

# Electrolytic precipitation of ammonium diuranate

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## SYNOPSIS

Continuous precipitation of ammonium diuranate from a solution of uranyl sulphate and ammonium sulphate in the cathode compartment of an electrolytic cell has been investigated. It is found that the rate of precipitation and the settling rate of the precipitate can be correlated with the current consumed per unit volume of catholyte solution. The weight fraction of uranium in the dried solid product appears to be constant over the range of operating conditions used.

## SAMEVATTING

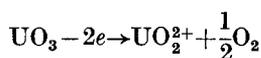
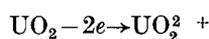
Die ononderbroke presipitasie van ammoniumdiuranaat uit 'n oplossing van uranielsulfaat en ammoniumsulfaat in die katodekompartement van 'n elektrolitiese sel is ondersoek. Daar is gevind dat die presipitasie- en besinktempo van die presipitaat gekorreleer kan word met die stroom per eenheidsvolume van die katolietoplossing verbruik. Die massafraaksie uraan in die gedroogde vaste produk is blykbaar konstant vir die bestek van die bedryfstoelestate wat gebruik is.

## INTRODUCTION

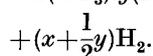
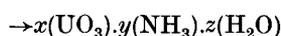
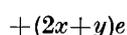
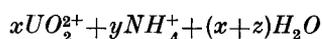
The production of ammonium diuranate (ADU) from ores containing the oxides  $UO_2$  and  $UO_3$  using the Purlex process involves essentially (1) acid-oxidation leach, (2) purification by filtration and solvent extraction, and (3) precipitation of ADU. A feature of the mass balance for such a plant is the net consumption of sulphuric acid and ammonia, and the production of an excess of ammonium sulphate. To circumvent this problem, an electrolytic process is proposed in which leaching takes place in the anode compartment and precipitation of ADU in the cathode compartment. The two compartments are separated by an anion-permeable membrane. Fig. 1 shows a schematic representation of the plant.

The overall reactions of interest are

1) anode compartment

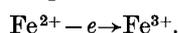
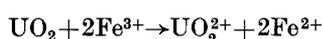


2) cathode compartment



It must be emphasized that these are the overall reactions, and many

intermediate stages may be involved. For example, the oxidation of  $UO_2$  is most likely to be accelerated by the presence of ferric ions that enter the cell as an impurity in the ore:



The present paper is restricted to a study of the precipitation process in the cathode compartment. The yield, composition, and settling rate of the ADU precipitate are determined at various current densities and solution flowrates.

The cathode reaction as given

above is based on the assumption that the chemical formula for ADU can be written as  $x(UO_3) \cdot y(NH_3) \cdot z(H_2O)$ , where  $x$ ,  $y$ , and  $z$  can take on a range of values. Birkill<sup>1</sup> has reviewed the results of a number of experimental investigations of ADU composition, which, in the main, support this formula.

For convenience in the present experimental work, the complex leaching process is replaced by oxygen evolution from a single-phase electrolyte (100g/l of ammonium sulphate solution). The flowrate of anolyte is set much higher than that

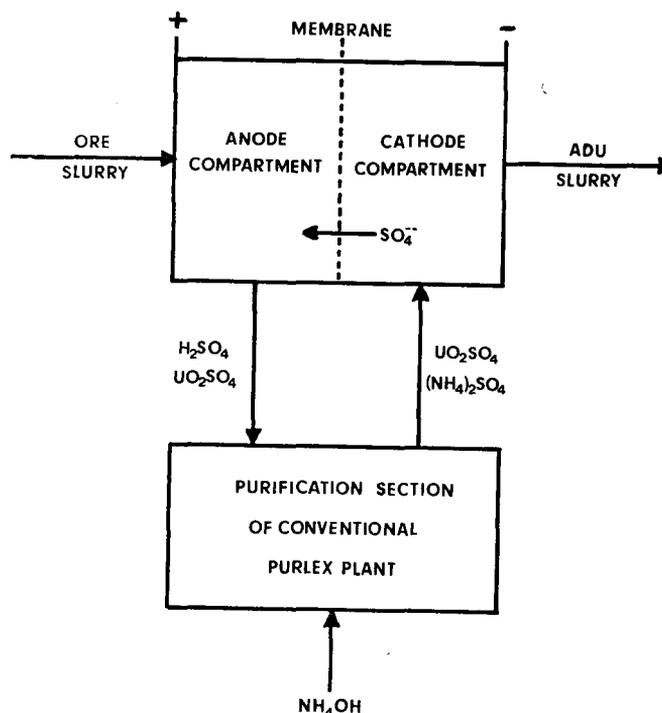


Fig. 1—Electrolytic uranium recovery plant

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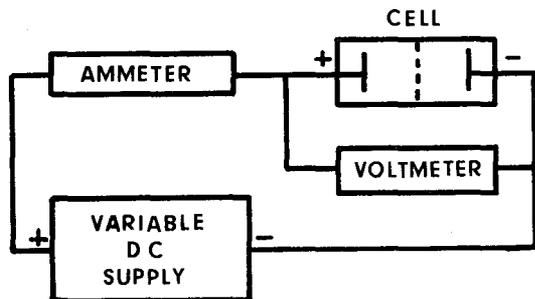
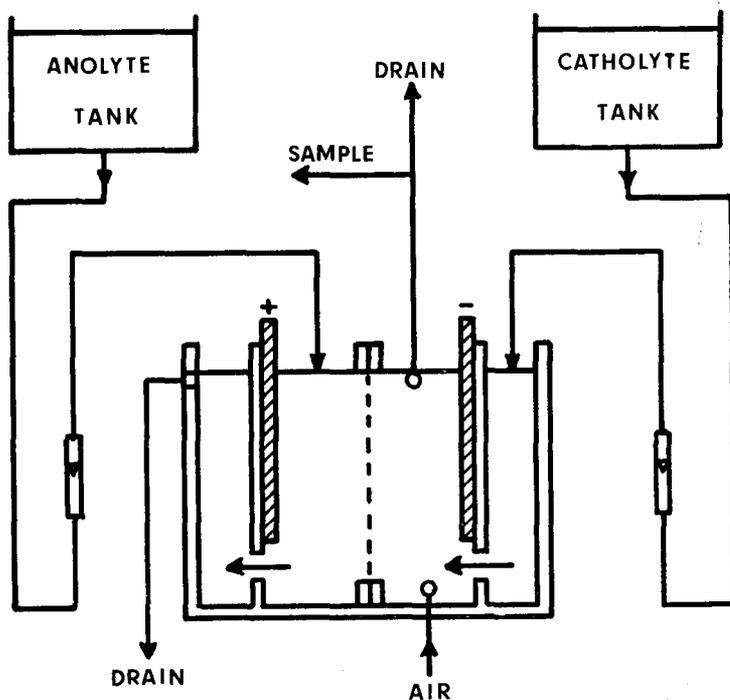


Fig. 2—Apparatus and electrical circuit

of the catholyte so that excess hydrogen ions will be flushed from the cell. Interference from the anode side was thus almost completely eliminated.

### EXPERIMENTAL INVESTIGATION

The apparatus is shown diagrammatically in Fig. 2. The catholyte is fed from a constant-head tank via a rotameter into the cathode compartment of the cell through a number of holes spaced regularly below the electrode. Air is passed through a distributor at the base of the cell to agitate the contents of the cathode compartment. The ADU precipitate tends to float to the surface and is removed with the spent solution through an overflow pipe, which also serves to maintain a constant level in the cell.

The cell is constructed of 6 mm rigid polyvinyl chloride sheeting. The volume of the cathode compartment is 300 ml and the effective cathode area is 84 cm<sup>2</sup> (14 cm wide by 6 cm high). The anode and cathode are graphite sheets of 6 mm thickness.

The electrolytes were prepared by the dissolution of analar-grade uranyl sulphate and ammonium sulphate in distilled water. The catholyte composition was 8 g/l of uranium and 100 g/l of ammonium sulphate. The anolyte contained 100 g/l of ammonium sulphate.

The range of experimental conditions were as follows:

current 2 to 10 A  
catholyte flowrate 0,26 to 1,23 ml/s.

The ADU slurry from the outlet of the cathode compartment was filtered, washed, dried, and weighed.

A sample of the dried cake was dissolved in sulphuric acid, and the uranium content was determined colorimetrically. A further sample of ADU slurry was collected from the outlet of the cell and its settling rate determined in a 2-litre measuring cylinder. It was found that this rate was reasonably constant over the first five minutes of settling, and it was thus assumed that unhindered settling was taking place during this period. The settling rate was corrected to 20°C by the application of the following relationship, which assumes that the viscosity of the fluid is the most sensitive parameter to changes in temperature:

$$U_{20} \approx \frac{\mu_t}{\mu_{20}} \cdot U_t, \dots \dots \dots (1)$$

where

$U_{20}$  = settling rate at 20°C

$U_t$  = settling rate at  $t^\circ\text{C}$

$\mu_{20}$  = viscosity of fluid at 20°C

$\mu_t$  = viscosity of fluid at  $t^\circ\text{C}$ .

### RESULTS

If the cathode process involves only the precipitation scheme given in the introduction, then by Faraday's law

$$W_T = \frac{M.I.V}{n.F.Q} \dots \dots \dots (2)$$

where

$W_T$  = theoretical weight of uranium precipitated

$M$  = atomic weight of uranium

$V$  = volume of cathode compartment

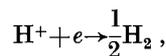
$F$  = Farady constant

$Q$  = volumetric flowrate of catholyte

$n$  = number of electrons transferred from cathode per atom of uranium precipitated

$$= \frac{2x+y}{x}$$

Other competing processes could also occur such as:



and therefore the actual weight of uranium precipitated,  $W$ , will be:

$$W = EW_T, \dots \dots \dots (3)$$

where  $E$  is the current efficiency for uranium precipitation. Combining equations (2) and (3) and inserting

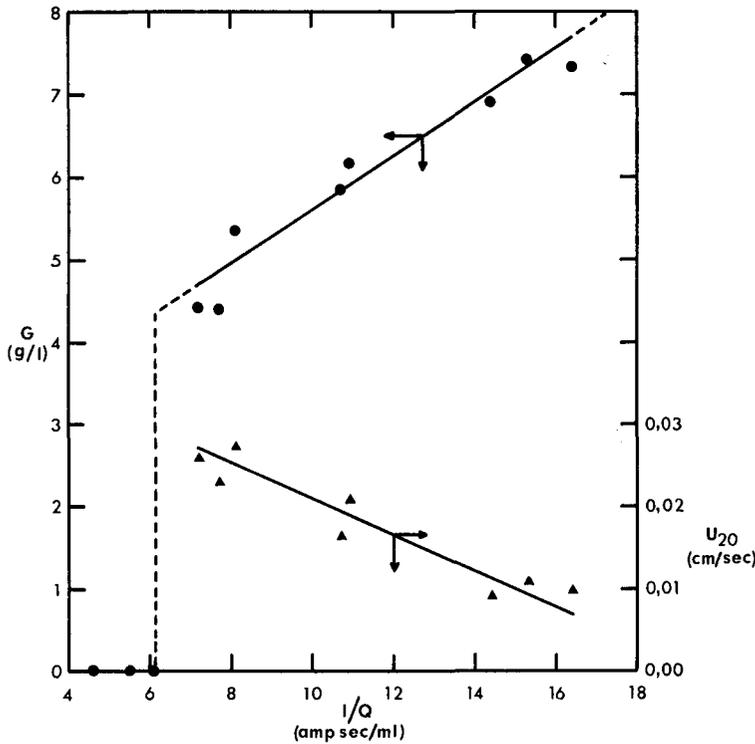


Fig. 3 The effect of current and solution flowrate on the rate of precipitation and settling velocity of the ADU precipitate

numerical values for M and F, we get:

$$W = \frac{2,47.E.x.I.V}{(2x+y).Q}, \dots (4)$$

If G is the mass of uranium precipitated per litre of catholyte, then

$$G = \frac{W}{V} = \frac{2,47.E.x.I}{(2x+y).Q} \dots (5)$$

Fig. 3 presents the experimentally determined values of G as a function of I/Q. It is found that below I/Q ≈ 6 A. s/ml, there is no ADU

precipitated, between 6 and 18 a reasonably linear relationship exists, and above 18 complete precipitation occurs. It is possible to explain the results in the region I/Q < 6 as due to the formation of either a soluble intermediate ammonia-uranium complex or a highly supersaturated solution of ADU.

Fig. 3 also shows the results of the settling tests. It appears that these can be correlated reasonably well with the ratio I/Q.

The weight fraction of uranium

in the precipitated ADU was found to be independent of operating conditions. The value obtained was 0,64 ± 0,03 g of uranium per gram of ADU.

## DISCUSSION

The feasibility of precipitating ADU from a sulphate solution in an electrolytic cell has been demonstrated. Control can be exercised on the rate of precipitation by adjusting the current or the flowrate of the solution. As a high settling rate is desirable for ease of ADU recovery, the results indicate that the test cell used in this investigation should be operated with I/Q ≈ 8 A. s/ml. This, however, will result in the precipitation of only about 60 per cent of the uranium. Economic considerations would necessitate the recycling of the clarified overflow from the cell as stripping solution to the solvent extraction section. As the concentration of ammonium sulphate will not build up in this stream (as it would do in a conventional plant), a recycle of this nature would be feasible.

## ACKNOWLEDGEMENT

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## REFERENCE

1. BIRKILL, R. S. Ph.D. Thesis, University of the Witwatersrand, 1972.