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To cite this article: Tai-Lee YU , Ying-Sheng LEE , Yii-Der CHUANG & Chau-Ting CHANG (1979) Scale-Up Preparation of Uranium Amalgam from Uranyl Ion Using Two-Compartment Electrolyzer, Journal of Nuclear Science and Technology, 16:7, 508-512, DOI: [10.1080/18811248.1979.9730936](https://doi.org/10.1080/18811248.1979.9730936)

To link to this article: <http://dx.doi.org/10.1080/18811248.1979.9730936>



Published online: 15 Mar 2012.



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Scale-Up Preparation of Uranium Amalgam from Uranyl Ion Using Two-Compartment Electrolyzer

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Received December 11, 1978

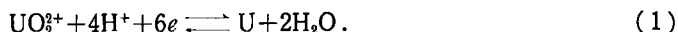
Revised April 2, 1979

A solid uranium amalgam containing as high as 1.7 g U/ml Hg was prepared electrolytically using a two-compartment electrolyzer separated with a cation exchange membrane at a kilogram scale. The design and operation characteristics of the electrolyzer is described. The results indicate that *ca.* 170 g of uranium ion in an aqueous solution could be reduced to metallic state by forming amalgam within 4 h with a current efficiency of 30% and uranium recovery of more than 80%.

KEYWORDS: *uranium amalgam, preparation, uranium ions, ion exchange materials, membranes, uranium, efficiency, feasibility studies*

I. INTRODUCTION

The conventional method for the preparation of nuclear fuels such as uranium metal, dioxide and carbides from the yellow cake $(\text{NH}_4)_2\text{U}_2\text{O}_7$ usually must undergo a series of tedious and energy-consuming chemical and metallurgical processes. Various attempts at simplifying and improving the manufacturing process have been made. Notable among them are the reduction of uranyl ion directly from an aqueous solution using a pre-prepared sodium amalgam⁽¹⁾. The thereby obtained uranium amalgam contains 50 mg U/ml Hg at most. The reduction of the uranyl ion to the metallic state is known to proceed according to Eq. (1):



The consumption of the hydrogen ion in the course of reaction will lead to the elevation of pH and to the precipitation of uranium hydroxides. Since the amalgamation was noticed to occur within a narrowly restricted pH range of 3 and 4, a two-compartment electrolyzer separated with an ion exchange membrane was developed for the preparation of uranium amalgam in our laboratories⁽²⁾. The pH of the cathode compartment where the reaction takes place is kept virtually constant during electrolysis by continuously supplying hydrogen ion *via* ion exchange membrane from the anode compartment. The solid amalgam which contains as high as 1.7 g U/ml Hg was found, besides for the preparation of nuclear fuels, to provide a facile route to the synthesis of organouranium compounds and to induce on various organic substrates interesting chemical reactions such as dehydrogenation and polymerization⁽³⁾.

In order to meet the increasing demand for the amalgam we have designed with a

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suitable modification an electrolyzer capable of continuous operation. The design and operation characteristics of the electrolyzer is described here.

II. EXPERIMENTAL

1. Cell Design

An electrolyzer having a surface dimension of 30×30 cm was constructed with acrylic resin. The anode and cathode compartments were separated with a Nafion 415 cation exchange membrane (DuPont Co.). The upper anode compartment was filled with Na_2SO_4 solution, whereas the uranium solution was placed in the lower cathode compartment. A platinum plate or gauze and a 10 mm deep mercury pool served as anode and cathode, respectively. The catholyte was forced to circulate between a reservoir chilled with ice water and the electrolyzer as shown in Fig. 1 for the purpose of controlling temperature at $20 \sim 25^\circ\text{C}$ and keeping the uranium concentration virtually constant during the electrolysis. In order to ensure a minimum Ohmic resistance the distance between the membrane and the mercury surface should be kept as short as possible, however, this would greatly impede the transport of the catholyte. The distance was actually kept at 5 mm. The applied voltage was kept at $10 \sim 11$ V.

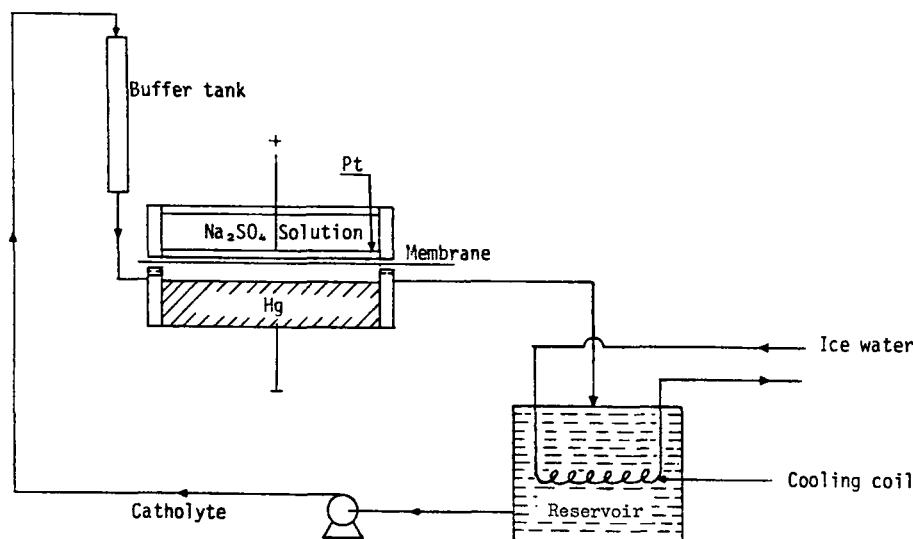


Fig. 1 Flow sheet of electrolysis

2. Reagents and Electrolyte Solutions

All the reagents used including $(\text{NH}_4)_2\text{U}_2\text{O}_7$, acetic acid, sodium sulfate and hydrochloric acid were of chemical reagent grade and without further purification. Deionized water was used for the preparation of electrolyte solutions.

The composition of catholyte has been found to affect the electrolytic process greatly. Two hundreds and fifty grammes of $(\text{NH}_4)_2\text{U}_2\text{O}_7$ were dissolved in 130 ml of 12 N HCl and 320 ml of glacial acetic acid, heated to 80°C to ensure complete dissolution and finally made up to 8 l with water. The solution contained *ca.* 25 mg U/ml and was at pH 1.6~1.8. One and a half liters of 1 M Na_2SO_4 was used as anolyte.

3. Chemical Analyses

The uranium content of the solid amalgam was determined gravimetrically. The

solid and liquid portions of the amalgam was first separated with a suction funnel under nitrogen. The amalgam was then digested with 6N HCl, precipitated with ammonia, ignited and finally weighed as U_3O_8 . Since the uranium content of the liquid portion was far lower than the solid portion, it was determined spectrophotometrically using arsenazo(III) at 665 nm. The solid amalgam was found to contain uranium in the range of 1.5~1.7 g/ml Hg, while the liquid portion 10 mg/ml Hg.

The catholyte was also analyzed for its uranium concentration at finite time intervals. One milliliter of the solution was titrated with a 0.1 M $Ce(SO_4)_2$ solution using ferroin as indicator.

III. RESULTS AND DISCUSSIONS

The electrochemical studies on the reduction of uranium ions have long been of active research interests for many workers. However, none of them have demonstrated the reduction of uranium ions into metallic state in aqueous solutions⁽⁴⁾. Our recent investigation by means of single sweep voltammetry with a hanging mercury electrode has revealed that U(III) ion is reduced into metallic state only in an acetate solution at -1.6 V *vs.* SCE (saturated calomel electrode), and not in other media such as chloride, sulfate, nitrate and perchlorate *etc.*⁽⁵⁾ The catholyte was therefore made up in acetic acid and the acidity was adjusted to pH 2~3 with hydrochloric acid. For the convenience of cell design and operation the electrolytic process was controlled at a constant current density and the potential shift was monitored with a calomel electrode occasionally.

Figure 2 shows the change of uranium concentration of the catholyte in the course of electrolysis. The concentration decreases virtually exponentially with respect to time and more rapidly for larger current density indicating a first order reaction as pointed earlier⁽⁶⁾. However, a closer scrutiny of the data by plotting the uranium concentration in logarithmic scale *vs.* time reveals that the slope becomes steeper as the amalgamation proceeds. The major reaction involved at the beginning stage of the electrolysis is therefore the reduction of U(VI) into U(IV) and possibly further into U(III), whereas the amalgamation takes place predominantly in the later stage, rapidly removing uranium ion from the solution. With the gradual depletion of uranium ion from the solution, the electrode potential was observed to shift cathodically from -1.6 to -3.0 V *vs.* SCE as easily expected from the Nernst equation. The effect of current density upon the electrolysis is tabulated in Table 1. The electrolysis at higher current density facilitates the higher recovery of uranium within a shorter time, whereas associated temperature elevation due to increased Ohmic resistance greatly impedes the amalgamation. The temperature control becomes necessary when the electrolyzer is to be operated at higher

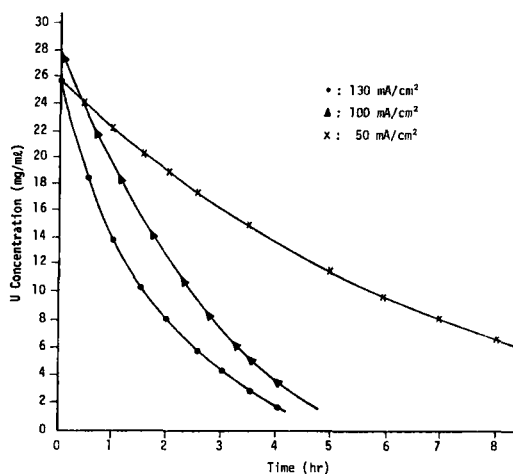


Fig. 2 Uranium concentration change of catholyte during electrolysis at different current density with flow rate of 5 l/min

current density. Since both anolyte and catholyte were made up with relatively highly conductive electrolytes such as sulfuric acid, sodium sulfate and chloride ion and the electrode distance was rather immune from the change of applied voltage, the major contribution to the potential drop might be ascribed to overpotential, membrane resistance and gas or bubble formation in the cathode compartment. The forced circulation of the catholyte between a reservoir and the cathode compartment was primarily aimed at reducing the concentration overpotential, removal of bubbles and thereby attaining a lowest possible voltage and a virtually constant temperature. However, no appreciable effect was observed for a flow rate larger than 4 l/min.

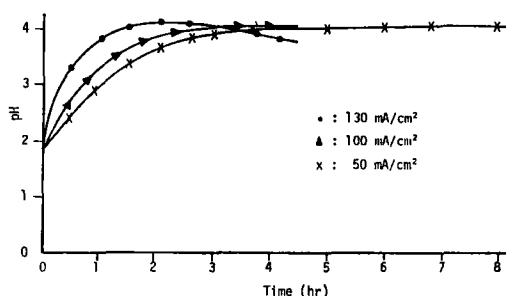
The acidity of the catholyte should be kept within a narrow pH region, or the uranium ion hydrolyzed and precipitated at higher pH, whereas at lower pH the amalgamation process would be retarded. The catholyte was adjusted to pH 2 at the beginning of the electrolysis and found to rise gradually up to a constant value of 4 as shown in Fig. 3. The ion exchange membrane thus plays the role of controlling the pH value.

The overall recovery and current efficiency shown in Table 1 is minimal at best, since the electrolysis was conducted at ambient conditions and no special caution was paid to remove oxygen in the electrolytes. Table 2 summarizes the semi-quantitative emission spectrographic determination of impurities on the uranium amalgam with a comparison with those of the yellow cake used. Except for the mercury content which could be removed down to 10 ppm order at *ca.* 1,300°C *in vacuo*, the impurities might be introduced mainly from the yellow cake, mercury and all chemicals used in the experiment. A separate tracer experiment shows that the alkali earths and lanthanides are not amalgamated under the same condition, and thus could be removed in the course of electrolysis.

Table 1 Effect of current density on electrolysis

Current density (mA/cm ²)	Recovery as amalgam (%)	Current efficiency (%)
130	88.2 (3 h)	34.5
100	84.1 (4 h)	31.9
50	74.0 (8 h)	28.2

Temperature: 20°C, Flow rate: 5 l/min

**Fig. 3** pH change of catholyte during electrolysis at different current density with flow rate of 5 l/min**Table 2** Analytical data for uranium amalgam and yellow cake

	Yellow cake UHg _x (ppm) [†]	(ppm) ^{††}		Yellow cake UHg _x (ppm) [†]	(ppm) ^{††}
Ag	1.0	1.5	Fe	30	40
B	0.2	0.6	Mn	5.0	<0.4
Cd	0.2	<0.1	Mo	1.0	—
Cr	10	<10.4	Ni	15	20
Cu	50	<1.4	Th	50	—

[†] Data from Eldorado Mining & Refining Ltd., Port Fork, Ontario, Canada.

^{††} Emission spectrographic analysis using Jerral-Ash Model 70-310.

IV. CONCLUSIONS

An electrolyzer designed for the preparation of solid uranium amalgam is described. A continuous operation for 24 h at a current density of 100 mA/cm² converted 1 kg uranium ion into amalgam, corresponding to a power consumption of *ca.* 24 kWh/kg U reduced. The electrolysis could be carried out more efficient at a higher current density,

provided the concentration and the temperature of the catholyte could be kept virtually constant during the process.

Besides the recognized fact that it furnishes an energy-saving facile route to the metallurgy of uranium and the synthesis of organouranium compounds, the present process further offers a possibility of selective amalgamation of uranium from a mixture.

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