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Jack L. Ryan
L. A. Bray
E. J. Wheelwright
G. H. Bryan

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Pacific Northwest Laboratory
Richland, Washington 99352

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CATALYZED ELECTROLYTIC PLUTONIUM OXIDE DISSOLUTION (CEPOD)

The Past Seventeen Years and Future Potential

J. L. Ryan, L. A. Bray, E. J. Wheelwright, and G. H. Bryan

Pacific Northwest Laboratory, Richland, WA 99352

Catalyzed Electrolytic Plutonium Oxide Dissolution (CEPOD) was first demonstrated at PNL in early 1974 in work funded by EXXON Corporation. That work was aimed at dissolution of Pu-containing residues remaining in mixed-oxide reactor fuels dissolution 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 are continuously regenerated at the anode. Catalysts used, in their oxidized form, include Ag^{2+}, Ce^{4+}, Co^{3+}, and AmO_2^{2+}. 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 scraps 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.

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Dissolution of PuO_2 in aqueous solutions has been a notoriously difficult task throughout the time Pu has been available on a weighable scale. Plutonium dioxide, particularly oxide heated to high temperatures, has been almost impossible to dissolve except in hot concentrated nitric acid

containing the fluoride ion. The difficult task of dissolving PuO_2, particularly on a process scale, in 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 acid 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 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 the second half century of plutonium chemistry and technology.

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) and 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 PuO_2 dissolution of Pu values 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 EXXON 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. 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 scraps 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):

$$PuO_2 \rightleftarrows PuO_2^{+} + e^- \qquad E^\circ = 1.58\ V \qquad (1)$$

$$PuO_2 \rightleftarrows PuO_2^{2+} + 2\ e^- \qquad E^\circ = 1.24\ V \qquad (2)$$

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

$$PuO_2^{+} \rightleftarrows PuO_2^{2+} + e^- \qquad E^\circ = 0.9164\ V \qquad (3)$$

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:

$$Ce^{3+} \rightleftarrows Ce^{4+} + e^- \qquad E^\circ = 1.74\ V \qquad (4)$$

$$Co^{2+} \rightleftarrows Co^{3+} + e^- \qquad E^\circ = 1.84\ V \qquad (5)$$

$$Ag^{+} \rightleftarrows Ag^{2+} + e^- \qquad E^\circ = 1.98\ V \qquad (6)$$

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

$$PuO_2 + 2NO_3^- + 4H^+ \rightarrow PuO_2^{2+} + 2NO_2 + 2H_2O \qquad (7)$$

or,

$$3PuO_2 + 2NO_3^- + 8H^+ \rightarrow 3PuO_2^{2+} + 2NO + 4H_2O \qquad (8)$$

The reduction of nitrate, particularly at high current densities, can be complex, and other products of nitrate reduction such as N_2O, N_2, and NH_4^+ have been observed. These other nitrate reduction products result in consumption of less nitric acid per amount of PuO_2 dissolved but are not readily converted back to nitric acid with O_2 and water in an off-gas scrub tower.

At high current densities, the rate of diffusion of 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 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

$$2H^+ + 2NO_3^- \rightarrow 2NO_2 + H_2O + 1/2\ O_2 \qquad (9)$$

$$2H^+ + 2NO_3^- \rightarrow H_2O + 2NO + 3/2\ O_2 \qquad (10)$$

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):

$$Ag^{+} \rightarrow Ag^{2+} + e^{-} \tag{11}$$

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-} \tag{12}$$

$$2Ag^{2+} + PuO_2 \rightarrow PuO_2^{2+} + 2Ag^{+} \tag{13}$$

$$2Ag^{2+} + H_2O \rightarrow 2Ag^{+} + 2H^{+} + 1/2\ O_2 \tag{14}$$

These increase the net positive charge in the anode compartment, and two events occur to balance this increase: 1) H^{+}, Ag^{+}, Ag^{2+}, and PuO_2^{2+} migrate through the diaphragm to the cathode compartment, and 2) 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 N_2O, N_2, or NH_4^{+} production occur at certain acidities, particularly at high current density, and H_2 is expected to be produced at low acidity):

$$2H^{+} + NO_3^{-} + e^{-} \rightarrow NO_2 + H_2O \tag{15}$$

$$4H^{+} + NO_3^{-} + 3e^{-} \rightarrow NO + 2H_2O \tag{16}$$

These all consume more H^{+} than NO_3^{-} and thus raise the negative charge in the catholyte. Again, neutrality is maintained by 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 HNO_3 by the continuous addition of 12 to 16 M HNO_3 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 shut down 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, NO_2, and dissolved HNO_2 can be reconverted to HNO_3 for recovery if desired by reaction with O_2 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. 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) perfluorinated cation exchange membranes. All are in principal and in fact usable, but some are not available in the most desired porosity. Workers in France are using a porous ceramic (11-14) and workers in England (19) 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 (20). As is also well known (20), 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 Ag^{2+} with particle surfaces. The temperature 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 3. 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 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 of 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 non-radioactive and in radioactive operation. This dissolver can be operated easily up to 1000 Amps. Heat transfer, mass transfer [including Ag(II) generation rates], and mixing (laminar versus nonlaminar flows at the electrode surface) studies were made. The CEPOD II dissolver system is 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 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 hydrogen concentration, off-gas flow, cell temperature, anolyte cooling water flow, catholyte cooling water flow, cell applied voltage, and cell current. Other control parameters that could be easily added include monitoring for and sounding an alarm if limits are exceeded for conductivity and radioactivity in the cooling water. 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. 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 PuO_2, product analysis and accountability, and PuO_2 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, 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 4 shows dissolution curves for 500°C, 950°C and 1700°C-fired pure PuO_2 in hot 12 M HNO_3 - 0.18 M HF. It can be seen that both increased oxide firing temperature (decreasing PuO_2 surface area) and increasing Pu-to-fluoride ratio significantly lower dissolution rates. 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 HNO_3-HF dissolution over those shown in Figure 4.

Figure 5 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 6 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.

Figure 7 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).

In processing and handling of 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 PuO_2. 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 ~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 through a matrix of other material. Three examples of these materials, incinerator ash, mixed oxide fuel pellets, and Pu-contaminated soils are described below.

Delegard (23) 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 (21)]. His results with one of these materials are shown in Figure 8. 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 9 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 100°C with 4 M HNO_3 to remove Cl^- (and other soluble ions such as Pb which forms PbO_2 on the anode if not removed). Approximately 97% of the Pu was dissolved in 2 hrs. using 200 g ash/L. Only about 1% of the total Pu was dissolved in the prewash with 4M HNO_3.

Unirradiated mixed oxide reactor fuel (40% PuO_2), made by ball milling UO_2 and PuO_2 together, pressing into pellets, and sintering at 1690°C in Ar - 8% H_2, 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 HNO_3 was used alone and in the other, dissolution was in 8 M HNO_3 - 0.1 M Ce in a CEPOD cell. Figure 10 shows that PuO_2 dissolution was incomplete (reaching ~91%) in 12 M HNO_3 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 70-90°C. One sample was leached in 4 M HNO_3 and the other was leached in a CEPOD cell in 4M HNO_3 - 0.1M 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.

TABLE 1. Leaching of Plutonium and Americium from Hanford Z-9 Crib Soil

Solution Composition(a)	Initial Activity of Sample, nCi/g of Sample(b)		Sample Activity After Leaching, nCi/g of Initial Sample(c)		Sample Decontamination Factor	
	Pu	Am	Pu	Am	Pu	Am
4 M HNO_3	46,400	7,200	12,200	3,000	3.8	2.4
4 M HNO_3 + 0.1 M Ce^{4+}	47,400	13,200	23	275	2,060	48

(a) Both experiments used 1.0 g soil/30 mL of solution at 70-90°C for 3 h.
(b) Calculated from the analyses of the residual solids(c) 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.

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 11 and 12 show results of two runs each on two different Pu-containing materials.

CEPOD Technology Transfer

Development work on the CEPOD process for dissolution of PuO_2 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 (19) have also recognized the potential adaptability of CEPOD technology developed for PuO_2 processing to destruction of organic wastes. The present authors have also studied the application of this technology to the removal of oxidizable gases from gas streams.

Organic Destruction. Both we and Steele et al. (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, cellulosic materials, PCBs, etc. The efficient destruction of tributyl phosphate, kerosene, etc. has been demonstrated by others (19).

As an example of this application, Figure 13 shows the removal of the carbon content of a synthetic complexant concentrate waste. Complexant concentrate waste is an alkaline, high $NaNO_3$-$NaNO_2$ 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 a early strontium recovery process. The synthetic waste used in these tests contained acetate, citrate, ethylenediamine tetraacetate, and

hydroxyethylethylenediamine triacetate. In the 76-80°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 (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 organics 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_3 for this purpose (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 14. Metal removal rates increase with both temperature and Ce(IV) concentration and above 45°C approach stoichiometric reaction with the metal 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^2, a total weight of 178 kg., and a void volume of 57 L. The tank was rinsed with 10 M HNO_3, treated with Ce(IV) in 4 M HNO_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 non-destructive assay). This amounted to 15 nCi of Pu remaining per gram of metal.

Future Potential

As we move into the second half century of the transuranium elements, increasing emphasis is being placed on accumulated transuranic and other radioactive wastes, on dismantling and disposal of closed or outmoded transuranic and general nuclear processing facilities, and cleanup of the sites themselves. The authors feel that CEPOD and CEPOD-related technology are quite suited to the treatment of many of the transuranic and nontransuranic waste problems.

The decontamination treatment of stainless steel equipment such as gloveboxes and hot cell equipment to the nontransuranic or low-level waste category, or even to recyclable levels, followed by removal of the

transuranics from the CEPOD solutions by ion exchange and/or solvent extraction is a very attractive option.

The wet oxidation of transuranic and other radioisotope contaminated organics, ranging from paper and gloves to solvents and cutting oils by CEPOD technology, certainly should be further studied. The extension of this technology to nonradioactive hazardous wastes is a logical technology transfer. Although the number of coulombs required per kilogram of organic waste is high, it has been shown that high current efficiencies can be obtained at high current densities (19). Also, the reduction of strong nitric acid at the cathode results in relatively low cell potential even though a very powerful oxidant is being produced at the anode. The conversion of produced nitrogen oxides back to nitric acid with air and the recovery of Ag means little chemical consumption or, more importantly, addition to the waste.

Finally, CEPOD technology shows great promise in treatment of at least the higher levels of transuranic-contaminated soils. The limited studies of this application should be expanded.

Acknowledgment

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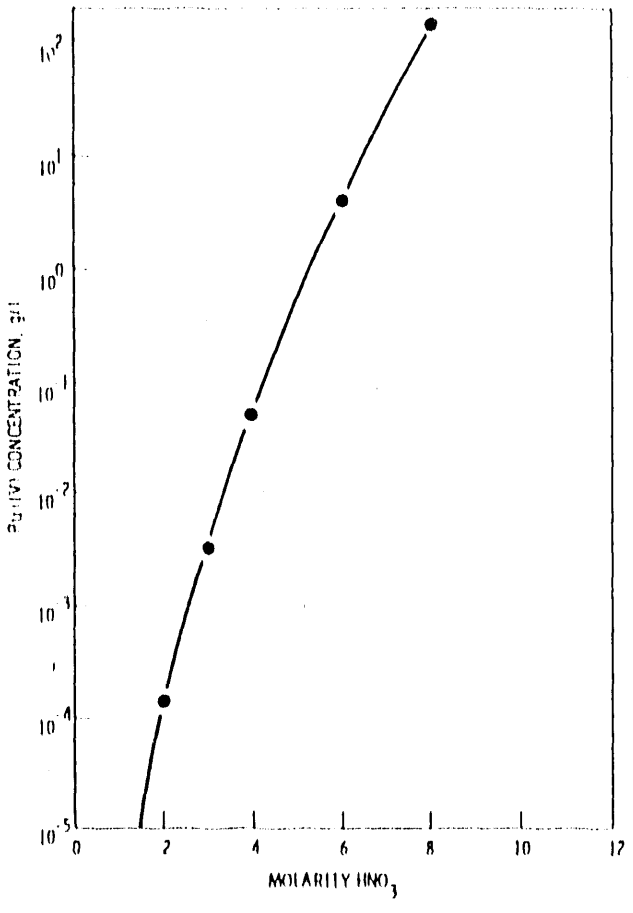


Figure 1. Thermodynamically calculated solubility of PuO_2 in HNO_3

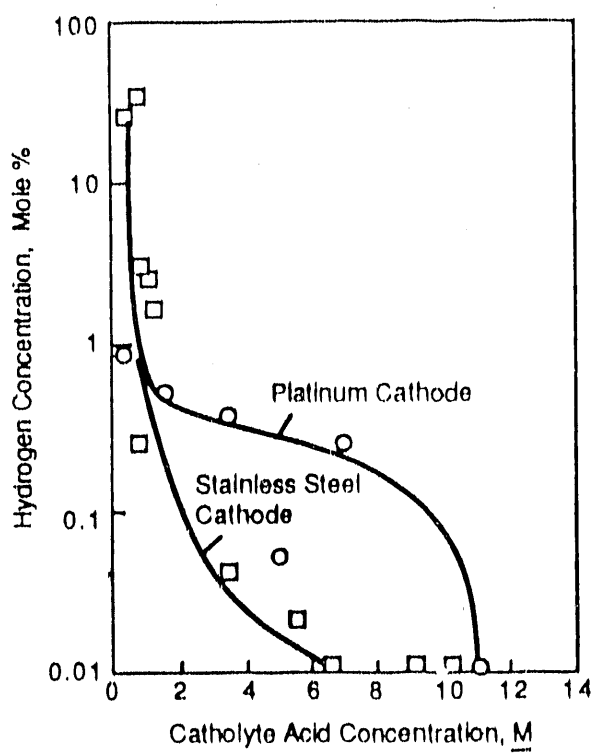


FIGURE 2. Effect of Catholyte Acid Concentration on Hydrogen Concentration of the Gas Evolved from the Cathode Compartment

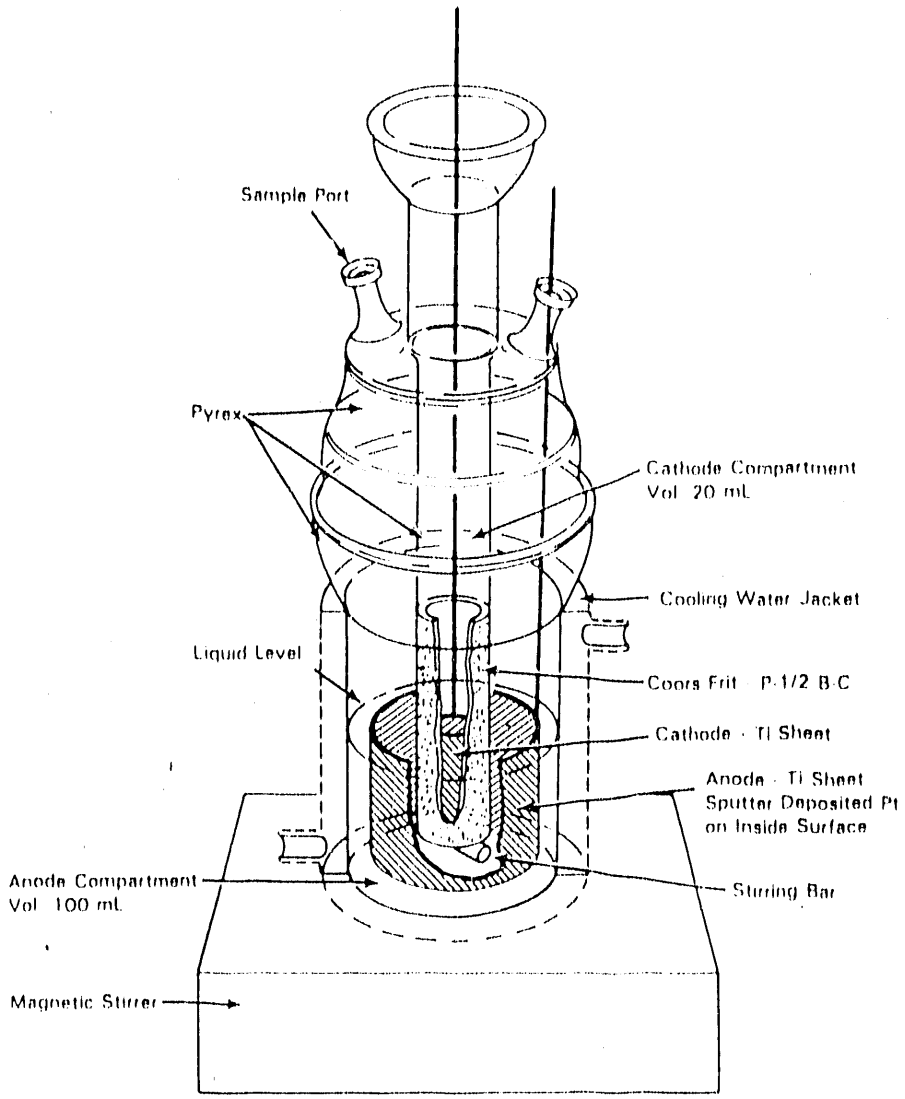


FIGURE 3. Laboratory-Scale CEPOD Dissolver

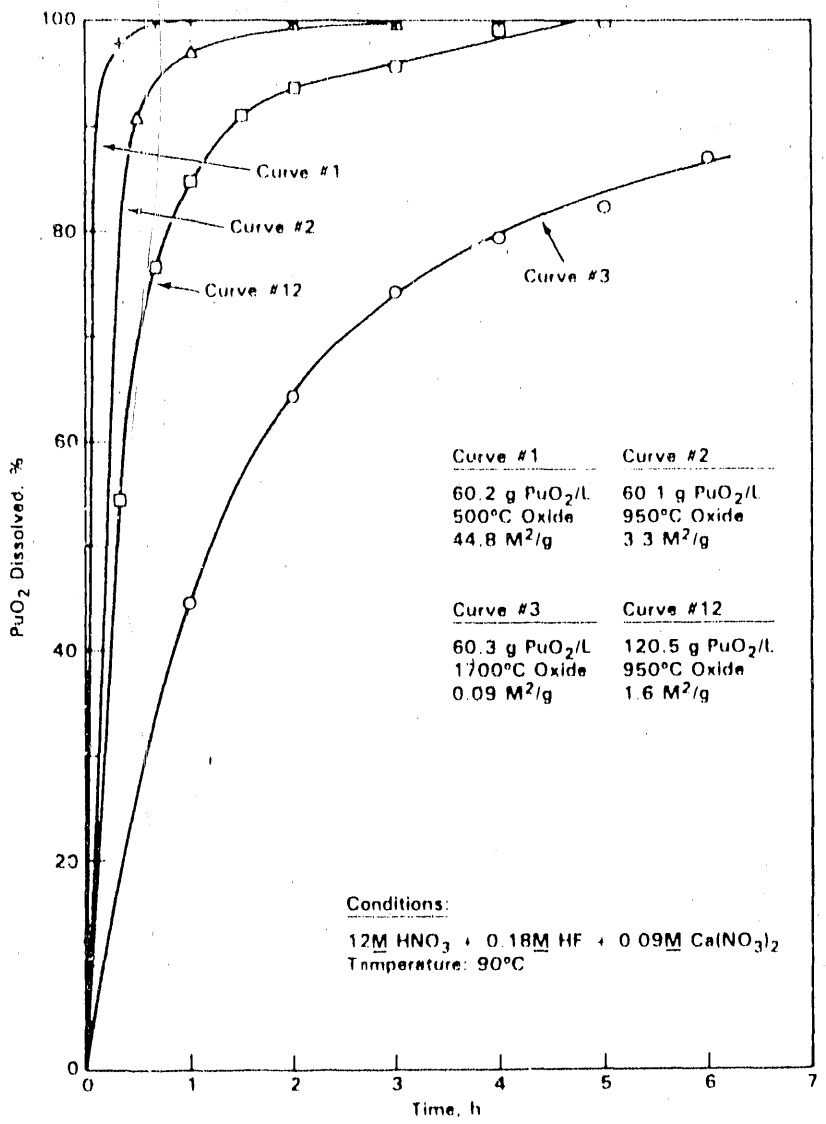


FIGURE 4. Rate of PuO_2 Dissolution Using 12 M HNO_3 + 0.18 M F^-

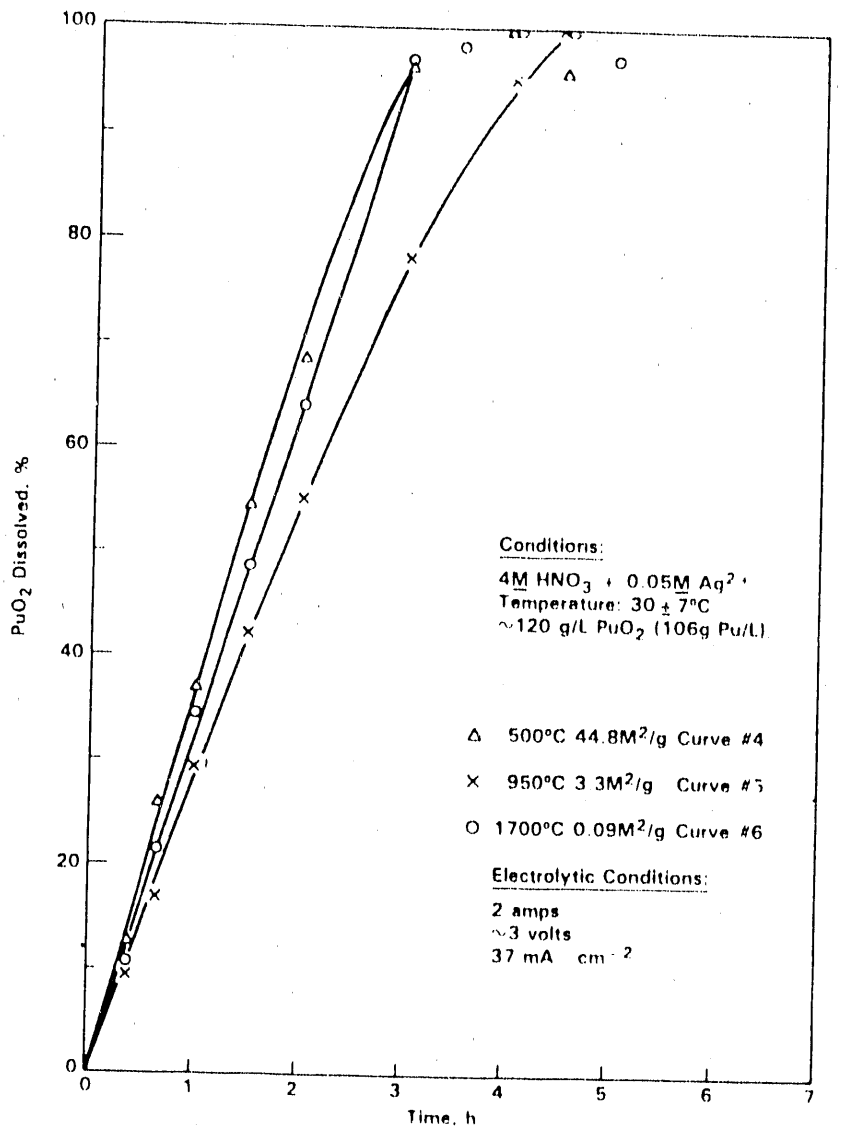


FIGURE 5. Effect of PuO_2 Surface Area on the Rate of Electrolytic Dissolution of PuO_2

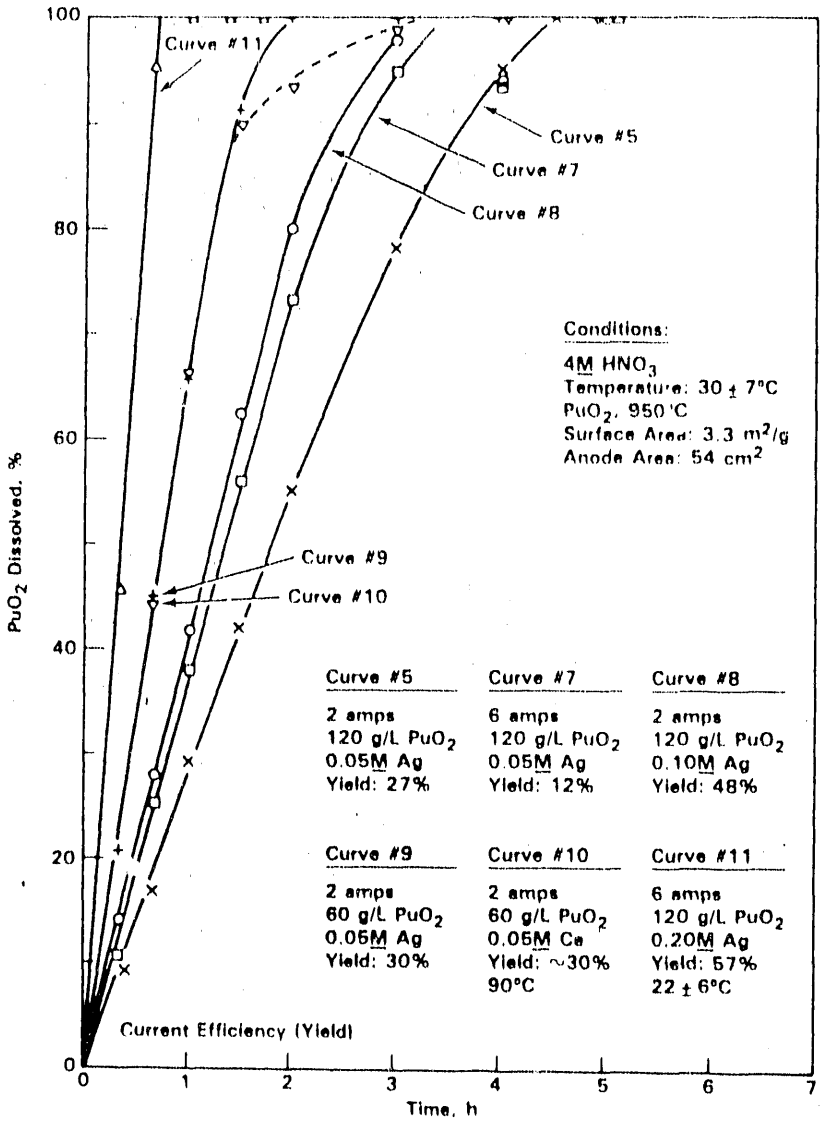


FIGURE 6. CEPOD Dissolution of PuO_2 With Varying Current Density, Plutonium and Silver Concentrations

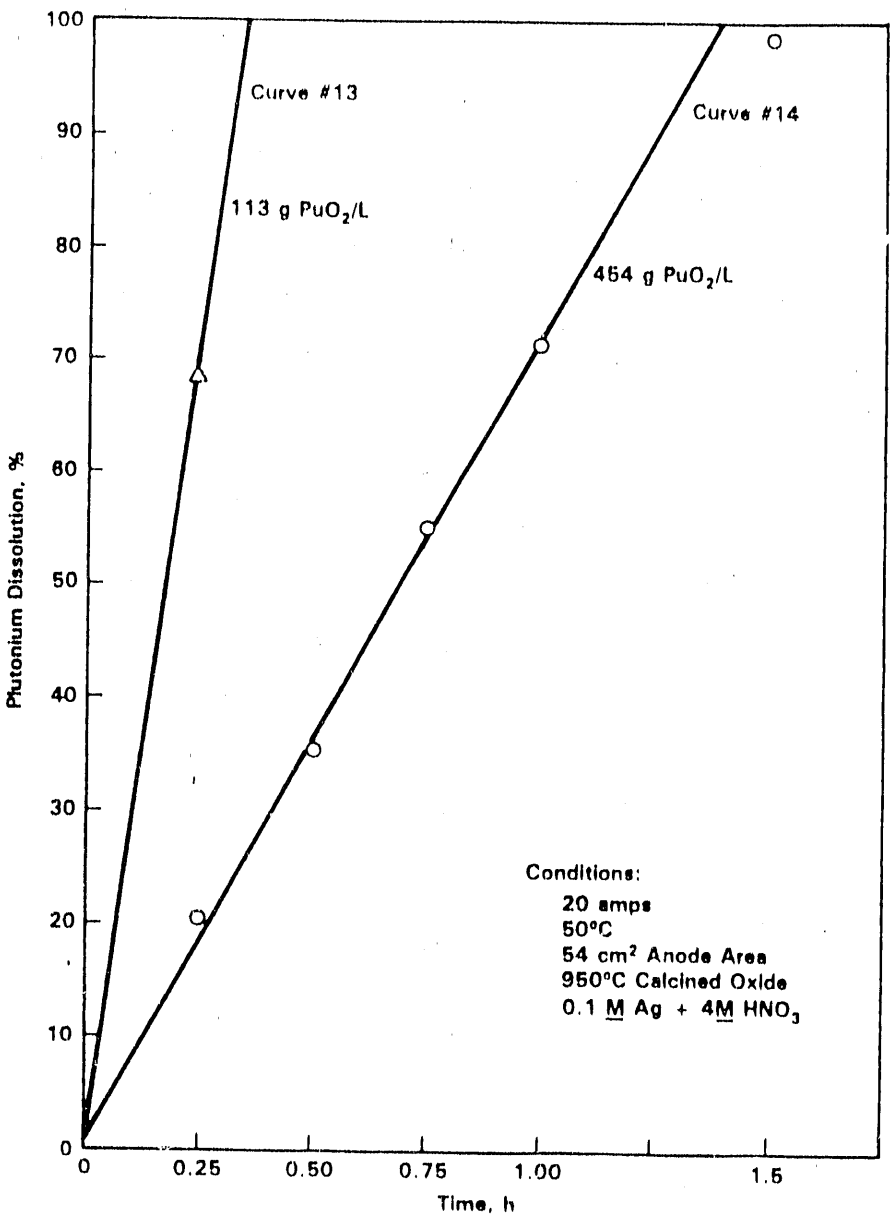


FIGURE 7. CEPOD Dissolution of PuO_2 at 50°C and High Cell Current

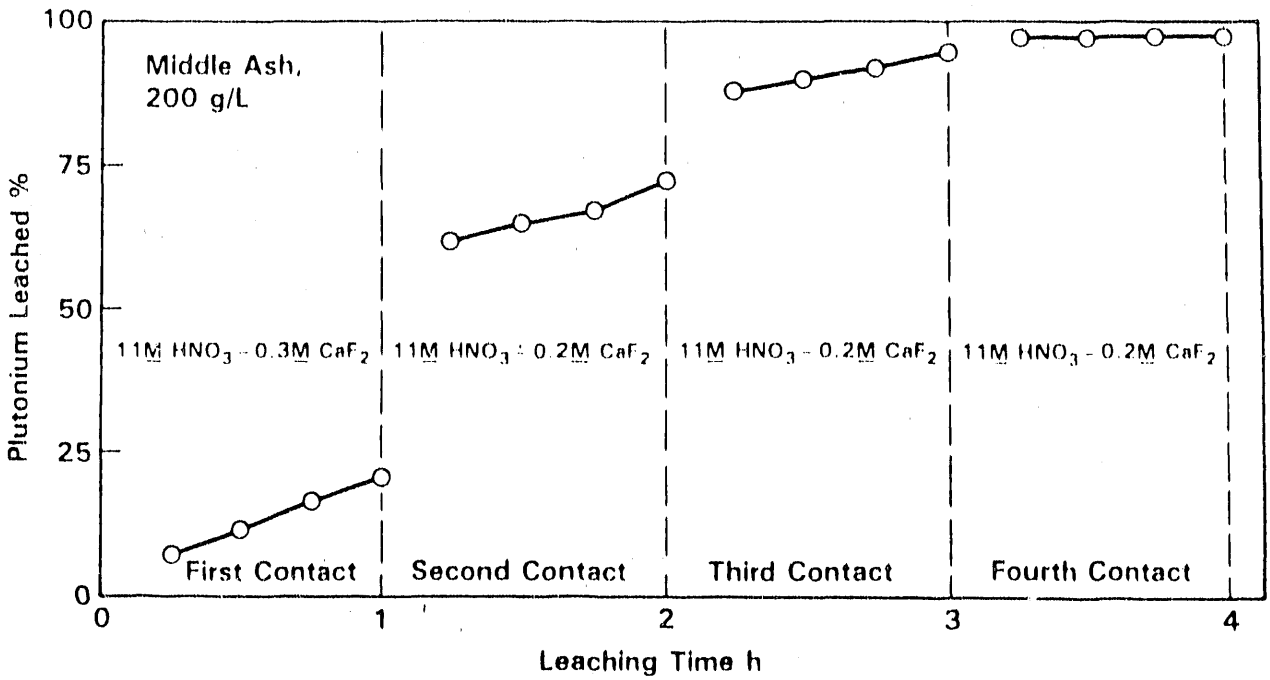


FIGURE 8. Multicontact Leaching Test Using HNO_3-CaF_2 (Data from 23)

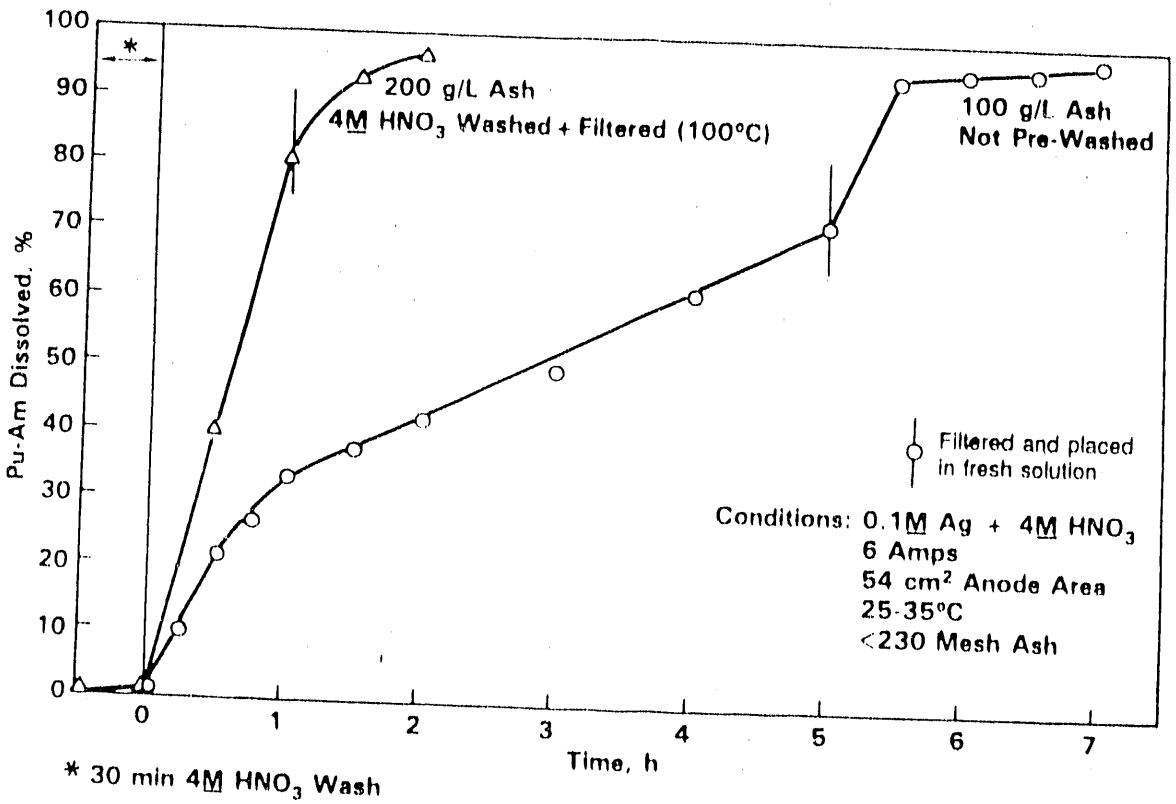
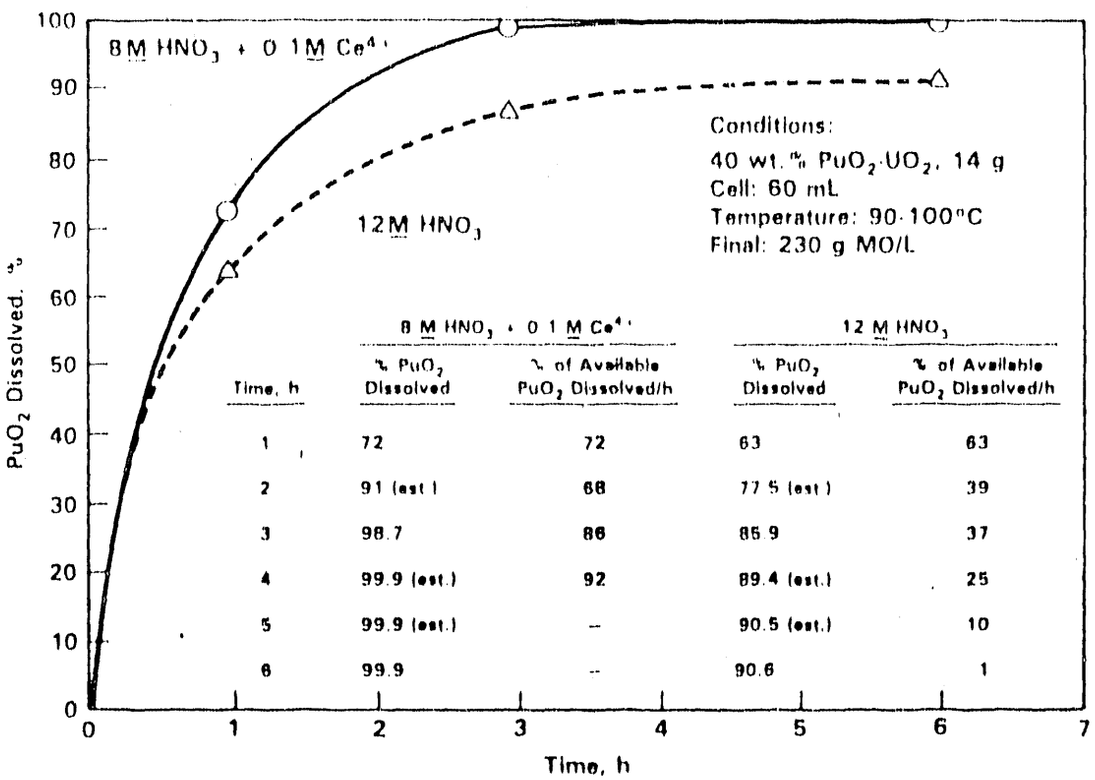


FIGURE 9. Effect of 4 M HNO_3 Prewash on CEPOD Leaching of Plutonium from Incinerator Ash



Time, h	8 M HNO3 + 0.1 M Ce4+ % PuO2 Dissolved	8 M HNO3 + 0.1 M Ce4+ % of Available PuO2 Dissolved/h	12 M HNO3 % PuO2 Dissolved	12 M HNO3 % of Available PuO2 Dissolved/h
1	72	72	63	63
2	91 (est.)	68	77.5 (est.)	39
3	98.7	86	85.9	37
4	99.9 (est.)	92	89.4 (est.)	25
5	99.9 (est.)	--	90.5 (est.)	10
6	99.9	--	90.6	1

Figure 10. Dissolution of 40% PuO_2 Mixed Oxide Fuel

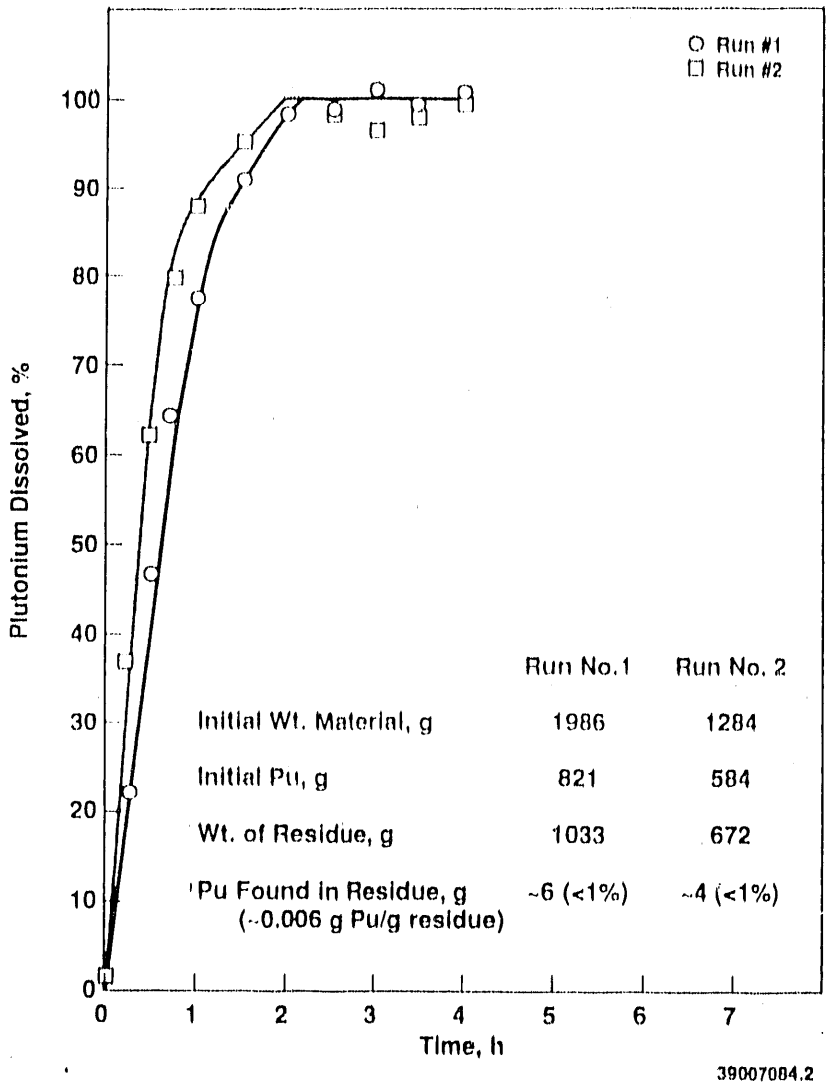


FIGURE 11. **CEPOD Leaching of Pu- Containing Material A With Ag Ion Catalyst**

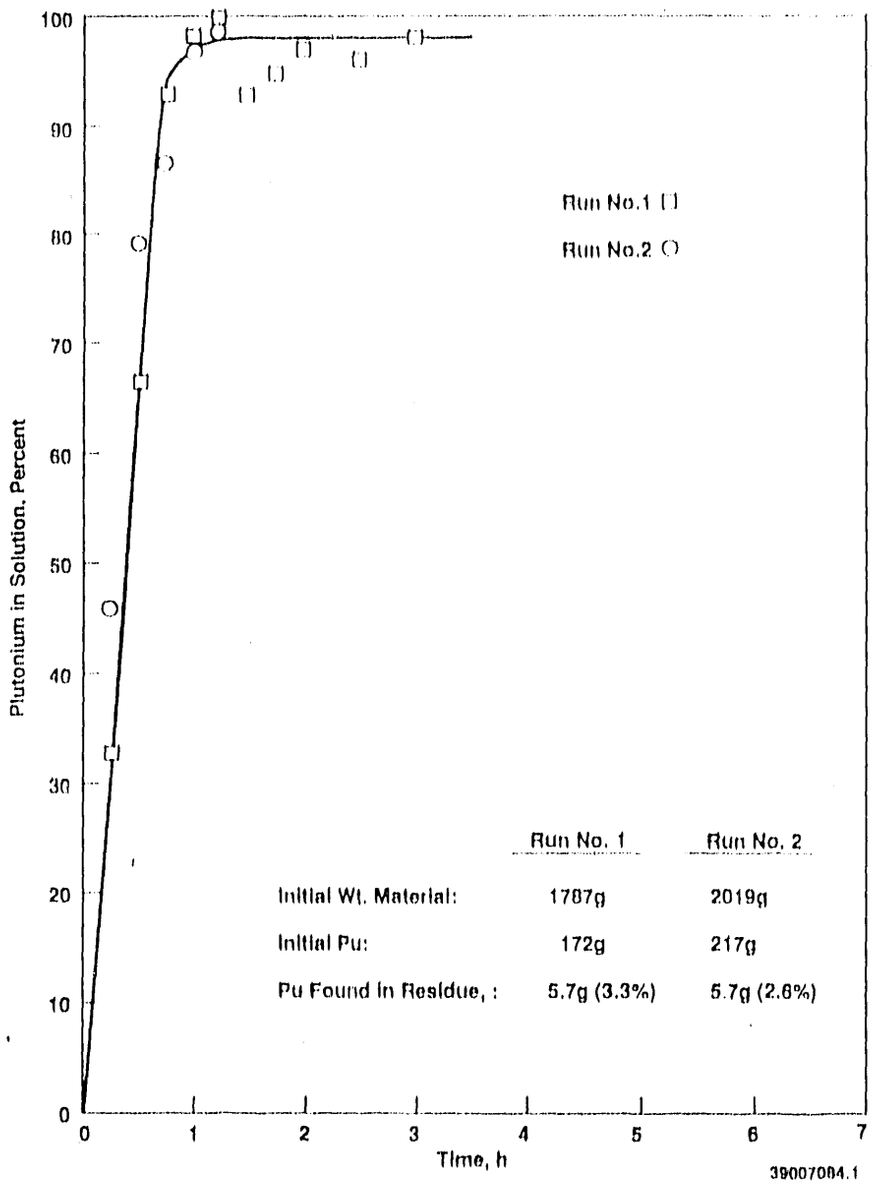


FIGURE 12. **CEPOD Leaching of Pu-Containing Material B with Ag Ion Catalyst**

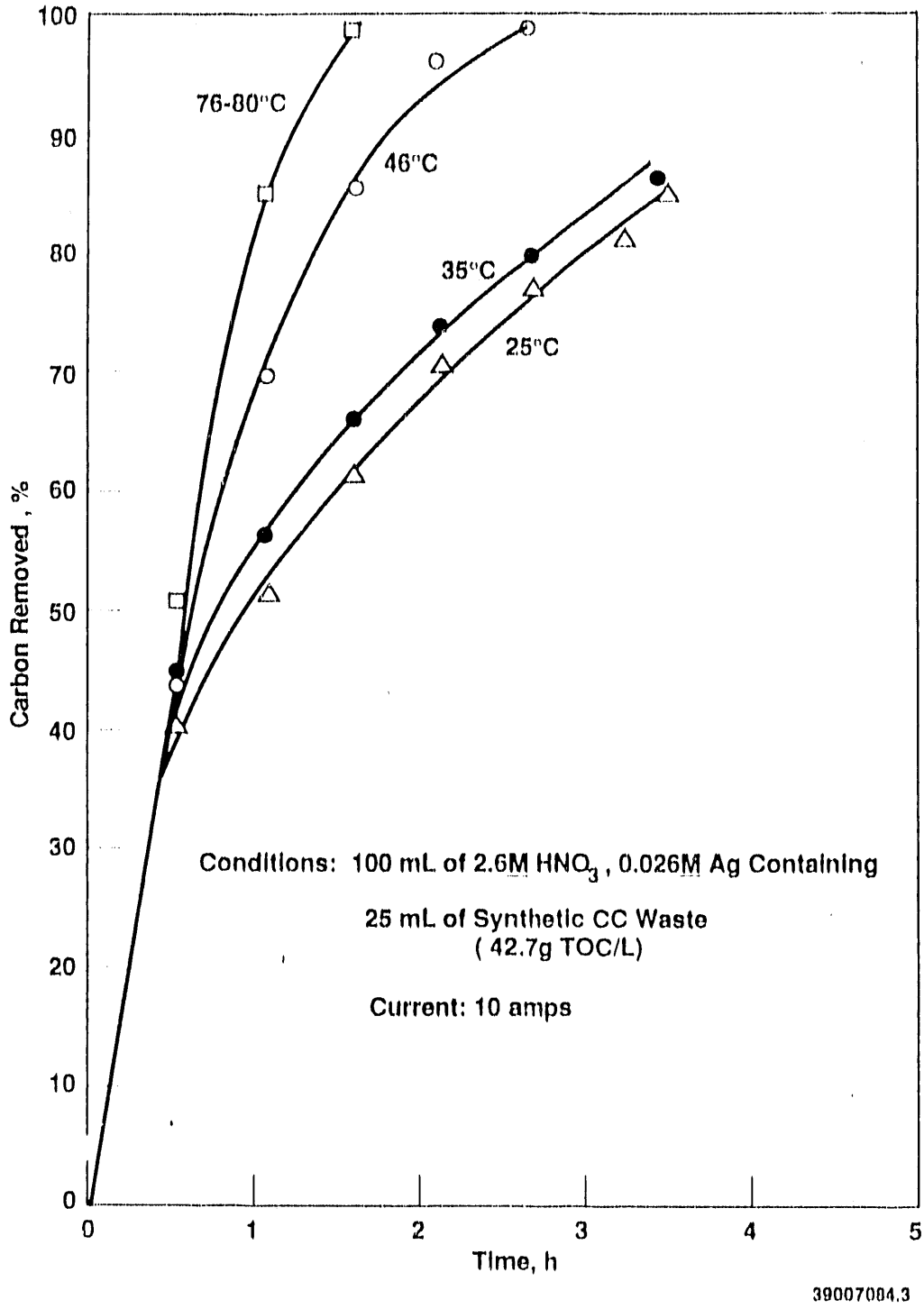


FIGURE 13. **Electrochemical Destruction of Organics in Complexant Concentrate Waste**

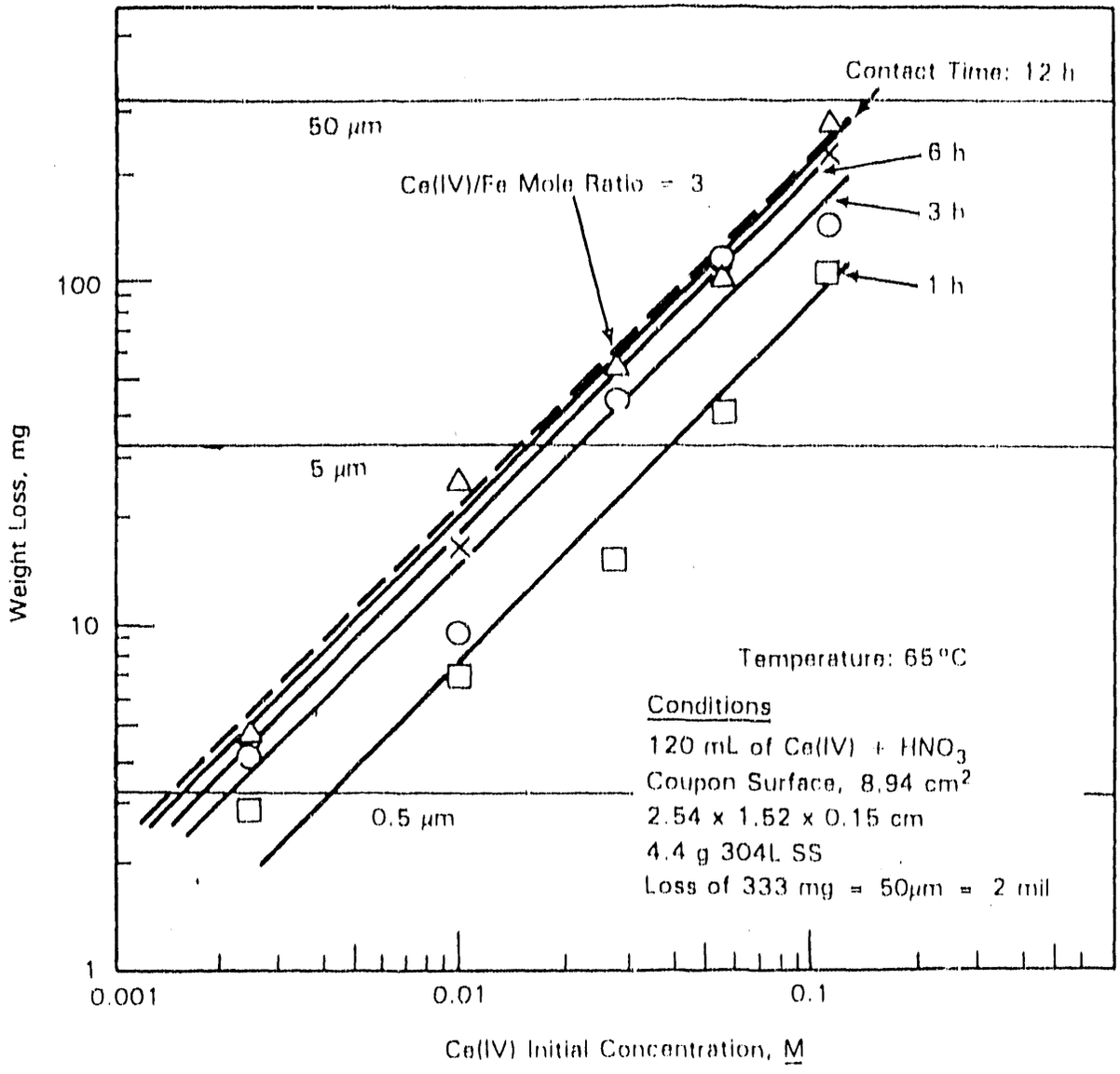


Figure 14. Effect of Cerium Concentration on the Dissolution of Stainless Steel, 65°C (Data from 27)

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