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Development of the CEPOD Process for Dissolving Plutonium Oxide and Leaching Plutonium from Scrap or Wastes

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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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SUMMARY

Laboratory-scale dissolving tests have demonstrated that PuO_2, fired at temperatures between 950 and 1700°C, can be dissolved at 25 to 35°C to concentrations exceeding 100 g Pu/L in an electrochemical dissolver using silver ion as a redox catalyst. The dissolution rates are 2 to 5 times faster than the rates obtained using the current process (12 $\underline{M}$ HNO_3-0.18 $\underline{M}$ HF at 90°C) and the corrosive fluoride ion is avoided.

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INTRODUCTION

Midway through FY 1985, the Albuquerque Operations Office of the Department of Energy provided funds through the Rocky Flats Plant for initial laboratory-scale development of the Catalyzed Electrochemical Plutonium Oxide Dissolution (CEPOD) process for dissolving plutonium oxide or leaching plutonium-contaminated scrap and waste. This process was originally conceived in 1974 (Bray, Ryan and Boldt 1974) as a part of a private contract with Exxon Nuclear Company. Work at that time was aimed at relatively low concentrations (5 g Pu/L) of PuO_2. The Exxon work was released for publication in 1981 (Bray and Ryan 1982). The current work is aimed at extending this concept to the dissolution of PuO_2 and Pu values in scrap to high aqueous Pu concentrations. This interim report was prepared to present the experimental progress achieved to date, and to describe some potential application of this new technology.

DESCRIPTION OF THE CONCEPT

In the past, plutonium oxide, particularly oxide heated to high temperature, has been almost impossible to dissolve except in hot concentrated nitric acid containing the very corrosive fluoride ion. Processes for leaching plutonium from many kinds of scrap have likewise employed repeated cycles using the same dissolvent. A new dissolving (leaching) concept has been proposed (Bray et al. 1974, Thompson et al. 1979, Bray and Ryan 1982) that uses electrical energy to force the nitric acid oxidation and dissolution of PuO_2 as the PuO_2^{2+} ion. This process, carried out in a two compartment electrolytic cell with the PuO_2 in the anode compartment, uses as a catalytic agent in the anode compartment, a kinetically rapid redox couple having a strongly oxidizing component such as the $Ag^{2+} + e^- \rightleftarrows Ag^+$, the $Ce^{4+} + e^- \rightleftarrows Ce^{3+}$ or other couple. The purpose of this catalytic agent is to rapidly transfer electrons from the PuO_2 surface to the anode surface thereby producing PuO_2^{2+} in solution and regenerating the catalyst. The catalyst can be used in quantities much below the amount of PuO_2 dissolved. The dissolution reaction (overall cell reaction) is: $3PuO_2 + 2NO_3^- + 8H^+ \rightleftarrows 3PuO_2^{2+} + 2NO + 4H_2O$ or the corresponding reaction producing NO_2. Prior proof-of-principle experiments (Bray and Ryan 1982) have shown the cerium catalyst to be quite effective, and the silver catalyst to be very fast. Later work (Koehly et al. 1984) using the silver couple confirmed our preliminary tests.

A schematic of the very simple two-compartment, laboratory-scale electrochemical dissolver is shown in Figure 1. The dissolver is mechanically stirred and heated by a hot plate for the elevated temperature tests. In the cell shown, an approximately cylindrical smooth titanium electrode having the inner surface ($54\ cm^2$) platinum-plated is used as the anode and an approximately cylindrical smooth titanium electrode ($17\ cm^2$) is used as the cathode. The PuO_2, catalyst, and nitric acid are in the anode compartment and nitric acid alone (10 - 16 $\underline{M}$) is used in the cathode compartment.

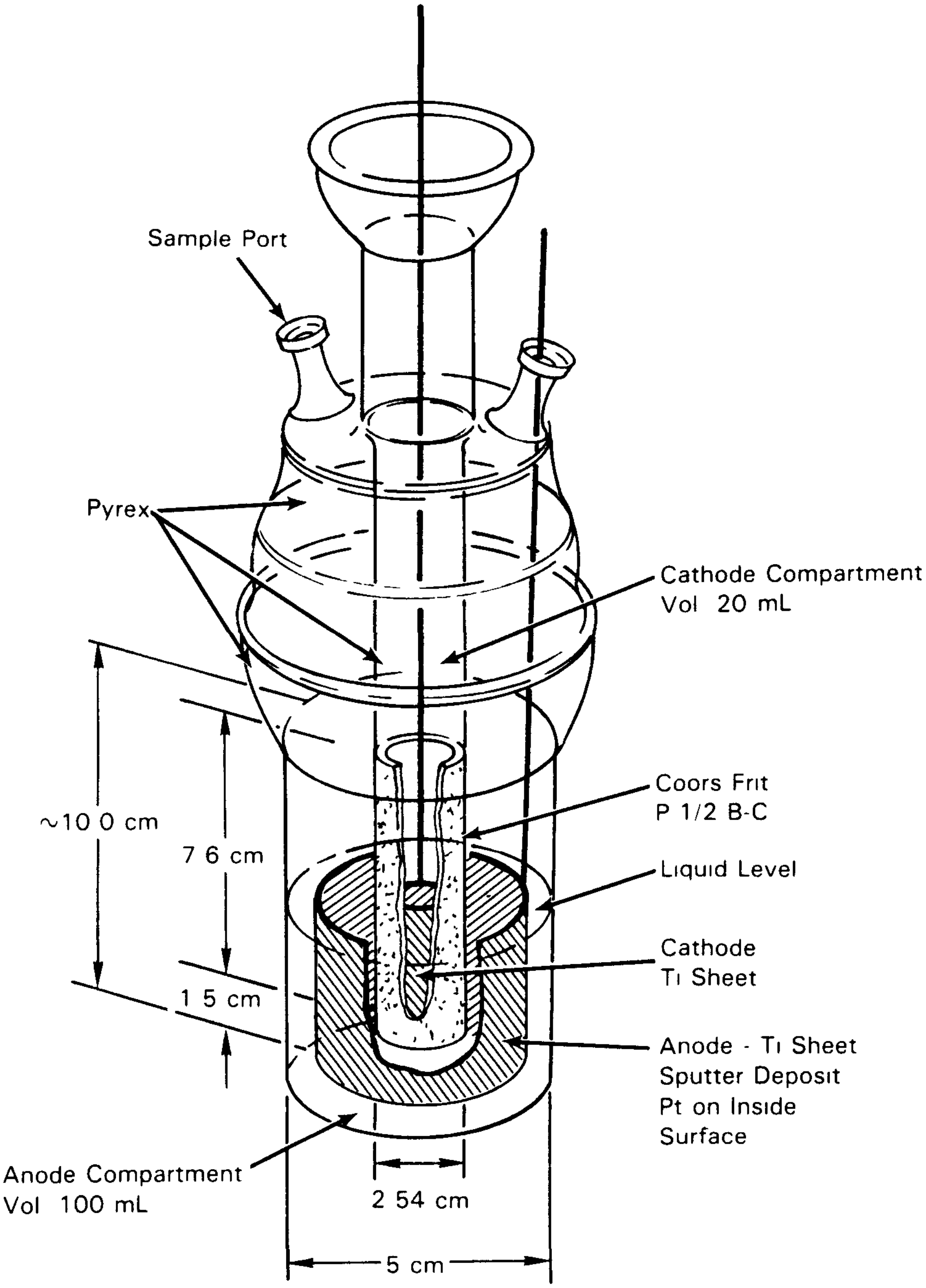

FIGURE 1. Laboratory - Scale Electrochemical Dissolver

SUMMARY OF PROGRESS ACHIEVED TO DATE

Preparation of Oxide

Plutonium oxide intended for use in the dissolution tests was specially prepared and characterized to eliminate any effects from unknown impurities and from americium. Following purification by nitric acid-anion exchange, hydrazine was added to suppress the nitrite ion concentration, ascorbic acid was added to reduce the plutonium to plutonium (III), and oxalic acid was added to precipitate the plutonium. The filtered plutonium (III) oxalate was dried and divided into two batches. The oxalate was calcined for two hours in air in alumina crucibles, one batch at 500°C and the other at 950°C. Part of the 500°C batch was re-calcined in a zirconia crucible at 1700°C in an atmosphere of water-saturated 92% Ar-8% H_2 to provide oxide that was highly sintered. The oxide calcined at 500°C had a surface area of 44.8 M^2/g, that calcined at 950°C had a surface area of 3.3 M^2/g, and that calcined at 1700°C had a surface area of 0.09 M^2/g as determined by a modified BET method. The importance of this difference in the surface area of the three batches of oxide is evident from the dissolving tests.

Dissolution Tests Using HNO_3-HF

Samples from each of the three batches of oxide were dissolved in a mixture of nitric acid and hydrofluoric acid at concentrations and conditions currently utilized in the plants at Hanford and Rocky Flats. This was done to provide a baseline to which results from the electrochemical dissolving tests could be compared. Because of the high concentration of fluoride, these tests were conducted in opaque Teflon® containers. The temperature was determined by use of a glass-mercury thermometer. The dissolver was heated on a stirring hotplate and the solution stirred by a Teflon-coated magnetic stirring bar. The dissolving solution was heated to the intended dissolving temperature, then the measured amount of oxide was added to avoid a heat up cycle. Samples were withdrawn at appointed time intervals, filtered, and the plutonium content in the aqueous phase was determined. The rate of dissolution,

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expressed as the percent of the original oxide dissolved versus time, and the dissolving conditions for each test are shown in Figure 2.

The oxide fired at 500°C (curve 1) dissolved completely in less than one hour. The oxide fired at 950°C (curve 2) dissolved in 3 to 4 hours. About 87% of the oxide fired at 1700°C (curve 3) had dissolved when the experiment was ended after 6 hours. Early in electrochemical dissolution tests, the amount of plutonium in each test was doubled to 12 g PuO_2 per 100 mL to provide a more desirable product solution. It was, therefore, appropriate to make another HNO_2-HF test on 950°C oxide at the higher concentration. The results of this test are expressed as dissolving curve 12 in Figure 2. The differences between curve 2 and curve 12 reflect the difference in plutonium concentration.

Electrochemical Dissolution Tests

Oxide samples from each of the three calcination temperatures were separately dissolved using Ag ion as the catalyst. The three dissolution curves, numbered 4, 5, and 6, and the dissolution conditions are shown in Figure 3. When comparing the electrochemical dissolutions (curves 4, 5, and 6) with the HNO_3-HF dissolutions (curves 1, 2, and 3) it is important to note that:

1. The plutonium concentration in the electrochemical dissolution tests is double the plutonium concentration used in HNO_3-HF tests 1, 2, 2 rerun and 3, and this must be taken into account when comparing dissolution rates.
2. The HNO_3-HF dissolution tests were done at 90°C while the electrochemical tests were performed without heating. The small increase in temperature above ambient in the electrochemical tests resulted from process self-heating. In a full-scale process dissolver, cooling may be required to control the temperature so as to minimize oxidation of water by Ag^{2+}.

In tests 5 and 7 through 11, samples of the 950°C-fired oxide were dissolved using different conditions. These conditions and results are summarized in

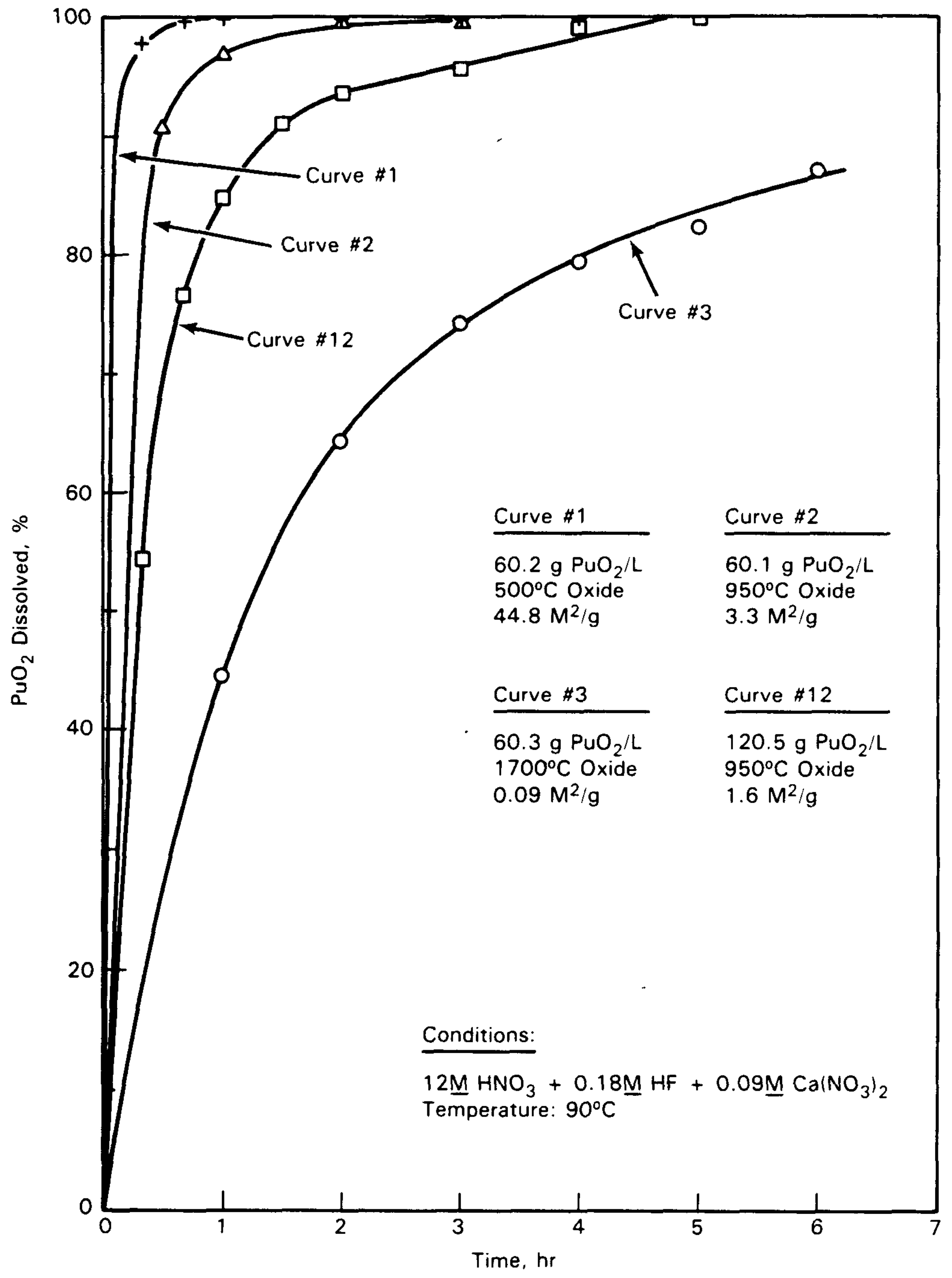

FIGURE 2. PuO$_2$ Dissolution Using 12 M HNO$_3$ + 0.18 M F$^-$

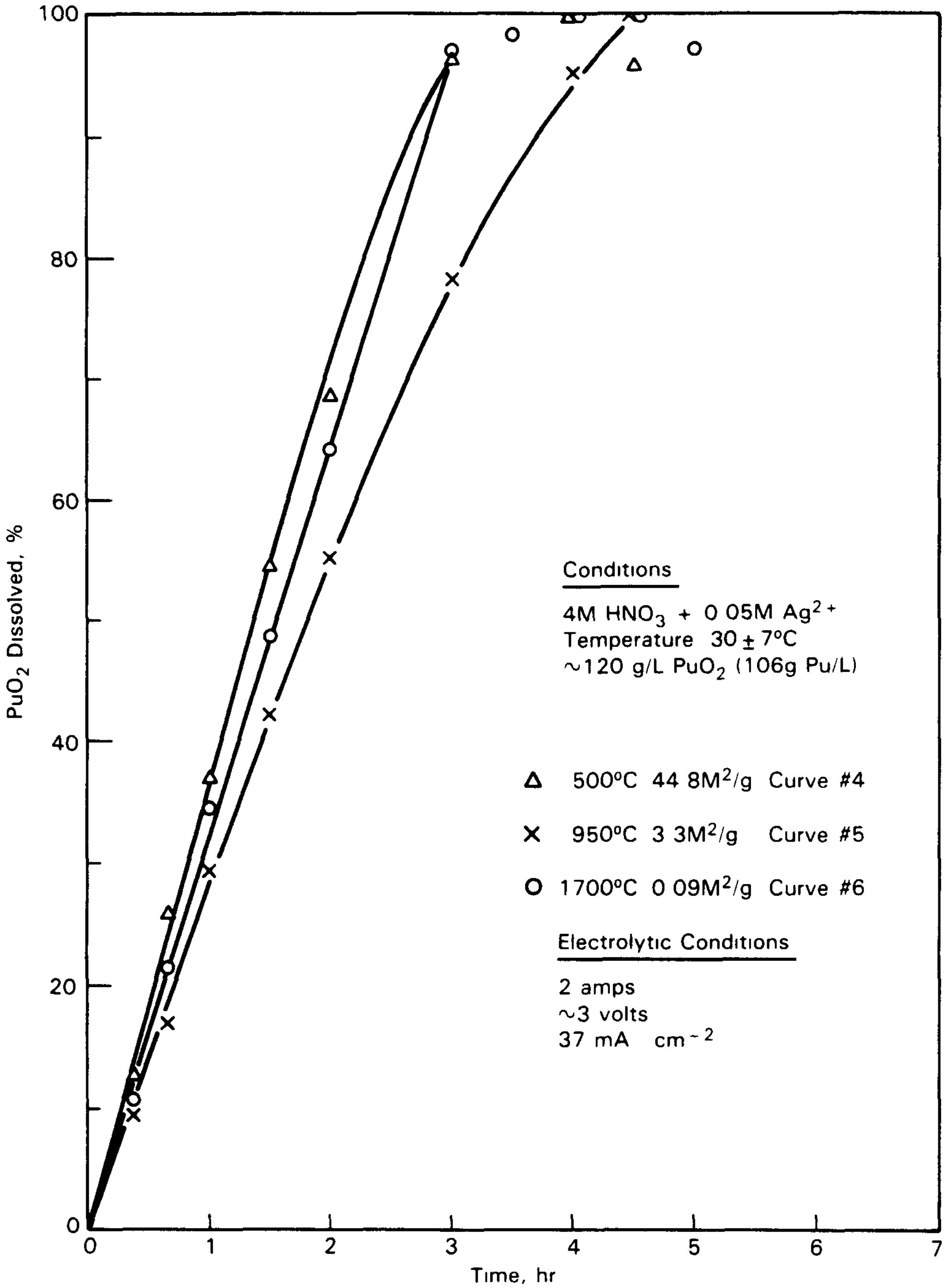

FIGURE 3. Electrolytic Dissolution of PuO_2 as a Function of Surface Area

Table 1 and the dissolution curves are shown in Figure 4. One test (No. 10) was done at 90°C using cerium in place of silver. The conditions were identical to those used for Test No. 9 except for the higher temperature.

Conclusions from Preliminary Tests

Some significant conclusions can be derived from the tests performed to date:

1. A comparison of curves 4, 5, and 6 with curves 1, 2, and 3 shows that the electrochemical process using silver will completely dissolve high-fired plutonium oxide two to five times faster than the currently employed 12 $\underline{M}$ HNO_3-0.18 $\underline{M}$ HF and will do so at near ambient temperature, at lower acid concentration, and without use of fluoride.
2. A comparison of curves 4, 5, and 6 indicates that the electrochemical dissolution rate with silver catalyst is essentially independent of the oxide surface area (calcination temperature). This indicates that the rate limiting step in this process is not the rate of reaction of Ag^{2+} with the PuO_2 surface.
3. Doubling the amount of PuO_2 present at a given cell current and Ag concentration (curve 9 vs curve 5) correspondingly increased the time required for complete dissolution. This indicates that the dissolution rate limiting step is the rate of Ag^{2+} generation. At the higher Pu concentration, tripling the cell current decreased the total dissolution time by only about 22% (curves 5 vs curve 7), indicating that the Ag^{2+} generation rate is not simply current limited. This is shown even more strongly by the fact that the current efficiency dropped from 27% to 12% on increasing the current density by a factor of three. (In this regard it should be noted that oxygen evolution at the anode competes with Ag^{2+} generation and accounts for the rest of the current passed.) This points to the Ag^{2+} generation rate being diffusion limited.
4. Doubling the total Ag concentration at a given amperage (curve 8 vs curve 5) almost halves the total dissolution time and almost doubles current efficiency. Quadrupling the Ag concentration, and tripling

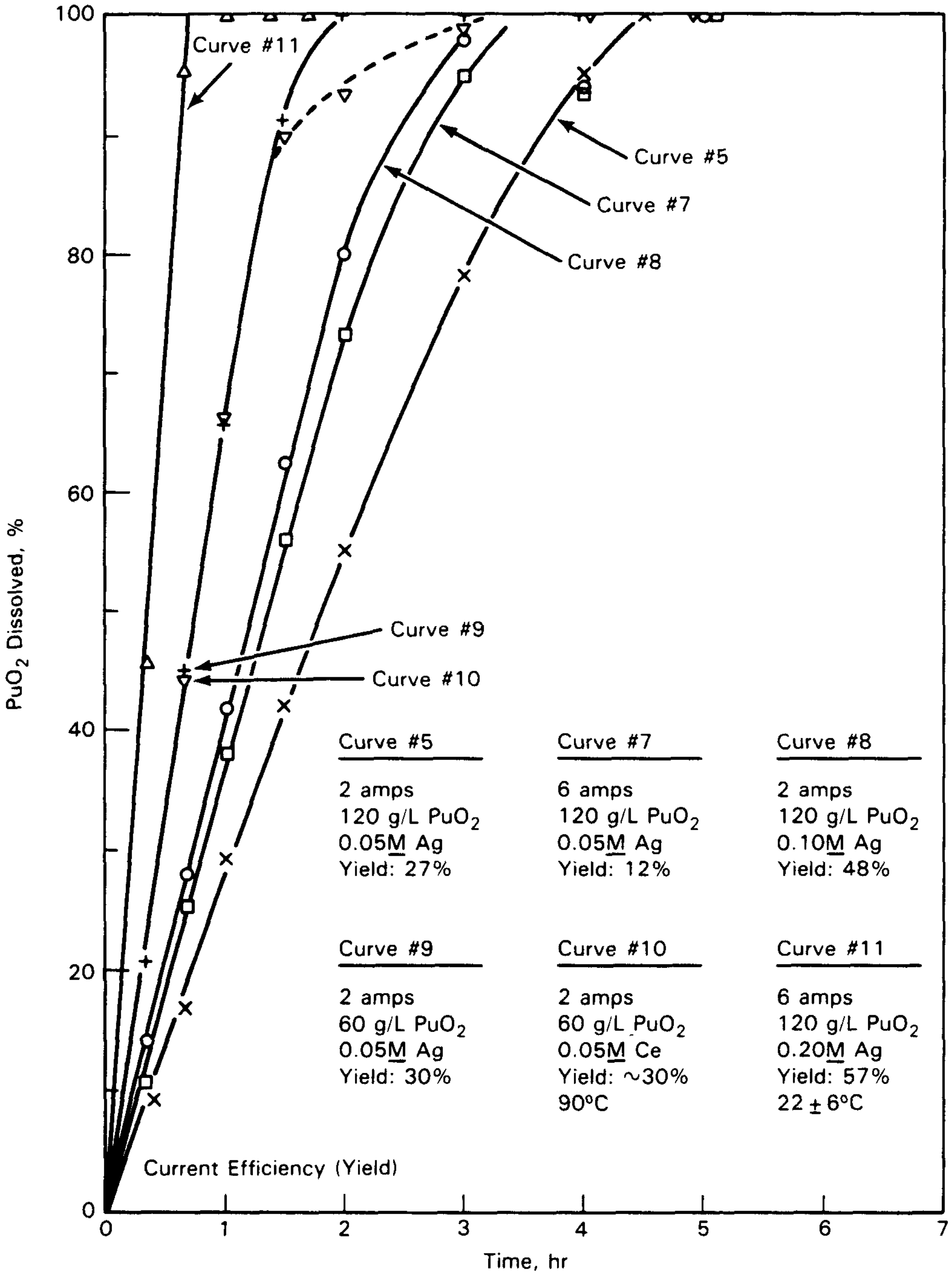

FIGURE 4. Electrolytic Dissolution of PuO_2 (950°C) Varying the Current Density, Pu and Ag Concentrations

TABLE 1. Dissolution of 950°C Fired Plutonium Oxide

PuO$_2$ Test No.		Initial Conc. (g/L)	HNO$_3$ Conc., M	Catalyst M	Cell Temp. (°C)	Current	
						Current (A)	Efficiency* (%)
5	121	4	0.05	Ag	30 ± 7	2	27
7	120	4	0.05	Ag	30 ± 7	6	12
8	120	4	0.10	Ag	30 ± 7	2	48
9	60	4	0.05	Ag	30 ± 7	2	30
10	60	4	0.05	Ce	90	2	~30
11	120	4	0.20	Ag	22 ± 6	6	57

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* Average current efficiency to the point of 100% dissolution.

current to avoid becoming current limiting at any stage in the dissolution, (curve 11 vs curve 7) decreased the total dissolution time by a factor of at least four and increased current efficiency by a factor of at least four. Therefore, the rate limiting step is not simply the rate of Ag^{2+} generation but is also the rate at which the Ag^+ ion diffuses to the anode surface for reoxidation to Ag^{2+}.

5. On the basis of known electrochemical technology, there are other ways of significantly improving diffusion limited electrode processes besides increasing reactant concentration. These include improved electrode design and improved stirring efficiency (ultrasonic stirring). On the basis of fundamental considerations of Ag^{2+} oxidation potential and kinetics (not discussed in any detail here) and on the basis of conclusion 2 above, it seems likely that with proper electrochemical cell design, dissolution rates much faster than any shown here can be achieved with the CEPOD process using silver as the catalyst.

IMPLEMENTATION OF NEW DISSOLVING TECHNOLOGY

Some additional work is required to optimize dissolving conditions applicable to pure plutonium oxide. The optimized conditions will then be used to demonstrate the leaching of plutonium from several kinds of scrap and waste. The probability seems high that the CEPOD process will show a significant advantage over HNO_3-HF when leaching several kinds of scrap. If this proves to be true, the necessary development work should be done as quickly as possible so that this advanced technology can be applied to three pressing problems: 1) recovery of plutonium from currently stored scrap and waste, 2) utilization of higher-fired oxide as a suitable shipping form, and 3) decontamination of soils to avoid TRU disposal costs.

The concept of electrochemical dissolving/leaching technology in an integrated scrap and waste processing facility is shown in Figure 5. A considerable amount of development work is required to assure performance of each processing step and to quantify the cost/benefit ratio. The potential for decontaminating much of the solid waste to less than TRU limits, thereby avoiding TRU disposal costs, should be given full consideration.

The shipping of plutonium has been a continual problem. High-fired oxide has been difficult to dissolve after shipment and low-fired material has resulted in pressurized containers due to degassing during shipment. Since the dissolution of 950°C-fired oxide is rapid when the silver-catalyzed CEPOD process is used and Ag^+ is easy to remove from the dissolver solution, this technology would allow safe shipment as high-fired oxide followed by rapid, economic conversion to pure nitrate solution at the receiving end. It is worth noting, since silver is considered a precious metal, that electrochemical dissolution to 100 g Pu/L using 0.05 $\underline{M}$ Ag catalyst amounts to use of only about $11 worth of silver per kg Pu and to less than $1 worth of electricity per kg Pu.

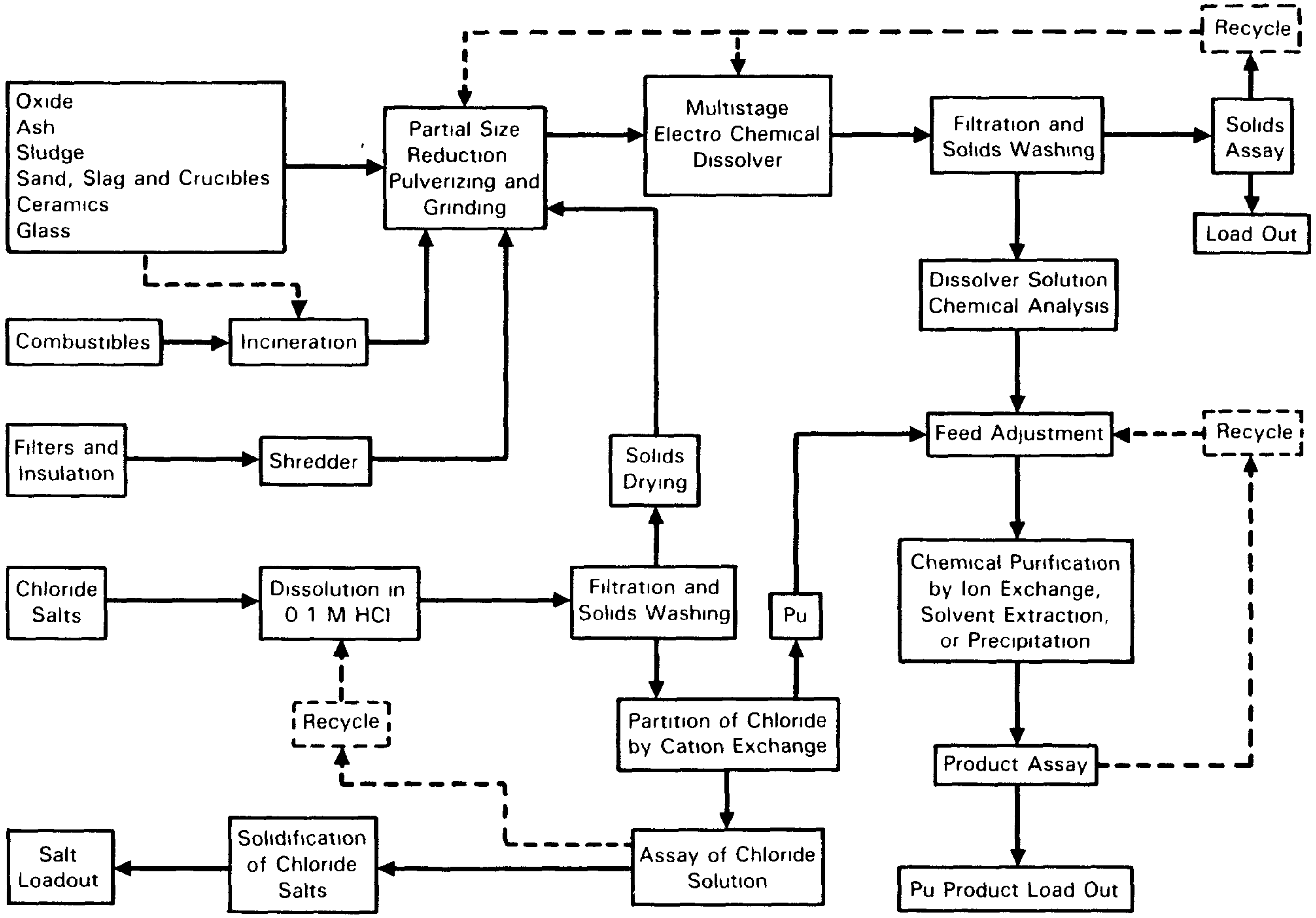

FIGURE 5. Integrated Plutonium Scrap Processing Facility

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