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## **Recovery of Plutonium from HEPA Filters by Ce(IV)- Promoted Dissolution of PuO<sub>2</sub> and Recycle of the Cerium Promoter**

F. M. Scheitlin  
W. D. Bond

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NUCLEAR FUEL AND WASTE PROGRAMS  
Waste Management Analysis for Nuclear Fuel Cycles  
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RECOVERY OF PLUTONIUM FROM HEPA FILTERS BY Ce(IV)-PROMOTED  
DISSOLUTION OF PuO<sub>2</sub> AND RECYCLE OF THE  
CERIUM PROMOTER

F. M. Scheitlin 03  
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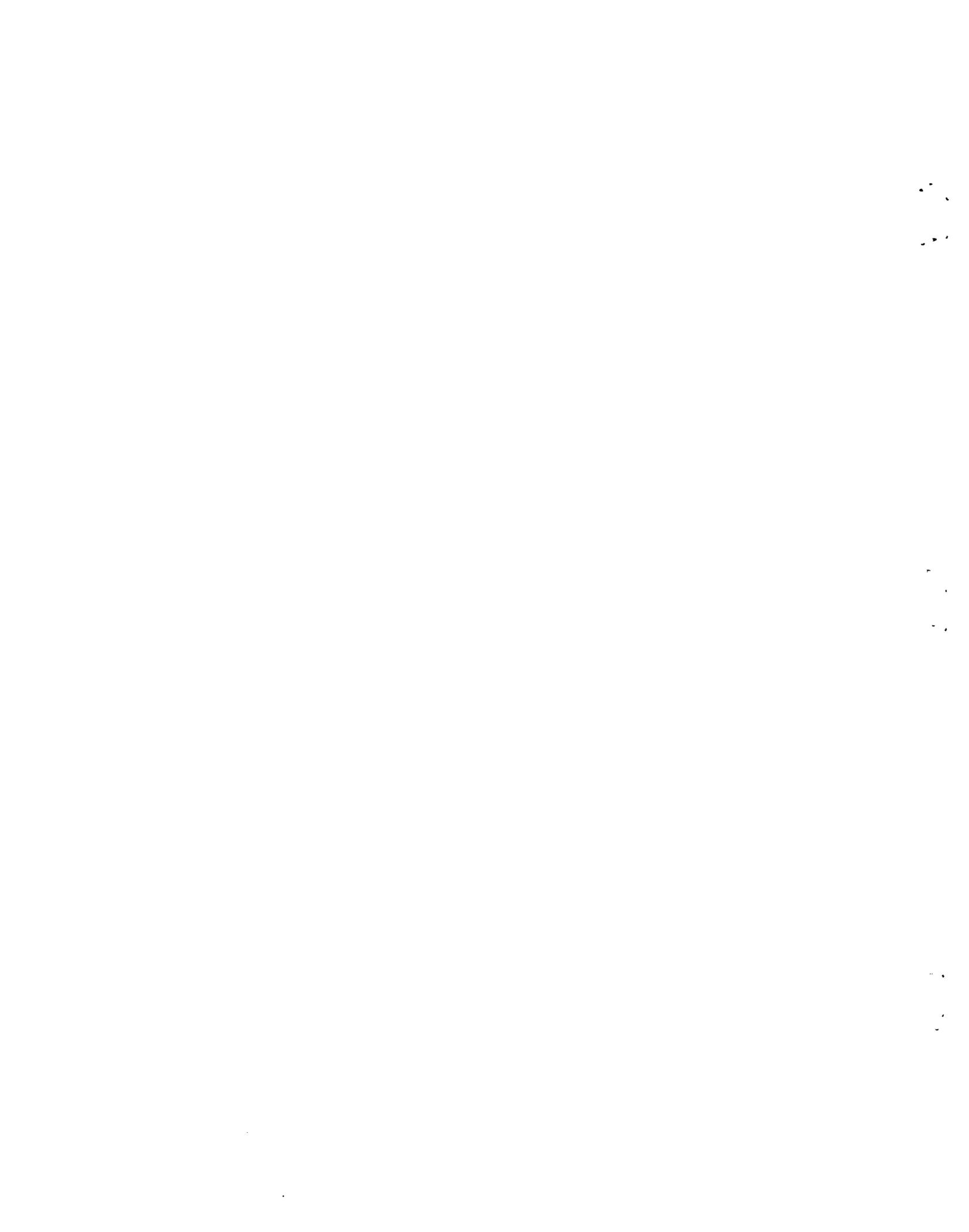
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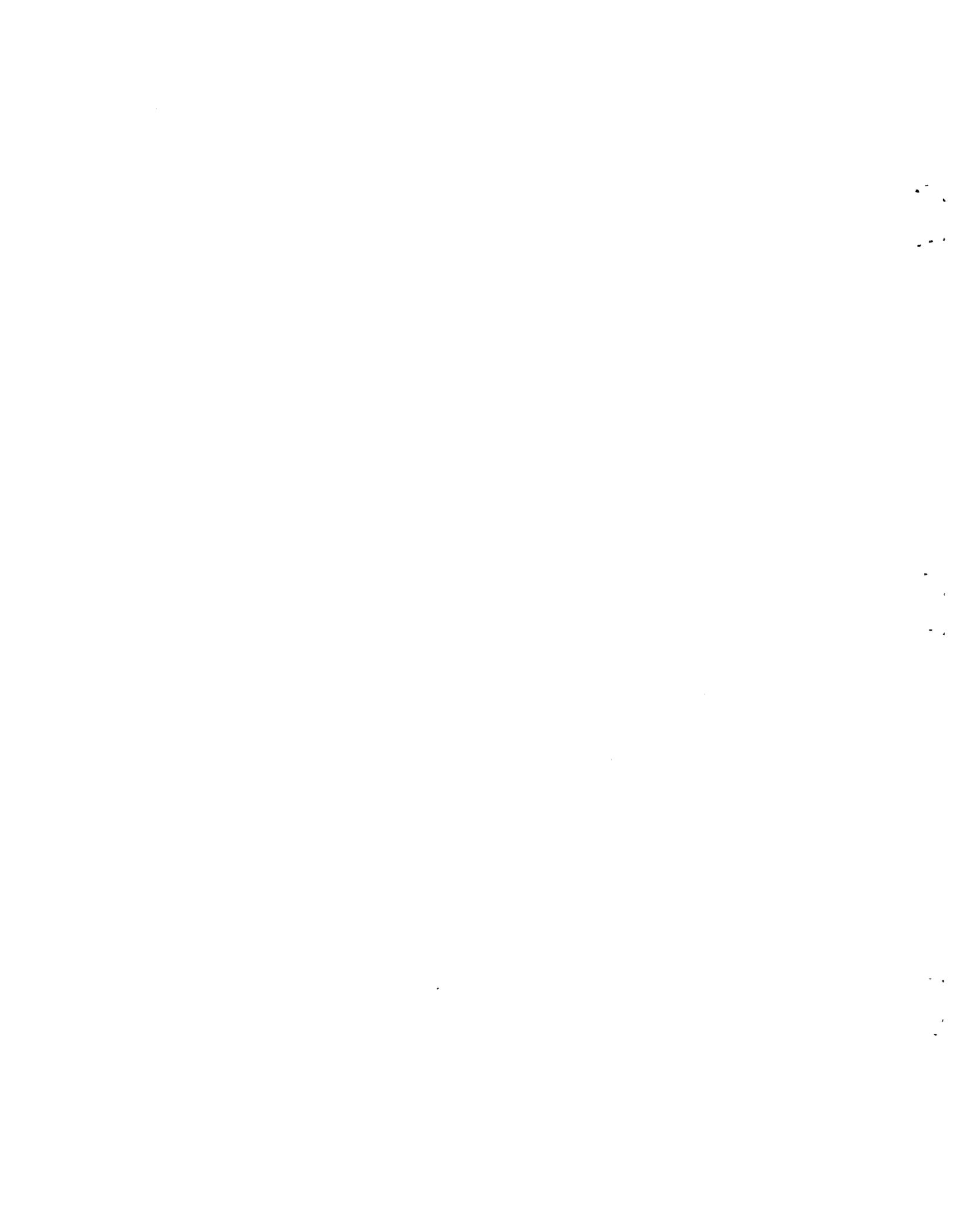
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RECOVERY OF PLUTONIUM FROM HEPA FILTERS BY Ce(IV)-PROMOTED  
DISSOLUTION OF PuO<sub>2</sub> AND RECYCLE OF THE CERIUM PROMOTER

F. M. Scheitlin  
W. D. Bond

ABSTRACT

The experimental studies carried out in this investigation included (1) the electrolytic production of Ce(IV) from Ce(III), (2) the leaching of refractory PuO<sub>2</sub> from HEPA filter materials with maintenance of Ce(IV) concentrations by anodic oxidation during leaching, and (3) evaluation of methods for contacting the HEPA solids with the leaching solution and for separating the solid residue from the leaching liquor. Anodic oxidation of Ce(III) was accomplished with an electric current efficiency of about 85% at current densities of 0.04 to 0.4 A/dm<sup>2</sup> at a platinum anode. Refractory PuO<sub>2</sub> was dissolved by a 4.0 M HNO<sub>3</sub> - 0.1 M Ce(IV) solution in 1.5 hr at 100°C using stirred-contact leaching of the solids or by recirculating the leachant through a packed column of the solids. Cerium(IV) concentrations were maintained continuously by anodic oxidation throughout leaching. Dissolution times up to 10 hr were required unless the HEPA media were oxidized initially in air at 300°C to destroy carbonaceous species which consumed Ce(IV) more rapidly than it could be regenerated by anodic oxidation. Leaching solids in packed columns avoided the relatively difficult liquid-solids separation by centrifugation which was required after stirred-contact leaching, however, the solids handling difficulties associated with charging and discharging of the packed columns in a remote environment remain a significant design obstacle.

On the basis of the experimental results obtained in this study and solvent extraction separations demonstrated in the literature, a chemical flowsheet is proposed for the recovery of actinides from HEPA filters. A 4 M HNO<sub>3</sub> - 0.1 M Ce(IV) nitrate solution is used as the leachant and the Ce(III) is recycled to the leaching operation using bidentate solvent extraction.

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## 1. INTRODUCTION

This work was carried out as a part of a program to evaluate the technical feasibility of partitioning and transmutation as a waste management concept.<sup>1,2</sup> In this concept, actinides (and perhaps other long-lived radionuclides such as <sup>129</sup>I) would be removed from waste streams and transmuted by neutron capture or fissioning to shorter-lived radionuclides. The purpose of partitioning and transmutation would be to reduce the potential risks associated with the long term (>500 years) geologic isolation of nuclear wastes. This has been discussed in detail by several investigators.<sup>1-5</sup>

The present experimental study deals specifically with the leaching of plutonium from HEPA filter materials using a 4 M HNO<sub>3</sub> - 0.1 M Ce(IV) nitrate leaching solution, and the recovery of Ce(III) from the spent leach liquor for recycle to the leaching process where it is oxidized to Ce(IV). Methods for the recycle of the Ce(III) ion have not been developed previously. In waste partitioning, the same type of leaching is also being considered for the recovery of plutonium from the ashes obtained from the burning of combustible wastes<sup>1</sup> and from the various solid wastes generated in fuel fabrication.<sup>2</sup> Of the alternatives examined, a 4 M HNO<sub>3</sub> - 0.1 M Ce(IV) nitrate solution has been shown<sup>6-8</sup> to be the most effective solvent for refractory PuO<sub>2</sub> that avoided the use of the corrosive fluoride ion.

The mechanism by which Ce(IV) promotes the dissolution of refractory plutonia in nitric acid is unknown. Maximum initial dissolution rates are obtained with solutions containing 0.1 M Ce(IV) and 4 M HNO<sub>3</sub> initially. During dissolution, the Ce(IV) is consumed by rapid reactions,<sup>9,10</sup> with

the soluble plutonium ( $\text{Pu}^{3+}$  and  $\text{Pu}^{4+}$ ) producing  $\text{Ce(III)}$  ion and  $\text{PuO}_2^{2+}$ . When the  $\text{Ce(IV)}/\text{Ce(III)}$  ratio is reduced to about unity the dissolvent becomes ineffective.<sup>6</sup> In addition to the oxidation reactions involving plutonium,  $\text{Ce(IV)}$  is also consumed by reactions with the carbonaceous species that are present in HEPA filter materials. The  $\text{Ce(IV)}$ , a powerful oxidant, oxidizes free carbon, organic compounds and most metals. The extent of  $\text{Ce(IV)}$  reduction during leaching depends on the amounts of  $\text{PuO}_2$  and carbonaceous species associated with the HEPA material. Since the carbonaceous species reacts more rapidly than does  $\text{PuO}_2$ , a method to oxidize  $\text{Ce(III)}$  and so maintain the  $\text{Ce(IV)}$  concentration during leaching is desirable in order to avoid the use of large quantities of  $\text{Ce(IV)}$  salts. Also, it is desirable to recover the  $\text{Ce(III)}$  from spent leach liquor and to recycle it to the leaching operation for oxidation to  $\text{Ce(IV)}$  in order to avoid a significant contribution to the salt wastes.

The experimental studies carried out in this investigation included (1) electrochemical production of  $\text{Ce(IV)}$  from  $\text{Ce(III)}$ , (2) leaching of refractory  $\text{PuO}_2$  from HEPA filter materials while maintaining the  $\text{Ce(IV)}$  concentration by anodic oxidation during leaching, and (3) methods for contacting the HEPA solids with the leaching solution and for separating the solid residue from the leaching liquor.

On the basis of the experimental results and solvent extraction separations demonstrated in the literature, a chemical flowsheet is proposed for the recovery of actinides from HEPA filters. A 4 M  $\text{HNO}_3$  - 0.1 M  $\text{Ce(IV)}$  nitrate solution is used as the leachant, and a two-cycle solvent extraction process employing tri-n-butyl phosphate (TBP) in the first cycle and dihexyl-N,N-diethylcarbamoylmethylene phosphonate<sup>1,2,11</sup> in

the second cycle is used to make the necessary separations for the recovery of the actinides and for the recycle of Ce(III) from the concentrated leach liquors.

## 2. ELECTROCHEMICAL PRODUCTION OF Ce(IV) FROM Ce(III)

In this study, the preparation of Ce(IV) from Ce(III) in  $\text{HNO}_3$  solution was investigated using three different electrode arrangements:

(1) anode and cathode compartments separated by a porous, fritted-glass barrier, (2) no barrier between anode and cathode compartments, and (3) a shrouded cathode and an unshrouded anode. In addition, several materials of construction were evaluated with respect to corrosion for their applicability as electrodes or process vessels.

### 2.1 Chemistry Involved in the Choice of Electrochemical Cells

The efficiency of electrochemical cells for carrying out the desired chemical reactions often depends on designs which prevent the products of the reactions in the anode and cathode compartments from intermixing and reacting to form either the original species or undesirable secondary products. Since nitrous acid ( $\text{HNO}_2$ ) is a cathodic reduction product of  $\text{HNO}_3$ , it must be prevented from diffusing into the anode region and reducing the Ce(IV) produced by anodic oxidation.

Previous studies by Smith and coworkers<sup>12</sup> showed that the principal reaction occurring at the anode was the oxidation of Ce(III) to Ce(IV). The high yields of Ce(IV) obtained by anodic oxidation of Ce(III) in  $\text{HNO}_3$  solution were attributed by them to the high stability of the hexanitratocerate anion,  $[\text{Ce}(\text{NO}_3)_6]^{2-}$ . They did not investigate the

products produced at the cathode.

Numerous studies<sup>13-16</sup> of the electrolysis of  $\text{HNO}_3$  solutions at Pt electrodes demonstrated the complexity of the reactions at the cathode. Ellingham<sup>13</sup> showed that either  $\text{HNO}_2$  or hydrogen ( $\text{H}_2$ ) may be the principal product depending on the conditions. He also determined the mechanisms of the principal reactions at the cathode. Ihle<sup>14</sup> showed that ammonium ion could be produced as a minor cathode reaction product when current densities were above certain critical values for any fixed concentration of  $\text{HNO}_3$ . Snider and Johnson<sup>17</sup> have recently reviewed the literature on studies of the cathodic reduction of nitric oxide ( $\text{NO}$ ),  $\text{HNO}_2$ , and nitrogen dioxide ( $\text{NO}_2$ ).

The primary cathode reaction in the electrolysis of  $\text{HNO}_3$  is generally regarded as:



where (H) denotes atomic hydrogen sorbed by the Pt cathode.

This process is followed by either of two secondary reactions:



depending on the conditions of the electrolysis. Hydroxyl ion is oxidized to oxygen and water at the anode in  $\text{HNO}_3$  electrolysis.

Reaction (2b) will occur only if reaction (2a) cannot proceed at a rate sufficient to remove (H) as fast as it is produced by reaction (1), but the rate of reaction (2a) is very slow even in solutions containing up to 5 M  $\text{HNO}_3$  unless  $\text{HNO}_2$  is present as a catalyst. Therefore, the magnitude of the current density which can be employed to maintain only reaction (2a) is governed by the concentration of  $\text{HNO}_2$  which is

established in the layer of solution in immediate contact with the electrode. But, the increase in  $\text{HNO}_2$  concentration at the cathode surface is limited by the following reactions and the resultant evolution of nitrogen oxide gases:



Thus the rate of reaction (2a) is limited by the maximum concentration of  $\text{HNO}_2$  which may be present at certain current density values for any given  $\text{HNO}_3$  concentration.

With a further increase of current density,  $\text{H}_2$  production by reaction (2b) commences at the cathode. The current density at which reaction (2b) becomes the dominant mechanism is designated by Ellingham<sup>13</sup> as the transition current density (TCD). Once vigorous  $\text{H}_2$  production begins and continues, it eventually sparges the solution free of any  $\text{HNO}_2$  formed previously at current densities below the TCD. The TCD values increase dramatically with  $\text{HNO}_3$  concentration and are presumably due to the mass action effect of  $\text{HNO}_3$  in reaction (2a).

The effect of  $\text{HNO}_2$  concentration on the TCD value is quite marked. For example, Ellingham<sup>13</sup> observed in the electrolysis of a 4 M  $\text{HNO}_3$  solution that the addition of 5 g  $\text{KNO}_2/\ell$  (0.06 moles  $\text{KNO}_2/\ell$ ) increased the TCD value from 0.07 to 1.5  $\text{A}/\text{dm}^2$ . In partially sparged solutions, Mailen and Horner<sup>16</sup> reported that  $\text{H}_2$  production was not completely suppressed by  $\text{NO}_2^-$  addition to 4 M  $\text{HNO}_3$  when current densities of 0.6 to 2.3  $\text{A}/\text{dm}^2$  were employed. Ellingham<sup>13</sup> also found that TCD values could be lowered considerably by stirring or sparging the  $\text{HNO}_3$  solutions with

air to promote decomposition of  $\text{HNO}_2$ . Increasing the temperature from 25 to 40°C greatly increased the TCD values.

In the early stages of the electrolysis of  $\text{HNO}_3$  solutions essentially free of  $\text{HNO}_2$ ,  $\text{H}_2$  is always the principal initial product and reaction (2b) is dominant even at current densities below the TCD value. However, as the  $\text{HNO}_2$  concentration builds up in solution a transition to reaction (2a) occurs at the cathode, and it becomes the dominant reaction. Transition times range from a few seconds at current densities well below the TCD value to 20 min for current densities approaching the TCD value.

Based on previous electrochemical studies, it appeared that several chemically feasible options were available for the design and operation of an electrolytic cell for producing Ce(IV) nitrate in high yield from Ce(III) nitrate- $\text{HNO}_3$  solutions by anodic oxidation:

1. The anode and cathode compartments could be isolated by a suitable porous diaphragm.
2. A shrouded cathode could be used with allowance for the escape of nitrogen oxide gases at the top of the shroud. If necessary, sparging with a carrier gas could be used to enhance removal of nitrogen oxide gases. The rates<sup>18</sup> measured for the reactions (3), (4), and (5) together with the effects of air sparging observed by Ellingham<sup>13</sup> indicated that the  $\text{HNO}_2$  concentration would be effectively controlled. Sparging could also promote the formation of  $\text{H}_2$  rather than  $\text{HNO}_2$  at the cathode, depending on the current density and  $\text{HNO}_3$  concentration employed.

3. The electrodes would not be isolated. Smith and coworkers<sup>12</sup> showed that solutions of Ce(IV) nitrate in  $\text{HNO}_3$  could be produced with high yields ( $\sim 80\%$ ) at current efficiencies of about 84% by employing a low current density ( $1.0 \text{ A/dm}^2$ ) at the anode and a high current density ( $100 \text{ A/dm}^2$ ) at the cathode. Although they did not study the cathodic reactions or production of gases at the cathode, it would appear from Ellingham's work<sup>13</sup> that a current density of  $100 \text{ A/dm}^2$  at the cathode would yield  $\text{H}_2$  as the major reduction product. Therefore, because little, if any,  $\text{HNO}_2$  may have been produced along with the  $\text{H}_2$ , it was not surprising that their method did not require the cathode to be isolated from the anode. Although these authors largely attributed the success of the method to the formation of the  $[\text{Ce}(\text{NO}_3)_6]^{2-}$  anion, the fact that  $\text{HNO}_2$  production was suppressed at the cathode appeared, to the present authors, to be the best explanation for the high yields of Ce(IV) obtained by the method.

## 2.2 Apparatus

The electrolytic cell using a porous, fritted-glass barrier for electrode compartment separation is shown in Fig. 1. Both anode and cathode were constructed of 60-mesh platinum screen, each with a surface area of  $2.7 \text{ dm}^2$ . The electrode compartments were approximately 250 ml in volume and were separated by a medium-porosity, fritted-glass barrier

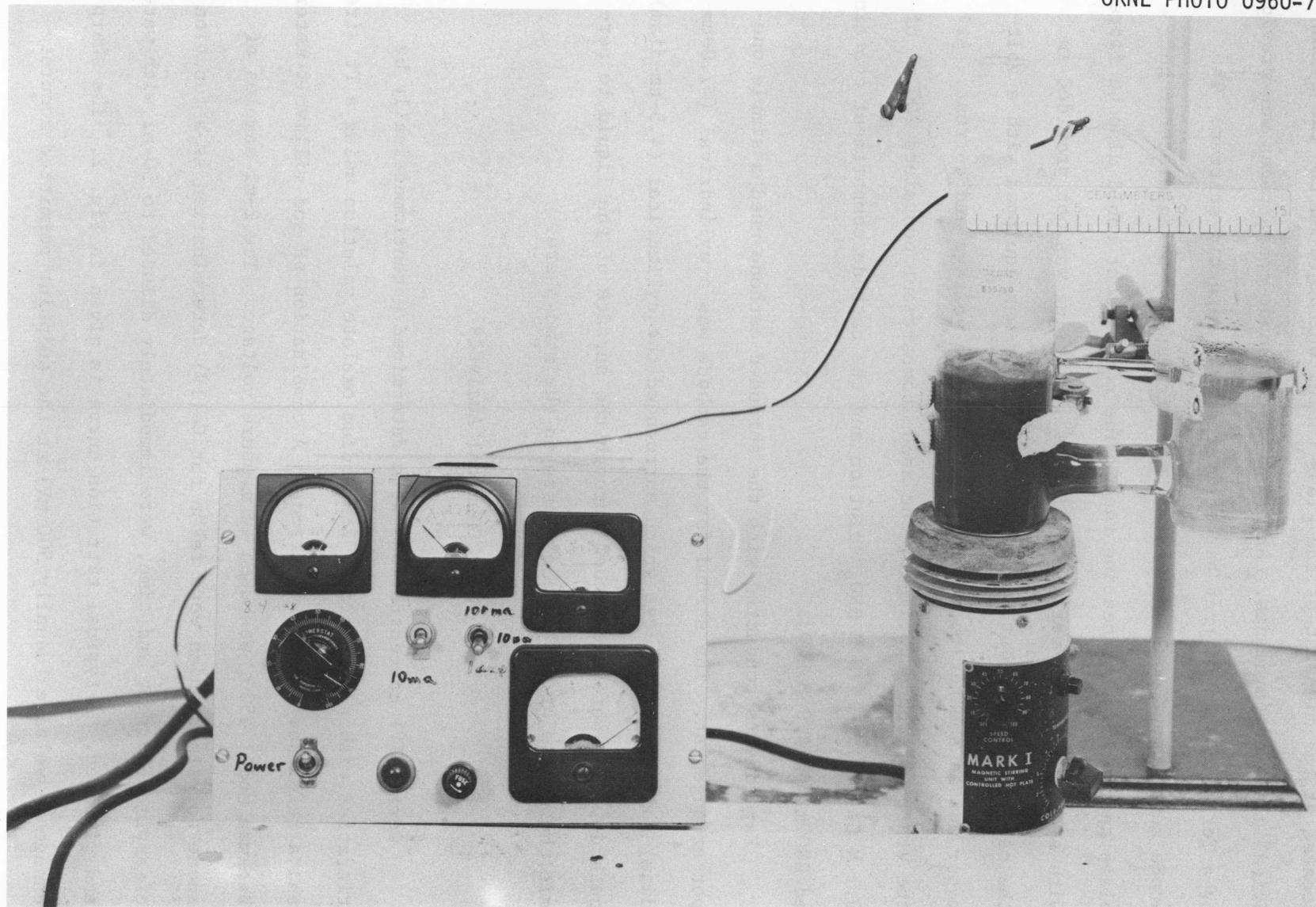


Fig. 1. The electrolytic cell with electrode compartments separated by a porous, fritted-glass barrier.

located at the midpoint of the glass tubing which joined the two cylindrical glass compartments. Stirring in the anode compartment was provided by a Teflon-coated stirrer bar activated by a magnetic stirrer. The anode compartment could be heated, when necessary, by an electric hot plate and an electric heating tape. The compartment could also be fitted with a condenser for reflux conditions. Stirring was not provided in the cathode compartment. The dc power supply was equipped with a voltmeter and an ammeter to measure the electrode voltage and current. At the start of each experiment, the anode compartment contained 200 ml of 0.1 M  $\text{Ce}(\text{NO}_3)_3$  - 4.0 M  $\text{HNO}_3$  solution and the cathode compartment contained 200 ml of 4.0 M  $\text{HNO}_3$ .

Experiments conducted with the shrouded cathode used a simple one-pot arrangement. The shroud for the cathode was a cylindrical ( $\sim$ 7.0-cm-diam) polyethylene sleeve which surrounded the cylindrical (4.5-cm-diam) cathode. The shroud extended through the surface of the liquid to permit the escape of any cathode gases to the atmosphere.

### 2.3 Chemical Analyses

Cerium(IV) concentrations were determined potentiometrically by titration with a standard 0.02 N sodium oxalate solution using a Pt wire and a reference calomel electrode. A combination pH and millivolt meter, Beckman Model 4500, was used to measure voltage. The 2-ml samples of anode solution, which were taken for Ce(IV) determination as a function of applied current and time, were immediately diluted to 50 ml with water and titrated. A typical titration curve is given in Fig. 2. The sharp change in voltage (usually 500 mV) at the endpoint permitted accurate

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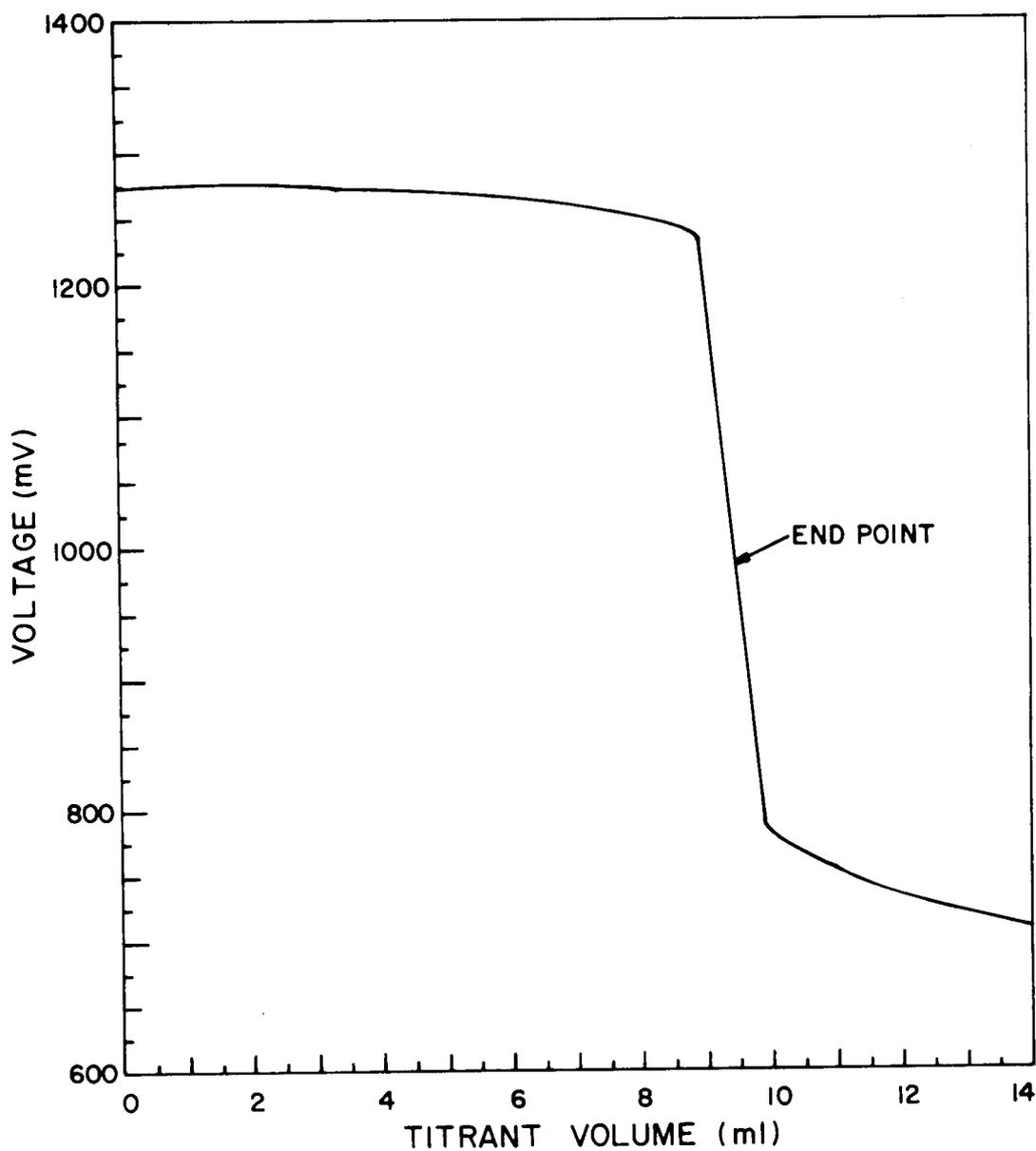


Fig. 2. Potentiometric titration of Ce(IV) with 0.02 N sodium oxalate.

determination of the Ce(IV) concentrations. We found this potentiometric method superior to the ferrous ion-ferroin indicator method<sup>12</sup> for end-point determinations. Nitrous acid was determined by adding a known amount of Ce(IV) and back-titrating the excess with a standard solution of sodium oxalate potentiometrically. Ammonium ion in the cathode solutions was determined by use of an ion-specific electrode and an ORION Research Model 901 specific ion meter.

#### 2.4 Results on Anodic Oxidation of Ce(III) to Ce(IV)

Good yields of Ce(IV) were obtained in the anode compartment of the electrolytic cell by using barrier-separated electrodes (Table 1 and Fig. 3). The yield of Ce(IV) increased in direct proportion to the time to ~85% conversion at a constant applied current. Calculations based on Faraday's law indicated that theoretical yields [1 milliequivalent of Ce(IV) per 965 coulombs] were attained over the linear portions of the curves shown in Fig. 3. Even at the highest applied currents, 0.5 - 1 A, ~85% of the Ce(III) was oxidized at the anode with theoretical efficiency. Analysis of the cathode solution after passage of 14,400 coulombs (1 A for 240 min) showed that 0.022 mole of  $\text{HNO}_2$  and 0.0008 mole of  $\text{NH}_4^+$  ion were present in the catholyte. Visual observations indicated that gas production in the cathode compartment was minimal. The few gas bubbles generated in the initial stages of the electrolysis disappeared after ~10 min of operation. Gas samples were not taken. This observation is in general agreement with that of Ellingham.<sup>13</sup> Therefore, under the conditions employed (current densities  $\leq 0.4 \text{ A/dm}^2$  and potentials of 1.5 - 6.0 V),  $\text{HNO}_2$  was the main product of the cathode reaction.

Table 1. Anodic oxidation of  $\sim 0.1$  M Ce(III) solution at  $25^\circ\text{C}$  using platinum electrodes separated by a porous, fritted-glass barrier

Initial Anode Solution: 200 ml of  $0.0960$  M  $\text{Ce}(\text{NO}_3)_3$  -  $4.0$  M  $\text{HNO}_3$   
 Initial Cathode Solution: 200 ml of  $4.0$  M  $\text{HNO}_3$

Run No.	1	2	3	4
Current, A	0.10	0.25	0.5	1.0
Voltage, V	1.70	2.25	2.95	4.20
Time, min	Ce(IV) concentration (M) <sup>a</sup>			
15	-	-	0.0250	0.0450
30	0.007	0.0265	0.0455	0.0850
45	-	-	0.0660	0.0925
60	-	0.0455	0.0870	0.0925
75	-	-	0.0860	-
90	0.0287	0.0750	0.0960	-
120	0.0385	0.0954	-	-
135	-	0.0956	-	-
150	0.0460	-	-	-
180	0.0580	-	-	-
210	0.0675	-	-	-
240	0.0775	-	-	-

<sup>a</sup>Complete oxidation of Ce(III) produces a  $0.0960$  M Ce(IV) solution.

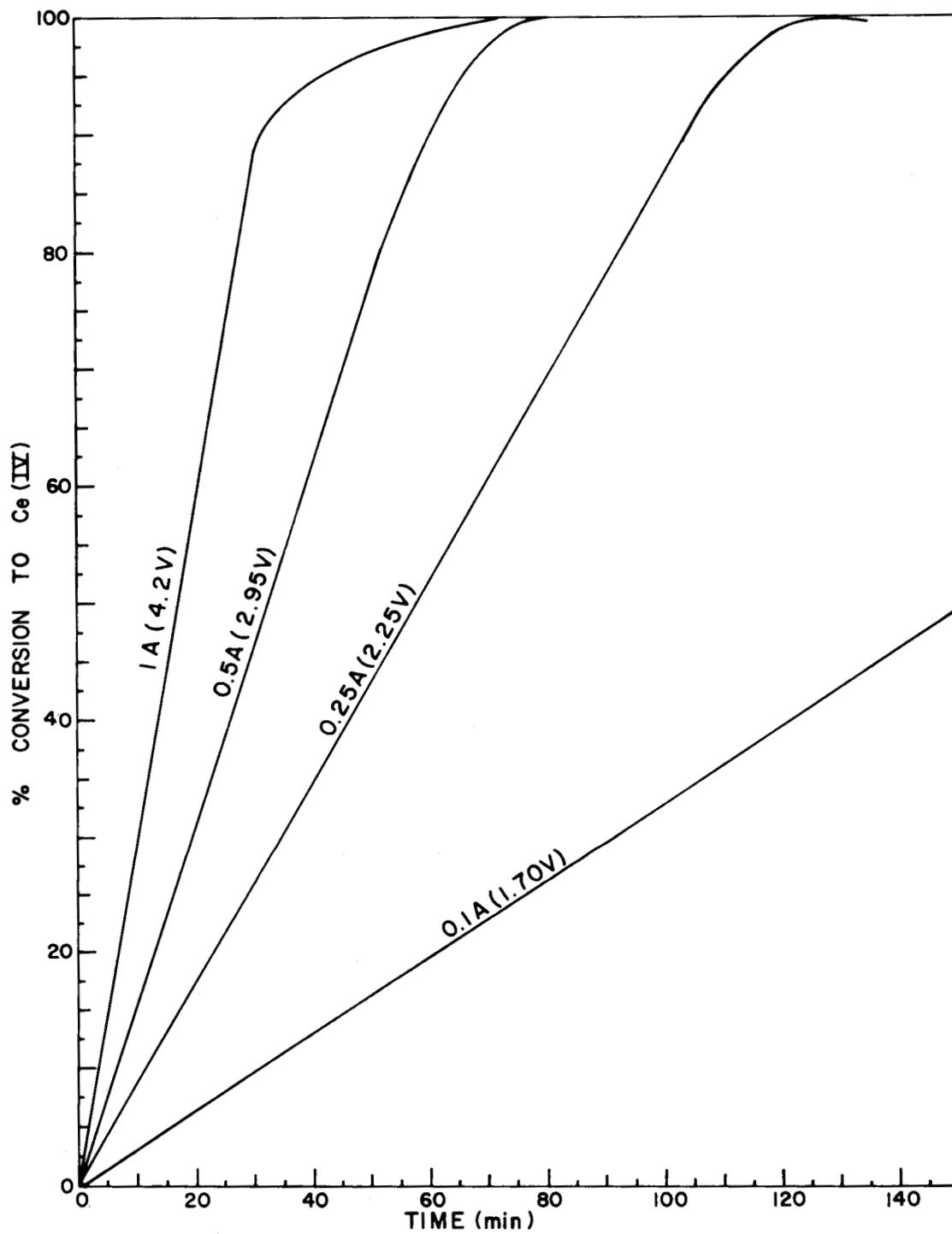


Fig. 3. Anodic oxidation of 0.096 M Ce(III) nitrate in 4 M HNO<sub>3</sub> solution at 25°C. Electrodes separated by a porous, fritted-glass barrier.

Results obtained with the stirred-pot electrolytic cell with both shrouded and unshrouded electrodes are shown in Fig. 4 and Table 2. It is seen that a simple shroud around the cathode effectively protects the Ce(IV) against reduction by  $\text{HNO}_2$ . The conversion of only 27% of the Ce(III) to Ce(IV) is achieved in the stirred-pot cell if protection against mixing of cathode and anode reaction products is not provided. A conversion of 88% is obtained using the shrouded electrode which permits the escape of nitrogen oxide gases to the atmosphere at the top of the shroud. Although sparging the catholyte with air may improve the conversion, the Ce(IV) concentration at 88% conversion is sufficient to promote the dissolution of  $\text{PuO}_2$ . No attempt was made to collect and analyze the cathode gases in these experiments.

Several materials of construction for use as either electrodes or for the fabrication of containment vessels for Ce(IV) in 4 M  $\text{HNO}_3$  were scouted with respect to corrosion (Table 3). The results showed that stainless steel was not suitable for construction of containment vessels, but that titanium, glass, or Teflon were satisfactory. Neither graphite nor titanium was suitable as an anode material; however, graphite appeared to be a satisfactory cathode material. These cursory corrosion tests indicated that for a practical system either glass-lined or titanium vessels were satisfactory for containment of solutions, platinum was suitable for the anode, and graphite could be used for the cathode provided that it could be satisfactorily isolated from the anode solution containing Ce(IV).

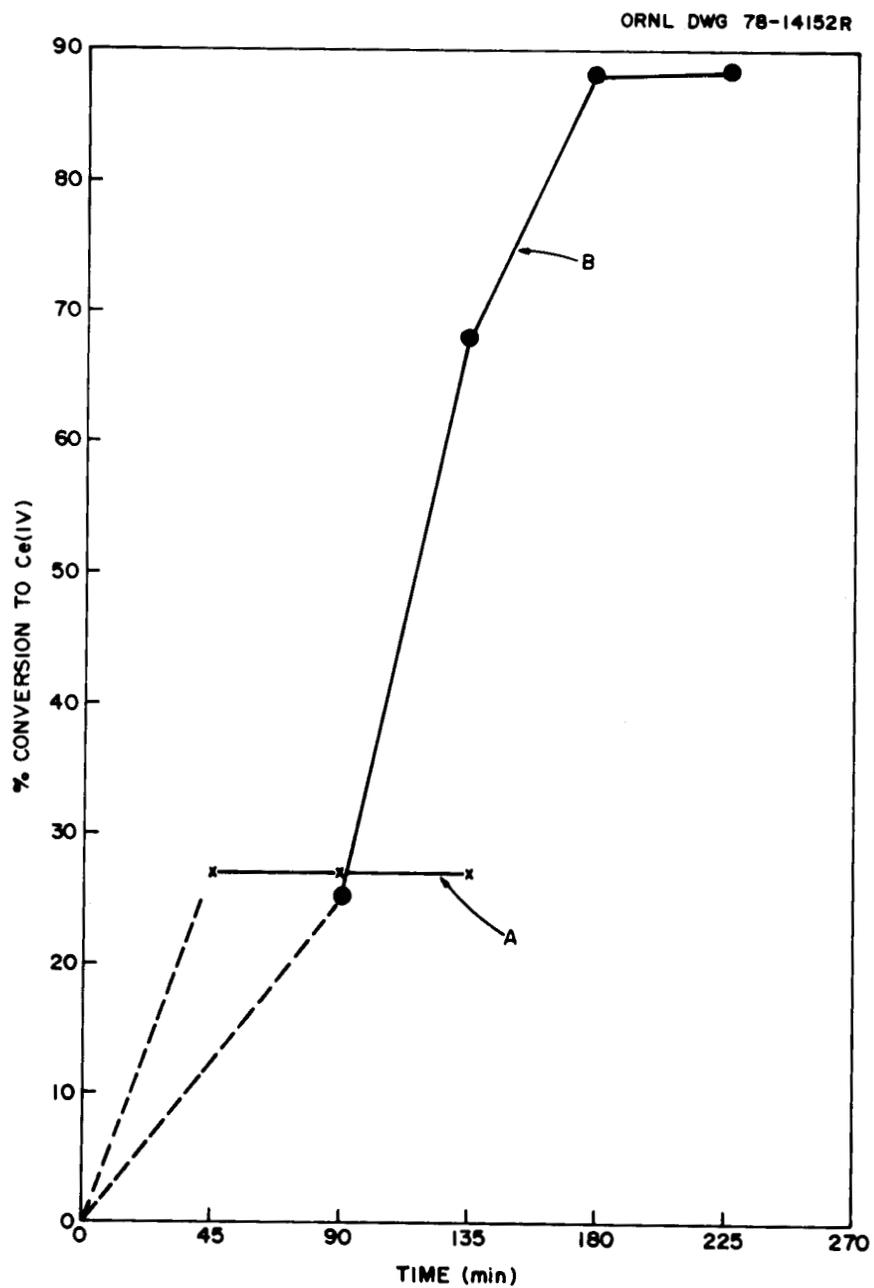


Fig. 4. Anodic oxidation of 0.096  $M$  Ce(III) nitrate in 4.0  $M$   $HNO_3$  solution using the stirred-pot electrolytic cell at 25°C.

Curve A - without cathode shroud

Curve B - with shrouded cathode

Table 2. Yields of Ce(IV) obtained using a stirred-pot electrolytic cell with and without a cathode shroud at a current of 1.0 A<sup>a</sup>

Cell type	Time (min)	Ce(IV) (M)	Ce(IV) yield (% of total Ce)	Net electrical efficiency <sup>b</sup> (%)
Without cathode shroud	45	0.0263	27	94
	90	0.0265	27	47
	135	0.0263	27	31
With cathode shroud	90	0.0245	25	44
	135	0.0654	68	78
	180	0.0850	88	76
	225	0.0850	88	61

<sup>a</sup>The cell initially contained 1 liter of 0.0964 M Ce(NO<sub>3</sub>)<sub>3</sub> - 4.0 M HNO<sub>3</sub>.

<sup>b</sup>Net cell efficiencies were calculated by Faraday's law.

Table 3. Reaction of various materials in  
0.1 M Ce(IV) nitrate - 4.0 M HNO<sub>3</sub> solutions

Material	Comments
1. Stainless steel	Rapidly corroded at slightly elevated temp. (~50°C). Quickly eroded at room temp. when used as an anode to electrolyze Ce(III) to Ce(IV).
2. Nylon	Deteriorated rapidly at room temp.
3. Carbon or graphite	Reacted at 60°C. Not suitable as an anode material due to spalling.
4. Titanium	Very little (if any) reaction even at 60°C, but not suitable as an anode material because the formation of an oxide coating caused high electrical resistance.
5. Platinum	Did not react at 100°C. Good as an anode material.
6. Teflon	Did not react at 100°C.
7. Alundum	Did not react at 100°C.

### 3. LEACHING OF PuO<sub>2</sub> FROM HEPA FILTERS

Cerium(IV)-promoted leaching of PuO<sub>2</sub> from synthetically prepared mixtures of refractory PuO<sub>2</sub> and HEPA filter materials was investigated using two techniques: (1) leaching of the slurried solids in the anode compartment of an electrolytic cell with continuous regeneration of Ce(IV), and (2) leaching of a packed column of PuO<sub>2</sub> - HEPA material with continuous recirculation of the leach liquor through the anode compartment of an external electrolytic cell.

Good dissolution of plutonium was achieved using either leaching technique. The packed-column method would avoid the difficult separation of gelatinous solids from leach liquors, but would present some difficulties in the remote or semi-remote loading and unloading of solids. Combustion of the carbonaceous species present in HEPA filter materials prior to leaching shortened the time required for dissolution of PuO<sub>2</sub>, probably because the Ce(IV) attacked the carbonaceous species preferentially so that the rate of PuO<sub>2</sub> dissolution was not appreciable until most of the carbonaceous species were oxidized. The combustion step might also help to avoid potential problems in the recovery of plutonium by solvent extraction from leach liquors containing soluble organic compounds unoxidized by Ce(IV).

#### 3.1 Materials Used

##### 3.1.1 HEPA filter media

The filtering media utilized in the leaching tests were obtained from the following two most common types of HEPA filters:<sup>19</sup>

- A. One type had pleated fiberglass media which were held

apart by corrugated aluminum separators and enclosed by a metal frame (Fig. 5). The media in this filter were attached to the frame by styrofoam that was formed in place. A proprietary binder held the fibrous filter media together.

- B. The other type had a wooden frame and corrugated-asbestos separators (Fig. 6). The fiberglass media were bonded together with a proprietary binder and joined to the frame by a rubber-base glue.

Values for the fluoride content, the reductive power, and the measured loss on ignition to 300°C of the media after their disassembly from the filter frame and the separators are listed in Table 4.

### 3.1.2 Preparation of PuO<sub>2</sub> and its mixtures with HEPA filter media

The PuO<sub>2</sub> powder was prepared by precipitating plutonium oxalate from ~1 M HNO<sub>3</sub> solution with oxalic acid, filtering, washing with dilute nitric acid, and then firing to temperature in a porcelain crucible heated in a muffle furnace. Two batches of PuO<sub>2</sub> were prepared in this manner using final firing conditions of 800 and 1000°C for 4 hr. Both oxide preparations were slightly reactive to 4.0 M HNO<sub>3</sub> at reflux temperatures (~104°C). About 5% of the PuO<sub>2</sub> sintered at 800°C was dissolved after a 6-hr dissolution period, whereas only about 1% of the PuO<sub>2</sub> sintered at 1000°C was dissolved under the same conditions. In the tests of the dissolution behavior of PuO<sub>2</sub> fired at either 800 or 1000°C, 50 mg of PuO<sub>2</sub> and 200 ml of 4.0 M HNO<sub>3</sub> were employed.

Mixtures of PuO<sub>2</sub>-HEPA filter media, 1.6 wt % PuO<sub>2</sub>, were prepared by mixing the fine PuO<sub>2</sub> powder with shredded HEPA filter media that had been ignited in air at 300°C in a muffle furnace. Frame materials and

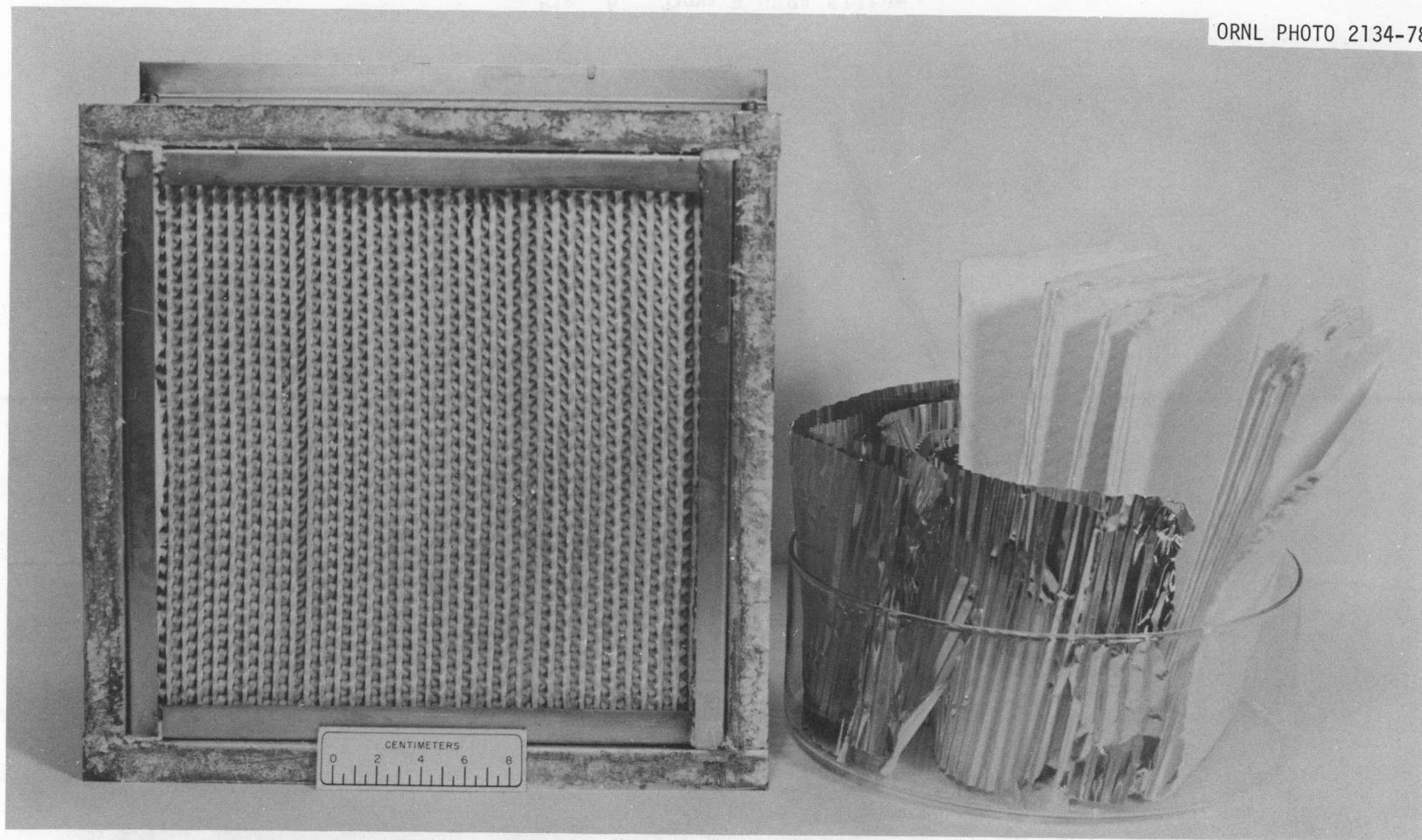


Fig. 5. Type A HEPA filter.

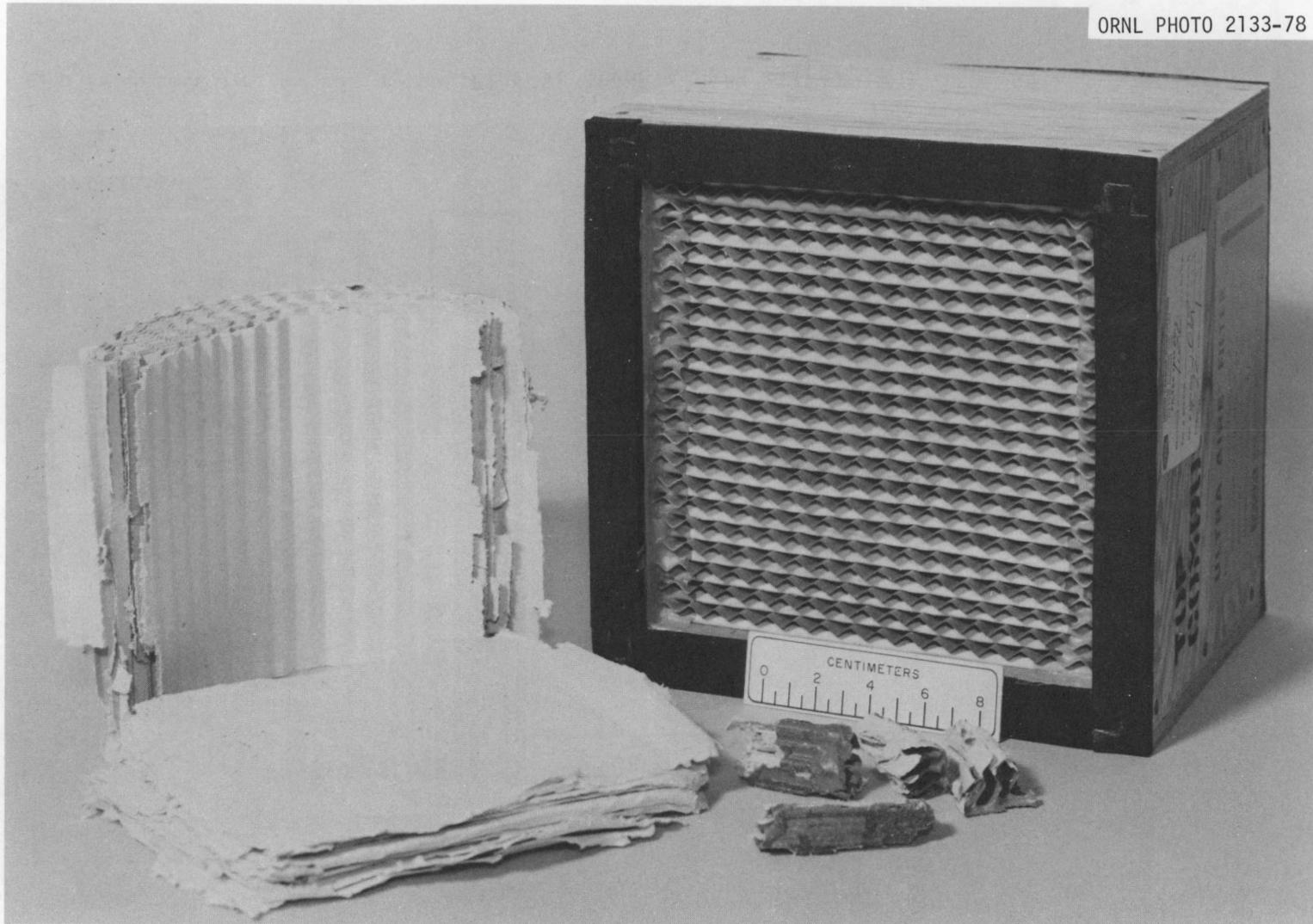


Fig. 6. Type B HEPA filter.

Table 4. Some properties of HEPA filters

	Type A <sup>a</sup>		Type B <sup>b</sup>	
	Glass fiber medium	Separator (aluminum)	Glass fiber medium + glue	Separator (asbestos)
Fluoride content, ppm	910	-	120	710
Relative weight <sup>c</sup>	0.5	1.0	4.0	1.0
Loss on ignition at 300°C, wt %	5	-	15	1
Reductive power, <sup>d</sup> meq/g	4	-	6	-

<sup>a</sup>See Fig. 5, Type A HEPA filter, p. 21.

<sup>b</sup>See Fig. 6, Type B HEPA filter, p. 22.

<sup>c</sup>Relative weight =  $\frac{\text{weight of medium}}{\text{weight of separator}}$ .

<sup>d</sup>As determined by the amount of Ce(IV) reduced in boiling 4 M HNO<sub>3</sub> after 1.5 hr.

and separator materials were not included in the mixtures since it was likely that in a processing facility these materials would be mechanically separated from the actinide-laden fiberglass prior to leaching. If the aluminum separators were included, their dissolution by the Ce(IV)-HNO<sub>3</sub> leachant would not only increase the quantity of aluminum nitrate waste, but also require additional time and electric current to regenerate the Ce(IV) reduced by the aluminum. The asbestos separators could be left with the media because they would not increase the Ce(IV) consumption.

### 3.2 Leaching Procedures

#### 3.2.1 Slurry leaching in anode compartment

Samples were leached in the anode compartment of the electrolytic cell described earlier (Fig. 1 and Sect. 2.2) with 200 ml of 0.1 M Ce(IV) nitrate - 4.0 M HNO<sub>3</sub> solution and an applied current of 1.0 A. The tests were carried out at the reflux temperature with stirring. All leachings were carried out with HEPA filter solids that had been ignited in air to 300°C except for those tests that were specifically designed to determine the effect of carbonaceous materials on the leaching process. All leaching experiments on PuO<sub>2</sub>-HEPA mixtures were conducted with a blend of 50 mg of PuO<sub>2</sub> and 3 g of HEPA media solids. In some experiments, only 50 mg of PuO<sub>2</sub> was used to determine the effects of the HEPA material and temperature on PuO<sub>2</sub> dissolution.

#### 3.2.2 Packed column leaching

A schematic diagram of the apparatus is shown in Fig. 7. Photographs of the overall equipment and of the column and electrolytic cell before installation in an alpha containment glove box are shown in Figs. 8 and 9,

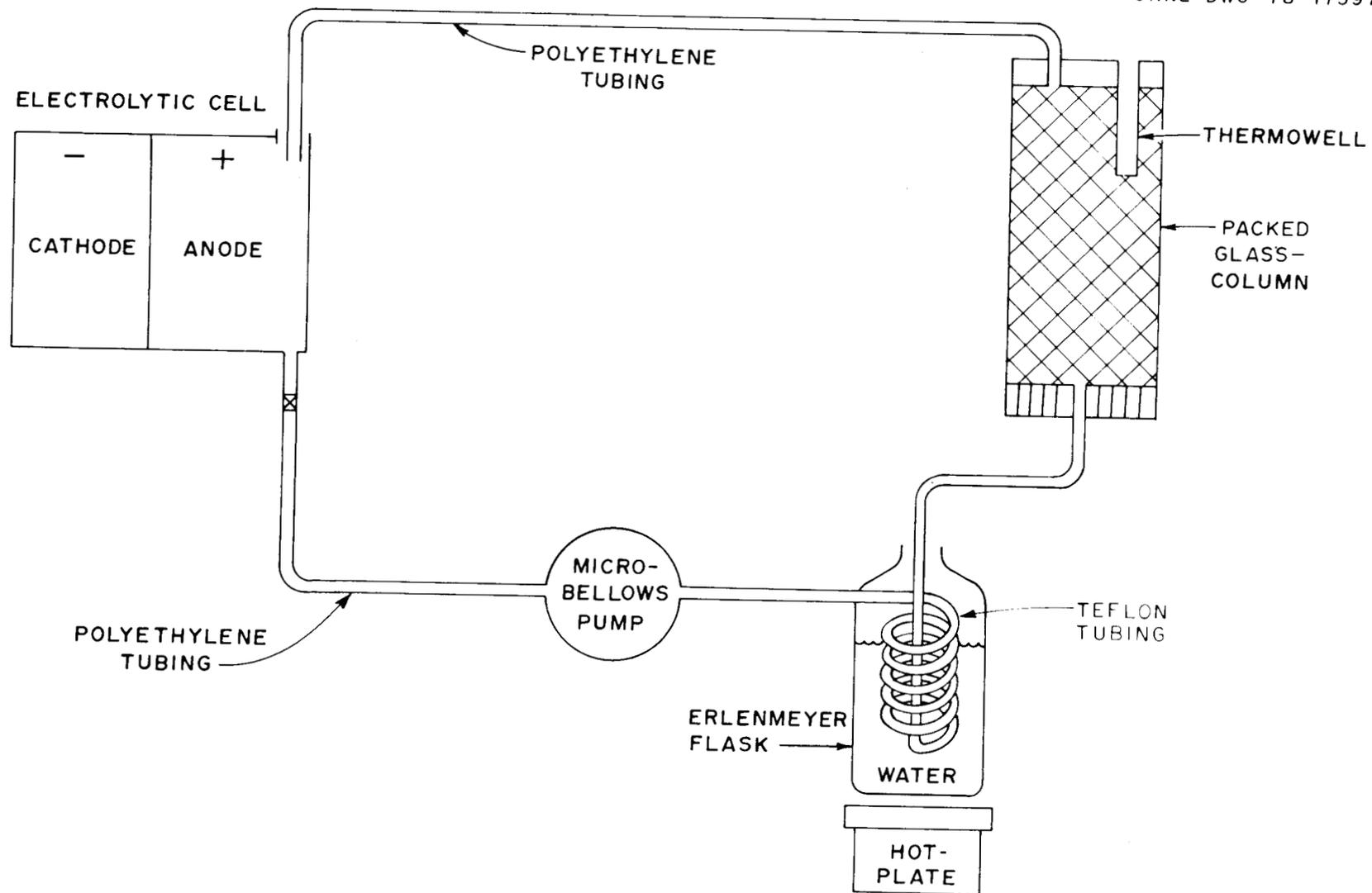


Fig. 7. Schematic diagram of the apparatus for leaching HEPA solids in a packed column with 0.1 M Ce(IV) nitrate - 4 M HNO<sub>3</sub>.

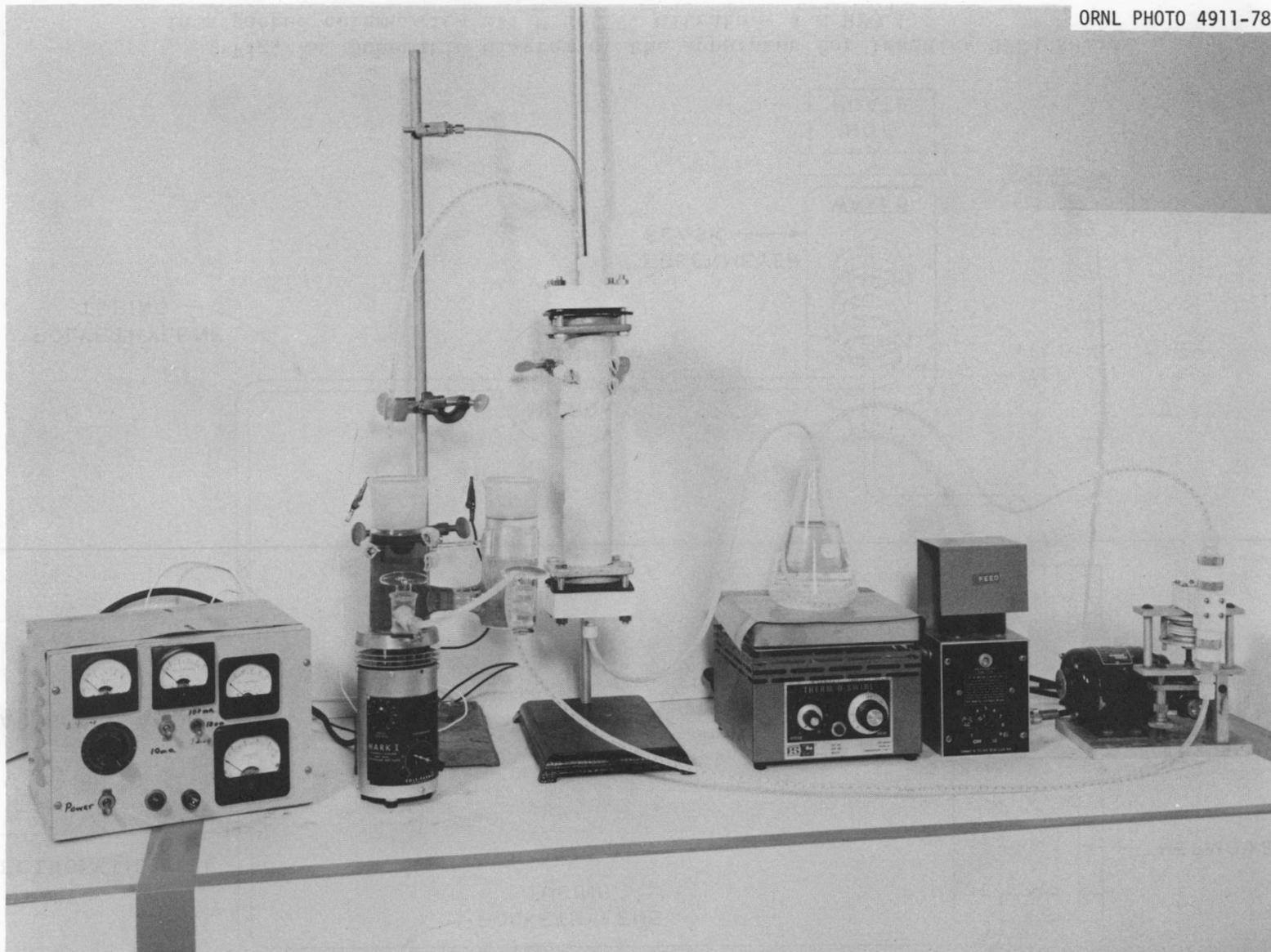


Fig. 8. The experimental equipment used in leaching a packed column of HEPA solids with 0.1 M Ce(IV) nitrate - 4.0 M HNO<sub>3</sub>.

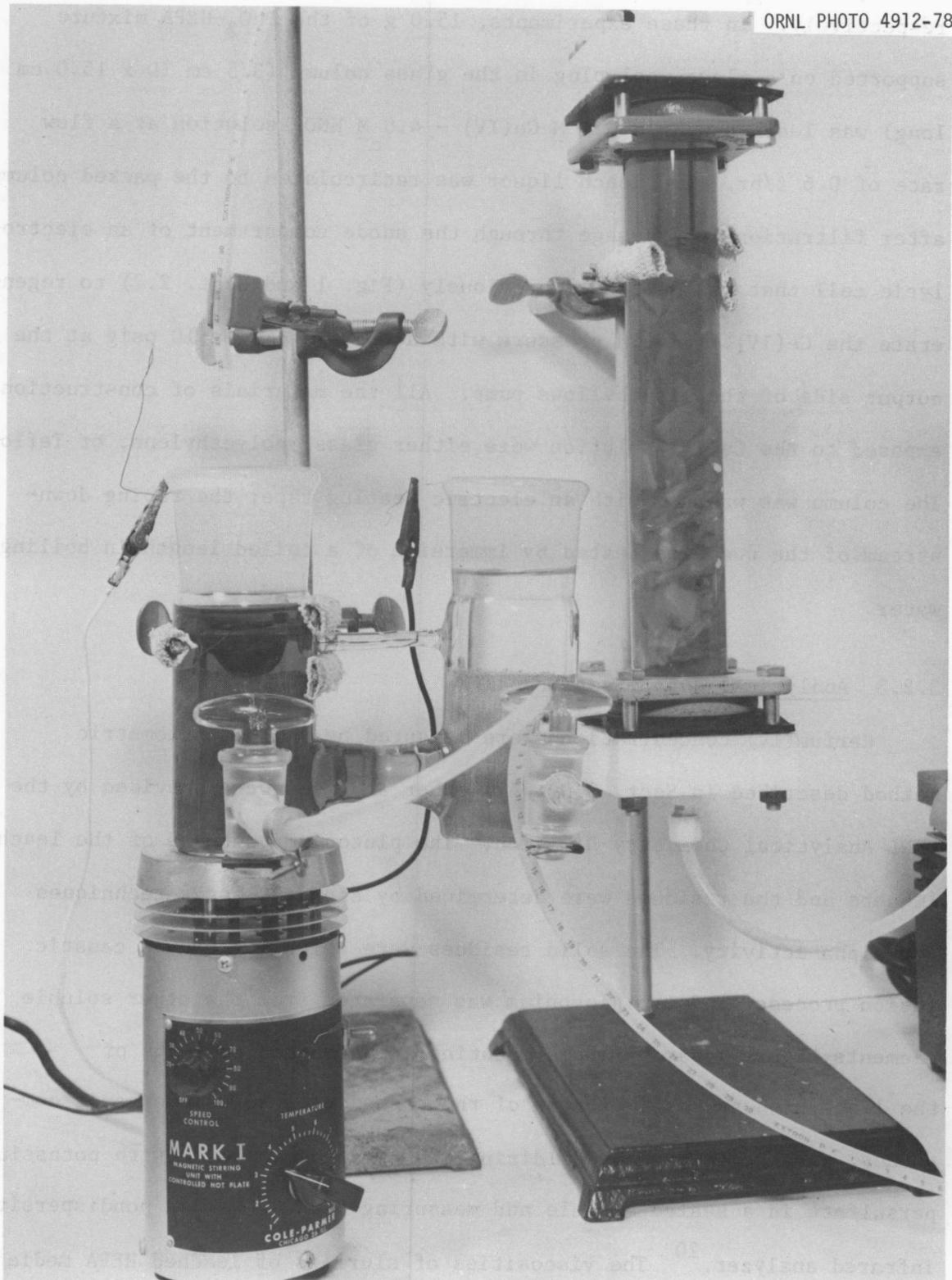


Fig. 9. A detailed view of the glass column packed with HEPA solids and the electrolytic cell.

respectively. In these experiments, 15.0 g of the  $\text{PuO}_2$ -HEPA mixture supported on a glass wool plug in the glass column (3.5 cm ID x 15.0 cm long) was leached with a 0.1 M Ce(IV) - 4.0 M  $\text{HNO}_3$  solution at a flow rate of 0.6 l/hr. The leach liquor was recirculated to the packed column after filtration and passage through the anode compartment of an electrolytic cell that was described previously (Fig. 1 and Sect. 2.2) to regenerate the Ce(IV). Liquid pressure within the system was 10 psig at the output side of the microbellows pump. All the materials of construction exposed to the Ce(IV) solution were either glass, polyethylene, or Teflon. The column was wrapped with an electric heating tape; the tubing downstream of the pump was heated by immersion of a coiled length in boiling water.

### 3.2.3 Analytical determinations

Cerium(IV) concentrations were measured by the potentiometric method described in Sect. 2.3. All other analyses were provided by the ORNL Analytical Chemistry Division. The plutonium contents of the leach liquors and the residues were determined by standard assay techniques for alpha activity. The solid residues were solubilized by a caustic fusion process, and the plutonium was separated from the other soluble elements before assay by alpha counting. The carbon contents of the leach liquors, an indicator of the presence of soluble organic compounds, were determined by oxidizing the organic compounds with potassium persulfate in a sealed ampoule and measuring the  $\text{CO}_2$  with a nondispersive infrared analyzer.<sup>20</sup> The viscosities of slurries of leached HEPA media were determined with a Brookfield viscosimeter.

### 3.3 Results and Discussion

#### 3.3.1 Effects of carbonaceous materials

In the initial tests, slurries of HEPA media were leached in the anode compartment of the electrolytic cell to determine the extent of the reaction of Ce(IV) with the organic species present in HEPA media and the concentrations of soluble organics in the leach liquor unoxidized by Ce(IV). In the HEPA media samples that contained substantial quantities of binder glue (Table 4, Type B), an applied current of 1.0 A was not sufficient to maintain the Ce(IV) concentration at its initial value even after a reaction time of 3 hr. Analyses of the liquors after leaching periods of 1 to 2 hr showed that aqueous-soluble organic compounds were present (Table 5). Subsequent tests with samples of HEPA media that had been ignited in air to 300°C prior to leaching showed that this was an effective pretreatment to reduce the production of soluble organic compounds and to facilitate the maintenance of Ce(IV) concentrations by anodic oxidation.

The introduction of foreign organic compounds should generally be avoided in solvent extraction separations because of the possible buildup of impurities in the extractants. Rather than introduce an uncertain factor into the subsequent recovery of plutonium from the leach liquors by solvent extraction, it would be prudent to eliminate the soluble, often difficult to identify, organic species previous to leaching to avoid the necessity of demonstrating that they have no effects in solvent extraction operations in which the extractant is recycled. Therefore, in all other tests reported here, the HEPA filter media were given the ignition treatment prior to leaching unless stated otherwise.

Table 5. Carbon content of liquors obtained from leaching HEPA filter media

Filter type	Run No.	Leaching ratio <sup>a</sup> (g/l)	Leaching time (hr)	Total carbon (mg/l)
B	C-1	25	1	336
B	C-2 <sup>b</sup>	25	1	140
B	C-3	25	2	228
A	C-4	10	1	40
A	C-5	10	1	52

<sup>a</sup>The leaching ratio is defined as grams of HEPA filter material per liter of 4 M HNO<sub>3</sub> - 0.1 M Ce(IV) leaching solution.

<sup>b</sup>HEPA samples in Run C-2 was preignited in air to 300°C. In all other runs, the samples were not ignited.

### 3.3.2 Separation of residues from leach liquors

Preliminary studies in which HEPA media without  $\text{PuO}_2$  were leached in the anode compartment of the electrolytic cell showed that moderately dilute slurries of the leached residues were very viscous and that the gelatinous solids were difficult to separate. In addition, the platinum anode was coated by a slimy deposit, but no difficulties were encountered in maintaining the desired 1.0-A current in the dissolution tests. Apparently, the mechanical force required for stirred-contact leaching of the slurries pulled apart the individual glass fibers which comprise the HEPA filter material and promoted their attack by the leachant. Subsequently, several leaching tests were carried out to determine the effect of solids concentration on the viscosity of slurries of HEPA residues and the ease of separation of the solids by centrifugation. Viscosities of slurries of leached Type A material were moderately high, 380 to 500 cP, at 10-g/l concentration and extremely high, 2400 cP, at 17.5-g/l concentration (Table 6). The latter slurries were almost gels. However, after separation of the solids the clear liquid phase had a viscosity ( $\sim 1$  cP) about equal to that of 4 M  $\text{HNO}_3$ . The problem of liquid-solid separation in slurries containing 10 g/l leached type A materials was illustrated by the results of some experiments using a laboratory centrifuge (Table 7). The settled solids volume of the most compact cake obtained by centrifugation was approximately 30% of the original slurry volume. The concentration of leached HEPA material in that cake was estimated to be approximately 30 g/l.

In contrast to the difficult problems with the separation of solids after stirred-contact leaching, tests with HEPA solids leached in a

Table 6. Viscosity of slurries of leached HEPA solids in 0.1 M Ce(IV) nitrate - 4.0 M HNO<sub>3</sub> solutions at 25°C<sup>a</sup>

Run No.	Filter type	Slurry concentration (g/l)	Viscosity (cP)
C-6	A	10	380
C-7	A	10	500
C-10	A	17.5	2400
C-8	B	25	350
C-9	B	37.5	680

<sup>a</sup>Conditions: stirred-contact leaching at reflux temperature (~104°C) for 1.5 hr in the electrolytic cell.

Table 7. Centrifugation tests at 25°C with 10 g/l slurries of HEPA materials (Type A) after stirred-contact leaching

Centrifuge speed (rpm)	Height (cm) of centrifuge cake in tube <sup>a</sup> at:				
	1 min	2 min	3 min	4 min	5 min
500	7.5	7.5	7.0	7.0	7.0
1000	5.3	5.0	4.5	4.5	4.5
1500	4.5	4.0	3.9	3.5	3.5
2000	3.7	3.5	3.5	3.5	3.5
2500	3.5	3.5	3.4	3.4	3.4
3000	3.3	3.3	3.2	3.2	3.2
3500	3.0	3.0	3.0	3.0	3.0

<sup>a</sup>A cylindrical, 2.5-cm-diam centrifuge tube having a height of 9.8 cm was filled to a 9 cm height with the slurry and centrifuged. The distance from the base of the centrifuge tube to the center of rotation of the centrifuge was 15.3 cm.

column showed that the expulsion of leach liquor and washing of the column were relatively easy. Application of about 2 psig air pressure to the column readily expelled liquids.

### 3.3.3 Leaching of PuO<sub>2</sub>-HEPA mixtures

The initial leaching studies were made with a slurry of PuO<sub>2</sub>-HEPA solids with 0.1 M Ce(IV) nitrate - 4.0 M HNO<sub>3</sub> in the anode compartment of the electrolytic cell. The HEPA material samples, which had not been ignited to remove carbonaceous species, were deliberately selected by visual inspection to contain considerable amounts of the organic-base binder glue (Table 4, Type B) so that the "worst case" for PuO<sub>2</sub> dissolution would be determined. The results of the preliminary tests confirmed expectations that the carbonaceous species would prolong the time to achieve appreciable PuO<sub>2</sub> dissolution beyond that required in the absence of the HEPA material (Table 8) because the Ce(IV) concentration necessary for PuO<sub>2</sub> dissolution could not be maintained by anodic oxidation at a current of 1.0 A until most of the carbonaceous material had been oxidized (Sect. 3.3.1 and Fig. 10). Although the Ce(IV) concentration was not measured during leaching of PuO<sub>2</sub>-HEPA samples, the color of the leaching solution indicated that the Ce(IV) concentration had been too low for efficient PuO<sub>2</sub> dissolution during the first 5 hr. Visual observation of color could be used as an indicator of the Ce(IV) content because it had been previously observed in the studies of anodic oxidation of Ce(III) to Ce(IV) that the color of the solution was yellow for a Ce(IV) concentration  $\leq 0.03$  M and red-orange for a concentration  $> 0.05$  M.

Plutonium dioxide powders sintered at 1000°C dissolved rapidly only at the reflux temperature, 104°C (Table 9). On the other hand, 98%

Table 8. Leaching of PuO<sub>2</sub> or PuO<sub>2</sub>-unignited HEPA material slurries with 0.1 M Ce(IV) nitrate - 4.0 M HNO<sub>3</sub> (initially) in the anode compartment of the electrolytic cell

Run No. <sup>a</sup>	Material	Applied current (A)	Temp. (°C)	Time (hr)	% Pu leached	
					Solution analysis	Final residue analysis
DS-4	PuO <sub>2</sub> -HEPA	0.8	Reflux <sup>b</sup>	5.5	43	
				12.5	101	
DS-5	PuO <sub>2</sub> -HEPA	0.8	Reflux <sup>b</sup>	5.5	82	
				12.5	97	99.99
DS-6	PuO <sub>2</sub>	1.0	25	18	98	
			Reflux <sup>b</sup>	5.5	100	
DS-8	PuO <sub>2</sub> <sup>c</sup>	1.0	25	18	30	
			Reflux <sup>b</sup>	6	101	

<sup>a</sup>In Runs DS-5 and DS-8, the solid-liquid mixtures were stirred by a magnetic stirrer. No stirring was used in Runs DS-4 and DS-6.

<sup>b</sup>Reflux temperature is ~104°C.

<sup>c</sup>1000°C-fired PuO<sub>2</sub> used; in other tests, it was 800°C-fired material.

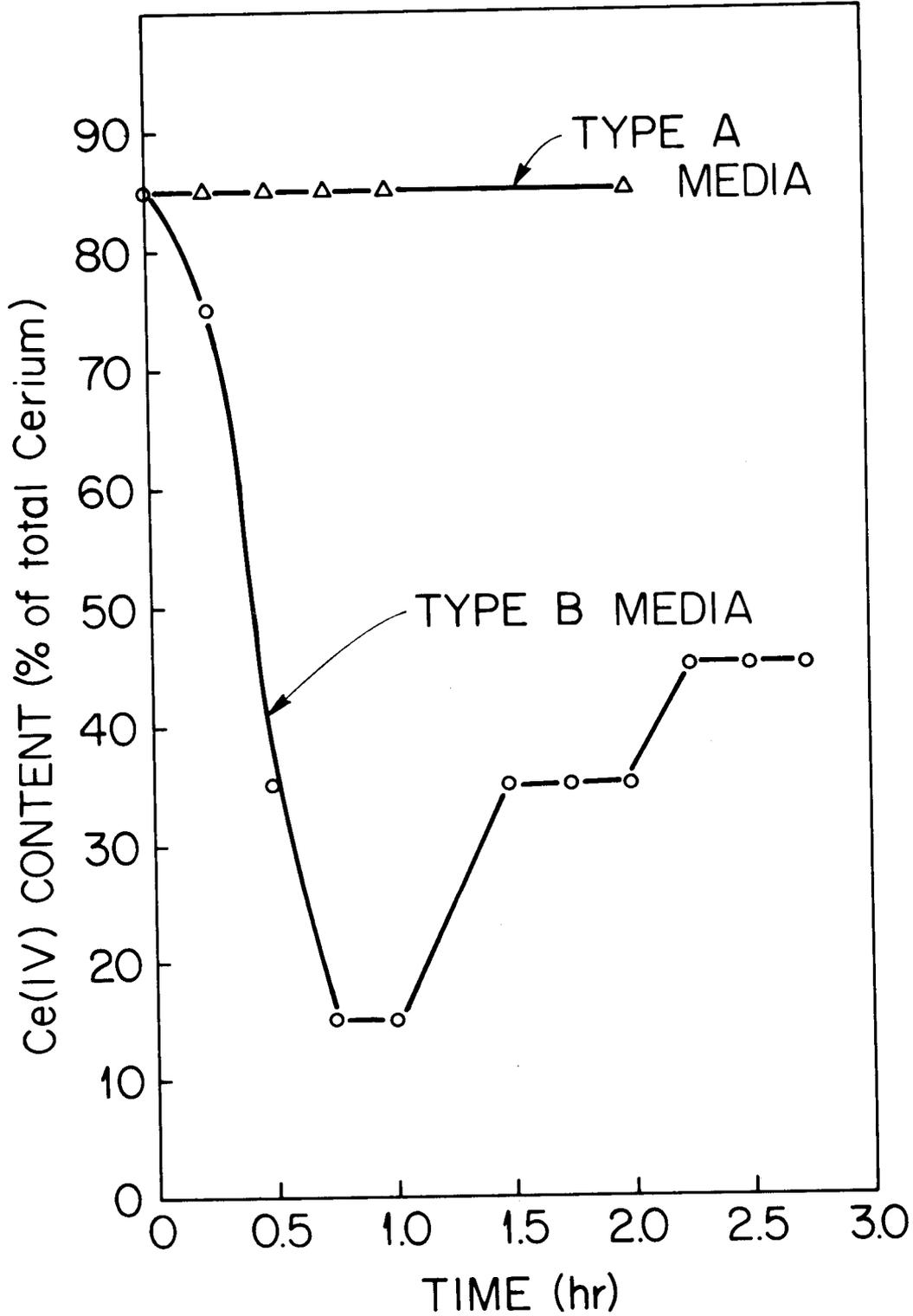


Fig. 10. Change in Ce(IV) content with time during the leaching of unignited HEPA media in the anode compartment at reflux temperatures.

Table 9. Effect of leaching time and temperature on the dissolution of sintered (1000°C) PuO<sub>2</sub> in the anode compartment of the electrolytic cell initially containing 0.1 M Ce(IV) nitrate - 4.0 M HNO<sub>3</sub> at a current of 1.0 A

Run No.	DS-9	DS-11	DS-14	DS-13
Temperature, °C	25	50	75	Reflux
Leaching time, hr	% Pu leached			
1	11.9	66.8	33.6	115
2	17.4	75.4	53.4	108
3	18.1	73.3	72.8	103
4	20.6	85.3	80.9	103
5	22.2	78.9	80.9	102
6	26.8	80.0	80.9	102
23	47.6	75.0	89.6	102

dissolution of  $\text{PuO}_2$  powder sintered at  $800^\circ\text{C}$  was achieved after 18 hr at  $25^\circ\text{C}$  (Table 8, Run DS-6). The decrease in  $\text{PuO}_2$  dissolution rates with increasing ignition temperature is well known<sup>21,22</sup> and was not investigated further.

No tests were made in the electrolytic cell on leaching plutonium from slurries of  $\text{PuO}_2$  and preignited HEPA material because it had already become apparent from work described in Sect. 3.3.2 that separation of HEPA residues from leach liquors would be difficult. Leaching tests in the packed column utilized  $\text{PuO}_2$  powder sintered at  $1000^\circ\text{C}$  and the ignited HEPA material since the separation behavior of HEPA solids from the slurries was identical for either the virgin or ignited materials. With the  $\text{Ce(IV)}$  concentration maintained by a current of 1.0 A in the electrolytic cell, the  $\text{PuO}_2$  dissolved after leaching for 1.5 hr at  $100^\circ\text{C}$  (Fig. 11) as determined by analyses of the leach liquors. It was not certain, however, that a small amount  $\leq 1\%$  had not remained with the HEPA residue. The study demonstrated that the  $\text{Ce(IV)}$  concentration necessary for  $\text{PuO}_2$  dissolution could be maintained during the leaching of HEPA filter solids and that the packed column concept was feasible.

#### 4. CHEMICAL FLOWSHEET FOR RECOVERY OF ACTINIDES AND RECYCLE OF CERIUM

The proposed chemical flowsheet (Fig. 12) for the recovery of actinides from HEPA filters was developed in a collaborative effort<sup>23</sup> with B. C. Finney and D. W. Tedder of ORNL. The HEPA filter material is mechanically separated from the frame and spacers and ignited in air to  $300^\circ\text{C}$  to remove carbonaceous materials present in glues and binders. Subsequently, the HEPA solids are leached with 0.1 M  $\text{Ce(IV)}$  nitrate -

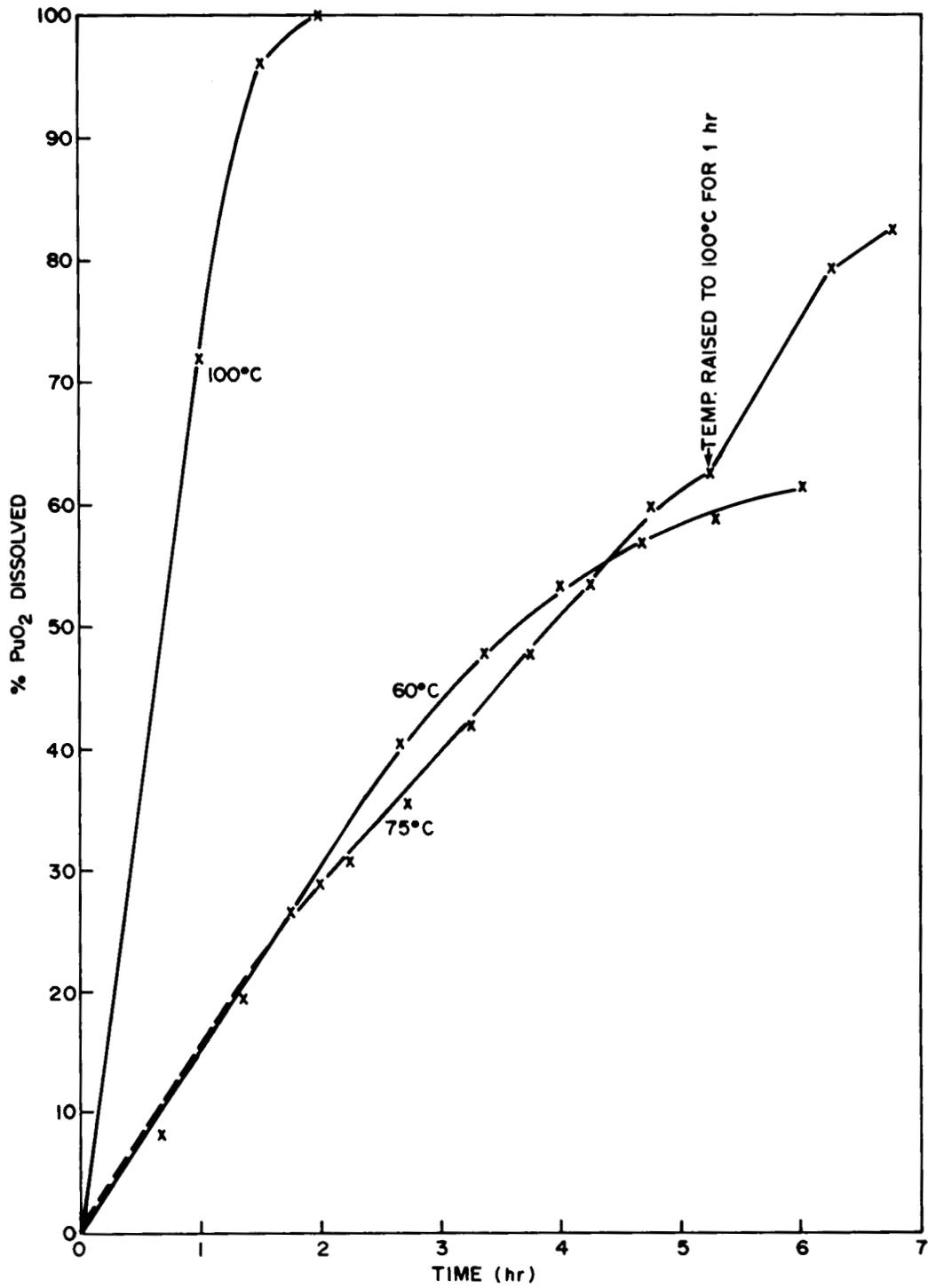


Fig. 11. Packed-column leaching of plutonium from sintered ( $1000^\circ\text{C}$ )  $\text{PuO}_2$ -ignited HEPA solids mixtures with  $0.1 \text{ M}$   $\text{Ce(IV)}$  nitrate -  $4.0 \text{ M}$   $\text{HNO}_3$ .

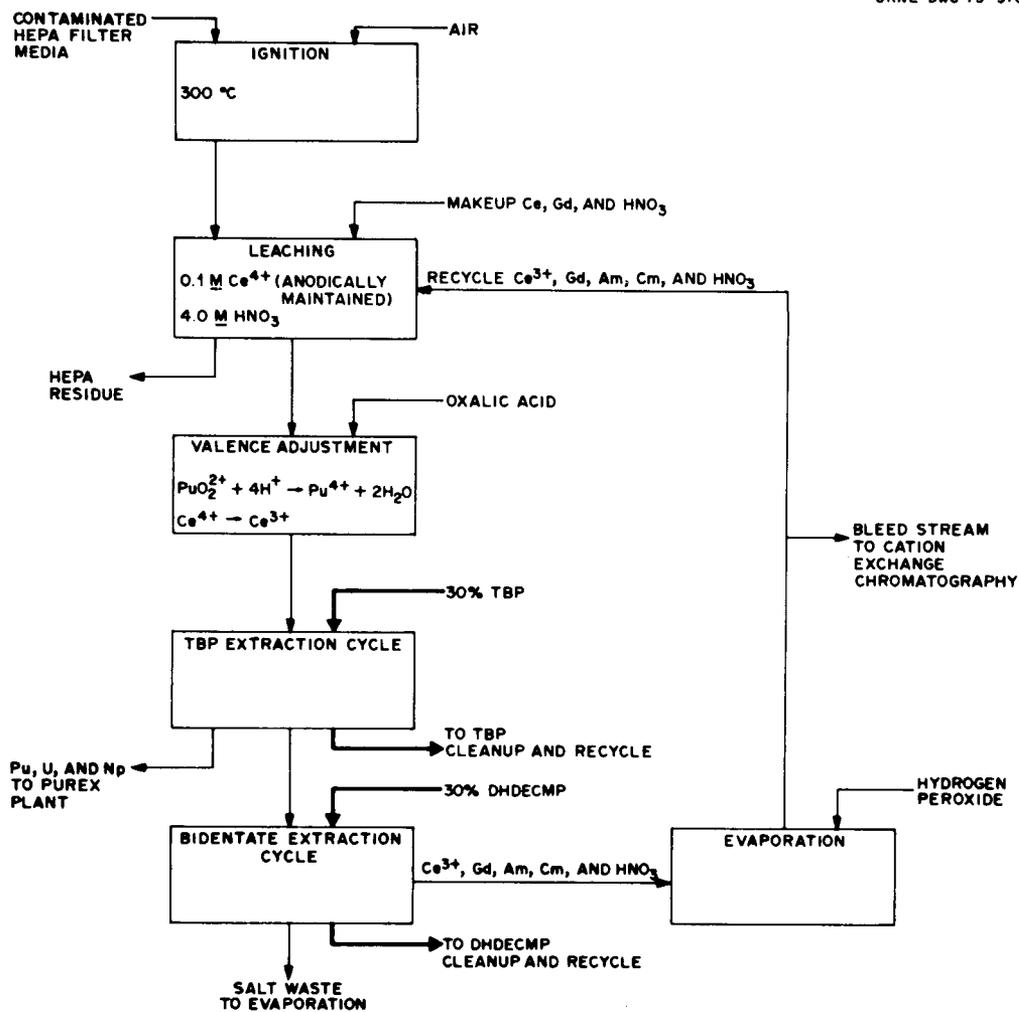


Fig. 12. Conceptual flowsheet for recovery of actinides from HEPA filter media.

4.0 M  $\text{HNO}_3$  solution by passing the leachant through a packed column of the solids while maintaining the Ce(IV) concentration in the leach solution by anodic oxidation. A soluble neutron poison, gadolinium nitrate, is used for criticality control during leaching.<sup>23</sup> Stirred-contact leaching is unsatisfactory because it produces a viscous slurry that cannot be readily pumped or centrifuged. The Ce(IV) that is reduced during the leaching process is regenerated continuously by reoxidation of Ce(III) at the anode of an electrolytic cell using an applied current density of 0.4 A/dm<sup>2</sup>.

The actinides, cerium, and gadolinium are recovered from the leach liquor by two cycles of solvent extraction. In the first cycle, plutonium, uranium and neptunium are recovered by TBP extraction after reduction of Pu(VI) to Pu(IV) and Ce(IV) to Ce(III) with oxalic acid in a valence adjustment step and separation of the leach liquor from solids.<sup>23</sup> Valence adjustment can be accomplished by sparging with NO or NO<sub>2</sub><sup>24</sup> rather than by oxalic acid addition, if desired. The recovered plutonium, uranium, and neptunium are recycled to the main Purex plant.<sup>23</sup>

The Ce(III), Gd, Am, Cm, and trace amounts of other actinide and lanthanide elements, which may be present, are recovered by the bidentate process which uses dihexyl-N-N-diethylcarbamoylmethylene phosphonate (DHDECMP) as the extractant. The bidentate process<sup>2,11,23</sup> will also extract the small amounts of the plutonium, uranium, and neptunium, that may remain after the TBP extraction. A valence adjustment step may be necessary to convert inextractable Np(V) to extractable Np(IV) or Np(VI). The actinides are recovered from the DHDECMP in two separate stripping operations. In the first, a solution of 0.005 M  $\text{HNO}_3$  - 0.05 M

hydroxylamine nitrate (HAN) is used to strip the trivalent actinides, trivalent lanthanides, and Np(V). The HAN reduces the extractable species, Pu(IV) and Np(VI), to the inextractable forms, Pu(III) and Np(V), respectively. Only about 20% of the uranium (present as hexavalent uranium) is stripped in this operation. In the second stripping, a solution of 0.005 M HNO<sub>3</sub> - 0.05 M oxalic acid is used to strip the residual uranium and trace amounts of Am, Cm, Gd, Pu, and Np that may remain after the first stripping operation. In addition to promoting the stripping of hexavalent uranium, oxalic acid promotes the stripping of Np(IV) and Pu(IV) into dilute HNO<sub>3</sub> by oxalate complexing. The Pu(VI), Np(VI), and Np(V) are reduced extremely slowly by oxalate ion at this low acidity.<sup>9</sup>

The products from the stripping operations are evaporated to adjust the HNO<sub>3</sub> concentration and to decompose the HAN and oxalic acid, the HAN by reaction with HNO<sub>3</sub><sup>25</sup> and the oxalic acid by reaction with a mixture of HNO<sub>3</sub> and hydrogen peroxide<sup>2</sup> in separate evaporators.<sup>23</sup> Since the reaction of HAN with HNO<sub>3</sub> proceeds autocatalytically and involves HNO<sub>2</sub> as an intermediate, it may be desirable to utilize a NO<sub>2</sub> gas sparge to assure smooth initiation of the reaction. After the evaporative treatment, the solution is recycled until the americium-curium concentration has increased sufficiently to be suitable for cation exchange chromatographic separation<sup>2,23,26,27</sup> of those actinides from cerium, gadolinium, and any fission product lanthanides. This could be accomplished by either a "bleed" stream to the cation exchange chromatographic process<sup>23</sup> or in a batch campaign manner. Recycle of HNO<sub>3</sub>, cerium, and gadolinium to the HEPA leaching step would reduce the amounts of cerium and gadolinium rejected to the salt waste<sup>2,23</sup> and hence minimize the quantity of that waste.

Some consideration was given to the use of TBP for the recovery and recycle of cerium, but flowsheets based on the extraction of either Ce(IV) or Ce(III) by TBP were more complicated than the one already described. A high recovery of cerium as Ce(IV) by extraction with 30 vol % TBP in n-dodecane would require the use of an electrolytic method to maintain the Ce(IV) concentration due to its slow reduction by the extractant (Fig. 13). In addition, special materials of construction would be needed to contain the corrosive Ce(IV) solutions. Cerium could also be recovered as Ce(III) simultaneously with gadolinium and the trivalent actinides by extraction with 100 vol % TBP in the second extraction cycle if the acidity of the aqueous phase were 12 to 14 M HNO<sub>3</sub>. Such a process would require an additional step to adjust the acidity and use of an organic phase with undesirable physical properties. Moreover, the distribution coefficients for the trivalent actinides between 30 vol % DHDECMP solution and 4.0 M HNO<sub>3</sub><sup>11</sup> are comparable to those between 100 vol % TBP and 12 to 14 M HNO<sub>3</sub>.<sup>28</sup> From the foregoing considerations, a flowsheet based on TBP as the sole extractant did not possess a marked advantage over one which used both TBP and DHDECMP.

## 5. CONCLUSIONS

This study permitted conclusions to be made regarding the electrolytic production of solutions of Ce(IV) nitrate in HNO<sub>3</sub>, leaching refractory PuO<sub>2</sub> from HEPA filter solids using 0.1 M Ce(IV) nitrate - 4.0 M HNO<sub>3</sub>, the separation of the solids and leach liquor, and methods for recycle of cerium from leach liquors.

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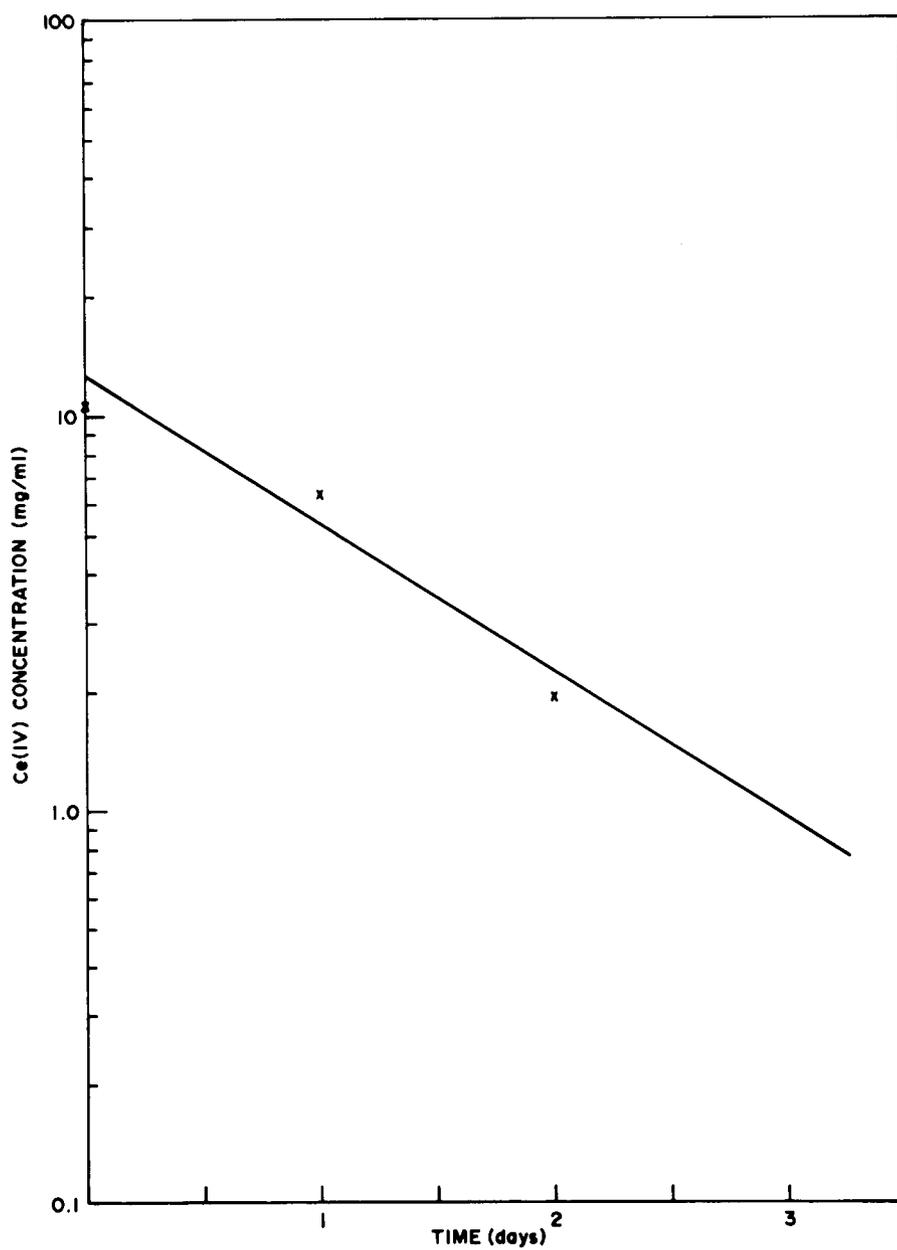


Fig. 13. The change in Ce(IV) concentration during the aging of a 30 vol % TBP extract containing Ce(IV) nitrate at 25°C.

### 5.1 Electrolytic Production of Ce(IV) Nitrate in HNO<sub>3</sub> Solutions

Cerium(IV) nitrate-HNO<sub>3</sub> solutions are produced in good yield by anodic oxidation of a 0.1 M Ce(III) nitrate - 4.0 M HNO<sub>3</sub> solution at platinum electrodes using a current density of 0.4 A/dm<sup>2</sup>. Over 80% conversion of Ce(III) to Ce(IV) was accomplished with good current efficiency when the anode and cathode compartments were separated either by a porous, fritted-glass barrier or simply by a shroud around the cathode. These electrode arrangements prevented the HNO<sub>2</sub> which was formed at the cathode from reducing the Ce(IV) produced at the anode to Ce(III). Tests showed that the Ce(IV)-promoted dissolution of refractory PuO<sub>2</sub> in 4.0 M HNO<sub>3</sub> was completely satisfactory if 80% of the cerium were present as Ce(IV).

Attempts to produce Ce(IV) nitrate-HNO<sub>3</sub> solutions that were satisfactory for effective dissolution of PuO<sub>2</sub> without isolating the anode or cathode were unsuccessful at current densities of 0.4 A/dm<sup>2</sup> because only 27% of the Ce(III) could be oxidized. The resulting Ce(IV) concentration was not sufficient for effective PuO<sub>2</sub> dissolution. This method could be successful with very high current densities at the cathode; for example, Smith and coworkers used 100 A/dm<sup>2</sup>.<sup>12</sup> At these high current densities, H<sub>2</sub> rather than HNO<sub>2</sub> is the major cathode reduction product and it is not necessary to isolate the cathode from the anode to obtain good yields of Ce(IV). Such a procedure, if employed, would require consideration of the disposal of hydrogen, a potential explosive hazard.

A few scouting tests were performed to determine suitable materials for electrodes and for liquid containment. Platinum was the only electrode material that was satisfactory for Ce(IV) nitrate - HNO<sub>3</sub> solutions.

Glass, Teflon, and titanium were satisfactory container materials, but titanium would be the only practical material for remote operations with highly radioactive materials.

## 5.2 Leaching HEPA Solids and Liquid-Solids Separations

Both stirred-contact leaching of HEPA solids and recirculating the leachant solution through a packed bed of HEPA solids were effective in dissolving  $\text{PuO}_2$ ; however, liquid-solids separation was much easier with the packed bed. Leach liquors and wash liquids were readily expelled from the bed using a slight overpressure (2 psig) of air. Stirred-contact leaching, on the other hand, produced very viscous slurries which were difficult to concentrate by centrifugation. At solids concentrations as low as 10 g/l, the viscosities were of the order of 500 cP. Prolonged centrifugation at 3500 rpm in a laboratory centrifuge did not dewater the solids satisfactorily. The suspended solids could be concentrated to only 30 g/l in the centrifuge cakes from an original concentration of 10 g/l in the slurries.

Visual observation indicated that in stirred-contact leaching the HEPA solids suffered attrition, probably due to both the physical force pulling apart the glass fibers making up the solid matrix and acid attack on the fibrous materials. In packed beds, it appeared that little, if any, disintegration of the original fibers occurred.

Ignition of the HEPA solids in air to 300°C was found to be beneficial in reducing the consumption of Ce(IV) by the carbonaceous compounds that were present as binder or glue materials. Therefore, the ignition step would also significantly reduce the electrical energy required for

the Ce(IV)-promoted leaching. Another potential benefit of the ignition step would be the significant decrease of soluble organic compounds in the leach liquor which might cause difficulty in subsequent solvent extraction operations.

### 5.3 Cerium Recycle

Based on information in the literature, it would be chemically feasible to recover the cerium as Ce(III) nitrate from spent leach liquors for recycle to the leaching operation where it would be oxidized to Ce(IV) nitrate. Bidentate extractants<sup>11</sup> have been demonstrated to give good recoveries of Ce(III), all other lanthanides, and the trivalent actinides from HNO<sub>3</sub> solutions. A chemical flowsheet for the recovery of actinides and the recycle of Ce<sup>3+</sup> based on two cycles of solvent extraction has been described. In the first, TBP is employed to recover plutonium, uranium, and neptunium. DHDECMP is employed in the second for Ce(III) recycle and for recovery of trivalent actinide elements.

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