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U-Th RECOVERY FROM PYROLYTIC CARBON-COATED CARBIDE FUEL PARTICLES BY ELECTROLYSIS IN NITRIC ACID

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ABSTRACT

Electrodissolver experiments were conducted with pyrolytic carbon-coated UC_2-ThC_2 fuel particles in both a direct contact anode dissolver and a U-shaped "series" dissolver. Under the conditions investigated (HNO_3 concentration, 4-10 M; current density, 1-10 amp/cm^2; temperature 25-80°C), uranium and thorium recoveries were less than 0.2%. The results of these experiments indicated that electrolytic methods are not adaptable to the processing of graphite-base reactor fuels containing carbon-coated particles.

1.0 INTRODUCTION

The purpose of this memo is to summarize laboratory electrolytic experiments relating to the recovery of uranium and thorium from graphite-base reactor fuel elements which contain carbon-coated fuel particles. Prior work on the direct contact anodic disintegration in nitric acid of fuels which did not contain coated fuel particles resulted in nearly quantitative uranium recovery.[1-3] However, in preliminary experiments at ORNL with fuel specimens containing carbon-coated particles, it was shown that although the graphite matrix readily disintegrated when the fuel was made an anode in a nitric acid electrolyte the coated particles were virtually unaffected and the uranium and thorium recoveries were less than 5% (ref. 4). Similar results were obtained at BMI with irradiated coated particle fuels.[5] To avoid the problems of direct contact of the anode with the fuel piece, "series" or "liquid contact" dissolvers were used at ICPP[6] and SRL[7,8] for the dissolution of metallic fuel elements. In this type of dissolver, the fuel pieces are not in contact with either electrode but become separate electrolytic cells under the influence of the overall potential gradient.

Two series of experiments, reported below, were conducted to determine cursorily the influence of nitric acid concentration, current density, and temperature on the recovery of uranium and thorium from a batch of carbon-coated fuel particles. It was hoped that conditions for penetrating the particle coatings could be discovered despite the prior evidence to the contrary. It was assumed that these conditions, if found, would also be satisfactory for recovering uranium and thorium from graphite-base coated particle fuels.

2.0 RESULTS

2.1 Disintegration of Graphite Fuel

Preliminary runs in the U-tube "series" dissolver (Sect. 3.0) using graphite fuel containing about 9% uranium as uncoated UO_2 particles, 10 M HNO_3 at 24°C, and an anode current density of about 1 amp/cm^2 indicated that under these conditions (which are probably not optimum) matrix disintegration does occur slowly with gas evolution at the anode end of the fuel piece. Reversing the polarity of the dissolver electrodes reversed the end of the specimen at which the gas was evolved. The electrodisintegration rate was much lower than the disintegration rate obtained with the same fuel in 90% HNO_3 (ref. 9). In 3- to 4-hr tests at 25°C, complete disintegration was achieved in 90% HNO_3 but only about 10% of the sample disintegrated in the "series" dissolver.

2.2 Experiments with Carbon-Coated UC_2-ThC_2 Particles

Two series of 7-hr experiments, one each in the direct contact anode and "series" dissolvers (Sect. 3.0), were conducted with Batch OR-1 carbon-coated UC_2-ThC_2

particles to evaluate the effects of nitric acid concentration, current density, and temperature on the recovery of uranium and thorium. The UC_2-ThC_2 particles were 147-417 microns in diameter and were coated with 55 to 60 microns of pyrolytic carbon. Only 0.006 and 0.025% of the uranium and thorium, respectively, was lost when a sample of the particles was leached for 5 hr in boiling 90% HNO_3. This test indicated that the integrity of the particle coatings was sufficient for the electrodissolver experiments.

Uranium and thorium recoveries, less than 0.04 and 0.2%, respectively, irrespective of the type of dissolver used (Table 1), were unacceptable for a fuel recovery process. These recoveries were essentially the same as those obtained by leaching the particles with nitric acid alone. Temperature had little effect on the recoveries; but, if a trend is indicated, the recoveries tend to decrease with increasing temperature (Table 1). At constant temperature and electrolyte concentration, an increase in current density from 1 to 10 amp/cm^2 increased recoveries by a factor of 2 to 3. Recoveries were 2- to 4-times higher in the direct contact anode dissolver than in the "series" dissolver, other pertinent conditions being the same.

The extreme conditions of (1) very high acid concentration at a high enough voltage to produce adequate current density and (2) low acid concentrations at high current density near the freezing points of the solutions were not scouted. The effects of additives to the nitric acid electrolyte, other electrolytes, and prolonged soaking of the particles prior to electrolysis were also not studied. Future work should probably be directed along these lines in addition to more experiments with pieces of coated particle fuels. However, the poor results obtained show that nitric acid electrolysis techniques do not warrant further major development effort. As time permits, additional scouting studies will be performed.

3.0 EXPERIMENTAL

The direct contact anode dissolver was a basket-type dissolver whose anode was fashioned from a small platinum crucible (about 0.7 cm^2 on the bottom) welded to a platinum wire. The cathode was a round disc of heavy platinum foil, about 2.5 cm in diameter, welded vertically onto a platinum wire electrode.

The "series" dissolver was a U-shaped, water-jacketed, tube similar to that described by Bomar[6]:

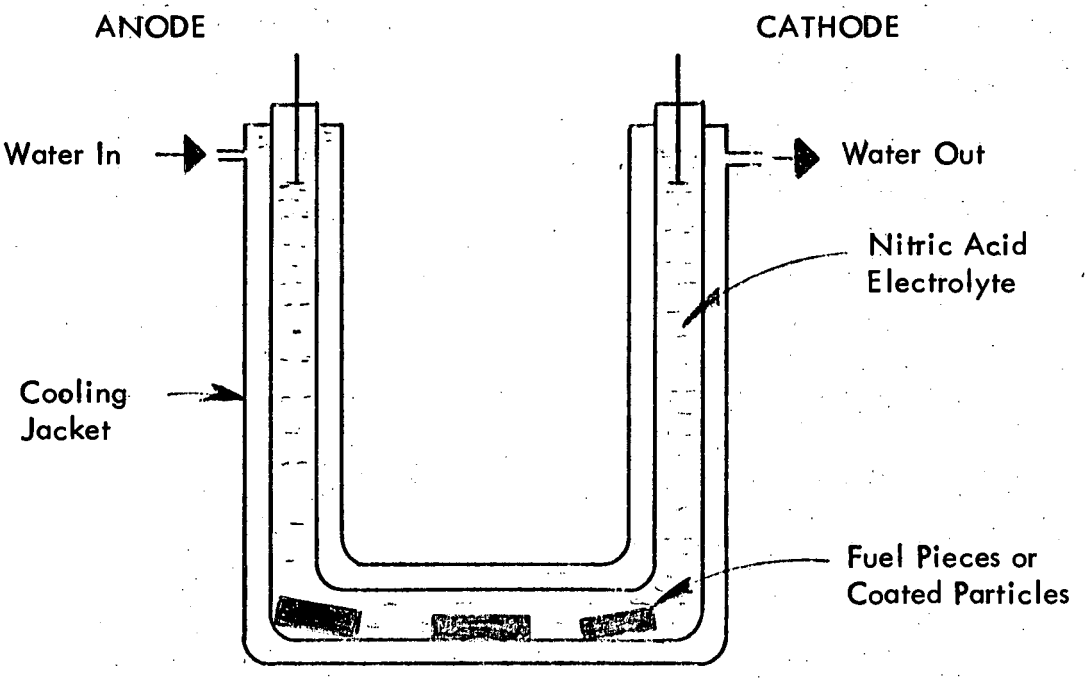
Table 1. Electrodissolver Experiments with Batch OR-1 Carbon-Coated UC_2-ThC_2 Fuel Particles

Conditions: Electrolysis time: 7 hr
Effective electrode areas: 0.7 cm^2

Run No., OR-1-	Type of Dissolver	Fuel Comp., % U	Fuel Comp., % Th	Temp., °C	Current Density amp/cm^2	HNO_3 Conc., M	Recoveries, % U	Recoveries, % Th
1B	None[a]	18.2	43.3	25	0	10	0.013	0.011
9	DA[b]	18.9	42.8	25	1.0	4	0.006	0.050
2	DA	15.0	33.8	30	1.0	10	0.020	0.16
11	DA	18.4	41.8	66	10	4	0.015	0.020
10	DA	18.1	42.3	67	10	10	0.030	0.050
8	Series	12.4	28.5	25	1.0	4	0.020	0.050
1	Series	17.1	37.4	25	1.0	10	0.015	0.014
3	Series	18.	41.	37	1.0	10	0.007	0.030
4	Series	19.2	42.6	52	1.0	10	0.014	0.035
5	Series	19.0	43.5	75-80	1.0	10	0.005	0.012
6	Series	18.7	43.6	32-45	10	10	0.008	0.009
7	Series	19.0	43.1	42	10	10	0.020	0.010

[a] No potential applied.

[b] DA = direct contact anode dissolver.



The electrodes (area of each, 0.7 cm^2) are inserted into the open ends at the top of the vertical U-tube. Current, which passes through the electrolyte, causes formation of a separate electrolytic cell in each piece of fuel or particle.

Temperature was difficult to control in both dissolvers, but was especially so in the direct contact anode equipment which was essentially an open beaker with no condenser or cooling jacket. The "series" dissolver could be immersed in a constant temperature bath and was equipped with condensers on the off-gas vents, but the temperature gradient between the electrode and fuel specimen was often as much as 15°C, since there was no provision for circulation of the electrolyte.

Nitric acid concentrations above 13 molar were found to be poor electrolytes (Fig. 1). The investigation, therefore, was limited to acid concentrations in the range of 4 to 10 molar since current densities of 1 to 10 amps/cm^2 were desired. Higher current densities required higher voltages, and the amount of heat generated rendered the modest cooling system ineffective for preventing boiling of the electrolyte. In addition, at current densities greater than 10 amps/cm^2, excessive foaming occurred which was attributable to increased electrochemical decomposition of the electrolyte at the higher voltage and elevated temperatures which resulted in rapid evolution of gaseous products.

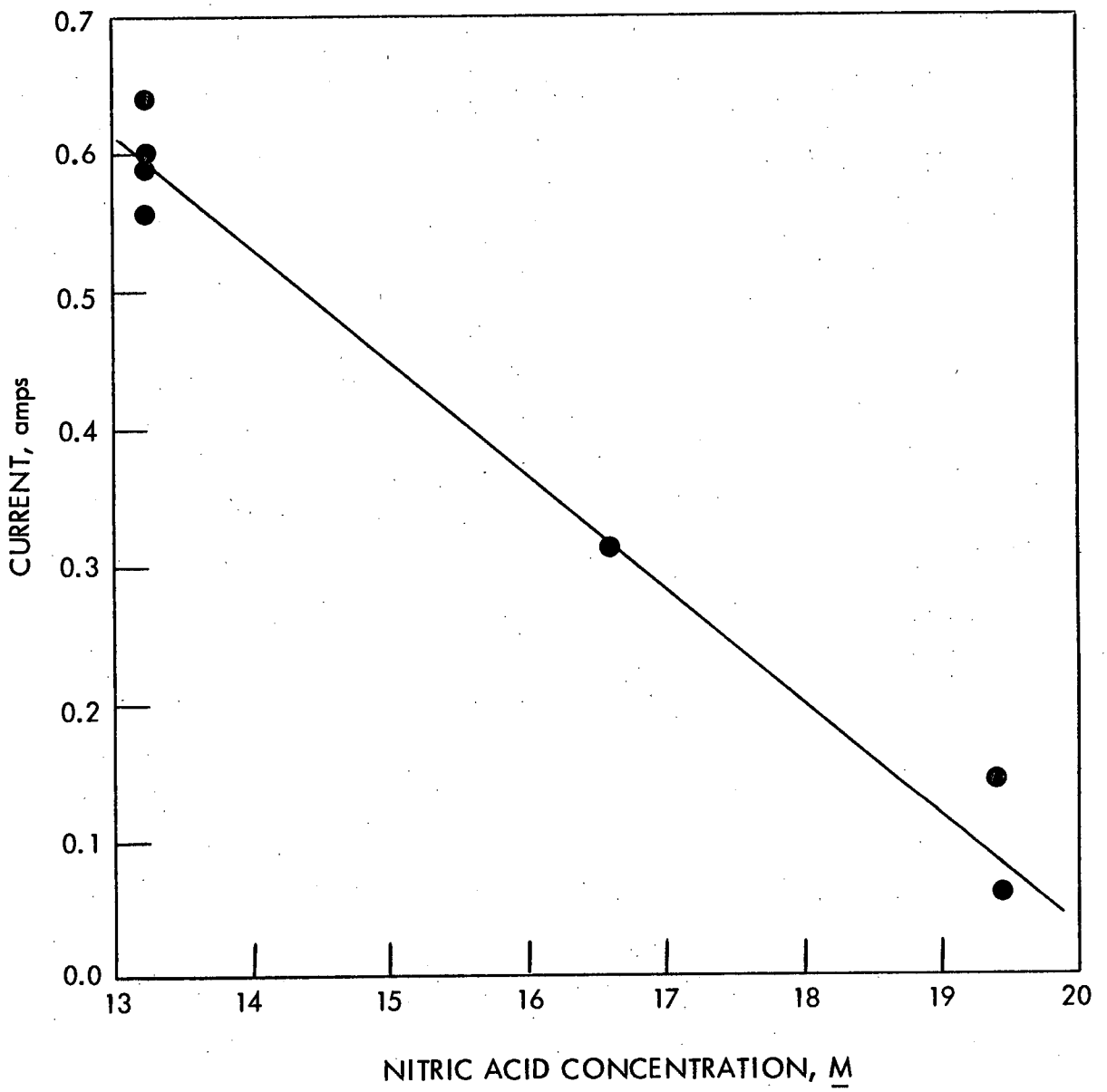


Fig. 1. Effect of nitric acid concentration on current density at constant voltage (18 volts) in the U-shaped "Series" Dissolver. Temperature, 25°C. Electrode area, 0.7 cm^2.

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