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 TO:
 FROM: I. R. Higgins

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ABSTRACT

Purification of Scrap Uranium by Electrolysis

by

I. R. Higgins

Industrial Technical Information Meeting

Uranyl fluoride-hydrofluoric acid solution may be electrolytically reduced to hydrated UF_4 with a current efficiency of 90% for a 99% reduction. A mercury cathode is necessary. The usual production rate is about 2 amps per sq. in. or about 2-1/2 lbs of uranium per hr per ft^2 of cathode. Either hydrochloric or sulfuric acids are added to the catholyte to increase conductivity. A cation exchange membrane is used to separate the cathode and anode compartments and prevent fluoride attack of the anode. Lead or lead alloy anodes are used in 0.5 M sulfuric acid solution. A plate and frame type construction is used for easy maintenance. Mercury is pumped through a header and forms a flowing film across a supporting plate or screen. The cell is operated between 90 and $100^\circ C$ to produce $UF_4 \cdot 3/4 H_2O$ rather than the higher 2-1/2 H_2O hydrate which forms at lower temperatures.

The electrolysis provides considerable decontamination. Decontamination factors between 100 and 1000 may be expected for Fe, Cr, Ni, Cu, Co, Mo, Mn, and V, 10-100 for Al, and 5 for rare earths. Decontamination factors for Na, Ca, K, Mg, and NH_4 are very low or nil because these ions form double salts with UF_4 .

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It is necessary to filter, wash, and dry the $\text{UF}_4 \cdot 3/4\text{H}_2$ product. Dehydration is accomplished by gradual heating to 400°C using nitrogen as a sweep gas. Hydrolysis, or the amount of UO_2 formed, is usually under 1%. Final water contents have been in a range between 0.2 and 0.5%.

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Purification of Scrap Uranium by Electrolysis

By

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INTRODUCTION

An electrolytic process is being developed as an alternate method of producing purified UF_4 . Originally the process was designed to process purified uranyl nitrate solutions from solvent extraction processes. Since appreciable decontamination was attained during the electrolysis, the scope of application was extended to less pure sources, such as high grade ore concentrate and uranium scrap. Crude uranium sources may be considered for electrolytic cell feed in the form of UO_2SO_4 , UO_2Cl_2 , or UO_2F_2 , if they are within specifications for alkali and alkaline-earth elements.^{1,2,3}

The development of both small and large scale electrolytic cells for preparation of $UF_4 \cdot 3/4 H_2O$ is progressing rapidly. In essence all cell designs use the same principles. Mercury is pumped over a vertical plate or screen for a cathode. A cation exchange membrane is used to separate the cathode and anode compartments and prevent the flow of fluoride from the cathode to the anode. A plate and frame type construction is used for easy maintenance.

STATUS OF DEVELOPMENT

Cell Design

The trial of several cell types and chemical studies is discussed in the Excer progress reports.^{1,2} The use of a cation exchange membrane solved

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a very difficult anode problem. A plate and frame construction combined features of compactness, mechanical simplicity, and rapid assembly and disassembly. Larger scale cell development is being carried out in conjunction with Ionics Inc. (see Figs. 1 and 2).

Purification

The decontamination of UF_4 during electrolytic reduction of UO_2F_2 has been discussed.^{1,2} At present studies are under way using synthetic feed solutions containing known amounts of impurities. The following general observations may be made about electrolytic cell decontamination. The alkali, alkaline earth, and ammonium ion are carried almost quantitatively with the UF_4 as double salts. Decontamination factors of 2 are sometimes observed. The rare earths act similarly but decontamination factors of 5 have been observed. Aluminum decontamination is about 10 to 50. The following metals are decontaminated by factors of 100-1000 Fe, Cr, Ni, Co, Cu, Mn, V, Mo. Corrosion products from stainless steel and copper alloys, when these materials are used in limited quantities in cell construction, are not a problem. Lead contamination of the product may be high when cell operation is poor. Excessive fluoride leakage into the anolyte corrodes lead and the lead in turn transfers through the cation membrane to the cathode compartment. Mercury contamination may be as high as 1000 ppm in the $UF_4 \cdot 3/4 H_2O$ but has not been detected in the dehydrated product.

Filtration and Drying

The most significant factors effecting filtration are tap density and particle size. Filtration studies have lagged until conditions are

established for forming high density, high particle size precipitates. Tap densities have been as high as 3.4 and as low as 2.2. Tap density and particle size do not necessarily correlate because granular, rapidly filtering products have been made with tap densities of 1.7 and filter plugging types of products have been made with tap densities of 2.7. One definite factor in favor of high tap density is operation of the cell above 90°C to form the 3/4 hydrate rather than the 2-1/2 hydrate.

Dehydration

Thorough chemical studies of dehydration carried out by Anderson et al.,^{4,5} showed that dehydration may be accomplished in a nitrogen atmosphere without excessive hydrolysis to UO_2 . These results have been confirmed in experiments at ORNL which showed that with gradual heating from 100° to 400°C over a 1 to 2 hour period with agitation the water content can be reduced to 0.2 to 0.5% with < 1% hydrolysis.

Continuous dehydration studies are under way using a 3-in. x 5 ft ribbon flight dehydrator.

REFERENCES

1. I. R. Higgins, J. T. Roberts, "Development of the Excer Process No. 1", ORNL-1696 (March 19, 1956)
2. J. A. Marinsky, "Development of the Excer Process No. 2", ORNL-1979 (March 27, 1956)
3. I. R. Higgins, "Recovery and Purification of Uranium by Continuous Ion Exchange and Electrolysis", ORNL-CF-56-6-138 (in press)
4. R. W. Anderson, et. al., "Electrochemical Preparation of Uranium Tetrafluoride", K-681 (Jan. 12, 1951)
5. L. L. Annas, "Dehydration of Uranium Tetrafluoride Hydrate", ORNL-CF-56-6-125 (in press)

Fig. 1. Preparation of $UF_4 \cdot \frac{3}{4} H_2O$ from Uranyl Salts by Electrolysis and Dehydration to UF_4 .