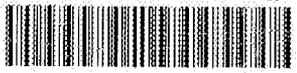


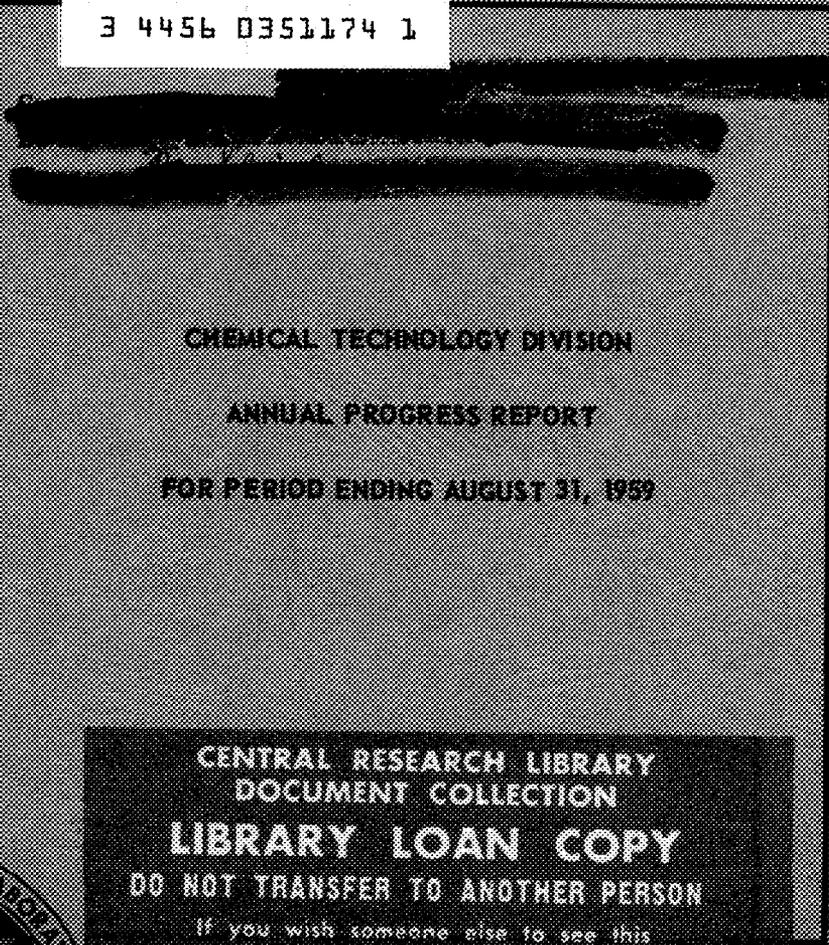
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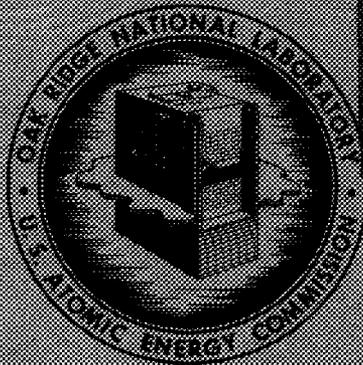


CHEMICAL TECHNOLOGY DIVISION

ANNUAL PROGRESS REPORT

FOR PERIOD ENDING AUGUST 31, 1959

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Contract No. W-7405-eng-26

**CHEMICAL TECHNOLOGY DIVISION**

**ANNUAL PROGRESS REPORT**

**for Period Ending August 31, 1959**

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J. E. BACON  
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TOTAL PERSONNEL	166	*DUAL CAPACITY
TECHNICAL	106	** RESEARCH PARTICIPANT
SCIENTIFIC	33	*** RESEARCH FELLOWSHIP STUDENT - UNIVERSITY OF LOUISVILLE
ADMINISTRATIVE AND CLERICAL	31	**** CONSULTANT, U.T.
TOTAL	305	
SUMMER EMPLOYEES	12	





## SUMMARY

### PART I. POWER REACTOR FUEL REPROCESSING

#### 1. Head-End and Solvent Extraction Processing

Development of the continuous Darex process for complete dissolution of stainless-steel-containing fuels on a small engineering scale was concluded. This process is applicable primarily to low-enrichment fuels because the 1 to 2% silica in highly enriched APPR fuels fouls the distillation column in ~10 hr. Of several batch chloride distillation processes tested, countercurrent addition of nitric acid through two buildowns gave the best chloride removal, to 28 to 51 ppm. Air-sparging during distillation improved chloride removal. A gaseous nitric oxide sparge at room temperature removed chloride from dissolver solution to 171 ppm.

Various methods were evaluated for removing silica from Darex-APPR feed solutions. Sand bed filtration and centrifugation were satisfactory, but hydrocloning and settling plus decantation were not. Removal of silica before chloride distillation was found feasible if the silica is first coagulated with gelatin and fluoride ion. Removal at this stage has the advantage of considerably smaller amounts of cake, since silica becomes highly hydrated during the chloride removal buildowns.

The Darex dissolvent declad stainless-steel-clad  $UO_2$ - $ThO_2$  fuels in tests with nonirradiated fuel. Maximum uranium and thorium losses were 0.4 and 0.04%, respectively, in a 2-hr decladding treatment. Chloride holdup by the oxide pellets was sufficiently low after water washing to produce uranium-thorium feed solutions containing <300 ppm chloride.

Corrosion tests on titanium as a material of construction for the standard Darex process were completed. The maximum rate under normal operating conditions was <1 mil/month, and was usually ~0.1 mil/month. Scouting tests on the use of titanium as a container for 13 M  $HNO_3$ -0.04 M NaF-0.1 M  $Al(NO_3)_3$  used in  $ThO_2$ - $UO_2$  dissolution indicated a vapor-phase corrosion rate of 0.8 mil/month; substitution of  $H_3BO_3$  for  $Al(NO_3)_3$  decreased this rate to 0.33 mil/month. Solutions containing 3 M  $HNO_3$ -60 g of stainless steel per liter and <800 ppm chloride did not corrode types 304L or 347 stainless steel at room temperature after two years of exposure, but produced severe

intergranular attack at boiling temperatures. Darex dissolver solution severely attacked type 304L stainless steel at 125°F.

In Sulfex process studies the passivation of stainless steel that occurs when stainless-steel-clad  $UO_2$  (Yankee Atomic type fuel) was declad with 6 M  $H_2SO_4$  was found to be caused exclusively by nitric acid carried over from prior  $UO_2$  core dissolutions. Passivation was produced by as little as  $10^{-4}$  M  $HNO_3$  in 6 M  $H_2SO_4$ . Addition of formic acid to destroy the nitric acid resulted in rapid initiation of the sulfuric acid-stainless steel reaction. Decladding was achieved in 1.75 to 2 hr. Uranium losses observed in decladding of stainless-steel-clad  $UO_2$  fuels increase with the degree of fuel pellet fragmentation and exposure time to the sulfuric acid. The rate of dissolution of  $UO_2$  in  $H_2SO_4$  varied from 0.04 to 0.8% per hour under various processing conditions. Uranium and plutonium losses in a 2-hr decladding of a Yankee Atomic fuel pin irradiated to 1440 Mwd/t were 0.045 and 0.052%, respectively. Irradiated  $UO_2$  dissolved much more rapidly in nitric acid than did unirradiated  $UO_2$ .

In the decladding of Consolidated Edison (stainless-steel-clad  $ThO_2$ -4%  $UO_2$ ) fuel with 6 M  $H_2SO_4$ , uranium losses were highly dependent on the amount of  $U_3O_8$  in the  $UO_2$ ; losses from air-fired (predominantly  $U_3O_8$ ) and hydrogen-fired  $UO_2$  varied by factors of 10 to 30. With 200% excess sulfuric acid the uranium losses for 6 hr decladding of unirradiated  $ThO_2$ - $U_3O_8$  Consolidated Edison fuel pins were 0.1 to 0.2% vs <0.02% for  $ThO_2$ - $UO_2$  pellets. Radiation-induced losses of uranium in Sulfex decladding solutions were inversely dependent on temperature. The maximum uranium and thorium losses during a 3-hr exposure of finely pulverized  $ThO_2$ - $UO_2$  irradiated to 5600 Mwd/t and decayed for four years were 3 and 0.3%, respectively. The dissolution rate of  $ThO_2$  in 6 M  $H_2SO_4$  decreased with exposure time since a relatively insoluble layer of  $Th(SO_4)_2$  formed on the pellets. This coating also decreased pellet dissolution rates in 13 M  $HNO_3$ -0.04 M NaF-0.1 M  $Al(NO_3)_3$ , and the presence of 0.1 M  $H_2SO_4$  in this dissolvent decreased the dissolution rate by a factor of 8. Treatment of Consolidated Edison fuel solution with silica gel gave a zirconium-niobium decontamination factor of 5 to 37.

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Ni-O-Nel was found to be the best material of construction for the Sulfex process. Corrosion rates under process conditions were ~1 mil/month.

In the Zircex process, zirconium-clad uranium-zirconium and uranium-zirconium-niobium fuels are hydrochlorinated at ~500°C to produce volatile  $ZrCl_4$  and nonvolatile  $UCl_3$ , thereby effecting a uranium-zirconium separation. For high zirconium-uranium (STR) fuels, a  $ZrO_2$ - $UO_2$  solid solution was formed which resulted in ~1.5% insoluble uranium loss during  $HNO_3$  leaching of the  $UCl_3$ . When the residue was contacted with gaseous  $CCl_4$ - $N_2$ , at 600°C,  $UCl_4$  and  $ZrCl_4$  were formed, which, when desublimed, were totally soluble in  $HNO_3$ . The resulting STR fuel solution contained 10 moles of zirconium per mole of uranium but only 2% of the zirconium originally present in the fuel.

In studies on the Zirflex process for Zircaloy-clad  $UO_2$  fuels uranium losses to the 6 M  $NH_4F$ -1 M  $NH_4NO_3$  decladding reagent were <0.2% from PWR pins irradiated to 1100 Mwd/t. The maximum corrosion rate of Ni-O-Nel in 6 M  $NH_4F$ -1 M  $NH_4NO_3$  was 12 mils/month. Addition of 0.05 M  $B_4O_7^{--}$  or 0.05 M  $SiO_3^{--}$  halved the above rate. The corrosion rates of Haynes 21 alloy and type 309Cb stainless steel in  $NH_4F$ - $NH_4NO_3$  were 2.3 and 8.5 mils/month, respectively.

Several flowsheets were developed to permit extension of the Zirflex process to reprocessing of zirconium-clad STR (1% U-Zr) and EBWR (93.5% U-5% Zr-1.5% Nb) fuels. In the first flowsheet the fuels are dissolved in 6 M  $NH_4F$ -1 M  $NH_4NO_3$  to produce a solution of  $ZrF_4$  and a precipitate of ammonium uranous fluoride. A solution of 2.7 M  $HNO_3$ -1.8 M  $Al(NO_3)_3$  (and 0.034 M  $CrO_4^{--}$  for STR fuel) is added to the dissolver solution to solubilize the uranium. The fuel solution is centrifuged to remove  $Nb_2O_5$  (EBWR core only) and then sent to solvent extraction. In a second flowsheet, developed to decrease the volume of solvent extraction feed, fuel solution obtained in the  $NH_4F$ - $NH_4NO_3$  dissolution is metathesized with  $NH_4OH$  to produce uranium, zirconium, and niobium hydrous oxides. These are filtered from the residual solution and redissolved in nitric acid, while the filtrate is recycled as dissolvent for additional fuel. A third flowsheet variation for EBWR fuel, which uses minimum fluoride, involves dissolution of the Zircaloy-2 cladding in 6 M  $HNO_3$  followed by addition of 8 M  $HNO_3$ -0.8 M  $Al(NO_3)_3$  to dissolve the uranium-zirconium-niobium alloy core in the same solution.

The Perfex process dissolvent,  $HF$ - $H_2O_2$ , readily dissolved 7% uranium-93% zirconium fuel samples. Neither Monel nor INOR-8 showed adequate corrosion resistance to  $HF$ - $H_2O_2$  for use as process containers.

Process flowsheet development for  $UC_2$ -graphite and  $ThC_2$ - $UC_2$ -graphite fuel compacts indicated that the uranium can be recovered quantitatively (99.8%) from the former by grinding the compact to 200 mesh and leaching with boiling 15.8 M  $HNO_3$ . Grinding and leaching of the latter fuel in 13 M  $HNO_3$ -0.04 M  $NaF$ -0.1 M  $Al(NO_3)_3$  resulted consistently in ~10% uranium and thorium insoluble losses; however, burning in air or oxygen permitted recovery of >99.9% of both uranium and thorium when the ash was dissolved in the latter dissolvent.

Foreign research reactor fuel (84% Al-15% U-1% Si) solutions in 7.5 M  $HNO_3$ -0.005 M  $Hg(NO_3)_2$  contain large amounts of highly hydrated silica; a satisfactory procedure for preparing the solution for filtration was to add 100 mg of gelatin per liter of feed and to digest at 85°C for 1 hr. The solution was then filtered on 30-mesh Ottawa sand, with Celite 545 used as the filter aid.

A modified three-step dissolution flowsheet was developed for the BORAX IV fuel ( $U_3O_8$ - $ThO_2$  clad with Al-1% Ni) in order to cope with the lead used as a bonding agent. The aluminum is dissolved in 2 M  $NaOH$ -1.8 M  $NaNO_3$ , the lead (and nickel) in 1.5 M  $HNO_3$ , and the  $U_3O_8$ - $ThO_2$  in 13 M  $HNO_3$ -0.04 M  $NaF$ -0.1 M  $Al(NO_3)_3$ . The use of neither 8 M  $HNO_3$ -0.005 M  $Hg(NO_3)_2$  to dissolve Al, Ni, and Pb nor 13 M  $HNO_3$ -0.04 M  $NaF$ -0.1 M  $Al(NO_3)_3$  to dissolve lead and  $U_3O_8$ - $ThO_2$  was satisfactory.

In tests on mechanical processing methods, abrasion-disk sawing of end boxes was done at rates up to 60 in./min although 25 to 30 in./min was optimum. At this rate about 7 g of metal is produced per gram of abrasive consumed. Only friction sawing appeared to be adequate for simultaneously sawing metal and oxide. Removal of ferrules from fuel bundles was studied; Microbraz 50 joints, which are quite brittle, can readily be broken by slabbing, but the more ductile Coast Metal braze material is more difficult to rupture.

Mechanical processing methods were developed for single-tube metal-clad Na-K-bonded alloy fuels and for multitube metal-clad oxide fuels. A device was designed, fabricated, and satisfactorily tested on unirradiated Na-K-bonded fuel tubes for discharging the alloy fuel slugs from the stainless

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steel cladding by hydraulic means. This device is being installed in cell A of Building 3026 and will be used to de-clad the Core 1 fuel from the SRE. This technique is also applicable to the fuel from the Consumer's Public Power District reactor and to the Power Reactor Development Corporation blanket.

Tests at ORNL and under subcontract to Birdsboro Steel Foundry and Machine Company and to Clearing Machine Corporation of U.S. Industries, Inc., demonstrated the feasibility of shearing stainless-steel-clad  $UO_2$  fuel bundles assembled with ferrules without prior disassembly of the bundles. Shearing of 0.4-in.-dia tubes to lengths of 0.5 in. or less was satisfactory, and tube closures were consistently <50%. The sheared pieces were leached in 8 to 10 M  $HNO_3$  at satisfactory rates (70 to 200  $mg \cdot cm^{-2} \cdot min^{-1}$ ). A 250-ton shear, a batch dissolver, and two types of continuous leachers are now being fabricated.

In Hermex process studies the solubility of uranium in mercury increased from 0.0067 to 1.18 wt % as the temperature was increased from 40 to 356°C. The calculated heat of solution for uranium in mercury was  $6.6 \pm 0.1$  kcal/mole. Thorium solubility increased from 0.0021 to 0.0295 wt % with a temperature increase from 40 to 356°C. A heat of solution of about 3 kcal/mole of thorium was calculated.

Satisfactory solvent extraction flowsheets were developed for Yankee Atomic-Darex, APPR-Darex, and foreign research reactor fuel solutions. The first uses a modified 30% TBP Purex flowsheet, and the other two use unmodified TBP-25 flowsheets. Preliminary tests indicated that  $Fe^{+++}$  salting is equivalent to  $Al^{+++}$  salting and that an aluminum-free waste can be produced in APPR-Darex-2.5% TBP solvent extraction processing and a waste containing >0.1 M Al in Consolidated Edison Thorex or Interim-23 processing.

Several Consolidated Edison (stainless-steel-clad  $UO_2$ - $ThO_2$ ) flowsheets were developed for both stainless-steel-free and stainless-steel-containing fuel solutions, using both the Thorex process (42.5% TBP), which permits recovery of uranium and thorium, and the Interim-23 (2.5 to 6% TBP) process for recovery of uranium only.

In a 0.1 M acid deficient 2.5% TBP Interim-23 flowsheet demonstration using a 1 M Th, 15 g of uranium per liter, 0.8 M  $Al^{+++}$  feed, the first-cycle decontamination factor was  $3.5 \times 10^5$  and that for the second cycle  $7.6 \times 10^4$ . In tests with >5%

TBP in Amsco an Interim-23 flowsheet containing only 0.1 M  $Al^{+++}$  (required in dissolution) appeared feasible.

Although nitric acid alone cannot be used for salting in a Thorex flowsheet using 42.5% TBP in Amsco, substitution of 42.5% TBP in Decalin gave flowsheet conditions where nitric acid salting was possible without formation of a second organic phase.

A new protactinium removal flowsheet using diisobutyl carbinol was demonstrated. About 99.5% removal of protactinium was achieved; decontamination factors for uranium, thorium, zirconium-niobium, ruthenium, and rare earths were  $10^2$  to  $10^3$ .

A new solvent recovery system using successive KOH, lime, and nitric acid washing was demonstrated.

In a program using both unirradiated and activity-spiked Darex and Niflex feeds, a considerable number of packed column-Redox runs were made. Data on decontamination factors, uranium losses, and column flooding and HETS values for a number of feed compositions and column operating characteristics are reported.

## 2. Power Reactor Fuel Reprocessing Pilot Plant

Operations of the former Metal Recovery and Thorex pilot plants were combined by the installation of interconnecting pipe lines. This combined facility is the Power Reactor Fuel Reprocessing Pilot Plant. Generally, feed preparation and first-cycle solvent extraction are performed in the Thorex plant, and second and third cycles of solvent extraction in the Metal Recovery Plant. This change permits processing of highly irradiated fuels at ORNL which could not be done if the plants were operated independently, owing to the individual limitations in each plant. Each plant can be operated independently on special programs if desired.

Among the materials processed were irradiated Th for  $U^{233}$  recovery, irradiated U and Pu-Al alloy for U and Pu recovery, Paducah fluorinator ash for U and Np recovery, and weapons debris for U and Pu recovery.

One Thorex process development run was completed in which the effect of bisulfite addition to the feed on ruthenium decontamination was demonstrated; this addition resulted in increases in ruthenium decontamination by a factor of 100.

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Approximately 900 g of uranium assaying 99.6%  $U^{233}$  was recovered from an isolated fraction of  $Pa^{233}$ . This uranium product, containing principally  $U^{234}$  as an isotopic contaminant, was further purified by the Isotopes Division by electromagnetic separation, producing 12.4 g of  $U^{233}$  containing <2 ppm  $U^{234}$  and a total isotopic contamination <5 ppm.

An additional 216 g of  $Np^{237}$  was recovered from Paducah fluorinator ash and converted to oxide for irradiation. Two additional demonstrations of the chemical flowsheet for the separation of neptunium from thorium were made, confirming the previously reported separation factor of about 200. The interim production program of recovering neptunium from fluorinator ash at ORNL was terminated with installation of a production plant at the Paducah site.

### 3. Fused Salt-Fluoride Volatility Process

Seventy-two kilograms of fully enriched uranium was recovered from fluoride used in critical experiments with a loss of about 0.01%. In runs spiked to study decontamination from fission product and plutonium decontamination, the gross gamma activity of the feed salt was  $9 \times 10^4$  counts/min per mg of U, but the  $UF_6$  product contained no detectable fission products and no activity other than that attributable to the uranium itself. Plutonium decontamination was satisfactory.

Pilot plant modifications and the associated process development required to process zirconium-uranium fuel elements are in progress. The dissolution capacity will be three S1W-1 or S2W-1 17-plate subassemblies per batch.

### 4. Molten-Salt Reactor Fuel Processing

Development of molten-salt reactor fuel processing methods has shown that a volatility procedure coupled with anhydrous HF solution leads to adequate recovery of uranium and  $Li^7F$ .

### 5. Homogeneous Reactor Fuel Processing

Development of hydroclone systems for separating insoluble fission and corrosion products from the aqueous uranyl sulfate fuel of the Homogeneous Reactor Test continued. In 2700 hr of operation with a single hydroclone, only 10% of the 22 kg of corrosion products formed in the reactor were collected. Competing mechanisms, mainly deposition on pipe walls, hold circulating solids

concentration at extremely low levels. Tests are in progress with a multiple hydroclone system containing 13 hydroclones in parallel to determine if higher processing rates can increase solids collection rates sufficiently to make this processing concept feasible. Periodic chemical dissolution of accumulated solids appears as the most attractive alternative processing method, and development work toward finding suitable reagents and operating conditions is in progress.

Fission product behavior predicted from laboratory studies was, in general, confirmed in reactor operations. Solubility of the important rare-earth poison group was somewhat lower than that measured in out-of-pile light-water tests. Iodine behavior is still not completely understood. The role of the tellurium precursor and an apparent equilibrium adsorption on corrosion products are factors which must be resolved. Performance of the charcoal fission gas adsorber beds was satisfactory, and additional basic data were obtained to permit design of beds for full-scale reactors.

Decontamination of samples of HRT fuel solution by  $UO_4$  precipitation was demonstrated. Electrolytic removal of nickel and manganese from  $UO_2SO_4-H_2SO_4$  solutions by use of a mercury cathode was shown to be a possible method for controlling nickel concentration in  $UO_2SO_4$ -solution-fueled reactors.

Studies of  $UO_2SO_4-H_2SO_4$  solutions at elevated temperatures showed that high nickel concentrations ( $>0.005 M$ ) or low  $H_2SO_4$  concentrations ( $<0.005 M$ ) can lead to solids formation at temperatures in the range 250 to 350°C. Boiling of such solutions in contact with hot metal surfaces even while the solution temperature is less than 320°C can produce solids at the metal-liquid interface.

### 6. Waste Treatment and Disposal

Evaporation and calcination are being studied as a means of converting high-level chemical reprocessing wastes to a solid state for permanent disposal. Synthetic waste solutions of the type expected from reprocessing of power reactor fuels were studied from the standpoint of the volumes and compositions of the off-gases and the physical and thermal properties of the solid residues obtained on evaporation and calcination. Calcination of high-level neutralized and acidic wastes resulted in less than 0.01% of the activity reporting to the off-gas. Pot calcination experiments with synthetic

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Darex, Purex, and TBP-25 waste solutions in an 8-in.-dia by 18-in.-deep pot at feed rates of up to 9 liters/min gave volume reductions to one-twelfth the volume of the feed.

The maximum temperature rise in radioactive solid cylinders, separated from an infinite solid medium by a 1-in. air space, was calculated over a range of cavity radii of 5 to 30 in. with heat generation rates of up to 2000 Btu·hr<sup>-1</sup>·ft<sup>-3</sup>. The thermal conductivity of the radioactive cylinders was varied from 0.1 to 1.0 Btu·hr<sup>-1</sup>·ft<sup>-1</sup>·(°F)<sup>-1</sup>. A maximum temperature rise of 1000°F would be produced with an initial heat generation rate of 1300 to 1600 Btu·hr<sup>-1</sup>·ft<sup>-3</sup> for the 5-in.-radius case, 350 to 450 Btu·hr<sup>-1</sup>·ft<sup>-3</sup> for the 10-in.-radius case, and 175 to 210 Btu·hr<sup>-1</sup>·ft<sup>-3</sup> for the 15-in.-radius case, with the thermal conductivity of the radioactive cylinder assumed to be 0.1 Btu·hr<sup>-1</sup>·ft<sup>-1</sup>·(°F)<sup>-1</sup>.

### 7. Fuel Cycle Developments

Preliminary criteria for evaluating fuel materials were established.

Two methods were developed for estimating the surface area and sinterability of ceramic-grade UO<sub>2</sub>, one based on acid titration of the hydroxyl ion adsorbed on the UO<sub>2</sub> particle surfaces and the other based on adsorption of methylene blue. With both methods correlations were good.

## PART II. RAW MATERIALS EXTRACTION

### 8. Amex Process

Several new amines were shown to be suitable extractants for uranium recovery from sulfuric acid liquors. A new quaternary ammonium compound also showed promise for extracting uranium from sodium carbonate liquors.

Two new uranium stripping methods, one using nitrate salt solution and the other ammonium sulfate solution, were tested. The concentrated uranyl nitrate solution product of the first method is more desirable as feed to subsequent purification operations than are the usual solid concentrates. The second method has extremely low reagent requirements and produces a sodium-free product which is a desirable feed for refineries using the reduction-hydrofluorination-fluorination flowsheet.

Study of the effect of silica on amine sulfate-aqueous sulfate phase separation suggested that aqueous-continuous emulsions are stabilized by

hydrogen bonding of silicic acid networks in the aqueous phase to amine sulfates at the surface of the organic droplets.

Engineering studies to provide scale-up data for design of both the extraction and stripping cycles in Amex mixer-settler plants were completed. The Amex process was installed in five American mills, in one Canadian mill, and in one Australian mill.

Processes were also developed for thorium recovery from monazite and from Canadian uranium-thorium ores. Two Canadian mills successfully piloted the Amex thorium process. In demonstrations of an economical two-cycle process for recovering both thorium and uranium from monazite liquors, >99.9% of the thorium was recovered. Uranium was 99.5% recovered.

### 9. Dapex Process

An ammonium carbonate stripping method was devised which shows advantage over the usual sodium carbonate method in providing a sodium-free product at lower reagent costs. A Dapex flowsheet in which ammonium carbonate stripping is used was successfully applied to uranium recovery from sulfuric acid leach slurry (20 wt % solids) of reduction-bomb liner slag. Reagent costs were considerably below those for the present ion exchange process.

Engineering studies on scale-up design of mixer-settler plants were completed. The Dapex process for uranium recovery has been installed in five mills in the United States; two of these have installed the process for vanadium recovery.

## PART III. FEED MATERIALS PROCESSING

### 10. Fluorox Process

The development program of the Fluorox process was terminated at the end of FY 1959. A continuous fluidized-bed reactor was developed in which the primary reaction,  $2UF_4 + O_2 \longrightarrow UF_6 \uparrow + UO_2F_2$ , was carried out at 700 to 850°C in a bed of UO<sub>2</sub>F<sub>2</sub>.

In the final runs with pure UF<sub>4</sub> and air or O<sub>2</sub> feed, more than 90% of the theoretical yield of UF<sub>6</sub> was collected in cold traps, the only significant product impurity being HF. The rate of corrosion of the Inconel reactor was low, 0.1 to 0.7 in./year. In tests with crude UF<sub>4</sub> from ore concentrates, UF<sub>6</sub> was produced and collected at 700 to 725°C, but Inconel corrosion rates were prohibitively high. In laboratory experiments the feasibility of the

hydrogen reduction of  $UO_2F_2$  to  $UO_2$  for recycle to hydrofluorination and oxidation was established, and kinetics data were collected with a thermobalance.

### 11. Production of Uranium Metal by Reduction with Alkali Metals

Uranium metal was produced by direct reduction of  $UF_6$  with lithium amalgam at  $25^\circ C$  with a metal yield of more than 80%. Total impurities due to processing were 417 ppm. In preliminary experiments  $UO_2$  was 100% reduced to metal with magnesium amalgam.

In experimental studies of the chemistry of the one-step Druhm process  $UF_6$  was completely reduced to uranium metal with an excess of sodium. The initiation temperature for the reaction is in the range 140 to  $200^\circ C$ . The adiabatic flame temperature was calculated to be  $1980^\circ K$ . As yet, a satisfactory reactor liner has not been found and efforts to develop an operable  $UF_6$  inlet nozzle have been only partially successful.

## PART IV. GENERAL RESEARCH

### 12. Equipment Decontamination Studies

Equipment decontamination research was reactivated as a formal project. Chromous sulfate was used to descale a pump from the HRT chemical plant, and several other descalers with low corrosion rates were demonstrated on HRT specimens. Trivalent uranium at very low acidity looks promising as a descaler. In general decontamination work, the proprietary Turco 4501 process was found superior to most of the older processes, and was successfully used to decontaminate Thorex pilot plant equipment. Successful procedures for decontaminating equipment used in the Fused Salt-Fluoride Volatility process were developed.

### 13. Thorium Oxide Slurry Development

In oxide preparation development studies, digestion of thorium oxalate precipitates virtually eliminated caking in oxide produced by their thermal decomposition. The addition of certain bi- and polydentate organic compounds, principally amines, to the oxalate precipitation system caused freshly precipitated thorium oxalate to grow on digestion into square-faced, more or less cubic particles, 1 to  $20 \mu$  on an edge, whose characteristics were essentially retained in the oxide product. Thoria spheres were produced by jetting

a thoria sol through an orifice along with an aqueous isopropyl alcohol solution, causing the sol to set into beads.

Two methods were developed for adding uranium to the thorium oxide in the production of engineering quantities of mixed oxide of controlled particle size for fuel slurry studies: coprecipitation of the thorium-uranous oxalates with subsequent decomposition, and precipitation of the uranium onto a  $650^\circ C$ -fired thorium oxide from ammonium uranyl carbonate solution with subsequent firing to incorporate the uranium in the solid. A 4-hr firing at  $1000^\circ C$  incorporated the bulk of the uranium in the solid from the second preparation method and gave a fairly homogeneous distribution of uranium in the solid.

Spherical thorium-aluminum-uranium oxide particles with a U/Th ratio of 0.08 and alumina contents of 2.5, 5, and 10 wt % were produced by flame denitration of methyl alcohol solutions of the nitrates. Fluidized-bed denitration of thorium nitrate solutions produced porous agglomerates of small thorium oxide particles instead of dense, spherical particles.

In the thorium oxide slurry development studies, hydroclones were successfully used on aqueous thoria slurries for separation of 0.5- to  $5\text{-}\mu$   $ThO_2$  particles, for batch collection of slurry from a circulating system into an induced underflow receiver, and for slurry transfer to effect concentration control. A rolling-ball viscometer of 6-ml volume was constructed and successfully used to determine the coefficient of rigidity and yield stresses of thorium oxide slurries. Adsorption-desorption studies of boric acid in slurries of  $1100^\circ C$ -fired thorium oxide indicated that the addition of boric acid to such a slurry might be a means of criticality control during startup. Studies on the effect of electrolyte concentration on leaching of uranium from fired mixed thorium-uranium oxide preparations by aqueous solutions at reactor temperature showed negligible uranium dissolution in pure water, but appreciable quantities were solubilized by a few hundred ppm of chromate.

In out-of-pile studies to develop a catalyst for the internal recombination of radiolytic deuterium and oxygen in a reactor slurry, pumping studies at  $280^\circ C$  were carried out with slurries of  $650^\circ C$ -fired  $ThO_2$ -5%  $UO_3 \cdot H_2O$  containing palladium and of  $1600^\circ C$ -fired  $ThO_2$  containing  $MoO_3$ . Samples of the slurry containing palladium pumped under a

reducing atmosphere in the temperature region 150 to 200°C showed high but temporary activities which appeared to be associated with reduced uranium species. Catalytic activities of the slurry samples at 280°C were not significantly affected by pumping under a reducing atmosphere but were lowered somewhat by pumping under an oxidizing atmosphere. Pumping the slurry containing the MoO<sub>3</sub> under an O<sub>2</sub> atmosphere impaired its catalytic activity, but subsequent pumping in a reducing atmosphere reactivated the catalyst.

Radiolytic gas production and recombination rates were measured in the ORNL Graphite Reactor with heavy-water slurries of ThO<sub>2</sub> containing 2.8% highly enriched uranium. Less than one molecule of D<sub>2</sub> was produced per 100 ev of energy absorbed under both oxygen and deuterium atmospheres. In 11 slurry irradiations carried out in Hole C-44 of the LITR at a thermal-neutron flux of  $2.7 \times 10^{13}$  neutrons·cm<sup>-2</sup>·sec<sup>-1</sup>, three methods of cooling in-pile autoclaves with water were investigated: varying the composition of a helium-air mixture in an annulus between the autoclave and a boiling water bath, injecting water into an air stream passing over the autoclave, and pumping water at high pressures through a capillary wound around the autoclave.

#### 14. Surface Chemistry

Studies on surface chemistry indicated that the technique of observing flow through a porous-plug electrolytic cell is the most feasible method for use with aqueous systems at high temperatures.

#### 15. Neptunium Recovery Process Development

Process methods were developed and used for final purification of the Np<sup>237</sup> product from processing of Paducah Feed Plant fluorination ash. A total of 663 g of Np<sup>237</sup> contaminated with 200 g of Th<sup>230</sup>, 700 g of uranium, 80 g of aluminum, and 150 g of corrosion products (iron, chromium, nickel) was processed, giving a final product of 660 g of Np<sup>237</sup> containing less than 0.5% impurities. The purification method was based on the solubility of hexavalent neptunium fluoride and the insolubility of tetravalent neptunium fluoride. Thorium and chromium were removed by fluoride precipitation while the neptunium was held in the hexavalent state. Treating the filtrate with SO<sub>2</sub> gas reduced the neptunium and precipitated NpF<sub>4</sub>, leaving aluminum, uranium, iron, and nickel in solution.

#### 16. Transuranic Studies

The first cycle of a proposed recovery process for plutonium, americium, curium, and rare earth fission products consists in: extraction of these elements from neutral aluminum nitrate feed into 40% TBP; selective stripping of americium, curium, and rare earths with nitric acid containing an oxidizing agent; and stripping of plutonium with dilute nitric acid containing a reducing agent. Batch countercurrent extractions with tracers indicate that satisfactory plutonium, americium, and curium recoveries can be obtained. Solvent extraction of rare earths into 0.5 M mono-2-ethylhexylphosphoric acid from 10.5 M LiCl-1.5 M HCl is a promising method for removing rare earth fission products from the less extractable americium and curium. In batch countercurrent extractions using macro rare earths and tracer americium, the aqueous raffinate contained 99.96% of the americium, 0.1% of the neodymium, 2.2% of the cerium, and 12% of the lanthanum.

#### 17. Uses of Depleted Uranium

Information was collected and a program organized to develop and promote nonnuclear uses for uranium depleted in U<sup>235</sup>. Nonreactor uses are insignificant, and possible nuclear use in fast breeders would use only a small fraction of the depleted uranium which will be produced in the next 40 years. A summarizing report is being prepared which will include the status of related programs at other sites.

#### 18. Solvent Extraction Technology

Selected neutral organophosphorus reagents, particularly the dialkyl phenylphosphonates, showed potential advantage over TBP as process extractants with respect to one or more of the following: ability to extract uranium (or uranium with plutonium and/or thorium) more selectively from fission products; ability to achieve this extraction from aqueous phases containing lower nitric acid and/or salting reagent concentrations; greater stability to hydrolysis and radiation; better separation of uranium from thorium.

Chemical flowsheets were proposed for recovery of uranium and plutonium from sulfuric acid solutions used for the removal of stainless steel cladding. The uranium and plutonium are extracted with a primary amine or a dialkylphosphoric acid.

Chemical flowsheets were proposed for recovery and separation of plutonium and neptunium from

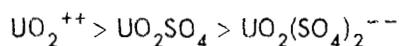
irradiated neptunium by extraction with a tertiary amine from acidic aluminum nitrate solution.

Study was concluded of the separation of natural rare earths, requiring an extraction system of high throughput capacity.

A chemical flowsheet was proposed for isolation of promethium from a fission-product rare earth concentrate by distribution between 12 N nitric acid and undiluted TBP.

The dialkylphosphoric acid extraction of iron(III) perchlorate appeared consistent at low iron loading with a formation of a chelate complex with singly ionized dialkylphosphoric acid dimers,  $Fe(X_2H)_3$ , in conformity with other II-, III-, and IV-valent cations studied. At higher loadings polynuclear complexes formed, involving  $OH^-$  and  $ClO_4^-$  in addition to the dialkylphosphate anion.

Metastable equilibria were demonstrated in the extraction of uranyl sulfate by amine sulfates, which may resolve anomalies noted in the dependence of extraction coefficient on reagent concentration and be significant in other extraction systems. Equilibration through a quiescent interface between slowly stirred phases showed power dependences of extraction coefficient on reagent concentration closer to theoretical than did equilibration by the usual violent shaking. Both sets of equilibria were reproducible in successive equilibrations alternating between the two methods of contact. Measurement of the kinetics of acid and uranium extraction by amines suggested rate control by diffusion through stationary layers at a quiescent interface and indicated that



in transferring uranium to the organic phase. The inability of aggregate formation to account for the anomalies was emphasized by light-scattering measurements that showed even lower degrees of aggregation in an aliphatic diluent than in benzene.

The practical activity coefficient for di(2-ethylhexyl)phosphoric acid dimer in *n*-octane was evaluated as  $\log \gamma_{(D2EHPA)_2} = -0.6432m_{(D2EHPA)_2}^{1/3}$ ,  $0.04 < m < 0.12$ . On this basis, isopiestic data gave estimates of the practical activity coefficients of tri-*n*-octylphosphine oxide and of triphenylmethane in *n*-octane as

$$\log \gamma_{TOPO} = -1.886m_{TOPO} + 0.245m_{TOPO}^2$$

and

$$\log \gamma_{TPM} = -0.737m_{TPM}$$

Studies on radiation decomposition of solvents showed the number of molecules of acid produced from tributyl phosphate per 100 ev of energy absorbed to be a linear function of the TBP concentration in Amsco. At a 400 whr/liter irradiation level the yield of unsaturated hydrocarbon in TBP-Amsco decreased linearly with increasing TBP concentration. Both di-*n*- and di-*sec*-butyl phenylphosphonate were more resistant to radiation damage than TBP.

Emulsion difficulties in solvent extraction systems in the presence of silicic acid were prevented by controlling the mixing to form solvent-continuous dispersions. The utility of solvent-continuous mixing has been demonstrated in uranium mills where feed liquors containing 2 g of silica per liter have been successfully processed. Continued engineering study of phase disengagement included promising preliminary testing of electrical phase coalescence.

## 19. Ion Exchange Technology

Equipment development achievements include operation of continuous ion exchange contactors at higher solution and resin flow rates, up to 3000 and 225 gph/ft<sup>2</sup>, respectively, and at higher solution/resin flow ratios, up to 1000/1, than heretofore demonstrated. Use of water-main pressure to move the resin, instead of using a pump or hydraulic accumulator as in the past, was demonstrated and a small contactor was relocated in an intermediate-level radioactive cell for study of problems of remote operation. Rate and equilibrium studies were made of the sorption of uranium(VI) on strongly basic anion exchangers from dilute sulfate solutions, of uranium(IV) and plutonium(IV) on weakly basic anion exchangers from concentrated sulfate solutions, and of cesium on phenolic cation exchangers from alkaline solutions.

Volumetric distribution coefficients for U(IV) and Pu(IV) on weakly basic polyamine resins in 3 M sulfuric acid were 4.5 and 8.5, respectively. The phenolic resin Duolite S-30 had about the same cesium distribution coefficient in alkaline solutions as the phenolic-methylenesulfonic Duolite C-3 resin but a better cesium-sodium separation

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factor and lower regeneration-acid requirements. Equilibrium loadings of U(IV) on Dowex 21K from 0.025 to 0.6 M sulfate solutions at pH 2 were fitted by Langmuir sorption isotherms, with initial slopes approximately inversely proportional to the sulfate concentration, which extrapolated to a maximum loading of 1 mole of uranium to about 4.8 moles of resin. The loading rates of U(VI) on Dowex 21K from similar dilute sulfate solutions could be correlated by the model of diffusion into a sphere of a single species with a diffusion coefficient of  $1.3 \times 10^{-7}$  cm<sup>2</sup>/sec.

#### 20. In-Line Instrumentation

In-line instruments are being developed for measuring high and low concentrations of uranium, plutonium, acid, gamma activity, liquid-flow rate, and neutron population in process streams.

#### 21. Chemical Engineering Developments

A method of measuring interfacial areas using a liquid scintillator was developed. The specific interfacial area measured in an agitated vessel was shown to be a function of the Weber number. Measurements of surface area made on photographs agreed with the results obtained by the scintillation technique.

The apparent integral diffusivity of uranium from an aqueous uranyl nitrate solution (50 g/liter) into 30% TBP in Amsco was determined to be  $6.7 \times 10^{-5}$  cm<sup>2</sup>/sec.

Sintered nickel tubes with 7- to 10- $\mu$  pores were protected, by transpirational flow of demineralized

water, from corrosion by aqueous ferric chloride. Corrosion rates were one-sixtieth of those without transpiration. A method of measuring concentration at a point on a porous wall, using Ag-AgCl electrodes in KCl solution, was developed. As determined by this method, in a water transpiration experiment with a porous glass frit in slab geometry, a 0.1 M KCl bulk solution showed 3- to 100-fold dilutions at the wall, depending on the bulk-solution mixing rate and transpiration rate.

A nonmechanical pulsing system for solvent-extraction columns, consisting of a boiler and, directly below it, a condenser connected to a column by a suitable transmission line, is being developed. It has been made to operate as a heat engine at pulse frequencies of 60 cpm and amplitudes of 10 in.<sup>3</sup>. The length and size of the transmission line must be tuned with the vapor space in the boiler to yield the desired frequency.

In thermal diffusion studies, CoSO<sub>4</sub> and CuSO<sub>4</sub> in aqueous solution were separated from each other by a factor of 1.05 in a horizontal column.

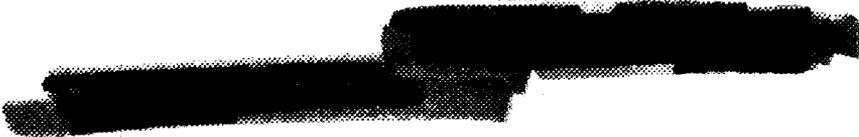
#### 22. Eurochemic Assistance Program

As part of the USAEC program of assistance in construction of a European plant for chemical processing of irradiated fuels, ORNL has assigned a design engineer to the program, has transmitted 500 USAEC-originated documents to Eurochemic, and has distributed 40 of their documents in the United States for information or for review and comment.

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**Part I**  
**POWER REACTOR FUEL PROCESSING**



## 1. HEAD-END AND SOLVENT EXTRACTION PROCESSING

Processes are being developed for uranium, plutonium, and thorium recovery by solvent extraction from reactor fuels containing aluminum, stainless steel, and zirconium. Fuel elements containing stainless steel may be dissolved by the Darex and Sulfex processes; those containing zirconium, by the Zirnex, Zirflex, and Perflex processes. For some fuel elements the jackets may be removed mechanically or the whole element may be chopped and the fertile and fissionable material leached.

### 1.1 PROCESSES FOR STAINLESS-STEEL-CONTAINING FUELS

#### Darex Process

The Darex process, applicable to all stainless steel-uranium (and aluminum-uranium) fuels, involves complete dissolution of the fuel in 5 M  $\text{HNO}_3$ -2 M HCl, quantitative distillation of the chloride from dissolver solution butted to 10 M  $\text{HNO}_3$ , and adjustment of the chloride-free distillation heel to correct metals and  $\text{HNO}_3$  concentrations for solvent extraction. The process is also usable as a decladding method for stainless-steel-clad  $\text{UO}_2$ - $\text{ThO}_2$  fuels. Flowsheet development has been done principally for APPR (stainless-steel-clad  $\text{UO}_2$ -stainless steel cermet), Yankee Atomic (stainless-steel-clad  $\text{UO}_2$ ), and Consolidated Edison (stainless-steel-clad  $\text{UO}_2$ - $\text{ThO}_2$ ) fuels. Small engineering-scale development of a continuous Darex process on unirradiated prototype fuels has been completed; laboratory- and engineering-scale development of a semicontinuous-dissolution batch chloride-distillation Darex process is continuing, and design of a pilot plant facility with a capacity of 5 to 8 kg of fully enriched  $\text{U}^{235}$  or 70 kg of low (<3%) enriched fuel is in progress.

**Continuous Process.** - The continuous Darex process loop, incorporating continuous dissolution, chloride stripping, and feed adjustment, was successfully operated for up to 10 hr with automatic control instrumentation on unirradiated prototype APPR and for longer times with Yankee Atomic fuel (Fig. 1.1). With APPR fuel the dissolution rate was 25 g of  $\text{U}^{235}$  per hour; chloride was removed to 40 ppm. However, the accumulation of silica during feed preparation rendered the equipment inoperable after 10 hr of

operation. The silica was easily removed from the glass and titanium equipment with boiling 10% NaOH. No further work on continuous stripping with APPR feed is planned because of the silica problem. The Darex APPR feed preparation system can be operated on a batch basis without major difficulty from silica deposition.

With Yankee Atomic fuel the rate was 600 g of uranium per hour and the final product contained 10 ppm of chloride; no silica problem developed with Yankee fuel.

**Batch Process.** - The major Darex effort was on the development of a semicontinuous-dissolution batch chloride-distillation and feed-adjustment flowsheet. Sufficient data were accumulated on dissolution, chloride removal, and solids separation to permit start of the design of a pilot plant facility.

Continuous dissolution of up to three unirradiated prototype APPR assemblies was demonstrated in a 6-in.-dia  $\times$  10-ft-high column dissolver. At a dissolvent (5 M  $\text{HNO}_3$ -2 M HCl) feed rate of 4.5 liters/min, the dissolution rate at boiling was maintained at 12 to 18  $\text{mg}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ ; the dissolver product contained 60 to 80 g of metal per liter. The total dissolving time for three elements was approximately 1 hr.

In batch laboratory tests with APPR fuel plates the stainless steel cladding became passivated when the chloride content of the dissolvent fell below 1 M; reaction was usually restarted by increasing the dissolvent HCl concentration to 2 M, and in all cases by addition of small amounts of metallic copper to the reaction mixture. Dissolution of braze-free samples resulted in 0.2% insolubles, which were satisfactorily removed on a 20- to 40-mesh Ottawa sand filter. These insolubles contained about 0.006% of the uranium in the fuel. Braze alloy containing ~13% silicon is insoluble in partially depleted dissolvent (5 M  $\text{H}^+$ -1.7 M  $\text{Cl}^-$ -27 g of stainless steel per liter) but dissolves readily in 5 M  $\text{HNO}_3$ -2 M HCl. The  $\text{SiO}_2$  remains as an insoluble residue with a particle size range of 0.06 to 26  $\mu$ .

In batch chloride removal studies three flowsheets were developed in which either 95% or 61%  $\text{HNO}_3$  was used. The 61%  $\text{HNO}_3$  flowsheets involve boiloff of a waste cut to purge excess water from the system, addition of concentrated

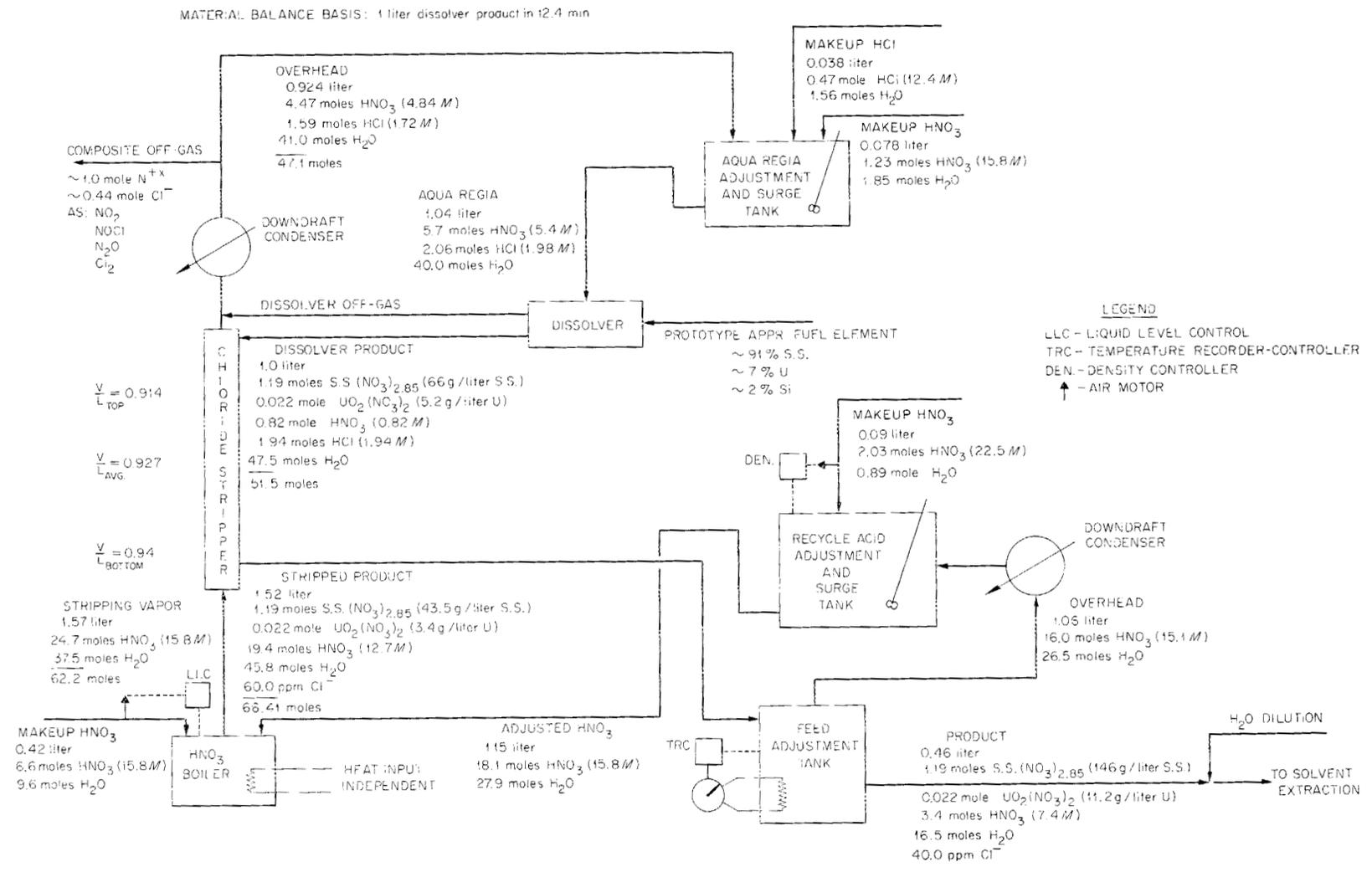


Fig. 1.1. Continuous Darex Process Equipment and Control Flowsheet, Including Material Balance.

HNO<sub>3</sub>, boiloff of a mixed acid cut for re-use after concentration adjustment as fuel dissolvent, and final boiloff of excess HNO<sub>3</sub> prior to addition of water and final feed adjustment for solvent extraction. The flowsheets for 95% HNO<sub>3</sub> are similar except that no excess water is added to the system, and therefore no waste cut is required. However, the use of 95% HNO<sub>3</sub> was abandoned to avoid the handling of a dangerous reagent and to avoid the possibility of a pyrophoric reaction<sup>1</sup>

between titanium and 97 to 100% HNO<sub>3</sub>. The three flowsheets using 61% HNO<sub>3</sub> differ principally in the method of nitric acid addition and recycle (Fig. 1.2, Table 1.1). The reference flowsheet (Fig. 1.3) is a compromise between the recycle and the reflux flowsheets and is superior to both in that it provides maximum chloride removal and involves the lowest maximum metal concentration at any point in the evaporation step. The reflux flowsheet produces the minimum waste cut volume. The reference flowsheet operated equally well with Yankee Atomic and MTR prototype fuels; the chloride in these fuel solutions is 64 and 23 ppm, respectively.

<sup>1</sup>A. Fitch, Jr., *Use of 95% Nitric Acid in Titanium Vessels*, ORNL CF-58-9-63 (Sept. 5, 1958).

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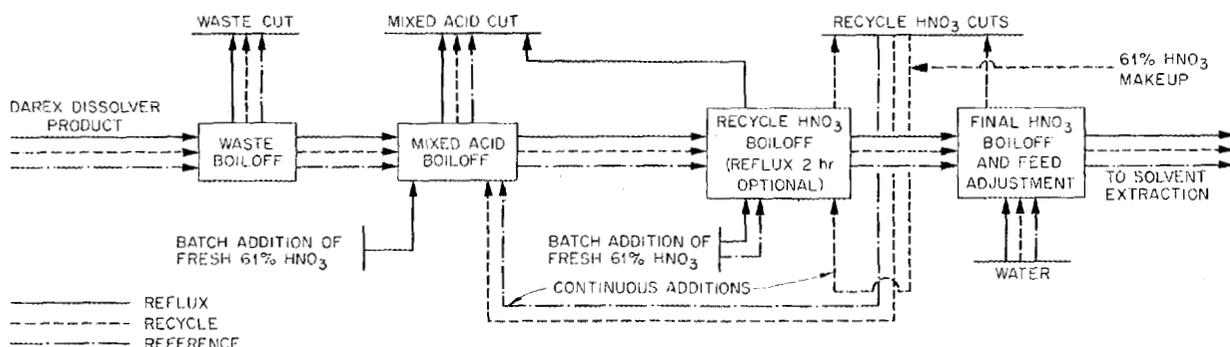


Fig. 1.2. Comparison of HNO<sub>3</sub> Addition Methods for Darex Reflux, Recycle, and Reference Cl<sup>-</sup> Removal Flowsheets.

Table 1.1. Comparison of Three Batch Darex Flowsheets Using 61 wt % HNO<sub>3</sub>

	Reference	Reflux	Recycle
Waste volume, % of aqua regia volume	27	19	32
First HNO <sub>3</sub> addition	Continuous 12 M	Batch 13.3 M	Continuous 13 M
Second HNO <sub>3</sub> addition (13.3 M)	Batch	Batch	Continuous
HNO <sub>3</sub> in acidified concentrate, M	11.1	9.0	9.2
Chloride in acidified concentrate, M	0.1-0.2	0.5-0.9	0.12
Reflux	If needed	Necessary	No provision
Volume of acid returned, % of aqua regia volume	167	90	225
Maximum metals loading, g of APPR fuel per liter	170	290	200
Chloride in solvent extraction feed, ppm	28-51	135-330	220

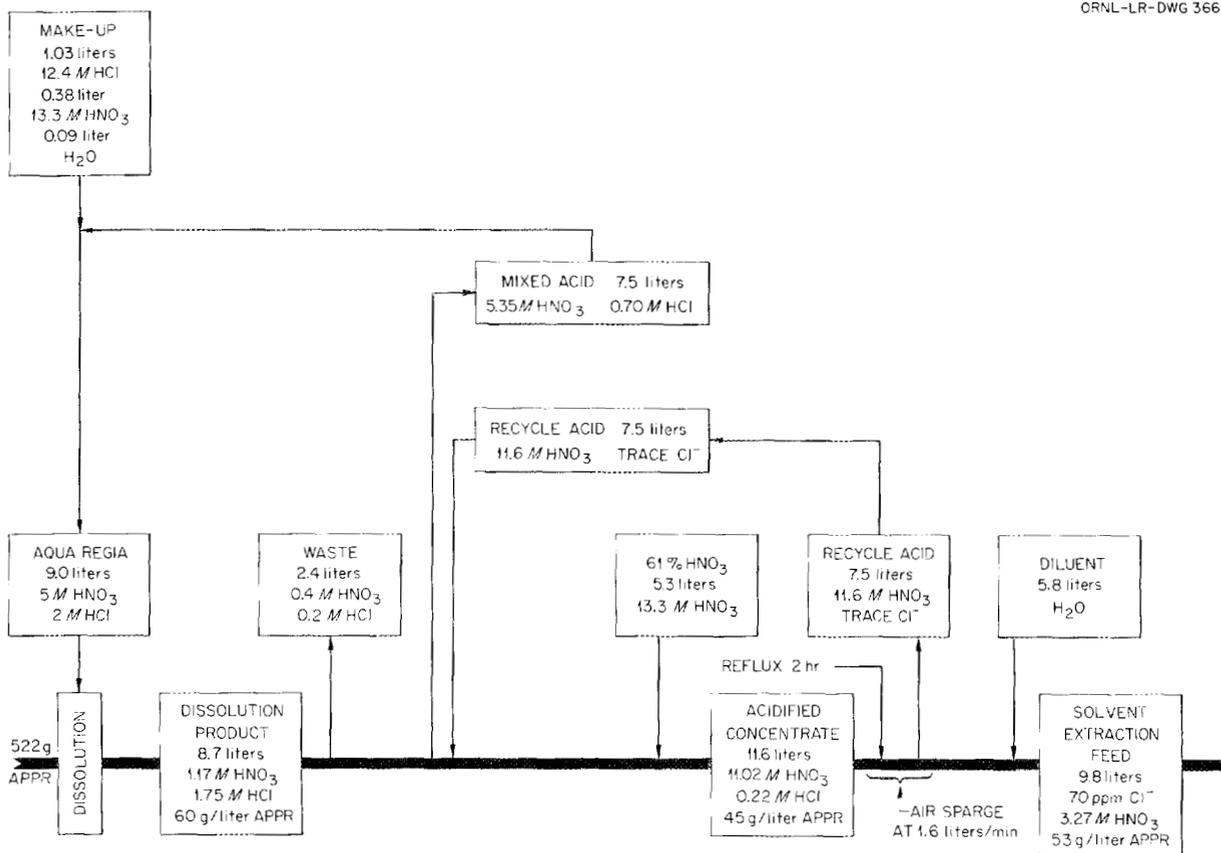


Fig. 1.3. Darex Process Reference Flowsheet for Batchwise Operation with 61 wt % HNO<sub>3</sub> (Run No. APPR-66).

In reference flowsheet development tests, air or nitrogen sparging and refluxing during the final boildown were shown to enhance chloride removal. For equal initial HNO<sub>3</sub> concentrations and refluxing times, air sparging produced a 10- to 75-fold increase in chloride removal; maximum improvement occurred at 12 M HNO<sub>3</sub>.

A titanium convective boiling loop evaporator, simulating the proposed pilot plant unit, was operated to determine heat transfer coefficients. Steam-to-boiling liquid coefficients of 170 to 320 Btu·hr<sup>-1</sup>·ft<sup>-2</sup>·(°F)<sup>-1</sup> were obtained in the range 25 to 64°F for the vaporization of HNO<sub>3</sub>-HCl mixtures. Coefficients for vaporization of water under the same conditions were 350 to 460 Btu·hr<sup>-1</sup>·ft<sup>-2</sup>·(°F)<sup>-1</sup>.

**Low-Temperature Chloride Removal.** - In preliminary equilibrium tests with the hydrochloric acid-nitric acid-nitric oxide-water system, chloride was removed from chloride-nitrate solutions

at 25°C by sparging with nitric oxide. In a typical experiment with a Darex feed solution containing 28 g of stainless steel per liter adjusted to 10 M HNO<sub>3</sub>, the chloride was decreased from an initial concentration of 1.23 M to 171 ppm; the total nitrate was simultaneously decreased from 10 M to 7.5 M. The chloride volatilized, as nitrosyl chloride, was recovered as 3 M HCl by scrubbing the off-gas with water in an 11-plate bubble-cap column.

The mechanism by which chloride removal is enhanced by gaseous nitric oxide involves the reaction of nitric oxide with nitric acid to form the intermediate oxides of nitrogen, which are considerably more effective in producing volatile nitrosyl chloride. The results of equilibration studies (Fig. 1.4) indicate that the volatility of chlorides relative to that of nitrogen oxides increases from 0.068 at 2.5 M HNO<sub>3</sub> to 9.0 at 8.5 M HNO<sub>3</sub>, thereby establishing the need for

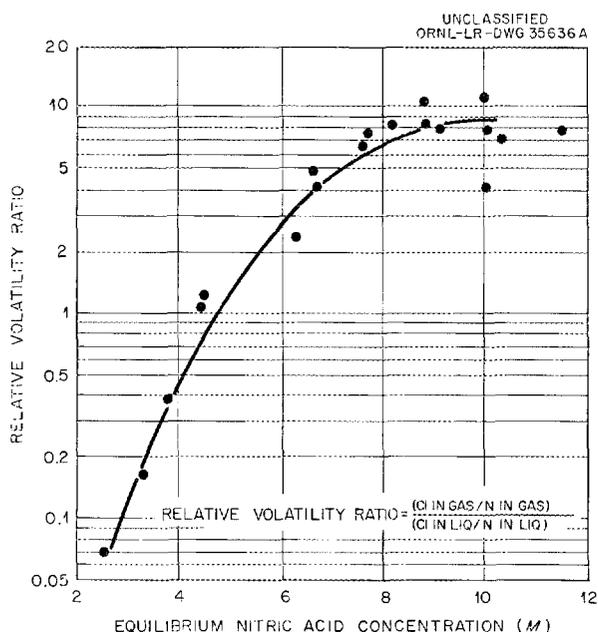


Fig. 1.4. Volatility Ratio of Chloride to Total Labile Nitrogen as a Function of Nitric Acid Concentration. Conditions: 25°C, 740 mm Hg.

fairly high nitric acid concentrations for good chloride removal.

A tentative batch flowsheet for low-temperature chloride removal is shown in Fig. 1.5.

**Feed Solids Separation.** — Laboratory studies are being conducted to determine possible techniques for silica removal from Darex solutions of APPR fuel. Immediately after batch dissolution of high-silica APPR fuel, the  $\text{SiO}_2$  is <50% hydrated and is a fine granular precipitate. During chloride removal the silica becomes highly hydrated and the bulky gelatinous precipitates that form after chloride removal contain about 3 wt %  $\text{SiO}_2$ , plus trace metals, the remainder being water of hydration.

Forty per cent of the  $\text{SiO}_2$  was removed by a medium-frit glass filter immediately after dissolution but before chloride removal, and 60% after 16 to 20 hr of standing. None was removed by a 30-mesh sand bed, even after standing for 24 hr. Addition of 0.4 g of gelatin per liter of dissolver product resulted in removal of 50% of the silica, as a precipitate (which was 23 wt %  $\text{SiO}_2$ ) on a Celite-coated sand filter. Fluoride ions were the most successful coagulant of several

tried; 98% of the  $\text{SiO}_2$  treated with 0.01 M HF was removed, as 3%  $\text{SiO}_2$ , by coated sand beds. With 0.005 M HF 40% was removed immediately as >50%  $\text{SiO}_2$ , and the remainder, after two days with no further treatment, as 9%  $\text{SiO}_2$ . Ammonium molybdate and ammonium tungstate were less effective as coagulants, and Celite, alumina, aluminum nitrate, and silica gel were all ineffective.

A number of methods were tried for removing silica from Darex-APPR feed solutions after chloride removal. Filtration and centrifugation were successful; the use of a hydroclone and gravity settling-decantation were not. Sand bed filtration was tested on the supposition that a sand bed filter could be developed that could be remotely cleaned by flotation or jetting of the bed. Sintered stainless steel filters of 20  $\mu$  mean pore size appeared to be better than sand filters because of equal performance and because considerably more filter area can be obtained with star filters in the same filter equipment volume. With both types of filter, the filtration rate was doubled by increasing the vacuum across the filter from 5 to 20 in. Hg and was doubled again by preheating the feed slurry to 60°C. Ten grams of filter aid per liter of feed slurry was required to achieve the maximum over-all filtration rate. The best over-all rates were achieved by settling the siliceous material, decanting and filtering the supernatant first, and then filtering the settled slurry. The APPR filtrate contained 10 to 30 ppm of soluble  $\text{SiO}_2$ , 43 g of stainless steel, and 5.5 g of uranium per liter. The filter cake, containing 3 to 6%  $\text{SiO}_2$ , occupied 25 to 30 cc (15 to 20 g of solids) per liter of feed slurry. Uranium losses on the cake were decreased to 0.1% with a single water wash one-fifth the volume of the filtrate and to 0.07% with two washes. The sintered stainless steel filters were easily cleaned by immersion in boiling 20 to 30% NaOH. Average filtration rates were 100 liters of feed slurry per hour for both sand bed and porous metal filters.

Sand was removed from sand bed filters by a steam jet, by a water eductor, and by pressurized water from a blow case; a steam jet was the most satisfactory. The optimum procedure was to fluidize the bed with a water backwash and immediately steam-jet the fluidized bed. With this

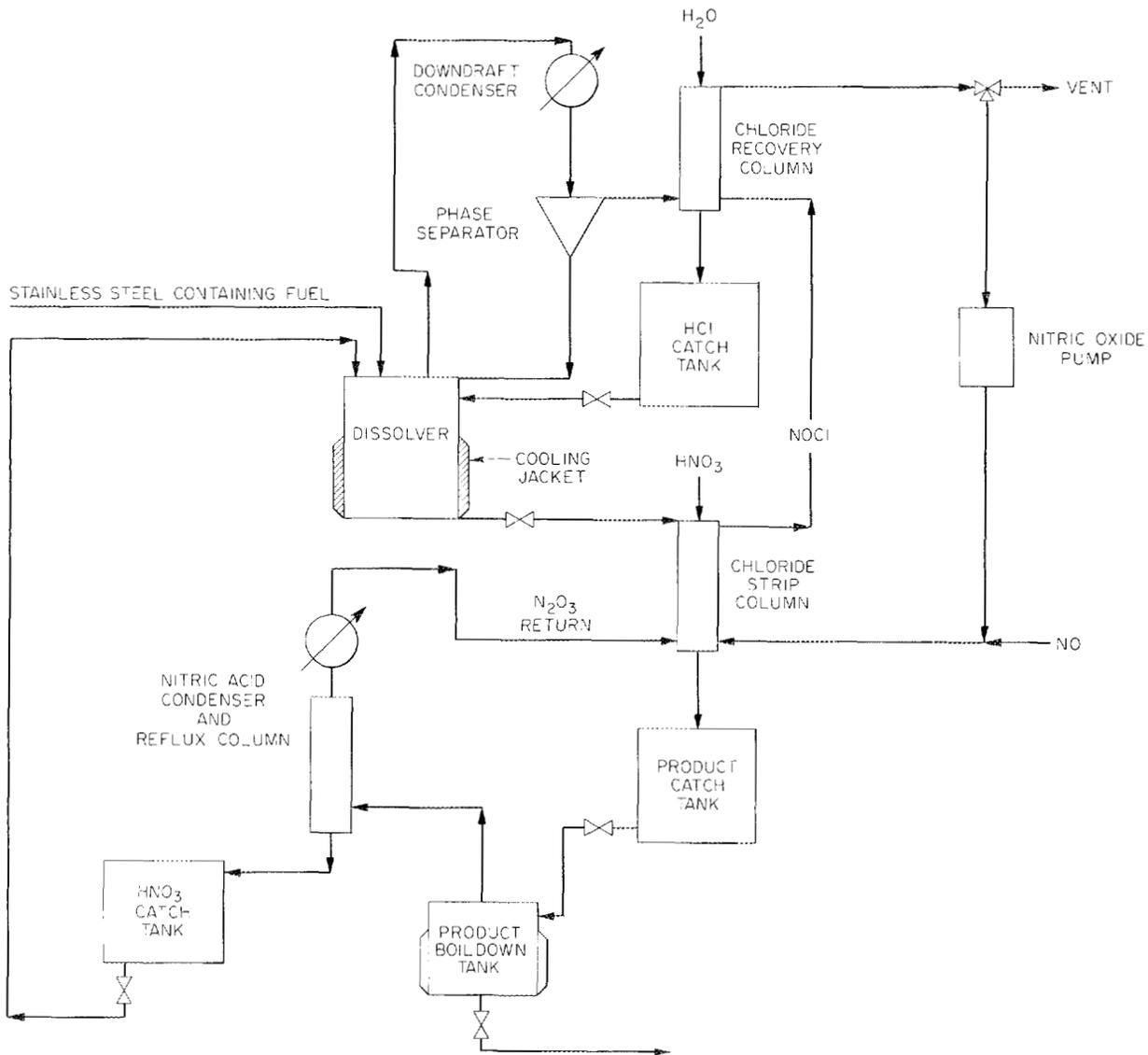


Fig. 1.5. Tentative Flowsheet for Batch Chloride Removal from Darex Dissolver Solution.

procedure a 12-in.-dia  $\times$  10-in. bed of 20- to 30-mesh Ottawa sand was removed in 15 gal of water in 2 to 3 min 97 successive times without failure.<sup>2</sup>

Separation of solids was also good on centrifugation in a 5-in. bowl centrifuge of 315 cc capacity. No solids over 1  $\mu$  were observed in the effluent

when the centrifuge was operated at 500g with a 1-min feed residence time. Uranium losses in the centrifuge cake were 0.1% after four water washes, each one-twentieth the filtrate volume.

A conical hydroclone was unsatisfactory for clarification of Darex feed; the very turbulent conditions in the clone resulted in high attrition of the siliceous material and little or no solids separation. Sedimentation was shown experimentally to be too slow. Further, it is probable

<sup>2</sup>C. O. Thornburg, *Methods of Remotely Removing the Bed from a Sand Filter*, ORNL-2613 (Nov. 20, 1958).

that fission product heating of the sedimentary solids would result in thermal convection currents which would prevent the settling of or would resuspend the silica particles.

**Decladding of Stainless-Steel-Clad  $UO_2$ - $ThO_2$  Fuels.** - Mixed  $UO_2$ -96%  $ThO_2$  is relatively insoluble in boiling fluoride-free 5 M  $HNO_3$ -2 M  $HCl$ . Darex solution may therefore be used for decladding of Consolidated Edison and Rural Cooperative stainless-steel-clad mixed-oxide-core fuels (Fig. 1.6). In laboratory tests with unirradiated simulated Consolidated Edison fuel the maximum uranium and thorium losses to Darex decladding solutions were 0.42 and 0.04%, respectively, when the final dissolved stainless steel concentration was 50 g/liter. Losses appeared to be independent of reaction time up to 2 hr. Similar tests on a small engineering scale resulted in average uranium and thorium losses of 0.21 and 0.019%, respectively. Washing tests on the declad mixed-oxide pellets indicated that three water washes, each one-sixth the volume of the de-jacketing solution, were sufficient to decrease

the crossover chloride content of the final core dissolver product to 90 to 300 ppm. This concentration of chloride is safe in stainless steel equipment at high nitrate concentrations; a chloride removal step is unnecessary. Darex decladding appears to be superior to Sulfex in overcoming the possible passivation of stainless steel and in cross-contaminating cladding and core dissolvents, but gives higher uranium losses.

When unirradiated Consolidated Edison  $ThO_2$ -4%  $U_3O_8$  pellets were exposed for 3 hr to 5 M  $HNO_3$ -2 M  $HCl$  in a  $Co^{60}$  gamma field, radiation-induced uranium losses were inversely dependent on temperature. After exposure in a field of 1 w/liter at 35°C the loss was 40% greater than in the absence of radiation (0.14% vs 0.10%); at 75°C in a 10-w/liter field the loss was 0.27% in both cases.

**Corrosion Tests.** - Corrosion testing of titanium as a material of construction for the Darex process has proceeded for a maximum of 4483 exposure hours and is now completed. Maximum rates under any foreseeable fluoride-free process conditions

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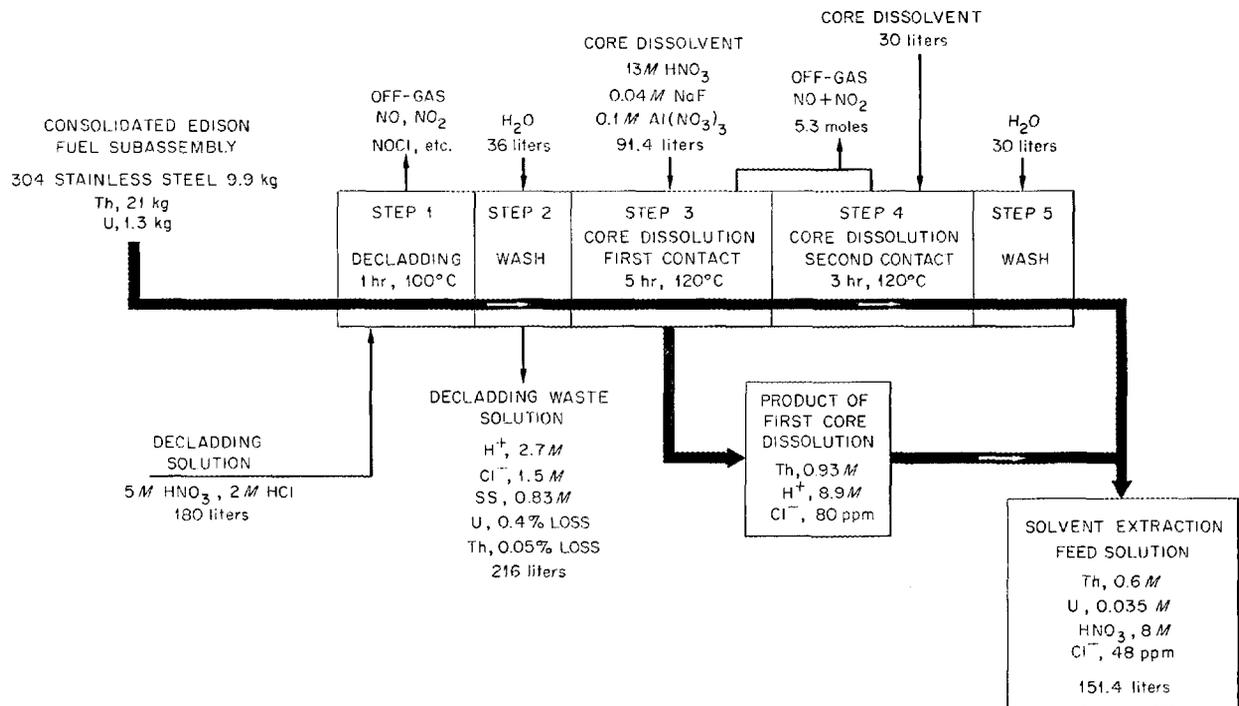


Fig. 1.6. Flowsheet for Reprocessing of Consolidated Edison Fuel, Darex Decladding.

are less than 1 mil/month and usually nearer 0.1 mil/month. Tests were made under numerous conditions. Both stressed and unstressed welded specimens were exposed in the liquid, interface, and vapor positions for up to 2008 hr; the specimens were cleaned weekly with boiling 10% NaOH. Selected specimens were scratched daily to break protective films. Metallographic examination of samples did not show any local attack. A welded hairpin tube through which steam at 135°C was passed for 2000 hr showed no appreciable attack.

Type 304L stainless steel exposed to Darex dissolver product solution at 105 to 125°F normally exhibited good corrosion resistance but was occasionally depassivated with subsequent serious attack. Boiling 3 M HNO<sub>3</sub> containing 60 g of stainless steel per liter and 0 to 800 ppm of chloride produced severe intergranular attack on both types 304L and 347 stainless steel; this attack appeared to be independent of chloride concentration in the 0 to 800 range. Similar two-year tests with type 347 stainless steel at room temperature resulted in negligible corrosion; no stress corrosion cracking was observed.

Exploratory tests were started on the corrosion of titanium by 13 M HNO<sub>3</sub>-0.04 M HF-0.1 M Al(NO<sub>3</sub>)<sub>3</sub> and 13 M HNO<sub>3</sub>-0.05 M HF-0.1 M H<sub>3</sub>BO<sub>3</sub>. After six runs, totaling 44 hr, with the first solution, the vapor phase corrosion rate was 0.6 to 0.8 mil/month; no liquid phase corrosion was observed. With the latter solution, after 253 hr, the liquid phase corrosion rate was 0.58 mil/month and the vapor phase rate was 0.33 mil/month. The use of boron, primarily as a criticality control soluble poison, was expected to result in lower vapor phase corrosion because of the formation of volatile BF<sub>3</sub>, thereby decreasing the amount of HF in the vapor phase.

### Sulfex Process

In the Sulfex process for stainless-steel-clad uranium and thorium oxide and alloy fuels the stainless steel is dissolved in boiling 6 M H<sub>2</sub>SO<sub>4</sub> and the core is dissolved by conventional methods: 8 to 10 M HNO<sub>3</sub> for uranium and UO<sub>2</sub> and 13 M HNO<sub>3</sub>-0.04 M NaF-0.1 M Al(NO<sub>3</sub>)<sub>3</sub> for thorium, ThO<sub>2</sub>, and ThO<sub>2</sub>-UO<sub>2</sub>. Development work has been concerned primarily with application of the process to Yankee Atomic (stainless-steel-clad UO<sub>2</sub>) and Consolidated Edison (stainless-steel-clad UO<sub>2</sub>-ThO<sub>2</sub>) fuels.

**Yankee Atomic Fuel.** - In dissolution tests with type 304L stainless steel samples and unirradiated Yankee fuel pins (stainless-steel-clad UO<sub>2</sub>) no passivation of stainless steel was noted in boiling 6 M H<sub>2</sub>SO<sub>4</sub>. However, seven out of nine fuel pin samples irradiated to 800 to 1440 Mwd/t were passive for at least 1 hr in boiling 6 M H<sub>2</sub>SO<sub>4</sub>. These pins were supported in a platinum basket. Metallic zinc and sulfamic acid added to the sulfuric acid did not break the passivation. Exposure of the pins to 0.8 M CrSO<sub>4</sub>-0.5 M H<sub>2</sub>SO<sub>4</sub> at 85°C was partially effective, but only wrapping of the pins with iron wire prior to sulfuric acid addition broke passivation consistently.

That the passivation increases with increasing amounts of nitric acid remaining in the process vessel from the preceding core dissolution was shown by refluxing passivated samples in 6 M H<sub>2</sub>SO<sub>4</sub> containing varying amounts of nitric acid. The depassivation times were directly proportional to the nitric acid concentration (Fig. 1.7). The depassivation time was much more dependent on temperature than on the sulfuric acid concentration. At a constant temperature of 97.5°C the depassivation time decreased by a factor of 4 as the

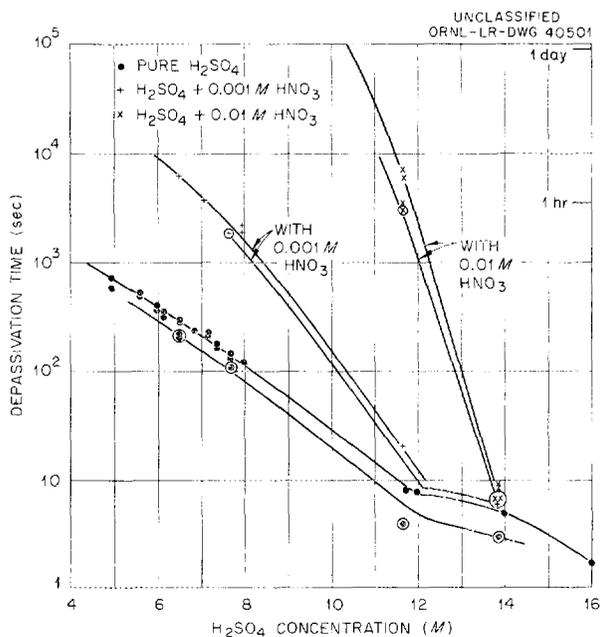


Fig. 1.7. Depassivation Time of Type 304 Stainless Steel in Refluxing Sulfuric Acid. Passivation treatment: 1 hr in boiling 15.8 M HNO<sub>3</sub>-0.025 M Cr(III) [circled points only, 0.25 M Cr(III)].

sulfuric acid concentration was increased from 5 to 10 M, but by a factor of 200 at the boiling point, which increased from 105 to 148°C with these sulfuric acid concentrations (Fig. 1.8). When 0.1 M formic acid was added to the boiling sulfuric acid-nitric acid mixtures, depassivation times were nearly equal to those in HNO<sub>3</sub>-free H<sub>2</sub>SO<sub>4</sub>. Passivated samples for study were prepared by refluxing type 304L stainless steel samples for 1 hr in 10 to 15.8 M HNO<sub>3</sub>-0.025 M Cr(III).

Samples of type 304L stainless steel Microbrazed together and passivated by the standard 1-hr HNO<sub>3</sub>-Cr(III) procedure began to react immediately when immersed in boiling 6 M H<sub>2</sub>SO<sub>4</sub>, both the braze material and the stainless steel.

Uranium and plutonium decladding losses did not increase with irradiation from 250 to 1440 Mwd/t (Table 1.2) except when the UO<sub>2</sub> surface area increased greatly as a result of fragmentation of the pellets. All decladdings, done under a nitrogen blanket, were complete in 1.75 to 2 hr

except for the stainless steel end plugs. The decladding operation can be monitored by observing the hydrogen evolution rate, which drops sharply when the cladding (except the end plugs) is completely dissolved.

The minimum rate of UO<sub>2</sub> dissolution (expressed as per cent uranium loss per hour) for oxide irradiated to ~1000 Mwd/t was 0.04% per hour. This rate was obtained by boiling oxide pellet fragments under a nitrogen blanket in 6 M H<sub>2</sub>SO<sub>4</sub> containing 35 g of stainless steel per liter and in the absence of dissolving stainless steel. The rate for the same solution with dissolving stainless steel present was 0.29% per hour and in the absence of dissolving stainless steel but air-sparged was 0.81% per hour. This high rate is attributed to the depletion of ferrous ion by the air sparging. The rate in nitrogen-blanketed fresh 6 M H<sub>2</sub>SO<sub>4</sub> and in the absence of dissolving stainless steel was 0.30% per hour. These tests emphasize the need of removing the decladding solution as soon as decladding is completed and of keeping all air out of the dissolution vessel.

**Consolidated Edison Fuel.** - In tests<sup>3</sup> in which unirradiated Consolidated Edison (stainless-steel-clad UO<sub>2</sub>-96% ThO<sub>2</sub>) fuel samples were declad in 200% excess of boiling 6 M H<sub>2</sub>SO<sub>4</sub>, a loss differential factor of 10 to 30 was noted between air- and hydrogen-fired mixed-oxide pellets. From the air-fired pellets, which were predominantly ThO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub>, uranium losses were 0.1 to 0.2% in decladding exposures of 1 to 6 hr. With 300% excess H<sub>2</sub>SO<sub>4</sub> the uranium loss increased to 0.34 to 0.41%. From hydrogen-fired oxide, predominantly ThO<sub>2</sub>-UO<sub>2</sub>, the uranium loss was <0.02% in 5 hr decladding in 200% excess of 6 M H<sub>2</sub>SO<sub>4</sub>. A comparison of loss for UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> vs exposure time to H<sub>2</sub>SO<sub>4</sub> is given in Fig. 1.9.

Radiation-induced losses in decladding tests were simulated by performing the tests in a Co<sup>60</sup> gamma field; the increase in loss over that in the absence of radiation was inversely dependent on temperature. With 6 M H<sub>2</sub>SO<sub>4</sub>, after 3 hr the loss increased 70% at 35°C in a gamma field of 1 w/liter, but increased only 40% at 75°C in a 10-w/liter field. In order to determine the effect of a large UO<sub>2</sub> surface area, a pellet irradiated to 5600

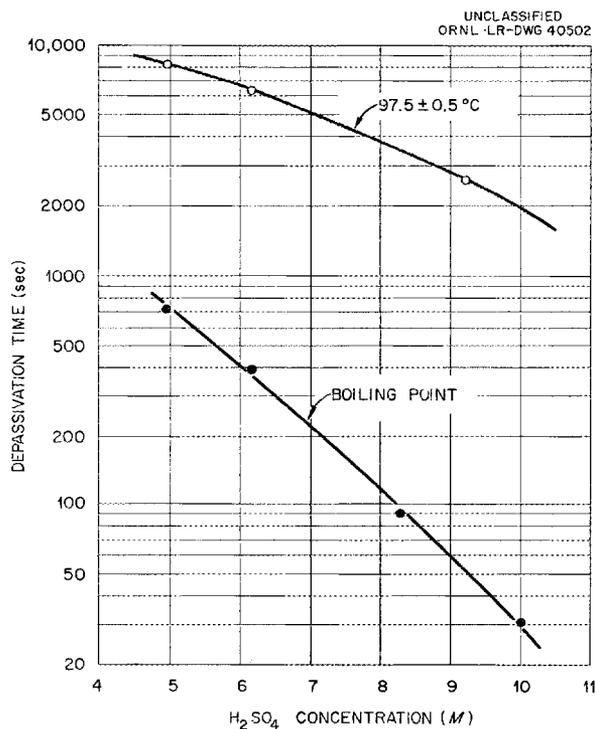


Fig. 1.8. Comparison of Depassivation Times of Type 304 Stainless Steel in Sulfuric Acid at the Boiling Point and at 97.5 ± 0.5°C. Passivation treatment: 1 hr in boiling 15.8 M HNO<sub>3</sub>-0.025 M Cr(III).

<sup>3</sup>L. M. Ferris and A. H. Kibbey, *Sulfex Process for the Dissolution of Consolidated Edison Power Reactor Fuel: Laboratory Development*, ORNL-2714 (in press).

Table 1.2. Uranium and Plutonium Losses During Sulfex Decladding of Irradiated Prototype Yankee Atomic Fuel Pins

Fuel pins: 42 g of sintered  $UO_2$  pellets encased in 20 g of type 304L stainless steel, 30 mils wall thickness, irradiated for 250 to 1440 mwd per ton of U and decayed for four months

Decladding solution: 370 ml of boiling 6 M  $H_2SO_4$

Irradiation (Mwd per ton of U)	U Loss (%)		Pu Loss (%)		Pellet Form
	In 2-hr* Decladding	In 4-hr Reflux	In 2-hr* Decladding	In 4-hr Reflux	
0	0.005				Intact
250	(0.003)		(0.06)		Intact
450	0.003	0.005	0.04	0.05	Intact
650	0.003	0.005	0.009	0.05	Intact
800	0.005	0.03	0.02	0.07	Fragmented**
1000	0.03	0.29	0.03	0.34	Fragmented**
1440	0.045	1.41	0.052	0.60	Fragmented**

\*Stainless steel cladding was dissolved in  $\sim 1.75$  hr.

\*\*Caused by thermal cycling at higher irradiation levels.

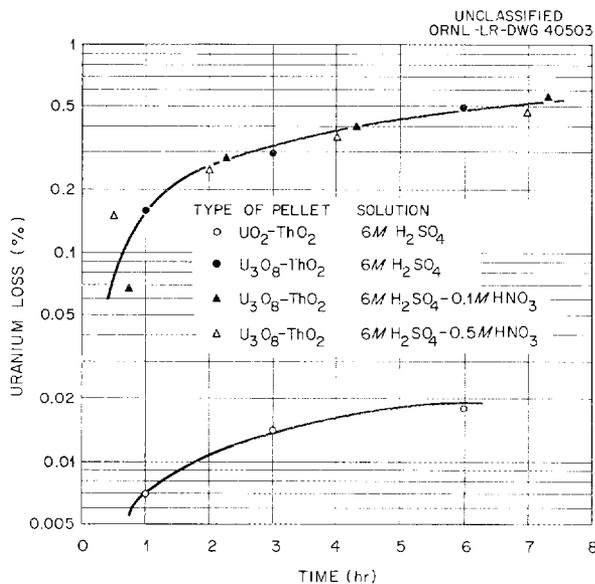


Fig. 1.9. Effect of Uranium Valence, Time, and Nitric Acid Concentration on Uranium Losses from Sintered 95.5% Thorium Oxide-Uranium Oxide Pellets Exposed to 6 M  $H_2SO_4$  Solutions (5 ml of Acid per Gram of Pellets).

Mwd/t and decayed for 3.8 years was crushed to powder and boiled in 6 M  $H_2SO_4$  for 3 hr; the uranium loss was 3% and the thorium loss 0.3%. The uranium loss increased relatively uniformly with time after 3 hr, being 15% at 50 hr, whereas the soluble thorium loss occurred completely within the first hour of exposure. Copious quantities of insoluble thorium sulfate were precipitated, preventing further soluble losses.

The use of good washing techniques and the avoidance of cross contamination of decladding and dissolving solution in the Consolidated Edison-Sulfex flowsheet are extremely important, not only in order to avoid stainless steel passivation but also to avoid a decrease in the already low  $ThO_2-UO_2$  dissolution rates.<sup>4</sup> Carry-over of 0.1 M sulfate decreased the amount of  $ThO_2$  dissolved in 1 hr in 200% excess of 13 M  $HNO_3$ -0.04 M  $NaF$ -0.1 M  $Al(NO_3)_3$  by a factor of 8. The decrease in dissolution rate was apparently caused by the

<sup>4</sup>W. D. Bond, *Dissolution of Sintered Thorium-Uranium Oxide Fuel in Nitric Acid Fluoride Solutions*, ORNL-2519 (Oct. 28, 1958).

formation of a film of  $\text{Th}(\text{SO}_4)_2$  on the  $\text{ThO}_2$  pellets, which is very slowly soluble in the dissolvent.

In order to determine the value of silica gel treatment for Consolidated Edison feed solution, a core solution (1 M Th, 0.6 M Al, 4 M  $\text{HNO}_3$ ) at  $50^\circ\text{C}$  spiked with fission product zirconium-niobium was decontaminated by silica gel by a factor of 37 initially; after 50 volume changes the decontamination factor was 5. Pretreatment of the bed with thorium or thorium and phosphate did not increase the decontamination.

An investigation of semicontinuous Sulfex-Thorex decladding and core dissolution was made because of the criticality control advantages which would accrue from the use of a geometrically safe dissolver. Semicontinuous decladding rates with 6 M  $\text{H}_2\text{SO}_4$  on individual pins were about half the batch rate of 8 to 11  $\text{mg}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ . The semicontinuous decladding solution loadings were 25 to 53 g of stainless steel per liter, compared with 50 to 100 g/liter in batch decladding. Average uranium losses in both batch and semicontinuous decladding were the same,  $\sim 0.1\%$ . In tests in which stainless steel tubing completely filled the

reaction zone, the decladding rates for semicontinuous and batch operation were approximately equal. In batch dissolution tests, 6 hr was required for complete dissolution of the  $\text{ThO}_2\text{-UO}_2$  in 55% excess of dissolvent [13 M  $\text{HNO}_3\text{-}0.04$  M  $\text{NaF}\text{-}0.1$  M  $\text{Al}(\text{NO}_3)_3$ ]; with only 30% excess dissolvent 12 to 16 hr was required. In semicontinuous tests considerably longer times were needed for complete dissolution; for example, with 80% excess dissolvent, dissolution was complete only after 9 to 12 hr.

The feasibility of hydraulically transferring (Fig. 1.10) chemically declad pellets from one vessel to another was demonstrated with brass pellets ( $\frac{1}{4}$  in. dia  $\times$   $\frac{1}{2}$  in.) whose density (8.4 g/cc) was approximately the same as that of the Consolidated Edison  $\text{UO}_2\text{-ThO}_2$  pellets. Fluidization was necessary to cause the pellets to flow from the decladding vessel into the pellet transfer line.

**Corrosion Tests.** - In determining the best material of construction for the Sulfex process, a number of alloys were cycled between boiling 6 M  $\text{H}_2\text{SO}_4$ , with and without dissolved stainless steel, and 13 M  $\text{HNO}_3\text{-}0.04$  M  $\text{F}^- \text{-}0.1$  M  $\text{Al}(\text{NO}_3)_3$ , with and without dissolved thorium. Alloys tested

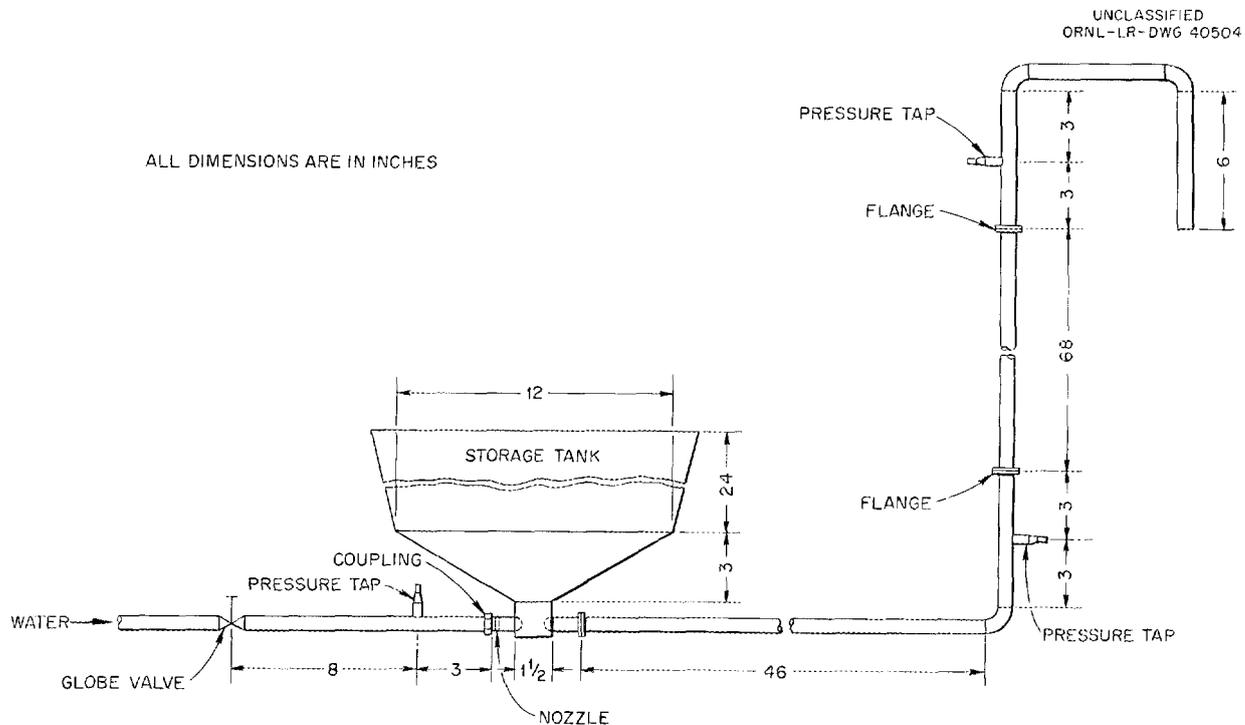


Fig. 1.10. Pellet Transfer Unit.

were Ni-O-Nel, Carpenter 20Cb stainless steel, Illium 98, Illium "R," Hastelloys C and F, Incoloy 804, titanium, zirconium, types 329, 319, and 17 PH stainless steels, Haynes alloys 21 and 25, high-cobalt alloys S-816 and S-590, and Inconel 700. Only Ni-O-Nel was corroded at a rate of <3 mils/month. In the presence of dissolved stainless steel, the rates in the two reagents were approximately 1 mil/month. Satisfactory corrosion resistance of weld zones was achieved by heat-treating to 1950°F after welding and either water- or air-quenching.

In boiling 6 M  $H_2SO_4$  the corrosion rate of titanium was 500 to 4000 mils/month.

## 1.2 PROCESSES FOR ZIRCONIUM-CONTAINING FUEL

### Zircex Process

The basic Zircex process for zirconium fuels involves the gas phase reaction at  $\sim 500^\circ C$  of anhydrous HCl with zirconium and uranium<sup>5</sup> to produce volatile  $ZrCl_4$  and nonvolatile  $UCl_3$ . The  $UCl_3$  is dissolved in nitric acid, the chloride is distilled off as in the Darex process (Sec 1.1), and the chloride-free uranium nitrate solution is solvent-extracted by conventional methods. Since  $UO_2$  does not react with gaseous HCl, the Zircex process can be used as a decladding process for zirconium-clad  $UO_2$  fuels.

With high zirconium-uranium (STR) fuel the nitric acid-insoluble uranium loss in the hydrochlorination residue leaching is 2 to 3%. This loss has been attributed to the existence of a nitric acid-insoluble  $ZrO_2-UO_2$  solid solution. Attempts to decrease this loss by using hydrogen chloride in which oxygen and carbon dioxide were only 0.02 and <0.01 mole %, respectively, resulted in losses of 1.1 and 1.9%, considerably greater than the 0.1 to 0.2% loss expected from the known oxygen content of the fuel alloy. When EBWR fuel (93.5% U-5% Zr-1.5% Nb) was hydrochlorinated, the nitric acid-insoluble loss was only 0.021%. However, a crust of uranium chloride formed on the fuel plates, resulting in an unacceptably low final reaction rate. The average hydrochlorination rate in a 10-hr test was  $3.3 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ .

<sup>5</sup>J. J. Perona et al., *Status of the Development of the Zircex Process*, ORNL-2631 (March 17, 1959).

The use<sup>6</sup> of  $CCl_4$ -saturated nitrogen as a final chlorination agent at 550 to  $600^\circ C$  has shown considerable promise as a means of decreasing the STR fuel nitric acid-insoluble uranium losses to acceptable limits. About 98% of the zirconium in the fuel is volatilized by the basic Zircex procedure, and then the  $ZrO_2-UO_2-UCl_3$  residue is contacted with the  $CCl_4-N_2$  gas mixture at 550 to  $600^\circ C$ , which converts the  $ZrO_2$  to volatile  $ZrCl_4$  and the  $UO_2$  and  $UCl_3$  to volatile  $UCl_4$  (Fig. 1.11). This gas mixture is passed to a desublimator and cooled to below  $300^\circ C$ , and the  $ZrCl_4$  and  $UCl_4$  are separated from the  $N_2$  and  $CO_2$  off-gas. The desublimed residue is totally soluble in  $HNO_3$ . For STR fuel the resulting solution contains about 10 moles of zirconium per mole of uranium but only 2% of the zirconium originally present in the fuel. Both  $ZrCl_4$  and  $Zr(NO_3)_4$  are soluble in nitric acid. A method of removing the fission products remaining in the hydrochlorinator would have to be developed because of their extremely high heat-producing capacity. In addition to solving the nitric acid-insoluble loss problem, the modified process circumvents the construction material problem by permitting the hydrochlorinator and desublimator-nitric acid dissolver to be made of Inconel and titanium, respectively.

### Zirflex Process

The Zirflex process for zirconium-containing fuels was originally developed as a method for decladding zirconium-clad  $UO_2$  fuels (PWR blanket, Commonwealth Edison) with 6 M  $NH_4F$ -1 M  $NH_4NO_3$ . The undissolved  $UO_2$  is subsequently dissolved in 8 to 10 M  $HNO_3$  by conventional means. The process has been modified to extend its use to the total dissolution of zirconium-clad uranium-zirconium-niobium fuels of the STR (high zirconium, highly enriched uranium) and EBWR (5% Zr-1.5% Nb-93.5% U) types.

Prototype PWR pins, both unirradiated and irradiated up to 2500 Mwd/t, were declad in 3 hr with boiling 6 M  $NH_4F$ -1 M  $NH_4NO_3$  in an amount sufficient to provide an F/Zr ratio of 6.5. The ammonium nitrate is used to solubilize the tin in

<sup>6</sup>T. A. Gens, *Recovery of Uranium from Residues Produced in Hydrochlorination of Nuclear Fuel Alloys*, ORNL CF-59-4-9 (April 10, 1959).

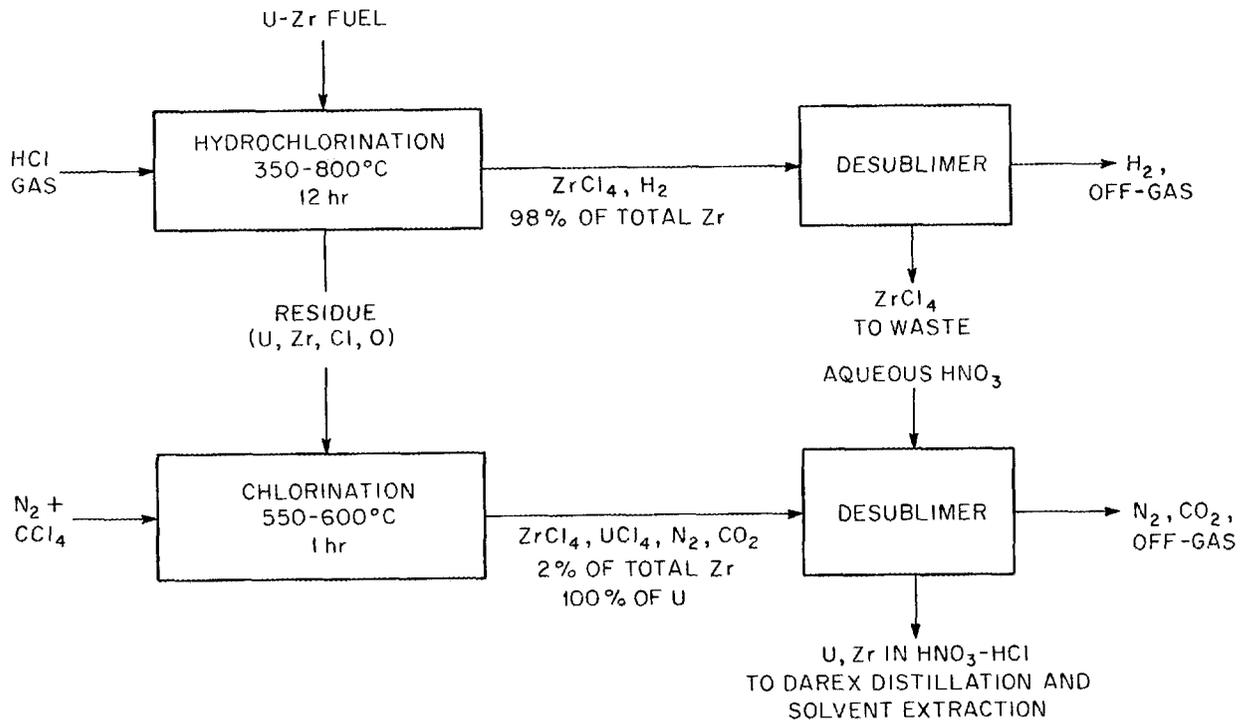
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Fig. 1.11. Modified Zircex Process: Gas-Phase Hydrochlorination Followed by Chlorination with Carbon Tetrachloride.

the Zircaloy-2 cladding,<sup>7</sup> which is insoluble in  $\text{NH}_4\text{F}$  alone, and to decrease the amount of hydrogen evolved during decladding.<sup>8</sup> Uranium losses to the decladding solution were unaffected by ammonium nitrate in concentrations below 1 M. Uranium losses from unirradiated pins were generally <0.09%; losses from pins irradiated up to 1100 Mwd/t were generally <0.2%. On cooling, the decladding solution must be diluted about fourfold to avoid precipitation<sup>9</sup> of  $(\text{NH}_4)_3\text{ZrF}_7$ .

Hydrogen-fired  $\text{UO}_2$  pellets exposed to 6 M  $\text{NH}_4\text{F}$ -1 M  $\text{NH}_4\text{NO}_3$  at 35°C for 3 hr in a 1-w/liter  $\text{Co}^{60}$  gamma field lost 0.00074% of the uranium to

the solution; the loss in the absence of radiation was only 0.00018%. Declad  $\text{UO}_2$  pellets absorbed sufficient fluoride to make the final core dissolver solution 0.1 to 0.2 M in fluoride, but when the pellets were washed with 0.05 M  $\text{Al}(\text{NO}_3)_3$ , the dissolver product was consistently <0.1 M in fluoride. In both cases aluminum nitrate must be added to the dissolver solution to inhibit corrosion of stainless steel equipment in subsequent process steps.

In corrosion tests made by exposing alloy samples alternately to 6 M  $\text{NH}_4\text{F}$ -1 M  $\text{NH}_4\text{NO}_3$  and to boiling 10 M  $\text{HNO}_3$  for a total of 72 hr, the most resistant material found, Haynes 21, showed corrosion rates in the two dissolvents of 2.3 and 2.8 mils/month, respectively, and type 309Cb stainless steel showed rates of 8.5 and 3.7 mils/month. In a 24-hr test Ni-O-Nel showed rates of 12 mils/month in  $\text{NH}_4\text{F}$ -1 M  $\text{NH}_4\text{NO}_3$ , and of 40 and 87 mils/month in the liquid and vapor phases, respectively, of 5 M HF. Addition of 0.05 M  $\text{B}_4\text{O}_7^{--}$  or 0.05 M  $\text{SiO}_3^{--}$  to the boiling ammonium fluoride-ammonium

<sup>7</sup>L. M. Ferris, *Decladding of PWR Blanket Fuel Elements with Aqueous Ammonium Fluoride Solutions*, ORNL-2558 (Sept. 25, 1958).

<sup>8</sup>L. P. Bupp, *Monthly Report, November 1957, Chemical Research and Development Operation*, HW-53961 (Dec. 9, 1957).

<sup>9</sup>G. V. Hevesy, J. A. Christiansen, and V. Berglund, *Z. anorg. allgem. Chem.* 144, 69 (1925).

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nitrate solution reduced the Ni-O-Nel corrosion rate to 6 mils/month and the type 309Cb stainless steel rate to 4 mils/month.

Several variations of the Zirflex process were developed for dissolution of STR and EBWR fuels (1% U-2% Sn-97% Zr and 93.5% U-5% Zr-1.5% Nb alloy, both clad in Zircaloy-2).<sup>10,11</sup> The STR fuel is dissolved in boiling 6 M NH<sub>4</sub>F, at an F/Zr ratio of 6.5, to produce a precipitate of ammonium

uranous fluoride (Fig. 1.12). A solution of 2.7 M HNO<sub>3</sub> containing 0.034 M CrO<sub>4</sub><sup>2-</sup> and 1.8 M Al(NO<sub>3</sub>)<sub>3</sub> is added to the dissolver solution to solubilize the uranium by converting U(IV) to U(VI). The chromate assures complete oxidation of uranium at room temperature in 1 hr. The aluminum nitrate is added to inhibit corrosion of stainless steel by the resulting solution. The uranium concentration in the final dissolver solution for 1% uranium alloy fuel is 0.0018 M. The flowsheet for EBWR fuel (Fig. 1.13) is similar except that no chromate is required for oxidation of uranium to U(VI) and an F/Zr ratio of 20 is required for complete dissolution of a fuel assembly in 28 hr. The insoluble niobic oxide is separated from the solution with a uranium loss of 0.03%. The uranium concentration in the final dissolver

<sup>10</sup>J. S. Swanson, *Dejacketing of Zircaloy Clad Fuel Elements with Ammonium Fluoride Solutions - Interim Progress Report*, HW-49633 (April 15, 1957).

<sup>11</sup>T. A. Gens and F. G. Baird, *Modified Zirflex Process for Dissolution of Zirconium and Niobium-bearing Nuclear Fuels in Aqueous Fluoride Solutions: Laboratory Development*, ORNL-2713 (in process).

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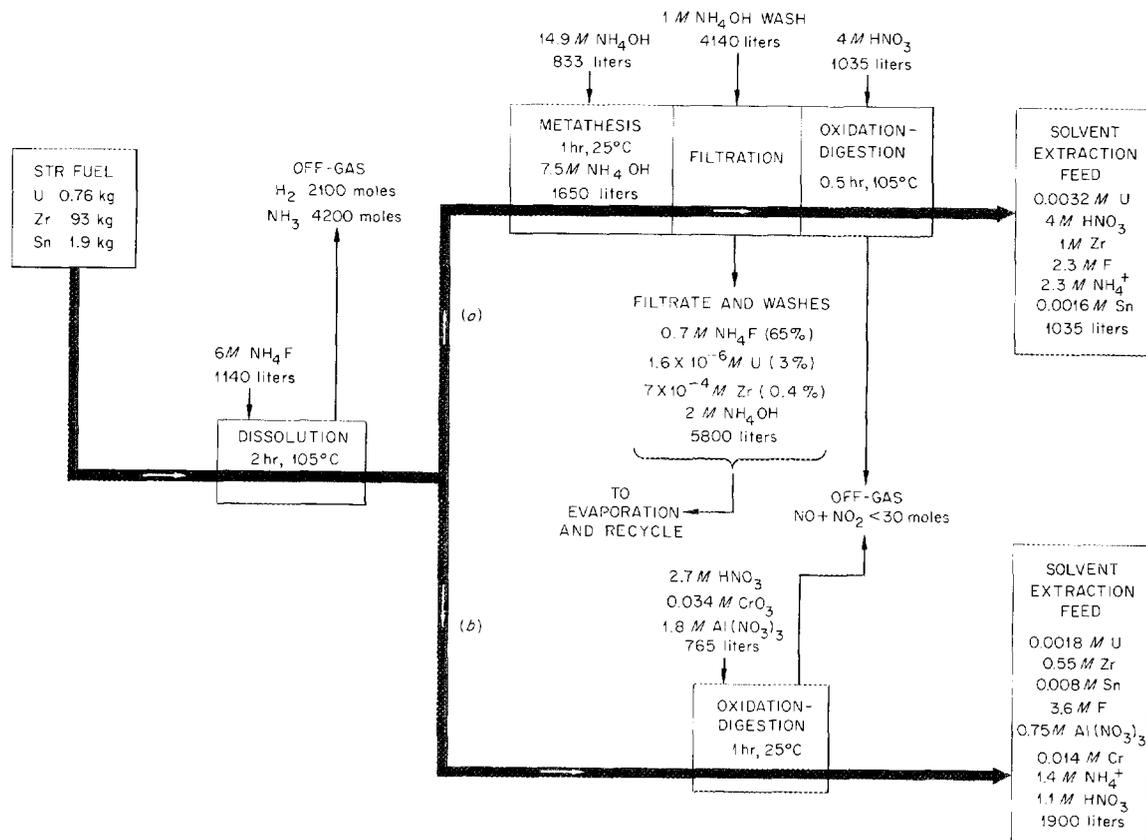


Fig. 1.12. Modified Zirflex Process for Dissolution of Low-Uranium (STR) Fuel Elements in Aqueous Ammonium Fluoride. Solvent extraction feed preparation by (a) metathesis and nitric acid oxidation and (b) chromic acid oxidation.

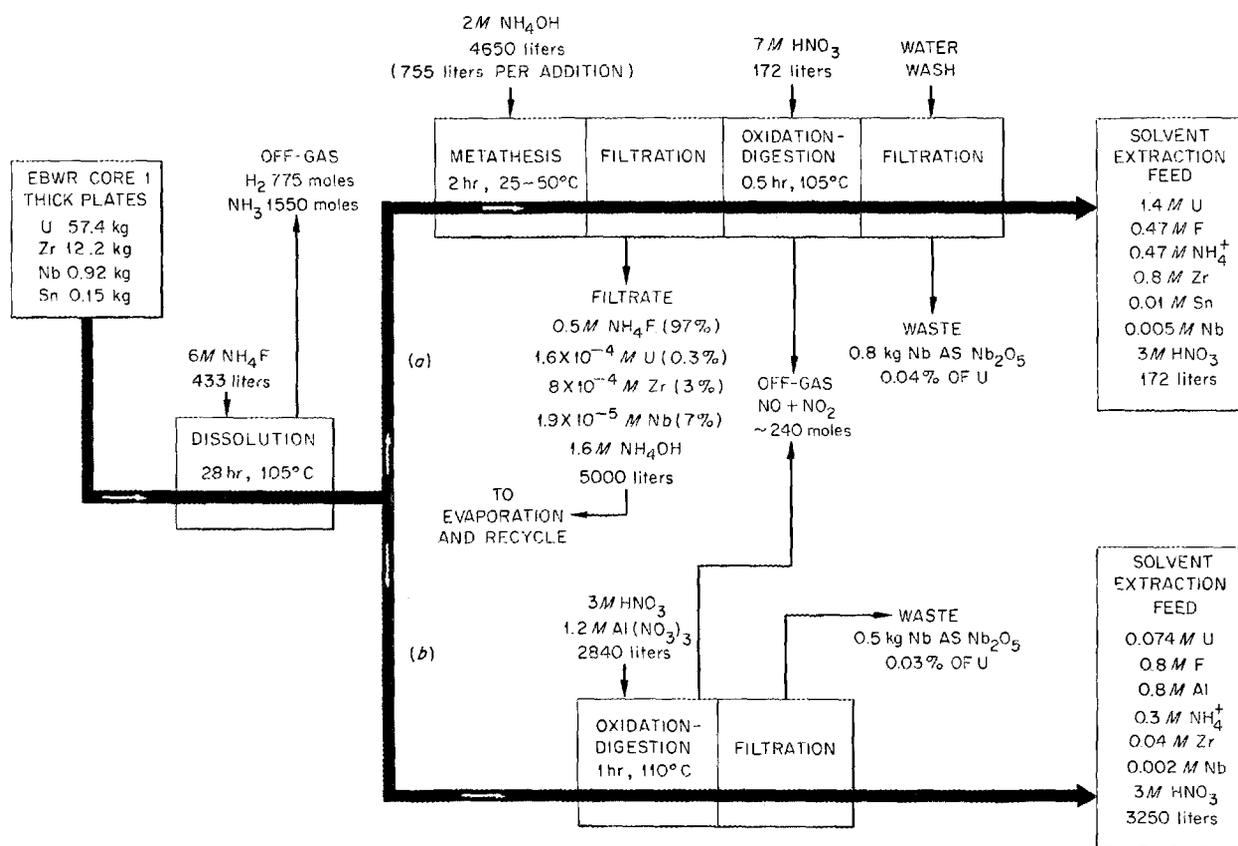


Fig. 1.13. Modified Zirflex Process for Dissolution of High-Uranium (EBWR Core 1) Fuel in Aqueous Ammonium Fluoride. Solvent extraction feed preparation by (a) metathesis and nitric acid oxidation and (b) nitric acid oxidation.

solution is 0.074 M; the volume per fuel element (57.4 kg of uranium) is 3250 liters.

With either fuel the volumes of final dissolver solution may be decreased by metathesis of the raw dissolver solution with ammonium hydroxide to precipitate uranium, zirconium, and niobium hydroxides, which are filtered and redissolved in boiling nitric acid. The STR fuel solution volume is lower by a factor of 2 and the EBWR fuel solution by a factor of 20 than in the oxidation and/or digestion method. The metathesis step regenerates ammonium fluoride, which is re-used in subsequent dissolutions. In the STR flowsheet three successive ammonium hydroxide metatheses are required to remove 97% of the uranium. The  $\text{NH}_4\text{F-NH}_4\text{OH}$  filtrate, containing 3% of the uranium, is evaporated to 6 M  $\text{NH}_4\text{F}$  and recycled. The

hydroxides of uranium and zirconium, after redissolution in 4 M  $\text{HNO}_3$ , contain 2.3 M fluoride and have an F/Zr mole ratio of 2.3, which is believed to be low enough to eliminate the need for addition of aluminum nitrate to inhibit corrosion. The EBWR flowsheet requires six ammonium hydroxide metatheses to remove 99% of the fluoride, which is recycled. The hydroxides, after dissolution in boiling 7 M  $\text{HNO}_3$ , are filtered or centrifuged to remove the insoluble  $\text{Nb}_2\text{O}_5$ , which contains 0.04% of the total uranium. The uranium-zirconium filtrate contains 0.8 M fluoride and has an F/Zr ratio of 0.5.

A third flowsheet variation (Fig. 1.14), for EBWR fuel only, uses just enough 6 M  $\text{NH}_4\text{F}$  to dissolve the zirconium cladding. The uranium-zirconium-niobium core is dissolved, in the presence of the

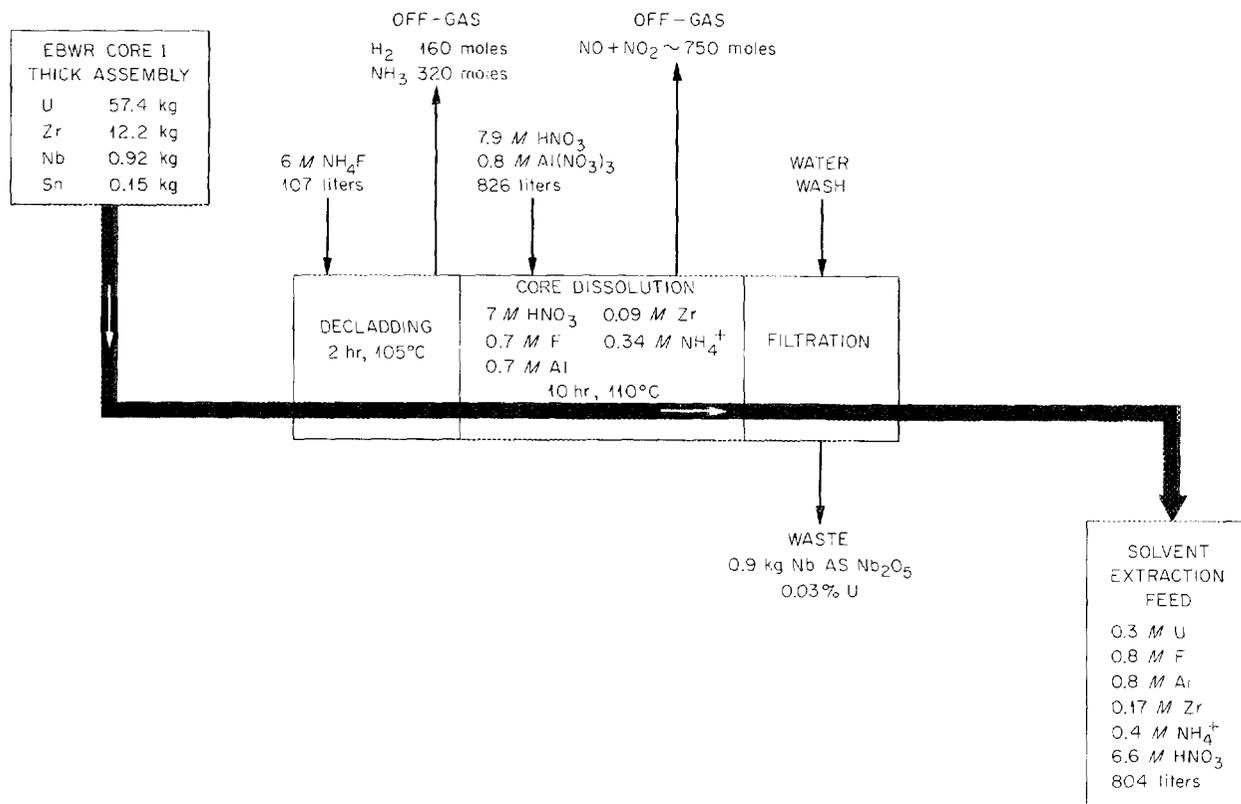


Fig. 1.14. Modified Zirflex Process for Two-Step Dissolution of High-Uranium (EBWR Core 1) Fuel in Aqueous Fluoride.

decladding solution, by the further addition of 8 M HNO<sub>3</sub>-0.8 M Al(NO<sub>3</sub>)<sub>3</sub>. The insoluble Nb<sub>2</sub>O<sub>5</sub> is filtered off, with a uranium loss of 0.03%. The time required is 12 hr. The resulting dissolver solution volume is five times that with the metathesis step but only one-fourth that with the digestion step. Although this flowsheet uses minimum fluoride, it may be unfeasible because of the chance of explosive reactions of nitric acid with epsilon-phase zirconium if fluoride concentrations are too low, and because of high corrosion rates in the core dissolution step.

**Perflex Process**

In the Perflex process zirconium-uranium alloy fuel is totally dissolved in an HF-H<sub>2</sub>O<sub>2</sub> solution.<sup>12</sup> In laboratory tests unirradiated 7% uranium-93% zirconium alloy fuel was immersed in water, and 34.4 M HF-1.7 M H<sub>2</sub>O<sub>2</sub> was added

continuously until the fuel was completely dissolved, producing a solution containing 0.032 M U, 1.1 M Zr, and 6.6 M F. Aluminum nitrate and nitric acid were then added to yield solvent extraction feed containing 0.016 M U, 0.55 M Zr, 0.75 M Al, 1 M H<sup>+</sup>, and 3.3 M F. No uranium or tin was precipitated even when the resulting solution stood at room temperature for one month. The hydrogen peroxide rapidly dissolved the tin and uranium, the latter by oxidation of U(IV) to U(VI), which has a wide solubility range<sup>13</sup> in HF. Niobium dissolved initially at 0.7 mg-cm<sup>-2</sup>.min<sup>-1</sup> in 1 M HF-1 M H<sub>2</sub>O<sub>2</sub>.

<sup>12</sup>Personal communication from M. Fortenbery and J. Perry, Y-12, Feb. 9, 1959.

<sup>13</sup>J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium*, NNES-VIII-5, p 571, McGraw-Hill, New York, 1951.

The Perflex process dissolvent is extremely corrosive to both Monel and INOR-8. The maximum corrosion rate for Monel in 4-, 10-, and 24-hr tests was 157, 111, and 24 mils/month, respectively, when all hydrogen peroxide was added at the start of the tests. The decreasing rate is believed to result from hydrogen peroxide decomposition. Rates with a nitrogen blanket and in the presence of dissolving zirconium were about half these. The rate for 1 M HF on Monel with a nitrogen blanket was 2.5 mils/month. Rates of INOR-8 in hydrogen fluoride-hydrogen peroxide were approximately 50% greater than those of Monel. Maximum rates of Hastelloy C over these exposures of 18 to 24 hr each varied between 4 and 5 mils/month.

### 1.3 PROCESSES FOR GRAPHITE-CONTAINING FUEL

Process studies were started on UC<sub>2</sub>-graphite and UC<sub>2</sub>-ThC<sub>2</sub>-graphite fuel mixtures. The former were readily processed by grind-and-leach methods, but grinding and leaching of the latter resulted in ~10% uranium and thorium losses. Only burning followed by leaching appeared capable of circumventing the loss problem with uranium-thorium fuels.

#### UC<sub>2</sub>-Graphite Studies<sup>14</sup>

In laboratory-scale grind-leach experiments uranium recovery from uranium-graphite mixtures increased with increasing uranium content, increasing nitric acid concentration, and decreasing particle size to 200 mesh. The highest uranium recovery, 99.8%, was achieved with -200-mesh particles and 15.8 M HNO<sub>3</sub>. First-leach uranium recoveries varied from 98.4 to 99.8% (Fig. 1.15) and second-leach recoveries from 0.2 to 0.8% of the original uranium. Samples of 2 to 14% uranium-graphite mixtures for dissolution studies were prepared by mixing UO<sub>2</sub>, graphite flour, and a binder, baking under vacuum at 800°C, and graphitizing at 2400 to 2800°C. The samples were then ground, classified, and leached twice, usually 4 hr for each leach, with nitric acid. The solutions were filtered from the graphite and the cake was washed after each filtration with water one-half the volume of the filtrate.

<sup>14</sup>M. J. Bradley and L. M. Ferris, *Recovery of Uranium and Thorium from Graphite Fuels. I. Laboratory Development of a Grind-Leach Process*, ORNL-2761 (in press).

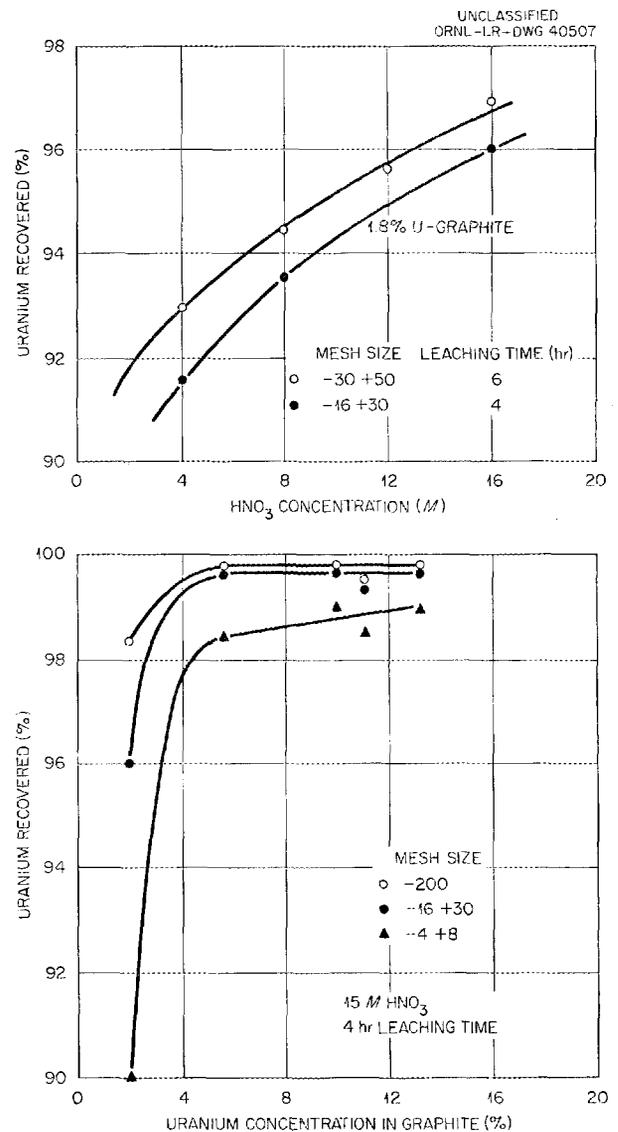


Fig. 1.15. Effect of Particle Size and (a) Nitric Acid Concentration of Leach and (b) Uranium Content of Solid on Uranium Recovery from Uranium-Graphite Fuel. Ten-gram specimens leached with 50 ml of boiling acid.

Two methods for the disintegration of graphite fuels by chemical means are being investigated: the use of swelling agents such as bromine, and formation of interlamellar compounds, for example, with potassium, and their subsequent reaction with steam and/or aqueous leaching agents. A sample of 9% uranium-graphite fuel was disintegrated at 25°C in liquid bromine in 5 hr to produce a powder with the following particle size distribution: +10 mesh, 6%; -10 +20 mesh, 21%; -20 +200 mesh,

73%. After leaching with two portions of boiling 15.8 M HNO<sub>3</sub>, 99.8% of the uranium was recovered. The same recovery can be obtained without the use of bromine by mechanically grinding to only -4 +8 mesh before leaching. Graphite fuels containing less than 1% uranium did not disintegrate in bromine.

#### UC<sub>2</sub>-ThC<sub>2</sub>-Graphite Flowsheet Studies

Samples of proposed High Temperature Gas Cooled Reactor fuel (1.5% uranium-7.2% thorium in graphite) in laboratory-scale experiments were ground to -325-mesh and leached with boiling 15.8 M HNO<sub>3</sub> and 13 M HNO<sub>3</sub>-0.04 M NaF-0.04 M Al(NO<sub>3</sub>)<sub>3</sub>. With both dissolvents about 10% of the uranium and thorium remained insoluble. Fuel samples were then burned in oxygen, and, after cooling, the U<sub>3</sub>O<sub>8</sub> and ThO<sub>2</sub> were dissolved in 13 M HNO<sub>3</sub>-0.04 M NaF-0.04 M Al(NO<sub>3</sub>)<sub>3</sub>. Recovery of both oxides was >99.9%.

Combustion of graphite fuels in air or O<sub>2</sub> would present an operating problem. Estimates show that the volume of gas to be processed would be 100 times greater than for conventional dissolution. In addition, the gas may contain as much as 10% of the total fission product activity, including all Xe, Kr, I<sub>2</sub>, and Te and some Cs, as well as small amounts of less volatile fission products.

### 1.4 PROCESSES FOR ALUMINUM-CONTAINING FUEL

#### Foreign Research Reactor Fuel

Foreign research reactors use chiefly aluminum-clad uranium-aluminum alloy plate fuels containing 1 to 2% silicon. The uranium is 20%-enriched U<sup>235</sup>, and at a burnup of 15% contains enough plutonium to require separation in order to meet U<sup>235</sup> specifications and possibly to be economically recoverable. This fuel (84% Al-15% U-1% Si) dissolves readily in 7.5 M HNO<sub>3</sub> containing 0.005 M Hg(NO<sub>3</sub>)<sub>2</sub> catalyst to produce 1.5 M Al(NO<sub>3</sub>)<sub>3</sub>-1.3 M HNO<sub>3</sub> dissolver solution. This is adjusted to 1.0 M Al(NO<sub>3</sub>)<sub>3</sub>-0.5 M HNO<sub>3</sub> for use in solvent extraction. The large quantity of hydrous, colloidal silica produced in dissolution can be dehydrated by extended refluxing at high acidity,<sup>15</sup> but is more simply readied for removal by the addition

of 100 mg of gelatin per liter and digestion at 85°C for 1 hr.<sup>16</sup> The resulting gelatin-silica polymer can be readily filtered or centrifuged and the cake washed free of uranium and plutonium with 0.1 M HNO<sub>3</sub>. The polymer was stable in radiation fields up to 2 to 4 whr/liter. In solvent extraction tests subsequent to the gelatin treatment for silica removal, phase separation times of approximately 20 sec were obtained with 6% TBP in Amsco for both unirradiated and irradiated extraction feeds, which is adequate for pulsed column use.

A sand filter using 30-mesh Ottawa sand, with 1- to 2-g/liter Celite 545 in the feed slurry, gave optimum filtration of the gelatin-silica polymer with rates of 1 to 2 ml·cm<sup>-2</sup>·min<sup>-1</sup>. The use of vacuum in filtration was not required. The filter bed was easily regenerated by backwashing with water, provided that the bed and cake were not allowed to dry before being backwashed.

The use of 0.05 M boric acid as a criticality control poison was satisfactory in that it was not removed by any head-end operation and was not extracted by 6% TBP.

#### BORAX IV Fuel

The BORAX IV reactor experiment used an M-388 clad (99% Al-1% Ni), lead-bonded multiplate fuel element with a ThO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub> core. The optimum dissolution technique was a three-step operation in which the aluminum was dissolved in 2 to 6 M NaOH (ref 17) or 2 M NaOH-1.8 M NaNO<sub>3</sub> (ref 18), the lead (and nickel) dissolved in 1.5 M HNO<sub>3</sub> at a rate of 3 to 16 mg·cm<sup>-2</sup>·min<sup>-1</sup>, and the ThO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub> dissolved in 13 M HNO<sub>3</sub>-0.04 M NaF-0.1 M Al(NO<sub>3</sub>)<sub>3</sub>. The use of mercuric nitrate-catalyzed nitric acid for aluminum and lead removal was unsatisfactory because of the high concentration of mercury (>0.5 M) required and because of the low solubility of divalent lead in concentrated nitric acid. Dissolution of lead and ThO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub> simultaneously in 200% excess of 13 M HNO<sub>3</sub>-0.04 M NaF-0.1 M Al(NO<sub>3</sub>)<sub>3</sub> following caustic dissolution of the aluminum jacket was also unsatisfactory because the ThO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub> dissolution rate is greatly decreased at the Pb/Th mole ratio of 0.77 required,

<sup>16</sup>H. J. Groh, *Removal of Silica from Solutions of Nuclear Fuels*, DP-293 (June 1958).

<sup>17</sup>R. G. Wymer and R. E. Blanco, *Ind. Eng. Chem.* **49**, 59 (1957).

<sup>18</sup>*Symposium on the Reprocessing of Irradiated Fuels*, TID-7534, p 25 (May 1957).

<sup>15</sup>J. R. Flanary et al., *Chemical Development of the TBP-25 Process*, ORNL-1993 (revised) (March 20, 1959).

and because the low-solubility lead nitrate prohibits the preparation of stable solutions with a thorium concentration greater than 0.1 to 0.2 M. Uranium losses in the two-step decladding procedure were less than 0.15%.

### 1.5 MECHANICAL PROCESSING

Mechanical head-end treatment may be required for several reasons: to remove non-fuel-containing sections from the fuel elements before processing, thus decreasing the quantity of material processed; to disassemble the fuel sections for ease of dissolver loading; and to remove or rupture the fuel jackets to expose the core material for chemical attack. Sawing, disassembly, slug removal from Na-K-bonded fuel tubes, and shearing of oxide fuels have been studied. The mechanical processing equipment now under development with nonirradiated material will be installed in the recently completed segmenting facility, which is provided with 6 ft of concrete shielding and is equipped to handle full-length and fully irradiated power reactor assemblies. Facilities for handling fuel element carriers weighing 50 tons and for horizontal charging of fuel assemblies to the segmenting facility have been provided. A preliminary sketch of the layout of the largest of the three cells in the facility is shown in Fig. 1.16. In a second cell various leaching devices will be tested; a preliminary layout is given in Fig. 1.17.

#### Sawing

Extensive abrasive-disk sawing tests, run to simulate end-box removal from fuel elements, were made on single and multiple stainless steel fuel bundles. A 16-in.-dia Manhattan No. 239 blade operated in air was used in these tests. In sawing through a triangular bundle of three 0.5-in.-dia type 347 stainless steel rods at a blade speed of 10,450 surface ft/min, the feed rate was varied from 10 to 60 in./min; smoothest cuts, fewest burrs, and best operation were observed at a feed rate of 25 to 30 in./min. At rates above 60 in./min, blade damage and an excessive amount of metal slivers were produced. At 10 in./min the volume and weight ratios of metal removed to blade consumed were 4 and 11.9, respectively; at 40 in./min the ratios were 2.5 and 7.7. About 43% of all particles produced in sawing were  $<150 \mu$  in diameter; 1.6% were  $>2000 \mu$ . Based on these data, the volume and weight of sawing debris produced in removing end

boxes from a Gas Cooled Reactor and a Consolidated Edison fuel element were calculated to be 16.3 and 184 cc and 123 and 1252 g per assembly, respectively.

#### Disassembly

Since many of the proposed power reactor fuels are assemblies of cylindrical tubes spaced by ferrules and joined by various brazing alloys, a number of tools for removing the ferrules or splitting the fuel tube bundles were built and tested. A multihole drawing die was unsuccessful because of buckling of the tubes during the drawing. An air-hammer-driven impact wedge split prototype Consolidated Edison assemblies into quarter sections, planes, and individual tubes when the ferrules and tubes were brazed with Microbraz 50, the 10% phosphorus in which imparts considerable brittleness to the braze. However, this technique did not break joints made with Coast Metals 50 brazing compound, which is more ductile than Microbraz 50.

#### Slug Removal from Na-K-Bonded Fuel Tubes

A device was designed, constructed, and tested on unirradiated prototype Sodium Reactor Experiment fuel tubes for removal of the Na-K-bonded uranium slugs from the stainless steel tubes. The end sections of single fuel tubes are first cut off with the abrasion saw. The slug removal sequence starts with the plugging of one end of the fuel, followed by application of hydraulic pressure to expand the jacket away from the core. The plug is then removed and core slugs are discharged with hydraulic pressure or by a ramrod, a screw follower for use when the slugs jam in the tube. The dejacketed slugs are freed from oil and Na-K by exposure to live steam under carefully controlled conditions.

The decladder and its auxiliary equipment are being installed in cell A of the segmenting facility (Building 3026) and will be used to mechanically disassemble the fuel from the SRE Core 1 (expected in December 1959). The declad slugs will be recanned in aluminum and transported to Building 3019 for chemical dissolution and solvent extraction.

#### Shearing of Oxide Fuels

A large number of shearing tests have been made on whole fuel tube bundles, quartered assemblies, and individual tubes both at ORNL and under

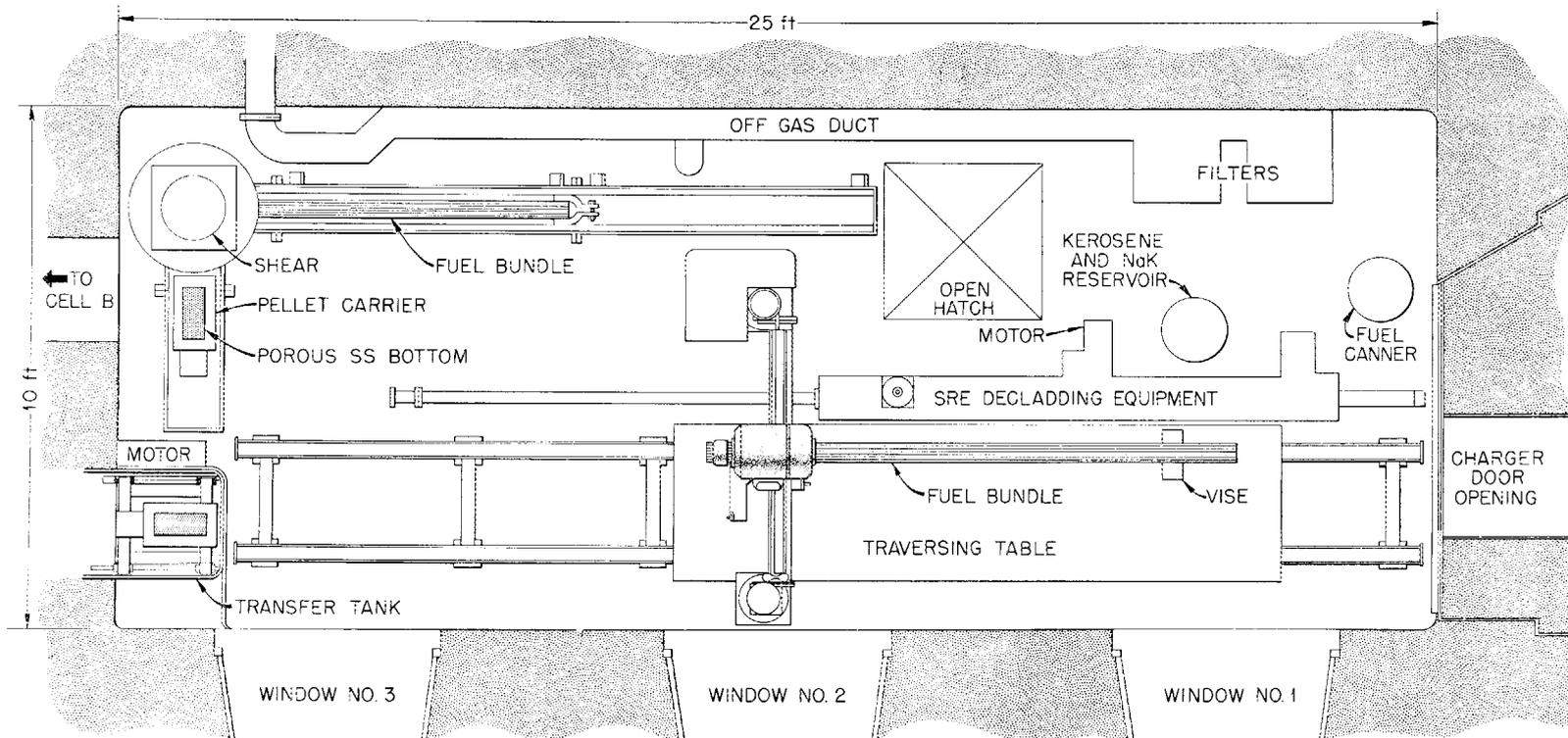
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Fig. 1.16. Preliminary Layout of Dismantling and Shearing Cell of the High-Level Segmenting Facility for Mechanical Reprocessing.

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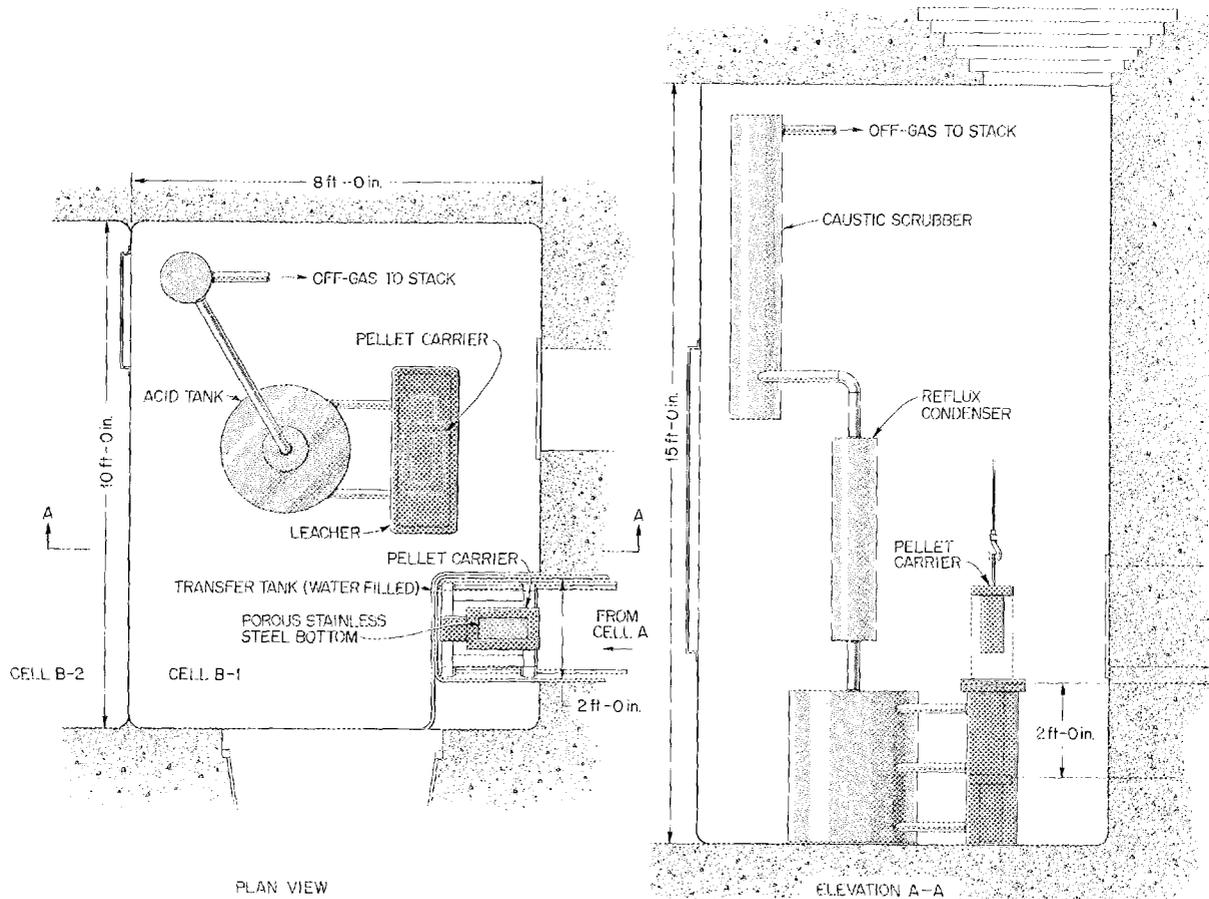


Fig. 1.17. Preliminary Layout of Leaching Cell in High-Level Segmenting Facility.

subcontract with Birdsboro Steel Foundry and Machine Company and with Clearing Machine Corporation of U.S. Industries, Inc. These tests indicate that shearing of a Yankee assembly will require a shear with a thrust of 270 tons and one adequate to shear an NS "Savannah" element will require a thrust of 370 tons. We have decided that a 270-ton thrust should be set as the upper limit, and that assemblies larger than those used by Yankee should be quartered longitudinally before shearing.

In shear blade tests performed by Clearing Machine Corporation,<sup>19</sup> 0.5-in. stainless steel

<sup>19</sup>Final Report on Designing and Testing of a Fuel Element Shear, U.S. Industries, Clearing Machine Division, 59-12, July 10, 1959; D. E. Willis, Trip Report to Clearing Division of U.S. Industries to Witness Shear Blade Tests, ORNL CF-59-7-96.

tube porcelain (stand-in for  $UO_2$ ) bundles, blade speeds of 55.2 and 0.833 in./sec were shown to be applicable, but galling and scoring were greater at the higher speed; longer blade life can be expected at lower speeds. The end openings of all cut pieces produced during the test exceeded 20% of the original cross-sectional area. Rounding of the cutting edge of the shear blade increased power requirements by about 25%, but the blade produced satisfactory cuts. Although blade life cannot be predicted by the results of these tests (only 300 cuts made per test blade), it is probable that greater than 10,000 cuts can be made without changing the shearing characteristics.

In order to provide minimum-cost materials for fuel disassembly and shearing tests, a prototype fuel assembly (Figs. 1.18 and 1.19), a 4 x 4 in. square containing 36 stainless steel tubes, was

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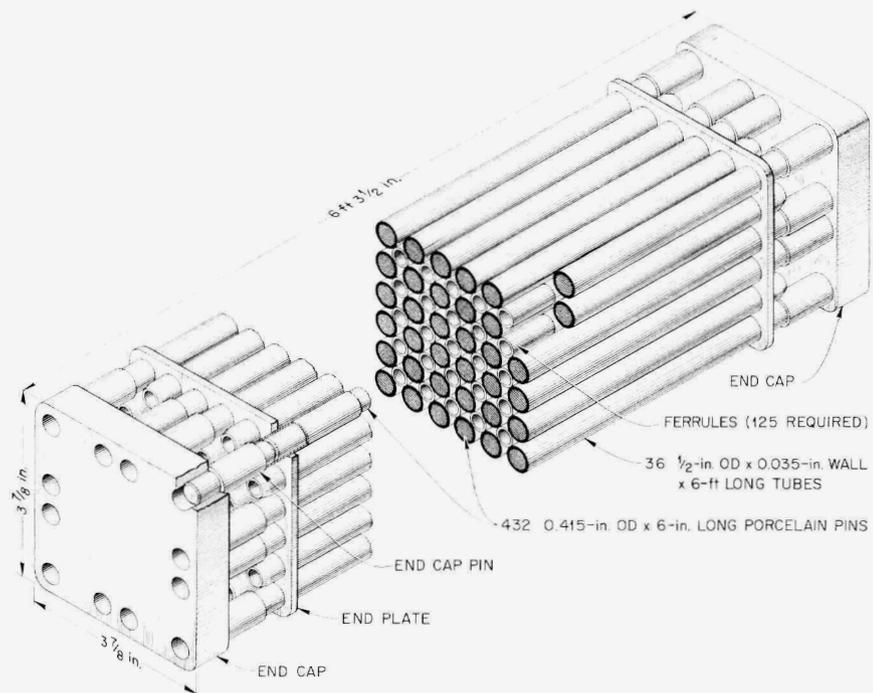


Fig. 1.18. Prototype Fuel Element Mark I.

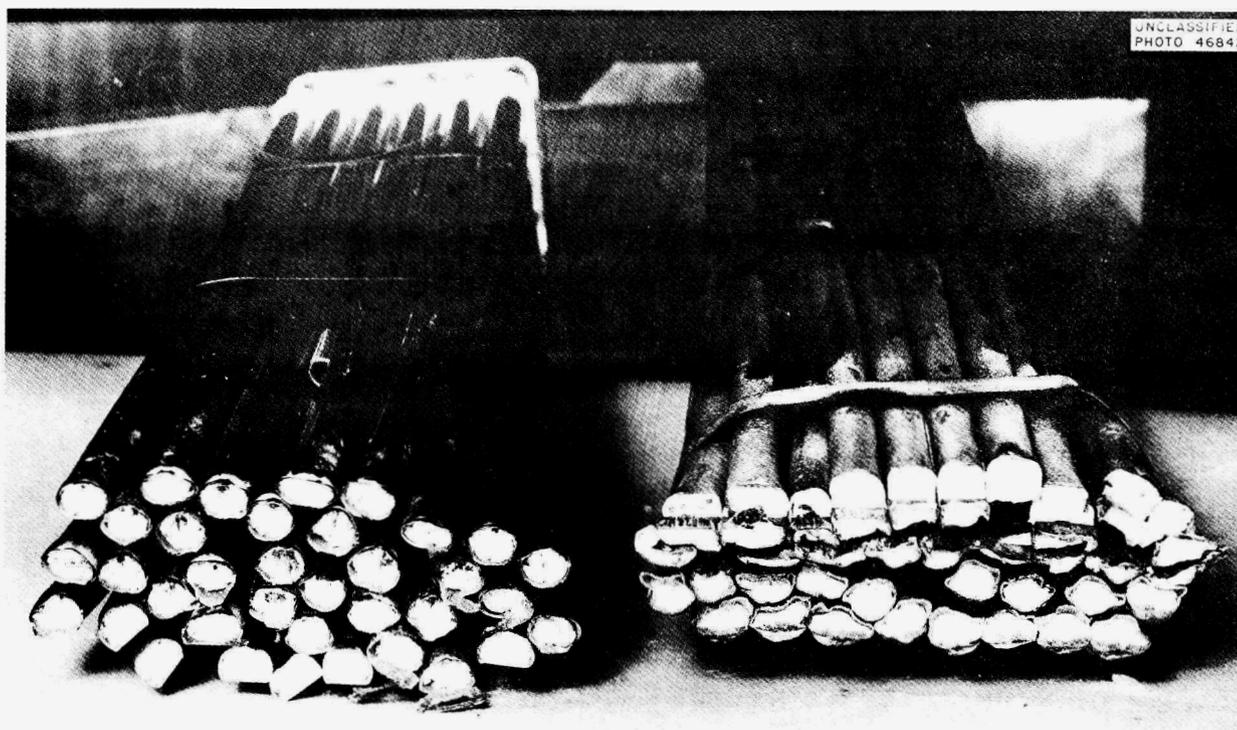


Fig. 1.19. Typical Sheared Sections of Mark I.

manufactured in quantity at a cost of ~\$500 each, 1 to 10% of the cost of rejected power reactor assemblies. Most of the simulated assemblies were filled with solid porcelain rods; a few, for use in leaching tests, were filled with  $UO_2$  and  $ThO_2-UO_2$  pellets.

Shearing tests were made with a Buffalo Forge shear, a 60-ton Manco shear, a 125-ton Manco shear, and a 150-ton Clearing shear. A variety of blade shapes were evaluated. Under optimum conditions cuts could be made to produce pieces with less than 50% closure of the tube area. Ferrules brazed to the tubes with Nicrobraz 50 were broken loose during shearing. Fines were produced by the action of the shear, mostly of oxide but also containing some of the stainless steel clad; the total amount of pulverized core material varied with the length of the cut section.

The quantity of fines produced in shearing single 0.4-in.-dia stainless-steel-clad  $UO_2$  rods varied linearly from 30% for  $\frac{1}{2}$ -in. cut lengths to 2% for those 5 in. long with a 60-ton shear (Manco) and a line-of-contact blade. The fines produced can be estimated empirically by the following expression, applicable to cut lengths from  $\frac{1}{2}$  to 5 in.:

$$\% \text{ fines} = 13(\text{cut length})^{-1.2}$$

The  $UO_2$  fines from  $\frac{1}{2}$ -in. cuts were 30%  $<40 \mu$ , 64%  $<200 \mu$ , 98%  $<1000 \mu$ , and 99.99%  $<2000 \mu$ .

Because fine fragments of cladding metal are produced by shearing action, as indicated by tests with stainless steel tubes, it is possible that shearing of zirconium-alloy-clad fuels prior to an acid leach might produce limited explosions or violent reactions between finely divided freshly cut zirconium; for this reason, shearing of zirconium-metal-containing assemblies may be unwise.

#### Leaching of Sheared Fuel

The leaching of unirradiated PWR  $UO_2$  pellets in stainless-steel-clad fuel tubes sheared into 1-in. lengths required 2 to 4 hr for completion. A 150% excess of boiling 10 M  $HNO_3$  was used. The dissolution time for the unclad PWR pellets ( $\frac{3}{8}$  in. dia  $\times$   $\frac{3}{8}$  in. long) was 20 to 40 min under the same conditions (Fig. 1.20). The range in dissolution rates was due to variations in individual pellets.

Both batch- and continuous-leaching equipment designs were completed, and a batch leacher

(Fig. 1.21) and a continuous vibrating spiral leacher (Fig. 1.22) were constructed and installed and are now being tested with unirradiated sheared fuel. An inclined-drum leacher is being fabricated. The capacity of the batch dissolver is 100 kg of uranium. The sheared fuel is transferred in screen or porous metal (1000  $\mu$ ) baskets to the critically safe 9-in.-dia out-riggers, where the  $UO_2$  is leached from the stainless steel with 8 to 10 M  $HNO_3$ . The stainless steel rings are removed in the porous basket. Insoluble fines ( $<1000 \mu$ ), which fall to the bottom of the out-riggers, are easily removed by fluidizing and jetting. The vibrating spiral leacher is a modified Syntron conveyer. Cut fuel tubes are thrown up the 30° slope counter-currently to nitric acid flowing downward. The vibration amplitude upward is  $\frac{1}{16}$  in.; the return vibration is damped. The device will hold about 53 lb of 0.5-in.-dia  $\times$  1-in.-long stainless steel tubes initially containing 164 lb of  $UO_2$ . Adequate liquid coverage of the tubing is maintained at a nitric acid flow of ~1 gpm; higher flow rates tend to wash the tubing down hill.

#### 1.6 HERMEX PROCESS

In the Hermex process, uranium or thorium metal fuel is dissolved in mercury to separate the uranium from fission products. Uranium solubility in mercury increased from 0.0067 to 1.18 wt % as the temperature was increased from 40 to 356°C. The heat of uranium solution was calculated to be  $6.6 \pm 0.1$  kcal/mole. In 0.1 wt % magnesium amalgam the uranium solubility was 0.0056 wt % at 20°C, increasing to 1.41 wt % at 356°C. The solubility of thorium in mercury increased from 0.0021 wt % at 40°C to 0.0295 wt % at 356°C. A heat of solution of approximately 3 kcal/mole of thorium was calculated.

Because of the great difference in the solubilities of uranium and thorium in mercury it was thought that a method of separation could be devised. However, extraction of uranium from thorium was incomplete because of coprecipitation of  $UHg_4$  with  $ThHg_3$  and coating of the alloy with an insoluble layer of  $ThHg_3$ , preventing further attack by mercury. In a mutually saturated solution of uranium and thorium, uranium solubility was approximately unchanged at the boiling point of mercury, but at 25°C the uranium solubility was only 20% of that in pure mercury. Thorium solubility at 25°C was half that at 356°C. The decrease

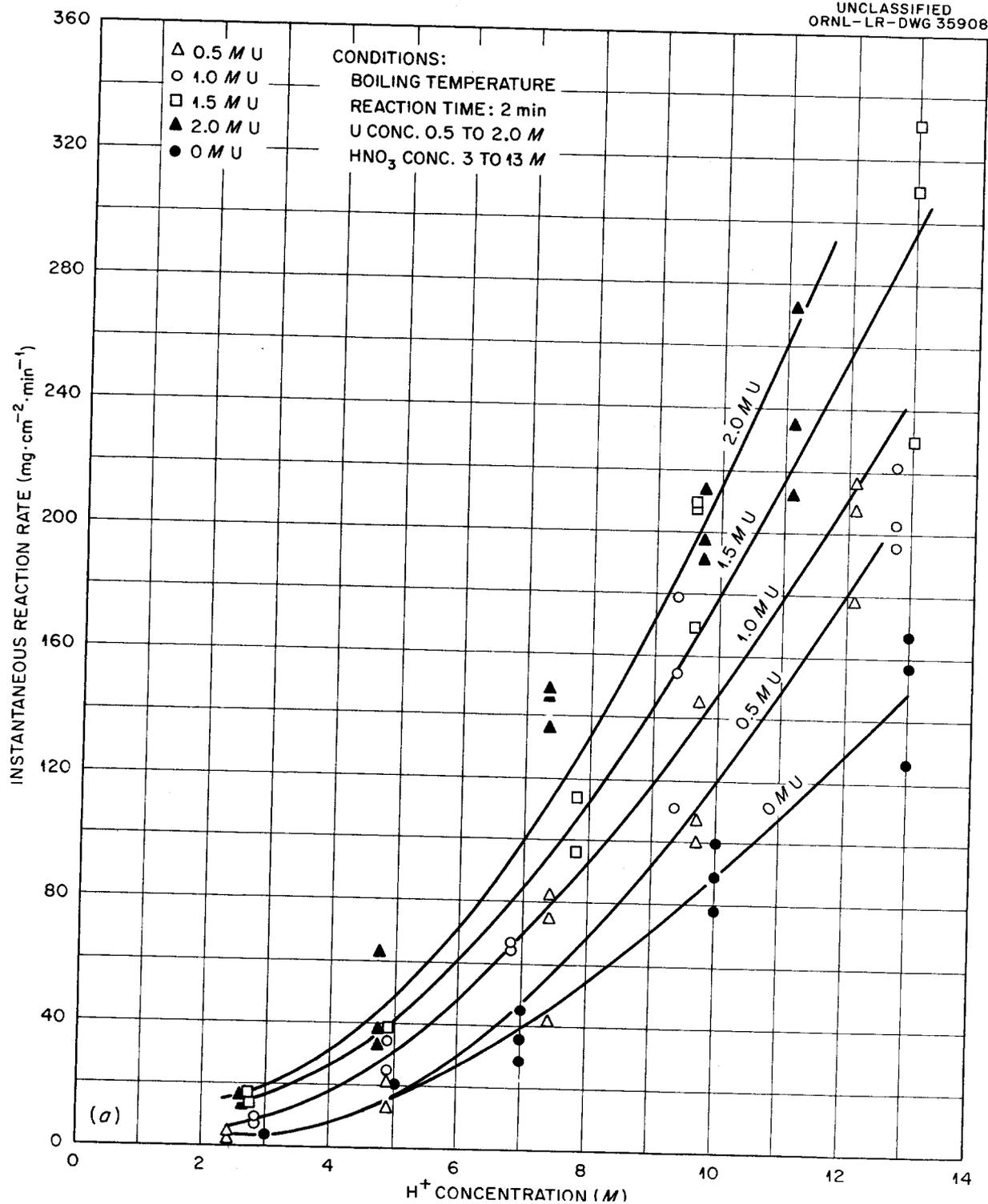


Fig. 1.20a. Effect of Nitric Acid Concentration on UO<sub>2</sub> Dissolution Rates at Various Uranium Concentrations.

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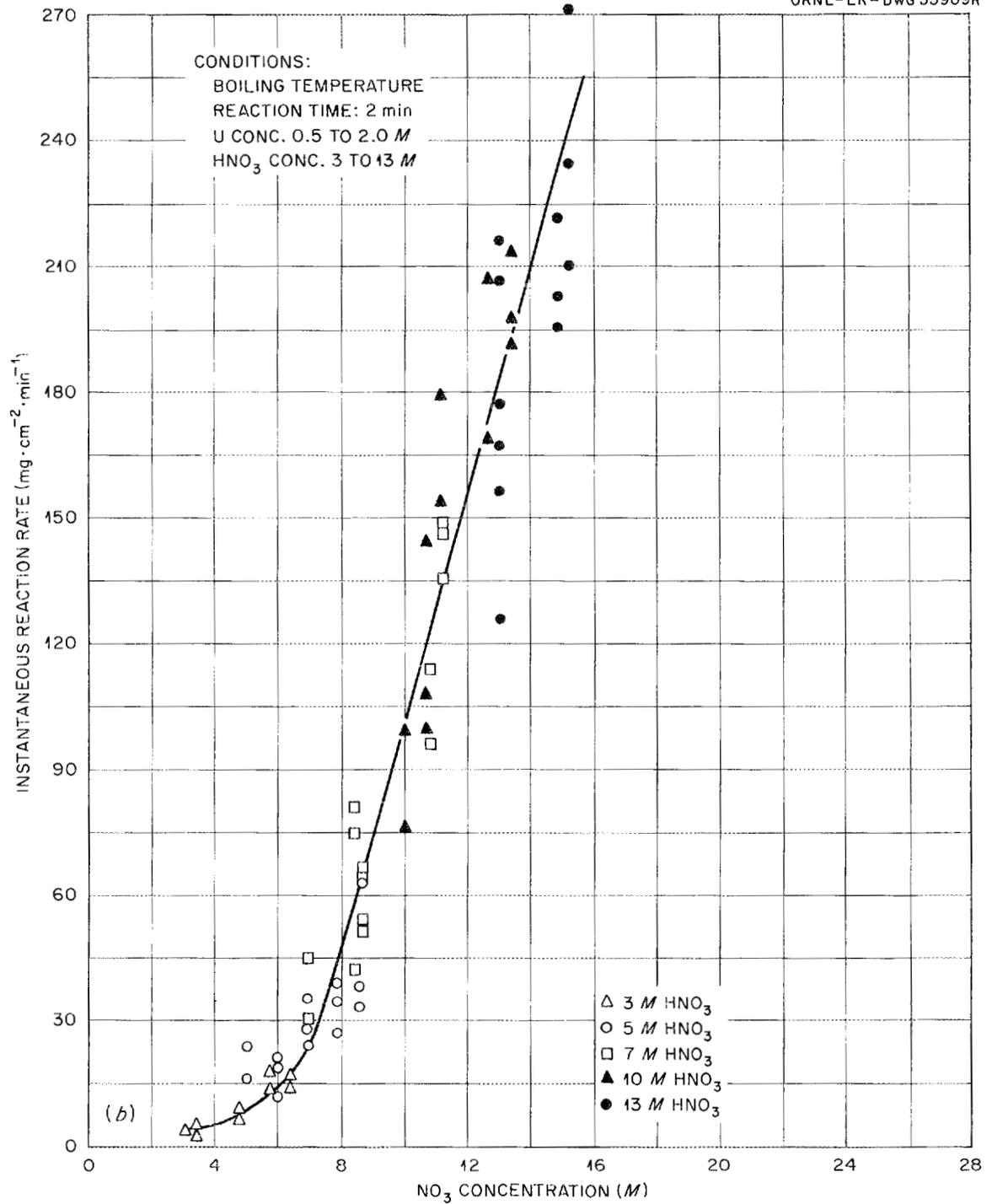


Fig. 1.20b. Effect of Nitrate Ion Concentration on UO<sub>2</sub> Dissolution Rates at Various Uranium Concentrations.

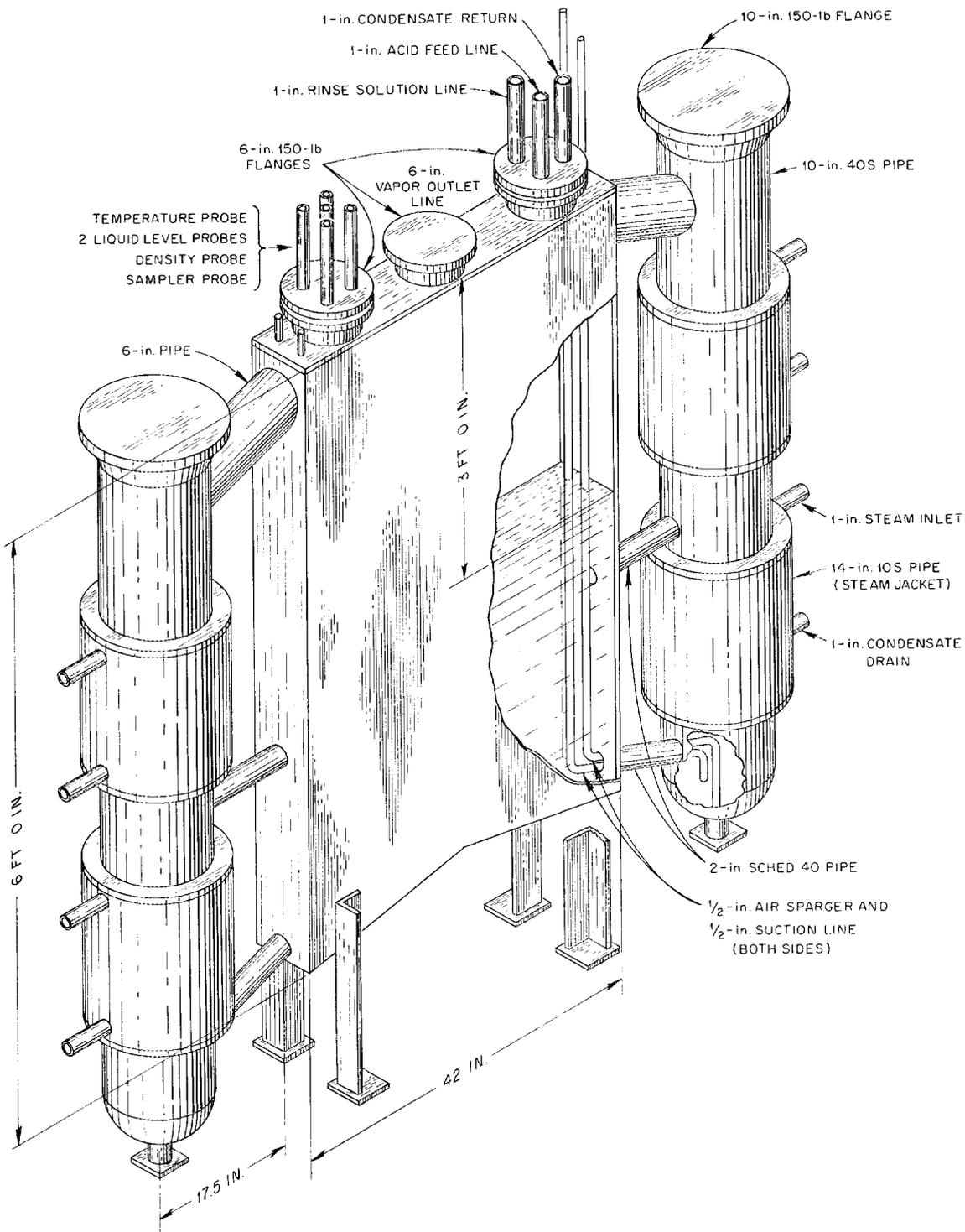


Fig. 1.21. PRFR Batch Dissolver for Mechanical Reprocessing of Spent Reactor Fuels.

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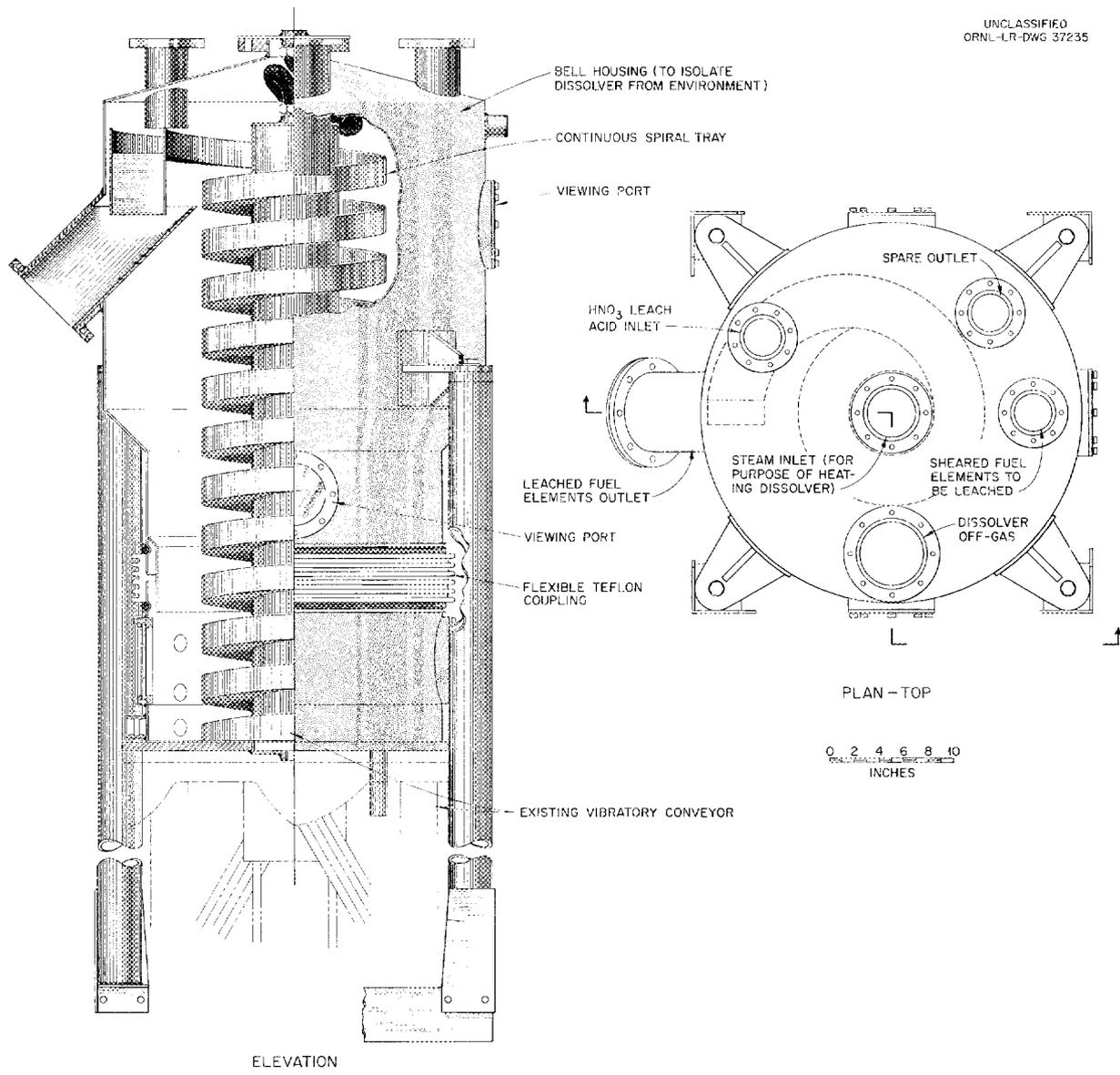


Fig. 1.22. Continuous Vibrating-Tray Leacher with Modified Syntron Spiral Conveyor.

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in solubilities is believed due to coprecipitation of the mercurides. From these data it was calculated that the uranium/thorium ratio in a single mercury extraction would be >400 times that in irradiated fuel of 4000 g of uranium per ton of thorium. In actual extraction experiments, however, this ratio in the mercury extract from a single extraction was greater by a factor of only 50 for a 0.4 wt % uranium-thorium mixture and by a factor of only 6 for an alloy of the same proportions.

### 1.7 SOLVENT EXTRACTION FLOWSHEET DEVELOPMENT

Feeds prepared by the various head-end methods described in the previous sections were solvent-extracted to evaluate decontamination from fission products, recoveries of uranium, thorium, and plutonium, flooding and HETS values, and interfacial solids and emulsion formation. Most of the work was with TBP systems. Four basic flowsheets were studied and modified as required: the Purex system for high and intermediate uranium concentrations (and plutonium) using 15 to 30% TBP and nitric acid or stainless steel salting; the TBP-25 system using 2.5 to 10% TBP and aluminum or stainless steel salting; the Interim-23 system for recovery of uranium using 2.5 to 10% TBP and aluminum or thorium salting, in which the thorium reports to the waste stream; and the Thorex system for simultaneous uranium and thorium recovery using 42.5% TBP and aluminum salting.

#### Purex Process Flowsheet

Feed prepared from unirradiated prototype Yankee Atomic fuel by Darex dissolution and chloride removal was successfully processed with 30% TBP in Amsco in a 2-in. glass pulsed column. Flooding occurred at 615 gph/ft<sup>2</sup> at a pulse frequency of 60 cpm; at 75% of flooding the uranium loss was 0.13% in 8 ft of extraction height; the HETS was 3.6 ft. The feed contained 30 g of stainless steel and 126 g of uranium per liter and <50 ppm of chloride and was 2.16 M in HNO<sub>3</sub>. The feed/scrub/solvent ratio was 10/2/15.

#### TBP-25 Process Flowsheet

Satisfactory flowsheets were developed for 20%-enriched U<sup>235</sup> foreign research reactor uranium-aluminum fuel and for APPR-Darex fuel solutions. The first-cycle solvent extraction feed for foreign

research reactor fuel is 1.0 M Al(NO<sub>3</sub>)<sub>3</sub>-0.5 M HNO<sub>3</sub> and contains gram quantities of uranium and milligram quantities of plutonium per liter. A 6% TBP flowsheet was selected (over 2.5%) to obtain maximum extraction efficiency consistent with criticality control. The uranium  $E_a^o$  is 20 for 6% TBP vs 2.7 for 2.5% TBP at 0.5 M HNO<sub>3</sub>. Nitrite was added to the unirradiated feed (which was spiked with plutonium) to obtain maximum plutonium extraction [ $E_a^o$  for Pu(IV) of 7.6] and 0.03 M Fe(NH<sub>2</sub>SO<sub>3</sub>)<sub>2</sub> added to the partitioning zone scrub to achieve maximum uranium separation from Pu(III). Nitric acid was unsatisfactory as an extraction scrub, the distribution coefficients for uranium and plutonium being 0.05 and 0.003, respectively, vs 1.15 and 0.04 when aluminum salting was used. The total uranium loss was 0.004%; the plutonium loss to waste was 0.03% and to the uranium product <1%.

For better criticality control, a 2.5% TBP flowsheet was developed for APPR fuel solution from the Darex process. Extraction conditions were as follows:

Feed	100 volumes; 5.65 g of U per liter, 3 M HNO <sub>3</sub> , 1 M Fe(NO <sub>3</sub> ) <sub>3</sub> , 0.21 M Cr(NO <sub>3</sub> ) <sub>3</sub> , 0.14 M Ni(NO <sub>3</sub> ) <sub>2</sub>
Scrub	40 volumes; 3 M HNO <sub>3</sub> , 0.75 M Al(NO <sub>3</sub> ) <sub>3</sub> , 0.03 M Fe(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub>
Solvent	200 volumes; 2.5% TBP in Amsco
Strip	50 volumes; 0.01 M HNO <sub>3</sub>

Addition of ferric nitrate to the feed sufficient to increase the iron content of the feed from its original value of 0.63 to 1 M assisted materially in decreasing uranium losses. The distribution coefficient for uranium, which was 1.6 at 0.63 M Fe<sup>+++</sup>, was increased to 3.8 at 1 M Fe<sup>+++</sup>, thereby decreasing the number of stages required for good uranium extraction to more practical values. Experiments were started in which ferric nitrate is used exclusively as scrub, which would eliminate aluminum from the extraction waste completely.

#### Thorex and Interim-23 Process Flowsheet Development

Solvent extraction flowsheets were studied for use with stainless-steel-clad ThO<sub>2</sub>-UO<sub>2</sub> (Consolidated Edison) fuel. In one, uranium only is recovered by an Interim-23 flowsheet with 2.5 to 7% TBP; in the other both uranium and thorium are

recovered by a Thorex system using 42.5% TBP and nitric acid, nitric acid-aluminum nitrate, or stainless steel nitrate salting. Two types of Consolidated Edison fuel solvent extraction feeds were investigated. The first, prepared by Sulfex or Darex decladding followed by Thorex dissolution of the  $\text{UO}_2\text{-ThO}_2$ , produced a  $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$  feed containing 0.04 M fluoride and  $>0.1$  M  $\text{Al}^{+++}$ . The second, prepared by combining Darex decladding solution with the Thorex dissolution product, is similar except that it also contains stainless steel nitrates.

A two-cycle 2.5% TBP Interim-23 acid flowsheet was developed in which the first-cycle feed contains 15 g of uranium per liter, 1 M  $\text{Th}(\text{NO}_3)_4$ , 1.2 M  $\text{Al}(\text{NO}_3)_3$ , and 1.0 M  $\text{HNO}_3$  and the scrub is 0.8 M  $\text{Al}(\text{NO}_3)_3\text{-}0.5$  M  $\text{HNO}_3$ ; the second-cycle feed contains 21 g of uranium per liter and 0.8 M  $\text{Al}(\text{NO}_3)_3$  and is 0.1 M acid-deficient; the scrub contains 1.0 M  $\text{Al}(\text{NO}_3)_3$  and is 0.1 M acid-deficient. Decontamination factors for uranium for the first and second cycles were  $3.5 \times 10^5$  and  $7.6 \times 10^4$ , respectively. The high decontamination factors were obtained by providing high TBP saturation.

In tests with a feed [1.5 M Th, 4 M  $\text{HNO}_3$ , 0.1 M  $\text{Al}(\text{NO}_3)_3$ , and 0.04 M fluoride] to which no aluminum was added beyond that in the dissolvent, a satisfactory Interim-23 flowsheet using  $>5\%$  TBP in Amsco now appears feasible. The scrub is 5 M  $\text{HNO}_3$ , 0.003 M phosphate, and 0.01 M ferrous sulfamate and the feed/solvent/scrub ratio is 5/10/2. The feed-plate uranium extraction factor was 1.3 at 50% solvent saturation.

Earlier Thorex studies indicated that thorium could not be extracted by 42.5% TBP-Amsco solvent with nitric acid salting without formation of a second organic phase if solvent saturation is sufficiently high to provide acceptable decontamination factors. Recent laboratory-scale tests with 42.5% TBP in Decalin indicated that use of Decalin diluent will permit nitric acid salting, thereby eliminating the addition of aluminum beyond that needed for fluoride corrosion inhibition in dissolution. The  $\text{Th}(\text{NO}_3)_4\text{-}2\text{TBP}$  complex has a higher solubility in Decalin than in Amsco. A laboratory-scale test of the first-cycle flowsheet was made with five extraction and six scrub stages used under the following stream conditions:

Feed	20 volumes; 1.5 M $\text{Th}(\text{NO}_3)_4$ , 4 M $\text{HNO}_3$ , 0.1 M $\text{Al}(\text{NO}_3)_3$ , 0.04 M $\text{F}^-$
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Extractant	100 volumes; 42.5% TBP in Decalin
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Scrub	20 volumes; 3.2 M $\text{HNO}_3$ , 0.003 M $\text{PO}_4$ , and 0.01 M ferrous sulfamate
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Preliminary data indicate a thorium loss of  $<0.07\%$ , and zirconium-niobium, ruthenium, and total-rare-earth decontamination factors of 300, 93, and  $6.3 \times 10^4$ , respectively. These decontamination factors are generally lower by a factor of 10 than those achieved with the pilot-plant-demonstrated Thorex flowsheet.

In preliminary tests with Consolidated Edison fuel solution containing stainless steel nitrate, ferric nitrate acted similarly to aluminum nitrate as a salting agent and had distribution coefficients close to those of  $\text{Al}^{+++}$ . No decontamination factors have been obtained for this system, but iron, chromium, and nickel were removed to below the limit of analytical detection ( $<0.1$  g/liter). Use of ferric nitrate salting appears satisfactory for both Interim-23 (2.5% TBP) and Thorex (42.5% TBP) types of flowsheets.

As noted in Sec 1.4, the use of soluble poisons for criticality control in Consolidated Edison fuel reprocessing was satisfactory in all head-end operations. The decontamination factors for boron, cadmium, and rare earths with an Interim-23 flowsheet (acid, 2.5% TBP) were 4000, 500, and 3000, respectively; corresponding values for an acid-deficient Interim-23 flowsheet were 9000, 1000, and 15,000, respectively.

#### Protactinium Removal

A new flowsheet using diisobutyl carbinol was demonstrated at  $50^\circ\text{C}$  on a tracer level for removal of protactinium from uranium, thorium, and fission products. The flow ratios and stream compositions were as follows:

Feed	100 volumes; 1.0 M $\text{Th}(\text{NO}_3)_4$ , 0.6 M $\text{Al}(\text{NO}_3)_3$ , 4 M $\text{HNO}_3$
Solvent	40 volumes; 0.6 M $\text{Al}(\text{NO}_3)_3$ , 2.0 M $\text{HNO}_3$
Scrub	75 volumes; diisobutyl carbinol
Strip	8 volumes; 1.0 M $\text{HNO}_3$ , 0.05 M $\text{F}^-$

Under these conditions 99.5% of the protactinium was extracted; decontamination factors for uranium, thorium, zirconium-niobium, ruthenium, and rare earths were  $6 \times 10^2$ ,  $6 \times 10^4$ ,  $2.5 \times 10^2$ ,  $5 \times 10^3$ , and  $4 \times 10^3$ , respectively.

### Solvent Recovery

The most satisfactory of several solvent recovery systems tested involves successively contacting the solvent with two 0.2 volumes of 0.1 M KOH, slurring with 20 g of CaO per liter, removing the lime with two 0.2 volumes of water, and removing the last traces of lime with one 0.2 volume of nitric acid. This treatment is more effective in removing thermal degradation products than irradiation products and was effective for 2.5% TBP-Amsco irradiated to 300 whr/liter and 50% TBP-Amsco that was 5% thermally hydrolyzed. The use of vacuum distillation to concentrate degradation products was unsuccessful because additional decomposition occurred during this operation.

Phosphorus-32-labeled TBP was used to study the solubility of TBP in the Thorex first-cycle product stream and its subsequent removal by Amsco washing or steam stripping. Under conditions duplicating those at the product end of the Thorex first-cycle strip column (aqueous phase, 40 g of Th per liter, 0.008 M  $\text{Al}(\text{NO}_3)_3$ ; organic phase, 7 g of Th per liter, 42.5% TBP in Amsco), the solubility of TBP and of TBP acidic degradation products in the aqueous phase was  $1.08 \times 10^{-3}$  M and  $7 \times 10^{-5}$  M, respectively. About 93% of the TBP was removed by two 0.1 volumes of Amsco washes, and 88% by steam distillation.

Contrary to what was anticipated, the addition of 0.05 M DBP to either freshly purified or used pilot plant solvent (42.5% TBP in Amsco) did not perceptibly increase the extraction of fission products from Thorex feed, probably because of the formation of thorium-DBP complexes in preference to similar fission product complexes. About 75% of the fission product activity was removed from solvents that contained added DBP when the thorium was stripped with a solution containing 0.008 M  $\text{Al}(\text{NO}_3)_3$ , and about 80% was removed from the solvent that did not contain added DBP. Under similar conditions about 1% of the DBP was removed from the solvent. Filtering of stripped solvent did not remove any additional fission product activity and only 0.1% of the DBP. At

least 99% of the DBP was removed from the stripped solvent by contacting with two equivalents of  $\text{Na}_2\text{CO}_3$ . When used filtered pilot plant solvent was treated with a 0.2-volume of 0.2 M  $\text{Na}_2\text{CO}_3$  and filtered again, the organic filtrate contained 1.6% of the fission products. About 18% of the fission products were distributed as solids in the two phases. If insufficient carbonate is used to remove DBP, fission products are also incompletely removed. It was concluded that washing with  $\text{Na}_2\text{CO}_3$  removes DBP completely and can decontaminate solvent from fission products by factors of  $\sim 5$ , but that solids removal is required to achieve higher decontamination consistently. Decontamination factors were  $>50$  on solvent that had been washed with carbonate and filtered.

### Redox Application to Darex and Niflex Feed

Extraction tests were made in packed 2-in. glass and stainless steel columns on Darex and Niflex feed solutions (Tables 1.3 and 1.4). (The Niflex process uses 1 M  $\text{HNO}_3$ -2 M HF to dissolve both stainless steel and zirconium-containing fuel.) The tests included a study of the effect of salting strengths and solvent flow ratios on decontamination and uranium losses and of the effect of silicon content on column flooding. Darex-Redox performance was, in general, more satisfactory than that of Niflex-Redox. With Darex feed, decontamination factors were generally twice those with Niflex feeds; however, the highest Darex decontamination factors were only about 16% of those with a standard Redox flowsheet. The decontamination factor was markedly increased, whereas uranium extraction efficiency was decreased, by decreasing the feed salting strength. The uranium extraction efficiency was improved without significant effect on the decontamination factor by increasing the solvent flow ratio. With increased silicon content flooding values were greatly decreased. However, addition of Mistron, a calcium magnesium silicate, or acidification of the feed markedly increased the flooding values.

Table 1.3. Efficiency and Decontamination Run Summary

Type	Stainless Steel Concentration of Feed (M)	Al Concentration of Feed (M)	Nominal Extraction Section Acidity <sup>a</sup> (M)	Solvent Flow Ratio <sup>b</sup>	Uranium Loss (%)	Scrub/Solvent Flow Ratio	Scrub Acidity (M)	Decontamination Factor	HETS (ft)
Standard <sup>c</sup>		1.18	-0.21	2.26	0.0017				2.0
Darex	1.3		-0.07	2.47	0.0018				3.6
	0.9		-0.26	1.99	0.0027				1.4
	0.8		-0.18	2.83	0.0128				
	0.8		-0.18	2.53	0.0373				
Standard <sup>d</sup>		1.09	-0.16	3.50	0.0322	0.07	0.2 <sup>e</sup>	1802	
Darex	1.2		-0.18	2.44	0.0019	0.13	0.2	59	
	1.2		-0.14	2.54	0.0004	0.20	0.2	35	
	1.2		0.40	2.66	0.0040	0.20	0.2	24	
	0.9		-0.27	1.49	0.1886	0.19	-0.15	221	1.2
	0.4	0.45	-0.04	1.95	0.0097	0.39	-0.15	283	
Niflex	0.25	0.84	0.24	1.34 <sup>f</sup>	0.0018	0.30	-0.15	34	
	0.25	0.84	0.19	1.68	0.0010	0.20	-0.15	27	
	0.16	0.8	0.08	1.80	0.0089	0.28	-0.15	53	
	0.15 <sup>g</sup>	0.75	0.15	1.67	0.1622	0.10	-0.12	135	

<sup>a</sup>Minus denotes acid deficiency.

<sup>b</sup>Relative to feed = 1.

<sup>c</sup>Extraction height for Unit Operations runs = 21.3 ft.

<sup>d</sup>Extraction height for pilot plant runs = 17 ft.

<sup>e</sup>Scrub length = 21 ft.

<sup>f</sup>Hexone for the run acidified to 0.1 M.

<sup>g</sup>Feed also contained 0.009 M Mo.

Table 1.4. Flooding Rate Determination Summary

Type	Aqueous/Organic Flow Ratio	Solvent Flow Ratio*	Feed Composition				Nominal Extraction Section Acidity (M)	Flooding Rate (gph/ft <sup>2</sup> )
			U (M)	Al + Stainless Steel (M)	Si (M)	Mistron (ppm)		
Standard	0.50	2.27	1.24	1.18			-0.22	581
Darex	0.60	2.50	0.66	1.3	0.0005		-0.07	594
	0.62	2.00	0.66	1.3	0.0005		-0.12	>644
	0.62	2.08	0.54	0.9	0.011		-0.25	370
	0.50	2.50	0.48	0.8	0.016		-0.23	333
Niflex	0.65	1.85	0.56	1.46	0.001		0.23	694
	0.60	1.90	0.14	0.84	0.0027		1.61	692
Darex	0.41	3.00	0.40	0.8	0.015		-0.18	378
	0.50	2.50	0.40	0.8	0.004		-0.18	484
	0.50	2.50	0.40	0.8	0.015	100	-0.18	815
	0.50	2.50	0.40	0.8		100	-0.18	>741
	0.50	2.50	0.40	0.8		57	-0.18	481
	0.50	2.50	0.40	0.8	0.004		0.38	778

\*Relative to feed = 1.

## 2. POWER REACTOR FUEL REPROCESSING PILOT PLANT

### 2.1 THORIUM PROCESSING

Thorex process development was completed. High-purity (99.6 isotopic %)  $U^{233}$  was separated from decayed protactinium solutions obtained in the short-decayed Thorex runs, all the available thorium was processed according to the Interim-23 flowsheet for  $U^{233}$  recovery, and the  $U^{233}$  product was reprocessed to remove the radioactive daughters of  $U^{232}$  decay.

**Thorex Process Development.** — The last of a series of runs to evaluate the effect of bisulfite addition to irradiated thorium feed on ruthenium decontamination<sup>1</sup> was completed. The plant was operated according to the one-cycle flowsheet. Dissolved thorium feed solutions were made 0.01 M in nitrite by batch addition of  $NaNO_2$ , simulating the feed conditions found in processing 30-day-decayed, 3000–4000 g/ton thorium metal. Ruthenium decontamination factors of 2–4, observed with nitrated feed, increased to 400–500 when the nitrite was destroyed by continuous addition of 0.06 M  $NaHSO_3$  to the feed stream as it was metered to the extraction column. Solvent extraction losses were not increased by the addition of bisulfite to the feeds in the range 0.04 to 0.06 M. Mercury in the feed catalyzed the destruction of bisulfite. Satisfactory dissolution of aluminum-canned irradiated thorium slugs was demonstrated by using only 0.04 M  $F^-$  as catalyst.

**High-Purity  $U^{233}$ .** — The first-cycle raffinates collected during three short-decay processing runs were combined and reprocessed for high-purity  $U^{233}$  recovery. A total of 885 g of uranium assaying 99.6%  $U^{233}$  was recovered and transferred to the Isotopes Division for the preparation of extremely high-purity  $U^{233}$ .

**Interim-23 Processing.** — A total of 10.5 tons of irradiated long-decayed thorium was processed according to the Interim-23 flowsheet for  $U^{233}$  recovery only. The use of the Interim-23 flowsheet increased the thorium processing rate to 400 kg/day, as compared with 180 kg/day with the Thorex process. The rate was limited by the

dissolver capacity. The thorium was discharged to waste storage, and the uranium was isolated by cation exchange. The uranium solvent extraction loss totaled 1.3%.

**$U^{233}$  Reprocessing.** — A total of 27 kg of  $U^{233}$  was reprocessed to remove the radioactive daughters of  $U^{232}$  decay. Approximately 20 kg of this material was processed for use by the Neutron Physics Division in measurements of nuclear properties of pure  $U^{233}$ . The additional 7 kg of  $U^{233}$ , consisting of fluoride-contaminated material, was processed for fluoride removal and decontamination.

### 2.2 URANIUM PROCESSING

Approximately 56,000 kg of irradiated uranium containing 30 kg of plutonium, from BNL, NRX (AECL), and SRO reactors, was processed. The BNL and NRX fuel was dissolved in the Metal Recovery Plant continuous dissolver. With 200% metal heel, uranium was dissolved at a rate of about 500 kg/day, using 7.5–8.0 M nitric acid as dissolver. These conditions produced a solution containing 350–400 g of uranium per liter in approximately 1.0–1.5 M nitric acid. In dissolution, 3.8–4.2 moles of nitric acid was consumed per mole of uranium dissolved. Aluminum cladding was dissolved with the uranium. A standard Purex flowsheet was used for the recovery and decontamination of uranium and plutonium from fission products. Product recoveries for uranium and plutonium exceeded 99%, based on measured losses from the plant. Equilibrium solvent extraction losses for uranium and plutonium were less than 0.25% for three cycles of solvent extraction. Some trouble was experienced in obtaining satisfactory decontamination of uranium from fission products, principally zirconium-niobium. Chemical flowsheet changes were made in an attempt to improve decontamination, but no significant improvement was observed until the first-cycle extraction column was operated with the organic phase continuous. A tenfold increase in gross decontamination in the co-decontamination cycle resulted from this change. Current plans include converting all plant extraction columns to organic-continuous contactors.

<sup>1</sup>Chem. Tech. Ann. Prog. Rep. Aug. 31, 1958, ORNL-2576, p 18.

### 2.3 PLUTONIUM-ALUMINUM ALLOY PROCESSING

Five AECL NRX Pu-Al alloy fuel assemblies containing 1150 g of plutonium were dissolved in 6.0 M nitric acid containing 0.05 M mercuric nitrate to catalyze the aluminum dissolution. The average dissolution rate of the alloy was in excess of  $10 \text{ mg}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ , and the final concentration of the dissolver solution was 0.5 M aluminum nitrate and 4.0 M nitric acid. These fuel assemblies had been exposed to less than 1 Mw of irradiation and did not have the low rate of dissolution that has been observed on highly irradiated fuels of this type. A modified Purex second plutonium cycle extraction flowsheet was used for the recovery and decontamination of plutonium from fission products, and a gross gamma decontamination factor of  $10^3$  was demonstrated for one complete solvent extraction cycle. Product recovery was 99.8%.

<sup>2</sup>See also sec 15.

### 2.4 NEPTUNIUM RECOVERY<sup>2</sup>

Approximately 12.0 tons of selected Paducah fluorinator ash from the recycle of uranium was processed to recover uranium and Np<sup>237</sup>. The flowsheet<sup>3</sup> for recovery and purification of neptunium and uranium provides for dissolution in 1.8 M  $\text{Al}(\text{NO}_3)_3$ -1.0 M  $\text{HNO}_3$  and one solvent extraction cycle, using 15% TBP as extractant.

Product recoveries for uranium and neptunium were 98 and 99%, respectively, and neptunium was separated from the uranium by a factor of  $10^4$ . Two additional runs were made to further test the chemical flowsheet<sup>1</sup> for separation of neptunium and Th<sup>230</sup>, which results from the decay of U<sup>234</sup> in natural uranium. In these two runs, neptunium was separated from thorium by factors of 268 and 211, and neptunium recovery exceeded 99%. This program for recovering neptunium from fluorinator ash was terminated.

<sup>3</sup>J. R. Flanary *et al.*, *Recovery of Np-237 by the Neptex Solvent Extraction Process*, ORNL-2235 (March 1957).

## 3. FUSED SALT-FLUORIDE VOLATILITY PROCESS

In the Fused Salt-Fluoride Volatility process, uranium is recovered from fused-salt reactor fuels and from reactor fuels soluble in fused salts. In this process, uranium fuel elements are dissolved by HF in a molten fluoride mixture. The fused salt is fluorinated to volatile  $\text{UF}_6$ , which is absorbed in NaF traps, and is then desorbed and collected in cold traps. Process development for the recovery of uranium from fused salt has been described.<sup>1-3</sup> Further development has been primarily concerned with the dissolution of zirconium-containing fuel in fused salt.

### 3.1 PILOT PLANT PROCESSING OF FUSED-SALT CRITICALITY FUEL

The fused salt (similar to ARE fuel) used in criticality studies was processed in nine runs in the Volatility Pilot Plant. The chemical and

engineering flowsheets<sup>4</sup> have been published previously. The feed salt contained 72 kg of fully enriched uranium, of which 99.21% was recovered as  $\text{UF}_6$  product and 1.2% was contained in recoverable aqueous solution of the adsorption bed and final equipment washes. The unrecoverable loss in waste salt was 0.01%, with an over-all material balance of 100.4%.

Some of the runs were spiked with highly irradiated material and/or plutonium to extend the limits of decontamination detection. The feed salt

<sup>1</sup>*Chem. Tech. Semiann. Prog. Rep. Sept. 30, 1955, ORNL-2000; Aug. 31, 1956, ORNL-2169; Aug. 31, 1957, ORNL-2392; Aug. 31, 1958, ORNL-2576.*

<sup>2</sup>G. I. Cathers, *Nuclear Sci. and Eng.* **2**, 768-77 (1957).

<sup>3</sup>R. P. Milford, *Ind. Eng. Chem.* **50**, 187-91 (1958).

<sup>4</sup>W. H. Carr *et al.*, *Chem. Tech. Monthly Prog. Rep. Nov. 1957, ORNL-2447, Figs. 10.1a and b; Dec. 1957, ORNL-2468, Fig. 9.1.*

activity in run L-7, the run with the highest beta-gamma activity, in counts per minute per milligram of uranium, was as follows:

Gross gamma	$9.26 \times 10^4$
Gross beta	$4.14 \times 10^5$
Cs gamma	$6.75 \times 10^4$
Nb gamma	$2.0 \times 10^4$
Zr gamma	$1.1 \times 10^4$
Ru gamma	<40
TRE beta	$3.41 \times 10^5$

The  $UF_6$  product had a gross gamma activity of only 8.4 counts/min per mg of U, which is attributed to the activity of the fully enriched uranium itself. There were no detectable fission products in the  $UF_6$  product.

In order to determine whether or not highly irradiated fuel could be processed without excessive plutonium contamination of the  $UF_6$  product, three runs were spiked with approximately 0.01, 1, and 10 g of plutonium, respectively. The plutonium concentration in the product of the run with the 10-g spike was only 3.4 ppb, which is well within tolerance. The plutonium was 99% accounted for:

Feed salt		10.25 g
Waste salt	10.08	
Complexible radioactive products trap	0.054	
First absorber	0.006	
Line washings	0.003	
Fluorinator walls	0.002	
Product	<u>0.00003</u>	
		10.15 g

Modifications to the Volatility Pilot Plant required for processing zirconium-uranium fuel elements are in progress. The new design provides for dissolution of two S1W-1 or S2W-1 subassemblies per batch in a fused salt with initial composition 37.5-37.5-25 mole % NaF-LiF-ZrF<sub>4</sub> and a melting point of 605°C. The final melt composition is 27.5-27.5-45.0 mole % with a melting point of 453°C and a volume of 50.5 liters at 500°C (see Sec 3.5). After successful operation of the plant on a batch basis, the capacity can be increased

to three subassemblies per dissolution by increasing the initial melt volume, drawing off only part of the melt, and leaving a heel of ZrF<sub>4</sub> for the next dissolution.<sup>5</sup>

### 3.2 DISSOLUTION STUDIES

The reaction of HF with zirconium in fused-salt dissolutions was determined to be predominantly gas-phase. This accounts also for the fact that, in all studies made to date, the reaction rate continually increases with increasing HF sparging rate. A laboratory study of the reaction of gaseous HF with Zircaloy metal was made in which temperature and gas composition were kept constant by limiting the amount of exposed metal surface. Since the volatilization of the product ZrF<sub>4</sub> is not complete even at 700°C, bare metal reaction rates for Zircaloy-2 were obtained by extrapolation to zero reaction time. These were found to be 35, 17, and 8 mg·cm<sup>-2</sup>·min<sup>-1</sup> with 35% HF at 725, 695, and 650°C, respectively, and 19 and 12 mg·cm<sup>-2</sup>·min<sup>-1</sup> with 100% HF at 650 and 600°C, respectively.

The hydrogen produced in the hydrofluorination reaction results in hydriding of Zircaloy-containing fuel. Nitriding occurs similarly and complicates the off-gas problem by subsequent formation of volatile ammonium fluoride. Both hydriding and nitriding increase the reaction rate with HF. An HF-H<sub>2</sub>O azeotrope is formed which will cause a serious corrosion problem in handling the off-gas in the processing of oxide fuels. Study of sludge present in the hydrofluorination process before reaction is complete indicated the existence of finely divided nickel metal while reaction with zirconium is proceeding. Dissolution is always accompanied by formation of nickel scale on the reactor wall. The hydrogen produced by the hydrofluorination reaction probably decreases the corrosion rate of the reactor. Corrosion results with hydrogen present confirmed this observation.<sup>6</sup>

### 3.3 FLOWSHEET TEST WITH STR FUEL

In an initial test of the flowsheet with STR-type fuel, the gross beta and gamma activities of the

<sup>5</sup>S. Mann, VPP Hydrofluorination: Choice of Various Na-Li-Zr Fluoride Salt Mixtures and Modified Procedures to Reduce Operating Temperature and Corrosion, ORNL CF-59-5-74 (May 19, 1959).

<sup>6</sup>Progress Relating to Civilian Applications During April 1959, BMI-1340, p 75-76.

product were within the limit of activity of the UY daughter of  $U^{235}$  ( $Th^{231}$ ). The initial dissolution salt composition was 57-43 mole % LiF-NaF, with the final salt composition being 31-24-45 mole % LiF-NaF-ZrF<sub>4</sub> (Fig. 3.1). The alloy fuel was hydrofluorinated at 700–600°C, the higher temperature being used initially because the initial liquidus temperature is 690°C. Uranium is fluorinated to UF<sub>6</sub> in the range 450–500°C to minimize corrosion and to achieve maximum product decontamination.

Over-all decontamination factors were as follows:

Ru gamma	$>5 \times 10^7$
Zr gamma	$>3 \times 10^6$
Nb gamma	$>6 \times 10^6$
Cs gamma	$>6 \times 10^8$
Sr beta	$>2 \times 10^8$
TRE beta	$1.5 \times 10^6$
Pu alpha	$8.5 \times 10^3$

None of the gamma activities were detectable in the product. Molybdenum and chromium appeared to be the major ionic impurities in the product, although the chromium content was decreased by operating with the second NaF bed at 400°C. Molybdenum hexafluoride passes through the NaF absorption-desorption step with the UF<sub>6</sub> product.<sup>7,8</sup>

<sup>7</sup>W. A. Brooksbank et al., *Volatility Studies of Some Fission Product Fluorides*, ORNL CF-58-6-86 (June 1958).

<sup>8</sup>Houdry Process Corporation, *Fluoride Volatility Process - Third Quarterly Report, 1958*, 58-OCR-52 (September 1958).

### 3.4 PROTOTYPE DISSOLVER STUDY

The dissolution of zirconium prototype Zr-U fuel elements by hydrogen fluoride in fused fluorides is a result of reaction between the gas and the metal. Maximum dissolution rates were obtained under conditions of mixing which promoted maximum contact between gas and metal and maximum reaction product removal by fused salt. The maximum dissolution found by optimizing these conditions was 3 mg per min per cm<sup>2</sup> of total surface present. The dissolution rate for totally and partially submerged elements increased rapidly with increasing superficial velocity of hydrogen fluoride, as a result of higher liquid phase mixing rates (Fig. 3.2). Partially submerged elements reacted more rapidly than totally submerged elements because of increased gas phase reaction rates. The gas phase reactions were carried to completion at 650°C because of continuous reaction product removal by fused salt. Variations in salt compositions had only small effects. In successive dissolutions in the same NaF-ZrF<sub>4</sub> bath the increased ZrF<sub>4</sub> concentration (from 38 to 44 mole % ZrF<sub>4</sub>) did not affect the rate significantly.

The dissolution rate studies were made with prototype fuel elements ranging from 0.6 to 6.0 kg in weight; initial salt compositions of 38-62 mole % ZrF<sub>4</sub>-NaF and 57-43 mole % LiF-NaF; salt temperatures of 600, 650, and 700°C; and hydrogen fluoride feed rates of 1 to 6 lb/hr. Three vessel configurations were used (Fig. 3.3). In all cases the anhydrous hydrogen fluoride was introduced below the fuel support plate; fuel assemblies were placed vertically on the support

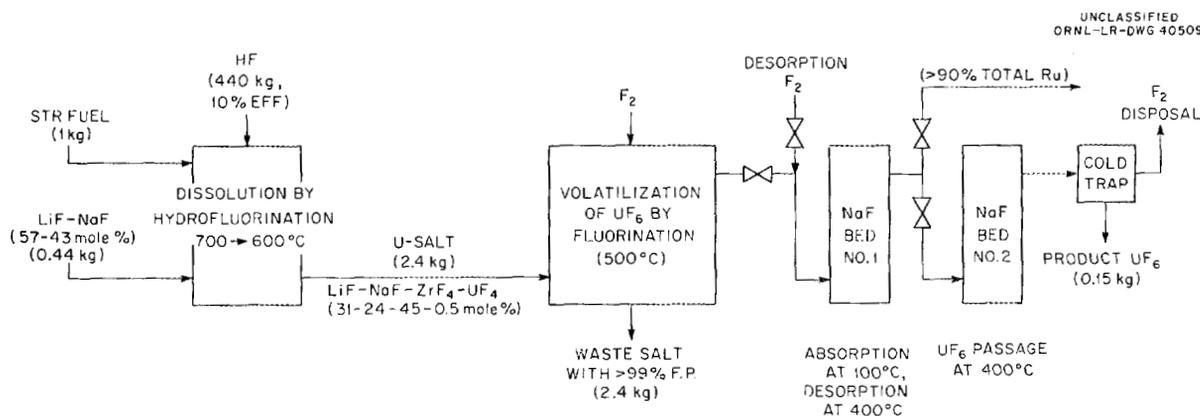


Fig. 3.1. Fused Salt-Fluoride Volatility Process for STR Fuel.

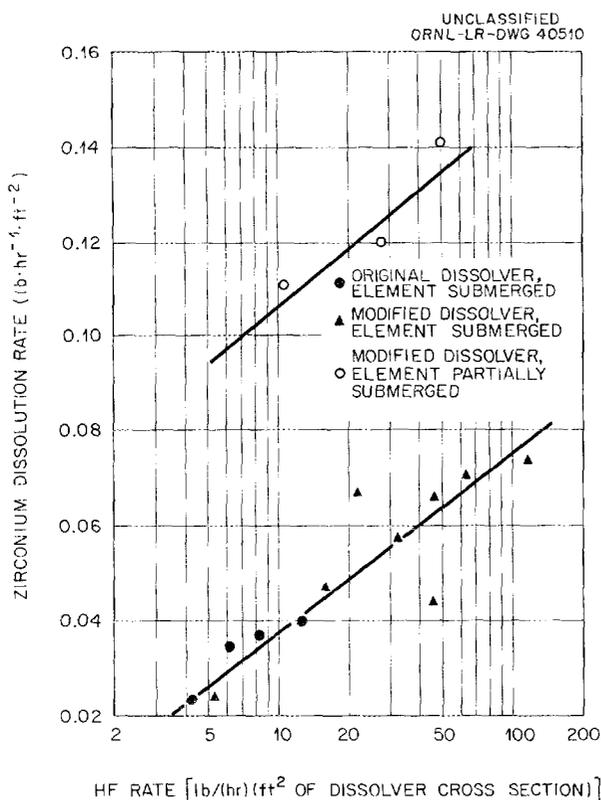


Fig. 3.2. Effect of Rate of HF Addition on Rate of Dissolution of Zirconium in Molten NaF-ZrF<sub>4</sub> (Initial Composition: 38-42 mole % ZrF<sub>4</sub>) at 650°C.

plate. In the modified copper-lined dissolver the decreased cross section at the point where acid contacted the fuel assembly submerged in salt made possible high gas velocities and good mixing in this region, with good de-entrainment in the upper portion. High gas velocities in the original vessel had resulted in carry-over of salt into the off-gas system. The INOR-8 dissolver was designed to provide a high-velocity region and included a draft tube intended to promote circulation of fused salt past the fuel assembly. The highest dissolution rates and acid utilization rates were obtained in this vessel.

### 3.5 HYDROFLUORINATOR CORROSION STUDIES

The Volatility Pilot Plant hydrofluorinator was fabricated from INOR-8 with a wall corrosion allowance of 125 mils. A penetration rate of 25 mils/month during exposure to HF-NaF-LiF at 20 lb/hr at an average temperature of 600°C is predicted, assuming that corrosion is proportional to the total amount of HF introduced into the vessel. This predicted rate was based on results of corrosion measurements of a draft tube in an ORNL prototype hydrofluorinator in which the penetration rate was 1 mil/month at 600°C and greater by a factor of 13 at 700°C.

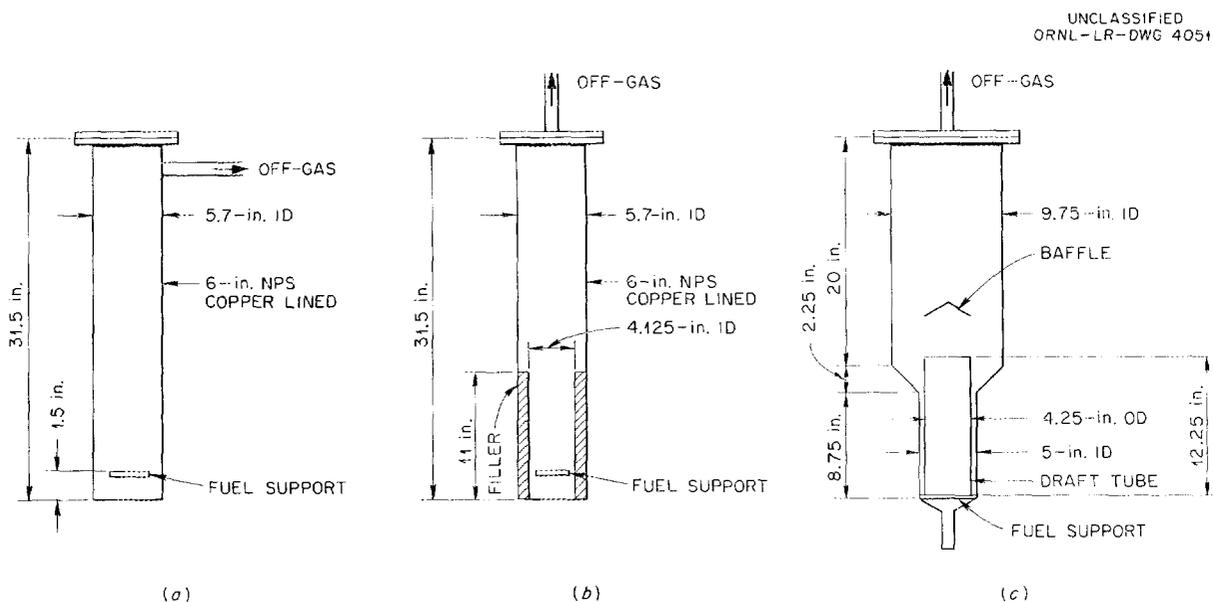


Fig. 3.3. Dissolver Vessels: (a) Original Copper-Lined Dissolver, (b) Modified Copper-Lined Dissolver, (c) INOR-8 Dissolver.

Laboratory-scale corrosion studies were made at Battelle Memorial Institute<sup>9</sup> with low HF flow rates and in the prototype hydrofluorinator at ORNL in which HF velocities are 100 times greater than those used at Battelle and approach those expected in the pilot plant. Tests at both locations substantiated the following conclusions: (1) The corrosion rate increases with increasing temperature and increasing rate of flow of HF through the melt; (2) the corrosion rate decreases when the concentration of  $ZrF_4$  in the melt is increased and when zirconium is being dissolved

in the melt; and (3) the highest corrosion rates are at the melt-vapor interface.

An average ORNL prototype hydrofluorinator wall corrosion rate of approximately 36 mils/month was found while dissolving Zircaloy-2 at 700°C with the HF rate at 4–6 lb/hr for half the run and at 1–3 lb/hr for the other half. Because of the large effect of temperature on corrosion rate, pilot plant flowsheet initial and final dissolution temperatures were decreased from 700 and 600°C, respectively, to 650 and 500°C. The lower dissolution temperature was accomplished by changing the initial melt composition from 57-43 mole % LiF-NaF (mp 652°C) to 25-37.5-37.5 mole %  $ZrF_4$ -NaF-LiF (mp 605°C).

<sup>9</sup>P. D. Miller *et al.*, *Construction Material for the Hydrofluorinator of the Fluoride-Volatility Process*, BMI-1348 (June 3, 1959).

#### 4. MOLTEN-SALT REACTOR FUEL PROCESSING

The Molten-Salt Reactor fuel, uranium fluoride dissolved in a mixture of fluorides, is processed by fluorination to recover the uranium (Fig. 4.1), and the solvent salt is purified by dissolution in concentrated aqueous HF. Uranium recovery by fluorination was reported previously.<sup>1</sup> Plutonium is not volatilized from the salt by fluorination at temperatures up to 750°C.

The fuel studied was 62 mole % LiF–37 mole %  $BeF_2$ –1 mole %  $ThF_4$  containing less than 1 mole %  $UF_4$ . The LiF- $BeF_2$  was separated from the major neutron poisons (rare earths and neptunium) by dissolution in essentially anhydrous HF, followed by distillation of the HF. The LiF and  $BeF_2$  solubilities varied with the HF concentration, being 60 to 80 g/kg for each in 90% HF. As the HF concentration increased to 100%, the LiF solubility increased to 110 g/kg and the  $BeF_2$  decreased to about 30. Evaporation of a solution of salt in 90% HF followed by fusion of the salt regenerated the LiF- $BeF_2$  without significant hydrolysis.

The rare-earth solubility in such HF solutions (based on dissolved LiF +  $BeF_2$ ) increased from  $10^{-4}$  mole % in 100% HF to 0.003 mole % in 80% HF. The decontamination factor was linearly dependent on the rare-earth concentration in the

fuel and therefore on the processing cycle time; with a one-year cycle the decontamination factors were found to be 50 and 16 for 100 and 80% HF, respectively. The solubility of neptunium was approximately the same as that of the rare earths, but decontamination was lower because of a lower initial fuel concentration. Neptunium(III) was less soluble than Np(IV), and the solubility decreased further when uranium, thorium, rare earths, and plutonium were present. When all these elements were present in concentrations expected in the fuel salt, the neptunium solubility was about  $5 \times 10^{-5}$  mole %. It appears likely that the trivalent metals – rare earths, plutonium, and probably neptunium – behave as a single group, so that the presence of all will repress the solubility of each. The tetravalent elements – uranium, thorium, and zirconium – behave similarly.

Investigation of alternative methods that might simplify or improve the process was started. Addition of 5 wt %  $ClF_3$  to anhydrous HF resulted in appreciable solubility of uranium, 3 to 6 g/kg, along with the LiF and part of the  $BeF_2$ ; without  $ClF_3$  the uranium solubility was of the order of 0.01 g/kg. Preliminary experiments indicated the feasibility of recovering LiF decontaminated from fission product cesium by dissolution of the fuel salt in 90% HF followed by partial distillation of HF to leave a 40–50% HF solution. The LiF was precipitated, the CsF remaining in solution.

<sup>1</sup>*Chem. Tech. Ann. Prog. Rep. Aug. 31, 1958, ORNL-2576, p 43.*

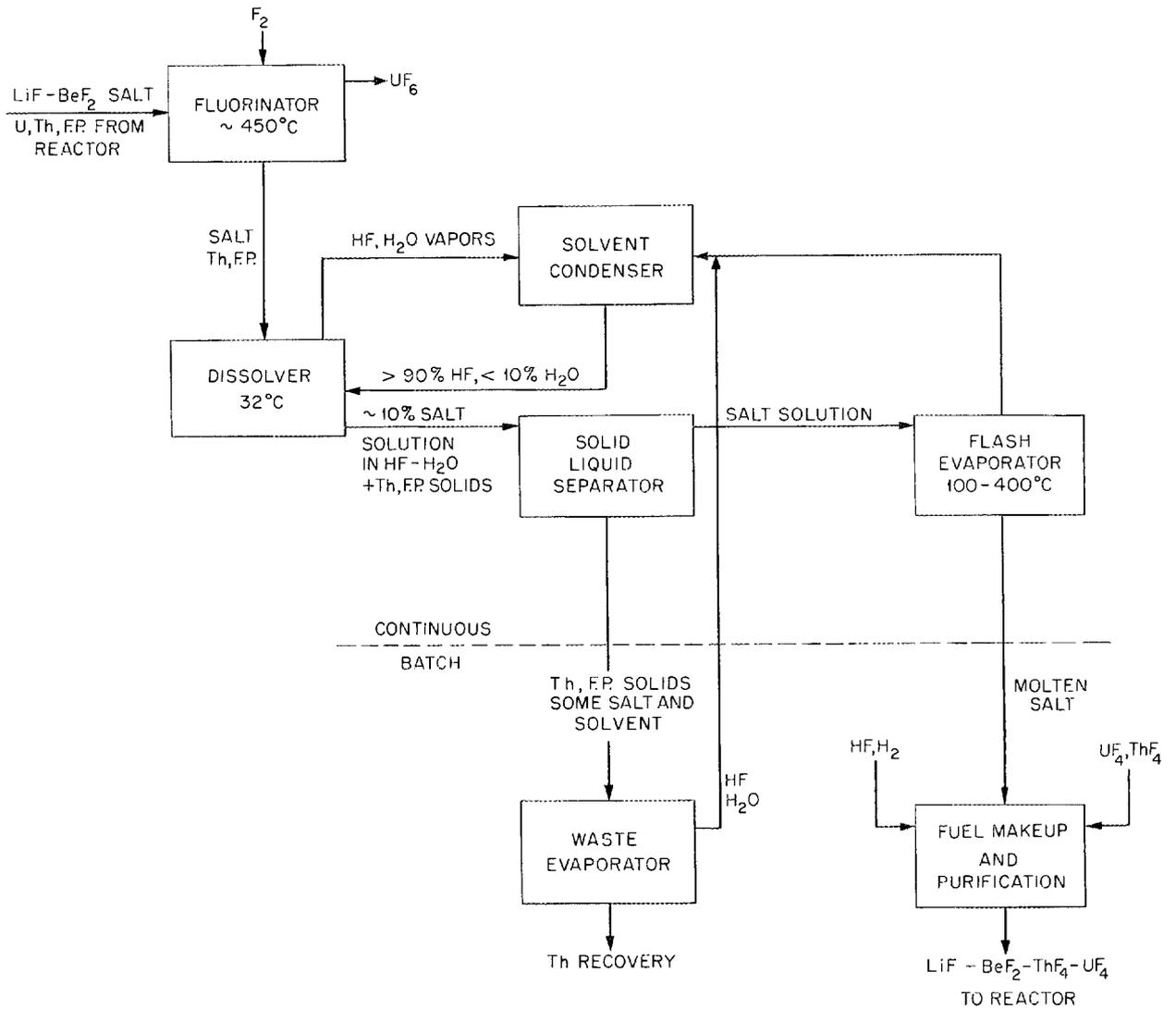


Fig. 4.1. Tentative Flowsheet for Fluoride Volatility and HF Dissolution Processing of Molten-Salt Reactor Fuel.

## 5. HOMOGENEOUS REACTOR FUEL PROCESSING<sup>1</sup>

The development of a scheme for processing the aqueous uranyl sulfate fuel of the Homogeneous Reactor Test by continuous centrifugation with hydroclones was continued. In the HRT chemical processing plant, fission and corrosion product solids collected in the hydroclone underflow receiver are periodically discharged to the low-pressure system for dissolution, sampling, and decay storage. Uranium associated with the solids will be recovered in existing solvent extraction facilities at ORNL. Disposal of all waste streams from the reactor, including the gaseous fission products held up on charcoal adsorber beds for decay, is an associated function of the processing plant.

Operation of the processing plant is governed largely by reactor operation. In the past year three major runs, the last still in progress, were made. In September the reactor was operated 1100 hr at power levels up to 4 Mw (run 17) with a corrosion specimen holder in the core. Very high core-tank corrosion rates were apparent from the large increase in zirconium content of the solids collected, but the reasons for the increase were not known. The power-dependent fuel instability problem was again confirmed. In December and January a 1250-hr run (run 18) devoted to fuel instability studies was terminated by the only reactor dump to date, which was initiated when activity backed up in an instrument line. A maximum power of 1.6 Mw was achieved in this run. Failure of both reactor circulating pumps at the beginning of the next run resulted in an extended maintenance period before the current run, which was started in June.

The hydroclone system was operated about 75% of the time during these runs. The only mechanical failure of chemical plant cell equipment occurred in run 18, when the small circulating pump rotor locked and could not be started. The pump was replaced by normal underwater maintenance techniques.

### 5.1 REMOVAL OF INSOLUBLE CORROSION PRODUCTS

In all runs up to run 20, a bypass stream of 1.3 gpm was circulated through the 0.56-in. hydroclone originally installed in the chemical plant. When it seemed apparent that processing at a

faster rate would increase the solids removal rates, a multiple hydroclone assembly was installed in the reactor cell, since connecting lines to the processing cell were not large enough to handle the increased flow. A primary flow of 10 gpm is circulated through the multiple clone, and the concentrated underflow stream (1.3 gpm) is routed to the original hydroclone for solids collection.

**Performance of Single Hydroclone.** - In laboratory and loop development work prior to operation of the HRT-CP hydroclone system, it became apparent that competing mechanisms for solids removal would seriously limit the fraction of corrosion product solids removed by a hydroclone system. In 2670 hr operating time with the HRT through run 18, 2.2 kg of corrosion product solids was collected, which is about 10% of those produced in the core system. The over-all average removal rate of 0.8 g/hr (compared with normal corrosion rates of ~3 g/hr) is largely a result of high removal rates in the first 200 hr of reactor runs. Rates varied from 0.6 to 2.6 g/hr in this initial period, but under all conditions dropped to and remained consistently at 0.3 g/hr after 250 hr of operation. The only factor that has significantly affected removal rates is reactor shutdown and startup. Two periods of high corrosion rate produced substantial quantities of solids above those normally expected, but the solids removal rate was not significantly higher in these periods. Other variables, such as reactor power and total accumulated solids inventory, have not appeared to have a marked effect on removal rates.

In laboratory studies, changing the geometry of the loop and hydroclone to several configurations had no effect on the fraction of solids collected by the hydroclone. Increasing the processing rate by using a 3-in.-dia hydroclone did not increase the amount of solids collected, possibly because of the lowered efficiency of the larger hydroclone for collecting particles smaller than 5  $\mu$ . In all tests only about 10% of the corrosion product solids calculated to have been formed were removed.

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<sup>1</sup>Reported in more detail in Homogeneous Reactor Project quarterly reports, e.g., ORNL-2696.

**Solids Removal at Faster Processing Rates.** — Data from the single hydroclone indicate that the circulating solids concentration is essentially independent of hydroclone operation; that is, circulating solids concentrations are controlled more by the competing mechanisms than by the hydroclone. Solids removal rates would therefore be proportional to processing rates, and, within limits, removal rates can be increased to any value by faster processing. A multiple hydroclone system containing thirteen 0.6-in. hydroclones in parallel was designed, fabricated, and installed prior to the present run (reactor run 20) to test this theory. The removal rates will not be directly proportional to the number of hydroclones, since, as installed, the flow rate through the 13 clones is 10 gpm compared with 1.3 gpm with the single unit. Additional losses are incurred in the overflow stream from the single clone, which is used as a final solids collector from the multiclone underflow stream. In the first two short runs with the multiclone, the predicted increase in removal rate of three to four times that with the single clone was realized. Approximately 300 g was collected in each of the runs, which were of 50 and 95 hr duration. Removal rates were 4 and 3 g/hr, while rates of 0.6 to 2.6 g/hr were obtained in comparable runs with the single hydroclone.

**Theory of Solids Behavior and Alternative Removal Methods.** — If the predicted removal rates with the multiple hydroclone are borne out, processing with hydroclones appears practical for scaleup to large systems. If, however, the rates drop off to values as low as with the single hydroclone, the process will not be feasible and alternative solids removal methods must be sought.

The most attractive alternative scheme is batch chemical dissolution of accumulated solids. Scale on corrosion specimens examined to date indicates that a substantial fraction of all corrosion products not removed are deposited more or less uniformly on all surfaces of the high-pressure system outside the core. Zirconium oxide from core tank corrosion is rapidly transported to regions outside the core, where it forms an integral part of the film with iron and chromium oxides. The dump tanks contain a substantial amount of solids, estimated at up to 25% of the total, but no accumulation of loose solids has been noted at any place in the high-pressure system. In the heat exchangers some

lowering of heat transfer coefficients has been noted, which eventually may necessitate chemical descaling to restore performance.

Laboratory- and loop-scale dissolution studies have shown markedly different results with different scales. Most scales from nonradioactive loops have no zirconium oxide and are more easily dissolved than reactor scale. Both chromous sulfate and uranous(III) sulfate have removed scale from any specimen tested, including some from the reactor itself. However, both are rather corrosive, and the question of whether hydrogen pickup by Zircaloy-2 is excessive in the reducing atmosphere has not been resolved. Many other reagents have been tested, and the studies are continuing in conjunction with decontamination studies.

In every hydroclone loop run since the period of high core tank corrosion in run 17, the chemical composition of solids collected has been remarkably consistent, with Zr running 38–43%, Fe 19–22%, and Cr 5–7%. Since the core tank corrosion is known to be low during low power runs, a large fraction of the solids being collected are those formed in previous runs. From removal rates and known hydroclone efficiencies the long-term equilibrium circulating solids concentration in the reactor is calculated to be only about 2 ppm, corresponding to a total circulating inventory of only 1 g, and the maximum concentration at the beginning of a run is no more than an order of magnitude higher. This concentration of solids can be of no consequence to reactor operations, but the long-term buildup or accumulation in such places as the reactor core or small lines may cause difficulties as yet uncovered. Since even with the present accumulation of 20 kg of solids the removal rates are only one-fourth of normal corrosion rates, it does not appear that the single hydroclone could ever maintain an acceptable equilibrium solids inventory.

Solids collected in the HRT Chemical Plant were satisfactorily dissolved by alternate treatments with boiling 10.8 M sulfuric acid and 4 M sulfuric acid. The uranium was decontaminated by ion exchange techniques and analyzed for isotopic composition in an effort to account for the disappearance of uranium during power operation of the HRT. Particle size analysis of two batches of solids from the HRT Chemical Processing Plant showed that about 85% of the solids are smaller than 5  $\mu$  and that 50% are smaller than 1  $\mu$ .

## 5.2 FISSION PRODUCT BEHAVIOR

The long-lived radioactive isotopes except cesium are relatively insoluble. A large group, including zirconium-niobium, ruthenium, and tellurium, are very insoluble, are intimately associated with the corrosion products, and are removed in approximately the same proportion as the corrosion products.

**Iodine.** – When laboratory and loop studies showed that iodine is easily volatilized from HRT fuel solutions, an iodine trap was installed in the reactor low-pressure system to remove iodine let down from the core. The primary objectives of iodine removal from the HRT were to minimize biological hazards and to prevent poisoning of the low-pressure recombiner catalyst. In power reactors, iodine removal on a 45-min processing cycle would effectively control xenon poisoning.

The discrepancy reported<sup>2</sup> from analyzing iodine data from the reactor by two methods has not been resolved. The mass of iodine in samples indicates removal at the letdown rate equivalent to an age of 2 hr, but the  $I^{133}/I^{131}$  activity ratio indicates an age up to 24 hr. If the latter analysis is correct, control of xenon by iodine removal will not be feasible. From a study of all factors affecting iodine data, the role of the tellurium precursors appears to be the most important. A poorly known fraction of the 131 chain is held up by the  $Te^{131m}$  isomer, and the partial solubility of tellurium further complicates calculations of the effect on iodine analyses. The exact effect of tellurium will be defined from analyses obtained in the present run at times designed to maximize the specific effects.

Limited laboratory studies showed that iodine is held up in an equilibrium condition by corrosion product solids, but the studies were not sufficient to define the variables involved. A further complication in the HRT is the presence of up to 50 g of silver dissolved from the low-pressure iodine trap and circulated with the fuel in the early part of each run. The effect this may have on holdup of iodine in the system is completely unknown.

Laboratory experiments indicated that radiation has little or no effect on the valence state of iodine under a variety of conditions, but the presence of hydrogen peroxide (0.01 M) resulted

in significant transfer of iodine from solution to the rubber closures used with the HRT sample containers. In laboratory experiments, solids produced in stainless steel corrosion loops adsorbed iodine at 250°C. In other experiments adsorbed iodine exchanged with iodine in solution. With the particular apparatus and solids used in these experiments, isotopic exchange equilibrium was reached in less than 5 min at 270°C.

**Rare Earths.** – Very limited data from radiochemical analyses indicate that the important rare-earth poison group may be even less soluble than anticipated from laboratory studies. The typical and important element neodymium appears to have a solubility of only 5 ppm. This level will result in a total poisoning from this group (excluding the very-high-cross-section rare earths) of less than 1.5% in a large reactor. Total mass levels from normal fission product buildup are not sufficiently high for the data to be checked by the more direct spectrographic analyses. A gross addition of four major rare earths is to be made in the present run to minimize these analytical problems.

## 5.3 WASTE SYSTEM

**Charcoal Fission Gas Adsorbers.** – Performance of the HRT charcoal adsorber beds has demonstrated that the capacity of the beds is adequate at flow rates up to five times the original design value. Heating in the beds is less than anticipated, mainly because the thermal conductivity of the charcoal measured experimentally was found to be four times the value used in the original design. A fire initiated in one bed by the recombination of  $D_2$  vented from the reactor resulted in a minor activity breakthrough due to elution of krypton and xenon by the  $CO_2$  formed. However, damage to the bed was minor, and after a short time for decay the bed has been used with no apparent signs of a lowered capacity. Extensive laboratory studies of the possible cause and effects of a fire confirmed that this is not a major hazard. Beds for large reactor systems have not been designed, but sufficient information is available to permit an adequate design. In dynamic laboratory experiments it was shown that when  $CO_2$  was used as the carrier gas instead of  $O_2$  to carry radioactive krypton through a charcoal-filled trap, the holdup time for krypton in the trap was reduced 50%. In mixtures of  $O_2$  and  $CO_2$ , holdup time was intermediate between the values for pure  $O_2$  and pure  $CO_2$  sweep gas.

<sup>2</sup>Chem. Tech. Ann. Prog. Rep. Aug. 31, 1958, ORNL-2576, p 49.

In laboratory experiments, activated charcoal at temperatures up to 100°C showed no catalytic effect on the reaction between H<sub>2</sub> and O<sub>2</sub>. However, when a combustible mixture of these two gases (30–78% H<sub>2</sub>) contained in a long tubular pipe filled with charcoal was ignited at one end of the tube, the explosion front was rapidly propagated through the length of the tube. As a result of the explosion, hot spots were created at many points throughout the bed. Upon introduction of O<sub>2</sub> these hot spots served as foci for combustion of the charcoal throughout the trap.

**Decontamination of Shield Water.** – Over 300 curies of activity has been discharged to the waste retention pond following periods of cell maintenance. An effective means for decontaminating this water before release to the environment was developed in the laboratory and demonstrated at the reactor site. Successive additions of 100 lb of trisodium phosphate to the 300,000-gal pond resulted in a fine precipitate of calcium phosphate which carried down the activity. Decontamination factors were 1.5 to 3 with each addition until levels were down to 100–200 counts·min<sup>-1</sup>·ml<sup>-1</sup>, which is acceptable for drainage.

**Transfer of Initial Fuel Batch.** – The first 6-kg fuel batch, which became unsuitable for reactor use because of high nickel concentrations, was transferred without incident to a solvent extraction facility where the uranium was decontaminated. An available 33-gal shield carrier was made critically safe by adding Gd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as a nuclear poison to the fuel.

#### 5.4 URANIUM DECONTAMINATION

Conventional solvent extraction processes could be used to remove such fission and corrosion product elements as cesium and nickel from aqueous UO<sub>2</sub>SO<sub>4</sub> solutions if a suitable plant was available and a long decay period prior to processing was not too costly. An alternative method which would allow for processing fuel solutions only a few days after discharge from the reactor and while still in the D<sub>2</sub>O system and which would use UO<sub>4</sub> precipitation as the basis of separation was tested with actual HRT fuel solution. Uranium losses during processing were less than 0.1%, and decontamination factors were as follows: Cu, 86; Ni, 14; gross beta, 5; Sr, 151; Ba, 72; Ce, 2.2; total rare earths, 11; Cs, 7; Ru, 6. Since the uranium so processed will be returned directly

to the reactor, such decontamination factors are adequate.

However, experience gained during operation of the HRT together with further laboratory studies on the stability of uranyl sulfate–sulfuric acid fuel solutions indicates that the nickel content of such solutions may determine the maximum temperature or power at which such fuel solutions can be used. Methods for maintaining a nickel concentration of 0.005 *m* or less in HRT fuel solution were therefore investigated, the most promising being electrolytic removal of nickel, copper, and manganese from the D<sub>2</sub>O fuel solution by a mercury cathode. In laboratory and small-scale runs all three elements were >99% removed. With solid metal cathodes, such as stainless steel or nickel, removal of copper from solution was rapid and complete, but the nickel concentration in the electrolyte was not decreased below 4 g/liter and manganese was not removed at all. Prior to use in the electrolytic cell the fuel solution was concentrated to about 60 g of U per kg of D<sub>2</sub>O, producing a solution about 0.25 *M* in D<sub>2</sub>SO<sub>4</sub>. At lower acidities reduced uranium was hydrolytically precipitated, while at higher acidities removal of the desired ions was impaired. The mercury cathode was regenerated by contacting it with 1 *M* HNO<sub>3</sub>–1.5% H<sub>2</sub>O<sub>2</sub> solutions both with and without an applied emf, although the latter procedure gave faster regeneration rates at a potential of 0.4 v. The fuel solution after being discharged from the cell was treated with an oxygen-ozone mixture at 25°C to regenerate UO<sub>2</sub>SO<sub>4</sub>. The process was developed through engineering scale, but there are at present no plans for continued study.

#### 5.5 FUEL SOLUTION STABILITY

The uncertainties in uranium inventory experienced during operation of the HRT and the apparent loss of uranium from solution at high power led to further investigation of the behavior of simulated HRT fuel solutions under a variety of conditions that could exist during reactor operation. In quartz tube experiments, solutions containing only small amounts of sulfuric acid (< 10% free H<sub>2</sub>SO<sub>4</sub>), when heated to a temperature sufficiently high to result in the formation of a second phase at approximately 330°C, produced a uranium-containing red solid which could be subsequently redissolved with difficulty.

Simulated fuel solutions containing more than 1200 ppm of nickel produced a second liquid phase, of unknown composition but presumably uranium-rich, which crystallized into a green solid phase. When this solid phase was cooled, it underwent a transformation, producing solid nickel sulfate which redissolved only slowly at 25°C. Other solids were observed under various conditions but could not be isolated from the liquid system.

When simulated fuel solutions were heated in the presence of corrosion product solids, the temperature of second-phase formation was not lowered by more than 1 or 2°C. However, when metal pins immersed in fuel solution contained in quartz tubes were inductively heated, second-phase formation on the surface of the metal was observed even when the bulk of the fuel solution was below the temperature at which a second phase would form in the solution.

## 6. WASTE TREATMENT AND DISPOSAL<sup>1</sup>

The objective of the waste treatment program is the development and demonstration of processes suitable for management of wastes produced in the power reactor economy of the future. Present methods of containment and disposal of reactor fuel reprocessing wastes are not generally conceded to be satisfactory for purposes of an expanding nuclear power economy. Storage of the high-activity liquid wastes in tanks is a temporary expedient which will suffice only until permanent means of containment with greater safety can be devised. Disposal of large volumes of low- and intermediate-activity liquid and gaseous wastes by dilution and dispersal in the environment will become more restricted with population growth and with the future likelihood of chemical reprocessing plants being located in areas of higher population density. In the case of high-activity liquid wastes, that is, those containing activities in excess of  $10^4$  times their maximum permissible concentrations (MPC), the objective is to convert to solids by evaporation and calcination. It is thought that the encapsulated solids could be permanently stored in specially prepared caves or concrete vaults on the plant site.

Low-activity liquid wastes (activities between  $10^2$  and  $10^4$  MPC) of high inert salt content, such as decladding wastes, could be converted by addition of proper reagents to solids such as gels or gypsum and stored in less expensive underground vaults or tanks. The larger volumes of low-activity waste containing small amounts of dissolved salts can best be handled by simple chemical treatment designed to decontaminate the water to levels that would permit discharge to the environment.

Emphasis has been placed on the treatment of high-activity wastes by evaporation and calcination (Fig. 6.1). In the proposed process, waste is first evaporated to a very concentrated solution or slurry and then fed to a stainless steel cylindrical pot in which it is calcined to the oxides. After being sealed, the pots would be removed from the furnace and stored in appropriate areas. The off-gas from the calciner, consisting principally of steam, nitrogen oxides, and fission products, must be decontaminated, possibly by scrubbing, before discharge to the environment. A concentrated solution of nitric acid and fission products would be recycled to the evaporator feed. To date, synthetic solutions representing wastes expected from reprocessing of power reactor fuels have been characterized from the standpoint of their evaporation to dryness and the nature of the solids produced by calcination of the residues. Calcination studies were performed with 200-ml samples of radioactive wastes containing activities up to  $2 \times 10^{11}$  counts·min<sup>-1</sup>·ml<sup>-1</sup> and with synthetic waste solutions in an electric furnace equipped with an 8-in.-dia stainless steel liner. A computer analysis was made of the problem of heat dissipation from calcined solids during storage.

### 6.1 EVAPORATION AND CALCINATION OF ACIDIC WASTES

The behaviors of four simulated high-activity fuel reprocessing solutions during evaporation and calcination were studied: Darex, Purex,

<sup>1</sup>See also secs 18 and 19.

Thorex, and TBP-25. Each waste was evaporated and then calcined to about 400°C in glass equipment. All solid residues were of high porosity, with volume reduction factors varying from 3 to 11 (Table 6.1). Nitrate recovery in the condensate ranged from 81% to better than 99%. In experiments on activity distribution during evaporation and calcination, greater than 99.94% of the radioactivity remained with the residue (Table 6.2).

Synthetic liquid waste was processed at feed rates as high as 9 liters/hr in an 8-in.-dia by 18-in.-high stainless steel electrically heated pot calciner. The wastes were evaporated to 25 to 50% of their original volumes before being fed to the calciner, which was operated at 900 to 1000°C. The off-gases were withdrawn continuously, and on passage through a water-cooled condenser yielded 6 to 12 M HNO<sub>3</sub>, NO<sub>2</sub>, and O<sub>2</sub>.

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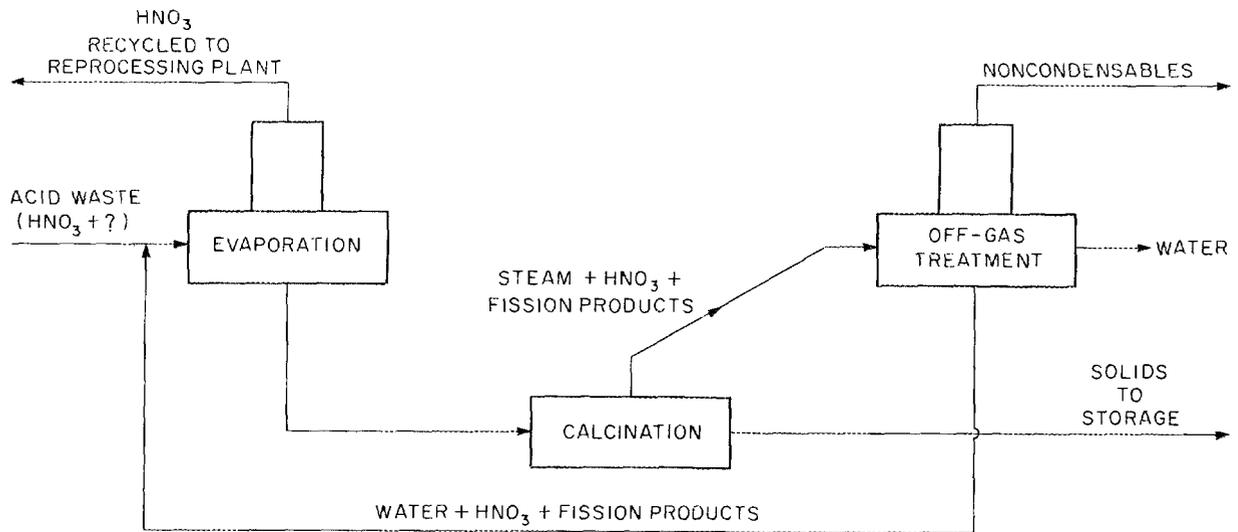


Fig. 6.1. General Flowsheet for Reduction of Radioactive Waste to Solids.

Table 6.1. Evaporation and Calcination of Wastes

Waste	Consistency and Color	Solid Residue				Condensate (% of Original)	
		Density at 24°C (g/cc)	Porosity (%)	Volume Reduction Factor	Nitrate (% of Original)	Volume	Weight
Darex (acidic)	Crumbly, dark brown	0.85	83	8	0.79	99.1	91.3
Purex (acidic)	Fairly hard, light brown	0.75	80	6.7	0.13	96.8	89.5
Thorex (acid-deficient)	Crumbly, off-white	0.31	92	11.4	4.0	101	97.5
TBP-25 (acidic)	Crumbly, off-white	0.56	86	3.3	16.8	95.7	84.5

Table 6.2. Activity Distribution During Evaporation and Calcination

Waste	Activity in Waste (counts/min/ml)		Activity (counts/million counts in feed)			
	Beta	Gamma	Condensate		Off-Gas	
			Beta	Gamma	Beta	Gamma
Darex (neutralized)	$9 \times 10^9$	$9 \times 10^9$	20	60	0.5	0.5
Purex (acidic)	$8 \times 10^9$	$8 \times 10^9$	400	600	1.0	2.0
	$2 \times 10^{11}$	$2 \times 10^{11}$	10	10	1.0	2.0
Purex (neutralized)	$8 \times 10^9$	$8 \times 10^9$	30	20	0.3	0.8
	$2 \times 10^{11}$	$2 \times 10^{11}$	50	100	0.07	0.2

The volume reduction from the unevaporated waste to the calcined solid was eight- to twelvefold. Densities of the solids were 0.8 to 0.9 g/cc for Darex waste, 0.6 to 0.8 g/cc for Purex, and 0.4 to 0.5 g/cc for TBP-25.

## 6.2 HEAT GENERATION IN STORED WASTES

For satisfactory storage of calcined high-activity wastes the heat generated by fission product decay would have to be removed since excessive temperature rises could adversely affect the safety of disposal by this method. The thermal conductivity of the solid, one of the most important factors affecting the temperature rise in stored solid wastes, may be measured by steady-state<sup>2</sup> or transient<sup>3</sup> temperature methods. Steady-state measurements showed thermal conductivities of calcined TBP-25 waste varying from  $0.396 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-1}\cdot(^{\circ}\text{F})^{-1}$  at  $1575^{\circ}\text{F}$  to  $0.065 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-1}\cdot(^{\circ}\text{F})^{-1}$  at  $235^{\circ}\text{F}$ . The waste was calcined at  $870^{\circ}\text{C}$  and had a density of 0.402 g/cc and a porosity of 89.9%. Transient-temperature measurements of calcined Darex waste gave thermal conductivity values of 0.042 to  $0.110 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-1}\cdot(^{\circ}\text{F})^{-1}$  in the temperature range 70 to  $500^{\circ}\text{F}$ . These measurements were made with a resistance-heated tube in a cylinder of the calcined waste, *in situ*.

<sup>2</sup>H. W. Godbee and J. T. Roberts, *Survey of the Measurement of Thermal Conductivity of Solids Produced by Evaporation Calcination of Synthetic Fuel Reprocessing Solutions*, ORNL-2769 (in press).

<sup>3</sup>H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2d ed., p 339, Oxford Press, New York, 1959.

## Calculation of Temperature Rise in Deeply Buried Radioactive Cylinders

The temperature rise in deeply buried radioactive cylinders was calculated as a first step in investigating the possibility of ultimate storage of the solid wastes. The results indicated that storage of cylinders of solid radioactive waste of a practical size and activity level is feasible without excessive temperature rise, that the maximum temperature rise increases linearly with heat generation rate over the ranges of parameters used in this study, and that the fission product spectrum is not significant in the determination of the maximum temperature rise.

The storage model studied was an infinitely long cylinder of radioactive solid in an infinite solid medium with an air space between them (Fig. 6.2). This model is pessimistic in that most other methods of storage would result in a lower temperature rise. Nevertheless, storage of waste cylinders of a practical size appears feasible even with the chosen model. The calculation was performed in two parts: (1) the problem of an infinite cylindrical cavity in an infinite solid medium with a decaying heat flux at the boundary was reduced to a set of difference equations which were solved on the Oracle and (2) the temperature differences from the axis to the surface of the radioactive cylinder and across the air space were calculated from analytical expressions. Over the ranges of thermal properties of interest, calculations with unsteady-state equations showed that steady-state temperature differences from the axis to the surface of the cylinder and across the air space consistent with the instantaneous heat generation

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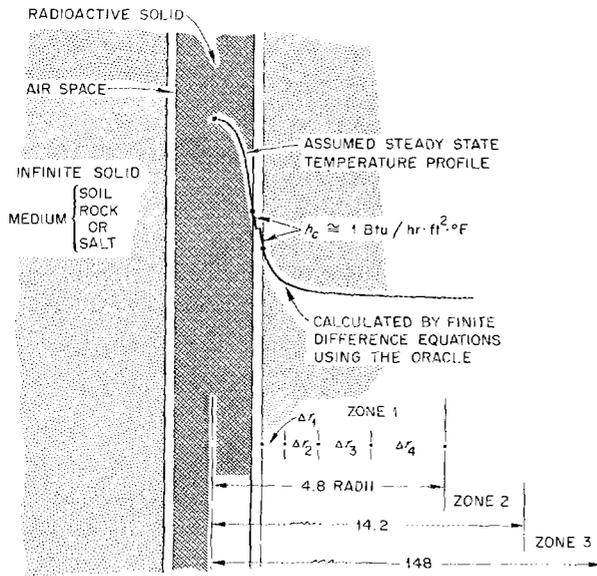


Fig. 6.2. Model for Temperature Rise Calculations.

rate were good approximations. Thermal properties were assumed to be independent of temperature, and the energy of fission product decay was assumed to be dissipated uniformly within the radioactive solid. The temperature difference across the air space was assumed to be determined by the instantaneous heat flux through two air films, and calculations were carried out with heat generation rates up to  $2000 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-3}$  solid for burial in an infinite solid medium of "average soil," "average rock," and salt.

For cavity radii ranging from 5 to 30 in. the maximum temperature at the cavity surface was reached in about three months with one-year-decayed waste, in six months with three-year-decayed waste, and in six years with eight-year-decayed waste. The properties for the infinite solid medium of "average soil," "average rock," and salt were used with thermal conductivities of  $0.56$ ,  $1.0$ , and  $2.80 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-1}\cdot(\text{°F})^{-1}$  and thermal diffusivities of  $0.0178$ ,  $0.0457$ , and  $0.101 \text{ ft}^2/\text{hr}$ , respectively.

The maximum temperature rise in radioactive solid cylinders, separated from an infinite solid medium by a 1-in. air space, was calculated over a range of cavity radii of 5 to 30 in. with heat generation rates of up to  $2000 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-3}$  (Fig. 6.3). The thermal conductivity of the radioactive

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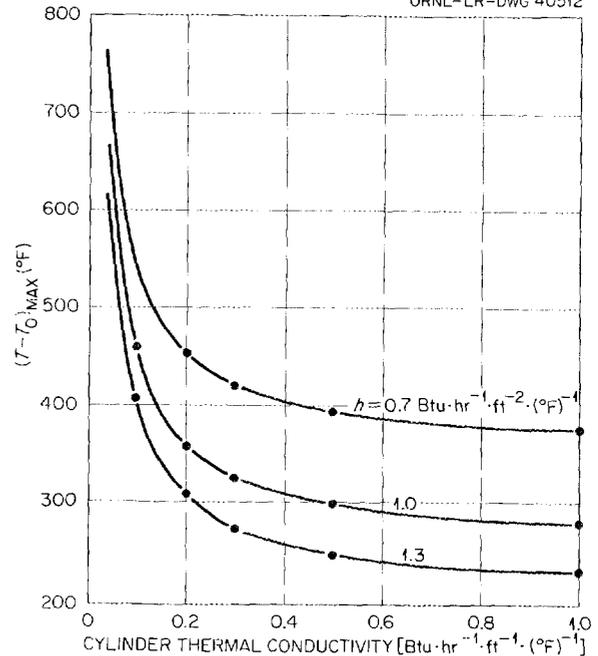


Fig. 6.3. Maximum Temperature Rise in a Cylinder of 1-yr-Decayed Waste as a Function of Thermal Conductivity and of the Thermal Convection Coefficient in the Air Space of a Salt Medium ( $Q_0 = 700 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-3}$ ; Cavity Radius = 5 in.).

cylinders was varied from  $0.1$  to  $1.0 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-1}\cdot(\text{°F})^{-1}$ . A maximum temperature rise of  $1000\text{°F}$  would be produced with an initial heat generation rate of  $1300$  to  $1600 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-3}$  for the 5-in.-radius case,  $350$  to  $450 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-3}$  for the 10-in.-radius case, and  $175$  to  $210 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-3}$  for the 15-in.-radius case, assuming a thermal conductivity of the radioactive cylinder of  $0.1 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-1}\cdot(\text{°F})^{-1}$ . The maximum temperature rise at the axis of the cylinder increased sharply as the thermal conductivity of the radioactive cylinder decreased below  $0.2 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-1}\cdot(\text{°F})^{-1}$ . The convection coefficient in the air space was varied from  $0.7$  to  $1.3 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-2}\cdot(\text{°F})^{-1}$ . It can be seen that maximum allowable temperatures ( $1300\text{°F}$ ) arbitrarily set lower than the calcination temperature are not exceeded with one-year-decayed wastes in 10-in.-dia cans if the thermal conductivity of the waste is greater than  $0.15 \text{ Btu}\cdot\text{hr}^{-1}\cdot\text{ft}^{-1}\cdot(\text{°F})^{-1}$ .

The specific heat generation rate of a radioactive material can be decreased prior to ultimate

storage by allowing the material to decay or by diluting with a nonradioactive material. By manipulating these two alternatives, wastes with different fission product spectra but the same specific heat generation rate can be produced. The waste with the lower decay rate would be expected to show a higher maximum temperature rise upon storage, but over the range of conditions studied the effect was found to be small. The difference in maximum temperature rise between one- and three-year-decayed wastes was about 2% and between one- and eight-year-decayed wastes was about 7%.

The effects of storage in media of different thermal properties are shown in Fig. 6.4. For a given initial heat generation rate and cylinder radius the maximum temperature rise for storage in "average soil" was 25 to 30% higher than for storage in salt and was 10 to 20% higher than for storage in "average rock." As the thermal conductivity of the cylinder increases, the choice of storage medium becomes more important because a larger fraction of the total allowable temperature rise occurs in the infinite solid medium.

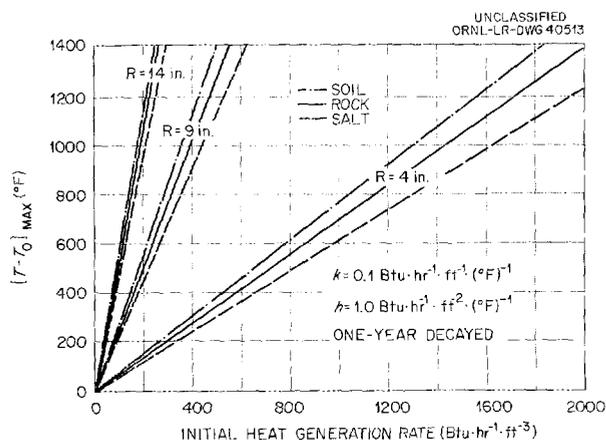


Fig. 6.4. Maximum Axial Temperature Rise as a Function of Heat Generation Rate and of Radioactive Cylinder Radius for Various Storage Media.

### 6.3 MARITIME REACTOR WASTE DISPOSAL STUDIES

Methods of converting ion exchange resins, radioactive gases, and other radioactive wastes generated on nuclear merchant ships of the NS "Savannah" type to a form suitable for disposal to the ocean are being studied. A stainless steel loop capable of circulating water at a rate of 10 to 20 ml/min under conditions simulating those of the NS "Savannah" reactor cooling system (1750 psi, 550°F) was constructed. Operation of this loop will furnish information on corrosion products, corrosion rates, effect of corrosion scale on ion-exchange resins, life of demineralizers, sizing of demineralizers, and reactor water chemistry. Radioactive tracers will be added to the feed to determine activity buildup on demineralizers.

Disposal of demineralizer resins by mixing with cement to form concrete blocks of low leachability is under investigation. A concrete block containing 200 ml of mixed-bed resin from the APPR demineralizers was placed in a bath and contacted with circulating synthetic sea water. After 117 hr, 0.27% of the activity was leached from the block.

### 6.4 PREPARATION OF DETAILED STATEMENT ON WASTE MANAGEMENT AT ORNL FOR CONGRESSIONAL HEARINGS

A report on radioactive waste management at Oak Ridge National Laboratory (ORNL-2601) was prepared in cooperation with the Health Physics and Operations Divisions to serve as the Laboratory's detailed statement before the public hearings on industrial waste disposal of the Joint Committee on Atomic Energy, Congress of the United States, January 28 through February 3, 1959. The report discusses the philosophy and history of waste management at ORNL and describes the collection, treatment, disposal, and monitoring of radioactive wastes (solid, liquid, and gaseous). The report constitutes an evaluation of ORNL waste management, concluding that the low degree of radioactive contamination of the air and water by ORNL does not represent a hazard to the local environment or population.

## 7. FUEL CYCLE DEVELOPMENTS

### 7.1 FUEL MATERIAL SELECTION CRITERIA

Many uranium, plutonium, and/or thorium compounds, alloys, cermets, intermetallics, and dispersions have been considered as possible power reactor fuels. In order to screen materials that are worthy of preliminary development and testing, rough economic selection criteria based on material properties are being developed (Table 7.1). The effect of uranium density on the fuel cycle cost is more difficult to define than the other criteria. IBM-704 calculations are being made to determine this effect and to check the other factors.

### 7.2 PLUTONIUM-THORIUM REACTOR SYSTEM CALCULATIONS

Reactivity lifetime values for plutonium-thorium reactors and U<sup>235</sup> thorium reactors have been

calculated with the IBM-704. Modified thermal group cross sections were used to determine the effect of heavy isotope poison buildup. These effective cross sections were obtained by adjusting the thermal values upward with a correction factor for resonance neutron density. This resonance neutron density was obtained as a function of the assumed resonance escape probability. Reactivity lifetime results were obtained for both systems using (1) batch irradiation methods and (2) continuous unmixed irradiation methods. In batch operation a reactor is completely charged with a loading of fresh fuel and then discharged when its excess reactivity is zero ( $k_{eff} = 1.0$ ). With continuous unmixed operation, only a fraction of the fuel is charged and discharged during each scheduled shutdown so that a steady-state operation is achieved and

Table 7.1. Selection Criteria for Fuel in Cylindrical Geometry

Property	Criterion*	Allowable Values and Remarks
Specific power	$\frac{K\Delta T}{\rho}$ , $\text{cm}^2 \cdot \text{cal} \cdot \text{sec}^{-1}$	0.3 minimum, 0.6–1.5 preferred; value of 0.7 represents ~0.4 mill/kwhr inventory; mills/kwhr proportional to $\rho/K\Delta T$
Thermal efficiency	$\frac{T_c - 310}{T_c}$	mills/kwhr proportional to $T_c/(T_c - 310)$
Heat generation per length of element	$K\Delta T$ , $\text{cal} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$	mills/kwhr proportional to fabrication cost/ft/ $K\Delta T$
Diluent poison	$\frac{\sigma_a N_p}{N_f}$ , $\frac{\text{barns}}{\text{fertile atom}}$	Thermal reactor < 3 barns/fertile atom, fast reactor < 0.1 barn (at 0.2 Mev)/fertile atom; value of 3 (thermal) or 0.1 (fast) equivalent to ~1 mill/kwhr
Atomic uranium density	$\rho$	Affects resonance escape probability and conversion ratio; limiting value yet to be determined

\*Nomenclature:

$K$  = thermal conductivity,  $\text{cal} \cdot \text{cm} \cdot ^\circ\text{C} / \text{sec}$ ,  
 $\Delta T$  = allowable temperature difference (center to surface of fuel),  $^\circ\text{C}$ ,  
 $T_c$  = coolant temperature,  $^\circ\text{K}$ ,  
 $\rho$  = fertile material density, g of fertile material/cc,

$\sigma$  = microscopic cross section, barns/atom,  
 $N$  = atom density,  $\text{atom}/\text{cm}^3$ ,  
 $f$  = fertile atom,  
 $p$  = poison atom,  
 $a$  = absorption.

$k_{eff}$  is constantly kept at a value only slightly greater than 1.0. Calculations were performed for resonance escape probabilities of 0.9, 0.85, 0.80, 0.75, 0.70, and 0.65, and  $k_{eff}$  values (based on fresh fuel) of 1.0 to 1.2. The plutonium studies assumed an isotopic analysis for plutonium of 56% Pu<sup>239</sup>, 25% Pu<sup>240</sup>, 14% Pu<sup>241</sup>, and 5% Pu<sup>242</sup> (equivalent to 10,000-Mwd/ton plutonium discharged from irradiation of 2%-enriched uranium).

Several examples of the maximum allowable irradiation exposures are listed in Table 7.2. The results indicate that, for the same initial fuel enrichment, higher exposures may be achieved by using U<sup>235</sup>. With low resonance escape probabilities, exposure may be increased by using high plutonium concentrations and continuous irradiation.

These reactor systems will be compared by using the 32-group GNU-II Burnup Code for the IBM-704 in order to get a more exact analysis of the allowable exposures for thorium irradiation and to compare the results of this more exact reactor computation model with the modified thermal model. The modified thermal model is intended as a quick check for a proposed reactor system since approximately 50 cases can be run in 1 hr. The output consists of exposure, conversion ratios, specific power, and isotopic composition for all important heavy isotopes through Pu<sup>242</sup> plus fission products.

### 7.3 MACHINE CALCULATIONS FOR PLUTONIUM AND U<sup>233</sup> RECYCLE

Calculations of the buildup of higher isotopes during many recycles of U<sup>233</sup> and plutonium in

power reactors using spiked or seed regions were made with the IBM-704. Isotopic contents were obtained for many cycles (1-400 and infinity) as a function of burnup per cycle, isotopic analysis of the plutonium or U<sup>233</sup> fed, and fraction of plutonium or uranium discarded following chemical processing. These studies are similar to those reported for U<sup>235</sup> in ORNL-2104.

The results of the plutonium calculations have been analyzed in light of the effects of Pu<sup>240</sup>, Pu<sup>241</sup>, and Pu<sup>242</sup> buildup on plutonium handling problems. Because of their high spontaneous fission rates, high Pu<sup>240</sup> and Pu<sup>242</sup> contents can seriously limit the permissible methods for fabrication of plutonium fuel elements. The buildup of Pu<sup>240</sup> and Pu<sup>242</sup> after infinite recycle can be reduced 30 to 80% by discarding (for possible sale to a fast-reactor operator) 5% of the total plutonium each pass.

The effect of this discarded fraction is illustrated by the values given in Table 7.3 (basis: 10% Pu<sup>240</sup> in initial plutonium feed). Similar results for the U<sup>233</sup> recycle have been obtained but have not been fully analyzed.

### 7.4 DETERMINATION OF SURFACE AREA OF UO<sub>2</sub>

The total surface area of UO<sub>2</sub> is one of the most important factors in its sinterability to high density, but the method used for determining the surface area, the BET nitrogen adsorption method, requires 4 to 8 hr per determination. Two methods were developed for determining the surface area of UO<sub>2</sub> powders, one based on acid titration of

Table 7.2. Examples of Maximum Allowable Radiation Exposures

Type	Fuel	Initial Enrichment, U <sup>235</sup> or Pu in Th	$k_{eff}^0$	Resonance Escape Probability	Exposure (Mwd/ton)	Net Conversion Ratio
Batch	U <sup>235</sup>	0.0308	1.084	0.8	28,396	0.61
Continuous	U <sup>235</sup>	0.0308	1.084	0.8	52,510	0.56
Batch	Pu	0.0469	1.089	0.8	10,387	0.54
Continuous	Pu	0.0469	1.089	0.8	22,045	0.58
Batch	U <sup>235</sup>	0.0536	1.085	0.7	85,620	0.61
Continuous	U <sup>235</sup>	0.0536	1.085	0.7	152,784	0.53
Batch	Pu	0.181	1.085	0.7	71,990	0.56
Continuous	Pu	0.181	1.085	0.7	192,012	0.52

Table 7.3. Effect of Discard Fraction on Buildup of Pu<sup>240</sup> and Pu<sup>242</sup> After Infinite Recycle

Burnup of Pu <sup>239</sup> per Cycle (%)	Discard Fraction (%)	Isotopic Ratios After Infinite Recycles		
		N <sub>40</sub> /N <sub>49</sub>	N <sub>41</sub> /N <sub>49</sub>	N <sub>42</sub> /N <sub>49</sub>
42.61	0	0.744	0.272	1.11
42.61	1	0.721	0.264	0.858
42.61	5	0.641	0.235	0.423
67.06	0	0.555	0.250	1.02
67.06	1	0.547	0.248	0.898
67.06	5	0.518	0.236	0.593

the hydroxyl ions believed<sup>1</sup> to be a primary adsorbed layer on the UO<sub>2</sub> and the other based on adsorption of methylene blue.

In the first method a 10-g sample of UO<sub>2</sub> is refluxed with 50 ml of 0.1 N NaOH for 2 hr and is then titrated potentiometrically with 0.1 N HCl from pH 7 to 3. The significant inflection points<sup>1</sup> in potentiometric titrations of UO<sub>2</sub> slurries by acid are at pH 3 and 7, but it was shown that the acid required to change the pH of UO<sub>2</sub> slurries from 7 to 3 varies and that anionic impurities, such as carbonate and fluoride, in the UO<sub>2</sub> powders also produce inflections. When the experimental results were corrected for fluoride interference, the milliequivalents of acid used correlated well with the sintered densities and surface areas of six ceramic-grade powders (Fig. 7.1).

The methylene blue adsorption method is quicker, easier to carry out, and more accurate for estimating sintered densities. Two grams of UO<sub>2</sub> is added to a boiling solution containing 0.001 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, as a dispersing agent, and 0.16 g of methylene blue per liter, buffered at pH 8 by phosphate (0.095 M NaOH + 13.6 g/liter of KH<sub>2</sub>PO<sub>4</sub>). The mixture (50 ml) is centrifuged, and the change in optical density (initially 30.1) at 6700 Å of the methylene blue supernatant is then determined. In experimental work the change in optical density correlated well with sintered density and surface area (Fig. 7.2).

An attempt to correlate the potential of UO<sub>2</sub> slurries for reduction of ferric ion to ferrous with sintered density and surface area was unsuccessful.

<sup>1</sup>T. L. Mackay and M. E. Wadsworth, *Trans. Am. Inst. Mining, Met. Petrol. Engrs.* 212, 597 (1958).

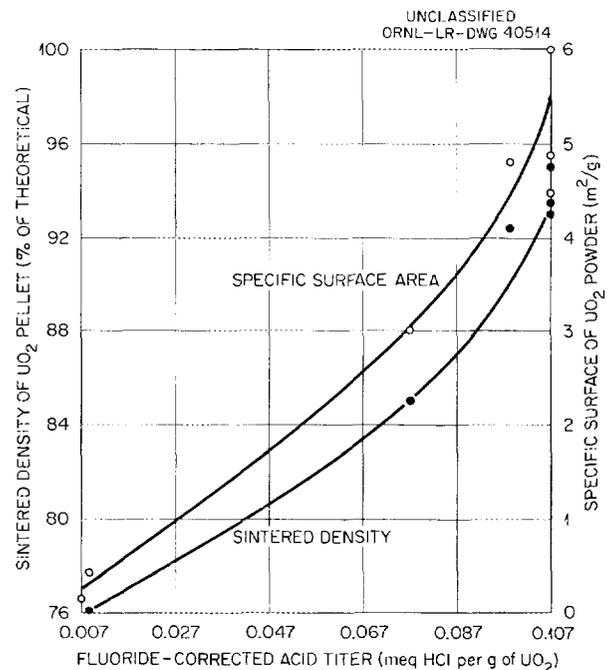


Fig. 7.1. Relation of Acid Titer to Sintered Density and Surface Area of UO<sub>2</sub>.

**Relation of Particle Size Distribution to Sintered Density and Surface Area.** — As the percentage of particles less than 1 μ in size increased from 1 to 22%, both sintered density and surface area increased sharply from 76 to 93% and from 0.5 to 4.4 m<sup>2</sup>/g (Fig. 7.3). Sintered density and surface area increased further with further increase in percentage of particles < 1 μ in size, but the effect was not so pronounced. For this work the particle size distribution of eight UO<sub>2</sub> powders was measured by a neutron activation method.

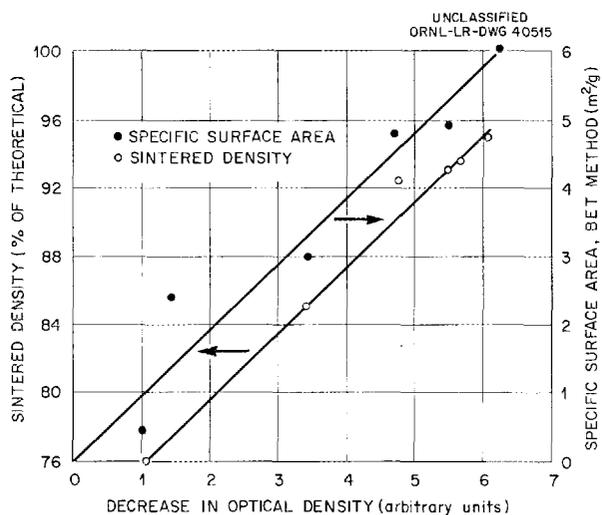


Fig. 7.2. Correlation of Methylene Blue Adsorption by  $\text{UO}_2$  Powders with Surface Area and Sintered Density.

**Precipitation Studies.** — Methods of precipitating intermediate compounds of uranium as source materials in the production of  $\text{UO}_2$  are being studied to determine the effects of precipitation variables on the properties of  $\text{UO}_2$  produced from the precipitates. Precipitation of  $\text{UO}_4$  from 0.15 M  $\text{UO}_2(\text{NO}_3)_2$  solutions with 2 N  $\text{H}_2\text{O}_2$ -0.2 N  $\text{HNO}_3$  solutions at 85 to 95°C in which the  $\text{UO}_2(\text{NO}_3)_2/\text{H}_2\text{O}_2/\text{HNO}_3$  ratio was 1/2/0.2 produced spheroidal aggregates of needles of 5 to 20  $\mu$  particle size. These were sintered to  $\text{UO}_2$  of high powder density (>10.5 g/cc). The mixture filtered rapidly, and the precipitate was decontaminated from uranium daughters by a factor of 125. Similar aggregates were precipitated from simulated  $\text{UF}_6$  solutions. The precipitation variables studied were temperature, concentration of reagent, order of addition, rate of addition, and aging of nuclei. The above conditions were those found optimum for production of clean, filterable, spheroidal aggregates.

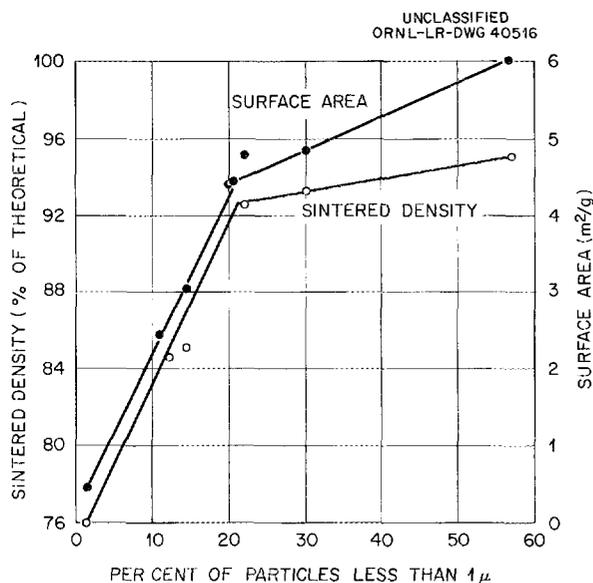


Fig. 7.3. Relation of Size Distribution of  $\text{UO}_2$  Particles to Surface Area and Sintered Density.

Fast-settling, fast-filtering ammonium diuranates were precipitated from 0.15 M uranyl nitrate solution at 95°C by slow addition of 7 M  $\text{NH}_4\text{OH}$ . The dry precipitate was free-flowing.

**Miscellaneous Studies.** — In studies to increase thermal conductivity of  $\text{UO}_2$  and to develop individual particle cladding, nickel phosphide coating was plated from an Electroless nickel solution onto  $\text{UO}_2$  pellets and powder. The coating resisted the attack of 3 N  $\text{HNO}_3$  for 24 hr.

Thorium perfluorobutyrate was prepared from perfluorobutyric acid and thorium nitrate. This salt is ether-soluble, and will be used to coat  $\text{UO}_2$  with  $\text{ThO}_2$  in a study of methods of preventing reaction between thorium metal matrix and dispersed  $\text{UO}_2$ .

**Part II**  
**RAW MATERIALS EXTRACTION**

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## 8. AMEX PROCESS

In the Amex process 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, dissolved in hydrocarbon diluents, first react (during extraction from acidic liquors) to form the alkylammonium salts. 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 Amex process<sup>1</sup> was originally designed for recovering uranium from ore leach liquors, but has been shown to be useful for thorium, vanadium, molybdenum, and rare earths also.

Uranium mills now using the Amex process are Eldorado Mining and Refining, Ltd., Port Radium, Canada; Texas-Zinc Minerals Company, Mexican Hat, Utah; Kermac Nuclear Fuels Corporation, Ambrosia Lake, New Mexico; Fremont Minerals Corporation, Riverton, Wyoming; Lakeview Mining Company, Lakeview, Oregon; Vitro Uranium Company, Salt Lake City, Utah; United Uranium, Coronation Hill district, Australia. Two Canadian mills have successfully piloted the Amex process for thorium recovery.

### 8.1 URANIUM STUDIES

**Evaluation of New Amines.** — Several new amines — including Amberlite XE-204, di(1-heptyloctyl), di(1-nonyldecyl), *N*-(1-undecylauryl)benzyl, and *N*-(1-nonyldecyl)benzyl — performed favorably in process tests. The last two compounds gave exceptionally high uranium extraction coefficients, typical of the *N*-benzyl-branched-alkyl secondary amines.

**Sulfate and Nitrate Stripping Studies.** — Continuous countercurrent tests of uranium stripping from a tertiary amine (Alamine 336) by contacting with 1 to 1.5 *M* ammonium sulfate solution adjusted to pH 3.5 to 4.5 with ammonia were partially successful. This stripping method has the potential advantage of producing a sodium-free concentrate

at low reagent cost. However, some emulsion difficulties were encountered in continuous tests, particularly at pH 4 to 4.5 where stripping was most efficient. Also, separations from molybdenum were poorer than are obtained by the chloride or nitrate stripping methods. Other tertiary amines, such as Amberlite XE-204 and triisooctylamine, which are weaker bases than Alamine 336, showed better response to this stripping method in batch tests but have not been evaluated in continuous equipment.

The results of survey tests indicated the possible use of a low-cost stripping method which produces a relatively pure uranyl nitrate solution instead of the conventional solid uranium product. A loaded tertiary amine extract is contacted with 2.5 *M* calcium nitrate to precipitate sulfate and convert the uranium in the solvent to an amine nitrate-uranyl nitrate complex. The uranium is stripped readily from the solvent with water, and nitrate is recovered from the amine, for recycle, by contact with a lime slurry. Shipment of the concentrated uranyl nitrate solution to the refinery offers potential cost savings since it would eliminate product precipitation, calcining, and packaging at the mill, simplify the transfer of uranium between mill and refinery, and eliminate nitric acid dissolution at the refinery. It would also allow production of pure  $UO_3$  or  $UO_2$  at the mill site, either directly from the strip solution or after further purification by tributyl phosphate extraction.

**Uranium Recovery from Carbonate Solutions.** — Interest in the recovery of uranium from sodium carbonate leach liquors by solvent extraction<sup>2</sup> was renewed upon the acquisition of a new commercial quaternary ammonium compound (Aliquat 336), which has better phase-separation properties than compounds studied previously. In preliminary tests effective uranium extractions were obtained by 0.1 *M* Aliquat 336 in kerosene-alcohol diluent. Uranium may be recovered inexpensively from the solvent by direct precipitation with 1 *M* NaOH-0.5 *M*  $Na_2CO_3$  solution. Possible limiting problems in this flowsheet are the separation of vanadium and the interference of organic matter contained

<sup>1</sup>K. B. Brown and C. F. Coleman, *Progr. in Nuclear Energy*. Ser. III 2, 3 (1958).

<sup>2</sup>K. B. Brown et al., *Progress Report on Raw Materials for February, 1957*, ORNL-2269.

in the aqueous leach liquors. These problems are currently being evaluated by tests on actual mill solutions.

**Emulsion Stabilization by Silicic Acid.** – A study was made of the effects of silica on emulsion formation in the Amex processes for uranium, with a view to predicting and testing specific remedies.<sup>3</sup> With a given amine (vs an aqueous phase containing silicic acid) the stability of the oil-in-water-type emulsion formed was dependent on the anion present in the order  $\text{SO}_4^{--}$  (most stable)  $> \text{Cl}^- > \text{ClO}_4^-$  (least stable). Emulsion stability increased with silica concentration and with the age of the silicic acid solution. Other organic solutes that also had electron-donating tendencies (e.g., oxygen atoms) showed smaller but real emulsion-forming abilities when contacted with silicic acid liquors. Organic additives with active hydrogen atoms decreased phase separation times of a typical silica liquor–amine sulfate solution dispersion by factors of 2 or more, presumably by competing with the silicic acid hydrogen atoms for bonding sites on the amine sulfate oxygens. It is suggested that silicic acid stabilizes oil-in-water-type emulsions by hydrogen bonding to electron-donating groups adsorbed on the surfaces of the organic droplets and by forming typical silicic acid networks in the aqueous phase.

**Solvent Extraction Mixer Settler Study.** – Batch studies of the kinetics of uranium extraction from sulfate solution showed that the rate of extraction in the Amex process is about one order of magnitude faster than in the Dapex process (Sec 9). Tests over a wide range of turbulence and interfacial area indicated that the extraction rate is directly dependent on area and virtually independent of turbulence. This is not usually the case for diffusion-controlled extractions but is in line with an ion exchange mechanism.

Continued studies of phase separation in the extraction circuit have shown settler flow capacities to increase nearly linearly with increased temperature over the range 15 to 45°C, being approximately doubled by the 30°C temperature rise for both solvent-continuous and aqueous-continuous dispersions. Because of this relatively large temperature effect on settler flow capacity, the settler size must be designed for the minimum

temperature expected, or facilities for heating to the design temperature must be provided.

Flow capacities of gravity settlers in the uranium stripping circuit were investigated with 1.0 M sodium chloride solution containing 0.05 M sulfuric acid as the stripping agent. Mixing was controlled to produce solvent-continuous dispersion at a 1/6 (a/o) phase ratio, which is in the range of typical mill stripping circuits. Only a thin dispersion band was discernible and the thickness increased very little with increased flow. However, the entrainment of aqueous in the solvent increased sharply between solvent flow rates of 2.5 and 3.0 gpm/ft<sup>2</sup>. Flooding was reached at only slightly higher flows. On this basis the maximum practical flow capacity should be designed at about 2 gpm/ft<sup>2</sup>.

## 8.2 THORIUM RECOVERY

Owing to the large variations in the relative extraction power of thorium and uranium by amines of different types and structure, the Amex process can be used for separate recovery of these two elements from sulfate solutions in which they coexist. Flowsheets have been devised for the treatment of Canadian Blind River ore leach liquors and monazite sulfuric acid digest liquors.<sup>4</sup>

**Monazite.** – An economical two-cycle process for recovering thorium and uranium from monazite liquors was demonstrated in bench-scale (3 liters of liquor per hour) continuous equipment. In the first cycle, >99.9% of the thorium was recovered in four mixer-settler stages with Primene JM as extractant. The extract was scrubbed with dilute sulfuric acid, stripped with ammonium nitrate solution, and precipitated with ammonia. The product, which analyzed 91.4% ThO<sub>2</sub>, <10 ppm U, 0.1% total rare earths, and <0.1% PO<sub>4</sub>, is more amenable to final purification by tributyl phosphate extraction than products obtained by the usual precipitation methods. Uranium was >99.5% recovered from the liquor, in eight stages, by triisooctylamine. Rare earths were recovered by adding sodium chloride or sodium sulfate to the thorium- and uranium-barren liquor to precipitate the sodium rare-earth sulfate or by extraction with a primary amine. Sulfuric acid (3–4 M) and dilute solutions of chloride, nitrate, or carbonate were

<sup>3</sup>K. A. Allen and W. J. McDowell, *Emulsion Stabilization by Silicic Acid*, ORNL-2771 (in press).

<sup>4</sup>D. J. Crouse and K. B. Brown, *Recovery of Thorium, Uranium, and Rare Earths from Monazite Sulfate Liquors by the Amine Extraction (Amex) Process*, ORNL-2720.

efficient agents for stripping rare earths from the amine.

**Blind River Ores.** - In Blind River mills using anion exchange and nitrate elution for uranium recovery the ion exchange effluent contains nitrate ion which severely impaired extraction of thorium with di(tridecyl)amine. Extractions with primary amines (Primene JM and 1-nonyldecylamine) were unaffected by nitrate. The latter compound, recently made available commercially, has negligible solubility loss to aqueous liquors and thus appreciable economic advantage over Primene JM for this application. In mills using chloride for eluting uranium, di(tridecyl)amine is a favorable

extractant for recovering thorium from the ion exchange eluate. Stripping this amine with ~4 M sulfuric acid and heating to precipitate a thorium sulfate product showed promise in preliminary tests.

In extractions from sulfate solutions the selectivity of primary amines for thorium over metal contaminants was greatly improved by addition of a long-chain alcohol to the kerosene diluent. For example, extraction coefficients for cerium(III) and iron(III) decreased by a factor of 6 and 20, respectively, on addition of 15 vol % tridecanol to 0.08 M Primene JM-kerosene, whereas thorium coefficients were virtually unaffected.

## 9. DAPEX PROCESS

The Dapex process<sup>1</sup> selectively recovers uranium from ore acid leach liquors by extraction with a kerosene solution of di(2-ethylhexyl)phosphoric acid (D2EHPA). Metal ions are extracted by cation exchange with the hydrogen ion in the dialkylphosphoric acid. To avoid excessive extraction of iron, most of the iron is reduced to ferrous. The loaded solvent is usually stripped with 1 M Na<sub>2</sub>CO<sub>3</sub>, and the uranium is recovered by acidification of the strip solution and precipitation with ammonia. The solvent is modified with a long-chain alcohol or a neutral organophosphorus compound, such as tributyl phosphate or a phosphonate, to prevent separation of the sodium salt of D2EHPA from the diluent as a third liquid phase during stripping. The alcohols depress the uranium extraction somewhat, whereas the neutral organophosphorus compounds operate synergistically with D2EHPA to enhance uranium extraction. The Dapex process can be modified for the recovery of vanadium and possibly of thorium.

Uranium is being recovered by the Dapex process by Kerr-McGee Oil Industries, Shiprock, N.M.; Climax Uranium Co., Grand Junction, Colo.; Gunnison Mining Co., Gunnison, Colo.; Union Carbide Nuclear Company, Rifle, Colo.; and Mines Development, Inc., Edgemont, S.D. Vanadium is being recovered by Union Carbide at Rifle and by Kerr-McGee.

<sup>1</sup>K. B. Brown and C. F. Coleman, *Progr. in Nuclear Energy. Ser. III* 2, 3 (1958).

### 9.1 URANIUM STUDIES

**Ammonium Carbonate Stripping.** - An ammonium carbonate stripping method (Fig. 9.1), developed through bench scale (1.2 lb of uranium per day), has shown advantage over the usual sodium carbonate stripping method in providing a sodium- and molybdenum-free uranium product at lower reagent costs. The system is operated at 1.2-1.5 M ammonium carbonate concentration and with strip-solution recycle in order to continuously precipitate uranium as ammonium uranyl tricarbonate, which has excellent settling and filtration characteristics. Calcination at 500°C eliminates the ammonia and carbonate from the product.

**Uranium Recovery from Reduction-Bomb Liner Slag.** - A Dapex flowsheet for the recovery of uranium from sulfuric acid leach slurry (20 wt % solid) of magnesium reduction slag was successfully demonstrated.<sup>2</sup> In continuous countercurrent tests with 0.24 M di(2-ethylhexyl)phosphoric acid in kerosene (modified with 5 vol % tributyl phosphate), using five extraction and three stripping stages, uranium recovery was 99.8% and the product contained no more than 500 ppm of any one impurity. The solvent loss was less than 0.5 gal per 1000 gal of slurry. The cost of chemicals for extraction, stripping, precipitation, and solvent loss was 13¢ per pound of uranium recovered.

<sup>2</sup>A. D. Ryon and F. L. Daley, *Solvent Extraction of Uranium from Reduction Slag Slurry*, ORNL-2744 (July 13, 1959).

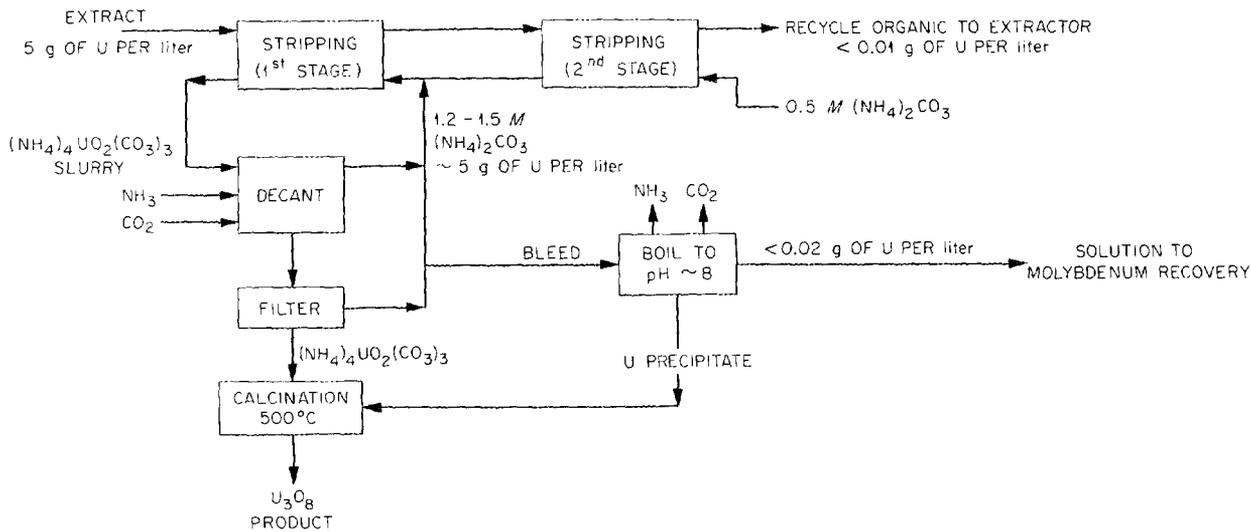


Fig. 9.1. Ammonium Carbonate Stripping of Uranium from Dapex Organic Solvent (0.1 M Di(2-ethylhexyl)phosphoric Acid + 0.05 M Diamyl Amylphosphonate in Kerosene).

**Solvent-Extraction Mixer-Settler Study.** — In continued study of phase separation, the effect of temperature on the flow capacity of gravity settlers was found to be similar to that measured for the Amex system (Sec 8). Increasing the temperature from 15 to 45°C approximately doubled the flow capacity of the settler for both organic-continuous and aqueous-continuous dispersions.

Small-scale phase separation tests of the uranium-stripping circuit using Dapex solvents and 10% sodium carbonate solution were made at a phase ratio of 1/6 ( $a/o$ ) with organic-continuous dispersions. Only a thin dispersion band was discernible, and the thickness increased very little with increased flow. However, entrainment of aqueous in the organic increased sharply and approached the flooding point at an organic flow rate of between 2.4 and 3.2  $\text{gpm}/\text{ft}^2$ . On this basis a flow of 2  $\text{gpm}/\text{ft}^2$  would be acceptable for plant de-

sign. Although scaleup tests of the settler for the stripping circuit were not made, in uranium-mill Dapex circuits phase separation was satisfactory in 7-ft settlers at a solvent flow rate of 1.8  $\text{gpm}/\text{ft}^2$ , in good agreement with results of laboratory tests.

The effect of phase ratio ( $a/o$ ), at a constant power input, on the rate of extraction of uranium from sulfate liquors was investigated. Organic-continuous mixing at phase ratios ( $a/o$ ) of 1/1 to 1/49 and aqueous-continuous mixing at phase ratios ( $a/o$ ) of 49/1 to 1/1 were examined. Preliminary evaluation of the data indicates that the extraction rate increases for both types of mixing as the proportion of the dispersed phase is increased. In other kinetic studies the rate of uranium extraction from perchlorate solutions was observed to be about ten times as high as that from sulfate solutions, indicating the large effect from sulfate complexing of uranyl ion in the latter case.

**Part III**  
**FEED MATERIALS PROCESSING**



## 10. FLUOROX PROCESS

In the Fluorox process,  $UF_6$  is prepared by oxidizing  $UF_4$  with dry  $O_2$  or air at 700–850°C in a fluidized-bed reactor. The uranyl fluoride by-product is recycled back to the  $UF_4$  feed stream by a two-step process. The experimental program was completed and evaluation of experimental data and economic studies are in progress.

### 10.1 FLUIDIZED-BED REACTOR DEVELOPMENT

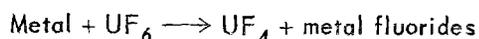
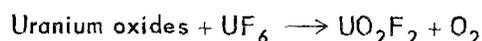
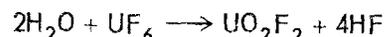
The chief engineering development work was aimed at the design and testing of a continuous fluidized-bed reactor for the primary oxidation reaction,  $2UF_4 + O_2 \longrightarrow UF_6 \uparrow + UO_2F_2$ . Sized  $UF_4$  was continuously fed into a  $UO_2F_2$  bed, which was fluidized with dry  $O_2$  or air at 700–850°C. The  $UF_6$  produced was removed in the off-gas stream and subsequently recovered in cold traps.

The final design of the all-Inconel reactor (Fig. 10.1) included a 4-in.-dia constant-volume fluidized-bed section in which a constant bed height was maintained by an overflow line, four porous metal filters for removing entrained solids from the off-gas stream and returning them to the fluidized-bed section, and a  $UF_4$  feeder made from a Jabsco pump adapted to meter  $UF_4$  into the bottom of the reactor as fluidized  $UF_4$ . The off-gas system was composed of 8-in. cold traps for collecting the  $UF_6$  product, chemical traps for removing trace amounts of  $UF_6$  from the off-gas, and a condensation pressure analyzer for measuring the  $UF_6$  concentration in the reactor off-gas.

During operation the reaction temperature was maintained in the fluidized-bed section by a combination of external heaters and gas preheaters. The fluidizing gas was predried in molecular sieves. The  $UF_4$  concentration in the fluidized bed was maintained below 10% to decrease sintering and caking of  $UF_4$  above 800°C and to retard formation of uranium fluoride intermediates such as  $U_4F_{17}$ . With 10%  $UF_4$  in the bed, approximately 5% of the feed is sent to the recycle stream before reaction occurs.

Five runs were made with pure  $UF_4$  and both  $O_2$  and air. The use of either  $O_2$  or air as the oxidizing agent is feasible in the system, and more than 90% of the theoretical amount of  $UF_6$  was recovered from or measured in the reactor off-gas. The remainder of the theoretical amount of  $UF_6$  was accounted for by various side reactions (Fig. 10.2)

in which the product  $UF_6$  reacted with water and uranium oxides introduced in the feed and with the metal walls of the reactor to form corrosion products:



The  $UF_4$  feed rate in these runs varied from 985 to 1600 g/hr and the total fluid bed weight was approximately 6000 g. Analysis of the  $UF_6$  product showed that it did not meet specifications. However, the only contaminant, HF, may be easily removed by volatilization (the boiling point of HF is 19°C, whereas that of  $UF_6$  is 56°C).

Two runs were made in the 4-in. fluidized bed system with crude  $UF_4$  (prepared from unpurified mill concentrate) as the feed material. This material contained up to 10% impurities, which resulted in relatively low melting ( $\sim 730^\circ\text{C}$ ) and sintering ( $\sim 690^\circ\text{C}$ ) points, necessitating operation at low temperatures (700–725°C) and low feed rates (300–400 g/hr). The product  $UF_6$  was highly contaminated with volatile fluorides, mainly vanadium and chromium fluorides and HF, and corrosion of the Inconel reactor was prohibitive ( $\sim 5$  in./year). Use of this type of  $UF_4$  feed may be possible if a suitable material of construction can be found.

Reaction-rate constants, in which the specific-surface-area term was eliminated, were determined for each run. At steady-state operation the reaction-rate constant in units of the reciprocal of time can be determined thus:

$$k = \frac{UF_4 \text{ reacting to } UF_6 \text{ per unit time}}{UF_4 \text{ holdup in the bed}}$$

Comparison of reaction-rate constants for the primary Fluorox reaction determined from both laboratory and batch fluidized-bed reactor data indicated a constant discrepancy equivalent to 20–40°C in reaction temperature (Fig. 10.3). However, there is good agreement between laboratory and continuous fluidized-bed data in the temperature range 700–800°C. The available reaction-rate data appear sufficiently precise for design of larger reactors.

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HOT OFF-GAS

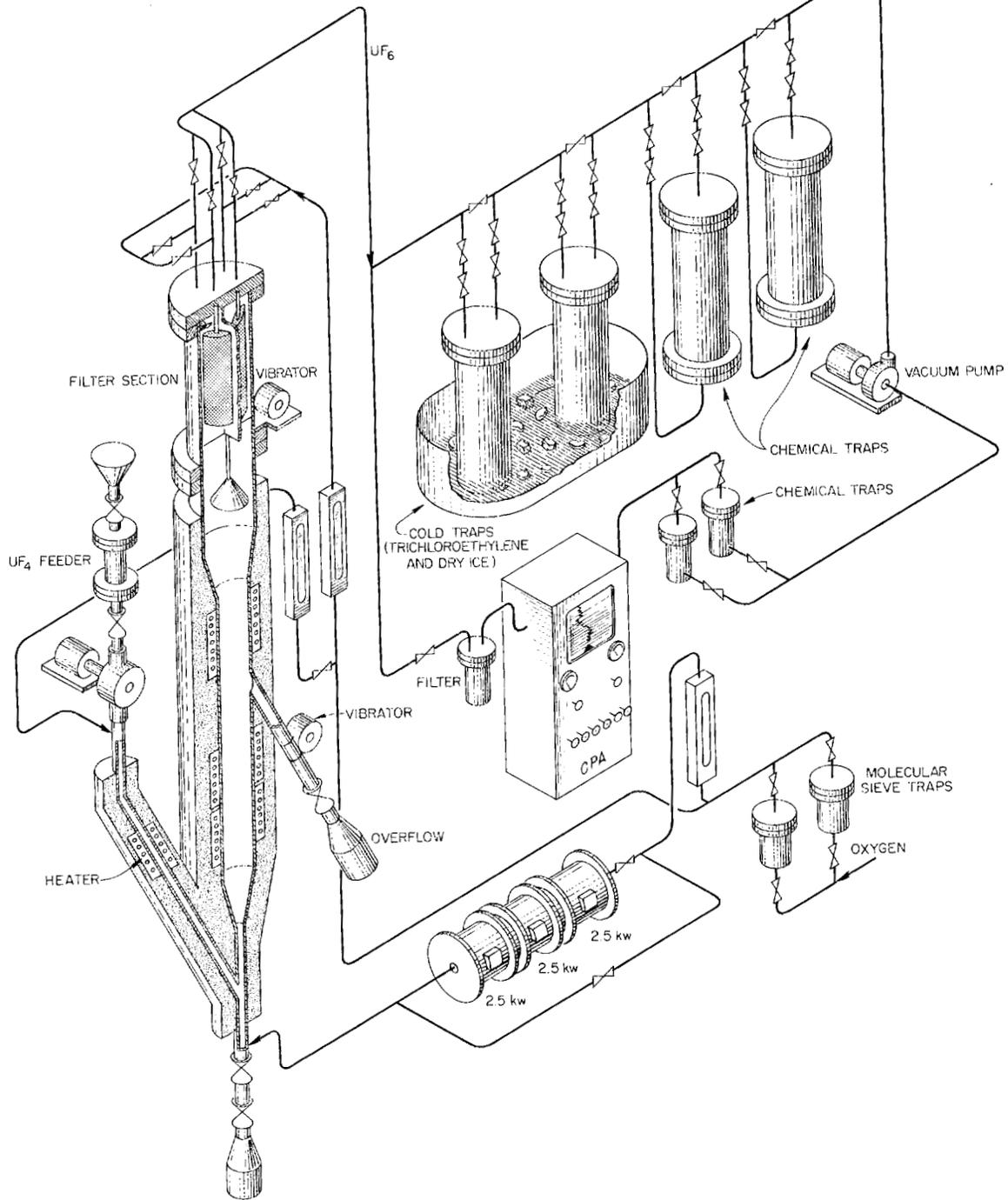
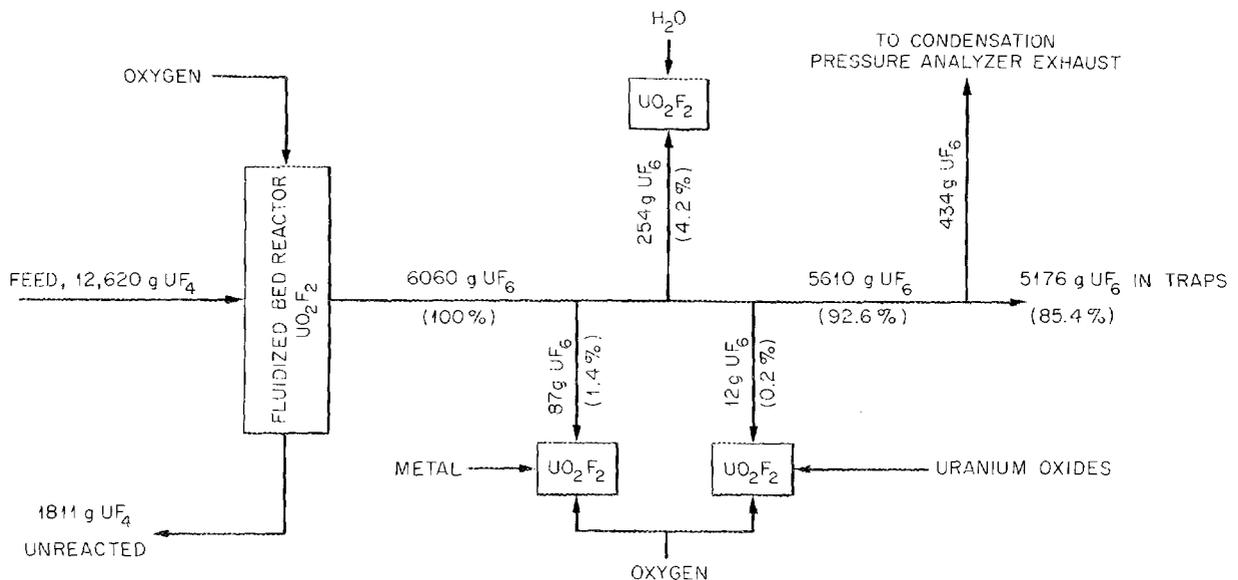


Fig. 10.1. Fluorox Fluidized-Bed Reactor Equipment.

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$UF_6$  MEASURED IN REACTOR OFF-GAS STREAM BY CONDENSATION PRESSURE ANALYZER

TOTAL  $UF_6$  ACCOUNTED FOR = 5529 g OR 91.2% OF THEORETICAL (BASED ON  $UF_6$  ACTUALLY TRAPPED FROM OFF-GAS STREAM)

= 5963 g OR 98.4% OF THEORETICAL (BASED ON  $UF_6$  MEASURED IN REACTOR OFF-GAS BY CONDENSATION PRESSURE ANALYZER)

Fig. 10.2. Sample Run in Fluidized-Bed Reactor.

Available experimental data indicate that Inconel will be a suitable material of construction for the reactor. Corrosion rates of 0.1 to 0.7 in./year were measured in the fluidized-bed section of the reactor during experimental runs at 800–850°C with temperature excursions in some runs. If the temperature is kept below 850°C, corrosion can be apparently kept to the lower values. Corrosion in the gas phase of the reactor is insignificant. A report summarizing the fluidized-bed reactor development program is being prepared.

### 10.2 FEED PREPARATION

The proper size range of  $UF_4$  for the Fluorox 4-in. fluidized-bed reactor is -20 +150 mesh

(U.S. standard sieve). Since  $UF_4$  feed from gaseous diffusion plants is much finer (80% -100 mesh), the size must be increased. The upgrading was done in two steps by compacting the fine material in a Chilsonator compactor to +8 mesh and decreasing the size of this material to the feed-size range by a granulating machine.

**$UO_2F_2$  Recycle.** — Since at least 50% of the uranium from the  $UF_4$  oxidation with  $O_2$  results in  $UO_2F_2$ , a complete process will require a method of recycling the  $UO_2F_2$  back to the  $UF_4$  feed stream. A two-step recycle is possible, in which the  $UO_2F_2$  is reduced with  $H_2$  to  $UO_2$ , which is hydrofluorinated to  $UF_4$  with HF. This recycle

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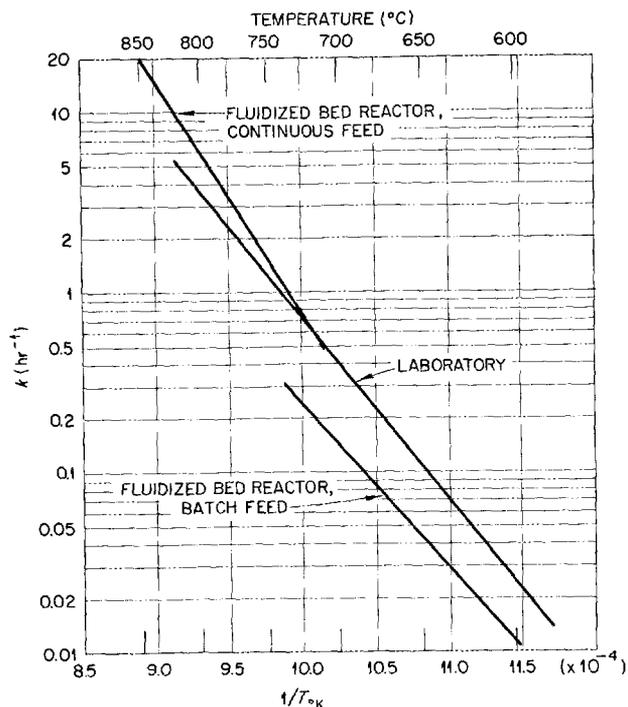


Fig. 10.3. Comparison of Reaction Rate Constants for the Reaction  $2UF_4 + O_2 = UO_2F_2 + UF_6$ , Determined from Laboratory and Fluidized-Bed Reactor Data.

scheme would give a complete process with  $UF_4$  as the feed and  $UF_6$  as the product, with some additional by-product gas streams (Fig. 10.4). The reduction of  $UO_2F_2$  with  $H_2$  was investigated in the laboratory, and the hydrofluorination of  $UO_2$  to  $UF_4$  is a well-known<sup>1</sup> reaction in feed processing.

**Reduction of  $UO_2F_2$  with  $H_2$ .** — The reaction of  $UO_2F_2$  with hydrogen at 700–850°C was investigated in the laboratory.<sup>2</sup> The reaction in this temperature range proceeds according to the equation  $UO_2F_2 + H_2 \rightarrow UO_2 + 2HF$ . Rates of the chemical reaction were not obtained, since, with the thermogravimetric technique used, the rate-controlling process was bed diffusion. However, the rate of chemical reaction is sufficiently high for the desired application. No significant amount of  $UF_4$  was formed by the back reaction,  $UO_2 + 4HF \rightarrow UF_4 + 2H_2O$ .

<sup>1</sup>M. Benedict and T. H. Pigford, *Nuclear Chemical Engineering*, p 149, McGraw-Hill, New York, 1951.

<sup>2</sup>L. M. Ferris and R. P. Gardner, *Recycle of  $UO_2F_2$  in the Fluorox Process. Reaction of  $UO_2F_2$  with  $H_2$* , ORNL-2690 (June 25, 1959).

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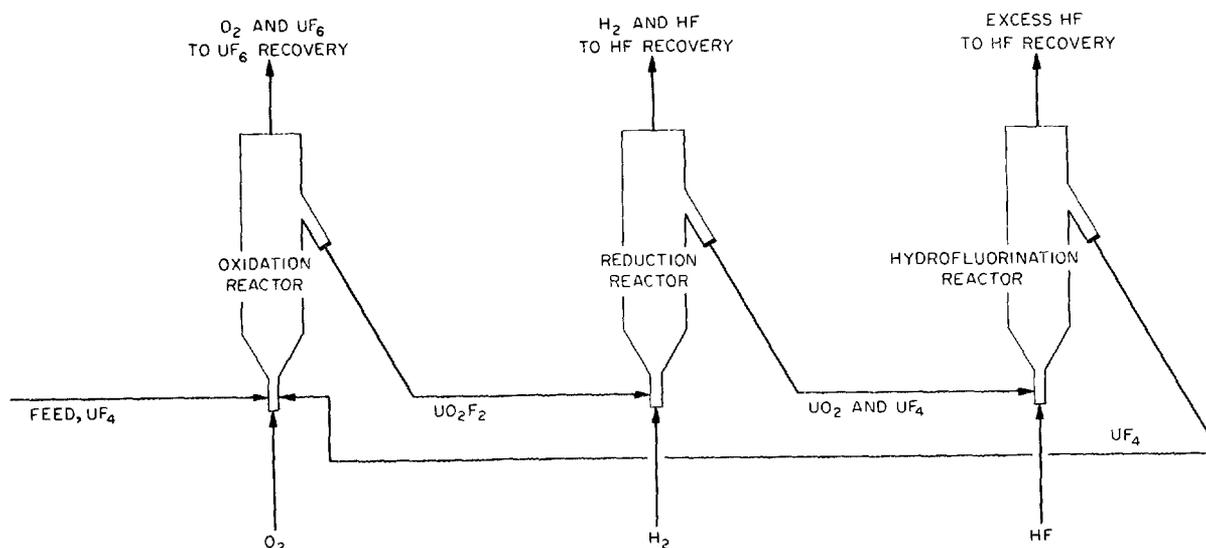


Fig. 10.4. Fluorox Flowsheet with  $UF_4$  as Feed.

## 11. PRODUCTION OF URANIUM METAL BY REDUCTION WITH ALKALI METALS

### 11.1 REDUCTION OF $UF_6$ WITH LITHIUM AMALGAM OR SODIUM AMALGAM

The laboratory study<sup>1</sup> of uranium production by lithium amalgam or sodium amalgam reduction of  $UF_6$  was completed. In the preferred process (Fig. 11.1), a slurry of 2 moles of lithium per liter of mercury is mixed at 25°C, under high-shear conditions, with  $UF_6$  vapor carried in argon. Approximately 86% of the uranium is converted to  $UHg_4$  by the reaction  $UF_6 + 6LiHg_3 \rightarrow UHg_4 + 6LiF + 14Hg$ . The  $UHg_4$  is wetted and protected from oxidants by the excess mercury. The product amalgam, a slurry of 0.5% uranium as  $UHg_4$ , unreduced  $UF_4$ , and by-product LiF in 0.7 M lithium amalgam, is vacuum-filtered. The solids, with some excess amalgam, are retained; the lithium amalgam passes through and is recycled to the reactor together with enough 6 M Li(Hg) from the electrolytic cell to give 2 M Li(Hg) in the reactor. The  $UF_4$  and LiF are water-washed from the uranium amalgam concentrate and recovered. The

washed uranium quasi amalgam, which makes up ~25% of the mercury stream and contains ~3 wt % uranium, is vacuum-dried or decanted from amalgamated phase separators to remove residual impurities and water. The mercury is separated from the uranium by vacuum distillation at 400°C in the upper section of a combined crucible and melting furnace; uranium sponge is produced. As the charge moves vertically down the furnace to the crucible, the sponge melts, at ~1200°C, and may be tapped off as molten uranium metal.

Suspended lithium-uranium fluoride and small particles of suspended mercury are removed from the amalgam wash slurry by centrifugation. Water and mercury are separated from the solids by calcination at 400°C;  $UF_4$  is separated from LiF by fluorination to  $UF_6$ . Residual LiF, reslurried with the supernatant LiF solution from the centrifugation step, is reconverted to LiOH by treatment with lime. After settling, the supernatant LiOH solution is concentrated by evaporation and recycled to the amalgam cell.

Six-molar lithium amalgam concentrate is produced by a combination of electrolysis of 2 M LiOH

<sup>1</sup>Chem. Tech. Ann. Prog. Rep. Aug. 31, 1958, ORNL-2576.

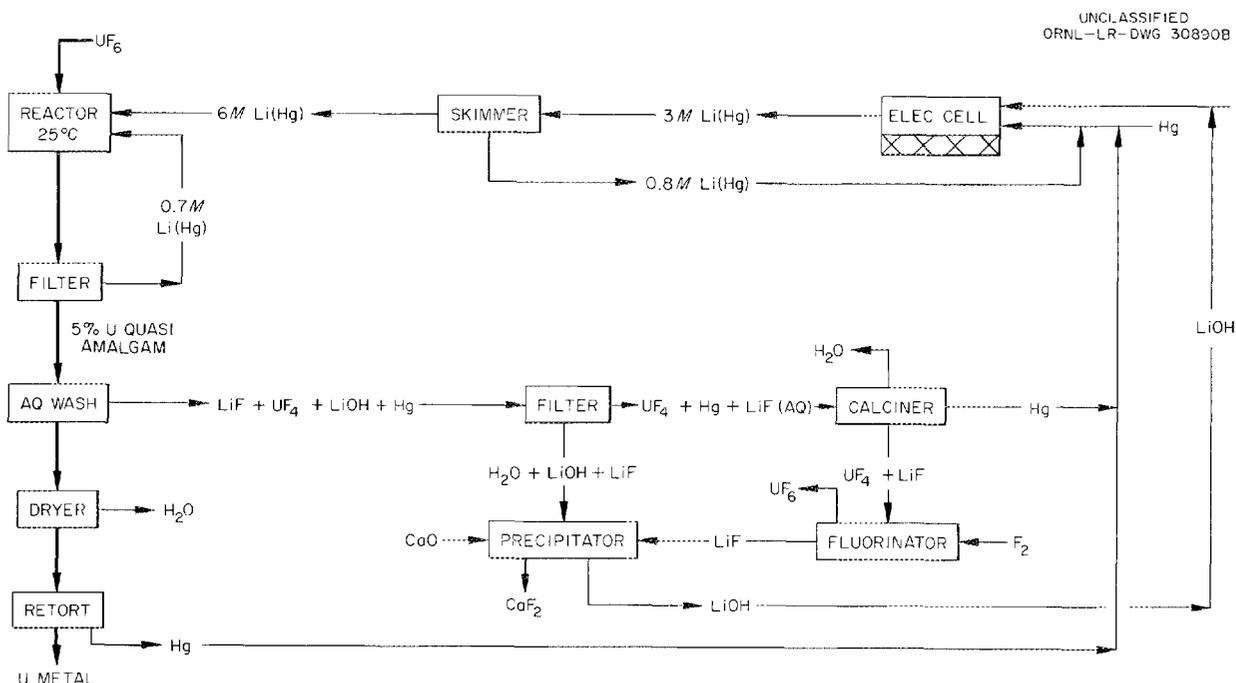


Fig. 11.1. Production of Uranium Metal from  $UF_6$  by Reduction with Lithium Amalgam.

over mercury and skimming. The solubility of  $\text{LiHg}_3$  in mercury at  $25^\circ\text{C}$  is 0.83 M. With a cell potential of 8 v, a slurry of 3 M  $\text{Li(Hg)}$  is produced. The  $\text{LiHg}_3$  floats and is skimmed off, producing a sludge of  $\sim 6$  M  $\text{Li(Hg)}$ .

One run was carried through to a 13-g uranium button. With the exception of mercury, the concentration of contaminants (in ppm) attributable to the processing was lower than for electrolytic-grade metal:

Lithium	10
Fluoride	20
Mercury	282
Iron	10
Oxygen	17
Hydrogen	2
Nitrogen	76

The high mercury content was thought to be due to recontamination from the vacuum-retort atmosphere on cooling.

When sodium amalgam was used as a reducing agent the maximum reduction yield was 40%. From experimental evidence it was thought that  $\text{NaF}$  complexed the  $\text{UF}_4$  intermediate product to irreducible  $\text{Na}_2\text{UF}_6$ , thus diverting a major portion of the uranium stream from the primary product.

### 11.2 REDUCTION OF $\text{UO}_2$ WITH MAGNESIUM AMALGAM

Amalgam reprocessing of high-fired uranium dioxide fuels is being investigated. In two runs,  $1700^\circ\text{C}$ -fired  $\text{UO}_2$  was reduced with magnesium at  $\sim 1000^\circ\text{C}$  under argon in the presence of magnesium chloride<sup>2</sup> with apparently 100% reduction yield. In the first experiment 93% of the uranium was extracted from the reaction mixture by mercury as the mercuride, while the remaining 7% was retained by a hard crust above the mercury surface. In the second run, 100% of the reduced uranium was recovered in the mercury.

### 11.3 DRUHM PROCESS

The reduction of  $\text{UF}_6$  to uranium with sodium metal in the vapor phase is being studied. The

<sup>2</sup>R. G. Bellamy and J. H. Buddery, *The Production of Uranium Powder by the  $\text{UO}_2$ -Mg Route*, AERE M/R-1049 (Oct. 28, 1952).

possible advantages of the process are: continuous operation with a primary uranium feed material in a low-pressure reactor; lower reagent costs than those of the calcium or magnesium reduction process; and lower operating and capital costs than those of existing processes for conversion of  $\text{UF}_6$  to metal.

After approximately a year of experimental work a satisfactory reactor liner has not been developed, efforts to develop an operable nozzle to feed  $\text{UF}_6$  gas to the reaction chamber have been only partially successful, and, as a result of many factors, high yields of consolidated uranium metal have not been obtained consistently. However, some results have been encouraging: (1) after the  $\text{NaF}$  slag melting temperature was lowered by the addition of  $\text{LiF}$  in a laboratory reduction of  $\text{UF}_4$  with 100% molal excess  $\text{Na}$ , reduction to metal was complete, the uranium crystals were large, and uranium settled to the bottom of the reactor, thus indicating that by operation at elevated temperature a high yield of consolidated, nonpyrophoric metal can be produced; (2) a helium-cooled copper inlet nozzle for  $\text{UF}_6$  was operated successfully at temperatures above  $1200^\circ\text{C}$ ; (3)  $\text{MgO}$  and graphite reactor liners were sometimes satisfactory at operating temperatures above the boiling point of  $\text{Na}$ ; (4) in one run high recovery of massive metal was observed.

**Laboratory Studies of the Reduction of  $\text{UF}_6$  with Sodium.** - A series of batch experiments in which  $\text{UF}_6$  and 100% excess sodium were heated in sealed nickel reactors was performed to determine the yields and rates for the reactions



at 25 to  $700^\circ\text{C}$ . At  $25^\circ\text{C}$ , the rate for both reactions appeared to be zero. The rate for the first reaction was significant at  $100^\circ\text{C}$ , and it increased with increasing temperature. In all experiments at temperatures above  $100^\circ\text{C}$ , a "firing point" was observed at  $140$ - $180^\circ\text{C}$  as the reactors were heated for the first reaction. The rate of the second reaction did not become significant until the temperature exceeded  $500^\circ\text{C}$ . The second reaction was therefore considered to be the slower and limiting step. It was also noted that the presence of  $\text{NaF}$  appeared to retard the first reaction.

**Laboratory Studies of the Reduction of  $UF_4$  with Sodium.** — A series of ten experiments was performed to study yields and reaction rates of the second reaction at temperatures from 800 to 1200°C. When a mixture of  $UF_4$  and NaF in a 1:2 mole ratio was reacted for 1–2 hr with 100% excess sodium at temperatures from 800°C to the melting point of the NaF slag (990°C), reduction to metal was 79.7% complete, but the uranium metal was pyrophoric and did not separate from the slag. When a  $UF_4$ -NaF-LiF mixture in a 1:5:8 mole ratio (mp 710°C) was reacted with 100% excess sodium at 800°C, the reduction to metal was complete, the uranium crystals were large and nonpyrophoric, and 70% of them settled to the bottom of the reactor. The results indicated that conversion of  $UF_6$  to metal is complete in operation with 100% excess sodium above 800°C, and that operation above the melting points of the NaF slag (990°C) and the uranium metal (1130°C) is required for separation of slag from metal.

**Consolidation of Uranium Metal and Evaluation of Reactor Refractories.** — In the above reductions of  $UF_4$  with sodium, the feasibility of consolidation of the uranium metal and the performance of reactor liner materials were studied. In all runs, reactor liners corroded, spalled, or cracked (Table 11.1); these effects limited the conclusions that can be drawn from the consolidation study. In runs where effects on liners were less severe, in which

the loss of uranium due to these side reactions was less than 25%, consolidation to small beads was observed. In one run, where 100 g of finely divided uranium was heated at 1200°C under vacuum for 7 hr with 50 g of NaF, 64% of the metal was recovered in a single button. The remainder reacted with NaF to produce  $UF_4 + Na$ , which vaporized and condensed on the reactor walls or reacted with the MgO liner to produce  $MgF_2 + UO_2$ . The latter was expected under vacuum, since sodium vapor pressure reaches 760 mm at 880°C and  $UF_4$  has a significant vapor pressure at 1000°C.

In the same series of  $UF_4$ -NaF reductions with sodium, nickel reactor liners were severely corroded, and all ceramic materials were corroded, eroded, or cracked under the operating conditions. In two special series the liners were heated with boiling sodium and with fused  $UF_4$ -NaF mixtures. It was concluded that cracking, spalling, and disintegration were due to the presence of liquid sodium, which penetrated pores and cracked the ceramic on flashing to vapor within the pores. In addition, the sodium reduced  $ZrF_4$  and  $AlF_3$  formed by the exchange of  $UF_4$  with  $ZrO_2$  and  $Al_2O_3$ . The formation of acetylene on contact of ceramic product with water indicated some chemical action between sodium and graphite. Magnesia and 3%-porosity graphite were least affected.

Table 11.1. Performance of Refractory Materials as Liners in the Reactor for the Reduction of Fluoride with Sodium  
Refractory material used in the form of a crucible as container for the reactants

Refractory Liner Material	Performance		
	In Sodium Alone, at 880°C	In $UF_4 + NaF$ at 1200°C	In Na + NaF + $UF_4$ at 1200°C
Norton Magnorite (fused magnesia, 20% porosity)	Cracked and spalled	Chemical exchange $UO_2 + MgF_2$	Cracked, chemical exchange $UO_2 + MgF_2 + Na$
National RH 0200 (graphite, 3% porosity)	Cracked, produced acetylene	Spalled, no cracking	Cracked, produced acetylene
Norton Alundum, 99% fused		Chemical exchange $UO_2 + AlF_3$	Disintegrated, produced $UO_2 + Al$
Norton 5% lime-stabilized zirconia	Cracked and spalled	Chemical exchange, spalled	Disintegrated
High-density graphite, 20% porosity	Shattered, produced acetylene	Spalled, no cracking	Shattered

**Reduction Reactor Development.** – Uranium hexafluoride was reduced with sodium in a 6-in.-dia reactor, which is essentially full-scale equipment for processing of highly enriched uranium. The equipment included a system for vaporizing and metering  $UF_6$ , a system for melting and metering sodium, and an Inconel reactor lined with graphite or a ceramic. An off-gas system was included for trapping out excess sodium and cleaning up the off-gas before it was sent to the radioactive off-gas system. The reactor was induction-heated to operating temperatures prior to feed introduction.  $UF_6$  vapor and sodium liquid were metered continuously into the reaction zone, where the sodium flashed to vapor and the reaction occurred in the vapor phase. The adiabatic flame temperature for the reactants at  $100^\circ C$  was calculated to be  $1980^\circ C$ . Reduction products were collected as a batch in the bottom of the reaction chamber.

Engineering development has been aimed at design and testing of suitable reactor components. Some operational data reflecting optimum operating conditions were also obtained. The two most serious problems in the development of the Druhm process have been the design of a suitable inlet nozzle for  $UF_6$  and the development of a satisfactory liner to contain the reaction and reaction products (molten uranium and sodium fluoride) at temperatures as high as  $1200^\circ C$ .

Thirty-four experimental runs were made in the semicontinuous reactor system. During the first 16 runs, various types of nozzles of Inconel, Lavite, magnesia, Monel, graphite, and tungsten were tried, but in all cases the nozzles either plugged or were consumed. In some of the late runs, a copper nozzle cooled internally with helium (Fig. 11.2) was used successfully at reactor temperatures above  $1200^\circ C$ . Although there have been occasional nozzle failures since, the basic nozzle design principle has been established. In future test models other materials, including Inconel and uranium, will be evaluated. Nozzle types that were found unsatisfactory included simple tubes and massive-metal and sodium-cooled nozzles fabricated from each of the materials tested.

Both magnesia and graphite were used successfully as reactor liners during the development runs. The MgO used was slip-cast or pressed with subsequent firing to  $1800^\circ C$ , and the graphite was a commercial grade. Both thin MgO ( $\frac{1}{8}$  in.) and

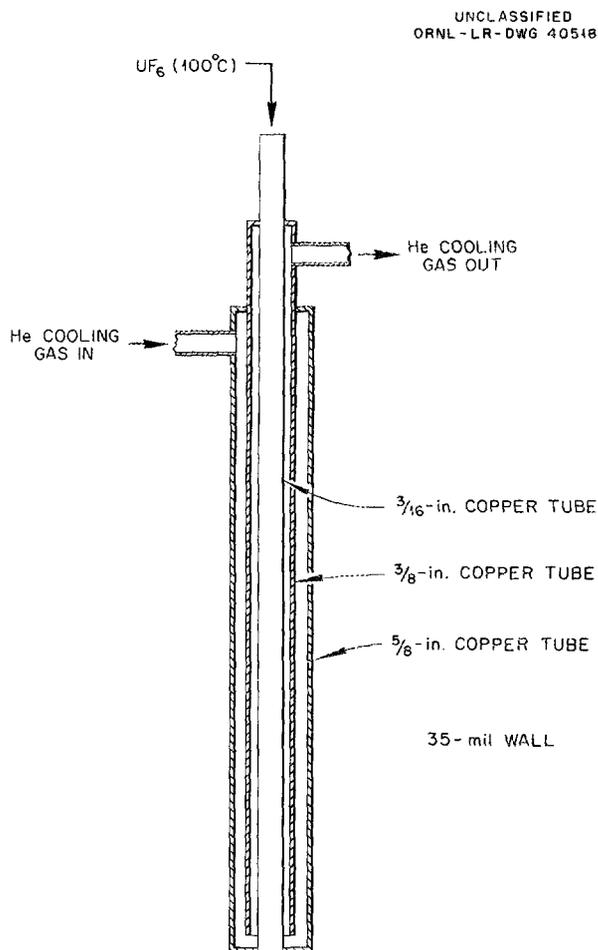


Fig. 11.2. Helium-Cooled  $UF_6$  Nozzle for Druhm Reactor.

graphite ( $\frac{1}{4}$  to 1 in. thick) tended to crack badly when the reaction-zone temperature was allowed to cycle up through the boiling point of sodium during the reaction. However, when the reaction-zone temperature did not go below the boiling point of sodium during the actual reaction, no cracks developed. There was some chemical attack on MgO during the reduction. This was especially true when there was a deficiency or low excess of sodium. In future development runs, graphite will probably be used for the lining material because of its availability and ease of fabrication.

In one semicontinuous reduction run, 88.3% of the uranium introduced as  $UF_6$  was recovered as massive uranium metal with a purity of 99.6%. There was also unconsolidated uranium metal in

the slag and in the liner walls; recovery of this uranium would have increased the efficiency. These experimental runs have shown the desirability of operating with the reaction zone above the melting point of uranium metal ( $\sim 1130^{\circ}\text{C}$ ) so that the product can be consolidated and separated. It also appears that a substantial excess of

sodium ( $>50\%$ ) will be necessary to ensure complete reduction to the metal.

Since design of the  $\text{UF}_6$  nozzle and choice of the liner material are complete, subsequent engineering work will be directed toward determining optimum operating conditions and testing of a completely continuous system.



Part IV  
GENERAL RESEARCH



## 12. EQUIPMENT DECONTAMINATION STUDIES

Decontamination research was concerned chiefly with developing methods for descaling and decontamination of the HRT with minimum corrosion. The chromous sulfate method of Baybarz<sup>1</sup> was used to descale a pump that had failed in service in the HRT chemical plant. Descaling was followed by flushing with dilute HNO<sub>3</sub> mixed with hydrogen peroxide, which is superior to the older alkaline tartrate peroxide for removing residual niobium. Decontamination was sufficient to permit disassembly and examination.

A simple and cheap method of preparing chromous sulfate in large quantities consists in heating slightly acidified chromic sulfate over mossy zinc in an inert atmosphere. The corrosion rate was somewhat decreased, without significant decrease in descaling power, by lowering the acidity to about 0.1 M H<sub>2</sub>SO<sub>4</sub>.

Several other reagents were used successfully to descale pieces of pipe from the HRT: alkaline periodate, which was also an efficient decontaminating reagent,<sup>2</sup> alkaline hypophosphite preceded by a short oxidative treatment with alkaline permanganate or periodate, alkaline periodate mixed with permanganate, pyrophosphoric acid, and concentrated nitric acid with long boiling. Deoxidine 170 (an inhibited phosphoric acid marketed by AmChem) and the Turco 4501 process (Turco Products Inc.) were also successful in HRT scale removal, although the latter process flaked scale off the steel instead of dissolving it cleanly. Turco 4512 is an inhibited phosphoric acid somewhat similar to Deoxidine 170. A descaling reagent of particular interest, still under development, is trivalent uranium, produced *in situ* by circulation of slightly acidified uranyl sulfate through zinc. Descaling of HRT specimens at HRT fuel concentration was demonstrated, with

corrosion rates of less than 1 mil/month. In addition to descaling research, decontamination effort was also directed toward removal of the stubbornly held niobium that remains on stainless steels after most other contaminants have been removed.<sup>3</sup> It was found that hydrogen peroxide with dilute nitric acid was superior to peroxide with alkaline tartrate, besides being cheaper and more stable. The best decontaminants for niobium were alkaline periodate (1 M KIO<sub>4</sub> in 2 M KOH at 90°C for 1 hr) and the Turco 4501 process. Both methods decontaminated stainless steels from niobium by factors of up to several hundred, compared to <5 for the controls boiled with nitric acid.

The corrosiveness of the old "3-20" reagent described by Bennett,<sup>4</sup> 3% HF in 20% HNO<sub>3</sub>, was lowered without loss in effectiveness by the inclusion of enough aluminum to complex the fluoride. In the Fused Salt-Fluoride Volatility process, an adequate decontamination method involving ammonium oxalate and HNO<sub>3</sub>-aluminum nitrate was developed by Jolley *et al.*<sup>5</sup> The effectiveness of the Turco 4501 decontamination process was demonstrated in the Thorex pilot plant by Parrott,<sup>6</sup> who found the process to be the best and cheapest ever used by that group on plant-scale equipment.

<sup>1</sup>R. D. Baybarz, *Decontamination of a Homogeneous Reactor*, ORNL CF-57-9-59 (Sept. 9, 1957).

<sup>2</sup>H. B. Whetsel, private communication, Nov. 10, 1958.

<sup>3</sup>D. O. Campbell, *Decontamination of Stainless Steel*, ORNL-1826 (Feb. 17, 1955).

<sup>4</sup>M. R. Bennett, *Evaluation of Reagent Decontamination - Quarterly Report for Period 8-10-51 to 11-10-51*, ORNL CF-51-11-123 (Nov. 21, 1951).

<sup>5</sup>R. L. Jolley *et al.*, *Equipment Decontamination Methods for the Fused Salt-Fluoride Volatility Process*, ORNL-2550 (Aug. 19, 1958).

<sup>6</sup>J. R. Parrott, *Evaluation of the Turco 4501 Process for Decontamination of the Thorex Dissolver*, ORNL CF-59-1-23 (Jan. 12, 1959).

13. THORIUM OXIDE SLURRY DEVELOPMENT<sup>1</sup>

Chemical development of an aqueous thorium oxide slurry for homogeneous reactor use was continued. The long-range aspects still emphasized the ultimate use of the slurry as a breeder blanket, but some attention was given to incorporating uranium in the solid and evaluating the characteristics of thoria-urania as a possible slurry fuel. The preferred method of preparing thorium oxide for slurry use is precipitation and thermal decomposition of thorium oxalate, and further work was done on the effect of precipitation conditions on particle size and shape and the adaptation of the method to the production of thorium-uranium oxide.

Approximately 4700 lb of thorium oxide and 3000 lb of thorium-uranium oxide with U/Th ratios of 0.005, 0.08, and 0.16 were prepared for slurry engineering studies – the thoria by the oxalate method, and the thoria-urania by adsorption of uranium on preformed thoria solids and subsequent firing.

The preparation of thorium-uranium oxides by flame denitration of alcohol solutions of the nitrates, of thorium oxide by fluidized- and agitated-bed denitration, and of thoria spheres by a gel technique were also studied.

Slurry development studies included the use of hydroclones for solids classification and transport, the development and evaluation of a small rolling-ball viscometer for use with slurries, the use of boric acid as a soluble poison in criticality control, the leaching of uranium from mixed oxide solids by aqueous solutions at high temperatures, and the coating of thoria with silicate to keep it dispersed at elevated temperatures.

Further work was carried out with  $\text{MoO}_3$  and palladium as catalysts for radiolytic gas recombination in slurries. Slurry irradiation studies continued, with particular emphasis on in-pile gas production and recombination. Improved methods of cooling the small stainless steel autoclaves used in the studies were also investigated, to permit irradiation at higher levels.

## 13.1 OXIDE PREPARATION DEVELOPMENT

**Thorium Oxalate Precipitation.** – Some properties of  $\text{ThO}_2$  slurries appear to depend partially on the conditions of preparation of the thorium oxalate from which the thoria is made. Digestion

of the oxalate did not change the average particle size of the oxide, and there was no change in the x-ray crystallite size of either the oxalate or oxide prepared from it as a result of the digestion of the oxalate up to 48 hr at 75°C. Crystallite sizes of the oxalate hexahydrate and dihydrate and the 800°C-fired oxide were 750, 300, and 150 Å, respectively. Caking of the oxide product, as indicated by a high cake resuspension index, was eliminated by digestion of the oxalate for 6 hr at 75°C or for >24 hr at 28°C. The surface areas of the oxides prepared from digested oxalates were about twice as great as those from the undigested. There were no consistent changes in water content of the oxalate as determined thermogravimetrically, or in adsorbed nitrate or water as determined by infrared absorption as a function of the oxalate digestion time.

**Cubic Particles.** – The addition of certain bi- and polydentate organic compounds, principally amines, to the oxalate precipitation system caused freshly precipitated thorium oxalate to grow on digestion into square-faced, more or less cubic particles, 1 to 20  $\mu$  on an edge, whose characteristics were essentially retained in the oxide product. The ratio of thickness to length of edge of the square face varied from about 0.2 to 1.0 and increased with decreasing thorium concentration; the ratio also increased with increasing oxalate-to-thorium ratio, complexing-agent-to-thorium ratio, and strength of the complexing agent. The effect of nitric acid depended on the nature of the complexing agent. A final concentration of 1.0 to 2.0 M  $\text{HNO}_3$  was necessary to produce any effect with urea, ethylenediamine, and propylenediamine, while triethanolamine affected the precipitation to about the same extent whether nitric acid was added or not; citric acid showed less effect with added nitric acid and an enhanced effect with added ammonia. The rate of recrystallization, in general, was increased by the conditions which increased the ratio of thickness to length of edge. The complexing agents, in order of effectiveness, were urea < guanidine < pentaerythritol < citric acid < ethylenediamine < propylenediamine < triethanolamine < Versene.

<sup>1</sup>Reported in more detail in Homogeneous Reactor Project quarterly reports, e.g., ORNL-2696.

**Thoria Spheres.** — An improved method of preparing  $\text{ThO}_2$  spheres by a gel technique is under development. A thoria sol produced by partial neutralization of a thorium nitrate solution with ammonia ( $\text{NH}_4/\text{Th} \geq 3.5$ ) was jetted through an orifice along with an isopropyl alcohol solution containing 12 to 14 vol %  $\text{H}_2\text{O}$ , causing the sol to set into beads, the size depending on the flow rates through the orifice. The beads were washed with more isopropyl alcohol, filtered, vacuum-dried, and slowly brought to  $1000^\circ\text{C}$ . The product had an average particle size of  $4.5 \mu$ , a surface area of  $0.65 \text{ m}^2/\text{g}$ , and a density, as measured pycnometrically, of  $6.8 \text{ g}/\text{cc}$ .

**Thorium-Uranium Oxide.** — Two methods of incorporating the uranium in thorium oxide in the production of engineering quantities of mixed oxide for fuel slurry studies were investigated: coprecipitation of the thorium-uranous oxalates and precipitation of uranium onto a  $650^\circ\text{C}$ -fired thorium oxide from ammonium uranyl carbonate solution, both methods followed by firing of the mixed solids. To coprecipitate the oxalates, uranous oxalate complexed with ammonium oxalate was added to the oxalic acid used as the precipitating agent. In the second method, a 4-hr firing at  $1000^\circ\text{C}$  was sufficient to incorporate the bulk of the uranium in the mixed oxide solid. The product retained the particulate properties of the oxide used. The upper firing temperature for the product from either method was determined by the effect of uranium in lowering the sintering temperature (i.e.,  $1300^\circ\text{C}$  for a U/Th ratio of 0.005;  $1000^\circ\text{C}$  for a U/Th ratio of 0.05).

Particle size was controlled in the coprecipitation method by controlling the temperature, precipitation rate, and reagent concentration during the precipitation. For the production of mixed oxide with a U/Th ratio of 0.05, total precipitation times of 45 to 60 min, precipitation temperatures of  $30$  to  $50^\circ\text{C}$ , and the use of  $0.5 \text{ M}$  thorium nitrate and oxalic acid gave mixed oxides of average particle sizes between  $1.6$  and  $4.2 \mu$ . With  $0.7 \text{ M}$  reagents the average particle sizes were  $1.1$  to  $2.0 \mu$ . The production of mixed oxides with U/Th ratios  $>0.05$  by this method was somewhat difficult, and uranium losses resulting from oxidation of the uranium oxalate during precipitation were hard to control. The most effective means of minimizing the uranium losses were metering of the uranous ammonium oxalate spike through a jet mixer into

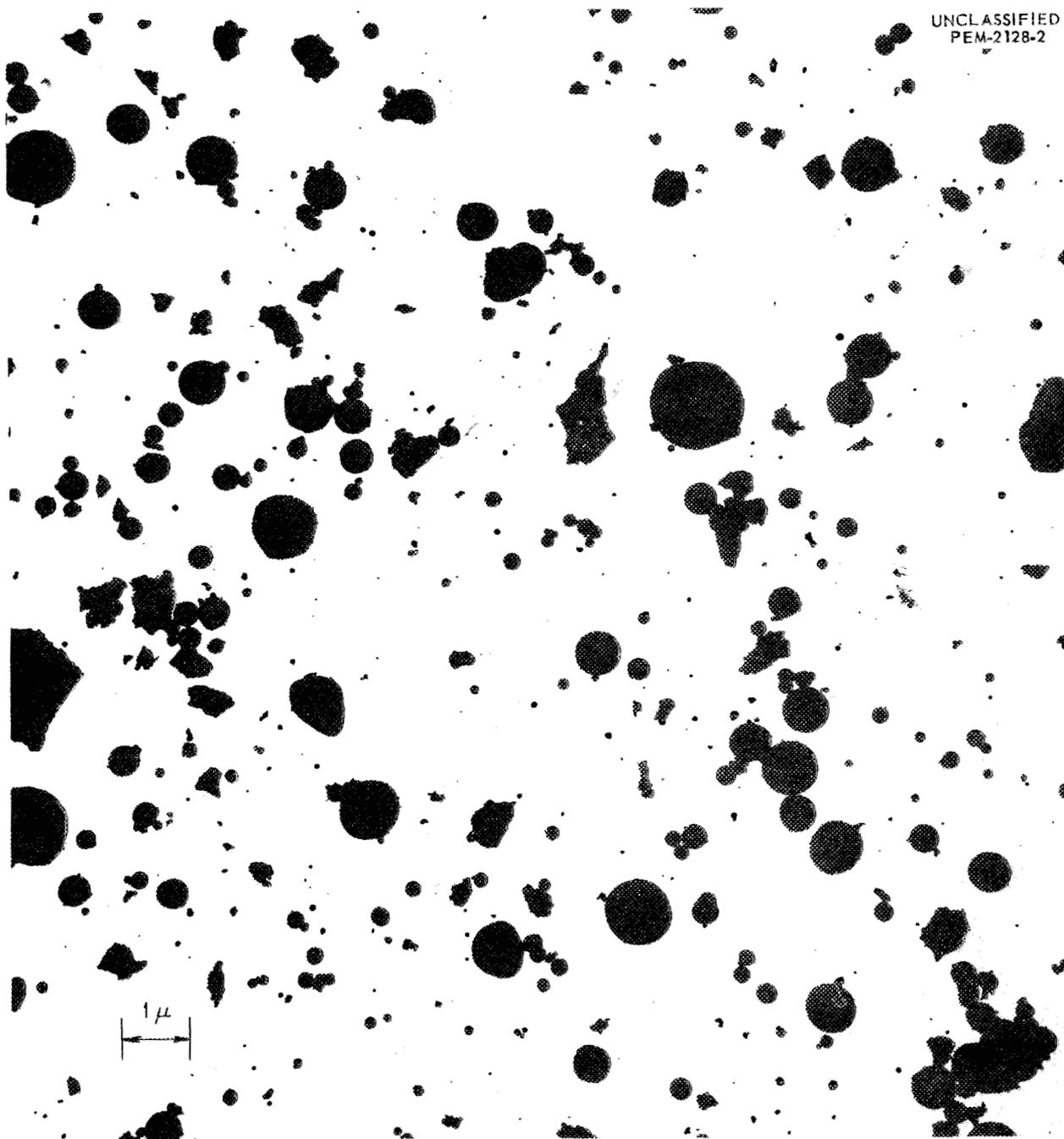
the oxalic acid precipitating reagent just upstream from the point of addition to the thorium nitrate solution and carrying out the precipitation as quickly as possible.

Thorium-uranium oxides with U/Th ratios from 0.005 to 0.33 were readily prepared by the adsorption method. In a typical preparation  $650^\circ\text{C}$ -fired thorium oxide was slurried in ammonium uranyl carbonate solution (solubility  $\sim 0.15 \text{ m}$ ) and the solution boiled until all the uranium had deposited on the thoria. The solids were filtered, washed, and refired. When a  $1000^\circ\text{C}$ -fired sample was autoclaved at  $300^\circ\text{C}$  for 24 hr as an aqueous slurry with an oxygen overpressure, the recovered supernatant contained only 0.2% of the total uranium; refluxing the solids 1 hr with  $8 \text{ M HNO}_3$  removed only an additional 0.07%. The uranium was distributed uniformly in the solids, as shown by successive refluxing with  $8 \text{ M HNO}_3$ ,  $4 \text{ M HNO}_3$  containing 5%  $\text{H}_2\text{O}_2$ , and  $4 \text{ M HNO}_3$  containing 10%  $\text{H}_2\text{O}_2$ . The thorium dissolved in the successive leaches amounted to 0, 25, and 40%, respectively, and U/Th ratios in the acid leaches and final solids were 0.1, 0.13, 0.12, and 0.09.

**Flame Denitration.** — Spherical thorium-uranium-aluminum oxide particles with a U/Th mass ratio of 0.08 and an alumina content of 2.5, 5, and 10 wt % were produced by flame denitration of methyl alcohol solutions of the nitrates (Fig. 13.1). Product was collected at reflector temperatures of  $800$  to  $1500^\circ\text{C}$  to give 120-g samples of classified product (95%  $<5 \mu$ ). Specific surface areas of the products were  $2.0$  to  $3.1 \text{ m}^2/\text{g}$ . Yield stresses of 2-g/ml aqueous slurries were 0.02 to 0.05 psf. At 1% alumina a partially rounded shape was obtained, but a "blackberry" surface appeared on the electron micrograph. Otherwise the 1% material appeared similar to the material of other alumina concentrations (Table 13.1).

Mixed thorium-uranium oxides (U/Th = 0.08) containing no alumina were also prepared by flame denitration at  $800$  to  $1500^\circ\text{C}$  reflector temperatures. These showed mean particle diameters after classification of  $1.6$  to  $2.5 \mu$ , surface areas of  $6.2$  to  $7.7 \text{ m}^2/\text{g}$ , and toroid erosion-corrosion rates (oxygen overpressure,  $280^\circ\text{C}$ , 26 fps, 200 g of Th-U per kg of  $\text{D}_2\text{O}$ ) on stainless steel of 2.7 to 7.0 mpy, which are acceptable and comparable to characteristics of oxides prepared by precipitation. Particle degradation during toroid tests was slight. Calculations indicate an economic advantage in

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CONDITIONS

U/Th MASS RATIO = 0.08  
OUTSIDE REFLECTOR TEMP = 1500°C  
CLASSIFICATION = 95% < 5 μ

OXIDE PROPERTIES

SURFACE AREA = 2.4 m<sup>2</sup>/g  
YIELD STRESS (ρ = 2 g/ml) = 0.02 lb/ft<sup>2</sup>  
MEAN PARTICLE SIZE = 1.7 μ

Fig. 13.1. Flame-Calcined Thorium-Uranium Oxide Containing 2.5% Al<sub>2</sub>O<sub>3</sub>.

Table 13.1. Flame Calcination Experiments: Characteristics of Flame Denitrated Thorium-Uranium Oxides Containing Alumina

U/Th ratio = 0.08 for all samples

Firing temperature, 1500°C

Run No.	Nominal Alumina Concentration (wt %)	Mean Particle Size ( $\mu$ )	Yield Stress of Slurry ( $\rho = 2 \text{ g/cc}$ ) (psf)	Surface Area ( $\text{m}^2/\text{g}$ )
62	5	1.5	< 0.02	2.0
63	2.5	1.7	0.02	2.4
66	1	2.0	0.026	2.6
69	10	1.6	0.05	3.1

using flame denitration for producing large amounts of mixed oxide or thorium oxide, but no significant economic gain for the present scale of pilot plant production.

**Fluidized Bed Denitration.** — Denitration of thorium nitrate solution in a fluidized bed was studied in an attempt to produce dense 50- to 500- $\mu$  thorium oxide particles. Production of porous agglomerations of small thorium oxide particles was observed under all conditions tested, instead of growth by addition of dense thorium oxide layers on particles. When temperatures were lowered to lower the rate of denitration, bed caking occurred at all temperatures tested for a  $\text{ThO}_2$  bed used with 1.5 M  $\text{Th}(\text{NO}_3)_4$  in  $\text{H}_2\text{O}$ . With 1.5 to 1.8 M  $\text{Th}(\text{NO}_3)_4$  in  $\text{CH}_3\text{OH-H}_2\text{O}$  mixtures, heat supplied by combustion of the  $\text{CH}_3\text{OH}$  in the fluidizing air eliminated caking problems. With 1.85 M  $\text{Th}(\text{NO}_3)_4$  in  $\text{H}_2\text{O}$ , a fluidized sand bed operated well at 700°C, poorly at 500°C, and caked quickly at 400°C. The formation of  $\text{ThO}_2$  fines was also indicated by rapid plugging of the off-gas filters when  $\text{CH}_3\text{OH-H}_2\text{O}$  or  $\text{H}_2\text{O}$  solution feeds were used at 700°C. The  $\text{ThO}_2$  produced from operation with a sand bed contained 550, 3400, and 5100 ppm of nitrate at temperatures of 700, 500, and 400°C. About 75% of the  $\text{ThO}_2$  formed at 700°C was present in 20- to 270-mesh fractions, but these agglomerations were easily broken up in  $\text{H}_2\text{O}$  to release 0.5- to 20- $\mu$  particles.

The system was operated with uranyl nitrate solution feed and a sand bed at 390°C. The  $\text{UO}_3$  coating formed on sand particles was relatively dense and homogeneous as compared with the

$\text{ThO}_2$ , the particles were not easily broken up in water, and the rate of filter plugging by fines was much lower.

### 13.2 SLURRY DEVELOPMENT

**The Use of Hydroclones.** — Hydroclones were successfully used on aqueous thoria slurries for separation of 0.5- to 5- $\mu$   $\text{ThO}_2$  particles, in batch collection of the slurry from a circulating system into an induced-underflow receiver, and in transfer of slurries to effect concentration control. Hydroclones commercially available as 0.40-in.-dia units can be used for classification of  $\text{ThO}_2$  with separation points of 1 to 3  $\mu$  or to remove oversize and undersize particles with separation points of up to 5  $\mu$  or down to 0.5  $\mu$  (Fig. 13.2). In a typical classification over 60% of the <0.6- $\mu$ -dia material and less than 6% of the >1- $\mu$ -dia material was recovered.

Hydroclones may be used to concentrate the slurry in one part of a system while maintaining constant fluid inventories throughout the system. Thoria slurries were collected in induced-underflow receivers by single hydroclones at rates of up to 2000 g of  $\text{ThO}_2$  per minute. For this batch collection the hydroclone was valved into the system so that it could be put into use with 40 to 200 ft of pressure drop. No flow control is required for this type of operation. Slurry transfer rates were higher with continuous underflow in hydroclone cascades. Starting with all the  $\text{ThO}_2$  slurry in one tank, tests demonstrated equilibrium concentrations of 0.5 g of  $\text{ThO}_2$  per liter in the other tank. Constant liquid levels and thorough

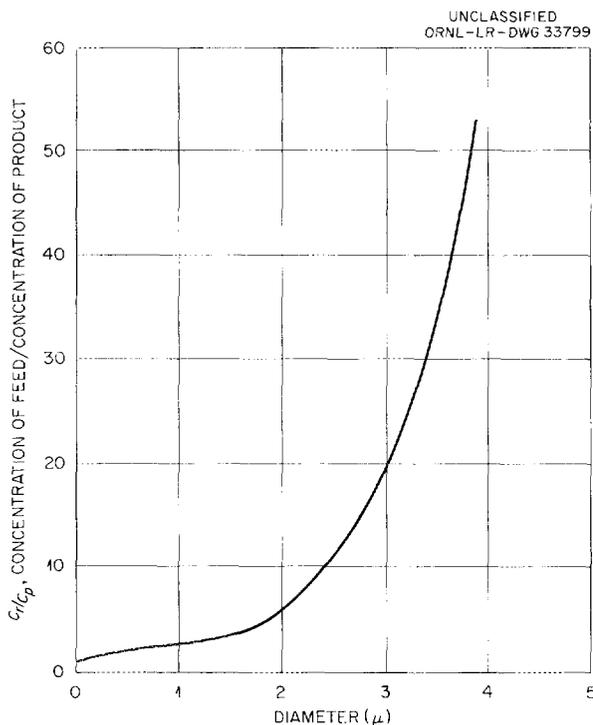


Fig. 13.2. Typical Separation Curve for a Single 0.4-in.-dia Hydroclone and a Thorium Oxide-Water Slurry.

agitation were maintained in both tanks throughout this test. Multiple hydroclones which have been fabricated could transfer 2- to 5- $\mu$  ThO<sub>2</sub> between a reactor system and high-pressure dump tanks at rates over 100 kg/min with no net transfer of D<sub>2</sub>O.

**Small-Volume Slurry Viscometer.** — A rolling-ball viscometer of 6-ml volume was constructed to determine the viscosity properties of small samples of irradiated thoria slurries. The terminal velocity of fall of a steel ball through fluid in a cylindrical tube is detected magnetically. Slurry is stirred by letting the ball roll freely while rocking the viscometer. The ball is suspended magnetically at the upper end of the tube until the viscometer is fixed in the chosen angle of inclination with respect to horizontal.

Room-temperature tests of the viscometer having a tube body of 0.2425 by 6 in. and ball diameters from 0.1885 to 0.2250 in. were made with Newtonian fluids of viscosity from 0.25 to 500 centipoises and on 650°C-fired thoria slurries at concentrations up to 800 g of thoria per liter.

Typical curves of terminal ball velocity vs effective force fraction of gravity on the ball are shown

for angles of inclination from 5 to 90° in Fig. 13.3. For an 0.1885-in.-dia ball in a 0.2425-in.-dia tube at 23 to 27°C, a sample calculation of the yield stress of a 600-g/kg slurry is given:

Extrapolate to zero velocity

$$\frac{\Delta\rho}{\rho} \sin \theta = 0.46$$

$$\text{Ball wt} = 0.986 \times 10^{-3} \text{ lb}$$

$$\text{Ball and parallel tube area} = 1.77 \times 10^{-3} \text{ ft}^2$$

$$\text{Yield stress} = \frac{0.75 \left( \frac{\Delta\rho}{\rho} \sin \theta \right)_{v=0}}{\text{Area of ball + tube}}$$

$$= 0.185 \text{ psf}$$

If the transition from laminar to turbulent flow occurs in the range of the instrument, the coefficient of rigidity may be estimated from the point of initial curvature on the graph by use of the critical Reynolds number and Hedström's *S* factor.

**Criticality Control in Slurries.** — One method of keeping a slurry reactor noncritical during startup would be to add boric acid to the slurry, which would be removed when operating conditions were achieved. Calculations based on a slurry reactor with a 2.5-ft core, 400 g of Th per liter and 0.1 g of U<sup>235</sup> per g of Th, indicate that the mole ratio of boron to thorium and uranium required for noncriticality under all conditions should be 0.02. Boron removal efficiency (i.e., desorption) for successful reactor operation after startup requires that less than 0.029 mg of boron per gram of solid remain with the solid (i.e., equivalent to 1% neutron loss to the boron) after removal of the boric acid from the system.

Experiments with a slurry of 650°C-fired thorium-uranium oxide indicate that the adsorption of boron by the solid and boron removal efficiency are such that boric acid could not be used as a soluble poison for criticality control. It appears, however, that in a slurry of 1100°C-fired thorium-uranium oxide such a method of operation is feasible. In a slurry (270 g of Th per kg of H<sub>2</sub>O) of the 1100°C-fired mixed oxide with an initial boron concentration 33% greater than that required for noncriticality (370 ppm boron in the supernatant), less than 0.029 mg of boron per gram of solid was adsorbed on the thoria solid on autoclaving above 60°C. Some 60% of the adsorbed boron could be desorbed from the solid in

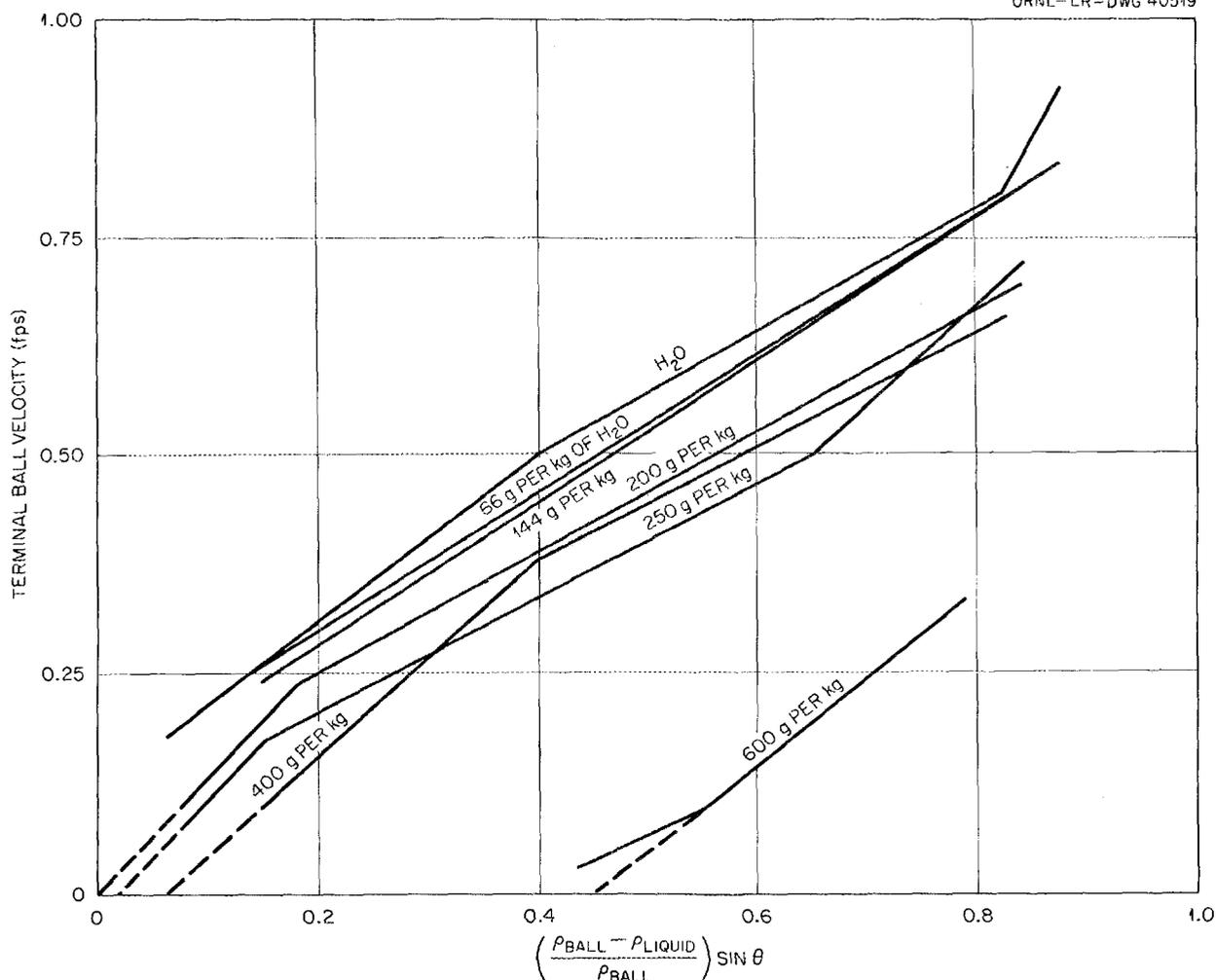
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Fig. 13.3. Force Fraction vs Terminal Velocity of Ball Falling Through Thoria Slurry.

fresh supernatant at 100°C in less than 2 hr. When enough boric acid was added to a slurry (233 g of Th per kg of H<sub>2</sub>O) of the 1100°C-fired mixed oxide to give 100% excess of boron required for non-criticality (713 ppm boron in the supernatant), the solid adsorbed less than the limit of 0.029 mg of boron per gram of solid at 240°C and above.

**Uranium Leaching Studies.** — Appreciable quantities of uranium were leached from thorium-uranium oxides pumped as aqueous slurries in high-temperature loop studies, presumably the result of a buildup of soluble chromium and a decrease in pH accompanying the corrosion process. A laboratory study with a thorium-uranium oxide having a U/Th ratio of 0.08, fired 72 hr at 1050°C, indicated that

a negligible quantity of uranium was solubilized by treating the mixed oxides with water alone at 280°C but that a solution containing a few hundred ppm of chromate (added as chromic acid) leached uranium from the solid at 280°C, the amount increasing with increasing chromium concentration from 125 to 1330 ppm. The ratio of ppm U to ppm Cr in the supernatant over this concentration range was about 2.6. The amount of uranium leached depended to some extent on the oxide firing conditions. There was also evidence from the laboratory studies that the past history of the autoclave, toroid, or loop in which the thorium-uranium oxide slurry is handled may considerably affect the amount of uranium that appears in the supernatant during high-temperature operation.

**Silica-Coated Thorium Oxide.** — Thorium oxides with chemically bonded silicate surfaces were prepared by treatment with chlorosilane vapors (G-E Dri-Film Sc-77), washing to remove chloride ion, and refiring to remove organic groups and leave a silicate surface. Thoria so treated showed no crystallite growth on being fired as high as 1000°C. At 1200°C pronounced sintering of the silicated oxide occurred, with consequent increase in crystallite size and decrease in specific surface area. The product from 1600°C firing was a completely sintered, dense cake. The silicated thoria fired at 1000°C or lower was completely dispersed as an aqueous slurry at temperatures up to 280°C.

### 13.3 RADIOLYTIC GAS PRODUCTION AND RECOMBINATION

The aqueous phase of a reactor slurry will be decomposed radiolytically into deuterium and oxygen. The amount of recombination necessary to prevent excessive gas pressure may be estimated from the fact that 0.2 to 0.4 mole of  $D_2$  and equivalent  $O_2$  will be produced per kilowatt-hour of energy absorbed. Both out-of-pile and in-pile experiments have indicated that  $MoO_3$  and palladium, either as the metal or hydrous oxide, are suitable for use in slurries for the liquid-phase recombination of the radiolytic gas. The  $MoO_3$  appears restricted to use in slurries of thorium oxide and thorium-uranium oxide with U/Th ratios of 0.005 or lower, fired at or above 1000°C. Higher uranium concentrations appear to deactivate the  $MoO_3$ . The palladium was an effective gas recombination catalyst in slurries of oxide or mixed oxide fired at all temperatures (650 to 1600°C) and appeared suitable for use in slurries of simple oxide mixtures.

Assuming that 100 psi is an acceptable radiolytic deuterium partial pressure at 280°C, a likely reactor operating temperature, the natural catalytic activity of a thorium or thorium-uranium oxide slurry was found sufficient to maintain a reactor power level of a few tenths of a kilowatt per liter. The  $MoO_3$  appeared capable of maintaining about 1 kw/liter per millimole concentration in slurries of the pure oxide (fired at 1000°C or higher) and of maintaining a power density an order of magnitude lower in the thorium-0.5% uranium oxide system. Higher uranium concentrations appear to

deactivate the  $MoO_3$  catalyst; with 5%  $UO_2$ , the recombination rate is less by a factor of approximately 100 than with pure  $ThO_2$  for a given catalyst concentration. The palladium will maintain a power density of 2 to 3 kw/liter per millimole concentration in slurries of oxides or mixed oxides fired at all temperatures (650 to 1600°C). It appears suitable also for slurries of simple mixtures of oxides of thorium and uranium.

**Out-of-Pile Studies.** — The out-of-pile work included studies on the effect of pumping at 280°C, under both oxidizing and reducing atmospheres, on the catalytic activity of a slurry containing palladium and of one containing  $MoO_3$ . The pumping studies were carried out as a joint effort between the Chemical Technology and the Reactor Experimental Engineering Divisions.

The slurry used in the palladium pumping study contained 454 g of Th per kg of  $D_2O$  of a 650°C-fired thoria to which uranium ( $UO_3 \cdot H_2O$ ) and palladium catalyst were added in the ratios of 5.15 mg of uranium and 0.158 mg of palladium per gram of thorium. The palladium was deposited on a 650°C-fired thorium oxide by heating an alcohol-acetone-palladium nitrate solution in which thoria was suspended. In the first phase of the study the loop was pressurized with argon and the slurry pumped 478 hr at 280°C. A partial pressure of deuterium gradually developed as a result of corrosion. In the second phase,  $O_2$  was substituted for the argon-deuterium atmosphere and pumping continued at 280°C for an additional 526.8 hr. Samples of the slurry were withdrawn from time to time and used in gas recombination experiments. The slurry pumped under argon showed a high catalytic activity, >5 moles of  $D_2$  per liter per hour at 100 psi  $D_2$  partial pressure in the region of 150 to 200°C, which was of temporary duration and probably associated with reduced uranium species. At reactor temperatures above 250°C and pumping times of 200 or more hours, recombination rates were 0.1 to 0.4 mole of  $D_2$  per liter per hour at 100 psi  $D_2$  partial pressure. At 280°C and a  $D_2$  partial pressure of 100 psi, the recombination rates of the slurry pumped under  $O_2$  were 0.04 to 0.08 mole of  $D_2$  per liter per hour. Very little activity was observed for these samples in the region 150 to 200°C.

The slurry containing 450 g of Th per kg of  $D_2O$  was prepared from 1600°C-fired oxide and pumped

for 200 hr under an  $O_2$  atmosphere before the addition of  $MoO_3$  to a concentration of 0.008 *m*. Subsequently, the slurry containing  $MoO_3$  was pumped an additional 300 hr under  $O_2$ , some 500 hr under  $D_2$ , and finally 300 hr again under an  $O_2$  atmosphere. After about 800 hr total pumping, the  $MoO_3$  concentration was increased to 0.012 *m*. The principal effect noted during the pumping of the slurry under an  $O_2$  atmosphere after the  $MoO_3$  addition was the development of an "induction period" before maximum catalytic activity was achieved. The slurry was apparently deactivated on pumping under  $O_2$  and reactivated when placed in a  $D_2$  and  $O_2$  atmosphere ( $D_2 + \frac{1}{2}O_2$ ) in the recombination tests. Substitution of a  $D_2$  atmosphere for the  $O_2$  atmosphere in the loop eliminated the induction period. The second pumping under  $O_2$  appeared to have but little effect on recombination activity, the induction period, if present at all, being of only a few seconds' duration. All rates observed after maximum catalytic activity was achieved in the out-of-pile tests were in excess of 2 moles of  $D_2$  per hour per liter of slurry at 100 psi  $D_2$  partial pressure and  $\leq 280^\circ C$ , which is a satisfactory rate for an internal recombination catalyst.

**In-Pile Studies.** — Radiolytic gas production and recombination rates were measured in the ORNL Graphite Reactor with heavy-water slurries of  $ThO_2$  containing 2.8% enriched uranium prepared without catalyst addition by firing the coprecipitated oxalates at 650 or 1000°C. Two experiments were run after sealing the in-pile autoclave in air, two after adding 250 psi excess  $D_2$ , and two with 250 psi excess  $O_2$ . The gas production rates in a light-water slurry sealed in air indicated a *G* value of about 0.8 (i.e., molecules of  $H_2O$  decomposed per 100 ev of energy adsorbed); they were 50% higher in the  $D_2O$  system. Under a deuterium atmosphere the gas production was initially suppressed sharply, but the effect was not reproducible. The production rate under oxygen was slightly lower than that under air. Recombination rates (Fig. 13.4) measured during reactor shutdowns were slower under excess deuterium than under air or oxygen. The air and oxygen rates were nearly the same, although a slightly increased temperature dependence was observed when oxygen was used.

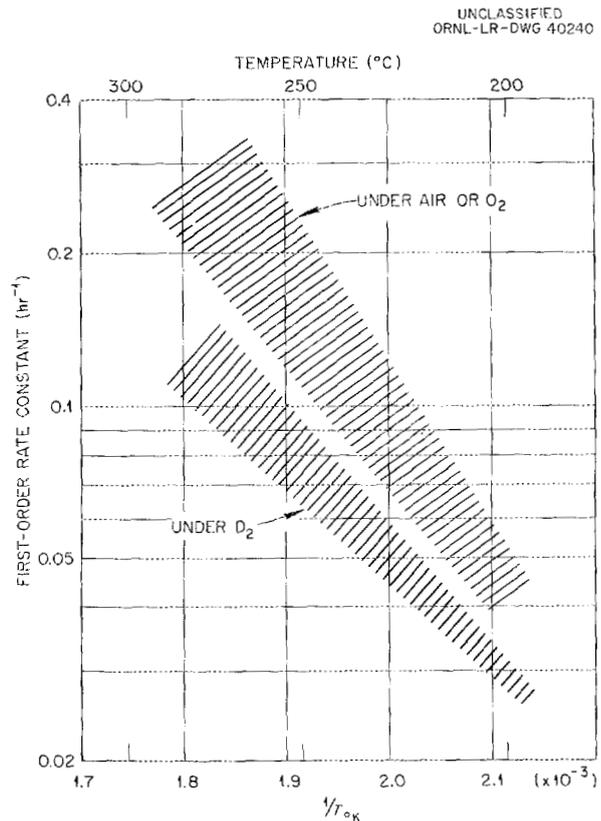


Fig. 13.4. First-Order Rate Constants for  $D_2$ - $O_2$  Reaction over Calcined  $ThO_2$ -2.8%  $U^{235}$  (500 g of Th per kg of  $D_2O$ ) in the ORNL Graphite Reactor.

### 13.4 SLURRY IRRADIATION STUDIES

Eleven slurry irradiations were carried out in dash-pot bombs located in Hole C-44 of the LITR at a thermal-neutron flux of  $2.7 \times 10^{13}$  neutrons·cm<sup>-2</sup>·sec<sup>-1</sup>. Five of these tests were on slurries of thorium oxide containing 5% natural uranium prepared by firing the coprecipitated oxalate at 1000°C. In four tests, all irradiated more than 300 hr, the slurry concentrations were varied from 250 to 500 g of Th per kg of  $D_2O$ , with a  $D_2$  gas overpressure in one case. In the other test the slurry contained 750 g of Th per kg of  $H_2O$ ; the run was terminated by a leak after only 49 hr of irradiation. Two similar tests were made on slurries containing 250 and 500 g of Th per kg of  $D_2O$  as thoria-8% natural uranium prepared by adsorbing uranium on thoria and refiring to 1050°C.

The purpose of these irradiations was to determine whether any radiolytic gas was formed. No catalyst was added to any of these slurries, and in no case was radiolytic gas buildup observed even at temperatures as low as 230°C.

The remaining four tests were on materials supplied by Westinghouse in connection with the PAR program. Two samples of pumped slurry and two of unpumped material were irradiated. The pumped material contained 3% natural uranium and was irradiated under an oxygen gas pressure in one test and a deuterium gas pressure in the other. The unpumped material was a 650°C-calcined ThO<sub>2</sub> and was irradiated under oxygen only. In all four tests, 122 to 145 ppm palladium was added as a gas recombination catalyst, and 0.5% U<sup>235</sup> was added to each slurry to raise the power density during irradiation. No radiolytic gas was observed in the tests with the pumped slurry at a concentration of 500 g of Th per kg of D<sub>2</sub>O. With the unpumped material at this concentration ~285 psi of radiolytic gas pressure was observed at 300°C. At a concentration of 250 g of Th per kg of D<sub>2</sub>O of the same material no excess pressure was observed.

All the slurries irradiated were recovered and examined. The fission products, corrosion products, palladium, and uranium were found predominantly associated with the solids as in previous tests. The presence of 5% uranium seems to decrease slightly the amount of iodine adsorbed on the solids, and in one case, the unpumped 650°C oxide supplied by Westinghouse, the supernatant could not be clarified and contained appreciable amounts of thorium and fission products in suspension.

A sample of 1600°C-calcined ThO<sub>2</sub> was irradiated at 280°C (autoclave sealed in air) as a settled slurry for 3235 hr in the C-43 facility of the LITR at a thermal-neutron flux of  $\sim 2.8 \times 10^{13}$  neutrons·cm<sup>-2</sup>·sec<sup>-1</sup>. During this time 0.22% of the material was converted to mass-233 isotopes. This corresponds to an effective cross section for LITR neutrons of 10.3 barns. The material was recovered as dark grainy particles, which were refluxed for 3 min in 4 N HNO<sub>3</sub> and then in 4 N HNO<sub>3</sub> containing 1.5% H<sub>2</sub>O<sub>2</sub>. Thirty-six per cent of the U<sup>233</sup>, 40% of the Pa, and only 0.2% of the thorium were dissolved in the first acid leach. The nitric acid-peroxide leach dissolved an additional 52, 35, and 36% of the U<sup>233</sup>, Pa, and Th, respectively. Sixty-five per cent of each of the gross gamma and beta activities was removed from the

solid by the two acid leaches (70 to 80% of the Sr, Zr, Cs, Fe; 58% of the Cr; 47% of the Nb; and 25% of the Ni). Thirty per cent of the Cs and 97% of the Ru appeared on the residual solids. Percentages leached were calculated on total activities recovered (leaches plus residual solid) and not on theoretical yields of activities.

**Cooling Methods for Slurry Irradiation Autoclaves.** — The slurry irradiations are carried out at present in small stainless steel autoclaves about 7 in. long and  $\frac{3}{4}$  in. OD at their largest diameter. Heat is removed by air cooling. Three methods of cooling with water were investigated. Heat loads for a slurry in the LITR are about 0.4 kw and in the ORR about 5 kw.

Five kilowatts of heat removal from a 1-in.-dia by 10-in.-long stainless steel bomb at 300°C was achieved out-of-pile with good temperature control by varying the composition of a helium-air mixture in a uniform 8-mil annulus between the bomb and a boiling water bath. The useful range of heat removal control was 1 to 5 kw. The lower limit of control is extended to 0.5 kw by substituting Freon-112 for air. However, this method of control is not easily adapted to the present in-pile bomb principally because the 8-mil annulus dimension is critical and difficult to obtain with any simple adaptation.

The use of water in a 30-lb·sec<sup>-1</sup>·ft<sup>-2</sup> cooling air stream passing a 1-in.-dia by 10-in.-long bomb at 300°C gave a heat removal of 5 kw at a water/air weight ratio of 0.43. Although the heat dissipation rate was adequate, uncontrollable temperature excursions, presumably the result of vapor binding at the bomb wall, were observed for bomb temperatures in excess of 200°C.

A heat removal of 1.8 kw was obtained from the present slurry irradiation bomb (7 in. long by  $\frac{3}{4}$  in. OD) at 300°C by using a tightly wound 20-mil-ID by 35-mil-OD stainless steel coil along the entire bomb length. Temperature control was good with pumping rates up to 80 ml/min and steady flow. Temperature cycling was observed when an intermittent-flow pump was used. At a heat dissipation of 0.4 kw, a temperature gradient of 40°C existed along the bomb when water was introduced into the coil at the bottom of the bomb and flowed upward. When water was introduced at the top of the coil and flowed downward, however, no temperature gradient was detected. The minimum heat generation rate that can be controlled at 300°C is approximately 100 w.

## 14. SURFACE CHEMISTRY

### 14.1 ADSORPTION EQUILIBRIA ON THORIUM OXIDE POWDERS

A group at the University of Utah (M. E. Wadsworth *et al.*) under subcontract have continued their studies of the adsorption of various ions on thorium oxide surfaces. Isotherms below 100°C have been obtained for sulfate, phosphate, and silicate ion adsorption, and in the case of silicate, to about 300°C. The adsorption of sulfate and silicate ions increases with increasing temperature, while that of phosphate ion decreases. Enthalpy and entropy values have been estimated. In the case of silicate adsorption a surprisingly high positive entropy led to the proposal of a micellular mechanism for the adsorption process.<sup>1</sup>

### 14.2 THE ZETA POTENTIAL, SURFACE CONDUCTANCE, AND PERMEABILITY OF THORIUM OXIDE POWDERS

Of the several available methods of studying electrokinetic transport, the technique of observing flow through a porous-plug, electrolytic cell seems most feasible for extension to high-temperature observations with aqueous systems. The transport phenomena through a porous plug with laminar flow can be described by the simultaneous transport equations for current and for flow (the Onsager reciprocal relations):

$$I = L_{11}E + L_e P, \quad (1)$$

$$V = L_e E + L_{22}P, \quad (2)$$

in which  $E$  and  $P$  are, respectively, the electric potential gradient and the pressure gradient. The  $L$ 's are the respective conductivities,  $L_{11}$  being the electrical conductance,  $L_e$  the electrokinetic conductance, and  $L_{22}$  the permeability. The  $L$ 's are each expressed in classical theory in terms of a specific conductance ( $\lambda$ ) and a suitable cell constant ( $k$ );  $\epsilon$  is the dielectric constant,  $\zeta$  is the zeta potential, and  $\eta$  is the viscosity:

$$L_{11} = \frac{\lambda}{k}, \quad (3a)$$

$$L_e = \frac{\epsilon \zeta}{4\pi \eta k}, \quad (3b)$$

<sup>1</sup>M. E. Wadsworth, private communication.

$$L_{22} = \frac{K_0}{\eta k}. \quad (3c)$$

These equations are correct without modification only if experimental factors meet the requirements of the assumptions involved in their derivation. There are several assumptions required; for instance, Eq. (3a) must be modified to include a parallel circuit if surface conductance is present ( $B$  = bulk,  $S$  = surface):

$$L_{11} = L_{11(B)} + L_{11(S)} = \frac{\lambda_B}{k_B} + \frac{\lambda_S}{k_S}. \quad (4)$$

If the conductance  $L_{11}$  is measured with increasing electrolyte concentration, the bulk conductance will, at sufficiently high concentration, overwhelm the contribution of the surface conductance, and each term of the right side of Eq. (4) may be separately estimated. A graph of  $L_{11}$  plotted against  $\lambda_B$  should approach a straight line at sufficiently high values of  $\lambda_B$ . The departure of the experimental points from this line at low values of  $\lambda_B$  is a measure of the contribution of surface conductance. The value of  $k_B$  determined in this way can then be used, along with the experimentally determined  $L_e$  and  $L_{22}$ , in Eqs. (3b) and (3c) to estimate the zeta potential and the specific permeability.

**Experimental.** - The apparatus currently being used consists of a thermostatted glass cell containing a porous plug of the thorium oxide sample confined between porous platinized platinum electrodes. A separate pair of platinized platinum electrodes is used to apply a d-c potential across the plug. The side arms of the cell are constant-bore glass tubing, vertical and parallel.

An experiment is performed by observing the rate of change of the difference in heights ( $b$ ) of the liquid in the side arms (of radius  $R$ ) with a constant potential gradient. Equation (2) may be rewritten in differential form as

$$\pi R^2 \frac{db}{dt} = L_e E + L_{22} \rho g b, \quad (5)$$

where  $\rho$  is the density of the liquid. A graph of  $db/dt$  (actually  $\Delta b/\Delta t$ ) against  $b$  should yield a straight line, the slope and intercept ( $b = 0$ ) of

which are determined by  $L_{22}$  and  $L_e$ , respectively, other quantities in the equation being known or measured constants. A determination of the resistance of the cell at some time during the experiment, when  $E$  and  $\rho$  are known, makes possible the calculation of  $L_{11}$  by virtue of Eq. (1). Thus all three conductivities are explicitly measured in a single experiment.

Preliminary experiments, in which no special precautions concerning the chemical integrity of the thoria and the solutions were taken, substantiate the validity and applicability of the method. Continued work will involve well-characterized and carefully purified thoria samples in water and a wide variety of dilute electrolyte solutions at 25°C, and construction of a pressure cell to permit analogous studies at elevated temperatures. A much more detailed discussion of the theory involved in this work, the early experimental results, and the interpretation of the data will be presented in a forthcoming topical report.

#### 14.3 CALORIMETRIC SURFACE STUDIES

Direct measurement of the heat involved in surface reactions, as in any chemical or physical process, is the foundation on which the thermodynamics of the processes rests. A program involving, in general, high-temperature aqueous-system calorimetry and, more specifically, the determination of heats of wetting and differential heats of adsorption of various materials on thorium oxide surfaces has been initiated. A preliminary design and cost estimate for a precision adiabatic calorimeter for this purpose was prepared.

Design and thermal factors will limit the operation of the calorimeter to temperatures less than about 300°C, the range of interest in aqueous reactor system applications. The design limit of detectability is  $(2 \times 10^{-5})^\circ\text{C}$  with an energy equivalent of 75 cal/deg or less, thus permitting the detection of  $1.5 \times 10^{-3}$  calorie.

#### 14.4 SURFACE POTENTIAL OF THORIA

As part of the surface-chemistry program, a study of the adsorption equilibrium between the  $\text{ThO}_2$  surface and various dilute aqueous solutions is planned. Simple Gouy-Chapman theory of the diffuse double layer can be used to calculate the electrical potential of the surface from such adsorption data. The particles of  $\text{ThO}_2$  suitable for such experiments should be nonporous and of a size that gives appreciable surface area but yet not much curvature of the surface. Initial experiments directed toward preparing such particles by use of homogeneous precipitation have given promising results.

If the surface potential is known, the degree of peptization of a  $\text{ThO}_2$  suspension can in principle be calculated by using existing theories of flocculation rates and of attractive and repulsive forces between suspended particles. These theories have already been used to calculate the surface potential required to give a particular degree of peptization under a variety of temperatures, particle radii, electrolyte valences, electrolyte concentrations, and suspension concentrations.<sup>2</sup>

<sup>2</sup>F. H. Sweeton, *Calculation of Suspension Peptization*, ORNL-2791 (in preparation).

### 15. NEPTUNIUM RECOVERY PROCESS DEVELOPMENT

A flowsheet was developed and used for final purification of  $Np^{237}$  product from the Metal Recovery Plant processing of fluorination ash.<sup>1</sup> Neptunium-237 feed contaminated with 11% thorium, 39% uranium, 4% aluminum, and 5% corrosion products (iron, chromium, nickel) was processed to give a final product containing 99.5% of the neptunium contaminated with less than 0.5% impurities.

The Metal Recovery Plant neptunium product was concentrated to 200 liters by evaporation and was purified in 30- to 200-g batches. The process used (Fig. 15.1) was (1) evaporation in glass equipment for volume reduction and acid removal, (2) fluoride precipitation of thorium and chromium after oxidation of neptunium to the hexavalent state with  $NaBrO_3$ , (3) fluoride precipitation of neptunium in the filtrate by reduction to the tetravalent state with  $SO_2$  gas, (4) dissolution of neptunium fluoride in 8 M  $HNO_3$ -0.5 M  $H_3BO_3$ , (5) precipitation of neptunium oxalate, and (6) calcination of the oxalate at 750°C to produce

neptunium oxide. This procedure gave 92% neptunium recovery containing less than 0.4% impurities. Product contamination was as follows:

Contaminant	Amount (mg per g of Np)	
	Feed	Product
Al	120	<0.2
Cr	40	<0.1
Fe	180	<0.7
Ni	15	<0.5
Pu	3	1
Th	290	0.9
U	1000	0.6

Process losses were as follows:

Waste Stream	Loss (%)
Distillate	0.15
$ThF_4$ precipitate	5.29
$NpF_4$ filtrate	0.75
Neptunium oxalate filtrate	1.66
<b>Total</b>	<b>7.85</b>

<sup>1</sup>Chem. Tech. Ann. Prog. Rep. Aug. 31, 1958, ORNL-2576, p 61.

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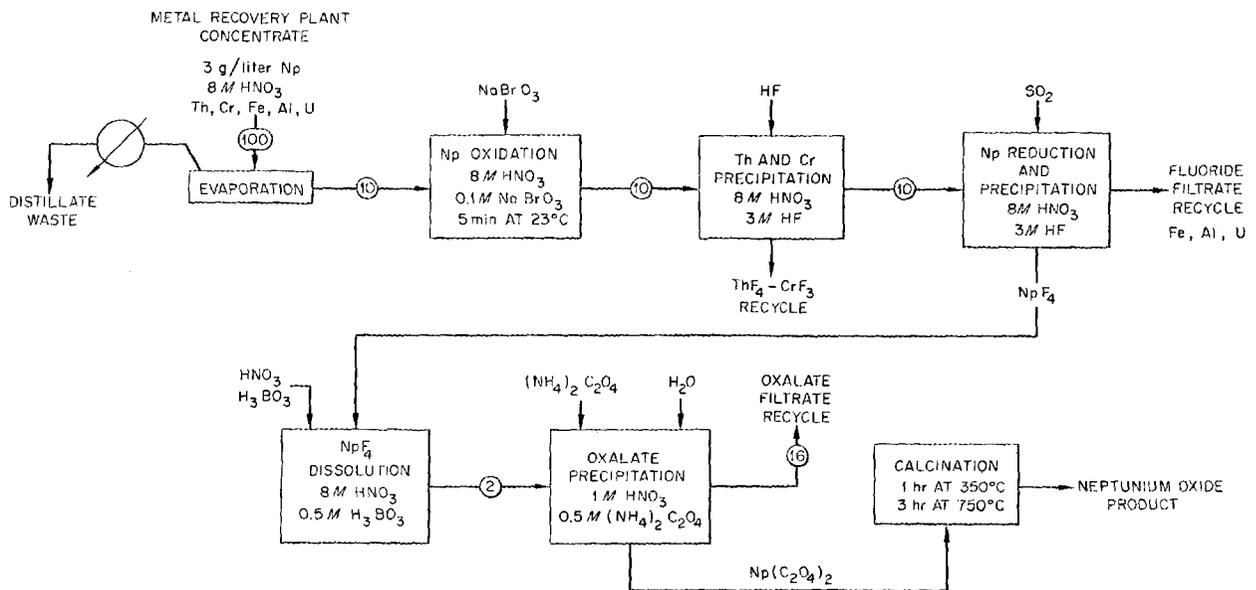


Fig. 15.1. Neptunium Isolation Flowsheet. Numbers in circles indicate relative volumes.

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The neptunium recycle flowsheet (Fig. 15.2) was used in recovering neptunium from the thorium fluoride precipitate, the neptunium fluoride filtrate, and the neptunium oxalate filtrate. The  $\text{Np}^{237}$  treated by these methods was recovered as a chloride product containing <1% impurities.

The program demonstrated that the oxidation-reduction fluoride precipitation method is satisfactory for neptunium purification if the amount of impurities is not too great. When the amount of

thorium plus chromium is more than twice the amount of neptunium, this method is not practical because of the large amount of neptunium carried on the thorium fluoride-chromium fluoride precipitate. The product of the solvent extraction separation of thorium and neptunium in the Metal Recovery Plant (Sec 2.4) provided satisfactory feed for this final purification step. This method is especially attractive for processing a single batch or a small amount of neptunium, since only ordinary laboratory equipment is required.

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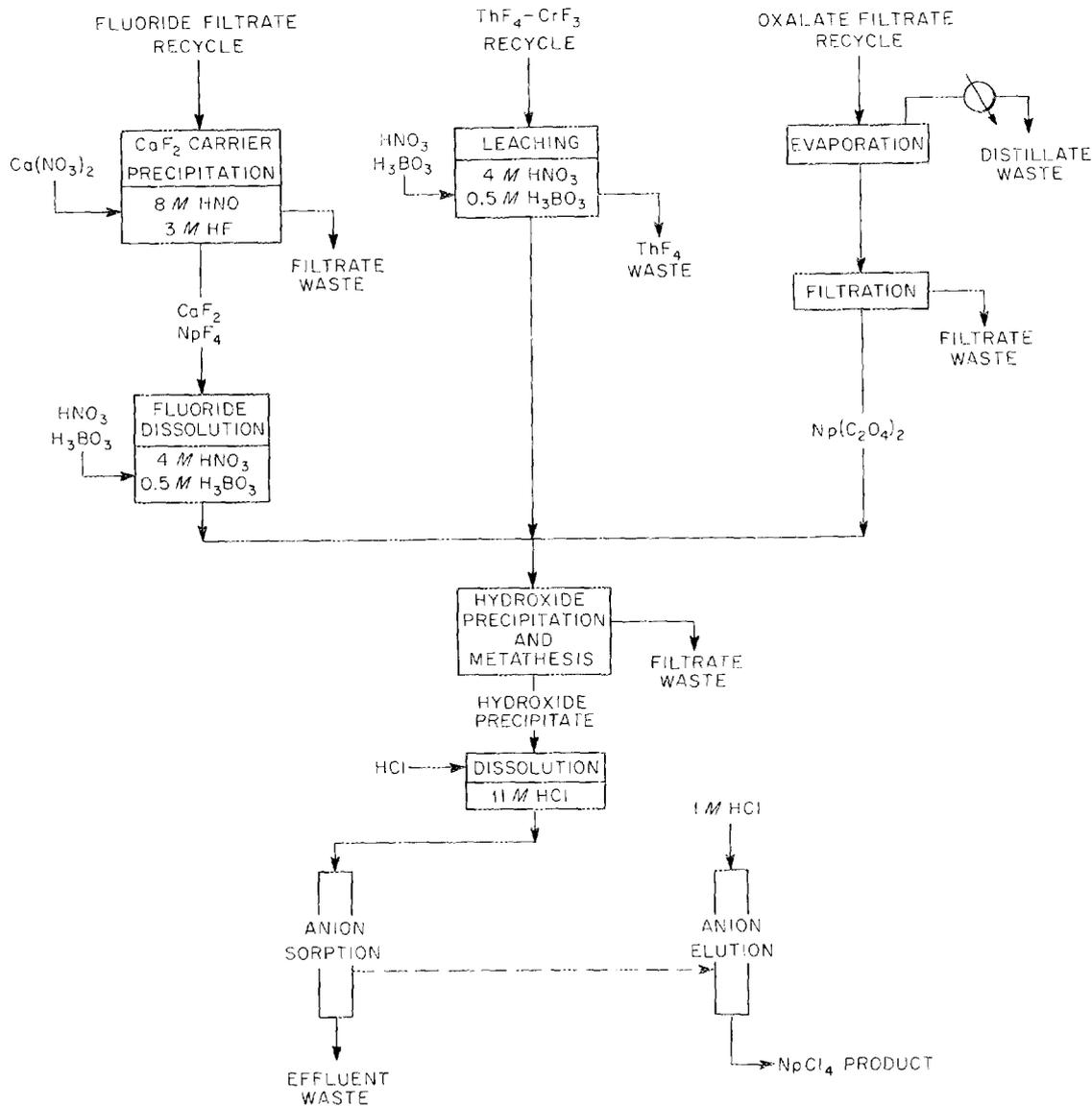


Fig. 15.2. Neptunium Isolation Recycle Flowsheet.

## 16. TRANSURANIC STUDIES

The purpose of the transuranic studies program is to develop processes for the separation of the transuranium elements from fission products and from each other. The program schedule is determined by the need for processes and facilities to recover plutonium, americium, and curium from highly irradiated  $\text{Pu}^{239}$  by July 1962. Chemical process development was carried out on a laboratory scale, preliminary design of a Transuranic Processing Facility was initiated, and irradiation of plutonium-aluminum fuel elements in the ORR was started to provide a supply of irradiated plutonium containing trace quantities of americium for process development.

### 16.1 PROCESS DEVELOPMENT

Transplutonium elements up to  $\text{Cf}^{252}$  can be produced by long-term neutron irradiation of  $\text{Pu}^{239}$ . Because of the large amount of heat generated during fission, the initial irradiation must be carried out at moderate neutron fluxes until more than 99% of the fissionable plutonium ( $\text{Pu}^{239}$  and  $\text{Pu}^{241}$ ) is consumed. The  $\text{Pu}^{242}$ , americium, and curium formed during this initial irradiation can then be irradiated at the highest neutron flux available for rapid formation of the higher isotopes. Chemical processing is required after each irradiation. To date, development studies have been limited to methods for processing after the first irradiation. This process must separate  $\text{Pu}^{242}$ , americium, and curium from fission products, major neutron poisons, and gross impurities so they can be fabricated into compact capsules for insertion into a neutron flux possibly as high as  $5 \times 10^{15}$  neutrons $\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$  as proposed for the High-Flux Isotopes Reactor.

The proposed process uses two solvent extraction cycles followed by ion exchange for final purification. The americium-curium product is to be precipitated and calcined for conversion to the oxide for reirradiation. In the preliminary flowsheet, plutonium, americium, curium, and rare-earth fission products are simultaneously extracted from a neutral aluminum nitrate solution into 40% TBP. Americium, curium, and the rare earths are stripped with nitric acid containing an oxidizing agent, and the plutonium is stripped with dilute nitric acid containing a reducing agent. Successful operation of this system depends on careful control

of the plutonium valence state. Since tetravalent plutonium will hydrolyze in neutral aluminum nitrate solutions, plutonium is reduced to the trivalent form during extraction. In the acid partitioning column, plutonium is converted to the more extractable tetravalent form in order to keep it in the organic phase. Plutonium is stripped after reduction to the less extractable trivalent form.

Batch countercurrent extraction tests were made with synthetic feed containing tracer plutonium, americium, and yttrium according to the flowsheet conditions in Fig. 16.1. Typical distribution coefficients ( $D$ ) for Pu(III), americium, and yttrium in the extraction section were 5.3, 8.5, and 14.5, respectively. With six extraction and four scrub stages, these tracers were quantitatively extracted, only about 0.01% remaining in the aqueous phase. Typical distribution coefficients for Pu(IV), americium, and yttrium in the partitioning column were 56, 0.05, and 0.07, respectively. With three partitioning and two organic scrub stages, only 0.5% of the americium and yttrium remained in the organic phase and about 0.001% of the plutonium was lost to the aqueous phase. In the plutonium stripping column, Pu(III) distribution coefficients were approximately 0.01, and four stages left only 0.005% of the plutonium in the organic phase. Although this flowsheet was not tested with curium tracer, satisfactory recovery is predicted, since distribution coefficients for curium are slightly higher than those for americium. Little is known about the behavior of other fission products as yet; however, ruthenium and zirconium decontamination factors were greater than 100 in tests with very low levels of these activities.

Extraction of rare earths into mono-2-ethylhexylphosphoric acid from concentrated chloride solutions is a promising method for removing rare-earth fission products from americium and curium.<sup>1</sup> In this system the lanthanides are more extractable than americium and curium. Although separations can be made from 12 M HCl, the distribution coefficients for lanthanum and cerium are low. By substituting LiCl for most of the HCl, distribution coefficients are increased by a factor of

<sup>1</sup>D. F. Peppard *et al.*, "Application of Phosphoric Acid Esters to the Isolation of Certain Transplutonics by Liquid-Liquid Extraction," *J. Inorg. & Nuclear Chem.* (to be published).

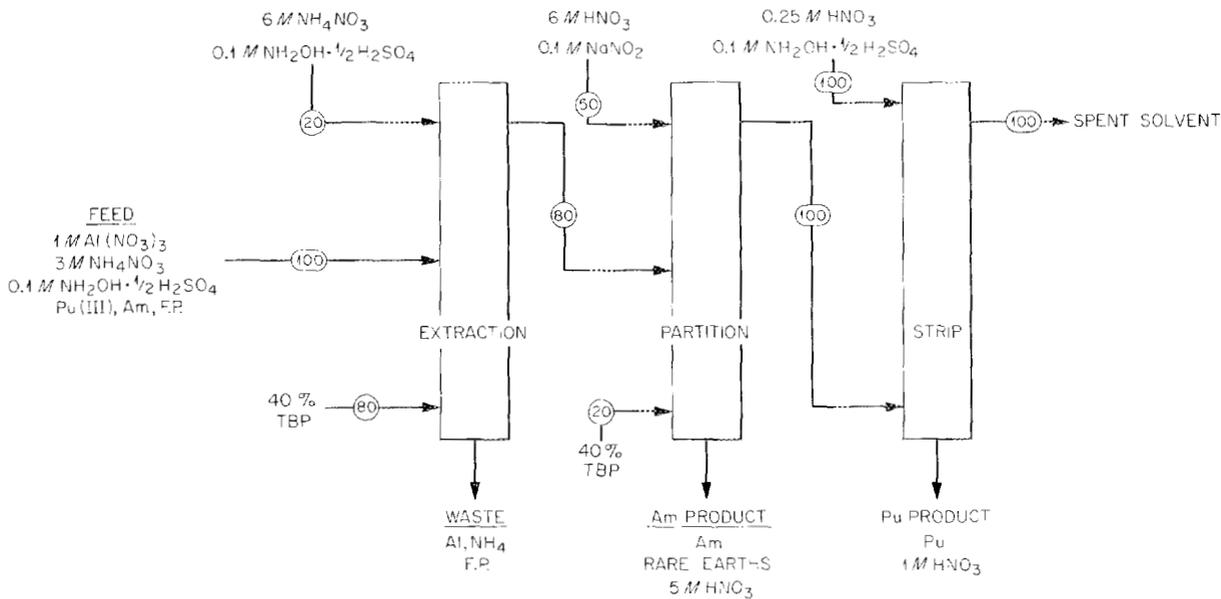


Fig. 16.1. Flowsheet for Simultaneous Extraction of Am, Pu, and Rare Earths. Numbers in circles indicate relative volumes.

5 to 8; however, separation factors remain essentially constant. Distribution coefficients ( $D/a$ ) for tracer amounts of neodymium, cerium, lanthanum, and americium between 0.5 M mono-2-ethylhexylphosphoric acid in xylene and 10.5 M LiCl-1.0 M HCl are 0.60, 0.50, 0.40, and 0.15, respectively.

Countercurrent extraction studies were made with one volume of a 10-g/liter rare-earth feed that was 11 M in LiCl and 0.2 M in HCl, four volumes of 0.5 M mono-2-ethylhexylphosphoric acid extractant, and one volume of 10 M LiCl-2 M HCl scrub. After equilibrium was reached, americium tracer was added to each stage to determine americium distribution coefficients throughout the system. With eight extraction stages and seven scrub stages, the aqueous raffinate contained 99.96% of the americium, 0.1% of the neodymium, 2.2% of the cerium, 12% of the lanthanum, and <0.1% of the samarium, europium, and gadolinium. Further development of this extraction process is needed to set optimum conditions and to make

certain that satisfactory curium recovery can be obtained.

### 16.2 TRANSURANIC PROCESSING FACILITY

Preliminary design of an addition to the Isolation Building was started. This addition will provide laboratories for work with alpha-active materials and cells for work with alpha-, gamma-, and neutron-active materials. The completed building will house essentially all the laboratory-scale alpha work of the Chemical Technology Division and the principal Analytical Chemistry Division laboratories for highly alpha-active samples.

### 16.3 SPECIAL PLUTONIUM IRRADIATIONS

Five plutonium fuel elements for the ORR are available. Irradiation of three of these has been started. They will be irradiated to greater than 90% burnup and will furnish material for process testing.

## 17. USES OF DEPLETED URANIUM

Information was collected and a program organized to develop and promote nonnuclear uses for uranium depleted in  $U^{235}$ . A summarizing report is being prepared which will include the status of related programs at other sites. Nonreactor uses are insignificant, and fast breeders would use only a small fraction of the depleted uranium that will be produced in the next 40 years.

The toxicology and radiology of uranium were reviewed to establish the least restrictive safe handling and accountability limits. An illustration of the restriction placed on handling depleted

uranium is that the maximum permissible concentrations for uranium or its compounds in air are greater than those of mercury or lead.

Literature reviews indicated the most promising large-scale uses of depleted uranium to be in these categories:

1. metallurgy, particularly in alloys and as sacrificial electrodes for cathodic protection,
2. ore dressing, for example, to form heavy media,
3. processing, for example, as a catalyst,
4. ceramics,
5. inorganic ion exchange work,
6. shielding.

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## 18. SOLVENT EXTRACTION TECHNOLOGY

Acid, basic, and neutral extractants with an increasing range of structures were examined in continuing chemical and engineering studies of their extraction behavior, and some of the many potential applications were investigated. Fundamental chemical reactions and the effect of irradiation on several solvents were studied.

### 18.1 URANIUM-THORIUM SEPARATION

In extractions from nitric acid solutions, phosphates and phosphonates with secondary alkyl side chains gave uranium-thorium separation factors 15-40 times greater than TBP (Table 18.1). Reagents with branching further along the chain (e.g., 2-ethylhexyl, 2-methylbutyl) or with a mixture of normal and cyclohexyl or phenyl groups were only slightly better than TBP, with separation factors about threefold greater. Phosphonates with straight alkyl chains showed separation factors down to half those with TBP.

The wide spread in uranium-thorium separation factors is a result of the large effect which reagent structural changes have on thorium extraction as contrasted to uranium extraction. Thus, the reagents listed in Table 18.1 showed a  $10^4$ -fold variation in thorium extraction coefficient, but only a 40-fold variation in uranium coefficient. The uranium-thorium separation factor with TBP in xylene was about three times higher than with TBP in Amsco 125-82. Similar differences have also

been observed with fission products. Di(sec-butyl) phenylphosphonate (DSBPP) and dibutyl phenylphosphonate (DBPP) require diluents of appreciable aromatic content in order to achieve sufficient organic phase solubilities of the uranium-organo-phosphorus complex.

### 18.2 URANIUM-PLUTONIUM EXTRACTION

DSBPP and DBPP showed higher extraction than TBP for uranium and plutonium (Table 18.2) and better separation factors for uranium from fission products (Table 18.3) from nitrate solution. Countercurrent tests under conditions simulating the usual Purex codecontamination cycle confirmed that both uranium recovery and decontamination from fission products are better with DSBPP in xylene than with TBP in Amsco 125-82 (Tables 18.4 and 18.5). The DSBPP has also been demonstrated to have higher stability to radiolysis than TBP (Table 18.6) (see also Sec 18.8).

**From Sulfuric Acid Decladding Solutions.** - Development continued of solvent extraction methods to recover plutonium and uranium lost from fuel cores to sulfuric acid decladding solutions. The two most promising flowsheets were tested through continuous countercurrent extraction in laboratory-scale mixer-settlers. These used successive extraction of uranium(IV) and plutonium(III) or (IV) with 0.1-0.3 M primary amine, followed by stripping of both together from the combined extracts

Table 18.1. Uranium-Thorium Separation Factors in Extraction from 4.0 M Nitric Acid with 1.0 M Organophosphorus Reagent

Reagent	Calculated Separation Factor	
	Amsco 125-82 Diluent	Xylene Diluent
Secondary Alkyl		
Di(octyl-2) phenylphosphonate		980
Di(sec-butyl) phenylphosphonate		370
Tri(octyl-2) phosphate	370	
Tri(sec-butyl) phosphate	240	
Di(isopropyl) 2-ethylhexylphosphonate	100	
Di(octyl-2) 2-ethylhexylphosphonate	55	
Branched Primary Alkyl		
Di(2-ethylhexyl) 2-ethylhexylphosphonate	27	
Tri(2-ethylhexyl) phosphate	26	
Tri(2-methylbutyl) phosphate	17	
Tri(isobutyl) phosphate	20	
<i>n</i> -Alkyl + Cyclohexyl		
Di( <i>n</i> -butyl) cyclohexylphosphonate	22	
<i>n</i> -Alkyl + Phenyl		
Di( <i>n</i> -butyl) phenylphosphonate		19
Straight Primary Alkyl		
Tri( <i>n</i> -butyl) phosphate	11	26
Di( <i>n</i> -hexyl) <i>n</i> -hexylphosphonate	8	
Di( <i>n</i> -pentyl) <i>n</i> -pentylphosphonate	6	
Di( <i>n</i> -butyl) <i>n</i> -butylphosphonate	13	

(Fig. 18.1a), and extraction of uranium(VI) alone with 0.3 M di(2-ethylhexyl)phosphoric acid-0.15 M TBP (Fig. 18.1b). Simulated decladding solutions were used at the expected concentrations<sup>1</sup> of 2-3 M H<sub>2</sub>SO<sub>4</sub> plus 1 M stainless steel sulfates, with addition of either 3 g of uranium and 0.001 g of plutonium or 2 g of thorium and 0.1 g of uranium per liter.

<sup>1</sup>J. R. Flanary et al., *Development of the Sulflex Process for Decladding Stainless-Steel Clad Power Reactor Fuel Elements with Sulfuric Acid*, ORNL-2461 (March 13, 1959).

Both uranium(IV) and plutonium(IV) are strongly extracted by primary amines from sulfate solution even at high acidity ( $E_a^0 > 1000$  from 3 M H<sub>2</sub>SO<sub>4</sub> with 0.1 M Primene JM-T). In the presence of uranium(IV) and iron(II), the plutonium is expected to be reduced to Pu(III), which is much less extractable. However, under the conditions shown in Fig. 18.1a plutonium was extracted with coefficients of 100. This ability to extract plutonium(III) is tentatively ascribed to enhancement of oxidation from Pu(III) to (IV), during extraction, by the complexing action of the sulfate and the amine. The addition of a relatively small amount of oxidant

[0.01 M Fe(III) added to the ~0.7 M Fe(II)] after the uranium extraction aided the plutonium extraction. Over 99% of the uranium and plutonium were recovered in continuous countercurrent tests,

Table 18.2. Uranium and Plutonium Extraction by DSBPP and DBPP

For U: 11.3 g of U per liter, 5.03 g of Th per liter; o/a ratio = 1.0

For Pu: 0.000055 M Pu(IV); o/a ratio = 1.0

HNO <sub>3</sub> Concentration in Aqueous Phase (M)	Extraction Coefficient		
	1.01 M TBP in Amsco 125-82	1.11 M DSBPP in Xylene	1.11 M DBPP in Xylene
Uranium Extraction			
3.0	31.0	37.8	52.7
0.8	6.2	16.5	19.4
0.2	2.9	7.5	11.1
Plutonium(IV) Extraction			
3.0	15.0	19.0	34.0
1.5	4.9	6.8	12.0
0.6	0.20	0.32	0.57
0.2	0.016	0.045	0.093

Table 18.3. Separation Factors for Uranium from 3.0 M HNO<sub>3</sub> with DSBPP, DBPP, and TBP in Batch Equilibrations

For U: 11.3 g of U per liter, 5.03 g of Th per liter; o/a ratio = 1.0

For Pu: 0.000055 M Pu(IV); o/a ratio = 1.0

Nuclide Separated from Uranium	Separation Factor		
	TBP (1 M in Amsco 125-82)	DSBPP (1.1 M in Xylene)	DBPP (1.1 M in Xylene)
Pu(IV)	2.1	2.0	1.6
Ru	720	1400	1550
Zr-Nb	890	1180	1000
Gross β	2000	5800	2400

with a concentration factor of ~2.5 in the extraction step.

A promising flowsheet similar to that in Fig. 18.1a combines the uranium and plutonium extraction sections into a single section. It is based on the ability of the plutonium, once extracted, to be retained in the organic phase while relatively large amounts of uranium(IV) are extracted in the upper stages. When the flow ratio was set to give uranium loading >95% of the maximum, plutonium was lost because of excessive refluxing in the upper stages. With the flow ratio adjusted to give ~80% of the maximum uranium loading, plutonium

Table 18.4. Uranium Extraction Factors (E<sub>d</sub><sup>0</sup>)

Counter- current Stage	1 M DSBPP in Xylene	1 M DBPP in 20% Xylene-80% Amsco 125-82	1 M TBP in Amsco 125-82
6-Sc	28.4	31.0	17.6
1-Ex	8.2	12.5	3.3
3-Ex	84.0	63.6	43.0

Table 18.5. Gross Beta Decontamination Factors

Counter- current Stage	1 M DSBPP in Xylene	1 M DBPP in 20% Xylene-80% Amsco 125-82	1 M TBP in Amsco 125-82
6-Sc	3900	840	1500
4-Sc	3380	570	1000
2-Sc	825	233	800
1-Ex	606	88	346

Table 18.6. Radiation Damage to Solvents

Product	Yield, G		
	DSBPP	DBPP	TBP
Gas	0.33	0.49	1.87
H <sub>2</sub>	0.13		>1.00
Mono acid	0.54	0.78	2.07

refluxing was considerably decreased. More than 99% of the uranium and plutonium were recovered, with a concentration factor of ~2.5 in the extraction step.

The combined extractant D2EHPA-TBP extracts<sup>2</sup> uranium(VI) ( $E_a^o \sim 10$  from 3 M H<sub>2</sub>SO<sub>4</sub> with 0.3 M D2EHPA-0.15 M TBP), but the extraction coefficients for plutonium(IV) are not high enough to overcome competition by high concentrations of

iron(III). When plutonium is absent or negligible, the iron can be reduced to (II) and uranium(VI) extracted according to the flowsheet of Fig. 18.1b. Over 95% of the uranium was recovered in continuous countercurrent tests, with a concentration

<sup>2</sup>C. A. Blake, D. E. Horner, and J. M. Schmitt, *Synergistic Uranium Extractants: Combination of Neutral Organophosphorus Compounds with Dialkylphosphoric Acids*, ORNL-2259 (Feb. 10, 1959).

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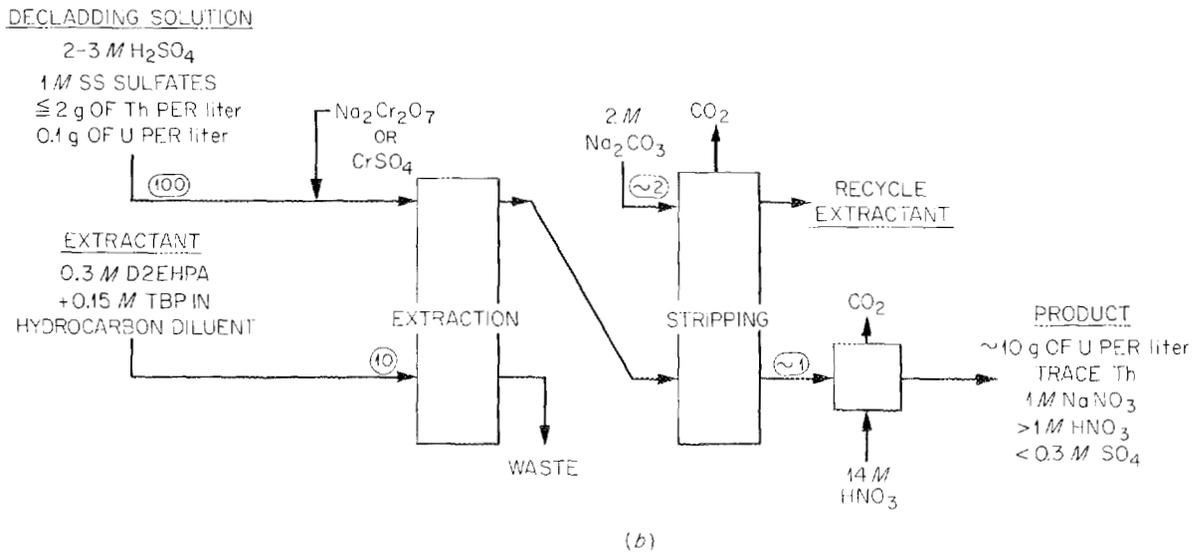
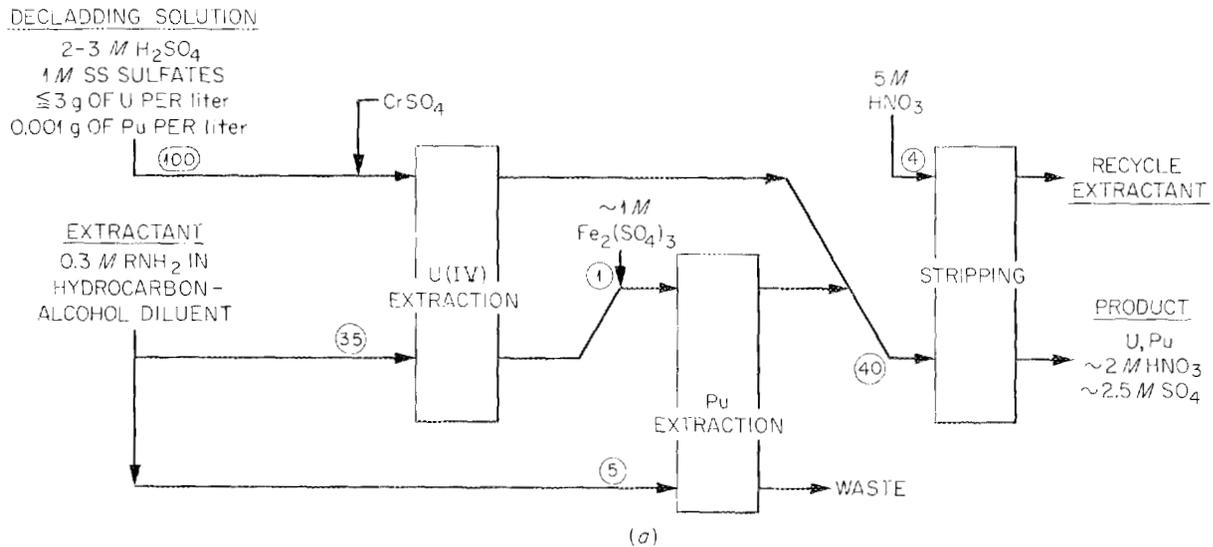


Fig. 18.1. Recovery from Sulfuric Acid Decladding Solution of (a) Uranium and Plutonium by Extraction with Primary Amine and (b) Uranium by Extraction with Di(2-ethylhexyl)phosphoric Acid. Circled numbers are flow ratios.

factor of 10 in the extraction step. About 2% of the thorium was extracted.

Uranium can also be recovered from uranium-thorium-bearing decladding solutions by extraction with a primary amine by the uranium portion of the flowsheet of Fig. 18.1a. The thorium will also be completely recovered. If there is much thorium in the decladding solution the relative product volume cannot be held as low as it can be in the absence of thorium because of the limited aqueous solubility of thorium (on the order of 10 g of Th per liter) in sulfate solutions.<sup>3</sup>

### 18.3 PLUTONIUM AND NEPTUNIUM RECOVERY

Study continued on extraction of plutonium and neptunium by amines, trialkylphosphine oxide, and dialkylphosphoric acid. Most attention was given to the highly extractable IV oxidation state from nitrate solutions, for application to the processing of neptunium and plutonium from irradiated neptunium, and to recovery of traces from waste streams.

The extraction coefficients for Np(IV) were generally lower than those for Pu(IV) by factors of 5 to 10. However, their variation with the major extraction variables was closely parallel over considerable ranges. This proved useful in interpolation and extension of plutonium nitrate extraction data by comparison with neptunium extraction curves, which are more readily established in detail with the use of Np<sup>238</sup> tracer.<sup>4</sup>

Certain aspects of Pu(IV) and Np(IV) extraction were similar with acid, phosphine oxide, and amine extractants. The extraction coefficients ( $D/a$ ) passed through maxima near 1 M HNO<sub>3</sub> and decreased sharply at lower acidities when no nitrate was added, but continued to increase with decreasing acidity down to ~0.2 N HNO<sub>3</sub> in the presence of ~6 M NaNO<sub>3</sub> (Fig. 18.2). With dialkylphosphoric acid the lower extraction at low acidity in the absence of salt is attributed to hydrolysis

<sup>3</sup>W. C. Waggener, "Thorium Sulfate Solubilities," letter to A. M. Weinberg, ORNL, April 17, 1953.

<sup>4</sup>B. Weaver and D. E. Horner, "Distribution Behavior of Neptunium and Plutonium Between Acid Solutions and Some Organic Extractants," paper presented at the 135th National Meeting of the American Chemical Society, Boston, April 1959.

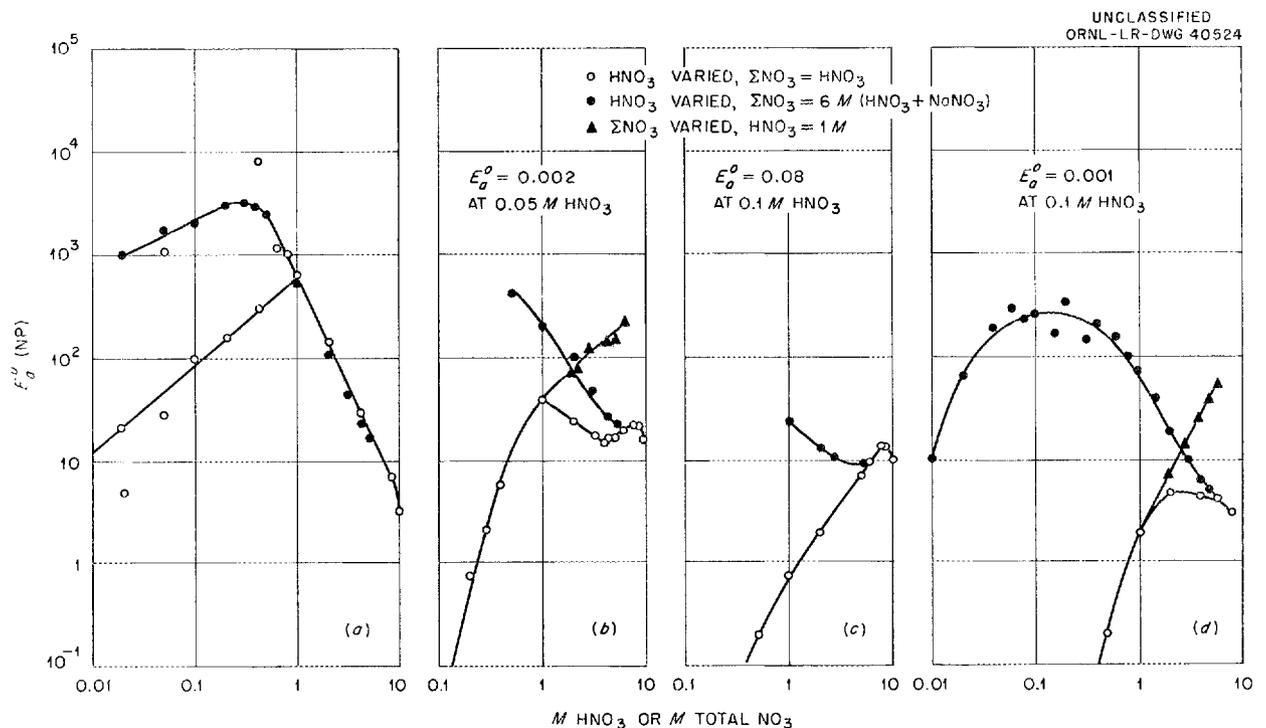


Fig. 18.2. Effect of Nitric Acid and Total Nitrate Concentrations on Extraction of Neptunium(IV) by: (a) 0.01 M Di(2-ethylhexyl)phosphoric Acid; (b) 0.01 M Tri-*n*-octylphosphine Oxide; (c) 1 M Tributylphosphate; (d) 0.1 M Triisooctylamine.

of the metal ion; with the phosphine oxide and amine it is attributed to both hydrolysis and insufficient nitrate complexing. Extraction coefficients varied with approximately the square of the concentration of each reagent. Neptunium-237 loading tests indicated saturation at an Np(IV)/D2EHPA mole ratio of  $\sim 1/3$  (0.001 M D2EHPA) and at an Np(IV)/amine mole ratio of  $\sim 1/4$  (0.025 M Alamine 336).

Extraction coefficients for Np(IV) from sulfate solutions were considerably higher than those for Pu(IV), the opposite of their relative extractabilities from nitrate solutions. The extraction behavior of neptunium was generally similar to that of plutonium, but less closely parallel than in the nitrate systems. For example, while both were strongly extracted by primary amines, they responded oppositely to varying acidity (Table 18.7). With both dialkylphosphoric acid and trialkylphosphine oxide, extraction was high at low sulfate concentrations and generally decreased with increasing sulfate. Extraction by phosphine oxide was impaired least when the sulfate was all present as sulfuric acid. Extraction by dialkylphosphoric acid was better at low acidity for Np(IV), but slightly better at higher acidity for Pu(IV).

Extraction of both Pu(IV) and Np(IV) varied with amine class in the order quaternary, tertiary  $\gg$  secondary  $>$  primary from nitrate solutions and primary  $\gg$  secondary  $>$  tertiary from sulfate solutions, the same orders as for most other III- and IV-valent metal ions.<sup>5</sup> With all the extractants examined, the relative extractability of the different oxidation states was Pu(IV)  $>$  Pu(VI)  $\gg$  Pu(III) and Np(IV)  $>$  Np(VI)  $\gg$  Np(V). Even Pu(III) was extracted, either as such or after enhanced oxidation to IV, by primary amines from sulfate solutions and by

tertiary amines from nitrate solutions at high salt concentration and low acidity.

As previously described,<sup>5</sup> the miscibility of amine salts with organic diluents depends on the anion, on the class, structure, and size of the amine, and on the type of diluent. The sulfate, bisulfate, and nitrate salts of all the amines<sup>6</sup> used in the foregoing studies are miscible at concentrations at least up to  $\sim 0.5$  M with aromatic hydrocarbons and with either aliphatic hydrocarbons or aliphatic hydrocarbon-heavy alcohol mixtures. However, 0.025 M triisooctylamine nitrate in xylene or 95% xylene-5% tridecanol separated into two organic phases when Np(IV) concentrations of the order of 0.005 M were extracted. Trilaurylamine at 0.025 M and Alamine 336 at 0.025 and 0.1 M in xylene each extracted Np(IV) up to saturation (1 mole Np to  $\sim 4$  moles amine) without separation of an extra phase. The higher solubility is attributed to the longer alkyl chains in Alamine 336 (*n*-octyl-*n*-decyl tertiary amine) and trilaurylamine than in triisooctylamine.

**Recovery Procedure.** - A possible process for plutonium and neptunium recovery from irradiated neptunium was developed (Fig. 18.3) using tertiary amine extraction. The dissolver solution containing  $\sim 6$  N aluminum nitrate is adjusted to  $< 0.1$  M HNO<sub>3</sub>. The neptunium is reduced to Np(IV), for example, with ferrous sulfamate, which also reduces the plutonium to Pu(III). Both are extracted by 0.3 M trialkyl amine, for example, trilaurylamine or Alamine 336. The extraction coefficient of neptunium is  $\gg 100$ . That of Pu(III) is more variable and much lower than that of Pu(IV), but high enough ( $> 10$ ) for extraction. The

<sup>5</sup>C. F. Coleman *et al.*, *Ind. Eng. Chem.* 50, 1756 (1958).

<sup>6</sup>Including, e.g., trilaurylamine, tri-*n*-octylamine, tri-*iso*-octylamine, Alamine 336, Amine S-24, N-benzylheptadecylamine, ditridecylamine, Primene JM.

Table 18.7. Extraction of Neptunium and Plutonium from Sulfate Solutions by Primene JM

Constituent Extracted	Concentration of Extractant (M)	Extraction Coefficient, $E_a^o$		
		0.5 M H <sub>2</sub> SO <sub>4</sub>	2.5 M H <sub>2</sub> SO <sub>4</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub> - 2 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
Np(IV)	0.001	50	600	80
Pu(IV)	0.01	35	8	200

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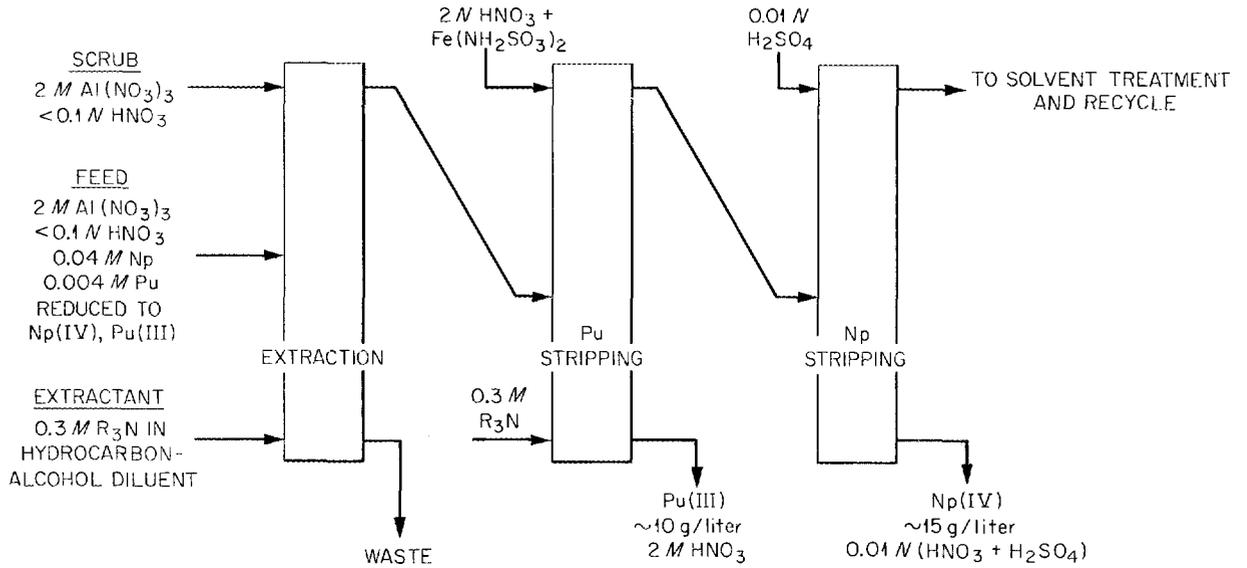


Fig. 18.3. Recovery and Separation of Plutonium and Neptunium by Tertiary Amine Extraction.

plutonium is stripped with 2 M nitric acid containing ferrous sulfamate as a reductant. The neptunium is then stripped with water containing enough sulfuric acid to prevent precipitation.

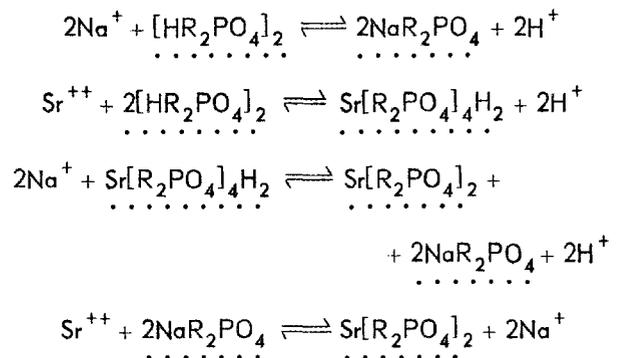
Two other methods examined also appeared promising for plutonium-neptunium recovery: (1) extraction first of Np(IV) from nitric acid solution, leaving Pu(III), and then of Pu(IV) after oxidation, and (2) simultaneous extraction of Np(IV) and Pu(IV) from low-acid aluminum nitrate solution. In the latter case, the presence of 6 N Al(NO<sub>3</sub>)<sub>3</sub> aids reduction of neptunium to IV and prevents its reoxidation when Pu(III) is oxidized to IV with nitrite. Sodium or ammonium nitrate (6 N) was sometimes, but not always, effective in reducing and protecting the Np(IV).

**Recovery from Wastes.** - The high extraction coefficients obtainable with several different extractants (cf. Fig. 18.2) may be useful in recovering traces of neptunium and plutonium from acidic nitrate waste streams. Either 0.3 M triisooctylamine or 0.01 M tri-*n*-octylphosphine oxide extracted Np(IV) with distribution coefficients of ~20 from 8 M HNO<sub>3</sub>, ~50 from 1 M HNO<sub>3</sub>, and >200 from 1 M HNO<sub>3</sub> salted to 6 M total nitrate. Di(2-ethylhexyl)phosphoric acid at 0.01 M extracted neptunium with distribution coefficients ~500 from 1 M HNO<sub>3</sub> and 3000 from 0.4 M HNO<sub>3</sub>

salted to 6 M total nitrate. The extracted metals can be stripped from all three extractants by dilute sulfate, oxalate, or carbonate solutions.

#### 18.4 FISSION PRODUCT RECOVERY

**Strontium.** - As previously reported,<sup>7</sup> D2EHPA extracts strontium from sodium nitrate solutions at pH ~3 to >12, with maximum extraction near pH 5. The following reactions (where the dots indicate the organic phase) account for a maximum in the  $E_a^o$  vs pH curve and for the observed slopes of ~2 below pH 5, ~(-2) from pH 5 to 7, and ~0 above pH 7:



<sup>7</sup>K. B. Brown, *Progress Report on Raw Materials for December, 1957*, ORNL-2486 (April 17, 1958).

They are also consistent with the concentration dependences near the strontium extraction maximum and in the presence of excess aqueous sodium ion:

$$E_a^o(\text{Sr}) \propto M_{\text{R}_2\text{PO}_4}^2 \quad \text{and} \quad \propto M_{\text{Na}}^2$$

$$\text{SF} = E_a^o(\text{Sr})/E_a^o(\text{Na}) \propto M_{\text{R}_2\text{PO}_4} \quad \text{and} \quad \propto M_{\text{Na}}^{-1}$$

Phenyl(1-hydroxy-2-ethylhexyl)phosphinic acid also extracted strontium but at lower pH, extraction starting at pH  $\sim 2.5$ , with a maximum at pH  $\sim 4.5$ . Bis(diisobutylmethyl)phosphoric and di(2-ethylhexyl)phosphinic acids showed only slight extraction maxima, near pH 7, but at pH 12 gave coefficients two to three times as high as D2EHPA, that is,  $\sim 30$ , from 0.5 M NaNO<sub>3</sub> solution with 0.1 M extractant.

**Separation of Rare Earths from Wastes.** – Rare earth fission products were extracted from 5.6 N Al(NO<sub>3</sub>)<sub>3</sub> solution containing no added nitric acid by di-*n*-butyl phenylphosphonate, TBP, and di-*sec*-butyl phenylphosphonate with extraction coefficients of 800, 270, and 100. Extraction of individual rare earths differed only slightly; for example, europium extraction coefficients were only about three times those for cerium(III).

The extraction coefficient was greatly affected by the salting agent (Table 18.8). Extraction from aluminum nitrate solution was about 30 times higher than from sodium nitrate, and more than 100 times higher than from ammonium nitrate, each at 5.6 N nitrate. Addition of 0.1 N HNO<sub>3</sub> at

constant total nitrate decreased coefficients to about  $\frac{1}{3}$  of those with no added acid.

A tentative flowsheet for recovery and concentration of rare earths, including cerium(III), uses extraction with dilute diamyl amyolphosphonate (DAAP) from 5–6 N Al(NO<sub>3</sub>)<sub>3</sub> or NaNO<sub>3</sub> solution, or with dilute TBP from 5–6 N Al(NO<sub>3</sub>)<sub>3</sub> solution, containing not more than  $\sim 0.1$  N HNO<sub>3</sub>. The extracted rare earths can be stripped readily by very dilute (unsalted) nitric acid.

**Separations of Rare Earths.** – As previously reported,<sup>8</sup> rare earth distribution between diluted TBP and 14 N HNO<sub>3</sub> nearly saturated with rare earth nitrates gave the theoretical separation factor between yttrium and erbium, 1.08 per stage, throughout an 86-stage extraction system operated at total reflux. Operation was also feasible at a 10 to 1 reflux ratio, with nearly constant concentrations being maintained through the extraction system although the separation factor dropped to 1.044 per stage. Attempts to operate with 10 N HNO<sub>3</sub> were unsuccessful. At the lower acidity the rare earths became concentrated beyond the solubility limits at one end or the other of the extraction system, so that steady state at total reflux was not attained. This part of the rare earth separations study – separations requiring high throughput capacity – was terminated.

<sup>8</sup>Chem. Tech. Ann. Prog. Rep. Sept. 23, 1958, ORNL-2576, p 113.

Table 18.8. Effect of Salting Agents on Extraction of Europium Nitrate  
Salting agent 5.6 N with no added acid

Reagent (1 M)	Eu Extraction Coefficient, $E_a^o$								
	LiNO <sub>3</sub>	NaNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	Al(NO <sub>3</sub> ) <sub>3</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>	Zn(NO <sub>3</sub> ) <sub>2</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub>	Fe(NO <sub>3</sub> ) <sub>3</sub>
Tributyl phosphate*	140	10	2	270	250	10	150	60	10
Diamyl amyolphosphonate	1800	230	50	3000	1400	40	1200	1200	90
Dibutyl butylphosphonate	1500	230	50	3000					
Di- <i>n</i> -butyl phenylphosphonate	320	25	7	800					
Di- <i>sec</i> -butyl phenylphosphonate	75	3	0.7	100					

\*Diluent for TBP was Amsco 125-82; for phosphonates, 80% Amsco 125-82–20% xylene.

The use of a continuous multistage TBP-nitric acid extraction system is attractive for the separation of fission product rare earths, which differs from the macro separation of natural rare earths in that high throughput (on a weight basis) is not needed. Separations of yttrium from the fission product lanthanons and of promethium from the lighter lanthanons and samarium by distribution between 12 N HNO<sub>3</sub> and TBP were demonstrated. Distribution coefficients and separation factors from 12 N HNO<sub>3</sub> were essentially the same with undiluted DAAP as with TBP. DAAP has a slightly lower density than TBP, and appeared to give better phase separation.

A process (Fig. 18.4) for isolation of promethium from a fission product rare earth concentrate was developed, based on experience with the natural rare earths, using ideal distribution and separation

factors. The operating conditions were tested and optimized first in the laboratory mixer-settler system used for the natural rare earths and then in the Knolls-type mixer-settlers obtained for use in the plant. The latter test work was done in cooperation with Isotopes Division personnel. The flowsheet uses distribution between 12 N HNO<sub>3</sub> and undiluted TBP to split the fission product rare earths first between promethium and neodymium, then between promethium and samarium. The separation factor between neodymium and samarium was 1.85 per stage. Promethium recovery with the 20 first-cycle and 34 second-cycle stages available for the plant was 90%, at 80% purity, from a 6% promethium feed. Recovery and purity could be considerably higher with more stages. Final tests with tracer neodymium, promethium, and samarium in the plant equipment corroborated the chemical flowsheet.

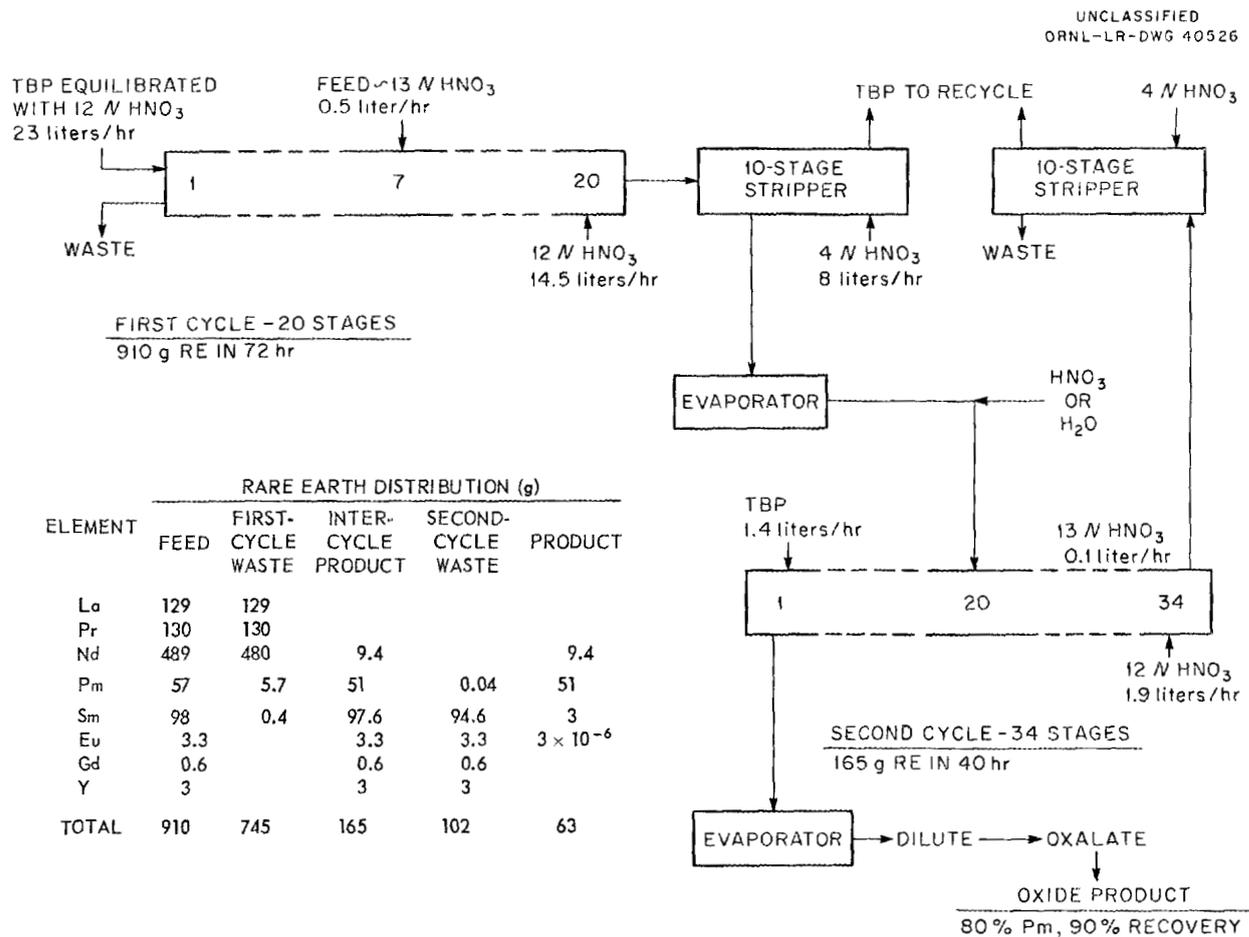
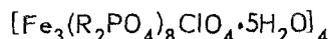


Fig. 18.4. Isolation of Promethium from Fission Product Rare-Earth Concentrate.

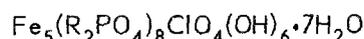
## 18.5 SOLVENT EXTRACTION EQUILIBRIA

## Iron Extraction by Dialkylphosphoric Acid.

Study continued of cation extraction by dialkylphosphoric acids, with principal attention to iron(III) distribution between acidic perchlorate solutions and di(2-ethylhexyl)phosphoric acid (D2EHPA) solutions in *n*-octane. The extraction isotherm for the system is complex, with inflections at metal/reagent mole ratios of 1/6 and 3/8 and saturation at 5/8. At low iron levels (metal/reagent < 1/10) the extraction complex  $\text{Fe}(\text{R}_2\text{PO}_4)_6\text{H}_3$  is indicated, corresponding to the complexes of uranyl and several other cations previously studied.<sup>9</sup> At higher iron levels polynuclear complexes are formed, analyses of which together with isopiestic and viscosity measurements suggest the formulas



and



The iron extraction coefficients at low iron levels varied with the cube of the aqueous acidity and between the square and cube of the free extractant concentration:

$$E_a^0(\text{Fe}) \approx (3.6 \times 10^4) [M_{\Sigma \text{R}_2\text{PO}_4} - 6M_{\text{Fe}(\text{o})}]^{2.65} (M_{\text{H}^+})^{-3}$$

These data also provided a basis for estimating activity coefficients for D2EHPA in *n*-octane (Sec 18.7).

**Thorium Sulfate Extraction by Amines.** – Thorium sulfate extractions from weakly acidic (pH 2) aqueous sulfate solutions by di(tridecyl P) amine sulfate in benzene indicated, from the isotherm plateau, a complex containing three amine sulfates per thorium, in close analogy with corresponding ratios for uranium loading by a number of the amine extractants. Di-*n*-decylamine and di(1-isobutyl-3,5-dimethylhexyl)amine behaved similarly. In addition, the latter two amines showed lower extraction coefficients, more favorable for analytical purposes. Since it is available in a pure form, di-*n*-decylamine will be used for the remainder of the thorium work.

<sup>9</sup>C. A. Blake *et al.*, *Proc. U.N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958* 28, 289.

**Anomalous Equilibria in Uranium Extraction by**

**Amine Sulfates.** – Uranium extraction coefficients obtained by the usual violent agitation procedures vary approximately linearly with the uncomplexed amine sulfate concentrations,<sup>10-12</sup> although the molar association ratios (amine sulfate/uranium) have been in the range 2/1 to 3/1, never as low as 1/1. Particle size determinations led to the prediction<sup>13</sup> that this dependence would be zero power with di-*n*-decylamine sulfate (DDAS) and second or third power with tri-*n*-octylamine sulfate (TOAS). A hypothesis which could account for these anomalies is that metastable conditions are induced by the agitation itself, such as organic droplets sufficiently small that all the extractant is adsorbed at the interface. On coalescence, the clear phase analyses obtained would thus reflect an interfacial adsorption equilibrium rather than a true extraction equilibrium, because of the slowness with which true equilibrium is established through the quiescent interface. In order to test this hypothesis, long-term equilibrations through quiescent interfaces were made. With DDAS the coefficients remained constant, within experimental error, over a 32-fold range of DDAS concentration, and with TOAS the dependence varied from third power below 0.05 *N* to nearly first power at higher concentrations (Fig. 18.5).<sup>14</sup> The slow equilibration technique has thus definitely established metastability due to violence of agitation as an important factor in the anomalous "equilibria" observed in at least one definitive parameter in the amine extractant systems. Also, it has replaced the previously anomalous dependences with nearly theoretically ideal results over a considerable range, and it shows promise of becoming a new and generally valuable tool in obtaining true thermodynamic equilibria in any extraction system where violence of agitation during equilibration may be leading to spurious results.

<sup>10</sup>K. A. Allen, *J. Am. Chem. Soc.* 80, 4133 (1958).

<sup>11</sup>W. J. McDowell and C. F. Baes, Jr., *J. Phys. Chem.* 62, 777 (1958).

<sup>12</sup>K. B. Brown *et al.*, AECD-4142 (May 27, 1954); AECD-4145 (June 24, 1955).

<sup>13</sup>K. A. Allen, *J. Phys. Chem.* 62, 1119 (1958).

<sup>14</sup>K. A. Allen and W. J. McDowell, "Agitation Rate Effects in Anomalous Solvent Extraction Equilibria," *J. Phys. Chem.* (1959) (to be published).

### 18.6 KINETIC BEHAVIOR OF THE AMINE EXTRACTANTS

In view of the rather startling results obtained on slow equilibration through quiescent interfaces (Sec 18.5), a kinetic study was made of acid and uranium extraction by amine sulfates in benzene, using an all-glass apparatus in which the phases could be stirred separately in opposite directions

at controlled speeds. All the extractions run so far appear to be first order, suggesting that the rate-controlling step is Fick's first law diffusion through the stationary layers at the interface. Under constant mechanical conditions, and at constant amine, uranium, and acid activity but varying aqueous sulfate ion concentration, a series of uranyl sulfate extractions by tri-*n*-octylamine sulfate in benzene has shown that the uranyl ion is three times as effective as the neutral monosulfate complex in transferring uranium to the organic phase, and that the neutral complex, in turn, is twice as effective as the dinegative disulfate complex.

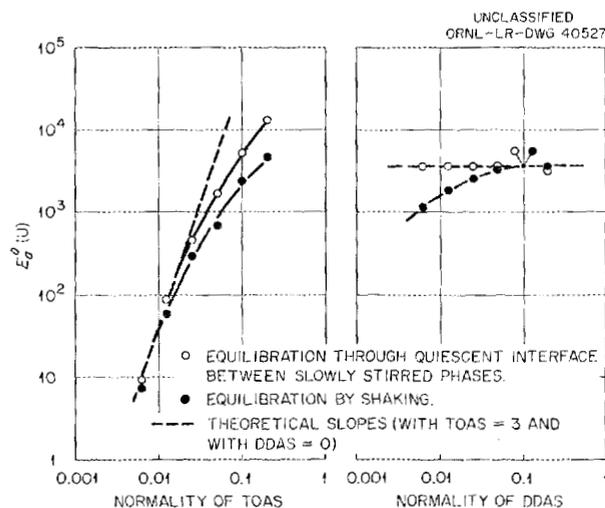


Fig. 18.5. Equilibria Obtained with Quiescent and Dispersion Contact in Uranyl Sulfate Extraction with (a) Tri-*n*-octyl- and (b) Di-*n*-decylamine Sulfate.

### 18.7 STUDY OF THE ORGANIC PHASE

**Aggregation in the Amine Extractant Systems.** — In continued study of the aggregation behavior of the amine sulfate extractants in hydrocarbon diluents, light-scattering measurements were extended to solvents other than benzene. Table 18.9 shows molecular weights and aggregation numbers for six amine salts in *n*-nonane containing 3% tridecanol, along with the previous results in benzene for comparison. Except for the 1-undecyl-dodecylamine sulfate, for which measurements were made on dry solutions and therefore do not apply to the corresponding two-phase equilibria, the particles were too small to provide a basis

Table 18.9. Aggregation of Amine Sulfates in Benzene and in *n*-Nonane

Solute	Benzene		<i>n</i> -Nonane (+ 3% Tridecanol)	
	Molecular Weight	Aggregation No.	Molecular Weight	Aggregation No.
Tri- <i>n</i> -octylamine sulfate	900	1	900	1
Trilaurylamine sulfate	1,100	1	1,300	1
Di(1-isobutyl-3,5-dimethylhexyl)amine sulfate	3,600	4	1,800	2
1-(3-ethylpentyl)-4-ethyloctylamine sulfate	8,000	11	4,200	6
Di- <i>n</i> -decylamine sulfate	30,000	40	3300-8100*	5-12
1-undecyldodecylamine sulfate**	140,000	180	800,000	1000

\* The DDAS results in modified nonane showed a smooth curvature corresponding to a continuous change in the average molecular weight from 3300 at  $c = 0.005$  g/ml to 8100 at  $c = 0.036$  g/ml.

\*\* The 1-undecyldodecylamine sulfate measurements were made on dry solutions, and the *n*-nonane did not contain tridecanol.

for the apparent (and probably spurious) constant activity observed in some of the equilibria previously studied.<sup>15</sup>

In a preliminary study<sup>16</sup> of the dielectric behavior of these solutes in benzene, the absence of a frequency dispersion for the large di-*n*-decylamine sulfate particle suggests that the individual molecules rather than the entire aggregates respond to the electric field. This, in turn, indicates that the bonds holding the micelles together may be quite weak, possibly only a few kilocalories per mole. At a fixed frequency of 1 Mc, the dependences of the dipole moments of this and other amine sulfates on concentration indicated that aggregation results in some cancellation of the moments due to the individual molecules.

#### Activity Coefficients in the Organic Phase.

Isopiestic measurements of solutions of tri-*n*-octylphosphine oxide (TOPO) and of D2EHPA in *n*-octane showed deviations from Raoult's law with either solute even at low concentration.<sup>17</sup> Activity coefficients could not be calculated directly from these results, since the activity of the reference solute, triphenylmethane, had not been established in *n*-octane. However, iron extraction data by D2EHPA (Sec 18.5) permitted evaluation of the practical activity coefficient of dimerized D2EHPA in *n*-octane as

$$\log \gamma_{(D2EHPA)_2} = -0.6432m_{(D2EHPA)_2}^{1/3}$$

in the range 0.04 to 0.12 *m*. On this basis, the isopiestic measurements gave estimates of the practical activity coefficients of both TOPO and triphenylmethane in *n*-octane:

$$\log \gamma_{TOPO} = -1.886m_{TOPO} + 0.245m_{TOPO}^2$$

$$\log \gamma_{TPM} = -0.737m_{TPM}$$

In addition to their general application to extraction systems, these activity coefficients will permit improved calculation of adduct formation constants in the interaction between D2EHPA and TOPO in synergistic extraction systems.<sup>18</sup>

#### 18.8 RADIATION DAMAGE TO SOLVENTS<sup>19</sup>

Radiation causes the decomposition of TBP to dibutylphosphoric acid (DBPA) and monobutylacid (MBPA), which can form stable compounds with thorium, plutonium, uranium, zirconium, and niobium. The yield of total acid,  $G_{acid}$ , in

molecules per 100 ev of energy absorbed, was found to be a linear function of the TBP concentration,<sup>20</sup> expressed as electron fraction  $F_{TBP}^e$  or weight fraction  $W_{TBP}$ , for solutions of TBP in Amsco 125-82. The concentration of total acid,  $M_{acid}$ , in moles per liter in a solution irradiated to a dose of  $D$  whr/liter is given<sup>21</sup> by

$$M_{acid} = 9.20 \times 10^{-4} DW_{TBP}$$

By use of this equation and knowing that the solubility of thorium dibutyl phosphate in TBP-Amsco solutions is less than 0.04 g/liter,<sup>22</sup> it can be shown that precipitation of thorium will start, in a nitric acid-free system, at a dose of 0.4 whr/liter. Correlation of uranium retention with dibutylphosphoric acid concentrations in TBP-Amsco solutions, after extraction of uranium from aqueous 2 M HNO<sub>3</sub>-0.2 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solutions and subsequent stripping with 0.01 M HNO<sub>3</sub>, showed that 1 mole of uranium was retained in the organic phase per mole of DBPA, rather than a maximum of 0.5 mole expected from stoichiometry. At the 400 whr/liter level, the yield of unsaturated hydrocarbon in TBP-Amsco solutions decreased linearly with increasing TBP concentration, from about 3.4 double bonds per

<sup>15</sup>C. F. Coleman *et al.*, *Ind. Eng. Chem.* 50, 1736 (1958).

<sup>16</sup>W. J. McDowell and K. A. Allen, *J. Phys. Chem.* 63, 747 (1959).

<sup>17</sup>C. F. Baes, Jr., *An Isopiestic Investigation of Di(2-ethylhexyl)phosphoric Acid and Tri-*n*-octylphosphine Oxide in *n*-Octane*, ORNL-2737 (in press).

<sup>18</sup>H. T. Baker and C. F. Baes, Jr., "Infrared and Isopiestic Investigation of the Interaction between Di(2-ethylhexyl)phosphoric Acid and Tri-*n*-octylphosphine Oxide in Octane," paper presented at the 134th National Meeting of the American Chemical Society, Chicago, September 1958.

<sup>19</sup>Work done by Stanford Research Institute under subcontract.

<sup>20</sup>R. M. Wagner and L. H. Towle, "Radiation Stability of Organic Liquids," *Stanford Research Institute Semi-Annual Report No. 4 on Subcontract 1081* (January 5, 1959).

<sup>21</sup>W. Davis, Jr. (ORNL) and R. M. Wagner (SRI), "Some Effects of Radiation on Solvent Extraction Processes," paper presented at the 135th National Meeting of the American Chemical Society, Boston, April 5-10, 1959; ORNL CF-59-1-90.

<sup>22</sup>R. M. Wagner and L. H. Towle, "Radiation Stability of Organic Liquids," *Stanford Research Institute Semi-Annual Report No. 3 on Subcontract 1081* (June 30, 1958).

100 ev for pure Amsco 125-82 to 1.0 for pure TBP.<sup>20</sup> Other studies<sup>23</sup> have shown that whereas the ratio DBPA/MBPA is about 10 when TBP is irradiated in the absence of nitric acid, in the presence of nitric acid it is only about 2. Since the total acid yield is affected only slightly by nitric acid, this change in ratio indicates that the mineral acid accelerates the hydrolysis of dibutylphosphoric acid to monobutylphosphoric acid. Addition of aromatic hydrocarbons, such as isopropylbiphenyl, amyl-naphthalene, and methylbiphenyl as 5 or 10 vol % solutions in Amsco containing 300 g of TBP per liter, had very little effect on the MBPA yields during radiolysis to the 200 to 400 whr/liter levels. These tests were performed with solutions that had been equilibrated with 2 M HNO<sub>3</sub>.

The radiation decomposition yield of an extractant is one measure of its potential value in nuclear fuel reprocessing; a second measure is the degree to which the decomposition products form complexes with uranium and fission products. Both di-*n*-butyl phenylphosphonate<sup>20</sup> and di-*sec*-butyl phenylphosphonate<sup>23</sup> are more resistant to

radiation damage than TBP. At 200 to 400 whr/liter, comparative values of  $G_{acid}$  for the three compounds are 0.78, 0.54, and 2.07 molecules per 100 ev of energy absorbed, respectively. These compounds as extractants for irradiated uranium have been compared by Gresky and Mansfield<sup>24</sup> (see Sec 18.2).

Diethyl carbonate<sup>21</sup> and five amines<sup>25</sup> were irradiated to 200 to 400 whr/liter and subsequently tested as extractants. Even with these high irradiation levels the extraction of fission products by any of the irradiated organic solvents tested was only slightly different from that by the control (Table 18.10).

### 18.9 ENGINEERING DEVELOPMENT

**Phase Separation in the Presence of Silicic Acid.** — Emulsion difficulties, caused by silicic acid in the feed solution, have been encountered in a number of solvent extraction systems in which mixing is aqueous-continuous. Although some

<sup>23</sup>R. M. Wagner and L. H. Towle, "Radiation Stability of Organic Liquids," *Stanford Research Institute Semi-Annual Report No. 5 on Subcontract 1081* (June 30, 1959).

<sup>24</sup>A. T. Gresky and R. G. Mansfield, *Comparisons of Organic Extractants for Irradiated Uranium: Tributyl Phosphate vs. Di-sec-Butyl Phenylphosphonate, Di-*n*-Butyl Phenylphosphonate, Tricapryl Phosphate, and Tri-sec-Butyl Phosphate*, ORNL CF-59-6-15 (June 5, 1959).

<sup>25</sup>C. F. Coleman, *Uranium and Fission Product Extraction by Irradiated Amines*, ORNL CF-59-3-12 (March 3, 1959).

Table 18.10. Radiolysis Yields and Fission Product Extraction

Each extractant was irradiated as the pure compound  
Each aqueous phase contained fission products

Compound	Dose (whr/liter)	Decomposition (molecules per 100 ev)	Ratio of Activity in Irradiated Samples to That in Control	
			Gross Gamma	Gross Beta
Diethyl carbonate	392	5.5	4.3*	1.3*
Primene JM-T	400	2.25	1**	3.4**
N-benzylheptadecylamine	200	2.14	7.5**	8.7**
Triisooctylamine	400		11**	10**
Alamine 336	400	3.49	1.5**	0.1**
Trilaurylamine	400		0.13**	0.86**

\*Pure diethyl carbonate contacted with aqueous 0.172 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>-1.57 M Al(NO<sub>3</sub>)<sub>3</sub>-0.99 M HNO<sub>3</sub>.

\*\*0.1 M amine in xylene as organic phase; 0.2 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>-8 M HNO<sub>3</sub> as aqueous phase.

relief from this problem can be obtained by either adding complexing agents or precipitating the silica with gelatin, the simplest remedy is control of the mixing to form a solvent-continuous dispersion, which is not stabilized by silica, so that primary separation is rapid and solvent loss is low. The importance and utility of controlled mixing in handling feed solutions containing silica has been demonstrated in uranium mills, which have successfully processed solutions containing of the order of 2 g of silica per liter of solution.

**Electrical Acceleration of Phase Coalescence.** — The use of electrical coalescence of water-in-oil-type dispersions in the petroleum industry suggested its usefulness in solvent extraction, both to improve phase separations in normal operation and to attain minimum contact times and volumes by means of high-speed separations. In preliminary tests with a small electrical source (150,000 cps, 50,000 v, low amperage), electrical coalescing of a 1/1 (a/o) phase ratio water-in-oil-type dispersion increased the flow capacity of a 0.2-ft<sup>2</sup> gravity settler about five times. A

10-kv, 30-ma-maximum a-c or d-c source has now been constructed, and further tests are under way.

**Prevention of Silica-Stabilized Emulsions by Solvent-Continuous Mixing.** — A number of sulfuric acid leach liquors from uranium mills contain emulsifying agents which stabilize oil-in-water-type dispersions when mixed with either Amex or Dapex process solvents. Emulsion difficulties are avoided by controlling the mixing to form water-in-oil-type (organic-continuous) dispersions which are not stabilized. Batch phase-separation tests (Table 18.11) show the relative effect of type of dispersion on primary break time for different plant liquors vs typical 0.1 M solvents at a 1/1 phase ratio.

With organic-continuous mixing, primary break times were less than 300 sec. Although the break times for each solvent varied with different liquors, there was no apparent dependence on silica concentration. With aqueous-continuous mixing, emulsion formation appeared to be a function of the concentration in the liquor of soluble silica, which cannot be removed by

Table 18.11. Batch Break Time of Plant Liquors Containing Silica vs 0.1 M Solvents

Settler: 3 × 3<sup>5</sup>/<sub>8</sub> in.  
Phase ratio: 1/1

Plant Liquor	SiO <sub>2</sub> (g/liter)	Break Time (sec)							
		Di(2-ethylhexyl)phosphoric Acid, 3% TBP		Rohm and Haas La-1 Amine, 3% TDA		Di(tridecyl P)amine, 5% TDA		Amine 336, 3% TDA	
		Aqueous Continuous	Organic Continuous	Aqueous Continuous	Organic Continuous	Aqueous Continuous	Organic Continuous	Aqueous Continuous	Organic Continuous
Slime <sup>a</sup>	<0.1	81	53	120	110	120	100		
KM-11 <sup>b</sup>	<0.1	64	79	120	160	110	130	73	120
Shiprock <sup>b</sup>	0.3	110	68	110	130	96	130		
Sect 10 <sup>c</sup>	0.7	120	80	150	130	120	80		
Holly <sup>c</sup>	1.0	>300	62	>300	170	130	110		
C-19 <sup>a</sup>	1.0	>300	87	>300	>300	>300	120		
Old Rifle <sup>d</sup>	1.6	>300	54	>300	120	150	51		
St. Anthony <sup>c</sup>	2.2	>300	62	>300	130	210	130		
New Rifle <sup>d</sup>	2.5	>300	75	>300	160	>300	77	>300	150

<sup>a</sup>Climax Uranium Co., Grand Junction, Colo.

<sup>b</sup>Kerr-McGee Oil Industries, Shiprock, N.M.

<sup>c</sup>Kermac Nuclear Pilot Plant, Golden, Colo.

<sup>d</sup>Union Carbide Nuclear Co., Rifle, Colo.

filtration or centrifugation. No difficulty was encountered at silica concentrations less than 0.7 g/liter. At concentrations greater than 1.0 g/liter, the break time was 24 hr or more; some stable emulsion was formed, the amount generally increasing with increased silica concentration. Addition of silicic acid to sodium sulfate solutions caused similar emulsification, demonstrating that silica is probably the main cause of difficulty with plant liquors.

Emulsion formation was less with di(tridecyl P)amine than with other solvents. With only two liquors were break times greater than 300 sec, and the amount of stable emulsion was much less than that formed with either Rohm and Haas LA-1 amine or di(2-ethylhexyl)phosphoric acid. The reason for this is not known, and the data are

not conclusive enough to recommend that di(tridecyl P)amine be used for aqueous-continuous mixing with silica-containing liquors. Rather, its use would provide an additional safeguard over the other solvents in case inversion occurred in a plant designed for solvent-continuous mixing.

The importance and utility of controlled mixing for handling feed liquors containing of the order of 2 g of silica per liter has been successfully demonstrated in uranium mills. The organic/aqueous ratio in the mixer is usually maintained in the range 1/1 to 2/1 to prevent inversion to aqueous-continuous in case of surges in flow rates. In the usual case, where the rate of aqueous feed to the plant is greater than that of the solvent, proper phase ratio in the mixer is attained by recycling solvent from each settler.

## 19. ION EXCHANGE TECHNOLOGY

The purpose of this program is to study ion exchange as a chemical-engineering unit operation with the goals of improving present AEC uses of ion exchange and of developing new uses. Present and potential uses of ion exchange include the recovery and/or purification of fertile elements, fissile elements, radioisotopes, reactor coolant water, and other materials of interest to the AEC, as well as removing fission products from waste streams prior to discharge. In spite of the wide application of ion exchange, basic engineering-design information is very incomplete in most cases. The scope of this program includes mathematical analysis, laboratory-scale rate and equilibrium measurements and process development, and engineering-scale equipment development.

### 19.1 DEVELOPMENT OF CONTINUOUS ION EXCHANGE EQUIPMENT

Two U.S. AEC plants and one Japanese AEC plant are using the Higgins continuous ion exchange contactor in uranium production. At Y-12 a 50-ft-high 12-in.-dia column operated successfully for a year on the recovery of slightly enriched uranium from reduction residues and, after the loading section was enlarged to 24 in.

in diameter to increase production rate, now has operated satisfactorily for several months on natural uranium.<sup>1</sup> At Hanford plutonium is processed through a contactor of critically safe dimensions to give a product of higher purity than was hitherto attainable.<sup>2</sup> The first Japanese uranium processing plant is now producing reactor-grade uranium tetrafluoride from ore concentrates,<sup>3</sup> using the Excer<sup>4</sup> chemical and equipment flowsheet. The ore concentrate is dissolved in hydrochloric acid and the solution is processed by continuous anion exchange to give high-purity uranyl chloride, from which UF<sub>4</sub> is

<sup>1</sup>J. M. Googin, G. B. Marrow, and N. J. Setter, "The Recovery of Uranium from Reduction Residues by Semicontinuous Ion Exchange," paper presented at the American Chemical Society Meeting in Boston, April 6, 1959.

<sup>2</sup>J. L. Ryan and E. J. Wheelwright, *The Recovery, Purification and Concentration of Plutonium by Anion Exchange in Nitric Acid*, HW-55893 (Jan. 2, 1959).

<sup>3</sup>"Process Pair Whittles Uranium Costs," *Chemical Week*, July 11, 1959, p 35-38; "Novel Process Tools Win First Job," *Chemical Engineering*, July 13, 1959, p 84-88.

<sup>4</sup>I. R. Higgins, W. J. Neill, and L. E. McNeese, "The Excer Process - An Aqueous Method for Production of Pure Uranium Tetrafluoride from Crude Uranium Sources," *Proc. U.N. Intern. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva, 1958* 4, 113 (1959).

subsequently prepared by electrolytic reduction and precipitation.

Development of continuous ion exchange equipment has been aimed at extending the range of practical operating conditions and testing simpler and more reliable components. A 2-in.-dia column has been operated for several months as a hydrogen-cycle water softener with solution flow rates greater than 2000 gph/ft<sup>2</sup> and resin rates less than 7.5 gph/ft<sup>2</sup> (12 in./hr). Operation for shorter times at solution and resin rates of 3000 and 3 gph/ft<sup>2</sup>, respectively, was satisfactory mechanically but the softening performance was substandard. These rates are the highest and lowest, respectively, known to have been used simultaneously in any moving-bed ion exchange equipment on a practical process basis.

The upper limit on solution throughput rate appears to be set by plastic deformation of the resin when the pressure drop plus static head across a contactor section exceeds a critical value characteristic of the resin used. With Dowex 50-X8 in the 2-in.-dia by 20-ft-high contactor and with Dowex 21K in the 12- and 24-in.-dia by 50-ft-high Y-12 contactor, and when the pressure drop plus static head across the loading section exceeds 60 psi, the resin packs so tightly that it is difficult to move around the loop; stresses on the resin particles break enough of them that the pressure drop rises still higher at the same solution flow rate unless the broken particles are backwashed out of the system.

There is no reason to believe that there is a lower limit on either resin or solution flow rates. The upper limit on resin flow rate appears to be set for practical purposes by the fraction of the time cycle that can be allowed for resin movement. A 1-in.-dia by 20-ft-high contactor was operated for several days at a solution flow rate of 1500 gph/ft<sup>2</sup> and a resin rate of 225 gph/ft<sup>2</sup>. The resin was moved 6 in. every minute with a gross resin movement time of 8 sec. This is the highest resin movement rate known to have been demonstrated on any type of moving-bed ion exchange equipment except at very low solution rates. It appears that if half the cycle time, as an upper limit, is allotted to resin movement a resin flow rate of 900 gph/ft<sup>2</sup> could be achieved. However practically all process requirements studied to date have fallen in the range of 10-100 gph/ft<sup>2</sup>.

The 1-in.-dia by 20-ft-high contactor was relocated in an intermediate-level radioactive cell and arranged to simulate remote operation in a radiochemical processing canyon in order to study operational problems that might arise in such an application. Hanford and Savannah River have process applications for remotely operated continuous ion exchange but have postponed installation of them because of lack of practical operating experience with remote control and maintenance of this type of equipment. The main difference between remote operation of pulsed solvent extraction columns and the ion exchange contactor are the large resin valves in the ion exchange and the greater difficulty in metering solid resin as compared with liquid solvent. In the experimental contactor the resin movement was actuated by water-main pressure rather than by a pump or a hydraulic accumulator as in all previous models, for several months without any trouble. Operation of the contactor for long periods without visual observation of the resin movement was reasonably satisfactory when the rate-time characteristic of the pulse-water injection was adjusted at intervals to keep it within predetermined limits. A television camera and sight glass were used to observe resin movement in the large Y-12 contactor with fairly satisfactory results. The only significant problem encountered with valves in the resin circuit has been leakage around the stem, requiring an occasional tightening of the O-ring seal.

#### 19.2 RECOVERY OF URANIUM, PLUTONIUM, AND CESIUM FROM WASTES

Flowsheets proposed<sup>5</sup> for the ion exchange recovery of uranium and plutonium from stainless steel sulfate decladding solutions require dilution of the decladding solution. Volumetric distribution coefficients for these elements on weakly basic polyamine resins in undiluted Sulfex decladding solution were found to be about 4.5 for U(IV) and 8.5 for Pu(IV) on either Dowex 3 or Amberlite IR45. These values are higher than those for previously tried resins but are much lower than those obtained with liquid primary

<sup>5</sup>W. J. Neill and I. R. Higgins, *The Recovery of Uranium and Plutonium from Stainless Steel Sulfate Decladding Solutions by Ion Exchange*, ORNL-2592 (Nov. 19, 1958).

amines (Sec 18). Primary amine resins are not commercially available.

Continuation of previous efforts<sup>6</sup> on the sorption of cesium from alkaline solutions by phenolic cation exchange has been directed at evaluating the use of Duolite S-30 resin instead of the previously proposed Duolite C-3. The S-30 contains only phenolic exchange groups whereas the C-3 contains methylene sulfonic groups also. The S-30 has about the same cesium capacity as the C-3 but a lower sodium capacity, giving a better separation factor. The S-30 requires much less acid for regeneration, giving higher concentration factors and lower chemical costs. Based on batch and fixed-bed laboratory tests with this resin, the volumetric distribution coefficient for cesium from neutralized waste supernatants of the type discharged to the seepage pits by the ORNL tank farm is about 100, the cesium-sodium separation factor is about 100, and the over-all solution-phase height of a transfer unit at a 1500-gph/ft<sup>2</sup> solution flow rate is about 3 in. In 1 N acid regenerant solutions the cesium distribution coefficient drops to less than 1. The 1-in. contactor in the intermediate-level radioactive cell mentioned above has been arranged to demonstrate a recovery flowsheet on actual ORNL waste.

### 19.3 EQUILIBRIUM URANIUM LOADING OF DOWEX 21K FROM SULFATE SOLUTIONS

The equilibrium uranium loading of Dowex 21K was determined for solutions 0.020 M in sulfuric acid, between 0.0005 and 0.005 M in uranium, and between 0.25 and 0.60 M in total sulfate. The data were correlated (Fig. 19.1) with these three concentrations as parameters since calculations of concentrations of the various uranium complexes had been made previously on this basis. The results extrapolated by fitting them to a Langmuir sorption isotherm indicate a maximum loading of 1 mole of uranium to 4.8 moles of resin. A sulfuric acid concentration of 0.020 M was sufficient to prevent hydrolysis of the  $\text{UO}_2^{++}$  ion. The desired total sulfate concentrations were obtained by adding the appropriate quantity of sodium sulfate.

<sup>6</sup>I. R. Higgins and A. F. Messing, *Development of a Continuous Ion Exchange Process for the Removal and Recovery of High-purity Cesium from Alkaline Waste*, ORNL-2491 (Oct. 23, 1958).

In order to specify the exact solution concentrations with which the resin approached equilibrium, a flow rather than batch method was used to contact the resin and solution. Between 4 and 8 liters of the loading solution was allowed to flow slowly through a fritted glass filter containing approximately 1 g of resin. This method of contacting required 3 to 6 days to ensure that the resin had approached equilibrium with the solution. The loaded resin was centrifuged for 30 min to remove any solution that remained on the surface of the beads. The resin was then eluted with 1 liter of 1 M NaCl solution, and the loading was determined by potentiometric analysis of the eluate. The resin in the chloride form was washed with water, dried 3 days at 55°C, and weighed.

### 19.4 MEASUREMENTS OF THE RATES OF SORPTION OF URANYL SULFATE ON DOWEX 21K FROM SULFATE SOLUTIONS

A technique was developed for studying the rate of uranium sorption on an ion exchange resin by radiochemical determinations of the resin loading as a function of time. Approximately 100 beads are dropped into a stirred 1-liter bath containing the loading solution. Beads are removed after various exposures, washed, and counted in a gamma spectrometer to determine the uranium loading. The diameters of the beads are measured with a calibrated microscope. With enriched uranium enough activity can be obtained in a single bead for an accurate determination. This technique eliminates the problem of obtaining quantities of carefully sized beads.

By this technique six runs were made with 1200- $\mu$  Dowex 21K resin beads and loading solutions with uranium and sulfuric acid concentrations maintained at 0.005779 M and 0.020 M, respectively. The total sulfate concentration was varied between 0.026 and 0.201 M. The data were correlated by means of the equation for diffusion of a single species into a sphere with a constant surface concentration.<sup>7</sup> The equation would apply to the diffusion of an uncharged molecule (e.g.,  $\text{UO}_2\text{SO}_4$ ) into the sphere or to the counter diffusion of two species

<sup>7</sup>J. Crank, *The Mathematics of Diffusion*, p 85-91, Oxford University Press, New York, 1956.

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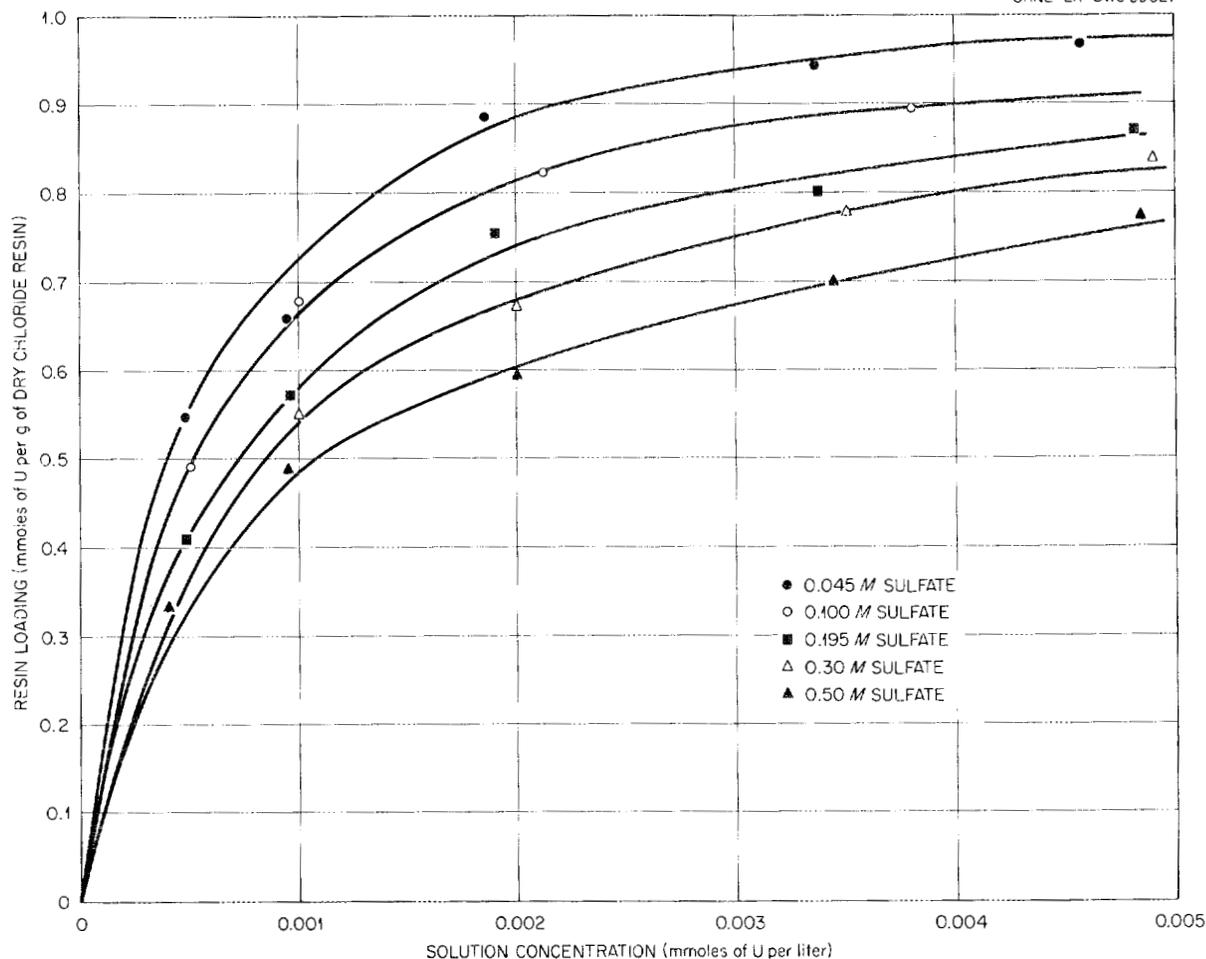


Fig. 19.1. Equilibrium Sorption of Uranium on Dowex 21K from Sulfate Solutions (0.020 M H<sub>2</sub>SO<sub>4</sub>) at 25°C.

[e.g., UO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>] with identical charges and diffusivities.

The equation may be written:

$$\frac{M}{M_{\infty}} = 6 \left( \frac{Dt}{r^2} \right)^{1/2} \left[ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} \text{ierfc} \frac{nr}{\sqrt{Dt}} \right] - 3 \frac{Dt}{r^2}$$

where

M = resin uranium loading, g/cc of resin,

M<sub>∞</sub> = equilibrium resin loading,

D = diffusion coefficient (or diffusivity), cm<sup>2</sup>/sec,

t = time, sec,

r = resin bead radius, cm,

ierfc = imaginary error function of the complement,<sup>8</sup>

$$\text{ierfc } x = \frac{1}{\sqrt{\pi}} e^{-x^2} - x \text{erfc } x,$$

$$\text{erfc } x = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-\xi^2} d\xi,$$

n = term number in an infinite series.

<sup>8</sup>H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2d ed., p 482, Oxford University Press, New York, 1959.

A plot of the diffusion equation with the fraction loading ( $M/M_\infty$ ) vs the reduced time,  $\sqrt{t/r^2}$ , would result in a family of curves with the diffusion coefficient  $D$  as the only parameter. For the experimental data collected in this investigation, all results for total sulfate concentrations from 0.050 to 0.201 M were correlated with a single curve and a single diffusion coefficient of  $1.3 \times 10^{-7}$  cm<sup>2</sup>/sec (Fig. 19.2). In only one run at 0.026 M total sulfate, the correlating curve differed and the diffusion coefficient was  $1.0 \times 10^{-7}$  cm<sup>2</sup>/sec. This difference may have been due to experimental error or a deviation from the simple diffusion model for low sulfate concentrations.

For all runs the initial fit of the data to the curve predicted by the model was poor (e.g.,

100% error at 10% loading). The agreement became progressively better; it was within the experimental scatter of the data after the resin was half loaded.

One possible explanation for the initial lack of fit is that at the initially high diffusion rates a significant resistance existed across the liquid film, and the surface concentration was not constant. To test this hypothesis, two runs were made with the same solutions but with different stirrer speeds (1250 and 1650 rpm). The results of the two runs were identical. Equations for different diffusion models will be studied in an effort to explain or predict the initial deviation. The first to be studied will be an equation which would allow for the difference in diffusivities of  $\text{UO}_2(\text{SO}_4)_2^{--}$  and  $\text{SO}_4^{--}$ .

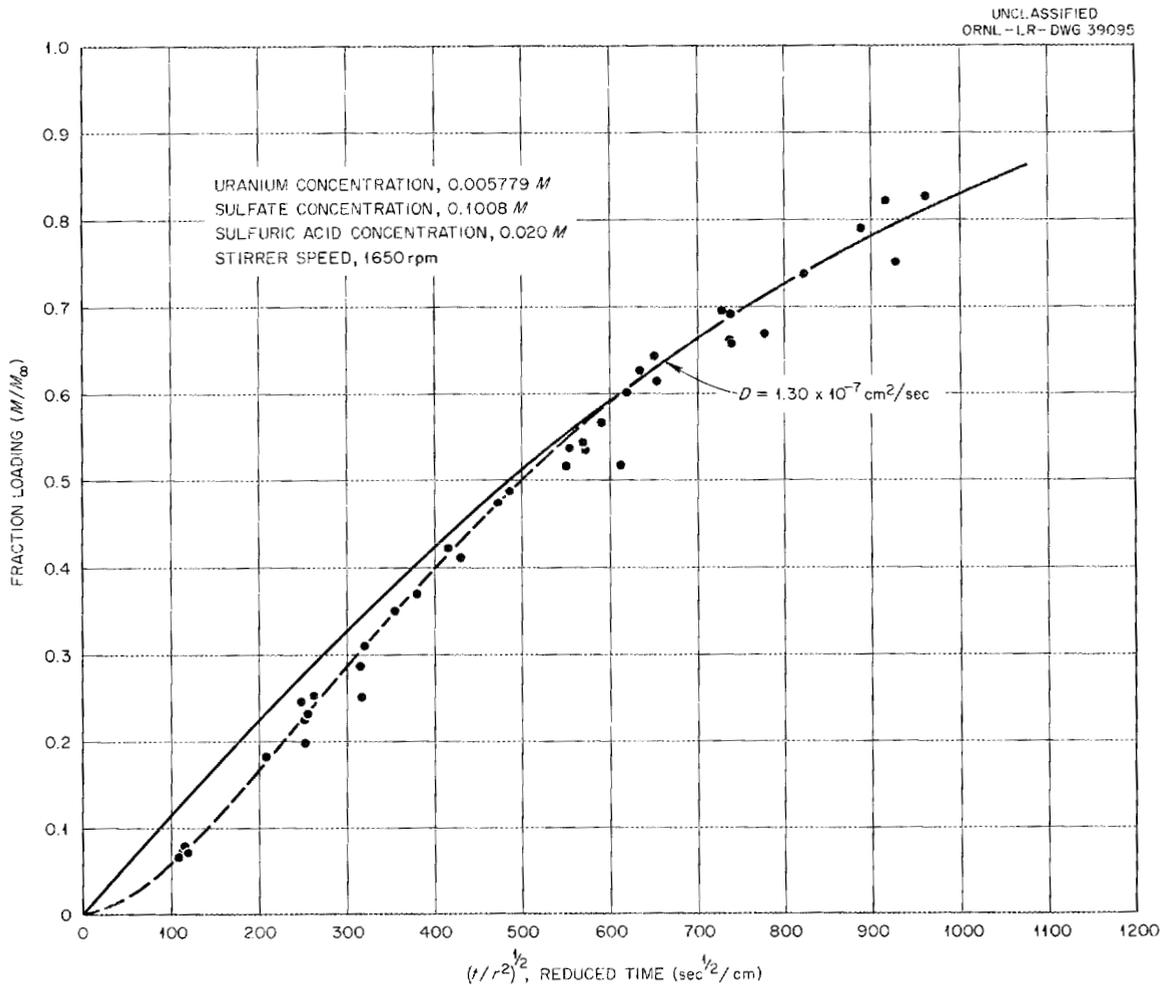


Fig. 19.2. Rate of Sorption of Uranium on Dowex 21K from 0.10 M Sulfate Solutions.

## 20. IN-LINE INSTRUMENTATION<sup>1</sup>

The purpose of the in-line instrumentation program is to develop instruments that will determine process stream compositions *in situ*, thereby improving process and hazard control and reducing analytical costs.

### 20.1 URANIUM COLORIMETER

An in-line colorimeter (Fig. 20.1) for continuously recording uranium-ion concentrations greater than 1 g/liter in either aqueous or organic process streams was fabricated and is being installed in the organic product stream of the Metal Recovery Plant extraction column. A carriage with a lamp, beam-splitter, filters, and phototubes moves between three transparent cells containing the product stream, the inlet solvent stream, and a standard solution. A dual-beam model (Fig. 20.2), which uses a single phototube and uses filters mounted on a motor-driven shutter, is being developed.

### 20.2 SINGLE-BEAM GAMMA ABSORPTIOMETER

An in-line single-beam gamma absorptiometer to continuously record uranium-, plutonium-, or thorium-ion concentrations of greater than 50

g/liter was tested on a simulated flowing process stream. It gives a linear plot of gamma-ray count rate vs heavy-metal-ion concentration on semilog paper for concentrations of 0 to 350 g/liter. The instrument uses the 60-kev gamma ray from a 10-mg Am<sup>241</sup> source. A dual-beam model is being designed for laboratory and plant testing in streams of high uranium-ion concentration (50 and 300 g/liter).

### 20.3 A-C POLAROGRAPH

A prototype model of an in-line a-c polarograph was constructed for continuously recording uranium-ion concentrations as low as a few parts per million in process raffinate streams. Design features are:

1. A three-electrode cell consisting of a platinum working electrode, a saturated calomel

<sup>1</sup>Cooperative program with the Analytical Chemistry and Instrumentation and Controls Divisions.

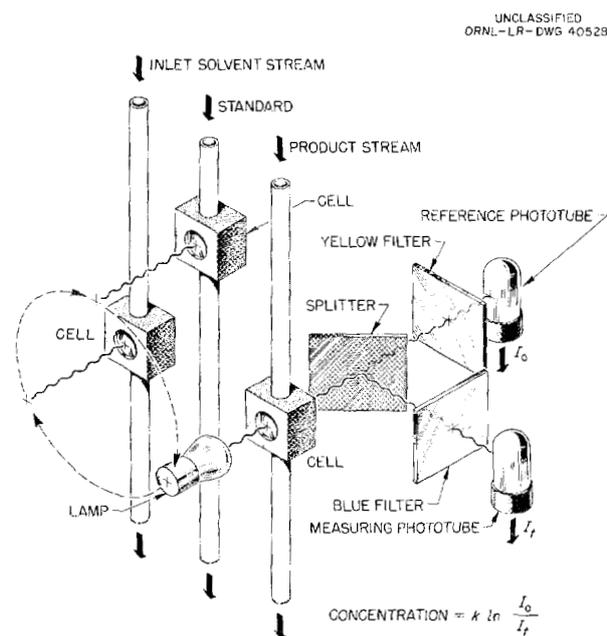


Fig. 20.1. In-Line Colorimeter for Measuring Uranium Concentration.

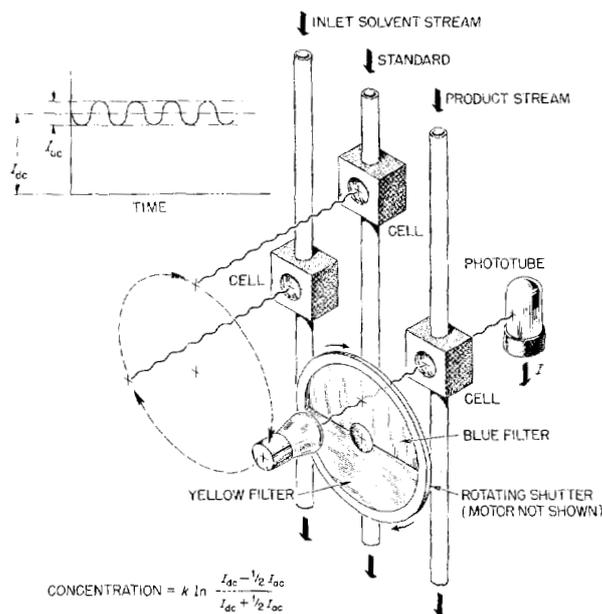


Fig. 20.2. Experimental Dual-Beam In-Line Colorimeter for Measuring Uranium Concentration. The alternating and direct currents are separated with a condenser. The instrument measures in per cent of the reading of the standard and reads in grams per milliliter.

reference electrode, and a dropping mercury electrode.

2. A controlled-potential system, based on computer operational amplifiers, that controls the potential of the dropping mercury electrode with respect to the saturated calomel electrode at every instant regardless of cell values.

3. A current amplifier with negative-feedback elimination of a high-valued current-measuring resistor in the cell circuit. Current ranges are from  $10^{-4}$  to 2000  $\mu\text{a}$ .

4. Phase discrimination rejection of the  $90^\circ$  component of the cell current. The a-c method is preferred for this polarograph application because it presents a derivative type of curve, is relatively free from interference of the diffusion current from irreversible chemical systems, and is highly sensitive because the charging current is rejected.

#### 20.4 PLUTONIUM ALPHA MONITOR

Development of an alpha monitor for determining low plutonium-ion concentrations by contacting an immiscible liquid scintillant with a flowing stream was discontinued. Small quantities of entrained radioactive solvent in process streams were mixed with the scintillant and contaminated it. Gaseous scintillants are being investigated for the monitoring of plutonium in process raffinate streams.

An alpha monitor is being tested with a mockup stream in which a very thin layer of the stream contacts a Lucite disk containing ZnS phosphor in the first few millimeters of thickness. This monitor is being tested for possible application as an in-line monitor for plutonium-ion concentrations in process raffinate streams.

Monitoring for plutonium by means of alpha-induced neutrons was found to be sufficiently sensitive for measuring plutonium losses of the order of a few parts per billion in process raffinate streams.

#### 20.5 ELECTROLYTE CONCENTRATION MONITOR

Work with the in-line radio-frequency monitor was resumed because it is an attractive means of performing an electrical conductivity measurement

on a flowing stream with high electrolyte concentration (2.5 M  $\text{HNO}_3$ ) and with no electrodes contacting the stream. The 300-Mc oscillator developed at ORNL operated stably on streams of high electrolyte concentration with good response to nitric acid concentration. However, in the presence of high salt concentration there was poor response to changing acid concentration.

#### 20.6 GAMMA MONITOR

A plant model of an in-line scintillation gamma monitor, which uses a free-falling cylinder of the process liquid, was tested in the Metal Recovery Plant extraction-column product stream. After a week of operation the instrument became inoperable because highly radioactive solids accumulated in a reservoir that supplied the cylinder and produced excessive background reading in the instrument. The reservoir and shielding are being modified.

A plant model of a scintillation gamma monitor, which uses a 12-in. length of 0.5-in. fluorothene tubing with a 10- $\mu\text{in}$ . finished bore to contain the stream, has been operating for six months in the Power Reactor Fuel Reprocessing Pilot Plant extraction-column product stream. The background reading stabilizes at approximately 25% of the instrument reading and, with background readings made every 48 hr, corrected readings agree within  $\pm 50\%$  with laboratory analysis of stream samples. Valves are provided in the instrument so that the fluorothene tube can be emptied for background measurement and also can be purged with decontaminating solution. If the tube is decontaminated once daily the background remains  $<10\%$  of the instrument reading and the instrument accuracy is improved. The instrument is used for monitoring gross gamma activity; Compton scattering effects limit its possible use as a spectrometer. The fast response of this instrument has enabled Pilot Plant operations personnel to correct a number of incipient operational malfunctions.

A test model of a continuous-scanning spectrometer, in which the volume of the stream sample and the position of the standardizing source are varied for subtraction of background and for stabilization of the instrument, is being fabricated. Fabrication and testing are complete for the continuous-scanning system.

### 20.7 EVALUATION OF POTTER FLOW-RATE METER

One of two Potter turbine flow-rate meters in the Metal Recovery Plant operated in an 8 M HNO<sub>3</sub> stream at 0.25 gpm and failed after six months. The other has been in use for a year and a half in a 13.4 M HNO<sub>3</sub> stream at 3 gpm. Plant operations personnel are of the opinion that, for nonpulsed flow rates greater than 1 gpm and for applications where a pressure drop of a few pounds per square inch is acceptable, this is a superior flow-rate meter. The Potter meters

installed in Thorex pilot plant streams operated satisfactorily in nonpulsed streams but were unsatisfactory in pulsed streams since the agreement with tank depletion rates was only within  $\pm 25\%$ .

### 20.8 NEUTRON MONITOR

An in-line neutron monitor was tested in which a BF<sub>3</sub> counter plus moderator was used to measure plutonium concentration. The sensitivity of the test model was not sufficient for direct use on waste streams.

## 21. CHEMICAL ENGINEERING DEVELOPMENTS

### 21.1 INTERFACIAL-AREA MEASUREMENTS WITH A LIQUID SCINTILLATOR

A method of measurement of interfacial area was described previously,<sup>1</sup> in which a solution of polonium-210 nitrate was contacted with a liquid fluorocarbon and the neutron flux generated at the interface due to the ( $\alpha, n$ ) reaction of F<sup>19</sup> was measured with an external counting device. Although the method had the advantage of being applicable to opaque or remote systems where normal photographic techniques could not be applied, it had the disadvantage of using as an alpha source an extremely hazardous isotope which was chemically unstable and had a tendency to deposit on metal surfaces. A much more convenient method has been developed for measuring interfacial area between an aqueous uranyl nitrate solution and a liquid scintillator (trans-stilbene in phenylcyclohexane). The technique consists in measuring the light produced at the interface by the excitation of the liquid scintillant by uranium alpha particles.

Studies were carried out in a 2-in. mixer (Fig. 21.1) over the range of Weber numbers from approximately 20 to 2,000. The Weber number ( $D^3 \omega^2 \rho_s / \sigma_i g_c$ ) is a ratio of the shear forces in a liquid caused by turbulent mixing to the interfacial tension forces between two liquid phases. Thus, the interfacial surface area would be expected to be proportional to the Weber number in a mixing vessel containing two liquid phases.

For Weber numbers of 100 or less the area measured by the liquid scintillator agrees quite

well with areas measured photographically (Fig. 21.2). At these low values of Weber number there was a cubic dependence of the specific interfacial area on the Weber number. This result indicates that, in a small mixing vessel, measurements of interfacial surface areas made at the bottom of the vessel to the depth of only a few millimeters are probably not representative of the average interfacial surface area throughout the vessel, due to a thick viscous boundary layer and coalescence of the heavy phase.

At Weber numbers between 100 and 200 the results of this study agree with the specific interfacial area predicted by the Rodger correlation.<sup>2</sup> Above a Weber number of 200 results of this work deviate sharply from Rodger's results, and the exponential dependence of the area on Weber number is 0.8 compared with 0.4 from his results. The reason for this difference is not known. Unfortunately, the available photoflash equipment was not sufficiently fast to produce satisfactory photographs at the higher Weber number, so the area measured by the liquid scintillator could not be checked photographically.

The interfacial area was calculated from the signal from a multiplier phototube optically coupled to the transparent bottom of the mixing

<sup>1</sup>Chem. Tech. Ann. Prog. Rep. August 31, 1958, ORNL-2576.

<sup>2</sup>W. A. Rodger, *Interfacial Area in Liquid-Liquid Dispersion Related to Fluid Motion in Mixing Vessel*, ANL-5575 (June 1956).

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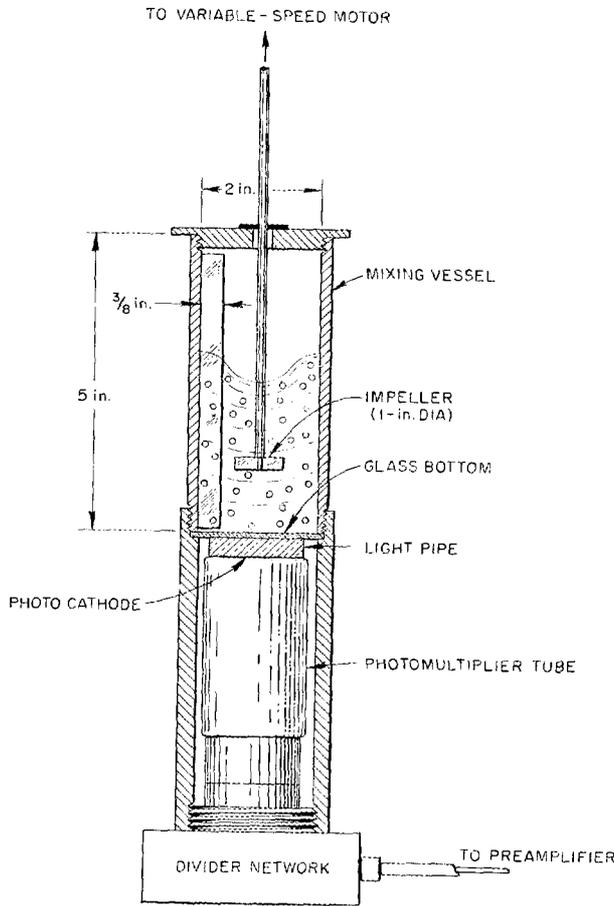


Fig. 21.1. Apparatus Used in Interfacial Area Measurement by Liquid Scintillator.

vessel. The relation between interfacial area and the tube signal, or count rate, is

$$a = \frac{4\mu N}{SAF - 4\alpha N}$$

where

- $a$  = specific interfacial area,  $\text{cm}^2/\text{cm}^3$ ,
- $\mu$  = emulsion light absorbency due to uranyl ion,  $\text{cm}^{-1}$ ,
- $N$  = count rate from tube,  $\text{min}^{-1}$ ,
- $S$  = source strength, alpha particles per  $\text{cm}^3$  per min,

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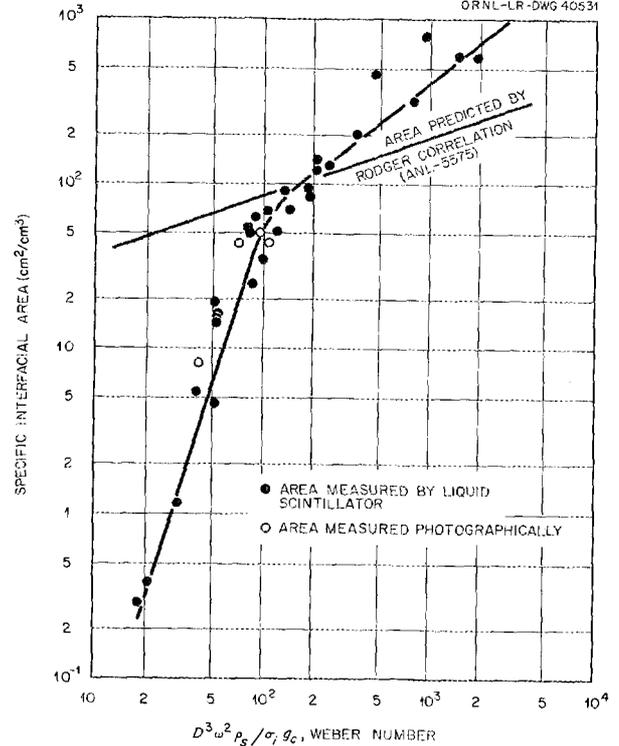


Fig. 21.2. Specific Interfacial Area (Measured by Liquid Scintillator) vs Weber Number.

$A$  = photocathode area,  $\text{cm}^2$ ,

$F$  = a complicated function of alpha energy and pulse-height-selector setting which is constant for any one experiment, cm,

$\alpha$  = light-scattering factor due to interfacial area (dimensionless).

The technique requires that a light absorber (uranyl ion in this case) be included in the emulsion. Otherwise, because of light attenuation from scattering by droplets, the light output, and hence the tube signal, would be independent of interfacial area. The absorber limited the depth of emulsion observed by the photocathode to a few millimeters.

21.2 MEASUREMENT OF RESISTANCE AT AN INTERFACE

An experimental study is being carried out to measure the resistance to mass transfer of the liquid-liquid interface between tributyl phosphate (TBP) in Amsco and aqueous uranyl nitrate. The purpose of the study is to verify the assumption, used in conventional chemical engineering calculations, of negligible resistance to mass transfer at the interface. While the resistance of a chemically pure system may be extremely small, certain impurities (particularly surface-active impurities) may significantly affect the transport of uranium across a solvent extraction interface, and a further purpose of this study is to determine quantitatively the effect of impurities on the kinetics of interfacial mass transfer.

Using a diffusion cell described in last year's report, attempts were made to measure photometrically a steady-state concentration gradient across

an interface in the presence of diffusing uranyl nitrate. In order to interpret the photometric results, it is necessary to know the diffusivity of uranyl nitrate at various temperatures and concentrations in aqueous and organic phases. In preliminary experiments in which an aqueous uranyl nitrate solution (50 g/liter) diffused from a capillary tube into an essentially infinite sink of either 0.02 to 0.1 N nitric acid or 30% TBP in Amsco, the apparent integral diffusivity of uranium was  $6.7 \times 10^{-5}$  cm<sup>2</sup>/sec (Fig. 21.3). There was no difference between the uranium diffusivity measured when the sink was aqueous and when it was organic. This means that, within the precision of these diffusivity measurements, there was no resistance to mass transfer at the interface.

When 10 ppm of a detergent (Tide) was added to the organic phase, the apparent uranium diffusivity decreased from  $6.7 \times 10^{-5}$  to  $4.4 \times 10^{-5}$  cm<sup>2</sup>/sec. This indicates that the interface was partially

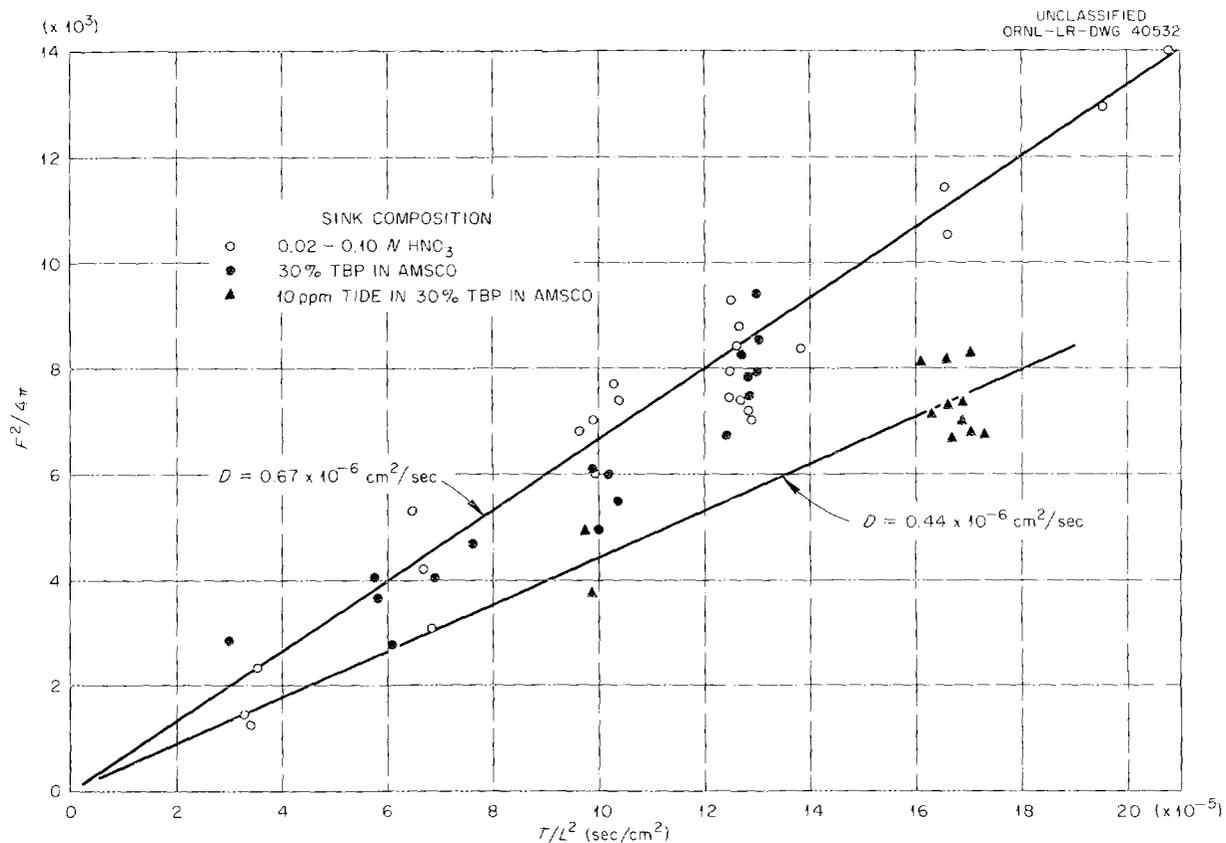


Fig. 21.3. Diffusion of Uranyl Nitrate in Aqueous Solution from Capillary Tubes into Infinite Sink.  $F$  = fraction of  $UO_2(NO_3)_2$  diffused from a capillary  $L$  cm long in  $T$  sec; 50 g of  $UO_2(NO_3)_2$  per liter. The slope of each line is the integral diffusivity.

blocked by the detergent and a resistance, equivalent to approximately 1 cm of diffusion length in water, was developed. Measurements of interface resistance due to the presence of surface-active impurities will be extended to those impurities normally encountered in solvent-extraction operations.

These preliminary uranium diffusivity data are lower by a factor of about 4 than those at room temperature reported in the literature. The reason for the discrepancy is not known. In order to determine whether there was a fundamental error in the design of the capillary diffusion equipment, the diffusivity of cesium ions containing the tracer  $Cs^{134}$  was measured in the same experiment. A 5-g/liter cesium chloride solution with  $5 \times 10^5$  counts/min per ml of tracer was diffused into water. The diffusivity under these conditions was  $1 \times 10^{-5}$  cm<sup>2</sup>/sec, which agrees quite closely with literature values for other alkali metals, such as potassium and rubidium.

The experimental procedures for all diffusion measurements involved the use of a gamma spectrometer with which the concentration of the diffusing ion was measured directly in the capillary as a function of time. In the uranium-diffusion experiments, fully enriched uranium was used in order that its concentration could be measured by a gamma-counting technique.

### 21.3 CORROSION PROTECTION BY TRANSPIRATION

An experiment was described previously<sup>1</sup> in which a nickel tube was protected from corrosion by a peroxide-catalyzed nitric or hydrochloric acid solution flowing through a porous nickel tube. The protection was achieved by transpiration of demineralized water through the wall of the tube. In a continuation of these experiments,<sup>3</sup> using a nickel tube with 7- to 10- $\mu$  pores and containing a 0.5 M ferric chloride solution, corrosion rates of the nickel tube were decreased to 1/60 of those without transpiration of demineralized water.

A fundamental study of transpirational protection was undertaken in order to measure the transport kinetics for diffusion of any corroding ion from the bulk of the flowing solution to the wall without

a simultaneous chemical reaction whose kinetics might be controlling under certain conditions. A direct physical measure of the concentration of migrating ions at the surface was made through the use of a 1-mm-dia electrode placed exactly at the surface of a porous plate. For the purpose of this experiment, the porous plate or disk was made of glass. The surface concentration was determined by the use of the Nernst equation for a silver-silver chloride electrode in a potassium chloride concentration cell. The potential difference between a silver-silver chloride electrode in the bulk solution and one at the surface was an exact measure of the concentration ratio from the bulk to the surface. The Nernst equation is as follows:

$$E = \frac{2T_+RT}{F} \ln \frac{\gamma_1 C_1}{\gamma_2 C_2},$$

$E$  = concentration cell potential, v,

$T_+$  = transference number for cation,

$R$  = gas constant,

$T$  = absolute temperature,

$F$  = Faraday's constant,

$\gamma$  = mean activity coefficient,

$C$  = molal concentration.

The applicability of the Nernst equation to the experimental system was determined by cell potential measurements with known concentration ratios (Fig. 21.4). Over a concentration ratio change of three orders of magnitude, the maximum deviation from the theoretical curve was only 12%.

The system is shown in Fig. 21.5. An 18-gage pure silver wire was coated with an adhesive and mounted through the center of a porous glass plate as shown in Fig. 21.6. The exposed surface (1 mm dia) of the wire was covered with silver chloride and the porous glass plate was mounted in the mixing tank. Potential differences were measured at various rotation rates of the plastic disk stirrer and various flow rates of demineralized water through the porous glass surface. In all cases the potassium chloride concentration of the solution was 0.1 M.

The results are shown in Fig. 21.7. As the rotation speed was increased at a constant transpirational flow rate, the concentration ratio decreased. That is, the surface concentration approached that of the bulk concentration. This

<sup>3</sup>S. H. Jury and C. R. Simpkins, *A Study of Transpirational Corrosion Protection in Porous Nickel Tubes*, ORNL CF-58-10-18 (Oct. 23, 1958).

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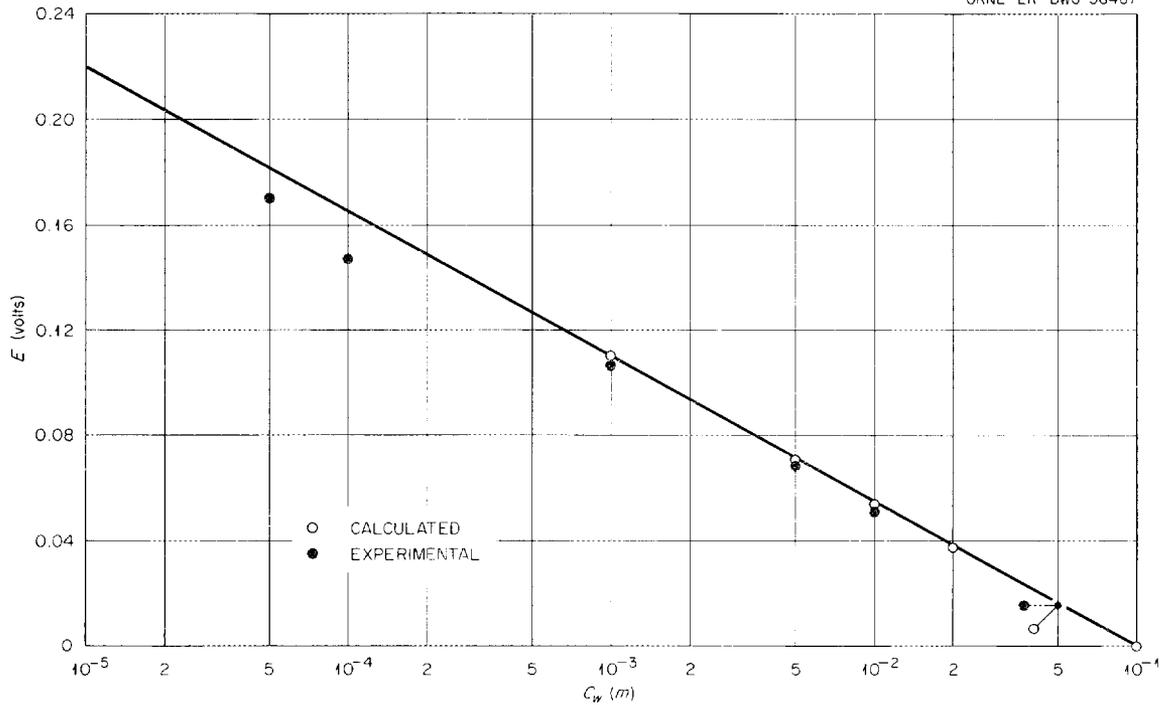


Fig. 21.4. Potential for Cell:  $\text{Ag, AgCl} | \text{KCl} (0.1 \text{ M}) || \text{KCl} (C_w) | \text{AgCl, Ag}$  at  $298^\circ\text{K}$ .

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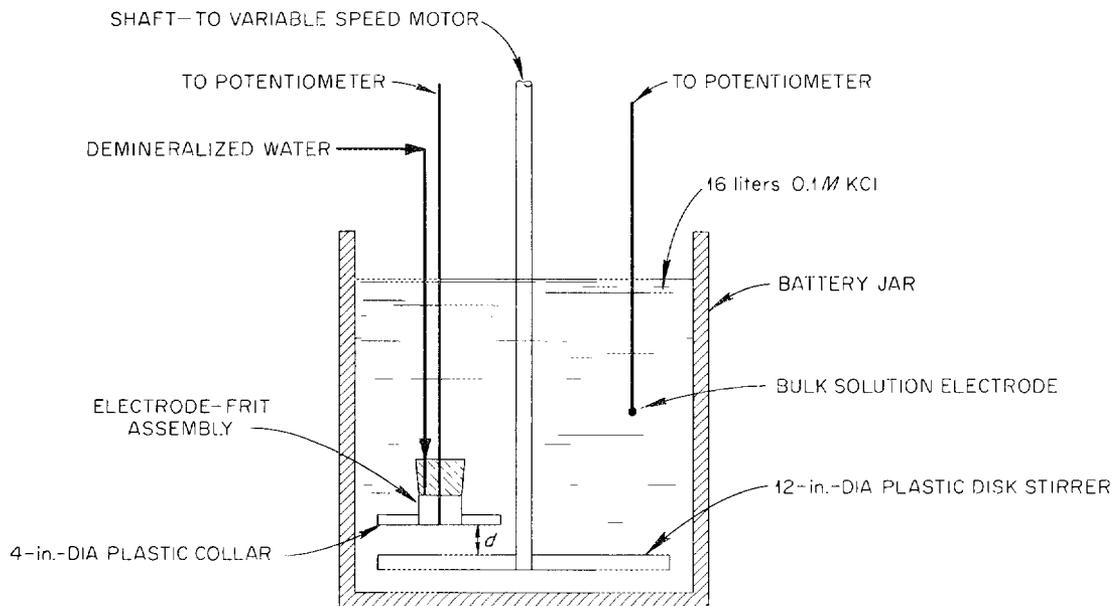


Fig. 21.5. Schematic Assembly for Slab Geometry Transpiration Experiment.

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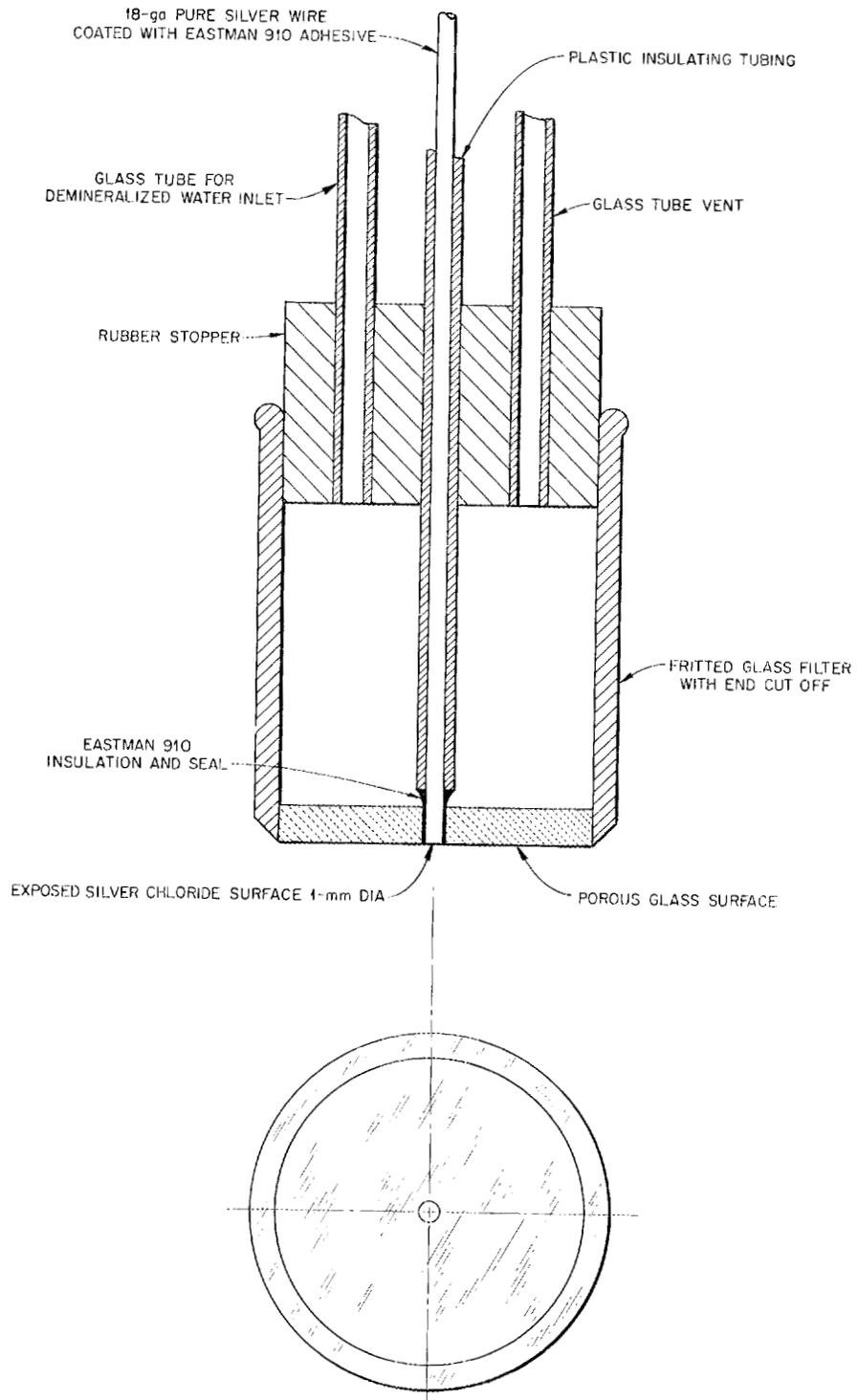


Fig. 21.6. Silver-Silver Chloride Electrode in Porous Glass Disk.

would be expected since the turbulent boundary layer would become thinner, and transport of the bulk solution to the surface would become faster at higher mixing rates. At a constant mixing rate, increasing the transpirational flow rate gradually increased the concentration ratio. This would be expected since the transpirational flow opposes the diffusion of the salt from the bulk solution to the wall.

The slab geometry used in these experiments was chosen since it is more susceptible to mathematical analysis than the two-dimensional flow patterns in a tube. The results of these experiments and others of the type described will be

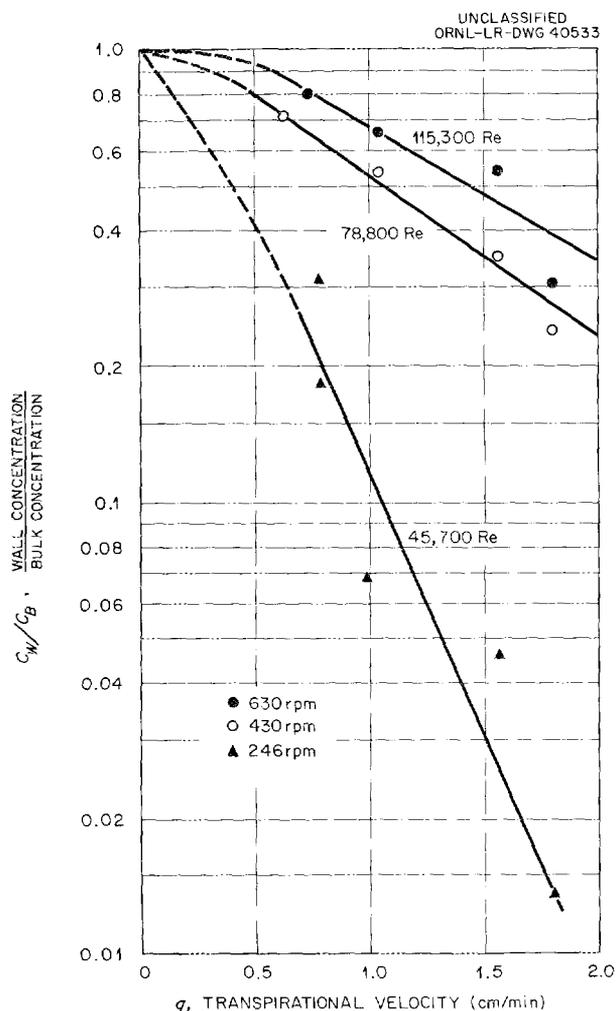


Fig. 21.7. Wall Dilution Factor vs Transpirational Velocity, at Various Reynolds Numbers (Run D-6). Disk-to-porous-plate spacing  $d$ , 2.54 cm; temperature, 298°K.

subjected to rigorous analysis in an effort to determine the quantitative effect of bulk turbulence and transpiration velocities on surface concentrations of various ions with differing diffusivities. From this correlation it should be possible to predict the surface reaction rates under various transpirational conditions that can be verified experimentally with porous metal surfaces.

#### 21.4 RESONATING STEAM PULSER

The resonating steam pulser, a nonmechanical pulser system<sup>1</sup> (Fig. 21.8) for solvent extraction columns, is being developed in an attempt to replace mechanical pulser systems to reduce maintenance problems in radiochemical reprocessing plants. The boilers used in a resonating steam pulser must provide a high heat input in a small volume. In further studies at ORNL a small shell-and-tube heat exchanger of conventional design was used with Dowtherm as the heating medium; concurrently, studies under subcontract were being conducted at Clemson College with a gas-fired boiler.

**Dowtherm-Heated Boiler.** - The Dowtherm-heated boiler operated satisfactorily at pulse frequencies

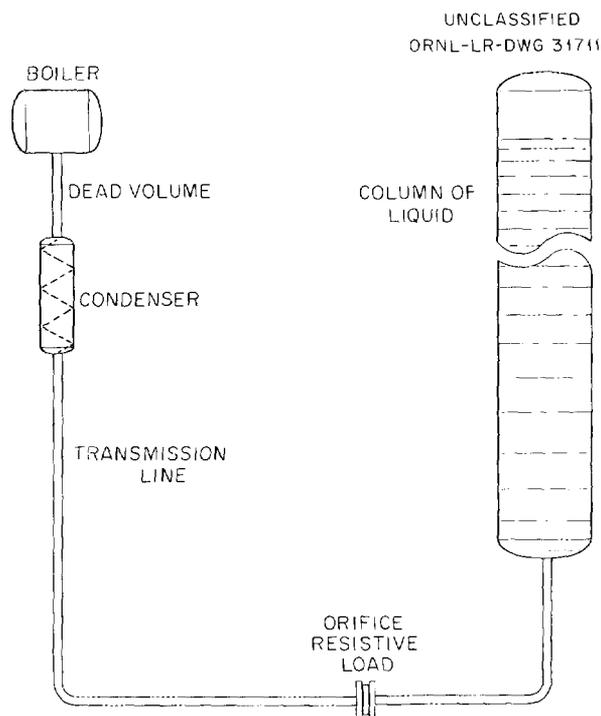


Fig. 21.8. Resonating Steam Pulser.

up to 60 cpm with amplitudes of 10 in.<sup>3</sup>. The working fluid for this unit was in the shell side of the two Ross 200-8 heat exchangers, and the heating and cooling fluids were in the tube side. The shells of the heater and cooler were connected by a close nipple. Inductance (the electrical analog of the length of a liquid-filled pipe) was varied by connecting additional lengths of tubing into the transmission line. The change in frequency was linear with the reciprocal of inductance (Fig. 21.9).

**Gas-Fired Boiler.** — Typical volume traces from the gas-fired boiler (Fig. 21.10) are shown in Fig. 21.11. The jagged traces from runs 10 and 13 are characteristic of the high wall temperatures and low surface area of the gas-fired heater. The smoother trace in run 12 was obtained by inserting in the heater a cruciform surface extender made of 1/8-in. copper plate which extended the length of the vapor space. The pulse frequency was observed to follow the predicted inverse relation:

with capacitance (the electrical analog of vapor-space volume). In all cases, increasing the resistive load on the system increased the frequency and decreased the pulse volume.

It was concluded from these experiments that a solvent-extraction-column pulser is feasible with

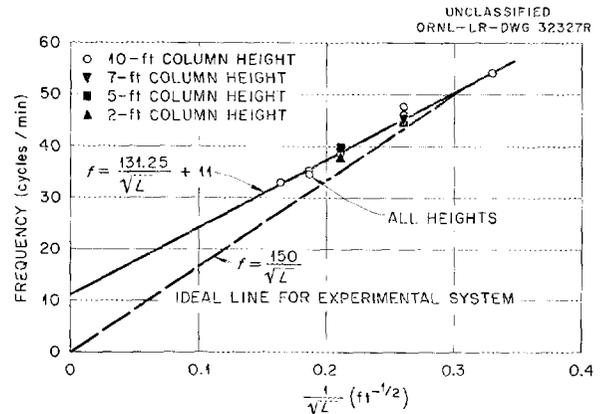


Fig. 21.9. Frequency-Inductance Correlation.

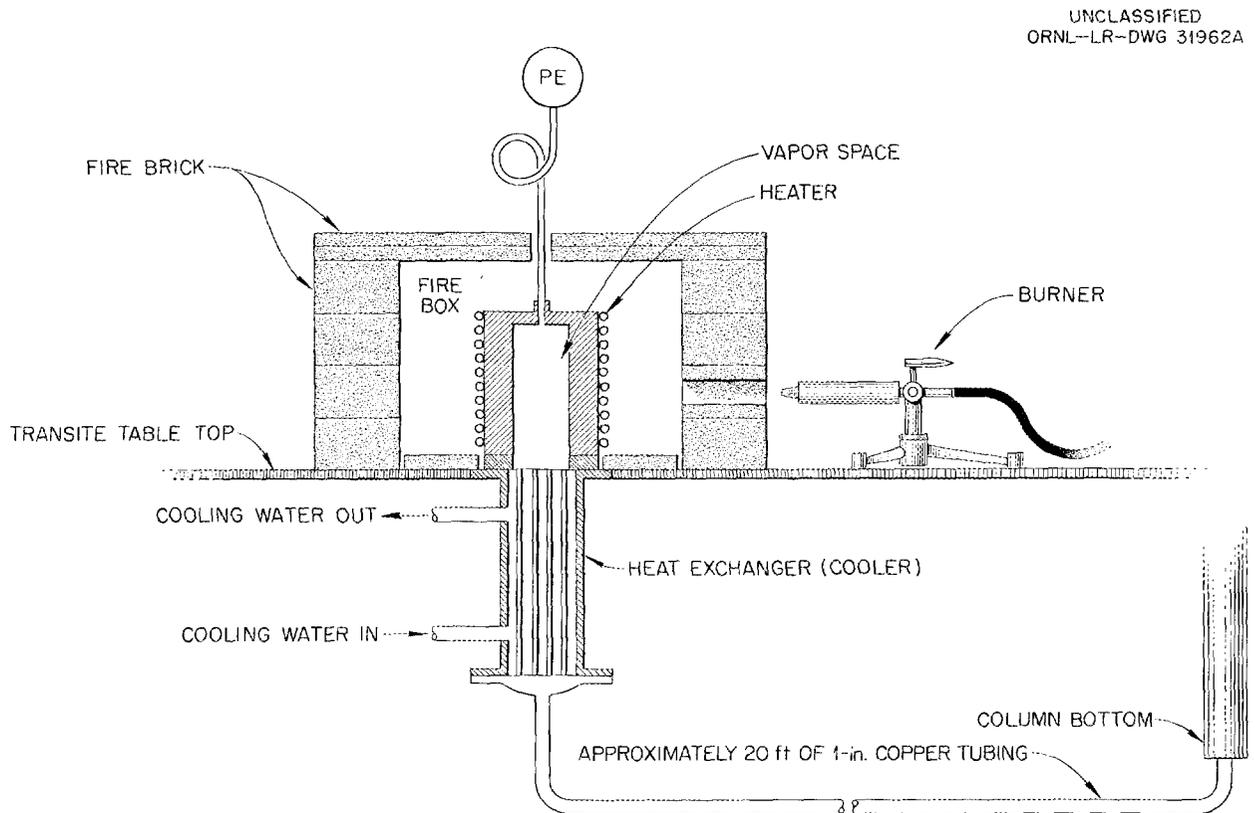


Fig. 21.10. Gas-Fired Resonating Steam Pulser: Preliminary Experimental Configuration.

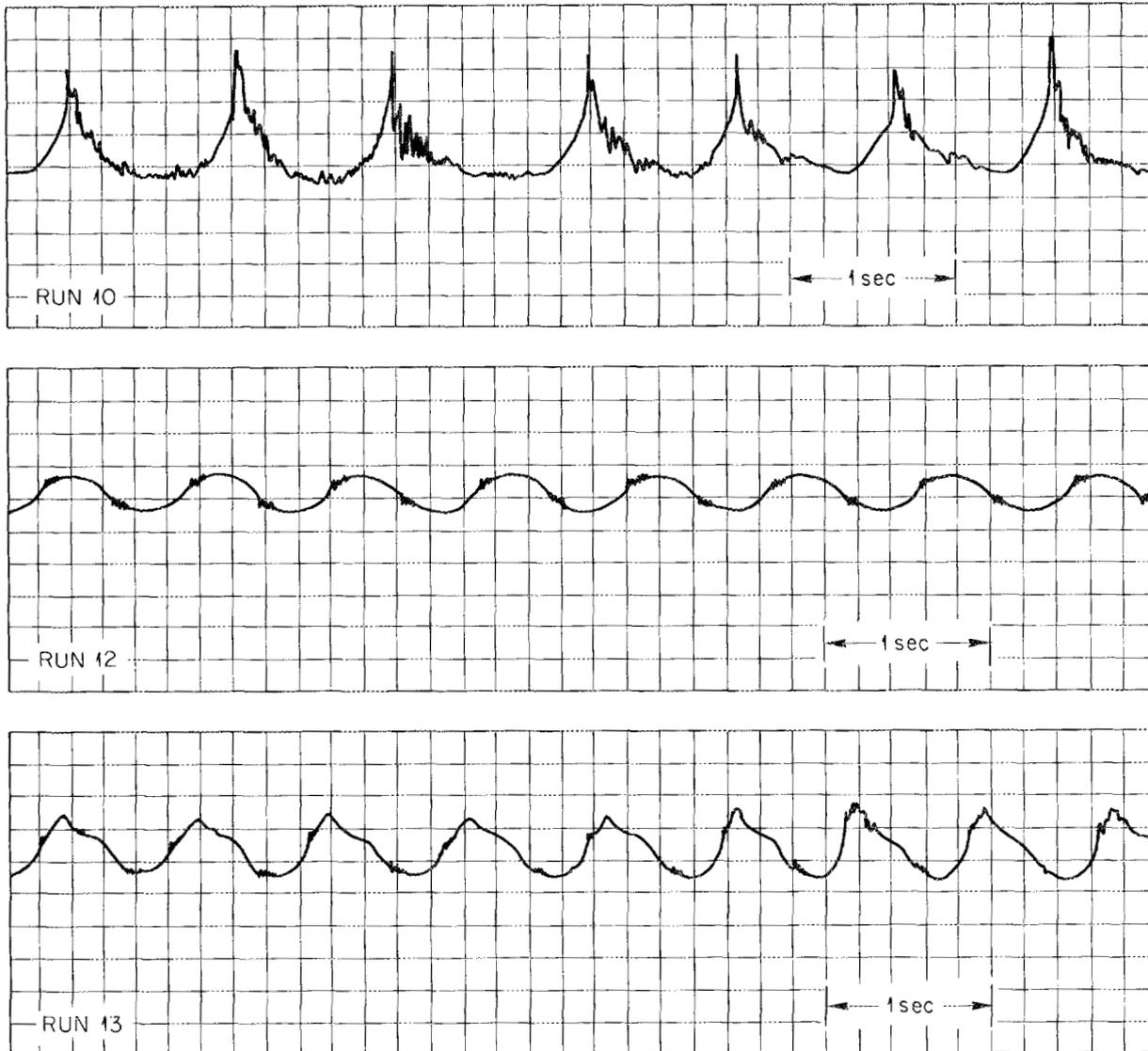


Fig. 21.11. Sanborn Traces of Pulse Volume in Gas-Fired Steam Pulser. One vertical division is 1-in, pulse in 2-in. column.

no moving parts, depending only on a heat engine operating at the system's natural resonance. The control of such systems must necessarily be indirect and by variation in the system resonance. A simple control system would be a regulating valve in the pulse-transmission line which could be opened and closed to increase and decrease the frequency-amplitude product of the column pulse wave.

#### 21.5 THERMAL DIFFUSION<sup>4</sup>

Studies of thermal diffusion in a horizontal column are being made to advance the basic understanding of this relatively new chemical-engineering unit operation. A cellophane membrane is

<sup>4</sup>Carried out under subcontract at the University of Tennessee, Knoxville.

used to separate the hot and cold sides to prevent bulk mixing of the streams and permit control of circulation, not possible in the vertical Clusius-Dickel column now in common use. The system studied was a 0.3–0.5 *m* aqueous solution of  $\text{CoSO}_4$  and  $\text{CuSO}_4$  in a 22.75-in.-long column (Figs. 21.12 and 21.13).

The two salts were separated by a factor of 1.05 at total reflux with the cold wall at 40°F and the hot wall at 140°F. The length of a transfer unit (LTU) in the column was about 1 ft. The logarithm of the separation ratio, defined as the ratio of the concentration of a particular salt in

the exit cold stream to that in the exit hot stream, was linearly proportional to the reciprocal of the flow rate (Figs. 21.14 and 21.15). The separation ratio of either salt from water was independent of the presence of the other salt.

Work will be continued with longer columns to verify the LTU values at total reflux and with feed and product withdrawal. The studies will also be extended to pairs of metallic ions of interest in atomic energy to determine the applicability of the unit operation to radiochemical separations.

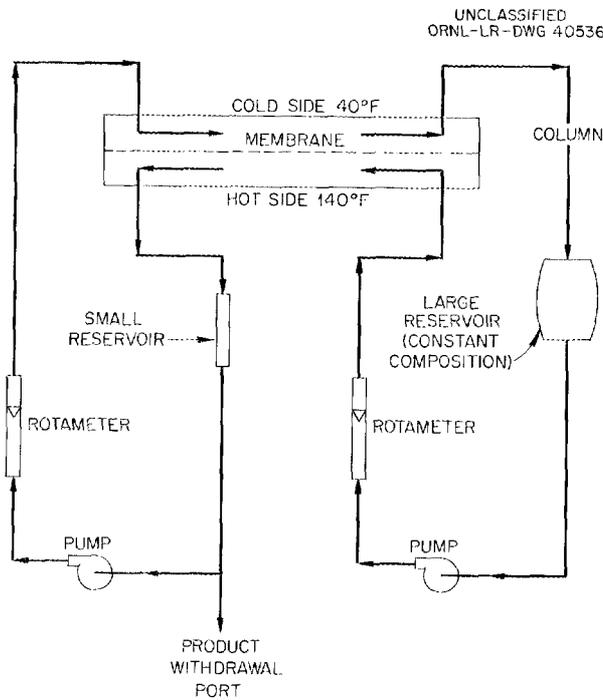


Fig. 21.12. Schematic of Thermal Diffusion Flow System.

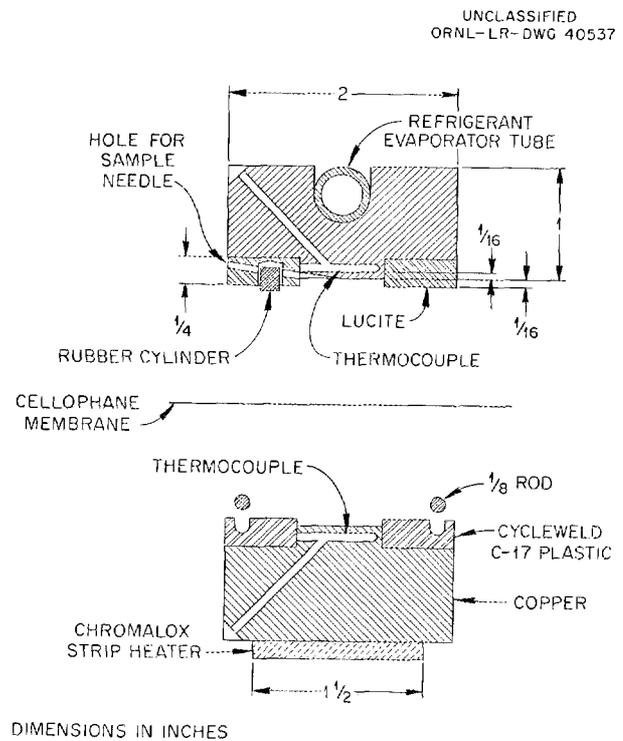


Fig. 21.13. Cross-Sectional View of Thermal Diffusion Column.

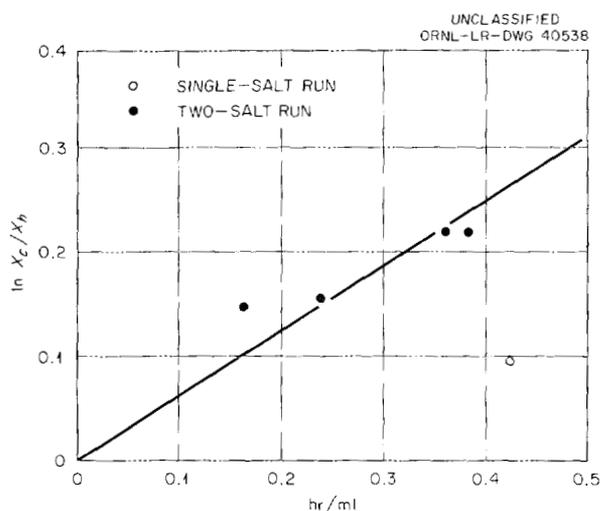


Fig. 21.14. Logarithm of Separation Ratio vs Reciprocal of Flow Rate for Total Reflux Separation of  $\text{CoSO}_4$  from  $\text{H}_2\text{O}$ .

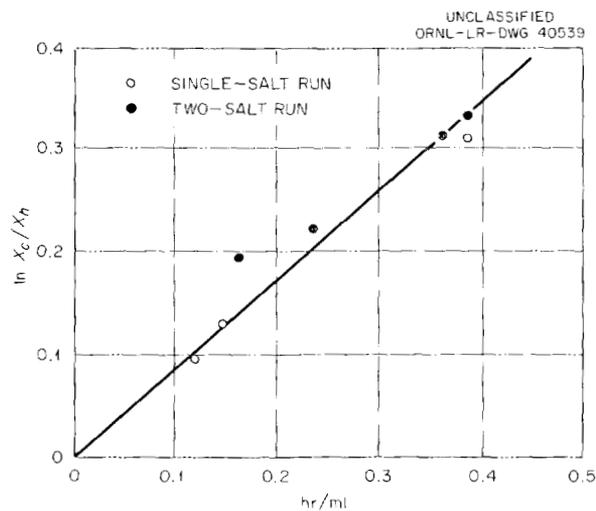


Fig. 21.15. Logarithm of Separation Ratio vs Reciprocal of Flow Rate for Total Reflux Separation of  $\text{CuSO}_4$  from  $\text{H}_2\text{O}$ .

## 22. EUROCHEMIC ASSISTANCE PROGRAM

The United States Atomic Energy Commission has entered into a program of assistance to The European Company for the Chemical Processing of Irradiated Fuels (Eurochemic). Assistance will take two principal forms: the loan of one to five technical people for periods of several weeks to several years and the exchange of technical and engineering data pertinent to the radiochemical reprocessing of irradiated fuels. The Eurochemic plant, which will be at Mol, Belgium, is to be used to process the various types of fuels from European research and test reactors. It will serve as a pilot plant for the construction, possibly on a joint basis, of the larger plants that will be necessary after 1965.

The plant will have sufficient versatility to be able to handle a variety of fuel elements of natural and slightly enriched uranium, and will be designed for 100 tons/year capacity. It will probably cost about \$12,000,000. The estimated annual operating cost is \$3,000,000, with an annual earning of \$1,500,000 during periods of full operation. The staff will consist of 400-450 people,

and the startup is scheduled for 1961. Ample research facilities will be available.

As coordinator for the program, ORNL has assigned a design engineer to the program, has transmitted approximately 500 USAEC-originated documents, has received, issued, and distributed about 40 Eurochemic documents for information or for review and comment (18 documents required translation prior to issue, and all documents were partially edited), and has issued, through the assistance of several USAEC contractors, about 20 specifically prepared documents for release and transmittal to Eurochemic.

A single-cycle, almost full-scale, nonradioactive solvent extraction pilot plant (described in Eurochemic Technical Reports 5, 9, 19, and 34) will be installed. The pilot plant will consist of extraction and stripping columns with the necessary tanks, evaporators, and solvent-recovery facilities. The design flow rate is 50 liters of uranium feed per hour to the extraction column (75% of the flow anticipated for the production plant). Completion is scheduled in seven months.

A laboratory has been set up for alpha work, and studies on anion exchange are to be started shortly to verify the data presented on this system.

The original design capacity was set at 100 tons of uranium per year, based on the predicted annual spent-fuel load that would be available in 1965. No allowance was made for fuels enriched more than 5% or for Euratom fuels. The fuel-canning materials being considered are aluminum, Magnox, stainless steel, and Zircaloy. It is estimated that 100 days/year should be allowed for maintenance and decontamination, and that 100 days/year total would be required to prepare the plant and clean it for the 20 different fuel batches. The indicated on-stream processing time was 150 days, giving 0.67 ton per on-stream operating day. The extraction columns were designed to operate at 40% of flooding at this throughput. This capacity was selected as a reasonable daily throughput to operate efficiently on the interim load of 100 tons/year, to permit expansion to 1.5 tons/day for the second-stage load, and, ultimately, when the maximum capacity was exceeded, to become the central European highly-enriched-fuel re-

processing center. A second design basis of 350 kg uranium/day (maximum) is also being investigated.

A research laboratory will be built as a supporting facility for the plant, to perform investigations in the fields of applied chemistry, chemical engineering, and instrumentation.

The proposed solvent extraction process will use the best available technology of the Purex process. The solvent extraction separation facilities will include a co-decontamination first cycle with exhaustive scrubbing; a partitioning cycle; final uranium and plutonium cycles; and a final purification treatment for each product. Backcycling of acid waste evaporator concentrates to the extraction column and of uranium evaporator condensate to strip makeup is planned. Solvent recovery is to be accomplished with turbine-mixer contactor units. Acid will be recovered in a small batch evaporator, which will use concentrate from the aqueous waste of each cycle as feed so that both acidity and volume of the fission-product-bearing wastes can be decreased as much as possible.

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