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FLUREX PROCESS - INTERIM REPORT

by

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Chemical Research Sub-Section
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INTRODUCTION

The present industrial processes for preparing both uranium hexafluoride and uranium metal utilize anhydrous uranium tetrafluoride as an intermediate. Uranyl nitrate is calcined to uranium trioxide which is reduced by cracked ammonia to the dioxide and then converted to the tetrafluoride by reaction with anhydrous hydrogen fluoride.

Attempts have been made to prepare uranium tetrafluoride by precipitation methods[1], but, in general, the resulting processes have not been wholly satisfactory. The principal difficulties are: (1) the nature of the precipitated product which tends to be difficult to wash and filter; and (2) the fact that the product is hydrated and must be dehydrated in a stream of dry hydrogen fluoride to prevent hydrolysis.

In contrast to the properties of precipitated uranium tetrafluoride, the alkali uranium double fluorides exhibit excellent physical properties with respect to filtering and washing; moreover, they precipitate as anhydrates and can be readily and completely dried in air.

Because of these superior qualities, the alkali uranic fluorides were considered a more desirable product than uranium tetrafluoride as a possible intermediate for production of uranium hexafluoride or uranium metal. In earlier methods of preparation of uranium tetrafluoride from uranyl nitrate, the reduction has been brought about either chemically by the use of ferrous ion[1] or electrolytically[2,3] as demonstrated by Oak Ridge investigators. This latter process, however, has the disadvantage of being unable to use uranyl nitrate as a feed without its preliminary conversion to the sulfate or fluoride.

From the above considerations, it appeared that a more ideal process would use uranyl nitrate directly as a feed for an electrolytic reduction process and have an alkali uranic fluoride as a product. These principal objectives have been incorporated in the design of the Flurex Process.

SUMMARY AND CONCLUSIONS

The Flurex process, in a single unit operation, converts aqueous uranyl nitrate into two products, an alkali uranic fluoride and nitric acid. This is achieved in an electrolytic cell which is divided into three compartments by an anion permeable membrane and a cation permeable membrane. Uranyl nitrate is introduced into the center (feed) compartment which is bounded by the two membrances. Uranyl ion migrates electrolytically through the cation permeable membrane into the cathode chamber which contains alkali and fluoride ions; here it is reduced at a mercury cathode and alkali uranic fluoride precipitates. The nitrate ion migrates through the anion permeable membrane to form nitric acid in the anode chamber.

Alkali uranic fluorides have been produced with current efficiencies of 80 to 100 percent. These salts are anhydrous and are readily dried in air. The sodium product has been reduced to uranium metal in a calcium-iodine bomb reaction with yields of greater than 90 percent. Conversion to uranium hexafluoride remains to be investigated.

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The preliminary flowsheet has been demonstrated in laboratory scale experiments with the cell under steady-state, continuous flow conditions. All components have been tested except concentration and recycling of the feed effluent and reduction of the excess catholyte volume.

CHEMISTRY OF THE FLUREX PROCESS

Two major electrochemical steps are performed simultaneously in the Flurex process; the uranyl and nitrate ions of the feed solution are separated from each other, and the uranyl ions are reduced at a mercury cathode to uranium(IV). The success of the reduction step is contingent on the previous separation since nitrate ions are capable both of being reduced at the cathode and of oxidizing uranium(IV) ions.

Salt-Splitting

Salt-splitting is the decomposition of a salt by electromigration of the component ions through permselective membranes. The membranes used in Flurex process experiments are commercially available ion-exchange resin membranes* which possess high selectivity for ion transport through them. The arrangement of membranes for salt-splitting in the Flurex process cell employs an anion membrane between the cathode and feed compartments. Upon electrolysis, the electric current is carried by nitrate ion through the anion membrane, and by hydrogen and uranyl ion through the cation membrane. A small fraction of the current through the anion membrane is carried by leakage of hydrogen ion. There does not seem to be any leakage of fluoride ion through the cation membrane since no fluoride has been detected in either the feed or anode compartment.

During the splitting of uranyl nitrate, some water is lost from the feed compartment by transport through the membranes. This transfer of water occurs only during the transport of ions, and the amount of water involved appears to be a function of the nature of the ion, its concentration, and the current density at the membrane(4). The amount of water transported in splitting uranyl nitrate is approximately 500 milliliters per mole of uranium transported, and 250 milliliters per mole of nitrate transported. For feeds of 0.2 molar uranyl nitrate, this amount of water represents 15 percent of the feed stream volume.

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* Ion-exchange resin membranes are available in either cation or anion forms. The cation form offers low resistance to the transport of cations, such as uranyl and hydrogen ions, but offers a high resistance to the transport of anions. The anion form offers low resistance to the transport of anions, such as nitrate, but offers a high resistance to the transport of cations. The permselectivity is not one hundred percent; in particular, hydroxyl and hydrogen ions tend to "leak" through the membranes by migration counter to the main flow of ions. With these two exceptions, however, the permselectivity of commercial resin membranes appears to be close to one hundred percent. Rohm and Haas "Amberplex" membranes are being used in Flurex experiments.

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Electrode Reactions

The overall cell reaction is given in equation (1). Equation (2) represents the anode reaction and equation (3) the cathode reaction. Although the equations indicate the use of sodium fluoride, potassium or ammonium salts may also be used. Sodium fluoride tends to form appreciable amounts of disodium uranic fluoride (Na_2UF_6) unless the sodium ion concentration is kept at or below about 0.05 molar.

$$UO_2(NO_3)_2 + 4\ HF + NaF \longrightarrow \underline{NaUF_5}\downarrow + H_2O + 2\ HNO_3 + 1/2\ O_2\uparrow \qquad (1)$$

$$H_2O - 2\ e^- \longrightarrow 2\ H^+ + 1/2\ O_2\uparrow \qquad (2)$$

$$UO_2^{++} + 4\ HF + NaF + 2\ e^- \longrightarrow \underline{NaUF_5}\downarrow + 2\ H_2O \qquad (3)$$

Uranium Reduction

The rate of reduction of uranium is proportional to the product of the current and the current efficiency. Preliminary experiments on the reduction have shown essential agreement with the conclusions and results for comparable electrolytic reductions reported by Oak Ridge investigators (2). The density of current actually causing uranium reduction at the cathode surface is the factor which dictates the physical size of plant equipment for any given rate of uranium production. To obtain maximum production from a plant of a given size, the product of current and current efficiency must be a maximum. This means that current efficiency of one hundred percent is not necessarily a maximizing condition.

The relation between current density and current efficiency is complex. Generally, the use of higher current densities under a given set of conditions results in lower current efficiencies, although there is often a range of current densities over which the current efficiency changes very slowly. A study is being made of the factors that enter into the relationship of current density and current efficiency for the Flurex process; the results will be reported later. Among the factors are: composition of the electrode, compositions of the catholyte and anolyte, stirring rates, cell resistance, shape and location of the electrodes in the cell, and temperature.

Preliminary experiments indicate the following are desirable conditions for the cathode compartment: a mercury cathode, a uranyl ion concentration of at least 0.2 molar, and a hydrofluoric acid concentration of about one molar. If these conditions are met, the physical factors become the important variables for study of the relation between current density and current efficiency.

Another efficiency figure of significance for an electrochemical process is the Power Efficiency (P. E.). This is the ratio of the useful work performed in the process to the total amount of energy expended. For a practical process it can be taken as:

$$P.E. = \frac{V_c + V_a}{V_t}$$

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where V_c and V_a are the voltages observed across the electrode-solution interfaces at the cathode and anode, respectively, and V_t is the total applied cell voltage. The expenditure of energy at both electrodes is the inescapable price of accomplishing the desired result; voltage drops across other parts of the cell and its contents should, of course, be reduced to the minimum practical level.

Most of the wasted work appears as heat, and results from the IR losses in the cell. The remainder of the wasted work may be attributed to the evolution of hydrogen from the cathode and to reduction of small amounts of nitrate that migrate through the cation membrane as a nitrate complex of uranium.

FLOW SHEET

A proposed flow sheet for the process is outlined briefly in Figure 1. Production of the sodium double salt is shown; the potassium and ammonium salts can be obtained by replacing the sodium hydroxide and fluoride with the appropriate potassium or ammonium compounds.

Feed Compartment

The uranium feed to the Flurex process is intended to be the uranium product stream from the Redox, Purex, or TBP process. It is possible to remove the uranium from the feed stream completely by salt-splitting alone, but it remains to be shown whether this would be more or less efficient than the 90 percent depletion and subsequent uranium concentrating and recycling indicated on the flow sheet. A variation under study is the use of concentrated feeds; this would eliminate the recycle step since at feed concentrations of 1.8 molar and above the water transport becomes one hundred percent of the feed stream volume. Dilute feeds from other processes would have to be concentrated prior to use under these conditions.

Cathode Compartment

The uranyl ions passing from the feed stream through the cation exchange membrane appear in the cathode chamber, where most of them are reduced to uranium(IV) and precipitate as the double fluoride. The catholyte slurry thus formed is recirculated through a filter or centrifuge at a volume rate which will give efficient removal of the solid product.

The total catholyte volume tends to increase because of the addition of concentrated hydrofluoric acid and caustic solutions as make-up reagents, and because of transport of water from the feed stream. This must be counteracted either by use of (a) a stripping cell where the uranyl present in the excess catholyte is reduced completely to uranium(IV), or (b) a concentrator, which will simply remove excess water from the recirculating catholyte. The former method has the advantage of providing an escape route for impurities.

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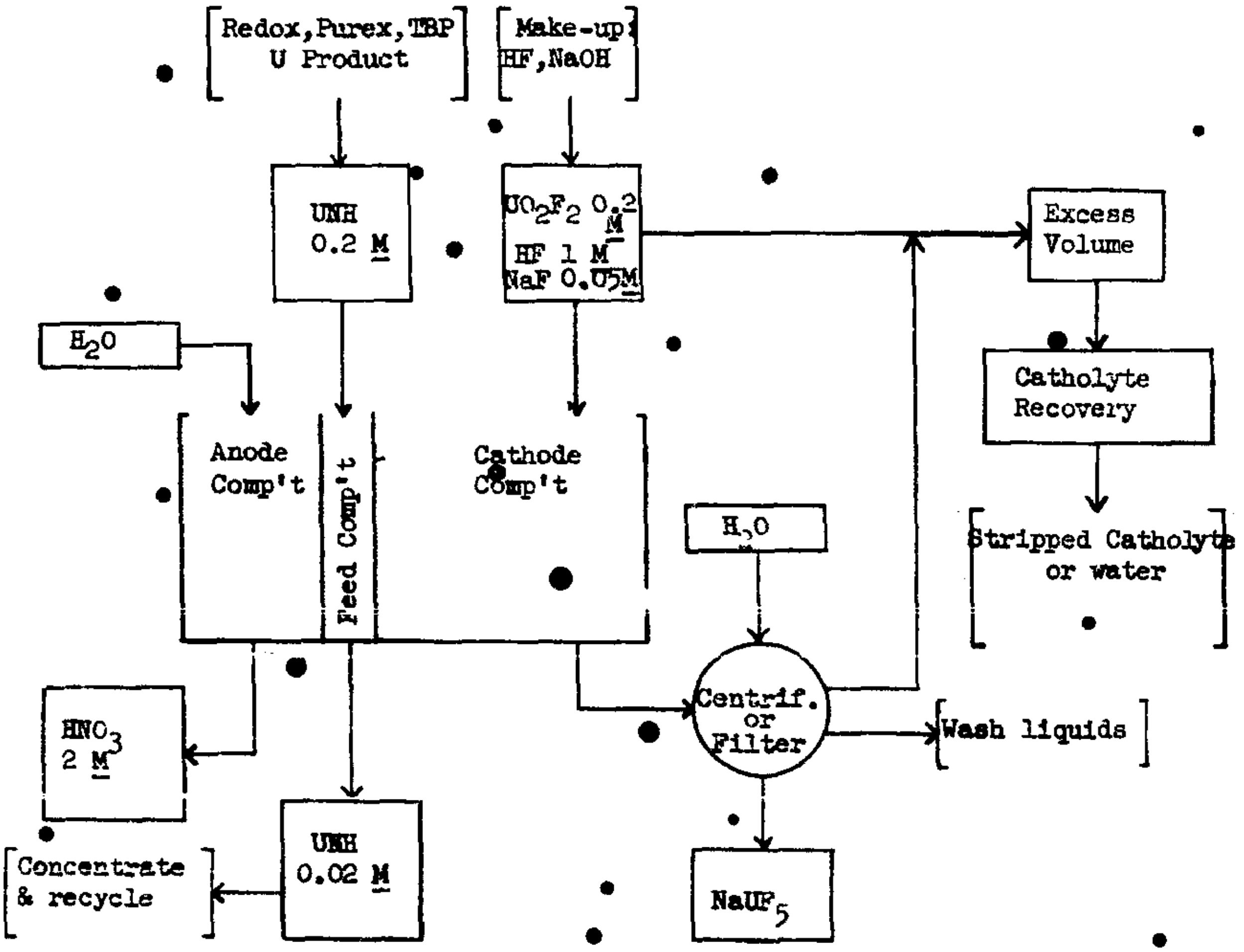
Figure 1

Flurex Flowsheet



Cathode - $UO_2^{++} + 4\ HF + Na^+ + F^- + 2e^- \longrightarrow NaUF_5 + 2\ H_2O$

Anode - $H_2O \longrightarrow 2\ H^+ + 1/2\ O_2 + 2e^-$

Net - $UO_2(NO_3)_2 + 4\ HF + NaF \longrightarrow NaUF_5 + 2\ HNO_3 + 1/2\ O_2 + H_2O$

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A second effect of the tendency toward increase of catholyte volume is the consequent dilution of the uranyl fluoride. The uranyl concentration could be maintained by operating at less than one hundred percent current efficiency, since this produces a net increase in the amount of uranium in the catholyte system. In practice, the concentration of uranium will tend to stabilize since the effect of dilution will be to lower the current efficiency to the point where the net increase in uranium transported balances the dilution. This has been shown to occur at a uranium concentration of about 0.2 molar.

Anode Compartment

Nitric acid is produced as a by-product in the anode compartment, and can be drawn off at any concentration up to about four molar; the limiting factor is the water transported through the anion exchange membrane with the nitrate ions.

The concentration of nitric acid in the anolyte is kept at two molar as a compromise between increase of solution resistance as the concentration is decreased, and the increase in hydrogen ion leakage into the feed compartment as the hydrogen ion concentration in the anolyte is increased. The latter results in a loss of efficiency in the salt-splitting step, since the overall reaction in this case is merely the transport of hydrogen ion from the anode to the cathode compartments. The feasibility of operation with two molar nitric acid has been demonstrated in the laboratory cells; however, this is not necessarily the optimum concentration for greatest overall efficiency of the process.

Product Recovery

The alkali uranic fluoride is removed as a catholyte slurry and is collected by settling, filtration, or centrifugation. The precipitate must be washed and dried. The drying can be done in air at 150 to 200 C without oxidation. The product in experimental runs has been a freely flowing dense powder that is readily filtered and washed.

The wash liquids from the product recovery step will contain appreciable amounts of uranium in solution too dilute for efficient electrolytic recovery. The relative costs will determine whether this material will be reclaimed by concentration followed by electrolytic stripping, or by precipitation at pH 10 of the alkali tetrauranate followed by dissolution in hydrofluoric acid and return to the catholyte.

SCOPE OF THE FLUREX EXPERIMENTS

Cell Operations

Over twenty separate runs have been carried out, each on a continuous process basis, with solution being fed and withdrawn from each of the three cell compartments. Ammonium, potassium and sodium fluorides have each been used in a number of the runs in this series. A few of the runs have been continued as long as four days (90 to 100 consecutive hours); most lasted approximately two days, although a few were interrupted in less than eight hours. Three different cells have been used, ranging in capacity from about thirty grams to about one-half kilogram of alkali uranic fluoride per day (24 hours).

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Production of Metallic Uranium

Bomb reduction experiments on a 25 gram scale using calcium-iodine booster have been carried out on six different product batches, among which both sodium and potassium uranic fluorides were represented. The recoveries of the metal in the charge have ranged from practically zero to better than 90 percent; to date, sodium salts have produced better results than potassium salts, but it is felt that proper adjustments in the conditions in the electrolytic cell and/or the reduction bomb would improve the yield from potassium salts.

Future Considerations

Numerous aspects of the Flurex process, itself, and potential utilizations of its products deserve further development. Much remains to be done with the physical design of the cell in order to achieve the best chemical performance consistent with economical operation. Little is yet known about the final distributions of the fission products which may be present in small amounts in the feed stream. One of the most important projects to be undertaken is the study of several possible methods of utilizing Flurex product materials in the production of uranium hexafluoride.

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