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AEC RESEARCH AND DEVELOPMENT REPORT

CHEMICAL TECHNOLOGY DIVISION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING MARCH 31, 1954

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CHEMICAL TECHNOLOGY DIVISION

SEMIANNUAL PROGRESS REPORT

for Period Ending March 31, 1954

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Reports issued during the past six months are as follows:

D. C. Overholt, D. A. Orth, F. W. Tober, R. H. Rainey, and D. G. Karraker, *Progress Report No. IV: Ion Exchange Isolation Processes for Plutonium and Uranium*, ORNL-1585 (Oct. 9, 1953) (Secret).

E. Lieberman and A. C. Jealous, *Application of the Pulse Column for Uranium Recovery from K-25 Wastes*, ORNL-1543 (Nov. 6, 1953) (Secret).

H. E. Goeller and F. L. Culler, *Idaho Chemical Processing Plant Design Capacity*, ORNL-779 (Feb. 4, 1954) (Secret).

D. O. Darby and J. M. Chandler, *Terminal Report for the ORNL Pilot Plant Investigation of the Purex Process*, ORNL-1519 (Feb. 8, 1954) (Secret).

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H. L. Hull and H. R. Zeitlin, *A Design and Cost Estimate Study of a Purex Plant*, ORNL-1558 (March 15, 1954) (Secret).

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F. R. Bruce, "Radiochemical Processing," Fifth Annual ONR Nuclear Sciences Seminar, Oak Ridge, Tenn., Dec. 3, 1953.

F. L. Culler, "The Design of Radiochemical Processing Plants," Washington University, St. Louis, Mo., Feb. 17, 1954 (ORNL-ORINS Traveling Lecture Program).

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W. K. Eister, "The Treatment of Radioactive Wastes," Fifth Annual ONR Nuclear Sciences Seminar, Oak Ridge, Tenn., Dec. 3, 1953.

W. K. Eister, "The Engineer in the Atomic Energy Program," Georgia Institute of Technology, Atlanta, March 8, 1954 (ORNL-ORINS Traveling Lecture Program).

Ibid., Catholic University of America, Washington, D.C., March 29, 1954 (ORNL-ORINS Traveling Lecture Program).

Ibid., University of Kentucky, Lexington, Feb. 18, 1954 (ORNL-ORINS Traveling Lecture Program).

D. E. Ferguson, "Chemical Processing of Aqueous Homogeneous Reactor Fuel," Reactor Information Meeting, Argonne National Laboratory, Chicago, Oct. 9, 1953.

H. E. Goeller, "Idaho Chemical Processing Plant Design," Reactor Information Meeting, Argonne National Laboratory, Chicago, Oct. 9, 1953.

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CHEMICAL TECHNOLOGY DIVISION SEMIANNUAL PROGRESS REPORT

ABSTRACT

Progress during the past six months is discussed on the following projects: U^{235} processing, recovery of plutonium and americium from Hanford waste, the Thorex and Excer processes, ARE fuel recovery, homogeneous reactor fuel and blanket preparation and processing, fuel-element processing, preparation of feed materials, the Idaho chemical plant process, studies in volatility, waste treatment, ion exchange, equipment decontamination, solvent extraction, and dissolution.

SUMMARY

Facilities are being installed at ORNL to recover Savannah River irradiated U^{235} by tributyl phosphate solvent extraction. The recovery cost is estimated to be $0.60 per gram of U^{235}, including amortization of the plant additions required. The proposed process flowsheet is designed for an over-all uranium loss of less than 0.04%. Acid dissolution of 7.5% uranium slugs in the 5.5-in.-dia dissolver was carried out at a rate of about 12 kg of uranium per day.

The Metal Recovery Plant recovered 95 tons of uranium and 208 g of plutonium from accumulated ORNL waste during the past year. The plant was converted to process Hanford slag and crucible waste, and in three weeks of operation it has recovered 1500 g of plutonium and 0.1 g of americium.

The Thorex pilot-plant installation is 35% complete, and startup is scheduled for August 1954.

Cost studies indicate that a moving-bed process may convert uranyl nitrate to uranium tetrafluoride at a cost of $0.20 per pound of uranium processed, which is $0.05 per pound less than the cost of conversion by the Excer process. Emphasis is being shifted to development of the Moving-Bed process.

Fused-salt fuel from the Aircraft Reactor Experiment will be transported to the ORNL Metal Recovery Building for recovery of uranium in open-top cans containing 4 kg of U^{235}. The uranium will be extracted from an aqueous aluminum nitrate solution of the fuel by tributyl phosphate. In preliminary studies on alternate methods for possible future use with ARE type fuels, 99% of the uranium was recovered as UF_6 by fluorination of the molten salt.

Thorium oxide that is less abrasive than fired Ames oxide, of interest as a possible blanket material for a two-region homogeneous power reactor, has been made by drying thorium hydroxide at 500°C and autoclaving the residue in water at 250°C.

Continuous removal of plutonium by precipitation from the blanket of a two-region homogeneous reactor is being considered. At 250°C, the reactor operating temperature, insoluble PuO_2 precipitates from the uranyl sulfate solution. Fission-product poisons, such as rare earths, are also insoluble in the core solution of uranyl sulfate and precipitate at this temperature. DorrClone separators, which are high-centrifugal-force liquid-solid separators, are now being studied for use in the removal of precipitates from circulating core and blanket solutions.

A method developed for processing stainless-steel-clad uranium dioxide fuel elements consists in carburizing the fuel elements, dissolving the iron, nickel, and some of the chromium of the stainless steel in copper sulfate–sulfuric acid, discarding the solution, and finally dissolving the uranium dioxide in nitric acid. Waste volumes from this procedure would be lower than those from other processes that have been proposed.

Thorium and uranium metal have been prepared

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at room temperature by lithium amalgam reduction of thorium tetrachloride and uranium tetrachloride dissolved in anhydrous propylenediamine.

Ruthenium decontamination of the U^{235} product in the Idaho Chemical Processing Plant 25 process was increased a thousandfold by making the second- and third-cycle feeds 0.05 *M* in sodium nitrite and simmering for 3 hr at 85°C.

In two alternative processes developed for producing low-fluoride uranium solution from a hydrochloric acid digest of uranium reduction bomb and liner waste at Feed Materials Production Center, the uranium is sorbed on Dowex A-1 anion-exchange resin. In one method it is converted on the bed to the nitrate and eluted with water, and in the other the chloride is eluted with water and precipitated as ammonium diuranate. The Higgins contactor was successfully used to recover uranium from unclarified leach liquors of low-grade uranium ores.

1. 25 PROCESSING

The recent decision to load the Savannah River reactors with enriched uranium led to the request that ORNL design, construct, and operate a plant for recovery of the uranium. Processing facilities are being installed in cells 1, 2, 3, and 4 of Building 3019, which formerly housed the Purex pilot plant. Completion is scheduled for April 1, 1955, and startup with radioactive material for May 1, 1955. The total cost of the new facility will be $3,600,000. The recovery cost is estimated to be $0.60 per gram of U^{235}, including amortization. Provisions will be included to remove 5 to 10 curies of I^{131} and to dilute 1800 curies of Kr^{85} per day liberated in dissolution. An entirely new waste system will be constructed southwest of the present ORNL site.

Recovery Process. The recovery process includes continuous acidic dissolution of irradiated uranium-aluminum alloy, two tributyl phosphate solvent-extraction cycles, product concentration by evaporation, and product purification by sorption of residual fission products on silica gel. The principal difference between this process and the 25 process now in use at the Idaho Chemical Processing Plant is the employment of tributyl phosphate instead of hexone as the extractant. A tentative first-extraction-cycle flowsheet has been developed which uses 6% TBP as the solvent; the feed is 0.1 *M* in nitric acid and 1.8 *M* in aluminum nitrate and contains 1.92 g of uranium per liter. The uranium is stripped with 0.01 *M* nitric acid, evaporated, and converted to second-cycle feed by addition of nitric acid. The second-cycle flowsheet uses 15% TBP. The feed is 3 *M* in nitric acid, and the strip solution is 0.01 *M* nitric acid. The flowsheets are designed for an over-all uranium loss of less than 0.04%.

Criticality Criteria. The criticality criteria used in the design of the ORNL 25 processing facility are considerably more liberal than those used in the design of the Idaho Chemical Processing Plant. In the slug handling and storage area, permission has been granted by the Criticality Review Committee to handle 200 slugs, containing a total of 4.4 kg of U^{235}, per basket. Spacing of baskets in a plane was reduced to 12 in., side to side, in both horizontal directions, and two baskets may be shipped in a single carrier. All process-equipment criticality limitations have been established except the diameter of the continuous dissolver, for which a special criticality experiment is now in progress. In general, no geometry control is required where U^{235} concentrations are kept below 12 g/liter; however, where this concentration is exceeded, 8-in.-dia vessels are limiting when there is no water moderation and 5-in.-dia vessels when moderation is unavoidable, as with jacketed equipment. Preliminary design considerations indicate that all first-cycle equipment except expanded column ends meet the former requirements, and for these cases geometry limitations have been set, based on maximum possible uranium concentrations. The second-cycle and product-handling-equipment dimensions are governed by the second requirement above, and all equipment can be designed within the limiting diameters.

Waste System. The yearly volume of the first-cycle acid waste will be around 10^6 gal following concentration. If neutralized before storage, the volume will be between 10^6 and 2×10^6 gal. In

either case, 10^6 Btu/hr will be generated. The Catalytic Construction Company staff in Oak Ridge has estimated the following costs exclusive of engineering and design, contingencies, and contractor's fees:

	Capital Cost	Yearly Operating Cost
1×10^6 gal acid system	$1,202,000	$ 741,000
1×10^6 gal neutralized system	1,119,000	788,000
2×10^6 gal neutralized system	1,376,000	1,045,000

These estimates are for self-supporting load-bearing tanks equipped with condensers and condenser-water cooling towers. The use of natural-convection and forced-draft condenser-water air coolers gave very similar cost figures. The estimates include tanks, neutralization or evaporation equipment, and piping and auxiliaries. Cooling coils for the storage tank were included in the acid-system cost estimate.

The main disadvantage of the acid system is the high corrosion rate observed with any type of stainless steel at elevated temperatures; that of the neutralized system is the precipitation of the metastable sodium aluminate with subsequent crusting, overheating, and eruption of large quantities of activity into the surrounding atmosphere.

Selection of the type of waste system to be used for the ORNL 25 process, the only major design decision still to be made, will be based on safety, operating preferences, and the fact that acid waste is the most suitable for use in multicurie fission-product production.

Storage Canal. A new slug-storage canal to be located adjacent to cell 3 south of Building 3019 has been designed and may be used for the ORNL 25 process in lieu of the existing Building 3001 canal. Use of the new canal would permit a more flexible process layout in Building 3019. Before the existing canal, which is dimensionally inferior to the new design, could be used for the 25 process, (1) the existing Building 3001 5-ton crane would have to be replaced with a 10-ton crane, (2) the present shielded canal-water ion-exchange equipment would have to be moved, (3) space to store 100 tons of uranium now in the canal would have to be found or built, and (4) a dam would have to be constructed to permit drainage of the part of the canal to be used for U^{235} storage. Furthermore, the drained canal would be very difficult to decontaminate. Cost of the new canal, including a protecting shed but excluding any equipment, is estimated at $17,000.

Slug Loader. Design of an automatic slug loader for either Hanford or Savannah River slugs has been completed and is now being mocked up for long-term testing in the reservoir west of the ORNL cafeteria. This automatic loader would deliver slugs to a continuous dissolver to be designed on the basis of the final data from the dissolution studies now in progress (see below) and within the criticality diameter limit now being determined.

Dissolution Studies. Preliminary laboratory-scale (1-in.-dia column) studies were carried out on continuous acid dissolution of extruded Savannah River type slugs (5% uranium–95% aluminum). Results with 6 *M* nitric acid indicated that, at a dissolution rate corresponding to 8 kg of uranium per day in a 5.5-in.-dia column, a solution with aluminum, acid, and uranium concentrations easily adjustable to those required for the solvent-extraction flowsheet may be obtained.

Experiments[1] were also carried out with 7 *M* nitric acid on Hanford type cast slugs, which contain 7.5% uranium, in a full-scale dissolver, 5.5 in. in diameter and 20 ft high. The dissolution rate was 12 kg of uranium per day. The reaction zone was in the bottom 10 ft and the acid feed at the 10-ft level. The off-gas was taken off at the 5-ft level, and the product was continuously withdrawn through a digester providing 15 min holdup at the bottom of the column. The dissolution rate was limited by flooding in the bottom section of the dissolver, as a result of which the liquid phase was entrained in the off-gas and carried out through the off-gas system. Off-gas withdrawal from the bottom of the column, which had originally been expected to give maximum capacity, resulted in a lower dissolving capacity and a much more dilute final product solution. With the 7.5% uranium slugs, when the 6 *M* acid was used instead of 7 *M*, the dissolving capacity was insufficient to give the desired salt concentration in the product.

[1]Based on earlier work. See: D. L. Foster and E. O. Nurmi, *Continuous Dissolution of Uranium-Aluminum Alloy Slugs*, ORNL-1672 (in preparation).

In batch studies on caustic dissolution, for possible future use, a rate equation was derived which fits the data for caustic dissolution of NP slugs under all conditions studied. The specific rate constant was 2.2×10^{-4} liter/min/sq cm, which corresponds to an aluminum dissolution rate of 36 mg/min/sq cm in 6 *M* sodium hydroxide. This rate is slightly higher than the theoretical maximum rate for the HNO_3-Hg^{++} system with 4.5 *M* nitric acid and zero aluminum concentration. Unlike the acid dissolution rate, which is optimized at 4.5 *M* acid and decreases with increasing aluminum concentration, the caustic rate is directly proportional to the sodium hydroxide concentration, at least over the range 3 to 7.65 *M* sodium hydroxide. No significant difference was noted between rate of dissolution of cast and extruded slugs.

Solvent-Extraction Flowsheet. In tests of the first-cycle solvent-extraction flowsheet in glass 2-in.-dia pulse columns, uranium losses of 0.05% were obtained with a 12-ft extraction height; this is equivalent to two stages giving an HETS of 6 ft. An extraction height of 16 ft will be required to obtain the desired goal of uranium loss of less than 0.01%. The flooding rate at 80 cycles/min and 1 in. amplitude in a 2-in.-dia by 28-ft extraction-scrub column was 780 gal/sq ft·hr (combined flow). With an 18-ft strip column uranium losses were 0.01%; this is equivalent to five batch countercurrent stages. The flooding rate at 60 cycles/min and 1 in. amplitude was 670 gal/sq ft·hr.

High Activity Level Analytical Facility. Provision is being made for use of the High Activity Level Analytical Facility (see Sec. 4) in the 25 processing program.

2. WASTE METAL RECOVERY

The Metal Recovery program, for recovery of uranium and plutonium from accumulated ORNL waste, was discontinued on January 23, 1954, to permit equipment modifications required to process Hanford metallurgical waste for recovery of plutonium and americium. During the one-year period January 2, 1953 to January 23, 1954, a total of 95,550 kg of uranium was recovered which met K-25 specifications (fission-product beta and gamma activities not exceeding 100% of natural-uranium background). A total of 208.3 g of plutonium was isolated.

Completion of the second uranium cycle installation has been postponed until work on recovery of the Hanford plutonium and americium is well under way.

Operation of the Metal Recovery Plant for recovery of plutonium and americium from Hanford plutonium-reduction slag and crucible waste was initiated on March 10, 1954. The plutonium process[1] consists of dissolution of crucible and slag in 13 *M* nitric acid followed by plutonium recovery by two cycles of tributyl phosphate extraction, and isolation on Dowex 50 ion-exchange resin. The americium process is described in Sec. 3.

To date 10 batch dissolvings have been made, and 1500 g of plutonium has been recovered. Visual inspection of dissolver and analyses of undissolved solids indicate complete dissolution of plutonium.

In general, the plutonium extraction process has been satisfactory. Increasing the solvent/feed ratio from the design value of $\frac{1}{4}$ to $\frac{1}{2}$ was found to be necessary to reduce losses in the aqueous raffinate. To increase extraction efficiency, a larger pulser will be installed and the extraction section will be increased by 4 ft.

[1] Development work on the plutonium-recovery process is described by R. L. Folger, E. B. Sheldon, and S. V. Castner, *Recovery of Plutonium from Metallurgical Wastes*, ORNL-1442 (April 17, 1953).

3. AMEX PROCESS

A process was developed for recovering the americium from the accumulated Hanford plutonium slag and crucible waste, which is estimated to contain from 10 to 20 g of americium. After the plutonium has been recovered by extraction with 30% tributyl phosphate (see Sec. 2), the excess acid (5 M) in the aqueous waste is neutralized with gaseous ammonia, and the americium is extracted with 30% tributyl phosphate. The organic extract is scrubbed with ammonium nitrate solution, and the americium is stripped with water, sorbed on Dowex 50 cation-exchange resin, and eluted with ammonium acetate–acetic acid solution. Process losses are about 1%.

The process was put in operation March 10, and about 0.1 g of americium has been extracted and sorbed on the resin column. Some difficulty was experienced because of a gradual plugging of the resin column. A micrometallic filter is being installed to remove solids from the americium stream before it enters the resin column.

Details of the chemical development work are given[1] in ORNL-1697.

[1]R. H. Rainey, *Development of the Amex Process for Americium Recovery*, ORNL-1697 (in press).

4. THOREX PROCESS

Design of the Thorex pilot plant for recovery of thorium and U^{233} is 80% complete, and installation of pilot-plant equipment is 35% complete. A thorium throughput of 200 kg/day is planned, with a 66% operating time. Operation of the plant is expected to begin by August 1, 1954. Because of space limitations, recovery of protactinium is not planned at the present time.

The Criticality Review Committee has approved the use of a 5-in.-dia by 25-in.-high Dowex 50 resin column for isolation of the U^{233}. A normal load of 1500 g and a maximum load of 1700 g are assumed.

If a need for protactinium recovery arises, it can be obtained in a batch process with 90 to 95% recovery from a concentrated extraction-column effluent stream by adsorption on a chromate precipitate. In the laboratory studies, the aqueous solution was concentrated by a factor of 3.3, adjusted to 0.1 M sodium chromate, and digested at about 100°C for 2 hr; the precipitate was separated by centrifugation or filtration. The chromate precipitate after centrifugation was about 5% of the concentrated extraction-column effluent volume, and therefore a concentration factor of 50 to 60 can be obtained. The precipitate may be dissolved or slurried in nitric or hydrochloric acid. The protactinium may be purified by a diisobutylcarbinol solvent-extraction process.[1]

Pulse Generator. Tests over a six-month period (equivalent to three months' continuous operation) on the hydraulic pulse-generator system that is to be used in the Thorex pilot plant showed it to be reliable. Variation of frequency, amplitude, and form of pulse wave is possible with this unit, which is composed of standard commercial parts. Specific conditions can be reproduced with a variation in frequency of not more than 2 cycles/min and in amplitude of 0.05 in. (in a 5-in.-dia column).

Sampler. A mockup of the preliminary design of the Thorex sampler was made and tested, and modifications necessary to correct the minor operating difficulties observed were incorporated in the final design.

The sampler unit operates on the existing fluid-recirculating system; however, the fluid to be sampled does not pass through the air jet, which is used only as a vacuum source. Each sampler station is a 10-unit system. A shielded chain-driven set of carts, each carrying 10 sample bottles, permits transfer of samples between sampler stations and a sampler unloading unit. A shielded bucket conveyor is being designed to transfer samples mechanically from the unloading

[1]A. T. Gresky *et al.*, *Laboratory Development of the Thorex Process: Progress Report, October 1, 1952 to January 31, 1953*, ORNL-1518, pp 55-57 (July 14, 1953).

unit to the High Activity Level Analytical Facility (see below).

Construction of the new sample gallery on the south side of Building 3019 is almost complete, and equipment is being installed.

High Activity Level Analytical Facility. The construction request for the new High Activity Level Analytical Facility was approved by the AEC in January, and the design, scheduled for completion in June 1954, is progressing on schedule. The conceptual design for the new facility is being developed jointly by the Analytical Chemistry and Chemical Technology Divisions, and the detailed design is being done by the Engineering Department. The facility will be used to handle radioactive samples from all ORNL areas and will initially receive samples from the Thorex and 25 processing areas and from the several reactor divisions.

The facility will be a single story, 18 ft high, 45 ft long, and 83 ft wide, located at the west end of Building 3019. It will include a concrete-shielded barricade containing one storage cell for approximately 2500 radioactive samples and seven working cubicles, a decontamination area, one office, and a limited amount of normal chemical-hood and work-bench space. Each cubicle will be equipped with a zinc bromide window, a pair of Argonne No. 8 manipulators, an access door, and miscellaneous services and analytical tools.

The original construction request grant for $334,000 has been increased by $150,000 in order to provide additional facilities for the new 25 processing program.

5. EXCER PROCESS

In a demonstration run on the flowsheet[1] of the Excer process for converting uranyl nitrate to uranium tetrafluoride (starting with a radioactive solution of uranium concentration 50 g/liter and 0.1 *M* in nitric acid), decontamination factors of 1500 for zirconium, 150 for niobium, and 17 for ruthenium were obtained. Dehydration of $UF_4 \cdot \frac{3}{4}H_2O$ in a hydrogen fluoride or nitrogen atmosphere at 400°C for 30 min gave a uranium tetrafluoride product containing only 0.1% water.

A compact electrolytic cell, 6 by 6 by 14 in., has been constructed for the uranium reduction step. In test runs, this cell, which uses a falling film of mercury on a wettable plate alternated with graphite anodes, reduced uranium at a rate of 50 to 100 lb/day at 85% current efficiency. The product settled rapidly. An unfavorable feature of this cell is the graphite anodes, which have to be changed frequently because of burnup.

A life test is being carried out on the Nepton demineralizer, an electrodialysis unit containing ion-exchange membranes, which has been proposed for use in recovering hydrofluoric acid from the uranium tetrafluoride precipitation step. The cell is still operating efficiently after 720 hr. The membrane components are apparently unaffected by the hydrogen fluoride.

Cost studies indicate that uranyl nitrate can be converted to uranium tetrafluoride at a cost of $0.20 per pound of uranium by means of the Moving Bed process. This is $0.05 per pound less than the cost now estimated for the Excer process. In the Moving Bed process, proposed by Catalytic Construction Company, the 0.2 *M* uranyl nitrate solution from the solvent-extraction plant would be evaporated to molten uranyl nitrate hexahydrate and then to the tetrahydrate. The molten tetrahydrate would be mixed with uranium trioxide, pelleted, and passed to a moving-bed heat-transfer unit where it would be denitrated with heated air to form uranium trioxide. Three-fourths of this uranium trioxide would be recirculated, and one-fourth fed to a moving-bed reduction unit where it would be reduced to uranium dioxide with hydrogen produced by cracking ammonia. The uranium dioxide would be converted to uranium tetrafluoride with hydrogen fluoride in another moving-bed unit.

Because of the economic advantage of the Moving Bed process over Excer, much of the development effort has been shifted from Excer to Moving Bed work.

[1] *Chem. Tech. Semiann. Prog. Rep. Sept. 30, 1953*, ORNL-1561, Fig. 3.1, p 4.

6. ARE FUEL RECOVERY AND REPROCESSING

The process that has been developed for recovering U^{235} from the ARE fuel, a $NaF-ZrF_4-UF_4$ mixture, calls for dissolving the solid fuel in an aqueous solution, extracting the uranium with 5% tributyl phosphate, and isolating it by ion exchange. A processing rate of about 5 kg of uranium per day, which is the maximum dissolution rate under proposed conditions, is anticipated. The fuel will be transported to the processing site in aluminum cans 8.5 in. in diameter and 17 in. long. Each can will have a capacity of 53 kg of fused salt, but the amount of salt per can will be limited to a quantity containing 4 kg of U^{235}, the maximum permitted in the dissolver by criticality considerations. A proposed flowsheet of the process has been submitted to the Criticality Review Committee for approval.

Calculations based on 15-Mwd fuel irradiation and 100 days of cooling indicate that 8 in. of lead shielding will be required for a carrier to handle one can at a time. Preliminary calculations indicate that most of the shielding at the Metal Recovery Building may be adequate for ARE processing, but heavier shielding will be required above the dissolver. The charging equipment to be built will also require shielding.

In a batch countercurrent extraction of uranium with 5% tributyl phosphate from dissolved ARE type fuel, a gross beta decontamination factor of 3×10^5 was obtained. The apparent improvement of this factor over the previously reported value[1] of 10^4 is due to greater reliability of analytical results gained by a tenfold increase in initial fission-product activity spiked into the dissolved fuel. A decontamination factor of 1×10^5 would lower the fission-product beta activity of the recovered U^{235} to below 200% of that of unirradiated U^{235}, the product activity specified[2] by Y-12.

Details of the ARE work are reported in the ANP quarterly progress reports.[3]

Chemical Processing of ARE Type Fuel by Fluorination. A new nonaqueous method for processing ARE type fuel from an actual aircraft reactor has been shown to be feasible. It consists of three steps: (1) recovery of the uranium by converting the uranium tetrafluoride in the molten $NaF-ZrF_4-UF_4$ mixture to the volatile hexafluoride, using elemental fluorine, (2) gas-phase reduction[4] of the partially decontaminated UF_6 to UF_4, and (3) refabrication[5] of the molten fuel from this UF_4, using fresh $NaF-ZrF_4$.

Scouting runs on the first step of the process showed that more than 99% of the fission products and less than 0.5% of the U^{235} would remain in the original $NaF-ZrF_4$ mixture and be discarded to waste. The process appears to be attractive from the standpoint of cost, inventory of fissionable material, and radioactive waste volume. Gross beta decontamination factors of 100 to 270 were obtained in the fluorination step, the major contaminants of the product being ruthenium and niobium. Resublimation of the UF_6 product gave an over-all gross beta decontamination factor of 4000 to 5000.

Details of the development work on the fluorination process are reported elsewhere.[6]

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[1] *Chem. Tech. Semiann. Prog. Rep. Sept. 30, 1953*, ORNL-1561, p 6.

[2] R. B. Lemon, memorandum to R. E. Torley, *Recommended Final Product Radioactivity Specifications*, ACCO-3234 (April 1, 1953).

[3] *ANP Quar. Prog. Rep. Dec. 10, 1953*, ORNL-1649; *ANP Quar. Prog. Rep. March 10, 1954*, ORNL-1692.

[4] Method demonstrated on a pilot-plant scale at K-25. See: S. H. Smiley, D. C. Brater, and R. H. Nimmo, *Metal Recovery Processes*, K-901, Part I (March 10, 1952).

[5] Method developed and demonstrated by the Materials Chemistry Division. See: *ANP Quar. Prog. Rep. Sept. 10, 1953*, ORNL-1609, p 15.

[6] G. I. Cathers, *Recovery and Decontamination of Uranium from Fused Fluoride Fuels by Fluorination*, ORNL-1709 (in press).

7. HOMOGENEOUS REACTOR FUEL AND BLANKET STUDIES

The development of an aqueous thorium oxide slurry for use in the blanket of a thermal power breeder reactor has continued.[1] Emphasis in the studies has been placed on the effect that the method of preparation has on the chemical, physical, and engineering properties of the oxide, in particular on its abrasiveness when dispersed as an aqueous slurry.

The desirability of a particular preparation method is determined by the ultimate use of the oxide in an aqueous slurry at 250 to 300°C in a thermal breeding blanket. This requires that the product have the physical characteristics of small particle size and minimum abrasiveness, be attainable in slurry form with a thorium concentration in excess of 1000 g/liter, and be sufficiently pure chemically that the slurry properties are not impaired when it is subjected to prolonged heating in water at 250 to 300°C.

The starting material for all oxide preparations has been thorium nitrate. Its conversion to oxide via the hydroxide, oxalate, formate, and oxycarbonate has been investigated.

Laboratory testing at room temperature (in a jet-impingement type of tester[2]) of aqueous slurries of the oxides showed that the abrasive property of the slurry varied significantly with the method of oxide preparation. Correlation of laboratory abrasion test results with abrasion observed in loop tests at 250°C has been indicated when engineering information has been obtained on specified preparations. Relative crystallinity rather than particle size seems to be the controlling factor in slurry abrasion.

The least abrasive slurries have been prepared from thorium hydroxide. The hydroxide precipitated from thorium formate solution with ammonium hydroxide was more easily handled and less gelatinous than that from thorium nitrate solution. Autoclaving the washed but undried hydroxide in water at 250°C for 90 hr yielded a bulky hydrous oxide slurry (maximum thorium concentration 300 g/liter) very much less abrasive than those slurries obtained from oxides prepared by the decomposition of the oxalate or formate. Drying the hydroxide at 500°C and autoclaving in water at 250°C permitted a slurry concentration of 1000 g of thorium per liter to be obtained and resulted in the least abrasive oxide slurry that has been prepared to date.

Thorium oxalate was found to be best prepared by the addition of excess solid oxalic acid to a 1 *M* thorium nitrate solution at 40°C. A systematic study of the effect of calcination temperature on the properties of oxide residues from the thermal decomposition of thorium oxalate was carried out. Particle size, abrasiveness, crystallinity, density, and chemical purity increased with increasing temperature of calcination, while surface area decreased. Investigation showed that the most desirable thermal decomposition method for a usable slurry material containing less than 10 ppm of nitrate was a calcination procedure with initial heating at 370°C and final heating at 600 to 650°C.

Pyrohydrolysis of thorium oxalate in water at 250°C in an aluminum-lined autoclave yielded fine-particle oxide (100 to 1000 Å) containing 10 to 30 ppm of nitrate. Subsequent calcination of the recovered solids at 250, 500, or 585°C removed organic contaminants and permitted the oxide solids to be dispersed as aqueous slurries having thorium concentrations greater than 1000 g/liter, but these slurries were moderately abrasive in laboratory testing. Reautoclaving the slurries at 250°C in the absence of an aluminum liner showed no impairment of slurry properties.

Thorium oxide slurries prepared by thermal decomposition of thorium formate at 500°C were similar to those prepared from thorium oxalate at this temperature. The thorium formate was precipitated from boiling concentrated formic acid as a sandlike crystalline solid by the addition of thorium nitrate. It readily dissolved in water at room temperature to give 52 to 62 g of thorium per liter and exhibited a negative solubility temperature coefficient. A saturated solution at 97°C contained only 24 g of thorium per liter. Decomposition of thorium formate to the oxide begins at 225 to 250°C and is substantially complete at 300°C. Thorium formate is completely decomposed to the hydrous oxide by steam distillation at atmospheric pressure.

[1] *HRP Quar. Prog. Rep. Oct. 31, 1953*, ORNL-1658; *HRP Quar. Prog. Rep. Jan. 31, 1954*, ORNL-1678; *HRP Quar. Prog. Rep. April 30, 1954* (in preparation).

[2] *Chem. Tech. Semiann. Prog. Rep. Sept. 30, 1953*, ORNL-1561, p 5.

Thorium oxycarbonate, prepared either by eluting thorium from an ion-exchange column or by metathesis of the hydroxide (from nitrate solution) with carbonate, was decomposed at 500°C to yield oxide products which contained less than 50 ppm of nitrate but which offered no advantages as a slurry material over the previous preparations.

Facilities for use in the irradiation of thorium oxide slurries in hole 11 of the ORNL Graphite Reactor are under construction. Initial studies will include the effect of irradiation on particle size, settling rate, abrasive hardness, and gas production. The dissolution of irradiated slurry will be studied along with the distribution of Pa^{233}, U^{233}, and fission products in the irradiated slurry.

8. HOMOGENEOUS REACTOR FUEL REPROCESSING

Processing schemes for aqueous homogeneous reactors capable of producing plutonium low in Pu^{240} are being considered. Three problems exist: continuous removal of plutonium from the blanket, continuous removal of neutron-absorbing poisons from the core, and removal of those fission products which would present a long-range biological hazard in the event of a major accident with the reactor.

Plutonium(IV) at the blanket operating temperature of 250°C is stable and hydrolyzes to produce insoluble PuO_2, with only about 3 mg of plutonium per liter remaining in solution. The PuO_2 that precipitates has an average particle size of about 0.5 μ and a density of about 11 g/cc. DorrClone slurry concentrators operating at reactor temperature and pressure are being considered for collecting the PuO_2 solids in a small volume of solution which can be removed for chemical processing; the large volume of clarified solution can be returned to the reactor.

The presently favored method of core processing is based on the low solubility of the rare-earth sulfates at high temperatures. In a uranyl sulfate core solution at 250°C the rare-earth solubility was found to be less than 0.2 g/liter. At this concentration the soluble rare-earth fission products would contribute less than 2% of the total poison to the core. The solubility at 300°C would be even less. Mechanical separation of the solids from the liquid phase promises to provide an economical method for the frequent reprocessing of a core solution necessary for good neutron economy. Laboratory data indicate that rare-earth removal can be increased by saturating an untreated core solution with calcium sulfate at room temperature, heating the solution to reprecipitate calcium and rare-earth sulfates, and mechanically separating the precipitate.

An alternate core process[1] is based on rare-earth removal on a bed of calcium fluoride. In this process, however, some fluoride ion is introduced into the fuel solution. Studies on fluoride removal showed that the lowest fluoride concentration obtainable by precipitating thorium fluoride would be 60 ppm. Studies on the corrosion effects of fluoride in the fuel are now under way in the Corrosion Section of the Reactor Experimental Engineering Division, but, until the results are obtained, it is not safe to assume that this concentration of fluoride can be tolerated with a zirconium core tank.

Fluoride may also be removed[2] from the fuel by precipitating calcium sulfate at 250 to 300°C and then evaporating the solution to dryness and heating the residue to 300°C for 1 hr. The solid product can be completely redissolved to give a fuel solution containing less than 1 ppm of fluoride. The estimated cost of treating the fuel by this process, without allowance for overhead, is $0.27 per gram of uranium processed; the cost of processing by the thorium fluoride precipitation method is $0.19 per gram of uranium; and the cost of processing without removing fluoride is $0.16 per gram of uranium.

Studies are under way to determine which fission products will be present in a concentration high enough to contribute significantly to the long-range biological hazard and how these products behave in the proposed core and blanket processing

[1] *Chem. Tech. Semiann. Prog. Rep. Sept. 30, 1953*, ORNL-1561, p 5.

[2] Vitro Corporation of America, *Homogeneous Reactor Fuel Reprocessing. Job 87. Quarterly Progress Report for October 1 through December 31, 1953*, KLX-1711 (Jan. 18, 1954).

schemes. The danger, in the event of an accident, from extremely short-lived isotopes can probably not be alleviated, and efforts will be centered on holding the concentration of iodine, alkali metals, and alkaline earths to as low a value as possible.

An evaluation was made of the magnitude and nature of fission- and corrosion-product poisoning of the core solution in the two-region Homogeneous Thermal Breeder up to 40 days of irradiation and extended to 150 days of irradiation by means of the Instrumentation and Controls Division analog simulator. This study indicated that there are 19 isotopes, 47% of the total, which add considerable poison to the core system. Approximately 72% of the fission-product poisons are contributed by the isotopes of the rare-earth group. However, if Tc^{99} and Si^{89}, which have high but uncertain cross sections, are included in the total poison contribution, then the rare-earth group contributes only 55% of the total fission-product poison. Corrosion products are significant poisons, and, if the corrosion rates are as high as 1.5 mils per year, the corrosion poisons become equal in magnitude to the non-rare-earth fission-product poisons.

9. HETEROGENEOUS REACTOR FUEL REPROCESSING

Development work on better methods for chemical processing of fuel elements from heterogeneous reactors has been started. Existing methods for processing stainless-steel- and zirconium-clad fuel elements require the use of very corrosive chemicals, which makes it difficult to select construction materials for the process equipment, and these methods produce large amounts of highly radioactive waste which is costly to store.

Limited laboratory work has been carried out on dissolution of stainless-steel-clad uranium dioxide fuel plates for the proposed 10-Mw package reactor. Untreated stainless steel is not attacked by either nitric acid or copper sulfate solutions, but heating the fuel element for 1 to 2 hr at 1000°C in a hydrocarbon atmosphere was found to introduce carbon into the stainless steel and destroy its resistance to solution. The chromium of the steel and the carbon are precipitated as chromium carbide in this carburization process. The iron, nickel, and some of the chromium of the carburized stainless steel dissolve readily in 2 *M* copper sulfate containing 0.05 *M* sulfuric acid, with no evolution of hydrogen but with deposition of metallic copper. The uranium loss in the step was 0.03%. The uranium dioxide of the fuel element was then dissolved, together with the deposited copper, in 12 *M* nitric acid. The uranium in the nitrate solution, 99.25% of that present in the original fuel element, can be separated and purified by a tributyl phosphate extraction process. The volume of radioactive waste to be stored from the solvent-extraction process would be only one-sixth that produced by present processing methods.

10. FEED MATERIALS PROGRAM

A survey of the feed materials preparation program, in an attempt to discover means of reducing costs, indicated that the metal reduction and fabrication steps are the most expensive. Efforts on this program have been directed toward consolidating steps between crude concentrate and metal.

In studies on uranium, 75% of the uranium present was reduced to metal by a single-stage contact of excess lithium amalgam with uranium tetrachloride dissolved in propylenediamine. Temperature changes in the range 25 to 120°C did not affect the yield, but more than 0.1% water in the solvent resulted in hydrolysis of the uranium tetrachloride to a nonreactive form of uranium. Centrifugation of the uranium–lithium amalgam phase produced a quasi-solid phase of uranium mercuride, which could be heated in an inert atmosphere to distil off the mercury, yielding pyrophoric uranium metal as a residue. Lithium amalgam reduction of uranium tetrachloride in anhydrous isopropyl alcohol gave a poor yield and was accompanied by side reactions.

Thorium chloride in propylenediamine solution was reduced to thorium metal by lithium amalgam at 100°C. Centrifugation of the amalgam phase produced a quasi-solid phase similar to that produced in the uranium studies.

In studies on the preparation of uranium tetrafluoride, a 95% yield of UF_4 was obtained by treating the double salt $UO_2 \cdot xNH_4F$ with 42% hydrazine hydrate, evaporating it to dryness at 100 to 150°C, and heating the residue at 300°C. The present cost of hydrazine makes this process unattractive, but large-scale commercial production of hydrazine, which is planned shortly, may reduce its cost.

Two processes were developed for possible use at the Feed Materials Production Center for producing low-fluoride uranium solution from a hydrochloric acid digest of uranium-reduction bomb and liner waste. Sorption of the uranium from the digest liquor on Dowex A-1 anion-exchange resin, washing with 10 *M* hydrochloric acid, conversion on the bed to uranyl nitrate with calcium nitrate, and elution of the uranyl nitrate with water gave a product containing 30 g of uranium and 24.7 g of calcium per liter, 6 ppm of fluoride, and less than 5 ppm of chloride (FMPC specifications permit up to 500 ppm of fluoride). In the second method, in which uranyl chloride was eluted from the resin bed with water and the uranium precipitated as ammonium diuranate, the product contained 800 ppm of fluoride and 79,000 ppm of chloride. The second method would require less change in FMPC's present operating procedure than the first. The uranium capacity of the resin in the scrap digest-liquor medium was 65 g of uranium per liter of resin.

Ammonium diuranate precipitated from aqueous uranium solutions by hydrolyzing urea was more crystalline and filtered 20 times faster than that precipitated with ammonium hydroxide. This may find application in the processing of uranium ores and in the recovery and separation of uranium from waste.

11. IDAHO CHEMICAL PROCESSING PLANT

During the startup of the Idaho Chemical Processing Plant, separation of U^{235} from fission products was considerably poorer than that predicted from early 25 process pilot-plant studies at ORNL. The ruthenium decontamination factor of 6×10^4 observed in the ICPP was twentyfold too low for the product to meet Y-12 specifications[1] (beta activity of not more than 200% of U^{235} background) when MTR assemblies cooled 120 days were processed. In studies on improving the process, the uranium product decontamination from ruthenium was increased from 6×10^4 to 1×10^7 by making the feed to the second and third cycles 0.05 *M* in sodium nitrite and simmering for 3 hr at 85°C. If the same decontamination is achieved in the plant as in these laboratory-scale studies, the U^{235} product from 120-day-cooled MTR assemblies would have a ruthenium beta activity of only 10% of that of unirradiated U^{235}.

A solvent-extraction process, using 1.5% tributyl phosphate as the extractant and aluminum nitrate as the salting agent, was developed for separating the U^{235} from STR and SIR fuel dissolver solutions. The process gave, in the laboratory studies, beta decontamination factors greater than 10^6 with a uranium loss of less than 0.1% in one cycle. The process is similar to the Interim 23 process.

A report[2] on the Idaho Chemical Processing Plant liquid-waste facilities is in preparation.

[1] R. B. Lemon, memorandum to R. E. Torley, *Recommended Final Product Radioactivity Specifications*, ACCO-3234 (April 1, 1953).

[2] F. N. Browder, *Design Report: Liquid Waste Facilities, Idaho Chemical Processing Plant*, ORNL-1687 (in preparation).

12. VOLATILITY STUDIES

A cost study was made of the Chlorine Trifluoride process (CTF) for converting irradiated uranium metal to decontaminated uranium hexafluoride.[1] Based on a hypothetical plant for recovering uranium and plutonium from 3 metric tons per day of uranium containing 550 g of plutonium per ton, the recovery cost, assigning all charges to plutonium, was $14.50 per gram. With a direct-maintenance Purex plant of similar capacity, the plutonium recovery cost was estimated to be $20.00 per gram (including the cost of converting uranyl nitrate to UF_6). This small differential in favor of the CTF process is not believed sufficient to justify an intensive development program of volatility processes for recovering plutonium from irradiated uranium.

Scouting runs were made to determine the feasibility of recovering uranium from irradiated zirconium- or aluminum-uranium alloys by direct hydrofluorination of the metal in molten fluoride, with subsequent fluorination to UF_6 and volatilization of the UF_6. The dissolution rate of zirconium, 7 mils/hr, in the molten $NaF\text{-}ZrF_4$ (50-50 mole %), through which HF was bubbled at 575°C, was rapid enough to justify further study. In the absence of HF, the rate was 3 mils/hr, showing that part of the reaction was between the metal and the salt. A black precipitate that formed during the process dissolved in excess HF. Faster penetration rates were obtained with excess molten KHF_2, but the ZrF_4 formed was insoluble in the melt and uranium could not be removed easily from the thick paste that resulted.

A survey of the literature on fractional distillation of inorganic substances indicated that design methods applicable to other inorganic substances may be used in designing columns for separating mixtures containing UF_6.

[1] Flowsheet is given in *Chem. Tech. Semiann. Prog. Rep. Sept. 30, 1953*, ORNL-1561, p 4.

13. WASTE TREATMENT STUDIES

It is now planned to store the radioactive wastes from Hope type processes and the ORNL 25 recovery process in open basins in the earth rather than in the carbon steel, stainless steel, or concrete tanks now used for similar wastes. These process wastes may have an activity of 600 curies/gal or higher and will be constantly boiling (230°F). It is expected that the basins will be lined to prevent any possibility of radioactive contamination of ground streams, which is especially likely to occur with acid wastes.

All the commercially available asphalts and tars that have been considered as lining material for these basins have deteriorated when they were exposed to activities considerably below those anticipated in the waste solutions. Two special modified asphalts with softening points of 278 and 256°F showed a 30% increase in volume when gamma irradiated to 5×10^8 r (equivalent to 20 to 100 years of exposure, through 2 ft of earth shielding, to 500-curie/gal waste) and were severely attacked when immersed in boiling synthetic Hope type process waste [1.6 *M* $Al(NO_3)_3$, 0.2 *M* HNO_3, 0.02 *M* H_2SO_4] for 3 hr. Four modified tars with softening points of 237, 199, 192, and 158°F were not affected by exposure to 5×10^8 r of gamma radiation or by immersion for two days in synthetic Hope process waste solution at 150°F.

14. ION EXCHANGE TECHNOLOGY

A major problem in the use of ion-exchange resin for recovery of uranium from South African leach liquor has been cobalt cyanide poisoning of the resin. It was found that 97% of the resin exchange capacity could be regenerated by passing 2 *M* potassium thiocyanate through the poisoned resin, followed by sodium hypochlorite (5% free chlorine). Only 75% of the capacity was regenerated with 2 *M* ammonium thiocyanate followed by 3 *M* sulfuric acid.

In preliminary studies on the use of the Higgins contactor for recovering uranium from unclarified leach liquors, more than 95% of the uranium was sorbed from an unclarified sulfuric acid leach of ground carnotite ore on IRA-400 resin. Only a small amount of the solid material suspended in the leach solution was filtered out by the resin, and this was easily removed from the resin by washing.

[redacted]

15. EQUIPMENT DECONTAMINATION

Gamma scintillation-spectrometer measurements showed niobium to be the primary contaminant on type 347 stainless steel exposed to mixed-fission-products solution (Purex process waste). Zirconium may contribute a few per cent of the gamma radiation, and other fission products are less important. Besides being the predominant contaminant, niobium appeared to be the most difficult to remove.

Contamination of type 347 stainless steel from dilutions of the Purex process waste solution was shown to follow the Freundlich adsorption isotherm relation between the amount of radioactivity adsorbed and its concentration in the contaminating solution.

The rate of decontamination with time of treatment was investigated for 8 and 16 *M* nitric acid, 5% oxalic acid, 10% sodium hydroxide, 2.5% sodium tartrate in 10% sodium hydroxide, and a solution of 2.5% sodium tartrate, 10% sodium hydroxide, and 1.5% hydrogen peroxide. Nitric acid was the least effective, and the alkaline-tartrate-peroxide solution was the most effective, removing about 90% of the contamination within an hour. All the reagents decontaminated rapidly at first, but the rate dropped to 60% removal of activity per day after several days. The most effective noncorrosive decontamination procedure found was alternate treatment with 16 *M* nitric acid and the alkaline-tartrate-peroxide solution. Ten cycles with this treatment on type 347 stainless steel contaminated with mixed fission products (Purex process dissolver solution), in which the nitric acid was used for an hour every day and the alkaline-tartrate-peroxide solution was used for the rest of each day, gave negligible corrosion and a decontamination factor greater than 10^4 (from 100 to 0.01 mr/hr).

The most effective reagent known, 3-20 solution (3% hydrofluoric acid, 20% nitric acid), is corrosive. However, microscopic examination of type 347 stainless steel exposed to 3-20 showed no corrosion after 5 min and a uniform attack, with no pitting or intergranular corrosion occurring within 20 min. Decontamination was initially rapid, a decontamination factor of 12 being obtained in 5 min.

Decontamination factors of less than 2 were obtained with water slurries of anion-exchange resins, cation-exchange resins, and Filtrol. Ultrasonic irradiation of the slurries increased the decontamination factors to 5–10.

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16. CHEMICAL ENGINEERING RESEARCH

Solvent Extraction. Studies in 2-in.-dia columns following Purex, Thorex, K-25 uranium recovery, and 25-process recovery flowsheets showed the concatenated pulse column to have a 10 to 30% greater capacity than vertical pulse columns of equivalent height. In all tests the efficiency of the concatenated unit was equal to or greater than that of the vertical unit.

A concatenated column with the top (last) section 5 ft lower than the other sections was shown to be operable. This point is of particular significance in cascade operations.

No failures or stoppages have occurred with the floating-disk check valves in over 600 hr of operation.

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