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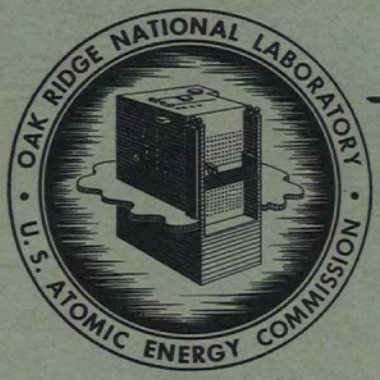
AEC RESEARCH AND DEVELOPMENT REPORT

ORNL-2468
Chemistry-Separation
Processes for Plutonium and Uranium

CHEMICAL TECHNOLOGY DIVISION

MONTHLY PROGRESS REPORT

FOR DECEMBER, 1957



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CHEMICAL TECHNOLOGY DIVISION MONTHLY PROGRESS REPORT FOR DECEMBER, 1957

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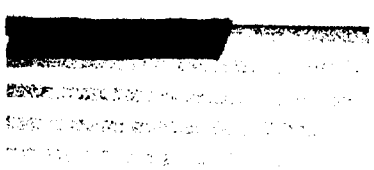

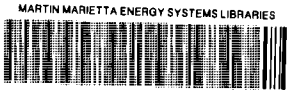

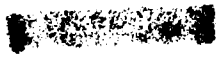

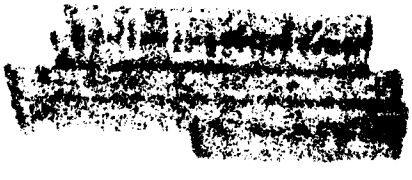

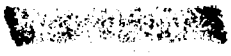

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Homogeneous Reactor Project Quarterly Reports:

For July 31, 1957, ORNL-2379 ($5.00) Oct. 31, 1957, ORNL-2432 ($5.50)

All studies reported here are preliminary and conclusions are subject to change The information is published as a formal report only to permit ready dissemination of data to interested persons.

ABSTRACT**

I. Feed Materials Processing

Metallex Process. Separation of thorium from approximately 180 gal of thorium amalgam remaining from previous reduction runs was completed.

Thirty-five grams of uranium as UF_6 was reduced at 356°C by 3.5 M sodium amalgam in ~20% yield. The mercury-insoluble slag contained $UF_4 \cdot 3NaF$, $UF_4 \cdot 2NaF$, NaF, and UF_3 but no UO_2 or HgF_2.

Druhm Process. A helium blanket around the UF_6 inlet line was partially effective in reducing inlet line corrosion.

Fluorox Process. In a 4-hr operation of the fluidized bed oxidation reactor, 80 g of uranium was recovered as UF_6 from the cold trap; 190 g of uranium, as UF_4, was charged. The run was shut down because gas and UF_4 dust were leaking from the packing of the continuous screw feeder. Evidence of volatile fluorides was found in the dust filter and the chemical traps.

II. Heterogeneous Power Reactor Fuel Processing

Head-end Treatments. In studies on the Darex process, a 13-hr loop run was made at an average V/L ratio of 0.88 and a stainless steel dissolution rate of 6.12 g/min. The stripper product contained 250 ppm of chloride. Chloride and nitrogen losses to the off-gas were 0.2 and 1.0 mole per mole of stainless steel dissolved, respectively. Overall material balances, based on net output relative to net input, were 106, 92, 95, and 95% for HNO_3, H_2O, chloride ion, and stainless steel, respectively. In small-scale continuous dissolution studies of 304L stainless steel–clad uranium oxide fuel (Yankee Atomic) in which fuel rods positioned

* This is the last report in this series.

** Work on raw materials processing, Chemical Development Section C, K. B. Brown Section Chief, is reported separately. Homogeneous reactor fuel and blanket processing and development studies are reported in the HRP quarterly reports.

vertically were immersed in 5 M HNO_3—1 M HCl, the dissolver product varied in uranium concentration from 112 to 144 g/liter. Batch chloride removal tests on simulated dissolver solution indicated that specification (30 ppm of chloride) solvent extraction feed could be made by 50% evaporation of the dissolver product, addition of an equal volume of 70% HNO_3, evaporation to 126°C, and dilution to the original volume. APPR fuel elements dissolved in aqua regia with a uranium loss of 0.0088% to residual solids.

In Zircex process studies the use of a sodium chloride bed in series and following a settling chamber resulted in recovery of >99% of the uranium chloride produced during hydrochlorination of U-Zr alloy. Recovery of uranium by nitric acid from the residue resulting from hydrochlorination of U-Zr-Nb alloy at 400, 500, and 600°C was 99.8, 99.5, and 99.0%, respectively; the rates of hydrochlorination were 1, 8.4, and 20 mg/cm^2.min.

In fluoride-catalyzed nitric acid the dissolution rate of 96% ThO_2—4% UO_2 pellets was maximum in 13 M HNO_3—0.04 M NaF. A simulated APDA fuel pin (Zr-clad U-Mo alloy) dissolved in 13 M HNO_3—0.5 M HF without the addition of heat, forming a stable solution.

The stainless steel cladding of an APPR fuel element (sintered UO_2—stainless steel core) in 4 M sulfuric acid followed by dissolution of the core in 8 M HNO_3 resulted in loss of 0.033% of the uranium to the residual solids. Contrary to previous results with APPR fuel elements, irradiation only slightly increased the uranium loss from Yankee Atomic fuel pins during dissolution of the stainless steel. The loss in the earlier experiments is considered due to formation of hydrogen peroxide.

Hydrofluoric Acid, added so that its concentration never exceeded 5 M, dissolved zircaloy-2 jackets from PWR fuel elements with a uranium loss of 0.24%. Irradiation did not increase the uranium loss significantly in a 2-hr dejacketing time. The increased loss in longer time is considered due to formation of hydrogen peroxide.

The liquid metal fuel 98.7% bismuth—1.3% uranium dissolved readily in 8 M HNO_3.

The alloy B-2 dissolved readily in hydrofluoric, hydrochloric, nitric, or sulfuric acid.

Solvent-extraction Studies. Solvent-extraction flowsheets for the APDA fuel element solution, using 6% TBP, and for a solution of the liquid metal uranium-bismuth fuel, using 2% TBP, were tested. Preliminary results were satisfactory.

Compounds containing a phenyl or phosphonate group appeared more stable to radiation than did tributyl phosphate. Acidic materials in irradiated organic compounds were removed by anion exchange.

Thorex Process. Two pilot-plant runs, HD-27 on long-decayed thorium and SD-3 on 4000-g/t, 30-day-decayed thorium, were completed. Run HD-27 lasted 325 hr and processed 720 kg of irradiated and 230 kg of recycled thorium. Run SD-3 processed 630 kg of irradiated and 420 kg of recycled thorium; it was terminated after 173 hr because of equipment failures.

In run HD-27 solvent-extraction losses averaged 4.3% for thorium and 0.3% for uranium, and overall gross γ decontamination factors were 4×10^3 and 1×10^4, respectively. In run SD-3, solvent-extraction losses averaged 3.3% for thorium and 0.6% for uranium, and gross γ decontamination factors across two cycles were 10^4 and 10^5, respectively. Increased solvent degradation was shown by a rapid buildup of solids in the 2C-column and by decreased partitioning efficiency.

The interfacial solids removal system was operated during runs HD-27 and SD-3. Radiation intensities approached 200,000 r/hr after 24 hr. Decontamination factors were 50, 10, and 40 from protactinium, ruthenium, and zirconium-niobium. The activity level at the extraction column interface decreased as the run progressed.

The lower product decontamination from ruthenium in the pilot plant than in the laboratory was shown to be the result of insufficient sulfite in the feed. In the large volumes of the plant, gamma energy is more efficiently absorbed and sulfite is more rapidly destroyed. At 53°C, with 0.06 M bisulfite in the feed, the decontamination factor was 320 compared to 2.5 in the control. Temperatures as high as 73°C were reached before the bisulfite was destroyed, indicating that the previously reported temperature effect was in error.

A 0.2 M KOH solution gave about twice the decontamination of used solvent as the 0.2 M Na_2CO_3 previously used.

A flowsheet for immediate recycle of the aqueous waste from the runs on short-decayed material to recover additional uranium was demonstrated. This will decrease the isotopic dilution of the U-232 recovered after protactinium decay. The off-gas from the tanks in which the waste from the runs on short-decayed material was stored did not contain appreciable hydrogen.

Waste Metal Recovery. The processing of ORNL tank farm wastes was completed. Seven tons of uranium was recovered during the latest phase of the program, increasing the total quantity reclaimed during the program to 136 tons. After plant cleanout and equipment modifications, 40 g of Am-241 will be recovered from solutions received from the Los Alamos Laboratory.

Waste Treatment and Disposal. The sodium and nitrate concentrations of synthetic waste were electrolytically reduced in membrane cells from 0.6 and 0.3 M to 0.06 and 0.02 M, respectively, in two or three stages.

Fused Salt--Fluoride Volatility Process. The pilot plant was modified to permit processing of the ARE fuel. A schematic engineering flowsheet is presented.

A simple mock-up of the dissolver using water, air, and a simulated 11-in. section of an STR fuel assembly was used to study flow patterns and contact for the HF--fused salt dissolver.

In tests with 400°C NaF beds in the volatility step, with 12-20 mesh and 1/8-in. pellet material, decontamination was greater with the higher-surface-area material. More than half the fission products, plutonium, or chromium removed was usually on the first quarter of the bed.

In fused NaF_4-ZrF_4 at 650°C with HF bubbled through, INOR-8 and Nickel-A were corroded at rates of 0.09 and 8.9 mils/month, respectively. The nickel suffered general intergranular cracking; the INOR-8 showed cracking only at the point of impingement of the HF bubbles.

Part I. FEED MATERIALS PROCESSING

1.0 METALLEX PROCESS
Program Leader: O. C. Dean

In the Metallex process, thorium or uranium chloride is reduced by sodium amalgam to the mercuride, and metal is recovered by pressure filtration and vacuum distillation.

1.1 Recovery of Thorium and Mercury from Stored Amalgams (G. K. Ellis, J. H. Thompson)

Separation of thorium from approximately 180 gal of thorium amalgam remaining from previous reduction runs was completed. The thorium was concentrated into a 35-gal volume by settling and decantation. Three separate washings removed impurities from the concentrate, which was pressure filtered into cakes weighing a total of 302 lb. Twenty pounds (7%) of the cakes was thorium metal in the mercuride form.

1.2 Reduction of UF_6 to Metal by Sodium Amalgam (O. C. Dean)

In earlier experiments on direct reduction of UF_6 to metal by sodium amalgam, UF_6 vapor was fed to sodium amalgam mechanically agitated at a high rate of shear; metal yields were up to 40%. In a new series of experiments the amalgam was agitated by sparging with argon in order to eliminate loss of metal from reaction with air leaking through agitator shaft seals. Of 35.3 g of uranium fed as UF_6, 19.6% was reduced to uranium metal, 3.6% to UF_3, and 75% to UF_4, and 2% was lost in the trap and lines as U(VI). The 127.3 g of mercury-insoluble slag remaining in the reactor after hot filtration contained ~50% metallic mercury in a finely divided state, and 61.9 g of true solids. X-ray diffraction analysis indicated the major components of the slag to be $UF_4 \cdot 3NaF$, $UF_4 \cdot 2NaF$, NaF, and UF_3. No UO_2 or HgF_2 were detected. A surge of gas was observed when the UF_6 flow was initiated, followed by a subnormal flow, and it is thought that all the uranium was delivered in the first 5 min of the 3-hr run.

The UF_6 (52.2 g) was fed to 2600 g of 3.5 M sodium amalgam at 356°C. Argon was passed over solid UF_6 in a cylinder at 25°C, picking up UF_6 vapor at a partial pressure of ~100 mm Hg, and then into the heated reactor. Uranium hexafluoride passing through the reactor unchanged was trapped on a weighed NaF trap. At the end of the reduction, the amalgam was withdrawn at 350°C through a type 316 stainless steel micrometallic filter of 55 μ average pore diameter at the bottom of the reactor to a receiver-crystallizer which had been evacuated and argon-purged. The mercury-insoluble slag in the reactor was removed, and the cold product amalgam was filtered and sampled under argon.

2.0 DRUHM PROCESS
Program Leader: J. C. Bresee
(C. D. Scott, W. G. Sisson)

In the Druhm process UF_6 is reduced to metallic uranium with sodium vapor.

A reduction run (VP-11) was completed in the revised 2-in. contactor. During the reduction step, 50 g of UF_6 was introduced to the contactor over a 1-min period, with a resulting temperature rise from 750°C to 1010°C. Inert gas flows of 0.5 cfh of helium were maintained both through the inlet line with the UF_6 and through the blanket line. The contactor inlet line was attacked but to a much smaller extent than in previous runs. The helium blanket around the inlet line was therefore at least partially effective in reducing nozzle corrosion.

The reheating step was discontinued after leaks developed in the contactor and the contactor gasket. Because of severe oxidation of the reaction products, no usable chemical reaction data were obtained.

3.0 FLUOROX PROCESS

Program Leader: J. C. Bresee
(J. B. Adams, C. D. Scott)

In the Fluorox process, UF_6 is prepared by oxidizing UF_4 with oxygen or air at high temperatures. The UF_4 may be obtained by simultaneous reduction and hydrofluorination of UO_3 and UO_2F_2, by the Excer process, or by conventional feed materials processes.

3.1 Fluidized Bed Reactor

The fluidized bed reactor was operated for 4 hr at 800°C. An attempt to feed UF_4 continuously to the reactor by a screw feeder was unsuccessful. The screw apparently fed material only erratically. The packing leaked small amounts of gas and dust throughout the run. The run was shut down when the packing failed and larger amounts of UF_4 dust and gas started leaking. The UF_4 charge to the reactor was estimated as 250 g. Eighty grams of uranium was recovered from the cold trap. This corresponds to almost stoichiometric recovery based on the UF_4 charged. However, part of the uranium recovered resulted from the decomposition ($9UO_2F_2 \longrightarrow 2U_3O_8 + 3UF_6 + O_2$) of part of the 12-lb charge of UO_2F_2 carried in the bed, thus making a material balance very inaccurate. An additional 44 g of uranium was found on the dust filter.

Visual observation in a small glass chemical trap directly following the cold trap showed an orange material being de-entrained. It appeared to be a fluid rather than a solid and had soaked into the calcium sulfate pellets before the trap was emptied. A sample of the pellets analyzed 0.16% chromium. X-ray analysis of material taken from the dust filter showed the presence of $CrF_3 \cdot 3H_2O$, and an orange solid removed from a small deposit on the top flange of the dust filter analyzed 2.87% chromium. Scale from the reactor wall analyzed 45.5% total U, 1.58% U(IV), 34.79% AOI, 12.66% F, and 0.57% Cr. Nickel (not analyzed for) is probably also a large component of the scale.

3.2 Reactor Solids Feeding Systems

Three systems are being fabricated for feeding UF_4 to the fluidized bed oxidation reactor during a run. Two of them are shown in Fig. 3.1. The third, a batch feeder, is similar to Fig. 3.1a without the pump.

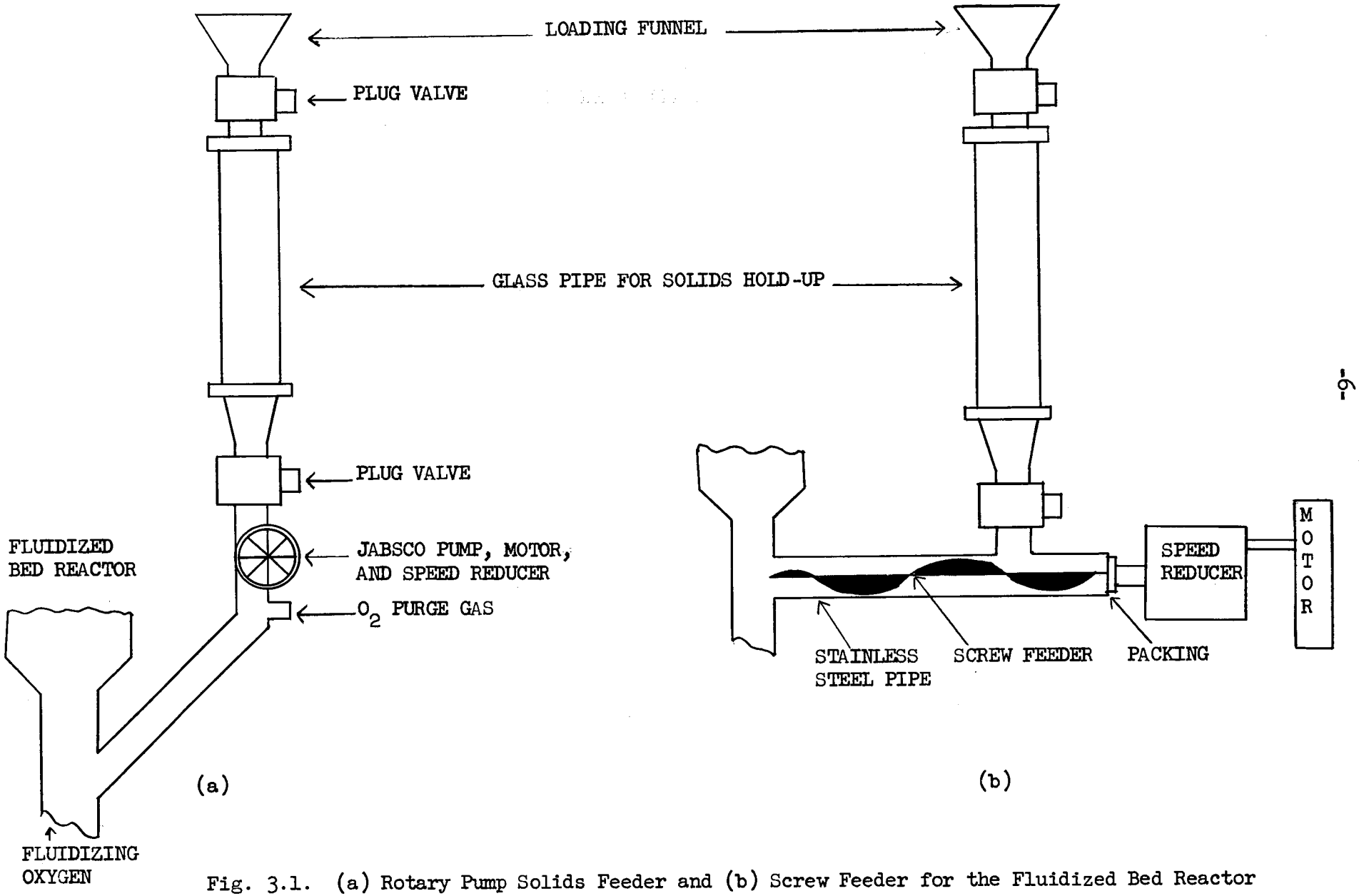

Fig. 3.1. (a) Rotary Pump Solids Feeder and (b) Screw Feeder for the Fluidized Bed Reactor

Part II. HETEROGENEOUS POWER REACTOR FUEL PROCESSING

4.0 HEAD-END TREATMENT

Program Leader: H. E. Goeller

Various head-end treatments, chemical and mechanical, are being investigated for preparing fuel elements with difficultly soluble components for solvent extraction. Considerable emphasis is being placed on the development of universal processes for entire classes of fuels.

4.1 Darex Process for Stainless Steel-containing Fuels

The Darex head-end treatment consists in dissolving fuel in dilute aqua regia and removing the chloride before the nitric acid solution is solvent-extracted.

Continuous Loop Operation (F. G. Kitts, B. C. Finney, J. Beams, F. L. Rogers). After preliminary shakedown runs in the Darex loop equipment to establish operating conditions with makeup nitric acid added directly to the dissolver, an extended run was made with 13 hr of steady-state operation. Chloride ion was removed in the stripper in 11 plates to an average of 225 ppm with an overall average V/L ratio of 0.88; 13.5% of the makeup acid was added directly to the dissolver. Losses to the off-gas averaged approximately 0.2 mole of chloride and 1.0 mole of nitrate per mole of stainless steel dissolved. Overall material balances (Fig. 4.1) on the basis of net output relative to net input were 106, 92, 95, and 95% for nitric acid, water, chloride ion, and stainless steel, respectively.

The stainless steel was added as 11-in. lengths of 3/4-in.-o.d. thick-walled tubing weighing ~199 g. An average dissolution rate of 6.12 g/min was calculated from the times required to dissolve individual pieces. The average time for 1 mole (55.4 g) of stainless steel was 9.05 min. The flow rates given for all streams are averages from the experimental operating data, rotameter readings, tank readings, etc. The compositions of the mixed streams were determined by averaging analytical results from five sets of samples taken at intervals. Densities were determined by direct weighing of 10-ml samples of each stream. The loading in the dissolver product stream was calculated from flow rates and the dissolution rate, but the strip product loading was calculated from analytical results and agrees with the calculated loading within 2 g/liter (5%). The overall material balance is accurate within 5% except for the water balances around the stripper and dissolver where the errors are 10 and 7%, respectively.

The composition of the off-gas was not well established although two reliable analytical techniques were used in gas analysis. The composition presented (Fig. 4.1) is a best guess from several sample analyses.

Continuous Dissolution of Yankee Atomic Fuel Elements (J. J. Perona) A small-scale engineering study of the continuous dissolution of prototype Yankee Atomic fuels (sintered UO_2 pellets in 304 stainless steel tubes) was carried out. Owing to the heterogeneous nature of the fuels and the absence of structural cohesion of the pellets upon dissolution of part of the stainless steel cladding, rigorous study of the dissolution characteristics of the system was not feasible; however, a few quantitative observations were made.

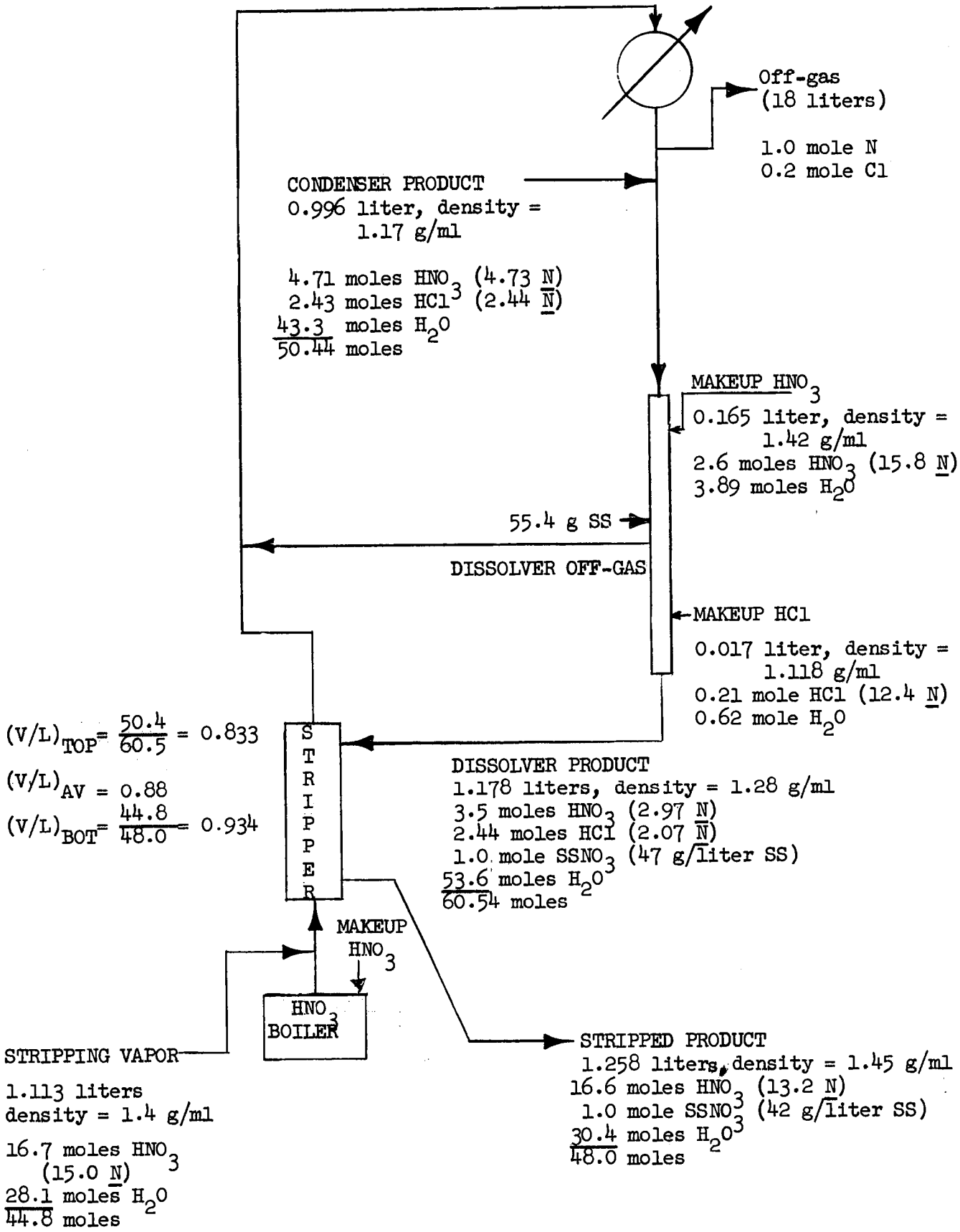

Fig. 4.1 Material Balance in Darex run 45.

Dissolution was carried out in a continuous pot dissolver in 5 M HNO_3--1 M HCl at initial F/S values less than 0.5 cm/min (see ORNL-2416). For the three values studied, dissolver capacity was maximum with an initial F/S of 0.22 cm/min:

Initial F/S, cm/min	No. of Fuel Rods Dissolved	Time, hr	Average U[a] Conc in Dissolver Effluent, g/liter	No. Dissolved per 24 hr (F = 50 ml/min)
0.09	20	16	112	30
0.22	8	5	144	38.5
0.47	4	3	120	32

[a]Instantaneous uranium concentrations in the effluent varied as much as 20% with time.

The initial F/S ratio (ratio of the acid feed rate to the surface area of the unreacted fuel rods exposed to dissolution) is not a fundamental characteristic of the system, but it may serve as an empirical scaleup factor for a given fuel over short increments of scaleup. The criterion for validity is that the surface area of the submerged UO_2 pellets and pieces of unreacted stainless steel be proportional to the initial surface area of the fuel and that the dissolution terms for UO_2 and stainless steel be equal.

The prototype rods dissolved were 0.43 in. dia by 16 in. long and contained about 270 g of UO_2 and 80 g of stainless steel.

Batch Preparation of Solvent-extraction Feed from Yankee Atomic Fuel Solution (J. R. Flanary, J. H. Goode). Solvent-extraction feed with a chloride concentration of 0.001 M, which is essentially the specification value of 30 ppm, was prepared from simulated Yankee Atomic Power Reactor fuel element solution. The solution, which was originally 3.17 M H^+, 0.92 M Cl^-, and contained 33 g of stainless steel and 122 g of uranium per liter, was evaporated to 115°C (50% volume reduction), 1 vol of 70% HNO_3 was added, the solution was re-evaporated to 126°C, and the still residue was diluted to the original volume of still feed. The chloride remaining in the still bottoms decreased linearly with increasing volume of acid added (Fig. 4.2a). During the 50% volume reduction, averages of 21.7 and 11.7% of the H^+ and Cl^-, respectively, were collected in the distillate.

Both the chloride decrease in the still bottoms and the increase in the distillate were approximately linear with increasing nitric acid concentration of the still feed (Fig. 4.2b) from 3 to 7 M. The dissolver feed used in these tests, before the addition of nitric acid, had the concentrations 1.8 M H^+, 1.8 M Cl^-, and 37 g of stainless steel and 15 g of uranium per liter. From the 7 M H^+ feed, chloride removal was 95%, but the chloride concentration of the solution formed by diluting the residue to its original volume was 0.03 M.

In a simple distillation, with no additive, the chloride concentration of the distillate increased as the still temperature increased (Fig. 4.2c), but less than 10% of the chloride was removed from the solution. Air sparging during the distillation resulted in removal of 13% of the chloride (9% in the distillate and 4% lost, presumably by oxidation), and steam sparging removed 22%. The presence of 40 g of potassium permanganate or manganese dioxide per liter during the evaporation, followed by dilution to the original volume and filtration, removed 73 and 38%, respectively,

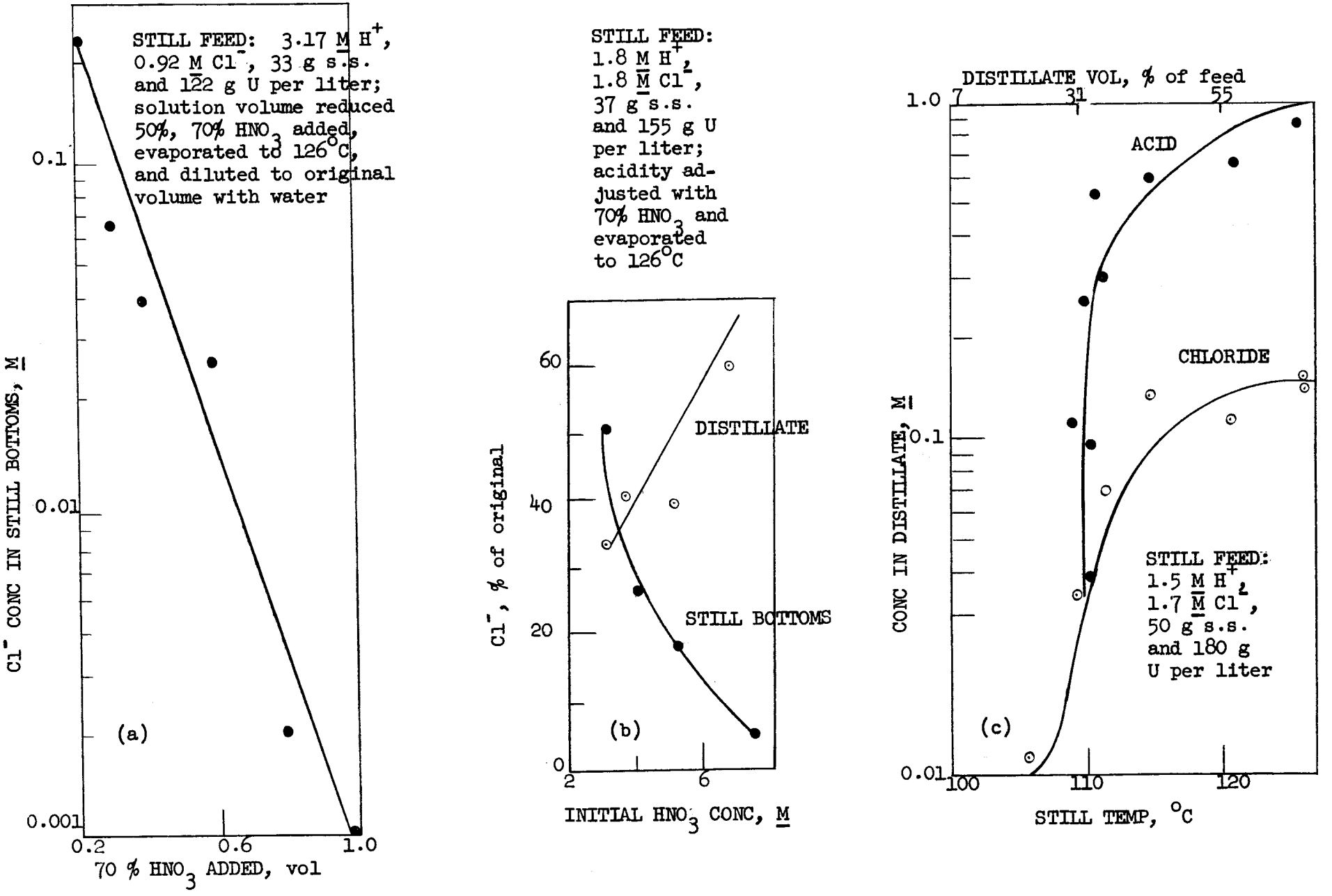

Fig. 4.2. Darex Process: Batch Removal of Chloride from Simulated Aqua Regia Solution of Yankee Atomic Power Reactor Fuel Element. Effect of (a) volume of 70% HNO_3 added to still feed on chloride concentration of still bottoms; (b) nitric acid concentration of still feed on chloride concentrations of distillate and still bottoms; and (c) still temperature on chloride and acid concentrations of distillate.

of the chloride. The feed to the still in these experiments was 1.5 M H^+, 1.7 M Cl^-, and contained 50 g of stainless steel and 180 g of uranium per liter. This composition would be obtained by using a minimum volume of aqua regia to dejacket a Yankee Atomic fuel element and a minimum volume of nitric acid to dissolve the UO_2 core.

Dissolution of APPR Fuel Elements (W. E. Clark). The uranium loss to solids when entire prototype APPR fuel elements (stainless steel--clad sintered UO_2—stainless steel) were completely dissolved in boiling 2 M HCl—5 M HNO_3 was 0.0088%. This is considerably lower than the loss in sulfuric acid (Sec. 4.4).

4.2 Zircex Process (T. A. Gens, J. E. Savolainen)

The Zircex head-end treatment consists in hydrochlorinating the fuel to form volatile $ZrCl_4$, dissolving the residue, containing uranium chloride, in nitric acid, and removing or destroying the chloride by distillation prior to solvent extraction. The uranium chloride residue may also be processed further by the Hermex or Fused Salt--Fluoride Volatility process (Sec. 9.1).

Uranium De-entrainment. Uranium chloride loss to the zirconium tetrachloride sublimate has been a serious problem in the Zircex process under certain operating conditions. Settling chambers maintained at temperatures slightly above the sublimation point of zirconium tetrachloride, but below the sublimation point of uranium chlorides, recovered most of the volatile uranium chloride. A sodium chloride bed recovered the uranium quantitatively.

Sodium chloride at 350°C was shown* to be a scavenger for zirconium tetrachloride. In further studies a bed of sodium chloride was placed in series with and following a short settling chamber, both at 350°C (Fig. 4.3a). Conditions were chosen so that a large amount of uranium chloride was volatilized during hydrochlorination of 85% of an 8.3-g sample of 80% uranium—20% zirconium alloy at 550°C. The average flow rate in the settling chamber was 50 ft/hr during the 76-min run. Ninety-nine percent of the uranium chloride was recovered in nitric acid from the reaction residue and the short settling chamber. The settling chamber walls were covered with uranium chloride, which would have been considered volatile loss by previous laboratory techniques. The amount of uranium insoluble in nitric acid was 0.17%. The remaining 1% of the uranium was found in the first centimeter of the sodium chloride bed. All zirconium tetrachloride was collected in the 10-in. bed of sodium chloride. Fusion of the sodium chloride bed had begun in the area in which uranium chloride was deposited. In a similar experiment at 480°C, the sodium chloride bed fused rapidly after a small amount of uranium chloride had passed through the settling chamber.

A similar experiment at a lower flow rate with a larger settling chamber maintained at 400°C was less successful. A large percentage of the uranium was volatilized from a 9.2-g sample of STR prototype fuel by hydrochlorinating at 800°C during 194 min. Eighty-seven percent of the fuel was hydrochlorinated. The exit gases were passed through the settling chamber at an average flow rate of ft/hr at 400°C (Fig. 4.3b). Forty-eight percent of the uranium and less than 1% of the zirconium was collected on the walls of the settling chamber. Only 12% of the uranium remained in the reaction area as salts soluble in nitric acid. Six percent remained as an insoluble residue. The zirconium tetrachloride deposit at the cool exit was

*CTD Monthly Progress Report for November, 1957, ORNL-2447.

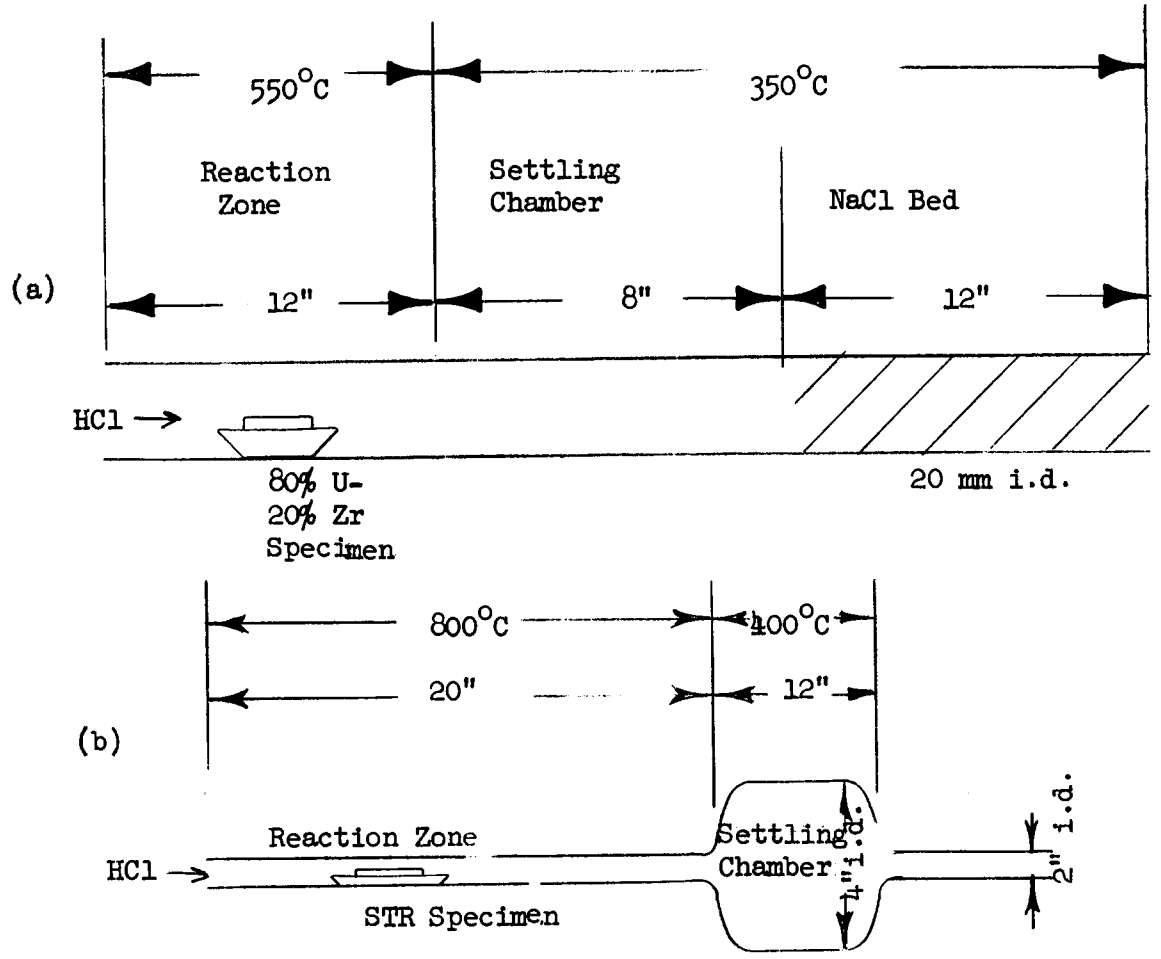

Fig. 4.3. Experimental Apparatus Used for Scavenging Uranium from Zirconium Tetrafluoride in Hydrochlorinator Off-gas. (a) Settling chamber and sodium chloride bed; (b) settling chamber alone.

divided into two portions. The inner portion contained 11% of all zirconium and 24% of all uranium. The outer portion contained 62% of all zirconium and 1.5% of all uranium. Uranium and zirconium not accounted for above was either deposited by convection currents in the hydrogen chloride entrance zone or was deposited on asbestos plugs used to decrease convection.

Hydrochlorination of 86% U—10% Nb—4% Zr Alloys. Hydrochlorination with the reaction zone at 400, 500, and 600°C, and the rest of the apparatus (Fig. 4.3a) at 350°C, gave a residue fromwhich 99.8, 99.5, and 99.0% of the uranium was recovered by nitric acid. At the two lower temperatures the loss was all in the insoluble residue; at 600°C, 0.1% of the uranium was found in the first centimeter of sodium chloride. Much ash (0.46 g) remained in a hard shell after the 600°C run. The runs were performed on 5.8-g samples and carried to 12, 68, and 100% completion at average rates of 1, 8.4, and >20 mg/cm^2.min at the respective temperatures. The rate at 600°C is not known exactly because the reaction was completed before the experiment was terminated. The average flow rate through the settling chamber was 50 ft/hr. The zirconium tetrachloride was recovered quantitatively in the NaCl bed.

4.3 Fluoride-catalyzed Nitric Acid

Dissolution of ThO_2—UO_2 (W. E. Clark, W. D. Bond). The dissolution rate of sintered 96% ThO_2—4% UO_2 pellets in boiling 2-15.8 M HNO_3 containing 0.04 M NaF was maximum in 13 M HNO_3 and decreased rapidly as the nitric acid concentration was decreased below 13 M and as the thorium nitrate concentration increased (Fig. 4.4). The optimum compromise between dissolution time and product solution compositions is attained by starting the dissolution in 13 M HNO_3 and allowing dissolution to proceed until a product solution composition of about 1 M $Th(NO_3)_4$—8 M HNO_3 is reached.

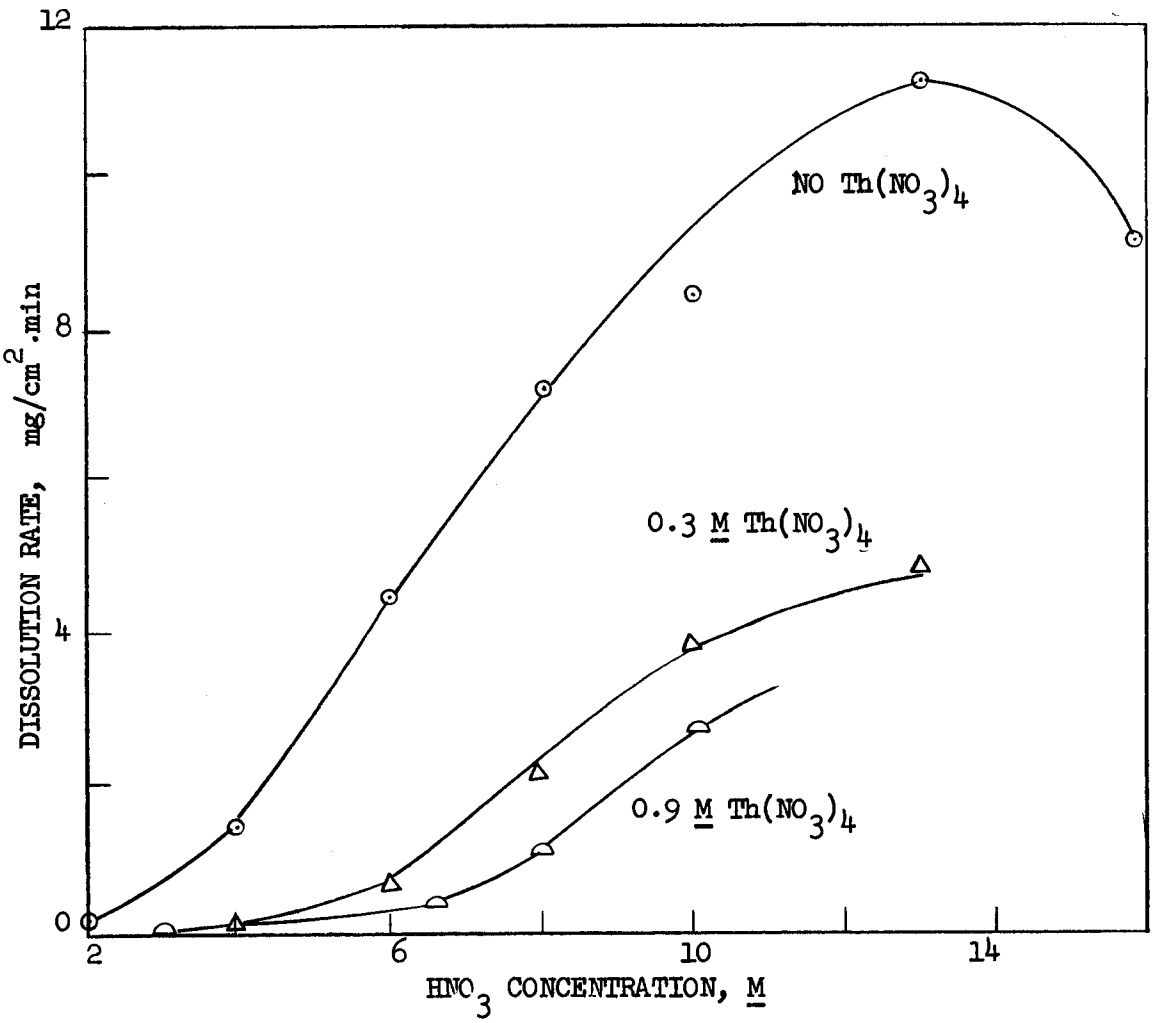

Fig. 4.4. Effect of Nitric Acid and Thorium Nitrate Concentration on Rate of Dissolution of 96% ThO_2--4% UO_2 Sintered Pellets in Boiling Nitric Acid--0.04 M NaF.

Dissolution rate studies of the pellets in 13 M HNO_3—0.04 M NaF at initial V/S ratios of 1.14, 1.90, and 3.84 were reported last month (ORNL-2447). Data from studies with V/S ratios of 0.795, 1.50, 2.60, and 6.45 showed the following conditions for production of 0.5, 1.0, 1.5, and 2.0 M $Th(NO_3)_4$ solutions:

$Th(NO_3)_4$ Conc, M	HNO_3 Conc, M	Dissolution Time, hr	V/S Ratio,[a] cm	Moles of Acid used per mole of ThO_2	Pellet Dissolution, wt %	Overall Dissolution Rate,[b] $mg/cm^2 \cdot min$
0.5	10.9	3.5	6.45	4.2	85	4.3
	11.0	0.90	2.60	4.0	34	6.6
	11.0	0.45	1.50	4.0	20	7.7
	10.7	0.20	0.795	4.6	10	9.3
1.0	8.7	3.3	2.60	4.3	68	3.7
	8.7	1.4	1.50	4.3	40	4.9
	8.8	0.55	0.795	4.2	20	6.7
1.5	6.6	3.6	1.50	4.3	60	2.9
	6.8	1.4	0.795	4.1	30	3.9
2.0	4.6	4.0	0.795	4.2	40	1.9

[a]Initial dissolvent volume to surface area ratio.

[b]Calculated from initial surface area.

In preliminary dissolution tests on 75% ThO_2—25% UO_2 sintered pellets in boiling 13 M HNO_3—0.04 M NaF, the average dissolution rate for obtaining a 0.2 M $Th(NO_3)_4$ solution was 4.04 $mg/cm^2 \cdot min$.

Dissolution of APDA Fuel (J. R. Flanary, J. H. Goode). A 10-g specimen of simulated APDA fuel pin (zirconium-clad uranium-molybdenum alloy) was dissolved in 500 ml of 13 M HNO_3—0.5 M HF without the addition of heat, forming a stable solution containing 11.8 M H^+ and 17.9 g of uranium, 2 g of molybdenum, and 1 g of zirconium per liter. The dissolution required less than 20 min, during which time the heat of reaction raised the temperature of the dissolvent from 60°C to 100°C. Dilutions of this solution were made with 1, 2, and 3 parts of water, also forming stable solutions containing 6, 4, and 3 M H^+ and proportinate amounts of metal ions.

4.4 Sulfuric Acid

Solubility of UO_2 during Dissolution of Stainless Steel (W. E. Clark, A. H. Kibbey). Dissolution rates of UO_2 in boiling 2, 4, 6, and 8 M H_2SO_4 over 2.5-hr periods, based on uranium dissolved, were 0.000124, 0.00124, 0.000639, and 0.00092 mg/cm^2.min, respectively. At these low rates the differences are not significant, but, in any case, the uranium loss to the decladding solution should be very small. In experiments in which the stainless steel constitutent of APPR fuel elements (stainless steel--clad sintered UO_2--stainless steel) was dissolved in sulfuric acid and the UO_2 filtered off, uranium losses to solution were about 0.3% compared to 0.04% when a centrifuge was used, indicating that some finely divided UO_2 probably passed through the filter.

Dissolution of the stainless steel of an APPR fuel element in 4 M sulfuric acid followed by dissolution of the UO_2 in nitric acid resulted in about a fourfold greater loss of uranium than when the Darex dissolution scheme was used (p.12). In the sulfuric acid procedure, after the stainless steel solution was poured off, the UO_2 was dissolved in 8 M HNO_3 and evaporated to 50% of the original volume. Concentrated (15.8 M) HNO_3 was then added to give a volume twice the original, and the solution was again evaporated to half the original volume. After the residue had been washed twice in 15.8 M HNO_3, the uranium remaining was 0.033% of that in the fuel element. With no boildown, 0.9-1.5% of the uranium remained undissolved.

Effect of Radiation on UO_2 Solubility (J. R. Flanary, J. H. Goode). In earlier experiments with highly irradiated APPR fuel elements (stainless steel--clad sintered UO_2--stainless steel), the uranium loss during dissolution of the stainless steel with 6 M H_2SO_4 was ~0.5% with unirradiated fuel and 94% with irradiated (ORNL-2362, p.20; ORNL-2385, p. 16). With sintered UO_2, the core material of Yankee Atomic fuel pins, the uranium dissolved in 4 M H_2SO_4 during 168 hr of Co-60 γ irradiation at 2.2×10^6 r/hr was only 2.5 mg/ml more than in an unirradiated control. Results were somewhat erratic. The experiment was made with duplicate 30-g specimens of UO_2 immersed in 50 ml of 4 M H_2SO_4 and irradiated in a Co-60 γ source. It was calculated that as much as 19 times (i.e., 0.01 mole) as much H_2O_2 was formed by the total γ irradiation, using a G value* of 0.8** for H_2O_2 production in sulfuric acid, as uranium was dissolved in the specimen with the higher uranium solubility (7.36 mg/ml).

In another experiment sintered UO_2 pellets clad in 304L stainless steel were irradiated 60 hr in the ORNL Graphite Reactor in a flux of 5×10^{11} n/cm^2.sec, allowed to decay 5 hr, and declad in 200% excess of 4 M H_2SO_4, at 100°C, over a 23-hr period. The 0.54 curie of β radiation associated with each pellet after 5 hr decay was calculated to produce and maintain up to 10^{-7} M H_2O_2 in the decladding solution. The uranium loss to the decladding solution was less than 0.01% (0.002 mg/ml) even though the UO_2 pellets had been disintegrated during fabrication of the specimens, exposing a large area to the acid. Gamma scanning indicated that essentially all radioactivity in the decladding solution was due to activated components of the type 304L stainless steel jackets.

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*G value = molecules of H_2O_2 produced per 100 ev.

**T. J. Sworski, J. Am. Chem. Soc., 76: 4687 (1954).

4.5 Hydrofluoric Acid

Dissolution of Zircaloy-2 Cladding (W. E. Clark, A. H. Kibbey). A prototype PWR fuel element (UO_2 pellets clad with zircaloy-2, was dejacketed in 2 hr with a uranium loss of 0.24%. The HF, 27 M, was added in increments such that the concentration of free acid was never greater than 5 M. The final concentration of fluoride was about 9 M, and the F^-/Zr ratio was 4.5. The temperature varied between 90°C and boiling. The cladding solution was 0.0048 M in uranium (about 1.14 mg/ml), compared to 0.0058 M predicted from UF_4 solubility data reported by Argonne.* It therefore appears that to achieve an appreciably lower uranium loss it will be necessary to increase the free fluoride concentration of the solution above that obtainable at a F^-/Zr ratio of 4.5.

Effect of Radiation on UO_2 Solubility in HF (T. A. Gens, J. E. Savolainen). An experiment simulating conditions expected during HF dejacketing at 25°C of irradiated PWR fuel rods indicated that the increase in uranium loss resulting from the radiation would be insignificant, 0.002%, in 2 hr. The increased loss could be as much as 0.1% if the contact time should be increased 100-fold, and with longer jacket dissolution times uranium recovery from the dejacketing solution would be required.

In the experiment a 6-g UO_2 pellet was contacted with 23.5 ml of 6 M HF at room temperature in a capped polyethylene bottle and irradiated (by H. A. Mahlman of the Chemistry Division) in a Co-60 source. A control sample was prepared simultaneously. Two-milliliter samples were periodically withdrawn from each bottle and analyzed for uranium. The calculated effective intensity of ionizing radiation produced by each reactor-irradiated UO_2 pellet (6.5×10^7 ev/min) was equal to the intensity of ionizing radiation absorbed per milliliter of hydrofluoric acid solution in the experiment.

The uranium in the control solution quickly reached a maximum of 0.001 N, apparently the solubility of UF_4 (TID-10089, op. cit.), but the uranium concentration increased nearly linearly in the irradiated solution (Fig. 4.5). The uranium loss per UO_2 pellet to the dejacketing solution, from ionizing radiation only, can be estimated at any contact time by subtracting curve B from curve A. Curve A does not show the expected loss from the sum of both radiation-induced loss and loss due to UF_4 solubility since under dejacketing conditions the loss from UF_4 solubility should approximately equal the product of the loss in curve B and the number of milliliters of hydrofluoric acid solution required per pellet, with some corrections necessitated by the differences in the amounts of free fluoride in solution in the two cases.

The increased loss due to irradiation is thought to be due to the formation of hydrogen peroxide (see also p. 14). The G value for hydrogen peroxide production has been found to be 0.78.** The calculated G value in this experiment for uranium going into solution at 2 hr was 0.3. These two values are close enough to suggest that hydrogen peroxide reacts with the uranium dioxide to produce soluble uranyl ions.

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*A. A. Jonke, V. H. Munnecke, R. C. Vogel, and S. Vogler, "Process for Recovering Uranium from Zirconium-Uranium Reactor Fuel," TID-10089 (1954).

**T. J. Sworski, op. cit.

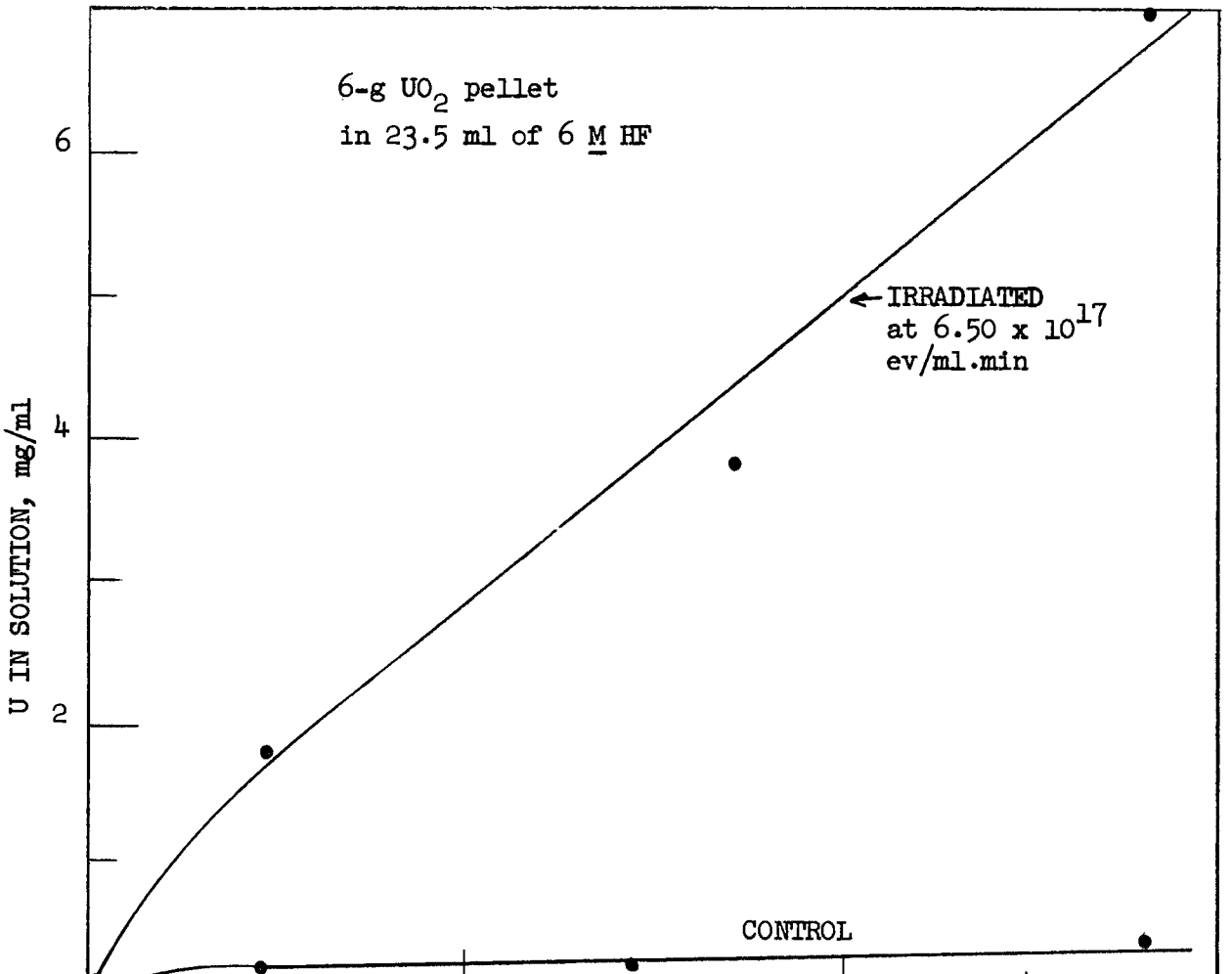

Fig. 4.5. Effect of Irradiation on Solubility of UO_2 in Hydrofluoric Acid.

Since dejacketing temperatures would probably be higher than 25°C, hydrogen peroxide would be less stable than in this experiment, and radiation-induced losses should be even lower. Catalysts which speed hydrogen peroxide decomposition might reduce the U loss to the decladding solution.

The intensity of ionizing radiation used here is comparable to that expected under actual dejacketing conditions, as estimated by E. D. Arnold of this Division for fuel irradiated to 7500 Mwd/t and decayed 120 days. Arnold's estimate was based on previous calculations* using further simplifying assumptions. Error

*T. W. Leland "Alteration of Beta Energy along a Straight Line Path Through Various Absorbing Media," ORNL CF-54-9-133 (1954).

arising from these assumptions should not exceed ± 30%. An additional assumption was that 50% of all γ radiation would be absorbed in the processing vessel. This assumption depends on the shape and size of the dissolver vessel, and only the calculation of γ radiation absorption is affected since β radiation is all absorbed near the surface of the pellet. The quantity of ionizing radiation arising from γ rays was calculated to be about the same as that arising from β radiation.

4.6 Dissolution of Liquid Metal Fuel (J. R. Flanary, J. H. Goode)

A total of 48 g of 98.7% bismuth—1.3% uranium alloy was dissolved in 40 min, without the addition of heat, in 300% excess 8 M HNO_3 (480 ml). The temperature of the dissolvent rose from 42°C to 56°C during the dissolution. A stable green solution was formed which analyzed 6.95 M HNO_3, 3.99 mg U/ml, and 78 mg Bi/ml. Acid consumption was about 3 moles per mole of bismuth.

4.7 Dissolution of Alloy DB-2 (W. E. Clark, A. H. Kibbey)

Two-minute dissolution rates of the new Martin Alloy DB-2* at 90°C indicated that fuel clad with this alloy would probably be amenable to integral dissolution in either dilute nitric acid or aqua regia and probably to decladding with sulfuric acid:

Dissolvent	Molarity	Dissolution Rate, $mg/cm^2 \cdot min$
HF	5	3.14
	9	12.5
	12	19.3
HCl	3	0.48
	6	1.96
	9	3.03
HNO_3	3	4.42
	6	2.67
	9	0.16
H_2SO_4	2	3.73
	4	4.83
	6	15.4
	8	3.09

4.8 Corrosion Studies** (W. E. Clark)

Gaseous Zircex Process. Cyclic hydrochlorinator-dissolver tests were continued to 75 cycles.

Microscopic examination of samples of Haynes 25 and S-816 showed that scaling and intergranular cracking had occurred, resulting in a much more severe attack than indicated by weight loss data:

*Approximate composition, wt %: 7 Al, >78 Fe, <5 Cr, <5 Nb, <5 Ti

**Work done by Battelle Memorial Institute under subcontract.

Solution Composition	Approximate Corrosion Rate, mils/100 cycles							
	Haynes 25				S-816			
	Wt Loss		Penetration		Wt Loss		Penetration	
	35	75	35	75	35	75	35	75
3 M HNO_3, 0.4 M UO_2^{++}, 1.2 M Cl^-	1.0	2.2	12.9	10.0	2.0	1.7	24.3	16.0
5 M HNO_3, 0.01 M UO_2^{++}, 0.03 M Cl^-	0.8	1.8	8.6	8.7	1.0	1.9	7.1	10.0
5 M HNO_3, 0.4 M UO_2^{++}, 1.2 M Cl^-	2.2	2.2	11.4	18.0	7.0	--	44.3	54.3
15 M HNO_3, 0.01 M UO_2^{++}, 0.03 M Cl^-	-->12		--	38.0	--	>10.5	--	32.0

However, these results do not necessarily rule out the use of Haynes 25 for construction of the hydrochlorinator-dissolver. For example, in 5 M HNO_3, 0.01 M UO_2^{++}, 0.03 M Cl^- the maximum rate shown by Haynes 25 corresponds to less than 3 mils/month under the most pessimistic conditions. If the concentration of nitric acid was lowered to 1-3 M, this rate could doubtless be decreased considerably.

Liquid Zircex Process. The series of scouting experiments run in refluxing (425°C) $AlCl_3.NH_4Cl$ was terminated. The data indicate that containment of this system is possible with dissolution rates of less than 3 mils/month for nickel, Hastelloy X, and molybdenum:

Material	Corrosion Rate, mils/month			
	24 hr		168 hr	
	Liquid	Vapor	Liquid	Vapor
Molybdenum	0.6	0.4-0.7	0.04	0.02
Nickel	6.4	0.2	1.2	0.08
Hastelloy X	8.2	0.5	2.7	0.07
Hastelloy C	8.2-13.0	0.9-1.6	8.4	1.6

Darex Process. Final results of Darex dissolver tests indicated that titanium 75A is entirely satisfactory for this application and superior to zirconium and the titanium—6% Al—4% V alloy:

Material	Location	Corrosion Rate, mils per month	
		Batch Dissolver	Continuous Dissolver
		1839 hr	2483 hr
Titanium (75A)	Vapor	0.01-0.07	0.02-0.03
	Interface	Gain*	Gain*
	Condenser	0.03	--
Tantalum	Vapor	0.01	0.00
	Interface	--	Gain*
			2207 hr
Haynes 21	Vapor	0.24-0.43	0.03
	Interface	--	0.38
	Liquid	0.35	--
Type S-816	Vapor	0.52-0.69	--
	Interface	0.73	--
	Liquid	0.81	--
			1000 hr
Titanium alloy, 6% Al-4% V	Vapor	--	0.15-0.19
	Interface	--	Gain*
			45 hr
Crystal bar zirconium	Vapor	--	67-69
	Interface	--	59-68

*Gain indicates a gain in weight of 100 mg or less on a 0.5 - by 2-in. specimen.

No appreciable embrittlement was indicated:

Exposure Time, hr	Continuous Dissolver		Batch Dissolver	
	Foil Radius, 64th in.	H_2 Content, ppm	Foil Radius, 64th in.	H_2 Content, ppm
0	1	20-41	1	20-41
190	-	-	1	42
483	-	76	-	-
832	-	-	1	42
1205	2	42	-	-
1839	-	-	1-3	-
1913	4	61	-	-
2483	2	63	-	-

During the long-term dissolver tests a hard scale formed on the titanium specimen in contact with dissolving stainless steel. X-ray analysis showed this material to be largely amorphous in character with small amounts of spinels and metallic silicon. Removal of this material may be a problem in a practical process.

4.9 Materials Evaluation (G. A. West)

Decontamination of Coatings and Plastics (J. S. Taylor, J. C. Rose). Tests on decontamination of protective coatings indicated higher decontamination factors for vinyl base paints than for other groups tested (Table 4.1). The decontaminability, in decreasing order, was vinyl, lacquer, epoxy, polyethylene, saran, phenolic, and alkyd. Ucilon system-K, a vinyl coating, had the best decontamination factor, $\sim 1.8 \times 10^2$, which is about three times greater than the next test coating. The panels, 2.5 by 2.5 in., 16 gage, used for the tests were contaminated in the center section with 2000 µl of a Thorex process IAWC waste (1.0 N acid) from reprocessing of short-decayed (30 day) thorium slugs and were air dried. The composition of the contaminating solution was, in c/m.ml: 1.68 U-233 α (4.7 mg/ml); 3.69×10^{10} gross β; 3.59×10^{10} gross γ; 3.0×10^{10} Pa-233; 4.19×10^8 Ru-106; 3.25×10^9 Nb-Zr-95; 1.26×10^5 I-131 β; 3.0×10^9 total rare earth β. The panel was first washed with water for 2 min and was then dried and the activity was read in milliroentgens per hour. It was then scrubbed in 3 M HNO_3 solution for 5 min, using a Gardner Wear Testing machine with Chinese hog bristle brushes. The brush was weighted for 1 lb total pressure on the panel and was operated 370 strokes during the 5-min period. The panels were finally rinsed with water and dried in air. The calculated decontamination factors accounted for decay of the contaminant.

Radiation Damage to Glass, Concrete, and Haveg (G. A. West). The vycor and pyrex glass rods, exposed at ORNL to 10^6, 10^7, and 10^8 r gamma, were tested by the Corning Glass Works for physical and chemical changes. There was no detectable change in strength by breakage tests or chemical resistance to 5% caustic or 5% HCl. These types of glass, along with Pfaudler glass on steel and an epoxy-base concrete, are undergoing irradiation to 10^{10} r gamma at the MTR facility in Idaho. The Haveg Corporation is currently performing physical and chemical tests on Haveg 41, 61, and 093 that has been exposed to 10^{10} r gamma at the MRT facility.

5.0 SOLVENT-EXTRACTION STUDIES

5.1 Flowsheets for Heterogeneous Power Reactor Fuel Processing (Program Leader: H. E. Goeller; J. R. Flanary, J. H. Goode)

APDA Fuel Element. The nitric acid solution of the simulated APDA fuel element containing fluoride (Sec. 4.3) was diluted 1 to 4, to give a composition

Table 4.1. Decontamination Tests on Protective Coatings

Manufacturer and Trade Name	Decontamination Factor						
	Water Flush		Acid Scrub		Overall		
	A[a]	B[a]	A[a]	B[a]	A[a]	B[a]	Avg
Vinyl Base							
Metal and Thermit, Ucilon System - K	43 366	-- --	30 6	-- --	1266 2350	-- --	1808
Amercoat, No. 31	40	52	11	15	418	825	621
Nukem Products, Nukemite-40	60	66	8	6	480	418	454
Amercoat, No. 35	28	104	3	6	83	600	342
Amercoat, No. 23	23	27	15	7	334	193	263
Amercoat, No. 33HB	69	41	3	5	212	223	218
DuBois, Peel Filmite	21	15	9	13	189	195	192
Amercoat, No. 33	22	32	3	6	59	193	125
Prufcoat Laboratories, Series A	18	--	6	--	102	--	102
Carboline, Polyclad 933-1DG	26	20	4	4	90	71	80
Nukem Products, Nukemite-33	21	23	4	3	88	69	79
Amercoat, No. 55	20	11	4	6	72	64	68
DuPont, Eng. 6200, System-2	18	21	4	3	67	65	66
DuPont, Eng. 6200, System-1	18	23	3	2	62	55	59
D. E. Long, Series-A	22	26	1	4	28	89	59
Metal and Thermit, Ucilon System-T	--	11	--	5	--	55	55
L. E. Carpenter, Virctex*	16	--	3	--	53	--	53
Carboline, Polyclad 120-1 DG	25	26	2	2	57	37	47
Amercoat, No. 88	12	13	3	3	37	37	37
DuPont, Eng. 1200	3	3	(acid attacked paint)				--

* Wallpaper

Table 4.1. Continued

Manufacturer and Trade Name	Decontamination Factor: Water Flush A[a]	Water Flush B[a]	Acid Scrub A[a]	Acid Scrub B[a]	Overall A[a]	Overall B[a]	Overall Avg
Epoxy Base							
Prufcoat Laboratories, Series EP	30	--	7	--	196	--	196
Amercoat, No. 74	29	28	8	4	244	122	183
Devoe and Raynolds, Devran-600	14	62	5	3	64	160	112
D. E. Long, Series-E	26	--	4	-	89	--	89
DuPont, Eng. 6426	20	33	3	3	63	98	81
Metal and Thermit, Unichrome XL-2535	--	16	--	2	--	30	30
Carboline, 180-57	14	4	2	3	30	11	21
Amercoat, No. 66	--	7	-	3	--	21	21
Lacquer							
Dittbrenner Associates, Polychem-1500	19	--	13	-	253	--	253
Hypalon (polyethylene)							
DuPont, 100-E-47394	32	16	4	7	135	118	126
Saran							
Peninsular Chemical, Penkote-500	36	--	1.4	-	52	--	52
Phenolic							
DuPont, Eng. 6102	20	11	2	2	39	18	29
Carboline, Phenoline-305	8	6	4	2	32	11	22
Alkyd							
DuPont, Eng. 5102	12	11	2	2	20	19	20

[a]Material prepared for study by (A) independent laboratory, (B) manufacturer.

3 M H^+, 4.5 mg U/ml, 0.50 mg Mo/ml, and 0.27 mg Zr/ml, and extracted with 4 vol of 6% TBP. The addition of 2 moles of aluminum per mole of fluoride in the feed, as a fluoride complexing agent, increased the O/A uranium distribution coefficient in the first equilibration from 3.5 to 6.8 and decreased the uranium in the aqueous phase after 4 equilibrations from 0.007 to 0.002 mg/ml. Consequently, the number of extraction stages required for adequate recovery of uranium and plutonium would be decreased by the addition of aluminum. The zirconium and molybdenum distribution coefficients were not affected by the addition of the aluminum and remained about 0.02, indicating adequate separation from the uranium.

Liquid Metal Fuel. Batch equilibrations with equal volumes of 2% TBP were made with the feed prepared in Sec. 4.3 and with a 1 to 1 water dilution. The O/A uranium distribution coefficients were 0.59 and 0.54, respectively. Equilibration of the undiluted feed with an equal volume of 5% TBP gave distribution coefficients of 1.54 for uranium and 10^{-4} for bismuth.

Scrub section uranium distribution coefficients after the second and fourth equilibrations were 6.8 and 6.6, respectively, assuming a flowsheet using 1 vol of 5% TBP, 1 vol of aqueous feed, and 0.25 vol of 3 M HNO_3 as an aqueous scrub. For the experiments an organic extract of 5% TBP containing about 2.5 mg U/ml and 0.17 M H^+ was equilibrated 4 times with 0.25 vol of 2 M HNO_3.

5.2 Solvent Radiation Stability* (Program Leader: R. E. Blanco; J. H. Goode)

Comparison of G values for various solvents and diluents (see ORNL-2447 and Table 5.1) indicated that compounds with a phenyl group and those with a phosphonate group are both more stable than tributyl phosphate; for example:

Solvent	G Value			
	Solvent Alone	Solvent + 50 w/v %[a] Amsco	Solvent Alone	Solvent + 50 w/v %[a] Amsco
Tributyl phosphate (TBP)	2.44	2.78	2.64	0.60
Dibutyl phenylphosphonate (DBPP)	0.45	1.04	0.36	0.24
Dibutyl butanephosphonate (DBBP)	1.79	2.05	0.14	0.08
Diamyl pentanephosphonate (DAPP)	1.30	1.79	0.19	0.10

[a] See Table 5.1 for meaning of abbreviation.

*Work done by Stanford Research Institute and reported in their progress reports for August, September, and October.

The phenyl group appeared to exert a protective effect and the aliphatic phosphonates appeared slightly more stable than aromatic, on the basis of acid produced. Diamyl pentanephosphonate was slightly less damaged by the irradiation than dibutyl butanephosphonate. The G values for acid produced in both cases were a factor of 10 lower than for TBP. The phosphonate system has one less C-O-P group and an inherently more stable C-P bond than the phosphate system.

The trend of emulsification studies was not clear, since at the high radiolysis levels studied three-phase phenomenons interfered, and necessitated dilution of some of the extractants with unirradiated material. The results were:

Solvent	Time to Clear[a] for Unirradiated, sec: As Received	Caustic Washed	Vacuum Distilled	Irradiation, w-hr/liter	Dilution with Unirradiated	Time to clear[a] for Irradiated, sec
TBP	22	18	--	1775	4 to 1	29
DBPP	21	--	--	1507	3 to 2	23
DBBP	31	24	--	1230	none	56
DAPP	37	--	22	1220	none	71

[a]"Time to clear" was the time required to obtain 90% of the initially clear organic phase after 2 min mixing.

The experiments were made with 0.2 M $UO_2(NO_3)_2$—2 M HNO_3. The extractants were 25 g of extractant diluted to 100 ml with Amsco 125-82.[3]

Attempts were made to remove the acidic materials from irradiated solvent, by ion exchange, so that polymers, if present, could be isolated. Duolite A-2 anion-exchange resin removed the acids from TBP irradiated to 1900 watt-hr/liter. Treatment with 0.5 M NaOH—0.05 M NH_4OH was also effective. Treatment with 1 M NaOH of the TBP irradiated to 1775 watt-hr/liter resulted in severe emulsions. Resin did not remove acids from such solvent that had been loaded with and then stripped of uranium.

The separation factors* for batch stripping of uranium with dilute nitric acid from irradiated TBP that had been washed with 1 M Na_2CO_3 or with 0.5 M NaOH—0.5 M NH_4OH were 0.60 and 0.33, respectively. The solvent was prepared by mixing 1 vol of TBP that had been irradiated to 1900 watt-hr/liter with 3 vol of unirradiated TBP, and diluting this mixture 1 to 1 with Amsco. For the experiment each of two samples of the prepared solvent was loaded with uranium by contacting it with 4 vol of 0.2 M $UO_2(NO_3)_2$—2 M HNO_3. The organic was stripped with 4 vol of carbonate or mixed hydroxide, washed with 0.1 M HNO_3, reloaded with uranium as before, and stripped again with 3- to 30-ml portions of 0.01 M HNO_3. Data obtained in continuous countercurrent spinner columns showed slightly more effective uranium stripping from irradiated TBP solvent that had been washed with the mixed hydroxides than with sodium carbonate. Distribution coefficients of 0.018 and 0.021, respectively, were obtained for the treated solvents compared with D.C.'s of greater than 0.5 for unwashed irradiated solvents.

*The separation factor is the ratio of uranium concentration in the organic phase to that in the aqueous strip, i.e., uranium distribution coefficient, UE_a^o.

Table 5.1. G Values[a] for Irradiated[b] Solvents and Solvent-Diluent Mixtures

Sample[c]	Irradiation, watt-hr/liter	G Values																
		Total Gas	Hydrogen	Methane	Acetylene	Ethylene	Ethane	Propylene	Propane	Butene	n-Butane	Isobutane	Pentene	Pentane	Pentanes, Hexanes, and Octanes	C_6 and Higher	Butanol	Amyl Alcohol	Monobasic Acid
DBBP	1230	1.79	1.42	0.04		0.03	0.05		0.05	0.04	0.12	0.04			<0.01		0.27		0.14
DBBP + Amsco	1325	2.05	1.40	0.18	<0.01	0.06	0.05	0.03	0.08	0.07	0.09	0.07			0.03		d		0.08
DAPP	1220	1.30	1.20	0.03	0.01	0.01	0.03	<0.01	0.01	<0.01	0.01	<0.01	<0.01	0.03				0.22	0.19
DAPP + Amsco	1325	1.79	1.33	0.16	<0.01	0.02	0.04	0.02	0.07	0.02	0.01	0.04	0.01	0.03		0.01		d	0.10

[a] Number of molecules produced per 100 ev of irradiation.

[b] Samples irradiated with 1-Mev (nominal) electrons; cooled in dry ice--methanol.

[c] For the mixtures 50 g of the extractant was diluted to 100 ml with Amsco 125-82.

[d] Determination of alcohol impossible because of interference from Amsco degradation products.

6.0 THOREX PROCESS
Program Leader: E. M. Shank

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

6.1 Pilot Plant Performance (E. M. Shank, J. R Parrott, W. T. McDuffee, G. S. Sadowski, R. H. Vaughan, O.O. Yarbro, C. V. Ellison, J R. Manneschmidt)

One pilot-plant development run on long-decayed thorium, HD-27, was completed to test the interfacial solid removal system. The third run on short-decayed material, SD-3, was completed on thorium irradiated to 4000 g of U-233 per ton and decayed about 30 days. Both runs were made with the ORNL Thorex co-decontamination flowsheet.

In run HD-27, a total of 325 hr of two-cycle solvent-extraction operation was maintained to process 720 kg of irradiated and 230 kg of recycled thorium. About 900 kg of thorium product, meeting ionic specifications, and 1000 g of U-233 were sorbed on ion-exchange resin. Column operation was interrupted frequently owing to malfunction of several pumps and to flooding of first- and second-cycle stripping columns. Thorium and uranium solvent-extraction losses averaged 4.3 and 0.3%, respectively. More than 99% of the thorium loss was from the extraction columns; the high loss reflects the effect of frequent column interruption. The average overall gross gamma decontamination factors were 4×10^3 for thorium and 1×10^4 for uranium; activity specifications were exceeded in both products for protactinum, ruthenium, and zirconium-niobium. After completion of run HD-27, all solvent-extraction equipment was flushed with nitric acid. Used solvent was continuously treated with 0.5 M KOH (see Sec. 6.3); residual activity in the recovered solvent was the lowest ever observed.

During run SD-3, a total of 173 hr of continuous two-cycle operation was maintained to process 630 kg of irradiated and 420 kg of recycled thorium. The run was terminated early because of equipment failures and excessive dispersal of radioactive contamination to the atmosphere. The irradiated feed contained about twice the specific activity as the feed for run SD-1. Bisulfite was added only to the 2AF owing to cooling of the 1AF being inadequate (the temperature was between 75 and 85°C) even with the use of ice water.

Thorium and uranium solvent-extraction losses for run SD-3 averaged 3.3 and 0.6%, respectively. Approximately 98% of the thorium loss was in the 1AW and 2AW streams. The high 1AW loss is attributed partly to a low aluminum concentration; the aluminum jackets apparently are not completely dissolved in the absence of mercury catalyst. The gross gamma decontamination factors across two solvent-extraction cycles were $\sim 10^4$ for the thorium and $\sim 10^5$ for the uranium:

	First Cycle		Second Cycle		Overall	
	Th 1AF/1CP	U 1AF/1CP	Th 2AF/2BT	U 2AF/IF	Th 1AF/2BT	U 1AF/IF
Gross γ	150	200	85	530	1.4×10^{4}	9.6×10^{4}
Pa	150	200	140	540	2.2×10^{4}	9.8×10^{4}
Ru	15	20	280	1800	4300	3.2×10^{4}
Zr-Nb	140	170	15	470	2300	7.5×10^{6}
TRE	3.5×10^{4}	4.3×10^{4}	240	230	7.0×10^{6}	7.2×10^{6}

The ruthenium decontamination factor increased a factor of 30 to 100 over that in run SD-1. The thorium product met tentative activity specifications for rare earth activity at time of separation, but the uranium product exceeded specifications for all fission products and Pa-233:

	Activity, c/min.mg						
	Gross γ	Pa γ	Ru γ	Zr-Nb γ	TRE β	I-131 β	Th-234 γ
Thorium							
1AF	1.4×10^{9}	1.3×10^{9}	5.2×10^{6}	4.2×10^{7}	3.5×10^{7}	1.2×10^{6}	2.4×10^{5}
1CP	9.6×10^{6}	8.9×10^{6}	3.7×10^{5}	3.0×10^{5}	1000	--	--
2AF	8.6×10^{6}	8.1×10^{6}	3.3×10^{5}	2.8×10^{5}	1200	--	--
2BT	1.0×10^{5}	5.9×10^{4}	1200	1.8×10^{4}	5	--	--
2BTC	1.1×10^{5}	7.6×10^{4}	1500	4200	9	4	4.5×10^{4}
Spec.	260	30	40	45	40	--	100
Uranium							
1AF	5.3×10^{11}	4.9×10^{11}	1.9×10^{9}	1.5×10^{10}	1.3×10^{10}		
1CP	2.7×10^{9}	2.5×10^{9}	1.1×10^{8}	8.6×10^{7}	3.0×10^{5}		
2AF	2.9×10^{9}	2.7×10^{9}	1.1×10^{8}	9.4×10^{7}	4.1×10^{5}		
2CU	5.5×10^{6}	5.0×10^{6}	6.0×10^{4}	2.0×10^{5}	1800		
IF	9.1×10^{6}	9.9×10^{6}	1.9×10^{5}	4.4×10^{5}	2000		
Spec.	9000	1000	280	8000	450		

Additional decontamination of the uranium product is expected from the ion-exchange step and the third uranium solvent-extraction cycle. Approximately 95% of the gamma activity in the uranium product was contributed by Pa-233. Pa-233 decontamination across the two solvent-extraction cycles was, generally, lower than in run SD-1. Solids appeared in the 2CU stream and partitioning efficiency in the second cycle was reduced during the latter part of the run. The difficulties are tentatively attributed to solvent degradation products. Radiation intensities at all column interfaces exceeded 200 r/hr after 24 hr of radioactive operation.

Use of Gamma Scintillation Spectrometer for Analysis of Thorex Solutions. With the assistance of John Cooper of the Analytical Division, a single-channel gamma spectrometer (ORNL Master Analytical Manual Method No. 900367) was used for analyses of all flowing stream or composite samples during run SD-2. These analyses could be made very rapidly for variations in the protactinum, ruthenium, and zirconium-niobium and corrections made much more efficiently than has been possible with previous analytical methods. Difficulties that have presented the

analysis of organic streams do not influence the gamma spectrum, and variations in the activity of the organic product from the extraction column were routinely determined. Since this stream rapidly reflects variations in the extraction column, many more process conditions were evaluated than previously. Analytical costs for process control were substantially reduced by this method of analysis.

6.2 Component Studies (R. J. McNamee, W. T. McCarley, F. L. Rogers)

The interfacial solids removal system (ORNL-2324, Fig. 7.2) was operated during runs HD-27 and SD-3. An aqueous-organic stream, drawn from the interface at about 500 ml/min, was passed through a Fulflo fiberglas filter and a Selas phase separator. The organic stream from the separator was routed to the 1AP stream and the aqueous stream was returned to the column below the interface. The 1AP stream was further clarified by passing it through a Fulflo filter. The activities of the organic portion of the stream withdrawn from the interface were factors of 1.5×10^3, 540, and 780 higher in protactinium, ruthenium, and zirconium-niobium, respectively, than the aqueous stream from the top of the column. As a result, the activities in the 1AP stream increased by factors of 30, 8, and 20 for protactinium, ruthenium, and zirconium-niobium, respectively, when the organic stream from the Selas separator was returned to it. This activity was removed by the 1AP Fulflo filter. Decontamination factors for these elements across the 1AP Fulflo filter were 50, 10, and 40, respectively. The activity level of the interface decreased with time, eliminating the necessity of interface jetting.

The Potter flowmeter was not a reliable flow-measuring device; the measurement of pressure drop across the Fulflo filter in the interface purge system indicated flow even when the flowmeter indicated zero flow. An inoperative sampler prevented determining the decontamination factors across the filter and the separator individually. Radiation intensities were about 120,000 r/hr at the interface filter after about 4 hr operation and reached a maximum of about 196,000 r/hr after 24 hr. Filters were removed and replaced remotely every 24 hr.

6.3 Process Development (R. H. Rainey)

Decontamination of Short-decayed Feeds from Ruthenium (A. B. Meservey). Results of laboratory experiments with short-decayed Thorex feed solutions indicated that the lower decontamination from ruthenium in the plant than in the laboratory is due to the use of insufficient bisulfite. By means of iodine-starch indicator, the concentration of bisulfite destroyers—e.g., nitrite and peroxide—in the feed was shown to be 0.02 M. The previously reported (ORNL-2416) value of 0.015 M was the result of the slow reaction between the sulfite and the destroyers, which requires several minutes. In a 10-ml sample the sulfite was destroyed at a rate of 0.02 mole/hr; in the pilot plant, where the large volumes result in more efficient absorption of gamma energy, the rate of destruction could be as high as 0.075 mole/hr.

The lower decontamination from ruthenium in the pilot plant is not due to too high a temperature, as previously reported (ORNL-2417). At 53°C treatment of the feed with 0.06 M bisulfite gave a decontamination factor from ruthenium of 320, as compared to one of 2.5 in the control. At 46°C with only 0.04 M bisulfite the decontamination factor was 5. Temperatures as high as 73°C were reached before the bisulfite was destroyed.

Hydrogen Production from Short-decayed Aqueous Waste (R. G. Mansfield). Analysis of the off-gas from the storage tank (N-22) containing short-decayed Thorex aqueous waste did not show appreciable concentrations of hydrogen. The air spargers to the tank were turned off 18 hr prior to the time of sampling to allow accumulation of the radiolytic gases. The off-gas composition was:

	Composition, %			Composition, %	
Gas	By Analysis	Analysis Corrected for Air Content	Gas	By Analysis	Analysis Corrected for Air Content
NO_2	<0.5	<2	H_2	<0.5	<2
NO	<0.5	<2	CO[a]	14.9	55
CO_2	4.0	15	N_2	61.0	--
O_2	18.6	24			

[a]Gas combustible to CO_2 with oxygen; probably largely Amsco, since the temperature was high (~70°C).

The conditions of the tank at time of gas sampling were:

Total volume of waste transferred to N-22, liters	3660
Evaporated to final volume, liters	2820
Pa content, corrected to time of dissolution, g	820
Temperature at sampling time, °C	~70
Sparging rate (with air), ft^3/hr	10
Time since sparging discontinued, hr	18
Tank free board volume, liters	~250
Average thorium concentration, mg/ml	~7
Average aluminum concentration, M	0.94
Gross γ, c/m/ml	$\sim 3 \times 10^{11}$
TRE β, c/m/ml	$\sim 9 \times 10^{9}$

Recycle of Short-decayed Aqueous Waste for Additional Uranium Removal (R. H. Rainey and R. C. Lovelace). The aqueous waste from the short-decayed Thorex runs will be stored to allow decay of protactinium and then processed for recovery of U-233. Uranium losses from the original extraction will contribute isotopic contamination to this recycle product. A flowsheet for the immediate recycle of this aqueous waste for additional removal of uranium and thorium was demonstrated in countercurrent batch extractions. This flowsheet provides for the concentration of the aluminum in the aqueous waste to 1 M, and extraction of the uranium and thorium with an equal volume of 4.25% TBP—Amsco. Thorium is added to a concentration of 70 g/liter before extraction. The organic is scrubbed with 1/5 vol of the regular Thorex scrub solution. Thorium losses were less than 0.01 g/liter, and the gross gamma decontamination factor was 670.

Solvent Recovery (R. G. Mansfield). Pilot plant used solvent decontamination with calcium, sodium, or potassium hydroxide was greater than with sodium carbonate, used previously. In laboratory experiments five contacts with 1/5 volume of sodium carbonate gave a decontamination factor of 10. A similar treatment with 40% lime slurry gave a decontamination factor of 100. These experiments reconfirm results

which have been reported frequently in the past. The use of 0.1 M HNO_3 to remove lime fines from treated solvent gave an additional decontamination factor of ~ 2. Since the pilot plant does not have facilities for treating the solvent with a slurry, the use of other solutions was investigated. Both 0.2 M NaOH and 0.2 M KOH gave about twice the decontamination factor obtained with 0.2 M Na_2CO_3 in a similar treatment. Treatment with these agents also gave an additional decontamination of 10 on solvent that had previously been treated with carbonate in the pilot plant. The addition of amonium hydroxide to any of the above solutions did not improve the decontamination. There was little difference between the use of 0.2 M or 1.0 M NaOH. Although sodium and potassium hydroxide gave the same decontamination, potassium is preferable because of the formation of less viscous emulsions (see Sec. 6.1).

Activated charcoal adsorbed activity from the solvent but had insufficient capacity for use in the plant. Decontamination factors as high as 10 were obtained by stirring bone black in treated solvent. However, when solvent was passed through a bed containing coconut charcoal, the activity in the effluent reached 90% of that in the feed in 4 volume changes.

7.0 WASTE METAL RECOVERY

Program Leader: W. H. Lewis
(R. E. Brooksbank, P. A. Goudreau, C. D. Hylton,
W. R. Whitson, J. L. Matherne, W. H. Lewis)

The recovery of uranium from tank farm wastes was completed, with 7 tons of uranium being transferred as purified product to Y-12 for conversion to the oxide form. To date, a total of 136 tons of uranium has been recovered from ORNL waste farm tanks since the recovery program was initiated.

After plant cleanout and decontamination, equipment revisions were started preparatory to the americium recovery program.

7.1 Tank Farm Program

The processing of 134,000 gal of uranium-bearing tank farm waste solutions resulted in the recovery of 7 tons of uranium. The uranium product recovered was 98.4% of that fed into the solvent-extraction equipment. The 1.6% process loss was due in most part to the periodic draining of the extraction column interface to remove interfacial emulsions. Equilibrium solvent-extraction losses were satisfactory, totaling 0.13%, and were distributed as follows:

Stream	U Loss, % of feed	Stream	U Loss, % of feed
1AW	0.03	1CW	0.09
1BP	0.01	Total	0.13

The overall gross gamma decontamination factor for the uranium product was 3.5×10^3. Approximately 1.5 tons of off-specification product was produced as a result of the relatively high salting strength of boiled-down feed, causing poor decontamination from zirconium and niobium. This condition, however,

produced uranium product with good decontamination from ruthenium, 1.86×10^4. Specification-grade product was obtained only by passing the product through a silica gel column for additional zirconium-niobium decontamination. The tendency of tank farm feed to emulsify in the extraction column, necessitating periodic draining of the interface, countributed to the quantity of product exceeding specifications. The activity spectrums for the feed and the uranium product solutions and the decontamination factors obtained were:

	Activity, c/min.ml		Decontamination Factor
	1AF	U Product	
Gross γ	9.4×10^6	1.9×10^4	3.5×10^3
Gross β	5.0×10^6	1.4×10^4	2.5×10^3
Ru γ	1.3×10^6	521	1.9×10^4
Zr γ	1.5×10^6	5.6×10^3	1.9×10^3
Nb γ	1.7×10^6	9.2×10^3	1.3×10^4
TRE β	7.7×10^5	75	7.4×10^4
Cs γ	3.5×10^6	728	3.4×10^4
UX β	--	1.2×10^4	--

7.2 Americium Recovery Program

Piping and equipment modifications were started to prepare the plant for the recovery of approximately 40 g of Am-241 from 72 gal of Los Alamos Scientific Laboratory solution. The process to be used consists of:

1. Neutralization of the feed solution, containing large amounts of lanthanum and cerium, with ammonium hydroxide to a pH of 2.

2. Solvent extraction of the americium and lanthanum from the feed with neutralized 100% TBP.

3. Stripping of the lanthanum from the organic in the presence of a high concentration of nitric acid (fuming nitric acid, 15.6 M) and acidified 100% TBP being used.

4. Final stripping of the americium from the organic phase with 2.0 M HNO_3, followed by product volume reduction by evaporation.

8.0 WASTE STUDIES

Program Leader: J. O. Blomeke
(I. R. Higgins, A. F. Messing)

Studies were continued on the practicability of recovering sodium hydroxide and nitric acid from ORNL wastes by electrolysis. With the cell designed by Ionics Inc., with ion exchange membranes spaced about 0.14 in. apart, 0.6 M sodium and 0.3 M nitrate in synthetic waste were reduced to 0.06 M and 0.02 M, respectively, in two stages. In a cell with membranes spaced 1 in. apart, the

same result was achieved in three stages (Table 8.1). However, the second cell design is attractive from the standpoint of simplifying the problems of remote operation and maintenance. Current efficiency, based on sodium transfer, was essentially the same for the two cells, but the power requirement for the second cell was 50% greater in the first stage and 20% greater in the second when operated at the same current density.

In the Ionics design cell, current efficiency was, in general, independent of current density, but power requirements increased with increasing current density. For the first stage, current efficiencies were 56-59% at 1.0-1.5 amp/in.^{2} and the power consumption was 4.9-7.3 kwh/lb NaOH produced. For the second stage, the current efficiency was 61-68%, the current density 0.5-1.0 amp/in.^{2}, and the power consumption about 8 kwh/lb NaOH.

9.0 NONAQUEOUS PROCESSES

9.1 Fused Salt—Fluoride Volatility Process (Program Leader: R. B. Lindauer)

Pilot Plant Studies (W. H. Carr, J. E. Bigelow, F. N. Browder, R. B. Keely, S. Mann, F. W. Miles, J. B. Ruch, C. L. Whitmarsh). The ARE fuel, a fused uranium-zirconium-sodium fluoride, is to be processed in the volatility pilot plant. Necessary modifications were made and most of the equipment was tested for operability. A freeze valve, which is essentially a jack-leg with a cross-over designed for transferring salt from the hold tank to the fluorinator, was tested with barren salt; the freeze valve was operable both in the jack-leg section used for pressure transfers and in the cross-over, which may be used for gravity transfer of the last batch. The dump tank furnace and the transfer line to the hold tank were also tested with barren salt; operation was satisfactory.

The engineering flowsheet for fluoride volatility processing of fused salts is shown in Fig. 9.1. For ARE fuel recovery the dump tank will be placed (upside down and sloped toward drain holes) in the retort, and the entire fuel charge will be melted and drained to the hold tank. The salt will be transferred from the hold tank to the fluorinator in batches of about 50 liters.

Fuel Element Dissolver (R. W. Horton, G. Jones, Jr.) A 4-in. glass column was constructed to observe flow patterns and degree of contact between an STR-type subassembly and a fused salt mixture during hydrofluorination. The design of the gas dispersal system allowed for replacement of the distributor so that the effect of perforation pattern and ratio of perforated area to column cross section may be observed. Preliminary data with the air-water system with an 11-in. section of a subassembly indicated that contact was satisfactory at gas flow rates of 2-3 ft^3/min when the subassembly was half or more submerged. Under these conditions, the water was circulated from the bottom to the top of the subassembly by an air-lift action. The most effective perforation pattern appeared to be a single row of perforations of approximately 3/32 in. diameter through the center of the disperser plate.

Table 8.1 Electrolytic Production of Acid and Base

Initial concentrations: 0.6 M Na^+, 0.3 M NO_3^-, 0.15 M $CO_3^=$

1st stage			2nd stage			3rd stage			Effluent Concentration, M	
Current Density, amp/in.^{2}	Current Eff., %	Power	Current Density, amp/in.	Current Eff., %	Power	Current Density, amp/in.^{2}	Current Eff., %	Power	Na^+	NO_3^-
0.4-in. spacing of membranes										
1	56	4.9 kwh/lb NaOH + 0.97 lb HNO_3	1	61	8.5 kwh/lb NaOH + 0.76 lb HNO_3				0.11	0.03
1.25	58	6.0 kwh/lb NaOH + 0.89 lb HNO_3	0.75	68	8.0 kwh/lb NaOH + 0.82 lb HNO_3				0.08	0.02
1.50	57	7.0 kwh/lb NaOH + 0.94 lb HNO_3	0.50	67	5.1 kwh/lb NaOH + 0.64 lb HNO_3				0.14	0.04
1.50	59	7.3 kwh/lb NaOH + 0.96 lb HNO_3	0.75	65	8.2 kwh/lb NaOH + 0.69 lb HNO_3				0.06	0.02
1-in. spacing of membranes										
1	62	7.5 kwh/lb NaOH + 0.9 lb HNO_3	1	63	9.9 kwh/lb NaOH + 0.9 lb HNO_3	0.5	68	12.2 kwh/lb NaOH + 0.52 lb HNO_3	0.06	0.01

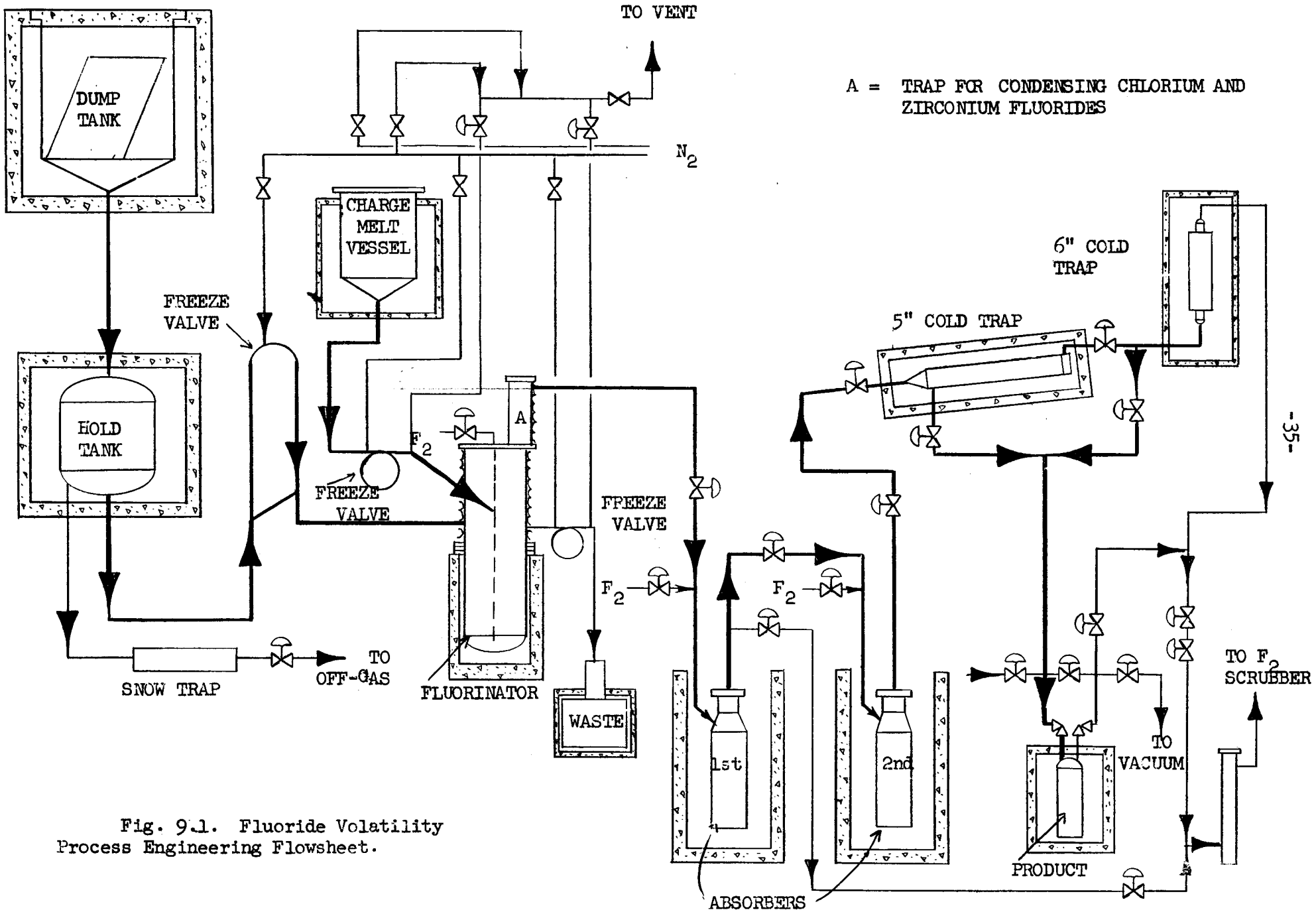

Fig. 9.1. Fluoride Volatility Process Engineering Flowsheet.

Effect of Grain Size on Effectiveness of 400°C NaF Bed (G. I. Cathers, R. L. Jolley). The relative effectiveness of two sizes of NaF was studied for use in the 400°C bed located after the fluorinator in the volatility process. Decontamination from all radioactive materials except plutonium was a factor of >10 higher for 12-20 mesh material than for 1/8-in. pellets:

	Decontamination Factors							
	Gr β[a]	Gr γ	Ru γ	Zr γ	Nb γ	Cs γ	TRE β	Pu α
	Run 1 (12-20 mesh NaF)							
Fluorination	6.8×10^{3}	3.0×10^{2}	5.3	1.0×10^{4}	96	2.7×10^{3}	1.0×10^{5}	12
NaF bed	7.0	35	9.7	7.4	2.2×10^{3}	2.6	3.2	18
Overall	4.8×10^{4}	1.0×10^{4}	51	7.4×10^{4}	2.1×10^{5}	7.1×10^{3}	3.2×10^{5}	220
	Run 2 (12-20 mesh NaF)							
Fluorination	5.2×10^{3}	1.5×10^{3}	36	2.5×10^{4}	1.1×10^{3}	3.8×10^{4}	5.2×10^{5}	79
NaF bed	9.5	97	45	4.6	122	6.9	40	6.3
Overall	4.9×10^{4}	1.4×10^{5}	1.6×10^{3}	1.1×10^{5}	1.3×10^{5}	2.6×10^{5}	1.6×10^{7}	490
	Run 3 (1/8-in. NaF pellets)							
Fluorination	5.9×10^{2}	74	4.1	2.2×10^{3}	18	4.9×10^{2}	2.0×10^{4}	66
NaF bed	5.0	11	6.2	3.2	66	1.8	1.7	21
Overall	3.0×10^{3}	830	25	7.1×10^{3}	1.2×10^{3}	9.0×10^{2}	3.4×10^{4}	1400

[a]Corrected for UX_1-UX_2 growth where necessary.

Results of analysis of the activity on the beds and of its distribution were inconclusive, possibly because of analytical inaccuracy at low activity levels. The activity distribution in each bed indicated two types of contamination in the UF_6 gas stream——volatile material which is chemically sorbed and particulate material which is filtered out. In all cases chromium was removed from the product stream.

Difficulty was encountered with plugging in both of the 12-20 mesh runs. In one case, the copper foil support for the NaF ignited; in the other the plugging was in the NaF. Although some of the difference in decontamination is attributed to the difference in NaF particle surface, part was due also to higher decontamination in the fluorination step itself, possibly influenced by the plugging difficulties with the 12-20 mesh material. Definite, but not altogether consistent, differences were observed in the way the various elements were distributed in the beds. The cesium and rare earth activities were usually present to a large extent in each part of each bed, emphasizing perhaps a poor filtration efficiency for fine particulates (cesium and rare earth fluorides are nonvolatile). The niobium activity (niobium forms a volatile fluoride) represented the other extreme in being efficiently trapped in the first quarter of each bed. Generally, including plutonium and chromium, more than 50% of the material was trapped on the first quarter of each bed.

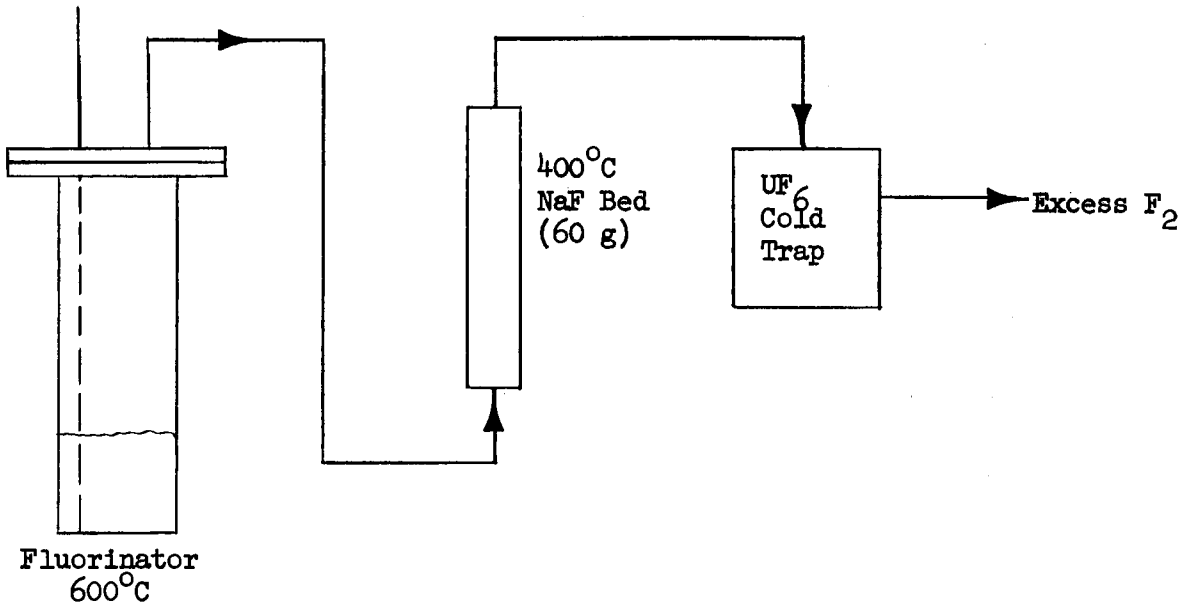

Fig. 9.2. Experimental Arrangement Used in Comparison of 1/8-in. Pellets and 12-20 Mesh NaF for Volatility Process.

The three runs were made without the normal absorption-desorption procedure of the volatility process, i.e., the UF_6 was trapped immediately following the 400°C NaF bed which was located after the fused salt fluorinator (Fig. 9.2). The 400°C NaF bed consisted of about 60 g of material held in a 1-in.-dia by 6-in.-long nickel reactor. The uranium charge volatilized from molten $NaZrF_5$ at 600°C by fluorine varied from 15 to 43 g. After each run all the UF_6 product was hydrolyzed with 1 M $Al(NO_3)_3$, while each NaF bed was roughly quartered, dissolved in 0.67 M $Al(NO_3)_3$—4 M HNO_3 solution, and then analyzed.

Corrosion Studies* (W. E. Clark). Hastelloy W showed the lowest corrosion rate in $NaF-ZrF_4$ + HF at 650°C, both by weight loss and by metallographic examination for cracking, of materials tested:

*Work done by Battelle Memorial Institute under subcontract.

Specimen Material	Time, hr	Corrosion Rate, mils/month	
		By Wt Loss	By Metallography
Inconel	2	2.0	1410
Inconel	24	38.6	--
Inconel	36	13.5	120
Inconel	96	22.2	85
Hastelloy W	250	Gained 80 mg	--
INOR-8	250	0.09	--
Nickel	192	8.9	--

No appreciable cracking was observed after 250 hr exposure. Both Nickel-A and INOR-8 showed intergranular cracking, but with the latter alloy cracking was observed only at the point of impingement of the bubbles of HF on the specimen.

10.0 APPENDIX

PUBLICATIONS AND SPEECHES

ORNL-2127, Part II, Vol 1., "Uranium-235 Fission-Product Production as a Function of Thermal Neutron Flux, Irradiation Time, and Decay Time. II. Summations of Individual Chains, Elements, and the Rare-Gas and Rare-Earth Groups," J. O. Blomeke and Mary F. Todd (Unclassified)

ORNL-2415, "Radioactive Waste Disposal, Report on Seepage Pit Liquid Waste-Shale Column Experiment," W. J. Lacy (Unclassified)

ORNL-2416, "Chemical Technology Division Monthly Report for September 1957," F. L. Culler et al. (Confidential)

ORNL-2443, "Progress Report on Raw Materials for September 1957," K. B. Brown et al. (Unclassified)

ORNL CF No:

53-5-172, Rev., "Cost Estimate Check List for a New Project," W. G. Stockdale, (Unclassified)

57-8-30, Supplement, "Nuclear Considerations in Design of High-Temperature Process Heat Reactors," J. T. Roberts (Unclassified - Internal Use Only)

57-8-30, Rev., "Nuclear Considerations in Design of High-Temperature Process Heat Reactors," J. T. Roberts (Unclassified)

57-10-34, "Thorex Pilot Plant Run HD-20 Summary," W. T. McDuffee and J. F. Manneschmidt (Secret)

57-11-69, "Trip Report: Power Reactor Fuel Reprocessing and Waste Efforts at Idaho Chemical Processing Plant and Hanford, September 25 to October 2, 1957," R. E. Blanco, J. J. Perona, and H. E. Goeller (Secret - Internal Use Only)

57-11-76, "Proposal to Irradiate Fluorocarbons in the New Cobalt Facility," T. A. Gens (Confidential - Internal Use Only)

57-11-120, "Aqueous Slurries: Information for AEC Reactor Handbook," J. P. McBride (Unclassified)

57-11-145, Supplement 2, "PAR Loop Schedule Review," B. B. Klima (Unclassified)

57-12-9, "An Evaluation of Asphalt and Other Materials for Lining Radiochemical Waste Storage Basins," A. J. Hoiberg, C. D. Watson, and G. A. West (Unclassified)

57-12-31, "Miscellaneous Information Concerning Thorex Short-Cooled Processing," W. L. Albrecht (Secret - Internal Use Only)

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57-12-78, "Preparation of U-233-Aluminum Alloy Fuel Elements: An Analysis of U-233 Availability and Anticipated Radiation Hazards," E. D. Arnold and A. T. Gresky (Secret)

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57-12-96, "Method for Separating Hafnium from Zirconium," T. A. Gens (Confidential - Internal Use Only)

57-12-108, "Heat Transfer Calculation for Irradiation of UO_2-Zr-2 Clad PWR Blanket Rods in the MTR," E. J. Frederick (Confidential - Internal Use Only)

57-12-116, "Activity Specifications for Thorium and U-233 Products of the Thorex Process," E. D. Arnold (Confidential - Limited)

57-12-120 Rev., "Program Proposal - Transplutonic Study," W. K. Eister, R. E. Leuze, E. D. Arnold, and H. E. Goeller (Confidential - Limited)

57-12-122, "Estimate of Potential Fuel Reprocessing, Rev. No. 21, Part A," J. W. Ullmann (Unclassified)

57-12-24, "Estimate of Potential Fuel Reprocessing, Rev. No. 21, Part B," J. W. Ullmann (Unclassified)

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"Continuous Centrifugation in a Disk Centrifuge," S. H. Jury and W. L. Locke, A.I.Ch.E. Journal, pp. 480-483, December 1957.

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