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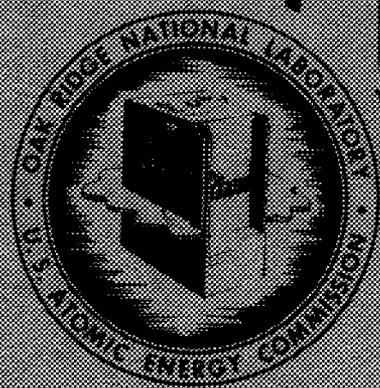


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CHEMICAL TECHNOLOGY DIVISION
ANNUAL PROGRESS REPORT
FOR PERIOD ENDING AUGUST 31, 1967

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Chemistry-Separation Processes
for Plutonium and Uranium
M-3679 (19th ed.)

Contract No. W-7405-eng-26

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for Period Ending August 31, 1957

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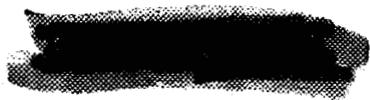
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CHEMICAL TECHNOLOGY DIVISION ANNUAL PROGRESS REPORT

ABSTRACT

This document reports progress for the past year on the Metallex, Fluorox, and Excer processes for feed materials processing; head-end treatments and solvent extraction for heterogeneous power reactor fuel reprocessing; waste metal recovery, Thorex process, americium recovery, waste treatment, the Hermex and fused salt-fluoride volatility nonaqueous recovery processes, HRT chemical processing plant, uranyl sulfate fuel reprocessing, uranyl sulfate blanket processing, thorium oxide slurry development studies, thorium oxide blanket processing, homogeneous reactor equipment decontamination, ion exchange technology, solvent extraction contactors, interfacial area measurement, in-line instrumentation, high-activity-level chemical development facility, Amex processes, Dapex processes, solvent extraction technology and fundamental chemistry of raw materials processing, and rare earth separations.

SUMMARY

PART I. FEED MATERIALS PROCESSING

1. Metallex Process

The quality of thorium metal produced by the Metallex process was improved by use of oxidation inhibitors in the amalgam wash solutions and decantation of the amalgam from an amalgamated container. Sintered thorium billets were hot-extruded directly into rods. A partial phase diagram for the thorium-mercury system was prepared. Approximately 200 lb of thorium metal as a ThHg₃-mercury slurry was continuously reduced and washed at a maximum rate of 3.4 lb of thorium per hour. Nineteen kilograms of thorium was prepared in a demonstration of Metallex equipment capable of a 3.6-lb/hr production rate.

2. Fluorox Process

Ten batch runs were completed in the fluidized-bed reactor for oxidation of UF₄ with air. Reaction rates agreed roughly with laboratory data indicating a very slow rate below 700°C but a large dependence of the rate on the temperature. Both fluidized- and moving-bed reactors were heated to 850°C with heat supplied internally by combustion of carbon monoxide. A flame reactor for oxidation of fine UF₄ powder in a CO-O₂ flame, at a temperature of 1400°C, was designed, constructed, and installed.

3. Excer Process

Precipitation of UF₄· $\frac{3}{4}$ H₂O at 90°C outside the electrolytic cell gave a product of high tap density, 3.0 g/cc. This permitted operation of the cell at room temperature and elimination of the flowing mercury cathode.

PART II. HETEROGENEOUS POWER REACTOR FUEL REPROCESSING

4. Head-End Treatments for Solvent Extraction Processing

In laboratory studies on the Darex process, in which dilute aqua regia is used to dissolve stainless steel-clad uranium fuel elements, the optimum acid concentrations were 2 M HCl and 5 to 6 M HNO₃. Continuous dissolution and chloride stripping were demonstrated on an engineering scale. Equipment was constructed to study these steps plus rectification and nitric acid evaporation as an integrated system.

Zirconium cladding was removed from UO₂ cores (PWR blanket) in 2.5 hr by the Zircex process (hydrochlorination) at 600°C with negligible loss of uranium. Uranium-molybdenum alloy clad with zirconium (APDA fuel) was completely hydrochlorinated in 9 hr at 370°C with little loss of uranium by volatilization. The method was equally successful with uranium-zirconium alloy,

but with niobium alloy the uranium loss when the residue was dissolved in nitric acid was somewhat higher. Engineering developments included large-scale determination of reaction rates, uranium losses, and heat transfer properties. In laboratory tests liquid-phase hydrochlorination, in molten $\text{AlCl}_3 \cdot \text{NH}_4\text{Cl}$, successfully converted zirconium to the chloride with negligible uranium loss.

Corrosion tests indicated that suitable materials of construction for the Darex dissolver are titanium or Haynes 21; for the Zircex hydrochlorinator-dissolver, S-816 or Haynes 25; and for the Darex or Zircex chloride stripping column and the Darex-Zircex acid rectifier, tantalum or titanium.

In studies of aqueous dissolvents alternative to nitric acid, type 304L stainless steel dissolved at a rate of 15 to 45 mils per 2.5 hr in refluxing 4 to 8 M H_2SO_4 , which is a feasible dejacketing rate for the Yankee Atomic fuel. Type 302B stainless steel from APPR fuel-element specimens dissolved readily in refluxing 4 to 6 M H_2SO_4 . Zirconium and Zircaloy-2 claddings dissolved readily in 5 to 9 M HF (>200 mg/cm²·min) with only very slow dissolution of UO_2 or U-10% Mo cores. Stainless steel dissolved anodically in 3 M HNO_3 with current efficiencies as high as 96%. Zircaloy-2 dissolved similarly in 3 M HCl containing <0.1 M HF.

Mechanical removal of some difficultly soluble claddings appears feasible. Methods investigated were electrical discharge cutting, abrasive disk sawing, derodding, and shearing followed by leaching of the soluble cores.

5. Solvent Extraction Studies

Chemical flowsheets were developed for solvent extraction processing of APPR fuel and APDA core and blanket material. All three use tributyl phosphate as the extractant.

Preliminary experiments on radiation damage to organic extractants indicated that the chief damage is formation of unsaturated compounds.

6. Metal Recovery

Approximately 37 tons of uranium, 22 g of Np^{237} , and 3.7 kg of plutonium were recovered in the Metal Recovery Plant from material that included ORNL tank farm waste, Chalk River uranyl nitrate and plutonium nitrate solutions, PuO_2 and miscellaneous plutonium metallurgical wastes, and K-25 fluorinator ash. A flowsheet for the recovery of

neptunium, plutonium, and uranium from irradiated uranium was developed and was demonstrated during the processing of 8.0 tons of Chalk River uranium. Uranium and neptunium product recoveries were 99.8 and 88%, respectively. The process, a modification of the Purex process, consists in oxidation of the neptunium to Np(VI) in the extraction column with 0.01 M BrO_3^- , extraction by tributyl phosphate, retention by the uranium-bearing solvent in the plutonium partitioning contactor by control of the nitric acid concentration, and, finally, stripping of the neptunium and uranium with water. In the second uranium cycle, the neptunium is isolated by selective stripping.

7. Thorex Process

The Thorex pilot plant was converted to the two-cycle co-decontamination flowsheet, with which process flexibility and fission-product decontamination are increased. In five runs 5.5 metric tons of irradiated thorium was processed, with separation of 11.8 kg of U^{233} . Average gross-gamma decontamination factors were 4×10^4 for thorium and 2×10^5 for uranium; both products met tentative activity specifications. Solvent extraction losses averaged about 1.3% for the thorium and 0.3% for the uranium. Since ruthenium and thorium extractabilities decrease with increased acid deficiency, the Thorex process feed has been set at 0.4 M acid deficiency to compromise between ruthenium decontamination and thorium loss. Satisfactory plant operation required a 25% reduction in plant capacity, preheating of the first-cycle strip solution, modification of the IC-column control, and installation of glass-fiber filters on all nonradioactive processing streams.

A modified U^{233} isolation system, a third uranium solvent extraction cycle, an interfacial-solids removal system, an I^{131} removal system, and a sample conveyor were installed in the pilot plant.

In laboratory studies, irradiation of the solvent diluent, Amsco 125-82, resulted in formation of unsaturated compounds; for every 100 ev of energy absorbed, 0.9 atom of I_2 reacted with the irradiated material. Irradiation of decahydronaphthalene (Decalin) gave similar results. The solubility of the $\text{Th}(\text{NO}_3)_4 \cdot 2\text{TBP}$ complex in Decalin is about 1.5 times that in Amsco; this increased solubility reduces the probability of third-phase formation and permits increased fission-product decontamination as a result of the increased loading. However,

in tests on Decalin in a 2-in.-dia glass pulsed column, extraction losses were 2.0% because of a long (5.6 ft) HETS, and the flooding rate was about 75% of that for Amsco.

Processing of short-decayed thorium results in I^{131} contamination of the organic phase and in almost complete loss of decontamination from ruthenium. In laboratory-scale tests, more than 98% of the I^{131} was vaporized during the dissolution step when I^{127} was added to the dissolvent as a carrier. Elimination of the mercury dissolution catalyst and inclusion of 0.01 M KI and 0.01 M NaHSO_3 in the extraction-column scrub effectively removed the remaining I^{131} . The addition of nitrite to the feed decreased the decontamination from ruthenium. A similar decrease in ruthenium decontamination was observed in the irradiation of aqueous feed solution. In laboratory-scale tests, the addition of sulfite, bisulfite, or sulfamic acid restored the decontamination factor.

The addition of 2 g of NaNO_2 per liter to a dilute uranyl nitrate solution reduced ruthenium sorption on cation exchange resin by a factor of 30. Modification of the uranium isolation system to incorporate upflow sorption and downflow elution simplified operation and permitted satisfactory use of 6 N HNO_3 as the eluant. About 1.2 kg of U^{233} was converted from uranyl acetate-citrate to uranyl nitrate.

The method for continuous interfacial-solids removal that was installed in the pilot plant was satisfactory in 2-in.-dia pulsed-column tests. This method consists in pumping a stream from the interface through a glass-fiber filter and a Selas separator, and reintroducing the two streams into their respective phases in the column. Radiation damage studies of the separator membranes indicated satisfactory stability.

8. Americium Recovery

In scouting tests with an americium-lanthanum solution of mole ratio 1/1000, the americium was separated from 99% of the lanthanum by anion exchange of the thiocyanate complex.

9. Waste Treatment

A comprehensive scheme proposed for waste treatment comprises scavenging, elimination of long-lived isotopes by ion exchange, and recycle of caustic by use of an electrolytic cell.

10. Nonaqueous Processes

Hermex process runs were made in larger scale, stainless steel equipment. Decontamination factors were lower than in the small-scale glass equipment. Mercury dissolution of refractory fuel elements does not appear feasible.

Construction of the volatility-sorption portion of the fused salt-fluoride volatility pilot plant was completed. All installed equipment was tested for operability and performance characteristics and found satisfactory. Design of the hydrofluorinator was started, the final design depending on corrosion- and dissolution-rate data now being obtained.

In process development studies, filtration of the $\text{UF}_6\text{-F}_2$ gas stream from the hydrofluorinator removed zirconium and niobium but not ruthenium or plutonium. A sodium fluoride bed at 400°C inserted in the line near the fluorinator outlet removed ZrF_4 snow and volatile chromium fluorides and improved the decontamination from ruthenium. Studies on the relative volatilities of uranium, plutonium, and fission products showed that all the transfer of activity except that of plutonium occurred during the UF_6 volatilization.

Dissolution rates of uranium-zirconium fuel elements with HF in fused NaF-ZrF_4 were sufficiently rapid to indicate the feasibility of a processing method based on this reaction. Dissolution of fuel elements containing stainless steel was unsatisfactory owing to preferential attack on chromium and very low dissolution rates.

PART III. HOMOGENEOUS REACTOR FUEL AND BLANKET PROCESSING AND DEVELOPMENT

11. HRT Chemical Processing Plant

The HRT chemical plant was operated, tied into the reactor, with natural uranium solution. Performance was satisfactory.

12. Uranyl Sulfate Fuel Reprocessing

Precipitation of uranium as UO_4 from the uranyl sulfate solution collected from the hydroclone underflow pot decontaminated the uranium sufficiently for return to the reactor. Uranium loss was 0.2%. Disappearance of fission-product and corrosion-product solids from a circulating stream was due to de-entrainment in stagnant areas. Hydroclone operation on a stream containing solids

concentrated the solids in the underflow pot by factors of 10 to 1000, depending on the amount of solids present.

The specific rate constant for reduction of iodate ion to free iodine under reactor conditions was measured as 0.1 min^{-1} . The oxidation of iodide ion to elemental iodine was too rapid to be measured.

In studies of charcoal adsorption of krypton under simulated HRT off-gas disposal conditions, both moisture in the charcoal and channels in the horizontal beds seriously interfered with adsorption.

13. Uranyl Sulfate Blanket Processing

Plutonium formed in simulated fuel solution under irradiation in titanium bombs was distributed between the bomb walls and the solution. Only negligible amounts appeared as a loose precipitate that could be concentrated with hydroclones.

14. Thorium Oxide Slurry Development Studies

Increasing the calcination temperature from 1000 to 1600°C in the preparation of ThO_2 increased its abrasiveness. The settling rate of aqueous slurries, from 25 to 300°C, as measured by the x-ray photography technique, was maximum for 1200°C-fired material. Addition of silicate decreased the settling rate, but the relative effect was less above 200°C. Thorium oxides with chemically bonded silicated surfaces showed complete dispersion in settling studies at 280°C. Mixed thorium-uranium oxide prepared by thermal decomposition of the coprecipitated oxalate was much more abrasive than either pure ThO_2 or the mixed oxide prepared by hydrothermal decomposition of the mixed-nitrate solution. Thoria microspheres were prepared by a gelling technique. Additional irradiations of both thorium oxide and thorium-uranium oxide slurries confirmed previous results on the lack of any gross irradiation effect. In further studies on MoO_3 as a catalyst for internal radiolytic-gas recombination, results with thorium-uranium oxide preparations were erratic, catalytic activity depending apparently on both the temperature and time of calcination of the oxide.

15. Thorium Oxide Blanket Processing

In scouting studies, lead and bismuth oxides added to a ThO_2 slurry adsorbed 0.1 g of ionic contaminants per gram of oxides. Treatment of ThO_2 with sulfate or sulfur decreased the adsorption of fission products on the ThO_2 by 90%.

16. Homogeneous Reactor Equipment Decontamination

Chromous sulfate in dilute sulfuric acid continued to be the best method of descaling stainless steel exposed to uranyl sulfate at 250 to 300°C. Chromous sulfate was prepared by electrolytic reduction of chromic sulfate in a 4-liter cell.

PART IV. CHEMICAL ENGINEERING RESEARCH

17. Ion Exchange Technology

A 12-in.-dia Higgins continuous countercurrent ion exchange contactor successfully processed 180 tons of Dysart ore with uranium losses of 0.2%. Operation of a 36-in.-dia contactor demonstrated that scaleup to larger diameter units is feasible from a hydraulic point of view.

A Jury continuous countercurrent ion exchange contactor was shown to be mechanically operable in runs to separate sodium from calcium.

18. Solvent Extraction Contactors

A three-stage countercurrent contactor with centrifugal pump mixer and hydroclone phase separator was built. It operated with 100% stage efficiency in extracting acetic acid from hexone with water.

19. Measurement of Interfacial Area

A method for measuring an organic-aqueous interfacial area was developed. It is based on the (α, n) reaction between Po^{210} in the aqueous phase and fluorine, as a fluorocarbon, in the organic phase, the rate of production of neutrons being proportional to the area and measurable outside the contactor.

20. In-Line Instrumentation

Development of the following in-line instruments is in progress: conductivity-type interface-level detector for contactors, alternating-current polarograph for monitoring uranium in waste streams, gamma monitor with a falling-stream cell or an electrically inhibited cell, radio-frequency monitor for nitric acid in feed streams, liquid flow-rate meters based on air-bubble flow rate, and chloride ion monitor for the Darex process.

21. High-Activity-Level Development Facility

The high-activity-level chemical development facility was completed. A high-activity-level laboratory was designed and was built in one cell of the building.

PART V. RAW MATERIALS PROCESSING

22. Amex Processes

Solvent extraction processes in which long-chain amines are used as extractants have been developed for recovering uranium from sulfuric acid ore leach liquors and have been successfully applied to liquors of widely varying compositions. The processes have been commercially installed in two uranium mills and are being evaluated in several pilot plants. Laboratory-scale studies have shown that the technique can be adapted to (1) the separate recovery of thorium, rare earths, and uranium from liquors from the digestion of monazite with sulfuric acid, (2) the separate recovery of thorium and uranium from Canadian Blind River ore leach liquors, (3) the recovery of vanadium from uranium process raffinates, and (4) the recovery of molybdenum as a by-product of uranium recovery from certain ores.

23. Dapex Processes

Solvent extraction processes in which dialkylphosphoric acids are used as extractants have been developed for recovering uranium from acid ore leach liquors. The efficiency of these processes is increased by the combination of neutral reagents, such as tributyl phosphate or dibutyl butylphosphonate, with the dialkylphosphoric acid. Good process economy has been shown for all liquor samples tested except those containing unusually large amounts of iron(III). A Dapex process has been installed in two uranium mills, and two other plants using the process are being constructed. A Dapex process adapted to the recovery of vanadium from acid leaches of uranium-vanadium ores has been installed at two mills.

24. Solvent Extraction Technology

In continued testing of organonitrogen compounds as extraction reagents for uranium, several amines potentially available in commercial quantities showed advantages for use in the Amex process. These included a tertiary amine with mixed *n*-octyl and *n*-decyl groups, trilaurylamine, and a tertiary amine with alkyl groups highly branched near the outer ends.

A new strong-base reagent, dimethyldidodecylammonium carbonate, appeared useful in the extraction of uranium from sodium carbonate solution.

In continued testing of organophosphorus compounds, unusually high uranium extraction power

was shown by an α -hydroxyalkyl arylphosphinic acid and by the reaction products of dialkylphosphoric acids with phosphorus pentoxide.

Neutral phosphonate esters with pentyl and hexyl groups have become commercially available and appear particularly promising for replacing tributyl phosphate in Dapex uranium extraction processes.

Survey tests of the extraction of rare earths, zirconium and hafnium, and cobalt and nickel from aqueous solutions indicated that useful separations may be obtained with amines, dialkylphosphoric acids, and trialkylphosphine oxides.

25. Fundamental Chemistry

The extraction of sulfuric acid from water by solutions of amines in benzene was well summarized by empirical equations similar to the mass-action equations expected for the apparent net chemical reactions. Only the normal sulfate salt of the amine extracted uranium effectively. The bisulfate/normal-sulfate ratio in the uncomplexed fraction of the amine depended only on the aqueous acidity. The amine/uranium ratio in the complex was constant over a range of uranium loading levels, but differed among different amines. Extraction results corroborated previous indications that the amine salts form aggregates in organic solutions.

In uranium extractions by dialkylphosphoric acid, the reagent was dimerized in alkane solutions. The extracted complex was mononuclear, $\text{UO}_2\text{X}_4\text{H}_2$, at low uranium loadings but was polynuclear at high uranium loadings, the uranium/reagent ratio approaching 1/2.

An empirical method was developed for the estimation of the dissociation of bisulfate and the actual ionic concentrations of H^+ , SO_4^{--} , and HSO_4^- in $\text{H}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ solutions ranging from pure acid to pure salt at total sulfate concentrations of 0.05 to 1 M.

The formation quotients of the aqueous uranyl sulfate complexes estimated from amine extraction data were in relatively good agreement with literature values for UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{--}$ but indicated very little formation of $\text{UO}_2(\text{SO}_4)_3^{4-}$.

26. Rare Earth Separations

Gadolinium was separated from samarium with a separation factor of 2.5 in single-stage extractions from 14 *N* HNO_3 with tributyl phosphate.



Part I
FEED MATERIALS PROCESSING

1. METALLEX PROCESS

In the Metallex process¹ chlorides of metals are reduced to mercurides by sodium amalgam and the metal is recovered by filter-pressing and vacuum distillation.

1.1 IMPROVEMENT OF METAL QUALITY BY AMALGAM PURIFICATION

The quality of sintered thorium improves with high bulk density, low free voidage, and low ThO₂ content.² The best of five aqueous-purification methods studied (Table 1.1) for removing impurities from thorium amalgam was decantation through an amalgamated outlet from an amalgamated-walled vessel following washing with oxidation inhibitors.

Nonaqueous Methods. — Results of preliminary tests on two nonaqueous methods, filtration and fused-salt-scrubbing, were unsatisfactory. Oxides and chlorides of sodium and thorium were removed

from thorium amalgams by filtration through glass and stainless steel filters after the ThHg₃ particles had been heated to boiling in mercury. With thorium amalgams prepared by sodium amalgam reduction of ThCl₄, 20 to 30% of the thorium passed through glass filters with a 40-μ pore size, and 60 to 80% passed a type 316 stainless steel filter of 55 μ pore diameter. With thorium amalgams prepared by dissolving metal in boiling mercury, less than 10% of the thorium passed through stainless steel filters of 55 μ pore size. With 0.74% uranium amalgams, more than 90% of the uranium passed a 55-μ stainless steel filter. Scrubbing of thorium amalgams with fused AlCl₃-NaCl mixtures and fused ZrCl₂ at 200–250°C effectively removed free sodium, sodium chloride, and feed ThCl₄ but also removed 60 to 70% of the reduced thorium.

1.2 DIRECT EXTRUSION OF METALLEX SINTERED THORIUM METAL

The production of massive metal by direct extrusion of sintered thorium billets rather than by arc-melting would have economic advantages. Six

¹O. C. Dean *et al.*, *The Metallex Process*, ORNL-2223 (in preparation).

²*Chem. Tech. Semiann. Prog. Rep. Aug. 31, 1956*, ORNL-2169, p 47.

Table 1.1. Effects of Amalgam-Washing Procedure on the Quality of Sintered Thorium

Source of amalgam: ThCl₄ reduced in 1.5-gal Dispersall mixer by sodium amalgam at 130°C; washed with 3 N HCl, then water, in a 4-in.-dia, 36-in.-long column

Scale: 10 g of thorium

Average of 2 to 5 values in each case

Secondary Washing Treatment	Bulk Density (g/cc)	Voidage (%)	ThO ₂ Content (%)
None	8.4	28	1.1
Further HCl-H ₂ O washing	8.4	28	0.9
Heating to 100°C and skimming	7.6	35	0.6
Vacuum drying at 25°C	9.4	20	0.7
Decantation from amalgamated vessel	9.4	20	0.7
Oxidation-inhibitor wash, followed by decantation to remove water			
Versene	9.4	20	0.5
Aniline	9.5	19	0.6
Pyridine	8.6	26	0.6

billets, $1\frac{1}{8}$ in. in diameter by $1\frac{1}{4}$ in. long, were hot-extruded at 700°C under an argon atmosphere into rods $\frac{1}{4}$ in. in diameter. Physical and chemical properties were close to specification.³ Densities were increased from 60–80% to 96–100% of the theoretical 11.7 g/cc. High iron and nickel found in three samples were probably due to exchange caused by volatilization of residual chlorides from the amalgam, reaction with steel retort walls, and reduction of metal chloride vapors on the surface of thorium metal. The ThO_2 content varied from 1.44 to 2.6 wt %. Tensile strengths and Vickers hardness numbers were close to those of thorium produced by the iodide (De Boer) process (18,000 psi and 45) and suggested that the rods were composed of metal of high purity interspersed by seams of segregated solid impurities. In tensile-strength tests, rods did not fail longitudinally, showing that cracks and voids in the original metal healed during the extrusion process.

Flat-rolling of No. 2 rod to 98.5% thickness reduction produced a ductile product without excessive edge cracking.

1.3 THE THORIUM-MERCURY SYSTEM

Constitutional Diagram. – Phase relations for the thorium-mercury system from 0 to 100% thorium and from 40 to 1000°C were investigated by Armour Research Foundation under subcontract to the Metallurgy Division.

By x-ray diffraction, electrical resistivity, and thermal analysis studies of 28 thorium amalgams at five temperatures, a partial constitutional diagram was constructed (Fig. 1.1). Pertinent details have been presented elsewhere.⁴ The significant aspects of the phase equilibria are: (a) the solubility of thorium in mercury is about 5% at 300°C and decreases to a negligible value at -32°C , the peritectic temperature; (b) the solid solubilities of thorium in mercury and of mercury in thorium are negligible; (c) two intermediate phases exist, ThHg_3 and ThHg , both of which are stable from room temperature to 1000°C in a small closed system but have a tendency to dissociate in a

dynamic vacuum at temperatures above 400°C ; (d) the diagram is not of an isobaric system, but one in which the phases are in equilibrium at the vapor pressure of mercury at the temperature stated.

Decomposition of Thorium Amalgams in a Vacuum. – The details of this study, also carried out by Armour Research Foundation, have been reported.⁴

For amalgams containing from 25 to 100% thorium, the rates of decomposition in a vacuum are exponential in time for a given temperature⁵ and approximately linear in temperature for a given decomposition time.⁶ The decomposition time required to achieve a given composition with an amalgam at different temperatures is equivalent and additive.

⁵*Ibid.*, p 10, Fig. 1.3, p 10.

⁶*Ibid.*, p 11, Fig. 1.4, p 11.

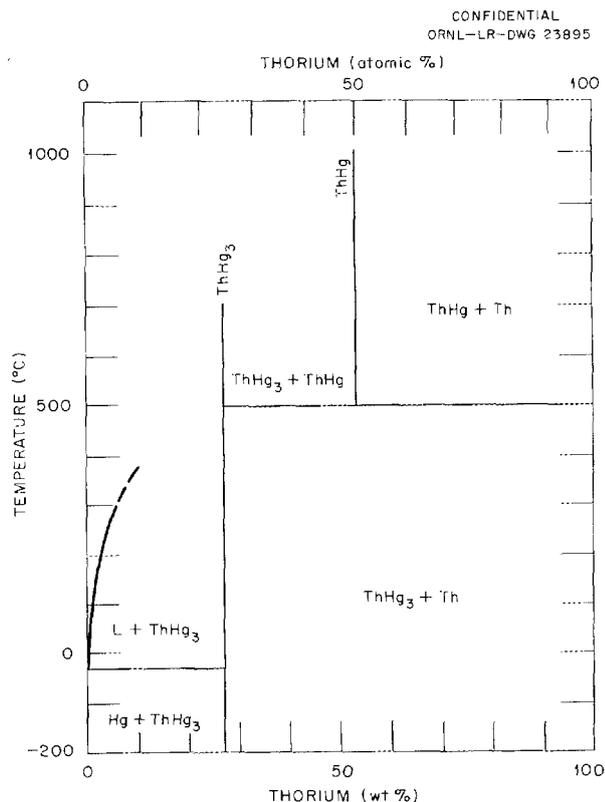


Fig. 1.1. Probable Phase Relations in the Mercury-Thorium System.

³Minutes and Recommendations of the Thorium Quality Working Committee, DPST 54-582 (Nov. 1954).

⁴Chem. Tech. Monthly Prog. Rep., Feb. 1957, ORNL-2270, p 7–12.

1.4 THORIUM REDUCTION IN 3.6-lb/hr EQUIPMENT

A large-scale (3.6 lb Th per hour) continuous unit (Fig. 1.2) for reduction of anhydrous thorium tetrachloride with sodium amalgam and for purification of the amalgam product was designed, fabricated, installed, and successfully operated after six months of component testing and revision. A total of 226 lb of thorium metal as ThHg_3 was produced in seven runs during 90 hr operation at an average rate of 2.5 lb Th per hour. The over-all reduction yield was 82.5%. The salt was reduced at 130°C in a 1.5-gal Dispersall contactor with a 20-min reaction time. A rate of 3.4 lb Th per hour was maintained over a 16-hr period in the last run, in which the sodium was in 18.5% excess over stoichiometric.

Development of a continuous reduction step was the primary concern of this engineering program. The most difficult problem, which was solved successfully, was continuous discharge of the semi-solid quasi-amalgam product from the dry contactor to the water-wash column while a contactor dewpoint of -35°F was maintained. Details have been given elsewhere.⁷

Filter-Pressing of Washed Amalgam. — Washed amalgam, ~1% thorium, was concentrated to a cake containing 7 to 15% thorium in a stainless steel filter press $5\frac{1}{8}$ in. in diameter by 17 in. long. Amalgam was fed to the press from a pressure tank under 50 to 800 psi of helium. Mercury filtrate emerged from the bottom through a porous stainless steel plate of $\sim 10\ \mu$ average pore size. When the entire system was at 800 psi, 3000 psi ram pressure was applied hydraulically to finish the cake. Cakes were 1 to 6 in. long and weighed 9 to 30 kg. Thorium losses in the filtrate varied from 50 to 80% as a result of leakage past seals, but were reduced somewhat by modification of a gasket on the filter plate of the press. Thorium losses were increased

by sudden surges of pressure and when the time between reduction and filtration was less than 24 hr. Solid impurities and water in the filter cake were reduced by installation of two amalgamated decanters in the product amalgam line between the wash column and the press.

Mercury Removal by Vacuum Distillation. — The remaining mercury was removed from the filter cakes by vacuum distillation in a large Metallex retort, whose capacity is 15 in. of $5\frac{1}{8}$ -in.-dia cake, or 20 lb of thorium metal. A retorting run, started at room temperature, approached 1100°C over a period of 6 hr and was held at 1100°C for 1 hr prior to cooling to room temperature. A total of 18.75 kg of thorium metal has been produced. Nine of the thirteen billets produced were in one piece, while four cracked into two parts. All contained large voids and cracks. The reduction in oxide content in the final six billets produced, to <0.7 wt %, was attributed to removal of water and solids from the amalgam. Bulk densities varied from 6.1 to 9.8 g/cc and the ThO_2 content from 0.38 to 1.80 wt %. With the exception of high iron and nickel content in five billets, the metal met chemical specifications.

1.5 VAPOR-PHASE METALLEX PROCESS

Three batch runs were made to determine whether the reduction reaction can be carried out continuously in the vapor phase. Small amounts of UF_6 vapor were contacted with sodium at temperatures of $450\text{--}800^\circ\text{C}$.⁸ Results showed that the UF_6 did react with the sodium at temperatures above 550°C and that solid products were formed. It was impossible to establish the valence state of the uranium in the solid product; therefore, the extent of the UF_6 reduction is not yet known.

⁷Chem. Tech. Monthly Prog. Reps. (see Appendix).

⁸Chem. Tech. Monthly Prog. Rep., Feb. 1957, ORNL-2270, p 24-25.

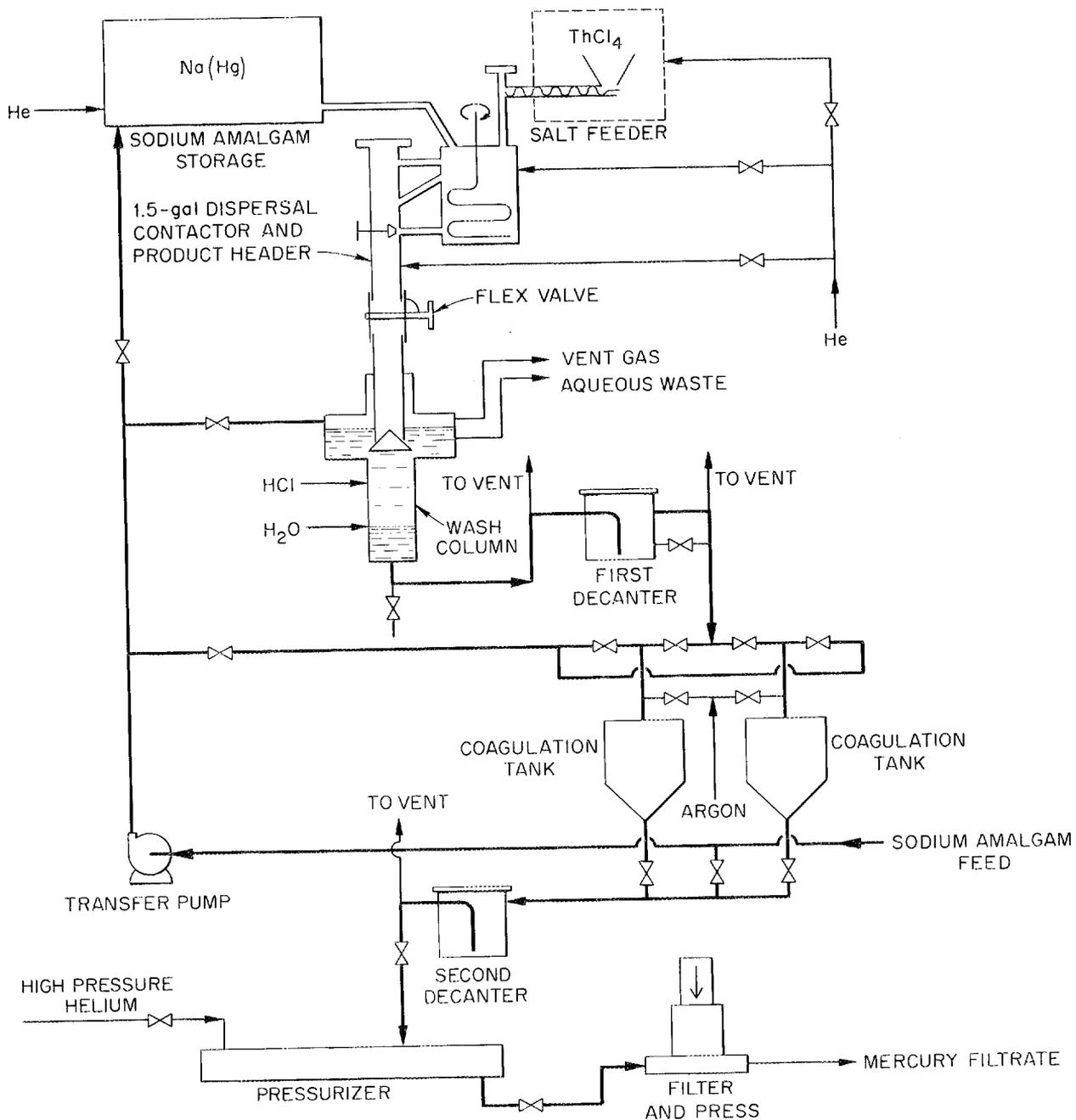


Fig. 1.2. Metallex Large-Scale Thorium Production Process (3.6 lb of Th per Hour).

2. FLUOROX PROCESS

In the Fluorox process, UF_4 is oxidized by dry oxygen or air to gaseous UF_6 . Solid UO_2F_2 or U_3O_8 residue may be recovered for recycle. Other by-products involving UF_4 and UF_4 - UF_6 intermediates may be formed under certain conditions. The UF_4 feed may be prepared in a moving-bed reactor from pelleted uranium trioxide by simultaneous reduction by starch contained in the pellets and hydrofluorination by a stream of anhydrous HF.

2.1 OXIDATION REACTOR

Laboratory studies have showed¹ that the oxidation of UF_4 to UF_6 with oxygen is feasible. Larger scale development work has been aimed at the designing of an oxidation reactor in which the high temperature required for the reaction can be readily obtained and controlled. Three types of reactors have been considered: fluidized-bed, moving-bed, and flame.

Fluidized-Bed Reactor. - A fluidized-bed reactor system (Fig. 2.1) was developed for UF_4 oxidation studies. External heating was successful at temperatures up to 750°C. With heat supplied internally from carbon monoxide and with sand in the bed, steady-state operation was obtained with both bed and wall temperatures of 850°C.

Ten runs with external heating were completed at temperatures of 565 to 735°C. Reaction rates could not be calculated from material balances, since complete product recovery was not possible with the off-gas equipment used, but they were estimated from bed compositions calculated from weights and analyses of samples. Specific surface area was taken as constant and was eliminated from the calculations. In the region of most practical importance, 700 to 735°C, these agreed well with rates calculated from laboratory data (Sec. 2.3) on the basis that the reaction is first order with respect to the UF_4 surface area. Agreement was only moderate over the entire temperature range studied (Fig. 2.2). Tentatively, it was assumed that reactor performance in the 735 to 850°C range can be estimated from laboratory rate data.

The components of the fluidized-bed system include a 3-in.-dia Inconel reactor equipped with

electrical resistance heaters; two porous nickel gas filters in parallel equipped for blowback cleaning and solids recovery; two 1-ft³ copper cold traps valved for parallel or series operation; and two calcium sulfate-packed UF_6 -scavenging traps valved for parallel or series operation. A continuously recording gas analyzer for monitoring the UF_6 concentration in the product stream is being constructed at K-25. The unit operates by condensation of UF_6 from a gas stream at a known temperature and total pressure to indicate the partial pressure of UF_6 in the stream. Six- to twelve-pound batches of UF_4 or mixtures of UF_4 and UO_2F_2 were charged in each run, and the reactor was raised to operating temperature while the bed was being fluidized with dry nitrogen. Oxygen was then fed at 24 to 40 scfh, and changes in composition were followed by withdrawal of samples at intervals for analysis. Preliminary tests in a 3-in.-dia glass column with sized sand and UF_4 had indicated 40 × 100 mesh material to be suitable for fluidization studies. Feed material in this size range was prepared from UF_4 by compacting and coarse grinding. Effects of variation of UF_4 surface area, entrainment from the bed, gas velocity, partial pressure of oxygen, and possible vaporization or decomposition of UO_2F_2 and UF_4 could not be evaluated effectively under the conditions.

Yields of UF_6 product were not determined,² but there were many evidences of UF_6 formation, the most frequent being a characteristic white mist of UO_2F_2 formed by reaction of UF_6 in the off-gas with moisture in the air. Off-gas samples taken in a miniature cold trap contained a white solid which sublimed when warmed with body heat and which was shown by analysis to contain U(VI). Other uranium fluorides isolated from parts of the off-gas system appeared to be UF_4 - UF_6 intermediates, such as U_4F_{17} , a chocolate-brown solid which was identified by x-ray diffraction, and a light-tan substance which was not identified. Both were extremely corrosive to glass, however, and probably exerted a UF_6 partial pressure. These intermediates were probably formed by the product of reaction of UF_6 with UF_4 , which sublimed as

¹Chem. Tech. Semiann. Prog. Rep. March 31, 1955, ORNL-1881, p 24.

²Equipment to permit material balances to be made has since been installed.

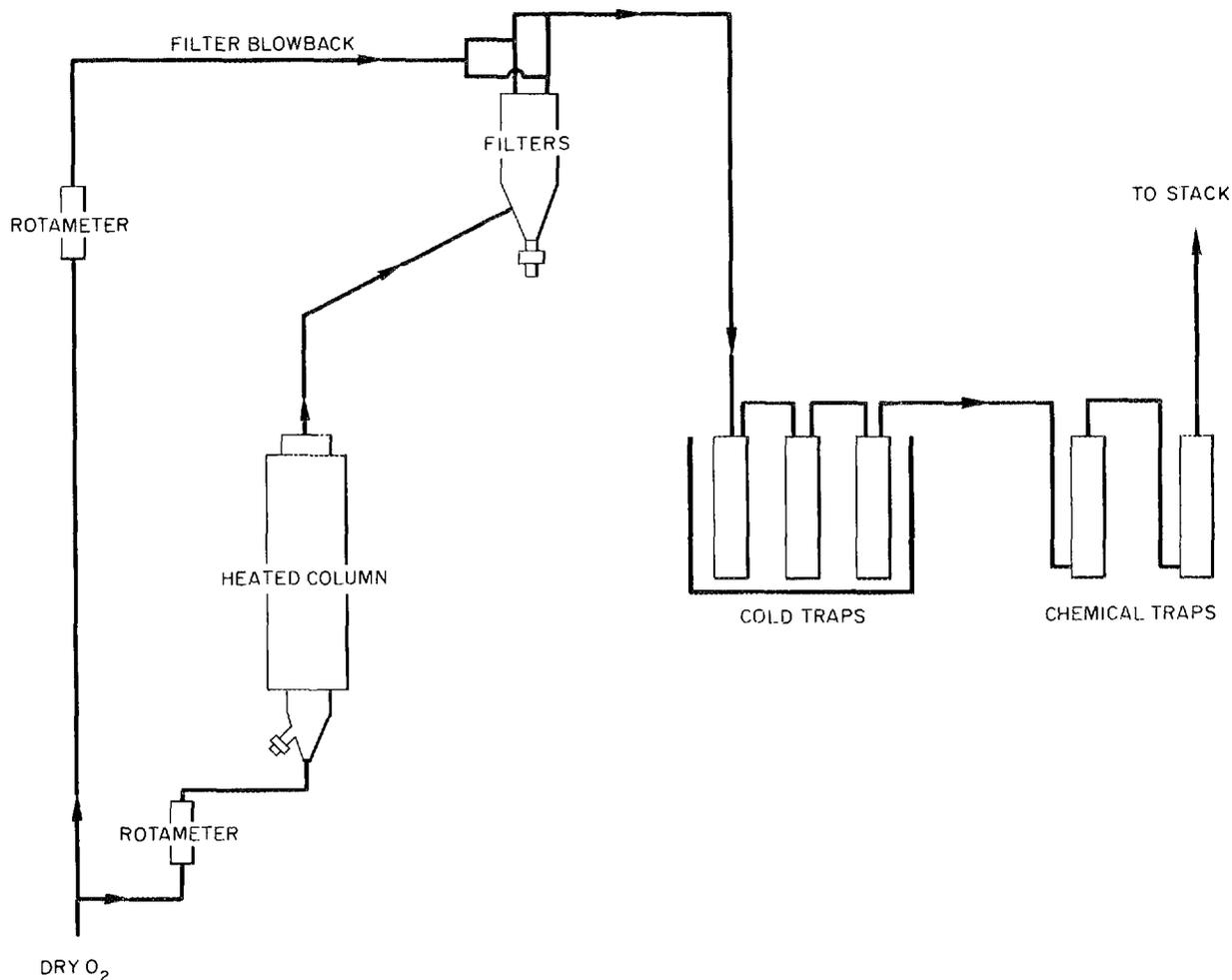


Fig. 2.1. Equipment Flowsheet for Oxidation in Fluidized-Bed Reactor.

$UF_5 \cdot UF_5$ and then disproportionated to gaseous UF_6 and the solid intermediates. This could have reduced the yield of UF_6 from 50% to as low as 25% of the uranium fed to the system.

Corrosion of metals by UF_6 at temperatures above $600^\circ C$ is a critical problem. The experimental Inconel fluidized-bed reactor operated remarkably well under a variety of conditions. The worst effects of corrosion and erosion, noted through thermocouple wells in the bed, were in the turbulent region at the interface between the fluidized

bed and the gas phase. During steady, well-controlled operation, a dense adherent film built up and apparently protected the metal from further attack. During intermittent operation, involving extreme temperature cycling in which the maximum temperature gradient as well as the most rapidly changing temperature was at the wall, the protective coating flaked off, exposing metal surfaces to further attack.

If neither Inconel nor any other alloy proves feasible, alternative methods of operation include

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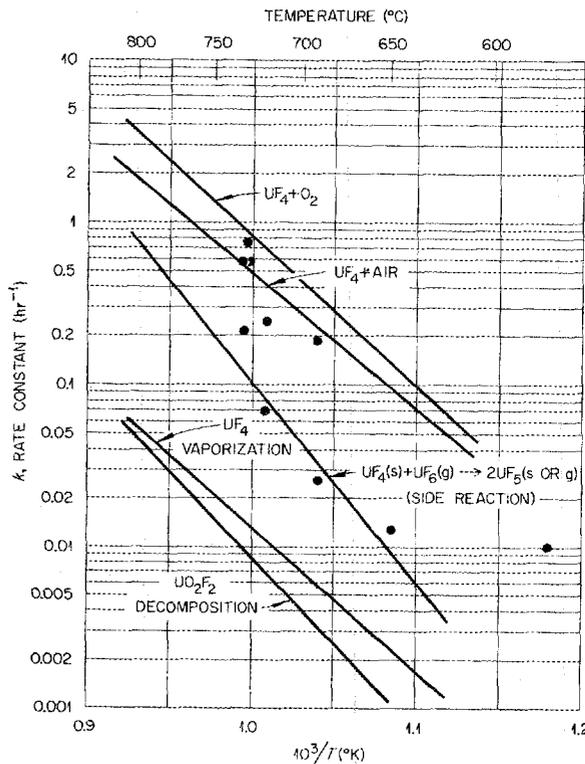


Fig. 2.2. Comparison of Fluidized-Bed-Reactor Data (Points) and Laboratory Data (Solid Lines) on Oxidation of UF_4 .

internal heating by combustion of carbon monoxide with oxygen in the fluidized bed, with either a refractory wall or liner (very high fired UO_2 or other suitable material) or a transpiration-cooled porous Inconel wall.

Moving-Bed Reactor. - Internal heating by carbon monoxide oxidation was successful in one 12-hr run in the 4-in.-dia moving-bed reactor. Internal heating by oxidation of particulate carbon included in the feed pellets was abandoned because of difficulty in temperature measurement and control; in every run, the bed fused as a result of excessive local temperatures.

Flame Reactor. - A flame reactor (Fig. 2.3), which will continuously contact fluidized UF_4 powder with oxygen in a $CO-O_2$ flame, was designed and built. The different components of this reactor (solids feeder system, pilot light assembly and burner assembly) have been tested individually, and the complete assembly is now ready for testing.

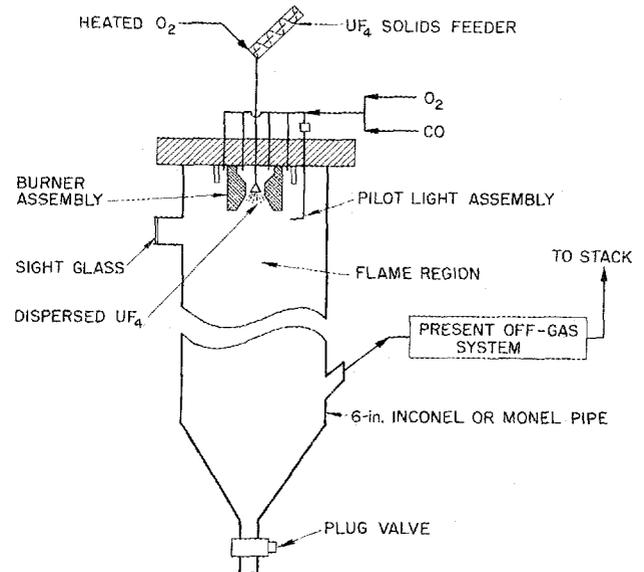


Fig. 2.3. Flame Reactor for Oxidation of UF_4 in an O_2-CO Flame.

The following optimum operating conditions were indicated from the component tests:

Flame temperature	1400°C
CO in fuel	50%
UF_4 feed	-200 +325 mesh
Feed rate	500 g/hr

In a preliminary test, black U_3O_8 was observed in the UF_4 powder that had passed through an approximately 1100°C flame.

2.2 REDUCTION-HYDROFLUORINATION REACTOR

A method was developed earlier³ for the preparation of UO_3 pellet feed, suitable for reduction in the moving-bed reactor, from UO_3-H_2O and $UO_3-starch-H_2O$ mixtures. In a combined operation, reduction and hydrofluorination of UO_3 to UF_4 would be followed by oxidation of UF_4 to UF_6 . In laboratory tests the addition of moderate amounts of

³Chem. Tech. Semiann. Prog. Rep. Sept. 30, 1955, ORNL-2000, p 43.

uranyl fluoride was not detrimental in the pelletizing of UO_3 -starch mixtures with water. In comparative attrition-impact tests on UO_2F_2 -containing pellets, physical properties were similar to those of standard pellets.

2.3 BASIC CHEMICAL STUDIES

Background information has been reported^{4,5} on the stoichiometry of the reaction of UF_4 with dry oxygen, $2\text{UF}_4 + \text{O}_2 \rightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$, together with side reactions and thermodynamics. The rates of decomposition of UO_2F_2 and of vaporization of UF_4 were negligible compared with the rate of reaction of UF_4 with oxygen at temperatures below 815°C . However, the compound UF_5 , indicated previously,⁶ was isolated at temperatures above 700°C , and appeared to be the product of a side reaction, $\text{UF}_4 + \text{UF}_6 \rightarrow 2\text{UF}_5$. The extent of this reaction depended somewhat on the packing of the powdered UF_4 samples. In thermobalance rate studies⁷ in which thin layers of 60-mesh UF_4

particles (~ 1 g) were used, this side reaction was not evident at temperatures below 750°C . Above this temperature approximately 20% of the UF_4 was consumed. In a kinetic study,⁸ the oxidation reaction between 550 and 815°C was found to be first order with respect to UF_4 surface area, to depend on the oxygen partial pressure, and to be highly temperature dependent. The rate constants for reaction with pure oxygen may be expressed as $\log k_o = 10,040/T + 6.9199$, where k_o has the units of moles/min \cdot m². The rate constant for the reaction with dry air, $\log k_a = -10,280/T + 6.9160$, was approximately half as large at each temperature as that with dry oxygen. No attempt was made to determine more exactly the effect of oxygen partial pressure on the reaction rate.

The rates were measured with a recording thermobalance. Two types of UF_4 were used, one with a specific surface area at 25°C of 0.3 m²/g, the other 1.26 m²/g. The material with the lower specific surface area showed typical first-order behavior between 700 and 750°C . Below 700°C , there were deviations from typical behavior as a result of sintering of the UF_4 . Sintering effects were prevalent at most temperatures when the material with the higher specific surface area was used. For these reasons and because of the marked effect of the UF_5 -producing side reaction above 750°C , rate constants were determined primarily from initial rates.

⁴L. M. Ferris, *Laboratory Development of the Fluorox Process: The Reaction of UF_4 with Dry O_2 . I. Side Reactions and Thermodynamics*, ORNL-2180 (March 13, 1957).

⁵L. M. Ferris, "A Chemical Study of The Reaction: $2\text{UF}_4 + \text{O}_2 \rightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$," Paper 113, presented at Miami, Florida, 132nd National American Chemical Society Meeting, April 7-12, 1957.

⁶*Chem. Tech. Semiann. Prog. Rep. Aug. 31, 1956*, ORNL-2169, p 42.

⁷L. M. Ferris and E. G. Carter, *Laboratory Development of the Fluorox Process. II. A Thermogravimetric Study of the Chemical Kinetics for the Reaction of UF_4 with Dry Oxygen*, ORNL-2216 (May 24, 1957).

⁸L. M. Ferris, paper in preparation.

3. EXCER PROCESS

The Excer process¹ is a method for producing pure UF_4 from uranium concentrates by aqueous reduction and precipitation. The concentrates may be prepared by ion exchange techniques. Detailed flowsheets² were prepared for adaptation of the Excer process to ore concentrate, ore leach, and solvent extraction uranyl nitrate products.

3.1 REVISED FLOWSHEET

The present Excer flowsheet differs from earlier³ flowsheets chiefly in that the $UF_4 \cdot 3/4H_2O$ product is precipitated outside the electrolytic reduction cell. This permits operation of the cell at room temperature rather than at $90^\circ C$, as required with simultaneous reduction and precipitation, and eliminates the necessity for the flowing mercury cathode.

3.2 REDUCTION STEP

Electrolytic. - A 9- by 10-in. electrolytic cell with a Hastelloy C cathode was used to reduce U(VI) to U(IV) in a chloride solution. It was run for 700 hr with no significant damage to the cell components. The anode was platinized tantalum in 0.5 M H_2SO_4 , separated from the uranyl chloride-hydrochloric acid catholyte by an Ionics, Inc., cation exchange membrane. Recent laboratory studies at Ionics indicated that current efficiencies were higher with a graphite cathode. An 18- by 20-in. ion exchange membrane cell was delivered by Ionics for testing at ORNL.

Iron. - Iron reduction is attractive because of low operating and equipment costs, and 100% reduction efficiency has been demonstrated. In laboratory tests the iron was completely eliminated from the UF_4 in the precipitation step. The recycle of waste acid with large quantities of iron present would not be a serious problem in an ore mill or in

an enriched-fuel recovery plant. Extra ion exchange equipment may be required in an ore concentrate plant, however, for removal of iron from the uranium product.

3.3 PRECIPITATION, WASHING, AND DRYING

Specifications require a minimum bulk density of 3.0 g/cc for UF_4 that is to be reduced to metal. The density of the dehydrated product is the same as that of the hydrate. Precipitation of the hydrated salt at temperatures below $90^\circ C$ gives $UF_4 \cdot 2.5H_2O$,⁴ which has a low bulk density. In laboratory experiments $UF_4 \cdot 3/4H_2O$ with a tap density of 3.0 g/cc was produced by addition of HF to a UCl_4 solution at $90^\circ C$. The density of the $UF_4 \cdot 3/4H_2O$ was increased from 3.0 g/cc to 3.5 g/cc by pressing at 10 tsi in a Stoker pill machine.⁵

In previous tests the product was filtered through laboratory filter paper or Buchner funnels. Tests are to be made with a leaf-type filter for consideration for plant-scale operation. From visual observation there should be no difficulties in filtering the $UF_4 \cdot 3/4H_2O$.

The filter cake has been dried in a simple tray drier. Twenty batches of precipitate, 1 to 5 lb per batch, have been dried to the hydrate in 12 hr each at $110^\circ C$.

3.4 DEHYDRATION

The water of hydration must be removed from the product material for use in either metal or UF_6 production. With the compressed and ground hydrate as starting material, initial studies were made in a Ribbon-Flite screw dehydrator.⁶ Recent work has been with a continuous two-stage fluidized-bed dehydrator (Fig. 3.1). Although this system was

¹A paper has been submitted to *Industrial and Engineering Chemistry* on the Excer process, and subsequent papers containing more recent information are being prepared for submission to *Chemical Engineering Progress*.

²*Chem. Tech. Monthly Prog. Rep. Feb. 1957*, ORNL-2270, p 40-42, Figs. 3.7-3.9.

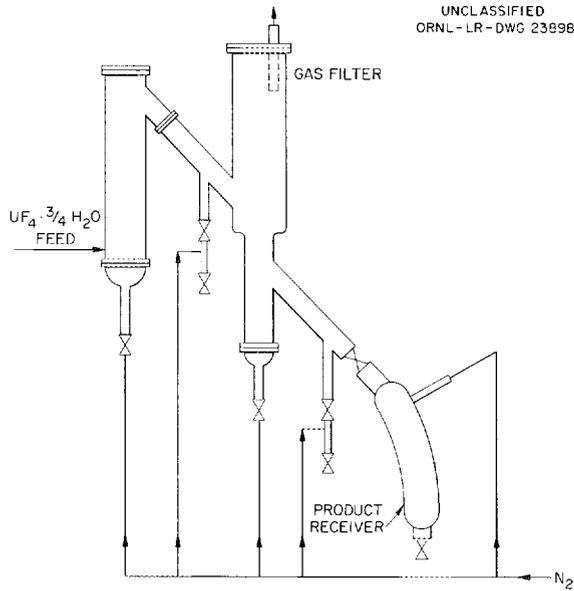
³I. R. Higgins and J. T. Roberts, *Development of the Excer Process. I.*, ORNL-1696 (April 13, 1956); J. A. Marinsky, *Development of the Excer Process. II.*, ORNL-1979 (April 17, 1956).

⁴A. L. Allen *et al.*, *Electrochemical Preparation of Uranium Tetrafluoride; Part I. Low Temperature Cell*, K-680 (Nov. 10, 1950); R. W. Anderson, A. L. Allen, and E. W. Powell, *Electrochemical Preparation of Uranium Tetrafluoride; Part II. High Temperature Cell*, K-681 (Dec. 22, 1950).

⁵In more recent tests, not yet completely evaluated, precipitation at the boiling point gave products of 3.5 to 3.7 g/cc tap density.

⁶*Chem. Tech. Semiann. Prog. Rep. Aug. 31, 1956*, ORNL-2169, p 45, Fig. 9.3.

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designed as a continuous unit, in preliminary tests it was operated as a batch unit. A drying time of 4 hr at 350°C followed by 4 hr at 450°C reduced the water content of the UF_4 to the desired specifications, that is, a maximum of 0.2% H_2O . The capacity of the equipment operating as a two-stage unit is estimated as approximately 3 lb/hr.

Fig. 3.1. Excer Dehydration Equipment Flowsheet.

Part II
HETEROGENEOUS POWER REACTOR FUEL REPROCESSING

4. HEAD-END TREATMENTS FOR SOLVENT EXTRACTION PROCESSING

Various head-end treatments, both chemical and mechanical, are being studied for preparing fuel elements with difficultly soluble components for solvent extraction. Development of processes for classes of fuels rather than for individual fuels is being emphasized.

4.1 DAREX PROCESS FOR STAINLESS STEEL-CONTAINING FUELS

The Darex head-end treatment is being developed for stainless steel-containing fuels. It consists in dissolving the fuel in dilute aqua regia and stripping the chloride¹ from the product.

On an engineering scale, continuous dissolution and stripping of HCl from the dissolver product as separate operations have been demonstrated. Equipment has been constructed to provide an integrated loop (Fig. 4.1) in which the four process steps - dissolution, chloride stripping, rectification, and nitric acid evaporation - will be operated together. The stripper-rectifier column is a 4-in.-dia Pyrex pipe with 11 Vycor bubble-cap plates in the stripping section and 12 in the rectifying section. In the stripper, the dissolver product is contacted with concentrated HNO_3 vapors. In the reboiler, the stripped product is boiled with makeup nitric acid to supply the stripping vapor. Concentrated product is drawn off the reboiler, diluted, and sent to solvent extraction. The stripping vapors, containing the chloride stripped from the dissolver product, flow overhead to the rectifier, where they are concentrated by removal of water. This dilute aqua regia condensate, along with makeup HCl, flows back to the dissolver, thus completing the loop. The effect of loop operating conditions on dissolution rates, chloride removal, rectification, reboiler operation, and off-gas evolution during dissolution of fuel with various stainless steel/uranium ratios in 5 M HNO_3 -2 M HCl will be studied.

Dissolution. - In laboratory batch studies the optimum acid concentration appeared to be 2 M HCl and 5 to 6 M HNO_3 (Fig. 4.2). These mixtures gave the highest dissolution rates and held the greatest amounts of dissolution products in solution. About 75 g of type 304 stainless steel and 80 to 85 g of APPR fuel elements per liter dissolved on refluxing. Under continuous process

¹Elimination of the chloride-stripping step has been considered; see Sec. 5.1.

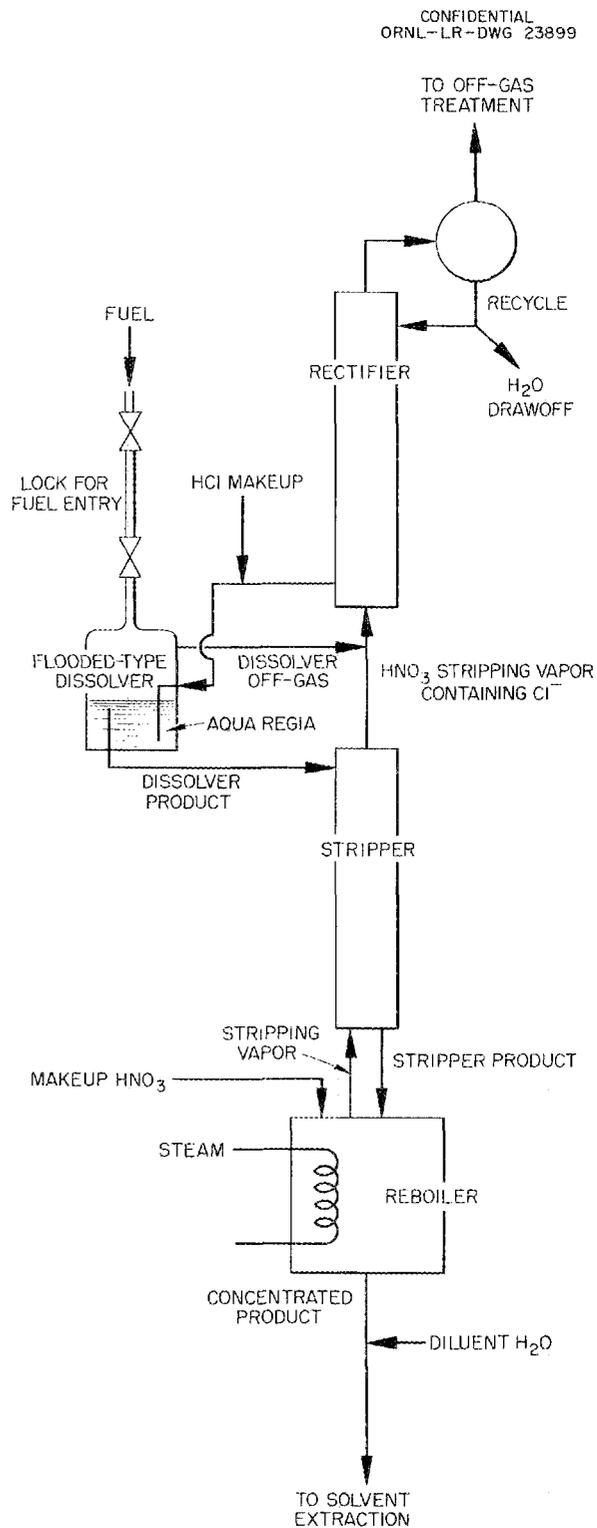


Fig. 4.1. Schematic Flowsheet of the Darex Head-End Process.

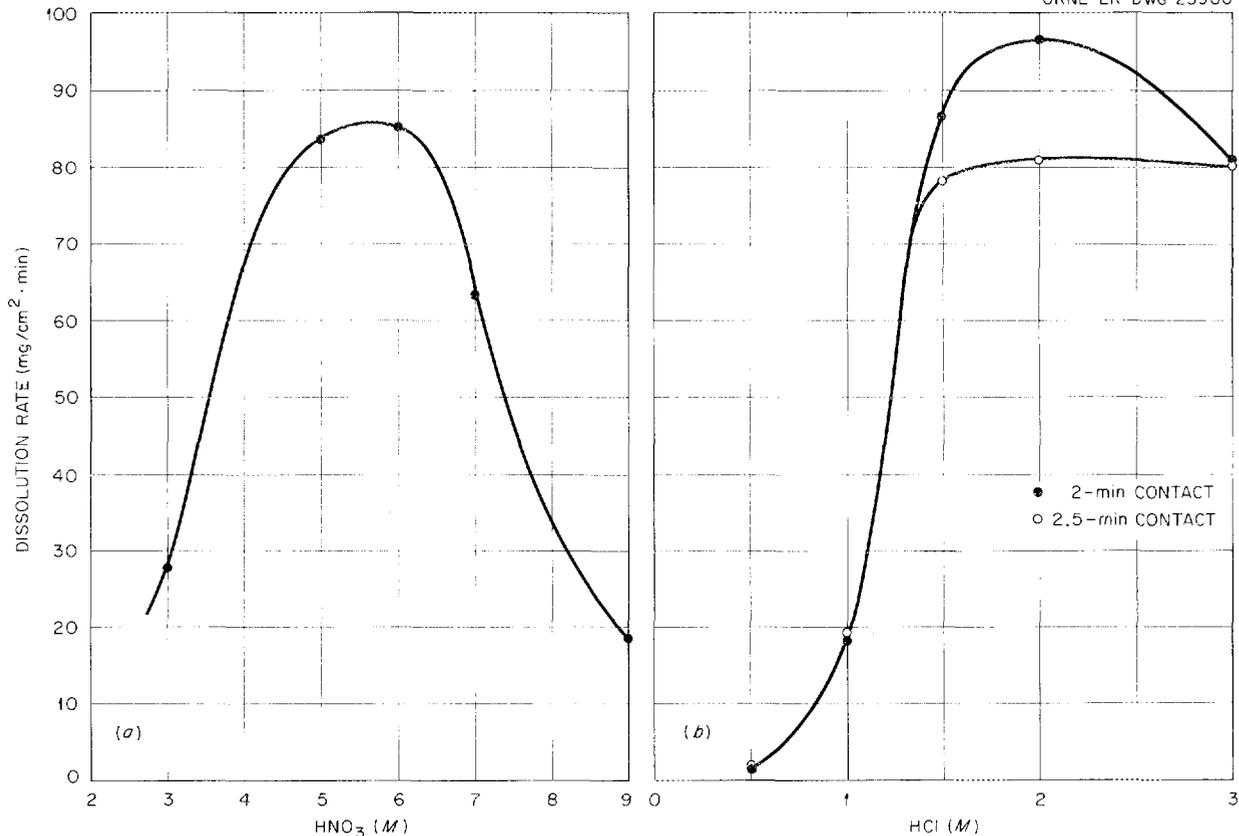
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Fig. 4.2. Rate of Dissolution, at 100°C, of Type 304L Stainless Steel in (a) 1.5 M HCl- x M HNO₃ and (b) 5 M HNO₃- x M HCl.

conditions, the weight of APPR fuel element dissolved and retained in solution was 50 to 55 g/liter. The solids remaining after dissolution were silica and metal carbides and contained only a trace of uranium. About 30% of the boron present remained in the dissolver and reflux condenser, the remainder escaping in the off-gas. Because of the relatively large amount of heat evolved during dissolution, the containment and control of the reaction on a batch scale presents a problem. Continuous dissolution, with the rate of reaction controlled by the level of the acid on the fuel element, appears more practical.

Since the chloride is removed before the solution is solvent-extracted, the initial chloride concentration should be as low as possible, and the investigation therefore did not include high concentrations of HCl. When the HCl concentration fell below about 1 M, the stainless steel was occasionally passivated, particularly when

fresh samples of metal were exposed to solutions containing dissolution products of stainless steel.

In engineering-scale tests, continuous dissolution was studied on 1-in. type 304 stainless steel tubing and on stainless steel-UO₂ strips containing 5.5 to 11% UO₂. The liquid phase was well mixed and no concentration gradient was noted. The surface area exposed to reaction was controlled by the liquid level in the dissolver. Reaction rates were high, which will permit use of a dissolver that is small compared with the stripper and rectifier. Chloride losses from the dissolver were negligible, and hydrogen was not present in the off-gases, showing that most of the hydrogen ion formed water.

Reaction rates for four acid feeds, 5 M HNO₃-2 M HCl, 5 M HNO₃-1.5 M HCl, 3 M HNO₃-2 M HCl, and 3 M HNO₃-1.5 M HCl, were in the range 15 to 60 mg/cm²·min and were correlated with the F/S (acid feed rate/metal surface area) ratio.

The presence of UO_2 did not affect the stainless steel reaction rate except with 3 M HNO_3 -1.5 M HCl, with which the reaction rates of the stainless steel- UO_2 strips were 50% higher than those of stainless steel alone. For F/S ratios below 0.5 cc/min/cm² the reaction rates of stainless steel- UO_2 were approximately the same for the four acid feeds, but the rates leveled off more quickly with the more dilute acid feed compositions at higher F/S ratios.

Metal ion concentrations in the dissolver product stream decreased as the F/S ratio increased. For a given ratio, metal loadings decreased as the feed acid concentration decreased. Although metal loadings were sometimes higher than 100 g/liter, there was evidence that loadings above 50 g/liter contained some metal in suspension rather than in true solution. No solids except silica built up in the stripping column. On cooling

to room temperature and standing for several weeks, the undissolved solids remained in suspension, but they were separated by centrifugation and readily dissolved in water at room temperature. They contained 13 to 15% nickel, compared with 8 to 10% in the stainless steel.

The dissolution rate of stainless steel alone was plotted as a function of H^+ and NO_3^- consumption rates. From the slope of the curves, consumption of 3.90 moles of H^+ per mole of stainless steel dissolved was calculated (Fig. 4.3a). For the 5-2 and 3-1.5 acid feeds, the nitrate consumption was 1.41 moles per mole of stainless steel dissolved, and for the 5-1.5 and 3-2 acid feeds, it was 0.35 mole (Fig. 4.3b). Nitrate decomposition to NO , NO_2 , and N_2 was the principal source of noncondensable off-gases (Table 4.1).

HCl Stripping. - In nine stripping runs with the Darex dissolver solution and synthetic feeds, high

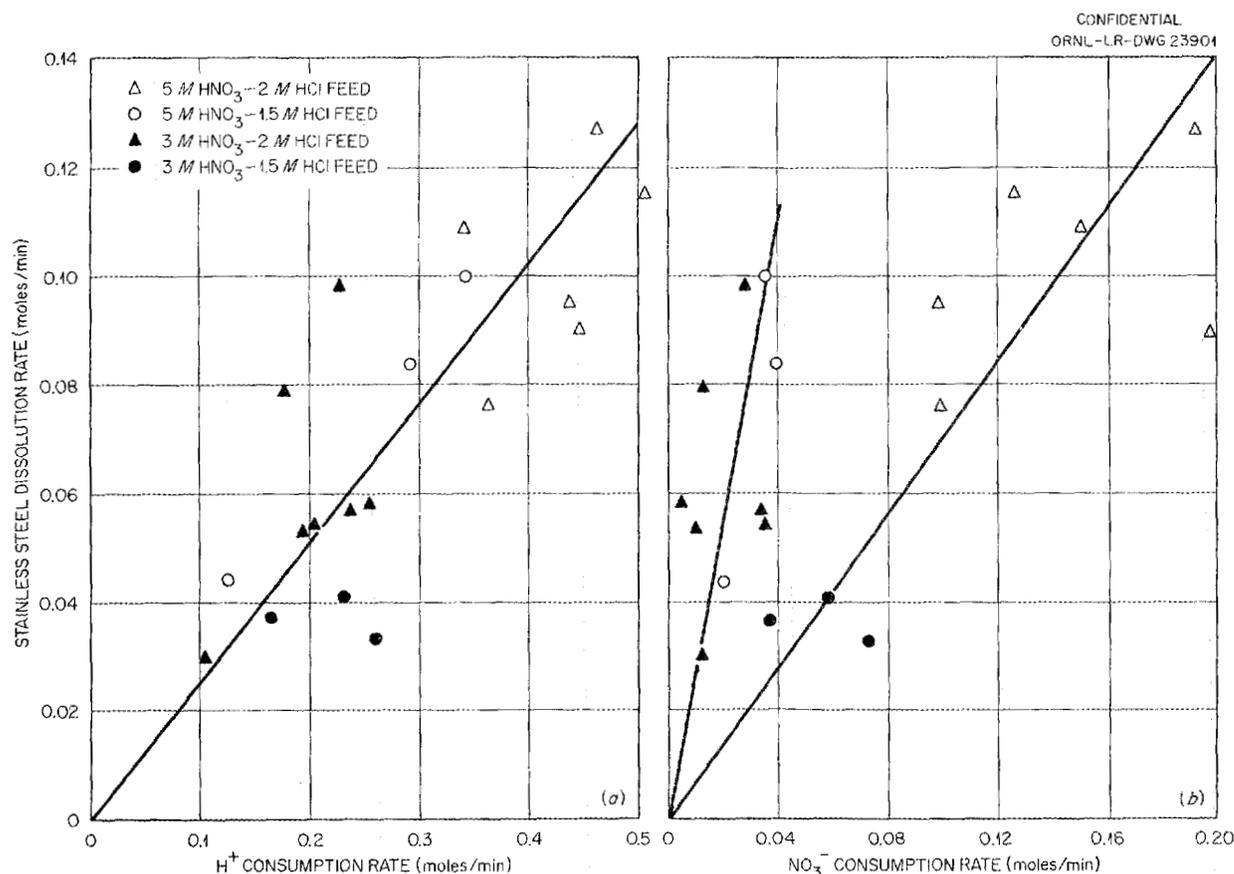


Fig. 4.3. Rate of Dissolution of Stainless Steel as a Function of (a) Rate of Consumption of H^+ and (b) Rate of Consumption of NO_3^- .

HNO₃ vapor concentrations and high V/L (vapor up the column/liquid down the column) mole ratios gave the best chloride removal. However, with less than 50 ppm chloride in the stripper product, with high HNO₃ in the vapor, and, in the case of the azeotrope (38.3 mole %), with high V/L ratios, volatile chloride losses were high because of decomposition. Stripping vapor compositions used were 20, 28, and 38.3 mole % HNO₃, and the V/L ratios ranged from 0.9 to 6.1.

Correlation of the experimental data from the first seven runs (Fig. 4.4) gave a method for predicting, for any stripping vapor concentration, the V/L ratio required for operation of the loop

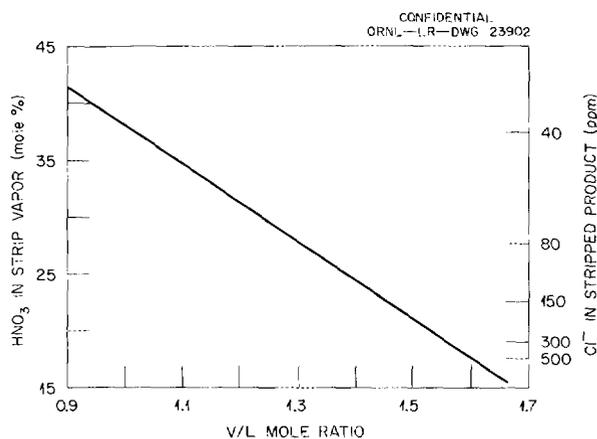


Fig. 4.4. Mole Ratio V/L Required to Reduce Chloride Concentration in Operation of Darex Loop Flowsheet with Various Concentrations of HNO₃ in Stripping Vapor. Dissolvent: 2 M HCl-5 M HNO₃.

flowsheet to reduce the chloride concentration of the dissolver product to the desired level.

In a total-reflux run made by boiling a nitric acid-water mixture in the column, plate efficiencies were 30 to 35%. This can be expected to change with boilup rate, however.

Reboiling-Feed Adjustment. - Solvent extraction requires a feed about 3 N in H⁺; the most economical way to remove HNO₃ from the highly acidic stripper product is to vaporize an HNO₃-H₂O mixture from it and to use this vapor as feed to the stripper. Stripper product was concentrated by batch boiling from about 30 to 260 g of stainless steel per liter. The normality of the HNO₃-H₂O distillate dropped from 15.3 to 14.0, and the H⁺ concentration of the solution dropped from 14 to about 2.5 N.

4.2 ZIRCEX PROCESS FOR ZIRCONIUM-CONTAINING FUELS

The Zircex process has been selected for intensive development for zirconium-containing fuels. It consists in hydrochlorinating the fuel to form volatile ZrCl₄ and processing the uranium residue either by dissolution in nitric acid, stripping off the chloride, and solvent extraction, or by the Hermex (Sec. 10.1) or the fused salt-fluoride volatility process (Sec. 10.2).

Decladding of Uranium Dioxide Cores. - Reactor elements of uranium dioxide clad with zirconium have high structural integrity and chemical stability. Removal of the zirconium cladding by hydrochlorination (Fig. 4.5a) with negligible loss of uranium appears feasible. The same vessel

Table 4.1. Darex Dissolver Off-Gas Compositions and Rates

Acid Feed Composition	UO ₂ in Stainless Steel (wt %)	Off-Gas Composition (%)				Cl Loss (%)	N Loss (%)
		Total Chloride	NO ₂	NO	N ₂		
5 M HNO ₃ , 2 M HCl	0	4.4	57.0	10.0	28.7	4.6	24.6
	9.3	1.1	75.1	7.1	16.6	1.0	20.2
3 M HNO ₃ , 2 M HCl	0	1.0	49.2	28.7	21.0	0.2	8.6
	8.0	<1	57.1	23.9	18.9	<0.3	20.3
3 M HNO ₃ , 1.5 M HCl	0	<1	50.6	23.3	25.8	<0.7	19.0
	10.0	1.0	41.0	41.0	17.0	1.0	28.3

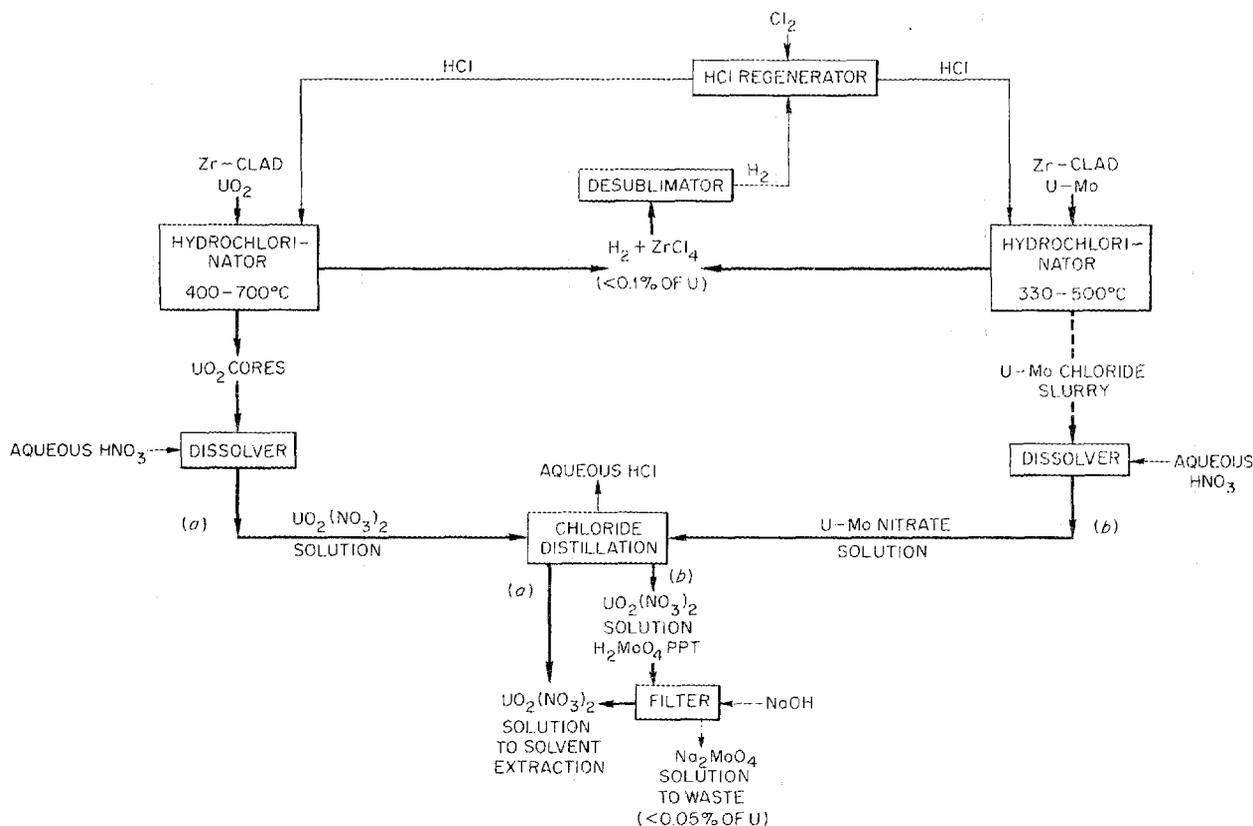


Fig. 4.5. Zircex Process Flowsheet for (a) Zirconium-clad UO_2 and (b) Zirconium-clad U-Mo.

may be used for the hydrochlorination and for the nitric acid dissolution in a batch process.

Sections of a PWR blanket element (zirconium-clad UO_2) were declad completely in 2.5 hr by hydrochlorination at 600°C (Table 4.2). Reaction between the hydrogen chloride gas and the uranium dioxide cores was insignificant, although a small amount of chloride, 0.1 to 16.3 mg per gram of uranium, was absorbed by the core. With the smaller amounts of chloride the nitric acid solution of the residue (325 g of uranium per liter) contained only 300 ppm of chloride, which is considered noncorrosive to stainless steel. About 0.5 mg of water-soluble zirconium per gram of uranium was found with the uranium dioxide residue, probably as the nonvolatile zirconyl chloride.

Zirconium-clad fuel elements that had been exposed to high-temperature pressurized water under simulated PWR conditions were coated with a layer of chemically inert zirconium dioxide, which

did not react with hydrogen chloride or dilute aqueous HF. This layer was ruptured in 10 to 15 min by passing small quantities of aluminum ammonium chloride vapor over the fuel element with the hydrogen chloride gas at 450°C. Hydrochlorination of the exposed zirconium metal then proceeded rapidly, and undercut and removed the oxide.

Decladding and Total Dissolution of Uranium Metal and Alloys. - Zirconium cladding can be removed from uranium alloy fuels by hydrochlorination, and the core can then be dissolved by aqueous reagents or hydrochlorinated completely. Some uranium chlorides form from the core alloy in most cases when the cladding is hydrochlorinated.

The feasibility of this process (Fig. 4.5b) was demonstrated with 1-in.-long sections of APDA fuel-element rods, which are $\frac{1}{8}$ -in.-dia uranium-molybdenum alloy cores clad with 4 mils of zirconium. Removal of the zirconium cladding and complete hydrochlorination of the core required

15 hr at 330°C or 9 hr at 370°C. Uranium losses due to the volatility of the uranium chloride were not prohibitive below 500°C (Table 4.3). The core disintegrated completely and was readily slurried with water. The uranium was converted to the uranyl form by addition of nitric acid, and the molybdenum was converted to water-soluble chloride complexes. Removal of the chlorides by distillation precipitated insoluble molybdic acid, which was filtered off with no retention of dissolved uranium.

Direct dissolution of uranium alloys containing 2 to 20% zirconium requires fluoride ion to reduce the accumulation of the explosive zirconium-

uranium intermetallic compound. Hydrochlorination of 98% uranium-2% zirconium alloy at 400°C followed by dissolution of the residue in nitric acid recovered 99.9% of the uranium (Table 4.3). The zirconium-uranium intermetallic compound is destroyed in the hydrochlorination.

Niobium alloys were attacked similarly, but the insoluble uranium losses were slightly greater, about 0.5% at 500°C.

Aluminum alloys of uranium had very high uranium volatility losses on hydrochlorination, for example, 29% loss at 400°C from a 15% uranium alloy.

Table 4.2. Zircex Decladding of PWR Blanket Element

Hydrochlorination		Zr Removal (%)	Uranium Distribution (%)		
Temperature (°C)	Time (hr)		Volatile	Soluble in 8-10 M HNO ₃	Insoluble in 8-10 M HNO ₃
400	4	90	0.001	99.0	0.03
500	4	100	0.1	99.85	0.05
600	2.5	100	0.03	99.87	0.1

Table 4.3. Hydrochlorination Behavior of Uranium Alloys

Alloy	Hydrochlorination		Sublimate	Uranium Distribution (%)	
	Temperature (°C)	Rate (mg/cm ² ·min)		Hydrochlorinator	
				Soluble in 8-10 M HNO ₃	Insoluble in 8-10 M HNO ₃
97.9% U, 2.1% Zr	400	1.25	0.003	99.9	0.08
	500	2.83	0.004	99.7	0.26
	600	9.55	0.09	99.3	0.65
98% U, 2% Nb	400	0.77	0.007	98.7	1.26
	500	0.79	0.04	99.5	0.48
	600	0.75	1.24	97.7	1.04
15% U, 85% Al	400	2.14	29.2	69.6	1.24
	500	0.77	16.2	83.6	1.11
	600	3.93	72.0	27.6	0.40
99.25% U, 0.41% Zr, 0.12% Nb, 0.22% Mo	400	0.132	0.22	97.8	2.18
	500	0.425	0.45	98.9	1.21
	600	2.22	6.54	93.2	0.24
10-12% Mo, 90-88% U	400	2.96	0.078	99.9	No solids
	500	10.33	0.58	99.4	No solids
	600	24.0	11.60	88.3	0.061

Engineering-Scale Developments. — Reaction rates, uranium losses, and heat transfer properties of vapor-phase hydrochlorination were investigated on an engineering scale.

Reaction rates increased as the temperature increased and as the uranium content of the alloy decreased. Uranium losses to the sublimate increased as the temperature increased and as the uranium content of the alloy decreased. With zirconium-uranium alloys containing 0 to 60% uranium at temperatures of 400 to 700°C and an HCl partial pressure of about 0.6 atm, the reaction rate varied from 2.5 to 27.0 mg/cm²·min. Rates for 1.5% Nb–5% Zr–93.5% U were 5.3 mg/cm²·min at 475°C and 7.9 mg/cm²·min at 545°C. Uranium losses to the sublimate ranged from 0.001 to 2.2% (Table 4.4). Losses of uranium to the nitric acid-insoluble residue showed no clear trend as a function of either composition or temperature. The uranium insoluble in 10 M HNO₃ appears to be in solid solution with zirconium oxide.² This uranium might be recovered by dissolution in a fused fluoride, but it is reported as a loss to serve as a guide to the feasibility of aqueous processing.

A promising application of the hydrochlorination reaction is the removal of Zircaloy-2 cladding from UO₂ fuel elements and blankets. Because of the large HCl concentration gradient in the gas phase

of production-size hydrochlorinators, the dependence of the reaction rate on the HCl concentration was studied. The empirical rate equation for the hydrochlorination of Zircaloy-2 at 475°C in the HCl partial pressure range 0.15 to 0.50 atm (Fig. 4.6) was

$$r = 1.43 p_{\text{HCl}}^{0.5}$$

where r is the reaction rate in milligrams per square centimeter per minute and p_{HCl} is the HCl partial pressure in atmospheres. Since the

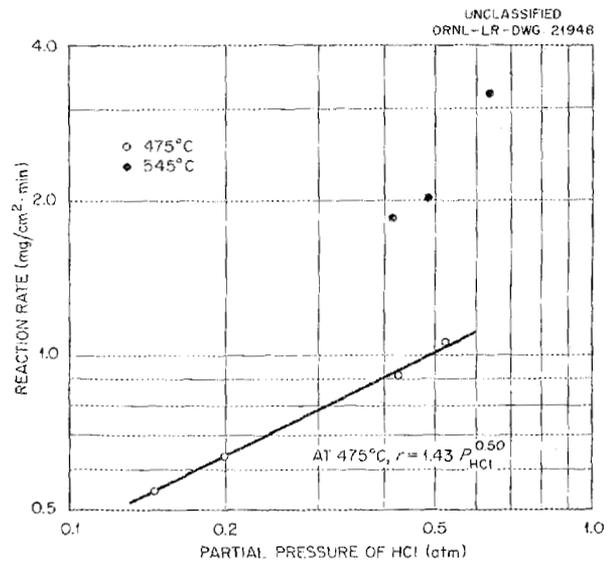


Fig. 4.6. Effect of Partial Pressure of HCl on Hydrochlorination Rate of Zircaloy-2.

²J. E. Savolainen and R. E. Blanco, *Chem. Eng. Progr.* 53(2), 78F (1957).

Table 4.4. Uranium Losses in Hydrochlorination of Zirconium-containing Fuel Prototypes

Composition	Hydrochlorination Temperature (°C)	Uranium Loss (%)	
		Sublimate	Insoluble in 10 M HNO ₃
PWR blanket rod (153 g of sintered UO ₂ pellets clad with 43.4 g of Zircaloy-2)	475	0.001	0.008
	~600	0.002	0.013
12% U, 88% Zr	448	0.05	0.53
	530	1.4	2.4
	694	2.2	0.58
60% U, 40% Zr	600	0.016	2.5
93.5% U, 5% Zr, 1.5% Nb	475	0.001	0.113
	545	0.028	0.045

reaction rates at 475°C are impracticably small, rate studies are continuing at higher temperatures.

A substantial temperature difference must be maintained between the reacting specimen and the hydrochlorinator walls for removal of the heat of reaction. Since the minimum wall temperature is limited to about 330°C by the sublimation temperature of $ZrCl_4$, an appreciable quantity of heat will be transferred by radiation. The emissivities of a few zirconium-uranium alloys undergoing hydrochlorination, estimated by energy balances, ranged from 0.22 to 0.89 and increased in general as the uranium content increased (Fig. 4.7). The energy balances were made by calculating the total heat removed during the reaction from the weight of the alloy reacted and a literature value for the heat of reaction.³ The heat removed by convection was estimated with the use of convection coefficients calculated from the Lorenz equation for natural convection; the values of the coefficients varied from 2.3 to 3.7 Btu/hr·ft²·°F. The rest of the heat was removed by radiation, and the emissivity was calculated from the equation for radiant heat transfer.

Liquid-Phase Hydrochlorination. — The serious problem of heat removal during the hydrochlorination reaction may be solved by the use of a refluxing liquid hydrochlorinating agent (Fig. 4.8). The molten double salt $AlCl_3 \cdot NH_4Cl$, which has a melting point of 304°C and a boiling point of about

425°C, dissolves metals, including zirconium, with the liberation of hydrogen and the formation of chlorides and aluminum chloride monoamine, which has a melting point of about 120°C and a boiling point of about 420°C:

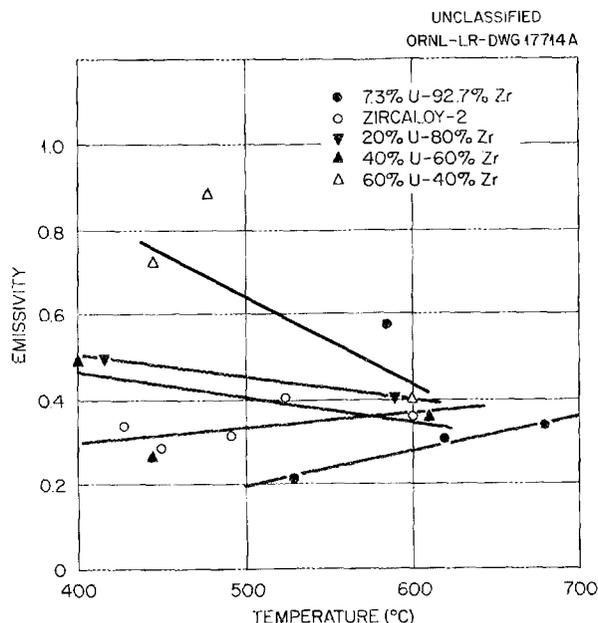
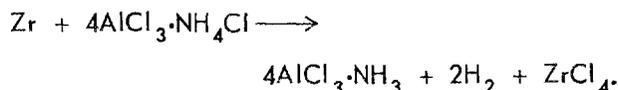


Fig. 4.7. Emissivity of Zirconium-Uranium Alloys vs Temperature.

³F. D. Rossini et al., Nat. Bur. Standards(U.S.), Circ. 500 (1952).

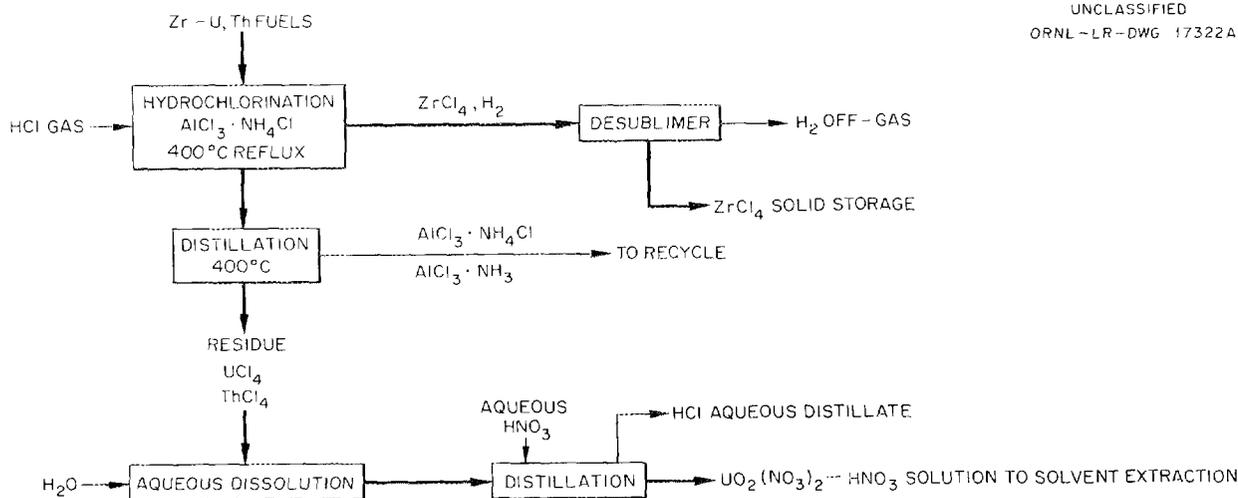


Fig. 4.8. Zircex Process Liquid-Phase Hydrochlorination.

When the reaction is carried out with zirconium near the boiling point of the double salt, the zirconium tetrachloride volatilizes.

The double salt dissolves both thorium and uranium metal. Uranium tetrachloride can form a 23.8% solution with the aluminum ammonium chloride at 350°C. Nonvolatile dissolved salts in the aluminum ammonium chloride can be concentrated by distillation of the double salt. For example, in a simple distillation, 67% of the double salt was removed, with recovery of 99.8% of the dissolved uranium chloride in the residue.

Corrosion is severe in molten-chloride processing. In preliminary laboratory tests gold and platinum resisted the corrosive attack of the fused double salt, but corrosion of other metals was proportional to the amount of dissolved HCl. In a melt with a composition indicated by $\text{AlCl}_3 \cdot \text{NH}_3$ the corrosion rate of nickel was 1 mil/month at 425°C. When the composition was $\text{AlCl}_3 \cdot \text{NH}_4\text{Cl}$ the corrosion rate was about 100 mils/month. The composition was maintained by bubbling gas through the melt. The laboratory work was conducted in Pyrex glass.

4.3 CORROSION STUDIES

Suitably resistant metallic materials for Darex and Zircex process equipment are:

Equipment	Material
Darex dissolver	Titanium, Haynes 21
Zircex hydrochlorinator-dissolver	S-816, Haynes 25
Darex-Zircex stripping columns	Tantalum, titanium
Darex-Zircex rectifier	Tantalum, titanium, possibly Haynes 21, S-816

Samples of these materials were exposed to liquid, vapor, and interface conditions.⁴ In 2 M HCl-5 M HNO₃, the initial Darex solvent, titanium was corroded at maximum rates of less than 1 mil/month and the rate decreased drastically with buildup of dissolution products. The presence of ruthenium in the solution further decreased the corrosion in liquid and interface positions by factors of 4 to 10. In continuous dissolution of stainless steel, the rate of corrosion of titanium reached a maximum of 0.03 mil/month after 1526 hr and then began to decrease. Holding the titanium for 66 days at the potential observed when it was

in contact with dissolving stainless steel resulted in no apparent embrittlement. The alloy 6% Al-4% V-90% Ti behaved similarly but was corroded at consistently slightly higher rates. Haynes 21 behaved satisfactorily, and its maximum rates were not much greater than those of titanium, although the average rates were much higher since the rates did not decrease with time nor with buildup of dissolution products. Tantalum was corroded at a negligible rate under all conditions but slowly became embrittled under impressed dissolver potentials. Zirconium and Zircaloy-2 failed (rates 60 mils/month) in the continuous Darex dissolver.

In the Zircex hydrochlorinator-dissolver tests, metal specimens were subjected alternately to HCl gas at 600°C for 11 hr and to boiling nitric acid containing uranyl chloride for 2 hr. In 25 test cycles, the high-cobalt alloys S-816 and Haynes 25 were by far the most resistant of the metals tested. It is planned to continue tests on these two alloys through 100 cycles. Tantalum and titanium failed immediately in the hydrochlorination part of the cycle, while Illium R, Inconel, Hastelloys B and C, type 304ELC stainless steel, Carpenter 20 and Carpenter 20S stainless steels, and the high-cobalt alloys S-590 and Haynes 21 suffered excessive corrosion. The high-nickel alloys, particularly Hastelloy B, showed the best resistance when exposed only to the dry HCl part of the cycle.

Under all Darex-Zircex stripper and acid-rectifier conditions, tantalum corrosion rates were negligible. Titanium rates were very low in liquid and interface positions; vapor-phase corrosion was more rapid but was always less than about 0.6 mil/month in the presence of NO₂, NOCl, or Cl₂. In the presence of gaseous HCl free from these inhibitors, titanium failed immediately, but there is no part of the stripping or rectifying steps in which this condition is encountered. In the liquid phase, HNO₃ and uranyl ion, as well as the dissolution products of stainless steel, effectively inhibited corrosion by HCl.

The high-cobalt alloys Haynes 21 and S-816 were corroded too rapidly in strong nitric acid to be used in construction of the stripping columns, but their resistance to the acid concentrations expected in the acid rectifier was relatively satisfactory, particularly in the case of Haynes 21. Vapor-phase corrosion was generally much less than that in the liquid phase.

⁴Work done by Battelle Memorial Institute under a sub-contract.

In corrosion tests at ORNL under actual operating conditions, the materials most resistant to the Darex dissolvent, 2 M HCl-5 M HNO₃, were tantalum, titanium, and glass-lined steel, with corrosion rates of 0.005, 1.4, and 0.2 mils/month, respectively. Grade "A" nickel and Hastelloy B were severely attacked.

In scouting tests anhydrous HCl gas at 500°C, used in the Zircex process, did not appreciably attack Inconel, "A" nickel, Hastelloy B, or type 304L stainless steel. However, all these materials were severely attacked by HNO₃-UCl₃ solutions, which would result from the dissolution in nitric acid of the UCl₃ produced by the hydrochlorination. Titanium resisted the above solution but failed in a cyclic test with HCl gas and HNO₃-UCl₃ solution.

Thirty-one different coatings are being evaluated for their ease of decontamination from mixed fission products at a concentration of 10⁹ counts/min·ml and for their chemical resistance to 3 M solutions of HNO₃, HCl, H₂SO₄, and NaOH and to hexone and water.

Protective coatings were obtained from 22 paint manufacturers for irradiation with both gamma rays alone and with gamma rays and neutrons in the shield tank of the Homogeneous Reactor Test. A total of 162 different coatings were suspended around the shield tank and are now awaiting the startup of the reactor.

4.4 ALTERNATE AQUEOUS DISSOLUTION STUDIES

Studies on aqueous dissolution procedures alternative to the usual nitric acid dissolution are emphasizing chemical decladding of fuels with nitric acid-soluble cores; sulfuric acid and hydrofluoric acid are being used to dissolve stainless steel and zirconium, respectively. Electrolytic dissolution is also being investigated.

Laboratory data on unirradiated materials indicated a good probability of removing stainless steel cladding from UO₂, U-Mo, and similar core materials with 4 to 5 M H₂SO₄ and of removing Zircaloy-2 cladding from UO₂, U-10% Mo, and possibly U-Nb alloys with aqueous HF. However, limited data on irradiated specimens differed from the data on unirradiated material.

4.4.1 Removal of Stainless Steel Cladding with Sulfuric Acid

Yankee Atomic Fuel Pins.— Type 304L stainless steel was penetrated at a rate of 15 to 45 mils per 2.5 hr in refluxing 4 to 8 M H₂SO₄ (Fig. 4.9), which is a feasible rate for dejacketing. The maximum solubility of type 304L stainless steel was 142 g/liter, obtained with 4 M H₂SO₄ (Fig. 4.10). At 25°C the solubility decreased as the sulfuric acid concentration increased and was 100 g/liter in 2 M H₂SO₄. Simulated core samples of uranium, UO₂, U-10% Mo, and U-10% Nb did not dissolve prohibitively under these conditions (Fig. 4.11). The uranium concentration of the dissolver solution increased with increasing acid concentration but was <0.1 g/liter with any fuel in 4 M H₂SO₄.

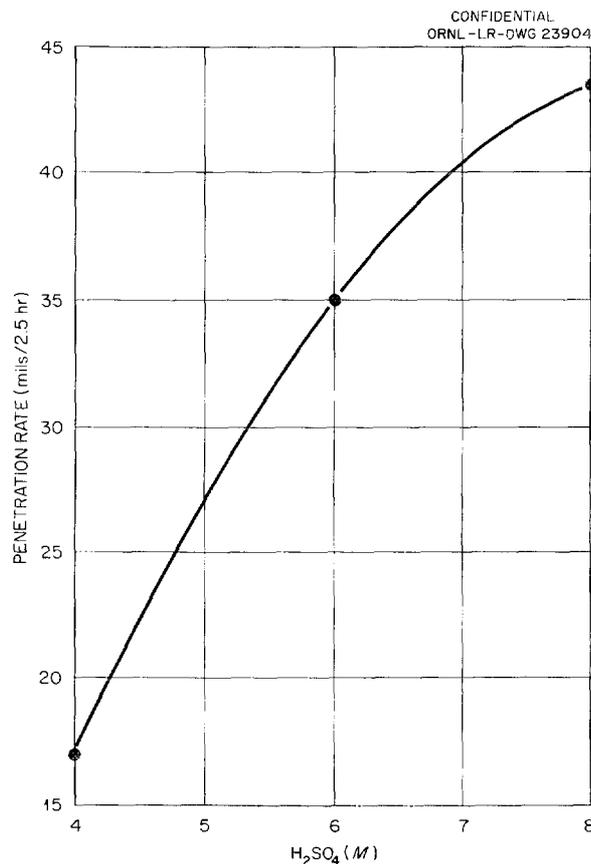


Fig. 4.9. Rate of Dissolution of Type 304L Stainless Steel in Refluxing Sulfuric Acid. Data obtained by immersing samples in acid for 2 min and extrapolating to 2.5 hr.

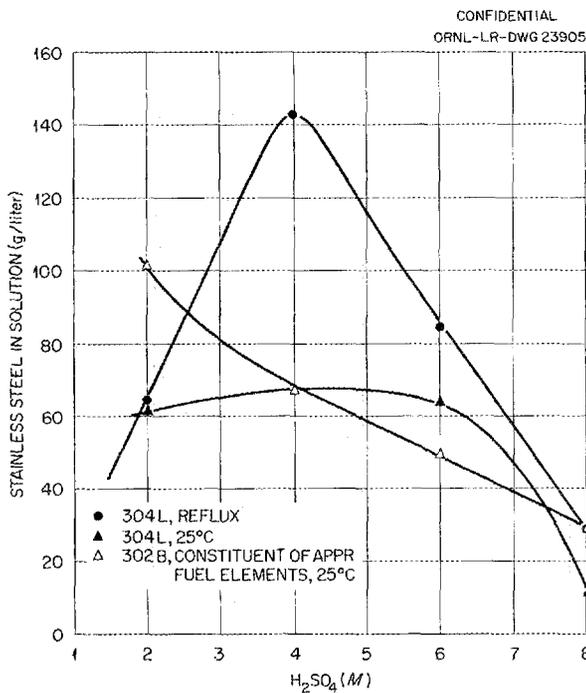


Fig. 4.10. Solubility of Stainless Steel in Sulfuric Acid at Reflux and Room Temperatures.

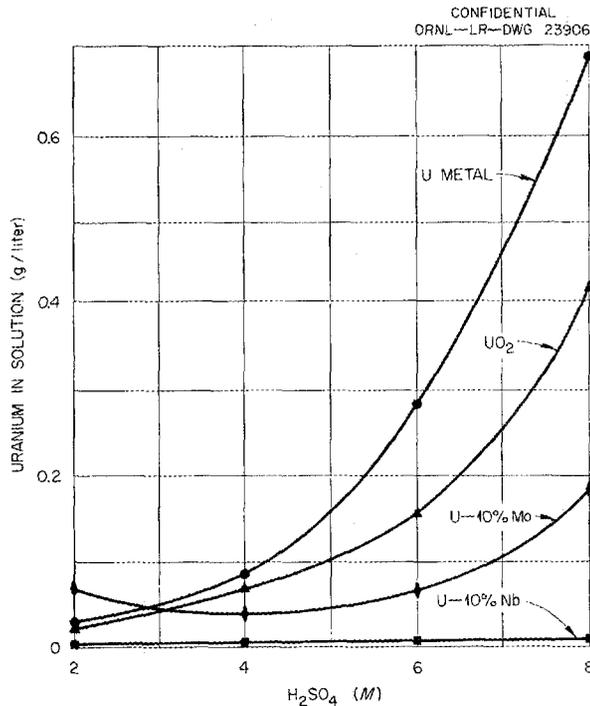


Fig. 4.11. Uranium in Solution after 2.5-hr Reflux of Various Fuel Core Materials in Sulfuric Acid.

Dissolution rates of type 304L stainless steel jackets on simulated Yankee Atomic fuel pins (UO₂ pellets with stainless steel) were 4 to 6 mg/cm²·min when the specimens were added to hot (95°C) 6 M H₂SO₄; when the specimens were added to cold acid and heated to 95°C, the rates were 2 to 3 mg/cm²·min. In 4 M H₂SO₄ the rates were about half these. Acid consumption was 2 moles per mole of stainless steel. Dissolution rates were essentially the same with 200, 300, 400, and 500% stoichiometric excess of acid. Uranium losses to the 6 M H₂SO₄ wastes were 0.01% (~0.0005 g/liter) or less. Stainless steel jacket heels, which had been passivated during dissolution of UO₂ pellets in 6 M HNO₃, were reactivated by contact with iron wire and could then be dissolved in sulfuric acid.

Army Package Power Reactor Fuel Elements. - The type 302B stainless steel cladding of APPR fuel elements (sintered UO₂-302B core) was completely dissolved by refluxing 4 and 6 M H₂SO₄ in 200 to 400% stoichiometric excess. The uranium loss to the solution was 0.3 to 0.5%, and the loss to residual solids insoluble in nitric acid was 0.9 to 1.6%. This type of solids problem should not be encountered with ordinary clad fuel elements where silica contents are low. With 8 M H₂SO₄, dissolution was incomplete and there were large amounts of flocculent solids, presumably silica.

The solubility at 25°C of type 302B stainless steel contained in APPR fuel specimens was constant at 65 g/liter for 2, 4, and 6 M H₂SO₄ but dropped sharply above 6 M. The difference in the 304L and 302B data may be due to passivation of the massive 304L pieces. In 5 to 6 M H₂SO₄ containing 20 to 24 g of stainless steel per liter, fresh APPR fuel samples consistently became passive.

Irradiated APPR Fuel Elements. - Two specimens of highly irradiated (~40% burned up) APPR fuel plate were dissolved in boiling 6 M H₂SO₄. Contrary to results with unirradiated fuel, 94% of the uranium and the bulk of the fission-product activity were found in the solution. Further tests will be made to determine the effect of radiant energy on the system.

U-10% Mo Cores. - In a few experiments on removal of Zircaloy-2 cladding from U-10% Mo cores with boiling concentrated sulfuric acid, removal was complete at reasonable rates and uranium loss to the solution was negligible only

with about 14 M acid at temperatures of 230 to 240°C. Because of the extreme temperature conditions and the large excess (>900%) of sulfuric acid required, this approach did not appear promising and work was discontinued.

Waste Treatment.—A 50% volume reduction of the partially spent decladding solution (5.6 M H₂SO₄; 22 g of Fe, 5 g of Cr, 3 g of Ni per liter) precipitated 63% of the iron and none of the chromium or nickel. Since only a small fraction of the salts was removed by this method, the supernatant would be unsuitable for recycling. Lime neutralization of the sulfate dejacketing waste produced a solid CaSO₄ waste of about the same volume as the original solution.

4.4.2 Removal of Zirconium Cladding with Hydrofluoric Acid

Data on dissolution of zirconium and Zircaloy-2 cladding and of core materials in aqueous HF are not so complete as those for stainless steel in sulfuric acid. In preliminary dissolution rate studies, zirconium and Zircaloy-2 dissolved readily in 9 M HF, while the core materials UO₂, U-10% Mo, and U-10% Nb dissolved only slowly (Table 4.5). Further processing of niobium alloys would present a problem since their dissolution in nitric acid in the presence of fluoride is slow and sometimes explosions are encountered.

In preliminary experiments on the dissolution in HF-HNO₃ and HF-HNO₃-Al(NO₃)₃ solutions of fuel elements containing zirconium and Zircaloy-2,

the dissolution rate increased with increasing nitric acid concentrations. However, an F/Zr mole ratio of 1.7/1 or greater was always required to obtain a satisfactory dissolution rate (i.e., >1.0 mg/cm²·min).

4.4.3 Electrolytic Dissolution^{5,6}

Anodic dissolution of fuel elements containing stainless steel and zirconium would permit dissolution in less concentrated acid than is required in straight chemical dissolution. A further advantage is the possibility that solutions of the two kinds of fuels similar enough to be processed by the same flowsheet might be obtained. Anodic dissolution of stainless steel-containing fuel elements in nitric acid now appears feasible. Zirconium-containing fuel elements have not dissolved in nitric acid satisfactorily, and the addition of HCl to the electrolyte is being investigated.

The problem of making continuous contact between the platinum portion of the anode and the fuel-element pieces so as to leave no undissolved heels was solved by the use of a conical glass vessel with the anode at the apex. The cone is inclined several degrees from the vertical, which facilitates continuous feeding of fuel elements

⁵E. C. Pitzer, *Electrolytic Dissolution of Stainless Steel Clad Fuel Assemblies*, KAPL-653 (Dec. 21, 1951).

⁶Work done in Carter Laboratories under subcontract.

Table 4.5. Dissolution Rates of Core and Cladding Materials in Hydrofluoric Acid at 90°C

Material	Dissolution Rate (mg/cm ² ·min)						
	1 M HF	2 M HF	5 M HF	9 M HF	10 M HF	12 M HF	15 M HF
Zirconium	11.8		236.5				
Zircaloy-2	5.37	20.9	78.7	284.3	164.9	118.6	126.9
UO ₂			0.15	0.08		0.036	
U-10% Mo			0.06	0.013		0.025	
U-2% Zr*			7.1	7.73		4.24	
U-9.7% Nb			0.032	0.083		0.14	

*Large amounts of insoluble UF₄ were produced.

during dissolution and tends to protect the anode from mechanical attrition during introduction of the fuel samples. No loss of platinum has been observed in the more practical dissolution systems studied. Ceramics will be investigated for larger vessels. When metal pieces of assorted sizes were dissolved in this equipment, the smaller pieces dissolved preferentially; thus any residual metallic heels were eliminated. Dissolution of both stainless steel and zirconium was more satisfactory with direct than with alternating current.

Stainless Steel-Containing Fuels. - Stainless steel was anodically dissolved in 3 M HNO_3 over a 12-hr period with current efficiencies as high as 96%. Current efficiencies appeared to be essentially independent of current density over the practical operating range, but were affected by the geometry of the cell, particularly the position and shape of the cathode. In experiments to evaluate this factor, the lowest current efficiencies obtained were about 60%.

The resistance of the stainless steel solution increased moderately with increasing concentration of stainless steel dissolution products until a concentration of about 0.6 M was reached. Above this concentration there appeared to be occasional passivation of small stainless steel particles, resulting in a metallic residue, although the overall anode current efficiency was not adversely affected. When the concentration of dissolution products was above about 1.1 M, resistance heating of the solution became prohibitively high. In the laboratory-scale continuous dissolution apparatus, heat was removed and the solution was clarified simultaneously by circulation of a part of the solution through a heat exchanger and a filter. Part of the solution was continuously removed, and an equal amount of fresh acid was fed back into the stream.

The anodic dissolution of stainless steel in hydrochloric and sulfuric acids was briefly explored, but current efficiencies were lower and cell resistance was higher than in nitric acid.

Zirconium-containing Fuels. - Zircaloy-2 dissolved continuously in 3 M HCl containing less than 0.1 M HF with current efficiencies greater than 100%.

In nitrate, chloride, and sulfate solutions, both with and without the addition of fluoride, peroxide, and oxalate, zirconium was intergranularly attacked,

producing a metallic sludge which was successfully eliminated only by the inclusion of small amounts (~ 0.1 M) of fluoride in the electrolyte. In nitric acid solutions enough fluoride must always be present to maintain a fluoride/zirconium ratio of 4/1 if the presence of finely divided metal is to be avoided. In chloride solutions metallic sludge was not produced in short-term experiments with a Cl/Zr ratio of 1.4/1. Sulfuric acid was intermediate in behavior between nitric and hydrochloric acids in its ability to hold zirconium in solution. Operation at acid concentrations above 3 N offered no apparent advantage.

The purity of the zirconium affected its behavior greatly. With reactor-grade zirconium in 3 M HCl-0.084 M HF, current efficiencies were 40 to 50%, while with Zircaloy-2 and commercial-grade zirconium (hafnium not removed) current efficiencies were well over 100%. The addition of peroxide or oxalate decreased the amount of residual solids somewhat, but only HF completely eliminated the finely divided metallic residue.

4.5 ION EXCHANGE TREATMENT

Scouting work was started on the use of ion exchange in head-end operations for fuel reprocessing. Investigations will include the recovery of uranium and plutonium from solutions resulting from sulfuric and hydrofluoric acid removal of zirconium and stainless steel claddings, which contain only small amounts of the fissionable core material and fission products. Ion exchange will also be evaluated as a substitute for the first solvent extraction cycle for use with highly enriched sintered UO_2 -stainless steel fuels dissolved in sulfuric acid.

In the preliminary runs >99% of the uranium present in a zirconium fluoride solution was sorbed by an anion exchange resin. Preparation of the feed to the ion exchange column by addition of hydrochloric acid or sodium chloride precipitated the zirconium as zirconyl chloride, which carried less than 0.1% of the uranium from the solution.

4.6 MECHANICAL PROCESSING

Since many of the newer fuels contain nitric acid-soluble active ingredients clad in nitric acid-insoluble stainless steel or zirconium, removal or destruction of the cladding by mechanical methods will permit conventional nitric acid dissolution of the fertile and fissionable

materials and subsequent solvent extraction by existing reprocessing technologies. An engineering development program is in progress to determine the feasibility of predissolution mechanical processing.

Evaluation of Mechanical Decladding Equipment.— Disassembling and decladding by electrical discharge cutting, abrasive disk sawing, fuel jacket derodding, and fuel shearing with leaching of cores are being studied.

Disassembling spent fuels by electrical discharge cutting with an Elox model M-500 electrical discharge cutting machine may be advantageous for close-tolerance cutting and for dissecting metallurgical specimens. The machine automatically maintains a 2-mil gap between the electrode and work piece, and the piece therefore does not need to be held as firmly as in milling operations. The electrodes were made of 1 to 2% leaded brass as recommended by the Elox Corp. Typical cutting rates are given in Table 4.6. The main disadvantage is the low cutting rate, which was about the same with the three types of electrodes studied — plate, rotating wheel, and continuously reeled wire. The type of electrode used would therefore be determined by the ease of electrode fabrication and the type and configuration of the material to be cut. The continuously reeled wire, 0.0201 in. in diameter, is considered the best electrode design for making cuts 1 to 2.5 ft long because field fabrication is not required and the length of the cut can be varied by adjustment of the pulleys. At the optimum reeling rate, 25 ft/hr, about 14% of the electrode was consumed. The fines produced were 30 to 100 μ in size.

In tests to obtain design information necessary to specify methods and machines for reducing spent fuel assemblies into subassemblies, 1-in.-OD

type 316 stainless steel rods were cut with five abrasive cutoff wheels to determine wear ratio, cutting rates, and sizes of particles produced. Aluminum oxide was superior to silicon carbide as the cutoff wheel abrasive. For the aluminum oxide abrasive, the wear ratio was 1 to 2 parts of wheel to 1 part of stainless steel, with 0.2 to 0.4 in.³ of metal cut per minute. For the silicon carbide abrasive, the wear ratio was 9 to 21 parts of wheel to 1 part of stainless steel, with 0.1 to 0.26 in.³ of metal cut per minute. The particles produced by the aluminum oxide abrasive ranged in size from 50 to 1500 μ and those produced by the silicon carbide abrasive from 20 to 600 μ . The tests were conducted with dry cutting and a disk peripheral speed of 10,500 ft/min.

A Mackintosh-Hemphill model AXY derodding machine successfully removed Al-Si bonded cladding and straightened or expanded rod-shaped fuel elements for other methods of disassembly. The machine would be serviceable in decladding Na-K bonded rods by straightening, if necessary, and expanding the cladding so that the fuel could fall out by gravity when the end cap was sawed off. The Al-Si bonded aluminum cladding of X-10 rejected slugs was removed in three to seven passes through the machine and expanded 14%. The uranium loss from this mechanical operation was <0.1%.

The machine will not handle materials shorter than 9 in. A special guide tube was designed that permits material of any length to pass through the three sets of rollers.

Prescoring the cladding before the fuel element was passed through the machine permitted jacket removal in one less pass. However, scoring would probably not be feasible because of the time and equipment required.

Rod- or slug-shaped fuels with nitric acid-insoluble claddings and nitric acid-soluble cores may be sheared and then leached with nitric acid. Fuels suitable for such treatment would be stainless steel- or zirconium-clad uranium metal, plutonium metal, UO₂, UO₂-ThO₂, and U-Mo and U-Si alloys. Since radioactive contamination will make shear blade replacement difficult and expensive, blade life is an important economic factor. A set of dies furnished with a Buffalo Universal Ironworker No. 2 shear made more than 6000 cuts on 1-in.-dia unirradiated uranium rod clad with 0.035-in.-thick type 321 stainless steel. Two grooves were worn by the cladding in the

Table 4.6. Rate of Electrical Discharge Cutting

Material	Cutting Rate (ca/hr)	Volume of Metal Cut per Unit Volume of Brass Electrode Consumed
Carbides	0.5	
Steels	0.6	2.0
Zirconium	0.8	2.5
Uranium	0.5-1.7*	3.0
Aluminum	18.7	

*Varying rate resulted from plating of vaporized metal on the electrode.

cutting face of the moving blade at the edge of the test hole (Fig. 4.12), indicating that the nature of the cladding may be more important than the core in determining blade life.

The hole diameter in the die is $1\frac{1}{8}$ in. The cutting edges of the hole were rounded to a radius of about 0.03 in., but this rounding did not substantially increase the deformation of the sheared pieces. Approximately 15% of the cross-sectional area of a slug was sheared before the rest failed by fracture. About 0.1% of the uranium was lost as fines, which consisted of about 40% stainless steel and about 60% uranium.

Continuous Nitric Acid Leaching of Sheared Fuel Elements. – An experimental continuous dissolver in which the soluble core could be leached out of sheared sections of fuel elements with nitric acid was designed (Fig. 4.13), and a Lucite model was constructed and operated.

The solids are continuously discharged by means of a flat cylindrical bucket assembly, rotating in the vertical plane in a stationary tank half full of acid. The buckets are fed from and discharged to pipes in the hub. The bucket assembly is supported on rollers around its periphery, and is rotated by the difference in weight of the freshly charged slug sections on one side and leached cladding on the other. A central shaft may be provided for regulation of speed.

Technical and Economic Study.⁷ – A design feasibility study to determine the technical and economic worth of mechanical processing of fuels prior to chemical dissolution is under way. Preliminary designs of individual machines, layout of the system, and cost estimates are about 60% completed.

⁷Work being performed under a subcontract by AMF Atomics, Inc.



UNCLASSIFIED
PHOTO 40356

Fig. 4.12. Grooved and Rounded $1\frac{1}{8}$ -in.-dia Hole in Moving Face of Cutting Die.

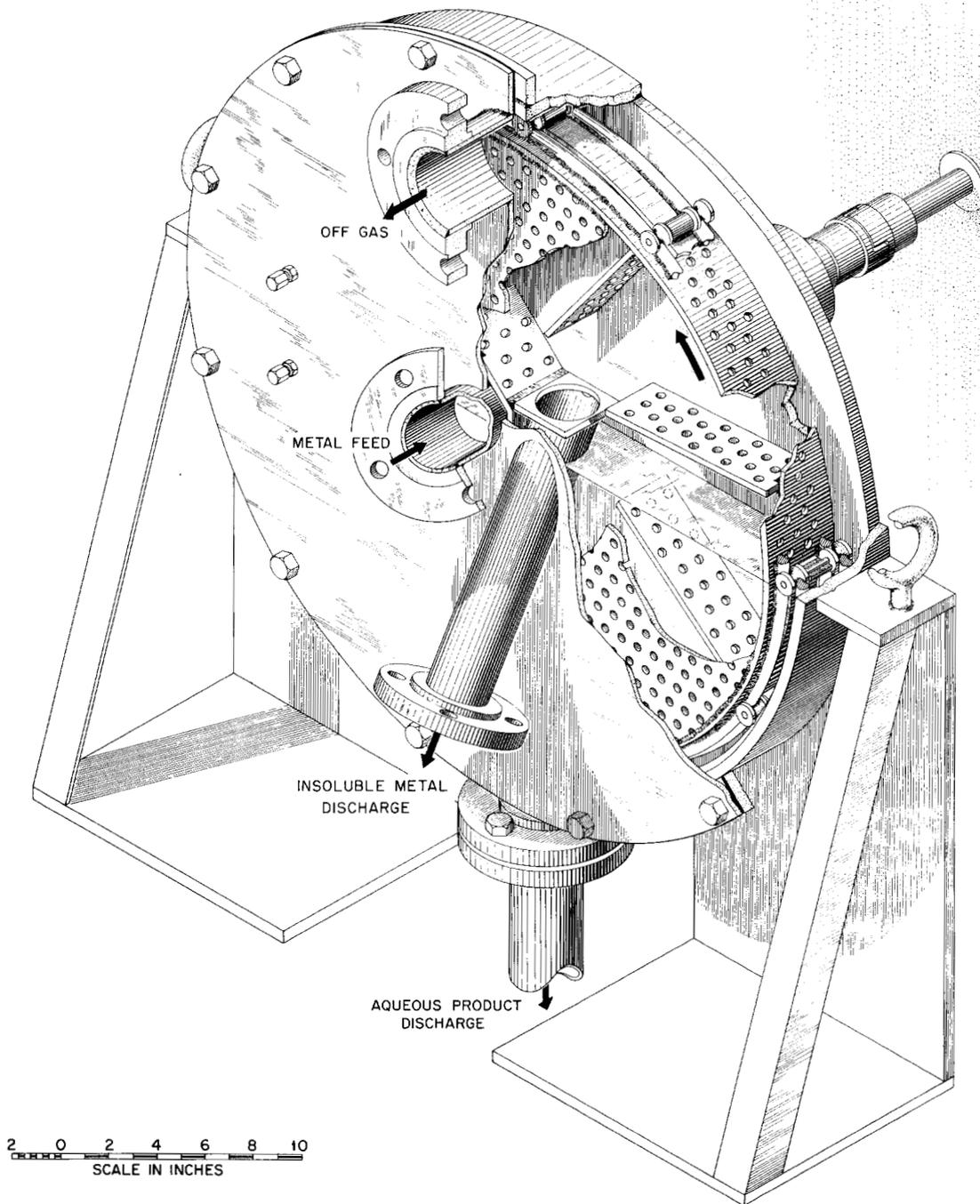


Fig. 4.13. Critically Safe Rotary Slab Dissolver with Continuous Solids Feed and Discharge.

5. SOLVENT EXTRACTION STUDIES

The head-end treatments discussed in Sec. 4 are designed to produce solutions that can be subsequently extracted with tributyl phosphate (TBP). In many cases the solvent extraction flowsheets will be slightly modified Purex, Thorex, or 25 process flowsheets. Three chemical flowsheets were developed for spent fuel and tested for product losses with nonirradiated fuels. These include the fuel from the Army Package Power Reactor and the core and blanket material from the Detroit Edison (APDA) reactor (Table 5.1).

5.1 APPR FUEL

It has been suggested that uranium--stainless steel fuels, for example, those from the APPR, after dissolution in dilute aqua regia (Sec. 4.1) and feed adjustment, might be solvent-extracted in the presence of hydrochloric acid. This would eliminate the chloride-stripping step but would introduce a corrosion risk in the first solvent extraction cycle and waste-treatment step. In batch countercurrent extractions of synthetic APPR feed solution containing 2 M HCl, uranium extraction was appreciably decreased; approximately 1% of the uranium was lost to the aqueous waste after five extraction stages. The stripping loss was unaffected. Chloride extraction by the solvent was less than 5 ppm after four scrub stages, indicating that chloride corrosion could likely be confined to the first-cycle extraction-scrub contactor and the aqueous waste equipment.

Approximately 200 g of representative APPR fuel specimens, irradiated to ~40% burnup and decayed one year, was dissolved in dilute aqua regia to supply feed for first-cycle flowsheet evaluation runs in the Mini mixer-settler equipment. As dissolution proceeded, large amounts of silica and other insolubles collected in the Pyrex batch dissolver. These solids contained no uranium. After batch chloride-stripping and evaporation to boil off excess nitric acid and dehydrate soluble silica, the fuel solution was adjusted to first-cycle feed. In the mixer-settler banks, eight stages each were used for the extraction, scrub, and strip sections. Uranium recovery and decontamination factors were satisfactory, that is, 99.98% recovery, and decontamination factors for gross beta, 4.8×10^5 ;

gross gamma, 6.1×10^4 ; Zr-Nb gamma, 2.6×10^4 ; Ru gamma, 3.9×10^5 ; total rare earth beta, 7.4×10^7 ; and Pu alpha, 86. Operation at elevated temperatures decreased the over-all decontamination from fission products. The addition of 0.01 M oxalic acid to the aqueous scrub during processing at room temperature appeared to increase the Zr-Nb decontamination factors, but further tests are required to confirm this point.

The 25-TBP¹ process second-cycle flowsheet has been proposed for the APPR second cycle. This flowsheet should give additional minimum decontamination factors of about 3.3×10^2 for gross beta and 2.5×10^3 for gross gamma.

5.2 APDA FUEL

A series of batch countercurrent experiments was made to test the solvent extraction flowsheets proposed for the head-end cycle and the first, or plutonium-partitioning, cycle of the APDA core processing scheme. Simulated feed was made up to correspond with that produced by nitric acid dissolution of the U-Mo alloy core after removal of the zirconium cladding with aqueous HF. Approximately 4 and 6 extraction stages in the head-end cycle were required to reduce uranium and plutonium losses to 0.01%, respectively. Approximately 5.5 stripping stages were necessary to reduce both uranium and plutonium losses to the stripped solvent to 0.01%. The experiment was carried out with a total of 1.02 g of molybdenum per liter in solution and the rest of the 1.28 g/liter as a suspension of MoO₃ in the feed. No emulsification was observed. The 8%-TBP solvent extracted 0.005 g of zirconium per liter and retained the same amount after 4 scrub stages. Two parts of molybdenum per million was found in the solvent at the feed plate, but it was completely removed in 4 scrub stages.

The first, or partitioning, cycle for the APDA core would use as feed the uranium-plutonium product from the head-end cycle. About 5 extraction stages in the extraction column and 5 partitioning stages and 4 back-extraction stages in the stripping column are required to reduce the plutonium losses to <0.01%.

¹J. R. Flanary *et al.*, *Chemical Development of the 25-TBP Process*, ORNL-1993 (Revised), (March 20, 1957).

Table 5.1. Solvent Extraction Flowsheet Conditions for Recovery of Source and Fissionable Materials from Typical Power Reactor Fuels

Stream	Conditions		
	APPR Core, Stainless Steel-Clad Stainless Steel-U ²³⁵ Alloy	APDA Fuel, Zr-Clad U-Mo Alloy	APDA Blanket, Stainless Steel-Clad Uranium
Head-End Step			
Feed (HAF)	5 g U/liter, 62 g SS/liter, 3 M HNO ₃ (100 vol)	12 g U/liter, 0.048 g Pu/liter, 6 M HNO ₃ , 1.28 g Mo/liter, 0.51 g Zr/liter, 0.01 M NaNO ₂ (100 vol)	215 g U/liter, 50 g SS/liter, 1 M HNO ₃ , 0.01 M NaNO ₂ , Pu (40 vol)
Scrub (HAS)	3 M HNO ₃ , 0.75 M Al(NO ₃) ₃ , 0.01 M Fe(NH ₂ SO ₃) ₂ (20 vol)	3 M HNO ₃ , 0.75 M Al(NO ₃) ₃ (50 vol)	3 M HNO ₃ (20 vol)
Solvent (HAX)	5% TBP in Amsco 125-82 (83 vol)	8% TBP in Amsco 125-82 (126 vol)	30% TBP in Amsco 125-82 (100 vol)
Strip (HCX)	0.01 M HNO ₃ (41.5 vol)	0.01 M HNO ₃ (47 vol)	0.01 M HNO ₃ (200 vol)
First Cycle			
Feed (1AF)	154 g U/liter, 3 M HNO ₃ (2.43 vol)	12 g U/liter, 0.048 g Pu/liter, 6 M HNO ₃ , 0.01 M NaNO ₂ (100 vol)	324 g U/liter, 2 M HNO ₃ , 0.01 M NaNO ₂ (100 vol)
Scrub (1AS)	3 M HNO ₃ , 0.02 M Fe(NH ₂ SO ₃) ₂ (1.49 vol)	3 M HNO ₃ , 0.75 M Al(NO ₃) ₃ (50 vol)	3 M HNO ₃ (67 vol)
Solvent (1AX)	18% TBP in Amsco 125-82 (7.44 vol)	8% TBP in Amsco 125-82 (126 vol)	30% TBP in Amsco 125-82 (333 vol)
Organic scrub (1BS)		8% TBP in Amsco 125-82 (32 vol)	30% TBP in Amsco 125-82 (89 vol)
Pu strip (1BX)		0.5 M HNO ₃ , 0.03 M Fe(NH ₂ SO ₃) ₂ (16 vol)	0.5 M HNO ₃ , 0.03 M Fe(NH ₂ SO ₃) ₂ (45 vol)
U strip (1CX)	0.01 M HNO ₃ (7.44 vol)	0.01 M HNO ₃ (59 vol)	0.01 M HNO ₃ (666 vol)

5.3 APDA BLANKET

Results of laboratory experiments with synthetic feed solution indicated that a dilute (215 g of uranium per liter) Purex-type feed containing 50 g of stainless steel per liter could be processed in a Purex plant for uranium and plutonium recovery. Feed solutions with higher uranium and stainless steel concentrations were unstable with respect to freezeout and precipitation of salts at ambient operating temperatures.

Results of batch-countercurrent tests of the first solvent extraction cycle flowsheet (Table 5.1) indicated that about 2 stages were required to extract 99.99% of the uranium and about 4.5 stages to extract 99.99% of the plutonium.

5.4 MTR FUEL

Laboratory studies indicated that a recently proposed MTR-type fuel element, aluminum-clad 97% U-3% Si-Al alloy core, may be processed by a slightly modified 25-TBP process.¹ A 150-160°C dehydration step will be required during feed preparation to minimize emulsification by colloidal silica. When such a step was included, phase-disengagement times of the subsequent extraction step were about 1 min, which are probably satisfactory for column operation. The 3- to 4-hr digestion of the feed at the boiling point, called for in the original flowsheet, had essentially no effect; digestion with high (4 M) acid was only slightly effective in reducing emulsification.

5.5 TBP STEAM-STRIPPING

Residual TBP is removed from uranyl nitrate solutions before they are concentrated by evaporation in order to prevent buildup of TBP hydrolysis products in the evaporator which may be explosive and/or may react with uranium to produce a non-strippable form. In the past, TBP has been steam-stripped from evaporator feed streams by introduction of the streams through a bubble-cap column countercurrently to the vapor. Sieve plates appear attractive for this service owing to their simpler construction and therefore lower cost and greater resistance to corrosion.

A series of tests was carried out on a 6-in.-dia sieve-plate column with plates of 2.73% free area

to determine their performance with tributyl phosphate-uranyl nitrate solution. For TBP concentrations between 1 and 200 ppm, the average plate efficiency was 25% over a range of f factors (the f factor is the product of the superficial vapor velocity and the square root of the vapor density) from 0.2 to 0.7. The efficiency decreased above f -factor values of 0.7 (Fig. 5.1a).

Uranium entrainment in the six-plate column (top two plates dry) was of the order of 50 to 100 μg per liter of condensate at f values from 0.2 to 0.5. At $f = 0.7$, uranium entrainment rose to about 300 μg per liter of condensate. This entrainment was reduced to less than 100 μg /liter by admission of water reflux to the sixth plate at a rate equal to 10% of the feed rate (Fig. 5.1b).

The column flooded at an f value of about 1.0, and began to weep at f values between 0.1 and 0.2.

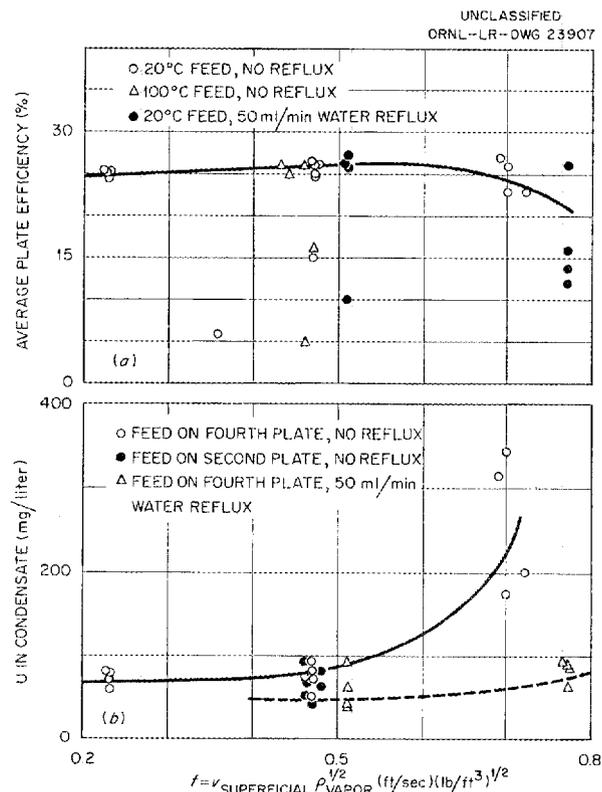


Fig. 5.1. Steam Stripping of Tributyl Phosphate from Aqueous Solution. The f factor vs (a) average plate efficiency, feed on fourth plate, and (b) uranium entrainment, 47 g of uranium per liter in feed. Conditions: 6-in.-dia sieve-plate column, 2.73% free area; $L/V = 1.15/1$.

5.6 RADIATION DAMAGE TO SOLVENTS

Study of the nature of the radiation damage to solvents used for metal extraction in fuel processing has been reactivated, and previously reported observations² have been correlated. As fuel irradiation increases and decay time decreases, such damage will become more important.

In general, the effects of radiolysis are those expected with organic molecules, that is, production of fragments, lighter molecules, and unsaturated compounds. Ultraviolet and infrared examinations of irradiated diluent have indicated that formation of unsaturates may be the primary form of radiation damage. This observation has been verified by determinations of the iodine number of selected, relatively pure diluents exposed to Co^{60} gamma radiation up to 68 watt-hours per liter (approximately 1.76×10^7 r) (Fig. 5.2).

The radiation damage to solvents now in use, usually tributyl phosphate with a diluent such as Amsco 125-82 (hydrogenated polymerized butene), results in lower decontamination from fission products; emulsification of, and formation of interfacial precipitates in, the organic-aqueous extraction mixtures; and retention of desired metals in the organic phase, rather than extraction to the aqueous phase, in stripping operations. These effects are primarily the result of radiolytic degradation of tributyl phosphate to dibutyl or monobutyl phosphate and/or subsequent polymer formation, with secondary effects arising from degradation of the diluent at sufficiently high levels of irradiation.

Work is in progress to determine the radiation sensitivity of the principally used diluent, Amsco 125-82. Individual components of the solvent are being separated³ by vacuum fractionation so that the radiation sensitivity of each may be determined.

The effects of radiation on tributyl phosphate and its mixtures with diluents are also being investigated.⁴ The G values⁵ for the production of radiolysis products are being determined, and the products are being identified with particular attention

²D. W. Sherwood, *Bibliography: Solvents for Extraction Processes*, ORNL CF-57-4-68 (April 24, 1957).

³At Georgia Institute of Technology under subcontract.

⁴At Stanford Research Institute under subcontract.

⁵The G value is the number of molecules produced per 100 ev absorbed.

to the effects produced by initial impurities (Table 5.2). Other phosphates, phosphonates, and phosphine oxides are being synthesized to determine the effect on radiation stability of the position of attachment of organic groups to the central phosphorus atom.

In recent work at ORNL the addition of protective agents, for example, benzene, to TBP-Amsco mixtures appeared to decrease the radiolysis of TBP, but increased chemical reactivity offset the gain. This approach is to be investigated further.

Vacuum distillation of tributyl phosphate effectively removed degradation products and fission products from used TBP-Amsco solvent. Data are being obtained for engineering evaluation of this method of purifying solvent for recycle.

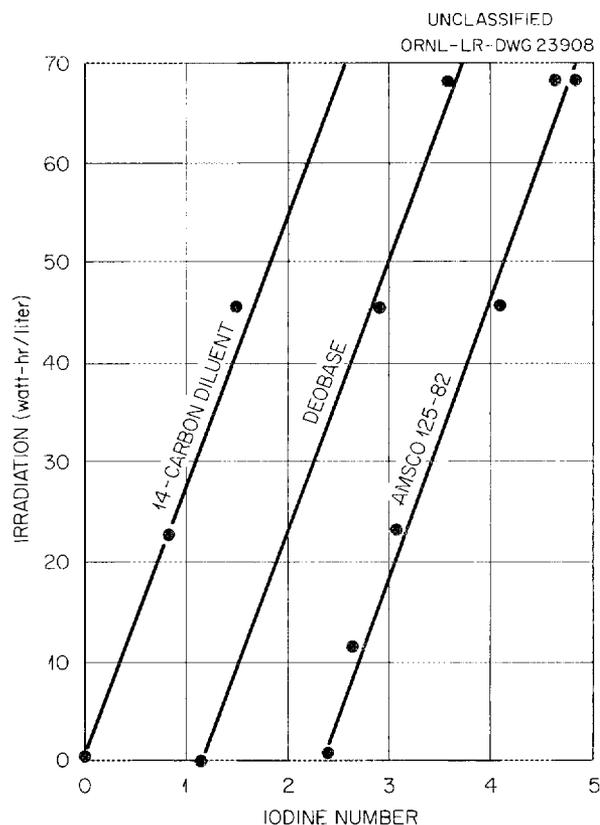


Fig. 5.2. Formation of Unsaturates, As Indicated by Iodine Number, in Hydrocarbon Diluents as a Function of Amount of Irradiation.

Table 5.2. Compounds Produced in Exposure of TBP to 1-Mev (nominal) Electrons

Component	G Value	Component	G Value
TBP Alone, 1072 watt-hours per liter			
Total gas	2.42	<i>n</i> -Pentane	0.02
Hydrogen	1.60	<i>n</i> -Hexane	0.004
Methane	0.10	<i>n</i> -Heptane	0.003
Acetylene	0.02	<i>n</i> -Octane	trace
Ethane	0.07	<i>n</i> -Butanol	0.16
Ethylene	0.03	Butyral	0.0006
Propene	0.02	Dibutyl phosphate	2.11
Propane	0.12	Monobutyl phosphate	0.40
Butene-2	0.09	Phosphoric acid	0.01
<i>n</i> -Butane	0.34		
20 wt% TBP in Amsco 125-82, 830 watt-hours per liter			
Total gas	3.47	Monobutyl phosphate	0.31
Dibutyl phosphate	1.47	Phosphoric acid	0.02

6. METAL RECOVERY

The Metal Recovery Plant has been operated to recover uranium, plutonium, and neptunium from various feed materials. The process for neptunium was developed as a modification of the Purex process.

6.1 PLANT OPERATION

Sodium diuranate sludge from ORNL waste tank W-10 and uranyl carbonate solution from tank W-7 were processed to recover 28.3 tons of uranium. Plant throughput averaged 450 lb/day and was limited by the uranium concentration of the tank farm material.

Approximately 8.0 tons of uranium and 3.5 g of Np^{237} were recovered from 3500 gal of partially decontaminated uranyl nitrate solution from Chalk River. Based on the development work conducted during this program, a modified Purex flowsheet

(Fig. 6.1) was proposed for recovering uranium, plutonium, and neptunium from irradiated uranium.

K-25 fluorinator ash resulting from the conversion of UO_3 to UF_6 was processed to recover 17.9 g of Np^{237} and 1.0 ton of uranium. Dissolution of the ash in 1.4 M $\text{Al}(\text{NO}_3)_3$ -1.0 M HNO_3 was followed by one cycle of solvent extraction and by evaporation to concentrate the product.

Chalk River plutonium nitrate solutions, PuO_2 , and plutonium-laden scrap were processed to recover 3.6 kg of purified plutonium as a nitrate solution. Of the total quantity of material handled, 1.8 kg required processing by ion exchange methods; the remainder required dissolution, one cycle of solvent extraction, and isolation by ion exchange.

6.2 PLUTONIUM OXIDE DISSOLUTION

Four PuO_2 dissolvings, each batch containing approximately 370 g of plutonium, were made during

the Chalk River plutonium program. Dissolution of PuO_2 was complete in 52 hr in 12 M HNO_3 -0.02 M HF (Fig. 6.2), the optimum concentrations. Nitric acid concentrations of 10 to 12 M and HF concentrations of 0.01 to 0.03 M were tried.

6.3 NEPTUNIUM RECOVERY PROCESS

Investigation of neptunium behavior in the Purex process¹ indicated that Np^{237} can be recovered directly as a by-product in this process. In the recovery scheme Np(VI) , which has been formed by oxidation of the feed in the column with 0.01 M NaBrO_3 or 0.05 M NaNO_2 , is extracted with the uranium and plutonium. In the plutonium-partitioning contactor the neptunium is kept in the uranium-bearing solvent by control of the nitric acid concentration. The neptunium is stripped with the uranium by water in the uranium-stripping contactor. In the second uranium cycle, neptunium is coextracted with the uranium in the first contactor and is separated from the uranium in a partitioning contactor. The flowsheet has been demonstrated in the laboratory and on a pilot-plant scale.

¹J. M. Chandler and D. O. Darby, *Terminal Report for the ORNL Pilot Plant Investigation of the Purex Process*, ORNL-1519 (Feb. 24, 1954).

Laboratory Development.—In batch equilibrations with Np^{239} tracer, the addition of 0.01 M NaBrO_3 to the feed after the normal nitrite adjustment step oxidized the neptunium to Np(VI) and permitted extraction; without the addition of NaBrO_3 , the neptunium, in the IV or V state, could not be extracted (Table 6.1). Sodium nitrite, 0.01 M, did not oxidize neptunium to the extractable VI state. However, a more recent experiment in the ORNL Metal Recovery Plant indicated that 0.05 M NaNO_2 in the extraction-scrub stream promoted neptunium extraction. Further work will be done to determine the effects of NaNO_2 concentrations greater than 0.1 M on neptunium extraction.

In a batch-countercurrent experiment neptunium, once extracted, was reduced to Np(IV) , probably by the TBP, in the scrub section and was eventually lost to the raffinate. This effect was counteracted by the addition of 0.01 M NaBrO_3 to the aqueous scrub. Extraction factors indicated that the 6- to 12-min contact time was adequate.

Batch equilibrations simulating the various stages of the partitioning column indicated that, although the neptunium would reflux, it would remain in the solvent and be carried into the first-cycle stripping column when the nitric acid concentration in the partitioning column was >1.1 M.

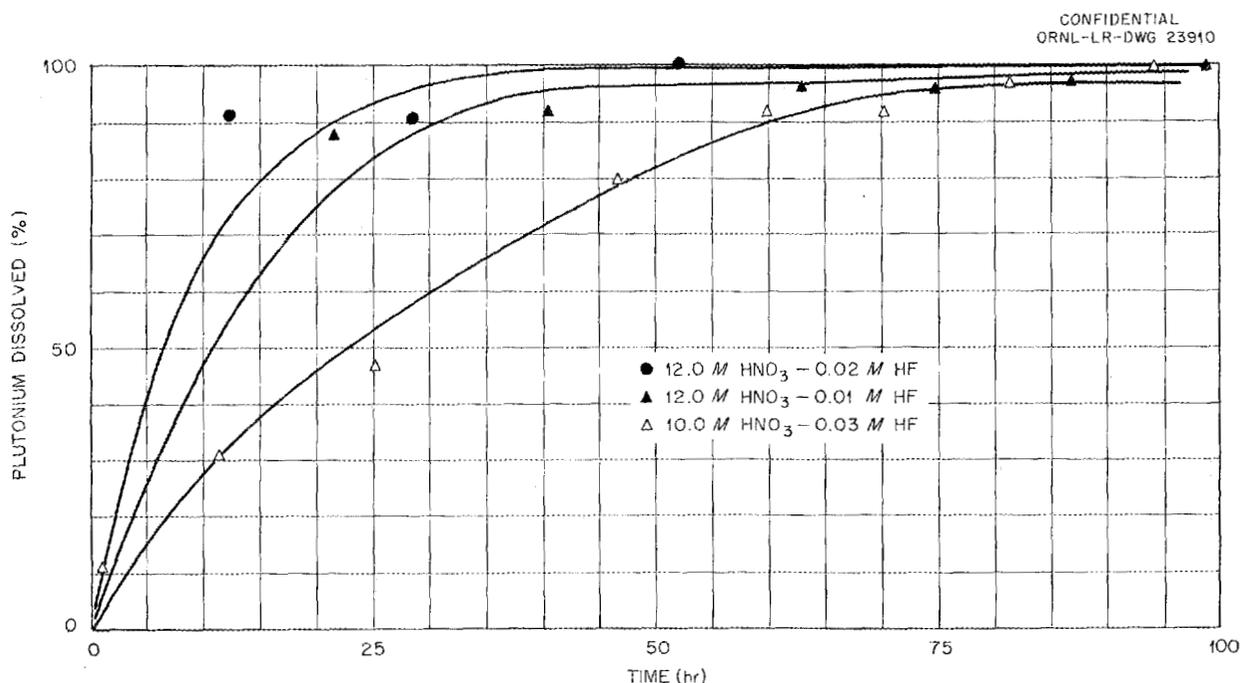


Fig. 6.2. Dissolution of Chalk River PuO_2 . Approximately 421 g of PuO_2 per batch.

Table 6.1. Neptunium Extraction Factors Under Purex Feed-Plate Conditions

Organic phase (2 vol): 103 mg U per ml, 0.17 M HNO₃
 Aqueous phase (1 vol): 35 mg U per ml, 3.75 M HNO₃

Feed Treatment	Distribution Coefficient	Extraction Factor*
None	0.18	0.36
0.01 M NaNO ₂	0.22	0.44
0.01 M Fe(NH ₂ SO ₃) ₂	0.29	0.58
0.01 M NaBrO ₃	1.01	2.02

*Extraction factor

$$= \text{distribution coefficient} \times \frac{\text{volume of organic phase}}{\text{volume of aqueous phase}}$$

An extraction factor greater than 1 is required.

A batch-countercurrent experiment verified the results of the equilibration.

In a test of the modified Purex flowsheet in 0.75-in.-dia pulsed columns with synthetic feed containing Np²³⁹ tracer, neptunium was extracted and carried through the first cycle with the uranium, for subsequent selective stripping in the second uranium cycle. Plutonium and uranium losses were less than 0.01% to all streams; neptunium losses were 0.17% to the extraction-column waste stream and 0.07% to the plutonium product stream from the partitioning column.

Careful control of the acidity in the partitioning column was necessary to avoid carrying the neptunium with the plutonium. When the acidity of the plutonium product stream was greater than 1.1 M, the neptunium remained with the uranium in the solvent. When the acidity of the plutonium product stream dropped below 0.8 M, the neptunium followed the plutonium.

Plant Tests. — Uranyl nitrate solution from Chalk River, which contained no plutonium, was processed by the modified Purex second-uranium-cycle flowsheet.¹ Over-all uranium and neptunium recoveries were 99.8 and 88.0%, respectively.

Uranium and neptunium were coextracted with 30% tributyl phosphate in a kerosene diluent with a uranium solvent saturation of 75%. Neptunium extraction losses under these conditions were less than 1%. A reductant, 0.05 M ferrous ion, which was added to the extraction column to convert the plutonium to the less extractable state, promoted neptunium extraction. When the reductant was omitted, neptunium extraction losses increased to 80%.

Neptunium was separated from the uranium with 0.01 M HNO₃, the acid concentration of the aqueous stream leaving the partitioning column being maintained at 0.8 M. Less than 1% of the neptunium went with the uranium and less than 0.001% of the uranium followed the neptunium. Increasing the acid concentration in the partitioning column from 0.8 M to 1.4 M caused the neptunium to remain with the uranium.

One 67-hr run was conducted to observe the fate of neptunium under Purex first-cycle extraction conditions. With 0.05 M NaNO₂ in the scrub, neptunium was extracted with the uranium and plutonium with a loss of <1%; omission of the nitrite resulted in neptunium extraction losses of 100%.

Neptunium Recovery from Fluorination Ash. — Possible modifications to the Neptex process flowsheet² for the recovery of neptunium from fluorination ash were studied to determine whether the unit cost for the Np²³⁷ product could be lowered. The major cost item in the Neptex flowsheet is the aluminum nitrate required in the ash-dissolution step, which gives a solvent extraction feed 1.8 M in Al(NO₃)₃. In laboratory experiments the feed uranium concentration was increased from 50 to 75 g/liter in 1.8 M Al(NO₃)₃ without adversely affecting the Np(IV) extraction coefficient. This change reduced the aluminum nitrate requirement 33%.

²J. R. Flanary *et al.*, *Recovery of Np²³⁷ by the Neptex Solvent Extraction Process*, ORNL-2235 (March 11, 1957).

7. THOREX PROCESS

In the Thorex process, thorium and U^{233} are separated from each other and from fission products and are recovered as aqueous solutions suitable for direct handling during subsequent processing to the metal. Irradiated thorium is dissolved in excess nitric acid, concentrated to remove the excess acid, and processed through two solvent extraction decontaminating cycles. The thorium and U^{233} are extracted by tributyl phosphate in a kerosene-type diluent (Amsco) and costripped with dilute nitric acid in the first cycle, are continuously concentrated and adjusted, and are re-extracted and partitioned in a second cycle. The thorium product is continuously evaporated to 2 M, and the U^{233} is further purified and concentrated by ion exchange.

7.1 PILOT PLANT OPERATION

The Thorex pilot plant was converted to the co-decontamination flowsheet (Fig. 7.1), which was developed in the laboratory.¹ In five runs (HD-20 through HD-25), 5.5 metric tons of irradiated thorium and 5 metric tons of recycle thorium were processed. A total of 10.5 metric tons of thorium product was recovered and 11.8 kg of U^{233} was separated.

Average decontamination factors for the thorium and uranium products, after ion exchange, are given in Table 7.1. Feed material for the five runs had been irradiated to 3400 g of U^{233} per metric ton of thorium and had decayed about 400 days. Both products met the tentative activity specifications (Table 7.2) established from considerations of the biological hazards encountered during subsequent processing. In laboratory-scale experiments, the two cycles had given comparable decontamination when processing the same feeds. In pilot-plant operation, decontamination factors for the second cycle were less than those for the first cycle but tended to compensate for first-cycle malfunction to provide satisfactory products. Solvent extraction losses averaged about 1.30% for the thorium and 0.29% for the uranium (see Table 7.3). The high thorium loss in the extraction

Table 7.1. Average Decontamination Factors for Thorex Products, Runs HD-20 Through HD-25

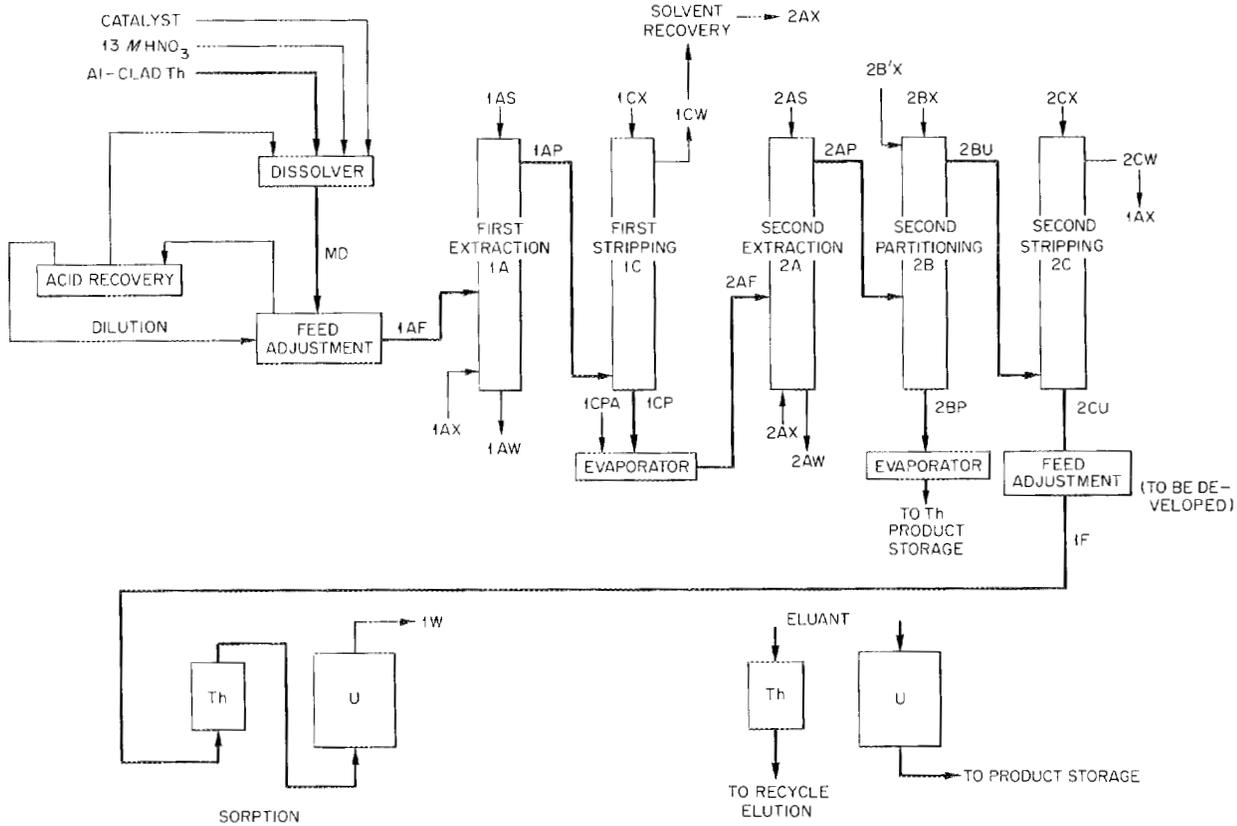
	Thorium	Uranium
Gross gamma	4×10^4	2×10^5
Pa	2×10^4	1×10^5
Ru	2×10^4	5×10^4
Zr-Nb	4×10^4	5×10^5
Total rare earths	2×10^6	1×10^7

columns is attributed to the acid deficiency in the extraction section and to degradation products from the intercycle evaporator. About 75% of the uranium loss was in the thorium product (55%) and in the 2CW stream (20%) and is therefore recoverable. The amounts of ionic contaminants in the products are shown in Table 7.4.

Satisfactory operation of the plant with the co-decontamination flowsheet required 25% reduction of the plant capacity owing to the increased rate of the aqueous strip (ICX) in the first cycle. Other operating modifications made to improve equipment performance consisted in preheating the ICX stream, replacing the IC-column pressure-pot level control with a remotely operated pump, stricter control on flow rates, and installation of glass-fiber filters on all nonradioactive process streams.

A modified U^{233} isolation system was developed in the laboratory and installed in the pilot plant, which incorporates upflow sorption and downflow elution. The new system simplifies operation by permitting a small uranium heel to be retained on the resin column, thus eliminating large volumes of dilute tailings that require recycle through solvent extraction. Elution with 6 N HNO_3 was satisfactory. At an eluant flow rate of 0.5 ml/cm²/min, 97% of the uranium was eluted to give a product with a uranium concentration of 86 g/liter and a nitric acid concentration of 4.88 N. This solution can readily be adjusted to a satisfactory feed for the third uranium cycle and eliminates the precipitation difficulties experienced with the acetate-citrate eluant.

¹Details of the laboratory development have been given in the *Chem. Tech. Monthly Prog. Reps.* (see Appendix).



Stream

Composition

MD	Th, 230 g/liter; U, 0.58 g/liter; H ⁺ , 6 N; Al, 0.4 M; F ⁻ , 0.038 M; Hg, 0.002 N
1AF	Th, 350 g/liter; U, 0.87 g/liter; Al, 0.6 M; H ⁺ , 0.3 N acid deficient; F ⁻ , 0.06 M; Hg, 0.004 M; PO ₄ , 0.002 M
1AX	Tributyl phosphate, 42.5%; hydrocarbon diluent, 57.5%
1AS	0.5 M Al(NO ₃) ₃ , 0.2 N acid deficient, 0.003 M PO ₄ , 0.005 M Fe ⁺⁺
1AP	Th, 67 g/liter; U, 0.18 g/liter in TBP-diluent
1CW	Contaminated TBP-diluent
1CP	Al, 2.3 M; H ⁺ , 1.4 N acid deficient
2AS	Al(NO ₃) ₃ , 0.5 M; H ⁺ , 0.2 N acid deficient; PO ₄ , 0.003; Fe ⁺⁺ , 0.005 M
2AP	Th, 67 g/liter; U, 0.18 g/liter in TBP-diluent
2B'X	HNO ₃ , 0.24 N
2BX	Demineralized water
2BT	Th, 58 g/liter; H ⁺ , 0.2 N
2BU	Th, 0.01 g/liter; U, 0.13 g/liter in TBP-diluent
2CX	HNO ₃ , 0.008 N
2CU	U, 0.26 g/liter; H ⁺ , 0.02 N
1F	U, 0.26 g/liter; H ⁺ , 0.02 N
1W	H ⁺ , 0.05 N
Eluant	NH ₄ acetate, 3 M; acetic acid, 1.5 M; NH ₄ citrate, 0.75 M

Fig. 7.1. Thorex Process Co-decontamination Flowsheet.

Table 7.2. Thorex Product Activity Spectra, Runs HD-20 Through HD-25

Contaminant	Activity (c/m/mg)			
	Thorium		Uranium*	
	Specifications	Observed	Specifications	Observed
Gross gamma	260	80	9000	6000
Pa gamma	30	3	1000	40
Ru gamma	40	10	280	130
Zr-Nb gamma	45	30	8000	1000
Total rare earth beta	10	5	450	60

*The uranium product radiation was 200 mr/hr, as compared with specifications of 300 mr/hr.

Table 7.3. Solvent Extraction Losses in Thorex Runs HD-20 Through HD-25

Process Step	Average Loss (%)	
	Thorium	Uranium
	Extraction	1.20
Partitioning	0.02	0.16
Stripping	0.07	0.06
Ion exchange	<0.01	<0.01
Product recovery	<0.01	<0.01
Total	1.30	0.29

Table 7.4. Ionic Contaminants in Thorex Products, Runs HD-20 Through HD-25

Contaminant	Amount (ppm)	
	Thorium	Uranium
Al	70	30
B		30
Ca, Mg	4	8000
Fe, Cr, Ni	200	600
Others	100	200
U	5	
Th		500

7.2 PILOT PLANT MODIFICATIONS

Design and installation were completed for the following additions to the Thorex pilot plant, preparatory to the processing of 4.5 metric tons of short-decayed thorium:

- (1) an ion exchange system for the isolation of U^{233} , incorporating upflow sorption and down-flow elution;
- (2) a third-cycle solvent extraction system for the final purification of the U^{233} product;
- (3) a 5,000-gal-capacity storage system for the concentrated raffinate from the first-cycle extraction column for the decay of Pa^{233} to U^{233} . Ten to fifteen per cent of the mass 233 available is present as Pa^{233} ; this can be recovered as isotopically pure U^{233} by reprocessing after decay of the Pa^{233} .

Modifications consisted in conversion of the plant to the co-decontamination flowsheet and installation of the following:

- (1) an interface purge system for the first-cycle extraction column for the continuous removal of interfacial solids by filtering through a glass-fiber filter medium;
- (2) a liquid-caustic scrubber for removal of I^{131} from the off-gases from dissolution and feed adjustment;
- (3) additional unit shielding of process equipment;
- (4) a sample conveyor for transporting samples from the plant to the high level analytical facility (Sec. 21).

7.3 PROCESS DEVELOPMENT

Ruthenium Chemistry. - Ruthenium decontamination factors have been the most uncertain variable

in the Thorex process. In further laboratory studies, ruthenium and thorium extractabilities decreased with increasing acid deficiency (Fig. 7.2). In the Thorex pilot plant, feeds are now adjusted to 0.4 M acid deficiency, which in laboratory studies gave ruthenium decontamination factors of 600 and thorium losses of 1.0% in the extraction column. This represents a compromise between desired decontamination and allowable thorium loss.

Decalin as a Diluent. - The use of Decalin (decahydronaphthalene) as a substitute for Amsco as a diluent has several possible advantages. The solubility of the $\text{Th}(\text{NO}_3)_4 \cdot 2\text{TBP}$ complex is about 125 g of thorium per liter in a 42.5% TBP-Decalin solution, as compared with about 86 g in 42.5% TBP-Amsco. This higher solubility would reduce the probability of third-phase formation in Thorex pilot-plant equipment. Since the extractability of fission products decreased with increased loading of the organic phase with thorium (Fig. 7.3), this diluent would increase product decontamination. In laboratory-scale experiments with 35% TBP-Decalin (to maintain the same organic density as 42.5% TBP-Amsco) and current-flowsheet flow ratios, the activity in the product was reduced to analytical limits. The increased loading increased the thorium loss by a factor of about 2. However, in tests in 2-in.-dia pulsed columns, the height of

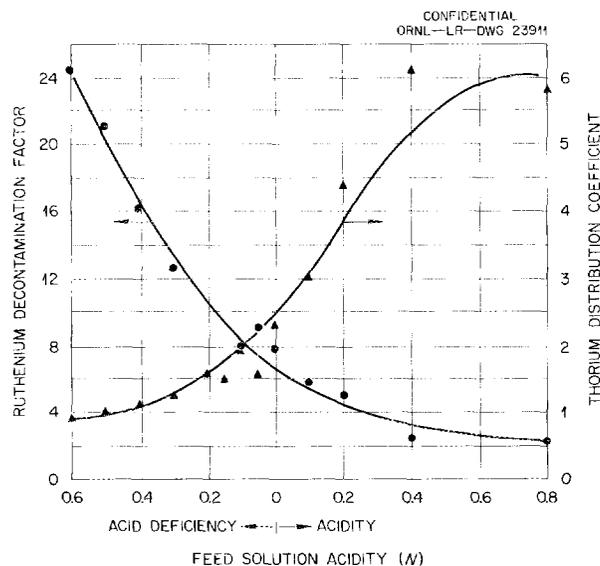


Fig. 7.2. Ruthenium Decontamination Factor and Thorium Distribution Coefficient at Various Feed Acidities under Feed-Plate Conditions.

column equivalent to one theoretical stage was 5.6 ft with 35% TBP-Decalin, as compared with 2.0 ft with 42.5% TBP-Amsco, and the flooding capacity was reduced about 25% with comparable pulse frequencies. Decalin offered no advantages over Amsco with respect to radiation stability; the irradiation degradation of both diluents, as measured by the reaction with iodine, was about 0.9 free radical formed per 100 ev of radiation.

Processing of Short-decayed Thorium. - In processing of highly irradiated thorium decayed less than 90 days, other difficulties arose. The 8-day ^{131}I formed in fission, which had not decayed, reacted irreversibly with unsaturated organic compounds present, so that recycled solvent was

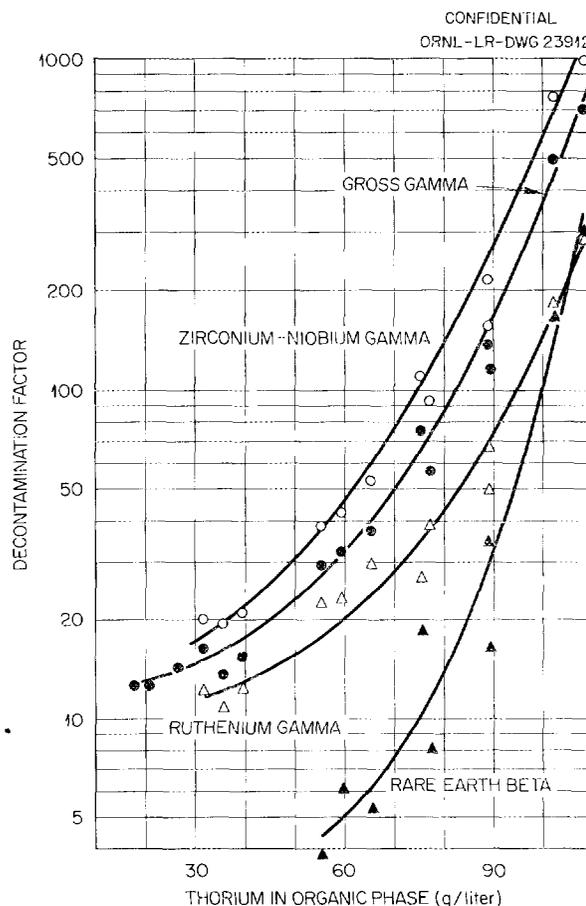


Fig. 7.3. Fission-Product Decontamination Factors for Various Concentrations of Thorium in the Organic Phase. Aqueous phase contained 0.55 M $\text{Al}(\text{NO}_3)_3$; single organic-aqueous contact.

very radioactive, and product decontamination from ruthenium was very unsatisfactory.

Only 30 to 60% of the I^{131} is vaporized during the thorium-dissolution step. The addition of 0.01 M I^{127} to the dissolvent as a carrier increased the I^{131} removal to about 95%. Over 50% of the unremoved iodine is extracted by the solvent extraction step as elemental iodine or as a mercury complex. Elimination of mercury as a dissolver catalyst was found possible, without decreasing the dissolution time cycle, and the inclusion of 0.01 M KI and 0.01 M $NaHSO_3$ in the scrub increased the over-all I^{131} removal to more than 99.5%.

The one-cycle decontamination factor from ruthenium, when material decayed more than 180 days is processed, is between 500 and 1000. With highly irradiated short-decayed thorium, this factor was decreased to 2-4. In laboratory-scale experiments with nonextractable ruthenium (decontamination factor 500), 0.01 M nitrite decreased the decontamination factor by a factor of 10 and 0.1 M nitrite decreased it by a factor greater than 100. Irradiation of the aqueous feed solutions to as little as 2 watt-hours per liter decreased the decontamination factor by a factor of about 2. Irradiation to 128 watt-hours per liter resulted in the ruthenium being over 90% extractable. It was assumed that the radiation from the short-decayed material produces nitrite, which reacts with ruthenium to form a highly soluble complex.

Heating the thorium solution with sulfite, bisulfite, or sulfamic acid restored the ruthenium to a nonextractable form. Decontamination factors were routinely in excess of 1000 when 0.01 M $NaHSO_3$ was added in the solvent extraction feed. Sulfite, when added in concentrations greater than molar equivalent to the nitrite produced, protected the ruthenium against the conversion to an extractable form by irradiation.

Decontamination of Uranium Product from Ruthenium. — In laboratory-scale tests, ruthenium in dilute uranyl nitrate solution was converted, by the addition of at least 2 g of $NaNO_2$ per liter and heating for 0.5 hr at 70 to 80°C, to a form that was

not sorbed on cation exchange resin. Use of this treatment before the uranium was sorbed on Dowex-50 cation exchange resin increased the ruthenium decontamination factor from 2.4 to 75. Full-scale tests are scheduled in the pilot plant to determine the effect of the added sodium on the capacity of the Dowex-50 resin for uranium.

Conversion of Uranyl Acetate to Uranyl Nitrate. — About 1.2 kg of U^{233} ion exchange product was converted from uranyl acetate-citrate to uranyl nitrate by precipitation of uranyl peroxide at pH 1.5, drying, and redissolution in nitric acid.

7.4 COMPONENT STUDIES

Removal of Interfacial Solids from Pulsed Columns. — A proposed method for continuous removal of interfacial solids from the Thorex extraction column was found satisfactory in tests in a 2-in.-dia glass pulsed column. The method consists in pumping a stream from the interface through a Fulflo glass-fiber filter and a Selas phase separator, and returning the resulting organic and aqueous streams to their respective phases in the column (Fig. 7.4). A Lapp pump is used in preference to a centrifugal pump to reduce further emulsification. The severity of emulsion formation was found to increase as the surface tension of the scrub solution to the column decreased (visual observation) and as the temperature of the recycle stream increased. Radiation damage studies of the Selas separator membranes indicated satisfactory stability. Such a system was installed in the Thorex pilot plant (Sec. 7.2). The flowsheet for the pilot plant provides an option for introducing the scrub onto the filter and for introducing the contaminated aqueous stream from the separator either below the column interface or tangentially at the interface. In the 2-in.-dia column tests, when the aqueous phase was reintroduced tangentially at the interface there was a definite optimum rate of recycle, below which emulsion was not removed fast enough and above which it seemed to re-form. However, reintroducing the aqueous phase below the column interface eliminated this operating restriction.

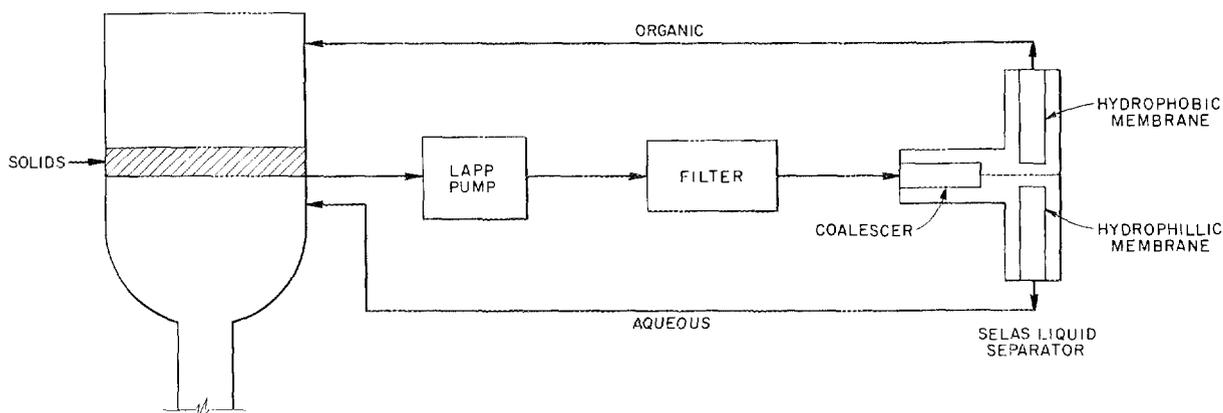


Fig. 7.4. Continuous Interfacial-Solids Removal System.

8. AMERICIUM RECOVERY

Scouting and development work has been aimed at purifying 40 g of Am^{241} contaminated with about 40 kg of lanthanum.

Since americium and lanthanum have very similar chemical properties, the best method of separation and purification seems to be ion exchange. Preliminary investigations indicated that thiocyanate complexing of the americium will permit ion exchange separation of the two elements.

The thiocyanate complex of americium is considerably stronger than that of lanthanum, and when americium was sorbed by an anion exchange resin from 5.0 M NH_4CNS , 90% of the lanthanum broke through. Passage of 2.0 M NH_4CNS through the column then removed 90% of the sorbed lanthanum, leaving essentially all the americium and about 1% of the original lanthanum on the column.

Elution of americium from a cation exchange resin column with 5.0 M NH_4CNS left 90% of the

lanthanum on the column, giving a product that contained nearly 100% of the americium and only 10% of the original lanthanum.

Laboratory scouting tests have shown that separation of lanthanum and americium by solvent extraction is feasible. Americium distribution coefficients between tributyl phosphate and nitric acid increased from 0.17 to 5.1 as the acid concentration increased from 7.5 N to 17.2 N. Over this same range of acidity lanthanum distribution coefficients increased from 0.046 to 0.53. In a laboratory batch countercurrent extraction consisting of four scrub stages, in which the nitric acid concentration was 15 M, and six extraction stages, in which the nitric acid concentration was 17 M, only 0.8% of the lanthanum was in the exiting organic phase. The calculated americium recovery was 99.96%.

9. WASTE TREATMENT

Waste studies have been concerned mostly with the removal of fission products from reactor cooling water and from aluminum nitrate first-cycle solvent extraction waste. Work is just starting with wastes bearing stainless steel and zirconium.

9.1 REACTOR COOLING WATER

The possibility of building a high-capacity, compact continuous ion exchanger for treatment of contaminated cooling water has been referred to the Illinois Water Treatment Company.

9.2 ALUMINUM-CONTAINING WASTE

The aluminum nitrate ion exchange process has gone through several stages of development. First, aluminum nitrate was treated directly by scavenging and ion exchange.¹ Fission-product separation was improved by converting the aluminum to dibasic aluminum nitrate² or by adding caustic

and forming sodium aluminate³ prior to ion exchange. The increase in ion exchange efficiency is largely the result of the very high affinity of phenolic cation exchange resins for cesium in alkaline solutions. However, at the high pH, strontium and rare earths were scavenged along with zirconium, niobium, and ruthenium. The addition of a large amount of sodium in the neutralization step greatly increases the volume of the waste, which is therefore recycled. The recycle of caustic is accomplished by electrolytic destruction of nitrate or by migration of nitrate in an ion exchange membrane cell (Fig. 9.1).⁴ This general approach to waste treatment has also been investigated by Barney *et al.*⁴ The purpose of the ORNL program is to evaluate a number of proposals and combine them into an effective comprehensive waste-treatment scheme.

¹R. E. Blanco, I. R. Higgins, and A. H. Kibbey, *Separation of Fission Products from Aluminum Waste Solutions by Ion Exchange*, ORNL-301 Revised (Aug. 2, 1956).

²I. R. Higgins and R. G. Wymer, *Diban-Ion Exchange Waste Disposal Scheme. I*, ORNL-1984 (Nov. 10, 1955).

³I. R. Higgins, *The Alkaline Method for Treatment of High Radiation Level Aluminum Wastes*, ORNL CF-57-1-139 (Jan. 17, 1957).

⁴D. L. Barney, R. C. Feber, and R. F. Blais, *Investigation of Methods for the Removal of Fission Products from Coating-Removal Solution*, KAPL-1460 (Jan. 30, 1956).

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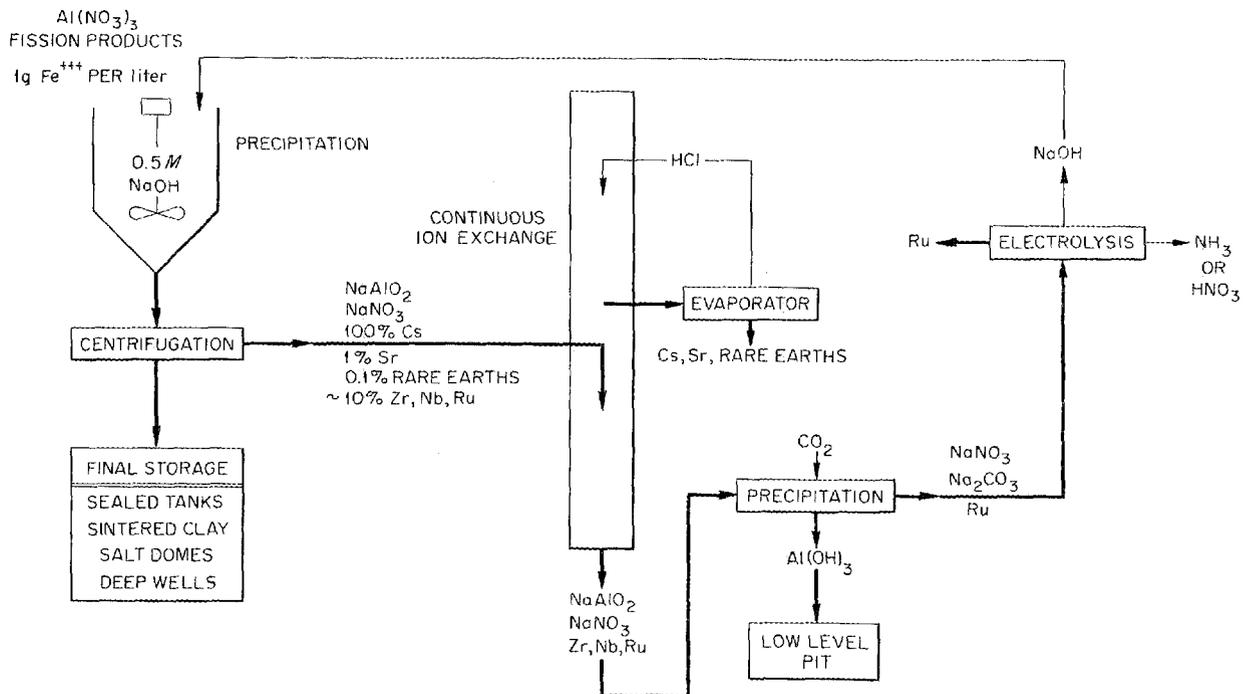


Fig. 9.1. Alkaline Treatment of High-Radiation-Level $Al(NO_3)_3$.

10. NONAQUEOUS PROCESSES

10.1 HERMEX PROCESS

The Hermex process¹ is a zero-valence-state process for recovering and decontaminating uranium from scrap metal or alloys. The uranium is dissolved in boiling mercury, from which it is separated by filtering, pressing, and retorting. The feasibility of the Hermex process for decontamination of irradiated uranium and purification of scrap uranium on a 30-g scale in glass apparatus has been reported.² More recently, stainless steel equipment has been built and operated to evaluate the various steps in the Hermex process.

Decontamination of Irradiated Uranium in Stainless Steel Equipment. - In a run in the stainless steel

equipment, decontamination factors (Table 10.1) were lower than in the glass equipment by approximately a factor of 100. The exact interdependence of decontamination and oxygen obtained from the atmosphere or from a vessel wall is not yet known. The dissolving step was the most effective step for removing fission products. Material balances were good for all components except plutonium (63%) and uranium (120%). Uranium losses were low. Low decontamination factors in the dissolving step for gross beta (2.6), for gross gamma (1.23), and particularly for total rare earth and strontium beta were attributed to small amounts of oxygen from the gas blanket. A system capable of producing vacuums of $<1 \mu$ and inert-gas atmospheres of <10 ppm oxygen is under construction to determine the effect of oxidation on uranium decontamination. Evaluation of the effectiveness of the dissolution and hot-filtration steps for fission-product removal in glass and in stainless

¹Chem. Tech. Semiann. Prog. Rep. March 31, 1956, ORNL-2079, Fig. 6.1, p 19.

²O. C. Dean et al., Status of the Hermex Process, ORNL-2242 (July 29, 1957).

Table 10.1. Removal of Fission Products from Irradiated Uranium
Uranium irradiated at 3.6×10^{17} neutrons per square centimeter, decayed 3.5 years

Component	Removal (% of total)			
	Dissolving and Slagging, Including Hot Filtration	Filtration, Including Cold Filtration After Crystallization	Aqueous Washing, Agitation of Quasi Amalgam with Cold 1 N HCl	Over-all, Including Experimental Handling
Uranium (losses)	5.12	0.474	0.417	6.47
Mercury (losses)	32.0			16.0*
Gross gamma	55.7	6.8	1.32	67.2
Gross beta	29.0	1.9	1.62	31.5
Cs beta	56.5	3.57	1.21	73.5
Sr beta	32.8	0.88	2.63	40.2
Total rare earth beta	16.0		1.77	23.0
Ru beta	25.0	1.87	0.28	36.6
Zr, Nb gamma	59.8	0.62	0.77	68.3
Pu alpha	4.2		1.1	64.5

*Inadequate condenser on dissolver.

steel apparatus is in progress. Results for glass apparatus showed very poor fission-product balances and are inconclusive.

Mercury Dissolution of Refractory Metals and Alloys. – Refluxing of STR-2 fuel samples in mercury at 800°C and 103 atm for 24 hr dissolved 14% of the uranium and 35% of the zirconium into the mercury phase. Hydriding at 350°C, annealing in argon at 600°C, and refluxing with mercury caused a separation of 26.2% of the uranium from the STR element into a floating slag phase; about 78% of the zirconium remained unchanged. Elemental niobium did not dissolve in mercury at 800°C and 103 atm. Refluxing of U-10% Mo alloy with mercury at 356°C dissolved 43.5% of the uranium in 48 hr.

Approximately half of a 4-g STR-2 sample was dissolved in 3.2 g of magnesium contained in a stainless steel bomb at 800°C for 24 hr. The remainder apparently was not immersed. Neither boiling mercury nor boiling dilute nitric acid extracted any uranium from the uranium-magnesium alloy.

Dissolution of Zirconium and Refractory Uranium Alloys in Fused Salts Floating on Mercury. – Low-melting combinations of fused chlorides floating on mercury were used to clean the metal sample surfaces to provide good metal-to-mercury contact. With $ZnCl_2$ - $NaCl$ - KCl salt mixtures of mole ratio 6/2/2 and $NaCl$ - $AlCl_3$ mixtures of mole ratio 1/1 containing 5 to 10 wt % $HgCl_2$ or 15 to 20 wt % NH_4Cl at 250°C, the oxide films were removed from zirconium, Zircaloy-2, and STR-2 prototype fuel elements so that the surfaces were completely amalgamated. Dissolution rates of the metals, when submerged in the mercury phase, were less than 0.03 mg/cm²·min. The addition of zinc, magnesium, or bismuth to the mercury phase did not increase the metal dissolution rate. When submerged in the fused-salt phase at 250 to 300°C over the mercury, the metals dissolved at rates of 0.3 to 76.9 mg/cm²·min as the $HgCl_2$ or NH_4Cl content was varied from 5 to 20 wt %. Negligible amounts of metal were transferred to the mercury.

Zircaloy-2 rod was anodically dissolved in fused $AlCl_3$ - $NaCl$, of mole ratio 1/1, over a mercury cathode at 300 to 350°C at the rate of 120 mg/cm²·min. The bath remained molten in this temperature range as aluminum ions were replaced by zirconium ions. Forty-five per cent

of the zirconium was found in the mercury and the remainder in the overlying fused salt.

Recovery of Uranium from Uranium-Magnesium Amalgam. – The operation of the Hermex process with magnesium amalgam was tested in one run. Ninety-two grams of FMPC uranium scrap was dissolved in 650 ml of 0.1 M magnesium amalgam at 365°C at an average rate of 2.5 mg/cm²·min. The amalgam was cooled, washed in 1 N HCl and water, and filtered to obtain a quasi amalgam containing approximately 3 wt % uranium. The quasi amalgam was pelletized and then vacuum-distilled in the Hermex retort and melting furnace at temperatures from 250 to 1200°C.

The product contained much slag, and the uranium had not consolidated into one billet. Individual pellets had a good appearance and a density of approximately 18 g/cc. The magnesium content was 55 ppm and the mercury content was 31 ppm. Approximately 45% of the uranium was in the slag as oxide with >99% of the magnesium. The high uranium loss was attributed to a high-oxygen furnace atmosphere.

10.2 FUSED SALT-FLUORIDE VOLATILITY PROCESS

In the fused salt-fluoride volatility process, uranium fuel elements are dissolved by HF in a molten fluoride mixture, and the UF_4 thus formed is fluorinated to UF_6 , which volatilizes, is absorbed in NaF traps, and is then desorbed and collected in cold traps.

Pilot Plant. – Construction of the volatility portion of the pilot plant was completed. The chemistry of the volatility process³ and the major equipment of the pilot plant⁴ have been described previously. Principal changes made since the flowsheet and description were previously published are: installation of a drier on the nitrogen supply, installation of a molten-salt sampler, substitution of NaF pellets for nickel mesh in the ZrF_4 snow trap and the addition of heaters on the snow trap, substitution of a nickel charge-melt vessel for the stainless steel vessel originally installed, addition of a sand seal on the charge-melt vessel and a liquid seal on the vent line to

³Chem. Tech. Semiann. Prog. Rep. Sept. 30, 1955, ORNL-2000, p 23 (classified).

⁴Chem. Tech. Semiann. Prog. Rep. Aug. 31, 1956, ORNL-2169, p 21.

maintain an inert atmosphere in the vessel, addition of heaters on the inlet and outlet lines of the absorbers, removal of the cold trap from the vacuum system, addition of a valve between the two process cold traps, and addition of steam coils and an agitator in the KOH surge tank.

Necessary equipment preparation and shakedown work were completed. For example, all fire brick used in the furnaces had to be cured in place. Vessels and instruments were calibrated, and operability of mechanical equipment such as pumps was checked. Fluorine disposal studies demonstrated that excess fluorine can be adequately disposed of in the present equipment.

The air-operated valves installed in the pilot plant are metal-to-metal-seating valves. The initial testing after installation showed that the majority of these valves were incapable of holding gas pressures without leaking. Remachining of the valves was necessary to avoid intolerable losses of UF_6 . A program is under way to obtain valves which will be more satisfactory for remote UF_6 service.

Studies were made to test equipment and develop operating techniques for transferring molten salt. The molten-salt-handling system is adequate at present, but additional study is needed covering design, construction, and operation.

Absorption and desorption studies were made by feeding UF_6 directly to the first absorber. These absorption and desorption studies revealed conditions under which losses at this stage could be held below 1%. The absorption of UF_6 by sodium fluoride releases sufficient heat to increase bed temperatures by 150 to 200°C. A high temperature in the absorber results in loss of UF_6 during absorption. Hence, it was necessary to start the absorption at 60 to 70°C, rather than 100°C as the original flowsheet specified, and to provide facilities for cooling the absorber during absorption.

In studies of desorption followed by reabsorption on a second NaF bed, losses (UF_6 not absorbed on the NaF) were as high as 10%. No explanation was found, and more laboratory work will be required before multiple-cycle absorption can be attempted in the pilot plant. During the absorption studies the possibility was investigated of loading absorbers with $NaHF_2$ and converting this material to NaF in the absorber. The performance of the resulting NaF was at least as good as, and was probably somewhat better than, that of purchased NaF. In addition, $NaHF_2$ is much cheaper than

NaF and can be obtained much more quickly and easily.

Experiments were made to check entrainment of salt from the fluorinator and vaporization of zirconium fluoride and chromium fluoride. At the low gas flow rates currently used (~ 0.5 scfm), physical entrainment was not serious. Vaporization of chromium fluoride (present as an impurity) and of zirconium fluoride was great enough to cause difficulty at points of condensation downstream. A nickel-mesh snow trap removed part of the ZrF_4 but no chromium. A sintered-nickel filter plate in the gas line removed most of the zirconium and chromium but plugged too rapidly. Sodium fluoride pellets, even at high temperatures, removed chromium and zirconium; the high temperature prevents retention of UF_6 .

Three complete flowsheet runs were made with nonirradiated salt containing approximately 10 kg of depleted uranium. In one of these three runs, 98.53% of the uranium reached the product cylinder. Recoverable losses in these three runs ranged from 3.5% to 1.0% (material remaining on sodium fluoride is considered recoverable). Nonrecoverable losses were 21% (caused by rupture of a fitting during product transfer), 0.45%, and 0.06%.

Design of a suitable hydrofluorination vessel was started. The two most troublesome points are the choice of a suitable material of construction and the rate of dissolution of fuel elements. In preliminary studies of the corrosion rates of various nickel-base alloys and copper-lined stainless steel in NaF- ZrF_4 with HF at Argonne National Laboratory,⁵ results with Hastelloy B were favorable. Corrosion rates of Ni-Mo alloys under hydrofluorination conditions will be compared with those of several high-nickel-base alloys and copper-lined stainless steel by Battelle Memorial Institute under a subcontract. Their work will, in part, parallel Argonne's work, but particular emphasis will be placed on studying the effect of sulfur in both the HF and the melt. Sodium fluoride-lithium fluoride melts will be used for part of the tests.

A system for studying the dissolution rates of actual SIW-type subassemblies was designed and is being installed in Building 4505. This unit will be capable of dissolving one-fourth of an unirradiated SIW-type subassembly in either NaF- ZrF_4

⁵Quarterly Reports of the Chemical Engineering Division at Argonne National Laboratory.

or NaF-LiF. The first hydrofluorinator will be of stainless steel lined with deoxidized copper, type DHP. Later, it will be replaced by one fabricated from a Ni-Mo alloy if Battelle corrosion results are favorable.

The feasibility of dissolving uranium-zirconium fuel elements by HF in NaF-ZrF₄ was established in laboratory studies.⁶ About 20 subassemblies each have been earmarked for use in dissolution and volatility-processing from both the S1W-1 and the first core discharged from the Nautilus (S2W-1). Phillips Petroleum Company's SIR-STR carrier-chargers will be used to transport these subassemblies from the National Reactor Testing Station to ORNL. Since these carrier-chargers have a bottom drawer which should preferably be opened to discharge the subassemblies while under about 4 ft of water, an underwater drawer operator was designed and fabricated. Tests at Idaho with an empty carrier-charger showed that the drawer operator is satisfactory.

Process Development. - In a series of four laboratory-scale flowsheet runs,³ the over-all UF₆ material balance was 97%, and the gross fission-product decontamination factor was >10⁶ for more than 80% of the material processed. The uranium in these tests had been irradiated at 600 Mwd/ton and had decayed 420 days.

Filtration of the UF₆-F₂ gas stream from the fused-salt fluorination step effectively removed

zirconium and niobium gamma, but not ruthenium gamma nor plutonium alpha activities. In a run with a grade H Micro Metallic nickel filter between the fluorination and absorption steps, the decontamination factors for the filtration step were 3600, 5200, 4, and 1.2, respectively, for zirconium, niobium, ruthenium, and plutonium activities.

Absorption by solids, as well as filtration, removed various activities from the UF₆-F₂ gas stream. Use of a special NaF bed at 400°C near the outlet of the fluorinator effectively removed ZrF₄ snow and volatile chromium fluorides, and improved the decontamination from ruthenium. Calcium fluoride at 100°C trapped plutonium from the UF₆ stream in addition to improving the product decontamination from ruthenium.

Studies on the relative volatilities of uranium, plutonium, and fission products in the fused-salt fluorination step showed that all the activity transfer occurs during the UF₆ volatilization, except for that of plutonium (Table 10.2).

Tests were made with 10 mole % UF₆ in N₂ as the flowing gas to determine the effects of flow rate, NaF particle size, and temperature on UF₆ absorption by NaF. Absorption was less efficient at 200 ml/min than at 100 ml/min, and it was less efficient with 1/8-in. pellets than with 12- to 20-mesh material. Increasing the temperature of absorption from 26 to 100°C also increased the absorption efficiency in one case; this indicates that the absorption reaction has an activation energy (Fig. 10.1).

Particle, bed, and over-all porosities of 48, 33, and 65%, respectively, were found for granular

⁶R. G. Wymer, *Dissolution of Uranium-Zirconium Fuel Elements in Fused NaF-ZrF₄*, ORNL-2183 (Jan. 24, 1957).

Table 10.2. Relative Volatilizations of Uranium, Plutonium, and Fission Products in the Fluorination Step

Sample	Time Interval (min)	Uranium Trapped (%)	Activity Trapped (% of total found in all fractions)						
			Gross Beta	Gross Gamma	Ru Gamma	Zr Gamma	Nb Gamma	Total Rare Earth Beta	Pu Alpha
1	25	0	1.0	0.5	0.1	0.4	0.5	0.3	0
2	10	10.7	37.2	31.9	47.5	21.4	32.6	30.3	0.1
3	10	24.1	39.3	43.2	31.8	30.2	42.3	32.8	0.3
4	12	31.4	17.4	17.8	12.5	11.7	18.6	25.0	0.9
5	10	25.7	3.9	5.7	4.7	34.7	5.1	9.2	4.0
6	20	6.5	0.7	0.6	1.8	1.3	0.5	1.3	30.0
7	55	1.6	0.5	0.3	1.6	0.2	0.2	1.1	64.7

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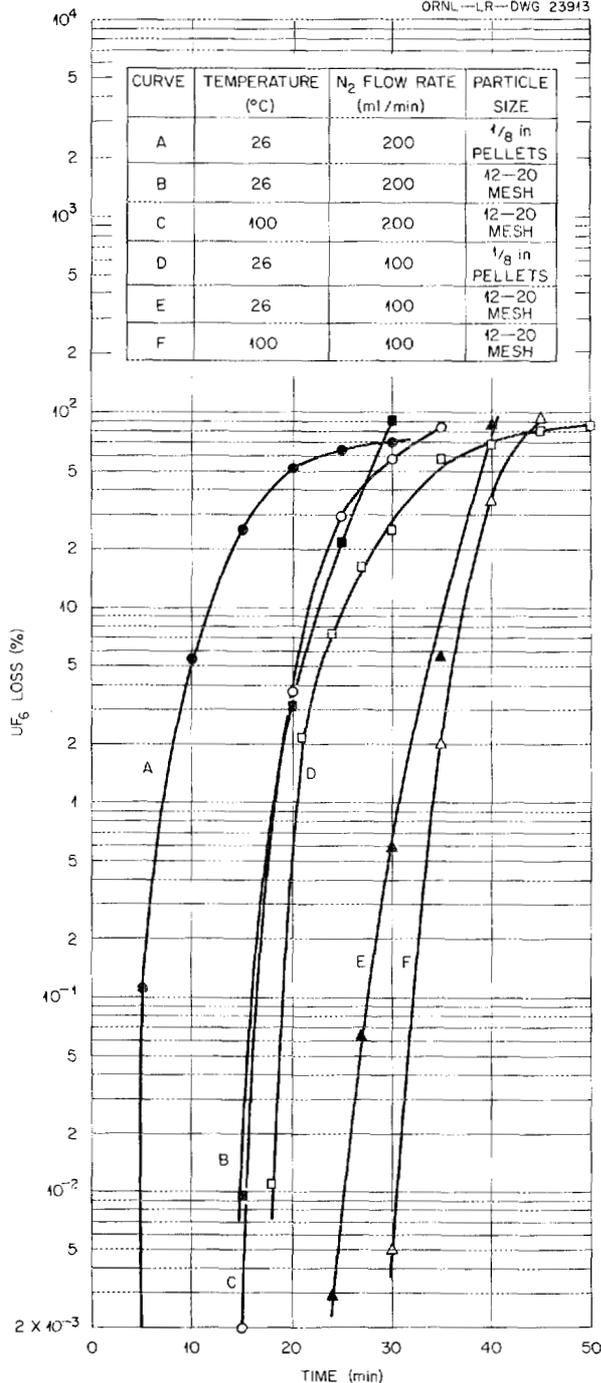


Fig. 10.1. Uranium Hexafluoride Loss in NaF Absorption Tests.

NaF (Harshaw Chemical Co.) from density measurements. There was no significant difference between three Harshaw lots, one being 12- to 20-mesh material, the others 1/8-in. pellets. Crystalline NaF from Allied Chemical & Dye Corp. was much denser, with an over-all porosity of 35 instead of 65%.

A brief study of the requirements for applying computer techniques to the prediction of the behavior of the fission-product absorber beds indicated that this experimental method is not applicable to this system.

The mixture 57 mole % LiF-43 mole % NaF (mp 675°C) was proposed as a melt in which to dissolve zirconium-uranium fuel elements, batchwise, with HF.⁷ This procedure is an alternative to the batch ZrF₄-NaF flowsheet outlined by Wymer⁶ and the semicontinuous ZrF₄-NaF plan proposed by Hyman *et al.*⁸ The main advantage of the LiF-NaF batch method is the higher average uranium concentration in each fluorinator charge, resulting in fewer subsequent fluorinations. Preliminary laboratory-scale runs showed that dissolution rates in this system (Table 10.3) were somewhat higher than in the ZrF₄-NaF system.⁶ Larger-scale tests are planned.

Equipment Decontamination. - A stainless steel NaF cold trap was easily decontaminated with 2.5% H₂O₂-10% sodium tartrate-10% NaOH solution. The trap read 600 mr/hr at contact before decontamination. Two 250-ml rinses with the alkaline reagent decreased the reading to 20 mr/hr, most of the activity being removed in the first rinse. More than 99% of the activity removed was ruthenium gamma.

Acid treatments were less effective.

Process Applications. - A survey of possible combinations of power reactor fuel processes, made by the MIT Engineering Practice School,⁹

⁷R. P. Milford, *Volatility Process - Use of NaF-LiF Melt for Batch Dissolution of Zirconium Type Reactor Fuels with HF*, ORNL CF-56-11-4 (Nov. 6, 1956) (classified).

⁸H. H. Hyman, R. C. Vogel, and J. J. Katz, "Fundamental Chemistry of Uranium Hexafluoride Distillation Processes for the Decontamination of Irradiated Reactor Fuel," chap. 6.1, in *Progress in Nuclear Energy, Process Chemistry*, Series III, McGraw-Hill, New York, 1956.

⁹G. Jansen and P. J. Birbara, *Zirconium-Uranium Fuel Element Processing Study*, KT-270 (Nov. 27, 1956).

Table 10.3. Initial Dissolution Rates
of Zirconium in Molten LiF-NaF
Saturated with Anhydrous HF
HF flow rate: 47 mg/min

Salt Mixture (mole %)			Temperature (°C)	Initial Dissolution Rate (mg/cm ² ·min)
LiF	NaF	ZrF ₄		
35	27	38	600	6
			700	8
26	19	55	600	1
			700	5
57	43		700	13

indicated that formation of uranium chloride from uranium fuel elements by the Zircex head-end treatment (Sec. 4.2) followed by fluoride volatility processing was worth further experimental study.

Dissolution of fuel elements containing type 347 stainless steel in molten NaF-ZrF₄ does not appear feasible. Estimates¹⁰ have indicated a solubility limit of 1.5 wt % stainless steel in the melt, which, with an APPR fuel element, would result in a uranium concentration of 0.1 wt % in the fused salt. In addition, the dissolution rate of this steel with HF in 53 mole % NaF-47 mole % ZrF₄ was very slow even at 700°C. Chromium in the stainless steel was preferentially attacked by HF, which resulted in disintegration rather than

¹⁰L. M. Ferris, *Preliminary Evaluation of the Fused Salt-Fluoride Volatility Process for APPR Fuel Elements*, ORNL CF-57-2-92 (Feb. 19, 1957).

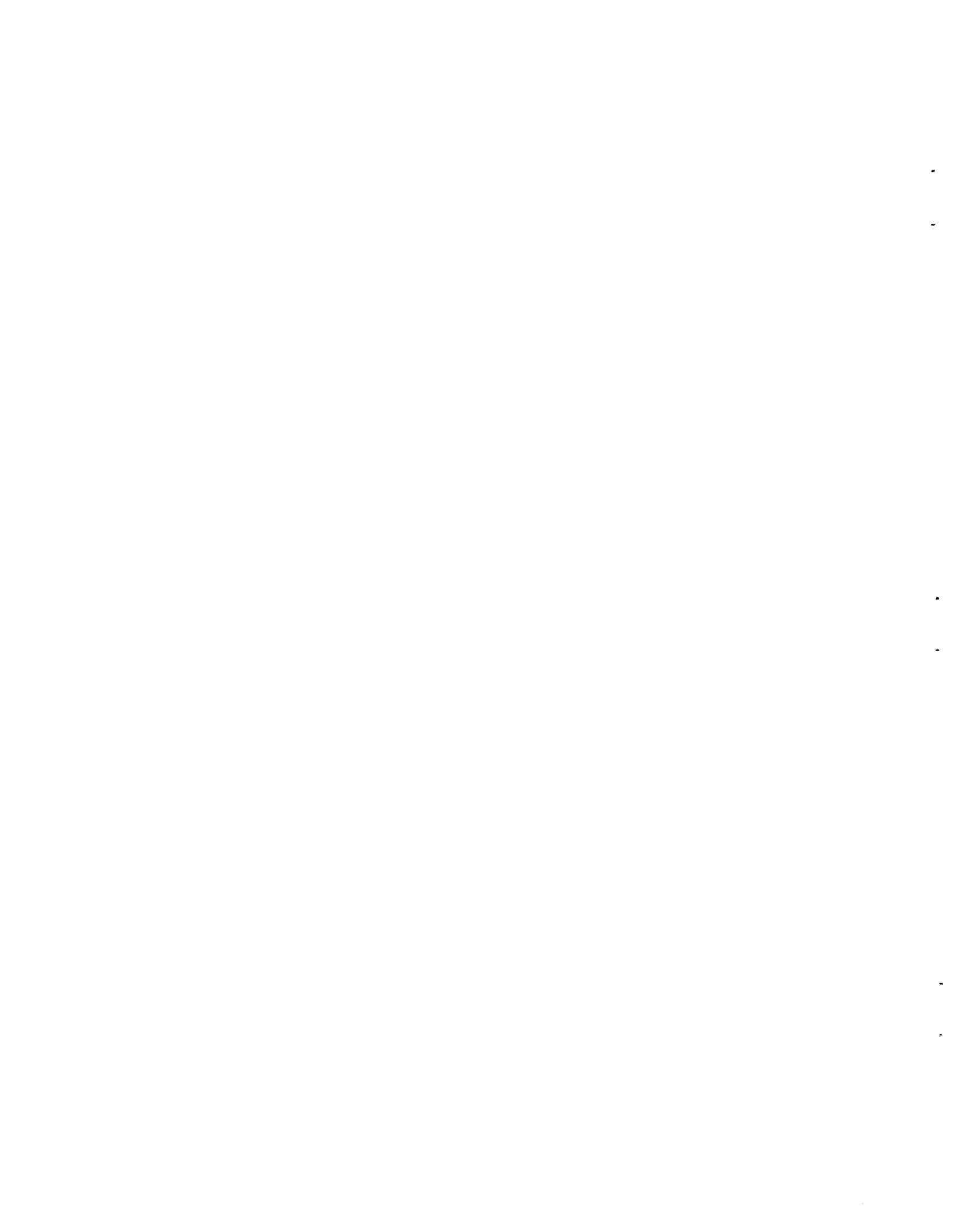
smooth dissolution of the fuel element, and metallic nickel was found in the resulting melts, which indicated an extremely low solubility of NiF₂.

The results of previously reported¹¹ corrosion tests had suggested that stainless steel-containing fuel elements could be oxidized or calcined in air at 650°C in the presence of fluorides, and that this process might serve as a head-end step to aqueous or volatility processing. The feasibility of this process was shown with an element having a UO₂-type 304 stainless steel core clad with type 304 stainless steel. The specimen, 30 mils thick, was completely converted in 1 hr to a substance completely insoluble, even in aqua regia. The product retained the shape of the original specimen. However, division through the thickness of the material occurred, possibly because of the nature of the core.

Aqueous leaching with 1.5 M HNO₃ for 0.5 hr at 95 to 100°C removed 95% of the uranium from oxidized material ground to -300 mesh. Fluorination of -100-mesh material with elemental fluorine at 350°C for 0.5 hr removed 97% of the uranium but increased the fluoride content of the oxide from 2% to 48%. Direct fluorination would therefore probably not be economic unless the oxides were previously hydrofluorinated. Thermodynamic evaluation of the conversion of Fe₂O₃ or Fe₃O₄ to fluorides indicated that this might be feasible at temperatures below 400°C. The temperature at which the free energy of reaction is zero was calculated to be 410°C for Fe₂O₃ and 475°C for Fe₃O₄.

¹¹Chem. Tech. Monthly Prog. Rep. Jan., 1957, ORNL-2251, sec 5.3, p 23.

Part III
HOMOGENEOUS REACTOR FUEL AND BLANKET PROCESSING AND DEVELOPMENT



11. HRT CHEMICAL PROCESSING PLANT

The high-pressure system, which contains the hydroclone and underflow pot, was completed in August 1956 and was then operated over 1000 hr at normal operating conditions of 280°C and 1700 psi. Approximately half this time was with water and half with natural uranium solution. A series of tests with simulated corrosion products, supplied by a pump loop in the adjacent cell, demonstrated operability and established performance characteristics of the hydroclone system. In March 1957 this system was operated, tied into the reactor system, for the first time. During 200 hr of operation, again with natural uranium solution, startup and shutdown procedures were perfected. The performance of the system was judged satisfactory.

Following the decision to sample the fission-product and corrosion-product solids removed from the reactor after complete dissolution in a light-water system, modification of the low-pressure system was undertaken to incorporate a tantalum-lined dissolver and decay storage tanks. Upon completion of these modifications in April, the entire low-pressure system was tested. A series of five tests established that essentially complete dissolution of the expected quantity of corrosion-product solids was attainable in a sulfuric acid system. In tests of the D₂O recovery system, complete separation of the light- and heavy-water systems was demonstrated with negligible losses of heavy water.

12. URANYL SULFATE FUEL REPROCESSING

During operation of a homogeneous thermal breeder reactor various fission and corrosion products will accumulate in the uranyl sulfate fuel solution and will adversely affect the operation of the reactor. Elements that will form insoluble solids under reactor conditions, such as zirconium, niobium, iron, and chromium, will be continuously removed from the fuel system by a hydroclone and concentrated into a receiver. Periodically these solids, accompanied by fuel solution, will be discharged from the high-pressure reactor system, and the uranium will be decontaminated from such soluble waste products as cesium, nickel, and rare earths before being returned to the reactor. Fission-product iodine will be concentrated, by a gas-liquid scrubber system operating at reactor pressure and temperature, into a small liquid stream for removal from the reactor. This method may provide a means of controlling Xe¹³⁵ poisoning without using a large-volume gas-liquid letdown stream. Radioactive noble gases purged from the reactor with a stream of oxygen will be retained in charcoal adsorption beds long enough to allow them to decay to a permissible activity level before being vented to the atmosphere.

12.1. URANIUM DECONTAMINATION

Laboratory studies have shown that a method, based on UO₄ precipitation, for decontaminating the uranium in the hydroclone underflow pot will make possible rapid return of the uranium to the reactor circuit. The process consists in separating soluble uranyl sulfate from insoluble fission and corrosion products at a temperature below 100°C and precipitating UO₄ from the clarified solution. The UO₄ is washed free of such soluble poisons as cesium and nickel and is dissolved in a stoichiometric amount of D₂SO₄ by heating to destroy the peroxide. This solution may then be returned to the reactor. Uranium losses for the process are 0.2%; decontamination from cesium and nickel is adequate.

12.2. BEHAVIOR OF FISSION- AND CORROSION-PRODUCT SOLIDS

The concentration of simulated HRT corrosion-product solids - mixed iron, zirconium, and chromium oxides prepared in the laboratory - added to circulating uranyl sulfate solutions in the HRT mockup and the HRT Chemical Plant decreased

exponentially with circulation time, whether or not a hydroclone was operating on the circuit, but the disappearance was much faster with the hydroclone operating. The concentration of solids in the underflow pot exceeded the concentration of solids in the circulating loop system by factors ranging from 10 to 1000, depending on the time the hydroclone operated and the amount of solids available for collection in the underflow pot. In laboratory studies agglomeration of particles of micron size into much larger masses was observed at 275°C, but such agglomerates disintegrated on cooling. Irreversible deposition on metal surfaces was observed only when such solids were in contact for some time with a surface hotter than the solution. In both glass and metal loops operating at room temperature, solids (ZrO_2) circulated for long periods of time without evidence of deposition. However, when identical solids were circulated in a metal loop at 250 to 325°C, 50 to 90% of the added solids disappeared from circulation within a short time. Evidence pointed to both mechanical de-entrainment in stagnant areas and deposition on hot walls in areas of highly turbulent flow. However, the contribution of each mechanism to the over-all process has not been determined, and the quantitative behavior of solids in the HRT reactor complex cannot be confidently predicted.

In initial operation of the HRT Chemical Plant (Sec. 11) the corrosion and fission products removed from the circulating fuel by the hydroclone will be dissolved in order that representative samples may be obtained. The dissolution procedure now recommended has given >99.5% dissolution of 400-g charges of corrosion-product solids. The procedure consists in two cycles, each a 4-hr reflux with 10.8 M H_2SO_4 and a 4-hr reflux with 4 M H_2SO_4 , at a ratio of 15 ml of 10.8 M H_2SO_4 per gram of solids. In the present dissolver the steam jacket is segmented to localize heating at the bottom of the uniformly heated dissolver and thus increase the agitation. In earlier studies with a rigid dissolver, dissolution was incomplete owing to insufficient agitation.

12.3 IODINE CHEMISTRY

In a circulating loop system containing 0.02 *m* UO_2SO_4 -0.005 *m* H_2SO_4 at 250°C, the specific

rate constant for reduction of iodate ion to free iodine was measured as 0.1 min^{-1} . The rate of oxidation of iodide ion to free iodine under the same conditions was too fast to be measured in the 1-liter loop used. The valence-state distribution and vapor-liquid equilibrium for iodine found in the loop system confirmed static laboratory data, but indicated a slightly greater tendency of iodine to go to the elemental form and to the vapor phase when only O_2 and H_2O were in the vapor phase. Addition of H_2 to the vapor phase and the presence of Co^{60} gamma radiation shifted the iodine valence-state equilibrium toward the elemental form.

At 100°C in 0.02 *m* UO_2SO_4 -0.005 *m* H_2SO_4 solution, iodate was more stable than elemental iodine in the presence of Co^{60} radiation as long as only O_2 was present. The stability of iodate was decreased by adding H_2 to the gas phase, by increasing the H_2SO_4 concentration, by raising the temperature, or by the presence of impurities such as Fe^{++} .

In the HRT mockup loop at Y-12, iodine added to the high-pressure system rapidly moved to the low-pressure system via the gas letdown system. In the low-pressure system the iodine collected in the platinum recombiner and impaired its efficiency. The efficacy of a silvered-alundum trap to prevent poisoning of the platinum catalyst was demonstrated.

12.4 RARE-GAS ADSORPTION

The characteristics of long charcoal-filled traps simulating the HRT charcoal beds for adsorption of fission-product rare gases are being studied. Data thus far accumulated show the capacity of Columbia grade G charcoal for krypton in an oxygen stream at temperatures above 0°C to be less than that indicated by extrapolation of lower temperature data. Charcoal containing water in equilibrium with the atmosphere had 25% less capacity than charcoal dried at 100°C. The presence of a small channel in horizontally situated traps decreased the breakthrough time of the trap by a factor of 10 when the channel constituted 3% of the total cross-sectional area of the trap.

13. URANYL SULFATE BLANKET PROCESSING

The proposed method for processing uranyl sulfate blanket solutions is to concentrate the precipitated PuO_2 , corrosion products, and fission products by means of solid-liquid hydroclones. The bulk of the solution is returned to the blanket, and the concentrated slurry is removed for further processing. Heavy water is recovered by evaporation, and the solids are dissolved in nitric acid to prepare a solvent extraction feed for plutonium recovery.

Plutonium formed in the uranyl sulfate blanket of the HRT can be expected to be distributed as follows: (1) in solution as Pu(IV) and Pu(VI), (2) as a loose precipitate, primarily PuO_2 , and (3) attached to vessel walls either as adsorbed ionic plutonium or as PuO_2 . At present, the amount of plutonium in each form can only be estimated. Experiments were carried out to determine the effect of different variables on plutonium behavior in 1.4 *m* UO_2SO_4 at 250°C. In addition, methods of dissolving corrosion products and PuO_2 were investigated.

13.1 PLUTONIUM VALENCE

When heated to 250°C in Pyrex containers, Pu(IV) dissolved in 1.4 *m* UO_2SO_4 was readily oxidized to Pu(VI) under an oxygen overpressure but not under a stoichiometric oxygen-plus-hydrogen overpressure. When heated in stainless steel vessels, Pu(IV) was readily oxidized by either an oxygen or a stoichiometric hydrogen-plus-oxygen overpressure. This oxidation is catalyzed by chromium dissolved in corrosion of the stainless steel. Even with an oxygen overpressure, plutonium remained in the tetravalent state when stainless steel corrosion was appreciable in the presence of 2 watts of gamma radiation per liter of solution.

13.2 PLUTONIUM ADSORPTION AND PuO_2 PRECIPITATION

Plutonium that does not remain in solution when 1.4 *m* UO_2SO_4 is heated to 250°C either is precipitated as PuO_2 or is adsorbed on the container walls. A very small amount of the adsorption is ionic, but most of the adsorbed plutonium is held

in the corrosion film as PuO_2 . Apparently plutonium will continue to be adsorbed on the walls and cannot be removed until the corrosion film itself is removed. Plutonium adsorption on titanium and stainless steel as great as 1 mg/cm² has been obtained.

Many of the variables affecting plutonium are not understood. The amount adsorbed seems to be a function of the type of metal, the plutonium concentration, and the ratio of exposed metal surface area to solution volume. It is probably also dependent on corrosion rate, radiation, and solution velocity.

13.3 PLUTONIUM BEHAVIOR IN 1.4 *m* UO_2SO_4 CONTAINED IN STAINLESS STEEL

When plutonium was added batchwise to 1.4 *m* UO_2SO_4 in a stainless steel container at the rate of about 6 mg per kilogram of H_2O per day, it was essentially all oxidized to Pu(VI), and it remained in solution until the concentration reached 45 mg per kilogram of H_2O . After the next plutonium additions, there was a rapid decrease of plutonium in solution to ~5 mg per kilogram of H_2O . The plutonium removed from solution was adsorbed on the stainless steel and also precipitated as PuO_2 .

13.4 IN-PILE EXPERIMENTS

Plutonium formed by LITR irradiation of 1.4 *m* UO_2SO_4 in titanium bombs was distributed between the bomb walls and the solution. Only negligible amounts were found as a loose precipitate that could be concentrated with hydroclones. The amount of plutonium in solution after irradiation varied from 12 to 50 mg per kilogram of H_2O . A considerable amount of the adsorbed plutonium was so tightly held that complete removal was possible only by the use of solutions that corroded the base metals. Neptunium formed in these experiments was largely in solution, with a small amount adsorbed on the titanium and negligible amounts in the precipitate.

13.5 DISSOLUTION OF BLANKET SOLIDS

Simulated HRT blanket solids containing 70% Fe_2O_3 , 18% Cr_2O_3 , 9.8% NiO, 1.2% ZrO_2 , 1% UO_3 ,

and 0.8% PuO₂ were dissolved readily and completely in anhydrous H₃PO₄ at 230°C. Complete solution was also obtained by heating the solids in 10.8 M H₂SO₄ at 156°C, dilution to 4.5 M H₂SO₄, and refluxing.

13.6 EXPERIMENTAL LOOP CONSTRUCTION

For study of the behavior of plutonium under reactor blanket conditions, loop P-1 was fabricated and installed. In initial tests with water, operation was satisfactory.

14. THORIUM OXIDE SLURRY DEVELOPMENT STUDIES

Further studies on ThO₂ slurries, which are potential homogeneous reactor fuel and blanket materials, were made to evaluate the effect of oxide firing temperature, particle size, and chemical additives on slurry properties. The study of the effect of neutron irradiation on slurry properties was continued, and the use of MoO₃ as a radiolytic-gas recombination catalyst was evaluated.

14.1 PARTICLE SIZE

Thorium oxide for slurry studies is usually prepared by calcination of thorium oxalate, which is precipitated from thorium nitrate by addition of oxalic acid. In studies on the effects of calcination temperature on thorium oxide, firing at 1000 to 1600°C did not affect the average particle size. For oxides of approximately the same particle size, the abrasive characteristic, measured on the jet impingement slurry abrasion tester, increased with increasing calcination temperature and showed a linear logarithmic dependence on reciprocal firing temperature ($^{\circ}\text{K}^{-1}$). This indicates an increase in the abrasive characteristic with increasing crystallite size, since the crystallite size increases markedly with increasing calcination temperature. Oxides fired at 1400°C for 64 hr and at 1600°C for 12 hr resisted degradation. Those fired at 1400°C for 12 hr and at 1600°C for 2 hr, as well as lower-fired oxides, were degraded. Grinding the oxides in a mortar, blending as a slurry in a Waring Blendor, and subjecting the slurries to ultrasonic treatment did not markedly affect the particle size of the oxides prepared from 10°C-precipitated oxalate and fired at 1000 to 1600°C.

14.2 SETTLING STUDIES

The settling rate, from room temperature to 300°C, of slurries of oxide prepared from 10°C-precipitated oxalate and fired at 1000 to 1600°C was maximum for the 1200°C-fired material. The settling results were obtained by the x-ray absorption technique. Oxide fired at 1600°C and pumped in a 100A loop at Y-12 showed relatively rapid settling and high flocculation compared with the unpumped material.

Hindered-settling rates from room temperature to 300°C decreased with decreasing particle size. Settling rates increased with increasing slurry temperature. Additional factors other than simple decrease in water viscosity appeared to be involved. Silicate addition slowed the rate at all temperatures and changed the shape and increased the slope of the temperature-dependence curve.

Local concentrations of ThO₂ at the bottom of the blanket in the slurry blanket mockup were considerably higher (1100 g of Th per kilogram of H₂O) than that expected from the x-ray settling data (700 g of Th per kilogram of H₂O). Settling studies with a 40-in.-dia column of slurry to determine the effect of bed height on slurry concentration at the bottom of a slurry column indicated that bed height alone does not explain the discrepancy and that the settling time, bed cross section, and dynamics all have a bearing.

Oxide prepared in the ORNL pilot plant (800°C-fired), on being pumped as an aqueous slurry, occasionally is converted to a product composed of large spherical agglomerates. Laboratory evaluation of a sample did not show any physical or chemical differences in this material.

14.3 EFFECT OF ADDITIVES

Dispersion effects at room temperature were marked in a slurry of 800°C-fired oxide, containing 250 g of Th per kilogram of H₂O, which had been heated overnight at 300°C with 13,000 ppm of hydrogen bentonite. Dispersion was also obtained with similar slurries heated with 5000 ppm SiO₂, based on ThO₂, added as Na₂O·SiO₂ or H₂SiO₃. Dispersion with this concentration of silicate appeared relatively insensitive to pH over the range 6 to 12.

With slurries of 800°C-fired pilot-plant thorium oxide (average particle size 2.6 μ) containing 250 g of Th per kilogram of H₂O, addition of Na₂O·SiO₂ up to 20,000 ppm SiO₂, based on ThO₂, decreased the settling rates up to slurry temperatures of 275°C. Above this temperature little change was observed as the result of the silicate addition. With slurries of oxide which had been micropulverized (1.0 μ) or of oxide prepared by hydrothermal decomposition of the oxalate (0.7 μ), settling rates were much slower at all temperatures, even 300°C, and at all silica concentrations. The effects were more pronounced below 225°C.

The slurries containing silicate were, however, less viscous than the untreated slurries, as indicated by the faster stirrer operation under set conditions when they were stirred in the dash-pot irradiation bomb. Slurries of thorium oxide and thorium-uranium oxide (750 g of thorium per kilogram of H₂O) decreased in viscosity with increasing sodium metasilicate concentration (0 to 7000 ppm SiO₂, based on ThO₂) in the temperature range 100 to 300°C. At all silicate concentrations and at comparable temperatures, the thorium-uranium oxide slurry was much more viscous than the thorium oxide slurry.

Thorium oxides with chemically bonded silicated surfaces were prepared by treating with chlorosilane vapors, washing to remove chloride ion, and refiring to remove organic groups and leave a silicate surface. Thorium so treated showed no crystallite growth on firing as high as 1000°C, and as an aqueous slurry was completely dispersed (no flocculated settling) in high-temperature settling studies up to 280°C.

The addition of aluminum oxide to thorium oxide, at aluminum concentrations of 250, 500, 1000, and

10,000 ppm, based on thorium, by the coprecipitation of the oxalates and subsequent thermal decomposition, resulted in oxide products with increased crystallite sizes, proportionately lower specific surface areas, and smaller, more uniform particles when compared with pure oxide similarly prepared. The settling characteristics of aqueous slurries of the thorium-aluminum oxides were similar to those of pure oxide slurries, as prepared and after being autoclaved at 300°C both in the absence and presence of sulfate (1000 and 2500 ppm based on ThO₂).

14.4 MIXED OXIDES

The effect of method of preparation on the properties of thorium-uranium oxides with a uranium-to-thorium mole ratio of 0.005/1 was studied. The methods were simple addition of UO₃ to ThO₂ followed by autoclaving in water, thermal decomposition of the coprecipitated thorium-uranous oxalates, and hydrothermal decomposition of thorium-uranium nitrate solution. All the products appeared to be suitable slurry materials. The mixed oxide prepared by thermal decomposition of the coprecipitated oxalates was much more abrasive than either the pure oxide similarly prepared or the other mixed-oxide products. No gross change was observed in the slurry properties of aqueous suspensions of any of the mixed oxides when they were autoclaved at 300°C with O₂, H₂, and CO₂ atmospheres and in the presence of 1000 to 10,000 ppm of sulfate.

The properties of a slurry of thorium-uranium oxide (250 g of Th per liter) prepared by thermal decomposition of the 10°C-coprecipitated oxalates resembled those of a pure oxide fired similarly. The hindered-settling rates and the critical concentration increased with increasing slurry temperature and increasing oxide calcination temperature to 1170°C. There was some evidence of gelation or foaming at 300°C.

14.5 SLURRY VISCOSITY AND FLOW RATE

Out-of-pile measurements of slurry viscosity were made in the dash-pot bomb with slurries of thorium-uranium oxides (0.5% U) prepared from the coprecipitated oxalates and calcined at 650 to 1600°C. At concentrations of 250 and 500 g of Th per kilogram of H₂O the viscosity was essentially

independent of both calcination temperature and slurry temperature. At a concentration of 750 g of Th per kilogram of H_2O , however, the viscosity increased markedly with slurry temperature, the effect becoming less as the calcination temperature was increased.

A 0.25-in.-ID glass elbow flowmeter is being evaluated for possible use with thorium oxide slurries (Fig. 14.1). With slurries having specific gravities of 1.8 and 1.5 the calibration of velocity vs ΔH in terms of head of fluid flowing is linear on a logarithmic plot, and the same calibration fits with either water or slurry as the flowing fluid.

14.6 THORIA SOLS

Thoria sols stabilized with nitrate ion were not stable under reactor conditions. Thoria microspheres with an average diameter of less than 10μ were prepared by coagulating thoria sols with hexamethylenetetramine solution. When calcined to oxide, the microspheres were less than 3μ in diameter.

14.7 SLURRY IRRADIATION STUDIES

The objective of the thorium oxide slurry irradiation program has been to confirm, by further in-pile experiments in the dash-pot bomb, the conclusions from previous studies that under irradiation conditions approximating those of a TBR blanket there is no gross change in slurry properties. Six additional thorium oxide slurries, four containing enriched uranium, were irradiated in the LITR at $300^\circ C$ and 2.7×10^{13} neutrons/cm².sec for an average irradiation time of 250 hr. The power density in the uranium-containing slurries (U/Th = 0.005/1) was of the order of 5 kw/liter, approximately the average power density of a TBR blanket. As in the past there was no apparent deterioration in the slurry (Table 14.1).

All irradiations were carried out in the dash-pot irradiation bomb, and 20,000 ppm of MoO_3 (0.15μ) was added as a gas recombination catalyst. A small oxygen overpressure was used with the slurries containing uranium. Less than 100 psi of radiolytic gas was observed in all experiments while under irradiation, indicating excellent radiolytic-gas recombination. Two of the uranium-bearing slurries also contained 3000 ppm SO_4^{--} (based on ThO_2), added as $Th(SO_4)_2$.

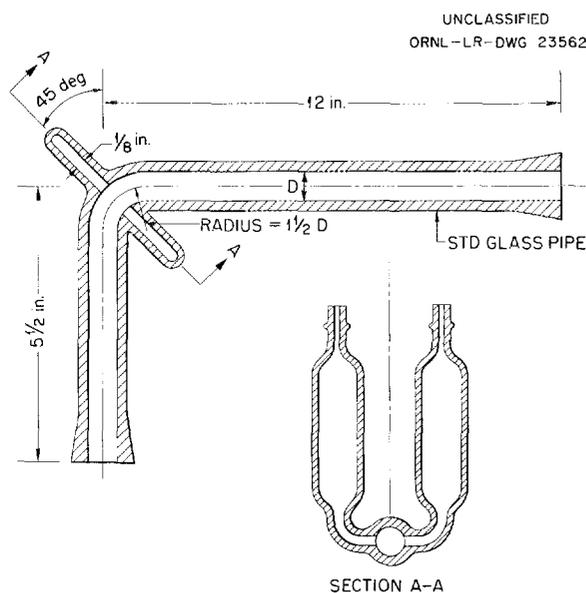


Fig. 14.1. Glass Elbow Flowmeter.

Chemical and radiochemical analyses were obtained on nine thorium oxide slurries – seven containing enriched uranium – that had been irradiated in the LITR. Uranium/thorium ratios were as expected. Corrosion-product pickup in the irradiated slurries agreed well with data from out-of-pile control experiments. The bulk of the radioactive materials was associated with the solids, only cesium appearing in the supernatant in significant amounts.

14.8 GAS RECOMBINATION STUDIES

Out-of-pile studies on the catalytic recombination of hydrogen and oxygen by thorium-uranium oxide slurries containing molybdenum oxide were continued. Studies were made on the effect on catalytic activity of (1) the method of preparing the molybdenum oxide; (2) the addition of sulfate, iron oxide, and rare earth to the slurry; and (3) the use of thorium-uranium oxides prepared from the coprecipitated oxalates (i.e., as opposed to a simple mixture of the oxides). In all cases the slurries were heated at 270 – $280^\circ C$ with an oxygen overpressure before being used in the combination experiment, and to obtain the maximum combination rate it was usually necessary to activate the slurries by additional heating at $280^\circ C$ under hydrogen.

Table 14.1. Effect of Radiation on Thorium and Thorium-Uranium Oxide Slurries

Irradiation conditions: 300°C , $\sim 2.7 \times 10^{13}$ neutrons/cm²·sec
 Thorium concentration of slurries: 750 g per kilogram of H₂O

Material	Radiation Time (hr)	Viscosity (centistokes)		Settled Concentration (g of Th per liter)	
		Control	During Irradiation	Control	Irradiated
ThO ₂ precipitated at 10 ^o C, calcined at 900 ^o C	198	16.0	16.0		1300
Pumped pilot-plant oxide (200A-6)	344	12.3	12.6	1200	1200
ThO ₂ -5%U, calcined at 800 ^o C*	44	13.1	13.0	1000	
	314	12.5	12.9	1000	1100
ThO ₂ -0.5%U, calcined at 800 ^o C plus 3000 ppm SO ₄ ⁻⁻⁻	247	**	**	1250	1300
	343	**	**	1250	1300

*Prepared by thermal decomposition of coprecipitated oxalates; 0.15 m MoO₃ added as gas recombination catalyst.

**Actual value of viscosity not determined (no calibration curve for stirrer timer), but no change was indicated in irradiated slurry.

The MoO₃ prepared by several different methods showed comparable activities at 0.05 m concentration in slurries of thorium-uranium oxide prepared from simple mixtures of 900^oC-fired thorium oxide and UO₃. Hydrogen-oxygen combination rates were more than sufficient to maintain a slurry blanket at less than 2000 psi total pressure under TBR conditions.

The addition of as much as 9600 ppm of sulfate (based on ThO₂) reduced slightly the catalytic activities of the slurries described above but did not impair their eventual usefulness in a blanket. The addition of 634 ppm of simulated rare earths showed no effect, but doubling the rare earth concentration decreased the catalytic activity slightly. The addition of 1000 to 1500 ppm of iron oxide resulted in a marked decrease in combination activity, indicating the need for a study of the

effect of corrosion-product buildup in a pumped slurry on its catalytic activity.

Somewhat erratic results were obtained with thorium-uranium oxide slurries containing 0.05 m MoO₃ in which the slurry solids were prepared by thermally decomposing the coprecipitated oxalates. Slurries of thorium-uranium oxides calcined at 1000^oC for 16 and 24 hr and at 1600^oC for 24 hr showed high catalytic activities (>>10 moles of H₂ per hour per liter). Slurries of the mixed oxides calcined at 800^oC for 24 hr and at 1000^oC for 4 hr and 8 hr showed low catalytic activities even after treatment with hydrogen. The low activities obtained with slurries of even the pure oxide fired at temperatures below 900^oC indicated the need for further study of the effect of oxide calcination temperature and calcination time on the catalytic activity of thorium oxide slurries containing the molybdenum oxide.

15. THORIUM OXIDE BLANKET PROCESSING

Scouting work was done on processing irradiated thorium oxide without going through a Thorex flowsheet. Calculations show that the recoil energy of U^{233} fission fragments is sufficient to eject them from a $1\text{-}\mu$ ThO_2 particle. Work has been concentrated on preventing irreversible adsorption of the fission fragments on the ThO_2 surface and on removal of the fission products by an inorganic ion exchanger.

In these preliminary experiments, as the calcination temperature of ThO_2 was increased the adsorption decreased, being ~ 60 parts of fission products per million parts of ThO_2 with ThO_2 calcined at 1600°C .

Lead and bismuth oxides showed the most promise in adsorbing the fission products in a thoria slurry, with adsorption of 0.1 g of ionic contaminant per gram of oxide. These oxides do not become refractory when heated at 250°C in water.

Treating the ThO_2 surface with various materials to prevent irreversible adsorption was only partially successful. Sulfate and sulfur adsorbed on the ThO_2 surface decreased the adsorption $\sim 90\%$. Other materials, such as silicates and phosphates, either had no effect or enhanced the irreversible adsorption.

16. HOMOGENEOUS REACTOR EQUIPMENT DECONTAMINATION

Chromous sulfate in dilute sulfuric acid continued¹ to be the best agent for descaling stainless steel exposed to uranyl sulfate at 250 to 300°C . Several more corrosion loops at Y-12 have been descaled with this solution. A solution of 2% H_3PO_3 -2% NaH_2PO_2 at 175°C , which gave some promise as a descaling solution in laboratory tests, was not satisfactory for defilming a corrosion loop.

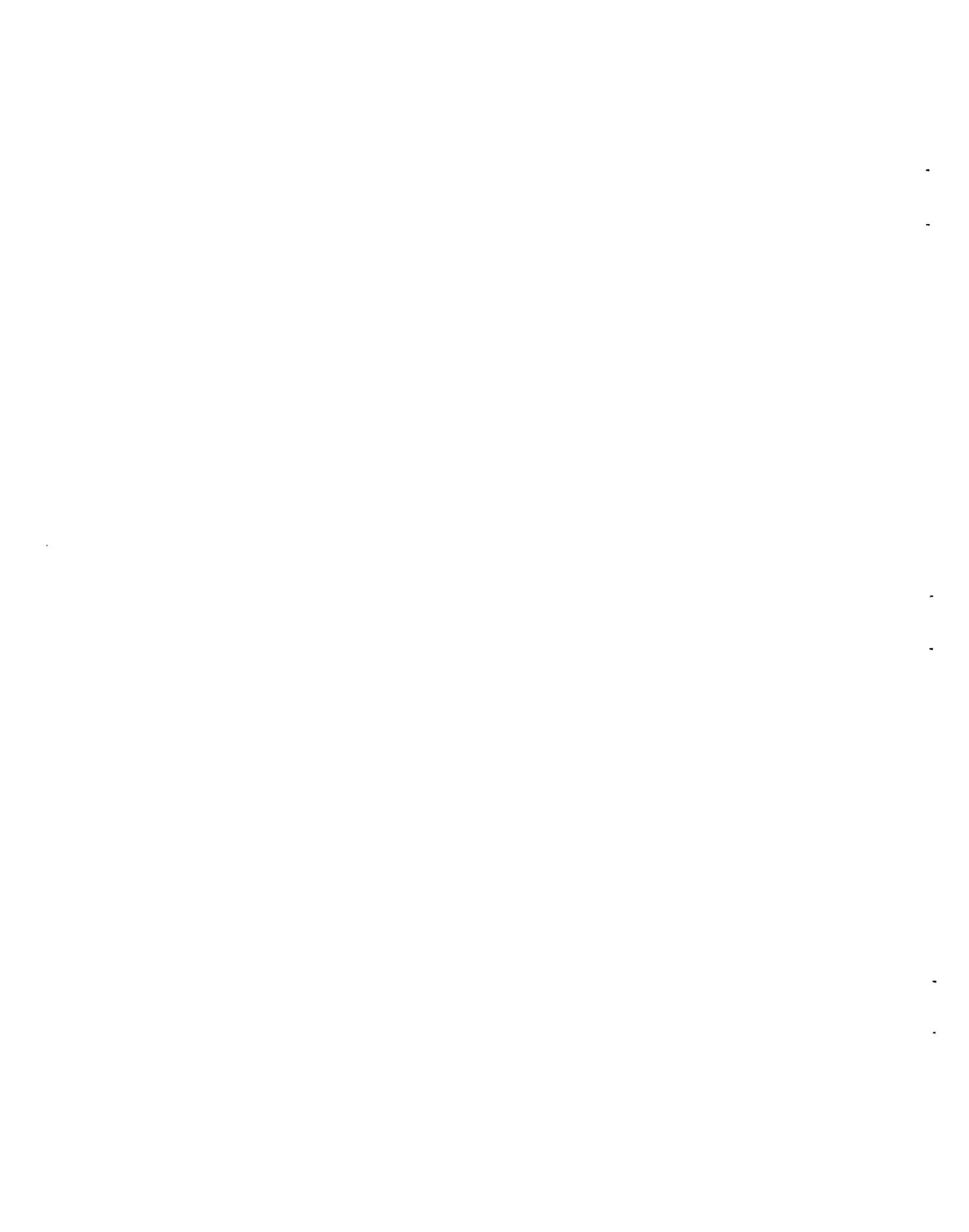
Electrolytic preparation of chromous sulfate was demonstrated in the laboratory.¹ The reduction of

Cr(III) to Cr(II) was carried out in an electrolytic cell with lead anodes and cathodes separated by anion exchange membranes. The current density used was 0.15 to 0.25 amp/in.². At a solution rate of 1.5 liters/hr, $>80\%$ of the chromium was reduced in a small (4-liter) 9-chamber cell with alternating anode and cathode compartments separated by Nalfilm-2.

Potassium and sodium dichromate are less expensive starting materials for preparation of chromous sulfate, but electrolytic reduction of chromate was not attractive because of chromate precipitation on the lead electrodes, which reduced the current efficiency. Chromate was rapidly and completely reduced to Cr(III) with SO_2 .

¹Preliminary work in *Chem. Tech. Semiann. Prog. Rep.* Aug. 31, 1956, ORNL-2169, p 9.

PART IV. CHEMICAL ENGINEERING RESEARCH



17. ION EXCHANGE TECHNOLOGY

Two continuous ion exchange columns were further evaluated, the Higgins column and the Jury column. Ion exchange techniques may be applied to recovery of uranium from ores, power reactor fuel processing, and waste treatment (Secs. 3, 4.5, and 9, respectively).

17.1 HIGGINS COLUMN

A 12-in.-dia Higgins ion exchange continuous contactor (Fig. 17.1) was operated at the Grand Junction ore leach pilot plant. One hundred and eighty tons of Dysart ore was satisfactorily processed as an 8-wt-% slurry in a 13-day run. The uranium loss ranged from 0.001 to 0.004 g of U_3O_8 per liter with an average loss of 0.002 g/liter (0.2% loss) (Table 17.1). The unit has been returned and is being installed at Y-12 in a bomb-liner scrap recovery plant (Fig. 17.2).

The 6-in.-dia Higgins unit was operated, in a joint test with the Y-12 Development Division, on the Fernald dolomite bomb-liner scrap. The scrap was ground and leached with sulfuric acid, and tests of uranium recovery were performed with unclarified and clarified feed streams. Although recovery did not exceed 95%, owing to the short loading section, the operating data indicated that the 12-in.-dia unit will perform satisfactorily.

A 36-in.-dia resin test loop was constructed and tested (Fig. 17.3). A study of resin movement indicated that even larger diameter Higgins-type contactors are feasible. The resin-to-wall friction decreased as the diameter increased, resulting in a lower slip-water ratio and a probable decrease in the height equivalent to one theoretical stage. A 12-in. butterfly valve was successfully used to replace a 12-in. plug valve in the resin phase. Butterfly valves are much cheaper and are more easily obtained in corrosion-resistant forms than are plug valves.

17.2 JURY COLUMN¹

A continuous countercurrent ion exchange contactor described by Jury^{2,3} (Fig. 17.4) was experimentally (Fig. 17.5) evaluated. The limiting

¹Work carried out at University of Tennessee under a subcontract.

²S. H. Jury, *U.S. Atomic Energy Comm. Nuclear Sci. Abstr.* 8, 20 (1954).

³T. A. Arehart *et al.*, *Chem. Eng. Progr.* 52, 353 (1956).

features of the operation were determined together with engineering data necessary for the scaleup of equipment. Auxiliary studies included the measurement of equilibrium and ion exchange kinetic data for the system Ca^{++} -Dowex 50W- Na^+ , the measurement of the fluidization velocity for 20-mesh Dowex 50W, and the determination of the frictional characteristics for a dense bed of resin moving relative to a solid wall.

Continuous steady-state operation was demonstrated with a calcium-loading-sodium-stripping water-softening cycle. Less than half the Ca^{++} was sorbed, there was no concentration of Ca^{++} in the regeneration stream, and the feed rate was about 20% of standard fixed-bed water-softening rates.

17.3 RESIN IRRADIATION DAMAGE

In preliminary studies on resin irradiation damage Permutit SK resin lost only 5 to 10% of its capacity per watt-hour of energy absorbed per gram.

Table 17.1. Summary of Second Grand Junction Test

Resin: Permutit SK (10 to 20 mesh)
Feed rate: 7 gpm (580 gal/ft ² /hr)
Ore consumption: 12 tons/day (180 tons total)
Pulse frequency: 1 per 5 min
Slip-water ratio: 4.2/1.0
Material balance: 104%
Flow balance: 101%

Stream	Flow Rate (gpm)	Uranium Concentration (g of U_3O_8 per liter)
Feed	7.00	0.98
Feed wash	0.90	
Strip, 1 M NH_4NO_3 , 0.1 M HNO_3	0.45	
Strip wash	0.57	
Acid wash, 0.5 M H_2SO_4	0.08	
Waste	8.20	0.002
Slip water	0.30	
Product	0.60	12.10
Resin	0.08	65.00

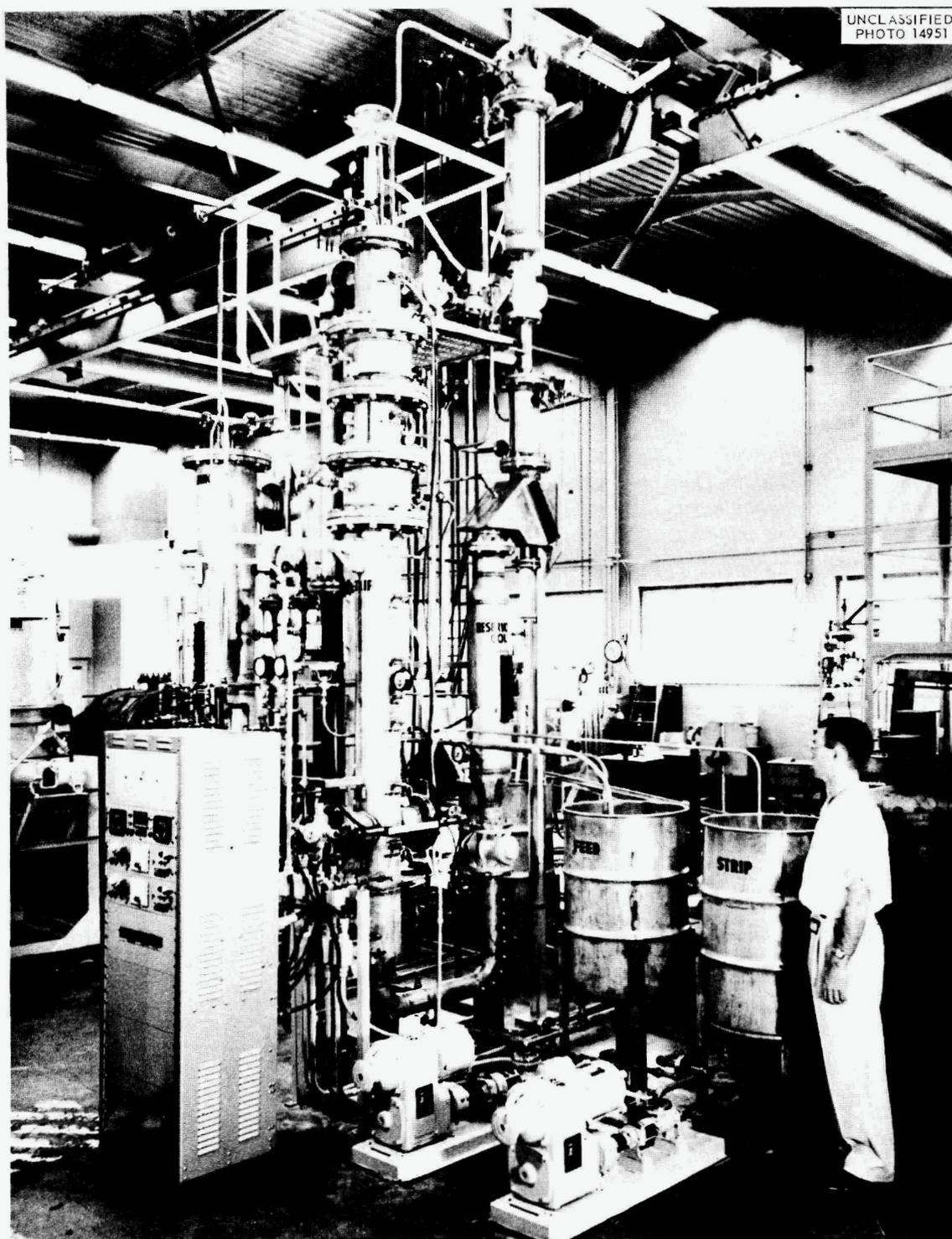


Fig. 17.1. Twelve-Inch-Diameter Higgins Continuous Contactor.

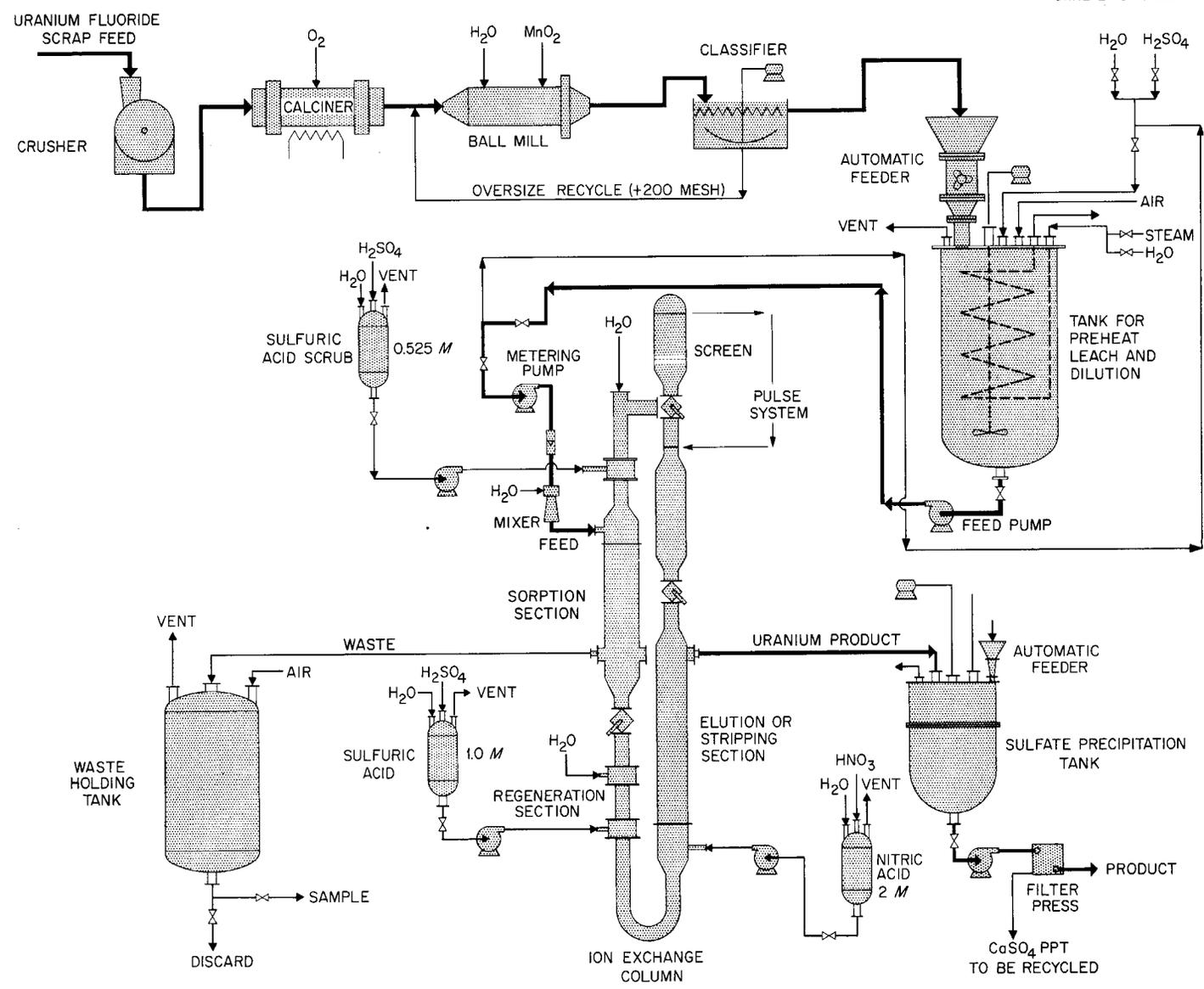


Fig. 17.2. Process Flow Diagram for Ion Exchange Unit. Y-12 uranium scrap recovery program.

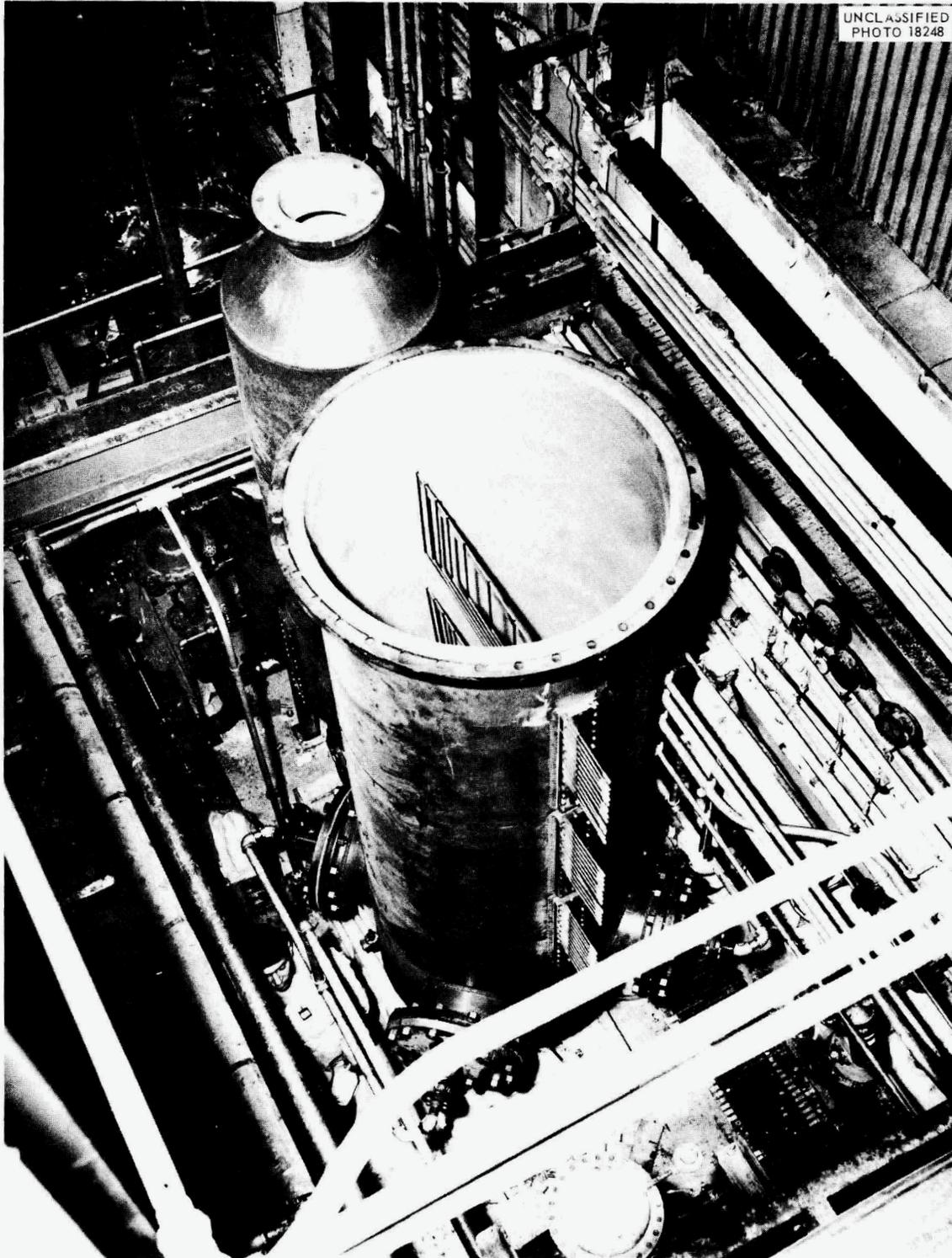


Fig. 17.3. Thirty-Six-Inch Resin Test Loop.

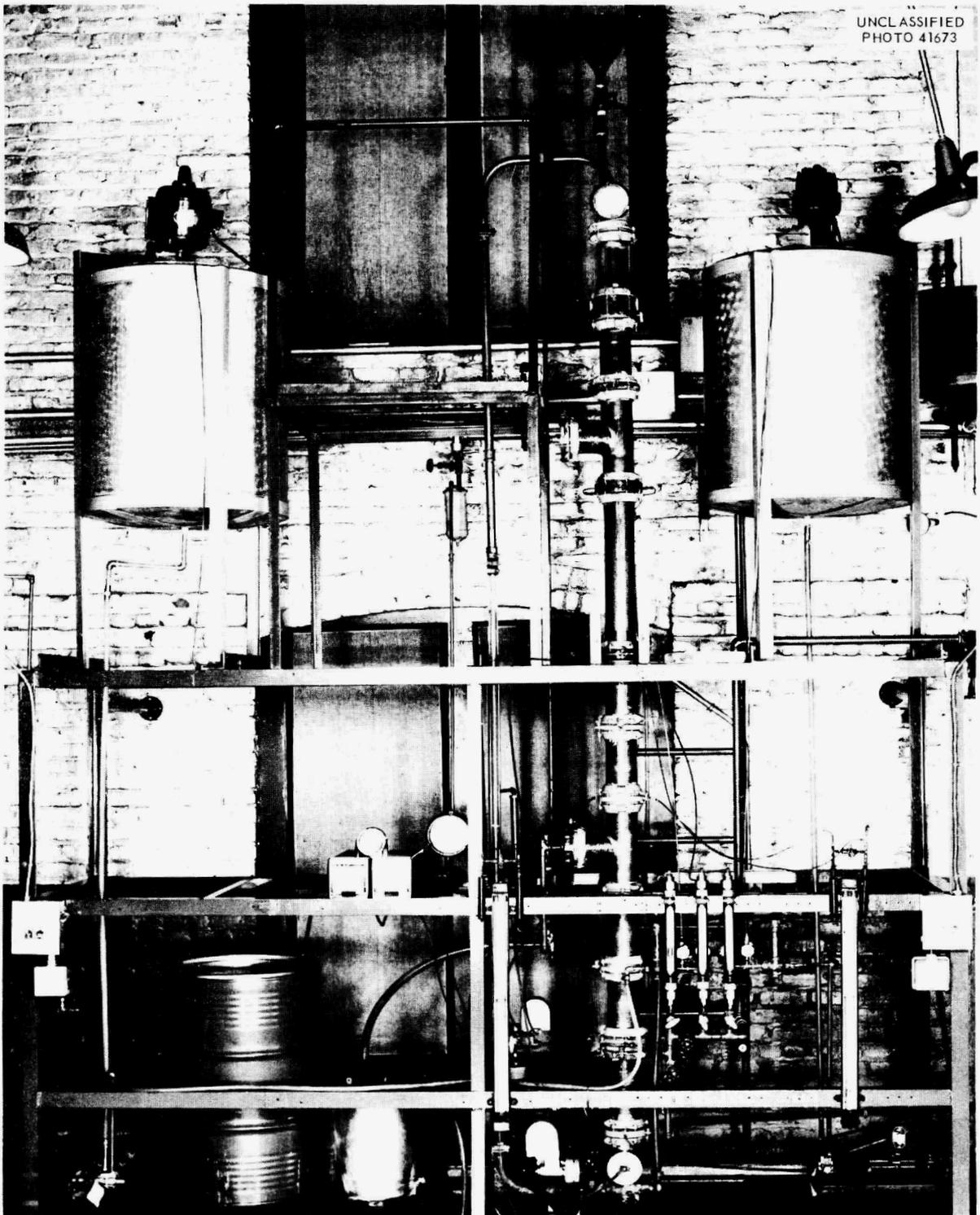


Fig. 17.4. Ion Exchange Equipment, Jury Column.

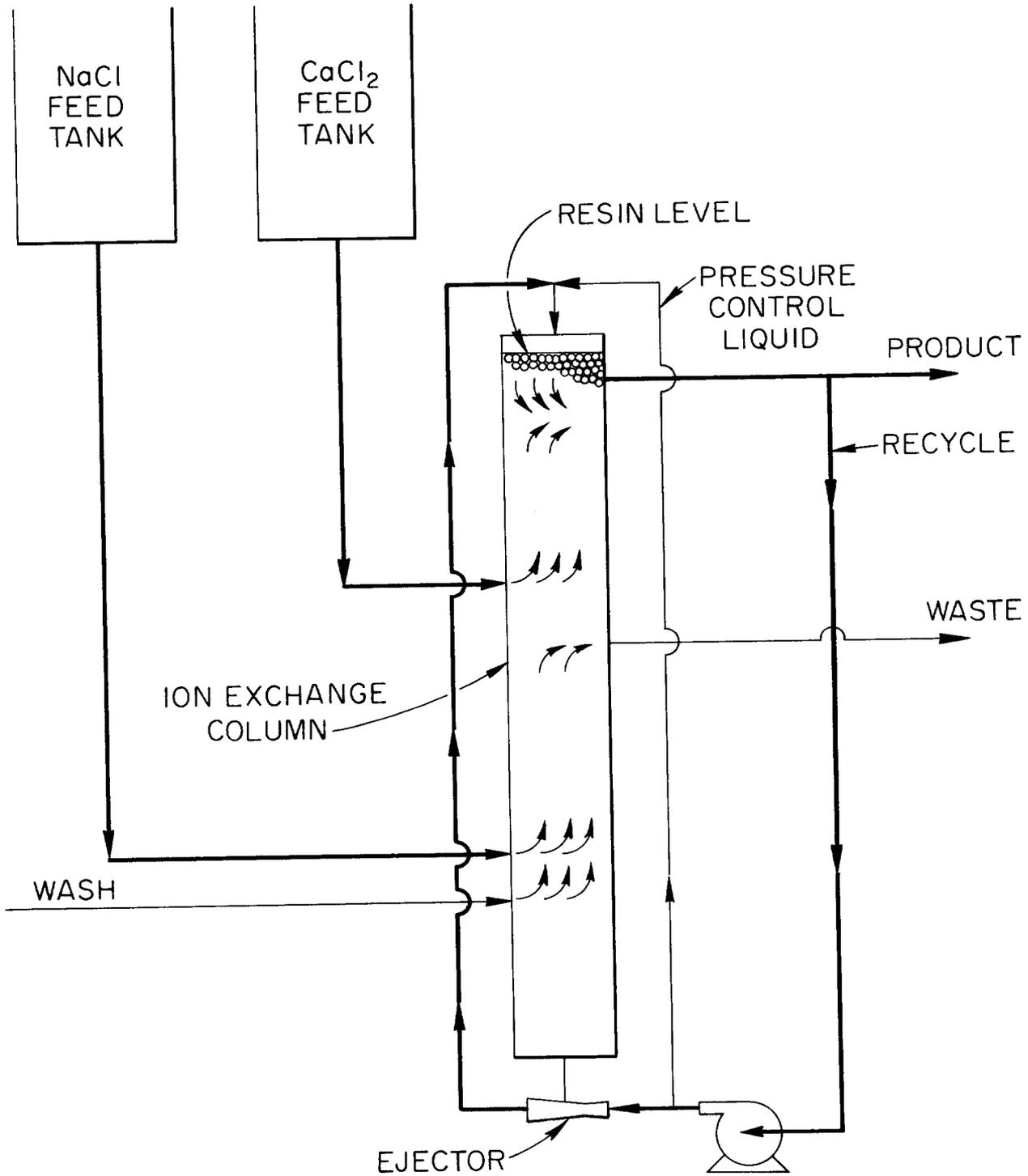


Fig. 17.5. Flow Diagram for Continuous Ion Exchange Equipment, Jury Column.

18. SOLVENT EXTRACTION CONTACTORS

18.1 HIGH-SPEED SOLVENT EXTRACTION SYSTEM

A method of rapidly contacting and separating aqueous and organic solutions is desirable for radiochemical processing plants in order to reduce radiation damage to solvents.

A three-stage countercurrent contactor in which centrifugal pumps are used for mixing and hydroclones for phase separation was built and tested. The contactor performed well with a hexone-water system, and extracted acetic acid from hexone into water with essentially 100% stage efficiency. It did not perform so well with a 30%-TBP-in-Amsco-water system, and uranyl nitrate was extracted from the organic phase by water with stage efficiencies of 70 to 90%.

It appears to be difficult to produce a solvent-free underflow with a single hydroclone unless the ratio of water to solvent in the feed is high, that is, approximately 4/1. A dual-hydroclone stage was operated with over-all separation factors for water and solvent greater than 30. Unfortunately, a method has not been developed for measuring the recycle-phase composition in a dual-hydroclone separator in the presence of dissolved salts, which would be necessary for a control system.

Analysis of the flow in a hydroclone indicated a basic difficulty of this device when used to

separate two liquids. All flow is introduced circumferentially and removed axially. To conserve angular momentum, the liquid must undergo angular acceleration as it approaches the axial takeoffs. This acceleration introduces large radial velocity gradients with proportionate liquid shear. The liquid shear may create a finer dispersion of the discontinuous phase, making separation more difficult.

18.2 COOLER FOR STEAM-JET DISCHARGE

Steam jets are being considered for mixing the two phases and providing the pressure to drive the separator in each stage of a high-speed solvent extraction contactor. However, a typical steam-jet pump may raise the temperature of the liquid pumped by as much as 35°F. To prevent excessive temperature rise in the cascade, heat exchangers must be inserted after each jet.

A high-performance helical-tube heat exchanger was designed and tested. It consists of 16.5 turns of $\frac{3}{8}$ -in. stainless steel tubing on 1-in. pitch in the annulus between concentric 17-in. lengths of 3- and 4-in. stainless steel tubing (Fig. 18.1). Cooling water circulates in the annulus and the jets discharge into the helix. The over-all heat transfer coefficient obtained with water at 1 gpm in the shell and 0.5 gpm in the tube was about 220 Btu/hr·ft²·°F.

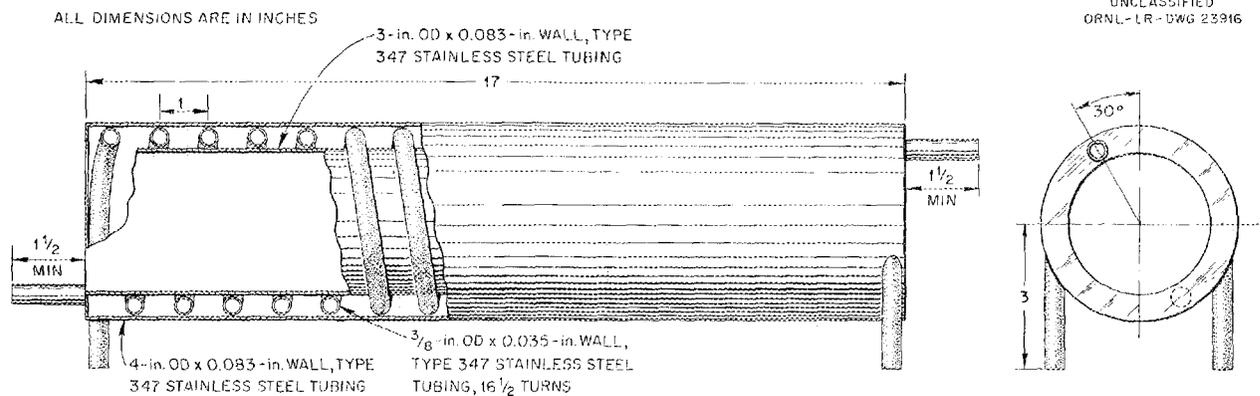


Fig. 18.1. Cooler for Steam-Jet Discharge. Length of helix, 15.5 ft.

19. MEASUREMENT OF INTERFACIAL AREA

A method of measuring the interfacial area between two liquid phases is important in the evaluation of liquid-liquid contactors. Since the mass transfer rate between two phases is proportional to the interfacial area, a knowledge of this area would also be useful in determining absolute mass transfer rates.

A successful method has been developed which is based on the (α, n) reaction between Po^{210} in the aqueous phase and fluorine, in the form of a fluorinated hydrocarbon, in the organic phase. Since mutual solubilities are extremely low, the (α, n) reaction can take place only at the interface. Neutrons are produced there and may be counted outside the liquid container (or contactor) without sampling.

A specific count rate of 0.116 ± 0.009 count per minute per square centimeter of interface was observed with an aqueous solution containing 1.1 millicuries of Po^{210} per milliliter in contact with

completely fluorinated cyclooctane. The counting efficiency was approximately 1%, so the actual production rate was about 12 neutrons per minute per square centimeter.

Current effort is directed toward refining the apparatus to improve counting geometry and toward using the method to (1) measure interfacial area in a model pulsed column and (2) check published correlations of the interfacial area produced in turbine mixers.

A method of interfacial-area measurement by chemical dosimetry was tried in which trichloroethylene in the organic phase was decomposed radiolytically by Po^{210} alpha particles emanating from the aqueous phase. The aqueous phase was analyzed for chloride concentration. Experiments with this method were inconclusive, and the method was deemed unsatisfactory owing to the necessity of handling the aqueous phase and analyzing it for chloride.

20. IN-LINE INSTRUMENTATION

The primary objective of the in-line instrumentation program is the development of special instruments for use in radiochemical processing plants to reduce analytical chemistry service cost and to improve process control. All the instruments described below are for in-line use.

20.1 DIGITAL PROBE FOR ORGANIC-AQUEOUS INTERFACE LEVEL

A digital probe for the measurement of organic-aqueous interface level is being tested in the IA column of the Metal Recovery Plant. Its operation depends on the difference in electrical conductivity between the organic and aqueous phases, and it indicates the interface level in the top section of the column to the nearest inch. The instrument indicates interfacial-solids conditions and is not affected by variations in liquid densities and pressures. A pressure-resistant probe is being prepared especially for controlling interface level in an organic-continuous column to be installed in the Metal Recovery Plant. It consists of a

molded assembly of stainless steel electrodes with insulators of a commercial plastic.

20.2 URANIUM CONCENTRATION DETERMINATION

Construction is about 75% complete on a prototype of a high-sensitivity alternating-current polarograph to monitor uranium in process raffinate streams. The instrument is designed to operate at uranium concentrations of the order of 10 ppm. The technique used is phase discrimination against the condenser current. A new type of polarographic electrode that may replace the customary dropping mercury electrode is being investigated for flowing-stream operation. This electrode depends on the rate of diffusion of a discharging species through an ion-permeable membrane. It retains the advantages inherent in the high overvoltage of a mercury electrode and eliminates the mercury disposal problem.

A flow colorimeter, which was developed at the Savannah River Laboratory, was tested in the

Metal Recovery Plant. It continuously recorded the uranium concentration within ± 1 g/liter in the ranges 25 to 35 and 45 to 55 g/liter. It is adaptable over a wide range of uranium concentrations and is regarded as a reliable plant instrument. A report of the test is in preparation.

20.3 NITRIC ACID CONCENTRATION

A radio-frequency monitor for nitric acid concentration in process feed was operated for four months on an air-lifted recirculating feed stream. The stability of the instrument was good despite concentration changes in the stream due to air-lifting. Sensitivity was good in the range for which it was designed (~ 0.5 M HNO_3) and this sensitivity was maintained even at higher concentrations (± 0.05 M HNO_3 at 4 M HNO_3). A study of the effect of a variation in $\text{Al}(\text{NO}_3)_3$ concentration around 1.8 M, with the HNO_3 concentration constant at 0.5 M, is in progress.

20.4 CHLORIDE CONCENTRATION

A chloride ion monitor was designed for the Darex process (Sec. 4.1) to measure HCl concentration in the recovered-acid stream. A silver chloride electrode versus a saturated calomel electrode is used in the design. Preliminary tests demonstrated good sensitivity, 12-mv scale reading, for the desired range, 1.5 to 2.5 M HCl in the presence of 5 M HNO_3 . The measurement is made on a side stream that is diluted 1 to 100 with water at constant temperature.

20.5 GAMMA ACTIVITY

Gamma monitors with two types of contamination-resistant samplers are being evaluated: the falling-stream cell and the electrically inhibited cell. Construction is about 75% complete on a prototype of the falling-stream gamma monitor to measure gross and specific gamma activities in the Thorex pilot plant first-cycle product stream (organic).

Electrically inhibited stainless steel cells were evaluated in a gamma monitor by MIT Engineering Practice School students as typical Purex feed and product solutions were circulated through the cell.¹ Application of 60 ma/cm² anodic current to a cell for 3 sec/min reduced the gamma contamination of the cell from the feed stream by a factor of 20, as compared with an untreated cell, and resulted in corrosion of 30 mils per year. The resistance to contamination was due mostly (about 90%) to the high surface polish maintained in the cell by the treatment. Anodic pretreatment of a cell reduced cell contamination from the organic stream by a factor of 30 as compared with a cell which was not pretreated. Prototypes of these cells are being designed for pilot-plant tests.

20.6 LIQUID FLOW RATE

Tests of a bubble-velocity meter for low liquid flow rates showed it to be accurate within $\pm 1\%$ over the range 0 to 60 gal/hr. A thyratron flip-flop circuit with stop clock is used for read-out. A model of another low-range flow-rate meter for radiochemical process streams was constructed for pilot-plant tests. It is expected to be accurate to within 10%. Like the bubble-velocity meter it contains no moving parts or flow restrictions. A process stream, along with air at a fixed flow rate, passes through a turn of tubing. The weight of liquid in the tubing is determined by means of an external air purge line and a pressure gage, which is calibrated in terms of both flow rate and density. The instrument is converted to a densimeter by shutting off the flow of air.

¹The results of evaluation studies are reported by A. E. Sherwood *et al.*, *In-Line Radioactivity Monitors*, KT-285 (May 8, 1957); G. Jansen, Jr., J. C. Bolger, and B. E. Prince, *In-Line Radioactivity Monitors*, KT-257 (Jan. 18, 1957).

21. HIGH-ACTIVITY-LEVEL CHEMICAL DEVELOPMENT FACILITY

Construction on a four-cell multicurie general-purpose manipulator facility (Building 4507) for chemical development work was begun in August 1956 by the Helrich Construction Company and completed in May 1957. The total estimated project cost was less than \$325,000, which includes the viewing windows and master-slave manipulators, both procured independently by ORNL. The building is now occupied by the Chemical Technology Division.

A high-level volatility laboratory was designed

and was installed in the facility. The equipment is designed to handle an initial salt charge of 880 g and to dissolve a 100-g uranium wafer. The highest activity level anticipated will be from the processing of enriched material with a 10% burnup and a ten-day decay. The system uses the hydro-fluorination, fluorination, adsorption, and cold-trap equipment used in past lower-activity-level development work. Most maintenance and process operations are to be conducted with a master-slave manipulator.

PART V. RAW MATERIALS PROCESSING



22. AMEX PROCESSES

The Amex process is a new technology in which the principles of anion resin exchange are applied on a liquid-liquid basis. The wide range of control obtainable through choice of reagent structure and diluent type is combined with the inherent advantages of liquid-liquid techniques.

The amines first react to form the alkylammonium sulfate and bisulfate salts, which are dispersed in the diluent as colloidal (perhaps micellar) aggregates. Subsequent extraction of metal or other ions follows closely the pattern for sorption with weak-base anion exchange resins and is assumed to occur by a mechanism analogous to anion exchange. The process was originally designed for recovering uranium from ore leach liquors, but potential utility has been demonstrated for thorium, vanadium, molybdenum, and rare earths.

In the process for uranium (Fig. 22.1), uranium is selectively extracted by long-chain secondary or tertiary amines in hydrocarbon diluents.¹ From the loaded solvent, containing 1 mole of uranium per 4 to 6 moles of amine, uranium is stripped with dilute solutions of chloride, nitrate, or carbonate. Uranium products suitable for feed to the refineries are obtained from these solutions by precipitation. In some cases direct product recovery from the organic solvent is also possible by alkaline precipitation, for example, by a magnesium oxide slurry.

22.1 URANIUM RECOVERY

Laboratory Development. — Continued counter-current testing in bench-scale mixer-settler equipment indicated the applicability of the Amex process to recovery of uranium from liquors with widely

variable concentrations of sulfate, sulfuric acid, and other metals. Several commercially available amines have given acceptable process performance, including trialkylmethyl dodecylamine (Amine 9D-178), bis(1-isobutyl-3,5-dimethylhexyl)amine (Amine S-24), di(tridecyl)amine, tri(isooctyl)amine, and a tertiary amine with mixed octyl and decyl radicals.^{2,3} Attempts to use the process on unfiltered ore leach slurries were unsuccessful owing to large losses of amine through sorption on the ore solids and large losses of total solvent through entrainment in the slurry phase.³ In treatment of clear liquors, phase separations were rapid and clean except with one liquor of unusually high dissolved silica content where appreciable amounts of stable emulsions formed in the settlers. This liquor was handled, however, by maintaining the contacting conditions in the mixer such that the organic phase was continuous.

Molybdenum is the only common metal constituent of ore leach liquors that is extracted in appreciable quantities with the uranium. Molybdenum was eliminated from the process circuit by selectively re-extracting uranium from the solvent with chloride solution; molybdenum was re-extracted from the uranium-barren solvent with an alkaline solution, sodium carbonate or ammonium hydroxide (Sec. 22.4).

With low-molybdenum extracts, direct precipitation of uranium from the solvent with MgO-water slurries^{2,4,5} may prove to be a more economical stripping method than the chloride, nitrate, or carbonate methods. In small-scale continuous tests with selected commercial magnesias, uranium stripping was essentially complete when the excess magnesia was only 10% above stoichiometric. The uranium precipitate was granular, in contrast with the slimy precipitates obtained in earlier tests

¹For previous reports, see: K. B. Brown *et al.*, ORNL-1734 (June 9, 1954) (classified); J. G. Moore, K. B. Brown, and C. F. Coleman, *Further Studies of Amines as Extractants for Uranium from Acid Sulfate Solutions*, ORNL-1922 (Aug. 9, 1955); B. B. Klima *et al.*, *Cost of Uranium Recovery by the Amine Extraction Process* (ed. by K. O. Johnsson), ORNL-1949 (Sept. 8, 1955); B. B. Klima *et al.*, *Design of an Amine Extraction Demonstration Plant* (ed. by K. O. Johnsson), ORNL-1963 (Sept. 8, 1955); R. H. Guymon *et al.*, *Uranium Raw Materials Process Cost Estimates One Through Ten* (ed. by K. O. Johnsson), ORNL-1998 (June 15, 1955); K. O. Johnsson (ed.), *Raw Materials Process Testing Progress Report*, ORNL-1914 (July 13, 1955) (classified), and the following ORNL reports in this series: 1970, 2025, 2026, 2034, 2035, and 2112.

²D. J. Crouse *et al.*, *Progress Report on Uranium Extraction with Organonitrogen Compounds*, ORNL-2099 (June 15, 1956).

³K. B. Brown *et al.*, *Progress Report on Raw Materials for June, 1957*, ORNL-2380 (in press).

⁴K. B. Brown *et al.*, *Progress Report on Raw Materials for April, 1957*, ORNL-2346.

⁵D. J. Crouse *et al.*, *Progress Report on Separation and Recovery of Uranium and Thorium from Sulfate Liquors by the Amex Process*, ORNL-2173 (Dec. 26, 1956).

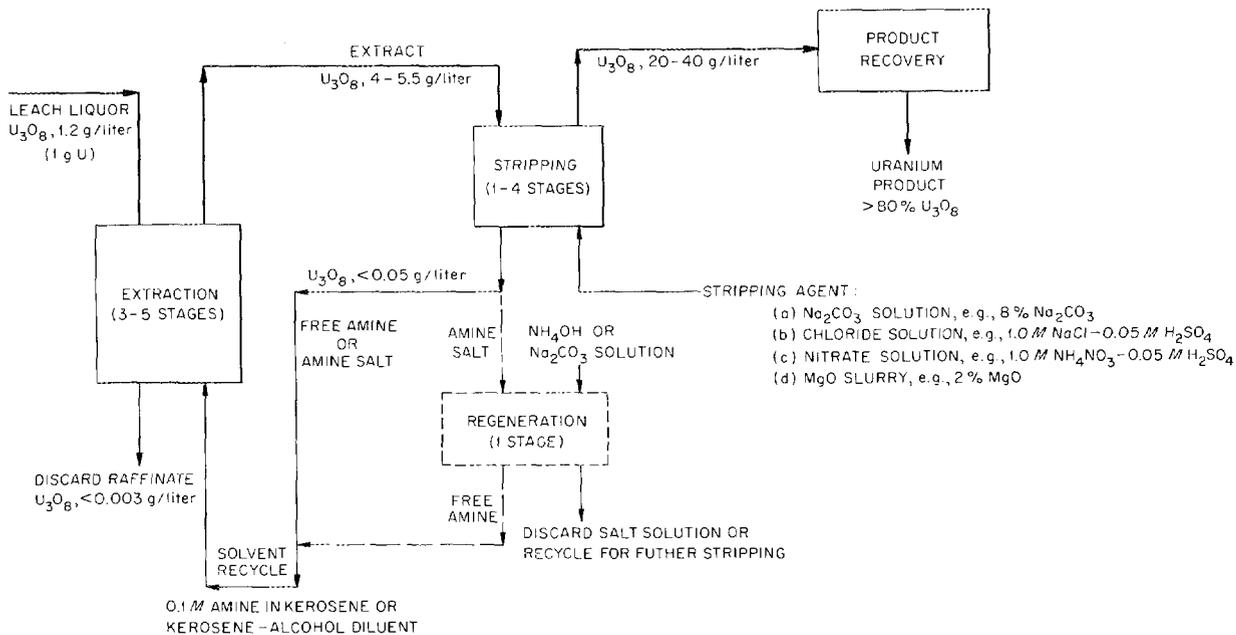


Fig. 22.1. Amex Process for Recovery of Uranium from Ore Leach Liquor.

with sodium and ammonium hydroxides, and settled readily into the aqueous phase. Phase separation was rapid and clean when the solvent was the continuous phase during mixing. Equipment is being constructed to evaluate the process on a larger scale.

Engineering Development. - Continued studies of the Amex process were made to develop fundamental data for mixing and phase separation and to determine scaleup factors for extrapolation to large-scale operations. In tests of uranium extraction from typical liquors in a 6- by 6-in. baffled turbine-agitated mixer, stage efficiency was >90% with an input of 0.01 hp per gallon of mixer contents and a liquid residence time of 0.3 min. Mixing requirements for chloride-stripping of uranium from the organic solvent were 0.03 hp per gallon with the same residence time. Comparison of the kinetics in batch tests of stripping by chloride, nitrate, and sodium carbonate showed no marked difference between the mixing requirements of these reagents.

In preliminary phase-separation studies in small-scale gravity settlers at flow rates of 1 to 5 gpm, settler capacities were 1 to 3.9 gpm of aqueous phase per square foot of settler area, depending on the phase ratio and the type of dispersion in the

mixer. The amount of residual solvent entrained in the raffinate was also dependent on the type of dispersion produced in the mixer; for water-in-oil dispersions the entrainment was consistently less than 0.2 gal of organic phase per 1000 gal of raffinate, while for oil-in-water dispersions entrainment was 0.2 to 2 gal per 1000 gal. After an additional settling time of 1 to 2 hr, the entrainment in the raffinate from oil-in-water dispersions was less than 0.2 gal per 1000 gal.

Mixing and settling equipment requirements were estimated for an Amex process treating 100,000 gal of liquor (~200 tons of ore) per day. In a plant designed for water-in-oil-type mixing and conservatively sized for flexibility, each mixer in the extraction section would have a capacity of about 50 gal with a 0.5-hp agitator, and each settler would be about 10 ft in diameter; each mixer in the stripping section would have a capacity of about 10 gal with a 0.3-hp agitator, and each settler would be about 4 ft in diameter.

Commercial Applications. - The Amex process is being commercially installed by the Eldorado Mining and Refining Limited at Port Radium, Canada, and the Texas Zinc Company at Mexican Hat, Utah.

22.2 VANADIUM RECOVERY

A tentative process for the recovery of vanadium by amine extraction has been proposed on the basis of preliminary batch and continuous small-scale tests (Fig. 22.2). The feed anticipated for this process is that obtained from a sulfuric acid cure or hot sulfuric acid leach of a uranium-vanadium ore, the uranium having been removed in a previous cycle by solvent extraction or anion exchange. Since extraction is appreciable only with vanadium(V) and at a relatively high pH, the liquor is oxidized with sodium chlorate or manganese dioxide and adjusted to a pH of 1.8 to 2.0 before extraction. Prolonged standing of the liquor after pH adjustment is avoided in order to decrease the likelihood of slow precipitation of polyvanadates or iron phosphates, which cause subsequent emulsion difficulties.

With secondary or tertiary amines at 0.1 M in the diluent, 95% of the vanadium is extracted in 5 to 7 countercurrent stages, giving a loaded solvent containing 15 to 20 g of V_2O_5 per liter. The vana-

dium is stripped from the solvent, as the soluble sodium vanadate, with a solution of sodium carbonate. Vanadium is recovered from the loaded strip solution (50 to 70 g of V_2O_5 per liter) by adding sulfuric acid to precipitate a conventional sodium polyvanadate ("red cake") product. Ammonium hydroxide is also a useful stripping agent.

Several facets of the process described have not been thoroughly examined, and commercial feasibility has not yet been proved by pilot tests. Chemical reagent costs, excluding those for pH adjustment, have been estimated at <10¢ per pound of V_2O_5 for liquors containing 6 g of V_2O_5 per liter.

22.3 THORIUM RECOVERY

The Amex process was developed through the laboratory stage for separate recovery of thorium and uranium from Canadian Blind River ore sulfate leach liquors.⁵ Continued studies further confirmed the feasibility of Amex for the separate recovery of thorium, uranium, and rare earths from

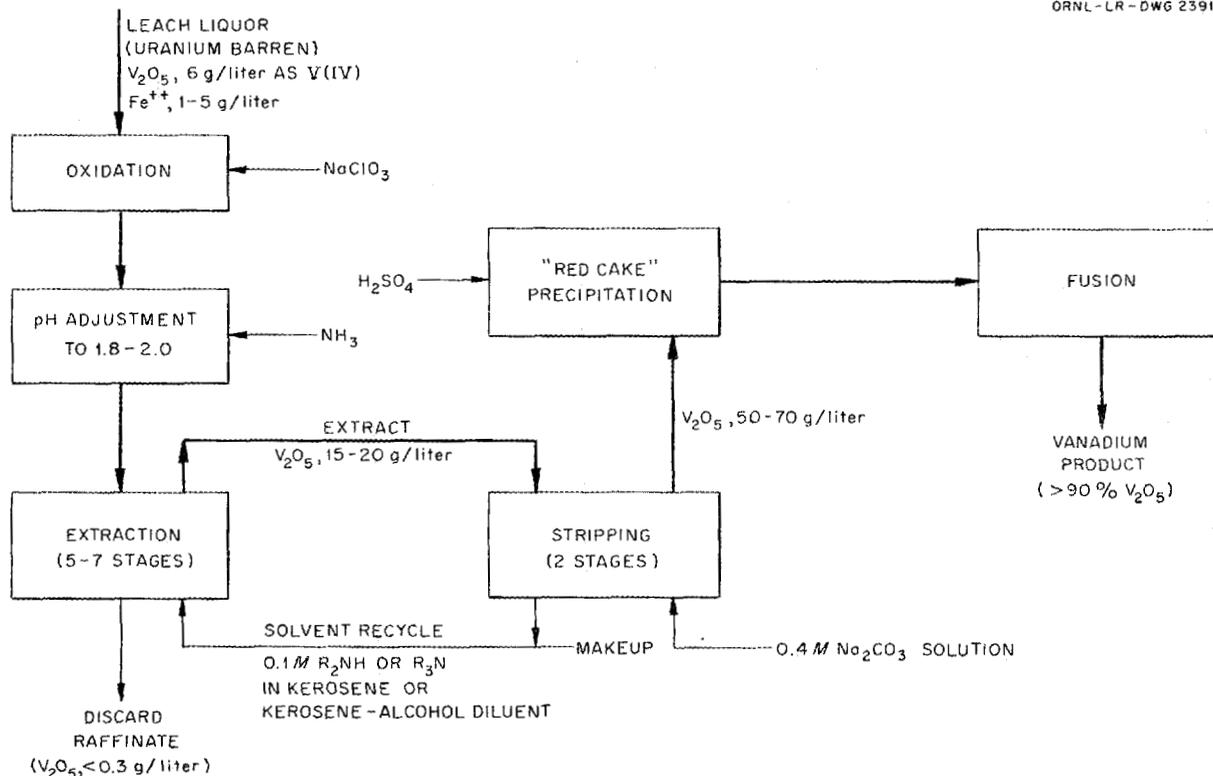


Fig. 22.2. Amex Process for Recovery of Vanadium from Ore Leach Liquor.

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liquors from the digestion of monazite with sulfuric acid.⁶ In both applications advantage is taken of the variation in extraction with amines of different types and structures (Table 22.1).

Blind River Ores. – The main constituents of a representative Blind River leach liquor, and their approximate concentrations in grams per liter, are: U₃O₈, 1.4; ThO₂, 0.2; Fe(III), 1; Fe(II), 2; and SO₄, 30. When the highly selective tertiary amines were used as extractants in the usual Amex flow-sheet (Sec. 22.1), uranium was completely recovered from this liquor in products containing <0.05% thorium. Uranium recoveries, in products containing only slightly more thorium, were also complete with the more selective secondary amines when the operation was controlled to give near-maximum uranium loading in the solvent.

The thorium was easily recovered, in high-grade products (>95% ThO₂), from the uranium-barren raffinate in a second cycle with an amine of high extraction power for thorium, for example, a primary or secondary amine with no branching or with branching distant from the nitrogen. Stripping was efficient by the chloride, nitrate, or carbonate methods developed for uranium. Of the extractants examined thus far, di(tridecyl)amine was the most suitable in that it has greater extraction power for thorium than other readily available secondary amines, and greater selectivity over Fe(III) and lower losses to the aqueous liquor than available primary amines. Based on results from continuous countercurrent extraction-stripping runs, total

⁶Preliminary tests were described by D. J. Crouse and J. O. Denis, *The Use of Amines as Extractants for Thorium (and Uranium) from Sulfuric Acid Digests of Monazite Sands*, ORNL-1859 (Feb. 1, 1955).

chemical costs for the thorium recovery cycle, including the cost of ammonia for product precipitation, were estimated at 13¢ per pound of ThO₂.

The existing Blind River plants use anion exchange resins for uranium recovery, and thorium is discarded with the raffinate. Direct recovery of the thorium from these raffinates is possible by the Amex process if chloride rather than nitrate solutions are used for elution from the resin. With elution by nitrate, the amounts of nitrate reporting to the raffinate are sufficient to seriously interfere with the amine extraction of thorium. However, modification of the process flowsheet to allow simultaneous recovery of thorium and nitrate appears feasible, and this possibility is being studied. The high extraction power of the primary amines for thorium and their relatively low extraction power for uranium have also suggested a process for recovering thorium before uranium in existing plants. Results of batch extractions from the initial Blind River liquor with these reagents have indicated that >95% of the thorium can be obtained in products containing <0.3% uranium. Subsequent recovery of uranium by anion exchange resins could proceed without the problem of incomplete decontamination from thorium which has been encountered in present plants.

Monazite. – The main constituents of a representative liquor from the digestion of monazite with sulfuric acid, at pH 0.0, and their approximate concentrations in grams per liter, are: ThO₂, 7; U₃O₈, 0.2; rare earth oxides, 44; SO₄, 130; and PO₄, 30. Results from preliminary tests have suggested that thorium can be recovered and separated from uranium and most of the rare earths in a first cycle by extraction with a primary amine, that uranium can be recovered and separated from rare

Table 22.1. Comparative Extraction of Thorium, Uranium, and Rare Earths by Various Types of Long-Chain Amines

Amine Type	Examples	Extraction Ability		
		Thorium	Uranium	Rare Earths
Branched primary	Primene JM-T or 1-(3-ethylpentyl)-4-ethyloctyl	Very strong	Moderate	Moderate
Secondary				
Straight chain or branching distant from N	Di(tridecyl) or dilauryl	Strong	Moderate to strong	Weak
Branching near N	Amine S-24 or Amine 9D-178	Weak	Strong	Negligible
Tertiary	Tri- <i>n</i> -octyl or triisooctyl	Negligible	Strong	Negligible

earths in a second cycle with a secondary or tertiary amine, and that the rare earths can be recovered and separated from phosphate in a third cycle with a primary amine. The uranium and thorium products are of a grade that can be purified for reactor use by a single-cycle tributyl phosphate process. The rare earth product (<1% PO₄) is a suitable feed for the existing rare earth industrial processes. The process has been demonstrated in batch tests, and continuous-countercurrent experiments are in progress.

22.4 MOLYBDENUM RECOVERY

The molybdenum content of some uranium ores is great enough to be of commercial interest. In preliminary studies molybdenum was recovered from these liquors as a by-product by coextracting the uranium and molybdenum with the amine, selectively stripping the uranium with chloride solutions, and subsequently stripping the molybdenum

with sodium carbonate or ammonium hydroxide solution (Sec. 22.1). Molybdenum concentrates can be precipitated from the alkaline strip solution as molybdenum sulfide or calcium molybdate.

Treatment of liquors containing relatively high levels of molybdenum in conjunction with phosphate or vanadium has imposed a greater limitation on choice of a suitable amine extractant than is encountered in usual practice. This is caused by the tendency of some amines to precipitate from the diluent as heteropoly phosphomolybdate or vanadomolybdate compounds during either the extraction or stripping cycles. Tertiary amines, such as tri-*n*-octylamine or triisooctylamine, are particularly prone to this. Tendencies to precipitate were much lower with secondary amines, such as Amine S-24 and Amine 9D-178, and these compounds have been used successfully for molybdenum-uranium recovery in several multicycle continuous runs.

23. DAPEX PROCESSES

The Dapex process (Fig. 23.1) was originally designed for the selective recovery of uranium from ore acid-leach liquors by extraction with kerosene solutions of appropriate dialkylphosphoric acids, usually di(2-ethylhexyl)phosphoric acid (D2EHPA).¹ Since these reagents have poor selectivity for uranium over ferric iron, the liquor is reduced before processing in order to convert most of the iron to the ferrous condition. The loaded solvent is ordinarily stripped of uranium with 1 M Na₂CO₃, although concentrated hydrochloric acid can also be used. Uranium products suitable for feed to the uranium refineries are recovered from the carbonate strip solution by first acidifying with sulfuric acid to destroy the carbonate and then precipitating with ammonia. Products are obtained from the HCl strip solution by precipitation with ammonia after most of the HCl has been evaporated and recovered for recycle.

¹C. A. Blake, K. B. Brown, and C. F. Coleman, *The Extraction and Recovery of Uranium (and Vanadium) from Acidic Liquors with Di(2-ethylhexyl)phosphoric Acid and Some Other Organophosphorus Acids*, ORNL-1903 (June 21, 1955).

During carbonate-stripping, sodium salts of the dialkylphosphoric acid extractants are formed, which tend to precipitate from the kerosene diluent or, as with D2EHPA, to form a third liquid phase containing the salt, some diluent, and some water. To prevent this formation, long-chain alcohols or neutral organophosphorus compounds such as tributyl phosphate (TBP) are added to the solvent. The alcohols depress the uranium extraction somewhat, whereas the neutral organophosphorus compounds operate in combination with the D2EHPA (and other dialkylphosphoric acids) to give a synergistic enhancement of uranium extraction (Sec. 24.1).

The Dapex process can be modified for the recovery of vanadium and possibly thorium. Metal ions are extracted by the dialkylphosphoric acid by cation exchange with the hydrogen ion. Like anion exchange extraction with amines (Sec. 22), this liquid-liquid cation exchange technology can, it is believed, be expanded to include applications other than those specifically examined thus far.

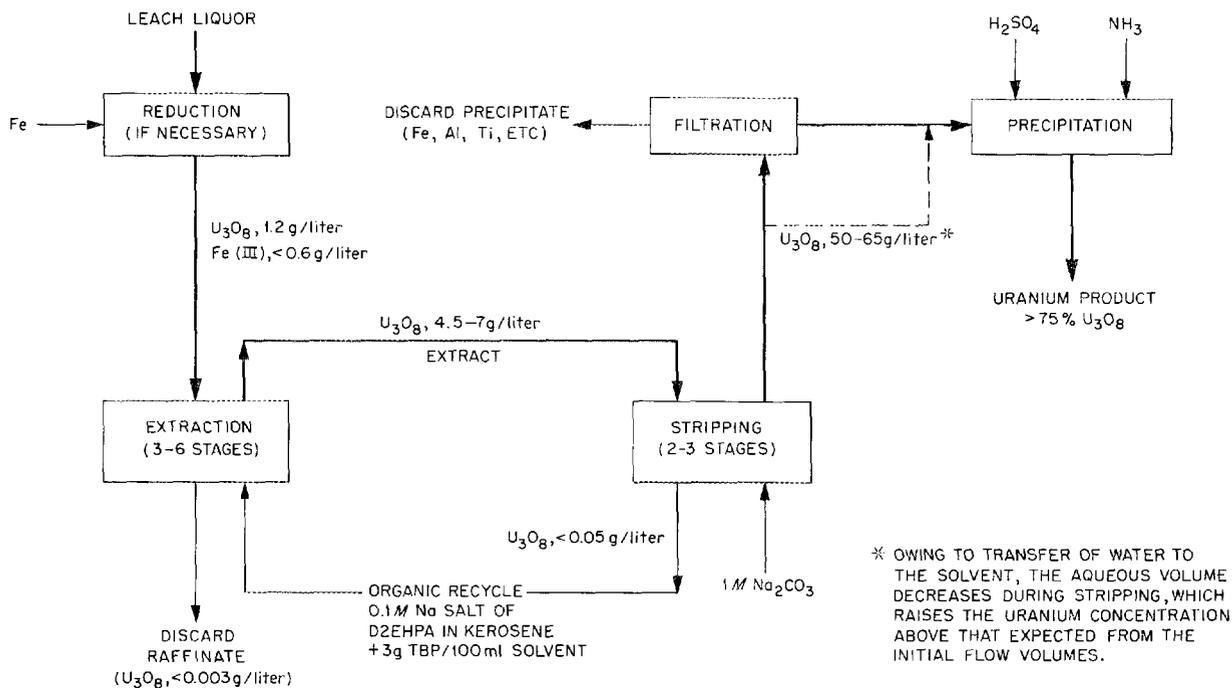


Fig. 23.1. Dapex Process for Recovery of Uranium from Ore Leach Liquor.

23.1 URANIUM RECOVERY

Laboratory Development. — In intensive testing of the Dapex process in bench-scale mixer-settler equipment, uranium was successfully recovered from a variety of sulfuric acid leach liquors.² Phase separation was rapid and clean with all the liquors when the organic solvent was the continuous phase during mixing. The nominal cost of chemicals, excluding costs for reduction of iron, amounted to only 14¢ per pound of U_3O_8 , which agrees with previous estimates from batch data. The process is not recommended for liquors of unusually high iron content because of the cost of reducing the iron.

The molybdenum content of some of the uranium products obtained during the test program was above specifications. In batch tests molybdenum was removed by digesting the products with dilute sodium hydroxide or by directly precipitating uranium from the sodium carbonate strip solution with

sodium hydroxide, rather than first adding sulfuric acid to destroy the carbonate and then precipitating with ammonia.

In some tests, ammonium carbonate solutions were successfully substituted for sodium carbonate in the stripping cycle. Products obtained by stripping with ammonium carbonate were free from sodium and would be a more desirable feed to the new refineries that use fluorination instead of solvent extraction for uranium purification.

Engineering Development. — Kinetic measurements in batch mixer tanks^{3,4} showed that the uranium extraction rates are well represented by first-order rate constants and that there was no significant difference in rate between oil-in-water and water-in-oil dispersions. The rate constants increased in proportion to turbine speed and to the cube root of power input, and doubled with a rise in temperature of approximately 15°C over the range from 15 to 55°C. The linear dependence on

²C. A. Blake et al., *Progress Report: Further Studies of the Dialkylphosphoric Acid Extraction (Dapex) Process for Uranium*, ORNL-2172 (Sept. 6, 1956).

³K. B. Brown et al., *Progress Report on Raw Materials for February, 1957*, ORNL-2269.

⁴K. B. Brown and C. F. Coleman, *Progress Report on Raw Materials for May, 1957*, ORNL-2366.

turbine speed, which implies nearly linear dependence on interfacial area, and the magnitude of the temperature dependence both suggest that the rate is controlled by reaction at the interface rather than by diffusion. In tests with 6-, 12-, and 20-in. mixers, the uranium extraction rate increased slightly with increased mixer size at constant power input per unit of mixer volume, so that scaleup on the usual basis of geometric similitude and power input would be conservative.

Kinetic measurements in a continuous-flow mixer^{5,6} agreed reasonably well with predictions from the batch studies. The stage efficiency was 80% in extraction from a typical uranium liquor (1.2 g/liter) at an aqueous/organic phase ratio of 4/1 and was over 90% in extraction from a high-uranium liquor (5 g/liter) at a phase ratio of 1/1 with a power input of 0.03 hp and an aqueous flow rate of 0.25 gpm per gallon of mixer contents. At 80% stage efficiency and an organic-phase uranium loading of 5 g/liter, with four countercurrent mixer-settlers, the raffinate from a feed containing 1.2 g/liter would contain 0.003 g/liter and would be discarded.

The extracted uranium was readily stripped with 1 M Na_2CO_3 in two countercurrent stages. A power input of 0.01 hp per gallon of mixer contents and a residence time of 0.5 min were used. The stage efficiency was over 90%.⁷

The nominal aqueous flow capacity (50% of flooding) of a 3-ft-deep horizontal gravity settler for water-in-oil dispersions was 1.1 gpm per square foot. For oil-in-water dispersions it was 1.5 to 3.9 gpm per square foot at aqueous/organic flow ratios of 1/1 to 4/1 (ref 8).

The entrainment of organic solvent in the aqueous phase was determined by the type and degree of dispersion and by the time of holdup of the aqueous phase after the primary phase separation. For water-in-oil dispersions it was consistently less than 0.2 gal per 1000 gal of raffinate, and for

oil-in-water dispersions it was 0.2 to 3.0. Batch settling tests demonstrated the rate of rise of the entrained organic droplets to be approximately 1 ft/hr, so that much of the entrained organic solvent could be recovered in a reasonable holdup time.

On the basis of the foregoing data, mixing and settling equipment requirements have been estimated for a Dapex process treating 100,000 gal of liquor (~200 tons of ore) per day. In a plant designed for water-in-oil-type mixing, each mixer in the extraction section would have about 300 gal capacity and a 10-hp agitator, and each settler would be about 10 ft in diameter; in the stripping section each mixer would have about 25 gal capacity and a 0.25-hp agitator, and each settler would be about 4 ft in diameter.

Commercial Applications. — Commercial plants using the Dapex process for uranium recovery have been operating since September 1956 at the Climax Uranium Company, Grand Junction, Colorado, and the Kerr-McGee Oil Industries, Shiprock, New Mexico. Other commercial plants are being constructed, including that of the Union Carbide Nuclear Company at Rifle, Colorado, and that of the Gunnison Mining Company at Gunnison, Colorado.

23.2 VANADIUM RECOVERY

Laboratory Development. — By adjustment of the conditions, the Dapex process may be applied to the recovery of vanadium from uranium-barren liquors and to the simultaneous recovery of vanadium and uranium. The latter process (Fig. 23.2) has been demonstrated in several continuous runs in bench-scale countercurrent equipment with leach liquors of the type obtained by a sulfuric acid cure or a hot sulfuric acid leach of a uranium-vanadium ore. Vanadium extractions are adequate with vanadium(IV) but only at high pH (~2) and relatively high extractant concentration (0.2–0.4 M D2EHPA in kerosene). Iron(III) is held to a minimum since it also is extracted well under these conditions.

Uranium recovery is essentially complete and vanadium recovery is 90 to 95% in 6–8 countercurrent stages. The vanadium is selectively stripped with 1.0 M H_2SO_4 to give a concentrated vanadium solution. To build up uranium in the solvent and thus reduce the amount of sodium

⁵A. D. Ryon and K. O. Johnsson, *Progress Report of Process Test Section for August, 1956*, ORNL-2214.

⁶K. B. Brown *et al.*, *Progress Report on Raw Materials for June, 1957*, ORNL-2380 (in press).

⁷K. B. Brown *et al.*, *Progress Report on Raw Materials for April, 1957*, ORNL-2346.

⁸K. B. Brown *et al.*, *Progress Report on Raw Materials for March, 1957*, ORNL-2306.

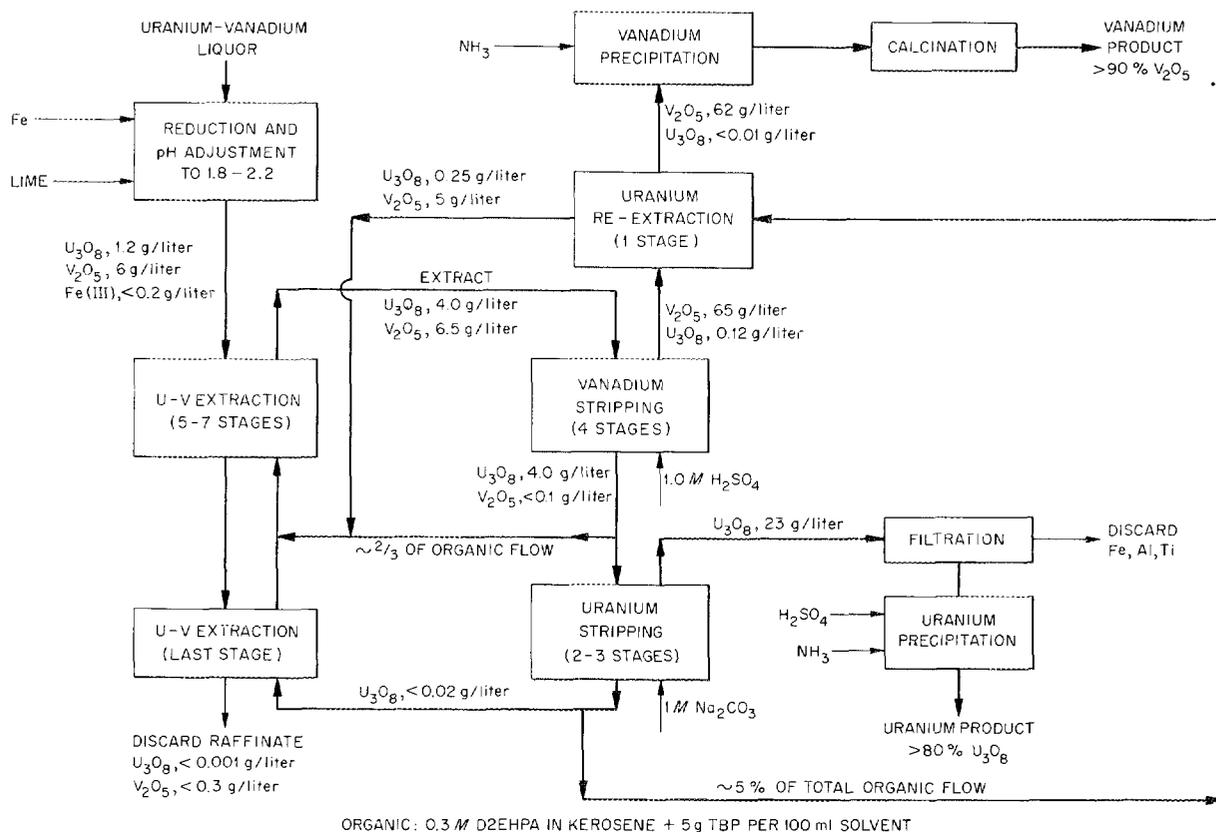


Fig. 23.2. Dapex Process for Simultaneous Recovery of Uranium and Vanadium from Ore Leach Liquor.

carbonate required for stripping, only about one-third of the solvent stream from vanadium stripping is sent to uranium stripping in each cycle.

Vanadium is recovered from the pregnant strip solution by neutralizing with ammonia to precipitate hydrated vanadyl oxide or by adding sodium chlorate and heating to precipitate a polyvanadate. In the latter method, precipitation of vanadium is not complete and some vanadium recycle is necessary. The vanadium products obtained by both precipitation methods contain 97 to 99% V_2O_5 . With ammonia precipitation the products sometimes contain more than the allowable amounts of phosphorus. In preliminary tests the amount of phosphorus in these products was decreased by scrubbing the extract with ammonium sulfate solution before stripping the vanadium or by precipitating phosphate from the pregnant strip solution with zirconium before precipitating the vanadium with ammonia.

Engineering Development. - In batch tests in 6- and 12-in.-dia baffled tank mixers the rate of vanadium extraction followed first-order kinetics, similar to the kinetics in uranium extractions (Sec. 23.1). As with uranium, the vanadium extraction rate increased in proportion to the turbine speed and to the cube root of power input. The value of the rate constant for vanadium was approximately two-thirds that for uranium under the same mixing conditions, so that the required residence time for vanadium extraction should be approximately 50% greater than that reported for uranium extraction.

Commercial Applications. - The Dapex process for vanadium recovery has been installed by the Kerr-McGee Oil Industries at Shiprock, New Mexico, and the Union Carbide Nuclear Company at Rifle, Colorado.

23.3 THORIUM RECOVERY

In preliminary batch experiments thorium was recovered from uranium process raffinates by the Dapex process. With 0.1 M D2EHPA in kerosene alone, kerosene plus 2 vol % primary decanol, or kerosene plus 0.1 M TBP, thorium was effectively extracted from simulated Blind River anion exchange raffinates, particularly when the aqueous pH level was above 1. In contrast with the effect in uranium extractions (Sec. 24.1), the thorium ex-

traction coefficients were decreased by the presence of TBP (Table 23.1).

The thorium may be stripped from the solvent by contacting with fluoride or bicarbonate solutions. Insoluble ThF_4 is precipitated when a fluoride strip is used. In carbonate-stripping, the thorium may remain dissolved in the strip solution or may precipitate; the result depends on the carbonate/bicarbonate ratio and total concentration.

Table 23.1. Extraction of Thorium from Sulfate Solutions by Di(2-ethylhexyl)phosphoric Acid

Molarity of Sulfate	Initial pH	0.1 M D2EHPA		0.1 M D2EHPA-0.1 M TBP	
		pH	Extraction Coefficient (Organic/Aqueous)	pH	Extraction Coefficient (Organic/Aqueous)
0.25	0.75	0.7	10	0.8	4
	1.0	0.9	35	1.0	10
0.52	0.6	0.5	1.4	0.5	0.6
	1.0	1.0	20	1.0	6
	1.8	1.8	2000	1.7	>400
1.04	0.3	0.3	0.2	0.25	0.05
	0.9	0.8	3	0.8	1
	1.8	1.7	1000	1.7	>400

24. SOLVENT EXTRACTION TECHNOLOGY

24.1 URANIUM EXTRACTION REAGENTS

The testing of organic compounds as potential extractants for uranium was continued, with more than a hundred new compounds being received from outside sources. Most of these were simple amines, other basic organonitrogen compounds, or organophosphorus acids. While many were research samples, an increasing number were samples of potentially commercial compounds submitted by manufacturers for evaluation as practicable uranium extractants.

Organonitrogen Compounds. — Several amines showed sufficiently good extraction performance and low aqueous solubility to be attractive for testing in specific process applications (Sec. 22.1). A tri-*n*-alkylamine containing mixed *n*-octyl and

n-decyl groups is available in development quantities. It was similar to tri-*n*-octylamine and triisooctylamine in extraction performance and showed less loss to the aqueous phase. A branched tertiary amine, tris(tridecyl)amine, showed some advantage over tri-*n*-octylamine and triisooctylamine in being compatible with unmodified kerosene diluent. Two primary amines having secondary straight-chain alkyl groups, (1-heptyloctyl)amine and (1-undecyldodecyl)amine, appeared promising for extraction of such metals as thorium (Sec. 22.3). As in previous tests, none of the organonitrogen bases other than the simple amines performed well enough to be of process interest. The compounds tested included some diamines, cyclic amines, aromatic amines, and compounds combining amino groups with other functional groups.

Extremely high uranium extraction power by N-benzylheptadecyl-, N-benzyltetradecyl-, and N-(2-naphthylmethyl)dodecylamine, in which the alkyl chains are highly branched, was reported previously.¹ Comparison of these with some other amines having related structures indicated that the aromatic substituent was an important factor in producing the high extraction power. This has been corroborated by further tests (Table 24.1) in which substituted N-cyclohexylmethylamines were compared with substituted N-benzylamines. The extraction power of these substituted N-benzylamines is high enough to permit effective recovery of uranium with low extractant concentrations from very low-grade liquors, for example, leach liquors of uraniferous shale.

A new strong-base reagent, dimethyldidodecylammonium carbonate,² extracted uranium from sodium carbonate solution more effectively than any quaternary ammonium compound previously available, and showed much better compatibility with practicable diluents. Both aromatic mineral spirits and alcohol-modified kerosene were effective. The uranium extraction power was improved considerably by increasing the alcohol content in

¹D. J. Crouse *et al.*, *Progress Report on Uranium Extraction with Organonitrogen Compounds*, ORNL-2099, p 2 (June 15, 1956).

²K. B. Brown *et al.*, *Progress Report on Raw Materials for February, 1957*, ORNL-2269, p 21.

either diluent (Table 24.2). The extracted uranium was readily stripped by chloride solutions, and stripping with sodium hydroxide solutions appeared promising. While the over-all extraction performance was still not good enough to be competitive with the best existing reagents for uranium recovery from carbonate solutions, the degree of improvement of this reagent over the reagents previously examined indicates that still better performance may be attained.

Table 24.2. Uranium Extraction from Carbonate Solution by Dimethyldidodecylammonium Carbonate

Aqueous phase: 0.5 M Na₂CO₃⁻⁻⁻, 0.004 M U
 Organic phase: 0.1 M (R₄N)₂CO₃, diluent modified with tridecanol as noted
 Organic/aqueous phase ratio = 1/1
 Room temperature

Tridecanol in Diluent (vol %)	Uranium Extraction Coefficient (Organic/Aqueous)	
	Amsco G	Kerosene
0	2	
5	7	6
10	12	14
15	17	21
25	10	30

Table 24.1. Comparison of Extraction Power of N-Benzyl- and N-Cyclohexylmethylamines

Aqueous phase: 1 M SO₄⁻⁻⁻, 0.004 M U, pH 1
 Organic phase: 0.1 M amine
 Organic/aqueous phase ratio = 1/1
 Room temperature

Amine	Uranium Extraction Coefficient (Organic/Aqueous)	
	Kerosene	Benzene
N-Benzyl-1-(3-ethylpentyl)-4-ethyloctyl	8000	2000
N-Cyclohexylmethyl-1-(3-ethylpentyl)-4-ethyloctyl	25	95
N-(2,4,6-Trimethylcyclohexyl)methyl-1-(3-ethylpentyl)-4-ethyloctyl	130	25
N-Benzyl-1-isobutyl-3,5-dimethylhexyl	1400	3000
N-Cyclohexylmethyl-1-isobutyl-3,5-dimethylhexyl	85	90
N-(2,4,6-Trimethylcyclohexyl)-1-isobutyl-3,5-dimethylhexyl	70	25

Organophosphorus Compounds. — Two new reagents, di(2-ethyl-4-methylpentyl)phosphoric acid and di(2-propyl-4-methylpentyl)phosphoric acid,³ appeared similar to D2EHPA (Sec. 23) and showed nearly the same uranium extraction power, suggesting that they should be competitive with D2EHPA if they became available in quantity at a competitive price.

Unusually high uranium extraction power was shown by an α -hydroxyalkyl aryl reagent, phenyl(1-hydroxy-2-ethylhexyl)phosphinic acid.⁴ The extraction coefficients obtained with this reagent were two orders of magnitude higher than those with phenyl(2-ethylhexyl)phosphinic acid, which is identical in structure except for the α -hydroxy group (Table 24.3). Higher reagent concentrations would be expected to give still higher extraction coefficients but could not be attained with this reagent because of its limited solubility in the common diluents. Incorporation of this type of acid group into a resin structure, at a high equivalent concentration, might achieve high enough extraction power for uranium recovery from, for example, commercial phosphoric acid.

The reaction of a dialkylphosphoric acid with phosphorus pentoxide produced a relatively stable

acidic polyphosphate reagent with high uranium extraction power. The reagent prepared from 0.1 M D2EHPA extracted either uranium(IV) or uranium(VI) from 5 M phosphoric acid, with extraction coefficients of 5 to 20. This approaches the extraction power of the dialkylpyrophosphoric acids, which are now used for uranium recovery from commercial phosphoric acid in spite of their relatively rapid hydrolysis. Hydrolysis of the polyphosphate reagent was slow, even when the extracted uranium was stripped with sodium carbonate solution.

Some polymeric compounds containing phosphate ester groups showed considerably higher uranium extraction power than has been found with simple monomeric phosphate esters. Although the particular samples examined had poor physical properties, the results may be useful for development of resinous extractants.

Synergistic Reagent Combinations. — Synergistic Dapex extraction reagents (Sec. 23) are certain combinations of neutral reagents with dialkylphosphoric acids that have greater uranium extraction power than the components individually.⁵ The high extraction power provides more efficient reduction of the raffinate uranium level in a small number of stages, permits higher uranium loading from dilute liquors, and extends the usefulness of the Dapex process to liquors difficult to extract otherwise.

The magnitude of the synergistic enhancement varies with the choice of the neutral component, increasing in the order phosphate < phosphonate < phosphinate < phosphine oxide (Table 24.4). Of the reagents listed, only tributyl phosphate and dibutyl butylphosphonate were formerly available in commercial quantities. Recently the other phosphonates listed have also become available commercially. The pentyl and hexyl compounds are particularly promising for process use, with enhanced extraction performance and decreased over-all operating costs more than compensating for a somewhat higher reagent price.⁶

Nearly all of various neutral organophosphorus compounds examined in combination with D2EHPA increased the uranium extraction, while all other neutral compounds tested either were indifferent

³K. B. Brown *et al.*, *Progress Report on Raw Materials for February, 1957*, ORNL-2269, p 4.

⁴K. B. Brown and C. F. Coleman, *Progress Report on Raw Materials for May, 1957*, ORNL-2366.

Table 24.3. Effect of α -Hydroxy Group on Uranium Extraction by Phosphinic Acids

Organic phase: 0.1 M reagent in CCl₄
 Aqueous phase: 0.004 M U
 Aqueous/organic phase ratio = 1/1
 Room temperature

Phosphinic Acid	Uranium Extraction Coefficient (Organic/Aqueous)			
	1.5 M SO ₄ pH 1	0.4 M PO ₄ pH 1	1.4 M PO ₄ pH 2	1.4 M PO ₄ pH 1.4
Phenyl(2-ethylhexyl)	15	15	1.5	0.5
Phenyl(1-hydroxy-2-ethylhexyl)	1000	1000	370	130
Di-n-octyl	20	20	2	1

⁵*Narrative Status Report, Raw Materials Chemistry Section*, ORNL-2002, p 2 (Dec. 13, 1955).

⁶K. B. Brown *et al.*, *Progress Report on Raw Materials for March, 1957*, ORNL-2306, p 4.

Table 24.4. Comparison of Extractions by Reagents Alone and in Synergistic Combinations

Neutral Reagent	Concentration (M)	Extraction Coefficient (Organic/Aqueous) for Uranium from 0.5 M SO_4 , pH 1	
		Neutral Reagent Alone	D2EHPA + Neutral Reagent*
None			135
Tributyl phosphate	0.1	0.0002	500
Dibutyl butylphosphonate	0.1	0.0002	1700
Dipentyl pentylphosphonate	0.1	0.0003	2000
Dihexyl hexylphosphonate	0.1	0.0004	2200
Didecyl decylphosphonate	0.1		600
Butyl dibutylphosphinate	0.1	0.002	3500
Tributylphosphine oxide	0.05	0.0025	7000

*Synergistic combination of 0.1 M di(2-ethylhexyl)phosphoric acid + neutral reagent at the molarity shown, in kerosene.

or impaired the extraction.^{7,8} Some enhancement, by a factor of about 2, was given by a basic additive, a high-molecular-weight branched-alkyl primary amine, but not by the secondary or tertiary amines tested.

Significant synergistic enhancement has so far been obtained only in the extraction of uranium(VI) and only with dialkylphosphoric acids as the acid component. Extraction by dialkylphosphinic acids was essentially the same in combination as alone, while extraction by monoalkylphosphoric and monoalkylphosphonic acids was severely impaired.⁹

24.2 EXTRACTION OF OTHER METALS

Survey tests of several metal ion systems have indicated that useful extractions and separations may be obtained with amines, dialkylphosphoric acids, and trialkylphosphine oxides.¹⁰

Rare Earths. — Tertiary amines (tri-*n*-octyl and triisooctyl) in kerosene-alcohol diluent extracted yttrium and yttrium-group rare earths from nearly

neutral nitrate solution. Extraction increased with increasing nitrate concentration and decreasing acidity. Dysprosium and holmium were extracted most strongly, with yttrium falling near ytterbium. Separation factors with respect to yttrium in a typical test were Gd, 4; Dy, 5; Ho, 5; and Er, 3. Under similar conditions, extractions with primary and secondary amines were low.

A solution of D2EHPA in kerosene extracted ytterbium best, with a gradual decrease to lanthanum, from nitrate, chloride, and sulfate solutions at acidities up to 1 M. Yttrium fell between holmium and erbium. Separation factors between adjacent elements were around 1.5.

Extraction with tri-*n*-octylphosphine oxide in kerosene from chloride or nitrate solution was maximum near samarium or gadolinium. Yttrium fell near erbium when the acidity was 1 M, shifting toward and past ytterbium as the acidity was decreased.

Zirconium and Hafnium. — Zirconium was extracted preferentially to hafnium from sulfate solutions by amines, with a separation factor of 5 in extraction from 1 M H_2SO_4 by tri-*n*-octylamine in kerosene-alcohol diluent. Extraction increased with decreasing sulfate concentration or

⁷C. A. Blake *et al.*, *Progress Report: Further Studies of the Dialkylphosphoric Acid Extraction (Dapex) Process for Uranium*, ORNL-2172, p 10 (Dec. 19, 1956).

⁸K. B. Brown *et al.*, *Progress Report on Raw Materials for February, 1957*, ORNL-2269, p 6.

⁹K. B. Brown *et al.*, *Progress Report on Raw Materials for April, 1957*, ORNL-2346, p 4.

¹⁰*Ibid.*, p 8.

acidity, but the separation factor remained nearly constant.

Scouting tests indicated stronger extraction of hafnium than of zirconium by D2EHPA from sulfate solutions, with separation factors greater than 40.

Cobalt and Nickel. – Cobalt was extracted effectively by tertiary amines from concentrated hydrochloric acid solutions, with maximum extraction at 8 M HCl. Nickel extraction under the same conditions was nil.

25. FUNDAMENTAL CHEMISTRY

Fundamental studies of systems related to raw materials process chemistry have continued, with increasing attention to aqueous-organic distributions in solvent extraction systems and to the nature of the extractant and the extracted species in the organic phase.

25.1 SOLVENT EXTRACTION EQUILIBRIUMS

Equilibrium liquid-liquid distributions are being studied in simple, well-defined systems related to the more complex systems encountered in actual process operation. Uranium distribution has been correlated with the principal variables in extraction both by dialkylphosphoric acid and by amines. Since the latter is actually extraction by amine salts, the equilibriums of salt formation and acid distribution were studied in the absence of uranium.

25.1.1 Acid Extraction by Amines

Sulfuric acid extraction by benzene solutions of tri-*n*-octylamine and di-*n*-decylamine and the equilibriums among free amine, amine sulfate, and amine bisulfate were measured as functions of the amine concentration in the organic phase and of the sulfuric acid activity in the aqueous phase. The results corroborated the conclusions from previous studies¹ that the amine salts exist in the organic phase as dispersions of approximately constant activity, instead of as true solutions, over a wide concentration range. With tri-*n*-octylamine sulfate in benzene this range extended down to 0.02 M and with di-*n*-decylamine sulfate down to 0.001 M or lower. The acid-extraction and salt-formation equilibriums were well summarized by empirical equations written in terms of equivalent

fractions of the amine salts.² These empirical equations were similar to but not identical with the mass-action equations expected for the apparent net chemical reactions, and were not identical for the two amines. The differences might be due to inadequacy of the equivalent fractions as a measure of the activities of the amine salts; other studies in progress on the nature of the organic phases (see Sec. 25.2) may help to resolve this.

Preliminary measurements were made of the relative base strengths of amine-diluent combinations for correlation with extraction performance. In the combinations examined thus far, the basicities varied with amine class, primary > secondary > tertiary; with branching, straight chain > branched chain; and with diluent, chloroform > benzene > *n*-nonane.

25.1.2 Uranium Extraction by Amine Sulfates

Uranium extraction by benzene solutions of sulfates of tri-*n*-octylamine and di-*n*-decylamine was measured as a function of uranium concentration, amine concentration, and aqueous sulfate concentration and acidity. The results showed that only the normal amine sulfate, and not the amine bisulfate, is effective in the uranium extraction, and that the bisulfate/normal-sulfate ratio in the uncomplexed fraction of the amine depends only on the aqueous acid activity, independent of the extracted uranium. Precise measurements of the amount of hydrogen ion released from amine bisulfate as a result of uranium extraction gave a measure of the number of amine groups associated with each extracted uranium atom. This was essentially constant over a wide range of uranium

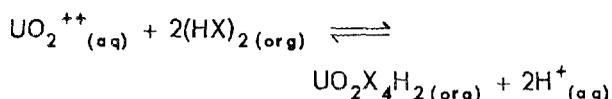
¹K. B. Brown *et al.*, ORNL-1734, p 112 (June 9, 1954) (classified).

²K. A. Allen, *J. Phys. Chem.* 60, 239 (1956); *J. Phys. Chem.* 60, 943 (1956).

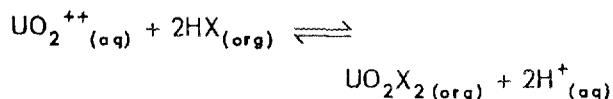
loading levels and agreed with the directly measured amine/uranium limiting ratios found near saturation, that is, approximately 6/1 with di-*n*-decylamine and a little more than 4/1 with tri-*n*-octylamine.

25.1.3 Uranium Extraction by Dialkylphosphoric Acid

Uranium extraction by *n*-hexane solutions of di(2-ethylhexyl)phosphoric acid (D2EHPA) was measured as a function of uranium concentration, D2EHPA concentration, and aqueous acidity. The uranium was extracted from perchlorate solutions at constant ionic strength in order to avoid the additional variable of changing uranyl complex formation in competition with the extraction. The results, together with the results of direct studies of the organic phase described below, indicated that the extraction reaction at low uranium/D2EHPA ratios is



in which X represents the di(2-ethylhexyl)phosphate anion. D2EHPA exists principally as dimers in the hydrocarbon solution, and at low uranium/D2EHPA ratios the extracted uranyl ion reacts with two of the dimers to form a 1:4 complex. At higher uranium/D2EHPA ratios polynuclear complexes are formed, $(\text{UO}_2)_x\text{X}_{2x+2}\text{H}_2$, and the limiting uranium/D2EHPA ratio approaches 1:2. These results show how and to what extent the originally assumed equation^{3,4}



(which ignored the D2EHPA dimerization) has served as a usefully close approximation for process applications, and they also account for the observed "distorted" shape of the extraction isotherms at higher uranium loadings.

³C. A. Blake, K. B. Brown, and C. F. Coleman, *The Extraction and Recovery of Uranium (and Vanadium) from Acidic Liquors with Di(2-ethylhexyl)phosphoric Acid and Some Other Organophosphorus Acids*, ORNL-1903, p 4 (May 13, 1955).

⁴*Narrative Status Report, Raw Materials Chemistry Section*, ORNL-2002, p 20 (Nov. 11, 1955).

Uranium extraction measurements and the corresponding direct investigation of the organic phase were extended to the synergistic extraction systems, in which the addition of a neutral organophosphorus compound to the D2EHPA solution enhances the uranium extraction coefficient by a large factor and at the same time increases the "distortion" of the extraction isotherm markedly. While these studies are still in the preliminary stages, they show evidence of direct interaction between tributyl phosphate or trioctylphosphine oxide and D2EHPA, which might be involved in the synergism.

25.2 STUDY OF THE ORGANIC PHASE

It has been recognized both in process development and in fundamental studies that many of the extractant phases are complex in nature and that the complexities have important effects on the extraction behavior. Some of these organic phases are being examined directly, with particular attention to amine salt aggregation, polymerization of D2EHPA and its uranium complexes, and interaction of D2EHPA with synergistic additives.

25.2.1 Amine Extractant Solutions

As was mentioned above (Sec. 25.1.1), recognition that the amine salts form aggregates has aided in the correlation of extraction variables, but more exact information about the nature of the aggregates is needed for satisfactory calculation of the activities of extracted acid and uranium. As one approach to this, the average molecular weights of amine species in organic solution are being estimated by measurement of their effectiveness in scattering light. The first species to be examined over a wide concentration range was di-*n*-decylamine sulfate in benzene. Results indicated a weight-average molecular weight between 2400 and 3000, corresponding to about 40 $(\text{R}_2\text{NH}_2)_2\text{SO}_4$ units per aggregate. The results also suggested that the di-*n*-decylamine sulfate aggregates are all of nearly the same size in this concentration range, which in turn suggests that they may be micelles of fairly definite size and structure. Measurements are in progress with benzene solutions of tri-*n*-octylamine sulfate, the bisulfates of di-*n*-decylamine and tri-*n*-octylamine, and the amines in the free-base form. Preliminary measurements indicated that the technique will also apply to amine salt solutions containing extracted uranium.

Equipment for measuring dielectric constants of organic solutions was assembled and tested for use in studying the dependence of amine salt aggregation on concentration in the organic phase.

25.2.2 Organophosphorus Extractant Solutions

In connection with the equilibrium measurements described above on the extraction of uranium by D2EHPA (Sec. 25.1.3), the mean molal concentrations of extractant and of extracted complexes in *n*-hexane were estimated by isopiestic balancing against reference solutes. The results showed that the effective (colligative) concentration of D2EHPA was half the nominal concentration, indicating the existence of D2EHPA in hydrocarbon solution as dimers, $(HX)_2$, rather than as monomers, HX. With a constant concentration of D2EHPA, the isopiestic results showed that the effective total concentration of solute particles decreased uniformly as the concentration of extracted uranium increased, $C_{\Sigma} = C_{(HX)_2} - C_{U(org)}$. This is consistent with the formation of a series of uranium-D2EHPA complexes with the general formula $(UO_2)_x X_{2x+2} H_2$. As was described above, the extraction equilibria were also consistent with this formulation.

Measurement of the viscosity of the organic phase was a useful auxiliary to the isopiestic measurements. As the uranium loading (and hence the average size of the polynuclear uranium complexes) increased, the total number (and hence the effective concentration) of solute particles decreased, until the isopiestic measurements, like other colligative measurements, lost sensitivity. At the same time the viscosity increased because of the increased size of the solute particles; it increased most rapidly near uranium saturation. The assumption that the polynuclear complexes are linear chains, increasing in size by increasing in length, permitted a fairly good correlation of viscosity with uranium loading and gave further support to the over-all interpretation of the extraction.

25.3 AQUEOUS SOLUTION CHEMISTRY

25.3.1 Bisulfate Ion Dissociation in Sulfuric Acid-Sodium Sulfate Solutions

In many of the aqueous-organic distribution studies described above, as well as in some other aqueous systems pertinent to raw materials chem-

istry, a knowledge of sulfuric acid activity and of the individual concentrations of sulfate, bisulfate, and hydrogen ions has been needed. Sulfuric acid activities in pure sulfuric acid solutions are available from Raman spectral measurements and potentiometric measurements reported in the literature. These were compiled and evaluated in connection with previously reported extraction measurements.^{5,6} In the absence of sufficient reported data for sulfuric acid-sulfate mixtures, an empirical method was developed to estimate the bisulfate dissociation and the actual ionic concentrations of H^+ , SO_4^{--} , and HSO_4^- in a useful range of H_2SO_4 - Na_2SO_4 solutions.⁷ Resulting values of the bisulfate ion dissociation quotient

$$Q = [H^+][SO_4^{--}]/[HSO_4^-]$$

and of the fraction of total sulfate present as bisulfate ion have been tabulated⁸ as functions of total sulfate concentration, ionic strength, and ratio of sulfuric acid to total sulfate. Raman measurements on sulfuric acid-sodium sulfate solutions which will test these calculations are under way at the University of Chicago. Preliminary measurements of the ratio of bisulfate to total sulfate have corroborated the calculated ratios.

25.3.2 Uranyl Complex Formation Constants from Solvent Extraction Equilibria

The measurements described above (Sec. 25.1.2) of uranium extraction from sulfate solutions by amine sulfates, together with the evaluation (Sec. 25.3.1) of sulfate and bisulfate ion concentrations in the aqueous sulfate solutions used, permitted estimation of the formation quotients of the successive uranyl sulfate complexes (calculated at unit ionic strength):

⁵C. F. Baes, Jr., *The Extraction of Iron(III) from Acidic Sulfate Solutions by Di-n-decylamine Sulfate in Benzene*, ORNL-1930, p 7 (Aug. 25, 1955).

⁶C. F. Baes, Jr., *The Extraction of Iron(III) from Acidic Sulfate Solutions by Di-n-decylamine Sulfate in Benzene*, Paper No. 220 presented at the Nuclear Engineering and Science Congress, Cleveland, Ohio, Dec. 12-16, 1955.

⁷C. F. Baes, Jr., "The Estimation of Bisulfate Ion Dissociation in Sulfuric Acid-Sodium Sulfate Solutions," *J. Am. Chem. Soc.* (to be published).

⁸K. B. Brown et al., *Progress Report on Raw Materials for March, 1957*, ORNL-2306, p 29.

$$K_1 = [\text{UO}_2\text{SO}_4]/[\text{UO}_2^{++}][\text{SO}_4^{--}] \approx 35 ,$$

$$K_2 = [\text{UO}_2(\text{SO}_4)_2^{--}]/[\text{UO}_2^{++}][\text{SO}_4^{--}]^2 \approx 100 ,$$

$$K_2/K_1 = 6 \pm 1 .$$

These values are somewhat lower than, but still in relatively good agreement with, formation quotients at unit ionic strength reported from spectrophotometric and potentiometric measurements.⁹ However, the present results indicate that very

⁹S. Ahrlund, *Acta Chem. Scand.* 5, 1151 (1951).

little if any trisulfate complex, $[\text{UO}_2(\text{SO}_4)_3]^{4-}$, is formed in solutions at concentrations up to at least 1 M sulfate; therefore, $K_3 \leq 125$. This is in disagreement with the potentiometric measurements, which led to a third formation quotient of ~ 2500 .

Extraction of uranyl ion from a complexing solution by dialkylphosphoric acid, in comparison with extraction from a corresponding perchlorate (non-complexing) solution (Sec. 25.1.3), offers a direct measure of the activity of uncomplexed uranyl ion in the complexing solution. This is expected to improve the accuracy in the evaluation of complex formation constants by means of systems such as those just described, and to permit evaluations in a wider range of systems.

26. RARE EARTH SEPARATIONS¹

The rare earth separations program originated from the need for large amounts of high-purity rare earths as charge material for the separation of their isotopes, and it has also supplied rare earths to other programs of the laboratory. It has been principally concerned with rare earth distributions in nitric acid-tributyl phosphate systems and with the multistage liquid-liquid separation of kilogram quantities.¹

The separation factor for gadolinium from samarium was ~ 2.5 in single-stage extractions with tributyl phosphate from $\sim 14 N$ HNO_3 solutions

saturated with a mixture of the two nitrates. This is close to the factor previously calculated on the basis of individual extractions from 14 N HNO_3 at low salt concentrations, rather than to the lower factor (1.1) indicated by individual extractions from 14 N HNO_3 solutions, each saturated with one of the nitrates.²

A pump-mixer-settler system with external reflux at each end, suitable for high salt concentrations, was developed. Seventeen stages gave a separation factor of ytterbium from yttrium of 630 (1.46 per stage) in extraction from 14 N HNO_3 nearly saturated with a mixture of yttrium-group rare earth nitrates. An 80-stage separation pilot plant, in which this system is used, was constructed and is ready for operation.

¹This work was recently transferred to the Chemical Technology Division from the Stable Isotopes Division. For previous reports see B. Weaver *et al.*, *Stable Isotopes Semian. Prog. Rep. Nov. 30, 1956*, ORNL-2236, p 15.

²B. Weaver *et al.*, *ibid.*, p 17.

APPENDIX

PUBLICATIONS

The following *Power Reactor Processing Status Reports* have been prepared:

ORNL CF-56-8-101, *Report for August 1956* (Confidential). \$0.30.

ORNL CF-56-9-101, *Report for September 1956* (Confidential). \$0.20.

ORNL-2210, *Report for October 1956* (Confidential). \$0.30.

ORNL-2228, *Report for November 1956* (Confidential). \$0.35.

ORNL-2247, *Report for December 1956* (to be issued).

The following *Feed Materials Processing Status Reports* have been prepared:

ORNL CF-56-7-100, *Report for July 1956* (Declassified). \$0.30.

ORNL CF-56-8-100, *Report for August 1956* (Declassified). \$0.30.

ORNL CF-56-9-100, *Report for September 1956* (Declassified). \$0.25.

ORNL-2209, *Report for October 1956* (Declassified). \$0.30.

ORNL-2227, *Report for November 1956* (Declassified). \$0.25.

ORNL-2246, *Report for December 1956* (to be issued).

The following *Chemical Technology Division Monthly Progress Reports* have been prepared:

ORNL-2251, *Report for January 1957* (Declassified). \$0.55.

ORNL-2270, *Report for February 1957* (Confidential). \$0.70.

ORNL-2307, *Report for March 1957* (Confidential). \$0.60.

ORNL-2324, *Report for April 1957* (Confidential). \$0.55.

ORNL-2361, *Report for May 1957* (Confidential). \$0.70.

ORNL-2362, *Report for June 1957* (to be issued).

ORNL-2385, *Report for July 1957* (to be issued).

ORNL-2400, *Report for August 1957* (to be issued).

The following *Progress Reports on Raw Materials* have been prepared:

ORNL-2268, *Report for January 1957* (Unclassified). \$0.20.

ORNL-2269, *Report for February 1957* (Unclassified). \$0.25.

ORNL-2306, *Report for March 1957* (Unclassified). \$0.25.

ORNL-2346, *Report for April 1957* (Unclassified). \$0.25.

ORNL-2366, *Report for May 1957* (Unclassified). \$0.25.

ORNL-2380, *Report for June 1957* (to be issued).

ORNL-2388, *Report for July 1957* (to be issued).

ORNL-2399, *Report for August 1957* (to be issued).

The following topical reports have been prepared:

Blake, C. A., D. J. Crouse, C. F. Coleman, K. B. Brown, and A. D. Kelmers, *Progress Report: Further Studies of the Dialkylphosphoric Acid Extraction (Dapex) Process for Uranium*, ORNL-2172 (Dec. 18, 1956) (Unclassified).

Bresee, J. C., C. D. Watson, and J. S. Watson, *Gamma Radiation Damage Studies of Organic Protective Coatings and Gaskets*, ORNL-2174 (Oct. 29, 1956) (Unclassified).

CHEMICAL TECHNOLOGY PROGRESS REPORT

- Chandler, J. M., and W. H. Lewis, *ORNL Metal Recovery Plant Activities During FY 1956*, ORNL-2335 (Aug. 13, 1957) (Confidential).
- Chester, C. V., *Evaluation of Sieve Plates for Steam Stripping of TBP from Evaporator Feed Streams*, ORNL-2339 (July 15, 1957) (Unclassified).
- Crouse, D. J., and K. B. Brown, *Progress Report on Separation and Recovery of Uranium and Thorium from Sulfate Liquors by the Amex Process*, ORNL-2173 (Dec. 26, 1956) (Unclassified).
- Culler, F. L., R. E. Blanco, H. E. Goeller, and C. D. Watson, *An Analysis of Power Reactor Fuel Reprocessing*, ORNL-2265 (March 7, 1957) (Confidential).
- Dean, O. C., E. Sturch, B. H. Morrison, and R. E. Blanco, *Status of the Hermex Process*, ORNL-2242 (July 29, 1957) (Unclassified).
- Ferris, L. M., *Laboratory Development of the Fluorox Process: The Reaction of UF_4 with Dry O_2 . I. Side Reactions and Thermodynamics*, ORNL-2180 (Feb. 19, 1957) (Confidential).
- Ferris, L. M., and E. G. Carter, *Laboratory Development of the Fluorox Process: II. Thermogravimetric Study of the Chemical Kinetics for the Reaction of UF_4 with Dry Oxygen*, ORNL-2216 (April 26, 1957) (Confidential).
- Flanary, J. R., *et al.*, *Chemical Development of the 25-TBP Process*, ORNL-1993 (March 20, 1957) (Confidential).
- Flanary, J. R., J. H. Goode, R. G. Mansfield, and R. P. Wischow, *Recovery of Np^{237} by the Neptex Solvent Extraction Process*, ORNL-2235 (March 11, 1957) (Confidential).
- Goode, J. H., *Radiation Damage to TBP and Diluents Covering Period October-December 1956*, ORNL-2287 (May 7, 1957) (Unclassified).
- Guthrie, C. E., *The Effect of the Radiochemical Reprocessing Industry's Growth on Spent Reprocessing Costs*, ORNL-2279 (May 29, 1957) (Confidential).
- Hancher, C. W., I. R. Higgins, and J. S. Taylor, *Uranium Recovery from Ore by a Higgins Ion-Exchange Contactor at Grand Junction Pilot Plant*, ORNL-2308 (June 17, 1957) (Unclassified).
- Higgins, I. R., *Development of the Higgins Continuous Ion Exchange Contactor for Recovery of Uranium from Leached Ore Pulps*, ORNL-1918 (Sept. 28, 1956) (Confidential).
- Hyman, M. L., *Laboratory Development of the Darex Process. I. Dissolution of a Nickel-Chromium Alloy*, ORNL-2239 (July 24, 1957) (Secret).
- Irvine, A. R., *Pulse Pumping: A Means for Transfer of Pulse Column Fluids*, ORNL-2377 (to be issued) (Unclassified).
- Kearsley, G. W. T., *Use of an Air Lift as a Metering Pump for Radioactive Solutions*, ORNL-2175 (Oct. 9, 1956) (Unclassified).
- Lewis, W. H., *Recovery of Uranium and $Np-237$ from Chalk River Uranyl Nitrate Solution in ORNL Metal Recovery Plant*, ORNL-2357 (Aug. 13, 1957) (Confidential).
- McCarley, W. T., *Analysis of Thorex Pilot Plant Radiation Exposures During 1955*, ORNL-2102 (Nov. 5, 1956) (Confidential).
- Sadowski, G. S., *The Organization, Administration, and Operation of a Radiochemical Pilot Plant*, ORNL-2132 (Sept. 14, 1957) (Unclassified).
- Shank, E. M., *Chemical Processing of Irradiated Thorium Oxide: Status Review for May 1956 to May 1957*, ORNL-2347 (July 29, 1957) (Confidential).

- Ullmann, J. W., *Throw-Away Fuel Cycle*, ORNL-2273 (March 7, 1957) (Confidential).
- Wymer, R. G., *Alloying of Zirconium-containing Fuels with Zinc and Magnesium*, ORNL-2184 (May 7, 1957) (Confidential).
- Wymer, R. G., *Dissolution of Uranium-Zirconium Fuel Elements in Fused NaF-ZrF₄*, ORNL-2183 (Jan. 24, 1957) (Confidential).
- Wymer, R. G., *Oxidation of Zirconium-Containing Fuels to Facilitate Uranium Recovery*, ORNL-2182 (Nov. 16, 1956) (Confidential).
- Yarbro, O. O., *A Criticality Study of the Thorex Pilot Plant*, ORNL-2332 (Aug. 28, 1957) (Unclassified).

The following papers have been published in the open literature:

- Allen, K. A., "Automatic Oxidimetric Micro-Method for Uranium," *Anal. Chem.* **28**, 1144 (1956).
- Allen, K. A., "The Equilibrium Between Di-*n*-decylamine and Sulfuric Acid," *J. Phys. Chem.* **60**, 943 (1956).
- Allred, V. D., S. R. Buxton, and J. P. McBride, "Characteristic Properties of Thorium Oxide," *J. Phys. Chem.* **61**, 117 (1957).
- Baes, C. F., Jr., "The Reduction of Uranium(VI) by Iron(III) in Phosphoric Acid Solution," *J. Phys. Chem.* **60**, 805 (1956).
- Baes, C. F., Jr., "A Spectrophotometric Investigation of Uranyl Phosphate Complex Formation in Perchloric Acid Solution," *J. Phys. Chem.* **60**, 878 (1956).
- Blake, C. A., C. F. Coleman, K. B. Brown, D. G. Hill, R. S. Lowrie, and J. M. Schmitt, "Studies in the Carbonate-Uranium System," *J. Am. Chem. Soc.* **78**, 5978 (1956).
- Blanco, R. E., "Processing of Power Reactor Fuels," *Nuclear Sci. and Eng.* **1**, 409-419 (1956).
- Bresee, J. C., J. R. Flanary, J. H. Goode, C. D. Watson, and J. S. Watson, "Damaging Effects of Radiation on Chemical Materials," *Nucleonics* **14**(9), 75-81 (1956).
- Bresee, J. C., and P. R. Larson, "A Continuous Cold Trap for Volatility Processing of Uranium," *Ind. Eng. Chem.* **49**, 1349 (1957).
- Bruce, F. R., "Chemical Processing of Aqueous Blanket and Fuel from Thermal Breeder Reactors," *Chem. Eng. Progr.* **52**, 347-352 (1956).
- Bruce, F. R., "Look for Nuclear Fuel Reprocessing by '65," *Chem. Eng.* **64**, 202-206 (1957).
- Dean, O. C., and J. M. Chandler, "The Preparation of Anhydrous Thorium Tetrachloride," *Nuclear Sci. and Eng.* **2**, 57-72 (1957).
- Goode, J. H., "How Radiation Affects Organics in Solvent Extraction of Fuel," *Nucleonics* **15**(2), 68-71 (1957).
- Haas, P. A., E. O. Nurmi, M. E. Whatley, and J. R. Engel, "Midget Hydroclones Remove Micron Particles," *Chem. Eng. Progr.* **53**, 203-207 (1957).
- Sadowski, G. S., "Decontamination of Processing Plants," *Nucleonics* **15**(3), 68-72 (1957).
- Savolainen, J. E., and R. E. Blanco, "Preparation of Power Reactor Fuels for Aqueous Processing," *Chem. Eng. Progr.* **53**, 78 (1957).
- Wymer, R. G., and R. E. Blanco, "U-Al Alloy Dissolution," *Ind. Eng. Chem.* **49**, 59-61 (1957).

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- Zeitlin, H. R., E. D. Arnold, and J. W. Ullmann, "Economics of Waste Disposal," *Nucleonics* 15(1), 58-62 (1957).
- Zingaro, R. A., "The Reaction of Uranyl Ion with Xanthates and Diethyldithiocarbamate," *J. Am. Chem. Soc.* 78, 3568 (1956).

PAPERS

The following papers were presented at the Symposium on Chemical Processing, Brussels, May 19-25, 1957:

- Blanco, R. E., *Alternate Processing Methods for Zirconium and Stainless Steel Containing Fuels*, ORNL CF-57-4-83.
- Blanco, R. E., *Dissolution and Feed Adjustment*, ORNL CF-57-4-85.
- Bruce, F. R., *Auxiliary Processes: Introduction*, ORNL CF-57-5-10.
- Bruce, F. R., *Ion Exchange Isolation Processes*, ORNL CF-57-4-6.
- Bruce, F. R., *Tail End Treatment for Zirconium-Niobium Removal*, ORNL CF-57-4-101.
- Bruce, F. R., *The Thorex Process*, ORNL CF-57-5-20.
- Cathers, G. I., *Fluoride Volatility Process for High Alloy Fuels*, ORNL CF-57-4-95.
- Culler, F. L., *General Economics of Chemical Reprocessing for Solvent Extraction Processing*, ORNL CF-57-4-100.
- Culler, F. L., J. O. Blomeke, and W. G. Stockdale, *Unit Costs and Economic Relationships for Certain Radioactive Waste Disposal Steps*, ORNL CF-57-5-25.
- Culler, F. L., and E. J. Frederick, *Development Facilities and Aids for Radiochemical Reprocessing*, ORNL CF-57-4-91.
- Gresky, A. T., *Radiochemical Separations Processes: Chemical Safety*, ORNL CF-57-4-59.
- Sadowski, G. S., T. W. Hungerford, R. E. Blanco, and F. L. Culler, *Radiation Exposure and Safety Experience in Radiochemical Plants*, ORNL CF-57-4-114.
- Ullmann, J. W., *Design for Criticality Control*, ORNL CF-57-5-4.
- Ullmann, J. W., *Heavy Element Isotopic Buildup*, ORNL CF-57-4-82.
- Ullmann, J. W., *Preparation of Wastes for Liquid Disposal*, ORNL CF-57-4-48.
- Unger, W. E., and F. L. Culler, *Auxiliary Radiochemical Equipment*, ORNL CF-57-5-17.

The following papers were presented at the Second Nuclear Engineering and Science Congress, Philadelphia, March 11-14, 1957:

- Dean, O. C., *Methods for the Production of Thorium Metal*, Paper 57-NESC-49.
- McBride, J. P., V. D. Allred, C. E. Schilling, and E. V. Jones, *Preparation and Properties of Aqueous Thorium-Uranium Oxide Slurries*, Paper 57-NESC-68.
- Savolainen, J. E., *New Developments in Preparation of Power Reactor Fuels for Aqueous Processing*, Paper 57-NESC-59.
- Ullmann, J. W., and E. D. Arnold, *Decay and Storage of Irradiated Fuel*, ORNL CF-56-4-51.

The following paper was presented at the Fifth Hot Laboratories and Equipment Conference, 1957 Nuclear Congress, Philadelphia, March 14, 1957:

- Watson, C. D., *Decontaminable Surfaces and Procedures for Hot Cells*, ORNL CF-57-3-159.

The following paper was presented at the Fifth Annual Atomic Energy in Industry Conference, Philadelphia, March 14-15, 1957:

Bruce, F. R., *Power Reactor Fuel Processing.*

The following papers were presented at the Industrial Technical Information Meeting at ORNL, September 13-15, 1956, and were published in TID-7518:

Blanco, R. E., and B. H. Morrison, *Reduction of UF_6 to Metal with Sodium Amalgam*, ORNL CF-56-6-157.

Cathers, G. I., and D. E. Ferguson, *Recovery of Uranium from Recycle Wastes by Fluoride Volatility - Industrial Technical Information Meeting*, ORNL CF-56-6-159.

Dean, O. C., *Recovery of Uranium from Scrap Metal by Amalgamation*, ORNL CF-56-6-156.

Higgins, I. R., *Purification of Scrap Uranium by Electrolysis - Industrial Technical Information Meeting on Processing of Cold Enriched Uranium*, ORNL CF-56-6-158.

Higgins, I. R., *Recovery of Uranium from Recycle Wastes by Ion Exchange*, ORNL CF-56-6-155.

The following papers were presented at the Uranium Institute of America Meeting, Denver, May 17, 1957:

Brown, K. B., *Recent Studies in Dapex Processing for Uranium and Amex Processing for Thorium.*

Higgins, I. R., *Treatment of Ore Leach Pulps by Continuous Ion Exchange.*

The following papers were presented at the American Chemical Society Meeting, Miami, April 7-13, 1957:

Baes, C. F., Jr., R. A. Zingaro, and C. F. Coleman, *The Extraction of Uranium(VI) from Acid Perchlorate Solutions by Di(2-ethylhexyl)phosphoric Acid in n-Hexane.*

Cathers, G. I., M. R. Bennett, and R. L. Jolley, *Formation and Decomposition Reactions of the Complex $UF_6 \cdot 3NaF$* , ORNL CF-57-4-25.

Ferris, L. M., *A Chemical Study of the Reaction $2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2$.*

Milford, R. P., *Engineering Design Features of the ORNL Fluoride Volatility Pilot Plant.*

The following paper was presented at the American Institute of Mining and Metallurgical Engineers Meeting, New Orleans, February 27, 1957:

Brown, K. B., D. J. Crouse and C. F. Coleman, *Some New Solvent Extraction Processes for Use in the Hydrometallurgical Treatment of Uranium, Thorium, and Vanadium Ores.*

The following paper was presented at the Sixth Annual AEC Corrosion Symposium, Columbus, June 19, 1957:

Clark, W. E., *Selection of Materials of Construction for Power Reactor Fuel Element Reprocessing Equipment.*

The following paper was presented at the Industrial Participation Meeting on Processing Uranium Magnesium Fluoride Slag, St. Louis, November 15, 1956:

Higgins, I. R., *Recovery of Uranium from Magnesium Fluoride Waste by Ion Exchange.*

CHEMICAL TECHNOLOGY PROGRESS REPORT

The following paper was presented at the meeting of AEC Nuclear Materials Management, New York, March 8, 1957:

Lewis, W. H., *Material Control Problems Associated with the Processing of Irradiated Uranium.*

The following speeches were given in the ORNL-ORINS traveling lecture program:

Baes, C. F., Jr., "Extraction of Uranium(VI) by Di(2-ethylhexyl)phosphoric Acid," Seminar at the University of Chicago, Chicago, Ill., February 4, 1957.

Bresee, J. C., "High-Speed Mixer Settler Equipment for Solvent Extraction," University of Tennessee, Knoxville, Tenn., January 21, 1957.

Browder, F. N., "Radioactive Waste," Clemson College, Clemson, S. C., January 8, 1957.

Eister, W. K., "The Engineer in the Atomic Energy Industry," Clemson College, Clemson, S. C., December 4, 1956.

Hancher, C. W., "Ion Exchange as a Unit Operation," Mississippi State College, Starkville, Miss., March 7, 1957.

Hancher, C. W., "Ion Exchange as a Unit Operation," University of Mississippi, Oxford, Miss., March 5, 1957.

Roberts, J. T., "Ion Exchange as a Unit Operation," University of Tennessee, Knoxville, Tenn., March 25, 1957.

Ullmann, J. W., "Reprocessing Economics of Power Reactor Fuels," University of Louisville, Louisville, Ky., May 9, 1957.

The following papers were presented at the Neptunium Information Meeting at ORNL, March 7-8, 1957, and are being published in TID-7542:

Arnold, E. D., *Neptunium Production: Future Potential.*

Flanary, J. R., *Introduction.*

Goode, J. H., *MTR Neptunium Second Cycle; K-25 Ash Processing.*

Goode, J. H., *Oak Ridge National Laboratory Purex Process.*

Kirslis, S. S., *Isolation of Gram Quantities of Neptunium.*

Lewis, W. H., *Neptunium Recovery from Chalk River Uranyl Nitrate Solution.*

Shank, E. M., *Neptunium Recovery from MTR Fuel Elements.*

Tomlin, W. E., *Neptunium Behavior in the Homogeneous Reactor.*

The following papers were presented at the American Nuclear Society Meeting in Washington, December 10-12, 1956:

Bresee, J. C., D. L. Foster, and E. O. Nurmi, *The Continuous Dissolution of Uranium-Aluminum Fuels in a Column Trickle-Type Dissolver.*

Cathers, G. I., J. T. Long, and R. P. Milford, *Uranium Recovery from Spent Fuel by Dissolution in Fused Salt and Fluorination*, ORNL CF-57-1-118 (to be published in *Nuclear Sci. and Eng.*).

Ferguson, D. E., *The Chemical Processing of Two-Region Aqueous Homogeneous Reactors*, ORNL CF-57-1-120.

Krohn, N. A., and J. P. McBride, *Reactor Irradiation of Thorium and Uranium Oxide Slurries*, ORNL CF-57-1-119.

- McNamee, R. J., *The Solvent Extraction of Thorium from Brazilian Monazite Sludge.*
 Morse, L. E., *Catalysts for Recombination of Radiolytic Gases over Thorium Oxide Slurries*, ORNL CF-57-1-117.

The following papers were presented at the American Nuclear Society Meeting in Pittsburgh, June 10-12, 1957:

- Arnold, E. D., *Economics and Hazards Potential of Waste Disposal.*
 Baybarz, R. D., *Decontamination of Homogeneous Reactor Systems.*
 Higgins, I. R., *An Alkaline Method for the Treatment of High Radiation Level Aluminum Wastes.*
 Kitts, F. G., and J. J. Perona, *Pre-Solvent Extraction Treatment of Stainless Steel-Uranium Fuels with Dilute Aqua Regia.*
 McBride, J. P., V. D. Allred, and J. M. Dalla Valle, *High Temperature Sedimentation Characteristics of Aqueous Thorium Oxide Suspension.*
 McBride, J. P., V. D. Allred, J. M. Dalla Valle, and R. L. Pearson, *Mass Subsidence of Thoria Slurries at High Temperatures and Pressures.*
 Nurmi, E. O., and D. L. Foster, *Thorium Dissolution Studies for Aqueous Fuel Re-processing.*
 Rainey, R. H., *Laboratory Developments in the Thorex Process.*
 Rainey, R. H., and A. B. Meservey, *Laboratory Developments in the Thorex Process.*
 Shank, E. M., *Pilot Plant Processing of Irradiated Thorium.*
 Weaver, B. S., and F. A. Kappelmann, *Separation of Rare Earths by Liquid-Liquid Extraction.*

The following papers were presented at the Civilian Power Reactor Conference at ORNL, May 1-2, 1957, and were published in TID-7540:

- Krohn, N. A., *Radiation Studies of Thorium Oxide Slurries.*
 Leuze, R. E., *Chemistry of Plutonium in Uranyl Sulfate Solutions.*
 McBride, J. P., *The Preparation and Characterization of Thorium Oxide and Its Aqueous Suspensions.*
 McNeas, R. A., *Homogeneous Reactor Core Processing Development.*
 Morse, L. E., *Catalytic Recombination of Radiolytic Gases in Aqueous Thorium Oxide Slurries.*

The following paper was presented at the University of Rochester Medical Research Center, Rochester, January 16, 1957:

- Culler, F. L., *The Hazards of a Radiochemical Processing Plant.*

The following paper was presented at the American Chemical Society Southwide Chemical Conference, Memphis, Tenn., December 6-8, 1956:

- Bresee, J. C., and D. C. O'Brien, *An Orifice Plate Pulse Column for Liquid-Liquid Extraction.*

The following paper was presented at the Second Annual Convention of the Wyoming Mining Association, Casper, Wyoming, April 13, 1957:

- Bresee, J. C., *Non-Military Applications for Uranium.*

[REDACTED]

The following papers were presented at the Gordon Research Conference on Ion Exchange, Meriden, N.H., August 5-8, 1957:

Blake, C. A., *Liquid Ion Exchange Media - Cation Exchange.*

Hancher, C. W., *A Comparison of Fixed and Moving Bed Ion Exchange.*