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THE ELECTROLYTIC DISSOLUTION OF METALLIC URANIUM

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J. J. Finley, J. H. Goode, J. A. Westbrook

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A B S T R A C T

Experiments have shown that uranium metal can be dissolved in a wide variety of acids, salts, and alkalies by anodic oxidation in an electrolytic cell. Uranium concentrations of 50 to 80 grams per liter have been obtained with sodium bicarbonate, tartaric, or nitric acids as electrolytes.

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THE ELECTROLYTIC DISSOLUTION OF METALLIC URANIUM

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INTRODUCTION

Uranium metal is dissolved with difficulty in common acids, salts, or alkalies unless an oxidizing agent is present to increase the rate of solution. Concentrated nitric and perchloric acid act as oxidizing agents to dissolve uranium rapidly. Oxidizing agents, such as oxygen or hydrogen peroxide, may be used to oxidize uranium metal for solution in a wide variety of acids, salts, or alkalies.

In commercial methods of electrorefining, anodic oxidation is used to dissolve the impure metals in the electrolytic cells. Copper, silver, and gold have been electrorefined for many years, and more recently, aluminum, lead, tin, and nickel have been purified by electrolysis in which the first step is anodic oxidation. Some metals, such as chromium, molybdenum, and tungsten, are passive and do not dissolve upon becoming anodic. In 1904 Muthmann and Fraunberger (1) observed that uranium gave no evidence of becoming passive. In 1913, U. Sborgi (2) dissolved a uranium anode in sulfuric acid and sulfates, nitric acid and nitrates, hydrochloric acid and chlorides, bromides, acetates, chlorates, phosphates, and various alkalies.

This report describes exploratory experiments on the electrolytic dissolution of uranium in which the metal was used as the anode in acid, salt, and alkaline electrolytes. Particular attention was paid to the conditions under which the metal could be dissolved to give high concentrations in alkaline solutions, and included the effects of types of current, deposits on the electrodes, and the addition of peroxide to the electrolyte, which may be used to form the highly soluble uranium peroxide complex. Qualitative experiments were also carried out in which the hydrogen from the cathode of the dissolving cell was combined with atmospheric oxygen in a primary cell to produce hydrogen peroxide.

EXPERIMENTAL

Apparatus and Reagents

Orientation experiments were carried out in Pyrex beakers containing about 200 ml. of the electrolyte under investigation. A piece of uranium metal was held by nickel, stainless steel, or platinum contact wires, and the cathode was generally nickel or platinum sheet or wire. Larger scale investigations in alkaline solutions were carried out in a three-liter polyethylene beaker fitted with a glass stirrer, a nickel "crowfoot" cathode, and a partially insulated nickel wire grill to support the uranium metal anode. (See Figure 1.) The electrolytes consisted of various salts and acids in distilled water.

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EXPERIMENTAL CELL FOR THE ANODIC DISSOLUTION OF METALLIC URANIUM

FIGURE 1

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Procedure

The uranium metal was connected with an anodic lead wire or placed in contact with the anode wire grill, the cathode was positioned over or near the weighed uranium anode, the stirrer started, and the electrolysis begun. The voltage drop across the cell and the current were measured during the electrolysis with ordinary voltmeters and ammeters. Periodic samples of the solution were taken for uranium analysis, and finally the uranium metal anode was reweighed to determine the weight loss.

RESULTS AND DISCUSSION

Dissolution in Various Electrolytes

Table I illustrates the results of preliminary orientation experiments on the anodic dissolution of metallic uranium in a number of electrolytes. Of the electrolytes tested, saturated tartaric acid, 1.5 N nitric acid, and sodium bicarbonate appeared to be the most satisfactory from the standpoint of concentration, rate of corrosion, and condition of the electrodes. Table II shows the results of two additional experiments on the dissolution of uranium metal in 1.5 N nitric acid and saturated sodium bicarbonate, using a two-compartment diaphragm cell.

Dissolution in Sodium Bicarbonate Solutions

Electrode Deposits. During the dissolution of uranium metal by anodic corrosion, it was noted that black coatings, presumed to be uranium oxide, formed on the electrodes or settled out of the electrolyte. The oxide formation, which decreased the cell current and increased the voltage, appeared to be dependent upon the electrolyte circulation and uranium concentration.

The coatings formed readily on electrodes in cells without mechanical circulation and on portions of the electrodes not exposed to the circulating electrolyte, for example, the electrode surface adjacent to the beaker wall. Table III indicates the electrode conditions at various uranium concentrations in a cell containing a platinum cathode, uranium anode, and sodium bicarbonate electrolyte. A momentary reversal of polarity restores the original current in the cell.

A second experiment indicated that the rate of formation of the electrode deposits increased at higher uranium concentrations, and that a nickel cathode permitted higher concentrations to be reached than did a platinum cathode, before interference by the electrode deposit. Upon reaching a uranium concentration of 65.6 g./l., the solution was withdrawn and fresh electrolyte was introduced into the cell; after 30 minutes of electrolysis, the electrode coatings had been dissolved and the current and voltage had returned to their initial values.

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TABLE I
ANODIC DISSOLUTION OF URANIUM METAL

<u>Electrolyte</u>	<u>Concentration</u>	<u>pH</u>	<u>Anode Current Density² amp./cm.</u>	<u>Anode Holder Material</u>	<u>Ampere- Hours of Electrolysis</u>	<u>Uranium Concentration, g./l.</u>	<u>Anode Condition</u>	<u>Cathode Condition</u>
Sodium acetate	Saturated	7.6	0.21	Stainless Steel	3.4	0.70	Green deposit	Black, orange deposit
Sodium tartrate	Saturated	6.2	0.12	Stainless Steel	10.0	21.4	Brown deposit	Black deposit
Potassium tartrate	Saturated	10.4	0.12	Stainless Steel	24.0	0.9	Green deposit	Black deposit
Tartaric acid	Saturated	0.4	0.12	Nickel	18.0	87.5	Polished	Clean
NH ₄ HCO ₃	Saturated	8.2	0.12	Nickel	2.0	4.6	Orange deposit*	Brown deposit
KHC0 ₃	Saturated	8.0	0.12	Insulated	0.7	5.4	Slight black	Slight black
KHC0 ₃	Saturated	8.2	0.12	Insulated	0.7	5.4	Slight black	Slight black
KHC0 ₃	Saturated	8.5	0.12	Insulated	10.0	38.6	Black flake	Slight black
H ₂ CO ₃ at 0 °C.	Saturated	3.3	Insufficient					
H ₂ CO ₃ + NaHCO ₃	Saturated at 0 °C.	6.6	0.12	Insulated	4.0	11.6	Green deposit	Slight black
NaHCO ₃	Saturated	8.0	0.44	Insulated	3.5	32.0	Clean	Slight black
NaHCO ₃ H ₂ O ₂	Saturated	---	0.12	Pt + U	3.0	33.1	Clean	Clean
Nitric acid	1.5 N	---	0.12	Platinum	3.57	46.0	Clean	Black precipitate

*Uranium precipitated.

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TABLE II
ANODIC DISSOLUTION OF URANIUM METAL IN 1.5 N NITRIC ACID

<u>Sample Number</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Dissolving time, minutes	5	30	60	110
Amperes	2	2	2	2
Volts	15	13	12	12
Normality of HNO ₃	1.5	1.28	1.24	1.17
Uranium concentration, g./l.	3	14	23	46
Dissolving efficiency, %	121	89.5	87.7	74.4

ANODIC DISSOLUTION OF URANIUM METAL IN SODIUM BICARBONATE

<u>Sample Number</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Dissolving time, minutes	5	30	60	110
Amperes	0.4	0.4	0.4	0.4
Volts	15	15	15	15
Uranium concentration, g./l.	0.6	3.6	6.2	15
Dissolving efficiency, %	124	117	97	89

TABLE III
ELECTRODE DEPOSITS

<u>Uranium Concentration, g./l.</u>	<u>Electrode Conditions</u>
29.4	No coating
48.4	Coating reduced current
56.5	Coating covered electrodes; low current

Effect of Current Types. It was noted that circulation of the electrolyte, around the electrodes without electrolysis dissolved the uranium deposits on the electrodes. Since a continuous electrolysis aided in the formation of these deposits, and since the deposits could be dissolved by the electrolyte, a single phase, half-wave rectified current was tested as the power source for the dissolving cell. Table IV illustrates the results of three experiments in which uranium metal was dissolved in a cell containing a nickel cathode and a saturated sodium bicarbonate electrolyte.

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An experiment was made to determine the effectiveness of alternating current for the dissolution of metallic uranium. A saturated sodium bicarbonate solution was used as the electrolyte in a cell containing platinum and uranium electrodes; a 10-volt, 60-cycle current was applied to the cell. Table V indicates the uranium concentrations reached and the electrode conditions. Although uranium may be dissolved with alternating current, it appears that higher concentrations may be reached with direct current.

TABLE IV
DISSOLUTION WITH HALF-WAVE POWER SUPPLY

<u>Run Number</u>	<u>1</u>	<u>2</u>	<u>3</u>
Temperature, °C.	80	25	25
Amperes	3.5	1.0	1.0
Volts	1.0	3.0	3.0
Time of electrolysis, hours	1.0	3.0	2.75
Uranium concentration, g./l.	32.1	33.1	28.7
Anode condition	Clean	Clean	Clean
Cathode condition	Slight deposit	Clean	Clean

TABLE V
DISSOLUTION WITH ALTERNATING CURRENT

<u>Time, hours</u>	<u>Uranium Concentration, g./l.</u>	<u>Remarks</u>
5	14.6	Electrodes clean; slight turbidity in solution.
10	28.2	Electrodes clean; precipitate in electrolyte.
20	36.0	Electrodes clean; large amount of precipitate.

Effect of Hydrogen Peroxide. It was noted that the addition of 0.5 ml. of 30% hydrogen peroxide to 1 liter of saturated sodium bicarbonate electrolyte would dissolve the deposits on the electrodes during the dissolution of a uranium anode. One experiment indicated that under suitable conditions hydrogen peroxide may be formed in the dissolution cell by electrolytic action, and that the uranium may be dissolved without the formation of a cell sludge or deposits on the electrodes. In a cell containing a large uranium anode, 36 hours of electrolysis, with a single-phase, half-wave rectified current, dissolved 82 grams of uranium per liter of saturated sodium bicarbonate containing an excess of hydrogen peroxide. Under these conditions, the calculated rate of dissolution was one kilogram of uranium per 2.31 kilowatt-hours.

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Uranium concentrations above 82 g./l. were not reached, but in the presence of peroxide the uranium continued to dissolve from the anode and precipitate as the carbonate.

In an auxiliary experiment, hydrogen was combined with atmospheric oxygen in an alkaline electrolyte, at platinized carbon electrodes, to form hydrogen peroxide and a primary cell for production of electricity. Such an arrangement could be used to form the hydrogen peroxide which appears necessary for obtaining high concentrations of uranium.

Demonstration Experiments

A piece of uranium metal, weighing approximately 250 grams and having an area of 42 square centimeters, was made the anode in the cell shown in Figure 1. The cathode was of nickel and had an area of 222 square centimeters. The electrolyte was 1.2 - 1.3 liters of sodium bicarbonate (83 g./l.). Operating conditions were room temperature, 1 ampere, and 3.5 volts; giving a cathode current density of 0.0045 amp./cm² and an anode current density of 0.024 amp./cm². The cell was operated, using a direct current, for 24.7 ampere-hours per liter (AH/l.) for the first electrolysis. A second electrolysis was then made under the same conditions for 35.4 AH/l. No hydrogen peroxide was added to the electrolyte. Table VI illustrates the results obtained during the two electrolyses. The uranium was dissolved in Run 1 at a rate of 1 kilogram per 2.4 Kwh., and at a rate of 1 kilogram per 2.9 Kwh. in the second run. Although some black precipitate formed on the cathode and settled out in the cell, there was no apparent interference with the rate dissolution of the anode.

TABLE VI
ANODIC DISSOLUTION OF URANIUM METAL

Run Number	Sample Number	Electrolysis, AH/l.	Uranium Dissolved, g./l.	Total Electrolysis, AH/l.	Total Uranium Dissolved, grams
1	1	4.08	4.8	4.08	5.92
	2	5.6	8.74	9.68	16.71
	3	15.0	22.15	24.68	44.07
2	1	35.4	42.0	35.4	52.5

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Preliminary investigations into the dissolution of metallic uranium by anodic corrosion have shown that such a method has a number of advantages over the usual dissolution in acids. Advantages of the electrochemical method includes: (a) low cost, (b) solution in both acidic and basic solvents, and (c) dissolution without the evolution of noxious gases, such as the oxides of nitrogen. One kilogram of uranium metal may be dissolved at a power cost of less than one cent using 3 Kwh. of electrolysis; this may be compared to the cost of the 1.5 kg. of 60% nitric acid (about twelve cents) theoretically required to dissolve the same weight of uranium in the reaction:

Maximum solubility appears to be dependent upon adequate circulation of the electrolyte around the uranium metal, low current densities to prevent oxide formation on the anode, and the presence of hydrogen peroxide in basic electrolytes containing high concentrations of uranium.

1. Muthmann, W. and F. Fraunberger, Ber. Bayr. Akad. 34 221 (1904) (J. W. Mellor, Comprehensive Treatise on Inorganic and Physical Chemistry, Vol. 12, page 26 (1932), London).
2. Sborgi, U., Z. Elektrochem. 19 115 (1913).

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