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RECOVERY OF U FROM PYROLYTIC CARBON-COATED

UC₂ SPHEROIDS

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H. Katz and J. Wagner
Brookhaven National Laboratory
Upton, L. I., N. Y.

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ABSTRACT

100% recovery of uranium from pyrolytic carbon-coated spheroids of uranium dicarbide has been accomplished by an aqueous electrolytic process at the small scale laboratory level. This result was obtained in a system which circulated 1 molar nitric acid through a thin bed of the spheres. The bed was supported between a glass frit and the anode, with which the bed was in contact. The anode was a spiral of platinum wire; the cathode was a grid of tantalum wire. Current density was about 0.2 amp/cm^2 based on geometric surface area calculated from the average particle size of 150 microns. Initial flow rate was about $1.3 \text{ ml/cm}^2/\text{sec}$. Reaction temperature was $72\text{--}82^\circ\text{C}$; time was 15 hours.

At $1/5$ the above current density and at the same temperature recovery was smaller and was independent of concentration of nitric acid over the range 1-4 molar; also recovery in 1 molar ammonium nitrate was about the same as in 1 molar HNO_3 .

About a 100-fold increase in recovery was obtained by going from a convection stirred cell at 90°C to the pumped type of cell at 54°C using ammonium nitrate as the electrolyte.

Various schemes for the recovery of uranium from nuclear fuels have been reported (1-6). Schweitzer, et al (7) detected U in solution following electrolysis of coated UC_2 particles in a static type cell, like our type II cell, Figure 4. In the present work pyrolytic carbon-coated UC_2 spheroids were electrolyzed in aqueous 1 molar HNO_3 to yield 100 per cent recovery.

RESULTS:

Recovery of U as a function of current density and temperature.

In Fig. 1, uranium recovery is plotted against reaction time. One hundred per cent recovery was obtained in 15 hours. The electrolyte was 1 molar HNO_3 ; current density was about 0.2 amp/cm^2 ; temperature was $72-82^\circ\text{C}$; initial flow rate was about $1.3 \text{ ml/cm}^2/\text{sec}$. The other data suggest that higher current densities and temperatures improve recovery. For example, at a current density of 0.04 amp/cm^2 and 49°C , about 30% recovery was obtained. This is compared with 70-86% recovery at the higher current density and temperatures. At zero current density a recovery of 0.9% was obtained in 18 hours. It also appears that there may be an optimum temperature since our results at 80° were better than at 90° and 64° . The two crosses (+) show the result of using 2 M and 4 M HNO_3 at 85° and 93° respectively, current density 0.04 amp/cm^2 .

EXPERIMENTAL

These results were obtained in a system which circulated the electrolyte through a thin bed of the UC_2 particles supported on a pyrex frit. Fig. 2 is a sketch of the electrolytic cell. The anode, which pressed the particles against the frit, was a flat spiral of 40 mil Pt wire. The cathode was a grid of 40 mil Ta wire. Initial flow rate through the frit was about $1.3 \text{ ml/cm}^2/\text{sec}$. Gas pressure above the anode ranged from 8.5 to 11.5 psig. The frit was standard pyrex, coarse pore size. The area used to calculate current density was obtained by adding the total wetted surface area of the anode to the geometric surface area of the UC_2 particles, assuming a uniform size distribution of spheres. The direction of flow across the bed was chosen so as to hold the particles against the frit and in contact with the anode. Earlier work had shown that contact with the anode was essential.

EARLIER EXPERIMENTS

Some of our earlier runs were made using 1 molar $NH_4 NO_3$ as the electrolyte. In Fig. 3 we have plotted the results on the same scale as the nitric acid data and compared them with the HNO_3 data. The solid lines are the nitric acid data. The triangles show results in $NH_4 NO_3$ obtained at $76^\circ C$. The solid black triangle was run at a current density of 0.02 to 0.03 amp/cm^2 ; the open triangles at 0.01. The circles show results at $54^\circ C$; solid circle at a current density of 0.02 - 0.03; open circles at 0.01.

The square data points were run at 91°C , current density 0.02 - 0.03, but differed from the other points in that they were obtained in a cell shown in Fig. 4. In this cell only force of gravity was used to keep the particles touching the anode, and the anode gas pressure was atmospheric. Going back to Fig. 3, one solid line shows the nitric acid data at 49°C , CD 0.04; and the other the best nitric acid data. The results in NH_4NO_3 suggest that recovery is about the same as in HNO_3 . Also, that the type of cell is very important. In the cell giving 100% recovery, the particles were pressed between the frit and the anode.

DISCUSSION

Fig. 5 is a photograph of the particles showing the appearance before reaction. Note the uniform size distribution. Fig. 6 shows how the particles look after reaction in the Type I cell. See how some have split open. One hollow fragment has a wall thickness about $1/4$ of its diameter, essentially that before reaction.

To get some idea of the current density required to rapidly rupture pyrolytic carbon, a flat specimen, prepared at Brookhaven National Laboratory, was mounted in silicone rubber so that edges and back were masked. It was placed in 1 molar HNO_3 and a current density of 3 amp/cm^2 applied. Within two minutes swelling and flaking occurred. The current density was then reduced to 1 amp/cm^2 .

Flaking continued but at a slower rate. These results suggest again that it may be possible to reduce reaction time by increasing the current density.

Fig. 7 is a comparison of the particle size distribution before and after reaction, plotted on log-normal probability scales.

Note that after reaction and 58% recovery the average particle diameter was about 16% greater than that of the unreacted material. Also, the maximum diameter of the particles was greater than that before reaction, and the proportion of both very large and very small particles was greater. The increase in small particles is attributed to flaking and that in large particles to swelling.

At 100% recovery the average particle diameter was about the same as that before reaction, maximum particle size was greater than before reaction; but less than at 58% recovery. The proportion of very small particles has increased considerably.

In earlier work done by Schweitzer, et al. (7), carbonate was detected in an NH_4NO_3 system, which, of course, suggests oxidation. If a surface oxidation were the only process, a parallel shift in particle size distribution toward smaller diameters would be expected. Since our data do not show this, we conclude that it is a mixed process of oxidation and swelling. This conclusion is also supported by the appearance of the particles after reaction.

A major problem was plugging of the glass frit. We have delayed plugging by placing a fine frit before the cell inlet.

Why is there an apparent temperature maximum for recovery? At 90°C gas bubbles larger than at the other temperatures were observed at the anode. These large bubbles may have blocked the current more than smaller bubbles so that the effective current density may have been less than calculated.

In summary, we have described a method for 100% recovery of U from pyrolytic carbon-coated UC_2 spheroids by electrolysis in an all aqueous solution. We did this in a system which circulated the electrolyte through a thin bed of the particles. The bed was pressed between a porous glass frit and the anode.

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Literature Cited

- (1) Fromm, L. W. Jr. (to U.S. Atomic Energy Commission),
U. S. Patent 2,903,402, (8 September 1959).
- (2) Ferris, L. M.; ORNL-TM-193, (3 April 1962).
- (3) Oak Ridge National Laboratory, p 1-57, ORNL-3314, (21 September 1962).
- (4) Hyde, K. R. and O'Connor, D. J., AERE-R4107, (August 1962).
- (5) Kibbey, A. H. and Ferris, L. M., ORNL-TM-384, (26 September 1962).
- (6) Slansky, C. M., Roberts, M. W., and Rohde, K. L., Nuclear
Science and Engineering 12, 33-38 (1962).
- (7) Schweitzer, D. G.; Singer, R. M.; and Hrabak, G.; Brookhaven
National Laboratory, private communication, 1962.

HIGHER CURRENT DENSITIES AND TEMPERATURE
IMPROVE RECOVERY IN 1 MOLAR HNO_3

FIGURE I

ELECTROLYTIC CELL-TYPE I

FIGURE 2

U RECOVERY IN 1 MOLAR NH_4NO_3

FIGURE 3

ELECTROLYTIC CELL - TYPE II
FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7