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Dissolution of Light Curium Oxide with a Catalyzed Electrolytic Process

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Nuclear Security and Isotope Technology Division

DISSOLUTION OF LIGHT CURIUM OXIDE WITH A CATALYZED ELECTROLYTIC PROCESS

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1. INTRODUCTION

1.1 BACKGROUND

The ability to produce transcurium elements and isotopes, such as ^{249}Bk and ^{252}Cf, requires the appropriate feed material and a high thermal neutron flux. Currently, at Oak Ridge National Laboratory (ORNL), the High Flux Isotope Reactor (HFIR) provides one of the world's highest steady state thermal neutron fluxes. The feed material consists of recycled curium from the decades of production of ^{249}Bk, ^{252}Cf, ^{253}Es, and $^{255/257}$Fm at the Radiochemical Engineering Development Center (REDC). Over time, the feed material has been depleted and needs to be replenished.

The current feed material is called "heavy recycled curium" and consists of over 50 wt% of $^{246/248}$Cm isotopes. In order to replenish this stock material, additional curium is needed. The only curium material that is currently available consists predominantly (greater than 80 wt%) of ^{244}Cm. This material also contains ^{240}Pu from the radioactive decay of the ^{244}Cm. Because of the amount of ^{244}Cm is greater than 50% of the total Cm, this material is termed "light curium."

Today, ^{249}Bk and ^{252}Cf are produced in only two places in the world: the United States and Russia. In the United States, the US Department of Energy and its predecessors have made these isotopes and others available to research agencies and commercial users since the late 1960s as part of the Department of Energy heavy-element production program located at ORNL. Currently these materials are provided through the DOE Office of Science Nuclear Physics-Isotope Development and Production for Research and Applications and the Basic Energy Science-Heavy Element Chemistry.

Feedstock for the production of ^{252}Cf and other transcurium element by-product isotopes was originally prepared by means of irradiation of multi-kilograms of ^{239}Pu in the large production reactors at the Savannah River Site. Products of the Savannah River Site irradiation were predominantly ^{242}Pu, ^{243}Am, and ^{244}Cm. These materials were shipped to ORNL for production of multi-milligram amounts per year of ^{252}Cf and other transcurium element isotopes by means of irradiation in the HFIR, followed by separation and purification processing in the Radiochemical Engineering Development Center (REDC). The transcurium element isotopes produced were distributed to other US and collaborating foreign laboratories for research studies to determine the nuclear and chemical properties of these rare materials.

The Cm feed material plays a key role in the efficient production of ^{252}Cf. The early targets irradiated in HFIR contained only the ^{242}Pu, ^{243}Am, and ^{244}Cm produced at Savannah River Site, and the rate of production of ^{252}Cf was less than 1 mg per 8 g of target material as shown in Figure 1. Also, shown in Figure 1 is the significant difference in ^{252}Cf production between the light and heavy curium; it differs by approximately 2 orders of magnitude.

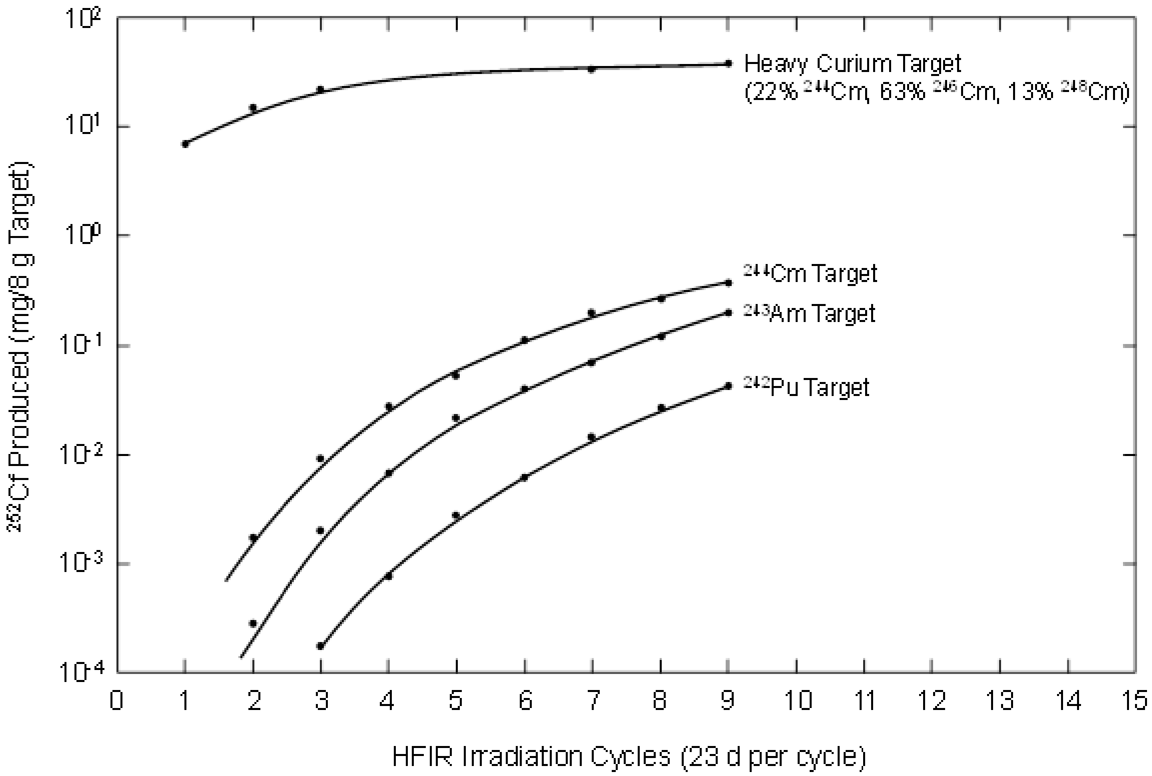

Figure 1. Production rate for ^{252}Cf.

1.2 FEED MATERIAL CONCERNS

Light curium, as mentioned previously, consists primarily of ^{244}Cm, which has an 18.1-year half-life and decays to ^{240}Pu via alpha-decay. The current inventory of light curium at REDC is over 40 years old and contains a significant quantity of ^{240}Pu. Because of the age of the material, the PuO_2 requires a special dissolution technique so that the Pu can be separated from the curium.

1.3 SUMMARY OF CEPOD TECHNOLOGY

Many of the problems faced with industrializing and reprocessing nuclear reactor fuels, often fabricated from mixed oxides, stem from the difficulties of dissolving PuO_2 and the separation of the material from the solution. The dissolution process is almost completely unsuccessful without the presence of concentrated HNO_3 containing fluoride ions. These fluoride ions successfully complex Pu^{4+} and therefore increase the solubility and rate of dissolution.

Although fluoride ions are known to enhance the solubility of PuO_2, they are corrosive to glass and many metals, thus they can attack and ruin tanks and piping they contact. Fluoride ions can also cause problems with absorbance spectrophotometric measurements that are used to monitor concentrations and valence states. Because of the undesirable properties of fluoride ions, it is advantageous to increase the dissolution of actinide oxides by using other methods, with the primary goal of limiting the production of waste materials.

Catalyzed Electrolytic Plutonium Oxide Dissolution (CEPOD) technology was first developed in the 1970s at Pacific Northwest National Laboratory and ORNL to accelerate the complex task of dissolving PuO_2 and other actinide oxides without problematic corrosive fluoride ions. Ryan et al. describe the electrochemical process to dissolve plutonium oxide with nitric acid and elements that form strong oxidizing ions, generally Ag^{2+}, Ce^{4+}, Co^{3+}, or AmO_2^{2+}. The oxidation capacity of these ions is illustrated by their ability to attack stainless steel [1].

Plutonium oxide is dissolved by placing the required components in an electrolytic cell. A platinum or platinum-coated electrode is used as the anode. When electrical current is applied to the cell, catalyzing ions such as Ag^{2+}, Ce^{4+}, Co^{3+}, or AmO_2^{2+} are converted from their base valence state to higher oxidation states on the surface of the anode to serve as strong oxidizing ions (e.g., $Ag^+ \rightarrow Ag^{2+}$). As a strong oxidizing ion encounters PuO_2, it is reduced back to its base valence state. Because base valence state ions are not oxidizers, these ions need to be reconverted again. When base-state ion comes in contact with the anode, it is re-oxidized, and the dissolution process continues. An electrical current is continuously applied to the electrodes of the electrolytic cell to continuously regenerate the oxidizing ions. Because the oxidizing ions can be regenerated, the concentration of the catalyzing ions can be low. It is typically necessary to perform downstream processing to separate the catalyzing ions from plutonium; therefore, it is beneficial to keep the concentration of the catalyzing ions low.

1.4 LITERATURE REVIEW

Numerous experiments throughout the years have been conducted to rapidly dissolve PuO_2, which is insoluble without the use of nitric acid or catalysts. In the past, it was found that plutonium oxide dissolution was increased by using hot concentrated nitric acid and fluorine ions, but this method is not desirable because of the corrosive solutions that are created. Experimentation dating back to the 1960s demonstrated early electrolytic dissolution processes to eliminate the use of HF and to promote faster dissolution rates.

In 1968, Berry and Miner demonstrated a process of rapid dissolution of plutonium in nitric acid containing fluorine ions using electrolysis. They determined that factors such as nitric acid concentration, fluorine concentration, and current density have a significant effect on the rate of dissolution, with current density having the largest impact. The optimal conditions observed in this experiment were with a nitric concentration of 15.0 *M*, a fluorine concentration of 0.13 *M*, and a current density of 10 A [2].

Several years later in 1977, D. E. Horner et al. in "Cerium-Promoted Dissolution of PuO_2, and PuO_2-UO_2 in Nitric Acid" demonstrated the use of cerium(III) to enhance the dissolution rate of plutonium oxide, credited with the oxidation of cerium(III) to cerium(IV). This study showed that the dissolution rate of plutonium oxide increased from 2 to 4 *M* nitric acid and drastically decreased after concentrations higher than 4 *M.* This experiment verified that catalysts other than fluorine were capable of enhancing dissolution rates [3].

After years of suboptimal dissolution methods, Ryan et al. successfully demonstrated CEPOD technology, introducing silver as a catalyzing oxidized ion. Further tests have been conducted to isolate variables that could influence the dissolution rate. In 2003, P. J. W. Rance et al. mirrored the experimentation performed by Ryan et al. to observe the contributing variables of dissolution rates. Ryan's work concluded that increasing the specific surface area of plutonium oxide affected by the calcination temperature increased the rate of dissolution. The process is most successful at moderate temperatures to limit the reaction of silver ions with water. Lastly, molybdenum, palladium, and ruthenium compounds have been proven to slow the dissolution rates [4].

2. DESCRIPTION OF CEPOD SYSTEM

The CEPOD system includes two chambers separated by a semi-permeably glass frit. Because the chemical reactions that occur in the cathode chamber would strongly interfere with desired reactions in the anode chamber, it is necessary to have separated chambers. The separation is achieved using a membrane that permits an electrical current to pass through it, while preventing or minimizing the transfer of liquids between the two chambers. The electrodes are positioned within the chambers and connected to a direct current power supply. A diagram of a CEPOD unit is displayed in Figure 2, and schematics of the anode and of the cathode chamber are shown in Figures 3 and 4.

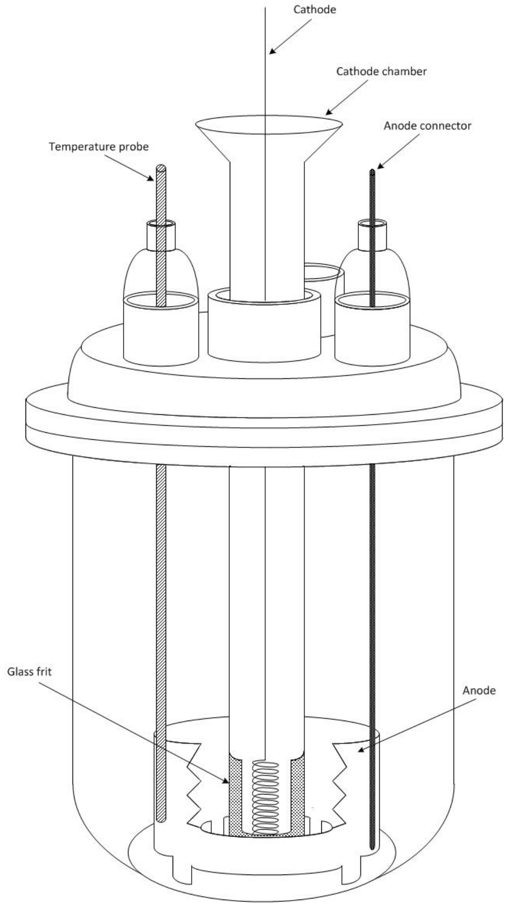

Figure 2. Diagram of CEPOD unit. Cutaways in the cylindrical anode and glass frit portion of the cathode chamber are included for clarity.

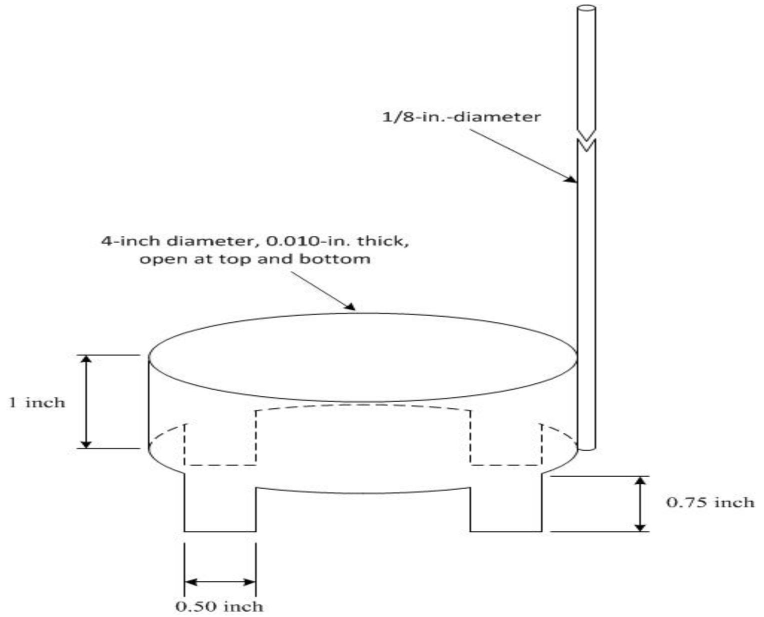

Figure 3. Schematic of anode and anode connector. The anode had a diameter of 102 mm (4 in.), with both the top and the bottom open. The platinum thickness was 0.25 mm (0.010 in.).

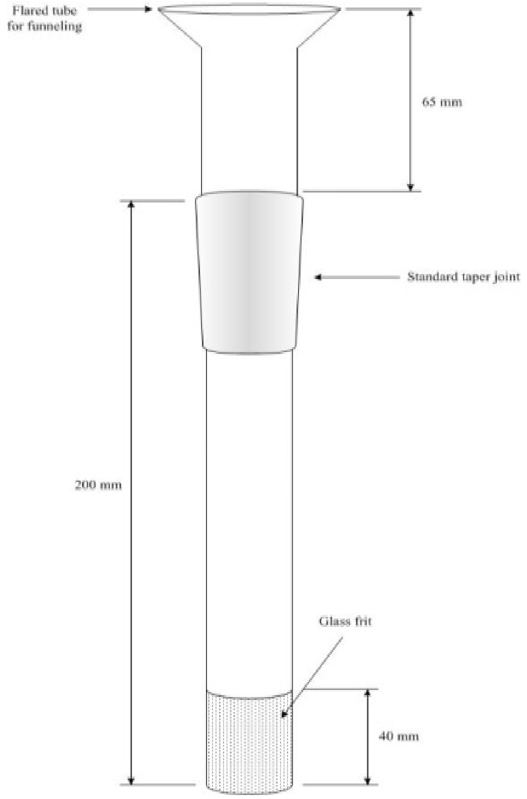

Figure 4. Schematic of cathode chamber. This tube was inserted through a standard-tapered joint opening through the top of the lid of the dissolution vessel.

2.1 DISSOLUTION VESSEL

A 2-L Pyrex® 6947 pot was used as the dissolution container for this experiment. Glass was selected as the vessel media primarily for its chemical resistance to the process components; however, it also provided researchers the ability to visually observe the process. The lid included four standard-tapered joint openings that allowed for the insertion of the anode, cathode chamber with inserted cathode, and temperature sensor, as well as for the addition of solutions. The height of the dissolution pot and lid was approximately 230 mm (9 in.).

2.2 ANODE

The platinum anode, illustrated in Figure 3, was custom fabricated into an open-ended cylinder. It had a diameter of 102 mm (~4 in.), height of 25 mm (1 in.), and thickness of 0.25 mm (0.010 in.). As shown in Figures 2 and 3, the platinum cylinder was positioned off the bottom of the pot with four legs. These legs allowed the stirring action of the spinning magnetic stirrer bar to (1) homogenize the solution on both sides of the cylinder and (2) agitate undissolved particles between the anode and walls of the pot. A ~3-mm-diameter (0.125-in.) connector rod was welded to the platinum cylinder. This connector rod was comprised of 90% platinum and 10% rhodium to provide rigidity. The connector rod extended through one of the ports in the lid. The positive side of the power supply unit was connected to the connector rod with an alligator clip.

2.3 CATHODE CHAMBER

A schematic of the cathode chamber is displayed in Figure 4. The cathode chamber was held in the center standard-tapered opening of the lid of the dissolution vessel. It was custom fabricated by Ace Glass Incorporated with a high-density porous-glass frit (~40 mm long) on the bottom end. The length of the chamber was designed so that the magnetic stirring bar would spin unimpeded. The glass frit had a porosity of 4–8 μm (Ace Glass porosity E). As illustrated in Figure 2, a cavity was formed in the glass frit to increase the surface area through which electrical current could flow. A flared lip was included at the top end of the chamber to aid in the addition of fluids to the chamber.

The cathode was formed from a titanium rod approximately 3 mm (1/8 in.) in diameter. The bottom end was coiled to increase the surface area of the cathode. As shown in Figure 2, the coil rested on the glass frit, and the rod extended above the flared lip of the cathode chamber to allow proper connection to the power supply with an alligator clip. The entire rod extended to a height of ~432 mm (17 in.).

2.4 TEMPERATURE MEASUREMENT

Temperature measurements during cold testing were observed with a glass thermometer. In the hot cell testing, a titanium-sheath type K thermocouple probe (1.6-mm diameter [1/16 in.] and 305 mm [12 in.] long) was used to monitor the temperature. The thermocouple probe was constructed with a titanium sheath to prevent chemical attack by the catalyzing ions (e.g., Ag^{2+}, Co^{3+}) on the thermocouple probe. The thermocouple probe was inserted into the solution in the dissolution pot through one of the outer ports in the lid.

2.5 HOT PLATE/MAGNETIC STIRRER

When desired, the solution in the dissolution vessel was heated and stirred by a hot plate/magnetic stirrer while the hot plate applied heat directly to the dissolution pot. The solution temperature was manually controlled with the hot plate's thermostat. Heat was also introduced into the solution by the electrical current flowing between the anode and cathode and from the ambient air within the hot cell. A 51-mm (2-

in.) Teflon^{TM}-coated magnetic stirring bar was used in the anode chamber to disperse solid particles, homogenize the liquid, and enhance transporting the reduced ions back to the anode for reconversion to the catalyzing state.

2.6 POWER SUPPLY

An Agilent Technologies Model E3644A power supply was used to provide and control the electrical current and voltage applied to the anode and cathode. This unit was located outside of the hot cell. This power supply unit has two supply ranges: (1) up to 8 V and 8 A, and (2) up to 20 V and 4 A. The 8 V/8 A range was used for the CEPOD operations. The 20 V/4 A range was used during cold testing for recovering silver from the solution. The power supply cables were connected to the anode and cathode by alligator clips.

2.7 SPECTROPHOTOMETRY

An Ocean Optics ultraviolet-visible (UV-VIS) and near infrared spectrophotometer was used to obtain spectrophotometric data. The analyses were performed with low-volume plastic cuvettes with a path length of 1 cm. Blank samples were taken with deionized water and various concentrations of nitric acid.

In this experiment, the spectrophotometric data was used to monitor the concentrations of plutonium(IV) and plutonium(VI) to determine the rate of dissolution and verify the effectiveness of the CEPOD unit. In reference [5], D. J. Mahildoss et al. demonstrated the use of spectrophotometric peaks to characterize the various oxidation states of plutonium (III), plutonium (IV), and plutonium (VI) [5]. Table 1 provides data for the adsorption peaks of the different oxidation states.

Table 1. Absorption peaks for Pu(III), Pu(IV), and Pu(VI)

	Peak 1 (nm)	Peak 2 (nm)	Peak 3 (nm)	Peak 4 (nm)
Pu(III)	566	602	660	—
Pu(IV)	422	476	660	800
Pu(VI)	831	—	—	—

Note: Table adapted from data provided in J. Mahildoss and T. N. Ravi, “Spectrophotometric Determination of Plutonium III, IV, and VI Concentrations in Nitric Acid Solution,” *Journal of Radioanalytical and Nuclear Chemistry* 294 (1): 87–91. © 2012 Springer. Experimental data determined that plutonium(VI) peaks at 950 nm and 980 nm as well.

3. EXPERIMENTAL ACTIVITIES

Cold testing (i.e., non-radioactive) and hot cell work was conducted at the REDC. The cold testing was conducted in a fume hood, and the hot work was conducted in a highly shielded hot cell. The hot cell runs were named 75ED-1 through 75ED-12.

The literature indicates that the Ag^{2+} ions are more aggressive than the Co^{3+} and Ce^{4+} ions [1]. However, literature also indicates that when the solution temperature exceeds 40°C, the effectiveness of the Ag^{2+} ions is limited because of a competing reaction of Ag^{2+} with water molecules in the solution. The hot cell's ambient temperature is typically 30°C–35°C. Because the application of current between the electrodes induces Joule heating, it was difficult to maintain the solution temperature under 40°C. In addition, cooling the solution in the existing facilities is difficult because chilled water is not piped into the hot cells except for pre-installed systems. Although, the dissolution pot could be outfitted with a cooling water jacket, experience has shown that the jacket can be easily broken in the hot cell environment. Once-through chilled water could be routed into hot cells from a tank in the chemical make-up area, but the temperature of the water would likely approach ambient by the time it reached to the pot. Dispositioning the once-through cooling water would also create an additional challenge because it would represent a significant volume of liquid waste. Finally, introducing a chiller unit into the hot cells is not an option because these units do not typically work well at the ambient temperature in the cells, and they would occupy valuable floor space, which is already limited.

After the CEPOD dissolution method is complete, the catalyzing ions typically need to be separated from the actinide product. For example, if cobalt was left in the product with the curium and subsequently used to prepare Cf-252 production targets for irradiation in HFIR, the neutron bombardment that converts the curium to californium would also cause cobalt to be converted to ^{60}Co. Because ^{60}Co emits high-energy gamma rays, its presence could complicate the handling and processing of the material.

Although, cobalt may introduce an issue as described above, it was considered easier to separate cobalt from the dissolution product than silver or cerium. Even though Co^{3+} is not as aggressive as Ag^{2+}, it was considered advantageous if cobalt could be demonstrated to effectively dissolve the plutonium and curium oxide materials.

3.1 COLD TESTING WORK

A series of cold tests was conducted with cobalt in various concentrations of nitric acid solutions to ensure that the cobalt ions could be successfully oxidized. Cold testing was also performed with silver in case the cobalt ions were not effective at dissolving the plutonium and curium oxides.

3.1.1 Cobalt

Process Parameters

The CEPOD unit was set up in a fume hood at the REDC. Cobalt nitrate hexahydrate (ACROS Organics, 99.0% minimum) was used to prepare cobalt nitrate solutions with concentrations ranging from 0.005 to 0.05 M in 4 M HNO_3. Nitric acid with a concentration of 6 M was placed in the cathode chamber. Both the anode and cathode were connected to the DC power supply providing a current ranging from 1 to 3 A to convert cobalt(II) ions to cobalt(III) ions. Equation (1) displays the chemical reaction for the cobalt ions at the anode. At the cathode, nitric acid is consumed, so it is necessary to periodically replenish the nitric acid in the cathode chamber. Ryan et al. present a more thorough discussion of the cell reactions that occur during the CEPOD process [1].

$$\mathrm{Co^{2+} \rightleftharpoons Co^{3+} + e^{-}} \qquad E^{0} = 1.82\ \mathrm{V} \tag{1}$$

Cobalt(II) has a pink color in aqueous solution of nitric acid while cobalt(III) has blue color. As the current was applied, the solution initially changed from pink to purple and finally to blue. The blue color became darker while the current was continued to be applied (see Figure 5). The color change from pink to blue is a visual indication that the cobalt(II) was successfully oxidized to cobalt(III).

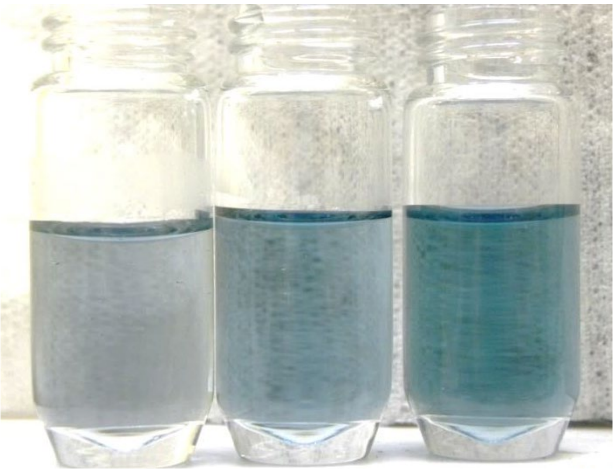

Figure 5. Cobalt(II) oxidation to cobalt(III). Samples were taken from the dissolution pot at various times. *Left* to *right*, samples taken after 41 min, 57 min, and 75 min of applied power.

When performing a valence conversion test, electrical current, voltage, and solution temperature were observed. UV-VIS spectrophotometry samples were taken intermittently to monitor the concentration of cobalt(II) and cobalt(III). A solution of 0.05 *M* Co–4 *M* HNO_3 was prepared and subjected to the electrolytic process. A sample of the resulting solution was analyzed by UV-VIS (Figure 6). The spectra showed that peaks were occurring at 410 and 606 nm, indicating that Co^{3+} was heavily prominent in the solution.

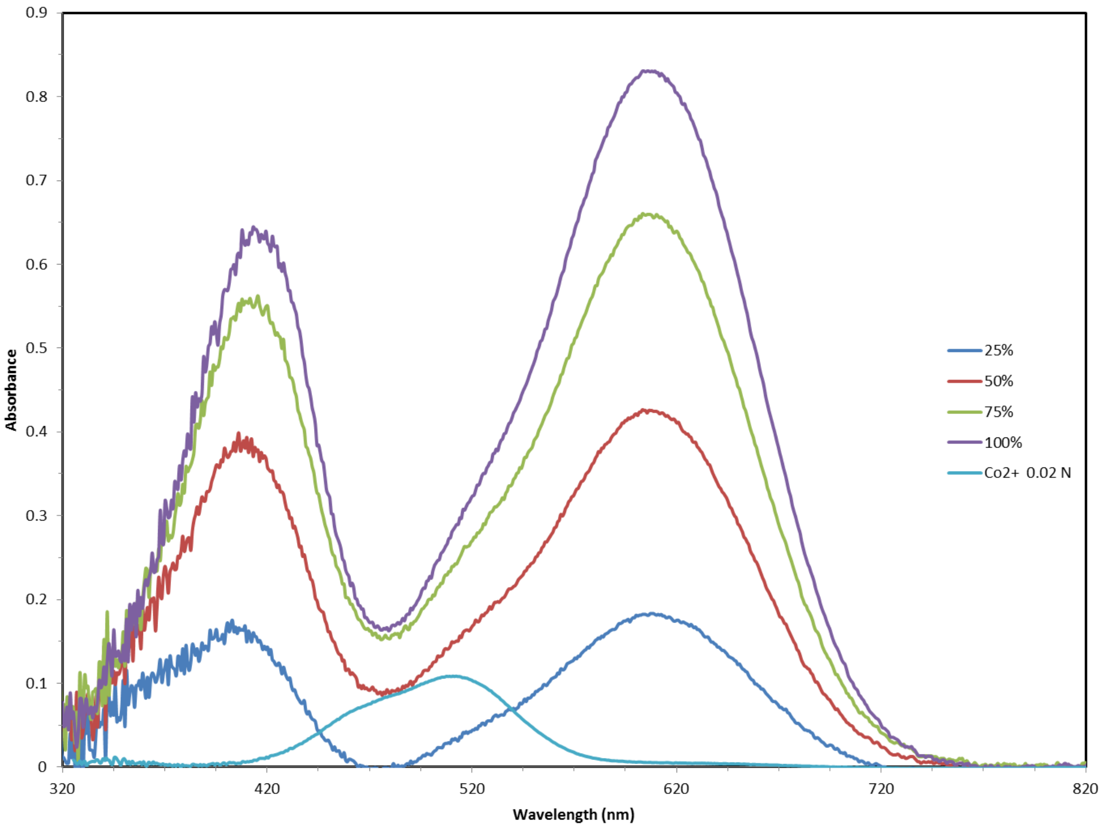

Figure 6. UV-VIS spectrum for 0.05 *M* Co–4 *M* HNO_3 solution following conversion of Co^{2+} to Co^{3+}. The actual conversion efficiency is unknown. The percentage values in the legend represent the concentration of Co^{3+} that resulted from the conversion process. For comparison purposes, a spectrum of Co^{2+} is included in the graph to show the difference in the peak positions.

Various dilutions with 4 *M* HNO_3 were made with the solution obtained following the conversion process, and then those dilutions were also analyzed using UV-VIS. For comparison purposes, a spectrum of 0.02 *M* Co^{2+} is shown in Figure 6 to illustrate the peak position differences between Co^{2+} and Co^{3+}.

Several hours after the voltage was discontinued, the solution color faded to a purple tint, and spectrophotometry results indicated that concentration of Co^{3+} was nearly depleted. To determine the effect of solution temperature on the concentration of Co^{3+}, the standard conversion process was performed to generate the blue-colored solution at ambient temperature. While continuing to apply current to the electrodes, the solution temperature was gradually increased by applying heat with the hot plate/magnetic stirrer unit. The solution temperature was increased up to ~90°C. The results showed that the blue color changed back to pink as the temperature increased. This indicates that the Co^{3+} is reacting rapidly with the water in the solution. Increasing the applied voltage did not appear to effectively overcome the reaction of Co^{3+} and water. Because of this, there was concern that it might not be possible to produce cobalt(III) in the hot cells because of their higher ambient temperature.

3.1.2 Silver

Process Parameters

Because there was a concern that cobalt would not be an effective catalyst in the hot cell environment, cold testing with silver in nitric acid was also evaluated with the CEPOD system. Equation (2) displays the oxidation reaction of silver at the anode. Nitric acid is consumed by chemical reaction at the cathode, so it is necessary to periodically replenish the nitric acid in the cathode chamber. Ryan et al. present a more thorough discussion of the cell reactions that occur during the process [1].

$$Ag^+ \rightleftharpoons Ag^{2+} + e^- \qquad E^0 = 1.98\ V \tag{2}$$

The anolyte contained 0.005 *M* Ag and 4 *M* HNO_3, and the catholyte contained 8 *M* HNO_3. Voltage was applied to the process at 3 V while nitric acid (70%) was metered into the cathode chamber at ~0.3 ml/min to continuously replenish nitrate ions reduced by the electrolysis process. When the voltage was applied, the anolyte immediately began producing brown plumes, a visual indication that Ag^{2+} ions were being produced, at the anode surface. Within minutes, the anolyte had changed from colorless to a dark brown color. Heat was applied to the solution to simulate the temperature of the hot cell, which is typically between 30°C and 35°C. Based on visual observation that the brown color dissipated, it was shown that the temperature had a negative impact on maintaining the concentration of Ag^{2+}. UV-VIS spectrophotometric measurements confirmed that the concentration of Ag^{2+} was depleted. The depletion of the Ag^{2+} is presumed due to the Ag^{2+} reacting with water molecules as displayed by Equation (3) [1].

$$2Ag^{2+} + H_2O \rightarrow 2Ag^+ + 2H^+ + \tfrac{1}{2}O_2 \tag{3}$$

Recovery of Silver

As previously discussed, it is desirable to remove catalyzing ions from the solution. One potential technique for removing silver is electroplating. In essence, electroplating is the reverse process of electrochemical dissolution. For our setup, the same electrodes were used, but the polarity was reversed so that the silver would plate out on the surface of the platinum electrode. In Figure 7, the electroplating process is shown in progress. The blackish color on the electrode was caused by the plating of the metallic silver. Upon removing the electrode from the liquid, the coating had a tannish-brown appearance. After removing the electrode from the pot, it was then placed in a solution of ~5 *M* HNO_3 to redissolve the silver.

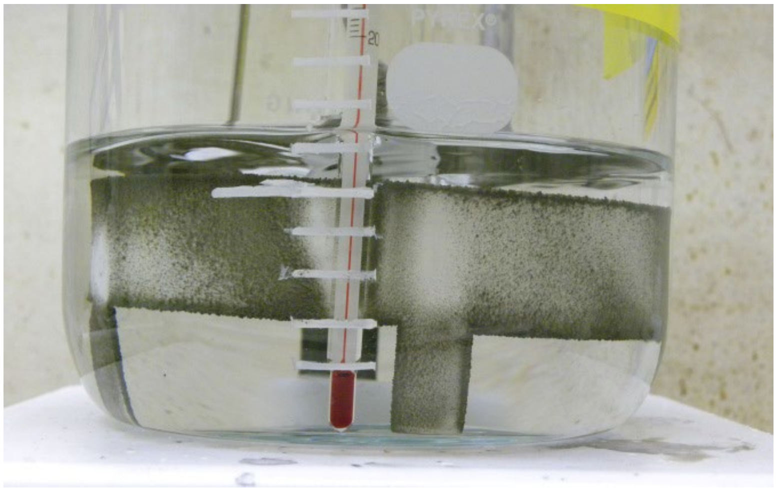

Figure 7. Electroplating silver. A coating of silver in solid form with a dark appearance on the anode indicates the successful reduction of Ag^{2+} to Ag (s).

Silver metal is soluble in nitric acid, so the electroplating process must be performed and the electrode with the plated silver removed from the solution soon after the current is stopped. The dissolution rate of silver can be increased by using higher concentration of nitric acid. Thus, it was thought that the electroplating process might be more successful at lower concentrations of nitric acid relative to higher concentrations of nitric acid (e.g., 1 *M* versus 5 *M*). A series of electroplating tests were performed with the silver concentration held constant at 0.01 *M* and the nitric acid concentration varying from 1 to 5 *M* at ambient temperature (nominally 20°C). The applied voltage was incrementally increased until electroplating of the silver was visually apparent. The results from these tests are shown in Table 2. As expected, the results indicated that electroplating could be accomplished at a significantly lower voltage in the 1 *M* HNO_3 mixture.

Table 2. Results of initial scoping study for electroplating silver

Catholyte	Anolyte	Catholyte temperature (°C)	Silver electroplating observed (V)
1 *M* HNO_3–0.01 *M* Ag	1 *M* HNO_3	21	7[a]
2 *M* HNO_3–0.01 *M* Ag	2 *M* HNO_3	21	18
3 *M* HNO_3–0.01 *M* Ag	3 *M* HNO_3	21	18
5 *M* HNO_3–0.01 *M* Ag[b]	1 *M* HNO_3	20	—

[a] As discussed below, when the test was repeated, electroplating did not begin until the applied voltage was ~18–20 V.

[b] Visually, the silver did not electroplate on the electrode; however, an increase in current was observed at 19.8 V. The applied voltage was increased to 20.6 V, but electroplating was still not observed. The anolyte solution turned milky white color, and the coloring was later determined to be caused by degradation of the particles from the glass frit membrane of the cathode chamber.

Because the hot cell's ambient temperature was nominally 35°C, testing was performed to determine if the solution temperature would have an effect on the electroplating capability. A new batch of 1 *M* HNO_3–0.01 *M* Ag solution was prepared. The anolyte solution was 1 *M* HNO_3. Based on the results in Table 2, the electroplating process was repeated and began with an applied voltage of 6 V. The voltage was then incrementally increased while watching for electroplating. Interestingly, electroplating did not occur until an applied voltage of 19 V. It is not known why there was a difference between the result of this test and the one reported in Table 2. Following the electroplating process, the electrode was left in the solution to redissolve the silver; however, the redissolution was slow. The solution was heated to ~82°C to assist with the redissolution of the silver. The heating was stopped, and the solution was allowed to set overnight to continue the dissolution process. The next morning, there was a small sphere (~2 mm diameter) that remained undissolved. Although the redissolution had not gone to completion, it had progressed enough to continue with repeating the electroplating process.

The catholyte solution was heated to ~40°C in preparation for the electroplating process. As in the previous test, the applied voltage was started at 6 V and incrementally adjusted until plating of silver could be visually observed on the platinum electrode; however, the time interval between voltage adjustments was reduced. Data were recorded at ~1-min intervals. The electroplating of silver occurred at 17.5 V. A graph of current versus applied voltage for the 20°C and 40°C tests is shown in Figure 8.

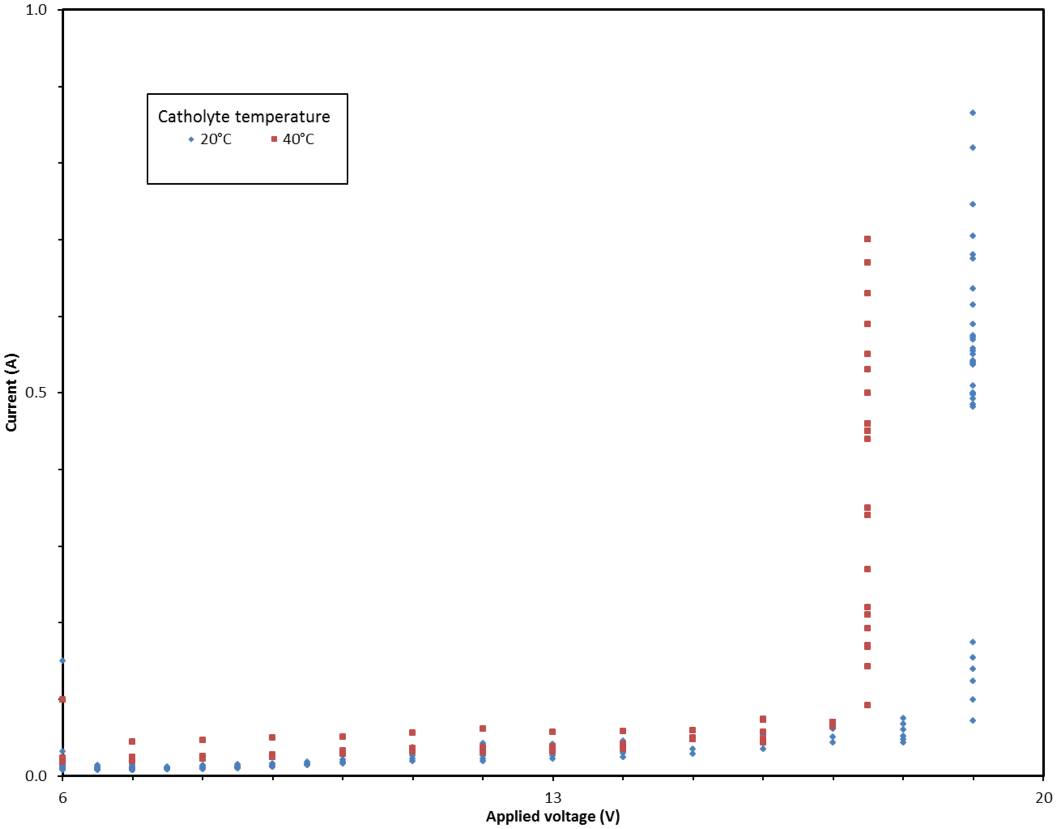

Figure 8. Response of current to the applied voltage during electroplating of silver from 1 *M* HNO_3 solution.

The electroplating results indicated that silver did not electroplate from the ~5 *M* HNO_3 mixture and that the electroplating process performed best with the ~1 *M* HNO_3 mixture. This primarily means that the acid concentration of the CEPOD solutions would need to be decreased for the electroplating process. Simple diluting of the acid would require increasing the volume by a factor of 5, so neutralization of the acid with a base was evaluated to minimize the generated volume. A mixture of ~5 *M* HNO_3–0.01 *M* Ag was prepared. The acidity of the mixture was reduced to ~1 *M* by adding 5 *M* NaOH. The resulting solution was 1 *M* HNO_3, 0.003 *M* Ag, and 1.3 *M* Na. The addition of the NaOH caused the solution to appear hazy (whitish), probably from formation of AgOH; however, the haziness disappeared after allowing the solution to stir for ~1 hour. This solution was heated and controlled at ~40°C and subjected to the electroplating process. Because of the low mass of silver in the solution, it was difficult to visually see the silver plate onto the electrode, but the electrical current data indicates that the plating began at 18 V. The inclusion of sodium in the mixture did not appear to have a large effect on the electroplating process.

Several samples were collected during the performance of the electroplating testing. The samples were analyzed for silver and titanium concentration by inductively coupled plasma mass spectrometry and acid concentration by titration. Titanium was included in the analyses because there was evidence that the titanium electrode was eroding during the process.

The analytical results are shown in Table 3 for the various tests. The results for the silver concentration before and after the electroplating process showed that the electroplating process significantly reduced the silver concentration for all of the tests except for the 5 *M* HNO_3 mixture, which was not analyzed because there was no visual indication of plating, and it was assumed that the silver concentration did not change significantly. The results also confirm that the silver was most effectively removed from the 1 *M* HNO_3 mixtures. The recovery of silver would likely be improved more by lowering the acid concentration to <1 *M* HNO_3 mixtures. The result for the mixture that included sodium may imply that sodium had a slight effect on the electroplating process. The testing with the 3 *M* HNO_3–0.002 *M* Ag mixture demonstrated that the electroplating process can achieve further reduction in the silver concentration, if necessary, by repeating the process.

During the electroplating process, it was observed that some erosion of the titanium electrode was occurring. The results in Table 3 confirm that the concentration of titanium increased during the electroplating process. The titanium concentration remained very low, so the ramification of the increased titanium concentration is likely negligible. In the setup, it is very easy to replace the electrode, but future operations may want to consider using a different material than titanium for the anode. Samples of the anolyte were also analyzed by inductively coupled plasma mass spectrometry.

Table 3. Analytical results obtained for the electroplating of silver testing

Nominal solution composition	Solution temperature (°C)	Before electroplating			After electroplating		
		Acid concentration (*M*)	**Silver concentration (mg/L)**	**Titanium concentration (mg/L)**	**Acid concentration (*M*)**	**Silver concentration (mg/L)**	**Titanium concentration (mg/L)**
1 *M* HNO_3–0.01 *M* Ag	20	—	—	—	0.99	2.9	0.28
5 *M* HNO_3–0.01 *M* Ag	20	4.71	1,100	0.22	—	—	—
3 *M* HNO_3–0.01 *M* Ag	21	2.77	1,100	6.9	2.82	240	23
3 *M* HNO_3–0.002 *M* Ag[*]	22	2.82	240	23	2.83	5.5	29
2 *M* HNO_3–0.01 *M* Ag	21	1.72	1,200	4.6	1.73	46	9.9
1 *M* HNO_3–0.01 *M* Ag	20	0.82	1,300	2.0	0.83	4.4	11
1 *M* HNO_3–0.01 *M* Ag	40	0.87	1,100	21	0.88	9.0	26
1 *M* HNO_3–0.01 *M* Ag–1.3 *M* Na	40	0.90	400	1.8	0.84	22	3.3

Note: Dashes indicate solutions that were not analyzed. The silver did not electroplate in the solution 5 *M* HNO_3–0.01 *M* Ag.

[*] This solution resulted from the previous test and demonstrates the feasibility of repeating electroplating processes to achieve lower concentrations of silver.

Overall, the results from the electroplating process show that it was efficient at removing the silver from the solution. The testing was performed on solutions ranging from 1 to 5 *M* HNO_3. The separation was most successful at 1 *M* HNO_3. This is likely due to the solubility of silver in nitric acid, and it would probably be even more efficient at nitric acid concentrations less than 1 *M.* The testing showed that the electroplating process would require applying 17–20 V. The electrical current remained relatively low (e.g., ~100 mA) until plating of the silver began on the electrode. The current typically peaked at ~1 A but was observed to reach ~3 A during at least one test. The current was dependent on the thickness of the silver that plated on the electrode.

3.1.3 Analysis of Cold-Testing Results

Cobalt(III) and silver(II) were successfully formed in cold-testing experiments. Silver is regulated under the Resource Conservation and Recovery Act if its concentration is 5 ppm or higher. If the silver remained in the liquid waste stream, it would cause the normally radioactive waste solution to be declared a mixed waste and make it more difficult to dispose of the solution. Electroplating was demonstrated as a potential method to remove silver from the acid solution; however, it may be necessary to repeat the electroplating process if the first attempt doesn't successfully reach the concentration limit.

The concentrations of cobalt(III) and silver(II) declined when the temperature was increased. However, a decrease in the concentration does not mean that there is not any in the solution. It was concluded that cobalt(III) would be evaluated to catalyze the dissolution of plutonium and curium oxide in the hot cell environment. If the cobalt was not successful, then silver could be evaluated as the catalyst.

3.2 HOT CELL WORK

The hot cell work was conducted at the REDC. The hot cells are heavily shielded concrete enclosures with viewing windows comprised of lead-impregnated glass panes and mineral oil. Mechanical arms are used to perform all operations within the hot cells.

Before beginning the CEPOD process, dissolution of aged curium-II oxide material was attempted with nitric acid. In a run designated as 75DS-3, approximately 3.2 g of material (~0.94 g ^{244}Cm) was added to a pot with 8 *M* HNO_3. After ~1 week of contact time, ~0.69 g of ^{244}Cm had dissolved. In dissolution 75DS-4, approximately 11.5 g of oxide (~1.7 g ^{244}Cm) was added to the dissolution pot. The solution underwent heated digestion for ~20 h. Sample analysis indicated that only 40 mg of ^{244}Cm dissolved. Hydrogen peroxide (15%) was added to the dissolution pot in three 100-mL aliquots during digestion. The solution was resampled, and the analysis indicated that the dissolved ^{244}Cm content had increased to ~0.25 g. Based on those results, six 100-mL peroxide additions were made while the mixture continued digesting. The solution was sampled again, and the results showed that the ^{244}Cm content had increased to ~0.37 g. Additional concentrated HNO_3 was added to the mixture, then the solution was digested, and additional hydrogen peroxide additions were performed. The solution was sampled again, and the results indicated that the dissolved ^{244}Cm had increased to ~0.50 g. The solution was separated from the undissolved solid matrix, and the undissolved solid matrix was then digested for ~20 h in ~11 *M* HNO_3 with periodic (~2 h intervals) hydrogen peroxide additions. This operation only resulted in dissolving ~74 mg of ^{244}Cm, so the liquid was separated from the undissolved solids. Following that separation, the undissolved solids were soaked in ~4 *M* HNO_3 for ~2 months. The solution was sampled, and the results indicated that ~0.63 g of ^{244}Cm had dissolved. The total amount of ^{244}Cm dissolved in run 75DS-4 was ~1.24 g. The solution was separated from the undissolved solids, and ~1 L of ~4 *M* HNO_3 was added back to the pot and mixed with the undissolved solids. An additional 1.05 g of oxide material was added into the pot in preparation for the electrolytic dissolution testing.

3.2.1 Electrolytic Dissolution Testing

The electrolytic dissolution system was set up in the hot cell with the remaining undissolved solids following the 75DS-4 operations. The run numbers for the electrolytic operations were designated as 75ED-1 through 75ED-12. Table 4 provides a listing of the oxide materials that were used during the non-electrolytic and electrolytic dissolution operations.

The operations during the various electrolytic dissolutions were similar, but specific parameters were varied during each run to attempt to achieve higher dissolution rates. The operations for the various runs are described in Tables 5–16 along with the results of radiochemical analysis. In addition, the progress of the dissolutions was periodically monitored using UV-VIS spectrometry. UV-VIS spectrometry analyses were not performed during run 75ED-12.

3.2.1.1 Operation notes and sample results from run number 75ED-1

The mixture of 4 *M* HNO_3 and undissolved oxide material (run 75DS-4) was settled, and a sample was obtained from the liquid phase to determine the starting conditions for the CEPOD processing (analytical sample code DSDP-476). Initially, no catalyst was added. The power supply to the electrodes was set to control at 4 V or 2 A, whichever was limiting. The CEPOD system was operated for ~2.6 h. The solution was settled and then sampled to determine the progress of the dissolution (DSDP-477). While waiting on sample results, the CEPOD system was restarted and operated for ~5.5 h. The anolyte was again settled, and then sampled (DSDP-478). Visual observation found the solution did not have much color, which led to speculation that dissolution was limited. Upon receiving the analytical results, dissolution was confirmed, but the process was very slow. Cobalt nitrate hexahydrate was added to the anode chamber such that the concentration of cobalt was ~0.01 *M*. The CEPOD system was operated as before. Following the electrolytic process, the solution was allowed to settle and then sampled (DSDP-479). The dissolution process with the CEPOD system was restarted and operated for ~6.5 h. The current was typically less than 2 A. The solution was settled, and the clarified solution was sampled (DSDP-480). The sample results indicated that the oxide material was dissolving very slowly.

The cold testing experiments showed that the concentration of Co^{3+} would quickly decline as the solution temperature was increased. This behavior did not mean that Co^{3+} was not being produced at the higher temperature but that it had a very brief presence. Theoretically, the Co^{3+} could attack the undissolved solid particles during that brief presence.

The solution was heated via a hot plate to ~80°C while applying current to the electrodes. The process was run at ~80°C for ~2.3 h. Following a settling period, the clarified solution was sampled (DSDP-481). While waiting on the results, the CEPOD system was restarted; however, the power supply was set to provide 8 V or 4 A, whichever was limiting. The system was operated for ~3 h without heating from the hot plate, followed by an ~2.4 h interval at ~80°C (the heat-up period required ~0.6 h) while continuing to apply power to the electrodes. The solution was allowed to cool and settle, and then the anolyte was sampled (DSDP-482). To speed up the dissolution process, the concentration of cobalt was increased to ~0.02 *M* in the anolyte. The cobalt was added to the dissolution pot. When the stirrer was turned on, the pink color of the solution became darker pink, but there was not a corresponding color change due to the suspension of undissolved solid particles. A visual investigation of the solution in the dissolution pot revealed that the dissolution was complete. Because the dissolution was complete, 82CM-7 oxide (13.12 g) was added to the dissolution pot. The material was stirred for ~10 h without the electrolytic process, and then sampled to determine the starting conditions for run 75ED-2 (DSDP-483).

Table 4. Listing of the oxide materials that underwent dissolution and characteristic data

Dissolution run no.	Origin of oxide	Oxide weight (g)	^{244}Cm weight (g)	^{240}Pu weight (g)	Predominant dissolution temperature[a] (°C)	Dissolution status
75DS-3[b]	LLNLSR72		0.94	1.7		
75DS-4[b]	82CM-5	11.5	2.0	8.6		Residue
75ED-1	82CM-5 +75DS-4 residue	1.05			40–80[c]	Dissolved
75ED-2	82CM-7	13.13	2.0	8.6	~80[d]	Residue
75ED-3	82CM-11 + 82CM-7 residue	13.16	2.0	8.7	80–95[e]	Dissolved[f]
75ED-4	SRO-20		3.5	14.7	90–95	Residue
75ED-5	72CM-1	21.10	2.7	11.5	90–95	Residue
75ED-6	82CM-10	13.14	2.0	8.7	90–95	Dissolved
75ED-7	82CM-6[g]		2.1	8.9	90–95	Dissolved
75ED-8	82CM-12		2.2	9.6	90–95	Essentially dissolved
	82CM-13		2.1	8.8		
75ED-9	82CM-15 + 75ED-4 residue	17.60	3.0	12.8	90–95	Residue
75ED-10	72CM-1	24.60	3.1	13.4	90–95	Residue
75ED-11	72CM-1 +75ED-10 residue	41.3	5.4	23.0	90–95	Residue
75ED-12	75ED-11 and 75ED-5 residues				~50[h]	Residue
		Total	**33.2**	**139.0**		

[a] Temperature values shown are the predominant range during the CEPOD processing. They do not necessarily include periods of ambient temperature.

[b] Runs 75DS-3 and 75DS-4 were performed without the electrolytic dissolution process.

[c] Initially the solution was only heated by Joule heating from the current. Approximately 50% of the CEPOD processing was conducted with the temperature at ~40°C, and ~50% at ~80°C.

[d] Current was applied while controlling the solution temperature at ~80°C with applied current for ~20 h, ~90°C–95°C for a period of ~3 h, and ~56°C for ~3 h.

[e] The early portion of the run was controlled at ~80°C (~6 h), but the solution temperature was controlled at ~90°C–95°C for ~21 h.

[f] There was some whitish-gray solid particles that did not dissolve, but based on the color of these solids, they were not believed to be curium or plutonium.

[g] This batch of oxide was added into the pot with the dissolution product from run 75ED-6.

[h] Silver was used as the catalyst during run 75ED-12. The goal was to keep the solution temperature less than 40°C so the hot plate heating was not used; however, the CEPOD processing induced heat into the solution.

Sample results from the various submitted samples during run 75ED-1 are shown in Table 5. The results show that the concentration of ^{240}Pu and ^{244}Cm were increasing as the operating time continued. Selected spectrums from radiochemically analyzed samples are presented in the figures below. Figure 9 compares spectra of DSDP-476, DSDP-479, and DSDP-482. The spectra show that the concentration of Pu (VI) is increasing in respect to operating time.

Table 5. Sample results from run number 75ED-1

Sample ID	Dissolved ^{240}Pu (g)	Dissolved ^{244}Cm (g)	Nitric acid concentration (*M*)
DSDP-476	0.114	0.025	4.0
DSDP-477	0.189	0.047	4.3
DSDP-478	0.280	0.065	4.4
DSDP-479	0.347	0.077	4.4
DSDP-480	0.414	0.099	4.9
DSDP-481	0.619	0.140	4.1
DSDP-482	0.749	0.226	5.3

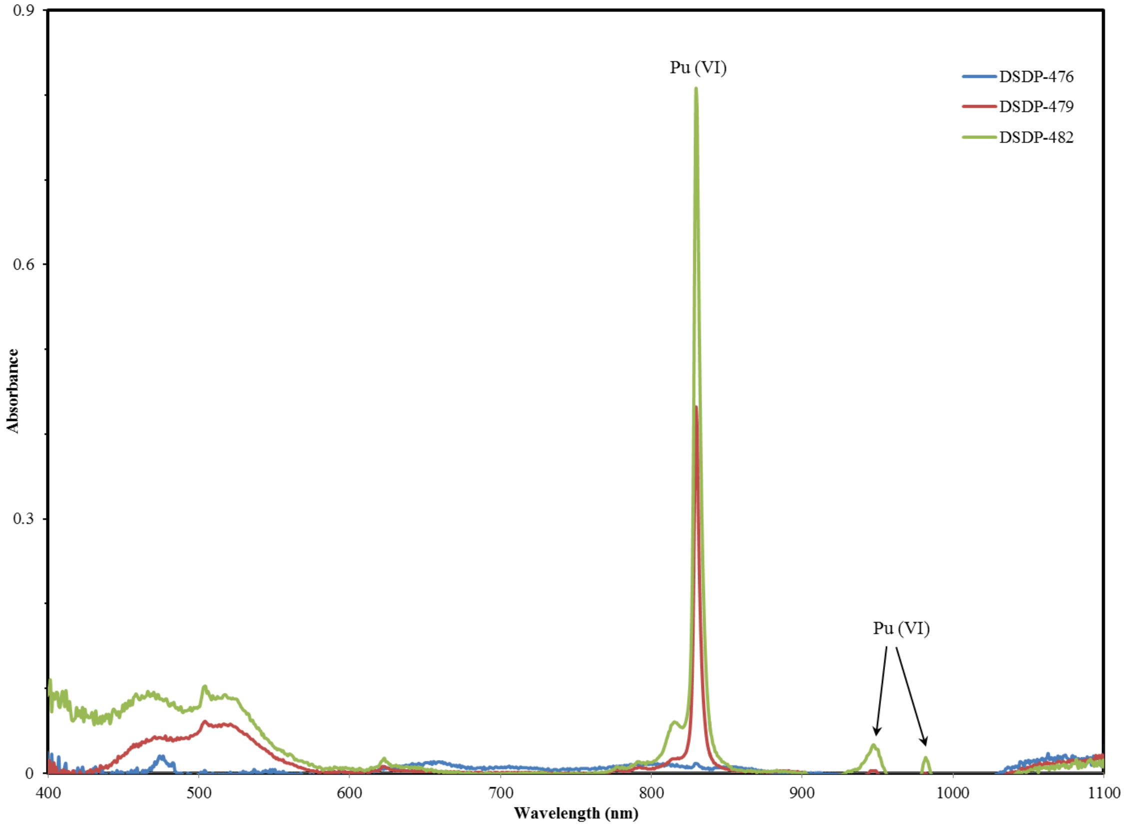

Figure 9. Spectrophotometric data for run 75ED-1. The blank sample for samples DSDP-476, DSDP-479, and DSDP-482 was taken with deionized water.

3.2.1.2 Operation notes and sample results from run number 75ED-2

Run 75ED-2 was initiated by adding 82CM-7 oxide powder to the anolyte generated from run 75ED-1. The starting conditions were determined by sample DSDP-483. The CEPOD system was operated at 4 V or 2 A (whichever was limiting) for ~3.4 h, and then the solution was heated to ~80°C while continuing to apply current. The CEPOD process was continued for ~2 h while controlling the solution temperature at ~80°C. Following a cooling and settling period (i.e., the undissolved solids were allowed to settle to the bottom so that the dissolved portion could be determined by sampling), the solution was sampled (DSDP-484). The UV-VIS analysis of the sample did not show much more dissolved plutonium than the initial conditions. The CEPOD system was restarted, but the power supply was set to control at 8 V or 4 A (whichever was limiting). The solution was heated to, and controlled at, ~80°C for ~5 h while applying current to the electrodes. The clarified solution (i.e., after settling) was sampled (DSDP-485) and the operation of the CEPOD system was restarted with power supply set as before. The power was applied to the electrodes for ~6.2 h without using the hot plate for heating. The solution temperature increased due to Joule heating provided by the applied current. The solution temperature was initially ~45°C and equilibrated at ~56°C. After the solution was settled, it was sampled (DSDP-486) to determine the dissolution's progress. Upon restarting the electrolytic process, the solution was heated to ~80°C for ~3.5 h, followed by the application of current for ~6.7 h. As before, the solution was settled and then sampled (DSDP-487). Operations were paused for ~1 week while the hot cells were in limited operations mode. When the hot cells returned to normal operations, the anolyte solution was mixed and sampled (DSDP-488). The results for the ^{240}Pu and ^{244}Cm indicated an increase in dissolved content relative to DSDP-487; however, the results for DSDP-487 showed a decrease in dissolved content relative to DSDP-486. It is not understood why there was a decrease in the dissolved content.

A portion of the anolyte was decanted from the dissolution pot to a flask, and the remaining anolyte was diluted with fresh nitric acid to obtain a mixture of ~4 *M* HNO_3–0.01 *M* Co. The CEPOD system was restarted with the typical power provided at ~6 V and 4 A for ~6.1 h. The solution was sampled as DSDP-489. Following this activity, the CEPOD operations were paused for ~1 week while the hot cells were in limited operations mode. Upon return to normal operations, the anolyte solution was sampled (DSDP-490), and the acid concentration was determined to be 7.0 *M*. It was elected to decant and adjust the anolyte's composition before proceeding.

Approximately 1/3 (i.e., ~200mL) of the anolyte solution was decanted to a flask, then fresh HNO_3 and cobalt nitrate were added to the remaining solution to adjust the constituents to ~4 *M* HNO_3–0.01 *M* Co. The contents were stirred for ~14 h, and then allowed to settle. The anolyte was sampled (DSDP-491), and the CEPOD system was operated at nominal settings of 6 V and 4 A for 3.6 h. The solution was heated and controlled at ~80°C during the operation. Following a settling period, the anolyte was sampled (DSDP-492). The results indicated that the remaining undissolved solids were slowly dissolving (Table 6). Figure 10 shows some UV-VIS data acquired in conjunction with radiochemical samples. It was decided to add more curium oxide material to the pot and allow the dissolution process to continue working on the undissolved solid particles while proceeding to dissolve the new batch of oxide.

Table 6. Sample results from run number 75ED-2

Sample ID	Dissolved ^{240}Pu (g)	Dissolved ^{244}Cm (g)	Nitric acid concentration (*M*)
DSDP-483	1.10	0.268	5.1
DSDP-484	2.46	0.625	5.1
DSDP-485	5.08	1.26	5.8
DSDP-486	6.44	1.55	6.3
DSDP-487	5.63	1.28	5.4
DSDP-488[a]	7.88	1.76	5.9
DSDP-489[a,b]	3.38	0.805	5.4
DSDP-491[b]	2.23	0.456	3.9
DSDP-492	2.33	0.487	4.4

[a] Following DSDP-488, a portion of the clarified anolyte was decanted to a flask, and then the remaining anolyte in the dissolution pot was diluted with fresh HNO_3 to obtain a concentration of ~4 *M* HNO_3–0.01 *M* Co.

[b] Following the acid concentration analysis of DSDP-490 (7.0 *M*), a portion of the clarified anolyte was decanted to a flask, and the remaining anolyte was adjusted to ~4 *M* HNO_3–0.01 *M* Co.

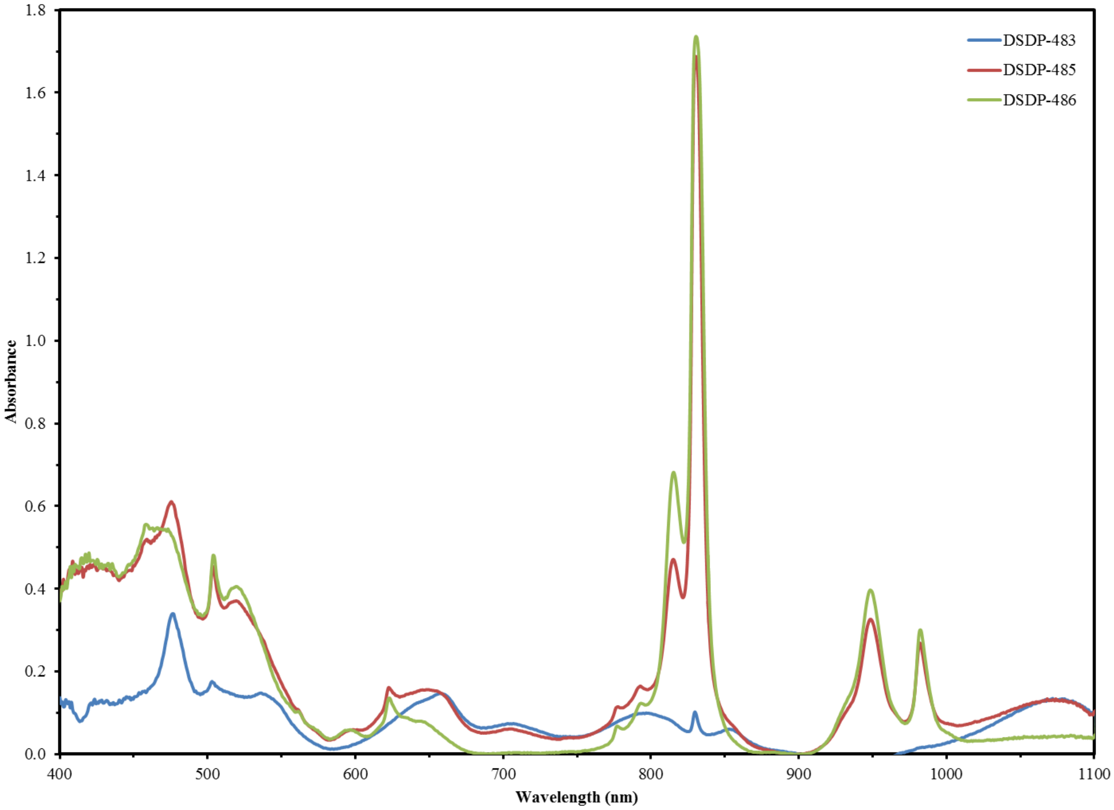

Figure 10. Spectrophotometric data for run 75ED-2. The blank sample for samples DSDP-483, DSDP-485, and DSDP-486 was taken with deionized water, 5 *M* nitric acid, and 6 *M* nitric acid, respectively.

3.2.1.3 Operation notes and sample results from run number 75ED-3

82CM11 oxide powder was added to the dissolution pot (anolyte is from 75ED-2). The CEPOD system was operated at nominal 6 V and 4 A for 2.1 h. The solution was heated and controlled at ~80°C during the process. After allowing a settling period, the solution was sampled (DSDP-493). Following the sample collection, the anolyte was reheated to ~80°C, and then the power was applied to the electrodes (nominal 5.8 V and 4 A) for ~4.1 h. A sample of the dissolution product was collected and analyzed by UV-VIS spectrometry. The electrical current was reapplied and operated at nominally 6 V and 4 A for 6.9 h while the temperature was held at ~90°C. Following a settling period, the solution was sampled (DSDP-495). The operation of the CEPOD system was paused for ~10 days for other hot cell activities.

The anolyte volume was adjusted with 0.1 *M* HNO_3 to replenish volume loss by evaporation. The operation of the CEPOD system was restarted at nominally 6 V and 4 A for ~6.8 h, and the solution temperature was controlled at ~90°C. After the customary settling period, the anolyte was sampled (DSDP-496).

Approximately 500 mL of anolyte was decanted from the dissolution pot (leaving 400 mL in the pot), and then ~750 mL of used catholyte solution (2.2 *M*) was added to the anolyte to dilute the acid. Prior to restarting the CEPOD process, a spot of "crud" was observed on the surface of the hot plate/stirrer during an inspection of the dissolution pot. Further inspection indicated that there was likely a hairline crack in the pot. The bulk of the anolyte solution from the dissolution pot was decanted, and the remaining contents from the pot were transferred into another container. The solids residue was rinsed from the pot into the container. The unknown material was rinsed from the hot plate/stirrer surface and the exterior surface of the dissolution pot to another container.

The material that was collected from inside the dissolution pot was transferred into a new dissolution pot, and the anolyte's composition was adjusted to ~1,100 mL of ~1 *M* HNO_3–0.02 *M* Co. Power was applied to the electrodes at nominally 6 V and 4 A for ~6 h. The solution temperature was heated and controlled at ~90°C during the electrolytic processing. Following a settling period, a sample was acquired from the anolyte and analyzed using UV-VIS spectroscopy. The analysis of the spectra indicated that the plutonium concentration was ~27 mg/L.

The CEPOD system was operated again with the power supply set to control at 4 A, and the solution temperature controlled at ~90°C. Power was supplied to the electrodes for ~6.7 h. The mixture was allowed to stir for several hours, and then the stirring was stopped to allow the undissolved solids to settle. The anolyte was sampled as DSDP-499. Sample results from this run are presented in Table 7.

Table 7. Sample results from run number 75ED-3

Sample ID	Dissolved ^{240}Pu (g)	Dissolved ^{244}Cm (g)	Nitric acid concentration (*M*)
DSDP-493	3.84	0.698	4.2
DSDP-495	5.56	1.31	5.8
DSDP-496[a]	3.72	0.767	5.7
DSDP-499[a,b]	0.342	0.077	1.7

[a] Following the collection of sample DSDP-496, a portion of the anolyte was decanted from the dissolution pot, and the anolyte was adjusted with fresh solution.
[b] The concentrations of Pu and Cm are lower because of the recovery from the cracked pot.

The cathode chamber was electively replaced in an effort to determine whether that might increase the dissolution rate. Following the replacement, the CEPOD system was operated at nominally 6 V and 4 A for ~3.6 h. Initially, the solution was not stirred to avoid suspending the undissolved solids, and it was observed that the anolyte color became blue (indicating the formation of Co^{3+} ions). The solution was heated and controlled at ~90°C during the processing. After a settling period, the contents of the pot were visually inspected. The inspection indicated that there were not any dark-colored particles (which are characteristic of the curium and plutonium oxide particles) in the pot. For confirmation, the magnetic stirrer was turned on for ~1 s and a whitish-gray cloud was observed to become suspended. It was speculated that the curium and plutonium components were likely dissolved and that the remaining undissolved solid particles were impurities.

Because the formation of Co^{3+} ions were observed in previous CEPOD operation, the system was operated again to visually verify that the conversion process was still operating properly. Initially the power supply was set to limit the applied current to 2 A and the nominal applied voltage was 4.5 V. After ~15 min, there was no visual indication of a color change. For confirmation, the solution was sampled and analyzed with UV-VIS spectrophotometry (Figure 11). The results of that analysis confirmed that there was not an increase in the concentration of Co^{3+}. The power supply was adjusted to control the applied voltage at 5 V, and the applied current was nominally 2.3 A. After a couple of minutes, it was observed that the solution appeared to be turning blue. After a few minutes, the power supply was adjusted to control at 6 V. The nominal applied current was 3.4 A; however, it was observed that the current decreased as the process time increased. It was speculated that the decrease in current was an indication that the catholyte was becoming depleted of acid. It was also observed that the blue color of the solution became darker when the applied voltage was 6 V. Because the curium and plutonium particles appeared to be dissolved, more oxide material was added to the dissolution pot and run 75ED-4 proceeded.

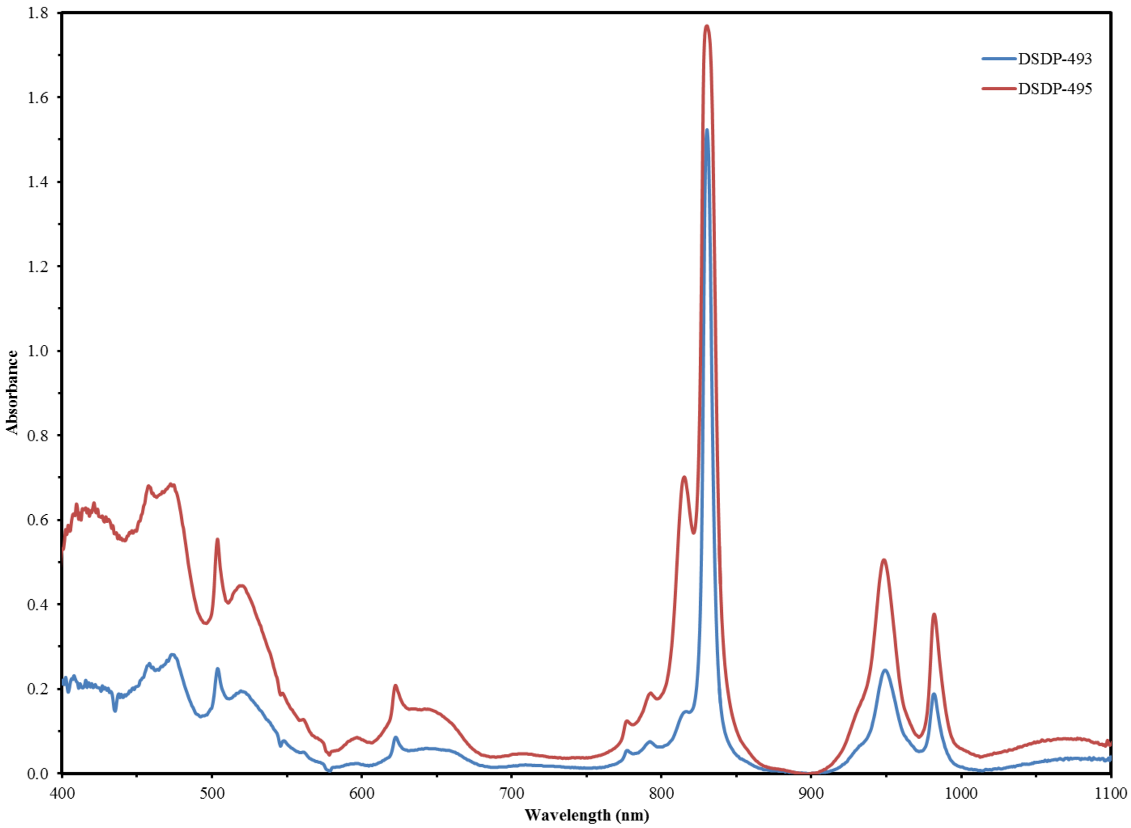

Figure 11. Spectrophotometric data for run 75ED-3. The blank sample for samples DSDP-493 and DSDP-495 was taken with 4 *M* nitric acid.

3.2.1.4 Operation notes and sample results from run number 75ED-4

SRO-20 oxide powder (~22–23 g) was added to the dissolution pot (anolyte from 75ED-3). The CEPOD system was operated at 6 V and nominally 3.5 A for 2.4 h. The solution was not stirred during the first 2.1 h of the operating period. The solution was not heated except for heat generated from the applied current between the electrodes. It was observed that the color of the anolyte solution was not turning blue like run 75ED-3; however, it was speculated that the Co^{3+} ions were probably reacting quickly with the oxide. After operating for ~1.5 h, the solution was analyzed using a UV-VIS spectrophotometer (Figure 12). The results indicated that there was a slight increase in the plutonium concentration (Table 8). The solution temperature began at 43°C and increased to 53°C during the processing period. The stirrer was turned on for the last 0.3 h of the processing period. The stirring did not appear to affect the current or temperature. The solution was allowed to settle overnight.

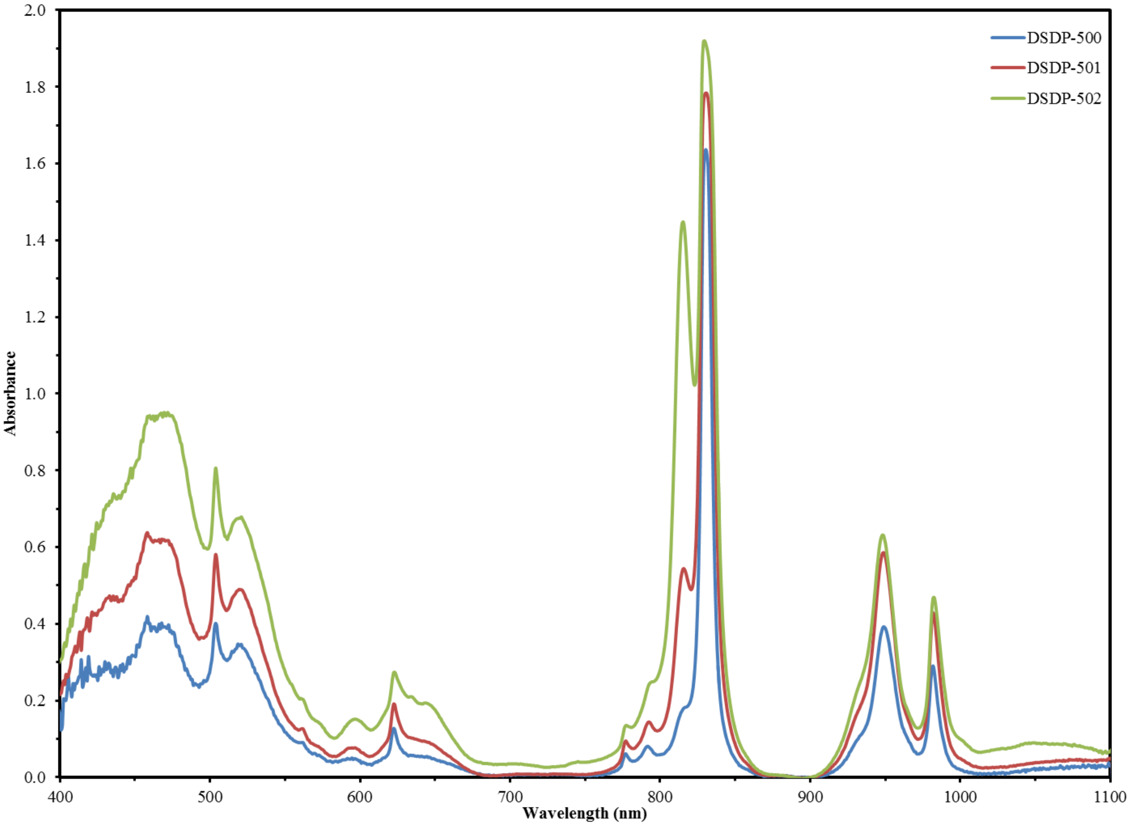

Figure 12. Spectrophotometric data for run 75ED-4. The blank sample for samples DSDP-500, DSDP-501, and DSDP-502 was taken with 3 *M* nitric acid, 5 *M* nitric acid, and 5 *M* nitric acid, respectively.

Table 8. Sample results from run number 75ED-4

Sample ID	**Dissolved ^{240}Pu (g)**	**Dissolved ^{244}Cm (g)**	**Nitric acid concentration (*M*)**
DSDP-500	3.83	0.932	4.2
DSDP-501	8.28	1.79	5.3
DSDP-502	9.57	2.20	6.8
DSDP-503	10.4	2.36	5.5

The CEPOD system was restarted and operated at nominally 6 V and 4 A for ~4 h. The temperature of the solution was 44°C at startup and 56°C when the system was shutdown. After allowing the solution to settle overnight, the solution was analyzed using UV-VIS spectrometry, and those results indicated that the amount of dissolved plutonium was very low. The CEPOD system was restarted with the same power settings; however, the solution was heated to ~90°C, and the operating time was extended (16.1 h). The solution was allowed to cool and settle, and then it was sampled to determine the progress (DSDP-500). The operation of the CEPOD system was restarted using the same parameters. The system was operated for 14.8 h. As before, the solution was allowed to cool and settle, and then it was sampled (DSDP-501). Following the sample collection, the CEPOD system was restarted using the same operating conditions. It was operated for 12.4 h. Following the cool down and settling period, the anolyte was sampled to determine the progress (DSDP-502). The acid concentration was reduced to ~5.2 *M* by adding water (while stirring) to replenish volume loss by evaporation. It was speculated that the replacement of the cathode chamber (following DSDP-499) improved the dissolution process, so a new cathode chamber was installed in the dissolution pot. The operation of the CEPOD system was restarted using the same conditions (i.e., 6 V, 4 A, ~90°C). The system was operated for 12.9 h, and then the solution was cooled and settled. The solution was sampled (DSDP-503), and after sampling, the anolyte solution was decanted from the dissolution pot. The remaining contents of the dissolution pot (including undissolved solids) were transferred to a storage container.

3.2.1.5 Operation notes and sample results from run number 75ED-5

A fresh batch of anolyte solution was prepared as ~1,100 mL of ~2 *M* HNO_3 + 0.02 *M* Co. Power was applied to the electrodes with the nominal settings of 6 V and 4 A. In approximately 10 min, the color of the anolyte had changed from pink to blue. A batch of 72-CM-1 oxide powder (~21 g) was added to the dissolution pot, and then the CEPOD dissolution process was started with the power supply controlling at 6 V. Interestingly, the current was initially being supplied at 2–3 A (where previously it had been ~4 A), but after a couple of hours, the applied current was back to the nominal 4 A. As before, the solution was heated to ~90°C. The power was applied to the electrodes for a total of 53.8 h; however, after ~46 h of operation, it was observed that the solution was not being stirred, and personnel were unable to get the stirring restarted.

After this discovery, the personnel were directed to continue operating the system until the predetermined time to allow the solution to cool and settle. Following the settling period, the solution was sampled (DSDP-505). Visually, the solution in the dissolution pot appeared as if it contained significant impurities. The solution was allowed to settle overnight, but the settling time did not improve the appearance of the solution. An attempt was made to get the stirring restarted, but the attempt was unsuccessful. The solution was allowed to settle overnight again, but again, the solution still appeared the same. The solution was transferred from the pot by decanting into a vacuum flask. The undissolved solids in the pot were mostly stuck to the walls of the pot instead of suspended in the solution. After the transfer, the magnetic stirring bar was retrieved from the dissolution pot, and the stirring bar was found to be hollow. Apparently, the Teflon coating had eroded (presumably from abrasion with the undissolved solid particles), and the acid had attacked and dissolved the magnet.

The walls of the pot were rinsed with 6 *M* HNO_3 to remove the film from the walls; however, this was not successful. Next ~650 mL of 2.6 *M* HNO_3 was added to the pot (for a total of ~900 mL), and the solution was allowed to set. After several hours, the anode was reinstalled in the dissolution pot, and a new magnetic stirring bar was placed in the pot. Upon turning on the stirrer, the solution's appearance was "muddy." The CEPOD process was restarted without adding cobalt to the solution using the nominal parameters of 6 V, 4 A, and ~90°C. The system was operated for 11.3 h, and then the solution was cooled and settled. Following the settling period, the solution was sampled (DSDP-506). Cobalt nitrate was added to the anolyte to return the cobalt concentration to ~0.02 *M*. The CEPOD system was restarted (nominally 6 V, 4 A, and 90°C) and operated for 16 h. Following the customary cooling and settling, the solution was sampled (DSDP-507). The contents of the dissolution pot were transferred to another container. Sample results from this run are presented in Table 9, and the results of the UV-VIS analysis are shown in Figure 13.

Table 9. Sample results from run number 75ED-5

Sample ID	Dissolved ^{240}Pu (g)	Dissolved ^{244}Cm (g)	Nitric acid concentration (*M*)
DSDP-505	2.57	0.58	6.1
DSDP-506	1.62	0.36	3.6
DSDP-507	2.34	0.45	4.4

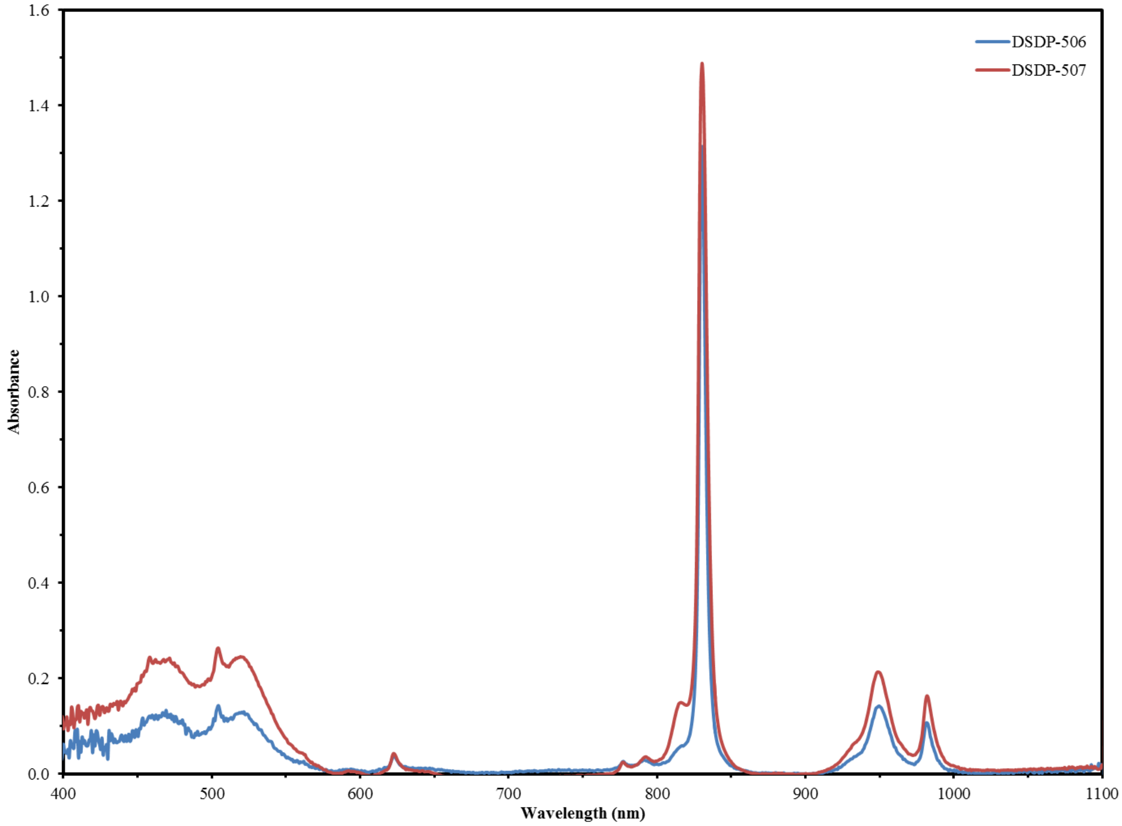

Figure 13. Spectrophotometric data for run 75ED-5. The blank sample for samples DSDP-506 and DSDP-507 was taken with 3 *M* nitric acid and 6 *M* nitric acid, respectively.

3.2.1.6 Operation notes and sample results from run number 75ED-6

A fresh batch of anolyte solution was prepared as ~1,100 mL of ~2 *M* HNO_3 + 0.02 *M* Co. A batch of 82-CM-10 oxide powder (~13 g) was added to the dissolution pot, and then the CEPOD system was started with the power supply controlling at 6 V, and the solution was heated to ~90°C. The CEPOD system was operated for ~10.2 h, then the solution was cooled, and the solid particles were settled. The clarified solution was analyzed using UV-VIS spectrometry. The results of the analysis estimated the dissolved plutonium content to be ~1.2 g.

The dissolution process was restarted with the same operating conditions, and it was operated for ~17.3 h. Following the cooling and settling period, the solution was sampled (DSDP-509). Following the sample collection, the operation of the CEPOD was restarted with the same controlling parameters and operated for 16.2 h. While preparing for collection of a sample, operating personnel observed that the dissolution appeared to be complete. It was decided that another batch of oxide should be added to the dissolution pot. Sample results from this run are presented in Table 10, and the results of the UV-VIS analysis are shown in Figure 14.

Table 10. Sample results from run number 75ED-6

Sample ID	Dissolved ^{240}Pu (g)	Dissolved ^{244}Cm (g)	Nitric acid concentration (*M*)
DSDP-509	3.85	0.91	3.6

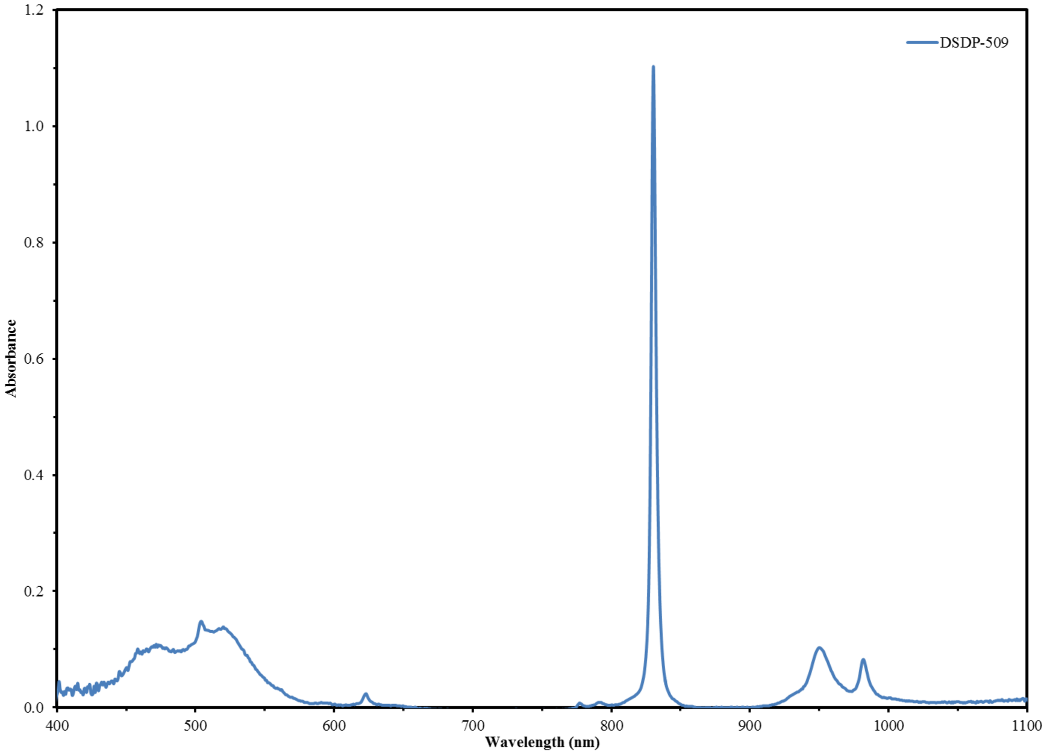

Figure 14. Spectrophotometric data for run 75ED-6. The blank sample for sample DSDP-509 was taken with 3 *M* nitric acid.

3.2.1.7 Operation notes and sample results from run number 75ED-7

Oxide from 82-CM-6 was added to the dissolution pot, and the solution was heated to ~90°C, and the operation of the CEPOD system was restarted. The system was operated for ~12.6 h. Following a cooling and settling period, the solution was sampled (DSDP-510). Following the sample collection, CEPOD operation was restarted with the same controlling parameters, and the system was operated for ~31.9 h. The solution was sampled as DSDP-511. Following the sample collection, the stirrer was restarted. Initially, it appeared that the dissolution was complete as there was not a visual dispersion of solid particles; however, after ~10 min, the solution appeared hazy. The solution was settled, and then a thin layer of undissolved solid particles on the bottom of the pot was observed. A portion of the anolyte solution was decanted from of the pot, and then the solution was adjusted to be approximately 2 *M* HNO_3–0.02 *M* Co at 1,100 mL. A sample of the solution was obtained (DSDP-512). The solution was heated to ~90°C, and then the electrical power was reapplied to the electrodes. Power was applied to the electrodes for ~46.7 h. Following this operation, it was determined that the undissolved solids had been successfully dissolved; however, the dissolution was probably complete earlier. The operating period was extended to try to ensure complete dissolution had occurred. The solution was sampled (DSDP-513), and the dissolution product was transferred from the dissolution pot to the product collection tank. Sample results from this run are presented in Table 11, and the results of the UV-VIS analysis are shown in Figure 15.

Table 11. Sample results from run number 75ED-7

Sample ID	Dissolved ^{240}Pu (g)	Dissolved ^{244}Cm (g)	Nitric acid concentration (*M*)
DSDP-510	9.71	2.32	6.0
DSDP-511	9.36	2.27	6.4
DSDP-512	2.60	0.87	1.8
DSDP-513	4.41	1.29	4.6

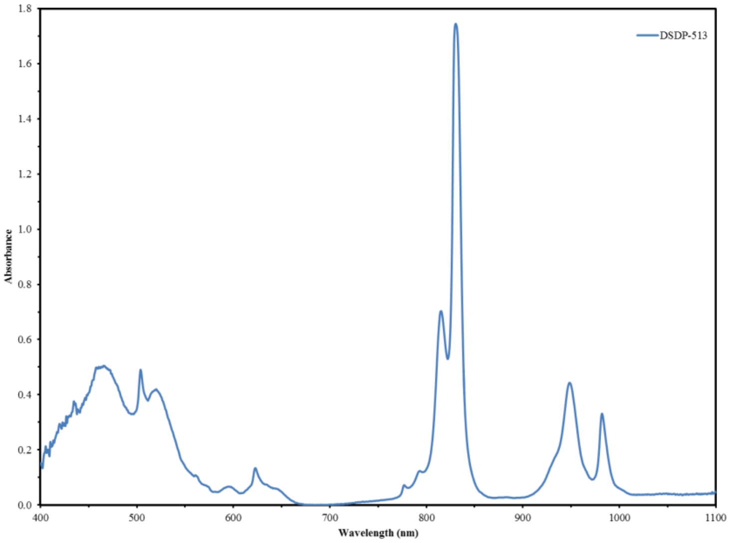

Figure 15. Spectrophotometric data for run 75ED-7. The blank sample for sample DSDP-513 was taken with 4 *M* nitric acid.

3.2.1.8 Operation notes and sample results from run number 75ED-8

A fresh batch of anolyte was prepared (~1,100 mL of ~1.5 *M* HNO_3–0.02 *M* Co). During the anolyte preparation, 82-CM-12 and 82-CM-13 oxide powders were mixed in the solution. A new cathode chamber and magnetic stirring bar was used. The solution was heated to ~90°C, and then the CEPOD process was restarted using the same power conditions (i.e., 6 V, 4 A). The system was operated for ~32.5 h. Following the cooling and settling period, the solution was sampled (DSDP-515). Following the sample collection, the electrical power was applied to the electrodes at 6 V without heating or stirring with the hot plate/stirrer. This was primarily to see if the solution changed color (i.e., from formation of Co^{3+} ions), but after operating for 2.3 h, a significant change in color was not observed. The system was turned off while waiting on the DSDP-515 results.

Upon receiving the sample results, the bulk of the liquid was decanted from the dissolution pot, then fresh acid and cobalt nitrate were added to reconstitute the contents to ~1,100 mL of ~1.5 *M* HNO_3–0.02 *M* Co. The CEPOD process was restarted and operated for ~40.4 h. It was stopped because of an increase in the frequency of changing the catholyte. Historically, the catholyte had to be replaced approximately every hour, but the frequency had increased to ~30 min. It was speculated that this increase may be due to a break in the cathode cable. The electrolytic dissolution process was paused until a new cable was fabricated. The solution was sampled (DSDP-516) for acid concentration analysis. The result was 5.0 *M*. It was decided to not decant the solution, but because the solution had lost volume by evaporation, water was added to the anolyte to reestablish the volume to ~1,100 mL. The resulting acid concentration was ~3.7 *M*.

Upon receiving the new cable, the electrolytic dissolution system was restarted (nominally 6 V, 4 A, and 90°C). The frequency of the catholyte replacements returned to approximately every hour. The system was operated for ~32.4 h. Following the cooling and settling period, the solution was sampled (DSDP-517). The dissolution of the oxide was nearly complete. Approximately 90% of the liquid was decanted and transferred to the product collection tank. Sample results from this run are presented in Table 12, and the results of the UV-VIS analysis are shown in Figure 16.

Table 12. Sample results from run number 75ED-8

Sample ID	**Dissolved ^{240}Pu (g)**	**Dissolved ^{244}Cm (g)**	**Nitric acid concentration (*M*)**
DSDP-515	5.70	1.51	3.9
DSDP-517	9.01	2.07	5.8

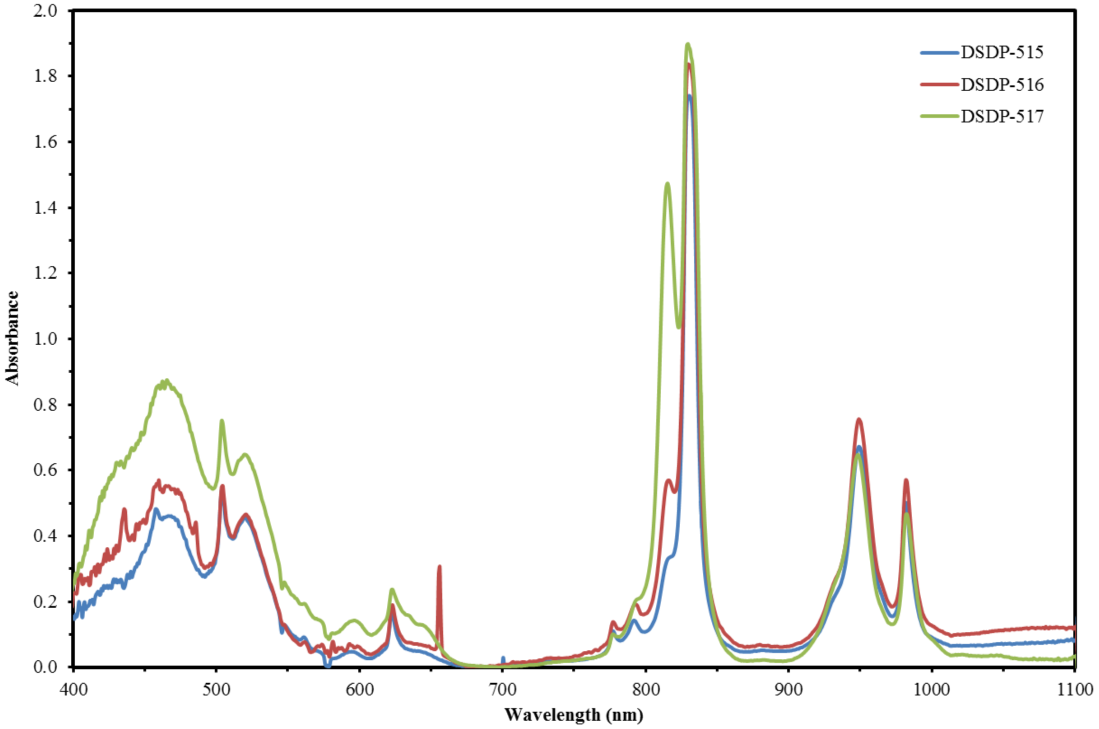

Figure 16. Spectrophotometric data for run 75ED-8. The blank sample for samples DSDP-515, DSDP-516, and DSDP-517 was taken with 4 *M* nitric acid.

3.2.1.9 Operation notes and sample results from run number 75ED-9

The anolyte for run 75ED-9 included the heel from 75ED-8, used catholyte from 75ED-8, undissolved solids from 75ED-4, and oxide from 82-CM-15. The solution was heated to ~90°C, and then the electrical power was applied to the electrodes and operated for ~59.5 h. Following the cooling and settling period, the solution was sampled (DSDP-519). Following the sample collection (Table 13), approximately 90% of the solution was decanted from the pot. The decanted solution appeared hazy, so the solution was allowed to settle overnight and was then decanted again. The second batch of decanted solution was transferred to the product collection tank. The results of the UV-VIS analysis are shown in Figure 17.

Table 13. Sample results from run number 75ED-9

Sample ID	Dissolved ^{240}Pu (g)	Dissolved ^{244}Cm (g)	Nitric acid concentration (*M*)
DSDP-519	15.4	3.47	6.0

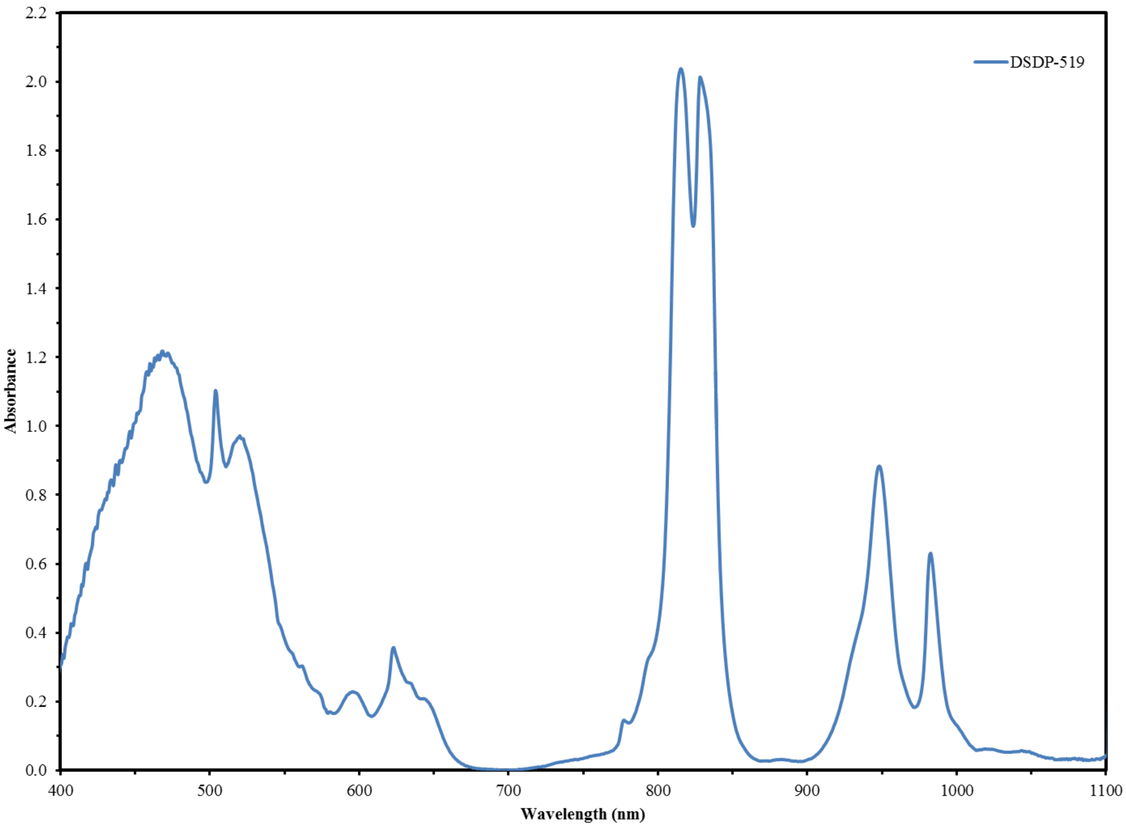

Figure 17. Spectrophotometric data for run 75ED-9. The blank sample for sample DSDP-519 was taken with 6 *M* nitric acid.

3.2.1.10 Operation notes and sample results from run number 75ED-10

The anolyte for run 75ED-10 included the heel from 75ED-9, used catholyte from 75ED-9, fresh HNO_3, and cobalt nitrate. The compositing of these solutions resulted in a mixture of ~1.8 *M* HNO_3–0.02 *M* Co. Oxide from 72-CM-1 was added to the dissolution pot. The dissolution process was started and operated for a cumulative ~50.2 h. After the cooling and settling period, the solution was sampled (DSDP-520). Following the sample collection, the CEPOD system was restarted and operated ~12.9 h. The solution was sampled after the standard cooling and settling period and analyzed using UV-VIS spectrometry (Table 14 and Figure 18). The results indicated no change from previous analysis. The system was allowed to set undisturbed over the weekend. Approximately 800 mL of solution was decanted from the dissolution pot. The remainder of the dissolution pot's contents was transferred into a storage flask. The dissolution pot was cleaned in preparation for the next run.

Table 14. Sample results from run number 75ED-10

Sample ID	**Dissolved ^{240}Pu (g)**	**Dissolved ^{244}Cm (g)**	**Nitric Acid Concentration (*M*)**
DSDP-520	7.57	1.68	Not determined

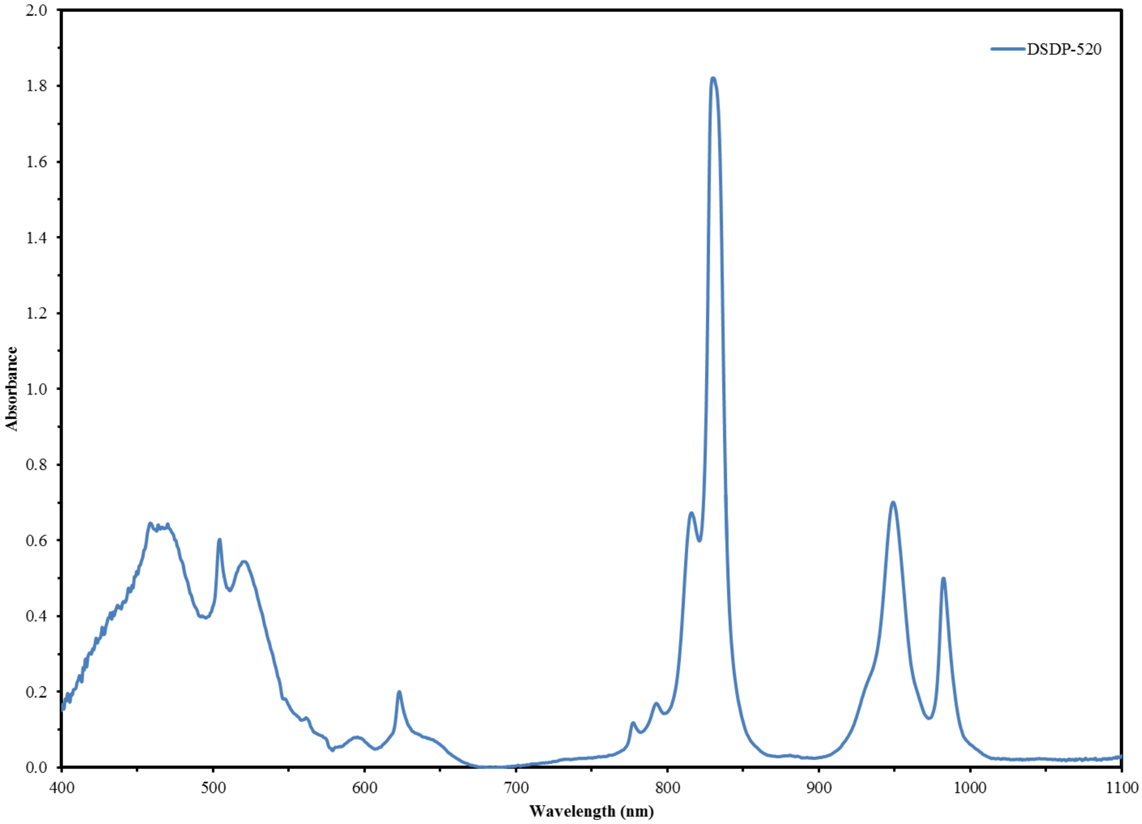

Figure 18. Spectrophotometric data for run 75ED-10. The blank sample for sample DSDP-520 was taken with 6 *M* nitric acid.

3.2.1.11 Operation notes and sample results from run number 75ED-11

The anolyte for run 75ED-11 included the undissolved solids and heel solution from 75ED-10, used catholyte from 75ED-10, along with fresh HNO_3 and cobalt nitrate. This composite was used to obtain a mixture (~1,100 mL) of ~2 *M* HNO_3 + 0.02 *M* Co. The contents were mixed and then allowed to settle overnight. A sample was obtained from the clarified solution to determine the initial conditions (DSDP-521). Following the sample collection, 72CM-1 oxide (~41 g) was added to the dissolution pot, and electrolytic dissolution operations were initiated. As before, the power applied to the electrodes was nominal 6 V and 4 A. The solution was heated to approximately 90°C, and the system was operated for ~15.8 h. The solution was cooled and settled to evaluate the progress. The solution was sampled and analyzed using UV-VIS spectrometry (Figure 19), and that analysis estimated that the solution contained ~9.5 g of plutonium (Table 15). The CEPOD system was restarted to continue the dissolution process. The system operated for ~1.8 h when personnel observed that the dissolution pot was empty because of a crack that formed near the bottom of the pot. The solution drained to the cubicle floor. The process operations were terminated, and a recovery effort was initiated.

Table 15. Sample results from run number 75ED-11

Sample ID	Dissolved ^{240}Pu (g)	Dissolved ^{244}Cm (g)	Nitric acid concentration (*M*)
DSDP-521	3.73	1.05	2.2

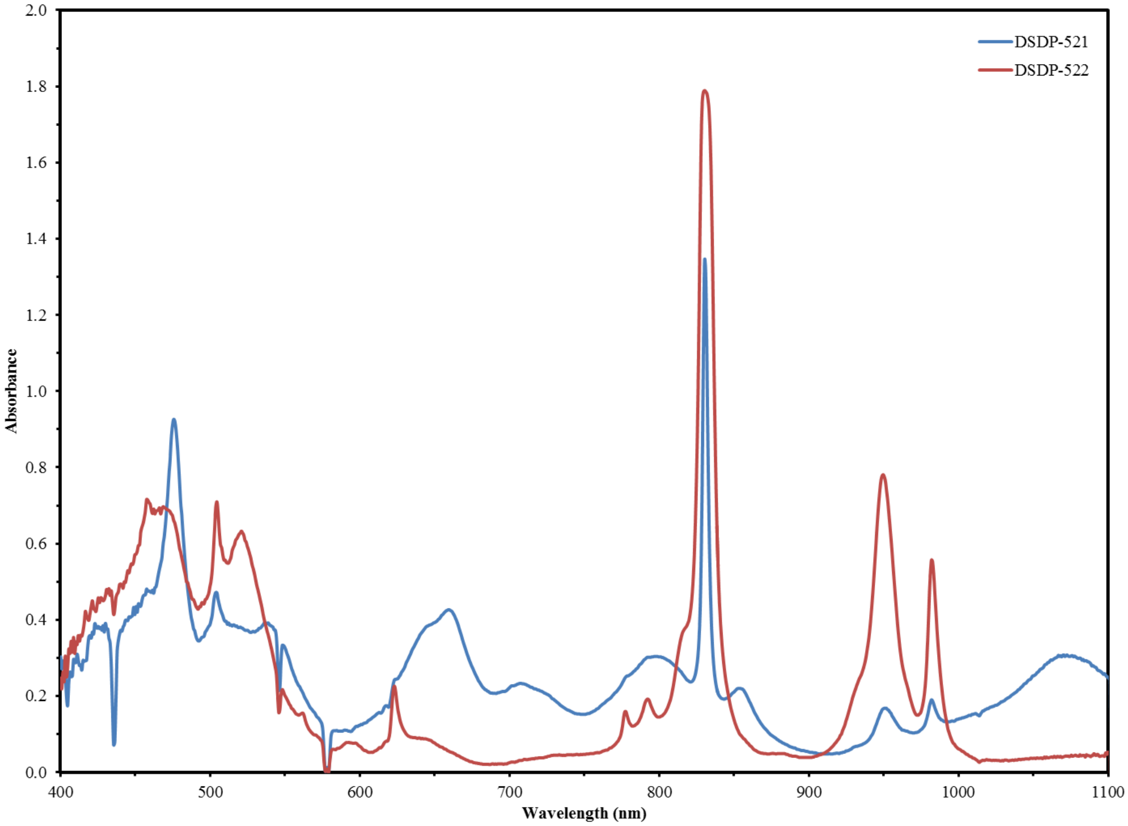

Figure 19. Spectrophotometric data for run 75ED-11. The blank sample for samples DSDP-521 and DSDP-522 was taken with 2 *M* nitric acid and 5 *M* nitric acid, respectively.

The solution in the floor was observed to be dark in color, and it was recovered into a flask. The solution in the sump was recovered into a separate flask. It was observed to be light in color, so it is speculated that the sump already had some liquid in it prior to the spill and that the solutions had mostly stayed segregated. After emptying the sump of solution, the floor was rinsed into the sump with 0.5 *M* HNO_3. A second rinse of the floor area was performed with 0.5 *M* HNO_3. The acid rinse was allowed to set in the sump overnight.

Following the floor rinse, the glass pot was examined. When the pot was lifted, the upper portion of the pot separated from the bottom of the pot. The bottom of the pot, platinum electrode, and magnetic stirring bar remained on the hot plate. The platinum electrode and magnetic stirrer bar were retrieved and rinsed with 0.5 *M* HNO_3 into a tray. The bottom of the pot was stuck to the surface of the hot plate, but it was removed relatively easily with a pair of forceps. A significant quantity of undissolved solid particles was observed on the bottom piece of the pot. Most of these solid particles were rinsed into a tray. Some of the particles had to be loosened by rubbing with the tips of forceps. Both sides of the pot's bottom were rinsed to recover undissolved solid particles. The walls of the upper portion of the pot were also rinsed. The hot plate's surface also contained undissolved solid particles. The hot plate unit was tilted over a collection tray, and the surfaced was rinsed with 0.5 *M* HNO_3. The base of the hot plate unit was rinsed to the cubicle sump. Following the recovery of the liquid rinses, the solutions were allowed to sit to allow the undissolved solid particles to separate, and the liquid was decanted. In some cases, this had to be done in two settling stages because the radiolysis from the undissolved solids tended to keep lighter weight solid particles suspended. The undissolved solids were washed with acid solutions to recover dissolved quantities of plutonium and curium; however, the washing process was also performed to reduce the cobalt to a very low concentration in preparation for a change to a silver catalyst in the next run.

3.2.1.12 Operation notes and sample results from run number 75ED-12

The anolyte for run 75ED-12 included the washed undissolved solids particles from runs 75ED-5 and 75ED-11, HNO_3, and silver nitrate to obtain a mixture of ~3 *M* HNO_3–0.01 *M* Ag. The solution was mixed, settled, and sampled (MSA-563). Following the sample collection, the CEPOD system was started with the supply power set at 3 V. Initially, the corresponding current was ~1.2 A, but it increased to ~2.1 A after ~7 min. The solution temperature was 42°C. The stirrer was initially left turned off so that the formation of the Ag^{2+} ions (i.e., brown plumes at the anode surface) could be observed, but none formed. The applied voltage was increased up to ~5.7 V and ~4.5 A, but formation of the brown plumes did not occur. There were other criteria that proved that power was being provided to the electrodes, such as the voltage and current measurements, and the formation of brown gas (i.e., NO_2) in the cathode chamber. Stirring of the solution was started ~2 h after applying power to the electrodes. The system was operated for ~2.8 h at the 5.7 V setting, the 4.5 A setting, or both settings.

The applied power to the electrodes resulted in the solution temperature rising to 51°C. As previously discussed, the Ag^{2+} ions rapidly react with water molecules when the solution temperature is >40°C, so the solution temperature may have been the reason that we could not see the formation of the indicative brown plumes of the Ag^{2+} ions. Later in the day, the power settings were reduced to provide 3.5 V to the electrodes to help control the solution temperature. After ~1.5 h of additional operating time, the solution temperature dropped to 49°C. The solution was allowed to cool and settle before sampling (DSDP-526). After cooling, the solution temperature was ~43°C. The CEPOD process was restarted again with the power supply set to control the voltage at 3V or the current at 4.5 A, whichever was limiting. The goal was to limit the amount of heat transferred into the solution to keep the temperature as low as possible. The CEPOD process was operated for ~20 h. At the end of the period, the solution temperature was ~49°C. Following a settling period, the anolyte was sampled (DSDP-527). The CEPOD system was restarted following the sample collection; however, the power supply was set to control the voltage at 4 V. The process was operated for ~18.7 h. At the end of the operating period, the solution temperature was 51°C. Following a settling period, the solution was sampled to determine the progress (DSDP-528). Following the sample collection, the dissolution process was restarted with the power supply set to control at 4 V again. The system was operated for ~13.3 h. After the settling period, the anolyte was sampled (DSDP-529). The CEPOD process was restarted again and operated for ~17.4 h. Following a settling period, the anolyte was sampled (DSDP-530). The dissolution process was restarted and operated for ~62 h. Following a settling period, the anolyte was sampled (DSDP-531). The sample results indicated that the amount of dissolved plutonium had not increased even with the long operating time with the CEPOD system (Table 16). The dissolution effort was electively stopped, and the dissolution product was decanted to a product collection tank. After decanting, the heel was washed to further recover the dissolved plutonium and curium. After the washing process, the undissolved solid particles were retrieved from the pot and stored for future operations.

Table 16. Sample results from run number 75ED-12

Sample ID	Dissolved ^{240}Pu (g)	Dissolved ^{244}Cm (g)	Nitric acid concentration (*M*)
MSA-563	1.11	0.12	3.0
DSDP-526	3.00	0.45	3.0
DSDP-527	4.92	0.89	3.6
DSDP-528	8.46	1.52	3.5
DSDP-529	8.25	1.60	4.2
DSDP-530	9.05	1.63	5.5
DSDP-531	9.08	1.90	5.0

4. CONCLUSIONS

A total of 33.63 g of ^{244}Cm and 141.07 g of ^{240}Pu material in several batches was processed using CEPOD dissolution. After the process was completed, 23.62 g of ^{244}Cm and 107.34 g of ^{240}Pu material were dissolved, with a dissolution percentage of 70.2% of ^{244}Cm and 76.1% of ^{240}Pu. Although the process did not dissolve all of the oxide material, the process was much more effective than attempting to dissolve the material with only nitric acid and avoided the complications of using HF. Undissolved material was stored in the hot cell for future dissolution efforts.

This experiment successfully demonstrated the use of the CEPOD process to dissolve plutonium and curium oxides using cobalt(III) ions. The advantage of using cobalt(III) ions over the commonly used silver(II) ions or fluoride ions resolves the issue of the difficult task of removing silver(II) from solution and the corrosive solutions that fluorine ions create. The electroplating method that was evaluated during for cold testing showed promising results at recovering silver from the solution and potentially recycling the silver for additional dissolutions.

Runs 75ED-1 through 75ED-12 were conducted in a hot cell located in REDC at ORNL. Runs 75ED-1 through 75ED-11 were conducted with cobalt(III) as the catalyzing ion in the reaction, whereas run 75ED-12 was conducted with silver(II). Very few differences in dissolution rates were observed between cobalt and silver ions as the catalyst. This can likely be attributed to the increased temperature of the hot cell, causing a negative impact on dissolution rates using silver ions, likely because of silver reacting with water at the higher temperature.

More experimentation is needed to isolate possible variables that affected dissolution rates. Unpredictable situations such as breakage of the dissolution vessels and in-cell wiring capabilities caused negative impacts on the dissolution rates.

5. REFERENCES

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