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ORNL-2417
Chemistry-Separation Processes for Plutonium and Uranium

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CHEMICAL TECHNOLOGY DIVISION

MONTHLY PROGRESS REPORT

OCTOBER 1957

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CHEMICAL TECHNOLOGY DIVISION

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July 31, 1957	ORNL-2379 ($5.00)
Oct. 31, 1957	ORNL-2432 (in press)

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. Washing of thorium amalgams, produced by sodium amalgam reduction of $ThCl_4$, with 1% versene decreased the oxide content of sintered billets by a factor of 2. In mercury recovery studies the thorium in dilute amalgams was decreased from 3000 to 60 ppm by anodic treatment in 1 M Na_2CO_3 for 8 hr at 8 volts; 15% of the mercury was lost to the aqueous phase.

Fluorox Process. In further tests on the flame reactor for oxidation of UF_4 to UF_6 with oxygen at temperatures above 1000°C, the CO flame used for heating the reactor to initiate the reaction was extinguished when fluidized UF_4 was introduced. This was probably the result of the quenching effect of the cold powder. In further tests on the 3-in.-dia fluidized bed reactor, UO_2F_2, a by-product of the oxidation, was fluidized at 800°C with nitrogen for 2 hr without agglomeration. CO was completely burned in O_2 in this reactor, but the temperature could not be maintained at the desired 840°C at the CO flow rate of 3-6 ft^3/hr used.

Excer Process. In tests on iron reduction, as a substitute for electrolytic reduction, of uranyl to U(IV) salts, Fe^{++} was removed from U(IV) by factors of 5-40 by continuous anion exchange in the 2-in.-dia column.

II. Heterogeneous Power Reactor Fuel Processing

Head-end Treatments for Solvent Extraction Processing. Engineering scale Darex process dissolver off-gas rectification tests indicated that it is not feasible to obtain a pure water rectifier overhead with the Darex flowsheet. The rectifier has been replaced with a downdraft condenser. In batch experiments on removal of chloride from dissolver solutions

*Work on raw materials processing, Chemical Development Section C, K. B. Brown, Section Chief, is reported separately.

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more than 1 vol of 15.8 M HNO_3 was necessary to oxidize the chloride and remove it from solution.

Following Zircex process hydrochlorination of Nb-Zr-U alloys at 400 and 600°C >99% of the uranium was recovered in aqueous nitrate solution. No finely divided metallic residues were observed after hydrochlorination and no violent reactions during nitric acid dissolution of the residues. Small amounts of impurities in the hydrogen chloride gas did not affect the hydrochlorination. Uranium alloys dissolved readily in molten $3ZrCl_4 \cdot 2POCl_3$ at 360°C in the presence of chlorine.

In laboratory-scale aqueous dissolution studies H_2O_2, CrO_3, MnO_2, or $Na_2Cr_2O_7$ contributed to uranium losses of up to 95% during sulfuric acid dissolution of stainless steel. Essentially all radioactivity in a sulfuric acid decladding solution was due to activated components of the stainless steel jacket. A total of 2.4% of the β and 9.1% of the γ activity from mixed fission products was leached from a $CaSO_4$ cake made by neutralizing H_2SO_4 decladding solution with lime. Uranium was quantitatively recovered on Dowex 1 resin from a simulated stainless steel sulfate decladding solution while plutonium tracer was not sorbed in the same experiment. Flowsheets were developed for the decladding and feed preparation steps and head-end solvent extraction cycle for the Yankee Atomic fuel processing by the Sulfex process.

A zircaloy-2 clad UO_2 fuel element was stripped by 9 M HF with a uranium loss of 0.5%. The decontamination factor for the separation of zirconium from uranium in a fluoride decladding solution, on Duolite C-65 cation exchange resin was 28 with 84% uranium recovery.

Dissolution rates of sintered 96% ThO_2—4% UO_2 pellets were fairly constant, 5.4-6.2 mg/cm^2.min, in 13 M HNO_3 containing 0.04-0.05 M fluoride. Insoluble ThF_4 formed at lower fluoride concentrations.

A simulated Yankee Atomic fuel element subjected to electrolytic dissolution at 50°C in 3 M HNO_3 containing 1.1 M stainless steel had 82% of its jacket and 5% of its core dissolved in 6 hr. The current efficiency was 71%. In 3 M HCl neither tin nor zirconium was preferentially attacked in the dissolution of zircaloy-2. Graphite was a satisfactory anode in 3 M HCl. After the dissolution of 1-1.5 kg of zirconium or zircaloy-2 and 2 kg of stainless steel in the 3 M HCl the platinum anode used showed a negligible weight loss.

In corrosion studies the tensile properties of Haynes 25, S-816, Inconel, Hastelloy C, Illium R, and Carpenter 20 were not adversely affected by the HCl-H_2 atmosphere during the Zircex hydrochlorination cycle. In boiling $AlCl_3$-NH_4Cl Hastelloy B was corroded at rates of 2.0 and 11.4 mils/month in the vapor and liquid phases, respectively, in a 24-hr test. S-816, Haynes 30, and Haynes 36 were less satisfactory in the liquid phase.

In preliminary tests in the ZrF_4.NaF-HF system Inconel was corroded at rates of 13 and 22 mils/month.

In materials evaluation studies, Chemfast, an epoxy resin base concrete, showed excellent resistance at room temperature to 3 M solutions of HCl, H_2SO_4,

HNO_3, and NaOH and to demineralized water for two weeks. Glascote, a polyester coating for concrete surfaces, blistered when irradiated to 10^9 r in water.

In liquid metal fuel processing studies, the average uranium separation factor was about 240 when equal volumes of molten U-Bi alloy and $BiCl_3$-LiCl-KCl were equilibrated at 550°C.

Waste Metal Recovery. Processing of the plutonium-aluminum alloy rod from the Chalk River NRX reactor was completed. A total of 181.82 g of plutonium was isolated as purified product, which represents 99.86% recovery. Two cycles of solvent extraction were required to obtain a gross gamma decontamination factor of 4.7×10^5.

Thorex Process. One pilot plant run, SD-2, was completed on thorium irradiated to about 3500 g/t and decayed 32 days; two-cycle operation was continuous for 329 hr. Potassium iodide in the dissolver and sodium bisulfite in the first and second cycle feeds were maintained by continuous metering. A total of 1400 kg of irradiated thorium was processed to isolate 4700 g of U-233 by ion-exchange and to separate 710 g of Pa-233 for decay storage. The thorium and uranium solvent-extraction losses averaged 4 and 0.47%, respectively. Average overall gross γ decontamination factors were 1.9×10^4 for thorium and 1.3×10^7 for uranium. Specifications were exceeded for the thorium product by 150 for gross gamma emitters and for the uranium product by 400 for ruthenium.

Equipment performance was good. The Fulflo filter elements in the organic streams were changed daily owing to the rapid rise in radiation intensity, which exceeded 100 r/hr after 24 hr. Additional shielding installed after run SD-1 effectively reduced the radiation levels in required access areas to permit continued operation. Operation of the third uranium cycle continued to be poor. Installation of the interface purge system was completed.

Additional 2-in.-dia pulsed column solvent-extraction runs made with specially prepared oleum-pretreated Decalin diluent indicated no improvement in flooding rates or HETS as compared to previous runs. Flooding rates at 50 and 80 cpm pulse frequencies were 554 and 310 gsfh, respectively. The HETS at 60 cpm was about 6 ft.

In laboratory studies Pilot Plant solvent was more efficiently decontaminated with a lime slurry than by the present carbonate treatment. Sulfite added to the Thorex feed to increase ruthenium decontamination reacted with nitrate at elevated temperatures to produce NO gas. Ruthenium was partially eluted from an ion-exchange resin column containing uranium without removal of appreciable uranium.

Waste Treatment and Disposal. In further studies synthetic alkaline waste was decontaminated from Cs-137 and Sr-90 in the continuous ion-exchange contactor with decontamination factors of 10^4-10^5 at rates of 2000 gal/hr.ft^2. In the first stage of a three-stage acid-base cell for the recovery of nitric acid and caustic from synthetic waste, current efficiencies were 75% and the power consumption was 6.2 kwh per pound of caustic produced. Nitric acid of 1.3 N and sodium hydroxide of 1.5 N were produced.

An adiabatic self-evaporating waste system is being designed.

Nonaqueous Processing. Final data on the seven volatility runs in the Fused Salt--Fluoride Volatility process Pilot Plant showed that 84% of the uranium entering the system as UF_6 was recovered in the product cylinders. Recoverable losses were ~11%, and nonrecoverable losses were 0.03%, for a material balance of 95%.

The facility for study of the dissolution of zirconium-containing fuel elements in fused salt and HF is undergoing minor modifications indicated by preliminary leak tests.

In laboratory tests the formation of the nonvolatile U(V) complex in the NaF absorption traps increased with temperature up to 450°C.

Installation of the portion of the high-activity-level-volatility laboratory covered by the initial design was completed. Equipment is being designed and fabricated to introduce an irradiated PWR fuel element into the cell, after which it can be charged to the hydrofluorinator. A handling device for small shielded carriers is also being designed.

Partial crystallization or freezing appeared promising as a method of separating fission products from ZrF_4-containing fuel. Non-zirconium-base fuels were partially purified by a CaO precipitation.

In studies on the Druhm process, 20 g of uranium metal was recovered from a UF_6 reduction run, about 30% yield. Difficulties in operation centered around the inlet nozzle design and the attack of uranium metal on the Inconel reactor walls.

III. Aqueous Homogeneous Reactor Fuel and Blanket Processing and Development

HRT Chemical Plant. The HRT Chemical Processing Plant hydroclone system was operated as a part of the reactor complex throughout the final 300-hour test operating period. Operation was normal except for gross leakage through two valves in series following a high-pressure sampling procedure. The system was isolated from the reactor to stop the leakage, which admitted fuel solution to the processing plant low-pressure system. Subsequently it was noted that the circuit for the interlok designed to divert such leakage back to the reactor dump tank had not been completed. One leaking valve was replaced to permit further operation and subsequent samples were obtained without incident.

Slight chloride contamination (5—10 ppm) was noted in the leak-detector-pressurization tank during replacement of a broken sight glass. The entire heavy water charge in this system (~10 liters) was removed and discarded and the system recharged with new D_2O.

Uranyl Sulfate Fuel Processing. Adsorption of simulated mixed corrosion product oxides traced with Fe-55 onto type 347 stainless steel test pins apparently reached an equilibrium value of 20 or 45 $\mu g/cm^2$ at 26°C with slurries containing

100 or 1200 mg of solids/kg H_2O. Similar slurries traced with Zr-95 continued to show activity buildup on the pins after 164 hr of contact.

Studies on the removal of iodine from steam-oxygen mixtures by some form of silver have continued in the laboratory and in the HRT mockup loop. With silvered alundum as the iodine trap in the low-pressure portion of the HRT mockup the trap efficiency was significantly increased by operation at 150°C instead of 120°C. In laboratory studies a column packed with silvered York mesh was less effective than one packed with silvered alundum. This lower efficiency was due to lower surface area per volume of packing and channeling. In a partially saturated silvered alundum bed the iodine decreased exponentially with distance traveled through the bed. As the silvered alundum approached saturation with iodine, diffusion of iodine through the AgI already formed controlled its rate of removal from the gas stream. The manner of firing the silvered alundum during that stage of its preparation affected its iodine-absorbing qualities. An atmosphere of hydrogen during heating and cooling as well as heating times longer than 1 hr at a temperature greater than 400°C are indicated.

Gaseous Fission-product Disposal. In dynamic studies of the adsorption of fission gases by charcoal, the number of theoretical chambers in a long trap was less than the sum of the chambers in its component parts. Linde's molecular sieves 10X and 13X were better adsorbents than 5A and 4A, which were about equal in performance. In laboratory equilibrium studies, however, the 5A material was 25 times better than the 4A and 1.5 and 1.9 times better than the 13X and 10X materials, respectively, at 28°C and 100 mm pressure of krypton.

Uranyl Sulfate Blanket Processing. In P-1 loop runs, using preformed ZrO_2 as a substitute for PuO_2, the half-time for solids disappearance from circulating 1.4 m UO_2SO_4 at 250°C was 2-4 hr. Only 6-16% of the ZrO_2 was removed in the hydroclone underflow, and 85-90% was removed by adsorption on loop walls.

The P-1 loop was operated 111 hr (93 hr at 250°C) with 1.2 m UO_2SO_4 containing 1.3-1.7 mg of plutonium per liter added as dissolved $Pu(SO_4)_2$. Of the 21.4 mg added to the loop feed, 93.4% remained in solution, 2.7% was adsorbed on the walls, and 0.1% was removed as solids in the hydroclone. Pu(IV) and corrosion product chromium were oxidized to the hexavalent states by the oxygen overpressure. Plutonium adsorption on well-conditioned type 347 stainless steel coupons averaged only 0.0004 $\mu g/cm^2$.hr compared to 0.009 $\mu g/cm^2$.hr previously obtained in static tests under similar conditions. Adsorption on well-conditioned titanium and zircaloy-2 was approximately the same as that on stainless steel, probably because they were covered with iron and chromium oxides and thus behaved as stainless steel. The corrosion rate, based on nickel analysis, was ~17 mpy. Of the 26 g of iron corrosion product, only about 0.5% was removed in the hydroclone underflow. The remainder accumulated in the loop.

In 16 hr, plutonium adsorption on titanium and zircaloy-2 at 250°C under 170 psi O_2 from 1.4 m UO_2SO_4 containing 0.54 m H_2SO_4 and 2.2 mg of plutonium per liter was only 0.007 and 0.008 $\mu g/cm^2$, respectively compared to 0.07 and 0.17 $\mu g/cm^2$ previously obtained in the absence of acid. The rate of plutonium adsorption from acidified uranyl sulfate appeared to decrease with time. In 242 hr the average plutonium adsorption rate on titanium and zircaloy-2 from

1.4 m UO_2SO_4 containing 0.54 m H_2SO_4 and 50 mg of plutonium per liter (at 250°C under 170 psi O_2) was 2×10^{-4} and 6.2×10^{-4} μg/cm^2.hr, respectively.

In scouting tests in which various solids were equilibrated at 250°C with 1.4 m UO_2SO_4 containing 15 mg of plutonium per liter, Zr, ZrO_2, $Zr(OH)_4$, and $Zr(SO_4)_2$ partially removed plutonium from solution. The $Zr(OH)_4$ was most effective, removing ~98% of the plutonium.

Thorium Oxide Slurry Development. Thorium oxalate of 1 μ average size, equivalent to 750 lb of oxide, was prepared in the coaxial-flow jet mixer. Sintering was pronounced in the high-fired oxides produced from this material. The precipitation setup is being revised in an effort to produce a purer and more uniform material.

Thorium oxide prepared by 1600 and 1400°C firing of jet-precipitated oxalate was discolored and contained a large fraction of sintered material, presumably the result of impurities. Test firing at 1600°C of thorium oxide prepared from batch-precipitated oxalate (800°C firing) resulted in apparently satisfactory products. The batch precipitation facility was reactivated for the production of small-particle material. The DX-908 flocculating agent was used to facilitate the filtering operation.

An 800°C fired pilot plant oxide prepared from the jet-precipitated oxalates showed a pronounced tendency to form "sized" spherical agglomerates during sieve analyses. Sieve analyses of 1600°C pilot plant fired oxide as prepared and after micropulverizing were readily carried out. Unlike the laboratory-fired oxide, the 1600°C pilot plant fired oxide was difficult to grind in small-scale laboratory tests and had a higher tap density.

Thorium oxide prepared by firing the hydroxide was much softer when the hydroxide was washed with alcohol rather than water or ammonia. The oxide products did not appear to be suitable slurry materials.

The Davison thoria sol as received, with 10% excess water, and diluted 1:1 with water was broken by heating in the dash-pot bomb at 300°C. In-pile and out-of-pile tests at 200°C were stirred for 322 hr and 363 hr, respectively, but the treatment destroyed the sol.

Out-of-pile studies on the effect of MoO_3 concentration on the recombination of hydrogen and oxygen in aqueous slurries of thorium-uranium oxide were continued. The recombination rate (after H_2 activation) in a slurry of a simple mixture of 1600°C fired thorium oxide and $UO_3.H_2O$ and containing 0.06 m MoO_3 was 20.8 moles H_2/hr.liter at 291°C and a hydrogen partial pressure of 500 psi. In a slurry of 1600°C fired thorium-uranium oxide, prepared from the coprecipitated oxalates, containing 0.012 m MoO_3, the rate after H_2 activation was 56.3 moles H_2/hr.liter at 250°C and a hydrogen partial pressure of 500 psi.

IV. Chemical Engineering Research

Interfacial Area Measurement. A procedure for measuring liquid-liquid interfacial areas by use of the $F^{19}(\alpha,n)Na^{22}$ reaction is being developed;

background and calibration measurements show practical relative values.

Inline Instrumentation. Development of the following inline instruments is in progress: a digital interface level controller based on differences in electrical conductivity of the two phases; an a-c polarograph for monitoring uranium and a falling-stream gamma activity monitor; and turbine and electromagnetic flow rate meters.

Part I. FEED MATERIALS PROCESSING

1.0 METALLEX PROCESS
Program Leader: O. C. Dean

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

1.1 Effect of Various Washing Procedures on the Integrity of Sintered Thorium Billets

In experiments to select washing procedures that would minimize cracking and production of large voids due to chloride volatilization, catholysis for 15 min at 3 volts with water, 1 N NaOH, or 1 N NH_4OH and washing with 1% versene were tried. Results were scattered, and the only procedure that demonstrated a consistent advantage over the conventional $HCl-H_2O$ wash was the 1% versene washing, which decreased oxide content by a factor of 2, and gave billets which, to visual inspection, contained the least cracks and voids.

The washed amalgam samples were dried in the amalgamated phase separator, filter-pressed, and vacuum distilled to thorium billets. Bulk densities and ThO_2 contents were measured, and each billet was visually inspected for cracks and voids.

1.2 Removal of Residual Thorium from Dilute Thorium Amalgams

In mercury recovery studies 8 hr anodic treatment of dilute amalgams decreased the thorium content from 3070 to 60 ppm, but 15% of the mercury was lost to the aqueous phase. The anolyte was 1 M Na_2CO_3, and the voltage was 8 volts.

Electrolytic removal of thorium by cathodizing the amalgam for 6 hr at 8 volts removed less than 1% of the initial 12,500 ppm of thorium.

2.0 FLUOROX PROCESS
Program Leader: J. C. Bresee

In the Fluorox process, UF_6 is prepared by oxidizing UF_4 with oxygen or dry 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.

2.1 Fluidized Bed Oxidation Reactor (J. B. Adams)

A fluidized bed of 40 x 100 mesh sand was maintained at a temperature of 800-840°C by burning CO only by use of an external wall heater. There was no detectable unburned carbon monoxide in the off-gas. The $CO-O_2$ reaction is probably surface-catalyzed and the large surface area of the fluidized bed helps bring the reaction to completion. In previous combustion studies commercial carbon monoxide contaminated with both hydrogen and hydrocarbons was used, water vapor being removed to a dew point of -100°F by an absorbent.

In the conversion of UF_4 to UF_6 with oxygen, a by-product is UO_2F_2. A fluidized bed operating at steady state will be predominately UO_2F_2 with relatively small amounts of UF_4 present to decrease the likelihood of reaction of the UF_6 with the UF_4 to produce undesirable intermediates. Also, UO_2F_2 is less likely to fuse on temperature excursions than is UF_4. In a preliminary run with no UF_4 addition, UO_2F_2 was successfully fluidized with nitrogen in the 3-in.-dia reactor at 800°C for 2 hr without agglomeration.

2.2 Flame Reactor (C. D. Scott, W. G. Sisson)

The flame reactor is used to react UF_4 continuously with O_2 in a CO-O_2 flame at temperatures in excess of 1000°C ($3UF_4 + O_2 \longrightarrow UO_2 + 2UF_6$).

Flame Tests. In flame tests with an all-metal burner assembly (Fig. 2.1) and pure (99.5%) dehydrated CO and O_2, the pilot light and main flame could be ignited only when water vapor was added to one of the gas streams. The main flame could be maintained without water vapor after it had been ignited and allowed to heat up the burner assembly and the reactor walls. Control of the flame was much more difficult than when commercial-grade CO was used. Decreasing the water vapor content in the fuel gases extended the flame length, probably because of the slower burning rate in the absence of the catalyzing water reactions ($H_2O + CO \longrightarrow CO_2 + H_2$; $H_2 + 1/2O_2 \longrightarrow H_2O$).

Analysis of the exhaust gases from the reactor, even with no water vapor present, indicated that there was complete combustion of the CO (less than 0.1% CO in exhaust gases at operating conditions of 3.0 cfm total gas flow with 50% CO).

Run with UF_4. In one experimental run (FR-3) with UF_4, approximately 3 cfm of gas, 50% CO, was used. When fluidized UF_4 was introduced to the flame at a rate of 200 g/hr by the fluidizing gas, the flame was immediately extinguished. This result was probably due to the quenching effect of the relatively concentrated and cold UF_4 powder. Removal of too much heat from the flame would reduce the flame temperature and burning velocity and thus cause the flame to blow off.

2.3 Thermodynamic Studies (L. M. Ferris)

A topical report (ORNL-2401) on the decomposition of UO_2F_2 at high temperatures, including data presented in ORNL-2416, is in press. The abstract of this report follows:

> The thermal decomposition of uranyl fluoride was studied by a thermogravimetric technique between 750 and 880°C. The decomposition reaction at atmospheric pressure is $3UO_2F_2 \longrightarrow 2/3U_3O_8 + UF_6 + 1/3O_2$. In dry helium the rate of reaction was first order in UO_2F_2 with indications that it was also dependent on the gas flow rate. The rate constants determined in dry helium (flow rate 300 ml/min at 25°C) may be expressed as log k (min^{-1}) = 11.57-15700/T. In preliminary experiments with dry air and oxygen the rate decreased with increasing oxygen partial pressure; however, insufficient data were obtained to derive a quantitative relation.

The effect of sublimation of UO_2F_2, as a parallel first order process, was observed at temperatures above 825°C.

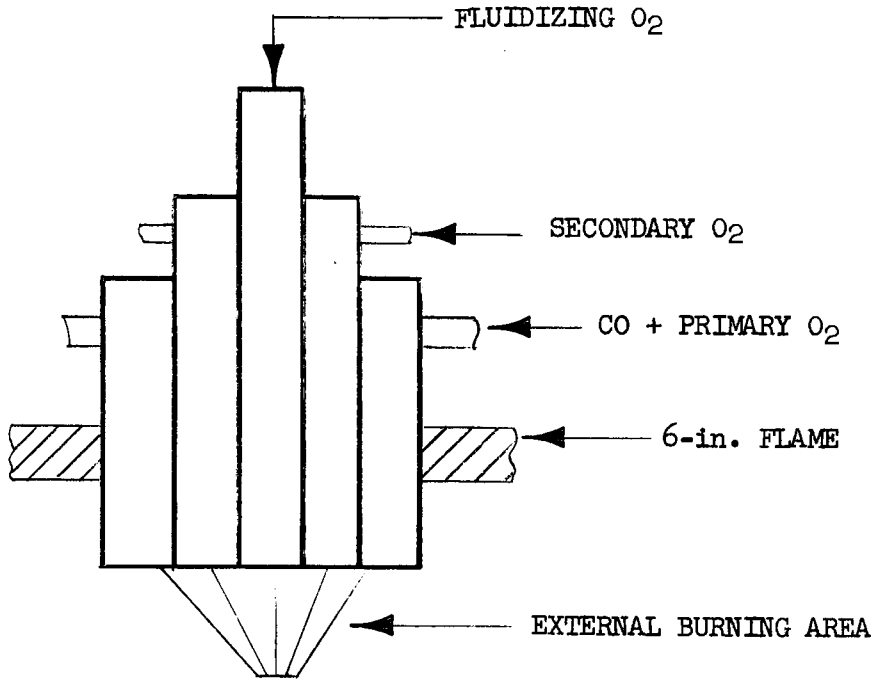

Fig. 2.1. All-metal Burner for Fluorox Flame Reactor.

3.0 EXCER PROCESS
Program Leader: I. R. Higgins

The Excer process is an aqueous process for the production of uranium tetrafluoride in which a uranyl salt is reduced to a U(IV) salt and UF_4 hydrate is precipitated and then dehydrated. The feed for the reduction step may be prepared by ion exchange.

3.1 Reduction by Iron (I. R. Higgins, R. R. Holcomb, W. J. Neill)

Reduction of the uranyl ion by iron has been considered in previous monthly reports. In tests on removal of iron from the reduced sulfate product by ion exchange in the 2-in.-dia continuous contactor, ferrous iron broke through an anion exchange bed immediately with a uranium loss of ~0.0001 g/liter.

Sulfate in the UF_4 hydrate product was decreased from 320 to 180 ppm in 2 hr of drying at temperatures up to 450°C and to 150 ppm in 3.5 hr drying at temperatures up to 500°C.

3.2 Precipitation (L. E. McNeese)

Precipitation of UF_4 hydrate was studied with a solution containing 9.8 lb of uranium produced by dissolving ore concentrate in acid recycled from a previous

precipitation step and processing through ion exchange and electrolytic reduction. The feed to the precipitation step had a uranium concentration of approximately 156 g/liter and was fed at a rate equivalent to 1.1 kg of uranium per hour. Five kilograms of dry hydrate was produced. The overall material balance for the run showed 6% loss, resulting in part from the precipitation of UF_4 from the recycled acid stream on cooling. The temperature dropped to between 90 and 93°C during precipitation (instead of the more desirable 100°C) and the dried filter cake had a low tap density, 1.6 g/cc. Photomicrographs of this material can be contrasted with material of tap density 3.8 produced in a previous run (Ex-P6) (Fig. 3.1). The material met all impurity specifications except calcium. The Monel precipitation vessels used showed severe attack, and have now been replaced with vessels and agitators of Hastelloy C.

3.3 Dehydration (L. E. McNeese)

Batch dehydration of the flow-sheet demonstration material was completed. The material was tabletted at 50,000 psi and then at 350°C for 8 hr and at 450°C for 8 hr. Feed and product analyses for water and AOI content have not been completed. Screen analyses for feed and product showed no significant changes in particle distribution. Tap density before and after dehydration was approximately 3.0 g/cc.

Part II. HETEROGENEOUS POWER REACTOR FUEL PROCESSING

4.0 HEAD-END TREATMENTS FOR SOLVENT EXTRACTION PROCESSING
Program Leader: H. E. Goeller

Various head-end treatments, both 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 the fuel in dilute aqua regia and stripping off the chloride before the nitric acid solution is solvent-extracted.

Engineering Studies (F. G. Kitts, B. C. Finney, J. J. Perona, J. Beams, F. L. Rogers). In further attempts* to obtain pure water overhead from a Darex rectifier located above the dissolver and HCl stripper two additional rectifier runs and several Gillespie still runs were made. Results of these tests indicate that rectification of pure water is not feasible in the range of interest of the Darex flowsheet.

In one experiment 1.5 M HNO_3—0.5 M HCl was fed to the rectifier, which was operated at a V/L ratio of 1.25. The 20% of the condensate withdrawn was 0.4 M HNO_3—0.4 M HCl. The same concentration existed throughout most of the column. In a second test, 5 M HNO_3—2 M HCl was fed to the rectifier, which was operated at total reflux. This run resulted in 2.0 M HNO_3—2.0 M HCl throughout most of

*Results of previous tests in ORNL-2416.

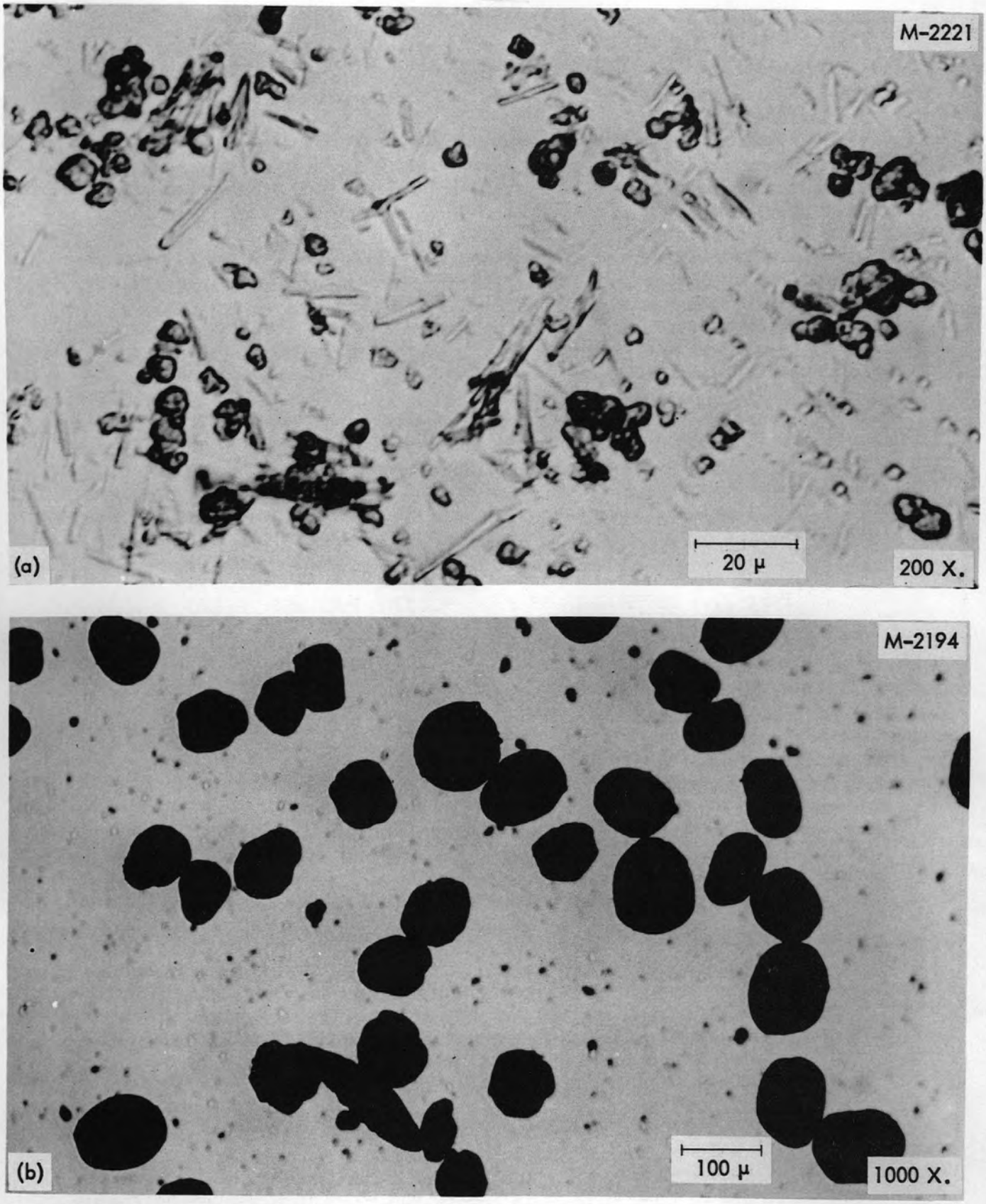

Fig. 3.1. UF_4 Hydrate Prepared by Excer Process. Tap density (a) 1.6 g/cc; (b) 3.8 g/cc.

the column. A third run with 0.315 M HNO_3—0.135 M HCl feed resulted in a nearly pure water overhead; however, the total H^+ at the bottom plate was only 0.1 M. A plot of acid normality versus plate number for the first two runs is given in Fig. 4.1.

These data indicate that gaseous decomposition products in the rectifier cause a shift in the HNO_3-HCl-H_2O equilibriums. Material balance calculations based on Gillespie still data show that >1% HCl decomposition occurs above 0.7 M HCl—5 M HNO_3 or 1.5 M HCl—3 M HNO_3 feed.

The Darex engineering-scale unit is being modified by substitution of a downdraft condenser for the rectifier. After the new loop—consisting of a dissolver, condenser, stripper, and nitric acid reboiler—has been operated satisfactorily, a feed adjustment tank and rectifier will be evaluated separately before incorporation with the overall loop system.

Batch Chloride Removal Studies (J. H. Goode). Several laboratory experiments were made to determine the minimum amount of nitric acid required to effectively remove HCl from Darex dissolver solution to 30 ppm in a batch chloride removal step. Tests were made on both APPR and Yankee Atomic fuel samples. Results show that a greater than equal volume of 15.8 M HNO_3 must be used. Earlier work had shown that addition of 2 vol of 15.8 M HNO_3 and evaporation to 130°C followed by dilution with water to the original dissolver solution volume was satisfactory.

APPR. In the new tests three specimens of APPR fuel plate were dissolved in 5 M HNO_3—2 M HCl to a concentration of about 50 g of stainless steel and 5 g of uranium per liter. An equal volume of 15.8 M HNO_3 was added to the first dissolver solution, which was then evaporated to 130°C, and brought back to original volume with water. About 0.14 M Cl^- remained in the raw feed solution, nearly 100 times greater than specifications. A second dissolver solution was evaporated to 130°C before any nitric acid was added; 50% of the chloride was removed in this operation. The addition of a volume of nitric acid equal to that of the initial dissolver solution and re-evaporation to 130°C brought the chloride in the raw feed to 0.14 M. In a third experiment evaporation to 130°C, followed by the addition of 0.5 vol of nitric acid and re-evaporation to 130°C, reduced the chloride concentration to 0.65 M.

Yankee Atomic. A series of experiments was also made simulating the dissolution and chloride removal steps as applied to Yankee Atomic fuel elements. Specimens of 304L stainless steel were dissolved in a heated pyrex flask equipped with reflux condenser in volumes of dilute aqua regia calculated to yield a solution containing 75 g/liter. The stainless steel samples became passivated, after 70-80% had dissolved, with 1.5 M HCl—5 M HNO_3, 1.6 M HCl—5 M HNO_3, or 1.7 M HCl—5 M HNO_3, but the reaction went to completion in 2.0 M HCl—4.7 M HNO_3. Analysis of the dissolvent showed that 4 moles of H^+ per mole of stainless steel was consumed during the dissolution; 0.24 mole of Cl^- per mole of stainless steel was also consumed or lost from the system.

A quantity of $UO_2(NO_3)_2$ solution was then added to the stainless steel dissolvent to simulate the material after the UO_2 fuel pellets had been dissolved; this solution contained 44 g of stainless steel and 178 g of uranium

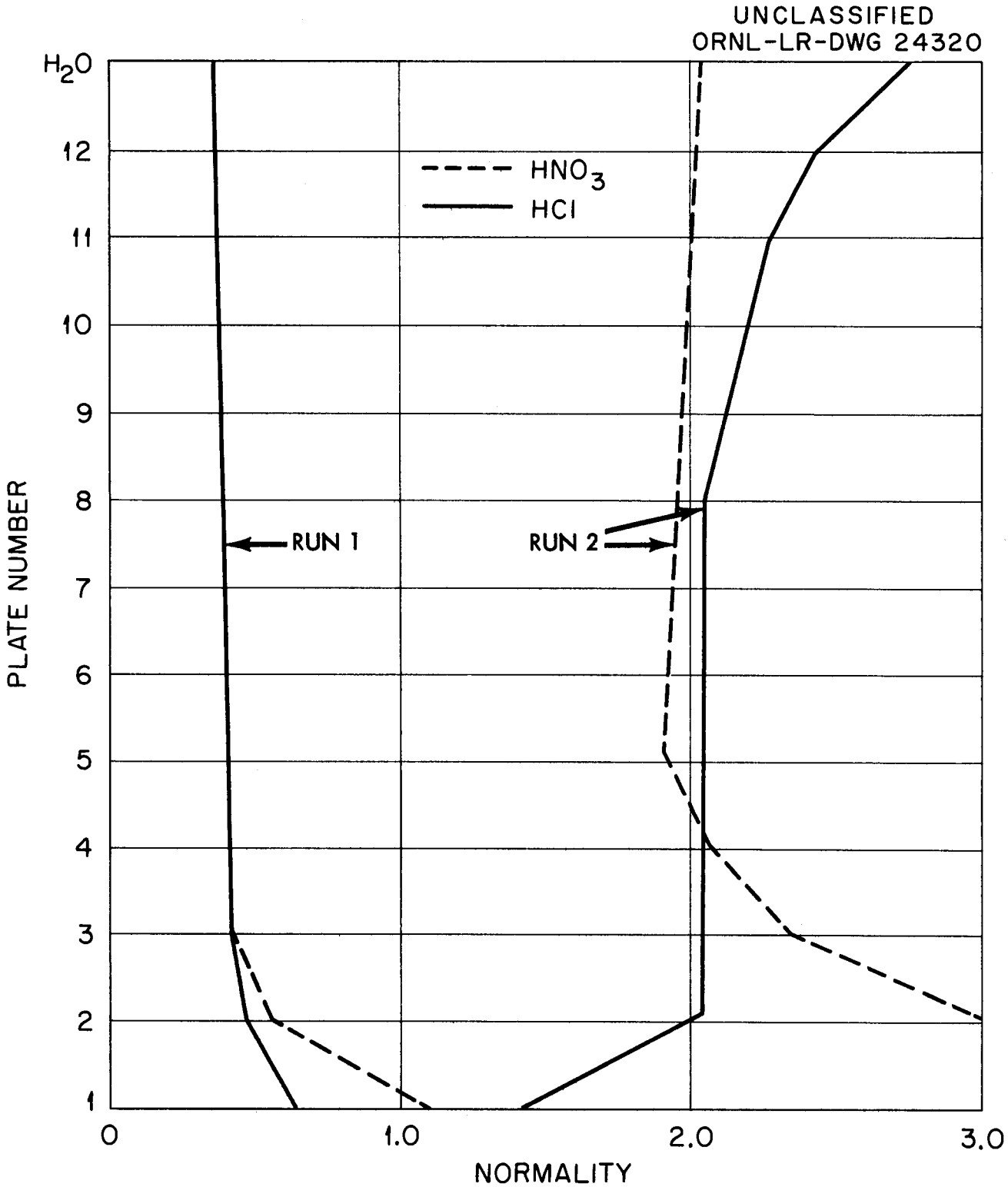

Fig. 4.1. Concentration Profiles in Rectifying Column.

per liter, and 1.26 M H^+ and 1.11 M Cl^-. The solution was evaporated to 126°C and held at this temperature for 30 min without adding excess nitric acid and then diluted back to the original volume with 2.25 M HNO_3 to make a stainless—steel—containing Purex-type of feed. A material balance on the chloride indicated that 88% remained with the feed (1.03 M), 4% was in the condensate collected at 110-126°C, and 8% was apparently oxidized to NOCl or Cl_2 and lost.

4.2 Zircex Process for Zirconium-containing Fuels (J. E. Savolainen, T. A. Gens)

The Zircex process 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 UCl_3 residue may also be processed further by the Hermex or Fused Salt—Fluoride Volatility process (Sec. 8.1).

Hydrochlorination of U-Zr-Nb Alloy. Hydrochlorination of 93.4% U—1.33% Nb—5.27% Zr alloy was studied at 400, 450, 500, and 600°C in a new hydrochlorinator especially designed to study UCl_3 ash nitric acid-insoluble losses. In general, increasing the hydrochlorination temperature increased the amount of niobium in the insoluble residue but did not affect the solubility of the uranium in nitric acid. Reaction rates varied from 1.7 to 4.4 mg/cm^2.min. Uranium losses at all temperatures were less than 1%:

Temp, °C	Reaction Rate, mg/cm^2.min	U Distribution, %			Nb Distribution, %			Total U Loss, %
			Residue			Residue		
		Vapor	HNO_3-soluble	HNO_3-insoluble	Vapor	HNO_3-soluble	HNO_3-insoluble	
400	2.6	0.001	99.7	0.26	13.1	85.9	1.0	0.26
450	3.9	0.33	99.6	0.006	20.0	70.0	~10	0.34
500	4.4	0.01	99.9	0.03	36.1	51.5	12.4	0.04
600	1.7	0.77	99.2	0.02	66.3	29.0	4.7	0.79

X-ray analysis of the nitric acid—insoluble material showed no metallic niobium or zirconium. Examination of the residues from incomplete hydrochlorinations showed that the unreacted metal was in a massive and not a finely divided form. In view of these repeated observations no violent reactions are expected in dissolving the hydrochlorination residue in nitric acid, and none have been observed.

The anhydrous HCl used in the experiment at 450°C was purified by distillation at liquid air temperatures through a phosphorus pentoxide absorber.

Effects of Hydrogen Chloride Purity. Impurities in the hydrogen chloride did not affect the rate of hydrochlorination. Mass spectrographic analysis of a sample of commercially available cylinder HCl showed 0.26% N_2, 0.61% CO_2, 0.07% H_2O, 0.02% Cl, 0.005% O_2, and a small but indeterminate amount of ethylene. The hydrochlorination rate of an STR specimen at 450°C with this cylinder HCl was the same as that with HCl purified by passage through a charcoal bed

that had been previously outgassed at 225°C for 16 hr, i.e., about 18 mg/cm^2.min. The rate of reaction was measured by collecting the hydrogen gas formed by the reaction; completion of the reaction was noted by abrupt termination of the hydrogen flow. No metallic residue remained after hydrochlorination with either gas.

Chlorination of Zirconium in $3ZrCl_4 \cdot 2POCl_3$. The complex compound, $3ZrCl_4 \cdot 2POCl_3$ which has been suggested* for zirconium processing was a satisfactory dissolvent for zirconium-niobium-uranium fuel alloys. Three alloy specimens were reacted in the molten $3ZrCl_4 \cdot 2POCl_3$ at its boiling point, 360°C, while agitated with a chlorine gas stream. Rates were higher for high uranium alloys:

85.4% U—10.6% Nb—4.0% Zr	11.2 mg/cm^2.min
93.4% U—1.33% Nb—5.27% Zr	14.9
90% U—10% Nb	11.7
2% U—98% Zr (STR)	7.5

The chlorinated products were separated by distillation. All the $3ZrCl_4 \cdot 2POCl_3$ complex distilled quantitatively at 360°C and no additional material distilled on heating the residue to 600°C. The residue appeared to consist of two types of materials, a porous gray mass and a dense black solid. Chemical analyses of the residues and distillate are not complete.

The rate of dissolution of zircaloy-2 in molten $3ZrCl_4 \cdot 2POCl_3$ without the use of chlorine was about 1 mg/cm^2.min.

The reaction rate of an STR fuel element section with $POCl_3$ at its boiling point, 105°C, was negligible, 0.0007 mg/cm^2.min.

4.3 Alternate Aqueous Dissolution Studies

4.3.1 Sulfuric Acid Processing of Stainless Steel--containing Fuels (Sulfex)

(J. R. Flanary, J. H. Goode, W. E. Clark, A. H. Kibbey, W. D. Bond)

The use of sulfuric acid is being studied both for removing the stainless steel cladding from fuels with nitric acid—soluble cores and for dissolution.

Effect of oxidants on dissolution of APPR fuel in H_2SO_4. In previous tests in which APPR fuel samples were dissolved in 4-6 M H_2SO_4, only 0.5% of the UO_2 in nonirradiated samples dissolved versus 94% of the UO_2 for fully irradiated specimens. These results indicate that the uranium in the irradiated fuel was oxidized, presumably by H_2O_2 formed in the irradiation, to the soluble UO_2^{++} ion. To test this hypothesis, several H_2SO_4 unirradiated fuel dissolution experiments, in which H_2O_2 was added, were made. It was also hoped that complete solubilization of UO_2 in H_2SO_4 could be achieved by H_2O_2 addition. The results indicated that uranium solubility was increased but never was complete.

In a series of fuel dissolution experiments with 6 M H_2SO_4, 0.01, 0.1, and 0.5 M H_2O_2 was added and the solutions were then heated to 95°C. The uranium solubility was 4% versus 0.5% with no H_2O_2. In another experiment in which an APPR sample was first dissolved without H_2O_2, sufficient H_2O_2 was added at 70°C to make the solution 0.5 M in H_2O_2. The solution was allowed to cool to

*W. C. Fernelius, "Recovery of Zirconium Tetrachloride from Its Complex Compounds," U. S. Pat. 2,695,213, Nov. 23, 1954.

30°C in 3 hr and was reheated to 95°C. The uranium solubilized in this experiment was 50%. When 3% H_2O_2 was added continuously during a 2.5-hr fuel dissolution in 4 M H_2SO_4 at boiling temperatures, 90-95% of the uranium dissolved. The total amount of H_2O_2 added was considerably in excess of that required to completely oxidize all the UO_2 to UO_2^{++}.

Addition of either chromic oxide or manganese dioxide increased the UO_2 solubility but not as much as H_2O_2.

In these tests the APPR fuel samples were first dissolved in 200% excess of 4 M H_2SO_4 at boiling until reaction ceased. Slight excesses of CrO_3 and MnO_2 were then added to each solution and boiling was continued for 2.5 hr. The resulting solutions were filtered and the residues washed first with 5 M HNO_2—2 M HCl and then with HF. The uranium in the HF wash was taken as the uranium loss to residual solids. Material balance data were:

Oxidizing Agent	Uranium Dissolved, %			Uranium Material Balance, %
	H_2SO_4	Aqua Regia Wash	HF Wash	
Continuous H_2O_2	88.1	9.0	1.3	98.4
CrO_3	65.8	31.1	0.4	97.3
MnO_2	66.2	39.4	0.4	106.0

The oxidizing effect of $Na_2Cr_2O_7$ in a 6 M H_2SO_4 decladding solution was shown by an increase in uranium losses from APPR fuel specimens. The losses rose from 0.5% in a dichromate-free control sample to 4% in the presence of 0.005 M $Na_2Cr_2O_7$ and to 69% in the presence of 0.05 M $Na_2Cr_2O_7$.

Calculations of H_2O_2 Formation in APPR and Yankee Atomic Fuel Decladding Solutions. The H_2O_2 formed in APPR and Yankee Atomic fuel decladding solutions was calculated to be 1.5×10^{-5} and 4×10^{-3} M, respectively.

An APPR type of fuel element, containing 500 g of U-235 and 5000 g of stainless steel, about 30% burnup and decayed about 150 days, would contain about 5×10^4 curies of residual β activity. Using an average energy for the radiation of 1 Mev and G value for H_2O_2 formation in unaerated H_2SO_4 of 0.80, calculations indicate that the H_2O_2 concentration in the 100 liters of well-mixed decladding solution would be about 1.5×10^{-5} M if all the energy was absorbed and none of the peroxide destroyed by the heat during the dissolution. It is possible that the OH^- free radical, formed by the radiation with a G value of about 2.7, would make the total oxidizing power of the decladding solution about 7×10^{-5} M, and thus contribute to additional oxidation of the UO_2.

Calculations based on 417 days' irradiation to 25.6% burnup and 90 days' decay indicated that 3.87×10^5 curies of fission product activity will be

associated with each Yankee Atomic fuel assembly. This activity should produce about 0.01 mole of H_2O_2 per minute in a H_2SO_4 decladding solution, maintaining a concentration of 0.064 M throughout the dissolvent. If the OH^- radical also contributes to the oxidizing power of the acid solution, about 0.015 M oxidant will be present in the dissolver during the decladding operation.

H_2SO_4 Decladding of Irradiated Yankee Atomic Fuel. The uranium loss to the sulfuric acid decladding solution with simulated Yankee Atomic fuel was 0.01%. The fission product β activity at the start of decladding was 0.54 curie per specimen. The activity in the decladding solution, 0.35% of the total β and 1.16% of the total γ activity involved, was essentially all due to activated stainless steel. The 0.54 curie of β radiation in the fuel was calculated to produce and maintain about 10^{-7} M H_2O_2 in the 250 ml of decladding solution; peroxide concentrations of this order apparently had no effect on the uranium loss to the sulfuric acid solution. The amount of β radiation in this experiment, as estimated from counting samples of the solution, was about 10% of that in the case where 94% of the uranium in the actual irradiated APPR specimen was dissolved.

In the experiments duplicate 6-g samples of sintered UO_2 pellets, clad in 304 L stainless steel, were irradiated for 60 hr in the Graphite Reactor, decayed for 5 hr, and reacted in 200% excess of 4 M H_2SO_4 at 100°C for about 23 hr to dissolve the jackets.

Metallographic Examination of UO_2 from Irradiated APPR Fuel Specimens. Metallographic examinations* of irradiated APPR-type fuel specimens indicated essentially no physical breakdown of the UO_2 particles except for possible voids caused by escape of fission gases, and sintering of UO_2 particles, which had been crushed during the fabrication, into larger aggregates by the irradiation. The results suggest that the chemical effects of the ionizing radiation during the dissolution of the fuel specimens were responsible for the high uranium losses.

Miscellaneous Sulfex Experiments. In miscellaneous stainless steel—H_2SO_4 dejacketing experiments, 2-min dissolution rates of UO_2 in boiling 4 and 6 M H_2SO_4 were 0.0015 and 0.0016 mg/cm^2.min, respectively. In the case of stainless steel passivated by treatment with 5 M H_2SO_4 containing 25 mg/ml of dissolved stainless steel, the passivation could be removed by either touching the specimen with iron wire or by treating the passivated sample with fresh boiling 4 M H_2SO_4. In the latter case, however, about 30 min was necessary to break the passivation.

Leaching of Neutralized H_2SO_4 Decladding Wastes. Simulated Yankee Atomic decladding solution, 6 M in H_2SO_4, containing 31 g of stainless steel per liter and spiked with 10^1 c/m/ml of mixed fission products, was neutralized with $Ca(OH)_2$ to a solid cake, dried, and leached with distilled water. The first leach, lasting 10 days, with about 3 vol of water removed 1.6% of the total β activity and 5.7% of the total γ activity that had been in the decladding solution. About 80% of the γ was due to Cs-137. The second leach, with about 10 vol of fresh distilled water and lasting 36 days, removed an additional 0.75% of the gross β and 3.42% of the γ, making a total of 2.4% of the β and 9.1% of the γ removed from the cake by the two leaches. Iron, chromium, and nickel were apparently

*Made by A. E. Richt, Solid States Division.

fixed, since the second leach contained less than 2 ppm of each.

Ion Exchange Recovery of Uranium from Decladding Solution (I. R. Higgins, W. J. Neill). In initial studies on the separation of Fe(II) from U(IV), in a stainless steel—sulfuric acid cladding solution, on Dowex-1 anion-exchange resin, uranium recovery was quantitative, with a decontamination factor of 3.8×10^3. Plutonium tracer was not sorbed, more than 99.5% following the zirconium into the waste solution. In the presence of the large amount of Fe(II) in the solution, the plutonium was assumed to be in the trivalent state.

Sulfex Decladding Flowsheet for Yankee Atomic Fuel. On the basis of data reported above and earlier, flowsheets (Figs. 4.2 and 4.3) were drawn up to cover the feed preparation and head-end solvent extraction cycle for processing of Yankee Atomic fuel elements, i.e., by the Sulfex process.

4.3.2 HF Removal of Zirconium Clads

Dissolution (W. E. Clark, A. H. Kibbey, W. D. Bond). A prototype fuel element consisting of UO_2 pellets clad in zircaloy-2 was chemically dejacketed by placing one end of the element in 9 M HF and allowing the element to feed itself into the solution. The temperature, initially 90°C, quickly rose to boiling. The volume of the solution was reduced 50% during the 2 hr required for completion of the reaction. The final F/Zr ratio was about 4.5/1; about 0.5% of the uranium was lost to the solution. It is believed that a lower uranium loss can be achieved by a different dissolving arrangement.

Ion Exchange Recovery of Uranium from Zirconium Cladding Solutions (I. R. Higgins, W. J. Neill). From a simulated zirconium cladding solution, uranium was preferentially adsorbed on Dowex-1 anion-exchange resin, and the decontamination factor from the zirconium was 5.4×10^4. Plutonium was only slightly absorbed, with 2.8% being found in the uranium product solution. The bulk of the fission product activity was in the zirconium waste solution, with only 1% of the gross γ and 0.5% of the gross β activity following the uranium. The cladding solution, containing trace plutonium and fission products, was adjusted to 2 M F^- and 6 M Cl^-.

The addition of excess ammonium fluoride to another sample of the zirconium cladding solution spiked with plutonium tracer decreased the uranium in solution from 0.2 to 0.05 g/liter. More than 99% of the plutonium tracer followed the $UF_4 \cdot NH_4F$ precipitate.

Preliminary work on Duolite C-65 cation-exchange resin, a phosphoric acid phenolic resin, indicated a promising separation of zirconium from uranium in a cladding solution. The minor constituent, uranium, was absorbed in preference to the zirconium. About 84% of the uranium was recovered from a simulated cladding solution (5 M F^-, 1 M Zr, 1.5 g/liter U) with a decontamination factor of 28 from the zirconium. In a similar experiment, with the addition of plutonium tracer, only 28% of the plutonium followed the uranium in the product solution. The eluting agents used thus far have been 6 M HCl, 10 M HCl, and 0.5 M dibasic ammonium citrate, all with similar results.

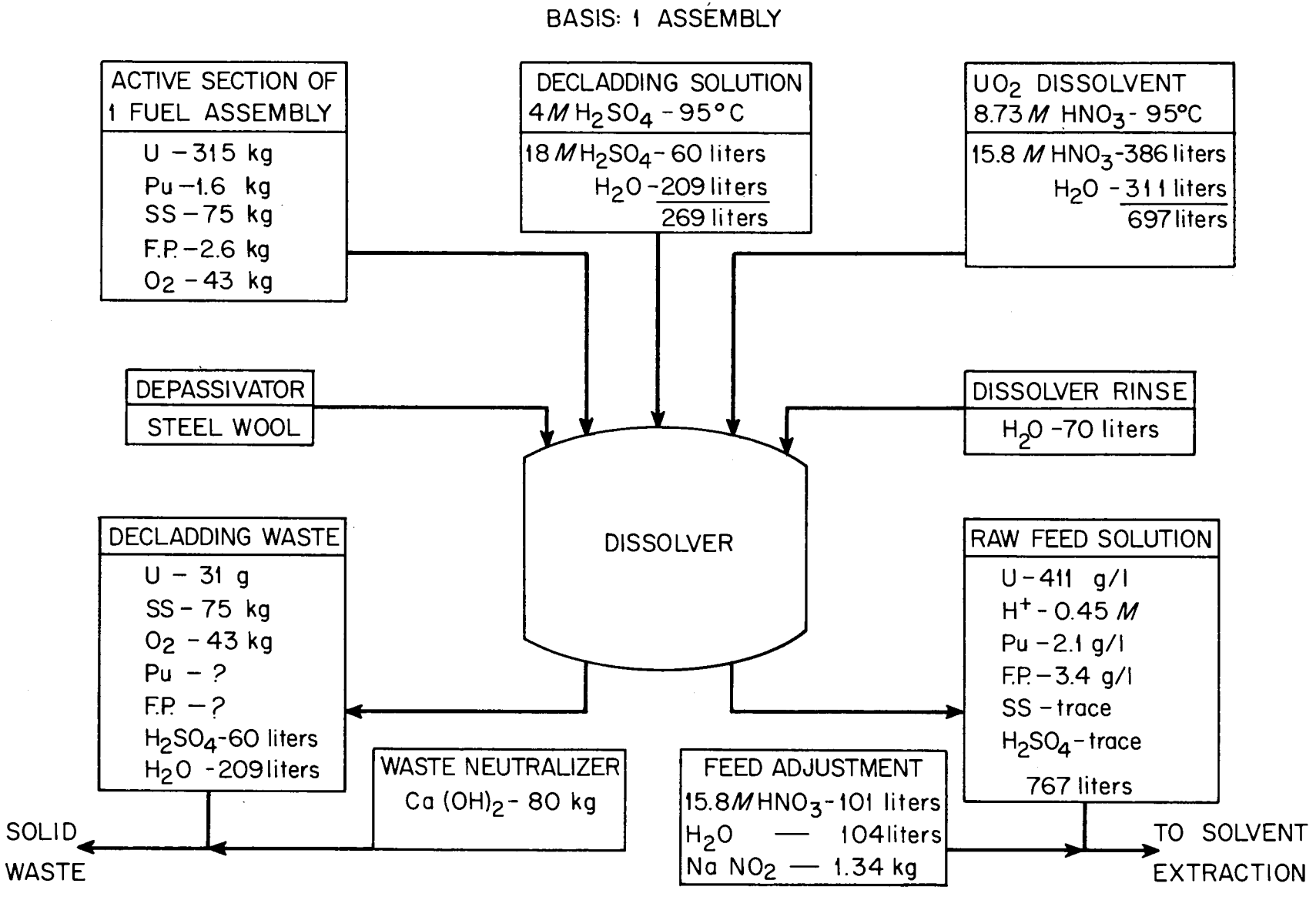

FIG. 4.2 SULFEX FEED PREPARATION
YANKEE ATOMIC FUEL REPROCESSING

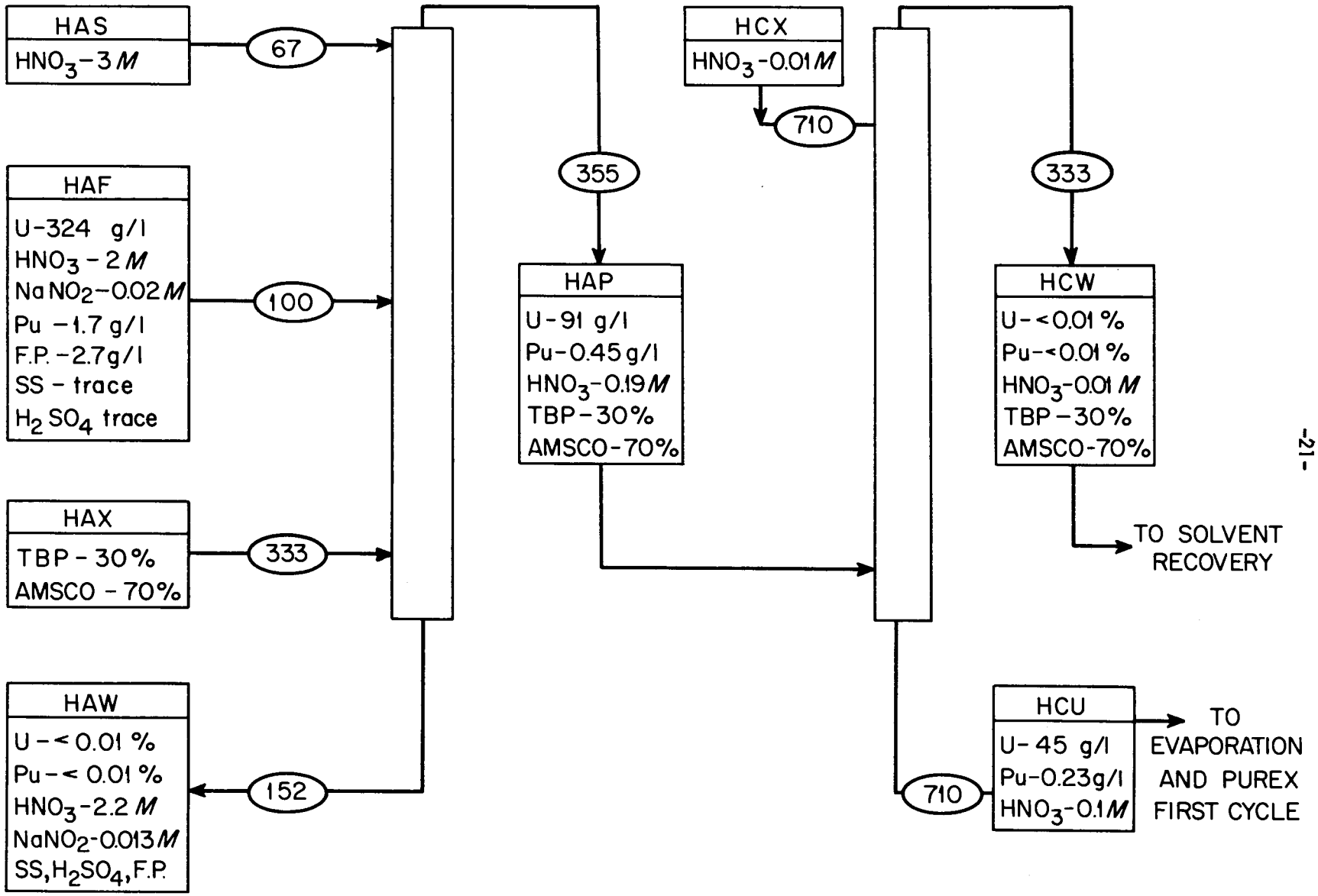

FIG. 4.3 HEADEND SOLVENT EXTRACTION CYCLE
YANKEE ATOMIC FUEL REPROCESSING

4.3.3 Dissolution Studies on Mixed UO_2-ThO_2 (W. E. Clark, A. H. Kibbey, W. D. Bond)

Work was started on the determination of a satisfactory dissolution procedure for mixed UO_2-ThO_2 fuels for possible use in reprocessing of the Consolidated Edison fuel. Short-term dissolution rates of ceramic 96% ThO_2—4% UO_2, fired at 1700°C, were negligible in 4 M H_2SO_4, in 3, 10, 13, and 15.8 M HNO_3, and in 2, 5, 9, and 12 M HF. In 3-hr tests at boiling temperatures dissolution rates were 0.057 and 0.037 mg/cm^2.min for this fuel in 6 M H_2SO_4 and in 2 M HCl—5 M HNO_3, respectively. The only effective dissolvents investigated were nitric acid containing catalytic quantities of fluoride similar to the Thorex dissolver solution. Rates on 96% ThO_2—4% UO_2 in 13 M HNO_3 with varying HF concentrations were high enough for a feasible process:

F in Dissolvent, M	Rate, mg/cm^2.min	ThF_4 Pptn	F in Dissolvent M	Rate, mg/cm^2.min	ThF_4 Pptn
0.01	5.5	None	0.5	2.9	Excessive
0.04	5.7	None	0.5	2.9	Excessive
0.04	6.2	None	0.5	5.4*	Excessive
0.1	5.1	Slight			

*The ThF_4 apparently did not adhere to the sample in this case as it did in the other two identical experiments. This specimen was run in a stainless steel container using a higher boil-up rate than was used in the Teflon pot employed for the other two experiments with 0.5 M HF.

4.3.4 Dissolution of Fe-Al-Mo Alloys (W. E. Clark, A. H. Kibbey, W. D. Bond)

Preliminary tests on dissolution of two iron-aluminum alloys of possible interest as fuel claddings indicated the feasibility of dissolving these materials:

Dissolvent	Dissolution Rate, mg/cm^2.min Thermenol**	Alfenol**	Dissolvent	Dissolution Rate, mg/cm^2.min Thermenol**	Alfenol**
5 M HF	14.0	16.4	3 M HNO_3	6.01	8.0
9 M HF	20.9	42.2	6 M HNO_3	2.30	71.2
12 M HF	27.9	63.1	9 M HNO_3	1.01	45.0
3 M HCl	0.17	1.8	2 M H_2SO_4	2.1	3.3
6 M HCl	0.60	6.6	4 M H_2SO_4	4.4	11.7
12 M HCl	0.31	25.2	6 M H_2SO_4	5.4	28.5
			8 M H_2SO_4	3.5	10.7

**Thermenol: 16 wt % Al, 81 wt % Mo; Alfenol: 16 wt % Al, 84 wt % Fe.

It should be noted that the substitution of molybdenum for 3% of the iron decreased the dissolution rate substantially in every dissolvent tested.

4.3.5 Criticality Control of Enriched Fuel Processes with Internal Neutron Processes (J. R. Flanary, J. H. Goode)

It was recently proposed that cadmium or other neutron poisons be added in the head-end operations as a means of criticality control in processing highly irradiated fuels. Such a poison would have to be removed quantitatively during subsequent solvent extraction for the fissionable material products to meet specifications. In laboratory tests on the solvent extraction removal of cadmium, there was no removal of cadmium in the Thorex feed adjustment steps and the cadmium in the solvent extraction feed was at a concentration of 3.79 mg/ml. In a series of batch countercurrent experiments the organic solvent at the feed plate contained 0.780 mg/ml and the stripped aqueous product contained 0.063 mg/ml. Based on the thorium, these values are equivalent to decontamination factors of 1.1 and 7.4, respectively; a decontamination factor of $\sim 10^6$ is required for a satisfactory uranium product.

In these tests, using the Thorex process flowsheet as an example, excess cadmium (0.02 M) was added to simulated Thorex dissolver solution and the material was carried through the feed preparation and first solvent extraction cycle of the modified Thorex co-decontamination flowsheet, dated 4/11/57.

A single batch equilibration, with macro amounts of $Cd(NO_3)_2$ in $Al(NO_3)_3$-HNO_3 and 42.5% TBP, indicated that the solvent would pick up essentially the same amount of cadmium as was found in the aqueous product of the Thorex test.

4.3.6 Electrolytic Dissolution* (W. E. Clark)

Stainless Steel—clad Fuels. The stainless steel cladding of a simulated Yankee Atomic fuel element (UO_2 clad in stainless steel) was 82% dissolved in 6 hr in 3 M HNO_3 containing 1 M stainless steel dissolution products. The anode current efficiency was about 71%. Only about 5% of the core dissolved at the low temperature ($\sim 50^\circ C$) at which the test was run. This experiment represents the worst case that would be encountered with stainless steel—containing fuels, since the solution represents the highest concentration of stainless steel dissolution products that can be obtained under optimum dissolution conditions.

Zirconium—containing Fuels. A series of experiments in which zircaloy-2 was dissolved in 3 M HCl at 40-45°C served principally to confirm previously reported results. Minimum sludge formation was 12-14% of the metal attacked and increased to a maximum of 21% as the zirconium concentration of the solution increased to 1.1 M. The use of 6 M HCl did not decrease sludge formation noticeably. Analysis of the sludge indicated that it had essentially the same composition as the original metal; no preferential attack of either tin or zirconium was indicated.

The graphite anodes used were not noticeably attacked: Cell resistance was considerably lower with graphite than with platinum as the anode material.

The platinum crucible used as anode for the dissolution of 1-1.5 kg of zirconium and zircaloy-2 in HCl and for the dissolution of approximately

*Work done by Carter Laboratories under subcontract.

2 kg of stainless steel in 3 M HNO_3 showed a negligible weight loss though there was some pitting due to arcing.

4.4 Corrosion Studies and Materials Evaluation

4.4.1 Corrosion Studies* (W. E. Clark)

The corrosion testing of materials of construction for the Darex and Zircex processes has now entered its final phase. Information was obtained indicating that Haynes 25 is not difficult to fabricate. The problem of materials of construction for Zircex and Darex equipment appears, therefore, to have been solved. Future tests in these systems will be confined primarily to testing the long-term resistance of the materials that have been selected for use (titanium, Haynes 25, S-816) and the investigation of weld and crevice corrosion.

Zircex. After 55 cycles in the Zircex hydrochlorinator-dissolver, Haynes 25 continued to corrode at relatively constant rates of <2 mils per 100 cycles (~0.5 mil/month) when cycled in 3 M HNO_3—0.4 M UO_2—1.2 M Cl^- and in 5 M HNO_3—0.01 M UO_2—0.03 M Cl^-. Rates for S-816 were slightly higher and were slowly increasing with time. Increasing the chloride concentration in the 5 M HNO_3 solution to 1.2 M gave maximum rates of 1.7 and 6.4 mils per 100 cycles for Haynes 25 and S-816, respectively, after 30 cycles. In duplicate tests on these two materials under these three test conditions the results after 15 cycles were very similar. Cyclic tests on Haynes 21, S-590, Carpenter-20, and Nb-stabilized Carpenter 20 alloys in 5 M HNO_3—0.01 M UO_2—0.03 M Cl confirmed previous results to the effect that the corrosion rates of these materials increase rather rapidly with the number of cycles.

Tensile, elongation, hardness, and embrittlement (bend) properties of alloy specimens that had been subjected only to the hot HCl part of the cycle were compared with those of original specimens and of specimens that had been subjected to similar thermal cycling in argon atmospheres. S-816, Haynes 25, Inconel, Hastelloy C, Illium R, and Carpenter 20 showed no marked ill effects, but type 304 ELC stainless steel and Haynes 21 became embrittled.

In 24-hr scouting tests in refluxing $AlCl_3.NH_4Cl$ at 325°C, only platinum and gold showed negligible corrosion:

Metal	Corrosion Rate, mils/month		Metal	Corrosion Rate, mils/month	
	Vapor	Liquid		Vapor	Liquid
Haynes 30	0.2	50.6	Hastelloy B	2.0	11.4
Haynes 36	0.4	40.2	Platinum	0	0
S-816	0.2	16.5	Gold	0	0

Purex Corrosion Tests. Stressed and unstressed samples of type 347 stainless steel have showed no appreciable weight change and no sign of stress corrosion cracking after exposure to chloride-contaminated Purex solutions for approximately 30 weeks. Chloride in these solutions varied from 3 to 10,000 ppm.

*Work done by Battelle Memorial Institute under subcontract.

4.4.2 Materials Evaluation (G. A. West)

Chemical Resistance. Chemfast, a special epoxy resin base concrete manufactured by the Truscon Laboratories, is being evaluated for possible use as a material of construction in radiochemical processing areas. The tests are being conducted in room temperature (75°F) solutions of 3 M HNO_3, 3 M HCl, 3 M H_2SO_4, 3 M NaOH, and demineralized water. The material has shown excellent resistance to these solutions for 14 days in tests which will continue for 30 days. There was no discoloration of the specimens and the weight changes, after 14 days, ranged from 0.2% gain in the H_2SO_4 to 0.01% loss in the demineralized water. Data were:

Solution	Weight Change, %	Solution	Weight Change, %
3 M HNO_3	+0.07	3 M NaOH	-0.02
3 M HCl	-0.05	Demineralized H_2O	-0.01
3 M H_2SO_4	+0.20		

Radiation Damage. The potential use of the various forms of glass and plastics as processing vessels in radiochemical reprocessing plants in high radiation fields has not been well established. Glascote, a protective coating manufactured by the Evershield Products, Inc., was irradiated to 10^9 r in air and in water in the Co-60 source at ORNL. Two colors, white and gray, on 1/4-in.-thick aluminum panels, were irradiated. The white specimens turned slightly yellowish but there were no blisters or visual damage which might indicate deterioration. The gray specimens became darker and the sample in water was blistered. The blistering may have been due to pin holes in the coating since the white sample was not affected.

Samples of glass from the Corning Glass Works (items 1 and 2 above) were irradiated to 10^6, 10^7, and 10^8 r at the ORNL Co-60 source, and specimens have been returned to Corning for physical properties tests.

Cylindrical tensile test specimens of Haveg 41, 61, and 093 have been irradiated to 10^{10} r at the MTR spent fuel γ facility in Idaho. All specimens were darkened and unchanged in size except 093 which was deformed. The irradiated alloys will be returned to the Haveg Corporation, who will conduct physical and chemical tests on the irradiated specimens. Other materials undergoing gamma irradiation to 10^{10} r in air and in water at the MTR γ facility are:

Vycor glass, 96% silica from Corning Glass Works
Pyrex glass from Corning Glass Works
No. 53 glass on metal from the Pfaudler Company
No. G-12 glass on metal from the Pfaudler Company
No. A-5 glass on metal from the Pfaudler Company
Chemfast (epoxy) concrete from the Truscon Laboratory

4.5 Liquid Metal Fuel Processing (J. E. Savolainen, L. M. Ferris)

Fused salt extraction has been studied as a head-end method for recovering uranium from liquid metal fuels in a small volume of salt. The salt extract would be dissolved in nitric acid and passed through the Darex system for chloride removal prior to solvent extraction.

Partial removal of uranium from molten U-Bi solutions by 24-hr extraction with 30 wt % $BiCl_3$—33.8 wt % LiCl—36.2 wt % KCl at 550°C was demonstrated. The average separation factor in seven equilibrations was 240:

Run	U in Salt, mg	U in Metal, mg	Sep'n Factor
1	Not analyzed	0.59	300
2	221	2.60	85
3	Not analyzed	3.3	116
4	85.4	0.2	427
5	23.0	0.13	177
6	51.6	0.177	292
7	59.5	0.216	275

Equal volumes of salt and alloy were used in each experiment. Formation of UO_2 by reaction of uranium with the glass vessels may have retarded the extraction.

The proposed process for extracting uranium and fission products from U-Bi solutions with $BiCl_3$ contained in a relatively inert solvent has a firm thermodynamic foundation.[3] A uranium separation factor in excess of 10^{10} was predicted from standard free energies of formation. Similar high separation factors were expected for the fission products. The low uranium separation factors are explained by the formation of a thin layer of UO_2 at the salt-metal interface by reaction of uranium with the glass vessels used in performing the experiments. This layer of UO_2 undoubtedly retarded diffusion of uranium and bismuth at the interface. The effect of this oxide layer was partially compensated for by periodically inverting the contactors to ensure attainment of equilibrium.

5.0 METAL RECOVERY PLANT
Program Leader: W. H. Lewis

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

The recovery of 181.82 g of plutonium from an irradiated NRX reactor plutonium-aluminum rod was completed and the resulting product, $Pu(NO_3)_3$, was transferred to Y-12 for conversion to $PuCl_3$. Following plant cleanout, the recovery of depleted uranium from ORNL tank farm wastes was resumed.

The plutonium-aluminum rod was dissolved in 6.0 M HNO_3 catalyzed by 0.05 M $Hg(NO_3)_2$. The solution was refluxed for 60 hr although analysis of the solution after 24 hr indicated complete dissolution. After the dissolver solution was jetted to the feed tank, a small (56 gal) heel dissolving and

rinse was made to assure complete removal of plutonium from the vessel. The dissolver solution was then blended with decontaminated uranyl nitrate solution and nitric acid and adjusted to Purex flowsheet feed specifications.

Two cycles of solvent extraction were used to recover and decontaminate the plutonium. Flowing stream losses during column equilibrium were:

Stream	Loss, % of total Pu	Loss, % of total U	Stream	Loss, % of total Pu	Loss, % of total U
1AW	0.01	0.01	1DFC	0.13[a]	--
1BP	--	0.01	2AW	0.01	--
1CU	--	--	2BW	0.01	--
1CW	0.02	0.15	2BPW	0.01	--
			Total	0.19	0.17

[a]Partially recovered as recycle.

The overall gross γ decontamination factor for the plutonium product was 4.7×10^5 through two cycles of solvent extraction. The activity spectrums for the feed and plutonium product solutions and the decontamination factors were:

	Gr γ	Ru γ	TRE β	Zr-Nb γ	Cs γ	Gr β
1AF	2.83×10^8	8.07×10^7	9.65×10^7	4.68×10^7	8.33×10^7	3.73×10^8
Pu product	2.26×10^5	1.09×10^5	1.0×10^4	5.19×10^4	1.18×10^2	1.57×10^6
DF	4.7×10^5	2.78×10^5	3.58×10^6	3.39×10^5	2.65×10^8	8.95×10^4

After all the plutonium was on the Dowex-50 resin column it was eluted into polyethylene bottles. The first phase of the elution was to remove the uranium from the column with 0.25 M H_2SO_4 solution; approximately 9 column volume changes were required to remove 2.6 g of uranium from the column. After the uranium elution the plutonium was eluted from the column with 5.7 M HNO_3 containing 0.3 M NH_2SO_3H in the downflow direction. After 4, 7, and 11 volume changes, 80, 96, and 98% of the plutonium was removed from the resin. An additional 35 volume changes removed only 2% of the plutonium; the elution was discontinued when less than 0.1 g/hr of plutonium was being removed. A total of 182.36 g of plutonium was removed from the column. Analysis of the rich product cut was:

Gr α	4.26×10^9 c/m/ml	Pu-239	63.87%
HNO_3	4.98 M	Pu-240	30.62%
U	0.01 mg/ml	Pu-241	4.51%
Sp. gr.	1.2054	Pu-242	1.00%
Pu (potentiometric)	29.51 mg/ml		

6.0 THOREX PROCESS
Program Leader: E. M. Shank

In the Thorex process thorium and U-233 are recovered as decontaminated aqueous solutions suitable for direct handling during subsequent processing to metal. Irradiated thorium is dissolved in excess nitric acid, concentrated to remove the excess acid, and processed through two solvent-extraction decontaminating cycles. The thorium and U-233 are extracted by tributyl phosphate in a kerosene-type diluent (Amsco) and costripped with dilute nitric acid in the first cycle and are continuously concentrated and adjusted and are re-extracted and partitioned in a second cycle. The thorium product is continuously evaporated to 2 M. 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. F. Manneschmidt, W. R. Winsbro, W. T. McCarley, R. J. Foltz)

The second short-decay pilot plant development run, SD-2, was completed with the ORNL Thorex Co-decontamination flowsheet. Thorium irradiated to about 3500 g/t, decayed an average of 52 days, was processed. Two-cycle operation was continuous for 329 hr, of which 23 hr was with recycled thorium product, 65 hr with 10% level feed, and 241 hr with full-level feed. A solution of potassium iodide was continuously added during the dissolution. The iodine scrubber was operated satisfactorily during the three dissolvings and three feed adjustments to provide an iodine decontamination factor of about 20. Sodium bisulfite was maintained at 0.01 M in the first and second cycle feed streams by continuous metering. Bisulfite was added every 4 hr to the scrub streams. Solvent from run SD-1 was discarded and new solvent was prepared with oleum-pretreated Amsco as the diluent.

A total of 1400 kg of SRP irradiated and 970 kg of recycled thorium was processed continuously to recover 2160 kg of thorium product, to isolate 4700 g of U-233 by ion-exchange, and to separate 710 g of Pa-233 for decay storage. Thorium and uranium solvent-extraction losses averaged 2.7 and 0.3%, respectively, with an overall material balance of 99.8% for thorium and 99.7% for uranium. The thorium and uranium losses to the 1A-column averaged about 1.7% and 0.2%, respectively. The 1A-column thorium loss was reduced to 0.5% during the last 75 hr of operation by increasing the extractant flow rate 10%. The initial high column losses cannot be attributed to poor column operation.

Average overall gross gamma decontamination factors were 1.9×10^4 for thorium and 1.3×10^7 for uranium (Table 6.1). The thorium product exceeded tentative specifications for γ emitters by a factor of 150 (Table 6.2). An additional 185 days will be required for the Th-234 to decay to specification, at which time the thorium will exceed specifications for ruthenium and zirconium-niobium by 65 and 10, respectively. The uranium product met tentative specifications after ion exchange for all activities except ruthenium (Table 6.2). After a third solvent-extraction cycle, the ruthenium specification was still exceeded by a factor of 2. In comparison, the uranium product from run SD-1 met the ruthenium specification after the third solvent-extraction cycle.

Equipment performance was, in general, good. Several Cuno filters on the

Table 6.1. Run SD-2: Average Decontamination Factors

	Decontamination Factors					
	Gross γ	Pa	Ru	Zr-Nb	TRE	I-131 β
Thorium						
First cycle	1000	1.6×10^{4}	3	2600	2.7×10^{4}	-
Second cycle	15	470	25	30	35	-
Overall	1.9×10^{4}	2.2×10^{6}	90	6.5×10^{4}	5.3×10^{5}	-
Uranium						
First cycle	1100	7600	4	2100	6.9×10^{4}	-
Second cycle	170	230	15	290	880	-
Isolation	9	740	5	40	35	-
Third cycle	15	60	450	~1	~1	130
Overall	1.3×10^{7}	1.9×10^{10}	1.5×10^{6}	3.3×10^{6}	3.5×10^{8}	5.0×10^{7}

Table 6.2. Run SD-2: Average Activity Spectrums

	Activity, c/m/mg					
	Gross γ	Pa γ	Ru γ	Zr-Nb γ	TRE β	I-131 β
Thorium						
1AF	6.1×10^{8}	5.5×10^{8}	1.7×10^{6}	3.8×10^{7}	1.9×10^{7}	4.9×10^{4}
1CP	9.7×10^{5}	6.9×10^{4}	7.9×10^{5}	1.8×10^{4}	3100	-
2AF	7.9×10^{5}	1.1×10^{5}	5.9×10^{5}	3.6×10^{4}	3200	-
2BT	4.5×10^{4}	730	2.4×10^{4}	1800	220	-
2BTC	3.8×10^{4}	360	1.9×10^{4}	750	30	6
Spec.	260	30	40	45	40	-
Uranium						
1AF	2.1×10^{11}	1.9×10^{11}	7.2×10^{8}	1.1×10^{10}	6.9×10^{9}	1.0×10^{7}
1CP	2.0×10^{8}	2.5×10^{7}	1.7×10^{8}	5.3×10^{6}	1.0×10^{5}	-
2AF	2.7×10^{8}	5.5×10^{7}	1.7×10^{7}	1.9×10^{7}	$[illegible].5 \times 10^{5}$	-
2CU	1.6×10^{6}	2.4×10^{5}	1.2×10^{6}	6.5×10^{4}	740	-
IF	1.8×10^{6}	4.3×10^{5}	1.1×10^{6}	1.3×10^{5}	230	-
IP	2.0×10^{5}	580	2.1×10^{5}	3100	7	25
3AF	1.3×10^{5}	600	1.2×10^{5}	5200	35	3
3CUP	1.6×10^{4}	10	470	3300	20	0.2
Spec.	9000	1000	280	8000	450	-

suction to organic metering pumps plugged frequently. The Fulflo filters on the organic streams were changed daily during the run; the radiation level of the filters increased daily to greater than 100 r/hr after about three days of operation. Following run SD-1, additional shielding was installed in the pipe tunnel and roof areas. This additional shielding reduced the radiation levels in these areas sufficiently to permit continued operation. The chief personnel exposure was in the changing of the organic stream Fulflo filters. Cell monitor during run SD-2 indicated radiation levels of 1.5-3 r/hr in front of the feed preparation cubicles, 200-500 mr/hr in the personnel cubicle in the feed preparation cell, 20-30 mr/hr in front of the solvent-extraction cubicles, and 20-30 mr/hr in the solvent-extraction cell personnel cubicles.

Operation of the third solvent-extraction cycle continued to be poor. Operation of the feed pump was not satisfactory except during one 24-hr run. Processing of acetate-citrate ion-exchange product was difficult owing to the poor performance of the feed pump and to poor column operation.

Installation of the interface purge system was completed and initial evaluation of the various components was started.

6.2 Diluent Studies (R. J. McNamee, B. C. Finney)

Previously reported solvent-extraction data (ORNL-2362) from 2-in.-dia pulsed column runs showed Decalin to be a poor diluent in the Thorex process because of higher HETS and lower flooding rates. In additional solvent-extraction runs with Decalin pretreated with oleum in a newly installed facility, results were not significantly different. Flooding rates at 50 and 80 cpm pulse frequencies were 554 and 310 gsfh respectively, as compared to 510 and 322 gsfh previously obtained. The HETS values at 60 cpm and 8 ft and 14 ft of extraction height were 6.3 ft and 5.8 ft, in good agreement with the 6.4 ft previously obtained.

6.3 Process Development (R. H. Rainey, A. B. Meservey)

Solvent Recovery. Treatment of used solvent with a 40 wt % lime slurry in water gave a gross γ decontamination of about 100 with essentially complete removal of protactinium and zirconium-niobium and a ruthenium decontamination factor of about 100. Dilute sodium hydroxide failed to give as good decontamination as the lime slurry, indicating that the lime particles scavenge the gelatinous precipitate from the solution.

Hydrogen Production in Short-decayed Aqueous Waste. Chemical analysis of the radiolytic gas formed by the radiation of a synthetic solvent extraction aqueous waste in a Co-60 source showed 5.6% hydrogen:

H_2, 5.6%	NO, 5.2%	CO, 8.4%
O_2, 10.5%	NO_2, < 3.0%	CO_2, 30.5%

The solution that was irradiated had the approximate composition of the aqueous waste from the Thorex short-decayed runs and a small amount of 42.5% TBP-Amsco to simulate entrained solvent. This solution was sealed in a glass

ampoule with an oxygen overpressure, irradiated in a Co-60 source for 130 hr, then opened and the gas phase analyzed.

Decontamination of Short-decayed Feeds from Ruthenium. Ruthenium decontamination factors in the pilot plant were improved by eliminating sulfite from feed solutions whenever the temperature went above 50°C. The sulfite ion apparently reacts with the ruthenium to produce a complex that is not extracted by TBP-Amsco but is easily reversed by a small excess of nitrite. At elevated temperatures destruction of the sulfite is accelerated, for example, the reaction of sulfite with nitrate to produce NO gas. This NO reacts with atmospheric oxygen to form NO_2, which then dissolves with the NO to produce nitrite. In the laboratory this reaction has required a temperature above 60°C, but it apparently proceeds at lower temperatures under pilot plant conditions. Losses of sulfite by air oxidation and SO_2 evolution are also increased by elevated temperatures.

Destruction of the nitrite in the solution by various oxidizing and reducing solutions not containing sulfite did not improve the ruthenium decontamination.

Behavior of Ru-106 on Cation Exchange Resin. In laboratory experiments the U-233 product was decontaminated from ruthenium by factors of only 2 by adjusting the acidity of the U-233 solution prior to passage through cation exchange resin. For the experiments uranium feeds were spiked with tracer ruthenium in the acid deficient and sulfited acid deficient forms and fed to a Dowex 50 column. Ruthenium was partially eluted from the 75% loaded column with 3 column volumes of 0.1 M $NaNO_2$ or 0.1 M $NaNO_3$, and then the uranium and the rest of the ruthenium were eluted with 6 M HNO_3 and the decontamination was calculated from this last elution:

Ru Form	Amount of Ru-106, %				Ru D. F.
	Sorbed	Desorbed by 0.1 M $NaNO_2$	Desorbed by 0.1 M $NaNO_3$	Desorbed by 6 M HNO_3	
Acid	53	20	2	40	2.5
Acid deficient	83	35	2	65	1.7
Sulfited acid deficient	62	25	---	37	2.7

7.0 WASTE TREATMENT AND DISPOSAL
Program Leader: J. O. Blomeke

7.1 Ion Exchange Treatment (I. R. Higgins, A. F. Messing)

In further studies synthetic alkaline waste was decontaminated from Cs-137 and Sr-90 in the 1.5-in.-dia continuous ion exchange contactor by factors of 10^4-10^5 with feed flow rates increased to 2000 gal/hr.ft^2 of resin. The feed-to-resin flow ratio was approximately 150, the resin being Duolite C-3. The cesium product was decontaminated from sodium by a factor of 10^4.

7.2 Electrolytic Treatment (I. R. Higgins, A. F. Messing)

In the first stage of a proposed two- or three-stage electrolytic cell for regeneration of caustic and nitric acid from ORNL waste, the current efficiency was 75% and power consumption was 6.2 kwh per pound of caustic produced.

The products were 1.32 N HNO_3 and 1.50 N NaOH. Calculation of the efficiency was based on the sodium transferred and took into account the water transferred with the migrating ions.

Each cell of the proposed assembly will be divided into an anode, feed, and cathode compartment separated by anion- and cation-exchange semipermeable membranes, respectively, spaced at 1-in. intervals. Platinum and stainless steel, with surface area of 20 $in.^2$, are used as the anode and the cathode, respectively. In the two- or three-stage cell, feed will enter the first, flow through the second and third, and then emerge. Nitric acid formed in the anode compartment and sodium hydroxide in the cathode compartment will be flushed out by a stream of water entering the third stage and emerging from the first. With this arrangement the ionic strength of any particular stage will be approximately the same in each of the three compartments.

In the experiments 1 N HNO_3 and 0.76 N NaOH were placed in the anode and cathode compartments, respectively. The feed, synthetic waste of 0.6 N sodium ion and 0.3 N nitrate ion, entered the feed compartment at a rate of 30 ml/min. Water was introduced to the anode and cathode compartments at a rate of 3-4 ml/min. The current density was 1 amp/$in.^2$

7.3 Adiabatic Self-Sintering (W. R. Winsbro)

A facility has been designed in which the heat generated by the fission products will heat stored waste, driving off water, nitric acid, etc. and eventually sintering the residue. It will consist of a mixing vessel, a well insulated sintering furnace, and an off-gas system. Waste simulated for testing the facility will be prepared by dissolving one 45-60 day decayed MTR fuel element, irradiated to 30% burnup, in nitric acid and adjusting to a final volume of 30 gal with the composition of 1.6 M $Al(NO_3)_3$—0.16 M HNO_3. To this waste will be added 30 lb of Na_2CO_3, 30 lb of limestone, and 100 lb of shale. A slurry thus formed sets to a firm gel in 10-30 min and must be dropped into the furnace before this occurs. The fission product heat will vary from 300 to 200 watts during the 60-120 day postirradiation time, raising the temperature of the cake to the desired sintering temperature of 800°C. The final cake is a porous, highly refractory, partially vitrified brick with a volume of 17.7 gal, ~40% less than the original waste volume. Preliminary data indicate that most fission products are reasonably well fixed to the matrix of such a cake. Estimates of the theoretical heat required to form 1 gal of final cake range from 20,000 to 30,000 Btu. On this basis, 30 to 60 days will be required to sinter the cake if heat losses can be reduced to 50% of that available from the fission products. An electrical heating system will be provided in the insulation surrounding the furnace to permit control of heat losses.

8.0 NONAQUEOUS PROCESSES

8.1 Fused Salt-Fluoride Volatility Process (Program Leader: R. B. Lindauer)

Pilot Plant Studies (W. H Lewis, J. E. Bigelow, F. N. Browder, W. H. Carr, R. B. Keely, F. W. Miles, C. L. Whitmarsh). Data summarizing the series of seven flowsheet runs are given in Table 8.1. Prior to this series,

Table 8.1 Data for Seven Pilot Plant Volatility Runs

Run No.	F_2 Flow Rate (std liters/min) During Fluorination	Uranium, g Feed	Uranium, g Product	Product Recovery %	Recoverable Losses, % Snow Trap	Absorption	Cold Trapping	Product Transfer	Total	Non-recoverable Loss in waste,[a] %	Total Accounted for, %
C-9	6.7	7,886	5,638	71.49	14.53	0.84	0.11	1.66	17.14	0.06	88.69
C-10	27.2	7,918	7,080	89.42	7.33	0.05	0.05	0.37	7.80	0.01	97.23
C-11	10.0	7,372	5,768	78.24	-	0.16	0.01	0.07	0.24	0.01	78.49
C-12	33.4	7,833	8,243	105.23	3.03[a]	1.30	0.08	1.52	5.93	0.04	111.20
C-13	20.7	7,947	5,592	70.37	20.12	0.88	0.20	0.89	22.09	<0.01	92.47
C-14	22.9	8,779	7,215	82.18	4.36	3.34	0.03	1.07	8.80	0.02	91.00
C-15	12.3	7,797	7,316	93.83	0.32	2.23	-	1.19[c]	3.75	0.04	97.62
Cleanout[b]									1.26		
Total		55,532	46,852	84.37	7.15	1.30	0.08	0.97	10.76	0.03	95.16

[a]Includes C-11 and C-12 losses.

[b]"Cleanout" shows recovery following runs; includes 620 g recovered by water-flushing of pipes, 46 g caught in heated duct chemical trap, and 32 g remaining on absorber NaF after desorption.

[c]Includes cold trapping and product transfer losses.

experimentation had been on the basis of individual runs; the primary purpose of the series was to study equipment reliability and absorber performance through a more extended period. Absorption losses were high in the last two runs; this does not necessarily indicate that NaF beds are good for only five runs, but it does emphasize the necessity for a close check of absorber losses.

Losses are listed as recoverable and nonrecoverable. Recoverable losses are those which can be recovered either by refluorination of the NaF on which the uranium is caught or by aqueous dissolution followed by concentration in an ion exchange column. Snow-trap losses were very high in all runs except the last one, because of inadequate temperature controls prior to the last run. The snow trap is a small bed of NaF added to the system to trap zirconium, ruthenium, and chromium; if any part of the bed is cooler than 375°C, UF_6 will also be absorbed.

Flowsheet (R. P. Milford). The flowsheet data to be used, based on most recent calculations, are shown in Table 8.2. These data are based on assumptions that may be proved impractical later. To date there is no operating experience for a hydrofluorinator, and the assumptions necessarily made for vessel dimensions, linear gas velocities, and actual subassembly dissolution progress may be in error. However, the cases as shown highlight certain differences between the two systems. For example, for the same final 50-liter batch volume at 600°C final temperature, the Na-Li system handles 3.7 subassemblies vs. 1.9 subassemblies for the Na-Zr system and requires an initial operating temperature of 700°C vs. 600 for the Na-Zr system. Also, the vessel diameter shown for the Na-Zr system is too small for practical dissolution; enlarging it to a more desirable size would be accompanied by either a lower linear gas velocity or shorter dissolution time.

For comparison, cases were calculated for both systems at 700°C operating temperature from start to finish. As shown in the second column of the table, this results in no increase in subassembly dissolution per 50-liter final batch for the Na-Li system, while the Na-Zr system capacity increases from 1.9 to 2.6 subassemblies.

Hydrofluorinator (R. W. Horton, M. E. Whatley). In preliminary tests of the hydrofluorinator numerous leaks in fittings and joints were located and corrected by simple tightening. Five more serious leaks were found in the welds of the copper piping of the HF cooler, and one leak was found in the HF condenser. The HF cooler coil is being replaced by a continuous section of tubing. Since it was necessary to remove the HF condenser for repairs, opportunity was taken to change its flow pattern. In the present design the HF stream enters the collecter and that which is not condensed here must pass up through an off-gas cooling coil (dry ice temperature) countercurrent to the returning condensate. This will bring the HF stream in through the cooling coil to the collector and out through another cooling coil. The increase in cooling area on the inlet stream should prevent the passage of appreciable quantities of condensibles into the off-gas coil, and minimize the probability of liquid HF entrainment.

Decomposition of UF_6·3NaF Complex (G. I. Cathers, R. L. Jolley). The retention of uranium on NaF in a nonvolatile form has been studied further in attempting to evaluate its importance in the volatility process. The effect

Table 8.2. Fused Salt--Fluoride Volatility Flowsheet Calculations

	600°C Final Operating Temp.				700°C Final Operating Temp.			
	Na-Li System		Na-Zr System		Na-Li System		Na-Zr System	
Final batch vol, liters	50		50		50		50	
Barren salt charged, kg	22.5		92.6		17.7		66.7	
No. of 17-plate cut subassemblies dissolved	3.7		1.9		3.7		2.6	
Wt. subassemblies dissolved, kg	77.4		40.1		77.3		54.2	
Wt. U dissolved, g	747		387		746		522	
Final batch composition	mole %	wt. %	mole %	wt. %	mole %	wt. %	mole %	wt. %
NaF	19.3	7.6	43.5	16.2	16.1	6.1	36.9	12.8
LiF	25.6	6.2	-	-	22.2	5.0	-	-
ZrF_4	54.9	85.6	56.4	83.5	60.8	88.3	62.9	86.8
UF_4	0.21	0.60	0.11	0.31	0.23	0.62	0.16	0.41
Barren salt composition								
NaF	43.0	55.0	62.0	29.1	43.0	55.0	65.0	31.8
LiF	57.0	45.0	-	-	57.0	45.0	-	-
ZrF_4	-	-	38.0	70.9	-	-	35.0	68.2
Vessel i.d. at 0.5 ft/sec gas velocity and 20 hr cycle, in.	18.2		7.22					
Initial dissolution temp, °C	700		600		700		700	
Final dissolution temp, °C	600		600		700		700	
Initial liquidus temp, °C	652		560		652		640-650	
Final temp, °C	550-560		530-540		650		640-650	

is due to formation of a U(V)-NaF complex. In tests at temperatures of 350 to 450°C, the rate of formation of the U(V) complex increased with increasing temperature. The rate between 350 and 400°C was variable. Although the decomposition effect appears large, it was less than maximum in the volatility process owing to some back-fluorination of the U(V) complex to the volatile U(VI) complex. No investigation of this back-fluorination rate has been made.

Two different reaction mechanisms are involved in the formation of U(V) complex at temperatures above and below 363°C, the atmospheric decomposition temperature of $UF_6 \cdot 3NaF$. Below 363°C, the reaction is represented by the equation

$$UF_6 \cdot 3NaF(s) \longrightarrow UF_5 \cdot xNaF(s) + 1/2\ F_2(g) + (3-x)NaF(s)$$

Above 363°C, $UF_6 \cdot 3NaF$ no longer exists as a solid phase, thus making the interaction proceed by the equation

$$UF_6(g) + xNaF(s) \longrightarrow UF_5 \cdot xNaF(s) + 1/2\ F_2(g).$$

This investigation was directed primarily toward study of the second reaction although some tests were made below 363°C to check previously reported work.*

In an Arrhenius plot (Fig. 8.1) there is some evidence of a linear relation between the logarithm of rate and reciprocal temperature over a limited range. Above 400°C the NaF percentage weight increase rate (calculated as due to UF_5) approached 5% per minute asymptotically, indicating that diffusion of the product F_2 gas from the solid is limiting the reaction. The scatter in the data between 350 and 400°C could also be due to differences in diffusion effects inherent in the various measurement techniques used.

An earlier investigation of the decomposition rate of $UF_6 \cdot 3NaF$ complex below 350°C was made by using a vertical bed of NaF saturated with UF_6, holding at the test temperature for a given time, then analyzing for U(V) without removal of the excess absorbed UF_6. Extrapolation of this work (dot-dash line in Fig. 8.2) does not appear inconsistent with the new high-temperature data, but it is much higher than recently obtained in the range 350-380°C. The present work was carried out with two methods somewhat different from the previous. In one method, a 1-g sample of 12-20 mesh NaF (Harshaw) was placed in a boat in a horizontal reactor (1/2-in. dia). In a second method, a vertical bed of NaF (2 g) was held in a 1/2-in. nickel tube. In both cases, the experimental material was conditioned with F_2 at the test temperature, flushed with N_2, then exposed to a flow of UF_6 for the test period. At the end of the test period, the excess UF_6 was rapidly flushed out with a fast flow of N_2. Reliance was placed on analyzing the bed for U(V) to determine the rate of formation. In some cases, a gravimetric check was also made on the sample bed to compare with the analytical result (Table 8.3). The boat method gave fairly reproducible results in the higher temperature range. However, at lower temperatures diffusion through the depth of the bed (several millimeters) apparently led to low results. No explanation has been found for the discrepancy between the new and old results with the vertical reactor bed method.

Fused Salt Reactor Fuel Processing (D. O. Campbell, G. I. Cathers). Trace rare earths, niobium, cesium, and strontium were concentrated in the liquid phase

*ORNL-CF-57-4-25.

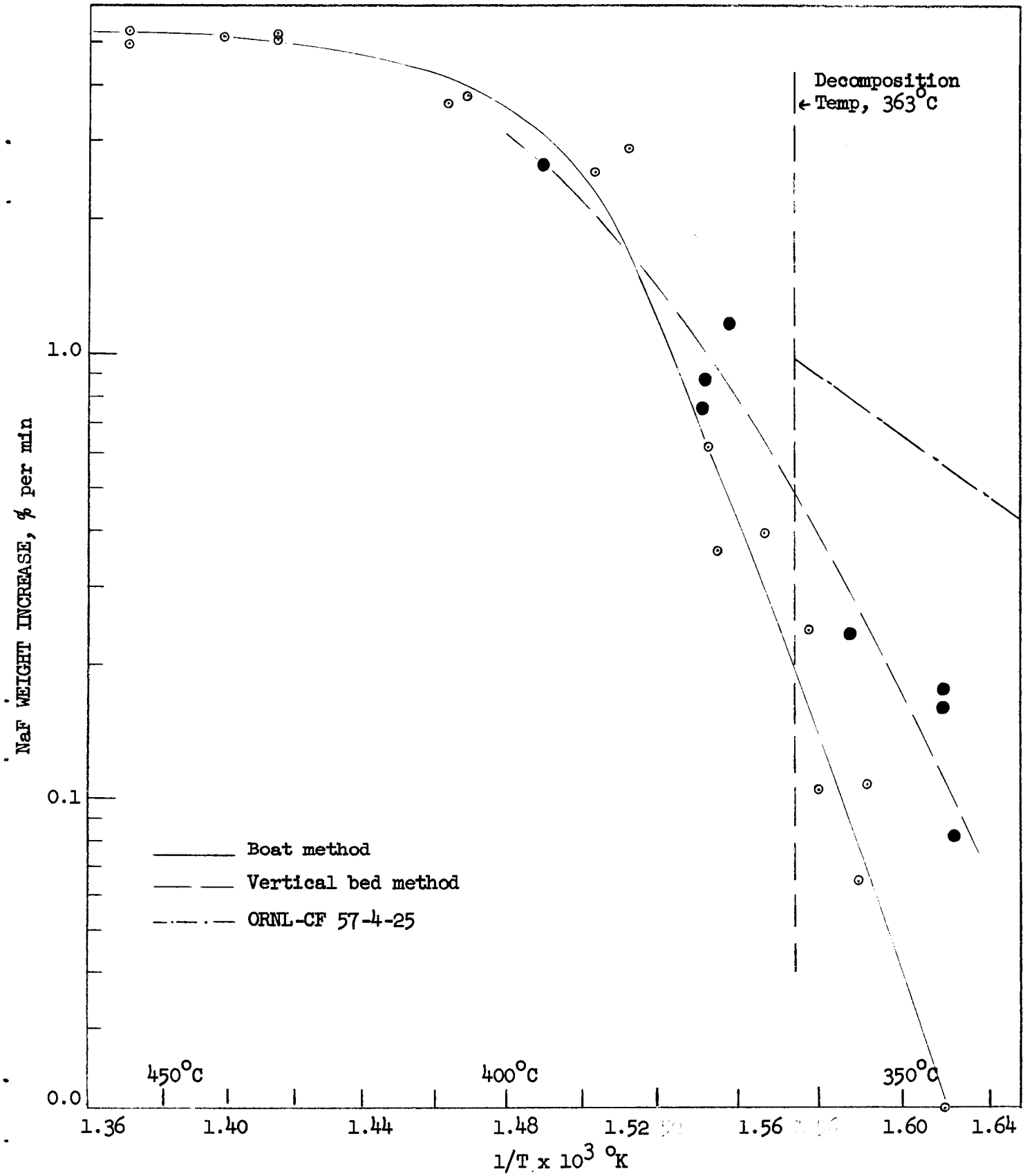

Fig. 8.1. Retention of Uranium as U(V) Complex on NaF as a Function of Temperature.

Table 8.3. Nonvolatile Uranium Retention on NaF from Contacting UF_6 Gas

Temp., °C	Time, min	UF_5 Content, wt %[a] Analysis	Gravimetric
		Boat Method	
345	38	0.76	
354	30	3.20	
355	30	1.96	
360	33	3.45	
361	15	3.53	
367	15	5.94	
372	15	5.44	
374	30	18.6	19.1
384	7.5	21.6	
388	15	38.2	37.0
405	5	18.8	
408	8	29.1	28.8
433	5	25.2	24.1
433	2.5	12.9	10.8
438	5.8	30.1	
455	4	19.9	19.1
456	3	15.8	
		Vertical Bed Method	
344	45	3.72	
345	34	6.02	5.6
345	32	5.12	4.6
356	31	7.27	
371	25	28.7	29.8
374	31	26.8	
374	30	22.6	25.2
395	10	26.1	27.3

[a]On original NaF weight.

when molten $NaZrF_5$ was partially frozen. Precipitation of fission products as oxides from zirconium-base salts does not appear promising; ZrO_2 precipitated first. The rare earths, zirconium, and niobium activities were largely removed from molten flinak (LiF-NaF-KF eutectic) by precipitation with CaO. An alkali metal fluoride-BeF_2 salt is presently favored for power reactor use, so similar experiments are being initiated with beryllium base salts.

Contaminated $NaZrF_5$ may be purified to some extent by partial freezing. The solid phase consists primarily of $3NaF.4ZrF_4$ and $7NaF\ 6ZrF_4$, with most of the fission products concentrating in the liquid phase. Experiments were completed in which 300 g of molten $NaZrF_5$ containing 1 mole % UF_4 and trace fission products with and without 0.2 mole % rare earth fluorides was slowly frozen without sparging. The top of the liquid was sampled and analyzed at intervals for fission products. A small auxiliary heater was dipped into the melt to prevent freezing across the top.

All the fission products except zirconium were concentrated to some extent in the molten salt phase (Table 8.4). The rare earths other than cerium (trivalent rare earths, which comprise about 10% of the total rare earth activity) appeared to concentrate to a somewhat smaller extent than cerium. Cesium concentrated slightly more than the rare earths, and niobium and strontium less. There was insufficient ruthenium present for determination of its behavior; it was largely removed by a preliminary hydrogen sparge. The uranium concentration in the molten salt was not affected in freezing.

Addition of CaO to molten $NaZrF_5$ containing UF_4 and fission products gave minor and inconsistent changes in the fission product activities in the melt. Activities of zirconium and cesium remained constant throughout. The other fission products were decreased by a factor of 2 by 3 and 30 mole % additions, but intermediate amounts of CaO had less effect. The melting point of the salt increased considerably with the larger additions, probably because ZrO_2 was being formed, leaving a higher melting $NaF-ZrF_4-CaF_2$ salt. Oxide precipitation of fission products from zirconium-base salts does not appear practical.

The constituents of flinak (NaF-LiF-KF, 11.5-46.5-42 mole %) containing 0.07 mole % ZrF_4, unlike $NaZrF_5$, were not precipitated by CaO addition, but rare earths, zirconium, and niobium were (Table 8.5).

With trace fission products only Zr and Nb activities were reduced measurably by CaO addition. With 0.2 mole % rare earths and 0.7 mole % CaO there was only little reduction in rare earth activity. This concentration is a realistic one for reactor fuel processing. With 1.2 mole % rare earth fluoride and excess CaO the rare earths, Zr, and Nb were effectively removed; a small part of the Sr and Cs was removed. The cause of the poor removal of rare earth activity with the 0.2 mole % rare earth concentration is not known.

8.2 High Activity Level Volatility Laboratory (R. P. Milford)

Electrical work is progressing satisfactorily and installation of thermocouples has begun. The 1-in. steel shield will be cut to allow access to the space below the work table area in the front part of the cell. At the same time a 6-in. channel will be placed under the absorber vessels and attached to the walls, thereby allowing the Unistrut framework now resting on the floor

Table 8.4. Concentration of Fission Products in Molten $NaZrF_5$ by Partial Freezing

Freezing Time, min	Concentration Factor of Fission Product in Liquid Phase						
	Zr	Nb	Cs	TRE	Ce	TriV*	Sr
Trace fission products, melt completely frozen in about 150 min							
90	1.01	1.22	1.70	1.62	1.60	1.42	1.24
105	0.98	1.27	1.74	1.63	1.71	--	1.30
135	1.04	1.62	2.68	2.19	2.31	2.08	1.77
0.2 mole % rare earth fluoride added, melt completely frozen in about 300 min							
145	1.08	1.05	1.67	1.75	1.85	--	1.38
210	1.04	1.27	2.64	2.16	2.30	--	1.77
240	1.05	1.37	2.88	2.46	2.40	1.95	1.81

*Trivalent rare earths, i.e., all rare earths except cerium.

Table 8.5. Oxide Precipitation of Fission Products from Flinak Containing 0.07 mole % ZrF_4, 550°C

Time, min	Activity Remaining in Solution, %					
	Zr	Nb	Cs	Ce	TRE	Sr
Add 0.25 mole % CaO						
20	60	76	99	104	96	91
60	89	53	106	101	98	91
Add 0.2 mole % rare earths and CaO to 0.45 mole %						
60	63	52	102	91	93	90
Add CaO to 0.7 mole %						
90	37	36	98	82	82	92
Add rare earths to 1.2 mole %						
60	<1	30	96	78	77	82
Add CaO to 3 mole %						
60	<2.5	<4	85	<4	<4	71

to be removed. This will also allow free access from the back to the front of the cell up to an elevation of approximately 30 in.

A 6-in.-dia hole was drilled through the concrete roof of the cell. Through this opening the charge material will enter the cell and the waste salt will be withdrawn. A steel sleeve is being fabricated. The design of the chute to receive the PWR assemblies when they are dropped into the cell was completed. This chute is mounted vertically and is a 3-in. NPS, Schedule 40 stainless steel pipe. It has a funnel section at the upper end to match the 6-in.-dia hole through the top of the cell. The lower end is closed with a 1/4-in. horizontal plate and has an 8-in.-high, ~180° cut-out. A 9-in. length of 3-3/4-in.-dia tubing with a 7-in.-high ~180° opening surrounds the lower end of the pipe and rests on the horizontal end plate. This provides a rotating closure which will contain a PWR fuel element after it is dropped into the pipe. The manipulator can then be used to rotate the tube to align the openings and remove the fuel element and place it in the hydrofluorinator. The 3-in. pipe is mounted on two heavy hinges which pivot it on a 9-in.-radius arc. This allows the pipe to be moved from under the roof opening to a position along the cell wall where it will be out of the way when waste salt cans are removed from the cell through the roof opening.

Now under study is a handling device to move small (600 to 1000 lb) shielded carriers in and out of the cell through the rear opening of the cell. This device is necessary to handle relatively low level unencapsulated charge material which cannot be introduced into the cell through the roof hole and charge chute.

8.3 Druhm Process (C. D. Scott, W. G. Sisson; Program Leader: J. C. Bresee)

The direct reduction of uranium hexafluoride to metal by use of sodium is being studied. From 76 g of uranium fed to a 2-in. contactor (ORNL-2416) as UF_6 (run UP-8), 20 g of uranium was recovered in a metal button, with a material balance of 87%. From the contactor walls 4.3 g of uranium metal was recovered by an aqua regia leach.

The metal button, weighing a total of 49 g, was on the bottom of the graphite liner, surrounded by slag. Part of the entrance line was melted or corroded away during the run. The graphite liner was penetrated in numerous small spots by both slag and metal; however, there was no other general deterioration of the liner.

Two runs were made; a graphite liner was used in each case. In both runs, VP-7 and VP-8, uranium metal in contact with the inconel walls formed low melting alloys and weakened the walls during the reheating to consolidate the reduced metal. In run VP-7 the was ruptured and results from that run are therefore not significant.

X-ray analysis of the slag showed the presence of NaF and of the $NaF.UF_3$ complex. The relative amount of the complex was not determined. Sodium analysis of the products gave inconclusive results, indicating that a nonhomogeneous sample was submitted from the graphite liner material. This incomplete reduction can probably be avoided by the use of larger amounts of sodium.

Part III. AQUEOUS HOMOGENEOUS REACTOR FUEL AND BLANKET PROCESSING AND DEVELOPMENT

Program Leader: D. S. Ferguson

9.0 HRT CHEMICAL PLANT

9.1 Operation of the Hydroclone Loop (W. D. Burch, W. L. Albrecht, R. H. Winget)

The HRT Chemical Plant hydroclone loop was operated throughout the final 300-hr test operating period of the reactor system. The system was started up, operated, and shut down four times without difficulty except leakage of two valves following a sampling operation. The two valves, in series, act as let-down valves, throttling flow from the hydroclone overflow stream at 1700 psi down to atmospheric pressure. Following a normal sampling operation these valves, when closed, leaked at a rate greater than 10 liters/hr for several hours until the leak was finally pinpointed and the plant was isolated from the reactor. The reactor continued operating normally for another 24 hr with a 10% reduction in fuel inventory, but was subsequently shut down in order for the exact inventory to be re-established. The solution leaked to the D_2O storage tank, filling it and overflowing into the vent system because the circuits for an interlock designed to divert such leakage back to the reactor dump tank had not been completed. One spare valve was installed and the other leaking valve repaired.

The hydroclone system sampler was tested for the first time during this period of operation. Except for the leaky valves the high-pressure sampler functioned properly. Following shutdown of the system, a sample of the underflow pot contents is obtained by circulating at atmospheric pressure through a second sampler via the circulating pump. During these tests, circulation was established, but misalignment of the sample flask holder prevented proper drainage of the sample into the sample flask. The holder has been realigned to permit normal draining.

Prior to this operating period, the leak-detector system was charged with heavy water (~11 liters) in anticipation of radioactive operation. All flanges remained leakfree throughout the runs.

Slight chloride contamination (5—10 ppm) was noted in the leak-detector pressurization tank during replacement of a broken sight glass. Pressurization manifolds and lines to individual flanges had been shown previously to be uncontaminated, and checks following detection of the contamination showed the lines still essentially free of chlorides. The pressurization tank was cleaned and recharged with clean D_2O.

9.2 Construction and Maintenance (W. D. Burch, W. L. Albrecht, R. H. Winget)

The roof shield plugs were installed in order that cell temperatures might be checked during operation. Design temperatures were easily maintained even without the space cooler. Seal pans, which are installed between the two layers of plugs, were fabricated and fitted.

To eliminate the tantalum tubes with tubing fittings piercing the dissolver top flange, a flange was fabricated of Carpenter-20. Corrosion resistance of this material had been established previously. Lines to the dissolver flange are now welded directly to the flange. The tantalum liner in the vessel and tantalum thermowell and transfer tube were retained. After fabrication the entire assembly was leak-checked with a helium leak detector with 100 psi helium pressure.

9.3 Holdup Tests on HRT Charcoal Adsorber Beds (R. E. Adams,* W. E. Browning*)

Experimental data from small laboratory charcoal beds indicated that the presence of a horizontal void space in a charcoal bed reduces the efficiency of the bed significantly. Therefore, holdup tests of the HRT charcoal beds are in progress under simulated operating conditions to determine their efficiency before reactor startup. A radioactive tracer technique developed for use in the laboratory adsorption study is being used. A pulse of Kr-85 is injected at the entrance of each bed and then swept through the bed by a stream of oxygen. Gases leaving the bed are monitored by a G.M. tube, and the activity is measured by a linear count rate meter.

Results of holdup tests on charcoal beds 10-A and 10-B run during the month of August are not considered valid because of temperature-induced changes in the field-mounted counting circuits and inaccuracies in sweep gas flow measurements. Holdup tests on these beds are to be rerun at a later date.

In tests on charcoal beds 10-C and 10-D the electronic equipment was moved into an air-conditioned building to eliminate temperature fluctuations. Wet-test meters were installed downstream from the counter to measure total gas flow leaving the beds. A graph of activity in the effluent gas versus time after injection of the pulse of Kr-85 is given in Fig. 9.1. Activity broke through bed 10-C, containing 250 lb of charcoal, after 186 hr and reached a maximum (t_{max}) after 211 hr. The average gas flow through this bed was 1.022 liters/min. Activity broke through bed 10-D, containing 360 lb of charcoal, after 140 hr and reached a maximum (t_{max}) after 170 hr. Average gas flow through the bed was 0.947 liter/min. These gas flows are approximately four times the design flow rate of 0.25 liter/min. Calculated values for t_{max}, based on laboratory data from small charcoal traps, are 300 hr for HRT charcoal beds 10-A, 10-B, and 10-C at a gas flow of 0.25 liter/min. It should be noted that holdup times are inversely proportional to flow rates, and the efficiency of the charcoal bed, as determined by these tests, is higher than anticipated. Calculated values for N (the number calculated from the pulse width, not from breakthrough times) were lower than expected (see ORNL-2416, Sec. 13.3). This indicated void spaces in the charcoal beds. However, on the basis of the holdup tests, beds 10-C and 10-D should be adequate for use under reactor operating conditions. The bed temperature ranged from 16 to 19°C during the test, and under reactor conditions the inlet end of the charcoal bed will be heated by decay of fission gases. This will tend to reduce the overall efficiency of the charcoal bed.

* Solid States Division.

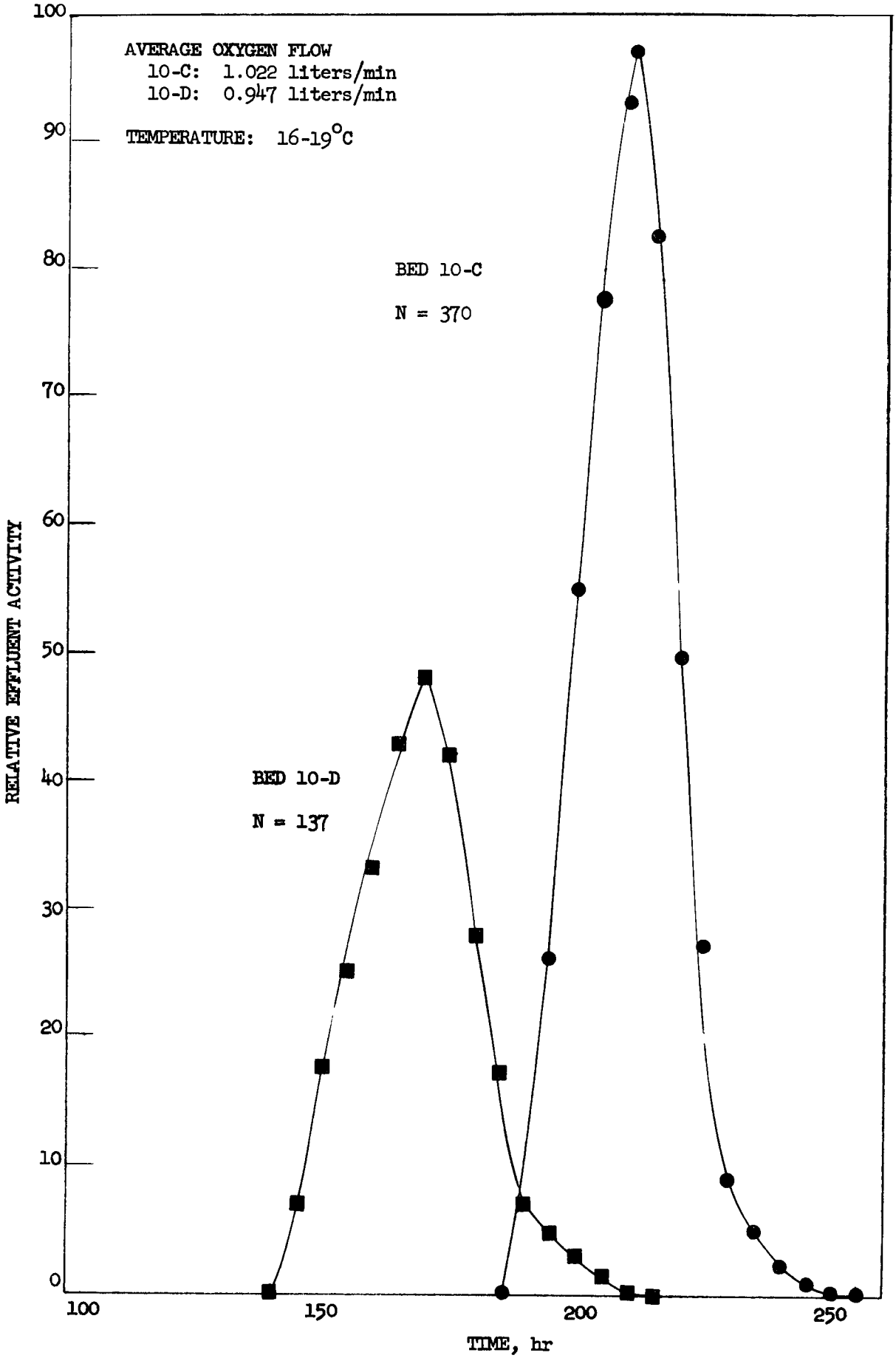

Fig. 9.1. Activity of Effluent Gas as a Function of Time after Injection of a Pulse of Kr-85 into HRT Charcoal Beds 10-C and 10-D.

10.0 URANYL SULFATE FUEL PROCESSING

10.1 Solids Behavior (R. A. McNees)

The hydroclone attached to a Y-12 loop which has been undergoing a thermal cycle from 300 to 100 to 300°C each day has removed signigicant amounts of corrosion product solids from the loop stream (Fig. 10.1). The estimated daily production of solids assuming a 0.1 mpy corrosion rate on 40 ft^2 loop area, is 80 mg if all corrosion product iron and chromium appear in the solids. A hydroclone and a 500-ml in-line sample bomb are being installed on another loop for use in estimating both the efficiency of the separation process under stable temperature conditions and the concentration factor for the hydroclone.

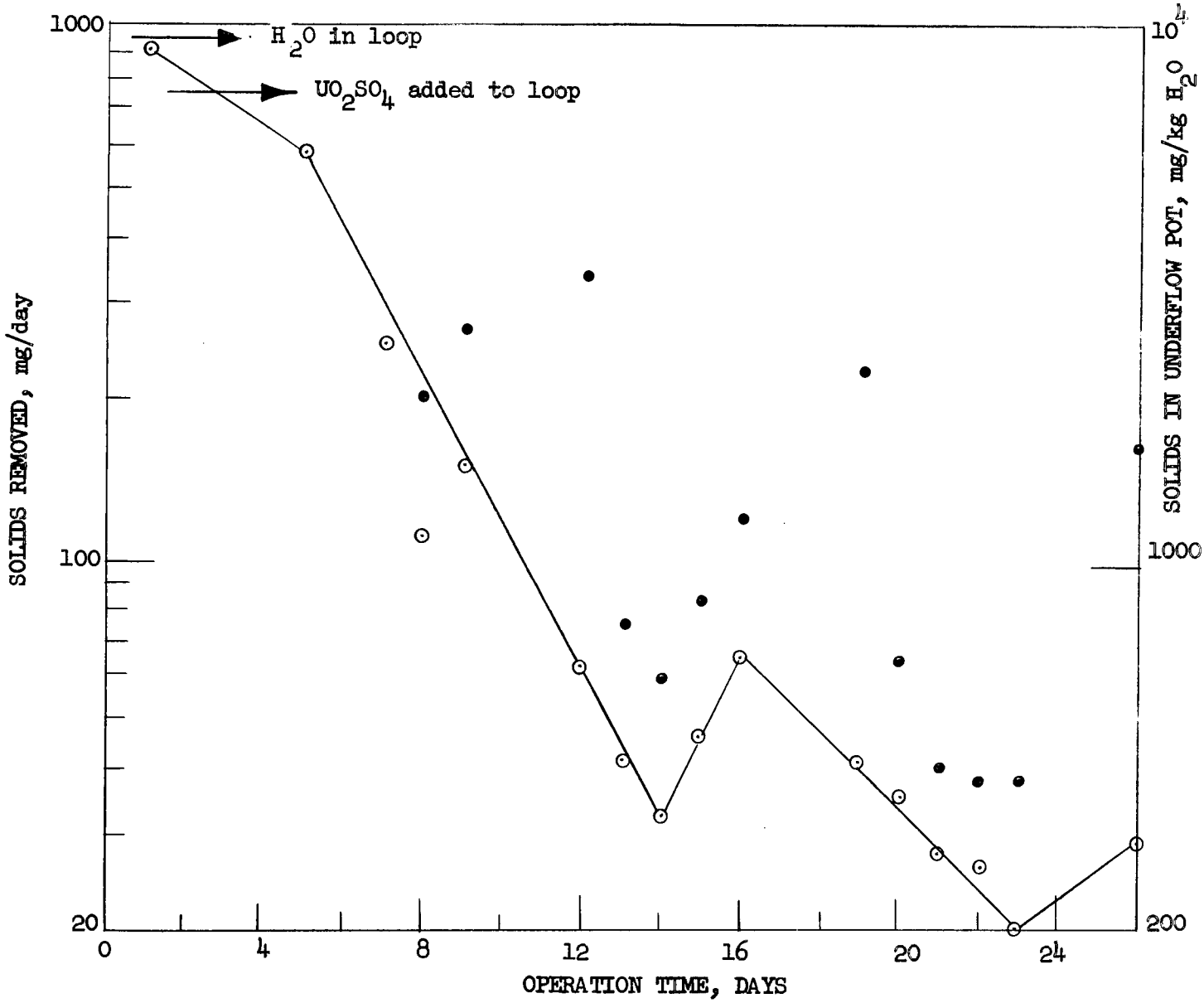

Fig. 10.1. Removal of Solids by Hydroclone from Thermally Cycling Loop and Concentration of Solids in Hydroclone Underflow Pot

The accumulation of mixed corrosion product solids on stainless steel pins exposed to dilute agitated slurries of such solids in 0.04 m UO_2SO_4 was studied with synthetic solids traced with either Fe-55 or Zr-95. The activity on the metal specimen exposed to iron-traced solids reached very nearly equilibrium conditions in about 100 hr while zirconium activity on similar pins continued to increase up to 184 hr (Fig. 10.2). The amount of iron activity on the pins was apparently doubled by increasing the solids concentration in the slurry by a factor of 12. For these tests metal pins of type 347 stainless steel in an unfilmed condition measuring 0.125 x 0.125 x 0.55 in. and with a surface area of 2 cm^2 were used. The experiment is being continued and will be expanded to include solids concentrations between 100 and 1200 mg/kg.

10.2 Iodine Chemistry (R. A. McNees, S. Peterson)

Loop Experiments. Iodine was very effectively removed from the HRT mockup by a silvered alundum bed kept at 150°C; a similar bed at 120°C was less effective (Fig. 10.3).

In each of two experiments, iodine was introduced into the stream being pumped from the dump tank to the high-pressure loop. As in a previous experiment, the iodine concentration in the high-pressure loop rose sharply until removal in the letdown stream competed with the iodine introduction, eventually becoming constant, and finally dropping sharply as the iodine feed was stopped. Iodine accumulated in the condensate tank until the source in the high-pressure loop diminished. The concentration of iodine in the pressurizer, which is fed from the condensate tank, reflected the concentration of iodine in the condensate tank with about a 1-hr time lag. Both these vessels acquired a smaller fraction of the iodine in the system when the silvered alundum was at the higher temperature. The dump tank leveled off at a low concentration, which dropped when the feed was stopped.

In each experiment the vapors from the dump tank passed through a bed, 6 in. dia by 8 in. high, packed with 4275 g of 0.25-in. silvered alundum rings. Samples of rings at 2-in. intervals had the iodine concentrations shown in Fig. 10.4. Included for comparison is a previous experiment with a 5-in. bed. Lines drawn in are the least-squares fit of the data. Bed efficiencies (percent of iodine retained in the bed) determined from the iodine distribution were:

Bed Height, in.	Temp, °C	Efficiency, %	
		From Bed Analyses	From Solution Analyses[a]
8	150	97.7	86.9, 85.5
8	120	81.0	79.7, 81.1
5	110	64.0	39.6, 38.6, 74.0

[a]Calculations made by Paul Harley of the Reactor Experimental Engineering Division.

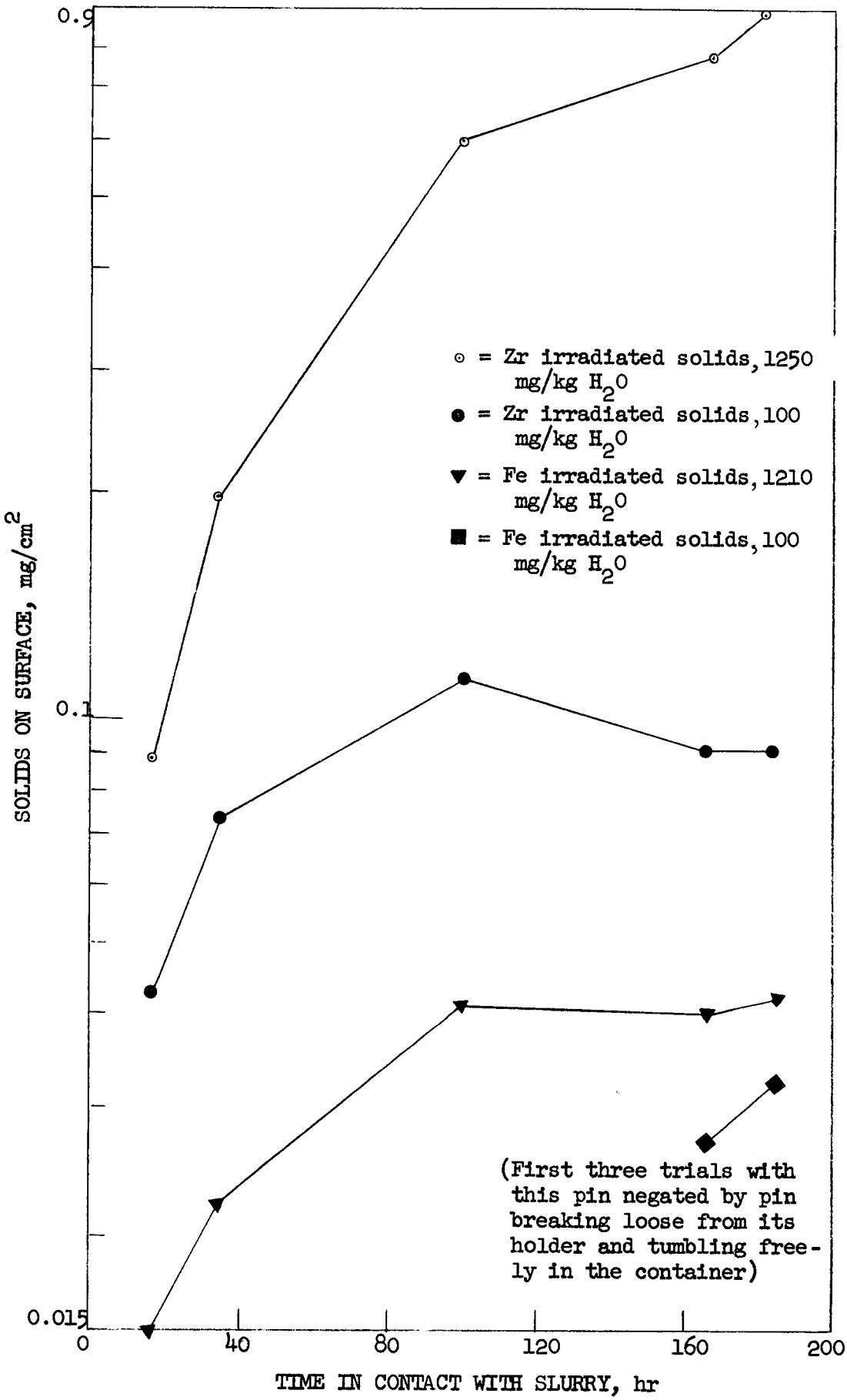

Fig. 10.2. Adsorption of Simulated Mixed Corrosion Product Oxides by Type 347 Stainless Steel at 26°C.

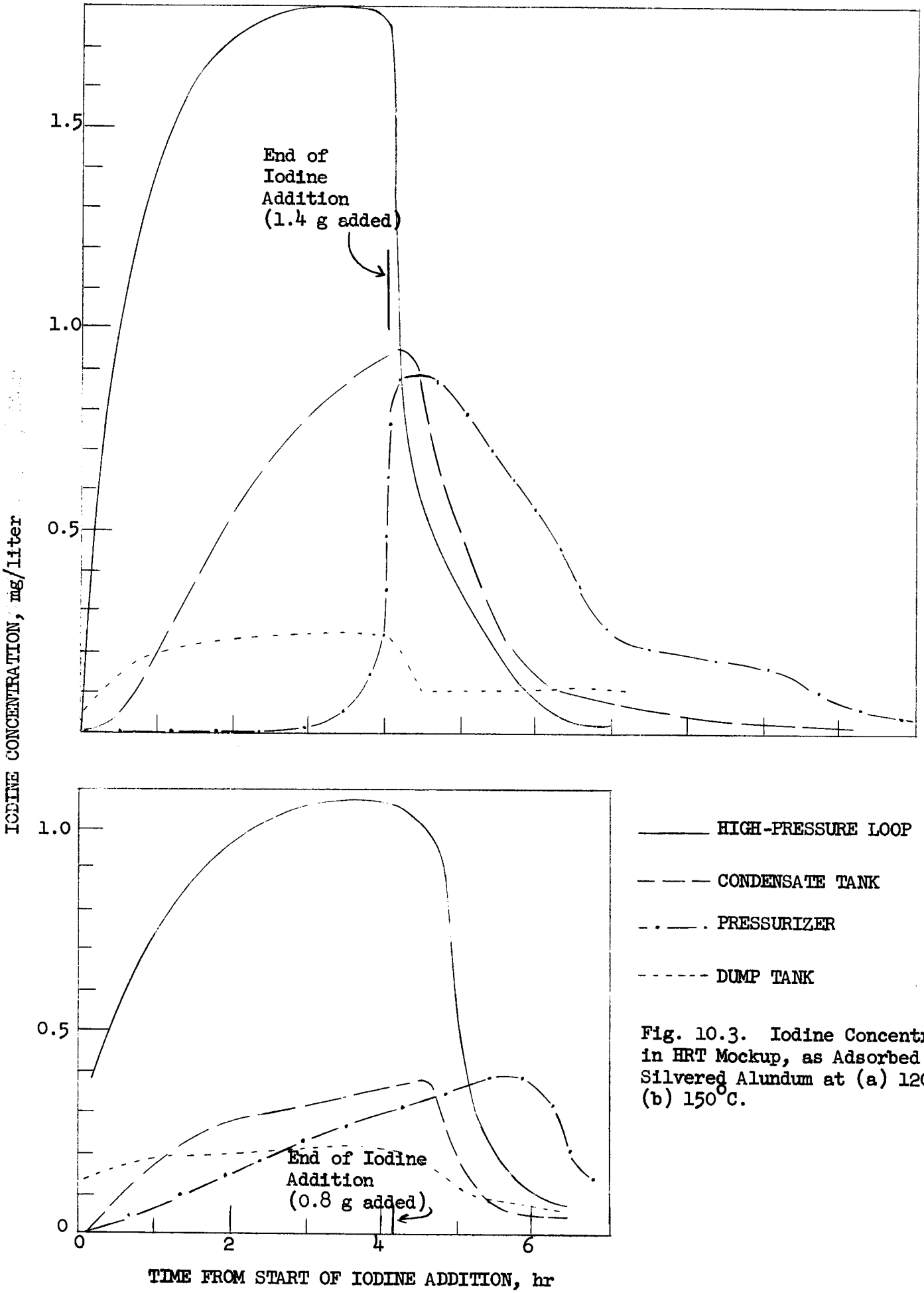

Fig. 10.3. Iodine Concentrations in HRT Mockup, as Adsorbed by Silvered Alundum at (a) 120°C; (b) 150°C.

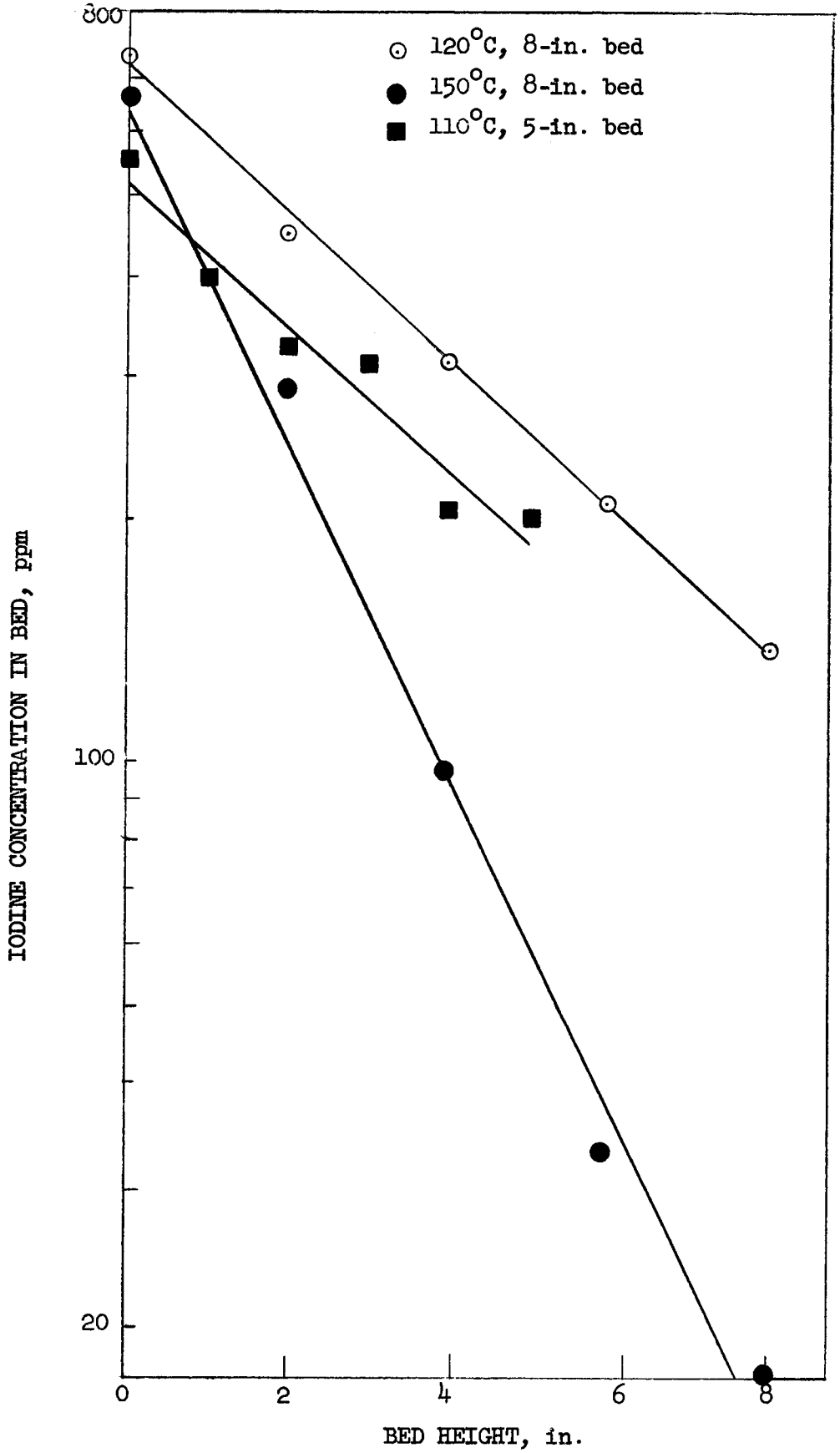

Fig. 10.4. Iodine Distributions in Silvered Alundum

The iodine distribution in the 5-in. bed corresponds to an efficiency of 80% for an 8-in. bed.

Laboratory Experiments. Silver-plated York mesh packing was less effective than silvered alundum pellets for removing iodine from steam-oxygen streams in the 1-in.-dia laboratory apparatus. This, along with an irregular distribution of iodine in the bed after partial saturation, suggests that in the small-diameter bed gases readily channel past portions of the mesh packing.

Silvered alundum on prolonged exposure to the stream adsorbs one atom of iodine per atom of silver. The iodine-removal efficiency for silvered alundum is enhanced by prolonged firing of the pellets in hydrogen and diminished by firing without hydrogen.

In the experiments metered oxygen was saturated, at controlled temperature, with tagged iodine and then introduced into the steam. The bed temperature was achieved by controlled preheating of the stream and heating of the iodine trap. Iodine was measured in portions of the trap by an ion chamber and in samples of condensed effluent by scintillation counting.

Iodine-removal efficiencies for silvered alundum (6 mg Ag/g alundum) and silver-plated York mesh (53.8% Ag) are compared at 120-126°C in Fig. 10.5. The beds compared were first, five sections of 15 g of pellets each; second, three sections of pellets alternating with two sections of wire, containing about 3 g of silver each; third, three sections of pellets; and fourth, a section of wire containing 17.5 g of silver. It appears from these experiments that the wire is much less effective than a pellet bed of the same length, although adding it to pellets adds to the iodine capacity. At the end of the experiment with the mixed absorber, the three-section pellets were each loaded to 90% of capacity. The upper (first contacted) wire bed contained 10.7 mg of iodine per gram of wire, the lower 7.6 mg. In the experiment with wire only, the absorber showed a similar decrease in iodine content with penetration, although irregularities suggested channeling of the iodine stream.

The iodine penetration of a silvered alundum bed (450 mg Ag on 75 g pellets at 137°C) on prolonged use is shown in Fig. 10.6. At the end of the experiment the bed contained 526 mg of iodine uniformly distributed among five sections. This is in excellent agreement with the 530 mg that would be equivalent to the 450 mg of silver present. This shows that all the silver in dilutely impregnated alundum is available for reaction with iodine.

The distribution of iodine in the absorber was determined in two partial-saturation experiments with ten 7.5-g sections of silvered alundum pellets (6 mg Ag per gram alundum) and in one experiment with 5 7-g sections of silvered York mesh. The features of these experiments were:

Experiment	Duration (hr)	Total Iodine in Experiment (mg)	Iodine Found in Condensate (mg)	Absorber
18	3.00	373	7.7	Alundum
19	1.00	108	17.2	York mesh
20	1.25	150	0.08	Alundum

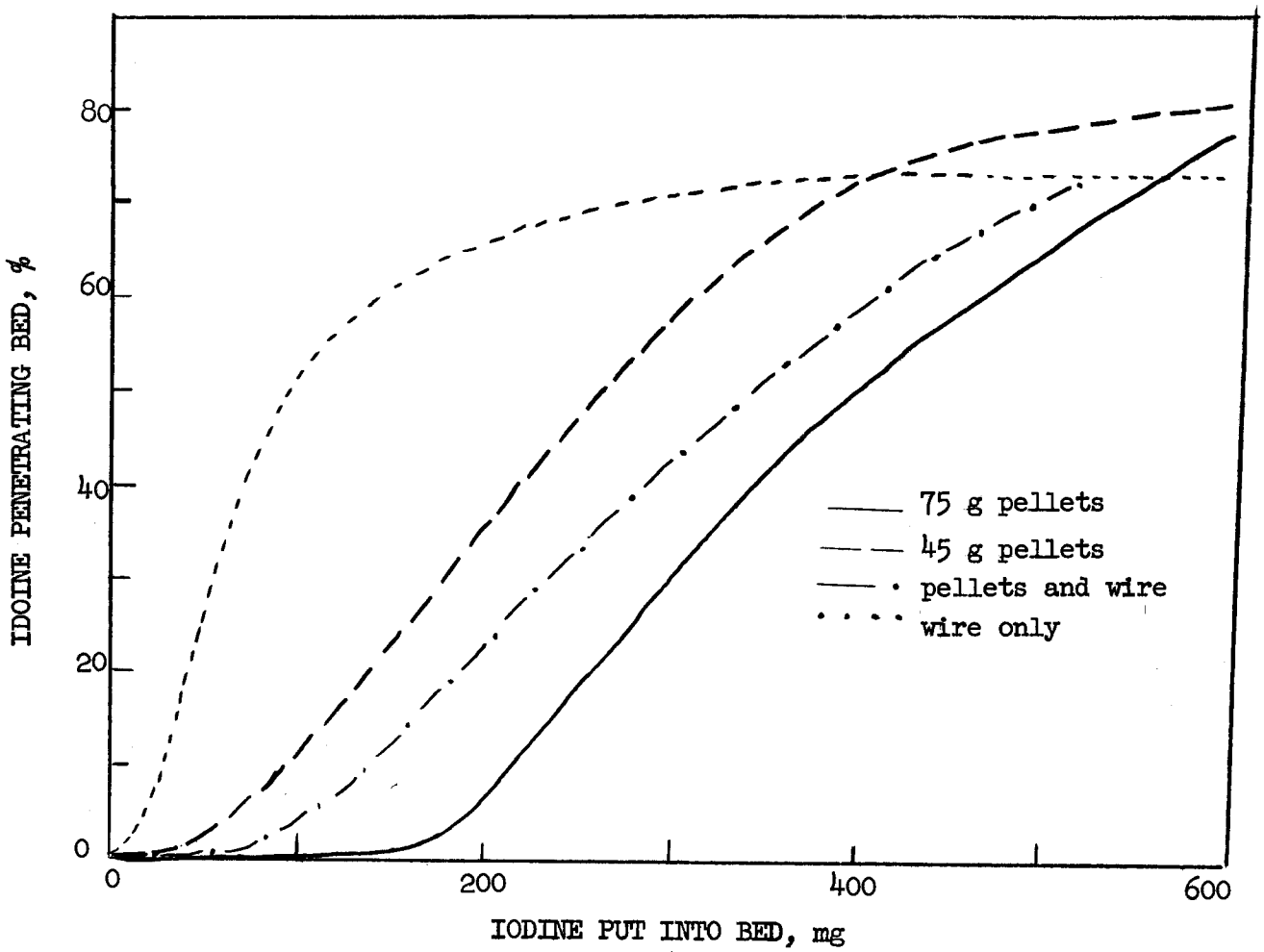

Fig. 10.5. Effect of Bed Packing on Iodine Penetration.

Fig. 10.7 shows the iodine distributions in the experiments with silvered alundum. The large fraction of saturation in the first sections leads to deviations from exponential distribution. With York mesh the concentration also decreased with bed depth, but results were erratic because of channeling:

Section	Iodine Concentration (mg per gram wire)
1	3.13
2	2.39
3	4.99
4	0.98
5	1.33

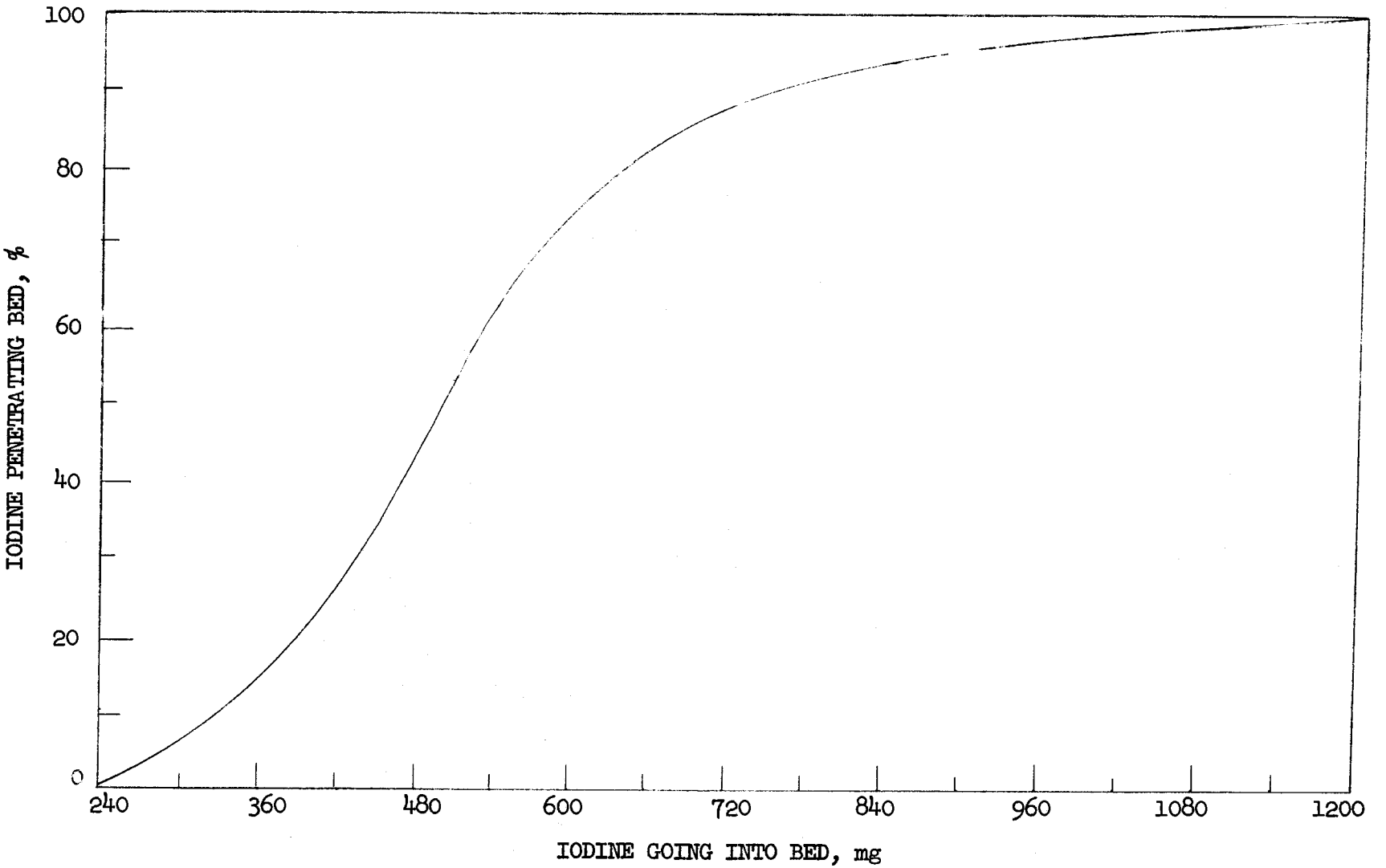

Fig. 10.6. Iodine Penetration of Silvered Alundum on Prolonged Exposure.

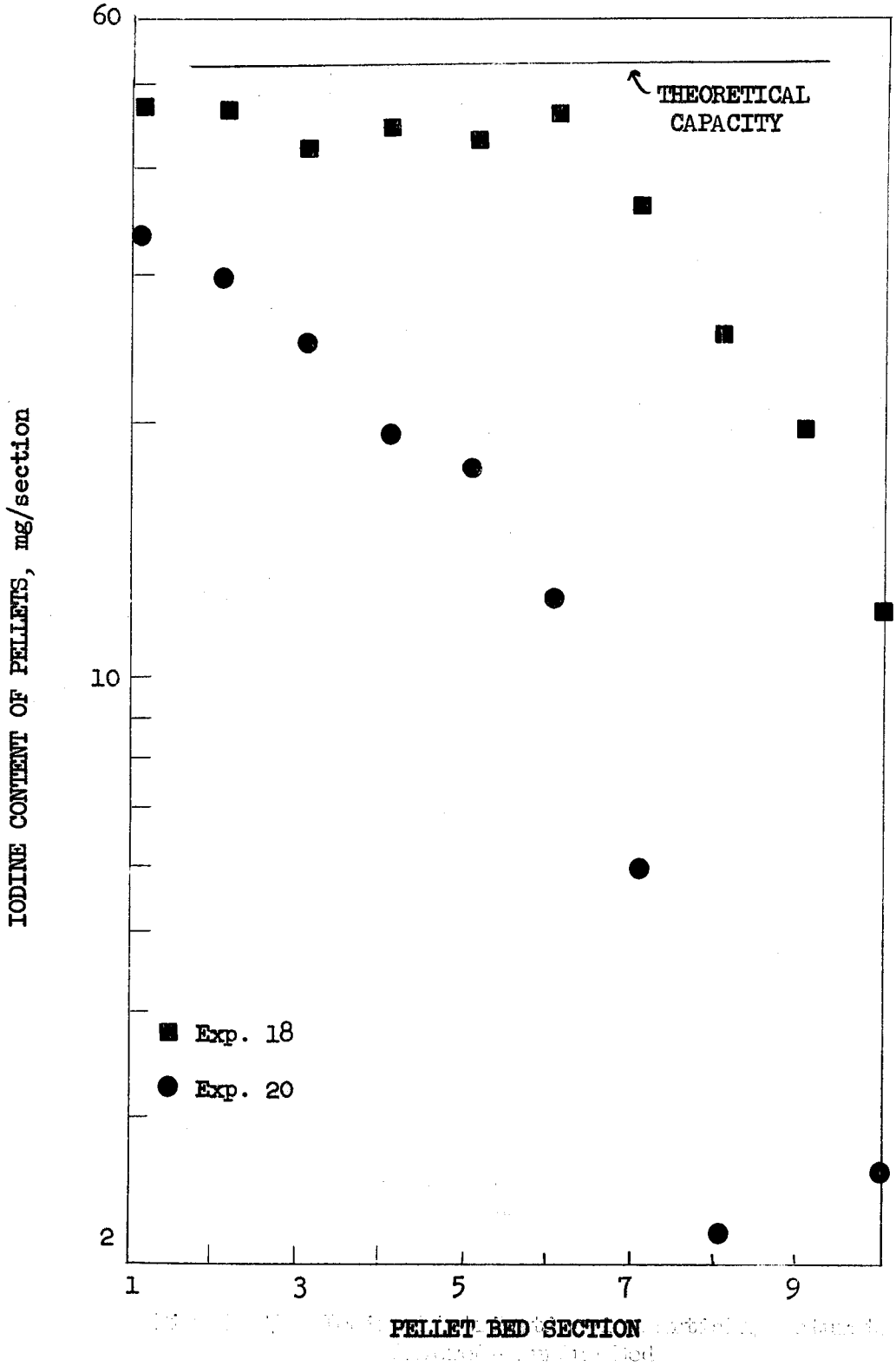

Fig. 10.7. Iodine Distribution in Partially Saturated Silvered-Alundum Bed

The effect of firing conditions on the efficiency of silvered alundum is illustrated by Fig. 10.8. The alundum was impregnated in one batch to 6 mg Ag/g alundum and four portions were fired separately as follows:

1. Heated in H_2 to 400°C
2. Heated in air 1 hr at 500°C, then 1 hr in H_2
3. Heated in H_2 1 hr at 500°C
4. Heated in H_2 approximately 6 hr at 500°C

The considerably greater penetration of the bed with preparation 2 clearly shows the adverse effect of firing without hydrogen. The other results show definite improvement of iodine absorption with increased firing of the pellets in hydrogen. This is also borne out by the iodine content of the effluent:

Iodine Addition	Iodine Absorbed, μg			
	Preparation 1	Preparation 2	Preparation 3	Preparation 4
In first 75 min	14	92	11	4.7
In next 15 min	18	82	14	6.3

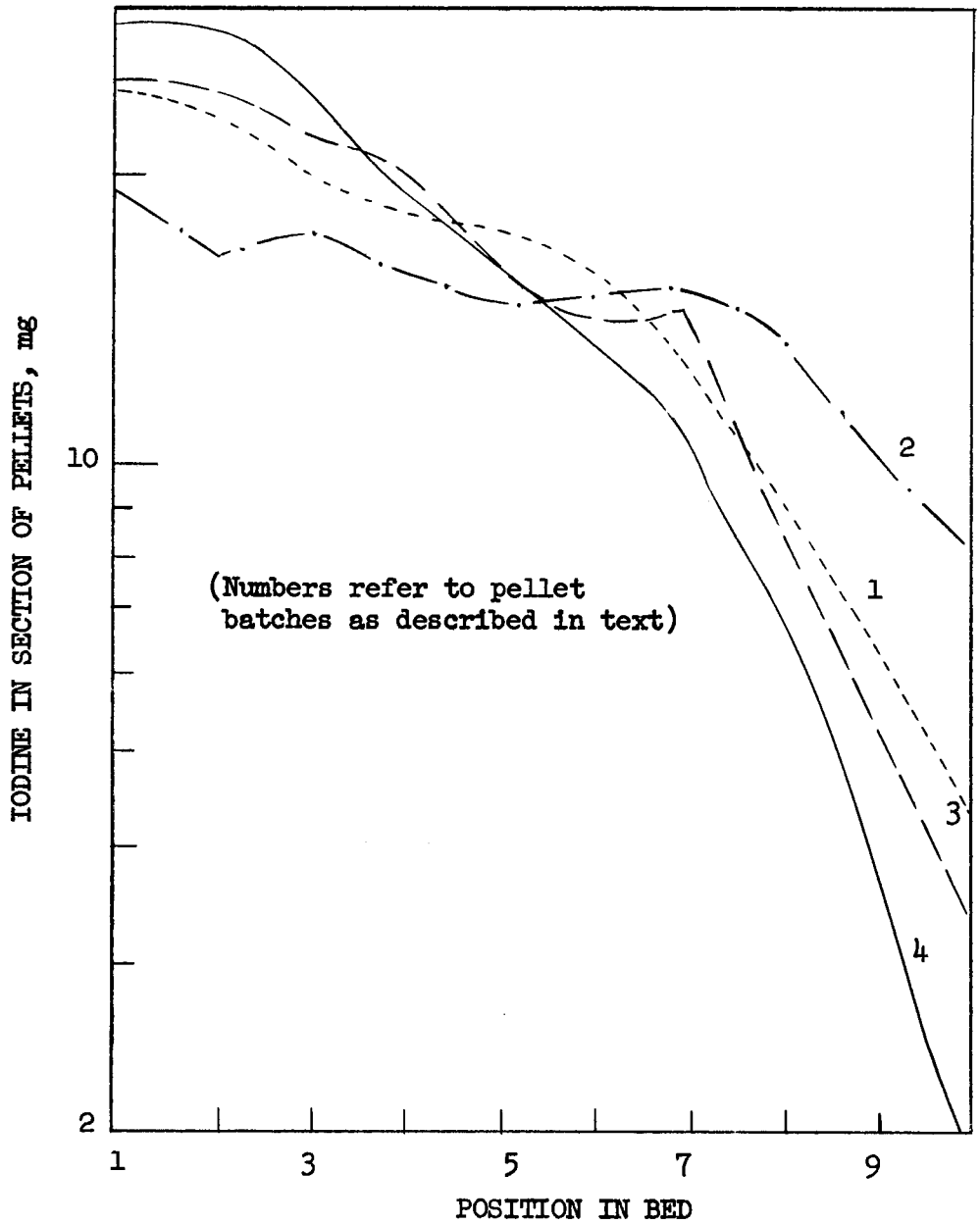

Fig. 10.8. Effect of Pellet Firing Conditions on Iodine Removal.

11.0 ADSORPTION OF FISSION GASES BY ACTIVATED CHARCOAL

11.1 Dynamic Studies (R. A. McNees, R. E. Adams,* W. E. Browning,* J. F. Krause*)

The study of N (the number of theoretical chambers in a particular charcoal trap) as a function of trap length was continued. Although sufficient data have not yet been obtained to warrant definite conclusions, it appears that N is not directly proportional to length. A vertically mounted charcoal trap consisting of 30 lengths of 3/4-in.-dia pipe is being used for this study. Each pipe is 7 ft long and contains approximately 360 g of activated charcoal with provisions for each length of pipe to be studied separately or in combination with other lengths. From data thus far obtained (Table 11.1) it is seen that the cumulative value of N as determined by separate examination of the four sections of the trap is approximately 340 but the average value determined by studying the four sections in series is only 249. The times to breakthrough and maximum activity for the series traps are longer than the sum of such times for the individual traps but such effects may be due to small temperature variations.

Evaluation of other adsorber materials was started in small traps fabricated from 0.5- by 12-in. glass pipes. Oxygen at a flow rate of 65 cc/min was used as the sweep gas with Kr-85 as the tracer. In these tests (but see Sec. 11.2) there was no difference between Linde molecular sieves 4A and 5A, while 10X and 13X were considerably more efficient:

Adsorber	Wt, g	Temp. °C	t_b, min	t_{max}, min	Efficiency, % of that of charcoal
Linde M.S. 4A	22.1	25.5	1.25	1.75	14
Linde M.S 5A	21.6	25.5	1.25	1.75	14
Linde M.S. 10X	20.8	25.5	2.75	3.5	28
Linde M.S. 13X	22.0	25.5	3 00	4.5	36
Columbia Charcoal G	18.7	25.5	6.75	12.5	100

The 13X and 10X materials are reported as having pore diameters of 13 and 10 A, respectively.

11.2 Equilibrium Studies (M. H. Lloyd)

Static adsorption isotherms showed considerably greater efficiency for Linde molecular sieves 5A than for 4A (Fig. 11.1). The 13X material adsorbed slightly better than the 10X. Adsorption for 13X was 4.48 mg of krypton per gram while adsorption for 5A was 7 mg of krypton per gram at a pressure of 128 mm.

The effect of mercury on the adsorption characteristics of Columbia charcoal grade 6G was determined by exposing the charcoal to mercury vapor at 28°C and then obtaining an isotherm with krypton. One gram of charcoal adsorbed 0.60 mg of mercury. Two hours was required for this amount of adsorption to take place; no further adsorption took place after this length of time. The adsorbed mercury had no effect on the krypton adsorptive capacity of the charcoal.

*Solid States Division.

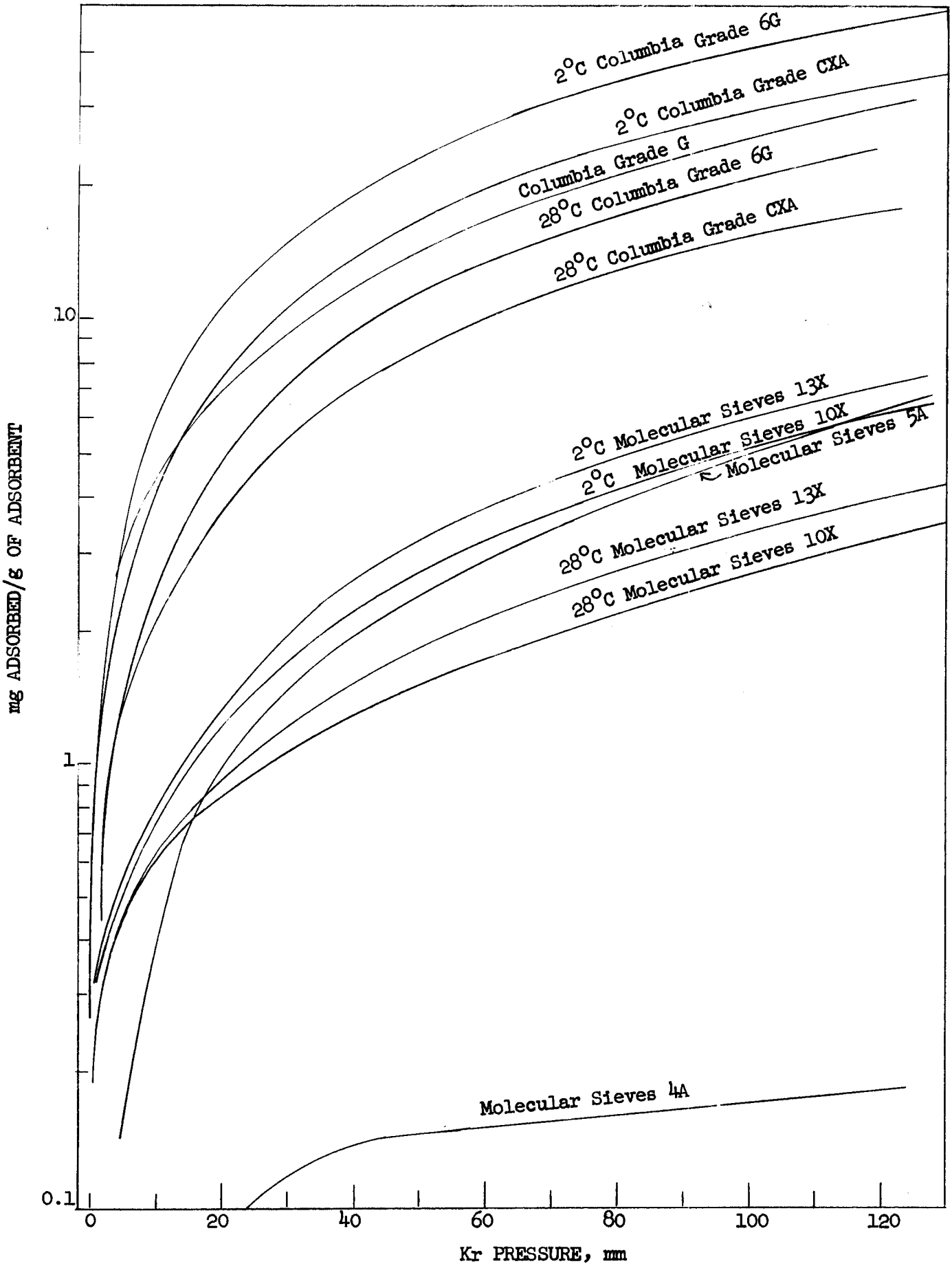

Fig. 11.1. Equilibrium Adsorption of Krytpon on Linde Molecular Sieves and Charcoal.

Table 11.1. Variation of Number of Theoretical Chambers with Trap Length

Trap Section	Run No.	Temp, °C	t_b, min	t_{max}, min	N
1	1	27	31	45	82.6
	2	27	31	45	82.6
2	1	26	31	44	85.7
	2	27	31	45	88.8
3	1	26.5	31	45	82.6
	2	28	31	45	82.6
4	1	24	33	49	88.7
	2	24.5	33	49	85.5
1 and 2	1	26	69	92	136.5
	2	26	70	94	145.2
1, 2, and 3	1	26	116	150	192.9
	2	24	126	160	256.0
	3	24	126	160	225.7
1, 2, 3, and 4	1	26	170	212	241.2
	2	25	172	213	256.0

12.0 URANYL SULFATE BLANKET PROCESSING

One of the most important problems in connection with uranyl sulfate blanket processing is the behavior of plutonium and, more specifically, the adsorption of plutonium on metals. Experiments were carried out in the P-1 loop to study plutonium behavior under dynamic conditions. In addition, static bomb tests were made to determine the effectiveness of added acid in decreasing plutonium adsorption on metals, and to determine plutonium adsorption on various solids, such as oxides and sulfates.

12.1 Zirconium Behavior in the P-1 Loop (R. E. Leuze, J. M. Chilton, R. L. Hickey)

In four runs in the P-1 loop preformed ZrO_2 was used as a substitute for PuO_2. In run P-22, two 5-g additions were made. The pressurizer containing Raschig rings was then replaced with one not containing rings, decreasing the surface area from 46.3 ft^2 to 10.4 ft^2. Runs P-23 and P-24 were conditioning runs and additional ZrO_2 was not added. In run P-25, 1 g of zirconium was added to determine ZrO_2 behavior in the loop without the Raschig rings.

Results (Table 12.1) were in general agreement with those previously reported+* When preformed ZrO_2 was added to the loop, the half-time for disappearance from the circulating solution was 2-4 hr both with and without the Raschig rings. Only 6-16% of the ZrO_2 was removed by the hydroclone and 85-90% was removed by adsorption on loop walls. An overall material balance for runs P-17 through P-25 showed that of the 15 g of zirconium added, 1.21 g was removed by the hydroclone and 14.1 g was adsorbed, with a material balance of 105%.

12.2 Plutonium Behavior in the P-1 Loop (R. E. Leuze, J. M. Chilton, J. H. Groover, R. L. Hickey)

The P-1 loop was operated 111 hr (~93 hr at 250°C) with 12-13 liters of 1.2 m UO_2SO_4 containing 1.3-1.7 mg of plutonium per liter, added as dissolved $Pu(SO_4)_2$. This run, P-27, is the first of a series of experiments in which plutonium behavior will be studied in simulated blanket solution in a dynamic system.

Plutonium Distribution in Loop. The principal object of this experiment was to investigate plutonium adsorption on metal surfaces from a solution in which the plutonium solubility is not exceeded. The plutonium distribution (Table 12.2) showed that most of the plutonium remained in solution. Only 0.60 mg, or 2.7%, of the plutonium was adsorbed on the loop walls. This value was determined by multiplying specific adsorption values determined from type 347 stainless steel coupons by the total loop surface area. Only insignificant amounts of plutonium were collected in the hydroclone underflow. Plutonium in the loop drain, loop holdup, and samples remained in solution. This totaled 19.97 mg, or 93.4% of the total. The overall material balance of 96.1% is considered good since the loop holdup volume is not accurately known but is probably between 0.5 and 1.5 liters.

Plutonium Concentration in Circulating Solution. Throughout the run, the plutonium concentration in the circulating solution was followed by analyses of flowing stream samples taken every 8 hr (Fig. 12.1a). No precipitate was

*R. E. Leuze et al., CTD Monthly Progress Report, August, 1957, ORNL-2400.

detected in any of these samples. Plutonium concentrations determined by analyses differed from concentrations calculated by assuming 12 liters of solution (only that added at start of run) and based on the amount of plutonium added and the amount removed in samples because of dilution by loop holdup and plutonium loss by adsorption. Feed dilution by loop holdup is probably not rapid, since the difference in the calculated and analytical values increased gradually over the first 5-10 hr.

Table 12.1. Zirconium Distribution in the P-1 Loop

10 liters of 1.4 m UO_2SO_4 circulated at 250°C under 350-400 psi O_2

Loop surface area: 46.3 ft^2 for run P-22
10.4 ft^2 for runs P-23 to P-25

Run No.	Time, hr	Zr Placed in loop, g	Zr Added as ZrO_2, g	Zr Removed from Loop, g: Hydroclone	Loop Drain	Samples	Zr Adsorbed,[a] g	Zr Material Balance
P-22A	21	0.007	5.000	0.293	---	0.081	10.00	111
P-22B	26	---	5.000	0.281	0.357	0.085		
P-23	29	0	0	0.007	0.024	0	b	---
P-24	22	0.024	0	0.002	0.004	0	b	---
P-25	78	0.004	1.000	0.086	0.001	0.002	0.944[b]	103

[a]Calculated by multiplying average plutonium adsorption on coupons by loop surface area.

[b]Adsorption coupons were not analyzed after runs P-23 and P-24.

Table 12.2. Plutonium Distribution in Run P-27

21.4 mg Pu added to 12 liters of 1.2 m UO_2SO_4 and circulated 110 hr at 250°C under oxygen pressure

Location	Plutonium Distribution: mg	% of Feed
Loop drain	15.54	72.6
Loop holdup[a]	1.39	6.5
Adsorbed on walls[b]	0.60	2.7
Hydroclone underflow	0.018	<0.1
Samples	3.04	14.2
Material balance	20.59	96.1

[a]Based on an estimated loop holdup of 1.0 liter.

[b]Calculated from adsorption on metal coupons.

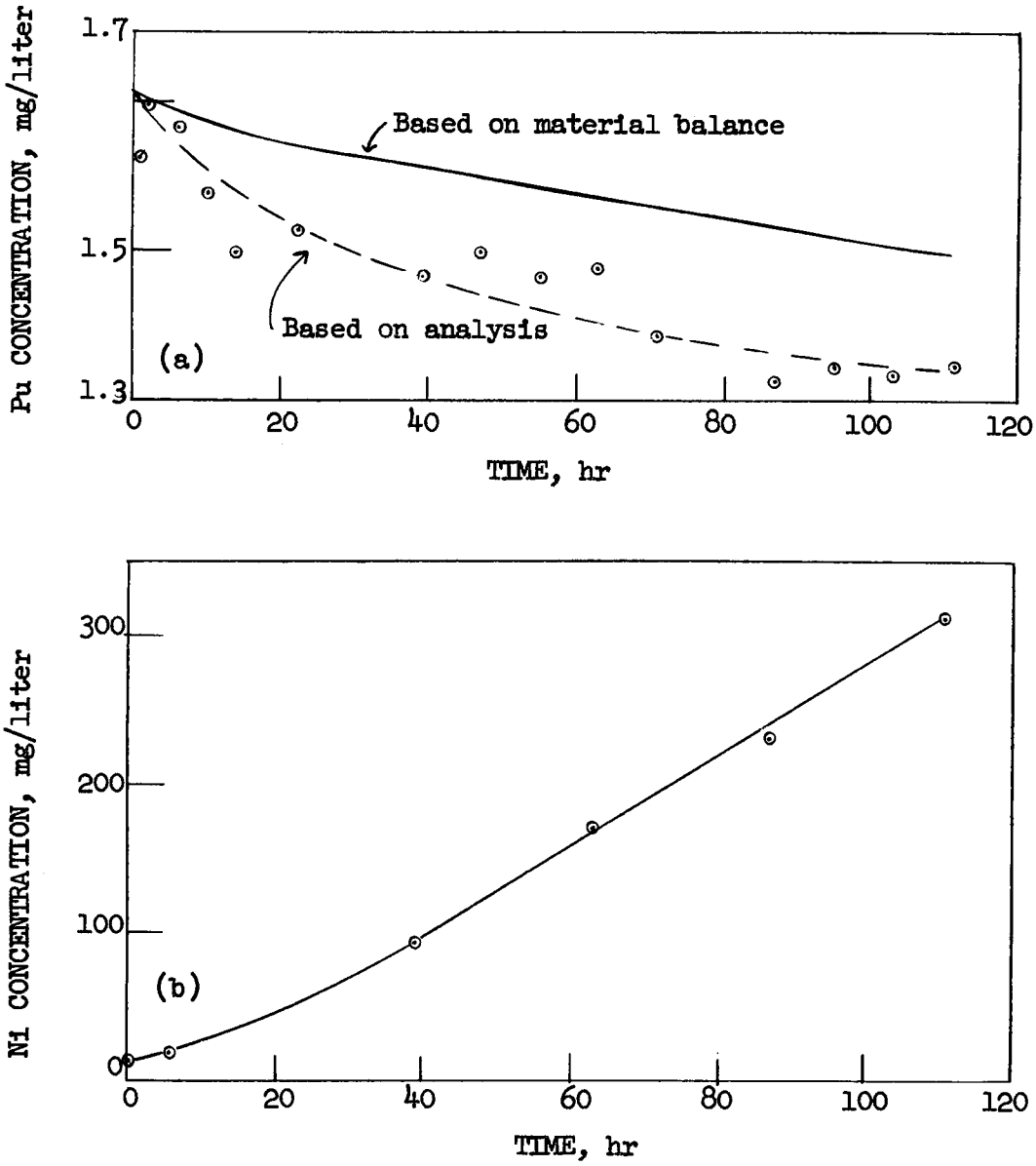

Fig. 12.1. Concentration of (a) Plutonium and (b) Nickel in Circulating 1.2 m UO_2SO_4. About 12 liters of solution circulated at 250°C under oxygen overpressure

In previous work in laboratory tests under static conditions oxidation of plutonium from Pu(IV) to Pu(VI) at 250°C was accompanied by a similar oxidation of Cr(III) to Cr(VI). In samples taken during the early part of this run both the chromium and plutonium were largely oxidized during the time the temperature increased from 200 to 250°C (Table 12.3). During the remainder of the run, both remained in the oxidized form.

Table 12.3 Plutonium and Chromium Valence in Run P-27

1.2 m UO_2SO_4 was circulated in the P-1 loop under 350-400 psi O_2

Time, hr	Temp., °C	Plutonium mg/liter	Plutonium % Pu(VI)	Chromium mg/liter	Chromium % Cr(VI)
0	30	1.74	17	4	~25
1	150	1.63	15	5	~20
2	200	1.70	18	4	~25
6	250	1.67	83	11	82
10	250	1.58	93	21	86
14	250	1.50	93	29	83
22	250	1.53	98	58	85
111	250	1.35	99	168	100

Plutonium Adsorption. Throughout this run, coupons of titanium, zircaloy-2, and 347 stainless steel were exposed to the circulating stream at velocities ranging from 1 to 3 ft/sec. At the end of the run the samples were washed and dried, and the alpha activity was counted on each side. The metal coupons were 0.5 by 0.5 by 0.03 in. Some of the coupons were those conditioned about 430 hr in the previous P-1 loop runs. These are labeled "old" in Table 12.4, while the remainder are called "new." From the alpha activity found on these samples a value was calculated for the amount of plutonium adsorbed on the total surface of the loop.

The data indicate that the velocity of the solution over this range had no significant effect on the adsorption. The well-conditioned stainless steel coupons adsorbed only 0.04 $\mu g/cm^2$, compared with 0.07 $\mu g/cm^2$ for the others. The conditioned samples are probably more representative of the wall surface of the loop. It is interesting that the adsorption on the conditioned titanium and zircaloy is approximately the same as on the conditioned steel. This may be due to the fact that they are probably covered with the same corrosion film from the steel loop.

The overall adsorption rate on the well-conditioned stainless steel samples throughout this run was about 0.0004 $\mu g/cm^2$.hr. This is considerably less than the value of 0.009 $\mu g/cm^2$.hr previously measured in static runs.*

Corrosion during Run P-27. During the plutonium run (P-27), the rate of corrosion was measured by means of nickel analyses of the circulating feed samples. The straight line portion of the graph in Fig. 12.1b shows that the corrosion rate is essentially uniform after the first few hours. Based on the total nickel found in this run, a corrosion rate of approximately 17 mils/year was calculated.

With this amount of nickel, there should be approximately 7.5 g of chromium and 26 g of iron in the corrosion products. In the final drain from the loop, approximately 25% of this amount of chromium was found in solution as chromate, and an insignificant amount, less than 2%, of the iron was found in solution.

*D. E. Ferguson et al., HRP Quar. Prog. Rep. April 30, 1956, ORNL-2096, p. 120.

Table 12.4. Plutonium Adsorption on Metal Coupons During Run P-27

Metal coupons 0.5 by 0.5 by 0.03 in. exposed to circulating 1.2 m UO_2SO_4 solution containing 1.35-1.7 mg/liter Pu under oxygen at 250°C for about 110 hr

Solution Velocity, ft/sec	Plutonium Adsorption, μg/cm²					
	Type 347 SS		Titanium		Zircaloy-2	
	Old[a]	New[b]	Old[a]	New[b]	Old[a]	New[b]
1.0	0.0426 0.0404					0.0433 0.0350
1.2		0.0750 0.0715		0.0150 0.0168		
1.3		0.0766 0.0717				
1.4			0.0414 0.0396			
1.5		0.0640 0.0841				
1.8					0.0478 0.0494	
1.9		0.0633 0.0657				
2.3	0.0417 0.0436					
2.5						0.0475 0.0294
2.8				0.0222 0.0230		
Avg.	0.0420	0.0715	0.0405	0.0192	0.0486	0.0388

[a]Conditioned in the loop about 430 hr at 250°C with 1.4 m UO_2SO_4 under oxygen.

[b]Unconditioned or conditioned in a static bomb 16 hr at 250°C with 1.4 m UO_2SO_4 under oxygen.

Throughout the run, the hydroclone was operated continuously and was discharged every 24 hr. The solid corrosion products, removed as solids by the hydroclone, totaled about 110 mg of iron and 10 mg of chromium. Most of the corrosion products therefore remained as scale on the walls of the loop.

12.3 Operating Procedures and Problems (J. W. Snider, R. D. Arthur, R. C. Early, D. A. McWhirter, G. E. Woodall, F. N. McLain, and S. G. Kent)

Pressurizer alterations were completed, the Raschig ring-free pressurizer giving an area/volume ratio of approximately 1 ft^2/liter at room temperature. Both the gas injection lines were plugged within the pressurizer but are now open for oxygen addition.

A third glove box was added to the loop facility, and is equipped to filter the spent feeds and sample both the filtrate and the solids removed. The filtered solutions may be reinjected into the loop or dumped into the underground tank.

Water was sometimes pulled from the loop can into the plutonium filter and the vacuum pump. An entrainment separator is being prepared for installation to prevent water damage to the filters. The condenser water cooling line was rerouted to by-pass the sump pump and relieve it of this additional load.

12.4 Static Adsorption of Plutonium on Metals (R. E. Leuze, R. L. Hickey)

In previous tests* excessive plutonium was adsorbed on metal container walls when plutonium was allowed to hydrolyze and precipitate from 1.4 m UO_2SO_4 at 250°C. In a series of scouting experiments the adsorption was considerably lower when the solution was acidified (Table 12.5). Preconditioning the metals with 1.4 m UO_2SO_4—0.54 m H_2SO_4 under oxygen at 250°C had little effect on the adsorption.

Plutonium adsorption on titanium and zircaloy-2 at 250°C under 170 psi O_2 from 1.4 m UO_2SO_4 containing 0.54 m H_2SO_4 and 2.2 mg of plutonium per liter was 0.007 and 0.068 $\mu g/cm^2$, respectively, in 16 hr. When an overpressure of 280 psi H_2 and 140 psi O_2 was used the adsorption was about 0.005 $\mu g/cm^2$ on titanium and varied considerably on zircaloy-2 (Table 12.5) but averaged about 0.02 $\mu g/cm^2$. This increase in adsorption was probably a result of holding plutonium in the tetravalent state. These adsorption values are less than 10% of previous data** (0.07 $\mu g/cm^2$ on titanium and 0.17 $\mu g/cm^2$ on zircaloy-2 when these metals were contacted for 16 hr at 250°C under stoichiometric H_2 and O_2 with 1.4 m UO_2SO_4 containing 1.9 mg of plutonium per liter but no free acid).

Plutonium adsorption on titanium and zircaloy-2 at 250°C under 170 psi O_2 from 1.4 m UO_2SO_4 containing 0.54 m H_2SO_4 and 50 mg of plutonium per liter was 0.04 and 0.13 $\mu g/cm^2$, respectively. When an overpressure of 280 psi H_2 and 140 psi O_2 was used, adsorption on titanium and zircaloy-2 averaged 0.06 and 0.36 $\mu g/cm^2$, respectively.

The data in Table 12.6 indicate that plutonium adsorption on titanium and zircaloy-2 from acidified 1.4 m UO_2SO_4 probably reaches a maximum, since the rate of adsorption decreased for long exposure times. The average rate of plutonium adsorption on titanium and zircaloy-2 during 242 hr exposure at 250°C under 170 psi O_2 to 1.4 m UO_2SO_4 containing 0.54 m H_2SO_4 and 2.2 mg of plutonium

*R. E. Leuze et al., HRT Quar. Prog. Rep. April 30, 1957, ORNL-2331, pp. 151-152.
** D. E. Ferguson et al., op. cit.

Table 12.5. Plutonium Adsorption on Metals from Acidified 1.4 m UO_2SO_4

Zircaloy-2 and titanium coupons heated at 250°C for 16 hr in 1.4 m UO_2SO_4

Plutonium adsorption determined by direct alpha counting of the metal coupons

	Pu Adsorption, μg/cm²				
	0.54 m H_2SO_4, 2.2 mg Pu/l		0.54 m H_2SO_4, 50 mg Pu/l		
Metal	170 psi O_2	280 psi H_2 140 psi O_2	170 psi O_2	280 psi H_2 140 psi O_2	50 mg Pu/l 170 psi O_2
Conditioned[a] titanium					
Top	0.0074	0.0004	0.038	0.058	0.120, 0.145
Bottom	0.0065	0.0060	0.036	0.057	0.074, 0.075
Unconditioned titanium					
Top	0.0082	0.0060	0.049	0.064	1.07, 0.147
Bottom	0.0073	0.0056	0.034	0.057	1.02, 0.074
Conditioned[a] zircaloy-2					
Top	0.0058	0.0089	0.137	0.170	1.07, 2.16
Bottom	0.0059	0.0411	0.126	0.450	2.04, 1.53
Unconditioned zircaloy-2					
Top	0.0096	0.0164	0.109	0.298	12.7, 7.62
Bottom	0.0096	0.0149	0.163	0.502	9.06, 2.06

[a]Metal preconditioned by heating under 170 psi O_2 at 250°C for 16 hr in 1.4 m UO_2SO_4 containing 0.54 m H_2SO_4.

per liter was 0.000050 and 0.000064 $\mu g/cm^2$.hr, respectively. Under similar conditions but with 50 mg of plutonium per liter, the average rates of plutonium adsorption on titanium and zircaloy-2 were 0.00021 and 0.00062 $\mu g/cm^2$.hr, respectively.

Table 12.6 Plutonium Adsorption on Metals from 1.4 m UO_2SO_4 at Various Exposure Times

Zircaloy-2 and titanium coupons were heated at 250°C under 170 psi O_2 in 1.4 m UO_2SO_4 containing 0.54 m H_2SO_2 and dissolved plutonium

Adsorption values are an average of 4 metal surfaces (except where noted)

Exposure Time (hr)	Pu Adsorption on Metal, $\mu g/cm^2$			
	2.2 mg Pu/liter		50 mg Pu/liter	
	Ti	Zr-2	Ti	Zr-2
16	0.0074	0.0077	0.039	0.134
16	---	---	0.043[a]	0.093[a]
32	---	---	0.061[a]	0.072[a]
80	0.0094	0.0086	0.053	0.168
242	0.0122	0.0156	0.050	0.150

[a]These results are each an average of 8 metal surfaces from another experiment under similar conditions.

Table 12.7. Effect of Added Solids on Plutonium Behavior in Uranyl Sulfate Solution

10 ml of 1.4 m UO_2SO_4 containing 15 mg of plutonium per liter and 1 g of solid heated at 250°C for 15 hr under 200 psi O_2

Solid	Solution			Pu Adsorbed, $\mu g/cm^2$	
	Pu, mg/liter	U, mg/ml	pH	Zr-2	Ti
Blank	15.4	---	0.98	0.54	0.016
$Zr(OH)_4$	0.27	343	1.91	0.41	0.18
Zr	1.9	238	0.45	0.17	0.015
ZrO_2	5.5	373	1.10	0.23	0.0066
$Zr(SO_4)_2$	2.7	---	0.10	0.048	0.023
TiO_2	8.7	---	0.98	0.52	0.031
C	6.2	401	0.66	0.33	0.014
Al_2O_3	14.9	---	2.02	0.71	0.010
$PbSO_4$	15.7	---	0.90	0.48	0.028
Ni	0.54	176	3.10	0.41	0.35

12.5 Plutonium Behavior in UO_2SO_4 Solution Containing Various Solids (R. E. Leuze, S. S. Kirslis)

Since plutonium deposition on system walls accompanied the precipitation of PuO_2 from uranyl sulfate blanket solution, scouting experiments were carried out on methods to recover plutonium other than by precipitation and removal with a hydroclone. Zirconium and its compounds effectively removed plutonium from solution (Table 12.7). Activated charcoal and TiO_2 were less effective, and Al_2O_3 and $PbSO_4$ had no apparent action. The result with nickel does not seem to have practical value since half the nickel dissolved and much of the uranium precipitated. Likewise, the result with zirconium metal powder (unconditioned) is of questionable value since some of the uranium was precipitated, as shown by the uranium analysis and by the pH.

The widely varying pH values found are generally interpretable in terms of hydrolysis of the added salt, reduction and hydrolysis of uranium, or the basic nature of the added solid. The decrease of pH to 0.66 for activated charcoal is puzzling.

Plutonium adsorption on zircaloy coupons was generally somewhat less when these various solids were present in the uranyl sulfate solution. Only for $Zr(SO_4)_2$ additive was the decrease in adsorption appreciable, and this may be due to the low pH of this solution. For the titanium coupons the least adsorption was obtained with the ZrO_2 additive, yielding one-third the adsorption observed on the blank. It may be noted that a high plutonium adsorption on metal would not necessarily preclude the use of an additive in a side stream off the reactor loop.

These tests were carried out by equilibrating 1.4 m UO_2SO_4 solution containing 15 mg of plutonium per liter with various solids at 250°C under 200 psi oxygen overpressure in a steel autoclave in pyrex tubes containing zircaloy-2 and titanium disks.

13.0 THORIUM OXIDE SLURRY DEVELOPMENT

13.1 Large-scale Preparation of Thorium Oxide

Thorium Oxalate Precipitation (P. A. Haas, W. M. Woods). Thorium oxalate of 1 μ average size, equivalent to 750 lb of oxide, was prepared in the coaxial-flow jet mixer. The oxide prepared from this material by multistage firing ending at 1600°C showed pronounced sintering, presumably the result of the presence of impurities (see Sec. 13.2).

The precipitation setup is being revised in an effort to produce a purer and more uniform material. A small-holdup vortex or centrifugal type mixer was fabricated and tested. Size analyses have not been received, but the precipitated $Th(C_2O_4)_2$ settled at a rate comparable to the 1-μ-dia material.

Thorium Oxide Production (E. M. Shank, C. V. Ellison). About 150 lb of jet-precipitated thorium oxalate was step-calcined to 800°C and recalcined in a gas-fired furnace: 60 lb to 1600°C for 4 hr and 90 lb to 1400°C for 12 hr. All the high-temperature calcinations produced dark, lumpy, and sintered material. None of the material was considered satisfactory. One additional calcina-

tion of jet-precipitated thorium oxalate was made at 1400°C for 12 hr, using a 4-hr interval in raising the temperature from 1200 to 1400°C; the oxide from this calcination was also unsatisfactory.

A test calcination to 1600°C was made with standard thorium oxide (LO-30), previously prepared and known to be free of contaminants. The oxide from this calcination was satisfactory (except for particle size). A second test calcination to 1600°C was made with previously prepared 10°C precipitated thorium oxalate (LO-15-2C). The oxide from this calcination was comparable to the oxide prepared from LO-30.

The 10°C precipitation facility was reactivated and modifications incorporated for the rapid addition of the thorium nitrate solution to the oxalic acid solution and for continuous metering of a flocculating agent to the thorium oxalate precipitate. One precipitation was made in the reactivated facility by adding 1.1 M thorium nitrate to 1.13 M oxalic acid solution at 25°C and metering a 1/6 volume of flocculating agent to the oxalate precipitate during transfer to the filter bed. The 25°C precipitated thorium oxalate was calcined to 1600°C. Analyses are not available but initial inspection of the calcined oxide showed no sintering and a high degree of crystal size uniformity.

Flame Calcination (P. A. Haas, C. C. Haws, Jr.). Three feeding methods for the flame preparation of thorium oxide are under investigation: (1) aspirating an organic solution of slurry containing thorium into the flame, (2) ultrasonic dispersion of a powder, and (3) critical-orifice expansion of a powder-gas suspension (suggested by Aerojet personnel). Preliminary tests with ether and alcohol solutions of thorium nitrate were particularly promising in that the oxide particles from the flame firing were too small to be handled by the spray collection chamber.

Ether and alcohol solutions of thorium nitrate were fed by a 1/4-in. aspirating nozzle into the flame of a conventional acetylene torch. Introduction of the organics appeared to cause no change in the flame characteristics. None of the thoria particles produced were caught in the previously adequate spray collection chamber. A small sample collected from an extended firing test under 1000X magnification under an optical microscope showed irregularly shaped particles with unusually jagged edges.

Several arrangements of flame-firing apparatus were tested to adapt ultrasonic dust dispersion to the thoria feeding problem. One fitting, consisting of a small (~100 ml) stainless steel beaker welded directly to the exponential probe of the transducer, worked effectively. Rough testings of this device as a feeder are being made.

Examination of a flame-fired sample of aluminum oxide (ORNL-2416) indicated that the particles that resembled spheres in electron micrographs had not been fused, although near fusion temperatures had been reached. The "spheroids" had a segmented surface, resembling a blackberry. A rounding of the general shape of the alumina particle had been achieved. Crystal imperfections showed the crystals to be in strain. The 75-μ particles that were fired were found under high magnification to consist of agglomerates of fine particles. Samples of Al_2O_3 and ZrO_2 were ground to give small-diameter feed for further flame evaluation tests. The samples of both alumina and zirconia were ground in a Fisher Scientific motor-driven mortar and pestle to fine particles. These materials, which were readily fed to the flame in their original state, now balled up into "bird-shot" as did the ThO_2 powders.

Component Development (P. A. Haas, E. L. Youngblood). The Szegvari pilot laboratory model attritor has been used to grind 1600°C fired thorium oxide to small particle size. The unit operated satisfactorily; however, the iron content of the material produced by the attritor was higher than micropulverized material owing to the wearing of the stainless steel balls in the attritor.

Test of the 3-in.-dia 400-cycle Chempump gave an output head of 18 ft at 1 gpm and 6400 rpm. This result is much lower than would be predicted for a 1.5- to 2-in.-dia impeller at this speed.

13.2 Laboratory Preparation of High-fired Oxide

The results of several firings indicated that the pronounced sintering of 1600°C fired thorium oxalate (Sec. 13.1) is not characteristic of pure thorium oxide and probably results from the presence of impurities. Laboratory studies were initiated to obtain information on the properties of high-fired oxide which will be useful in evaluating the pilot plant oxide and also in determining the characteristics of high-fired oxide suitable for use in slurry engineering studies.

Sieve Analyses (J. P. McBride, R. L. Pearson, W. L. Pattison). Sieve analyses, with standard screens and a Cenco sieve shaker, of 800°C fired pilot plant oxide as prepared and 1600°C fired pilot plant oxide as prepared and after micropulverizing showed the following particle size distribution:

Sieve Mesh Size (Passing/Retained)	Material Retained on Smaller Sieve, %		
	800°C, as Prepared	1600°C, as Prepared	1600°C, Micropulverized
20	2	62	0
20/40	4	21	0
40/60	6	5	0.1
60/80	6	2	0.1
80/100	7	2	1
100/200	20	3	72
200/325	50	2	22
325/400	1	1	2
400	4	3	4

All oxides were prepared from the jet-precipitated oxalates, and 100-g samples were sieved. The 800°C burned ThO_2 was sieved for 1 hr to clean the sieve screens of foreign material and check technique. The material retained on each screen except the 325 mesh formed into apparently uniform spherical agglomerates. The bottom pan, containing material smaller than 400 mesh, had spherical agglomerates about 1/32 in. dia and rather firmly bonded together. The agglomerates continued to grow after being trapped on any one screen but there was no appreciable degradation after they once formed. About half the sample was retained on the 325 mesh screen after passing the 200 mesh and was not agglomerated to any appreciable extent, i.e., there were no spheres on this screen (see below). This may have been due to the presence of a node in the shaker action at this position. There was no spherical agglomeration evident on any of the screens with the (TP-12) 1600°C fired pilot plant oxide.

This was the material that formed "clinkers" at 1600°C and included some of the "clinkers". The 1600°C fired ThO_2 that had been micropulverized in three passes showed only a very slight tendency to agglomerate in loosely bonded spheres. The agglomerates broke easily with slight shaking.

Grinding of High Fired Oxide (J. P. McBride, R. L. Pearson, W. L. Pattison). A Fisher motor-driven mullite mortar and pestle was used to grind the TP-12 1600°C, micropulverized 1600°C, and TP-12 1400°C fired pilot plant oxides. Less than 2.0% loss of material, accompanied by sharp, brittle fracture and much flying around of splintered material, occurred during the grinding of the TP-12 1600°C material. No further degradation of the micropulverized 1600°C material was accomplished. Both TP-12 1600°C and TP-12 1400°C material were ground to fine powders of rather high tap density, 5 and 4 g/cc, respectively.

Pilot plant 800°C fired thorium oxides fired in the paint bucket laboratory furnace at 1300-1600°C were relatively easily ground in the mullite motor-driven mortar in 1 hr time without the sharp, brittle fracture and loss of material found with TP-12-1600°C. Tap densities after grinding were 3-4 g/cc, much lower than those of the ground TP-12-1600°C and TP-12-1400°C materials.

13.3 Preparation of Oxide from Thorium Hydroxide (J. P. McBride, E. V. Jones)

Studies on the effect of reagent concentration and washing techniques on the properties of oxide prepared from thorium hydroxide by firing at 650°C were completed. Oxide products from the water- or ammonia—washed hydroxide, in the absence of DX-908 flocculant used in product recovery, were almost universally gritty and glasslike. The DX-908 was much less efficient in alcohol suspensions than in water. Alcohol-washed hydroxide yielded a much softer and more powdery oxide (Table 13.1).

The hydroxide was precipitated by a rapid-mixing technique, and the solid was recovered by filtration, washed several times with ammonia and/or water, and finally with 95% alcohol.

Early precipitations (see also ORNL-2416) were carried out with 2 M $Th(NO_3)_4$ solutions with the expectation that the higher reagent concentrations would give better slurry products. In later experiments, however, the lower reagent concentration (i.e., 1 M $Th(NO_3)_4$ and 6 M NH_4OH) gave the softer oxides. The oxide products have on the whole appeared to be unsuitable slurry materials.

13.4 Slurry Irradiation Studies (J. P. McBride, N. A. Krohn, P. P. Haydon, H. F. Soard)

In-pile Gas Recombination Studies. Experiments in the Graphite Reactor to determine the rate of production and recombination of radiolytic gas were continued. Varying the stirring rate from 1.5 to 5 cycles/sec had no measurable effect on the steady-state pressure in the temperature range 200-250°C. The range 250-300°C is now being investigated.

Equipment Development. A new stirring device for use with the slurry in-pile autoclaves was built* and tested with water at 260°C. The stirring mechanism consists of an eight-pole magnet, rotated by an air motor, which couples

*Designed and fabricated by F. R. Duncan of the Instruments Division.

Table 13.1. Oxide Preparation from Thorium Hydroxide: Effect of Reagent Concentration and Washing

Conditions: 20 ml $Th(NO_3)_4$ solution + 20 ml NH_4OH solution; filtered, oven dired at 150°C, calcined at 650°C

Expt. No.	Reagnet Conc., M		Final pH	Special Treatment	Characteristics of Oxide Product		
	$Th(NO_3)_4$	NH_4OH			Appearance	Surface Area, m^2/g	X-ray Crystallite Size, A
13	2	8	7.8	Flocculant added; water wash	Soft, white lumps	8.1	---
14	2	7.6	8.6	Same	Soft, white lumps	8.6	---
15	2	8.0	9.0	Flocculant in $Th(NO_3)_4$; water wash	Soft, white lumps	16.8	100
16	2	7.6	8.6	Same	White, lumpy, harder than Expt. 15	14.9	107
17	2	7.6	9.0	Water wash	Soft white lumps	10.1	113
				Alcohol wash; air dried	Massive product, readily broken	14.1	113
18	2	8.0	8.3	Same	Soft white mass	12.1	---
				Alcohol wash	Soft white mass	48.6	86
19	1	6.5	8.6	Same	Soft white mass	29.6	110
20	2	15.4	10.1	Same	Soft white mass	40.2	95
21	Solid	15.4	---	Same	Soft white mass	32.2	91
22	1	5.4	9.7	Water wash	Soft white	68.8	75
				Alcohol wash	Soft white	73.0	73
23	1	5.0	9.0	Water wash	White, very hard	---	106
				Alcohol wash	Hard glassy layer	---	102

with a second eight-pole magnet canned in stainless steel. The second magnet is connected in turn to a stirrer in the autoclave by a shaft entering the autoclave through 1/4-in.-high pressure tubing. The device seems especially interesting for use in the ORR, since gamma heat removal from the slurry autoclave will be easier than with the current dash-pot autoclave where the stirrer drive coils interfere. The device is also more adaptable for corrosion studies.

Evaluation of Davison Sols. Two sols submitted for evaluation by Davison Chemical Company were heated in the dash-pot autoclave to 300°C. Both gelled, one in 10 min, the other in 40 min. With 10% excess water or diluted 1:1 with water, the sol was stirred readily at 300°C in the dash-pot bomb for 206 hr, but was no longer a sol after this treatment. In-pile (LITR) and out-of-pile tests at 200°C were stirred for 322 hr and 363 hr, respectively, but again the treatment destroyed the sol. The recovered materials were slow-settling slurries.

13.5 Gas Recombination Studies (J. P. McBride, L. E. Morse)

Studies on the effect of MoO_3 oxide concentration on the reaction of stoichiometric H_2-O_2 mixtures in aqueous slurries of thorium-uranium oxide were continued. Slurries of simple mixtures of 1600°C fired ThO_2 and $UO_3.H_2O$ with 0.06 m MoO_3 and 1600°C fired Th-U oxide, prepared from the coprecipitated oxalates, with 0.012 m MoO_3 gave very rapid combination rates.

Reaction Rates of Stoichiometric H_2-O_2 Mixtures in Aqueous Slurries of Simple Mixtures of 1600°C Fired ThO_2 and $UO_3.H_2O$. The reaction rates of stoichiometric H_2-O_2 mixtures in aqueous mixed ThO_2-UO_3 slurries as a function of MoO_3 catalyst concentrations were determined up to 0.06 m MoO_3 (Table 13.2). At this concentration the reaction rate in the slurry as prepared was 12.8 moles H_2/hr. liter of slurry and in the H_2-activated slurry, 20.8 moles H_2/hr.liter at 291°C and a partial pressure of 500 psi H_2. The increase in reaction rate in the H_2-activated slurry with increasing catalyst concentration appears to be leveling off, but the rate in the slurry as prepared doubled with the same catalyst increment.

The thorium oxide used in these experiments was calcined at 1600°C for 4 hr and then circulated as a slurry for 268 hr at about 300°C in a REED loop (run BS-16). After the addition of $UO_3.H_2O$ and each 0.012 m MoO_3 aliquot, the slurry was heated at 280°C for 3 hr with a small oxygen overpressure.

Reaction Rates of Stoichiometric H_2-O_2 Mixtures in Aqueous Slurries of Th-U Oxide Calcined at 1600°C. The reaction rate in the slurry of Th-U oxide prepared by calcining the coprecipitated oxalates at 1600°C for 24 hr and with 0.012 m MoO_3 added, as prepared, was 35.5 moles H_2/hr.liter of slurry at 250°C and a partial pressure of 500 psi H_2. The reaction rate in the slurry after H_2-activation was 56.3 moles H_2/hr.liter for the same conditions (Table 13.3).

The Th-U oxide was prepared by calcining the 10°C coprecipitated oxalates at 1600°C for 24 hr. The slurry was prepared by heating the oxide in water at 280°C for 3 hr in a small oxygen overpressure. The slurry was reheated under the same conditions after the addition of 0.012 m MoO_3.

Table 13.2. Reaction Rates of Stoichiometric H_2-O_2 Mixtures in Aqueous Slurries of Sample Mixtures of 1600°C Fired ThO_2 and $UO_3.H_2O$

Th - 500 g/kg H_2O (1600°C-4 hr calcined ThO_2)

U - 0.25 g/kg H_2O ($UO_3.H_2O$)

Reaction Temperature - 291°C

Slurry Composition	Combination Rate (P_{H_2} = 500 psi), moles H_2/hr.liter	
	Slurry as Prepared	H_2-Activated Slurry[a]
ThO_2	< 0.1	0.1
0.5 mole % U ($UO_3.H_2O$) added	< 0.1	0.2
MoO_3 additions		
0.012 m	0.4	0.24
0.024 m	0.5	0.27
0.036 m	1.2	3.1
0.048 m	5.2	17.28
0.060 m	12.8	20.81

[a]Slurry heated with H_2 (250 psi at 25°C) for 2 hr at 270°C.

Table 13.3. Reaction Rates of Stoichiometric H_2-O_2 Mixtures in Aqueous Slurries of 1600°C Calcined Thorium-Uranium Oxide

500 g Th-0.5% U/kg H_2O, coprecipitated oxalates calcined at 1600°C for 24 hr

Slurry Conditions	Reaction Temp., °C	Combination Rate, (P_{H_2} = 500 psi) moles H_2/hr.liter
Slurry as prepared	289	0.17
H_2-activated	291	0.45
0.012 m MoO_3 added	250	35.5
H_2-activated	250	56.3

Part IV. CHEMICAL ENGINEERING RESEARCH

14.0 INTERFACIAL AREA MEASUREMENT

Program Leader: J. C. Bresee
(C. V. Chester, J. L. Whitten)

A method of measuring a liquid-liquid interfacial area by neutron activation was described in ORNL-2385, Sec. 17.0. The specific rate of neutron production at a fluorocarbon-aqueous interface was measured as 106 neutrons/cm^2.min, and the specific background from the α,n reaction of O^{17} and O^{18} in the water was 180 neutrons/cm^3.min. The concentration of polonium in the solution was 1.03 curies/liter.

The interfacial area measurements were carried out in a 12-in. length of 2-in.-dia fused quartz tubing. The tubing was surrounded by nine boron trifluoride neutron counter tubes. The whole assembly was immersed in water, which served as a neutron moderator and reflector.

The geometry of the counting system was determined with a calibrated radium-beryllium neutron source (Fig. 14.1). Stainless steel trays containing hexadecafluoro-n-heptane were lowered into the polonium solution and the count rate was determined. From the known geometry of the system and the known interfacial area, the specific neutron production rate from the interface and the volume of the solution were calculated (Fig. 14.2).

15.0 INLINE INSTRUMENTATION

Program Leader: W. H. Lewis
(M. J. Kelly, J. W. Landry, T. S. Mackey, R. W. Stelzner)

Various instruments are being developed for use in radiochemical separation plants to improve process control and to reduce analytical costs.

15.1 Interface Level Control System

Design and fabrication were completed for a digital interface level controller which will be installed in the bottom of the Metal Recovery Plant 1S organic-continuous column. This controller is of the electrical conductivity type and will be tested concurrently with a hydraulic dip-tube controller after the column is installed.

15.2 Concentration Monitors

Uranium. Construction is 95% completed for a prototype a-c polarograph designed for monitoring uranium concentrations of the order of 10 ppm in process raffinate streams.

Gamma Activity. The prototype gamma activity monitor was tested and found satisfactory in the Thorex Pilot Plant 1AP stream, which had a gamma activity level of 10^5 c/m/ml. Background effects were minimized in this instrument because the sample was a continuous stream which fell through the gamma spectrometer cell without touching the cell surfaces. The instrument is being modified

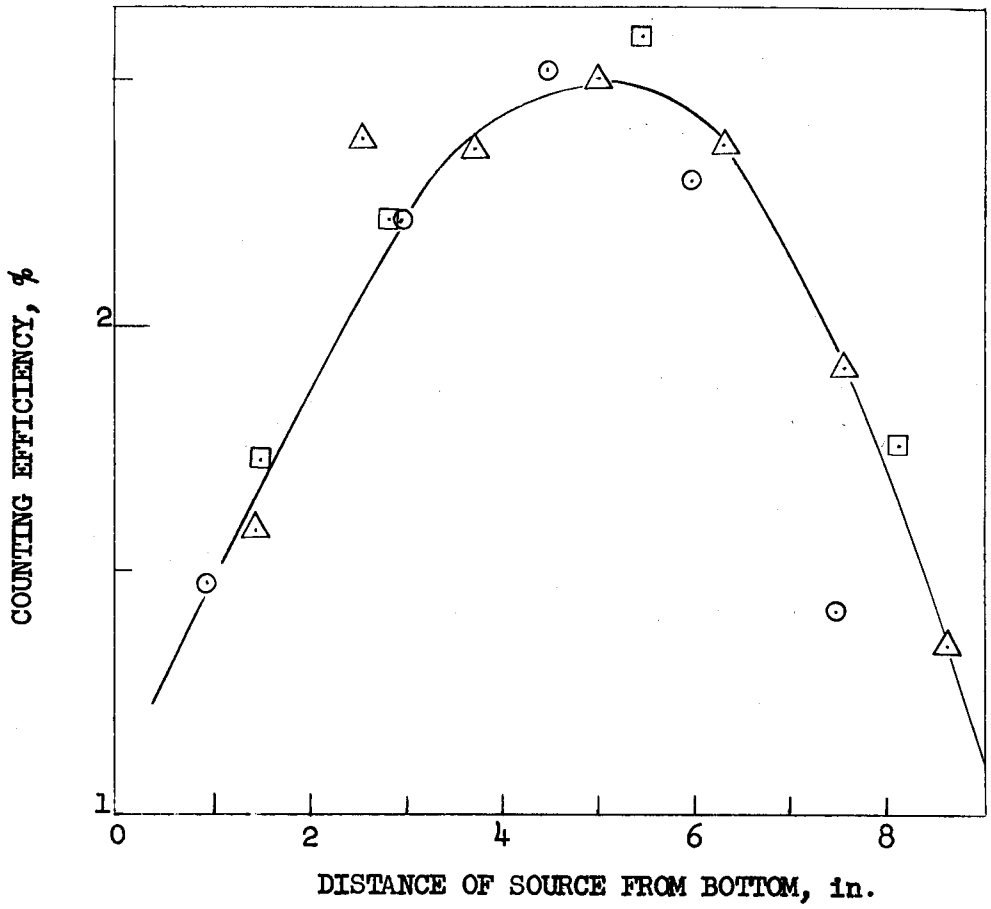

Fig. 14.1. Absolute Counting Efficiency Determination with a Standard Radium-Beryllium Neutron Source of 2.5×10^6 n/min.

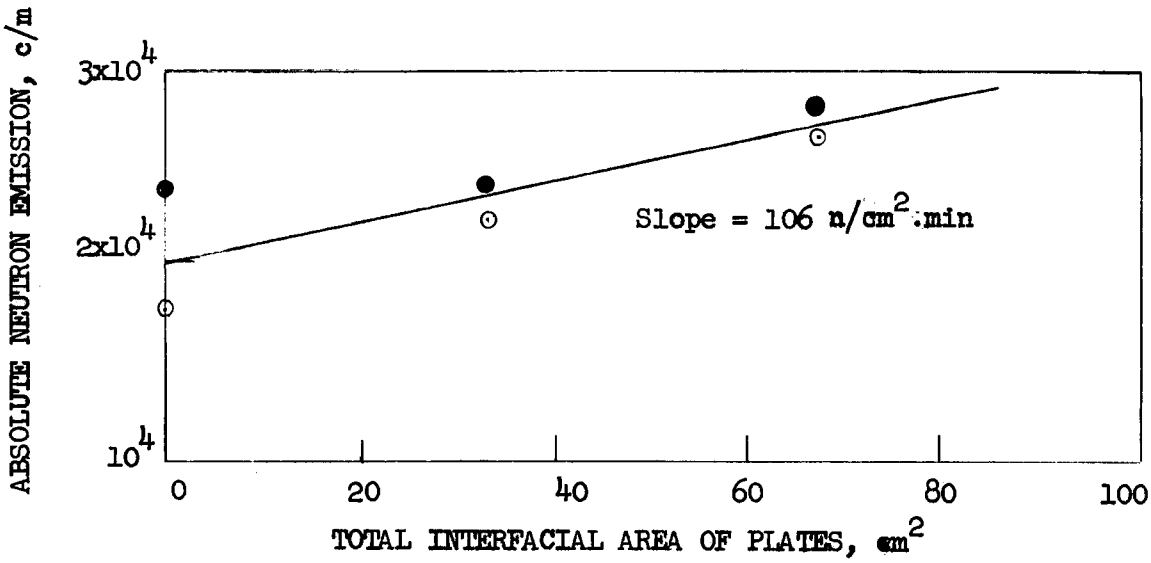

Fig. 14.2. Determination of Specific Neutron Production Rate.

for use in the Thorex Pilot Plant 1AP stream when the gamma activity level will be 10^8 c/m/ml. These modifications include: shielding the sampler piping; adding a liquid level alarm to shut off the sampler in case the 1AP stream stops; and changing the recorder circuit to optimize its response to transient conditions.

15.3 Flow Rate Measurement

Turbine Meter. The Potter turbine meter that was installed in the Metal Recovery Plant's acid addition line operated satisfactorily during the first week of use. The one in the interface purge system of the Thorex Pilot Plant stopped but was restored to service by backflushing; the stoppage was believed to have been caused by a slug of weldment metal temporarily lodging in the turbine. Both meters measure flow rate as well as total flow.

Electromagnetic Meter. The electromagnetic flow rate meter, which was purchased for installation in the 1AF stream of the Metal Recovery Plant, was rebuilt. Adjustments, previously located on the flow head, were transferred to the panel. The rebuilding included removal of the tar, with which the instrument was filled, and resoldering of connections, many of which were cold-solder joints.

16.0 APPENDIX

REPORTS AND SPEECHES MADE

ORNL-2377, "Pulse Pumping: A Means for Transfer of Pulse Column Fluids," A. R. Irvine (Unclassified)

ORNL-2388, "Progress Report on Raw Materials for July, 1957," K. B. Brown et al. (Unclassified)

ORNL-2392, "Chemical Technology Division Annual Progress Report for Period Ending August 31, 1957," F. L. Culler et al. (Confidential)

ORNL-2399, "Raw Materials Progress Report for August 1957," K. B. Brown et al. (Unclassified)

ORNL CF No.:

57-7-93, Supplement No. 1, "Revised Estimate of Heat Requirements for Self-Sintering," J. O. Blomeke (Unclassified - Internal Use Only)

57-8-117, "Radioactive Waste Treatment and Disposal--A Bibliography of the Classified Literature," P. E. Novak, D. L. Africk, and J. O. Blomeke (Secret)

57-10-21, "A Discussion of the Possibility of Using Oxygen Difluoride as a Fluorinating Agent, Including a Preliminary Cost Estimate," T. A. Gens (Confidential - Internal Use Only)

57-10-30, "HRP - Comparison of Several Line Connectors for High Pressure and/or High Temperature Disconnects," C. C. Haws, Jr. (Unclassified)

57-10-59, "Recovery of Plutonium from Chalk River Solution, Oxide and Scrap," C. D. Hylton (Confidential)

57-10-89, "A Continuous Darex Process Flowsheet," F. G. Kitts (Unclassified - Limited)

57-10-119, "S1C (SRS) Data Sheet," J. W. Ullmann (Confidential)

57-10-123, "Volatility Pilot Plant Run C-4," C. L. Whitmarsh (Unclassified - Internal Use Only)

57-10-125, "Process Design Section Status Report for Period September 15 to October 15, 1957," H. E. Goeller (Confidential - Internal Use Only)

57-10-129, "Proposal for Installation of Equipment for Treatment of ORNL High Level Waste," I. R. Higgins (Unclassified - Internal Use Only)

57-10-135, "Monthly Program Summary, October 1957, Chemical Technology Division," (Unclassified - Limited)

Subcontract Reports:

Houdry Process Corporation, Subcontract No. 2010, "First Quarterly Report, 1957, Period Ending September 30, 1957," (57-OCR-18) (Unclassified)

Houdry Process Corporation, Subcontract No. 904, "Preparation of Thorium Oxide Sols, Third Quarterly Report, 1957," (57-OCR-19) (Unclassified)

Houdry Process Corporation, Subcontract No. 2010, "Fluoride Volatility Process Monthly Status Report for October 1957," (57-OCR-22) (Unclassified)

Houdry Process Corporation, Subcontract No. 904, "Preparation of Thorium Oxide Sols, Monthly Status Report for October 1957," (57-OCR-23) (Unclassified)

Speeches:

The following papers were prepared for presentation at the Annual Meeting of the Engineering Liaison Program of the Union Carbide Corporation, October 14-16, 1957, New York City:

57-10-3, "High-Speed Mixer-Settler Equipment for Solvent Extraction," J. C. Bresee

57-10-4, " Developments in Continuous Ion Exchange Equipment for AEC Applications," J. T. Roberts

The following papers were prepared for presentation at the American Nuclear Society meeting, October 28-31, 1957, New York City:

57-10-26, "An Engineering Evaluation of Decalin as a Thorex Solvent Diluent," R. J. McNamee

57-10-28, "The Preparation of Thorium Metal by Sodium Amalgam Reduction of Thorium Chloride: The Metallex Process," O. C. Dean and G. K. Ellis

57-10-38, "Radiation Exposure to Operating Personnel in a High-level Radiochemical Plant," G. S. Sadowski

Open Literature Publications:

"The Estimation of Bisulfate Ion Dissociation in Sulfuric Acid-Sodium Sulfate Solutions," C. F. Baes, Jr., JACS 79, 5611

"Cost of Packless Pumps," B. B. Klima, Cost Engineering , October 1957