The Use of Catalyzed Electrolytic Plutonium Oxide Dissolution (CEPOD) for Waste Treatment

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Abstract
Catalyzed Electrolytic Plutonium Oxide Dissolution (CEPOD) was first demonstrated at Pacific Northwest Laboratory (PNL) in early 1974 in work funded by EXXON Nuclear Company, Inc. That work was aimed at dissolution of Pu-containing residues remaining from mixed-oxide reactor fuels dissolutions, and was first publicly disclosed in 1981. The process dissolves PuO$_2$ in an anolyte containing small (catalytic) amounts of elements that form kinetically fast, strongly oxidizing ions. These ions are continuously regenerated at the anode. Catalysts used, in their oxidized form, include Ag$^{2+}$, Ce$^{4+}$, Co$^{3+}$, and AmO$_2^{3+}$. This paper reviews the chemistry involved in CEPOD and the results of its application to the dissolution of the Pu content of a variety of PuO$_2$-containing materials such as off-standard oxide, fuels dissolution residues, incinerator ash, contaminated soils, and other scrap or wastes. Results are presented for both laboratory-scale and plant-scale dissolvers. Spin-off applications such as decontamination of metallic surfaces and destruction of organics are discussed.

Introduction
Dissolution of PuO$_2$ in aqueous solutions has been a notoriously difficult task throughout the time Pu has been available in weighable amounts. Plutonium dioxide, particularly oxide heated to high temperatures, has been almost impossible to dissolve except in hot concentrated acid containing the fluoride ion. The difficult task of dissolving PuO$_2$, particularly on a process scale, is scrap recovery, in Pu metal production, in fuels preparation operations, and in mixed-oxide reactor fuels dissolution has been critically reviewed.\(^{1}\)
That review showed that not only is crystalline PuO$_2$ kinetically very difficult to dissolve in nitric acid solutions, but it is also thermodynamically insoluble in nitric solutions below about 4 M (Figure 1). The use of the fluoride ion, then, is based on its ability to complex Pu(IV) in strongly acidic solutions where it acts to increase both the rate of PuO$_2$ dissolution and its thermodynamic solubility. Because this dissolution process is based on formation of the Pu(IV) fluoride complex, the fluoride concentration often must exceed the final dissolved Pu concentration.

In irradiated mixed-oxide fuels, many scraps, and various Pu-contaminated wastes, other contaminants such as Si, Zr, U, and various fission products also form fluoride complexes. They virtually prevent the dissolution of PuO$_2$ when present in large quantity relative to PuO$_2$ unless a large excess of fluoride is used. Processes for leaching Pu from various scraps have often employed repeated cycles of leaching by fluoride-containing nitric acid solutions. Not only has this produced large volumes of solutions, generating eventually more wastes, but significant amounts of Al$^{3+}$ are generally added to the solutions (further increasing waste) to complex the fluoride both to allow normal Pu processing by ion exchange or solvent extraction and to minimize fluoride corrosion of equipment. When silica or silicates are present, the volatilization of SiF$_4$ can produce significant problems in off-gas systems, and silica often precipitates when Al is added to prepare the solution for further processing.

An alternative dissolution (leaching) concept has been proposed by Ryan and Bray that uses electrical energy to force the nitric acid oxidation and dissolution of PuO$_2$ as the PuO$_2^{2+}$ ion.\(^{2,3}\)
This concept was first publicly presented in 1981.

(a) All authors from Pacific Northwest Laboratory, Richland, Washington
Figure 1. Thermodynamically Calculated Solubility of PuO$_2$ in HNO$_3$

at the 182nd National Meeting of the American Chemical Society in New York. The purpose of this paper is to review this concept, to discuss further development of the concept, to discuss spinoffs of this technology to other applications, and to discuss some potential applications of this technology to waste treatment; the ultimate goal being conversion of transuranic (TRU) waste to low-level waste.

History

The use of Ce to increase the rate of dissolution of PuO$_2$ by nitric acid was reported by Wilson in 1961.\(^4\) Actually Wilson carried out only very limited experiments using Ce(III) in 15.7 M HNO$_3$ and reported PuO$_2$ dissolution rates for very low-fired PuO$_2$ which, while measurably faster than in nitric acid alone (by about a factor of five), were still low from a practical standpoint.

Uriarte and Rainey\(^5\) studied the effect of Ce(IV) on PuO$_2$ dissolution in nitric acid. They, unlike Wilson, adequately showed that Ce(IV) increases the rate of PuO$_2$ dissolution in nitric acid. They mistakenly concluded that at 4 M HNO$_3$ the dissolution rate was simply proportional to the concentration of Ce(IV). They also were incorrect in concluding that Ce(IV) does not enhance dissolution at 7, 10, and 14 M HNO$_3$ and that Ce(IV) below 0.005 M has no effect.

In 1973, Bray and Ryan at Pacific Northwest Laboratory (PNL), under a private contract with EXXON Nuclear Company, Inc., recognized that Wilson's results were due to slight oxidation of Ce(III) to Ce(IV) by the concentrated HNO$_3$. They found that reasonably high-fired (950°C) PuO$_2$ could be dissolved in hot solutions of Ce(IV) in ~4 M HNO$_3$. In January 1974, they demonstrated the rapid dissolution of 900°C-fired PuO$_2$ in the anode compartment of a two-compartment electrolytic cell in which either Ce, Ag, or Co ions were present in less than stoichiometric amounts in the anolyte to act as oxidation catalysts. At that time they found that dissolution using Ag ions as the catalyst was very fast, achieving practical dissolution rates at 25°C. This work, reported to EXXON Nuclear in January 1974,\(^6\) eventually led to two patents.\(^3,7\)

Others\(^8,9\) also independently recognized the potential applicability of Ce(IV) to dissolution of Pu in mixed oxide fuels dissolution. They apparently abandoned this approach because various oxidizable fission products (such as Ru metal) consumed unacceptably large amounts of Ce(IV) with resultant large addition to the high-level waste.

The EXON sponsored work was aimed at dissolving PuO$_2$ residues remaining after treating irradiated mixed-oxide fuels with nitric acid alone. As such, the proposed concept was to use the fission product Ce present in the dissolver solution as the oxidation catalyst. This level of Ce (~0.005 M in the dissolver solution) was found to be effective in dissolving the ~2 g PuO$_2$/L not dissolved by the initial direct nitric acid dissolution of mixed oxide fuels. This work was not released by EXXON for public disclosure until
1981.(2) Work with Ag as the catalyst under EXXON sponsorship was limited, but information was presented at that time to indicate that the PuO$_2$ dissolution rate with Ag(II) might be as much as $10^4$ times that of Ce(IV).

After EXXON work was discontinued because of the U.S. government decision not to reprocess power reactor fuels, but before EXXON's formal release of the work, Thompson et al.(10) examined the use of electrolytically regenerated Ce(IV) in the dissolution of PuO$_2$ in combustible waste. Also after the 1981 release, French workers(11-14) carried out studies based on Bray, Ryan, and Boldt's European Patent(7) that were aimed at process-scale CEPOD dissolution of PuO$_2$ using the Ag ion catalyst.

Starting in 1985, a significant U.S. Department of Energy (DOE) funded program was started at PNL aimed at development of CEPOD for application to a range of PuO$_2$ dissolution and Pu leaching applications. This work involves a variety of Pu-containing residues and wastes. Considerable development of the CEPOD process itself, as well as of spin-off applications also started during the 1970s, has now occurred.

Dissolution Theory

In the CEPOD process, PuO$_2$ is dissolved in an anolyte containing small (catalytic) amounts of elements that form kinetically fast, strongly oxidizing ions. The oxidizing ions are regenerated at the anode; they act in a catalytic manner, carrying electrons from the solid PuO$_2$ surface to the anode of the electrochemical cell. The standard potentials for the oxidative dissolution of PuO$_2$ have been calculated:(1)

$$PuO_2 + e^- = PuO_2^+ \quad E^o = 1.58 \text{ V} \quad (1)$$

$$PuO_2 + 2e^- = PuO_2^{2+} \quad E^o = 1.24 \text{ V} \quad (2)$$

It was pointed out by Bray and Ryan(2) that because

$$PuO_2^+ + e^- = PuO_2^{2+} \quad E^o = 0.9164 \text{ V} \quad (3)$$

the final product of oxidative dissolution will be PuO$_2^{2+}$. It is assumed that the dissolution proceeds through reaction (1) because greater than one-equivalent electron transfer reactions are of low probability.(15)

Based on the above potentials and the assumption that dissolution proceeds through reactions (1) and (3), it can be seen that catalyst couples for this process probably need to have a potential of about 1.5 V or greater and it is assumed, as discussed previously,(2) that rapid electron exchange between the oxidized and reduced forms of the couples is necessary. The following couples are found to be applicable:

$$Ce^{3+} = Ce^{4+} + e^- \quad E^o = 1.74 \text{ V} \quad (4)$$

$$Co^{2+} = Co^{3+} + e^- \quad E^o = 1.84 \text{ V} \quad (5)$$

$$Ag^+ = Ag^{2+} + e^- \quad E^o = 1.98 \text{ V} \quad (6)$$

The formal potentials for reactions (4), (5), and (6) in 4 M HNO$_3$ are 1.61, 1.85, and 1.93 V, respectively.(16-18) In addition to the three couples above, the Am(VI)-Am(V) couple at 1.6 V appears to be effective. Of these couples, the Ag(II)-Ag(I) couple (reaction 6) has by far the highest rate of electron exchange, the rate being about $10^4$ times those of Co and Ce (reactions 4 and 5).(2) Indeed, the dissolution rate of pure PuO$_2$ (950°C-fired) in a Ag catalyzed CEPOD cell appears to be strictly diffusion limited. If adequate amounts of PuO$_2$ are present and sufficient cell current is used, this diffusion limit is the rate at which Ag$^+$ can diffuse to the anode surface to be reoxidized.

The Ag(II)-Ag(I) couple can also be used as a catalyst for the dissolution of PuO$_2$ by ozone. The reaction of O$_3$ with Ag$^+$ at 25°C was found to be first order in O$_3$ concentration and first order in Ag$^+$ concentration with an overall second-order rate constant of 0.18 M$^{-1}$sec$^{-1}$. At practical O$_3$ partial pressures that can be prepared and aqueous solubilities at these partial pressures, the Ag(II) generation rate (and thus maximum possible PuO$_2$ dissolution rate with O$_3$) is very much less than that achievable with electrolytic generation.
Overall Cell Reactions

All current flowing through an electrolyte solution must cause electrode reactions to occur at both the anode and cathode, with the amount of reaction at each electrode defined by Faraday's Law. In the CEPOD process, the desired overall cell reactions are

\[ \text{PuO}_2 + 2\text{NO}_3^- + 4\text{H}^+ \rightarrow \text{PuO}_2^{2+} + 2\text{NO}_2 + 2\text{H}_2\text{O} \]  

or

\[ 3\text{PuO}_2 + 2\text{NO}_3^- + 8\text{H}^+ \rightarrow 3\text{PuO}_2^{2+} + 2\text{NO} + 4\text{H}_2\text{O} \]

The reduction of nitrate, particularly at high current densities, can be complex, and other products of nitrate reduction such as \( \text{N}_2\text{O}, \text{N}_2, \) and \( \text{NH}_4^+ \) have been observed. These other nitrate reduction products result in consumption of less nitric acid per amount of \( \text{PuO}_2 \) dissolved but are not readily converted back to nitric acid with \( \text{O}_2 \) and water in an off-gas scrub tower.

At high current densities, the rate of diffusion of \( \text{Ag}^+ \) to the CEPOD cell anode is limiting, and current efficiencies are typically in the range of 30 to 70%. This is not objectional in \( \text{PuO}_2 \) dissolution because electrical costs are insignificant relative to other costs but may be objectional in some of the spin-off applications. The rest of the current passed results in reactions such as

\[ 2\text{H}^+ + 2\text{NO}_3^- \rightarrow 2\text{NO}_2 + \text{H}_2\text{O} + 1/2\text{O}_2 \]  

\[ 2\text{H}^+ + 2\text{NO}_3^- \rightarrow \text{H}_2\text{O} + 2\text{NO} + 3/2\text{O}_2 \]

In a separated compartment (diaphragm) cell, two separate solution compartments are present, and the separate electrode reactions may occur under widely differing conditions. Electrical neutrality is maintained by ionic migration through the porous diaphragm (separator).

Anode Reactions

The following four reactions occur in the anode compartment (the first two at the electrode surface):

\[ \text{Ag}^+ - \text{Ag}^{2+} + e^- \]  

\[ 2\text{H}_2\text{O} + \text{O}_2 + 4\text{H}^+ + 4e^- \]  

\[ 2\text{Ag}^{2+} + \text{PuO}_2 - \text{PuO}_2^{2+} + 2\text{Ag}^+ \]  

\[ 2\text{Ag}^{2+} + \text{H}_2\text{O} - 2\text{Ag}^+ + 2\text{H}^+ + 1/2\text{O}_2 \]

These increase the net positive charge in the anode compartment, and two events occur to balance this increase: 1) \( \text{H}^+, \text{Ag}^+, \text{Ag}^{2+}, \) and \( \text{PuO}_2^{2+} \) migrate through the diaphragm to the cathode compartment, and 2) \( \text{NO}_3^- \) migrates from the cathode compartment into the anode compartment.

Cathode Reactions

The following overall reactions occur in the cathode compartment (others such as \( \text{N}_2\text{O}, \text{N}_2, \) or \( \text{NH}_4^+ \) production occur at certain acidities, particularly at high current density, and \( \text{H}_2 \) is expected to be produced at low acidity):

\[ 2\text{H}^+ + \text{NO}_3^- + e^- \rightarrow \text{NO}_2 + \text{H}_2\text{O} \]  

\[ 4\text{H}^+ + 2\text{NO}_3^- + 3e^- \rightarrow \text{NO} + 2\text{H}_2\text{O} \]

These all consume more \( \text{H}^+ \) than \( \text{NO}_3^- \) and thus raise the negative charge in the catholyte. Again, neutrality is maintained by \( \text{H}^+ \) diffusing from the anode compartment into the cathode compartment and to a lesser extent by nitrate diffusing into the anode compartment.

The net mass transfer in a CEPOD cell is a fairly complex function of transference numbers, ionic concentrations, amperage, and the relative extent of the various electrode reactions such as reactions (11) through (16); the latter in turn being influenced by such things as cell mixing efficiency. In general, the nitric acid concentration increases in the anode compartment and decreases in the cathode compartment under normal CEPOD cell operating conditions.
Hydrogen production at the cathode is undesirable for two reasons. One is the obvious safety hazard, and the other is that hydrogen embrittlement can occur in certain metals such as titanium that might be used in the construction of the electrodes. Figure 2 shows the percent hydrogen in the cathode off gas from a small-scale CEPOD dissolver as a function of nitric acid concentration. Based on these data, acidities in CEPOD catholyte are kept above 4 to 6 M HNO₃ by the continuous addition of 12 to 16 M HNO₃ accompanied by continuous vacuum aspiration of gas and overflow liquid from the cathode compartment. In process-scale cells, both the flow of incoming acid and the density of the out-flowing acid are continuously monitored with automatic power shutdown if either drop below predetermined set points. This, combined with the large gas dilution factor resulting from the aspiration process, insures that hydrogen levels are far below explosive limits. The aspirated NO, NO₂, and dissolved HNO₂ can be reconverted to HNO₃ for recovery, if desired, by reaction with O₂ in air in a scrub tower.

**Cell Description**

The CEPOD cell is a two-compartment cell with an electrode in each compartment. The compartments are separated from each other by a porous diaphragm chosen to minimize solution mixing while maintaining adequate electrical conductivity (Figure 3). Such mixing must be kept to a minimum because nitric acid reduction products in the catholyte will rapidly reduce Ag(II) if they get into the anode compartment. Various barriers or diaphragm materials have been examined including porous ceramics, porous valve-metal (Ti, Zr, Nb, etc.) frits, porous fluorocarbon polymers, and Nafion® (DuPont, Wilmington, Delaware) perfluorinated cation exchange membranes. All are in principle and in fact usable, but some are not available in the most desired porosity. Workers in France are using a porous ceramic, and workers in England are using the Nafion membranes in the production of Ag(II) in nitric acid for the destruction of organics (a spin-off of CEPOD to be discussed later).

As is well known in the electrochemical industry, few anode materials can be used at the high anode potentials required to anodically produce highly oxidizing species in solution. Because of its high oxygen overvoltage and its corrosion resistance, shiny Pt is the usual choice for such application. As is also well known, the so-called valve-metals (Ti, Zr, Nb, etc.) that form protective anodic films and thus do not anodically dissolve at reasonable voltages can be plated with Pt by various means and thus serve very well as Pt anodes.

The anode compartment is vigorously stirred to move Ag(I) rapidly to the anode surface for oxidation to Ag(II) and to properly suspend the solid plutonium-containing particles to be dissolved or leached so as to optimize contact of Ag²⁺ with particle surfaces. The temperatures of the anode and cathode compartments are controlled by a heat exchanger system or systems to an optimum temperature range. The heat exchangers remove the thermal energy produced by Joule heating in the cells at high current densities.
Laboratory-Scale CEPOD Dissolver

A laboratory (100-mL anode compartment) dissolver, which incorporates the criteria discussed above, is shown in Figure 4. This cell makes use of a Pt-plated anode (inside surface only) of 54-cm$^2$ surface area. The cathode is either Ti sheet or Pt-coated Ti sheet as desired. Cooling is by water jacketing of the anode compartment. This cell design was used for all laboratory-scale PuO$_2$ dissolution, Pu-containing scrap leaching, and Pu-contaminated waste leaching studies, as well as for studies of electrolytic destruction of contaminated or hazardous wastes. Cells of other designs were used in the laboratory for measurement of gases produced, for testing and measurement of the resistance of cell diaphragms, and for testing of other cell materials.

Process-Scale CEPOD Dissolvers

Two full-process-scale CEPOD dissolvers of significantly different design have been built by PNL. Both of these were designed to be safe with respect to nuclear criticality at all possible concentrations of Pu. Both dissolvers were built of materials resistant to attack by the reagents present in the process.

The first of these dissolvers (CEPOD II) was extensively tested in nonradioactive and in radioactive operation (Figure 5). This dissolver can be operated easily up to 1000 amps. Studies were conducted on heat transfer, mass transfer [including Ag(II) generation rates], and mixing (laminar versus nonlaminar flows at the electrode surface). The CEPOD II dissolver system was designed to be automatically controlled by a PC-based data acquisition and control system that will control the temperature and the concentration of nitric acid in the catholyte. Temperature control is by feedback control of the cooling water flowrate. Control of the concentration of nitric acid in the catholyte is achieved by feedback control of the catholyte feed rate. Feedback control of the current could be achieved by spectrophotometrically
monitoring the progress of the dissolution process. Development of such a spectrophotometric monitoring system is in progress.

The computer will also monitor several safety or operational control parameters and will automatically shut off power if prechosen limits are exceeded. These parameters include catholyte density, catholyte flow, off-gas flow, cell temperature, anolyte cooling water flow, catholyte cooling-water flow, cell applied voltage, and cell current. Other control parameters that could easily be added include monitoring the limits for conductivity and radioactivity in the cooling water and sounding an alarm if these limits are exceeded. The data acquisition system provides a ready record of all these parameters.

After adequate cold-testing of the dissolver and control system, CEPOD II was installed in a glovebox in a research and development facility and tested with a variety of Pu-containing materials, none of which were pure PuO$_2$. Most of these materials are known to or, based on their composition, expected to pose a difficult problem for conventional HNO$_3$-HF dissolution or leaching.

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Figure 5. Production-Scale, Batch CEPOD II Dissolver
Because of a 2-kg Pu limit allowed in the facility, the dissolver has operated only a small percentage of this testing period with the bulk of the time devoted to Pu material receiving and associated accountability, ion-exchange purification of the dissolved Pu, conversion of purified Pu to pure PuO₂, product analysis and accountability, and PuO₂ shipping. At the time of this writing approximately 5 kg of Pu had been processed through the CEPOD II system.

Another process-scale dissolver of significantly different design (CEPOD III) has been designed and built, and is currently being cold-tested. This dissolver operates easily at currents up to 1500 A. This dissolver will also be operated with a PC-based data acquisition and control system.

Results

Laboratory-Scale Studies

Figure 6 shows dissolution curves for 500°C, 950°C, and 1700°C-fired pure PuO₂ in hot 12 M HNO₃ - 0.18 M HF. It can be seen that both increasing oxide firing temperature (decreasing PuO₂ surface area) and increasing Pu-to-fluoride ratio lowers the dissolution rates significantly. It is also known⁽¹⁾ that the presence of impurities which complex fluoride (such as Al, Si, Zr, etc.) can very drastically reduce the rate of HNO₃-HF dissolution over those shown in Figure 6.

Figure 6. Rate of PuO₂ Dissolution Using 12 M HNO₃ + 0.18 M F⁻
Figure 7 shows the dissolution, to a final concentration of 106 g Pu/L, of the same three oxides in the laboratory CEPOD dissolver at only 30°C and 0.05 M Ag. It is apparent that the dissolution rate is essentially independent of PuO$_2$ surface area and is virtually constant until dissolution is almost complete. This indicates that the rate-limiting step in the process is not the rate of reaction of Ag(II) with the PuO$_2$ surface.

Figure 8 shows the dissolution rate of 950°C-fired PuO$_2$ in the CEPOD cell with various PuO$_2$ and Ag concentrations and various amperages. As discussed previously,$^{(21)}$ these results show that the rate-limiting step in PuO$_2$ dissolution using Ag ions as catalyst is the rate of diffusion of Ag(I) to the electrode surface to be reoxidized to Ag(II). The rate of diffusion of Ag(I) to the electrode surface is increased by increasing the Ag(I) concentration, by increasing stirring efficiency near the electrode surface, and by increasing the temperature. Increased temperature increases the parasitic consumption of Ag(II) by water oxidation,$^{(22)}$ but it also presumably increases the rate of Ag(II) diffusion to and reaction with the PuO$_2$ surface. The increased Ag(II) loss rate and increased Ag(II) reaction rate with PuO$_2$ will tend to compensate.

![Graph showing dissolution rate of PuO$_2$ with different temperatures and Ag concentrations.](image)

**Figure 7.** Effect of PuO$_2$ Surface Area on the Rate of Electrolytic Dissolution of PuO$_2$
Figure 8. CEPOD Dissolution of PuO$_2$ with Varying Current Density, Plutonium and Silver Concentrations

Figure 9 shows the rate of dissolution of 950°C-fired PuO$_2$ in the CEPOD cell at 0.1 M Ag and 50°C. It is clear that the rate is the same at 113 g PuO$_2$/L and 454 g PuO$_2$/L, indicating again that reaction rate is controlled by the rate at which Ag(I) is converted to Ag(II). Figure 10 shows the rate of dissolution of a plant oxide residue in the laboratory-scale CEPOD dissolver. Dissolution is shown to be rapid with only 0.3% of the initial plutonium remaining in the final undissolved residue. The results from CEPOD dissolution of the same residue but using Ce(IV) rather than Ag(II) is shown in Figure 11. The dissolution results from Figure 10 are provided in Figure 11 for comparison purposes and show the dramatic rate advantage of Ag(II) compared with Ce(IV).

In processing and handling Pu, a large range of Pu scraps, recycle materials, mixtures, and wastes may be produced. These vary widely in Pu...
content, ranging from wastes such as contaminated soil containing small amounts of Pu to off-standard oxide which is principally PuO₂. We have carried out Pu-leaching studies on a wide range of these materials in the laboratory-scale and/or process-scale CEPOD dissolvers. In all of these but one low-Pu-content, very high-fired scrap material, 98 to 100% Pu recovery was typically achievable in \( \sim 2 \) hr dissolution times. In the case of the one low Pu, high-fired scrap, over 60% recovery occurred in minutes followed by no further recovery. In many materials of relatively low Pu content, it was clear that dissolution rate was not limited by Ag(II) generation rate but was more likely limited by diffusion of Ag(II) to the Pu throughout a matrix of other materials. Three examples of these materials (incinerator ash, mixed oxide fuel pellets, and Pu-contaminated soils) are described below.
Delegard\(^{22}\) characterized, reburned at 650°C, and carried out HNO\(_3\)-HF dissolution tests on several Pu-containing incinerator ashes resulting from incineration of Pu-contaminated combustibles (see also Reference 21). His results with one of these materials are shown in Figure 12. Note that the first contact was at a higher fluoride concentration than the other three and that the final total leachate volume corresponds to only 50 g ash/L solution. Figure 13 shows two CEPOD runs with ash.\(^{21}\) One of these runs with 100 g ash/L was with ash that had not been washed to remove its chloride content. Leaching of Pu was slow because of precipitation of the Ag catalyst as AgCl, although we later found [as did Steele et al.\(^{19}\)] gradual oxidation of AgCl by Ag(II) to Ag\(^+\) and Cl\(_2\). After 5 hr, the solution was replaced with fresh 4 M HNO\(_3\) - 0.1 M Ag\(^+\), and most of the remaining Pu was quickly dissolved. The other run was made with ash prewashed at

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*Figure 10. CEPOD Dissolution of Plant Oxide Residue*

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100°C with 4 M HNO₃ to remove Cl⁻ (and other soluble ions such as Pb²⁺ which forms PbO₂ on the anode if not removed). Approximately 97% of the Pu was dissolved in 2 hr using 200 g ash/L. Only about 1% of the total Pu was dissolved in the prewash with 4 M HNO₃. The two methods resulted in similar total Pu recoveries. In order to achieve this with HNO₃-HF, however, four separate 1-hr leaching steps were required versus a 2-hr single leaching for CEPOD; the final leachant volume was four times as dilute in Pu for the fluoride process as for the CEPOD process, and a very large molar excess of fluoride relative to Pu was present in the fluoride leachant to complicate further processing.

Unirradiated mixed oxide reactor fuel (40% PuO₂), made by ball milling UO₂ and PuO₂ together, pressing into pellets, and sintering at

Figure 11. Comparison of CEPOD Dissolution of Plant Oxide Residue Using Silver or Cerium Catalyst
Figure 12. Multicontact Leaching Test Using HNO₃-CaF₂ (Data from 23)

Figure 13. Effect of 4 M HNO₃ Prewash on CEPOD Leaching of Plutonium from Incinerator Ash

* 30 min 4 M HNO₃ Wash
1690°C in Ar - 8% H₂, was crushed and screened to -100 mesh. This was dissolved in two separate experiments at 230-g mixed oxide/L and 90 to 100°C. In one case, 12 M HNO₃ was used alone and in the other, dissolution was in 8 M HNO₃ - 0.1 M Ce in a CEPOD cell. Figure 14 shows that PuO₂ dissolution was incomplete (reaching ~91%) in 12 M HNO₃ but was complete in 4 hr in the CEPOD run. CEPOD dissolution studies of irradiated mixed-oxide fuels using Ce(IV) have also been published.² It is anticipated that dissolution would be much faster using Ag as the catalyst instead of Ce.

Two aliquots of Pu-contaminated Hanford soil were leached for 3 hr at 70 to 90°C. One sample was leached in 4 M HNO₃ and the other was leached in a CEPOD cell in 4 M HNO₃ - 0.1 M Ce. Results are shown in Table 1. It is clear from the data that CEPOD has a real potential for leaching Pu (and the accompanying Am) from soils to below the limits for definition as nontransuranic waste. Again, much better results would be expected with Ag catalyst.

**Process-Scale Studies**

A large variety of Pu-containing scraps and recycle materials have been leached in the process-scale CEPOD II dissolver (~5 kg of Pu total). In all cases, Ag was the catalyst. No significant operational problems were encountered. Providing Cl⁻, if present in significant amount, was removed by prewashing, recoveries of Pu were typically >98% in 1 to 3 hr of operation. Figures 15 and 16 show results of two runs, each on two different Pu-containing materials.

![Figure 14. Dissolution of 40% PuO₂ Mixed Oxide Fuel](image-url)
Table 1. Leaching of Plutonium and Americium from Hanford Z-5 Crib Soil

<table>
<thead>
<tr>
<th>Solution Composition(^{(a)})</th>
<th>Initial Activity of Sample, nCi/g of Sample(^{(b)})</th>
<th>Sample Activity After Leaching, nCi/g of Initial Sample(^{(c)})</th>
<th>Sample Decontamination Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4\ M\ \text{HNO}_3)</td>
<td>Pu 46,400  Am 7,200</td>
<td>Pu 12,200  Am 3,000</td>
<td>Pu 3.8  Am 2.4</td>
</tr>
<tr>
<td>(4\ M\ \text{HNO}_3 + 0.1\ M\ \text{Ce}^{4+})</td>
<td>Pu 47,400  Am 13,200</td>
<td>Pu 23  Am 275</td>
<td>Pu 2,060  Am 48</td>
</tr>
</tbody>
</table>

(a) Both experiments used 1.0 g soil/30 mL of solution at 70 to 90°C for 3 hr.
(b) Calculated from the analyses of the residual solids\(^{(d)}\) and the filtered leachate.
(c) Residual solids were filtered, washed, and analyzed by fusing with sodium peroxide; dissolved in HCl; and the Am and Pu separated by solvent extraction, followed by liquid scintillation counting of the separated fractions.

Figure 15. CEPOD Leaching of Pu-Containing Material A with Ag Ion Catalyst

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CEPOD Technology Transfer

Development work on the CEPOD process for dissolution of PuO₂ has served to create an interest in adapting the chemistry of the strongly oxidizing couples (equations 4 to 6) used for CEPOD catalysts to other applications. This has resulted in two major applications: 1) the wet oxidation and thus destruction of radioactively contaminated or noncontaminated organic wastes, and 2) the decontamination of stainless steel. The present authors have been actively involved in both of these for some time.²⁴⁻²⁶ British workers (Steele et al.)¹⁹ have also recognized the potential adaptability of CEPOD technology developed for PuO₂ processing to destruction of organic wastes. We have also studied the application of this technology to the removal of oxidizable gases from gas streams.
Organic Destruction

Both the present authors and Steele et al.\textsuperscript{19} have carried out research on the wet electrolytic oxidation of organics using oxidation catalysts such as Ag and Ce. This has been done in what is basically a CEPOD cell, but if significant Pu is not present, the lack of nuclear criticality concern allows significant differences in cell design and size. We have shown the ability of such an approach to destroy a wide variety of organic wastes, both materials finding their way into wastes (often mixed with radioactive isotopes) in the nuclear industry and hazardous non-nuclear industry wastes. We have demonstrated the destruction of ion-exchange resins, cellulose materials, PCBs, etc. The efficient destruction of tributyl phosphate, kerosene, etc., has been demonstrated by others.\textsuperscript{19}

As an example of this application, Figure 17 shows the removal of the carbon content of a synthetic complexant concentrate waste. Complexant concentrate waste is an alkaline, high NaNO\textsubscript{3}-NaNO\textsubscript{2} solution containing significant amounts of radioisotopes such as $^{137}$Cs, $^{154}$Eu, $^{60}$Co, and transuranics. This material is currently stored in Hanford high-level waste tanks. It contains about 45 g of total organic carbon per liter present as complexing agents (and degradation products thereof) that were used in an early strontium recovery process. The synthetic waste used in these tests contained acetate, citrate, ethylenediamine tetraacetate, and hydroxyethyl-ethylendiamine triacetate. In the 76 to 80°C range, current efficiency remained at 100% until 85% of the organic carbon was removed. The improved organic destruction with an increase in temperature has also been noted by others.\textsuperscript{19}

The Ce catalyst results (not shown) are considerably poorer than those for Ag catalyst, and in fact are the same for this synthetic waste as that for no catalyst being present.

This demonstrates the potential of the electrochemical method for the destruction of organic constituents in radioactive wastes. The method has definite potential for the destruction of non-radioactive hazardous organic wastes as well.

Stainless Steel Decontamination

Solutions of Ce(IV) or Ag(II) attack the surface of stainless steel reasonably rapidly and in a relatively uniform manner. These reagents can thus be used in either a once-through or an electrolytic regeneration mode to chemically mill and thus decontaminate stainless steel surfaces. Ce(IV) has a cost advantage as well as an insignificant rate of reduction by water that allows long-term solution storage. Considerable development work has gone into the use of Ce(IV) in HNO\textsubscript{3} for this purpose.\textsuperscript{27} The rates of surface removal as a function of Ce(IV) concentration and temperature were measured, and an example of the results is shown in Figure 18. Metal removal rates increase with both temperature and Ce(IV) concentration, and above 45°C are such that stoichiometric reaction with the metal is approached within 12 hr.

Very high decontamination factors have been achieved with this technique, and it has been applied to both Pu and other transuranic-contaminated and fission-product-contaminated stainless steel equipment. Pu and Am purification equipment (such as ion exchange column end fittings) have been decontaminated adequately to be reused in nonradioactive, open laboratory work.

As an example of the potential of this process, five tanks that had been removed from concentrated Pu service in the PNL Critical Mass Laboratory were decontaminated to nontransuranic (<100 nCi/g of metal) levels without dismantling. These tanks had been water and steam rinsed, wrapped in plastic, and stored for 15 to 20 years. One 12-in.-diameter tank contained 159 kg of stainless steel Raschig rings resulting in a total inside surface area of 27.8 m\textsuperscript{2}, a total weight of 178 kg, and a void volume of 57 L. The tank was rinsed with 10 M HNO\textsubscript{3}, treated with Ce(IV) in 4 M HNO\textsubscript{3}, and rinsed with dilute nitric acid. A total of 176 g of Pu was removed from the tank and purified by ion exchange, leaving 0.044 g Pu (as determined by nondestructive assay). This amounted to 15 nCi of Pu remaining per gram of metal.
Figure 17. Electrochemical Destruction of Organics in Complexant Concentrate Waste
Use of CEPOD for Treating Solid TRU Waste

Current development efforts are focused on developing CEPOD technology and integrating it with suitable extraction technology to provide a processing system by which solid TRU waste can be processed into a small volume of TRU waste and a much larger volume of low level waste without increasing the total volume of waste. Figure 19 shows a schematic flowsheet of such an integrated process and the kinds of materials that could be processed.

The development effort is divided into three tasks:

- recovery and recycle of silver
- demonstration of complete leaching of TRU to less than the 100 nCi/g limit on low level waste
- design, fabrication, and demonstration of a multi-stage, continuous counter flow dissolver system.
Figure 19. Integrated Scrap/Waste Processing Schematic Flowsheet
Figure 20. CEPOD IV Multistage Countercurrent Dissolver System for Processing TRU and/or Hazardous Chemical Contaminated Particulate Solid Waste
Laboratory experiments have shown that silver can be reduced to metal particles and removed from the dissolver solution by filtration down to below the current limit of 5 ppm prior to or following the extraction of plutonium and other TRUs. Figure 20 shows a schematic view of a dissolver concept now under development. Both silver and nitric acid will be recovered and recycled. Only electrical power will be consumed.

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References


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