Cy. 4

ORNL-2490

Chemistry-Separation Processes for Plutonium and Uranium

Cy. 4

DEVELOPMENT OF THE EXCER PROCESS. IV. CHLORIDE SYSTEM

I. R. Higgins
W. J. Neill
L. E. McNeese

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

Printed in USA. Price 150 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

ORNL-2490

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

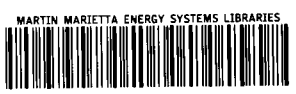
DEVELOPMENT OF THE EXCER PROCESS. IV CHLORIDE SYSTEM

I. R. Higgins, W. J. Neill, L. E. McNeese

DATE ISSUED

NOV 19 1958

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION



ABSTRACT

An Excer flowsheet for the recovery of uranium from a chloride system by anion exchange is presented. Ore concentrate was dissolved in HCl, purified by anion exchange, electrolytically reduced to uranium tetrachloride and then precipitated as hydrated uranium tetrafluoride by the addition of HF. The hydrated uranium tetrafluoride was filtered, dried, pelletized, granulated and then dehydrated in a fluidized bed dehydrator at 450°C.

In the anion exchange purification step decontamination factors of greater than 10^3 were realized for all impurities except trivalent iron, pentavalent vanadium and molybdenum. These three impurities were removed in the uranium tetrafluoride precipitation step with a decontamination factor of 10^3. The final dehydrated uranium tetrafluoride was contaminated primarily with stainless steel products which probably were introduced in the dehydration step.

Three kilogram batches of Excer uranium tetrafluoride were bomb-reduced to the metal by the Mallinckrodt Chemical Works. The first and second runs were reduced as received and reduction yields of 0 and 14% were obtained. The third batch was ball-milled for 24 hours, improving its blendability with the magnesium reductant, and a yield of 76% was obtained.

CONTENTS

1.0 INTRODUCTION

This report presents a flowsheet for the ion exchange recovery of uranium from a chloride system in the Excer process. The Excer process was originally developed for economical conversion of hexavalent to tetravalent uranium by electrolytic reduction, the feed to the electrolytic cell being prepared by ion exchange, and may be applied to low-grade uranium ores as well as to feed materials.

Conditions in the ion exchange step must be varied depending on the crude uranium source,[1,6] and other systems, the sulfate[7] for example, have been developed. The chloride system has certain advantages over the sulfate; namely, the hydrochloric acid can be distilled from waste liquors and reused; uranium concentrations in the chloride ion exchange system may be a factor of 10 higher; and the problem of sulfate contamination of the product is avoided. Batch and continuous tests in the 2-in.-dia glass contactor were made. The UF_4 was bomb-reduced in test batches of 1 and 5 lb at the Mallinckrodt Chemical Works. Acid losses in recycle steps were determined in laboratory distillation tests.

Electrolytic rather than chemical reduction[8] was chosen because it had been more thoroughly developed and there was less likelihood of contaminant build-up in recycle.

The authors are indebted to G. R. Wilson and Marvin Murray of the Analytical Chemistry Division for analyses and to R. O. Payne, C. C. Nance, and W. E. Shockley of the Chemical Technology Division for nontechnical operational assistance. P. N. Rigopulos and A. J. Guiffrida, on loan from Ionics, Inc., and K. O. Johnsson of the ORNL Chemical Technology Division were responsible for much of the unit operation work on precipitation, dehydration and electrolysis. W. G. Stockdale assisted in the preparation of the cost estimate.

2.0 FLOWSHEET

The Excer process chloride flowsheet (Fig. 2.1) provides for leaching of ore concentrate with hydrochloric acid, continuous ion exchange sorption of uranyl chloride from the leach followed by continuous elution, electrolytic reduction of uranyl to uranous chloride, continuous precipitation of uranium tetrafluoride hydrate, filtration, drying to a free-flowing powder, densification by pressing, granulation of the pressed pellets, and dehydration in a fluidized bed.

Feed for the anion-exchange step is prepared by dissolving ore concentrate, an impure yellow cake, in hydrochloric acid. Technical grade hydrochloric acid or recycle liquor from green-salt precipitation (Sec. 8.0) of previous runs may be used. The recycled acid contains 10% excess fluoride, used to precipitate UF_4, any contaminants that follow the uranium

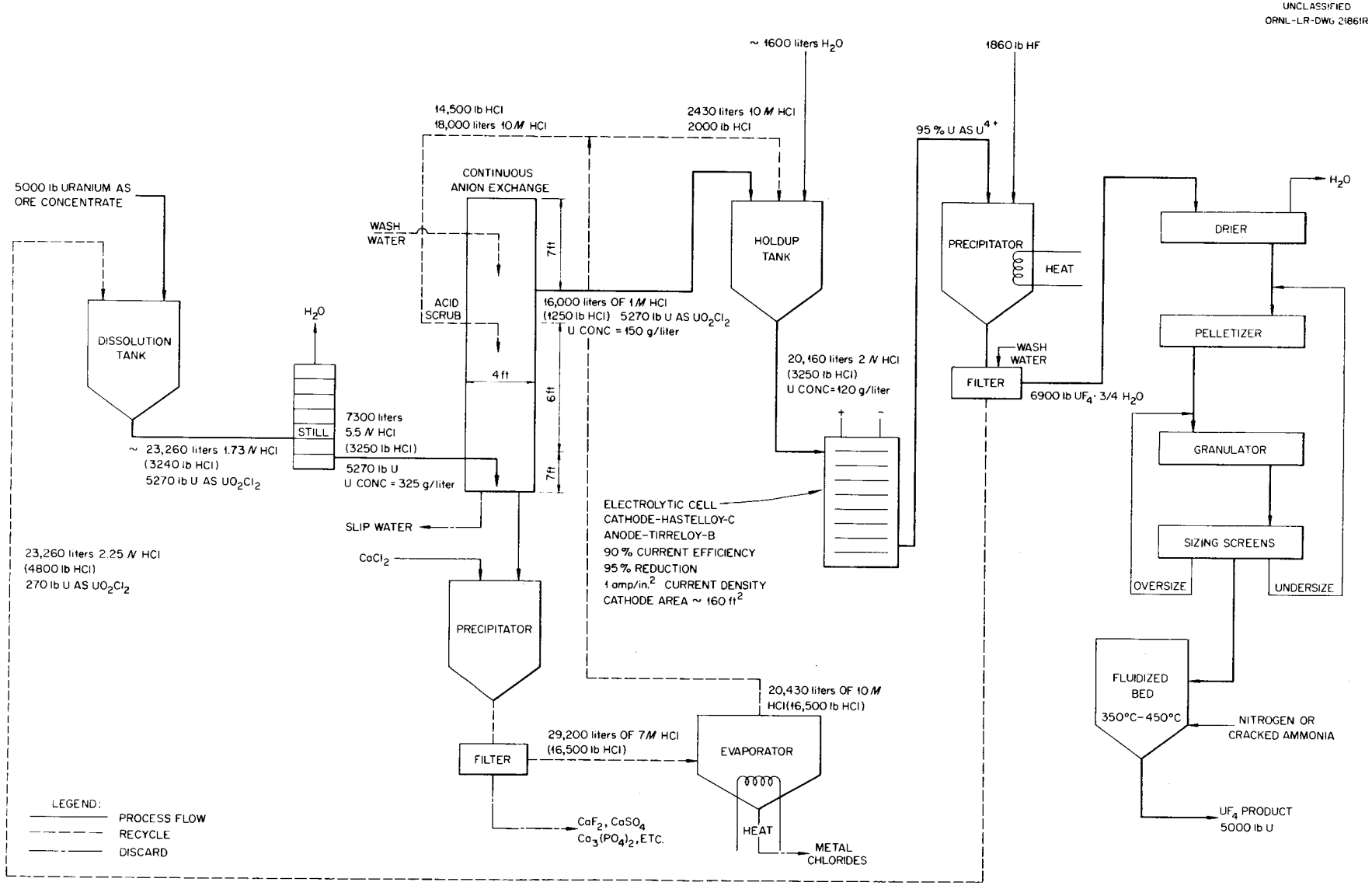


Fig. 2.1. Treatment of Ore Concentrate by the EXCER Process, Chloride System, for Recovery of Uranium.

through the ion exchange step, and any that are introduced during electrolysis. It also contains the unreduced uranyl chloride.

The uranium concentration of the feed to the anion-exchange column may vary from 50 to 500 g/liter, but the total chloride must be at least 5 M. The anion-exchange resin is loaded to about 50 g of uranium per liter of resin, and the feed flow rate may therefore be lower than the resin flow rate. The loaded resin is scrubbed with 5-10 M HCl, the minimum flow rate of scrub solution required being over 40% of the resin flow rate, which corresponds to the void-volume flow rate. In the scrub section weakly sorbed anions are displaced, and the resin sorbs uranium to its maximum capacity.

Uranyl chloride is eluted with water, the water eluant being essentially a diluent for the chloride present. The uranium concentration of the product may be greater than 200 g/liter if the uranyl chloride is allowed to build up at the product take-off point. The uranyl chloride that thus builds up scrubs out HCl, down to 1 or 2 M. Withdrawal of some acid with the uranyl chloride product is desirable, since acid is required in the electrolytic reduction step.

The uranyl chloride product of the anion exchange treatment is reduced in an Ionics, Inc. membrane electrolytic cell. For 95% reduction the current efficiency is 80%. The uranium (IV) chloride solution is then heated to 100°C in the precipitator and UF_4 hydrate precipitated by the addition of HF. The hydrated UF_4 is then filtered and tray-dried in a steam-heated air-oven at 110°C to a water content of 6%. In case the tap density of the dried precipitate is less than 3.0 g/cc, the material is densified by pelletization and then ground to a -4 + 100 mesh. The UF_4 hydrate is then dehydrated in a fluidized bed, in two stages, the first operating at 350°C and the second at 450°C.

The hydrochloric acid in the anion exchange column waste is recovered by distillation to provide a scrub for the anion column. The hydrochloric acid in the UF_4 supernatant is reused for the dissolution of ore concentrate, the solution being evaporated to the optimum chloride concentration for loading on the anion exchange column.

3.0 ANION EXCHANGE STEP

The proposed flowsheet was tested with ore concentrate from South Africa.

3.1 Feed Preparation

The concentrate was dissolved in about 2.25 N HCl, 1 lb HCl per pound of uranium in the concentrate, to give a feed containing about 200 g of uranium per liter.

3.2 Sorption and Elution

In the flowsheet run, using Permutit-Sk anion resin in the 2-in.-dia Higgins contactor, sorption and elution produced a product having a uranium

UNCLASSIFIED
ORNL-LR-DWG 32655

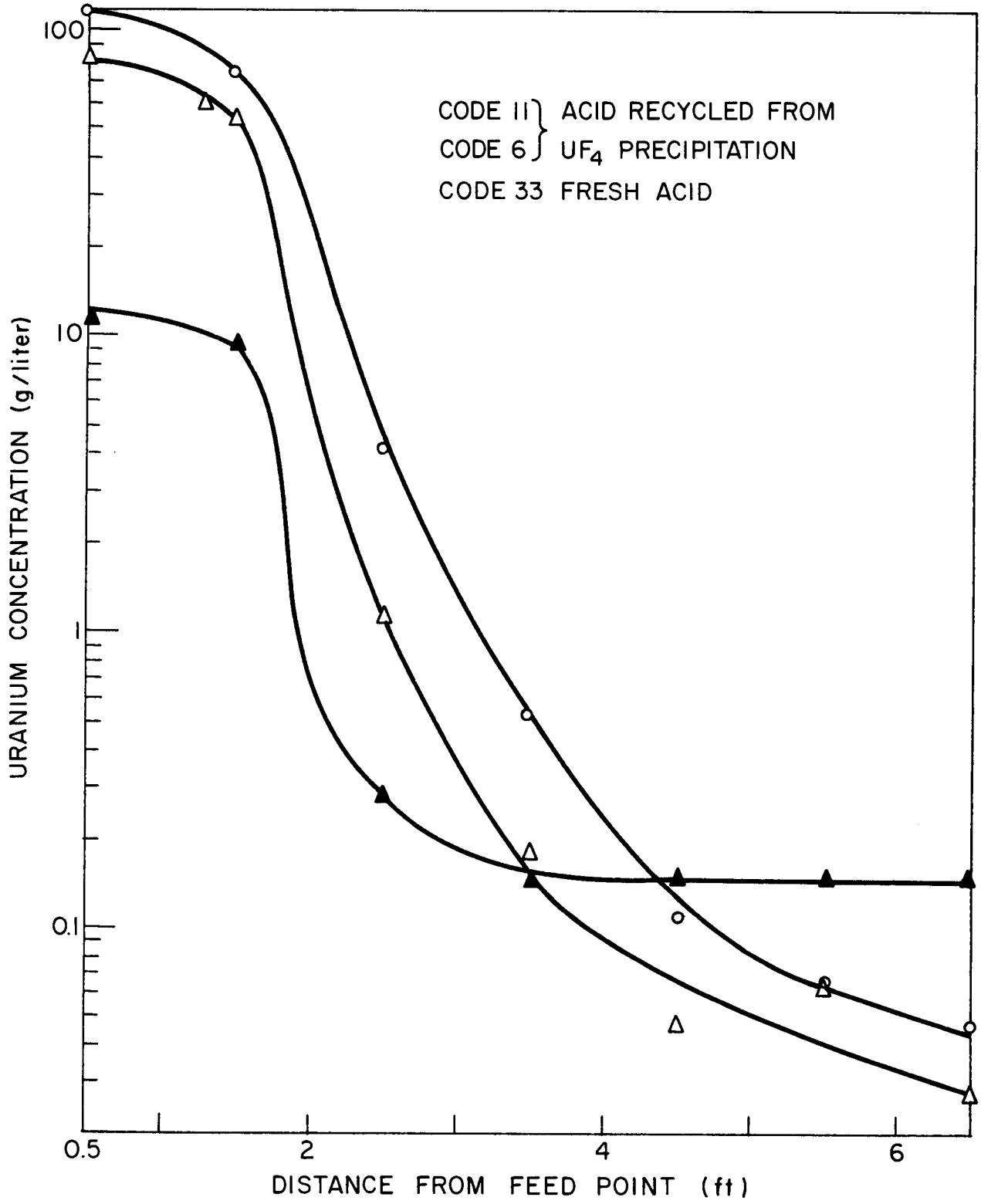


Fig. 3.1. Uranium Profile in Loading Section of the 2-in.-dia Continuous Anion Exchange Contactor.

UNCLASSIFIED
ORNL-LR-DWG 32657

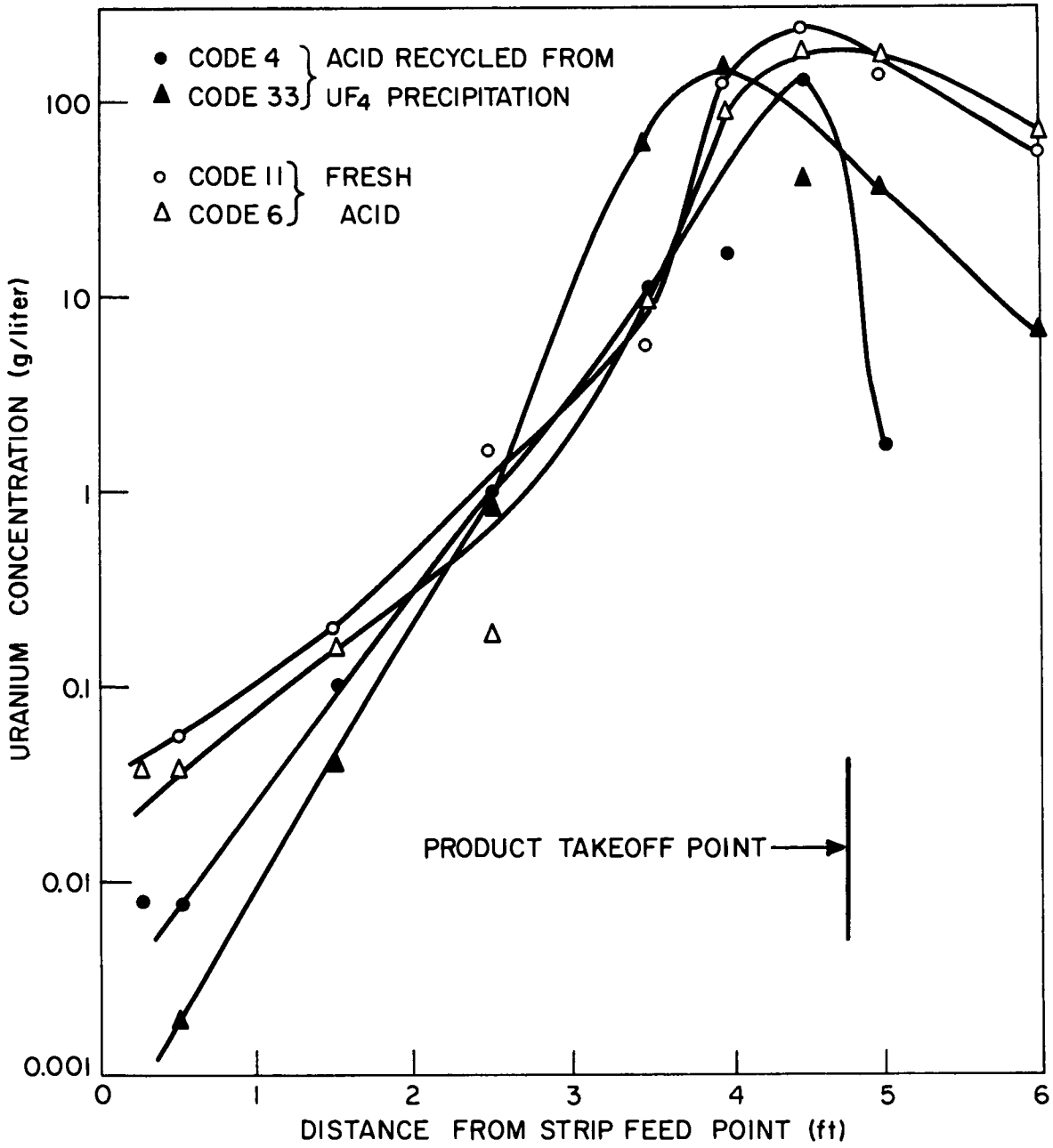


Fig. 3.2. Uranium Profile in the Stripping Section of the 2-in.-dia Continuous Anion Exchange Contactor.

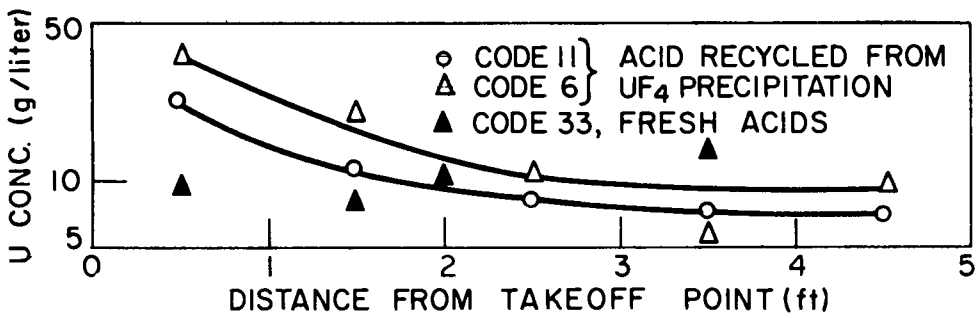


Fig. 3.3. Uranium Profile in the Scrub Section of the 2-in.-dia Continuous Anion Exchange Contactor.

concentration of 200 g/liter at a rate of 150 g uranium per hr (Table 3.1). The concentration of uranium in the wastes was 0.004 to 0.285 g/liter, the higher losses having been the result of withdrawing product too slowly, consequently overloading the resin. Results were the same whether the feed was prepared with recycled or fresh acid.

The uranium profiles for the different sections of the column (Figs. 3.1-3.3) were typical of normal operation. They were plotted from data obtained by analysis of samples drawn with a hypodermic needle inserted through rubber gaskets between the 1-ft pipe sections.

The concentration profile for each section is characteristic but is affected by operating conditions in other sections. In the loading section profile (Fig. 3.1) the uranium content at the feed point was abnormally high when product was not being withdrawn fast enough. The waste loss was abnormally high when the column was too short. When the scrub flow rate was too low, the chloride concentration in the loading section gradually decreased below optimum loading concentration and the uranium losses to the anion-column waste stream were excessive.

Table 3.1 Concentration of Uranium in 2-in.-dia Higgins Continuous Contactor

Feed: South African ore concentrate dissolved in 2.85 N HCl

Eluant: H_2O

	Feed		Scrub		H_2O Strip	Product		Waste		Resin
Run No.	U Conc, g/liter	Flow Rate, ml/min	HCl, M	Flow Rate, ml/min	Flow Rate, ml/min	U Conc, g/liter	Flow Rate, ml/min	U Conc, g/liter	Flow Rate, ml/min	Flow Rate, ml/min
1	196	10-12	10	22-25	58-75	98-158	15-19	0.09	42-72	50
2	196	22-25	10	27-39	92-100	163-225	19-22	0.05	68-83	75
3	196	23-64	10	30-37	66-100	46-120	17-22	0.004	50-116	75
4	287	13-28	9	28-42	92-125	134-193	12-40	0.285	66-162	75

In the scrub section profile the solution uranium concentration should be constant for the full length of the section or slightly higher near the product takeoff point. The concentration indicates roughly the resin loading. The sharpness of the uranium concentration rise near the scrub feed point indicates the extent of uranyl chloride buildup around the product takeoff point. The scrub was maintained closely at the minimum value, i.e., at about 50% of the resin flow.

UNCLASSIFIED
ORNL-LR-DWG 32653

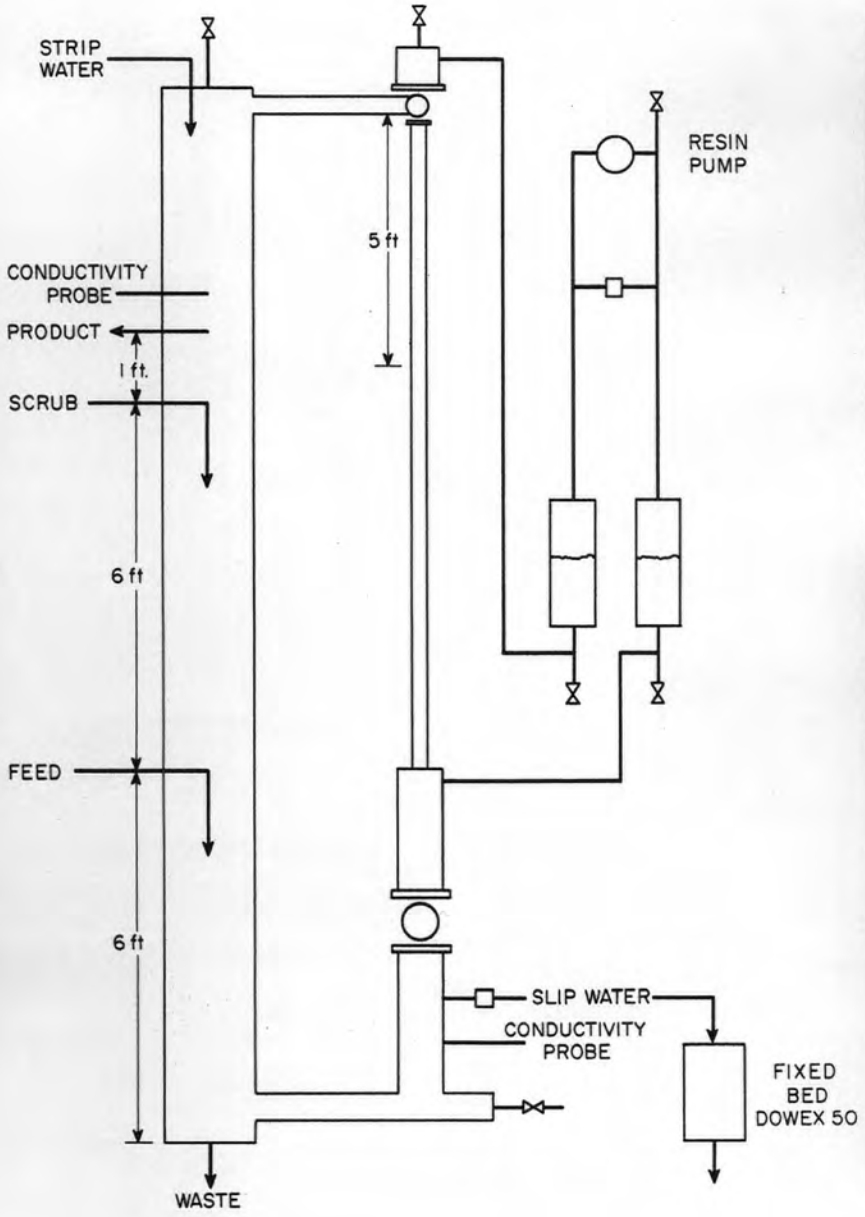


Fig. 3.4

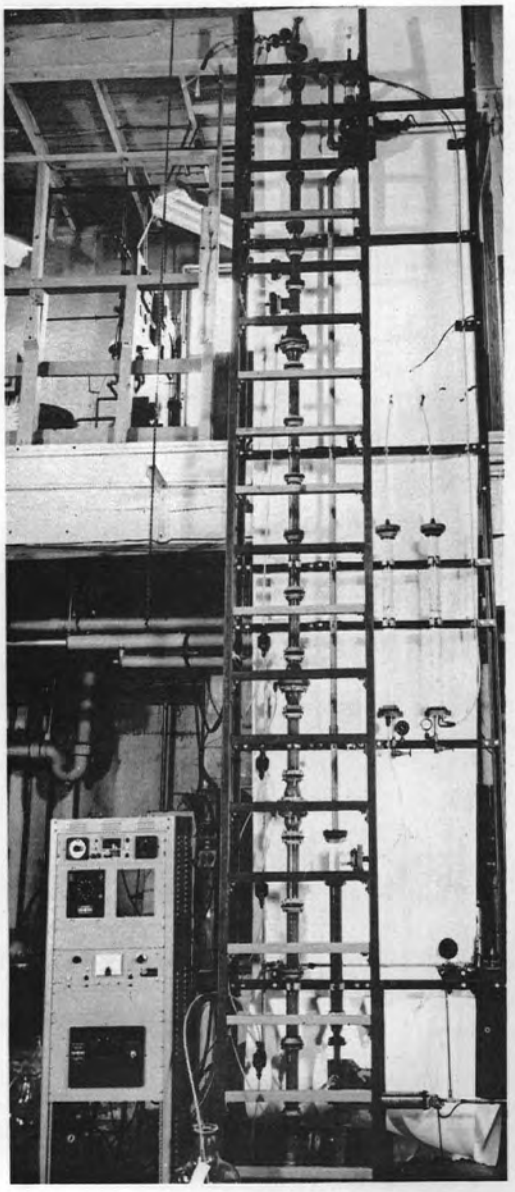


Fig. 3.5

Higgins Continuous Ion-Exchange Contactor.

UNCLASSIFIED
ORNL-LR-DWG 32656

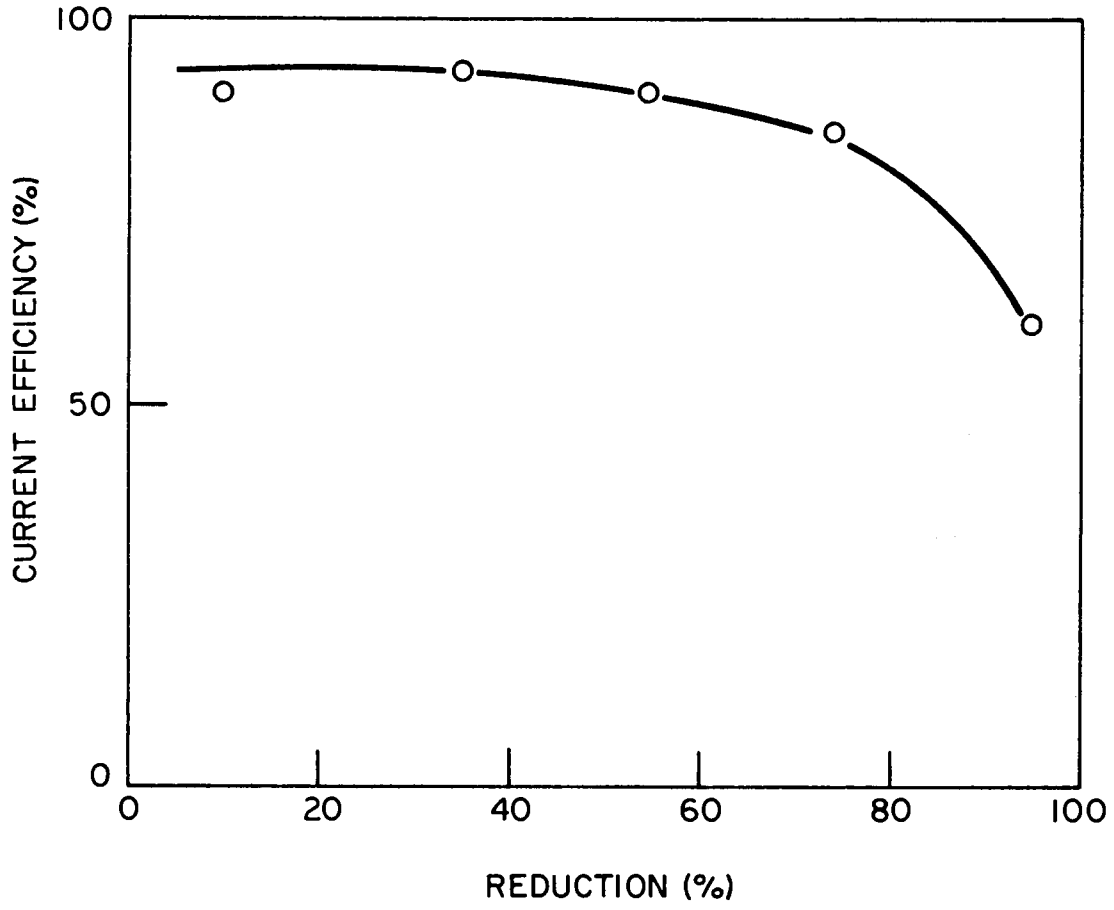


Fig. 4.1. Variation of Current Efficiency with Per Cent of Reduction of UO_2Cl_2.

The strip section profile indicates the column height required for adequate stripping and the amount of chloride buildup around the product takeoff point. A sharp peak indicates optimum rate of product withdrawal.

The quantity of strip water used is practically a void-volume displacement. About 5 ft of column is needed to reduce the uranium in solution to 0.01 g/liter. A conductivity instrument is used to indicate the interface between the uranyl chloride solution and water so that a product uniformly high in uranium may be drawn off. Stripping with water is efficient, producing the high uranium concentration (200 g/liter) in the product, which is desirable for high efficiencies in the subsequent electrolytic reduction. With an adequate detector and control on the product takeoff the strip section might be shorter, and the uranyl chloride would not have to build up so high to scrub out excess acid.

3.3 Ion-Exchange Equipment

The ion-exchange contactor used in the Excer development work is diagrammed in Fig. 3.4 and illustrated in Fig. 3.5. Much of the Excer process efficiency may be attributed to use of the Higgins continuous ion exchange contactor.

The Higgins contactor retains the low stage-height and high throughput features of the conventional fixed bed. Mechanically the contactor is simple and rugged in construction, easy to control, and is not curtailed in its application by varying pressures, flow rates, or solution densities. An additional feature is the ability to handle unclarified feeds. Although the over-all effect of the operation is continuous, the solution and resin flow are intermittent. Each column section operates as a fixed bed, with the resin stationary. When the resin is moved, solution flow in and out of the bed is interrupted and the resin is shoved from one column section to the other by a sudden hydraulic thrust.[9-12] The over-all advantage gained in any chemical process application is attributed to the countercurrent flow of liquid and solid; for example, increased throughput, higher product concentration, less resin inventory, uniformity of products, etc. The particular mechanical device chosen to effect this countercurrent flow is evaluated on its efficiency, its operational reliability, and the initial capital cost. The Higgins contactor is a young development and still largely in the pilot plant stage, but has performed admirably so far.

4.0 ELECTROLYTIC REDUCTION OF U(VI) TO U(IV) CHLORIDE

The uranyl chloride products of the ion exchange treatment were reduced in batches in an Ionics, Inc. membrane electrolytic cell.[13] The current efficiency varied with the per cent of reduction (Fig. 4.1), averaging 82% for 96% reduction. At a current density of 1 amp/in.^{2} the theoretical reduction rate is 130 g (0.35 lb) of uranium per hour. The only uranium lost was that which passed through the membrane into the anolyte. At the end of the run 0.36 g of uranium was detected in the anolyte, 0.01% of the total. This uranium could be recovered on a small fixed-bed anion exchange column or by recycling the anolyte to the ion exchange step.

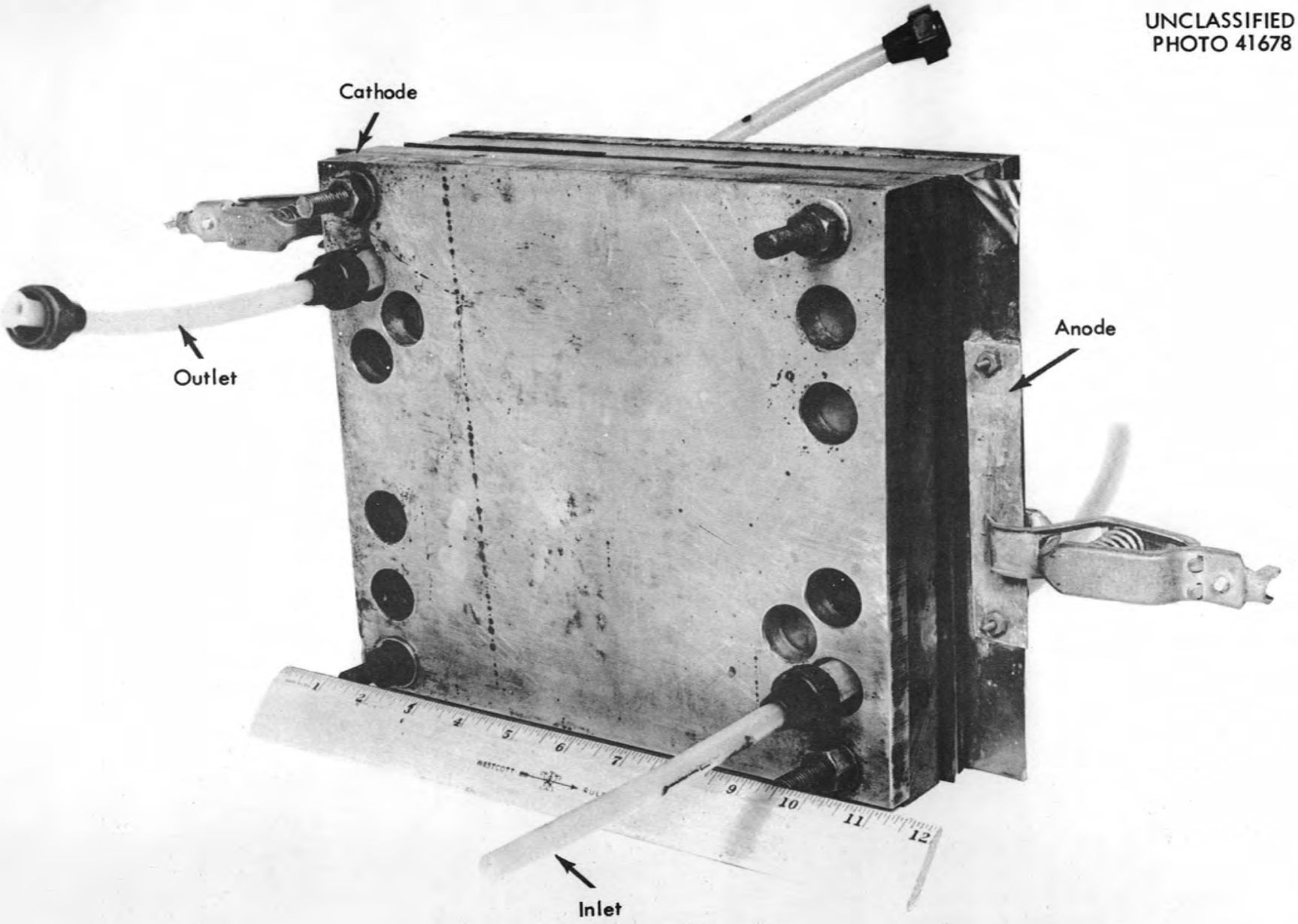


Fig. 4.2. Assembled Excer Membrane Electrolytic Cell.

UNCLASSIFIED
PHOTO 41677

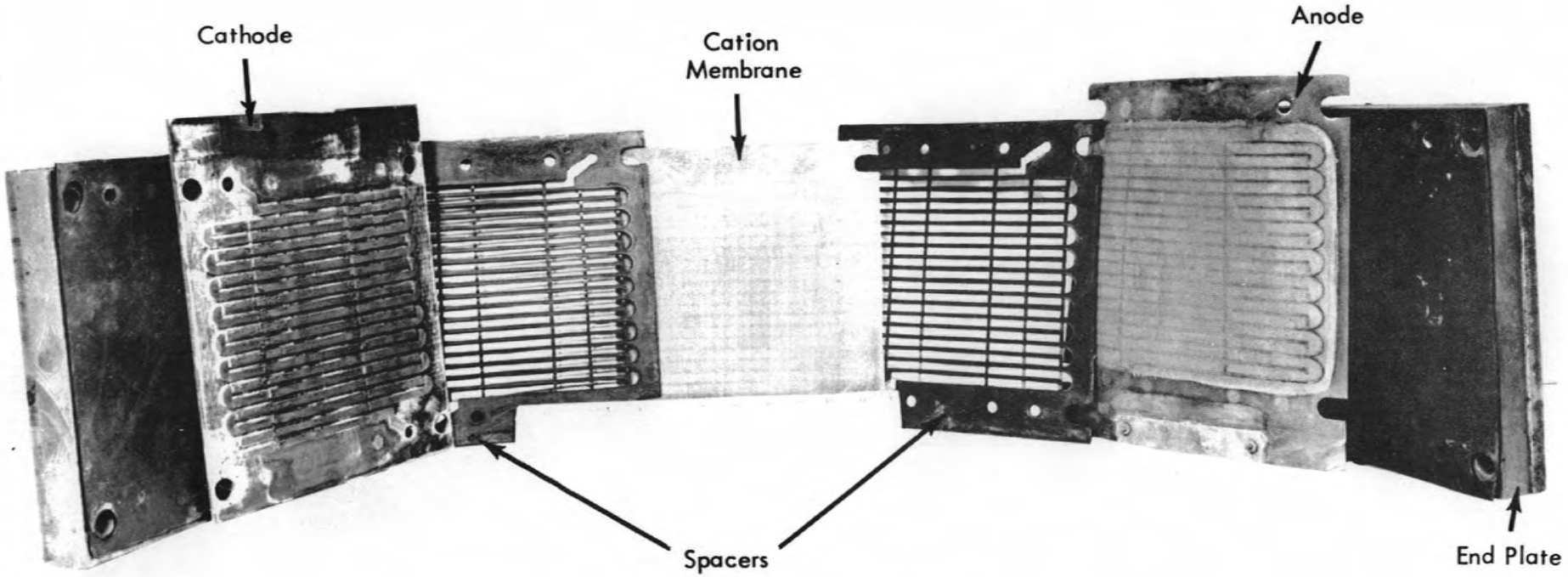


Fig. 4.3. Disassembled Excer Membrane Electrolytic Cell.

The electrolytic cell (Figs. 4.2 and 4.3) used in the reduction step has over-all dimensions 9 x 10 in. and an effective electrode are of 30 $in.^2$ The cathode is Hastelloy C and the anode Tirrelloy B, platinized-tantalum. Acehide flow-guide spacers form thin-spaced cathode and anode compartments, which are separated by a cation-permeable membrane. The membrane prevents reoxidation of the uranium at the anode and minimizes the amount of chloride in the anode compartment, thus retarding deterioration of the anode. The membrane efficiency for excluding anions was not determined but was less than 100% since some chloride ion appeared in the anolyte, reaching a steady-state value of 0.02 M with chlorine being evolved at the anode. The uranium was transferred through the membrane at a rate of 1.3 mg/liter/hr and reached a final value of 90 mg/liter by the end of the run.

The uranyl chloride catholyte, 145 g of uranium per liter and 1.5 N in H^+, and the 0.5 M H_2SO_4 anolyte were recycled from the storage vessels until the desired per cent of reduction was obtained. The flow rate was 250 ml/min and the current density was kept constant at 1 amp/$in.^2$. The reactions in various parts of the cell were:

Cathode	$UO_2^{++} + 4H^+ + 2e$	$\longrightarrow$	$U^{4+} + 2H_2O$
Across Membrane	$2\ H^+_{anode}$	$\longrightarrow$	$2\ H^+_{cathode}$
Anode	H_2O	$\longrightarrow$	$2\ H^+ + 1/2\ O_2 + 2e$
Net	$UO_2^{++} + 2H^+$	$\longrightarrow$	$U^{4+} + H_2O + 1/2\ O_2$

The cell has been operated 700 hr with the same components with no visible damage to either the cathode or the anode.[14] An analysis of the anolyte and the catholyte showed only traces of platinum and nickel. There was no change in the membrane efficiency, as shown by the relative constant rate at which the uranium built up in the anolyte. The spacers in the anode compartment were embrittled by the chlorine liberated at the anode, but those in the cathode compartment appeared unchanged.

A larger scale Ionics, Inc. electrodialysis cell, 18 x 20 in., with an electrode area of 180 $in.^2$, has been successfully operated.[15] The cell components are made of the same materials as the smaller-scale laboratory cell. Uranium is 100% reduced at a rate of 2.43 lb/hr at a current density of 1 amp/$in.^2$ and a current efficiency of 68%. The cell was operated for a total of 162 hr, the longest continuous run being 73 hr. During the operations 210 lb of uranium was reduced.

Two electrolytic reduction cells, which could be operated independently of each other, were used in this system. The unit could be operated in a batch manner or in a continuous feed-and-bleed manner where the stages were in series for higher over-all current efficiencies.

Fig. 5.1. Hydrated Uranium Tetrafluoride, $UF_4 \cdot 2.5\ H_2O$.
6000X. Reduced 9%.

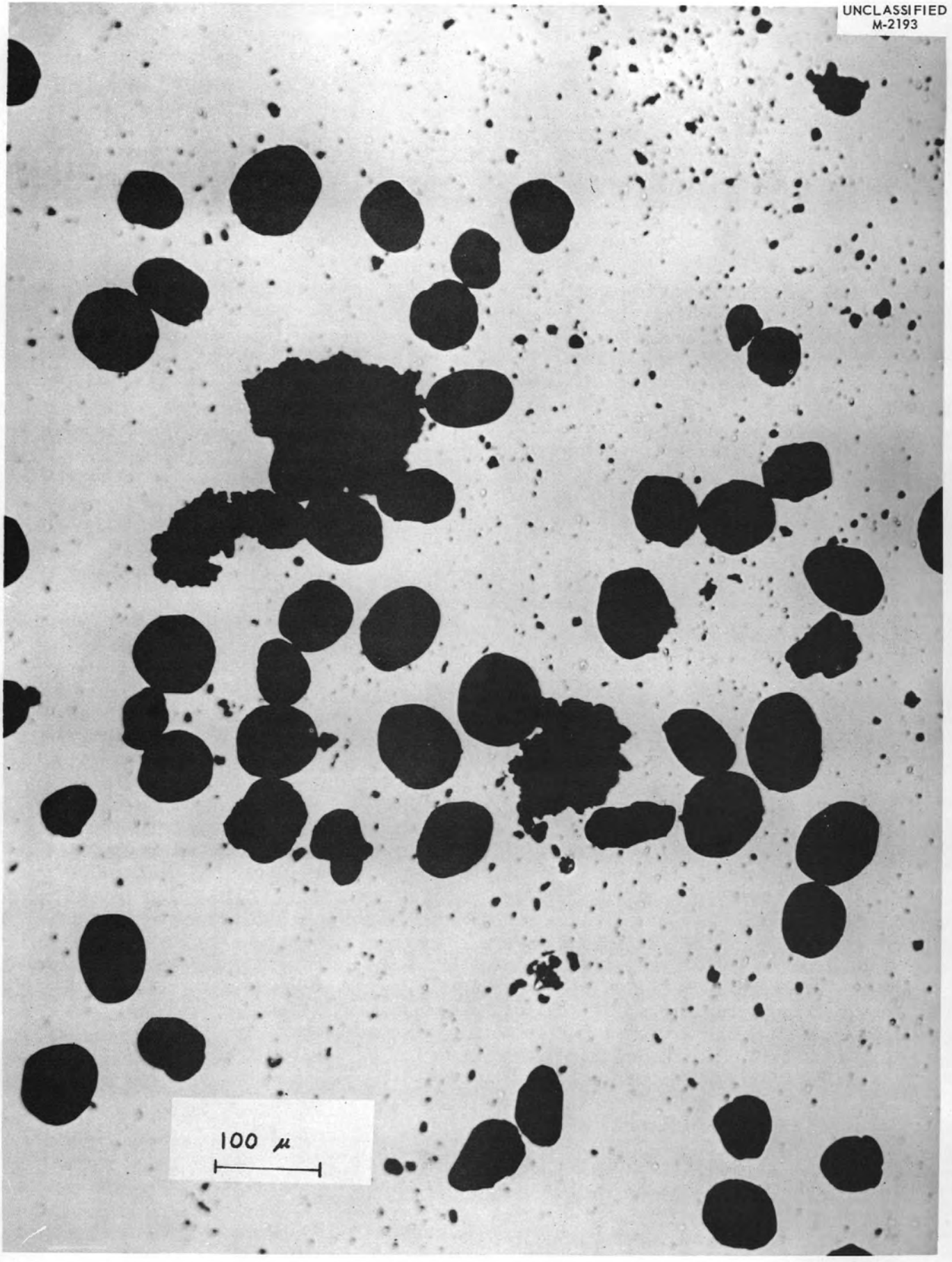


Fig. 5.2. Pseudo-Cubic Hydrate of Uranium Tetrafluoride.
200X. Reduced 9%.

5.0 URANIUM TETRAFLUORIDE PRECIPITATION

Uranium tetrafluoride for metal production must have a tap density of 3.0 g/cc or greater so that it may be charged to reduction bombs in adequate amounts. The settling rate and filterability of the wet UF_4 precipitate and the tap density of the filter cake dried at 110°C for 24 hr are dependent upon temperature, fluoride ion concentration and aging time during precipitation, but independent of order of reagent addition, concentration of reactants, hydrogen ion, and feed purity.

Several hydrates of uranium tetrafluoride have been reported. The highest hydrate definitely to be established is $UF_4 \cdot 2.5\ H_2O$; this was prepared by Von Grosse[16] by suspending ordinary precipitated uranium tetrafluoride in dilute aqueous hydrofluoric acid overnight. Khlopin and Gerling[17] and Khlopin and Yashenko[18] claim to have isolated three hydrates; $UF_4 \cdot 2\ H_2O$, $UF_4 \cdot 1.5\ H_2O$, and $UF_4 \cdot 0.5\ H_2O$ by electrolytic reduction of uranyl fluoride in aqueous hydrofluoric acid. Bolten[19] observed that addition of aqueous hydrofluoric acid to aqueous uranous chloride solution produced a precipitate with the composition $UF_4 \cdot H_2O$ after vacuum-drying or air drying at 100°C. X-ray diffraction studies[20] later revealed that the hydrates below $UF_4 \cdot 2\ H_2O$ have the same structure. There are probably only two hydrates of uranium tetrafluoride, $UF_4 \cdot 2.5\ H_2O$ and $UF_4 \cdot nH_2O$ where $0.5 < n \leq 2.0$. The crystal structure of the compounds $UF_4 \cdot 2.5\ H_2O$, $UF_4 \cdot nH_2O$, and UF_4 have been observed to be orthorhombic, pseudocubic, and triclinic, respectively.

In the pseudocubic crystal, the water molecules occupy vacant uranium sites and are hydrogen bonded to the fluorine. Since cell dimensions vary little over the range $UF_4 \cdot 2\ H_2O$ to $UF_4 \cdot 0.75\ H_2O$,[20] it is possible that a large change in cell structure occurs when the amount of water per uranium atom becomes less than 0.75. This could account for the fact that the two most widely recognized hydrates of uranium are $UF_4 \cdot 2.5\ H_2O$ and $UF_4 \cdot 0.75\ H_2O$.

The theoretical densities[20] of uranium tetrafluoride and some of its hydrates as calculated from X-ray diffraction data are:

UF_4	6.63 g/cc	$UF_4 \cdot 2\ H_2O$	6.32 g/cc
$UF_4 \cdot H_2O$	5.98 g/cc	$UF_4 \cdot 2.5\ H_2O$	4.74 g/cc

Apparently the variations in the characteristics of the precipitate depend on the relative amounts of each hydrate in the precipitate. Material which is largely $UF_4 \cdot 2.5\ H_2O$ is shown in Fig. 5.1. As can be noted the crystalline form is that of long slender needles. This material would pack similarily to straw with a large amount of void volume, resulting in a low tap density. The tap density of the material shown is 0.5 -1.0 g/cc as compared with its theoretical density of 4.74 g/cc. This material is flocculent, sticky, and very difficult to filter. It has a settling rate of approximately 6 in./hr.

The pseudocubic hydrate is shown in Fig. 5.2. Immediately after precipitation, the material is present as an agglomerated mosaic crystal with no regular shape. As expected, this material settles rapidly and has good filtration characteristics. The tap density of the dried precipitate is approximately 3.5 g/cc.

Fig. 5.3. Pseudo-Cubic Hydrate of Uranium Tetrafluoride.
200X. Reduced 10%.

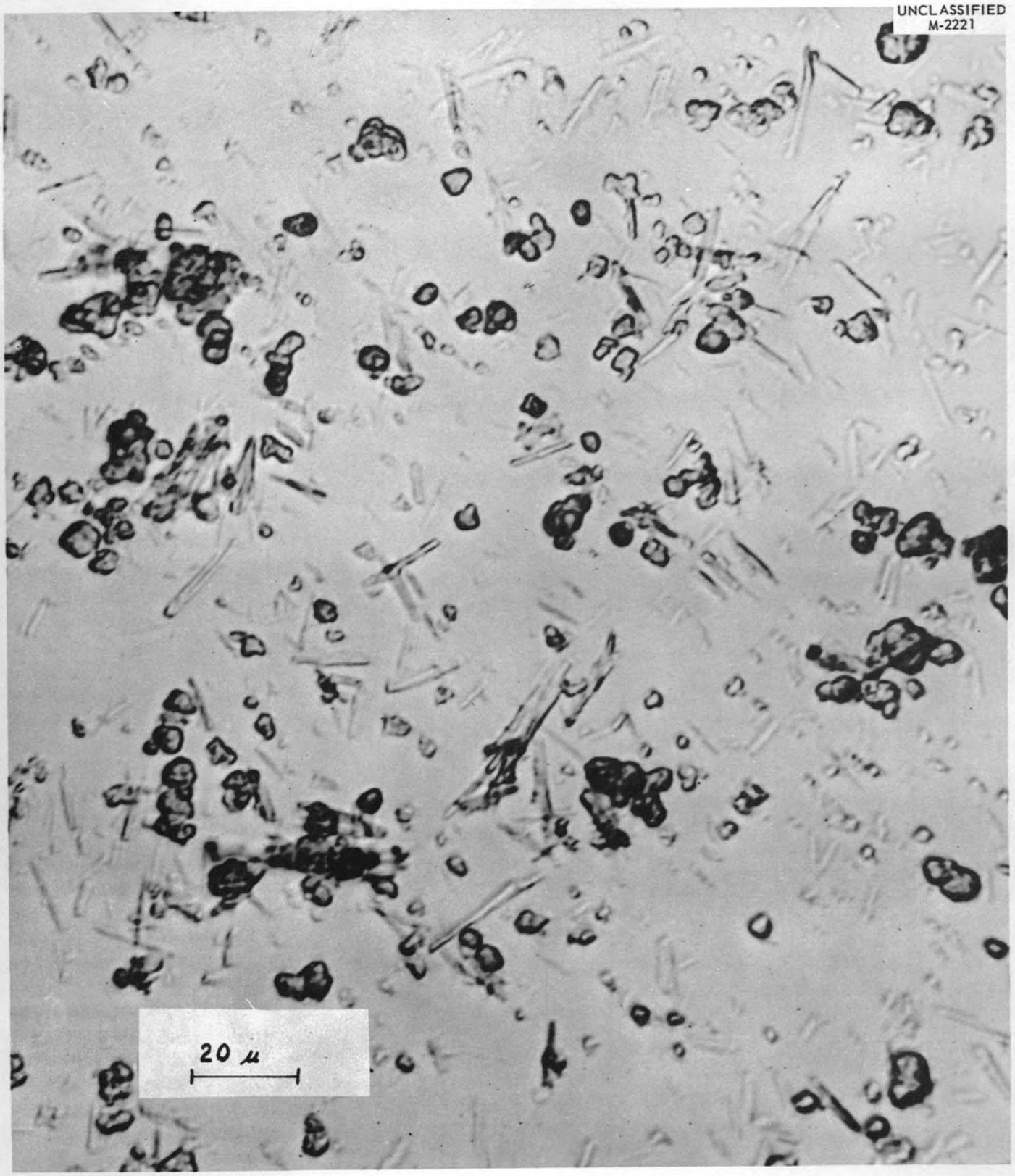


Fig. 5.4. Mixture of Uranium Tetrafluoride Hydrates.
1000X. Reduced 10%.

If an aqueous slurry of either of the hydrated forms is heated at 100°C for 24-36 hr, crystals of $UF_4 \cdot nH_2O$ (Fig. 5.3) result.[21] These crystals are more nearly regular in shape than freshly precipitated crystals.

Usually the precipitate is a mixture of the two crystalline forms (Fig. 4), and the properties of the mixture are intermediate. The tap density of this particular mixture is 1.6 g/cc; normally the tap density is approximately 2.3 g/cc owing to a smaller relative amount of the needlelike crystals.

5.1 Effect of Precipitation Conditions on Product

The characteristics of uranium tetrafluoride precipitated from aqueous solutions of uranous ion with aqueous hydrofluoric acid are very dependent on precipitation conditions. The precipitate may be described by comparing settling rates and filterabilities of the wet material and the tap densities of the dried material. Before the tap density is measured, the wet precipitate is dried for 24 hr at 110°C in air to a water content of approximately 6% and ground in a mortar.

The variables that might determine the crystalline form or the ratio of the two forms in the precipitate include the order of addition of reactants, concentration of reactants, fluoride ion concentration, hydrogen ion concentration, seeding, aging, feed purity, temperature, and treatment of precipitate.

5.1.1 Effect of Temperature on Properties of Uranium Tetrafluoride Precipitate. The most important variable affecting the properties of the precipitate is precipitation temperature. Dried filter cake having a tap density > 3.5 g/cc has been produced at 94-100°C; however, the tap density is usually lower than this, and the determining factor is not known. At lower temperatures a mixture of UF_4 hydrates is formed whose dry tap density is 2.0 g/cc or lower.

The product formed at >94°C settles and filters rapidly, while that formed at lower temperatures is slimy and difficult to filter and settles very slowly (~6 in./hr).

5.1.2 Effect of Order of Addition of Reactants. Settling rate, filterability and tap density of the precipitate are apparently unaffected by order of addition of UCl_4 and HF solutions, but purity is probably greater when UCl_4 is added to hot HF.

If aqueous hydrofluoric acid is added to aqueous uranium tetrachloride, no precipitation occurs until 50% of the stoichiometric quantity of HF has been added. It has been postulated[22] that a soluble complex,

$$\left[UCl_4F_2\right] = \left[H_2^{++}\right],$$

is formed which accounts for this. For this reason an excess of at least 10% of the stoichiometric quantity of HF must be added to achieve nearly complete precipitation of the uranous ion.

When a solution of uranous ion is added to a large volume of hydrofluoric acid, precipitation is instantaneous. The likelihood that the precipitated product will be contaminated by coprecipitation (particularly in the sulfate system where the sulfur remains in the product), or occlusion of the complexion is greater when acid is added to uranous solution- where precipitation is delayed - than when uranous is added to acid solution-- where precipitation is instantaneous.

In spite of the sacrifice in product purity, because of hazards and container corrosion involved in heating aqueous HF, the procedure chosen for precipitation was the addition of a relatively small stream of aqueous HF to a large volume of agitated heated uranous chloride.

5.1.3 Concentration of Reactants. In all precipitation work stockroom concentration hydrofluoric acid (60 wt %) was used. There have been no indications that less-concentrated acid could not be used except where the uranous ion concentration was low in the feed stream.

Uranous ion concentrations of 25-150 g/liter have been used with no observable effect on precipitate characteristics. With concentrations less than 10 g/liter, the particles of uranium tetrafluoride formed are very small and may require 3-5 hr to settle.[20]

5.1.4 Fluoride Ion Concentration. During batch precipitation of uranium tetrafluoride by addition of uranous ion to aqueous hydrofluoric acid solutions, a very dense precipitate forms initially, but as the addition of uranous ion proceeds the precipitate becomes less dense.[23] This indicates that high fluoride ion concentrations, and hence rapid precipitation, produces material with a high tap density.

5.1.5 Hydrogen Ion Concentration. Owing to the necessity of high fluoride ion concentrations, it was not possible to operate at low hydrogen ion concentrations. Addition of excess hydrogen ion as HCl produced no visible change in the precipitate.

5.1.6 Seeding. This variable was not studied sufficiently to show a definite effect. During two different precipitation tests the product near the end of the run was almost entirely the high-tap-density hydrate $UF_4 \cdot nH_2O$. Since the only difference in conditions between the earlier part and the end of the run was the added time (which allowed for possible coalescence of the suspended particles) it might be thought that seeding was responsible for the change in dried precipitate tap density from approximately 2.0 g/cc to approximately 3.5 g/cc.

5.1.7 Aging. Although extended aging of freshly precipitated material will produce crystals such as those in Fig. 5.3 from either of the hydrated forms of uranium tetrafluoride, the necessary aging period of 24-36 hr is impractical. If the precipitation vessels are so constructed that 30-60 min aging or holdup time is provided, good mixing and precipitation are ensured.

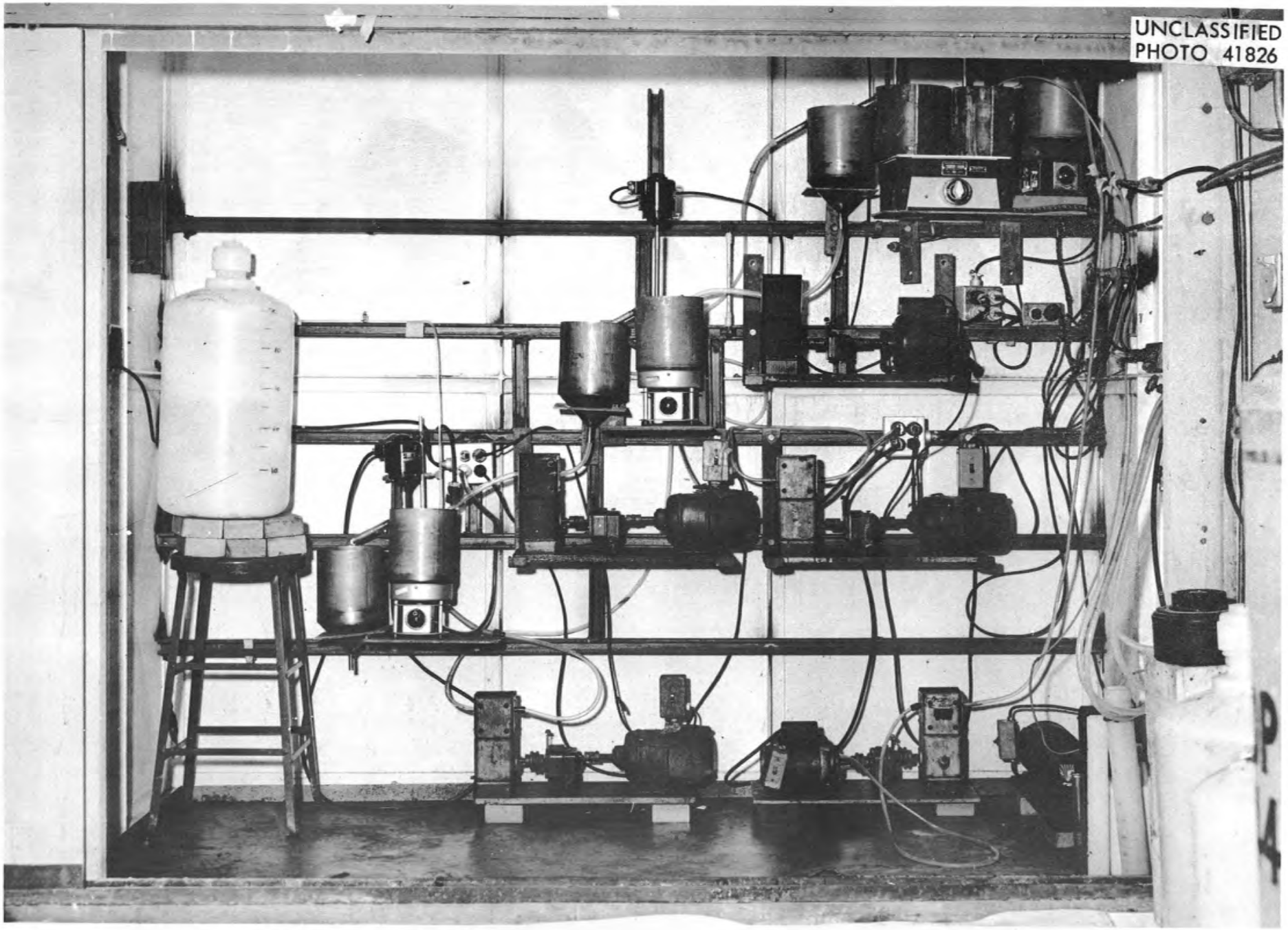


Fig. 5.5. Equipment for Continuous Precipitation and Countercurrent Decantation of Uranium Tetrafluoride.

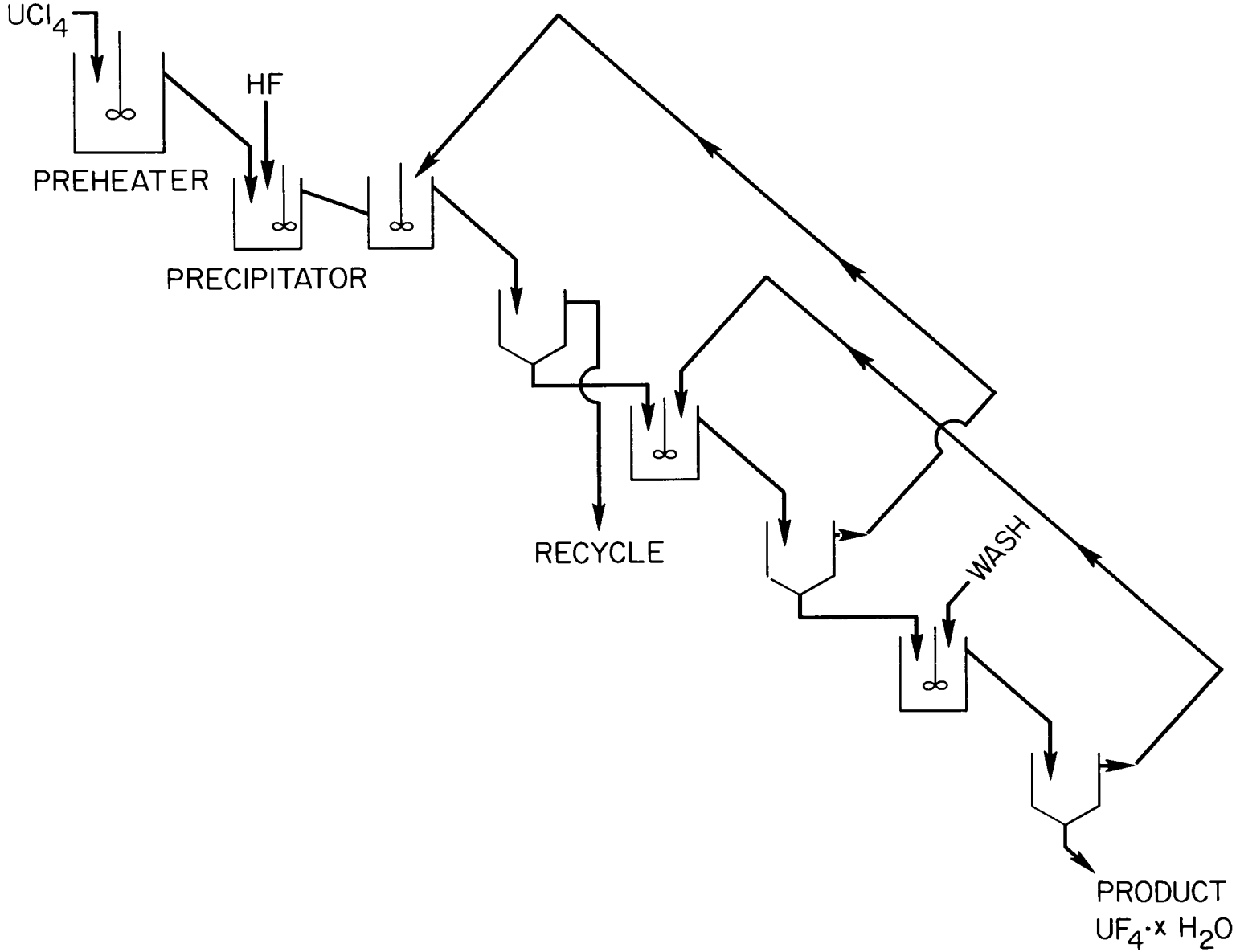


Fig. 5.6. Precipitation and Decantation Flowsheet.

5.1.8 Feed Purity. The presence of various feed stream contaminants even in concentrations as high as 2250 ppm iron (based on uranium) did not seem to affect the characteristics of the precipitate.

5.2 Materials of Construction

A number of materials were tested before one was found suitable for the precipitation vessels. Among these were Lucite, Bakelite, Monel, Hastelloy C, and Haveg-42. Only the last two were acceptable. (The Bakelite vessels were made of two sections, a thick bottom plate and a thin-walled tubular section which rested on the bottom plate. The bottom plate gave good service but the tubular section suffered severe attack from the hot solutions containing hydrofluoric and hydrochloric acids. Perhaps a thick-walled Bakelite vessel would serve.)

Hastelloy C vessels have given good service and are probably the best of the metals. An agitator of Hastelloy C in an abrasive slurry with 40% HF at 90°C has a life of one year.[24] Two tanks made of Haveg-42, 200 and 800 gal each, show no visible attack when containing 40-50% HF at 100°C.[24]

5.2.1 Description of Equipment. Material with a tap density in excess of 3.5 g/cc has been produced in equipment such as that shown in Fig. 5.5. The precipitation temperature was near 100°C, and 10% excess of the stoichometric quantity of hydrofluoric acid was used. The vessels and agitators are made of Hastelloy C. Sigmamotor pumps are used to move both slurry and aqueous streams. Tygon tubing was satisfactory for all streams except the aqueous hydrofluoric acid stream where Saran was used. A short section of rubber tubing was used in the pump section since the Saran is not flexible.

As shown schematically in Fig. 5.6, the equipment provides for preheating the uranous chloride feed solution, precipitation, and three stages of countercurrent decantation. The precipitation recycle stream containing unprecipitated uranium, dissolved uranium tetrafluoride, impurities removed by countercurrent decantation, excess hydrofluoric acid, and hydrochloric acid formed by the reaction is sent to the hydrochloric acid recovery step. After removal of the hydrochloric acid, the stream is sent to the feed dissolution vessel. Typical precipitating conditions were:

Temperature	98°C
Uranous Feed Stream	144 g/liter uranium at 50 ml/min
Hydrofluoric Acid Stream	60 wt % at 4.8 ml/min
Wash water flow rate	100 ml/min
Precipitation rate	432 g/hr of uranium

Filtering, washing, and handling the $UF_4 \cdot nH_2O$ precipitate at 95-100°C is recommended, because it tends to react with water at lower temperatures to form the low-density 2.5 hydrate.[20]

6.0 FILTRATION, DRYING, DENSIFICATION, GRANULATION

The uranium tetrafluoride slurry discharged from the countercurrent decantation vessels was filtered in large Buchner funnels using filter paper. The precipitate produced at high temperature was very granular in appearance and filtered easily. The filtered precipitate, in the form of 1-in.-thick filter cakes, was tray-dried in a steam-heated air-oven at 110°C for 24 hr to a final water content of 6%. No oxide formation was observed during this step.

At the K-25 plant,[25] experiments were performed in order to obtain an estimate of the optimum filtration conditions and the required filtration area for material precipitated at high temperatures. Specific filter-cake resistances (Table 6.1) were calculated from the following equation.

$$\alpha = \frac{\Delta 0}{\Delta V} \frac{\Delta P A^2}{\mu W}$$

where α is the specific resistance

$\Delta 0$ is the time in minutes

ΔP is the vacuum across the cake in inches of mercury

A is the filter area in square inches

ΔV is the volume of the wash water in ml

μ is the viscosity of water in centipoises

W is the weight of the dry cake in grams.

Table 6.1 Specific Filtering Resistances

15/32-inch cake		11/32-inch cake	
ΔP	α	ΔP	α
5.0	0.77	5.0	0.69
10.0	0.81	19.9	1.46
26.7	0.84		

In the cases where the tap density of the dried precipitate was less than 3.0 g/cc, the material was tabletted in a Stokes Tabletting machine using a pressure of approximately 40,000 pounds per square inch. No die lubricant was used. The tablets were ground in a Stokes oscillatory granulator to -40 + 100 mesh.

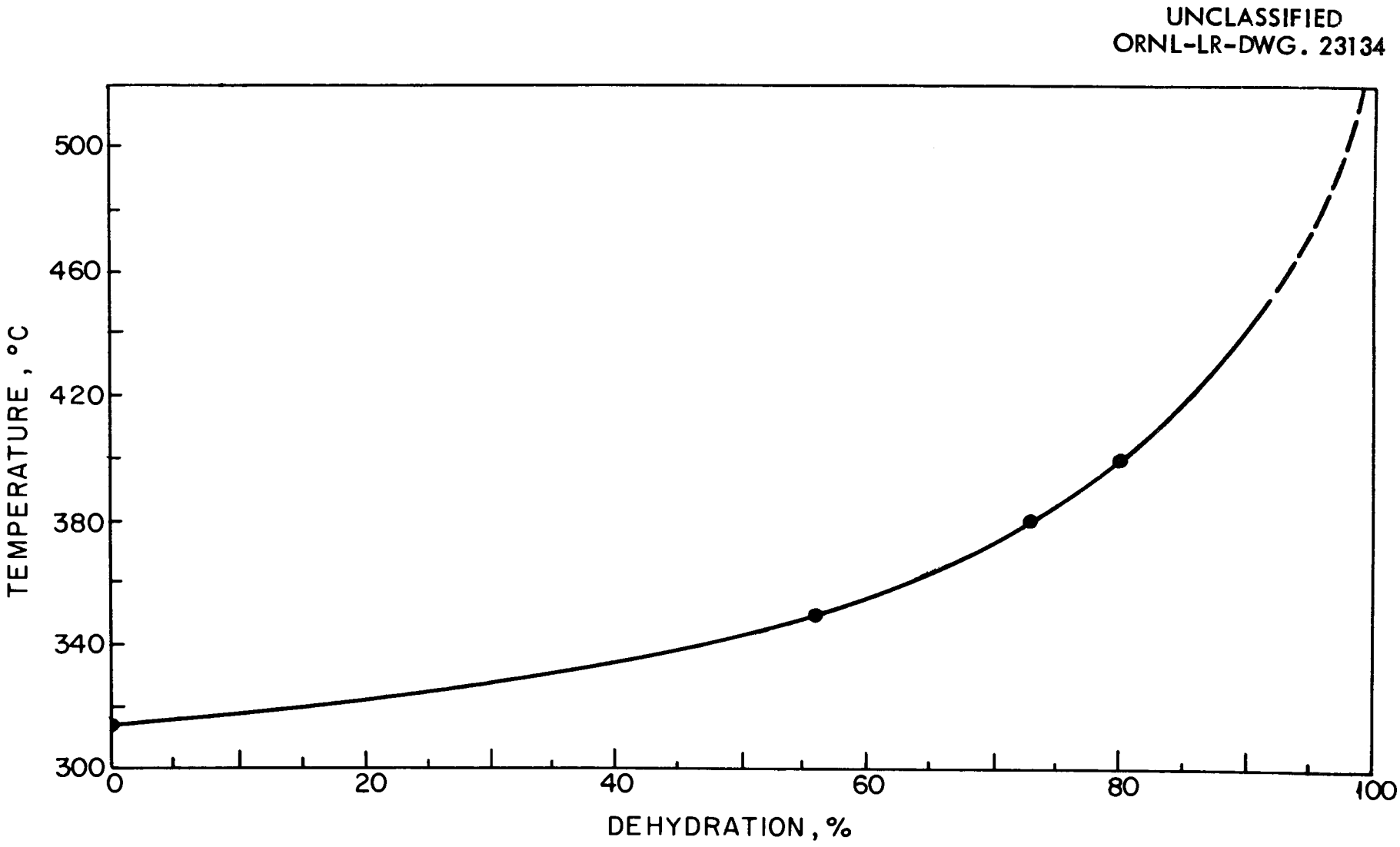


Fig. 7.1. Limiting Temperatures for the Dehydration of $UF_4 \cdot 3/4\ H_2O$ in Flowing Nitrogen. Above the temperatures on the curve, UO_2 is formed. (From reference 1)

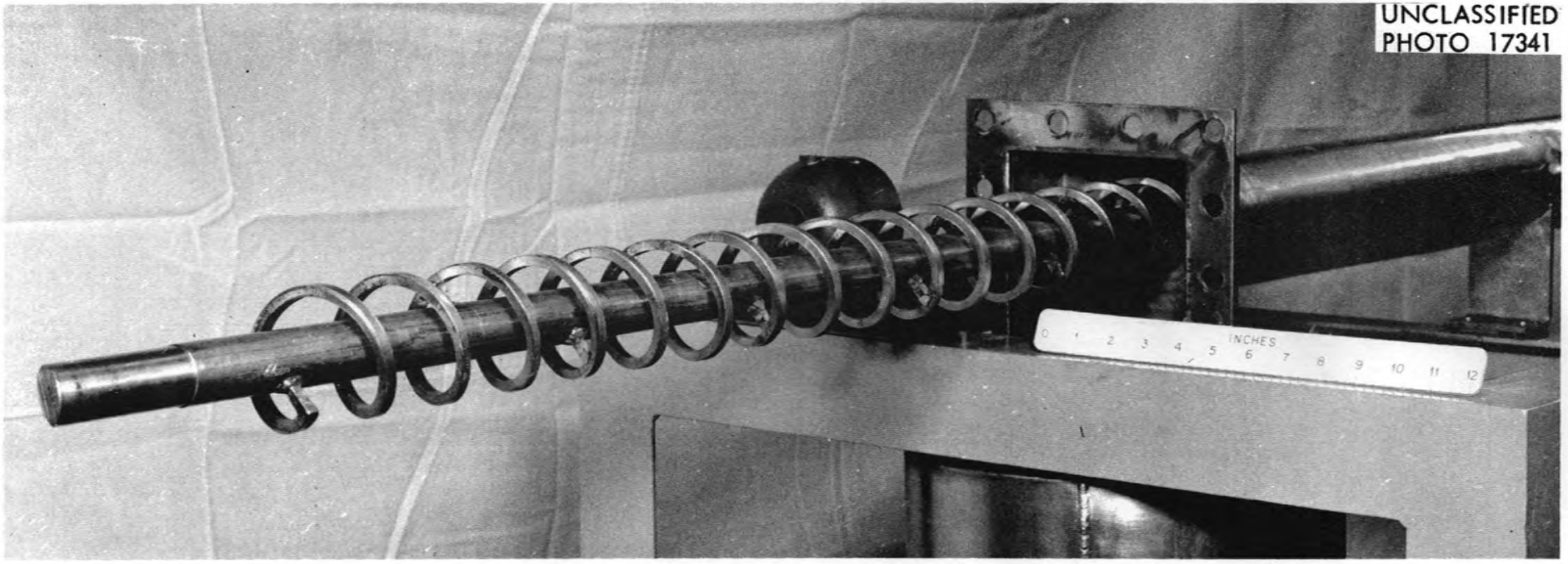


Fig. 7.2. Ribbon-Flite Dehydrator Hollow Screw and Unlagged Tube.

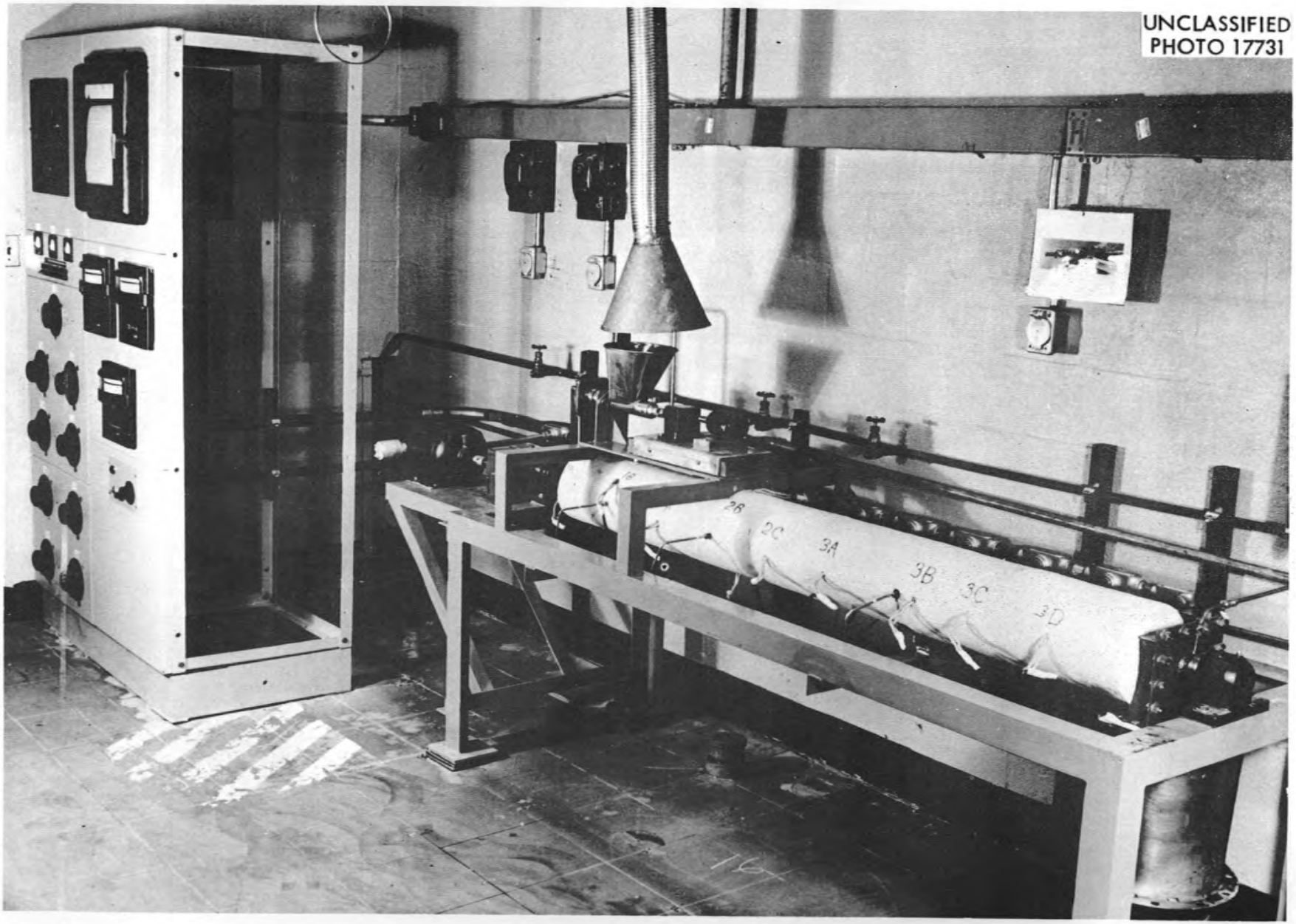


Fig. 7.3. Ribbon-Flite Screw Dehydrator for Producing UF_4, 6 ft. long by 3 in. dia.

UNCLASSIFIED
ORNL-LR-DWG 32654

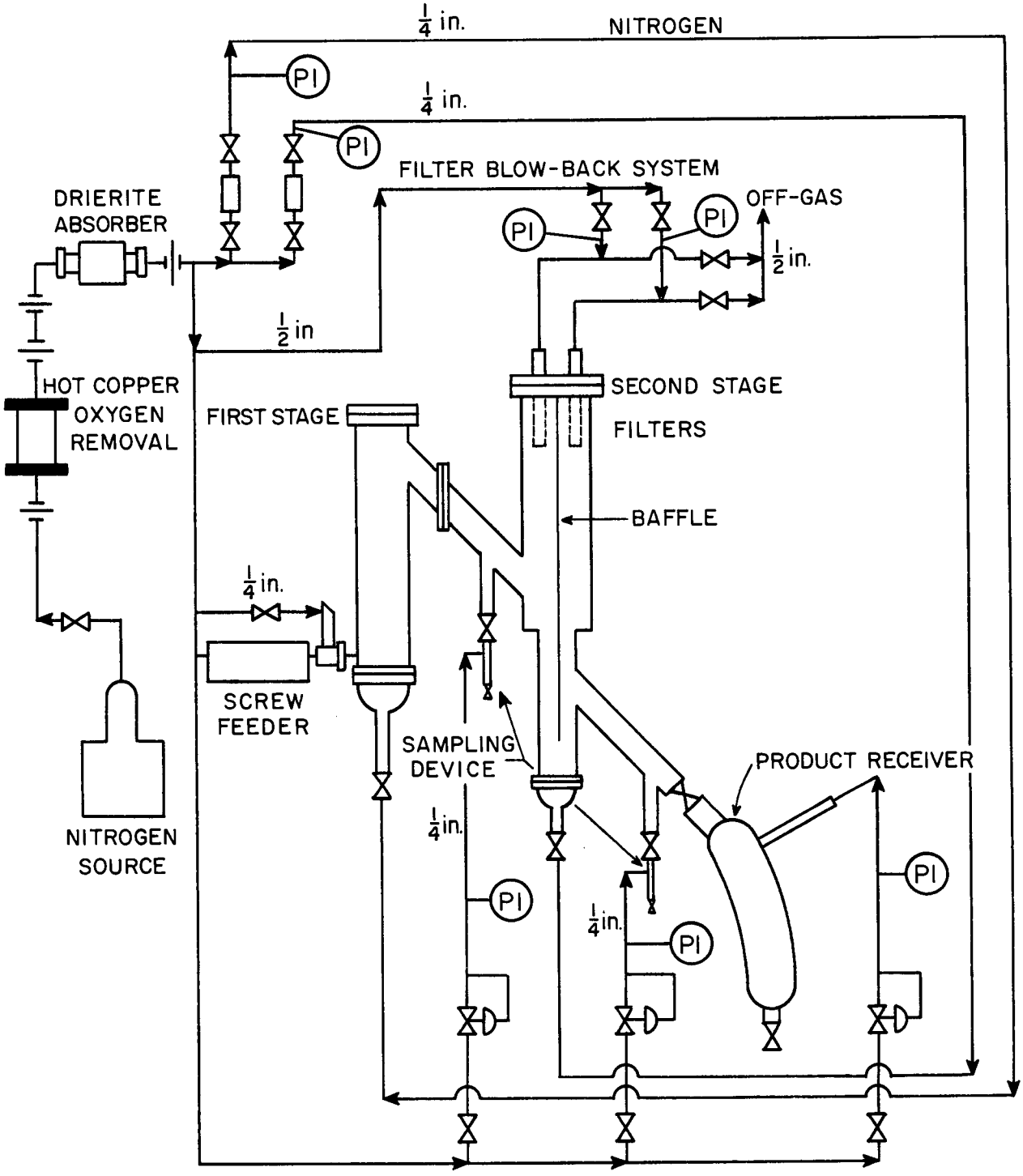


Fig. 7.4. Excer Dehydration Flowsheet.

7.0 DEHYDRATION

Laboratory work[5,26,27,28] has shown that the water content of uranium tetrafluoride can be reduced to less than 0.2% by weight in an atmosphere of nitrogen with subsequent formation of less than 1.0% by weight AOI (ammonium oxalate insoluble). The allowable dehydration temperature is dependent on the water content of the material (Fig. 7.1). In order to avoid the formation of AOI, the initial dehydration temperature must be kept below approximately 325°C. As the dehydration proceeds, the maximum allowable temperature increases, and near complete dehydration temperatures may be used in the range 425-475°C. Since the pyrohydrolysis reaction is catalyzed by traces of oxygen, very pure nitrogen must be used.

The first large dehydrator (Fig. 7.3) used consisted of a heated tube containing a hollow screw (Fig. 7.2) for moving the solid material. Dry nitrogen flowed countercurrently to the solid material. The drying time was controlled by adjustment of the angular velocity of the screw. Heat was supplied by external heaters.

AOI formation was low during the operation of this dehydrator; however, extremely low feed rates were required. The major problem was that of heat transfer. A small amount of uranium tetrafluoride in the clearance space between the screw and the tube wall was a very good insulator and seriously reduced heat transfer to the center of the bed.

For better heat transfer and solids-gas contact, a fluidized bed dehydrator was designed (Fig. 7.4). The uranium tetrafluoride hydrate was fed to the bottom of the first stage by a screw feeder where it was fluidized by a nitrogen stream. The material overflowed from the first to the second stage. A baffle extending to within 4 in. of the bottom of the second stage prevented material's by-passing this stage. After dehydration the material was collected in the product tank.

The unlagged dehydrator is shown in Fig. 7.5. The heaters were provided in two sections on each stage and six thermocouple wells were inserted into each stage. Fig. 7.6 shows the completed dehydrator. Traces of oxygen and water were removed from the nitrogen feed stream by a hot copper oxidifier and by a Drierite column respectively.

The rates of dehydration of uranium tetrafluoride hydrate at 250°C and 350°C are shown in Fig. 7.7 (a) and Fig. 7.7 (b), respectively. Traces of naphthalene and stearic acid were present from the tabletting step where they served as die lubricant. The addition of these compounds was later discontinued since a large amount of carbon remained in the product after dehydration.

As can be noted in Fig. 7.7 (a), the dehydration rate becomes almost zero at a water content of 1.0%. At 350°C, water content is reduced to 0.2% in approximately twenty-four hours. In order to obtain good dehydration rates with low AOI formation, the first stage of the dehydrator was operated at 350°C and the second at 450°C.

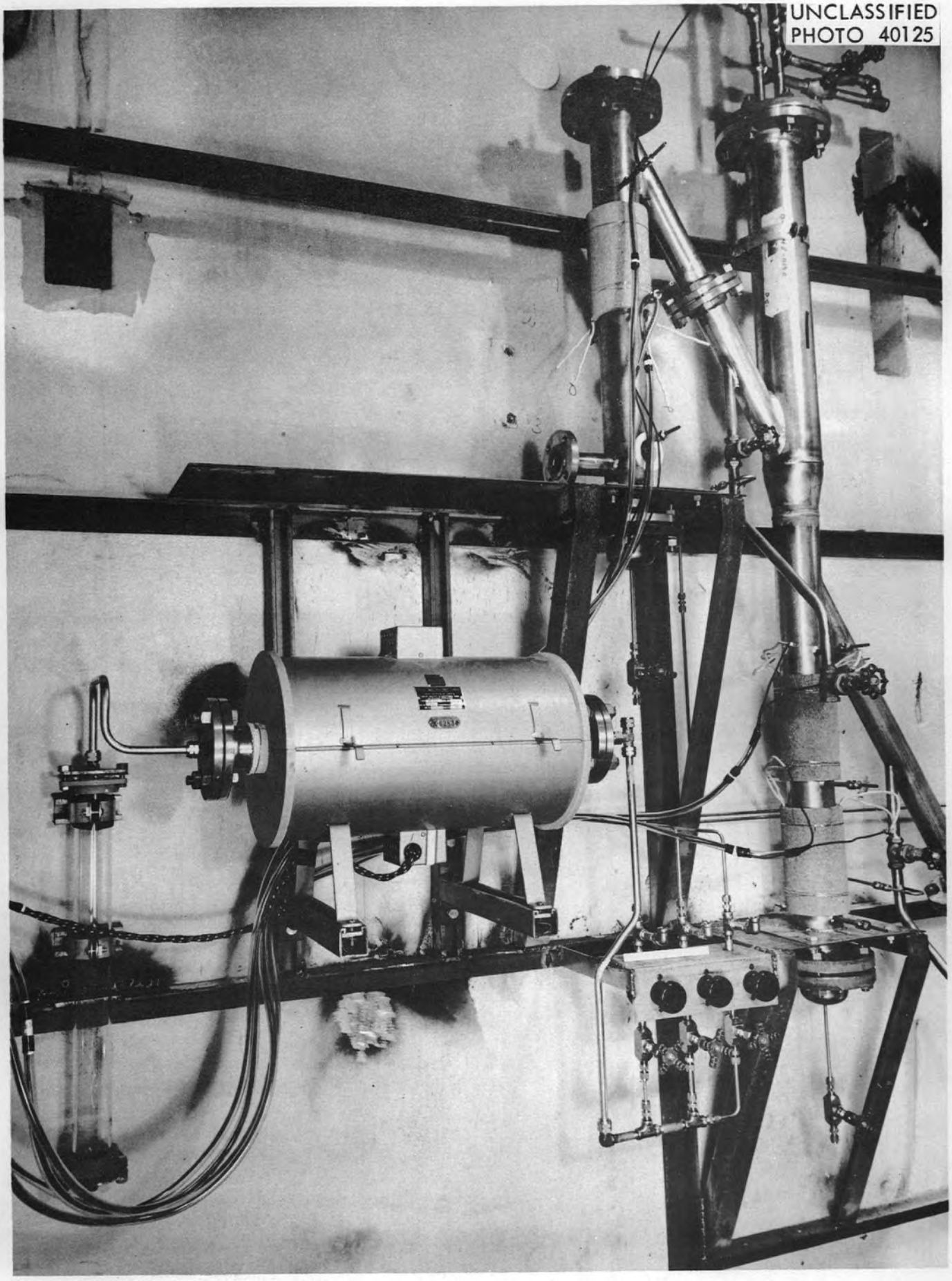


Fig. 7.5. Unlagged Fluidized Bed Dehydrator.

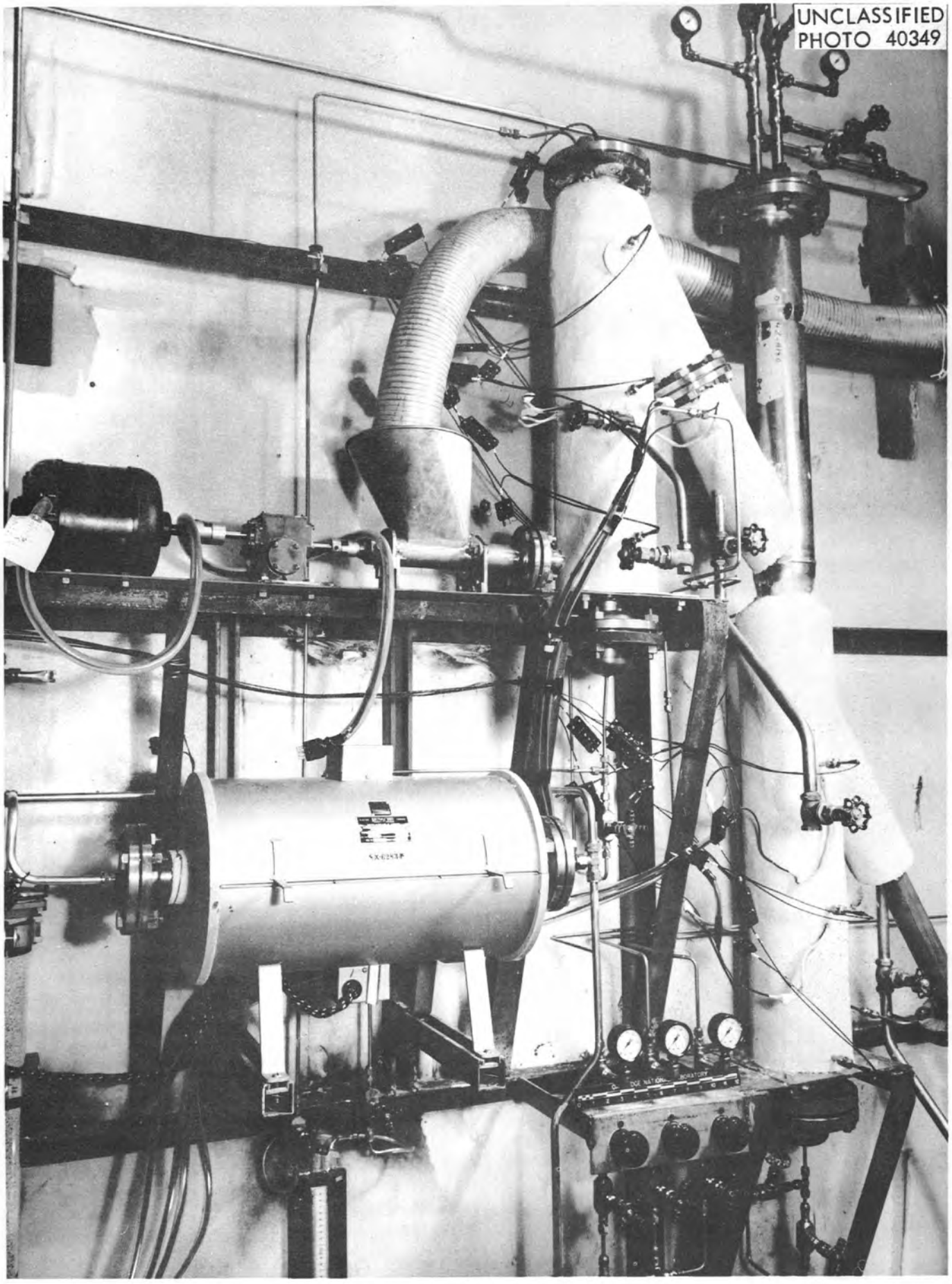


Fig. 7.6. Fluidized Bed Dehydrator.

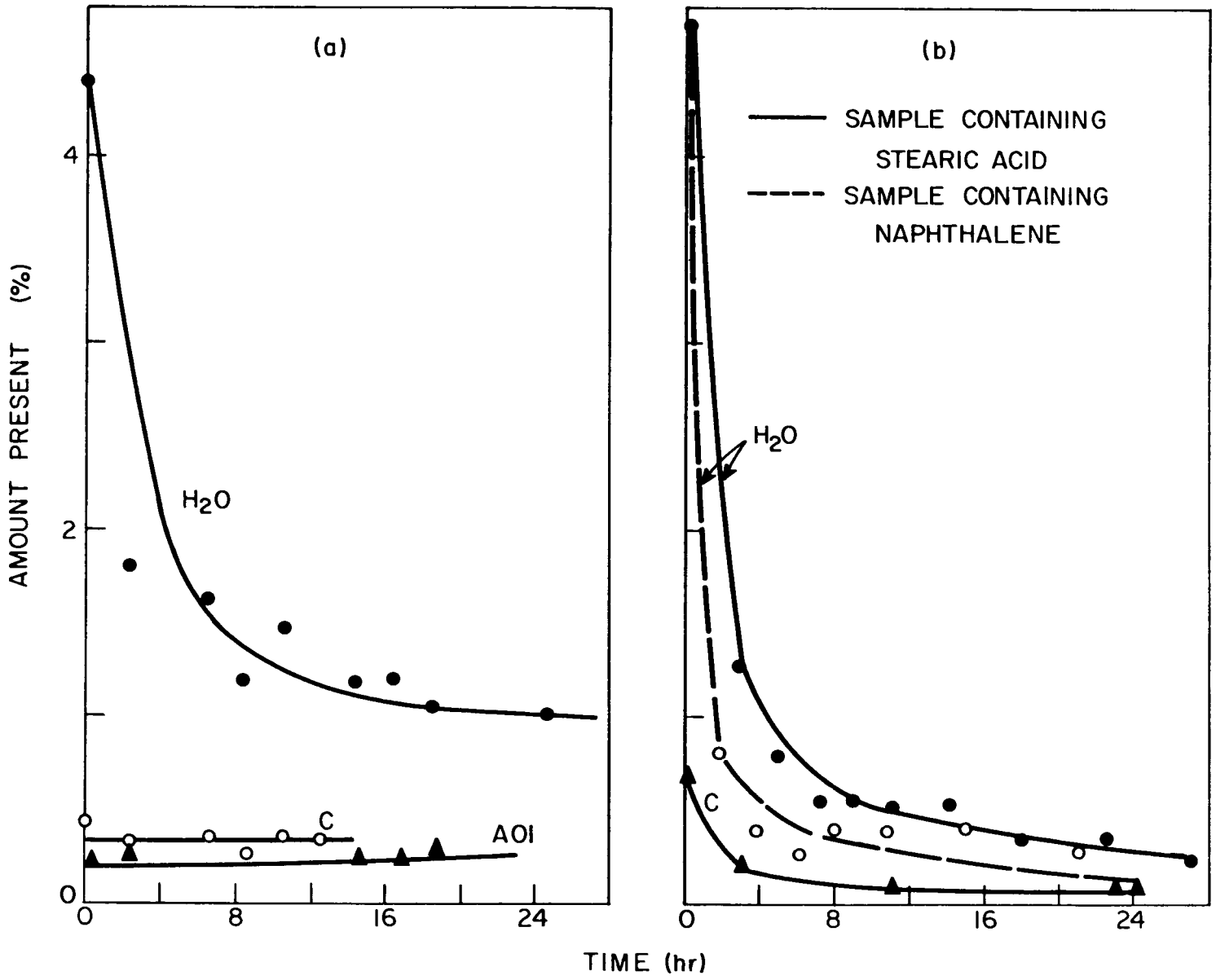


Fig. 7.7. Dehydration of $UF_4 \cdot \frac{3}{4}H_2O$ at (a) 250 ± 25°C and (b) 350 ± 25°C.

In general the operation of the fluidized bed was satisfactory. Owing to the absence of insulation on the top section of the second stage, water vapor condensed. Since the filters were located at the product exit, moist material that collected on the filters, dropped off later and contaminated the product.

The solids feeding device was a source of trouble. During normal operation of the dehydrator, a small volume of nitrogen leaked from the first stage through the feeder. Traces of moisture carried with the gas adsorbed on the feed material and increased its tendency to cake. Pressurization of the feeder improved its operation.

Early results indicated that a large amount of particle-size degradation was occurring in the dehydrator. Later studies showed that little change occurred when the sizing operation was thorough. Results from one of the later tests are given in Table 7.1. The change which occurred was probably due to poor sizing since this operation is difficult.

Although the fluidized bed offers good heat transfer and solid-gas contact, it complicates the process as a whole since the feed must be a certain particle size; in this case, -40 + 100 mesh. An improved screw dehydrator or a rotary kilm would probably prove more satisfactory for this operation.

Table 7.1 Screen Analysis of Feed and Product for Dehydration

Tyler Mesh Size	Feed, Weight %	Product, Weight %
-40 + 60	33.23	23.19
-60 + 80	33.97	33.01
-80 + 100	13.47	15.77
-100 + 150	10.40	15.45
-150 + 200	2.94	4.45
-200	6.01	8.05
Totals	100.02	99.92

8.0 WASTE ACID RECYCLE

The hydrochloric acid in the anion exchange column waste was recovered by distillation to provide a HCl scrub for the column. The hydrochloric acid in the supernatant from the precipitation of UF_4 was reused in dissolution of ore concentrate, the solution being evaporated to the optimum chloride concentration for loading on the anion exchange column. In laboratory-scale experiments HCl was 99% distilled from synthetic column waste and the precipitation supernatant was evaporated with negligible loss of HCl.

The distillation of HCl from resin column waste was investigated in open beakers with no attempt at recovering the evolved HCl. The synthetic waste solution contained calcium and iron chlorides. The HCl retained by the solution was about 1% or less in all runs (Table 8.1).

Supernatant from UF_4 precipitations was distilled in all-glass reflux equipment. Two hundred milliliters of a solution containing 125 g of UO_2Cl_2 per liter in 0.7 N HCl was evaporated to a final volume of 45 ml and samples were taken of the distillate at intervals. The HCl concentration in the distillate samples was less than 10-2 M. The hydrochloric acid recovered in the distillate represented less than 0.01% of the original chloride in the uranyl chloride solutions. The chloride ion concentration in the residue was increased from 1.8 to 7.2 M during the evaporation.

Table 8.1. Distillation of HCl from Resin Column Synthetic Waste

	Original Waste				Residue in Still				
Run No.	Vol, ml	$FeCl_2$, g/liter	$CaCl_2$, g/liter	HCl, N	Vol, ml	$FeCl_2$, g/liter	$CaCl_2$, g/liter	HCl, N	HCl, % of orig.
1	1000	101	---	2.8	300	337	---	0.13	1.4
2	1000	81	---	2.7	220	345	---	0.07	0.4
3	1000	---	720	4.0	440	---	3350	<0.001	~ 0
4	500	18	15	7.2	48	180	150	0.43	0.6

9.0 PRODUCT PURITY

The product obtained in the flowsheet demonstration run with South African concentrate was very pure (Table 9.1). The final anhydrous UF_4 contained 97.7% UF_4 and the acid from the supernatant could be used directly for dissolving more ore concentrate. The only contaminants in the original ore concentrate above 1000 ppm were sulfur, aluminum, magnesium, and iron. Insolubles, or silica, were 3.47%. With such pure feed to the process, high decontamination factors could not be demonstrated, but the product recovered from Vitro ore concentrate, which is very contaminated because of a different ore extraction process, was likewise very pure (Table 9.2). The

waste acid after UF_4 precipitation was so contaminated that it could not be reused until it was distilled. In general, in the flowsheet run, contaminants built up during dehydration of the hydrated greensalt. The iron, chromium, and manganese resulted from slight corrosion of grinding and dehydration equipment. A Monel precipitator used during part of the run, later changed to Hastelloy C, contributed copper and nickel. The high carbon was not expected but may have come from a Karbate heat exchanger. Many of the values were at background levels.

The purification obtained in ion exchange and precipitation complement each other to the extent that high-purity product may be made from very contaminated concentrate. The anion exchange-chloride system gave good separation of uranium from all impurities except trivalent iron, pentavalent vanadium, and molybdenum.

At the time the Vitro continuous run was made, there was no reduction in emf in order to reduce iron to Fe^{++} and vanadium to V^{4+}. In a later continuous run with UO_2^{++} and Fe^{++}, 80% of the iron was removed from the uranium. Separation of UO_2^{++} from V^{4+} was not tried in the chloride system, but has been studied by the Dow Chemical Co.[12] In the chloride system about 20% of the molybdenum stayed with the uranium, 60-70% went in the waste, and, by difference, 10-20% remained on the resin. If the resin is poisoned by molybdenum, a periodic caustic treatment is recommended, as is common practice in the sulfate system.

The greensalt precipitation step consistently rendered good separation from Cr, Fe, Mo, V, Cu, Ni and B, by factors of 10^2 and 10^4. The alkali, alkaline earths, and rare earths form double salts with UF_4 and are usually carried quantitatively, although decontamination factors of 5 have frequently been observed. The calcium contamination (Table 9.2) is not characteristic for either the ion exchange or precipitation step.

During the Excer development program calcium and boron were the most consistently high in the greensalt products, even when demineralized water was used and glass equipment was avoided. Boron analyses were frequently higher in the product than in the original feed. When feeds were spiked with 10,000 ppm of boron, decontamination factors were greater than 10^3 in both the ion exchange and the precipitation steps.

9.1 Bomb Reduction Test

Three kilogram batches of Excer uranium tetrafluoride were bomb reduced to the metal by the Mallinckrodt Chemical Works. The first and second batches were reduced with 90% >30 mesh and -40 +50 mesh magnesium with reduction yields of 0 and 14%, respectively. The third batch was ball milled for 24 hr, improving its blendability with the 90% >30 mesh magnesium, and a yield of 76% was obtained.

Table 9.1. Product Impurities in the South African Ore Concentrate Flowsheet Run (ppm, based on U)

Contaminant[a]	Ore Concentrate		Anion Exchange Product		UF_4 Hydrate					Anhydrous UF_4
	Solid	HCl Solution	Fresh Acid[b]	Recycle Acid[c]	Batch 1, 11 lb	Batch 2, 4 lb	Batch 3, 1 lb	Batch 4,[c] 8 lb	Composite	
Ag	X	X	X	X	---	---	X	X	1.45	---
Al	10,740	10,740	6.2	24	13.2	12.3	18.5	22.4	81.8	11
AOI	X	X	X	X	X	X	X	X	X	0.14%
B	---	X	---	---	---	---	---	---	---	---
C	0.042%	X	X	X	---	X	X	356	X	330
Ca	390	390	66	95	29	25	171	59.3	145	92.3
Cd	---	X	X	X	---	X	X	---	X	---
Cl	X	X	X	X	106	X	X	416	X	11.9
Cr	X	X	3.7	---	0.4	1.2	1.9	23.7	14.5	99
Cu	X	X	14	$2x10^4$	15.8	22.8	15.8	26	27.7	29
Dy	---	X	X	X	---	---	---	---	---	---
Fe	5,750	5,750	2,850	6,500	11.1	13.2	19.8	210	256	356
Gd	---	X	X	X	---	---	---	---	---	---
H_2O	X	X	X	X	X	X	X	X	6.27%	0.17%
K	---	X	X	X	13.2	X	X	6.6	13.2	6.6
Mg	1,950	1,950	2	32	1.2	1.3	5.9	2.8	3.3	5.9
Mn	X	X	51	470	0.4	0.4	0.26	2.77	2.4	11.5
Mo	49	49	5	12	---	X	X	---	4.1	4.3
Na	340	109	730	1000	74.8	X	X	53	198	23.7
Ni	X	X	---	10	30.3	46.2	26.4	33	43.5	10.7
P	1,270	1,270	47	X	7.9	X	X	10.5	X	10.5
S	31,000	31,000	112	X	---	X	X	---	X	---
Si	3.47%	12.3	---	X	66	X	X	53	X	26.4
Th	123	123	X	X	---	X	X	---	X	---
V	293	293	---	---	---	X	X	---	---	---

[a]The lower limits of detection of the contaminants were, ppm: Ag, 0.2; B, 2.0; C, 132; Cd, 18; Cr, 3; Dy, 6; Gd, 1.5; S, 4; Th, 100; V, 12.

[b]Fresh acid used for dissolving ore concentrate.

[c]Recycle acid used for dissolving ore concentrate.

Key:

Concentrations based on ppm uranium or % by weight

X = not analyzed for

--- = not detected

Table 9.2. Purification of Vitro Ore Concentrate by the Excer Process

Contaminant	Amount, ppm based on U		
	Ore Concentrate	Ion Exchange UO_2Cl_2 Product	UF_4 Hydrate
Al	42,000	---	2.9
B	< 0.1	---	---
Ca	3,650	1,760	11
Cu	X	---	0.6
Cr	X	X	---
Fe	48,500	32,000	29
Mg	X	N.T.	0.1
Mo	43,500	8,000	38
Na	1,700	43	10
Pb	X	X	12
Si	(high)	X	0.7
V	5,200	3,600	---
Mn	X	---	---
K	220	96	---

--- = not detected

X = not analyzed for

The following comments are quoted from a personal communication from R. F. Liefield and N. F. Newmann of the Mallinckrodt Chemical Works.[29]

"The separate portions received (2 of approximately 7 lbs each) were combined and rotary cone blended. Considerable Fe_3O_4 "scale" (X-ray analysis) was noted and magnetic separation was used for partial removal. A total of 3.3 grams of Fe_3O_4 was removed from 4400 grams of UF_4; the UF_4 remaining still contained 330 ppm iron. Reductions of this material were made in a dingot bomb scaled to produce 1 kilogram of uranium metal. A summary of reduction runs is also attached. It was found that the "as received" material did not blend well with our standard size magnesium and although finer magnesium (-40 + 50 mesh) produced improved blends, they were still unsatisfactory and resulted in very low yields. Ball milling the UF_4 for 24 hours improved its blendability and resulted in an improved (76%) yield. However, this is still considerably below the 90+% average obtained routinely with dry-process UF_4.

Based upon these limited data, it appears likely that size reduction will be necessary before this type UF_4 will uniformly produce satisfactory yields via bomb reduction. Because of the generally poor slag-metal separation, the metal produced was not analyzed. However, as large decontamination factors are not obtained in the reduction step, specifications for reactor-grade metal would very probably be exceeded by iron and nickel with boron on the borderline. Chromium and copper would probably be higher than dingot metal but might be acceptable."

9.2 Impurity Buildup in Recycle Scheme

Insufficient data were obtained for determination of the relation between the decontamination factor in the ion exchange step and the ultimate buildup of impurities in the feed solution since only one recycle was carried out. However, by using several assumptions we can arrive at an estimate of the buildup. The three main assumptions would be: (1) the decontamination factor is constant throughout the operation, (2) all the impurities following the uranium product from the ion exchange step appear in the uranium tetrafluoride supernatant and thus are recycled, and (3) only slight amounts of impurities are added after ion exchange. These assumptions appear reasonable and are used below in the derivation of a value for a given contaminant buildup after an infinite number of recycles.

If for a given contaminant the concentration in the original feed is A grams per liter and the decontamination factor for this element is r, the buildup is

Original amount of contaminant	A
Contaminant in 1st recycle	$A + 1/r(A)$
2nd recycle	$A + 1/r(A + 1/rA)$
3rd recycle	$A + 1/r[A + 1/r(A + 1/rA)]$

for three recycles. This procedure may be continued indefinitely; the sequence of terms, when simplified, have the form

$$A,\ A + 1/rA,\ A + 1/rA + 1/r^2A,\ A + 1/rA + 1/r^2A + 1/r^3A,$$
$$A + 1/rA + 1/r^2A + 1/r^3A + \ldots\ldots\ldots + 1/r^{(n-1)}A,\ \ldots.$$

For this geometric progression the sum of n terms, S_n, is

$$S_n = A\,\frac{(1/r^n - 1)}{(1/r - 1)} \qquad (1)$$

and as n increases without limit

$$S_\infty = \frac{A}{1 - 1/r} \qquad (2)$$

To illustrate the use of eq. 1 and 2 we may assume that iron has a decontamination factor of 2; for four recycles we would obtain from eq. 1, if the original iron was 5 g/liter,

$$S_4 = 5\ \frac{1/2^4 - 1}{1/2 - 1} = 5\left(\frac{-15/16}{-1/2}\right)$$

$$= 5 \times 15/8 = 75/8 = 9.4 \text{ g Fe/liter}$$

For the iron buildup after an infinite number of recycles from eq. 2,

$$S_\infty = \frac{5}{1 - 1/2} = 10 \text{ g Fe/liter}$$

For decontamination factors of greater than 100 the buildup is insignificant.

10.0 COST ESTIMATE

A summary of plant investment and operating costs for Excer plants processing ore concentrates at production capacities of 2.5 and 25 tons of uranium per day was prepared. The estimated mill costs per pound of uranium are 45¢ and 26¢, respectively.

The 2.5 ton/day plant is based on one 4-ft-dia Higgins contactor and four electrolytic stacks (40 electrode pairs per stack, three stacks on stream, one spare). The 25 ton/day plant is based on four 6-ft-dia Higgins contactors and 32 electrolytic stacks (30 on stream, 2 spare).

Table 10.1. Capital Investment (Summary) for Excer Plant

	2.5 tons/day		25 tons/day	
	Process Equip.	Elect.	Process Equip.	Elect.
A. Estimated total major equipment costs (less Tirrelloy)	$ 216,025	$ 41,800	$ 960,100	$ 167,200
B. Installed cost (140% of A)	300,000	58,500	1,344,100	234,100
C. Piping (50% of B)	150,000	---	672,100	---
D. Instrumentation (10% of B)	30,000	---	134,400	---
E. Total Physical Plant w.o. building	480,000	58,500	2,150,600	234,100
F. Engineering and Construction Supervision (35% of E)	168,000	20,500	752,300	81,900
G. Total Physical - No building	648,000	79,000	2,902,900	316,000
H. Contingencies (30% of G)	195,000	23,700	870,870	93,200
I. Total	843,000	102,700	3,773,770	409,200
Tirrelloy	44,000		352,000	
	887,000		4,125,770	
	102,700		409,200	
Total Capital Investment	989,700		4,534,970	

Table 10.2. Cost of Basic Equipment for Excer Plant (2.5 tons/day)

Equipment	No.	Process Equip.	Elect.
Ore conveyor	1	$ 2,000	
Storage hopper	1	1,000	
Scales	2	2,000	
Dissolver		6,000	
Surge tank		1,500	
10 M HCl storage tank		5,000	
Recycle 10 M HCl surge tank		2,600	
Higgins contactor		40,000	
Cell solution surge tank		1,700	
Elect. cells,* Tirrelloy- $44,000, Rest- $52,500		96,500	
Rectifier			29,300
Cell heating element		1,725	
Precipitators	2	3,000	
Rotary filter		13,200	
Conveyor belt and feeder		8,800	
Dryer		20,000	
Pelletizer		5,800	
Granulator		3,300	
Dehydrator		17,500	
Dust collector		2,200	
Fume scrubber		5,500	
H_2SO_4 storage tank		1,000	
Dilution tank (H_2SO_4)		500	
HCl still burners		2,000	
Barrens preheater		1,000	
Barrens still pot		3,000	
Barrens condenser (a)		2,300	
Barrens condenser (b)		900	
Recycle HCl still		3,000	
Recycle still pot		3,000	
Recycle preheater		700	
Recycle condenser		2,300	
Recycle cooler		1,000	
Elect. substation at $50/kw			
Cell load 150 kw			7,500
Dehydrator 50 kw			2,500
Misc. load 50 kw			2,500
Total equipment cost including Tirrelloy		260,025	
Tirrelloy		-44,000	
		216,025	41,800

*Costs based on single-faced anodes.

Table 10.3. Operating Costs (Summary) of Excer Plant

	2.5 tons/day			25 tons/day		
	$/day	$/day	¢/lb U	$/day	$/day	¢/lb U
A. Labor		454.2	9.1		1,307	2.6
B. Overhead (100% labor)		454.2	9.1		1,307	2.6
C. Materials						
Chemicals	555.0			5,555.0		
Utilities	111.1			1,111.0		
Resin (2 yrs.)	33.7			337.0		
Membranes (1 yr.)	5.4			54.0		
Tirrelloy Recoat	10.9			109.0		
Maintenance (at 4% of total plant)	120.0			550.0		
Total Materials	836.1	836.1	15.56	7,716.0	7,716.0	15.4
D. Decontamination		18.0	.4		165	.33
Process equipment at 20%	540.0					
Electrical equipment at 5%	16.0			2,500		
Total depreciation		556.0	11.1		2,562	5.1
Total mill cost		2,318.5	45.26	62	13,057	26.1

Table 10.4. Operating Costs (Itemized) for Excer Plant

	$/day		¢/lb U	
Labor				
Direct labor and supervision	274.2			
Maintenance labor (6% of plant cost)(0.06) (989,000)/330	180.0			
Total Labor		454.2		9.1
Overhead (100% of total labor)		454.2		9.1
Chemicals				
H_2SO_4, 1250 lb at $23.50/ton	15.0		.3	
HF, 3000 lb (60%), at 0.18/lb	540.0		10.8	
Total Chemicals		555.0		11.1
Utilities				
Electricity, cells, 3220 kwhr				
Dehydrator 700 kwhr				
Misc. 1000 kwhr				
4920 kwhr at $0.007/kwhr	34.50		0.7	
Steam for stills, precipitator, drier, 100 x 10^3 lb at $0.68/$10^3$ lb	68.0		1.4	
Process water, 200 x 10^3 gal at $0.028/$10^3$ gal	5.6		0.1	
Demineralized water, 20,000 gal at $0.15/$10^3$ gal	3.0		0.06	
Total Utilities		111.1		2.26
Miscellaneous				
Resin, 2 yr life, $22,000/660	33.7		0.7	
Membranes, 1 yr life, $120 x 15/330	5.4		0.1	
Tirrelloy Recoat, 1 yr life, $30 x 120/330	10.9		0.2	
Maintenance materials (4% of total plant), (0.02)(989,000)/330	120.0		1.2	
Total Miscellaneous		170.0		2.2
Decontamination (30% of maintenance mat. cost)		18.0		0.4
Depreciation				
Process equipment at 20%/yr, (0.20)(887,000)/330	540.0		10.8	
Electrical equipment at 5%/yr,(0.05)(102,700)/330	16.0		0.3	
Total Depreciation		556.0		11.1
Total Mill Cost		2,318.5		45.26

11.0 REFERENCES

1. I. R. Higgins, J. T. Roberts, "Development of the Excer Process. I," ORNL-1696 (April 13, 1956).

2. J. A. Marinsky, "Development of the Excer Process. II," ORNL-1979 (March 12, 1957).

3. Chemical Technology Division Monthly Report, January 1957, ORNL-2251.

4. Chemical Technology Division Monthly Report, February 1957, ORNL-2270.

5. Chemical Technology Division Monthly Report, August 1957, ORNL-2400.

6. I. R. Higgins, "Recovery and Purification of Uranium by Continuous Ion Exchange and Electrolysis," CF-56-6-138 (June 26, 1956).

7. R. R. Holcomb, I. R. Higgins, W. E. Shockley, "Development of the Excer Process. V: Recovery, Purification, and Iron Reduction of Uranium Using a Sulfate Ion Exchange System," ORNL-2554.

8. W. J. Neill, I. R. Higgins, "Development of the Excer Process. III. Preparation of Uranium Tetrafluoride from Uranyl Chloride by Iron Reduction and Precipitation," ORNL-2469 (In press).

9. I. R. Higgins, "Mechanical Features of the Higgin's Continuous Ion Exchange Column," ORNL-1907 (Sept. 29, 1955).

10. I. R. Higgins, U. S. Patent 2,815,322.

11. I. R. Higgins, J. T. Roberts, C. W. Hancher, J. A. Marinsky, "Preparing Uranium Tetrafluoride by Ion Exchange and Electrolysis," Ind. Eng. Chem., 50, 285 (March 1958).

12. T. A. Arehart, J. C. Bresee, C. W. Hancher, S. H. Jury, "Countercurrent Ion Exchange," Chem. Eng. Progr., 52, 353 (Sept. 1956).

13. N. W. Rosenburg, Progress Report on Subcontract No. 947 (Excer) for the Month of February, 1957, CF-57-2-145.

14. Chemical Technology Division Monthly Report, June 1957, ORNL-2362.

15. A. J. Giuffrida, L. E. McNeese, M. E. Whatley, Excer: Evaluation of Ionics Electrolytic Cell, CF-58-1-112 (Jan. 31, 1958).

16. J. J. Katz, E. Rabinowitch, The Chemistry of Uranium, First Edition, p. 360, New York: McGraw Hill Book Co., 1951.

17. Khlopin and Gerling, "Zhur. Obschey Chim.," (1936) 6, 1701.

18. Khlopin and Yashenko, "Invest. Akad. Nank., U.S.S.R., Otdel Khim. Nank," (1942) 87.

19. H. C. Bolton, "Bull. soc. chim." Paris, (2) 6:450.

20. J. K. Dawson, R. W. M. D'Eye, A.E. Truswell, J. Chem. Soc. 3922-9, November 1954.

21. K. J. Fritz, "Precipitation of Uranium Tetrafluoride," CF-57-9-63 (Sept. 30, 1957).

22. E. Lofthouse, "The Manufacture of Uranium Tetrafluoride by the Wet Way Process," Imperial Chemical Industries, AERE-X/R-249, (May 13, 1949).

23. W. K. Eister, et al, Progress Report for May 1957, ORNL-2361.

24. R. H. Capp, Personal Communication, Niagara Falls, Electro. Metal Corp., July 1, 1957.

25. R. W. Anderson, A. L. Allen, E. W. Powell, "Electrochemical Preparation of Uranium Tetrafluoride, Part II, High Temperature Cell," K-681 (Nov. 10, 1950).

26. Chemical Technology Division Monthly Report, May 1957, ORNL-2361.

27. Chemical Technology Division Monthly Report, Sept. 1957, ORNL-2416.

28. Chemical Technology Division Monthly Report, Nov. 1957, ORNL-2447.

29. R. F. Leifield, N. F. Newmann, Personal Communication, St. Charles, Mo., Mallinckrodt Chemical Works, May 19, 1958.

12.0 APPENDIX

Table 12.1. Ion-exchange Run Data

Time	Resin	Flow Rate, ml/min: Feed	Scrub	Strip Water	Waste	Product	Slip Water	U Analysis, g/liter: Product	Waste	Slip Water	H^+ (N) Product
		Feed: 196 g uranium per liter					Scrub: 10 M HCl				
March 26, 1957											
9:00											
11:00	50	10	23	75	72	17	75	136	0.053	---	---
1:00		11	25	58	50	18	75	109	0.083	---	---
3:00		12	22	67	50	16	46	147	0.082	---	---
5:00		11	25	75	42	19	46	109	0.042	---	---
7:00		12	25	75	67	17	46	98	0.051	---	---
9:00		12	25	75	50	16	46	103	0.062	---	---
11:00[a]		12	25	75	58	15	46	158	0.061	0.047	---
March 27, 1957											
9:00											
11:00	75	25	29	92	68	21	58	163	0.027	---	---
1:00		22	37	92	82	21	58	200	0.041	---	---
3:00		23	35	100	83	19	62	218	0.044	---	---
5:00		25	39	100	75	22	62	218	0.042	---	---
7:00		23	36	92	78	---	58	220	0.045	---	---
9:00		22	35	92	71	22	58	211	0.032	---	---
11:00		22	36	100	75	20	58	225	0.023	---	---
March 28, 1957											
9:00											
11:00	75	---	32	75	50	20	41	---	---	---	---
12:00		27	30	66	66	18	50	---	---	---	---
1:00		23	37	83	66	23	66	46.3	0.0012	---	---
3:00		36	33	67	75	17	58	79.6	0.0037	---	---
4:00		59	33	66	100	18	67	---	---	---	---
5:00		64	33	87	116	22	67	73.5	0.0013	---	---
7:00		---	33	92	92	18	58	87.1	0.0008	---	---
9:00		63	37	100	116	19	67	141.6	0.0016	---	---
11:00		63	37	92	116	18	67	119.8	0.0012	0.0024	2.13

Table 12.1. continued

Time	Resin	Flow Rate, ml/min						U Analysis, g/liter			H^+ (N)
		Feed	Scrub	Strip Water	Waste	Product	Slip Water	Product	Waste	Slip Water	Product
		Feed: 287 g of uranium per liter						Scrub: 9 M HCl			
August 21, 1957											
8:30											
9:30	75	13	33	92	115	12	17	134	0.113	---	---
10:30		20	37	116	162	13	20	199	0.106	---	---
11:30		28	33	116	116	25	40	182	0.272	---	3.2
12:30[b]		18	42	116	116	25	57	161	0.146	---	---
1:30		20	42	160	66	40	83	174	0.421	---	---
3:30[c]		21	28	120	66	28	83	193	0.262	---	2.8
4:30		18	35	116	95	33	50	166	0.285	---	---
5:30		23	40	116	98	33	50	166	0.050	---	---
7:30		18	41	117	100	30	41	164	0.055	---	---
9:30		18	29	125	100	31	41	157	0.044	---	4.0
11:30		22	25	125	83	30	67	166	0.039	0.0004	---
12:00[d]		---	---	---	---	---	---	---	---	---	---

[a,b,c,d] Times of sampling for data plotted in Figs. 3.1-3.3

ORNL-2490
Chemistry-Separation Processes for
Plutonium and Uranium
TID-4500 (14th ed.)

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-26. Laboratory Records Department
27. Laboratory Records, ORNL R.C.
28. A. M. Weinberg
29. L. B. Emlet (K-25)
30. J. A. Swartout
31. J. P. Murray (Y-12)
32. E. H. Taylor
33. E. D. Shipley
34-35. F. L. Culler
36. M. L. Nelson
37. W. H. Jordan
38. C. P. Keim
39. J. H. Frye, Jr.
40. S. C. Lind
41. A. H. Snell
42. A. Hollaender
43. K. Z. Morgan
44. M. T. Kelley
45. T. A. Lincoln
46. R. S. Livingston
47. A. S. Householder
48. C. S. Harrill
49. H. E. Seagren
50. D. Phillips
51. W. K. Eister
52. F. R. Bruce
53. D. E. Ferguson
54. R. B. Lindauer
55. H. E. Goeller
56. C. W. Hancher
57. R. A. Charpie
58. J. A. Lane
59. M. J. Skinner
60. R. E. Blanco
61. G. E. Boyd
62. W. E. Unger
63. R. R. Dickison
64. A. T. Gresky
65. E. D. Arnold
66. C. E. Guthrie
67. J. W. Ullmann
68. K. B. Brown
69. K. O. Johnsson
70. J. C. Bresee
71. C. E. Winters
72. P. M. Reyling
73. L. E. McNeese
74. D. L. Katz (consultant)
75. G. T. Seaborg (consultant)
76. M. Benedict (consultant)
77. C. E. Larson (consultant)
78. L. Squires (consultant)
79. J. H. Rushton (consultant)
80. ORNL- Y-12 Technical Library, Document Reference Section

EXTERNAL DISTRIBUTION

81. Division of Research and Development, AEC, ORO
82-598. Given distribution as shown in TID-4500 (14th ed.) under Chemistry-Separation Processes for Plutonium and Uranium category (75 copies - OTS)