*Transpassive Electrodeposition of
Depleted Uranium in Alkaline Electrolytes*

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ABSTRACT

To aid in removal of oralloy from the nuclear weapons stockpile, scientists at the Los Alamos National Laboratory Plutonium Facility are decontaminating oralloy parts by electrodisolution in neutral to alkaline electrolytes composed of sodium nitrate and sodium sulfate. To improve the process, electrodisolution experiments were performed with depleted uranium to understand the effects of various operating parameters. Sufficient precipitate was also produced to evaluate the feasibility of using ultrafiltration to separate the uranium oxide precipitates from the electrolyte before it enters the decontamination fixture.

In preparation for the experiments, a potential-pH diagram for uranium was constructed from thermodynamic data for fully hydrated species. Electrodisolution in unstirred solutions showed that uranium dissolution forms two layers, an acidic bottom layer rich in uranium and an alkaline upper layer. Under stirred conditions results are consistent with the formation of a yellow precipitate of composition $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, a six electron process. Amperometric experiments showed that current efficiency remained near 100% over a wide range of electrolytes, electrolyte concentrations, pH, and stirring conditions.

INTRODUCTION

The United States has initiated removal of 200 tons of fissile material from its nuclear weapons stockpile. Oak Ridge enriched uranium (oralloy) constitutes a significant portion of the material for decontamination and consolidation. Los Alamos scientists at the Plutonium Facility have developed an electrolytic process for removing a 1–10 μM -thick layer of oralloy by electrodisolution. Under neutral to alkaline conditions, significant quantities of plutonium and americium contaminants are removed and tend to remain with the oralloy precipitate.

Within the electrolytic process, electrolyte containing the precipitate is recirculated to the decontamination fixture where electrodisolution takes place. After electrodisolution is complete, a high velocity stream of wash water removes remaining precipitate from the oralloy part.

Electrodisolution experiments were designed to understand the effects of various operating parameters, and to produce sufficient precipitate for ultrafiltration studies. While the decontamination process has been effective, we are interested in understanding the impact of variables upon current efficiency, namely, current density, electrolyte concentration, choice of electrolyte, pH, and changing hydrodynamics. Use of ultrafiltration to improve decontamination efficiency, through removal of the precipitate, was also of interest to us. A final goal in our study was to produce sufficient uranium oxide for ultrafiltration tests.

SUMMARY OF THE THERMODYNAMICS AND ELECTROCHEMISTRY OF URANIUM

A potential-pH diagram for uranium species in aqueous solution is given in Figure 1. This figure is based upon work by Pourbaix.¹ A compilation of the properties of uranium species in solution was also helpful.² Pourbaix gave two figures, one for uranium where no hydrates are included and another where some hydrates are found. Figure 1 is derived for fully hydrated species that are expected to precipitate from aqueous solution.

Figure 1 consists of three sets of lines representing water oxidation and reduction, regions for stability of soluble uranium species, and regions of predominant precipitates in aqueous solution. At 0–0.826 V versus the potential of the normal hydrogen electrode (NHE), hydronium ions in water are reduced to hydrogen gas. At more positive potentials, oxidation of water to oxygen gas takes place by the following reaction

This reaction also represents the oxidizing potential of oxygen gas.

Regions of stability of soluble species are separated by dotted lines. Uranium(III) species are most electronegative and are in equilibrium with uranium metal. They are unstable with respect to water and are slowly oxidized to uranium(IV) species as hydronium ions are reduced to hydrogen gas. Uranium(IV) is most stable in acidic solution, but is hydrolyzed to the UOH^{3+} species in alkaline solutions. Uranium(VI) is highly stable because of the formation of the uranyl complex, UO_2^{2+} .

Figure 1. Electrochemical potential, a pH diagram for uranium in solution. The numbers 0, -3, and -6 at the top of the figure represent concentrations of 1 M, 10^{-3} M, and 10^{-6} M of the soluble species.

Uranium(V) species are least stable. They are formed by electro-reduction of uranium(VI).² Electro-reduction of uranium(V) to uranium(IV) does not occur because the reaction is kinetically hindered. Uranium(V) disproportionates into uranium(IV) and uranium(VI) by the following reaction:

The U^{5+} species is produced during cyclic voltammetry as observed below.

EXPERIMENTAL APPARATUS AND PROCEDURES

Electro-oxidation of uranium was studied in beaker tests in an open-faced hood. A 100 ml beaker was filled with 80 ml of 200 g/L NaNO_3 solution. After weighing, a 2.5 cm length of 0.95 cm-diameter depleted uranium rod was immersed in the bath. The counter electrode consisted of a 5 cm² platinum flag spot welded to a platinum wire. Electrical contact was made to the wire with an alligator clip outside of the electrolyte. A double-junction silver/silver chloride reference electrode essentially eliminated contamination of the electrolyte with chloride ions. The rest potential of a silver/silver chloride reference electrode with 4 M KCl inner electrolyte is +0.204 V NHE.³ The electrode tip was located approximately 0.6 cm from the uranium rod. The bath was stirred except as noted.

Cyclic voltammograms and amperometric experiments were performed with a PAR 273 Potentiostat. A Gateway 2000 Pentium computer controlled the potentiostat with Corrware software purchased from Scribner and Associates.

RESULTS

Physical Observations

The depleted uranium rod was initially covered with a thick oxide layer. In air, uranium is oxidized at room temperature to form a thick dark film of UO_2 .² During electrodisolution, some of the layer flaked off and accumulated in the bottom of the beaker. After electrolysis, additional flaking generally occurred as the rod dried and was transferred to a balance for weighing.

Unstirred experiments were performed to explore the effect of convection upon dissolution. We observed interesting phenomena described below that have implications for stainless steel dissolution.

During dissolution in 200 g/L NaNO_3 electrolyte, a convective current of dense, soluble uranium-rich solution flowed down the submerged portion of the rod and formed a column at the end of the rod, which moved to the bottom of the beaker (Figure 2). After 10 min of electrolysis, sufficient heavy phase formed so that two layers were apparent, a bottom layer with yellow color indicating uranium in solution and an upper layer with a slight amount of precipitate. The pH of each layer was measured with a pH probe. The bottom layer had a pH of 1.42–1.75, while the top reached a pH of 11.6. When the two layers were mixed a yellow precipitate formed and slowly settled to the bottom of the beaker. Final solution pH was 5.16, a value slightly lower than the initial value.

Figure 2. Schematic of unstirred beaker solution with formation of two layers.

Cyclic Voltammogram Behavior

Four sets of voltammograms were performed to understand the electrochemical behavior of uranium in a 200 g/L NaNO_3 solution. The potential sweep began at the rest potential, moved initially in the cathodic direction (to more negative potentials), and then anodically to the maximum value before completing the cycle. Multiple cycles were performed to differentiate between initial and steady-state behavior. The solution was not stirred during these experiments.

During some of the voltammograms, the voltage loss between the working and reference electrode was measured and mathematically removed so only the kinetic overpotential was found. This was accomplished with the built-in current interruption feature available in the PAR 273 potentiostat. With this device, the current is interrupted at a specified interval (every second) and the initial drop in current is rapidly recorded. Because the potential drop in solution occurs much more rapidly than potential changes in the double layer at the electrode/solution interface, the solution potential drop, or IR drop, can be measured. The IR drop value is then subtracted from the total working electrode potential relative to reference electrode potential to obtain a closer estimate of the actual interface voltage.

Voltammograms without IR compensation are given in Figure 3. At potentials more negative than -1.0 V versus the potential of the silver/silver chloride reference electrode, water reduction and hydrogen evolution were observed at the working electrode. When scanning in the anodic direction, no active dissolution was apparent. Transpassive dissolution of the uranium rod began at potentials greater than 0.3 V. During uranium dissolution, no oxygen evolution was observed at the working electrode. A heavy yellow solution was observed to flow down the side of the rod and pool at the bottom of the beaker.

Voltammograms with IR compensation were then performed with the same electrolyte that was used above (Figure 4). The first cycle exhibits only hydrogen oxidation and reduction reactions at less than 0.0 V NHE. In the transpassive region, more anodic potentials are observed in the initial cycle compared with subsequent cycles to obtain the same current density for uranium dissolution.

After the first cycle, a cathodic wave with half-wave potential of 0.1 V NHE was observed along with an anodic peak with half-wave potential of 0.2 V. The cathodic peak might be attributed to reduction of U^{6+} , formed during electrodisolution, to uranium U^{5+} .² The half-wave potential of 0.1 V for the reduction reaction compares well with +0.063 V for U^{6+} reduction in 1 M $HClO_4$.⁴ The anodic wave at 0.2 V may correspond to the oxidation of U^{5+} formed in the boundary layer to U^{6+} .

Uranium dissolution occurs as follows. Initially, the uranium electrode is covered with a layer of UO_2 that formed in air. This film appears to peel off the electrode during initial uranium metal dissolution. Uranium dioxide is not oxidized to UO_2^{2+} . In subsequent cycles, the scan in the anodic direction requires less overpotential for the same current.

Figure 3. Second voltammogram with depleted uranium, no IR correction, 200 g/L NaNO_3 , pH = 5.3, 5 mV/s scan rate.

Amperometric Experiments

We performed a total of 11 amperometric (constant current) experiments to determine the current efficiency for uranium dissolution. An earlier study found that uranium metal oxidized in nitrate solution during transpassive dissolution by a six electron reaction when a stainless steel counter electrode was used.⁵ This observation provided the basis for current efficiency calculations. Most of the experiments were performed at 30 mA/cm² for 10 min to simulate processing parameters. Experimental conditions and results are presented in Table 1.

For the two electrolytes explored, variations in electrolyte concentration, pH, and stirring conditions yielded a constant current efficiency near 100%, assuming a six electron reaction.

Figure 4. Third voltammogram with depleted uranium, IR correction, 200 g/L NaNO₃, pH = 5, 50 mV/s scan rate.

Table 1. Summary of Experimental Conditions and Results

Electrode	Electrolyte	Current Density (A/cm ²)	Stirrer Setting #	pH Initial	pH Final	Total Time (min)	Weight Initial (g)	Weight Final (g)	Temp (°C)	WE Voltage	Weight Removed (mg/cm ²)	Current Efficiency (%)
DU1_03-1	200 g/L NaNO ₃	0.030	0	8	5.16 mix	10	107.0762	107.0221	21.3	0.76	7.12	96.2
DU1_03-2	200 g/L NaNO ₃	0.030	1	5.12	5.02	10	107.0221	106.961		0.8	8.04	108.7
DU1_03-3	200 g/L NaNO ₃	0.030	1	10.8	9.61	10	106.9459	106.8878		0.74	7.65	103.3
DU1_03-4	200 g/L NaNO ₃	0.125	1	9.65	8.12	2.4	106.8878	106.8301		1.4	7.60	102.6
DU1_03-5	0.2 M Na ₂ SO ₄	0.030	1	8.42	6.34	10	106.8301	106.7706		1.15	7.83	105.8
DU1_03-6	0.4 M NaNO ₃	0.030	0	8.4	5.1	10	106.7706	106.7125		1.15	7.65	103.3
DU1_03-7	0.4 M NaNO ₃	0.030	1	8.9	6.07	10	106.7125	106.6552		1.21	7.54	101.9
DU1_12-8	0.4 M NaNO ₃	0.125	1	8.55	6.23	2.4	106.6552	106.5982		2.8	7.50	101.4
DU1_03-9	0.4 M NaNO ₃	0.030	1	11.02	9.85	10	106.5982	106.5415	21.8	1.37	7.46	100.8
DU1_03-10	0.4 M NaNO ₃	0.030	1	11.04	10.01	10	106.5415	106.4784	21.4	1.09	8.31	112.2
DU1	0.4 M NaNO ₃	0.125	1	11	9	61.6	106.4784	105.0245	22	2.1	191.38	100.7

During our series of experiments, the resulting solutions were allowed to settle and we noted the color of the solution above the precipitate (Table 2). The solubility transition for the primary soluble species occurs at a pH between 5.0 and 6.3.

Table 2. Solubility of Uranium Species as a Function of pH

Solution Composition	Final pH	Decanted Solution Color
200 g/L NaNO ₃	1.4	Yellow
200 g/L NaNO ₃	5.0	Yellow
200 g/L NaNO ₃	8.1	Clear
200 g/L NaNO ₃	11.0	Clear
0.2 M Na ₂ SO ₄	6.3	Clear

DISCUSSION

Based upon the initial measurements by Nelson et al.,⁵ uranium is oxidized to the uranium(VI) oxidation state when an inert counter electrode is used. Our data in Table 1 confirms, for a valence change of 6, that a current efficiency of 100.7% is obtained when a large amount of metal is removed (test #11, depleted uranium [DU] 1). We also know from the literature that UO₃•2H₂O is a dominant stable species in aqueous solution. This observation was confirmed by analysis of the precipitate. Carbon, hydrogen, and nitrogen analysis of the precipitate after washing indicated no measurable carbon or nitrogen, indicating no nitrate complex. Hydrogen analysis was in good agreement with the UO₃•2H₂O formula. Hydrogen content was also in agreement with U(OH)₄. Thus, a nearly pure hydrolyzed oxide is formed. Because oxygen evolution is not observed at the anode, predominant overall electrode reactions are as follows:

At the anode

while at the cathode

Based upon these reactions, the anode fluid becomes acidic while the cathodic fluid becomes more alkaline. This was indeed observed for unstirred experiments as described above.

For unstirred conditions, production of H⁺ during dissolution leads to dissolution of uranium at a pH of about 1.5. Thus, uranium undergoes dissolution in an acidic environment to form UO₂⁺² in solution. Only after mixing with the alkaline layer does UO₃•2H₂O precipitate. Equation [2] is better represented by the sum of the following two reactions:

followed by precipitation during mixing

It is also noted that the overall reaction is pH neutral.

During electrodisolution of stainless steel with a stainless steel counter electrode, breakdown of nitrate is observed by a movement toward higher pH and the odor of ammonia. The drift toward higher pH was also observed in full-scale oralloy part decontamination tests with stainless steel counter electrodes.

In these bench tests, the pH has been observed to become more acidic with time (Table 1). We propose that the slow acidification arises from hydration of the uranyl complex. As an alternative to Eq. [5], the following reaction occurs:

Addition of three of Eq. [3], three of Eq. [4] and one of Eq. [6] yields the formation of a net excess of two hydronium ions. Formation of numerous hydrolysis products has been proposed and confirmed.²

Different pH behavior has been reported for full-scale operations when oralloy parts are decontaminated. In these experiments at Los Alamos, a slow movement to alkaline pH is observed. While the area ratio of the anode to cathode is near unity for both the full-scale and bench-scale experiments, the full-scale unit has a stainless steel cathode, but the bench-scale rig has a platinum cathode.

We ran additional bench tests which indicated that the difference in pH drift was tied to counter electrode composition. When a platinum counter electrode of similar or larger size than the working electrode is used, nitrate reduction is minimal and pH drift is governed by other reactions. A 304 stainless steel (SS) electrode of the same size, however, causes a slow drift toward higher pH. It is suspected that poor hydrogen evolution kinetics on SS, leading to counter electrode operation at more cathodic potentials, enhances the possibly favorable kinetics of nitrate reduction on SS.

Cyclic voltammetry, with IR correction, yields an estimate of dissolution potential for comparison with the Pourbaix diagram (Figure 1). At 30 mA/cm², dissolution occurs between 0.66–0.834 V NHE. For the pH range from 1.5–10, uranium(VI) is indicated as the stable species.

One might wonder why oxygen is not evolved during dissolution like that observed during transpassive dissolution of stainless steel.⁶ At a pH of 10, oxygen evolution is favored at potentials greater than 0.64 V NHE. The overpotential of 0.19 V is insufficient to drive oxygen evolution at a significant rate.

Validity of Figure 1 may be further tested with Table 2. A soluble species, as indicated by a yellow solution, appears in the pH range from 5.0–6.3. This corresponds to a calculated concentration on the Pourbaix diagram of about 10^{-3} – 10^{-6} M. Thus, the calculated value is in approximate agreement with qualitative observations. No concentration measurements were made to quantitatively confirm the calculated values.

Based upon a six electron oxidation, Table 1 outlines operating conditions and calculated current efficiencies. Under essentially all conditions, uranium underwent dissolution at a current efficiency near 100%. In a number of cases, values were significantly above 100%. For test #10, the rod was flipped end-for-end so the UO_2 -covered portion of the rod was submerged. A current efficiency of 112% may be attributed to loss of the oxide layer which did not participate in the electrochemical reaction.

We also note that a change in concentration of the nitrate anion or use of sulfate salts did not change the current efficiency. No difference in surface properties was readily apparent, although microscopy was not performed on the resultant surfaces. Current efficiency was also independent of current density over the range of 30–125 mA/cm². Stirring rate changes or pH changes from 5–11 had little effect. This might be expected since the potential range for dissolution occurs where UO_2^{+2} is the predominant species and oxygen evolution is not favored.

CONCLUSIONS

We explored the impact of current density, electrolyte composition and concentration, pH, and stirring rate upon transpassive dissolution of depleted uranium. Over the range of variables we explored, dissolution was identified as a six electron process in agreement with the following information:

- earlier measurements with inert counter electrodes by Nelson et al.,⁵
- current efficiency values of near unity for a six electron process,
- lack of oxygen evolution at the cathode, and

- dissolution in the potential region where formation of uranium(VI) is favored.

In further support of the potential pH diagram, a qualitative loss of yellow solution color corresponds to the pH range where $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ becomes the dominant species.

Amperometric experiments show that current efficiency remained near 100% for two electrolytes over a range of electrolyte concentrations, pH, and stirring conditions. The pH should be maintained at a value greater than 7 to minimize the solubility of uranium. To reduce contamination of wash water with NaNO_3 , an electrolyte concentration of 0.4 M is recommended in future decontamination operations. No loss in current efficiency is expected. Finally, current density range from 30–125 mA/cm^2 may be applied with equal effectiveness. Other factors, such as the capacity of current feedthroughs or IR heating of the solution, may further limit the preferred current density range.

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