



INITIAL TESTING OF MEDIATED ELECTROCHEMICAL OXIDATION FOR INCLUSION IN THE PLUTONIUM-238 PRODUCTION PROGRAM

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Oak Ridge National Laboratory is currently restarting the United States' capability to produce kilogram quantities of ²³⁸Pu annually for space power applications. This involves the purification of ²³⁸Pu from neutron-irradiated ²³⁷Np targets and conversion to heat-source plutonium oxide product for shipment to Los Alamos National Laboratory. Dissolution of the plutonium oxide product material is required to obtain an isotopic assay and impurity analysis of the product material. In addition, any off-specification product will need to be dissolved for re-purification. An electrochemical method that produces highly oxidizing ions in solution is currently being investigated as a rapid method for dissolving these plutonium oxide samples.

I. INTRODUCTION

Radioisotope thermoelectric generators are a key enabling technology for space exploration because they can provide power for many years without reliance on the Sun. This is demonstrated by the successful continued operation of the Voyager space probes for over 40 years, which are now both over 11 billion miles from the Earth and Sun. Radioisotope thermoelectric generators provide power by converting the decay heat of radioisotopes into electricity through the thermoelectric effect. Although other radioisotopes may be used as a heat source for space applications, ²³⁸Pu is the preferred radioisotope for the radioisotope thermoelectric generators produced in the United States.

Recently, Oak Ridge National Laboratory (ORNL) began to reestablish the United States' capability to produce large quantities of ²³⁸Pu with a targeted average production rate of 1.5 kg of plutonium oxide per year. The ²³⁸Pu is produced by irradiating ²³⁷Np in a nuclear reactor, such as the High Flux Isotope Reactor at ORNL and the Advanced Test Reactor at Idaho National Laboratory. The purified plutonium oxide material is produced through radiochemical processing of the irradiated targets at the Radiochemical Engineering Development Center (REDC) at ORNL. Refractory plutonium oxide samples, which are notoriously difficult to dissolve, are produced during this production process and need to be analyzed. Traditional dissolution approaches involve the use of hydrofluoric

acid [1,2]. This results in a more complicated waste stream due to the presence of fluoride. Additionally, the hydrofluoric acid approach takes several days. This may negatively impact production efforts when, for example, continued progress is dependent on analytical sample results. It is also necessary to dissolve in the hot cell any off-specification product that is produced. Solutions containing fluoride cannot be used inside REDC's hot cells due to incompatibility with infrastructure materials. It is for these reasons that an alternative dissolution method is desired that does not use hydrofluoric acid. One such method, called Mediated Electrochemical Oxidation (MEO), is to use an electrochemically produced oxidizing agent, such as Ag(II) [3-9]. It should be noted that this method has historically been called Catalyzed Electrochemical Plutonium Oxide Dissolution (CEPOD), and MEO is a generalized term for the approach. CEPOD has been used to dissolve plutonium oxide at production scale for several decades and continues today [3-9]. This paper summarizes results from initial testing of MEO for inclusion in the ²³⁸Pu production program's radiochemical processing scheme as a method for dissolving plutonium oxide material.

II. EXPERIMENTAL

The electrochemical cell used for these initial tests was a bulk electrolysis cell kit (MF-1056) purchased from Bioanalytical Systems Inc. The components used from the kit were a reticulated vitreous carbon working electrode, a coiled platinum auxiliary electrode, an auxiliary electrode chamber with a glass frit separator, a 100 mL glass cell vial, a Teflon cell top, and a Teflon stir bar. An additional platinum gauze working electrode (NM-D001) was purchased along with the bulk electrolysis cell kit. Experiments were completed with either the reticulated vitreous carbon electrode or the platinum gauze electrode. A picture of the electrochemical cell with the platinum gauze working electrode set up in the glovebox is presented in Figure 1. The larger compartment contained the dissolver solution (anolyte) and the plutonium oxide samples. The smaller compartment contained the catholyte solution. The use of silver as the oxidizing agent required the use of a double electrochemical cell to

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prevent electroplating of the silver onto the cathode. The catholyte and anolyte solution compartments were separated by the glass frit in the auxiliary electrode chamber. A constant voltage of 5 V was used for the dissolutions.

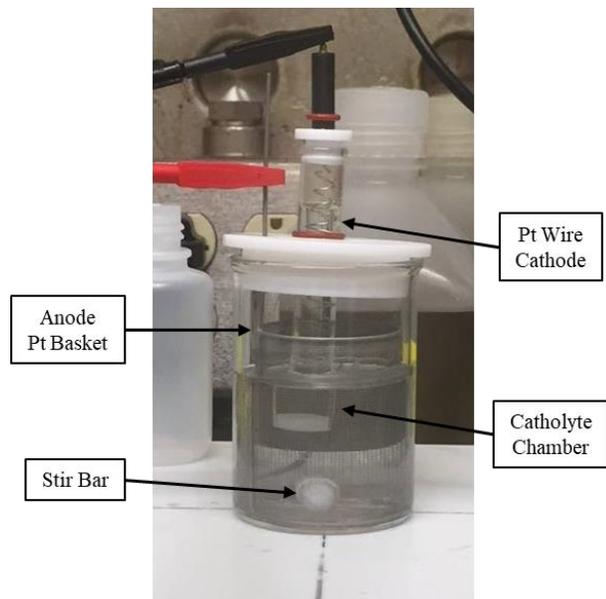


Fig. 1. Electrochemical cell used for initial testing in a glovebox.

The anolyte solutions used were either (a) 0.01 M Ag(I) in 2 M HNO₃ or (b) 0.1 M Ag(I) in 4 M HNO₃. The catholyte solutions were always 8 M HNO₃. These solution parameters were based on recent work at the National Nuclear Laboratory in the United Kingdom [7, 8]. The samples were analyzed using total pulse height alpha analysis and alpha spectroscopy to determine the total amount of dissolved material. The ²³⁸Pu has a strong alpha emission around 5.5 MeV. Results were compared to those obtained by calorimetry of the bulk oxide material in the hot cell before obtaining a small sample for transfer to the glovebox laboratory where MEO testing was performed.

III. RESULTS AND DISCUSSION

The first dissolution test with plutonium used 24 mg of a plutonium oxide sample that was 97 wt.% plutonium oxide with the ²³⁸Pu present as 88% of the total plutonium. Thus, 18 mg of ²³⁸Pu would be expected to be dissolved with 100% dissolution of the plutonium oxide in the sample. The plutonium oxide had been heat treated to 850 °C. Two different anolyte solutions were used for the first test. The first 1.5 hours of dissolution used a 0.01 M Ag(I) in 2 M HNO₃ anolyte solution. After 1 hour of dissolution time, the power supply and magnetic stirrer were turned off. It was then observed that the dark grey

color, which indicates the presence of Ag(II) ions, disappeared from the bottom upward. In contrast, solutions with Ag(II) ions that did not contain plutonium oxide took significantly longer to lose the dark grey color and did so evenly throughout the entire solution volume. It was then concluded that the Ag(II) ions were continuing to react with the undissolved plutonium oxide powder that was seen in the corners of the glass cell. Figure 2 shows several pictures of a solution containing electrochemically produced Ag(II) ions and undissolved plutonium oxide powder at different times. This can be used as a simple indicator to determine whether the sample has completely reacted with the undissolved solid material.

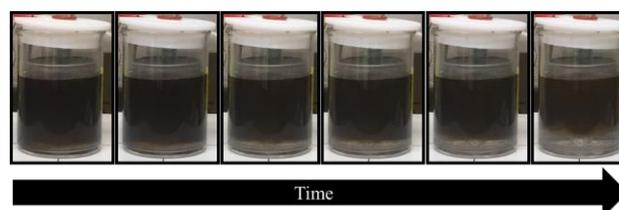


Fig. 2. Electrochemically produced Ag(II) containing solution in contact with plutonium oxide powder at different times.

The power supply and magnetic stirrer were turned on again for another 0.5 hours. The experiment was then paused to obtain results from radioanalytical measurements of sample aliquots taken at 1 and 1.5 hours of dissolution. After obtaining the results (see Table 1) for 1 and 1.5 hours of dissolution time, it was seen that only 44% of the sample had dissolved within 1.5 hours, and a relatively small amount of plutonium had dissolved in the 0.5 hour between samples. The anolyte was then switched to 0.1 M Ag(I) in 4 M HNO₃ solution for the remaining 1.5 hours. A higher concentration of silver and nitric acid was expected to increase the dissolution rate. It was noticed during the dissolution that the liquid volume in the anolyte compartment was increasing. This was due to solution from the catholyte compartment, which required refilling every 0.5 hour, leaking into the anolyte compartment through the glass frit separator. After 3 hours of total dissolution time, there was no observable solid powder remaining in the dissolution cell, and the experiment appeared to be complete. Radioanalytical results, however, measured only 73% of the expected plutonium in solution. This was due to the original anolyte solution volume being used despite a noticeable increase in solution volume. This would account for the complete disappearance of plutonium oxide powder, indicating complete dissolution, while measuring only 73% of the material dissolved through radioanalytical measurements.

To overcome the anolyte solution volume error associated with the first dissolution test, the mass of the anolyte solution for the second dissolution test was measured before the experiment was started and at each point a sample was taken. A density of 1.1 g/mL (based on 4 M HNO₃) was used to convert from the measured solution mass to solution volume. The second dissolution test was accomplished with 286 mg of a plutonium oxide sample that was 34 wt.% plutonium oxide with the ²³⁸Pu present as 72% of the total plutonium. Thus, 62 mg of ²³⁸Pu would be expected to be dissolved with 100% dissolution of the plutonium oxide in the sample. A noticeable difference between the two samples is the percentage of plutonium oxide. The first sample was close to pure plutonium oxide, whereas the second sample was only 34 wt.% plutonium oxide. The remaining mass is likely to be mostly carbon and had a sludge-like appearance. It was therefore not expected to fully dissolve. Rather, it was expected that the plutonium could be dissolved from the material for assay.

Samples of the anolyte solution for the second test were taken at 1 and 4 hours. Radiochemical analysis showed that 78% of the plutonium had dissolved in 1 hour, and 95% had dissolved in 4 hours. These results matched well with those obtained using the hydrofluoric acid to dissolve the sample. However, the hydrofluoric acid dissolution took several days, whereas the same percentage of dissolution was achieved using MEO in only 4 hours.

	Time (h)	²³⁸ Pu by alpha (mg)	Percent dissolved (%)
Test One	1	7.0	39
	1.5	8.0	44
	2.5	12.7	71
	3	13.2	73
Test Two	1	48.0	78
	4	58.6	95

Table 1. Table of experimental results from the first two tests of MEO to dissolve plutonium oxide samples. The final result for test one of 73% is suspect because of the noticeable volume increase in the anolyte solution. It is likely that the plutonium oxide was completely dissolved based on the absence of any visible material in the anolyte solution at 3 hours for test one. The results from test two have been corrected for the volume change by measuring the mass of solution before, throughout, and after the dissolution.

IV. CONCLUSIONS

A preliminary test of dissolving plutonium oxide samples for assay and impurity analysis using MEO was completed. The results from initial tests were promising. A significant improvement in the dissolution time of plutonium oxide samples was achieved. Instead of several days of dissolution with hydrofluoric acid, dissolution only took several hours using the MEO approach. This shows that MEO will be useful for rapid dissolution of off-specification product in hot cells and that it has promise as for routine analytical sample dissolution. It is expected that the procedure can be improved through the study of parameters including electrochemical cell geometry, electrode material, and solution composition. These and other parameters are currently being evaluated through further testing. It is expected that MEO will be routinely used for dissolving plutonium oxide samples for radiochemical analysis at REDC once a final, optimized procedure is developed.

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