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QUARTERLY PROGRESS REPORT

FOR PERIOD ENDING FEBRUARY 20, 1953

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CHEMICAL TECHNOLOGY DIVISION

QUARTERLY PROGRESS REPORT

for Period Ending February 20, 1953

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T. S. McMillan and W. L. Johnson, *Removal of Nitrous Oxide and Krypton from Uranium Dissolver Off-Gas*, ORNL-1300 (Dec. 3, 1952).

A. T. Gresky, M. R. Bennett, S. S. Brandt, W. T. McDuffee, and J. E. Savolainen, *Progress Report: Laboratory Development of the Thorex Process*, ORNL-1367 (Dec. 17, 1952).

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).

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

C. D. Hylton, *Separation of* U^{233} *in the ORNL Pilot Plant*, ORNL-1425 (Dec. 11, 1952).

Chemical Technology Division Quarterly Progress Report for Period Ending November 20, 1952, ORNL-1448.

I. R. Higgins, *Radiation Damage to Organic Ion-Exchange Materials*, ORNL-1325 (Feb. 18, 1953).

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CHEMICAL TECHNOLOGY DIVISION QUARTERLY PROGRESS REPORT

ABSTRACT

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

INTRODUCTION

The major effort in the Chemical Technology Division during the past quarter was expended on Thorex process development and waste metal recovery. The Purex process demonstration was virtually completed, and the Idaho project work was being brought to a conclusion.

In the Chemical Development Section, studies on isolation by ion exchange were continued. Work was done on the flowsheets for Thorex, waste metal recovery, and chlorine trifluoride processes. Investigations were carried out on the preparation and properties of slurries for use as a type of homogeneous reactor fuel. Further studies were made on electrochemical development of surfaces on electrodes. Studies were made on the separation of two elements in order to evaluate the Higgins continuous ion-exchange contactor.

In the Unit Operations Section, both fundamental and applied studies were made in continuous metal dissolution and solvent extraction, especially as applied to the Thorex process.

In the Pilot Plant Section, the metal recovery pilot plant was completed, and plans were made for Thorex process studies.

In the Process Design Section, preliminary plant design for the Thorex process was completed, and some cost studies were made. The Purex plant cost analyses were continued.

SUMMARY

Purex Process. Five runs on Hanford slugs were completed, and the data were reported directly to Hanford for use in their Purex program. Ion-exchange isolation of the Purex solvent-extraction product was completely satisfactory.

Waste Metal Recovery. The metal recovery pilot plant was completed, and a satisfactory uranium product was obtained in the early runs.

Thorex Process. Improvements were made in the Thorex flowsheet, and data were obtained on satisfactory dimensions for solvent-extraction columns and on dissolution of thorium slugs for preparation of feed.

Volatility. Preliminary flowsheets were prepared for both batch and continuous chlorine trifluoride processing of irradiated uranium.

Electrochemistry. The effective surface of a silver anode was found to be increased by electrochemical formation and reduction of a chloride layer.

Ion Exchange. Results of separation studies in the Higgins contactor showed that it gives separations satisfactorily close to the results calculated for an ideal continuous countercurrent contactor.

1. PUREX PROCESS

The Purex solvent-extraction process for separation and decontamination of plutonium and uranium from irradiated uranium metal has been developed through the laboratory and pilot-plant stages and has been shown to be both efficient and economical, as compared with other processes.

The five additional runs (HCP-16 through 20), on 60-day-cooled Hanford slugs,[1] were completed with satisfactory results. The data obtained were reported directly to Hanford for use in their Purex program. Detailed run summaries and the flowsheet modifications that were used will be given in the terminal report[2] on the Purex project, which is now being prepared.

About 1900 g of plutonium, including 370 g from the 60-day-cooled material, was isolated from the solvent-extraction product by ion exchange. The over-all performance of the ion-exchange process was excellent, plutonium losses were low, and all products met specifications.

The effects of routine cyclic operation, omitting the uranium elution, increasing the normal column loading to 50%, and increasing the plutonium elution flow rates have been investigated to determine the operating limits of the plutonium ion-exchange isolation process for the Savannah River plant.

Decontamination of the Purex solvent (ICW stream) prior to its reuse was carried out on both a laboratory and a pilot-plant scale, but the laboratory results were more satisfactory. Some evidence was obtained that failure to decontaminate successfully on a pilot-plant scale was due to carry-over of suspended matter on which activity was adsorbed. Sodium hydroxide was shown to give better decontamination than sodium carbonate. Emulsions that formed when used solvent was washed with the aqueous phase were quickly broken with as little as 10^{-3} *M* HNO_3, and the activity appeared to favor the aqueous phase. Attempts to remove iodine from the solvent were not very successful, and it was concluded that much of the iodine is present as fixed iodine.

The procedure used in denitrating the uranyl nitrate product affects the purity and physical characteristics of the uranium trioxide formed. This, in turn, affects the reactivity of the uranium trioxide in its conversion to uranium tetrafluoride. Laboratory-scale apparatus has been constructed for denitration of uranyl nitrate and the reduction and fluorination steps. Experience has been gained in the reduction and fluorination steps, which comprise the reactivity test used at K-25 for determining the suitability of recovered uranium trioxide for conversion to UF_6. Study has begun on the denitration process, with emphasis on its effect on the reactivity of the oxide produced.

An all-metal denitrator capable of handling 5-gal batches of Purex uranyl nitrate product (300 to 400 g of uranium per liter) is being constructed. It will be used to obtain information on large-scale reaction steps and characteristics, off-gas composition and absorption, acid recovery, energy input to the denitrator, and product purity and particle size. These data will be useful in evaluating the denitration characteristics of the uranyl nitrate product from various processes.

[1] *Chem. Tech. Quar. Prog. Rep. Nov. 20, 1952*, ORNL-1448, p. 2.

[2] D. O. Darby, *Terminal Report for the ORNL Pilot Plant Investigation of Purex Process*, ORNL-1519 (to be published).

2. WASTE METAL RECOVERY

The purpose of the Waste Metal Recovery project has been to develop a chemical process for recovering uranium from Hanford metal waste and uranium and plutonium from ORNL metal waste. Since Hanford is now operating its own metal-recovery plant, future studies will be concentrated on chemical and equipment studies and the design, construction, and operation of the ORNL metal-recovery plant.

Air sparging of ORNL W-10 metal wastes yields slurries with a uranium concentration ranging from 40 to 55 g/liter. A feed uranium concentration of 100 g/liter is considered optimum, and the best method of preparing such a feed is considered

to consist in allowing the waste to settle for 12 hr, acidifying to 1.35 *M* HNO_3, evaporating, adjusting the acid to 4.5 *M* HNO_3, and allowing this preparation to settle to free it from near-colloidal particles.

The major revisions[1] in the Scrup equipment were completed, and 2.5 tons of uranium was processed to give a product that meets the K-25 specifications for feed material. The capacity of the metal-recovery plant during February is not expected to exceed 200 lb of uranium per operating day, but the necessary equipment to bring the capacity up to 500 to 750 lb of uranium per day is to be installed. The plant is expected to be operating near the design capacity by March 1.

Laboratory studies aimed at improving the modified Purex flowsheets[2] used in the metal-recovery work have been made. There are indications that plutonium losses in the IIA column are due to the increased sulfate concentration brought about by evaporation of the highly acid IBP solution, which is 0.03 *M* in ferrous sulfamate. After the solution volume is reduced to one-third its former value, about 99% of the plutonium is in the IV valence state, and addition of sodium nitrite before extraction in the IIA column is not necessary. Since the reaction

$$Pu^{4+} + HSO_4^- \rightleftharpoons PuSO_4^{++} + H^+$$

reaches equilibrium very slowly, a longer contact period of aqueous solution with solvent, and hence a greater number of equilibrium stages, is recommended.

Plutonium stripping in the IIB column is also improved by increasing the contact time.

Studies on plutonium recovery indicate that the ion-exchange isolation of plutonium from the ORNL waste-metal-recovery solvent-extraction process is feasible with a uranium-to-plutonium ratio of 100 to 1.

The design of equipment for the second uranium cycle is almost complete, and piping and equipment layouts are under way.

(1) *Chem. Tech. Quar. Prog. Rep. Nov. 20, 1952*, ORNL-1448, p. 3.

(2) T. C. Runion and C. V. Ellison, *Application of the Purex Process to ORNL Metal Waste Recovery*, ORNL-743 (Aug. 24, 1950).

3. HOMOGENEOUS REACTOR FUEL REPROCESSING

Past work in the Homogeneous Reactor Fuel Reprocessing program has been concentrated on the development of a chemical process for recovering the products from a homogeneous plutonium producer. The program is being changed to work on the development of processes applicable to experimental breeder reactors. Studies will include chemical and equipment development on both a laboratory and a pilot-plant scale.

During the past quarter, work continued on the basis of the old program;[1] details of the work are given in HRP quarterly reports.[2] It was established that in the presence of the mixture of hydrogen and oxygen expected in the reactor, hexavalent plutonium is reduced and precipitates in 24 hr at 250°C. If this plutonium is removed as it precipitates, the concentration of Pu^{240} in the product will not exceed 0.2%. At 100°C, some reduction of hexavalent plutonium was observed with the fuel solution in contact with mixtures of hydrogen and oxygen, but no precipitation of plutonium occurred in 72 hours. Special provision, other than precipitation, would therefore have to be made for removing plutonium from a reactor operating at 100°C to limit the Pu^{240} concentration to as low as 2%.

Preliminary experiments had indicated that radiation damage to the 30% tributyl phosphate–Amsco solvent would not be noticeable in a Purex process operating in the presence of less than tenfold the radiation level expected in the processing of 15-day-cooled material from a homogeneous reactor. Two series of Purex batch countercurrent tests have been completed that confirm these earlier results. Noticeable changes did occur in the decontamination factors of products and residual activities in used solvents in the tenfold level, and very large changes occurred at the hundredfold level. The effect of the radiation was more pronounced in the presence of nitric acid and uranium.

(1) *Chem. Tech. Quar. Prog. Rep. Nov. 20, 1952*, ORNL-1448, p. 3.

(2) See, for example, F. R. Bruce, D. E. Ferguson, G. I. Cathers, W. B. Howerton, O. K. Tallent, and W. E. Tomlin, *HRP Quar. Prog. Rep. Jan. 1, 1953*, ORNL-1478, p. 113.

The processing of uranium-bearing material salvaged from homogeneous reactor experiments was completed.[3] A total of 411 g of U^{235} was recovered, which represents about 90% of the U^{235} in the material processed and more than 99% of the U^{235} in the feed to the solvent-extraction process.

About 425 g of enriched uranium is being recovered from material salvaged from homogeneous reactor experiments. Tributyl phosphate solvent-extraction and ion-exchange processes are being used.

[3] C. E. Schilling and J. H. Goode, *Completion Report – 7500 Area Recovery Program*, ORNL CF-52-12-112 (Dec. 12, 1952).

4. THOREX PROCESS

The purpose of the Thorex program is to develop a process for the separation and decontamination of U^{233}, Pa^{233}, and thorium from irradiated 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 on the laboratory phase of Thorex development work is in preparation.[1] A flowsheet incorporating primary engineering features of the Thorex process and late revisions in the chemical flowsheet has been issued (see Fig. 4.1).

The continuous dissolving operation appears to be the most operable in a two-stage unit. An AF stream whose chemical composition varied ±3% in thorium concentration and ±10% in nitric acid concentration was produced at flow rates that varied ±20% (cf. "Metal Dissolution," this report). Provisions for possible continuous head-end treatment of the AF solution, e.g., reagent addition and/or digestion, have been included in the dissolver system to permit control of ruthenium decontamination in the process.

Protactinium separation in the A column was shown to be markedly dependent on the presence of phosphate ions. The inclusion of 0.002 *M* H_3PO_4 in the AS stream was found to be the optimum condition for controlling the protactinium separation and preventing significant thorium losses in the AP stream.

In order to improve conditions of the CU stream and to permit better operation of the U^{233} ion-exchange isolation step, a neutralization column has been included to remove nitric acid from the BU stream. This has been shown to permit lower CU or CX flow rates with lower acidity and higher uranium content. The device used in the scheme involves scrubbing the BU stream with the AS stream at a BU/AS flow ratio equivalent to that prescribed by the primary flowsheet. The AS stream is provided initially with a sufficient nitric acid deficiency to absorb the nitric acid from the BU stream and leave the neutralization column at proper conditions for A-column use. Each of the improved conditions mentioned above was known to promote higher efficiency in the isolation step.

The optimum system for protactinium recovery from the AP stream has not been determined, and alternate procedures are being investigated and evaluated for preliminary plant design. It is doubtful whether the silica-gel adsorption system described previously[2] is adaptable to efficient plant operations. In addition, certain unknown variables adversely affecting protactinium adsorption have been encountered, and radiation instability of silica-gel structures under prospective high exposures has caused uncertainties regarding its use as a "protactinium sponge." The solvent-extraction scheme indicated in the January 1953 flowsheet reflects an alternate consideration by the Chemical Development group to provide for high recovery and large volume-reduction factors. Final isolation of protactinium and/or U^{233} separation techniques are realistically considered as problems requiring close laboratory control, owing to the unique problems of handling extremely high activity levels.

[1] A. T. Gresky, *Laboratory Development of the Thorex Process – Progress Report September 30, 1952 to January 31, 1953*, ORNL-1518 (to be published).

[2] A. T. Gresky, M. R. Bennett, S. S. Brandt, W. T. McDuffee, and J. E. Savolainen, *Progress Report: Laboratory Development of the Thorex Process*, ORNL-1367, p. 80; 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).

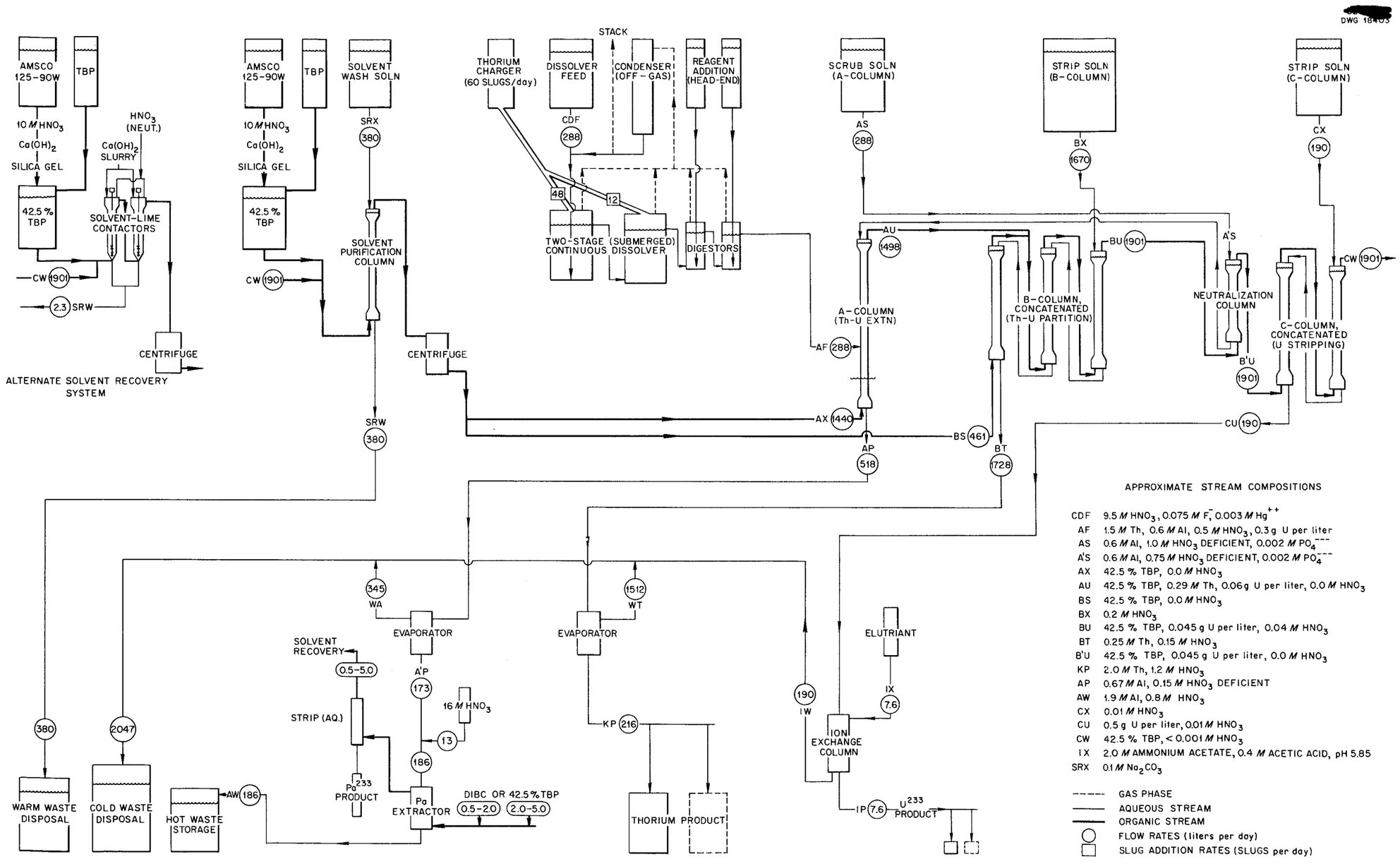

Fig. 4.1. Thorex Process Chemical Flowsheet, January 1953. Basis: 100 kg of thorium per day.

[redacted]

[redacted]

Extraction- (A) and preferential-strip-column (B) geometries have been established for a Thorex pilot plant having a capacity of 100 kg/day and meeting the requirements given in the last quarterly report.[3]

The vertical extraction column should be 3 in. in diameter and should include 8 ft of extraction section to give losses of only 0.02% each for uranium and thorium. Startup is currently carried out at half the operating flow rates, and the rates are increased to normal after 1 to 2 hours. Optimum methods of startup are still under investigation.

A 4-in.-dia preferential strip column would be required to process 100 kg of thorium per day at 60% of flooding. If a concatenated construction was used, a 12-ft height would reduce uranium losses to less than 0.1%, and a 24-ft stripping height would effect thorium separation from uranium by a factor of 8×10^3. Startup would have to be carried out by filling from the bottom.

A change in U^{233} stripping conditions to facilitate ion-exchange isolation has necessitated a recheck of C-column geometry.

[3] *Chem. Tech. Quar. Prog. Rep. Nov. 20, 1952*, ORNL-1448, p. 4.

Calcium hydroxide contactors with an inside diameter of 6 in. and a height of 4 ft were operated satisfactorily in the processing of new and used nonradioactive Thorex solvent; they consistently produced a solvent that was satisfactory for use in nonradioactive pulse-column development tests. The original contactor design,[3] with minor changes, was found acceptable. The optimum composition of the calcium hydroxide reagent was found to be a slurry of 330 to 400 g of dry $Ca(OH)_2$ per liter of water; the amount of slurry (6 liters) used was sufficient to fill the lower third of the contactor. Satisfactory operation of these contactors can be maintained at up to double the design capacity of 18 liters/hr. With two contactors in series, a slurry-treating capacity of 660 liters of solvent per kilogram of calcium hydroxide per contactor (66 hr at 18 liters/hr for these contactors) was proved under nonradioactive conditions, and a usable life of several times this seems probable. The spent calcium hydroxide slurries can be simply and easily dissolved in place in the contactors with dilute nitric acid.

Preliminary plant design for the Thorex process was completed, and cost studies are being made. Some necessary revisions were made in the pilot-plant design.

5. 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. A total of 2.64 kg of U^{233} was produced.

In order that criticality studies could be made on the U^{233} system in a nonpoisoning medium, a process was developed for converting $U^{233}O_2(NO_3)_2$ to $U^{233}O_2F_2$. The process consists in sorbing the uranyl ion on a cation-exchange resin and eluting with 4 *M* HF. About 85% of the uranium is eluted at a concentration of 380 g/liter and an acidity of less than 0.05 *M*; this product is satisfactory for use in the criticality studies. The remaining 15% of the uranium, which is eluted at too high an acidity (1.0 *M* HF) to be used, is sorbed on an anion-exchange resin, eluted with 0.2 *M* HNO_3, and recycled to a subsequent cation sorption. About 1 kg of $U^{233}O_2(NO_3)_2$ has been converted to $U^{233}O_2F_2$.

6. IDAHO CHEMICAL PROCESSING PLANT

Construction of the Idaho Chemical Processing Plant has now been completed, and operation with radioactive feed is scheduled to follow immediately a final mechanical check and Freon leak test. ORNL personnel assisted in the design, field engineering, and plant acceptance tests, and they are remaining to assist the operating contractor during the cold-run testing period and preliminary radioactive runs.

Construction, mechanical testing, and calibration of all areas in the Idaho Chemical Processing Plant have been completed. Foster Wheeler Corp.,

the architect-engineer, terminated its responsibilities on the job November 15, 1952, after supervising construction, testing, and preparation of as-built drawings for the plant. Bechtel Corp., the construction-contractor, recalled its remaining construction crew December 5, 1952 and released the plant for operational checks to the Idaho Operations Office of the Atomic Energy Commission and to the operator, American Cyanamid Co.

Approximately 50 runs have been made in which unirradiated natural uranium fuel elements of various types were used. Dissolution of the elements proceeded with no more than normal operating difficulties. Filtration of feed solution from MTR slugs presented a problem involving slow filtration rates, which has now been partially resolved as a result of studies made by the American Cyanamid Co. Works Laboratory. The solvent-extraction cascade – three cycles of hexone extraction from aluminum nitrate–salted aqueous uranium solution – operated satisfactorily with the smaller first-cycle columns designed for a uranium capacity of 1 kg/day. Uranium losses are acceptable, but decontamination has not yet been checked, since no fission products have been processed. Problems of control that developed during cold runs of the continuous-falling-film intercycle evaporators have been corrected. Analyses of product uranium for ionic contamination indicate that a product acceptable to the Production group at Y-12 can be prepared. The HETS values for the first-cycle extraction and stripping column vary between 2.2 and 2.9 ft, depending upon the type of feed, whereas the HETS values for second- and third-cycle columns have been measured to be 1.9 feet. These values are well within design assumptions.

The liquid-waste system has been thoroughly checked and is ready for operation. The evaporator, designed for a capacity of 300 gal/hr, has been operated satisfactorily at rates as high as 1100 gal/hr with water as the feed.

All units in the waste-gas systems required for plant startup have been operated successfully. The rare-gas removal system for the dissolver off-gas, in which radioactive operations will be started sometime after initial operation of the main plant has begun, has been mechanically checked and is now ready for test runs.

7. WASTE TREATMENT STUDIES

It is hoped that the Waste Treatment program, which is designed to reduce the radioactivity discharged from ORNL processes to a nonhazardous level, will lead directly to efficient means of waste disposal from large-scale radiochemical plants. The program includes chemical, equipment, pilot-plant, and design work on contaminated gaseous, liquid, and solid wastes.

During the past quarter, work has been concerned chiefly with means of decreasing the formation of foam in the ORNL waste evaporator. The foam, which is formed in spite of the use of appreciable quantities of Dow Corning-A antifoam agent, reduces the capacity of the evaporator considerably. Results of experiments indicate that if cold feed is sprayed on the foam, the foam collapses completely. If the spray is used hot, however, it creates more foam than it destroys. The experiments were carried out in equipment physically designed to simulate the ORNL waste evaporator on a reduced scale.

8. HOMOGENEOUS REACTOR SLURRIES

Efforts to develop a method for preparing uranium and thorium systems to be used as fuel media in homogeneous reactors were continued during the past quarter, emphasis being placed on uranium trioxide for use in slurry types of fuel. 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. Studies will include an investigation of methods of preparing slurries and the determination of their radiation stabilities. Details of the work are given in the HRP quarterly reports.[1]

[1] See, for example, F. R. Bruce, *HRP Quar. Prog. Rep. Jan. 1, 1953*, ORNL-1478, p. 97.

During the past quarter, the metathesis process[2] of preparing uranium trioxide was investigated more extensively, and kilogram quantities of the product were successfully prepared. The process consisted in treating uranyl nitrate with ammonium hydroxide to form ammonium diuranate. This was allowed to react with ammonium carbonate to give ammonium uranyl carbonate, which was decomposed to uranium trioxide. The anhydrous trioxide was washed and then calcined to UO_3 and finally hydrated to the desired monohydrate rods. The soluble uranium content of the supernatant was 1.1 ppm.

There were no difficulties with the metathesis step. A small amount of uranium went into the supernatant because of the solubility of ammonium uranyl carbonate, but this could be recycled. The product settled rapidly and could be filtered easily. There was some indication that iron contamination of the uranyl nitrate used as the starting material would be objectionable.

The crystal structure of $UO_3 \cdot H_2O$ was investigated[3] over the temperature range of 150 to 250°C, and crystals were prepared that exhibit the same x-ray diffraction patterns as those of the α-$UO_3 \cdot H_2O$ and β-$UO_3 \cdot H_2O$ reported by Zachariasen.[4] A transition from the low-temperature alpha rods to the high-temperature beta platelets occurs at approximately 200°C. This transition may not occur, however, if the alpha form is first annealed by heating in water at 150 to 180°C for several hours before the temperature is raised past the transition point. Transition from the beta back to the alpha form does not occur when the monohydrate is cooled past the transition point at a rate of about 2°C per minute. Reversion to the alpha form does occur when the β-$UO_3 \cdot H_2O$ is ground at room temperature in a fluidized energy mill.

Investigations on uranyl carbonate slurries, reported earlier,[2] were continued in an attempt to find the conditions of preparation that give the most desirable product. Reaction of $UO_3 \cdot H_2O$ at room temperature with carbon dioxide at pressures of 225 to 840 psi was found to yield much better slurries than reaction at higher temperatures and pressures. The addition of 0.005 *M* Na_2CO_3 before the reaction had a peptizing effect on the resulting carbonate slurry.

Experiments have been carried out to determine the effect of such variables as temperature, the presence of electrolytes, and the carbon dioxide pressure on the hydrolytic decomposition of uranyl carbonate slurries. Slow hydrolysis was found to occur during prolonged boiling. At 250°C and in the absence of sufficient carbon dioxide to maintain the carbonate, almost complete hydrolysis to the oxide occurred in 2 to 3 hours. In the absence of electrolytes, the oxide formed in rods 10 to 20 μ long, although the original carbonate from which the slurry was prepared was in the form of elongated platelets much less than 1 μ in average diameter. The presence of 0.005 *M* concentration of Na_2CO_3, NaOH, or Na_2SiO_3 appeared to promote the growth of large rods and platelets during the hydrolysis. Small, thin, uniform platelets were formed when 0.005 *M* Na_3PO_4 was present, and 5- and 10-μ agglomerates of small particles, which appeared to approximate the original carbonate particles in size, were formed in the presence of 0.005 *M* $Na_4V_2O_7$. Preliminary experiments indicate that the partial pressure of carbon dioxide at 250°C required to maintain UO_2CO_3 in the presence of 0.005 *M* Na_2CO_3 is less than 500 ppm.

Earlier studies[5] indicated that uranium trioxide slurries are stable at a relatively low power density. During the past quarter, uranium trioxide slurries at 250 to 295°C were irradiated with neutrons at a flux of 7×10^{11} neutrons/cm^2·sec. The rate of gas production ($H_2O \rightarrow H_2 + \frac{1}{2}O_2$) was approximately one-third as large as that found for uranyl sulfate solutions of the same uranium concentration. Steady-state pressures were higher with the slurries, which indicates that the rate of recombination is much slower than it is with solutions.

The material recovered from the bomb at the end of the irradiation showed no impairment of slurry-forming properties, but only 30% of the original material could be readily transferred from the bomb. There was no indication of caking, and the nontransferable material may have been deposited as a film on the interior of the bomb. Photomicrographs showed that the slurry had undergone considerable degradation during the irradiation,

(2) *Chem. Tech. Quar. Prog. Rep. Nov. 20, 1952*, ORNL-1448, p. 10.

(3) The x-ray studies were carried out by R. D. Ellison of the Chemistry Division.

(4) W. H. Zachariasen, "The Crystal Structure of β-$UO_3 \cdot H_2O$," *Report from July 1 to December 31, 1946.* Mass Spectroscopy and Crystal Structure Division, CP-3774, p. 20.

(5) *Op. Cit.*, ORNL-1448, p. 11.

with the production of many small fragments and fines plus a number of large, thin, irregularly shaped particles, 20 to 40 μ in average diameter, with no definite crystalline form. (Significant crystalline growth would not be expected in slurries of this uranium concentration.) These large particles may have been fragments of the nontransferable film, if it is actually formed. The soluble uranium concentration of the slurry at the end of the irradiation was less than 8 ppm.

9. VOLATILITY

Experiments designed to study the application of volatility techniques to the solution of AEC separation problems continued to be concerned chiefly with the chlorine trifluoride process for preparation of uranium hexafluoride.

Preliminary flowsheets were prepared for both batch and continuous chlorine trifluoride processing of Hanford-type uranium, but available data are not sufficient to permit an accurate economic analysis of the process to be made. A small dissolver (50 g of uranium) has been constructed for determining reaction rates as a function of the ClF_3/HF ratio, the uranium hexafluoride concentration, and the temperature.

The fluoro chemical N-43, a perfluoro tributyl amine, is being considered as a carrier for PuF_3 and fission-product fluorides. It was found to be reasonably stable under a radiation exposure equivalent to 2500 watt-hr/liter. A 0.5-ml sample formed only 0.5 ml of gas under these conditions, whereas an Amsco control formed 1.5 ml of gas. The N-43 does not extract uranyl nitrate or nitric acid from an aluminum nitrate solution. The time required to dissolve uranium tetrafluoride in aluminum nitrate solution was not affected by the presence of N-43.

Calculations based on Raoult's and Dalton's laws were made to determine the concentration of the tellurium in various portions of the proposed continuous dissolver system. The highest tellurium concentration will be in the liquid leaving the $-60°C$ dissolver condenser, where it is estimated to be 70 times that in the uranium metal feed. The tellurium concentration in the dissolver will be about 3.5 times that in the uranium metal feed.

10. ELECTROCHEMISTRY

Studies in the Electrochemistry program are directed toward reducing the costs of chemical processing by application of electrochemical techniques. Fundamental data will be obtained on such problems as production of deuterium oxide, production of source and fissionable materials, removal of poisons from homogeneous reactors, electrolytic reduction of uranyl fluoride to uranium tetrafluoride, and equipment decontamination.

During the past quarter, studies have continued[1] on the separation of hydrogen isotopes by means of a cathode of low overpotential and a hydrogen anode to recover power and increase the separation. Experiments on the cathodic deposition of hydrogen in palladium have shown that the separation factor may vary from below 5 to above 10 with variation in the surface structure of the cathode.

The initial hydrogen anode was prepared by using a reversible nickel oxide element from an alkali battery. Succeeding hydrogen anodes were prepared from the first anode. The life of the battery cycle is measured by the faradaic efficiency of the cathodic and anodic processes. Experimental efficiencies between 90 and 100% have been obtained.

A cell has been built with a number of porous electrode surfaces through which ions may flow during anodic or cathodic electrode processes. A study of electrolytic migration of the hydrated ion is in progress, including measurements on the concentration of ions at the cathode, the formation of an alkali-metal amalgam, and the regeneration of an alkali-metal hydroxide electrolyte.

Mass-spectrometer parts of stainless steel and other parts of nickel have been electropolished in order to decrease the true area of the metal surfaces. The polished metal has a smaller adsorptivity, and polishing may decrease the "memory effect" at metal surfaces in the gaseous-diffusion plants.

[1] *Chem. Tech. Quar. Prog. Rep. Nov. 20, 1952*, ORNL-1448, p. 12.

In contrast to electropolishing to reduce the effective surface area, a method of electrochemical development has been used to increase the surface of a silver anode by electrochemical formation and reduction of a chloride layer on the surface of the anode. An anode on which a silver surface had been developed was found to operate at much greater current densities than the original anode. A silver anode was used to remove chloride and radioactive iodine from solutions of uranyl sulfate in the homogeneous reactor.

A miniature cell, which contained platinum electrodes, was constructed for insertion in the homogeneous reactor fuel-sampling system to test the continuous removal of cationic fission products and impurities involved in corrosion couples and neutron absorption.

11. ION EXCHANGE

Investigations for developing applications of ion-exchange techniques to AEC separation problems have continued with emphasis on further evaluation of the Higgins continuous contactor.

Sodium-lithium separation runs in the Higgins contactor gave results close to the values calculated for an ideal continuous countercurrent contactor based upon equilibrium and fixed-bed studies. It is not yet known whether the differences between the results obtained with the contactor and the calculated ideal values are inherent in this type of apparatus or whether better results can be obtained by mechanical refinements.

The sodium-lithium system was chosen for the tests because it is a moderately difficult separation, with a separation factor of about 2.7 under the conditions used, and because analysis for the elements concerned (by a flame spectrophotometer) is relatively easy and accurate. The laboratory-model contactor[1] was set up to operate as a $\frac{3}{4}$- by 39-in. total-reflux lithium enricher with 2.4 *M* NaOH–0.024 *M* LiOH flowing countercurrently to the hydrogen-form resin (50- to 100-mesh Dowex 50W, 12% cross linked) at a superficial flow rate of 3.6 cm/min. At steady state, the lithium was enriched with respect to sodium by factors of approximately 360 at 15 in. below the feed point, 40,000 at 27 in., and 530,000 at 39 inches. At the 39-in. position, the sodium concentration in the 2.4 *M* LiOH was down almost to the background level contributed by the sodium present in the hydrogen-form resin, which had been regenerated with reagent-grade nitric acid. The results at the 15- and 27-in. positions correspond to an HETS, calculated from the Fenske equation, of about 2.5 in., which is about twice the ideal value indicated by fixed-bed studies.

A second run was started that was similar to the first, except that 2.4 *M* LiOH product was withdrawn slowly at the 39-in. position. This run had to be stopped before steady state was reached because of the buildup of insoluble lithium carbonate in the column.

Satisfactory removal of trace amounts of chloride ion from a synthetic homogeneous reactor fuel solution by ion exchange was demonstrated.

Investigations now in progress include (1) a study of the use of ion exchange instead of evaporation for coupling the first and second uranium solvent-extraction cycles and (2) a study of the decontamination obtained in the conversion of uranyl nitrate to uranyl fluoride (see following section).

Contactor development work has included the demonstration of a "folded" column, designed to conserve building height when necessary, and the near completion of a "pilot-plant" model for demonstrating the practicability of operation on a larger scale.

CONVERSION OF URANYL NITRATE TO URANYL FLUORIDE

A preliminary cost estimate indicates that the solvent-extraction strip solution of uranyl nitrate can be converted to uranium tetrafluoride by an ion-exchange–electrochemical-reduction process for 20 to 25 cents per pound of uranium, which is considerably cheaper than present costs. Studies during the past quarter have indicated that electrochemical reduction is to be preferred over the use of hydrogen or ammonia gas at high temperature and pressure, zinc, ferrous ion, or stannous ion. It has also been found that conversion to and electrolysis of UO_2–HF is to be preferred over direct electrolysis of $UO_2(NO_3)_2$–HF. The ion-exchange

[1] *Chem. Tech. Quar. Prog. Rep. Nov. 20, 1952*, ORNL-1448, p. 13.

and electrolysis steps have been demonstrated batch-wise in the laboratory, and a continuous demonstration with the Higgins column and electrolysis cell in series is planned. Since this proposed process offers two or three opportunities for uranium decontamination, the possibility that the second solvent-extraction cycle can be eliminated is being investigated. Decontamination from iron, aluminum, sodium, and fission products present in first-cycle uranium will be studied.

12. LITR COOLING SYSTEM

A new cooling system for the LITR has been designed and installed. This system saves approximately $60 per day in operating cost over the former system at the present LITR operating power level.

Operation of the Trane fluid coolers was started November 25, 1952, and they have given satisfactory performance, with minor interruptions. The heat-removal capacity meets design specifications for current air temperatures, but it will be necessary to wait until next summer to determine the capacity under the most adverse temperature conditions.

About half of the 10,000 gal of water in the LITR cooling system has had to be dumped each week and replaced with fresh demineralized water. A "hot" demineralizer, which eliminates the need for dumping the water, has been installed and operated satisfactorily for more than a month; an estimated saving of $200 per month is effected.

13. CHEMICAL ENGINEERING RESEARCH

The Chemical Engineering Research program is a long-range program that has as its objective the reduction of radiochemical processing costs. The high cost of radiochemical processing 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 reported in this quarterly as general projects include solvent extraction, equipment decontamination, metal dissolution, radiation resistance of coatings, and cost analyses. Applications of these and other fields studied are continually being made in the various processes being developed and are reported under the specific process headings.

SOLVENT EXTRACTION

Various types of contactors, including packed, pulsed, and Scheibel columns, mixer-settlers, and the Podbielniak centrifugal contactor, have been evaluated as a part of the Solvent Extraction program. At present, emphasis is being placed on pulsed concatenated columns.

Continued studies on concatenated pulse columns[1] have (1) verified the reliability of the floating-disk type of check valves, (2) shown more effective phase separation with an end settling section incorporating an enlarged tangential entrance, and (3) indicated the optimum size of the transfer tubes.

The first two floating-disk type of check valves have been in operation without failure for over 400 hours. An end-settling-chamber cross section approximately twice the actual column cross section, which incorporates a tangential entrance, permits effective phase separation and less recirculation of the organic phase. Tests indicate that $\frac{3}{4}$-in.-dia transfer tubes are optimum for a 4-in.-dia concatenated pulse column.

Startup must be carried out by filling the unit from the bottom end. Tests in a 4-in.-dia column have shown that 400 to 500 cc of air per minute entering the system is purged immediately, with no apparent difficulty. Larger amounts of air entering the column during operation would fill the organic transfer tube with air and reduce the pulse action. Tests in a 4-in.-dia concatenated column indicated that the amplitude was reduced from 1 to 0.5 in. with larger amounts of air. Countercurrent flow over a 3-hr period was maintained.

Final evaluation of operating procedures and equipment integrity will depend on additional tests, including tests of means for purging large volumes of air.

[1] *Chem. Tech. Quar. Prog. Rep. Nov. 20, 1952*, ORNL-1448, p. 15.

EQUIPMENT DECONTAMINATION

At present, research on improving the methods for decontaminating radiochemical process equipment is chiefly chemical, although electrolytic methods have been studied and are considered preferable in some cases.

At the request of the Pilot Plant Section, a series of experiments was carried out in an attempt to find an alkaline or low acid decontamination reagent for type 347 stainless steel. Appreciable decontamination was obtained in a procedure involving a ½-hr treatment of the metal with vigorously agitated 6.5 *M* NaOH–0.67 *M* sodium tartrate at 85°C followed by 1 *M* sodium oxalate–0.1 *M* NaF under the same conditions. Somewhat less, but still satisfactory, decontamination was obtained with 6.1 *M* NaOH–0.1 *M* NaF followed by 1 *M* oxalic acid–0.1 *M* NaF under the same conditions as those in the first procedure. The relatively high pH of the first reagent decreases the corrosion of the equipment during the treatment and decreases the volume of waste to be stored, since acid waste would have to be neutralized.

METAL DISSOLUTION

The applicability of the continuous dissolution method[2] to the preparation of feed for the Thorex process was studied with canned thorium slugs. With the use of a two-stage dissolver that operated at a rate of 50 kg of thorium per day, a consistent product was obtained when steady state was reached, and results indicated that a two-stage dissolver with a capacity of 50 gal per stage could accommodate as much as 100 kg of thorium per day.

The trickle type of dissolver did not produce a consistent product. Under the best conditions, the thorium concentration varied as much as 30 or 40 g/liter from one hour to the next. The size of a trickle type of dissolver that would be required to produce a product of average composition approaching specifications would be exorbitantly large if it were to meet the dissolving rate requirements for the Thorex pilot plant.

[2] *Ibid.*, p. 17.

[redacted]TINGS

Sixteen coating samples were irradiated in demineralized water to 10^6, 10^8, and 10^9 r (in air) in order to determine the effect of gamma radiation on wet coatings as compared with dry coatings. The damage to the wet coating – color change, softening, and blistering, followed by embrittlement, and halogen release – appeared to be of the same type as that suffered by specimens irradiated dry.[3] Failure appeared to occur no sooner in a wet environment than in a dry one. There was no appreciable damage to any of the coatings at 10^6 r; a total radiation exposure of 10^8 r is considered the limit that any of them will stand.

COST STUDIES

The program of obtaining cost data on radiochemical plants, with the ultimate purpose of reducing costs, has been continued. Data are being accumulated, and the effects of various factors such as accountability, criticality, radiation, and waste disposal on plant costs will be determined. Preliminary economic studies will be made for future plants.

The costs of processing equipment components and instrumentation have been analyzed, and the studies of four other phases of the work are in the final stages. The processing equipment components studied included such prefabricated items as process vessels, heat exchangers, funnels, pumps, agitators, and other pieces of equipment that come into direct contact with the raw material, reagents, or final product.

An unsuccessful attempt was made to determine the correlation between vessel volume and cost, but a rough relation was found to exist, with certain exceptions, between the weight of a vessel and its cost when modified by nozzle cost. The exceptions to this rule were small vessels under 150 lb in weight and those with 5¼-in.-o.d. seamless tubing for the shell.

Material and equipment lists for the Purex plant cost analysis have been revised to include recent developments. Work on equipment costs and cell layouts is in progress.

[3] *Chem. Tech. Quar. Prog. Rep. Aug. 20, 1951*, ORNL-1141, p. 80.