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DEVELOPMENT OF THE EXCER PROCESS. II

J. A. Marinsky

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CHEMICAL TECHNOLOGY DIVISION

DEVELOPMENT OF THE EXER PROCESS. II

J. A. Marinsky

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0.0 ABSTRACT

Two revised Excer process flowsheets are presented for the production of UF_4 from uranyl nitrate solution. In both, the uranium is sorbed on a cation-exchange resin and eluted with aqueous HF. In one, the resulting UO_2F_2 in dilute HF is mixed with dilute sulfuric or hydrochloric acid and electrolytically reduced in a cation-exchange-membrane cell, and the precipitated $UF_4 \cdot 0.75H_2O$ is dried and dehydrated to anhydrous UF_4. A cost of 20¢ per pound of reduced uranium is estimated. In the other, ammonium fluoride is also added to the uranyl fluoride solution before the electrolytic reduction step, and the precipitate is $UF_4 \cdot 0.4NH_4F$. A flowsheet for preparing UF_4 from raw ore is also shown. The uranium is sorbed on an anion-exchange resin from a sulfuric acid leach liquor and eluted with dilute HCl. Ammonium fluoride and HF are added to the UO_2Cl_2-HCl solution before the uranyl ion is electrolytically reduced to precipitate $UF_4 \cdot 0.4NH_4F$. Decontamination factors as high as 45 and 9 for gross beta and gamma activities and of 10 to 5000 for light metal impurities were obtained in the electrolytic reduction step.

1.0 SUMMARY

The revised Excer process is presented for the production of pure UF_4 from uranyl nitrate solutions or raw ores by ion exchange and electrolytic reduction. Alternate proposed flowsheets for production of $UF_4 \cdot 0.75H_2O$ or $UF_4 \cdot NH_4F$ are given (Figs. 1, 2, and 3). These flowsheets as units have not been demonstrated with ore or concentrate as the starting material, since the development work used synthetic solutions and single-step evaluations. In a demonstration run reactor grade metal was produced by reduction of UF_4 prepared in the Excer cell from a synthetic feed containing 1000 ppm each of representative contaminants.

Anode corrosion in the electrolytic reduction-precipitation step was eliminated by the use of a cation-exchange membrane to separate the anode from the fluoride process solution. Since the product was protected from the anode by the membrane, partial reoxidation was avoided. Precipitation of $UF_4 \cdot 0.75H_2O$ from a solution containing a stoichiometric amount of fluoride

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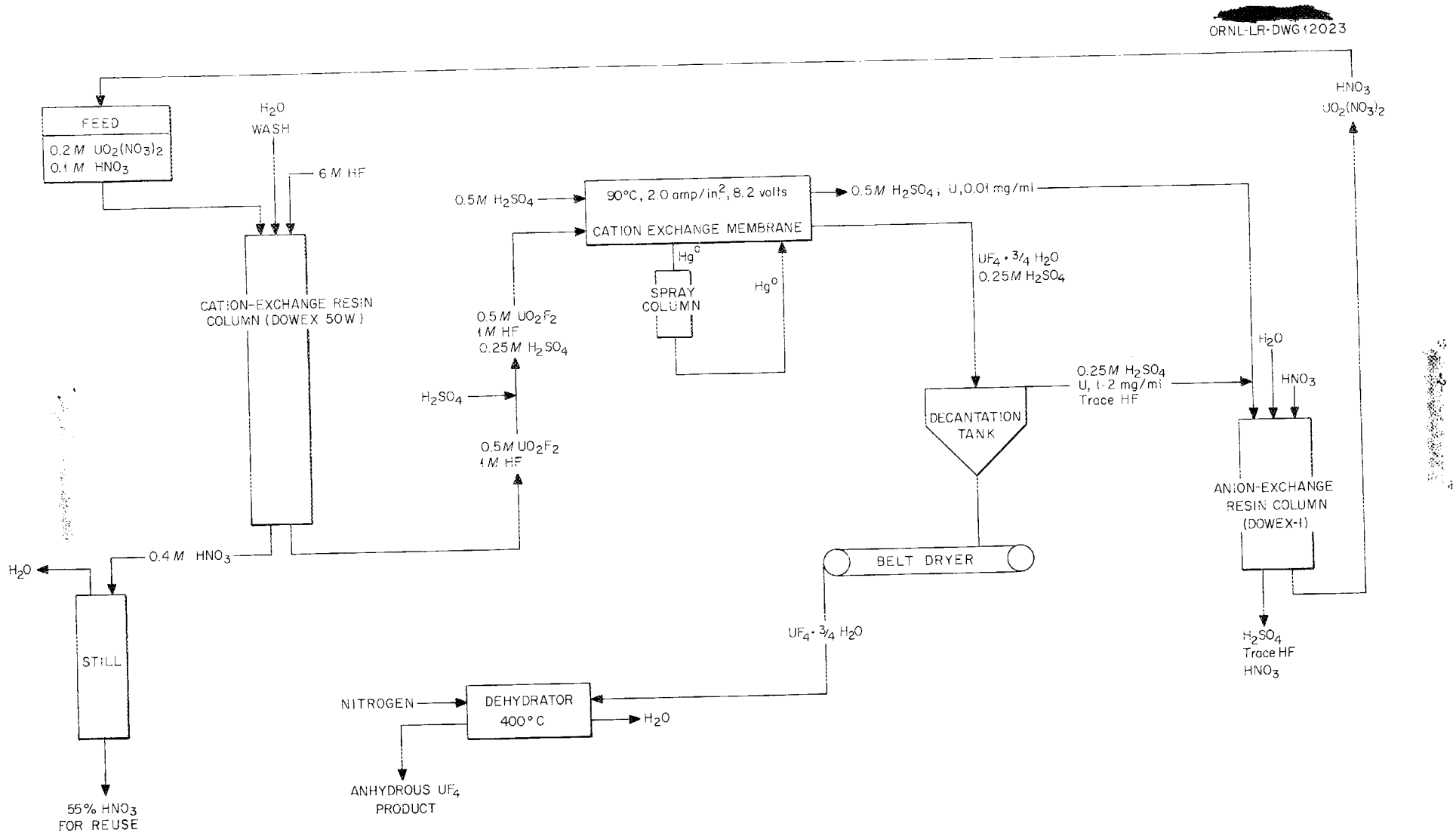

Fig. 1. Modification of Excer Flowsheet.

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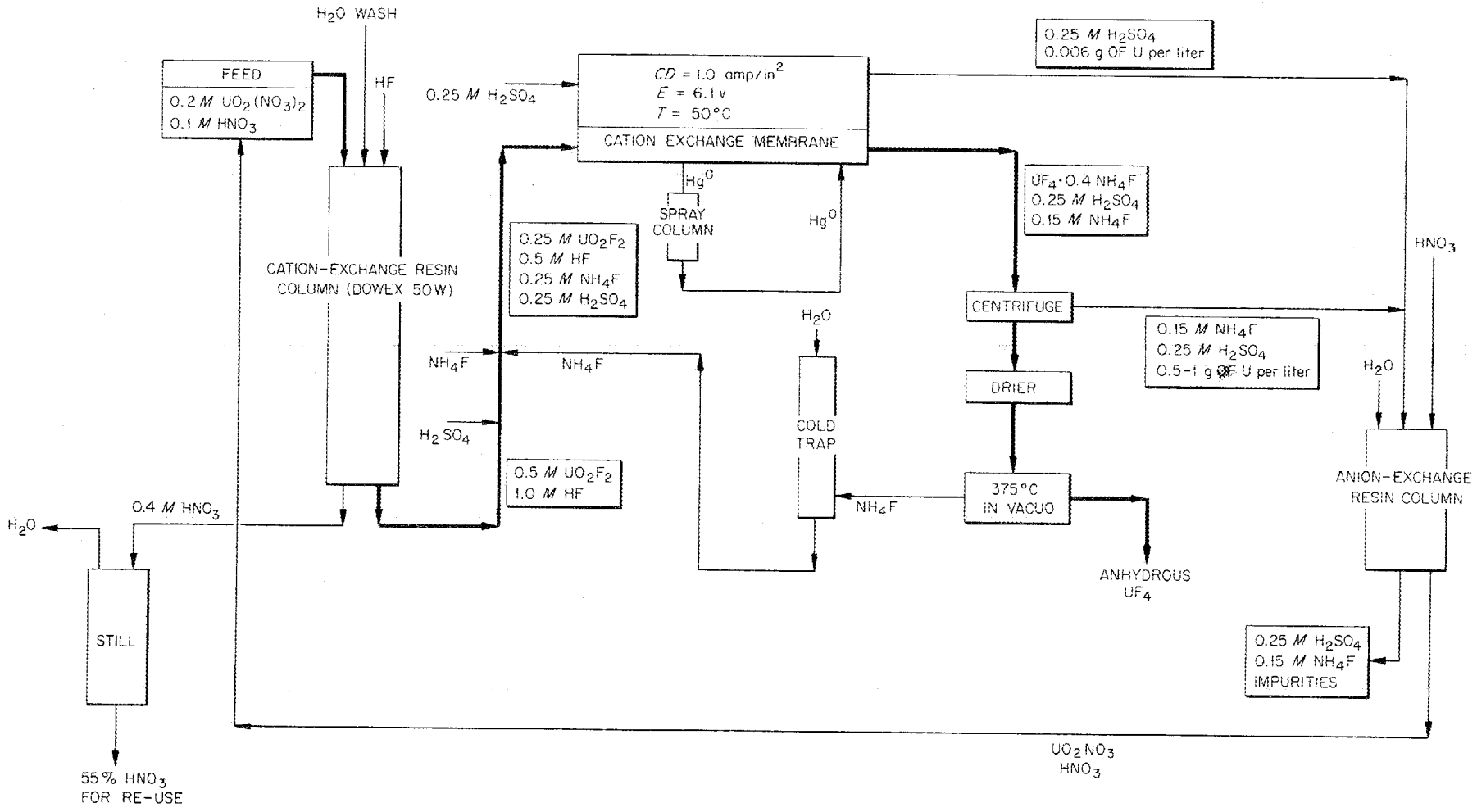

Fig. 2. Chemical Flowsheet for Excer Process Using the Double-Salt System.

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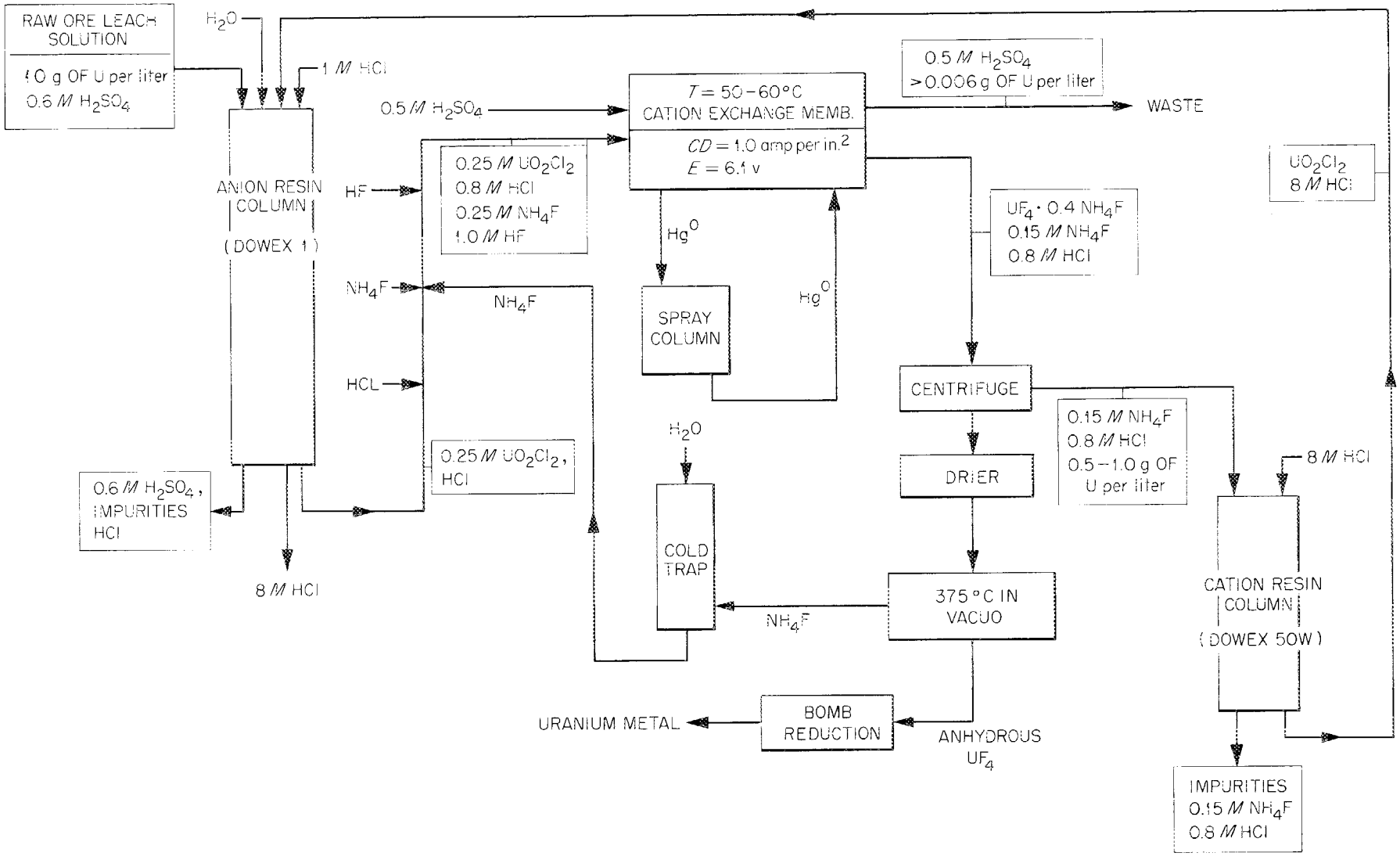

Fig. 3. Chemical Flowsheet for Preparation of Metal-Grade Uranium from Raw Ore.

using sulfuric acid to carry the current produced a denser and more crystalline product which was more easily separated from the supernatant than that formed in the presence of excess fluoride.

When the electrolyte contained a stoichiometric amount of fluoride, excess sulfuric or hydrochloric acid, and significant amounts of ammonium ion, the precipitate was a double fluoride salt of tetravalent uranium and ammonium. Apparent advantages of double salt over hydrate precipitation include ease of washing with less tendency to peptize; cell operation at 50°C rather than 90-100°C so that membrane life should be longer; and the reputed anhydrous character of the double salt so that hydrolysis is not serious on thermal decomposition at 400-500°C to form anhydrous UF_4.[1]

Current efficiencies as high as 95% at a current density of 2 amp/in.[2] were obtained with the hydrate system in a single-stage reduction of about 90% of the uranium. In two-stage operation with a current efficiency of about 90%, reduction was complete in both the hydrate and double salt systems. In the reduction-precipitation step in the membrane cell, decontamination was particularly good for the transition elements, with factors ranging from 30 to 5000 for Al, Cu, Co, Fe, Ni, Sn, V, Mo, Mn, Cd, and Cr. The decontamination factor for Zr-Nb was 10, which was the highest obtained for any fission product.

With the membrane cell, the estimated cost of converting uranyl nitrate solution to anhydrous UF_4 was reduced from the 25.1¢ reported previously[2] to about 20¢ per pound of uranium.

2.0 INTRODUCTION

The Excer process has been proposed as a method for producing uranium tetrafluoride from uranyl nitrate, ore concentrates, or ore pulp slurries.[2] In this process uranyl nitrate is converted to the fluoride by ion exchange at room temperature; the uranyl fluoride is reduced electrolytically at 100°C to $UF_4 \cdot 0.75H_2O$; and the tetrafluoride is dehydrated at 350-400°C.

The Excer process should be cheaper than the dry process now in use, and, unlike the dry process, it achieves considerable decontamination. A disadvantage of the process has been the rapid corrosion of the anode during electrolysis. Other workers[3, 4] had found that the UF_4 was partially reoxidized to UO_2F_2 by contact with the anode. Also, the cell must be operated at temperatures above 90°C in order to obtain a dense precipitate; below 90°C the bulky $UF_4 \cdot 2.5H_2O$ is obtained.

Laboratory-scale experiments were carried out in an electrolytic cell in which the anode was protected from the fluoride ion in the electrolyte by an ion-exchange membrane. The nature of the precipitate formed under these conditions, the efficiency of the cell, and the decontamination achieved were investigated. Precipitation of a double fluoride of uranium and ammonium was studied for possible advantages.

On the basis of the results, two modified flowsheets for the Excer process were prepared, and the cost estimate was revised. A flowsheet for preparing anhydrous UF_4 directly from the ore is suggested.

In other experiments[5-7] on electrolytic reduction of the uranyl ion to uranous, reduction efficiency was found to be increased by simultaneous precipitation of UF_4 in excess HF. Reduction without precipitation was carried out in the UO_2Cl_2-HCl and UO_2SO_4-H_2SO_4 systems to study the reduction step alone.

A portion of the laboratory work was carried out by L. L. Annas and A. F. Giuffrida. F. E. Harrington was responsible for a major part of the economic study reported in Sec. 7.0. Analyses were made under the supervision of G. F. Wilson, J. Edgerton, W. Laing, and C. Feldman.

3.0 EQUIPMENT AND PROCEDURE

3.1 Description of Cell

The cell used in the reduction-precipitation experiments had an Ionics CR-61 cation-exchange membrane hydraulically sealed between the electrode compartment (Figs. 4 and 5). The membrane was backed with teflon or saran cloth and was

supported by a 9- by 10-in. haveg plate, 1/4 in. thick, containing 1/2-in. holes closely spaced in a 5- by 6-in. section in the center. A 1/2-in. saran fitting was screwed through the plate. The membrane was connected firmly to the haveg support by tightening a rubber-gasketed teflon nut onto the saran coupling. The coupling extended beyond the membrane surface through a 5/8-in. hole in its center.

The anode compartment contained a 1/8-in.-thick lead plate anode sandwiched between two 1- by 9- by 10-in. polyvinyl chloride blocks. Sections 5 by 6 in. were cut out of their centers* to coincide with the perforated section of the haveg plate, and 1/2-in. holes evenly spaced 1/2 in. apart were cut into the corresponding section of the lead plate. A hole about 1-1/2 in. in diameter was drilled into the center of the lead plate. An inlet and outlet for the anolyte solution were provided by two separate 1/4-in. holes drilled into the center of one edge of each polyvinyl chloride frame. The top of the anode compartment was a solid polyvinyl chloride block, 1 by 9 by 10 in., with a 5/8-in. hole in its center to provide convenient access to a stirrer shaft.

The cathode compartment was also defined by two 1- by 9- by 10-in. polyvinyl chloride blocks with 5- by 6-in. cutouts in their centers. Two 1/4-in. holes were drilled through opposite edges of one block, and a single 1/4-in. hole was put through an edge of the second block. The two holes were inlets for components of the catholyte solution, and the single hole in the lower polyvinyl chloride frame provided an entry for mercury. Electrical contact for the mercury cathode was a 9- by 10-in. monel sheet, 1/16 in. thick, which was held in place between the lower polyvinyl chloride frame and a solid 1- by 9- by 10-in. block of polyvinyl chloride. A 3/8-in. hole in the center of the monel sheet coincided with another 3/8-in. hole in the center of the polyvinyl chloride block for convenient withdrawal of the mercury.

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*A second cell used in this program had a 5-in.-dia compartment instead of a 5- by 6-in. rectangle.

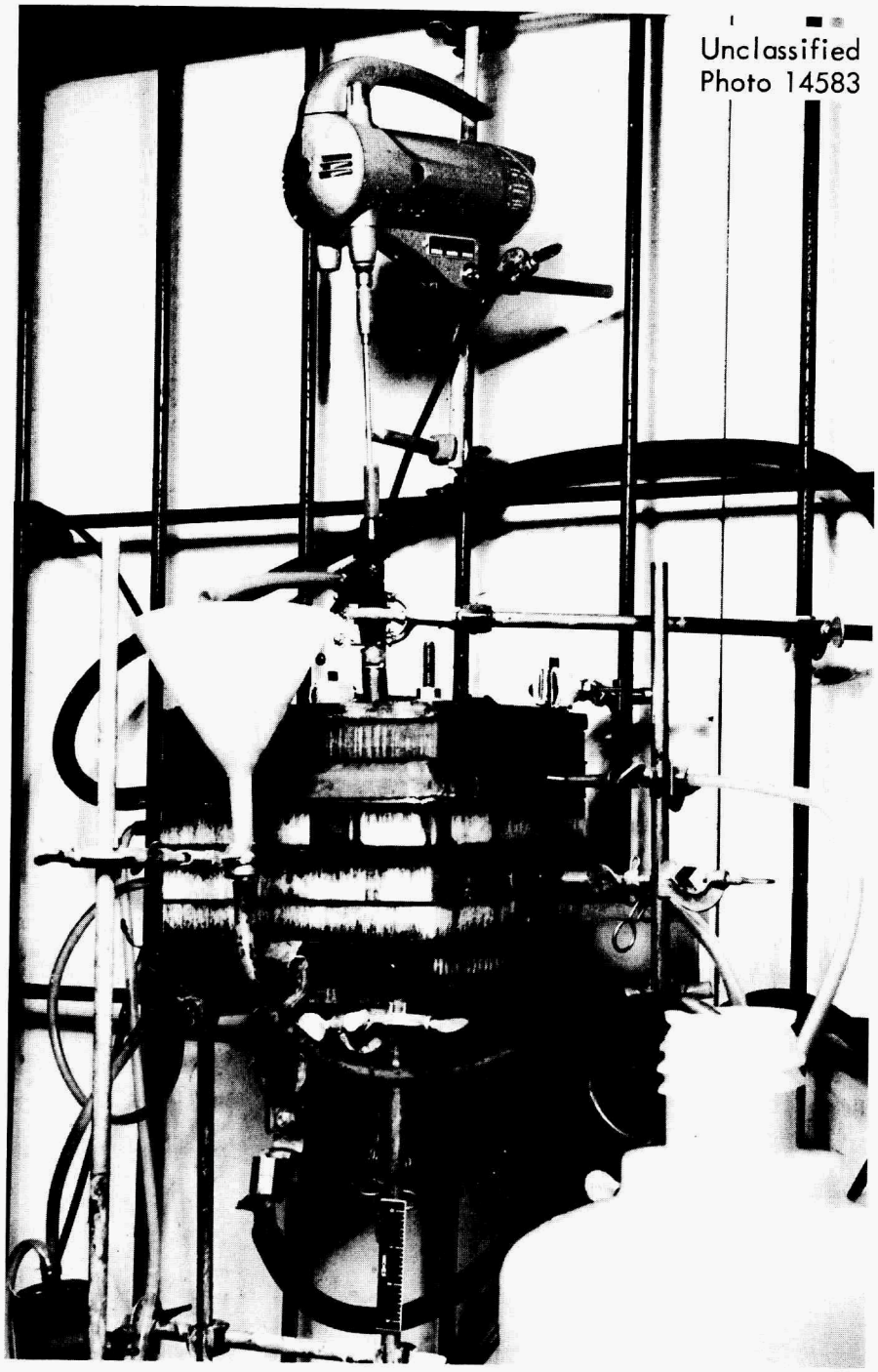

Fig. 4. Electrolytic Reduction Cell.

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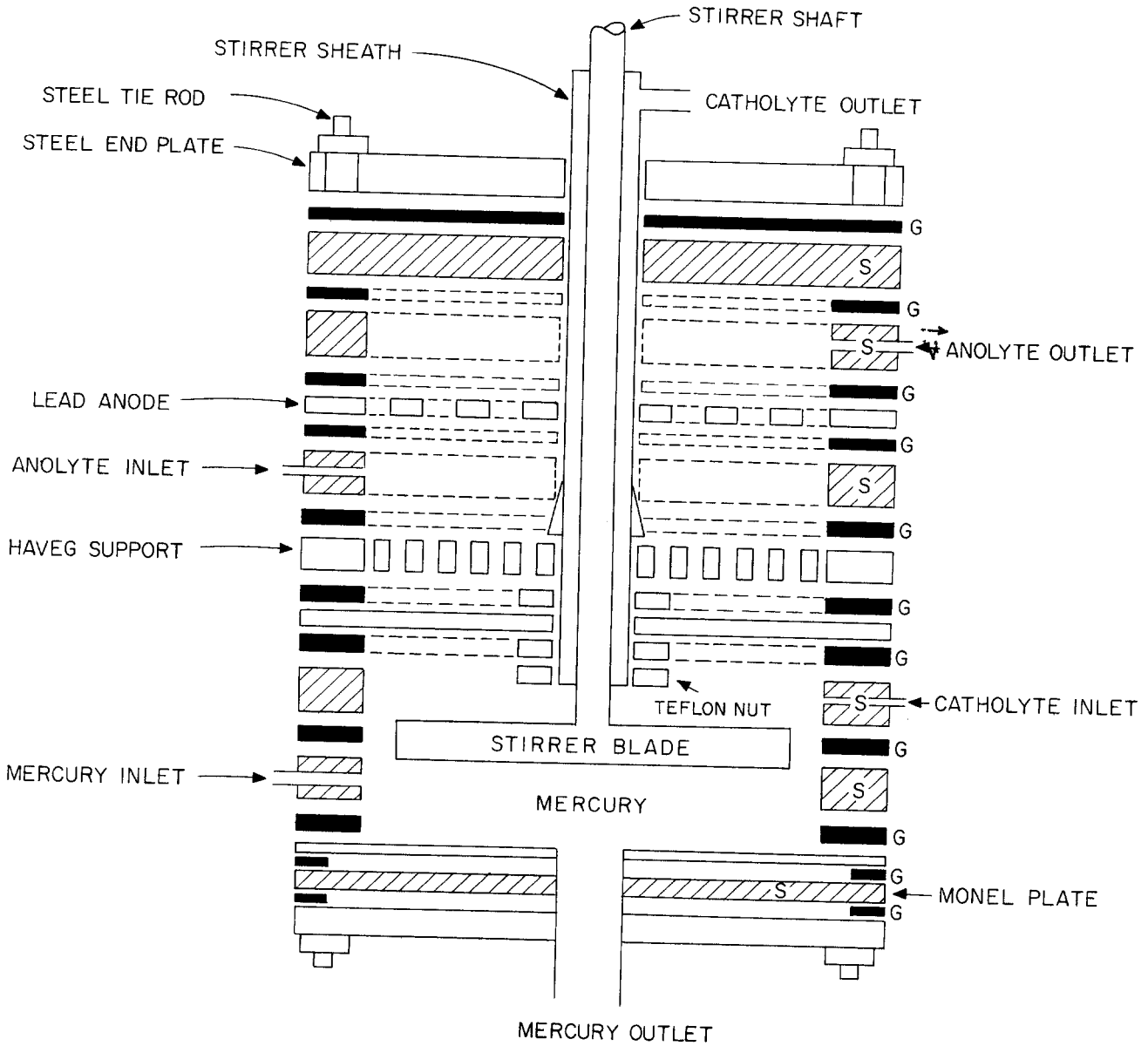

G, RUBBER OR NEOPRENE GASKET

S, SARAN FRAME

Fig. 5. Diagrammatic Cross Section of Electrolytic Reduction Cell.

A monel stirrer with a twisted 3/32- by 1/2- by 4-in. blade welded to a 1/4-in. shaft extended from the cathode compartment into the fitting holding the membrane to its haveg support and through the anode compartment into the chuck of a Mix-Master motor outside the cell. The shaft was hydraulically sealed from the anolyte by a sheath of 3/8-in. saran tubing connected to the saran fitting fastened to the haveg plate. The thick UF_4 slurry produced percolated up around the spinning shaft of the stirrer and left through a saran tubing fitted perpendicularly to the sheath.

During assembly the component parts of the cell were compressed between two 9- by 10-in. plates, 3/8 in. thick, by means of threaded stainless steel tie rods extended through 1/2-in. holes drilled in each corner of the end plates, the polyvinyl chloride blocks and frames, the membranes, and the haveg support. To ensure hydraulic seals between all the component parts, rubber or neoprene gaskets were used wherever needed. The tie rods were electrically insulated by tygon sleeves.

A narrow-channel cell was used to study the efficiency of the reduction step alone. A 0.0002-in.-thick platinum anode was used rather than a lead anode since expansion of lead oxide film into the channels could have plugged the anode compartment. The cathode and anode compartments were defined by channels in 1/8-in.-thick plastic gaskets that provided a hydraulic seal between the cation-exchange membrane and the platinum anode and the lead cathode. The electrode area exposed to the current was 0.23 ft^2. The platinum anode was cemented to a 1- by 9- by 10-in. block of lucite, and the 1/8- by 9- by 10-in. lead cathode plate was supported by another 1- by 9- by 10-in. lucite block. Access of solution to each electrode compartment was through a 3/8-in. hole in the lucite blocks. On assembly, the unit was compressed between two 3/8- by 9- by 10-in. steel plates by means of tie rods extended through the four corners of the cell. The tie rods were insulated with tygon tubing.

Rapid recirculation of solution was used in place of stirring to provide

optimum mass transfer characteristics, and air traps were placed in the solution lines just before the entry of the recirculating streams into the unit to absorb the pulsation caused by the steel fingers of the Sigma pump kneading the rubber tubes. Pressure gages were inserted in the lines between the cell and pulse absorber. Weir type overflow devices emptied the influent solutions after they were completely mixed with the recirculating solutions held up in the system piping.

3.2 Operating Procedure

In the study of the reduction-precipitation step, the cathode compartment was half-filled with mercury by means of a Sigma pump. In the experiments on precipitation of the 3/4 hydrate of UF_4, the cathode compartment was filled with 2 M HF and the anode compartment with 0.5 M H_2SO_4. The voltage was applied, rapid stirring of the catholyte was begun, and the anolyte flow was continued at a controlled rate by an Ionics constant-displacement pump. The system was heated by the current, and, when the temperature had reached 90°C, continuous pumping of 0.5 M UO_2F_2--1.0 M HF solution containing 0.5 M H_2SO_4 was started into the cathode compartment by a Sigma pump. In the double-fluoride experiments, because of the low solubility of these salts, 1.0 M UO_2F_2--1.0 M HF containing 0.5 M H_2SO_4 and ammonium fluoride solutions were fed separately to the cathode compartment at equal rates in order to maintain the uranium concentration at 0.5 M. The uranyl ion concentration during steady-state operation was always much lower than 0.5 M, so that the solubility of the salt $UO_2F_2 \cdot NH_4F$ was not exceeded. When the uranium concentration was 0.25 M or lower, solutions containing no more than 0.25 M NH_4F were stable for several hours, and in studies of the double-fluoride system at this concentration, the catholyte feed was uranyl fluoride solution containing ammonium fluoride. For the double-fluoride system, where high temperatures were not required, and in the second-stage experiments the catholyte and anolyte feeds were both started as soon as the current was turned on.

An experiment was continued until steady state was approached, the current being kept constant. Influent and effluent catholyte flow rates were determined by the volumes collected in 1-liter polyethylene graduates in known times. Density and weight measurements made on samples collected over a specified time interval provided a more accurate measurement of flow rates. Anolyte flow rates were determined periodically from the volumes collected in 500-ml glass graduates. Representative samples were collected at the start and during steady-state operation for analysis. During the course of a run, the time, cell current, cell voltage, and flow rates were recorded at intervals.

In experiments on the reduction step in the absence of precipitation, operation was similar, but rapid recirculation of anolyte and catholyte streams through the channels of the electrode compartments was used as a substitute for the stirring used in the other cell. The pressure drop across each compartment was equalized at 5-6 psi.

3.3 Preparation of Catholyte Solutions

Uranyl fluoride feed solution was prepared by dissolving a weighed amount of UO_3 in a mixture of hydrofluoric and sulfuric or hydrochloric acids and diluting with water to the desired uranium fluoride, hydrogen, and sulfate or chloride concentrations.

Feed solution to test second-stage operation in both systems was the supernatant liquid separated from the slurry produced during reduction-precipitation of hydrated tetrafluoride and double fluoride.

Studies of the reduction step alone were carried out with 0.5 M UO_2SO_4 and with 0.5 M UO_2SO_4 made 1.3 N in acid by dissolving UO_3 in a calculated excess of acid. For one experiment, a solution about 0.4 M in uranyl chloride and 0.7 N in acid was prepared from uranium recovered in the Higgins contactor[8] from low-grade Los Ochos uranium ore.

4.0 MEMBRANE CELL PERFORMANCE

Rapid agitation of the mercury surface was necessary for successful operation of the reduction-precipitation cell. The efficiency of operation was not directly dependent on slurry density, as was the case in earlier work[6] where agitation of the mercury surface was inefficient and did not keep the surface free of the precipitate.

The most serviceable membrane used in the study was the Ionics CR-61 cation-exchange membrane, which is backed with teflon cloth. It did not become distorted at temperatures above 90°C, as did a saran-backed CR-61 membrane. However, it did tend to erode. After 50 hr of operation at the higher temperatures (Expt. 22), continuous impact of the membrane against the haveg support during stirring of the mercury resulted in removal of all ion-exchange material at the points of contact. In the area where the membrane was exposed only to current, it was physically unchanged. The teflon-backed membrane could therefore probably be used for long periods of time in an electrochemical cell designed to provide continuously a clean mercury surface, such as mercury flowing over a screen, without stressing the membrane surface.

The teflon-backed membrane also appeared to provide a surface to which the $UF_4 \cdot 0.75H_2O$ and the $UF_4 \cdot 0.4NH_4F$ precipitate did not stick. The double-fluoride precipitate adhered to the saran-backed membrane and also to a membrane backed with a saran-teflon mat.

Loss of uranium to the anode compartment was less than 0.01% in a properly operated cell.

4.1 Corrosion

In the earlier studies[2] the unprotected platinum anode was corroded at a rate of about 0.9 mg/amp-hr. Under these conditions the loss of platinum would result in excessive processing costs. With the protected lead anode, corrosion was slight during an experiment, although some corrosion did occur between experiments when hydrofluoric acid diffused

into the anode compartment from the cathode compartment. It was estimated that a 1/8-in. lead anode would have to be replaced three or four times a year in a cell that was operated continuously.

4.2 Hydrofluoric Acid Recycle

Because of the presence of the membrane, sulfuric or hydrochloric acid can be used instead of hydrofluoric acid to carry the current when uranium and fluoride ions have been removed in the precipitation. There is therefore no excess hydrofluoric acid in the supernatant from the final product to be recycled. The cell performed equally well with sulfuric, hydrochloric, or excess hydrofluoric acid. Since the supernatant from the $UF_4 \cdot 0.75H_2O$ precipitation contains only traces of fluoride, the uranyl fluoride remaining in the supernatant may be recovered and concentrated by recycling this liquid through a cation-exchange column.

4.3 Reoxidation of UF_4

The high current efficiencies obtained at the high current densities used in these studies indicated that there was no reoxidation of the UF_4. These high current efficiencies were obtained in the absence of excess HF. In the unprotected system excess HF is required to keep the U(IV) out of solution (precipitated) and unavailable for reoxidation.

4.4 Nature of $UF_4 \cdot 0.75H_2O$

The dark-green $UF_4 \cdot 0.75H_2O$ precipitated at 90°C in the presence of sulfuric or hydrochloric acid was more crystalline and was denser, with a dry tap density of 3.2 g/cc, than that precipitated in the presence of excess HF, which has a tap density of 2.7-3.0 g/cc.[2] The denser precipitate settled rapidly, and the supernatant could be easily decanted without loss of product.

In part of one run (Expt. 22) with sulfuric acid present, a bulky, lighter green precipitate formed, probably as a result of the temperature dropping below 90°C. The voltage remained constant during this 50-hr run except when the stirrer slipped and had to be readjusted.

4.5 Precipitation of Uranium Ammonium Fluoride

When the electrolyte contained both uranium and ammonium ions, a dense, crystalline double fluoride, 2.4 g/cc, precipitated at moderate temperatures (25-60°C) as well as at the elevated temperature of 90°C (Table 1). The double fluoride is easily centrifuged or filtered and, unlike $UF_4 \cdot 0.75H_2O$, does not tend to peptize when washed with water. The uranium ammonium fluorides are reported[1] to be anhydrous. They may be decomposed in vacuum at 450-500°C after being washed with ether and air-dried. $UF_4 \cdot 0.75H_2O$ can be dehydrated at 350-400°C in a dry nitrogen atmosphere with $< 1\%$ hydrolysis.

Current efficiencies of up to 87% were obtained with 84% reduction of a 0.5 M UO_2SO_4 solution at 70 and 90°C (Expts. 33 and 34). The efficiency of the reduction-precipitation step was essentially unchanged by increasing the current density from 1.5 to 2.0 amp/in.^{2} However, at the higher current density and higher temperature, the precipitate contained less water and less ammonium fluoride. Neither product was a true double salt, $UF_4 \cdot 0.75NH_4F$ being formed at the lower current density and $UF_4 \cdot 0.6NH_4F$ at the higher. The physical properties of the two precipitates were similar.

During reduction-precipitation of a 0.25 M UO_2F_2 solution, the current efficiency did not vary with the amount of excess HF. The amount of ammonium fluoride in the precipitate did vary with HF concentration, however. The true double salt $UF_4 \cdot NH_4F$ was formed at 40-60°C when there was a large excess of HF (Expt. 52), but the quasi-double salt, $UF_4 \cdot 0.35NH_4F$ formed when the HF/U ratio was approximately stoichiometric (Expt. 56). The double salt $UF_4 \cdot 0.5NH_4F$ precipitated from the uranyl fluoride-hydrochloric acid system in the presence of excess HF (Expt. 40), and $UF_4 \cdot 0.4NH_4F$ formed when stoichiometric amounts of HF were used in the HF-HCl system (Expts. 42 and 44). The precipitate formed in these systems contained as much as 2.7% water (Expts. 42 and 53). A small amount of ammonium uranyl fluoride slowly crystallized and settled out from those feed solutions that contained more than stoichiometric amounts of HF.

Table 1

Summary of Reduction- Precipitation Runs

Time: Runs 53 and 56, 30-40 hr; run 22, 50 hr; all others, 2-6 hr.

Expt.	Feed Solution Composition (M)					Current Density (amp/in.^{2})	Temp. (°C)	Voltage (volts)	Current Eff. (%)	Reduction (%)	Precipitate Composition (wt %)					(ppm)				Formula
	UO_2F_2	HF	NH_4F	H_2SO_4	HCl						Total U	F[a]	O	NH_4	H_2O[b]	U(VI)	Hg	SO_4	Cl	
33	0.50	1.2	0.73	0.26	---	1.5	~70	8.3	87	84	68.3	25.4	---	3.8	4.2	180	< 50	300	---	$UF_4 \cdot 0.7NH_4F$
34	0.50	1.1	0.67	0.28	---	2.0	>90	9.6	86.5	83.5	69.5	25.7	0.27	3.3	0.9	---	< 50	800	---	$UF_4 \cdot 0.6NH_4F$
52	0.24	1.25	0.28	0.21	---	1.0	40-60	6.2	91	91	64.8	26.3	---	4.7	---	---	200	< 10	---	$UF_4 \cdot NH_4F$
53	0.24	1.0	0.24	0.26	---	1.0	40-60	6.2-7.0	87	87	68.8	26.2	---	3.2	2.1	---	505	---	---	$UF_4 \cdot 0.6NH_4F$
56	0.26	0.6	0.23	0.29	---	1.0	40-60	6.5-8.1	90	90	66.7	24.2	---	1.8	---	---	35	2300	---	$UF_4 \cdot 0.35NH_4F$
40	0.23	1.25	0.28	---	1.3	1.0	40-60	6.1	90	90	68.1	25.3	---	2.5	---	---	< 50	---	---	$UF_4 \cdot 0.5NH_4F$
41	0.23	0.75	0.29	---	0.8	1.0	40-60	6.1	88	88	74.4[c]	21.5[c]	---	0.2[c]	0.3	670	---	---	<500	$UF_4 \cdot 0.04NH_4F$
42	0.22	0.5	0.35	---	0.8	1.0	40-60	6.0	90	90	72.9	24.3	---	2.1	2.7	690	---	---	---	$UF_4 \cdot 0.4NH_4F$
44	0.23	0.5	0.25	---	0.8	1.0	40-60	6.1	88	88	71.3	25.2	---	2.2	---	530	---	---	---	$UF_4 \cdot 0.4NH_4F$
55	0.27	1.25	0.05	0.30	---	1.0	~25	6.7	86	86	66.0	22.6	---	0.8	12.5	---	309	4200	---	$UF_4 \cdot 2.5H_2O$
51	0.49	1.85	---	0.28	---	2.0	>90	10.2	92	92	67.5	23.2	---	---	4.0	---	< 25	---	---	$UF_4 \cdot 0.75H_2O$
49	0.50	1.0	0.07	0.28	---	2.0	>90	9.4	90.5	90.5	69.9	23.2	---	0.4	5.9	---	---	---	---	$UF_4 \cdot 0.75H_2O$
22	0.50	1.0	---	0.50	---	2.0	>90	8.2	94	94	72.9	22.9	---	---	4.0	---	< 25	---	---	$UF_4 \cdot 0.75H_2O$
45	0.46	1.5	<0.07[d]	---	1.3	2.0	>90	8.0	93	93	73.6	23.7	---	0.3	1.0[e]	490	< 25	---	---	$UF_4 \cdot 0.75H_2O$
46	0.45	2.4	<0.07[d]	---	1.3	2.0	>90	8.2	94	94	73.6	23.9	---	0.3	1.0[e]	180	< 25	---	---	$UF_4 \cdot 0.75H_2O$

[a]The fluoride concentration of representative samples was determined by back-titrating the standard alkali used to absorb the HF that was steam-distilled during complete hydrolysis of the samples. The values given are corrected for neutralization of the HF by ammonia also evolved during the hydrolysis.

[b]Water was determined by direct absorption in Anhydrone of water evolved into a nitrogen stream from samples heated in a sodium carbonate bed to 500°C. The values are corrected for absorption of ammonia by Anhydrone.

[c]This sample was analyzed after ignition for 2 hr in air at 300-400°C to volatilize the ammonium fluoride. The samples remained uniformly green, indicating no significant conversion of UF_4 to UO_2.

[d]No ammonium fluoride was added. The ammonium ion in the supernatant waste solution and the precipitated product probably came from residual ammonium fluoride used in earlier experiments.

[e]The low water content is not easily explained; a 0.75 hydrate is expected under the conditions of Expts. 45 and 46.

In the presence of trace amounts of ammonium ion, the precipitate was the same hydrated UF_4 that would have formed with no ammonium ion present. At 25°C, the bulky $UF_4 \cdot 2.5H_2O$ precipitated (Expt. 55), while above 90°C the precipitate was $UF_4 \cdot 0.75H_2O$ (Expts. 22, 49, and 51). The smaller percentage of water observed in the UF_4 product in Expts. 45 and 46 could not be repeated in Expt. 49.

Most of the runs lasted 2-6 hr. In two runs (Expts. 53 and 56) which lasted 30-40 hr, the voltage rose steadily. Disassembly of the unit after the runs showed that the increase in resistance was due to precipitate sticking to the cathode face of the membrane. Three different types of precipitate were obtained in these runs. In Expt. 56, there were two different crystalline precipitates, one dark green and dense and the other lighter green and more bulky (Table 2). Both precipitates settled rapidly and could be washed and filtered easily. The operating parameters during the formation of these precipitates were identical, and there was no difference in their chemical composition (Table 2). The third type of precipitate (Expt. 53) was gelatinous, and its formation may be attributable to a more than 10% decrease in the flow rate of the feed solution, as a result of which more current than was required for 100% reduction of uranyl ion was passed continuously through the system. At the beginning of Expt. 53, when feed flow was faster, a dark-green, dense, crystalline precipitate formed. The gelatinous precipitate contained 15% less ammonium fluoride than the crystalline.

One run (not reported in Table 1) was made in which NaF was used instead of NH_4F. The precipitate, $UF_4 \cdot NaF$, was bulky, and current efficiency was 79% at 70% reduction.

4.6 Efficiency of Membrane Cell

Single-Stage Operation. Current efficiency during precipitation of $UF_4 \cdot 0.75H_2O$ was not affected when sulfuric or hydrochloric acid was substituted for excess hydrofluoric (Fig. 1). The highest current efficiency was

Table 2

Composition of Different $UF_4 \cdot xNH_4F$ Precipitates Formed During Electrolytic Reduction

Expt.	Solution Composition (M) UO_2F_2	HF	NH_4F	H_2SO_4	Precipitate Composition (wt %) F	NH_4	U	Density (g/cc)	Description of Precipitate
56	0.26	0.6	0.23	0.29	22.1	1.8	66.8	2.4	Crystalline, dark green
					22.6	1.8	66.6	2.1	Crystalline, light green
53	0.24	1.0	0.24	0.26	25.6	4.1	65.3	1.4	Gelatinous, light green
					24.3	3.5	65.8	1.8	Crystalline, dark green

obtained in reduction-precipitation of the hydrated tetrafluoride, with 97% efficiency at 80% reduction and 91% at 95% reduction. In reduction-precipitation of uranium ammonium fluoride, the current efficiency was 87% with 84% reduction. Lowest current efficiency was obtained in the reduction-precipitation of $UF_4 \cdot NaF$ (Fig. 6). In studies on the reduction step alone, a current efficiency of 87% was obtained with the uranium chloride—hydrochloric acid system. A current efficiency value was not obtained for the uranium sulfate—sulfuric acid system, but it was considered low because of gas evolution at the lead cathode in one experiment designed to reduce only 40% of the uranyl sulfate.

Since the products of the anode reaction were isolated, current densities of 2 amp/in.^{2} were possible, which are higher than any reported in previous studies. With chloride and sulfate systems, current densities were 1.8 and 1.6 amp/in.^{2}, respectively.

With the fluoride-chloride system, the operating voltage was 7.1 volts, while with the fluoride-sulfate system the voltage required to precipitate $UF_4 \cdot 0.75H_2O$ was 7.9-8.4. Voltages recorded during steady-state operation were 9.6, 8.6, 6.2, and 6.6 volts, respectively, for the formation of $UF_4 \cdot 0.7NH_4F$, $UF_4 \cdot NaF$, UCl_4, and $U(SO_4)_2$, respectively. The lower voltages with the chloride and sulfate systems were a result of the somewhat lower current densities used in these systems and the smaller distances between electrodes in the narrow-channel cell that was used.

Two-Stage Operation. About 99% of the uranium should be reduced and precipitated in the electrolytic reduction step in order to minimize uranium recycle. This reduction was not achieved with high current efficiency in a single-stage operation (Figs. 6 and 7 and Table 1), but it was in two-stage operation (Table 3). Reduction and current efficiency values of more than 90% were obtained during the second-stage reduction, giving an overall reduction of about 99% in the double fluoride system when a stoichiometric amount of HF was available (Expts. 35 and 36). In the presence of excess HF, as much as 97.5% of the uranium was precipitated

[redacted]

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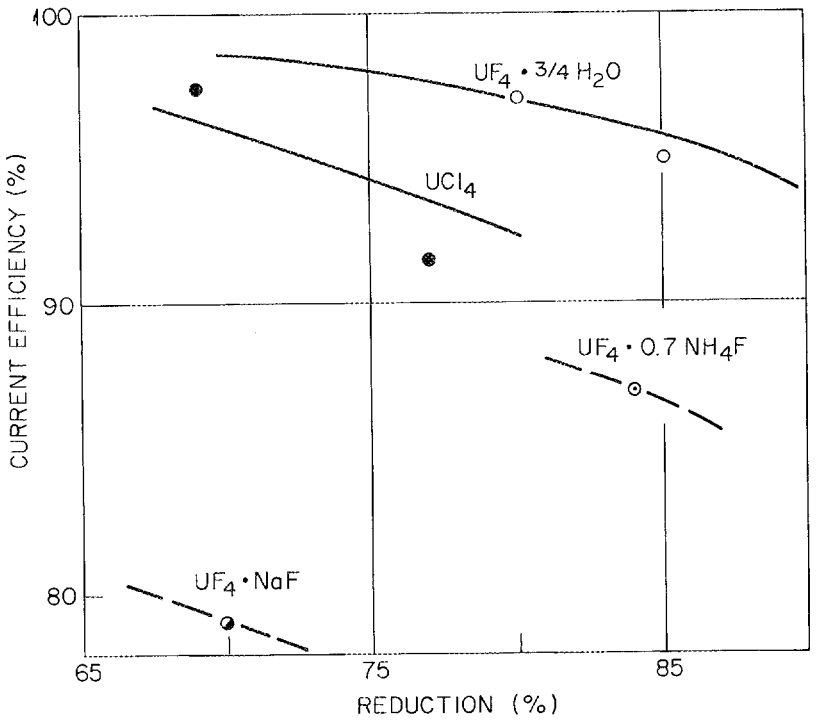
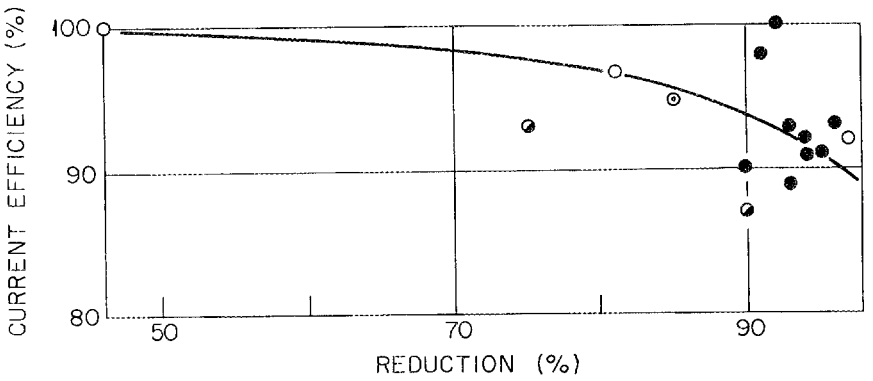


○ 0.5 *M* UO_2F_2 in (1) 3.0*M* HF and (2) 0.9*M* HF--1.0*M* HCl
● 0.5*M* UO_2F_2 in 1.3*M* HCl
⊙ 1.0*M* UO_2F_2-- 1.0*M* HF--0.5*M* H_2SO_4
◐ 1.0*M* UO_2F_2-- 1.0*M* HF--0.5*M* H_2SO_4--1.0*M* NaF

Fig. 6. Dependence of Current Efficiency on Nature of Reduced Product.



ADDED

○ 3.0*M* HF
⊙ 0.9*M* HF, 1.0*M* HCl
◐ 0.9*M* HF, 0.2*M* H_2SO_4
● 0.9*M* HF, 0.5*M* H_2SO_4

Fig. 7. Dependence of Current Efficiency on Solution Composition and Percentage Reduction during Precipitation of $UF_4 \cdot 3/4 H_2O$ from 0.5*M* UO_2F_2 Solution.

Table 3

Summary of Two-Stage Reduction-Precipitation Runs

Temperature: 40-60°C

Run 57, 30-40 hr; run 54, 20-30 hr; runs 35, 36, 38, about 2 hr

Expt.	Feed Solution Composition (M) UO_2F_2	HF	NH_4F	H_2SO_4	Current Density (amp/in.^{2})	Voltage (volts)	Current Eff. (%)	2nd stage	Over all	Precipitate Composition (wt %) U	F	NH_4	H_2O	Formula
35[a]	0.075	~0.2	0.32	0.26	0.25	3.9	93	93	98.8	---	---	---	---	---
36[b]	0.082	~0.1	0.38	0.30	0.30	4.2	91	90.5	98.5	---	---	---	---	---
54[c]	0.031	0.45	0.10	0.26	0.30	4.3	d	84	99.7	65.2	26.4	4.0	2.8	$UF_4 \cdot 0.8NH_4F$
57[e]	0.028	f	0.17	0.27	0.10	3.5	84	97.5	98.2	65.9	21.8	0.4	---	$UF_4 \cdot 0.08NH_4F$
38[g]	0.053	~0.05	---	0.34	0.20	3.6	88	84	98.4	---	---	---	---	$UF_4 \cdot 2.5H_2O$

[a]Feed was supernatant solution from Expt. 33.

[b]Feed was supernatant solution from Expt. 34.

[c]Feed was supernatant solution from Expt. 53.

[d]Much more current was passed than was necessary for this reduction step.

[e]Feed was supernatant solution from Expt. 56.

[f]Feed was deficient in HF.

[g]Feed was supernatant solution from Expt. 22.

in the second stage as the double salt (Expt. 54), giving an overall reduction of greater than 99%. When there was a deficiency of HF (Expt. 57), the second-stage reduction dropped to 84% at 84% current efficiency.

The current efficiency was 88% for 84% reduction in precipitation of the 2.5 hydrate of UF_4 (Expt. 38). This is less than would be expected on the basis of the efficiency of the first-stage reduction to the 3/4 hydrate. Operation at a high enough temperature to produce the 3/4 hydrate might improve the second-stage reduction efficiency. However, an overall reduction of 98.4% was obtained in precipitation of the higher hydrate, which is sufficient to demonstrate the effectiveness of two-stage operation.

The experiments were carried out with supernatant solution from the slurry produced in the first-stage reduction. Since the efficiency of the reduction was not expected to vary with the degree of hydration of UF_4 and temperature is unimportant in precipitation of the double fluoride, no attempt was made to control the temperature.

A current density of about 0.2 amp/in.^{2} was used in the second-stage reduction of 0.5 M UO_2F_2. Uranium was produced at a rate of about 1.35 lb/hr per square foot of mercury cathode during two-stage reduction, and 1 kwhr of energy per pound of uranium reduced was required at this rate of reduction. For 99% reduction of 0.25 M UO_2F_2, the current density was halved; 0.75 kwhr was required for reduction of 0.7 lb of uranium per square foot of mercury cathode.

4.7 Decontamination

In the earlier studies[2] the uranium was separated from fission and corrosion products by large factors in the Excer process. With the revised cell, exclusive of decontamination achieved in the preceding ion exchange step, factors for decontamination from corrosion products were as high as 5000. Gross beta and gross gamma decontamination factors of up to 45 and 9, respectively, were obtained (Table 4). The maximum decontamination from the light elements was obtained with the fluoride-chloride system (Expts. 44

Table 4

Decontamination Efficiency of the Excer Process

Element	Ion Exchange Max	Ion Exchange Min	Reduction - Precipitation Run 51	Run 52	Run 33	Run 34	Run 44	Run 45	Run 53	Run 54	Run 56	Run 57	Overall Max	Overall Min
Gross β	16	--	1.2	45	--	--	--	--	--	--	--	--	720	20
Gross γ	27	16	4	9	--	--	--	--	--	--	--	--	240	110
R.E.'s	300	70	1	5	--	--	--	--	--	--	--	--	1,500	70
Sr	5000	--	1	2	--	--	--	--	--	--	--	--	10,000	5000
Cs	500	--	3	1	--	--	--	--	--	--	--	--	500	---
Zr-Nb	50	--	8	18	--	--	--	--	--	--	--	--	900	400
Ru	20	--	3	3	--	--	--	--	--	--	--	--	60	60
Na	3	--	--	--	--	--	--	--	--	--	--	--	--	---
Al	14	1	--	--	30	30	43	230	--	--	--	--	3,200	30
Cu	400	--	--	--	--	--	--	--	--	--	--	--	--	---
Co	29	--	--	--	--	--	> 50	> 50	--	--	--	--	1,450	---
Fe	3	--	--	--	200	130	2000	2000	9[a],15[b]	64	13[c],24[b]	118	6,000	27
Pb	40	--	--	--	--	--	--	--	--	--	--	--	--	---
Mg	9	--	--	--	--	--	--	--	--	--	--	--	--	---
Hg	2000	--	--	--	--	--	--	--	--	--	--	--	>14,000	>1100
Ni	>28	--	--	--	--	--	>500	>500	38	500	34[c],54[b]	> 770	> 1,600	---
Sn	25	--	--	--	--	--	> 65	> 65	--	--	--	--	--	---
Zn	22	--	--	--	--	--	--	--	--	--	--	--	> 600	30
V	3	--	--	--	> 50	>50	>200	>200	10[a],40[b]	45	13[c],15[b]	295	--	---
Si	> 77	--	--	--	--	--	--	--	--	--	--	--	--	---
Mo	--	--	--	--	--	--	--	> 500	> 70	>300	140	2950	--	---
Mn	--	--	--	--	--	--	5000	5000	--	--	--	--	--	---
Cd	--	--	--	--	--	--	> 200	> 200	>55	>265	740	> 280	--	---
Cr	--	--	--	--	--	--	5000	4000	>180	760	38[c],97[b]	> 580	--	---

[a]Gelatinous precipitate.

[b]Dense precipitate.

[c]Fluffy precipitate.

and 45). The minimum decontamination factors were obtained with the gelatinous and fluffy precipitates. Spectrographic analysis of uranium metal prepared from the Excer UF_4 product indicated that it was of metal-grade purity (Table 5). On the basis of these results the solvent-extraction step might be eliminated in preparation from ores of uranium metal for use in reactors, and the second and/or third solvent-extraction cycle might be eliminated in reprocessing of spent fuel.

The test to determine whether metal-grade uranium could be prepared from the Excer product was made with a solution 0.25 M in UO_2F_2, 0.25 M in NH_4F, and 0.25 M in H_2SO_4 which was contaminated with iron, cobalt, nickel, vanadium, manganese, tin, chromium, cadmium, molybdenum, and boron. The impurity level of these components was 1000 to 2000 ppm with respect to the uranium. The uranyl ion was reduced in two-stage operation of the membrane cell to $UF_4 \cdot 0.3NH_4F$ (Expts. 56 and 57). The precipitate was washed with water and absolute alcohol and dried under a heat lamp. The double salt was decomposed at 400°C in an atmosphere of HF, and the precipitate was reduced with calcium in a thermal-bomb reduction step. The final product was 84% uranium metal and 16% CaF_2 slag. The high slag content was attributed to the small charge (about 1 kg) that was available for the reduction step (Table 5).

In this flowsheet (Fig. 3) an anion-exchange resin column is used to sorb uranium from sulfuric acid leach solution of the raw ore. The uranium is eluted as uranyl chloride with water after pretreatment with 8 M HCl. The rest of the flowsheet is the same as illustrated for the double-salt system until the uranium recovery step from the supernatant catholyte from the centrifugation. The uranium, after sorption on a cation-exchange resin column, is eluted with 8 M HCl and is resorbed on the anion-exchange resin column.

In all three processes, impurities separated from the uranium during the reduction-precipitation step should be removed by the resin column during the waste recovery step. Impurities which remain with the traces of uranium are those not removed by the first ion-exchange step. In each case, the

Table 5

Spectrographic Analysis of Uranium Metal Prepared from Excer UF_4 Product

Electrolyic cell feed initial metal content: 1000-2000 of each per million parts of uranium

Element	Amount in Metal (ppm)	Element	Amount in Metal (ppm)
Al	30	Mn	35
B	< 1	Sc	35
Ba	<10	P	<100
Be	< 0.3	Sn	20
Ca	>1600	Ni	< 25
Cr	18	Na	< 10
Cu	< 2	V [a]	1
Fe	58	Cd [a]	5
Hg	< 1	Co [a]	3
Li	< 2	Mo [a]	< 2
Mg	30		

[a] These impurities are as reported for the double salt. They were not reported for the metal.

two ion-exchange steps involve use of oppositely charged resin beds and impurities not picked up by the cation exchanger, for example, should be removed by the anion exchanger.

5.0 MODIFICATION OF EXCER PROCESS

Two modifications of the Excer process for use with uranyl nitrate solutions, to reduce costs and to improve the operation, are suggested as a result of this study.

In the first flowsheet (Fig. 1) the modifications which derive solely from the use of a membrane to separate catholyte and anolyte are incorporated. The still used to recover HF is eliminated, and an anion-exchange resin column is added to recover uranium from the anolyte and from the supernatant solution exiting from the catholyte. Because a more dense $UF_4 \cdot 0.75H_2O$ precipitate is formed in the presence of dilute sulfuric acid, the centrifuge is replaced by a decantation tank.

The second flowsheet (Fig. 2) incorporates those changes which result from use of the double-salt system. The still to recover HF again is eliminated. The centrifuge is returned to the operating scheme because it is believed that the double-salt is not dense enough to permit use of decantation. An anion-exchange resin column is used to recover uranium from the anolyte and from the supernatant catholyte. No scrubbing tower and no anhydrous HF are required during the dehydration step, but a cold trap is added to recover the ammonium fluoride that is volatilized.

A more drastic modification of the Excer process is proposed for the handling of raw ores (Fig. 3). In this case the cation-exchange column for conversion of $UO_2(NO_3)_2$ to UO_2F_2 and removal of chloride was eliminated. It was assumed that the anion-exchange product would be sufficiently pure and that excessive chloride corrosion could be prevented in succeeding steps.

6.0 MODIFICATION OF COST ESTIMATE

In an earlier detailed cost estimate[2] the cost to produce UF_4 by the Excer process was estimated to be 25.1¢ per pound of uranium. Continuous operation at a uranium production rate of 22 tons per day, 7 days a week and 315 days per year, was assumed.

Subtraction of those cost items which no longer exist as a result of major modifications, i.e., elimination of anode corrosion and HF recovery problems, gives a cost estimate of about 20¢ per pound of uranium. The items eliminated are a still for HF recovery and labor to operate this still, anode replacement costs, and the replacement cost of anode stockings that were used to sheath the anodes.

The estimated basic equipment costs are given in Table 6 and the detailed costs are converted to total capital investment in Table 7. The building cost was estimated by making a rough building layout in a cubical shape and charging $1.00 per cubic foot. The estimated annual operating costs are also summarized in Table 7.

Table 6

Capital Investment

A	Basic equipment costs	$456,000[a]	$358,000[b]
B	Installed equipment costs (140% A)	$638,400	$501,000
C	Piping (50% B)	319,200	
D	Instruments (10% B)	63,800	
E	Total physical without building	$1,021,400	$501,000
F	Engineering and construction supervision (35% E)	357,500	175,000
G	Building		220,000
H	Total physical	$1,378,900	$896,000
I	Contingencies (30% H)	413,500	268,800
J	Total	$1,792,400	$1,164,800
	Grand total		$2,957,000

[a]Includes $351,800 for general equipment; $82,500 for electrolytic cells and membranes; and $21,700 for rubber-lined-steel ion-exchange system.

[b]Includes $300,000 for power supply and $58,000 for bus bars.

Table 7

Annual Operating Costs

22 tons/day,
315 days/year

Labor			$332,500
Operators, 6 men per shift		$100,000	
Foreman, 1 man per shift		24,000	
Other, 25% of above 2 items		31,000	
Maintenance labor, 6% of total capital investment		177,500	
Materials			1,604,000
Chemicals		987,000	
Utilities		429,000	
Electricity at $0.007/kwhr	$108,000		
Steam at $0.68/1000 lb	306,000		
Water at $0.028/1000 gal	2,000		
Demineralized H_2O at $0.015/1000 gal.	13,000		
Miscellaneous		188,000	
Pb anodes and membranes	30,000		
Maintenance, 4% of total capital investment	118,000		
Other	40,000		
Decontamination, 30% of maintenance material costs			35,000
Overhead, 100% total labor cost			332,500
Depreciation			417,000
Process equipment		358,500	
Electrical equipment		58,500	
Total annual costs			
Excluding depreciation			$2,304,000
Including depreciation			2,721,000

Cost of UF_4 = 19.95¢ per pound of uranium

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