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Chemistry - Separation Processes for
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DEVELOPMENT OF THE EXCER PROCESS III. PREPARATION OF URANIUM TETRAFLUORIDE FROM URANYL CHLORIDE BY IRON REDUCTION AND PRECIPITATION

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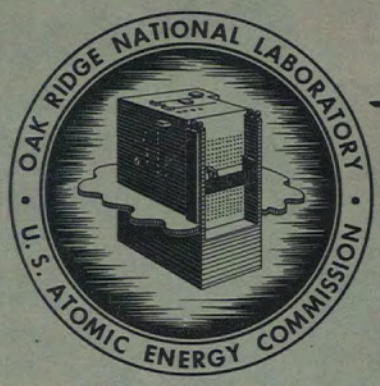

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ABSTRACT

A flowsheet, based on laboratory-scale experiments, is presented for preparation of uranium(IV) chloride solution by reduction of uranyl chloride with metallic iron. The reduction was rapid, with 95% efficiency for 100% reduction. Precipitation of $UF_4 \cdot 3/4\ H_2O$ from this solution with HF separated the iron from the uranium by a factor of 10^3.

CONTENTS

1.0 INTRODUCTION

The use of iron for the reduction step of the Excer process was investigated. In the original Excer process[1,2] uranyl solutions are purified by ion exchange, electrolytically reduced, and converted to uranium tetrafluoride. Chemical reduction would use simpler equipment and operating procedures, but would involve possibly higher reagent costs and the necessity of removing the reagent from the product. The low cost of iron and the possibility of good decontamination of the product from iron led to the laboratory-scale investigations of metallic iron as a reductant for uranyl chloride.

Metallic iron reduction of uranyl sulfate[3] and of uranyl chloride[4] has been reported by other workers. Iron(II) has been used in the presence of fluoride to reduce uranyl nitrate solutions.[5-7]

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2.0 IRON REDUCTION FLOWSHEET

An Excer process flowsheet, incorporating iron as the reducing agent, for ore leach pulp is presented in Fig. 2.1. This flowsheet provides an adequate recycle for the uranium and acid values in the UF_4 supernatant without contamination of the uranium product by the large quantities of iron in the supernatant.

In the iron-reduction flowsheet for ore leach pulp, the sulfuric acid ore leach liquor is treated by continuous anion exchange for purification, concentration, and conversion of the uranium to the chloride form. This uranyl chloride is reduced with iron, and UF_4 hydrate is precipitated by the addition of HF. The UF_4 hydrate is dried and is subsequently oxidized to UF_6 or reduced to uranium metal. The supernatant is recycled to the ore leach tank for recovery of residual uranium and utilization of the acid value for ore dissolution. As an alternative recycle, the HCl in the supernatant may be distilled and concentrated for use in the anion exchange column before the uranium is recycled to the ore leach tank.

Since the volume of the ore leach solution is $\sim$200 times that of the UF_4 supernatant, the chloride ion will be diluted sufficiently that the uranium loading in the anion exchange step will not be hindered. The iron will be separated from the uranium in the anion exchange step by a factor of $\sim 10^3$.

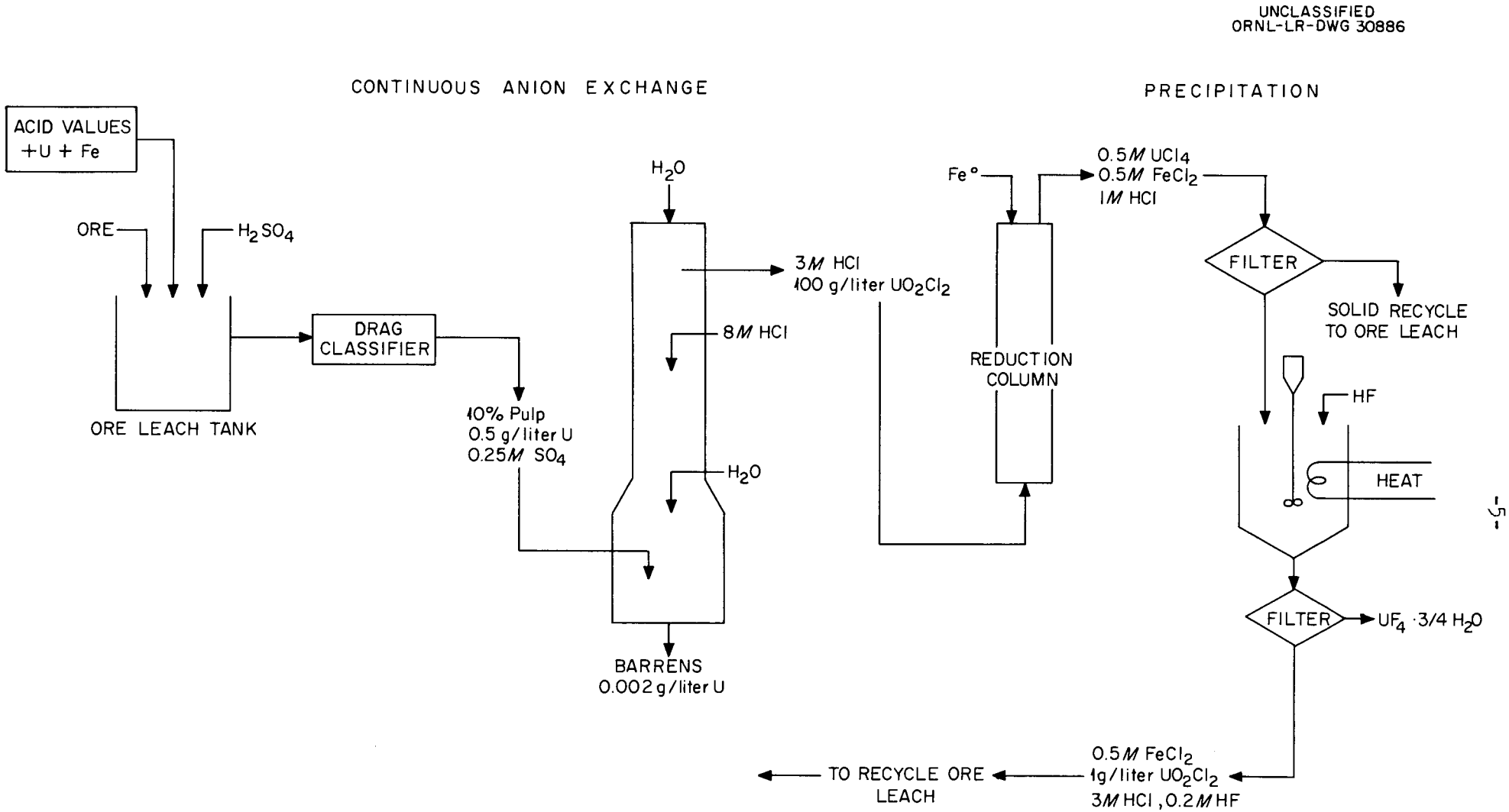

Fig. 2.1. Treatment of ore leach pulp by the Excer process with iron reduction step.

3.0 REDUCTION EXPERIMENTS

Uranyl chloride solutions were 100% reduced in 30 min with 88-95% efficiency (Table 3.1). The reaction, $Fe + UO_2Cl_2 + 4HCl \longrightarrow UCl_4 + FeCl_2 + 2H_2O$, began at room temperature but was exothermic. Samples were taken every 15 min.

Table 3.1. Variation of Time Required for Complete Reduction with Uranyl Chloride Concentration in Preparing Uranous Chloride by Iron Reduction with Sponge Iron

UO_2Cl_2, g/liter	Max Temp, °C	Reduction Time, min	Reduction Efficiency,[a] %
50	35	15	92
105	43	30	95
150	53	15	89
160	54	15	88
170	50	30	92

[a]The reduction efficiency was calculated from the iron in excess of stoichiometric quantities found by analysis of the reduced solution.

Most of the uranyl chloride solutions were prepared by dissolving uranium trioxide in hydrochloric acid. Sufficient HCl was used in all cases to form UCl_4 and $FeCl_2$ during the reduction and to have the final solution 1 M in HCl. Some of the uranyl chloride solutions were prepared from an African ore concentrate to which HCl was added to the same concentrations as used with UO_3. The ore concentrate was in most cases passed through Permutit SK regular anion exchange resin and in some cases also through Dowex 50 cation exchange resin. The contaminants in the various solutions were:

Feed	Contaminants, ppm of U								
	Fe	V	Al	Ca	SO_4	Mg	P	Mo	Si
UO_3 + HCl untreated	40.5	a	7.1	332	a	2.6	a	a	7.5
with anion exchange	45	a	1	400	a	24	a	a	1
Ore concentrate, untreated	5,800	294	10,800	392	95,000	1,960	1,470	49	b
with anion exchange treatment	2,250	330	6	66	1,500	2	200	30	b
with anion and cation exchange treatment	2,050	55	38	100	175	3	50	10	b

[a]Analyzed for but not found.

[b]Not analyzed for.

The metallic iron used for most of the reductions was Ancor 40-200 mesh sponge iron manufactured by Hoeganaes Sponge Iron Corp. In other runs, Baker's nitrogen-free iron filings, 100 mesh, or iron nails were used. The sponge iron contained 890 ppm calcium, <80 ppm phosphorus, <380 ppm sulfur, and <80 ppm molybdenum. When it was dissolved in HCl, a distinct hydrogen sulfide odor was observed and $\sim 4\%$ was insoluble; this residue was predominantly carbon.

For the runs with sponge iron or iron filings the uranyl chloride solution was reduced in batches by adding 10% excess iron, with stirring, to the solution. For the runs with iron nails, the nails were packed in a column and the uranyl chloride was pumped through the column. In pumping the solution down through the column the evolution of hydrogen sulfide and hydrogen hampered the operation. This difficulty was eliminated by pumping the solution up through the column. The volume of gas was kept at a minimum by controlling the flow rate since uranium reduction proceeded in preference to hydrogen evolution.

The final uranous chloride product in all cases contained finely divided carbon particles. The reduced solution was therefore filtered before precipitation of uranous fluoride. After being washed with HCl, the residue on the filter contained $<0.1\%$ of the original uranium.

4.0 PRECIPITATION OF $UF_4 \cdot 3/4\ H_2O$

The nature of the UF_4 hydrate precipitated from the uranous chloride solution by addition of hydrofluoric acid varied with the percent excess HF, the uranium concentration, and the filtration temperature. In general, the greater the excess HF, up to 50%, the more granular the precipitate and the lower the uranium loss in the filtrate. Ten percent excess HF was considered an economic compromise. With uranium concentrations varying from 50 to 170 g/liter, tap densities varied from 1.0 to 2.6 g/cc. The precipitate was finer and settled more slowly at the higher concentrations. The optimum concentration appeared to be 60-100 g/liter, at which concentration product tap densities were consistently higher.

The UF_4 must be precipitated at a temperature above 90°C in order to form $UF_4 \cdot 3/4\ H_2O$, which is much denser than the $UF_4 \cdot 2.5\ H_2O$ product formed at lower temperatures.[8,9] The filtration also had to be carried out above 90°C to prevent plugging of the filter paper by this flocculent 2.5 hydrate formed on cooling. Therefore either the uranous fluoride slurry was filtered hot, through a Buchner filter with Whatman No. 40 filter paper, or the supernatant was decanted and the precipitate was slurried with 90°C water and filtered.

The uranium concentration of the hot filtrate was approximately 3 g/liter, which decreased to 0.1 g/liter on cooling. The excess uranium in the hot supernatant precipitated as the 2.5 hydrate as the supernatant cooled to room temperature. This could be recovered by another filtration step and recycled to the precipitation feed.

In the event the uranyl chloride is not completely reduced in the iron reduction step, further reduction occurs in the precipitation step. Uranyl ion in the presence of fluoride ion is reduced to uranous ion:[5,6]

$$Fe^{++} + UO_2^{++} \longrightarrow Fe^{3+} + U^{4+}$$

$$U^{4+} + 4\ F^- \longrightarrow UF_4$$

The filtered precipitate was washed with several volumes of 0.1 N HCl and then with water before being dried under a heating lamp.

5.0 PRODUCT PURITY

The UF_4 hydrate precipitated from the UCl_4 solution consistently contained low amounts of iron. In most cases calcium was higher in the product than in the original uranium. Typical values of the contaminants in the $UF_4 \cdot 3/4\ H_2O$ are given in Table 5.1.

Table 5.1. Contaminants in $UF_4 \cdot 3/4\ H_2O$ Product

Feed	Reducing Agent	Contaminant, ppm of U												
		S	Cl	Fe	B	Si	Mo	V	Na	Ca	Mg	Ni	Al	Rare Earths
Ore concentrate														
No treatment	Sponge iron	1,900	425	13	1.6	a	a	a	7	90	3	a	52	60
Anion treatment	Sponge iron	35	b	57	0.2	1.5	a	a	30	40	b	b	b	b
Anion and cation treatment	Sponge iron	23	2,200	7	10	5	a	a	80	140	120	a	4.5	a
UO_3														
No treatment	Sponge iron	45	14	23	1.5	a	a	a	b	470	b	b	b	a
	Iron nails	b	b	16	b	b	b	b	b	b	b	b	b	b
Anion treatment	Sponge iron	82	410	27	a	a	a	a	b	420	b	b	b	b
	Baker's iron filings	41	b	150	b	b	b	b	b	300	b	b	b	b

[a]Analyzed for but not found.

[b]Not analyzed for.

In one precipitation experiment the uranous chloride solution was spiked with gross fission products. The decontamination factors of the uranium from the fission products were

Sr	5	Ru	28	Nb	400
Cs	2.3	Zr	6	Rare earths	1

Several samples of the hydrated UF_4 were dehydrated at 450°C.[9] The only contaminants removed to any extent were chloride and sulfate, which were decreased from 410 ppm to 14 ppm and from 82 ppm to 30 ppm, respectively.

6.0 RECOVERY OF URANIUM AND HCl SUPERNATANT

In the Excer process for ore leach concentrate, the UF_4 supernatant could be recycled to the anion exchange column. Since the uranium concentration of the supernatant is less than 0.1 g/liter, the HCl may be distilled off and re-used for dissolution of UO_3 or ore concentrate and the residue discarded if the material being processed is natural uranium. If the uranium is enriched or if the concentration in the supernatant is higher than 0.1 g/liter, the uranium could be separated from the iron in the supernatant by ion exchange.

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