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MASTER

# RECOVERY OF PLUTONIUM FROM HEPA FILTERS BY Ce(IV)-PROMOTED DISSOLUTION OF $PuO_2$ AND RECYCLE OF THE CERIUM PROMOTER*

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Fig. 1. Electrolytic cell with fritted-glass barrier between electrodes.

Fig. 2. Anodic oxidation of cerium in an electrolytic cell with fritted-glass barrier between electrode.

Fig. 3. Anodic oxidation of cerium in a stirred-pot electrolytic cell.

Fig. 4. Type A HEPA Filter.

Fig. 5. Type B HEPA Filter.

Fig. 6. Schematic diagram of equipment for leaching HEPA media in a packed column.

Fig. 7. Experimental equipment for leaching HEPA media in a packed column.

Fig. 8. Rate of leaching $PuO_2$ from HEPA media in a packed column.

Fig. 9. Conceptual flowsheet for recovery of actinides from HEPA filters.

# INTRODUCTION

This experimental investigation was part of a program to evaluate the technical feasibility of partitioning and transmutation as a waste management concept.[1,2] In this concept, actinides (and perhaps other long-lived radionuclides such as $^{129}I$) 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.[1-5]

The experimental study presented here dealt specifically with leaching of plutonium from HEPA filter materials using a 4 M $HNO_3$ - 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). A more detailed account of this work has been prepared.[6] A 4 M $HNO_3$ - 0.1 M Ce(IV) nitrate solution has been shown[7-9] to be the most effective solvent for refractory $PuO_2$ 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; however, it has been found that maximum dissolution rates are obtained with solutions containing 0.1 M Ce(IV) and 4 M $HNO_3$. During dissolution, the Ce(IV) is consumed by rapid reactions,[10,11] with the soluble plutonium ($Pu^{3+}$ and $Pu^{4+}$) producing Ce(III) ion and $PuO_2^{2+}$. When the Ce(IV)/Ce(III) ratio has decreased to about unity, the dissolvent becomes ineffective.[7] In addition to the oxidation reactions involving plutonium, Ce(IV) is also consumed by reactions with the carbonaceous species that are present in HEPA filter materials. The Ce(IV), a powerful oxidant, oxidizes free carbon, organic compounds and most metals. The extent of Ce(IV) reduction during leaching depends on the amounts of $PuO_2$ and carbonaceous species associated with the HEPA material. Since the carbonaceous species reacts more rapidly than does $PuO_2$, a method to oxidize Ce(III) and so maintain the Ce(IV) concentration during leaching is desirable in order to avoid the use of large quantities of Ce(IV) salts. Also, it is desirable to recover the Ce(III) from spent leach liquor and to recycle it to the leaching operation for oxidation to 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 Ce(IV) from Ce(III), (2) leaching of refractory $PuO_2$ from HEPA filter materials while maintaining the 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 residues from the leaching liquor.

On the basis of the experimental results and solvent extraction separations reported previously in the literature, a conceptual chemical flowsheet is proposed for the recovery of actinides from HEPA filters. A 4 $\underline{M}$ $HNO_3$ - 0.1 $\underline{M}$ Ce(IV) nitrate solution is used as the leachant, and a two-cycle solvent extraction process employing tri-$\underline{n}$-butyl phosphate (TBP) in the first cycle and dihexyl-N,N-diethylcarbamoylmethylene phosphonate[1,2,12] 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.

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

In this study, the preparation of Ce(IV) from Ce(III) in $HNO_3$ 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.

## 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 ($HNO_2$) is a cathodic reduction product of $HNO_3$, it must be prevented from diffusing into the anode region and reducing the Ce(IV) produced by anodic oxidation.

Smith and coworkers[13] 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 $HNO_3$ solution were attributed by them to the high stability of the hexanitratocerate anion, $[Ce(NO_3)_6]^{2-}$. They did not investigate the products produced at the cathode.

The primary cathode reaction[14] in the electrolysis of $HNO_3$ is generally regarded as:

$$H^+ + e \rightleftarrows (H) \ , \qquad (1)$$

where (H) denotes atomic hydrogen sorbed by the Pt cathode. This process is followed by either of two secondary reactions:

$$HNO_3 + 2(H) \rightleftarrows HNO_2 + H_2O \qquad (2a)$$

or

$$2(H) \rightleftarrows H_2,$$

depending on the conditions of the electrolysis.

Reaction (2b) will occur only if reaction (2a) does not 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 $HNO_3$ unless $HNO_2$ 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 $HNO_2$ which is established in the layer of solution in immediate contact with the electrode.

With a further increase of current density, $H_2$ production by reaction (2b) commences at the cathode. The current density at which reaction (2b) becomes the dominant mechanism is designated by Ellingham[14] as the transition current density (TCD). The TCD values vary widely and increase dramatically with $HNO_3$ concentration, $HNO_2$ concentration, and temperature.

Ellingham[14] also found that TCD values could be lowered considerably by stirring or sparging the $HNO_3$ solutions with air to promote decomposition of $HNO_2$.

Based on previous electrochemical studies, it appeared that several 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-$HNO_3$ solutions by anodic oxidation:

1. The anode and cathode compartments could be isolated by a suitable porous diaphragm, thus preventing $NO_2^-$ from coming in contact with and reducing the Ce(IV).
2. A shrouded cathode with allowance for the escape of nitrogen oxide gases at the top of the shroud could be used to prevent gross amounts of the $NO_2^-$ from reacting with the Ce(IV).

3. The electrodes would not be isolated, but by operating with a high current density (100 $A/dm^2$) at the cathode, the principal product would be $H_2$ gas so little or no $HNO_2$ will be in solution to reduce the Ce(IV). This type of cell which generates large amounts of $H_2$ has serious safety related problems so it was not considered suitable for this application.

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 $cm^2$. The electrode compartments were approximately 250 ml in volume and were separated by a medium-porosity, 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 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 $Ce(NO_3)_3$ - 4.0 M $HNO_3$ solution and the cathode compartment contained 200 ml of 4.0 M $HNO_3$.

Experiments conducted with the shrouded cathode used a simple one-pot arrangement. The shroud for the cathode was a cylindrical (∿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.

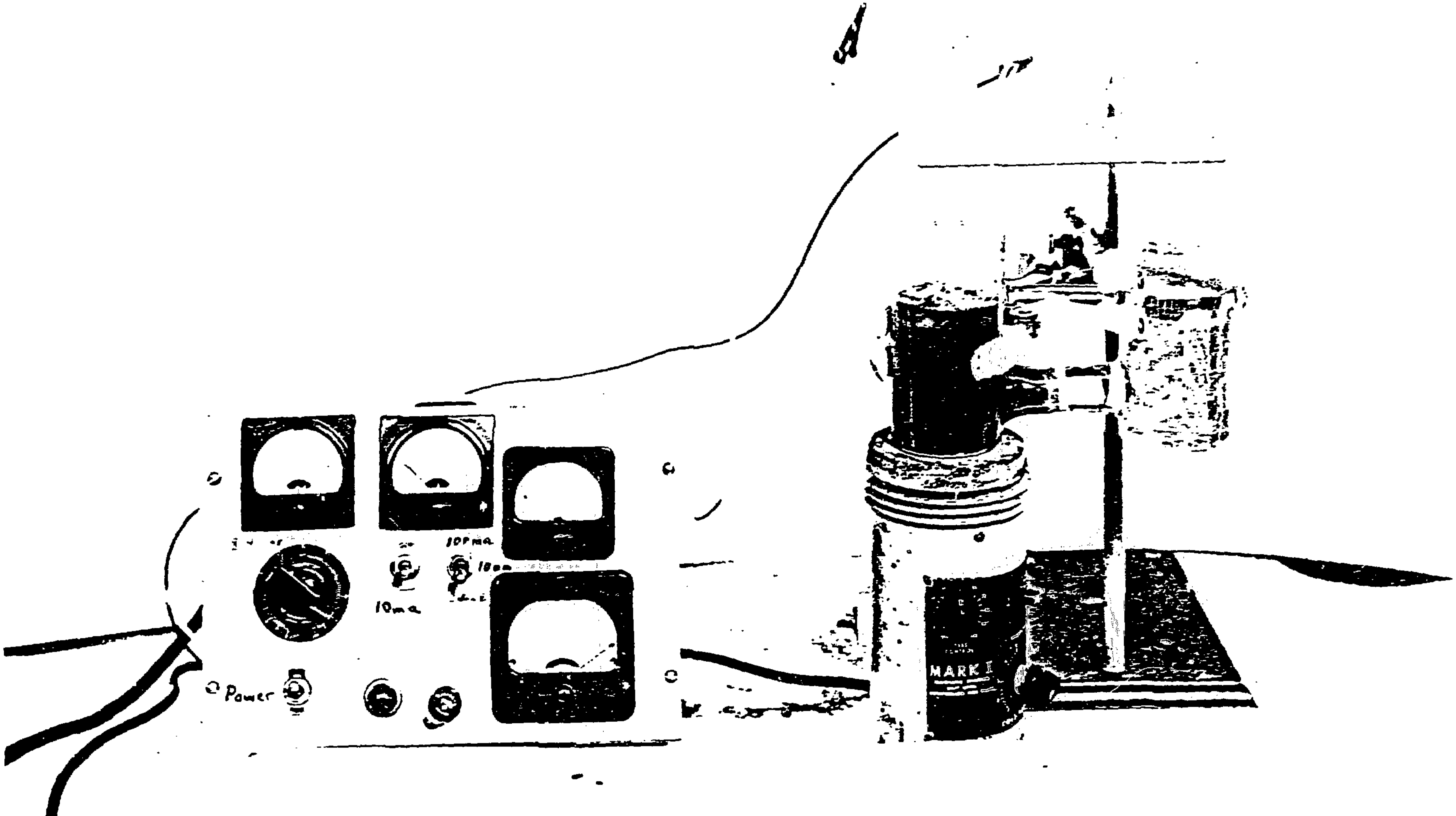

Fig. 1.

## 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 (Fig. 2). The yield of Ce(IV) increased in direct proportion to the time to $\sim$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. 2. Even at the highest applied currents, 0.5 - 1 A, $\sim$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 $HNO_2$ and 0.0008 mole of $NH_4^+$ 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 $\sim$10 min of operation. This observation is in general agreement with that of Ellingham.[14] Therefore, under the conditions employed (current densities $\leq$0.4 A/dm$^2$ and potentials of 1.5 - 6.0 V), $HNO_2$ was the main product of the cathode reaction.

Results obtained with the stirred-pot electrolytic cell with both shrouded and unshrouded electrodes are shown in Fig. 3. It is seen that a simple shroud around the cathode effectively protects the Ce(IV) against reduction by $HNO_2$. 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% was obtained using the shrouded electrode which permits the escape of nitrogen oxide gases to the atmosphere at the top of the shroud. Conversion of 88% to Ce(IV) is sufficient to promote the dissolution of $PuO_2$. No attempt was made to collect and analyze the cathode gases in these experiments.

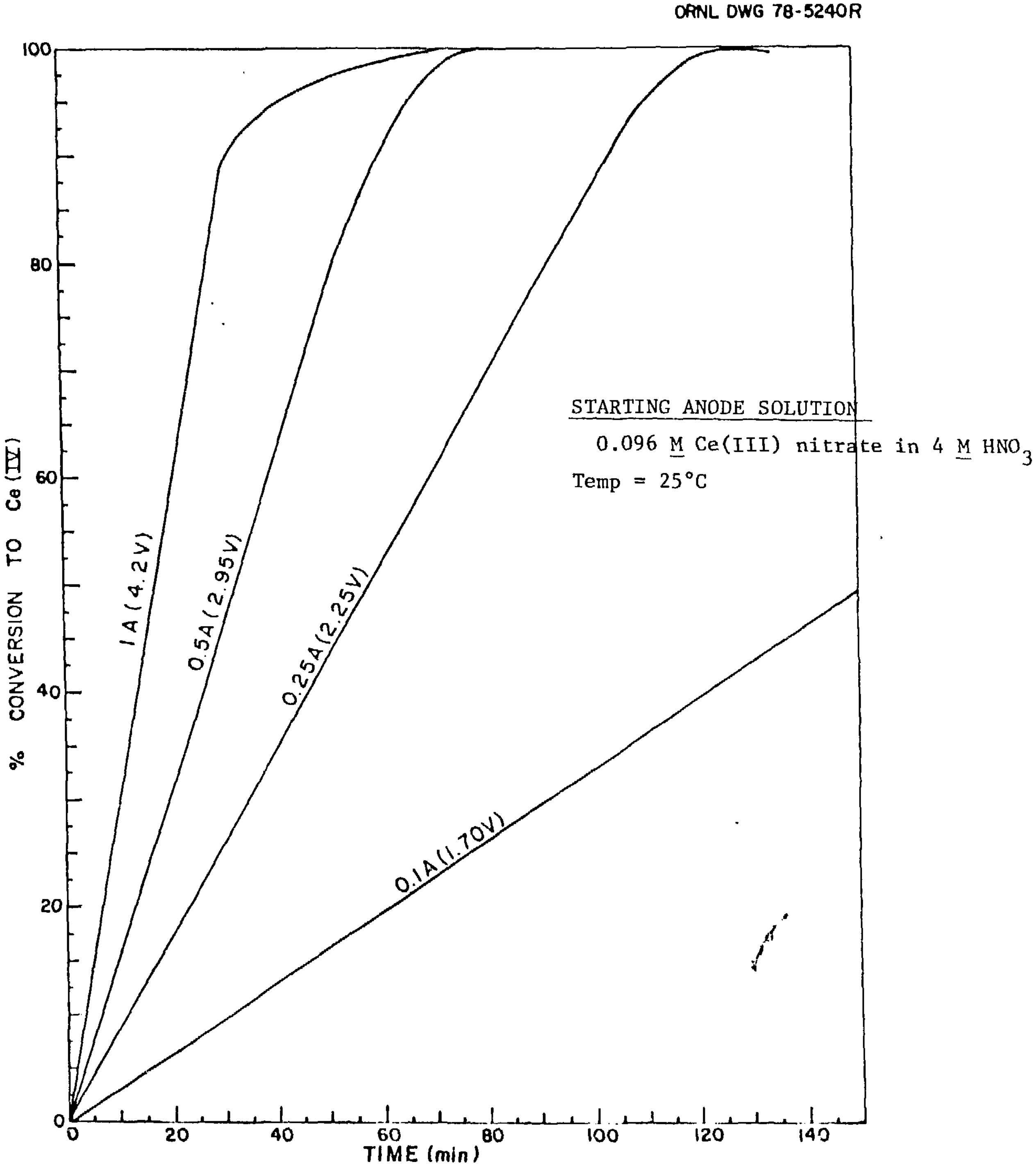
ORNL DWG 78-5240R
% CONVERSION TO Ce(IV)
0
20
40
60
80
100
TIME (min)
0
20
40
60
80
100
120
140
1A (4.2V)
0.5A (2.95V)
0.25A (2.25V)
0.1A (1.70V)
STARTING ANODE SOLUTION
0.096 M Ce(III) nitrate in 4 M HNO3
Temp = 25°C

Fig. 2.

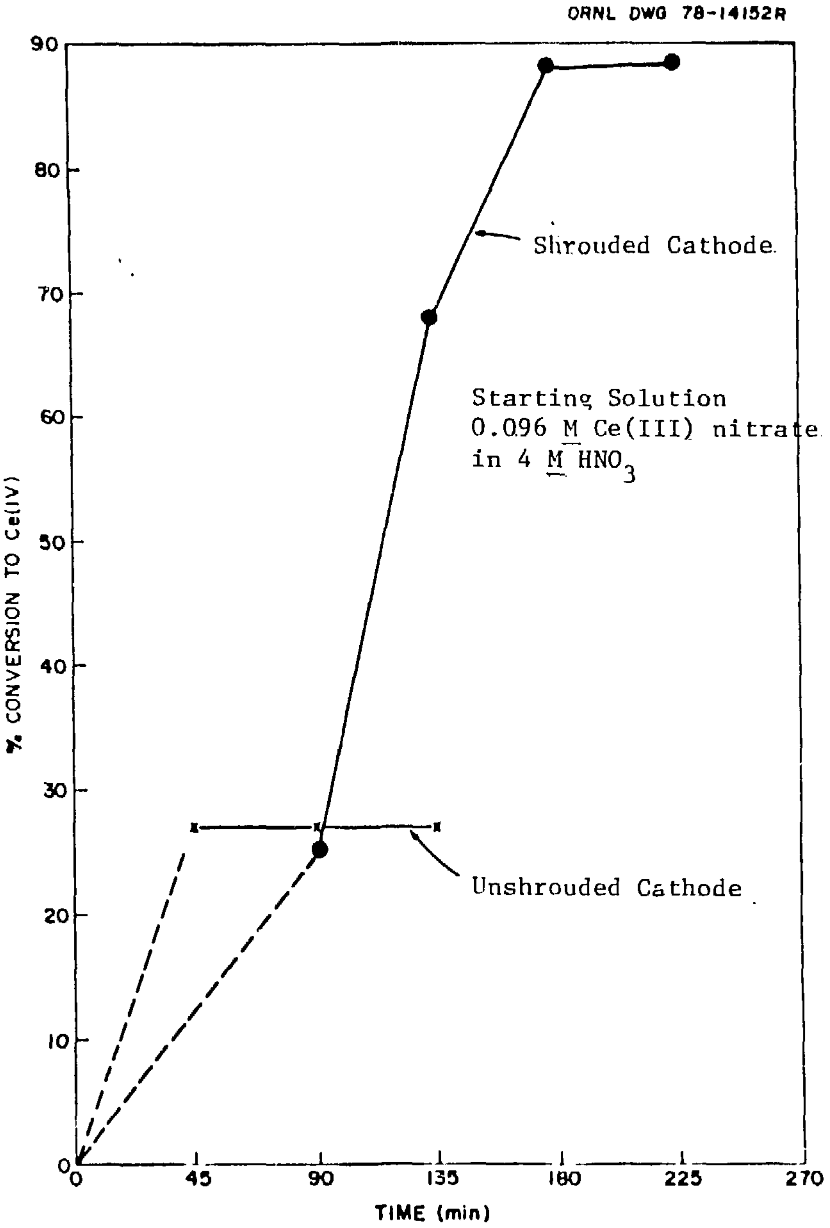
ORNL DWG 78-14152R
% CONVERSION TO Ce(IV)
90
80
70
60
50
40
30
20
10
0
0
45
90
135
180
225
270
TIME (min)
Shrouded Cathode
Starting Solution
0.096 M Ce(III) nitrate
in 4 M HNO3
Unshrouded Cathode

Fig. 3.

Several materials of construction for use as either electrodes or for the fabrication of containment vessels for Ce(IV) in 4 M $HNO_3$ were scouted with respect to corrosion (Table 1). 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).

## LEACHING OF $PuO_2$ FROM HEPA FILTERS

Cerium(IV)-promoted leaching of $PuO_2$ from synthetically prepared mixtures of refractory $PuO_2$ 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 $PuO_2$ - HEPA material with continuous recirculation of the leach liquor through the anode compartment of an external electrolytic cell.

### Materials Used

The filter media utilized in the leaching tests were obtained from the following two most common types of HEPA filters:[15]

Table 1. Reaction of various materials in 0.1 M Ce(IV) nitrate - 4.0 M $HNO_3$ 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. |

A. One type had pleated fiberglass media which were held apart by corrugated aluminum separators and enclosed by a metal frame (Fig. 4). 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. 5). The fiberglass media were bonded together with a proprietary binder and jointed 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 2.

The $PuO_2$ powder was prepared by precipitating plutonium oxalate from ∿1 $\underline{M}$ $HNO_3$ 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 $PuO_2$ 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 $\underline{M}$ $HNO_3$ at reflux temperatures (∿104°C). About 5% of the $PuO_2$ sintered at 800°C was dissolved after a 6-hr dissolution period, whereas only about 1% of the $PuO_2$ sintered at 1000°C was dissolved under the same conditions. In the tests of the dissolution behavior of $PuO_2$ fired at either 800 or 1000°C, 50 mg of $PuO_2$ and 200 ml of 4.0 $\underline{M}$ $HNO_3$ were employed.

Mixtures of $PuO_2$-HEPA filter media, 1.6 wt % $PuO_2$, were prepared by mixing the fine $PuO_2$ powder with shredded HEPA filter media that had

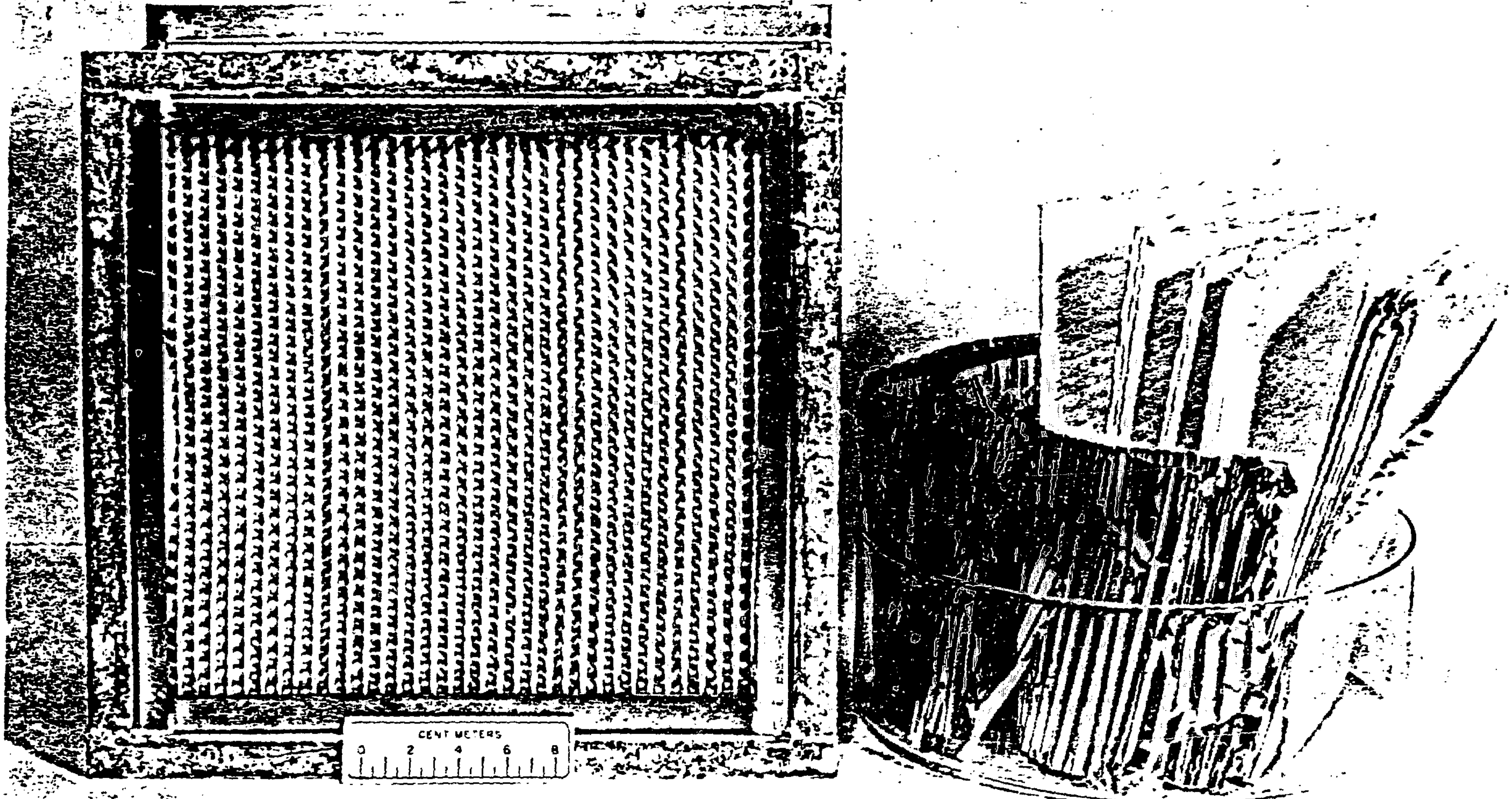

Fig. 4.

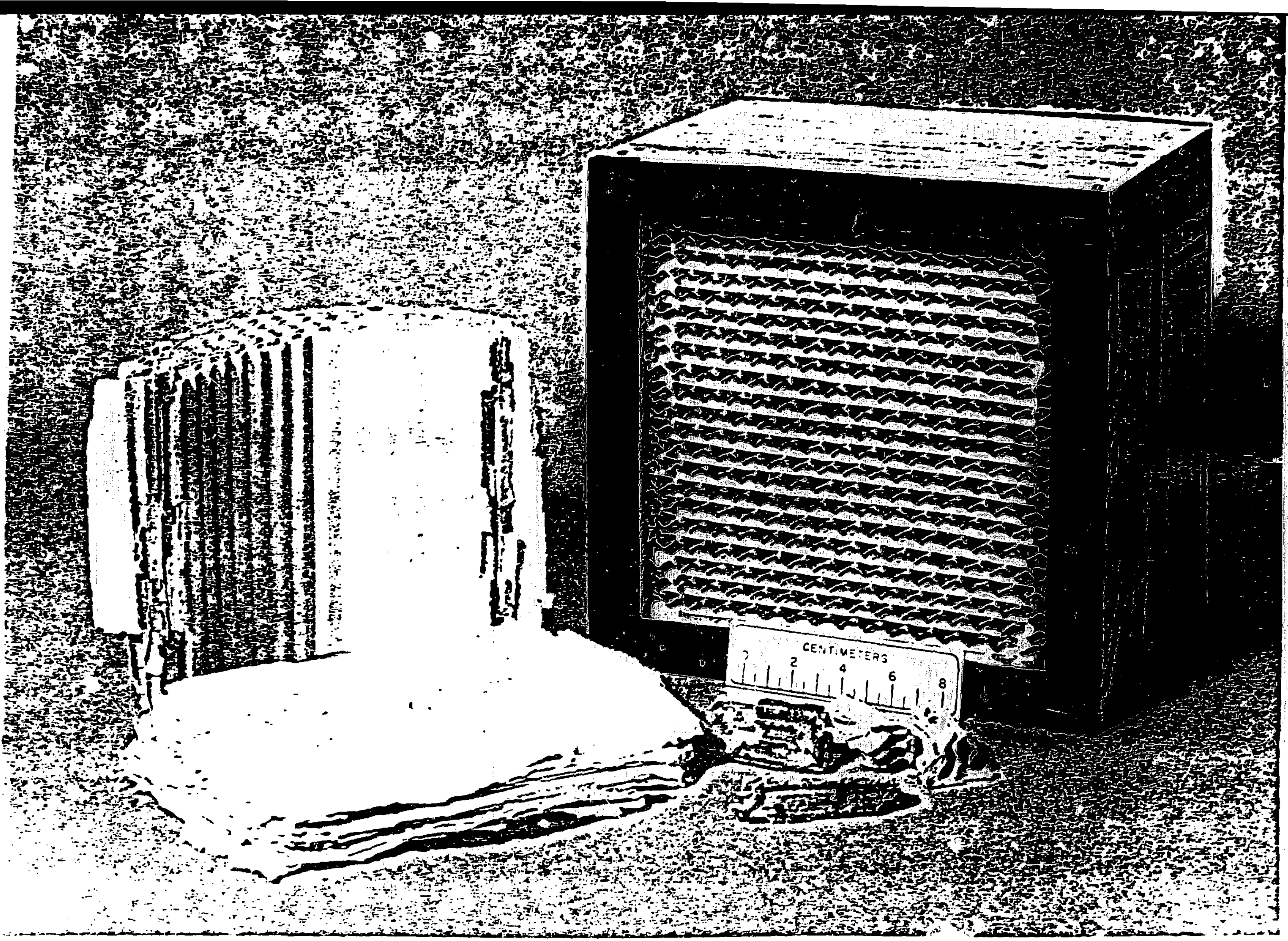

Fig. 5.

Table 2. Some properties of HEPA filters

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

[a] See Fig. 4, Type A HEPA filter, p. 21.

[b] See Fig. 5, Type B HEPA filter, p. 22.

[c] Relative weight = $\frac{\textit{weight of medium}}{\text{weight of separator}}$.

[d] As determined by the amount of Ce(IV) reduced in boiling 4 M $HNO_3$ after 1.5 hr.

been ignited in air at 300°C in a muffle furnace. Frame materials 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)-$HNO_3$ 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.

## Leaching Procedures

Slurry leaching of samples was carried out in the anode compartment of the electrolytic cell described earlier (Fig. 1) with 200 ml of 0.1 M Ce(IV) nitrate - 4.0 M $HNO_3$ solution and an applied current of 1.0 A. The tests were carried out at the reflux temperature and 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 $PuO_2$-HEPA mixtures were conducted with a blend of 50 mg of $PuO_2$ and 3 g of HEPA media solids. In control tests, only 50 mg of $PuO_2$ without HEPA media was used to determine the effect of temperature on $PuO_2$ dissolution.

A schematic diagram of the apparatus used for packed column leaching is shown in Fig. 6. A photograph of the equipment before installation in an alpha containment glove box is shown in Fig. 7. In these experiments, 15.0 g of the $PuO_2$-HEPA mixture supported on a glass wool plug in the

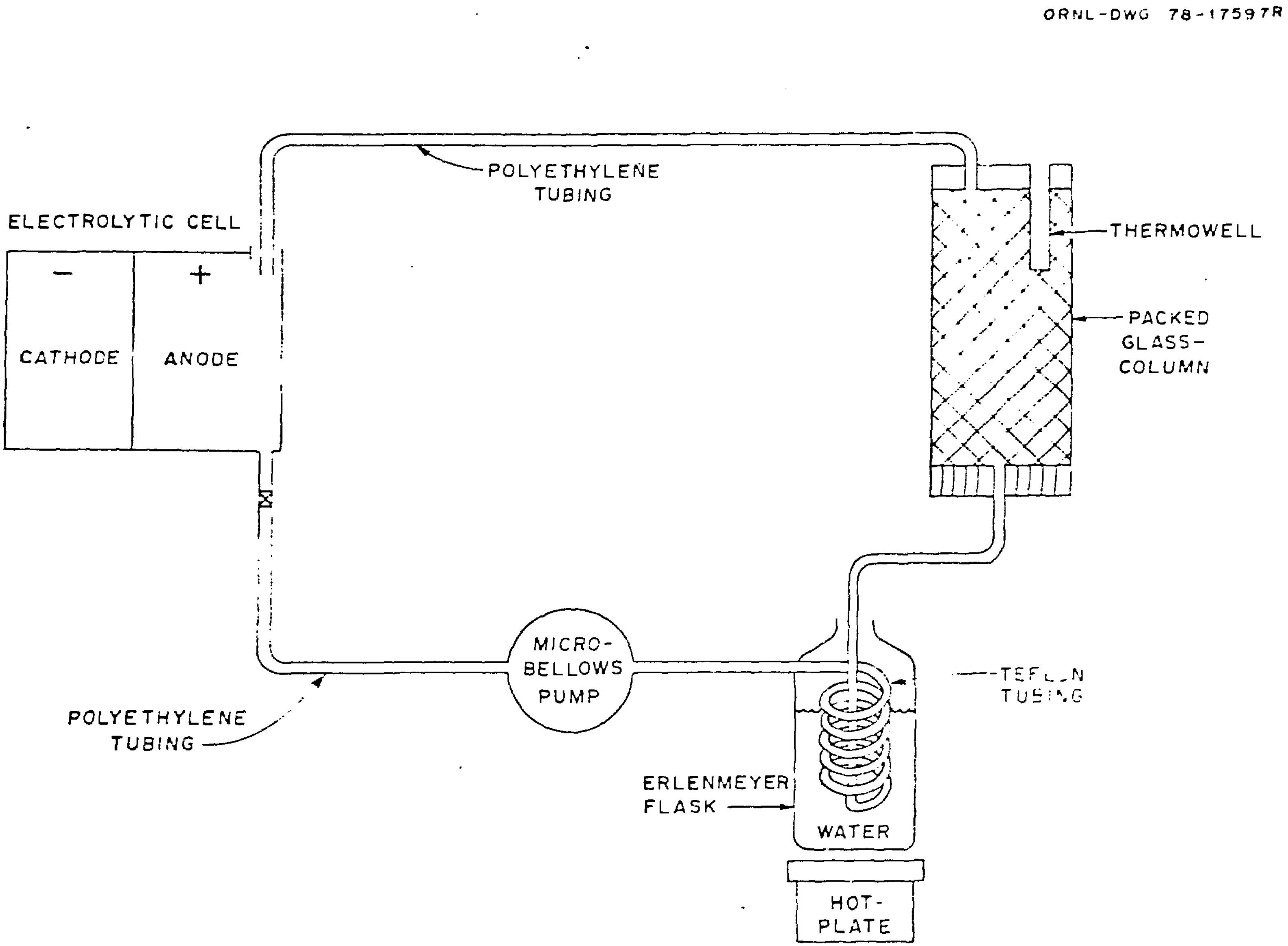
ORNL-DWG 78-17597R
POLYETHYLENE TUBING
ELECTROLYTIC CELL
THERMOWELL
−
+
CATHODE
ANODE
PACKED GLASS-COLUMN
MICRO-BELLOWS PUMP
TEFLON TUBING
POLYETHYLENE TUBING
ERLENMEYER FLASK
WATER
HOT-PLATE

Fig. 6.

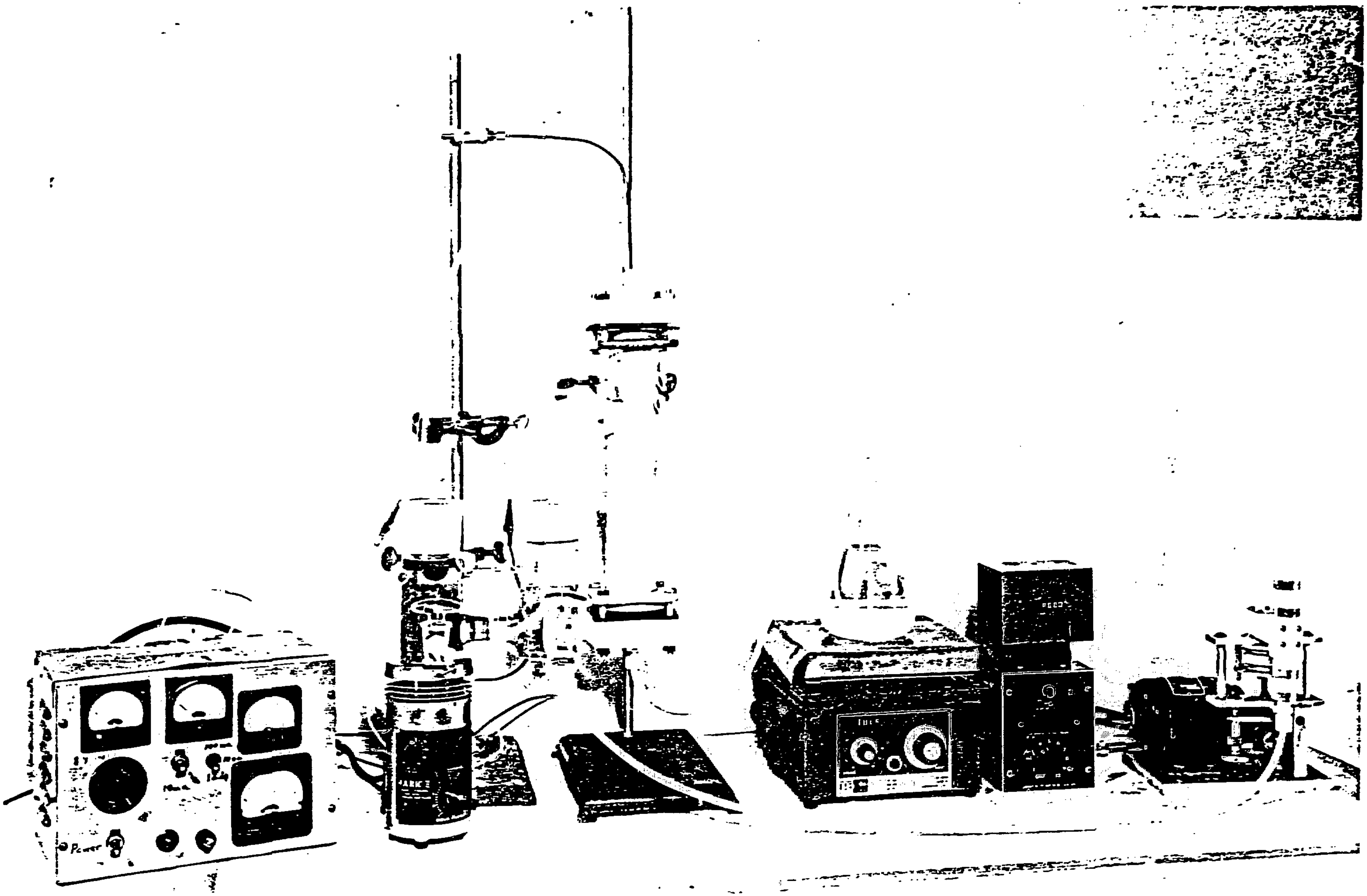

Fig. 7.

glass column (3.5 cm ID x 15.0 cm long) was leached with a 0.1 M Ce(IV) - 4.0 M $HNO_3$ 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) 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.

## Effects of Organic Material in the HEPA Media

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 2), 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. 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.

## Handling Problems with Slurry Leaching

Preliminary studies in which HEPA media without $PuO_2$ 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 leach 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. The latter slurries were almost gels. However, clear liquid separated from the solids had a viscosity (∿1 cP), about equal to that of 4 M $HNO_3$. 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. 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. The problem with Type B material was less severe. Slurry concentrations of 25 and 37.5 g/ℓ had viscosities of 350 and 480 cP, respectively.

### Mechanical Ease of Packed Column Leaching

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

### Slurry Leaching of $PuO_2$-HEPA Mixtures in the Anode Compartment

Because of the problems with separating HEPA filter media from the leach solution, only a few tests were made of slurry leaching in the anode compartment. These included dissolution of $PuO_2$ without filter media and leaching of $PuO_2$ in the presence of filter media containing considerable amounts of organic-base binder glue (Type B filter-unignited). The purpose of these tests was to confirm the adverse effect of organic material on the leaching of $PuO_2$. Rapid dissolution of $PuO_2$ calcined at 1000°C required refluxing the anode solution at a temperature of ∿104°C (Table 3). Plutonium dioxide that was calcined at only 800°C was 98% dissolved in 18 hr at 25°C and was completely dissolved in less than 5.5 hr at reflux temperature.

The adverse effect of the organic binder can be noted by the longer times required to dissolve the $PuO_2$ from a slurry containing unignited, Type-B filter material. After 5.5 hrs of refluxing, only 43% of the $PuO_2$ was dissolved when the anode compartment was not stirred and 82% when it was stirred. However, dissolution was essentially complete in 12.5 hours. This slower dissolution was a result of low Ce(IV) content during the early part of the runs.

## Leaching of $PuO_2$-HEPA Mixtures in a Packed Column

Leaching tests in the packed column utilized $PuO_2$ powder sintered at 1000°C and ignited HEPA material since the organic material interferes with $PuO_2$ dissolution. With the Ce(IV) concentration maintained by a current of 1.0 A in the electrolytic cell, the $PuO_2$ dissolved after leaching for 1.5 hr at 100°C (Fig. 8) 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 Ce(IV) concentration necessary for $PuO_2$ dissolution could be maintained during the leaching of HEPA filter solids and that the packed column concept was feasible.

## CONCEPTUAL FLOWSHEET FOR RECOVERY OF ACTINIDES AND RECYCLE OF CERIUM

The proposed chemical flowsheet (Fig. 9) for the recovery of actinides from HEPA filters was developed in a collaborative effort[16] with B. C. Finney

Table 3. Slurry leaching of $PuO_2$ in the anode compartment

Initial solution composition: 0.1 $\underline{M}$ Ce(IV) nitrate – 4.0 $\underline{M}$ $HNO_3$
Unignited Type-B HEPA filter material was used

| Material | Stirring of slurry | Applied current (A) | Temperature °C | Time hr | % Pu[b] leached |
|---|---|---|---|---|---|
| 1000°C fired $PuO_2$ | Yes | 1.0 | 25 | 18 | 30 |
| | | | ∿104[a] | 6 | 101 |
| 800°C fired $PuO_2$ | No | 1.0 | 25 | 18 | 98 |
| | | | ∿104[a] | 5.5 | 100 |
| 800°C fired $PuO_2$ plus HEPA | No | 0.8 | ∿104[a] | 5.5 | 43 |
| | | | ∿104[a] | 12.5 | 101 |
| 800°C fired $PuO_2$ plus HEPA | Yes | 0.8 | ∿104[a] | 5.5 | 82 |
| | | | ∿104[a] | 12.5 | 97[c] |

[a] Reflux temperature.

[b] Determined by analysis of plutonium dissolved.

[c] Analysis of residue indirect 99.99% complete solution of $PuO_2$.

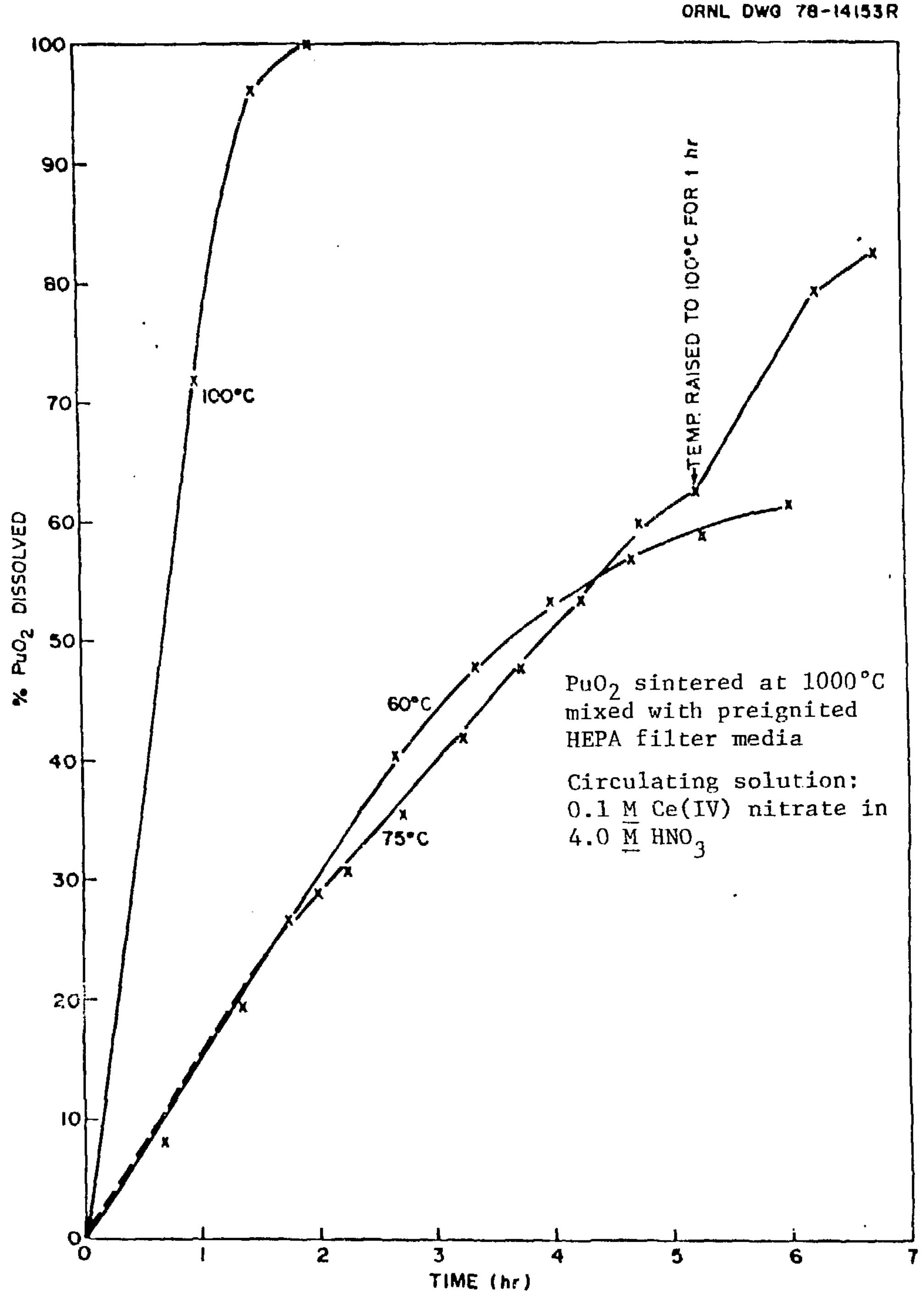
ORNL DWG 78-14153R
% $PuO_2$ DISSOLVED
100
90
80
70
60
50
40
30
20
10
0
TIME (hr)
0
1
2
3
4
5
6
7
100°C
60°C
75°C
TEMP. RAISED TO 100°C FOR 1 hr
$PuO_2$ sintered at 1000°C
mixed with preignited
HEPA filter media
Circulating solution:
0.1 M Ce(IV) nitrate in
4.0 M $HNO_3$

Fig. 8.

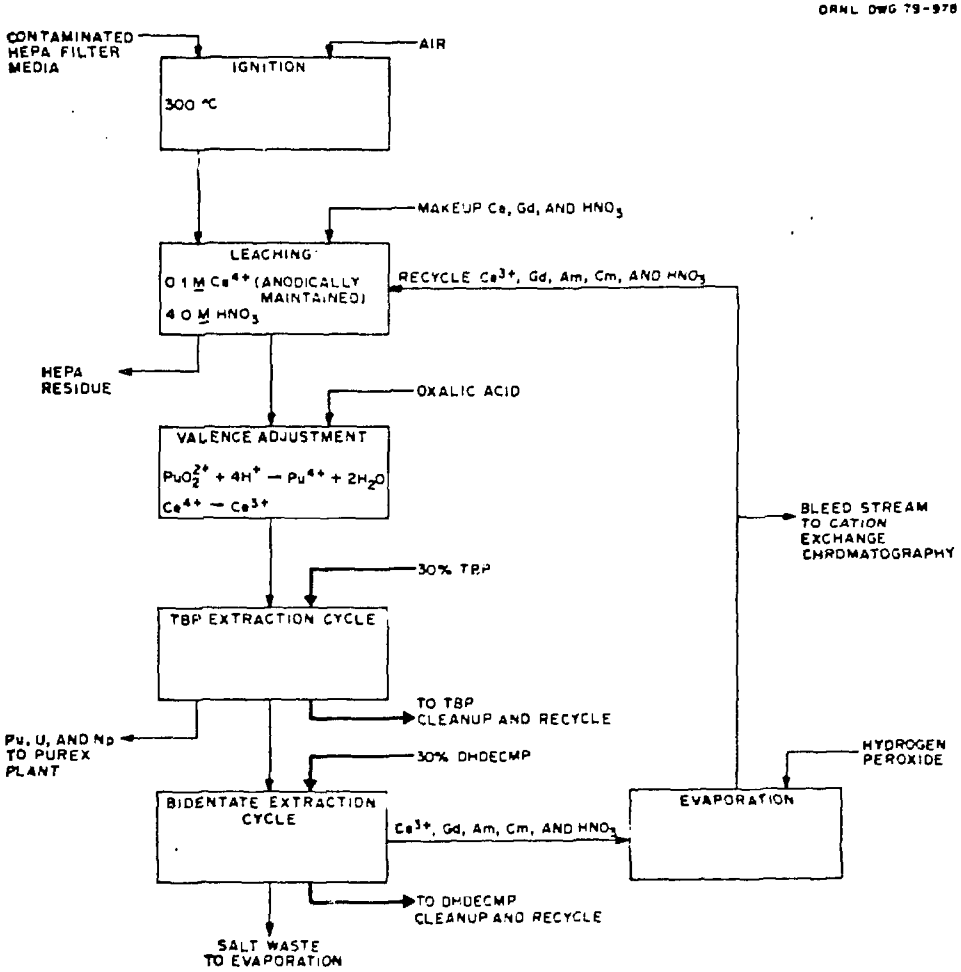
ORNL DWG 79-978
CONTAMINATED HEPA FILTER MEDIA
AIR
IGNITION
300 °C
MAKEUP Ce, Gd, AND $HNO_3$
LEACHING
0.1 M $Ce^{4+}$ (ANODICALLY MAINTAINED)
4.0 M $HNO_3$
RECYCLE $Ce^{3+}$, Gd, Am, Cm, AND $HNO_3$
HEPA RESIDUE
OXALIC ACID
VALENCE ADJUSTMENT
$PuO_2^{2+} + 4H^+ \rightarrow Pu^{4+} + 2H_2O$
$Ce^{4+} \rightarrow Ce^{3+}$
BLEED STREAM TO CATION EXCHANGE CHROMATOGRAPHY
30% TBP
TBP EXTRACTION CYCLE
TO TBP CLEANUP AND RECYCLE
Pu, U, AND Np TO PUREX PLANT
30% DHDECMP
HYDROGEN PEROXIDE
BIDENTATE EXTRACTION CYCLE
$Ce^{3+}$, Gd, Am, Cm, AND $HNO_3$
EVAPORATION
TO DHDECMP CLEANUP AND RECYCLE
SALT WASTE TO EVAPORATION

Fig. 9.

and D. W. Tedder of ORNL. The HEPA filter material is mechanically separated from the frame and spacers and ignited in air to 300°C to remove carbonaceous materials present in glues and binders. Subsequently, the HEPA solids are leached by passing a 0.1 M Ce(IV) nitrate--4.0 M $HNO_3$ solution 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.[16] 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$^2$.

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.[16] Valence adjustment can be accomplished by sparging with NO or $NO_2$[17] rather than by oxalic acid addition, if desired. The recovered plutonium, uranium, and neptunium are recycled to the main Purex plant.[16]

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[2,12,16] 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 HDHECMP in two separate stripping operations. In the first, a solution of 0.005 M $HNO_3$ - 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 $HNO_3$ - 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 $HNO_3$ by oxalate complexing. The Pu(VI), Np(VI), and Np(V) are reduced extremely slowly by oxalate ion at this low acidity.[10]

The products from the stripping operations are evaporated to adjust the $HNO_3$ concentration and to decompose the HAN and oxalic acid, the HAN by reaction with $HNO_3$[18] and the oxalic acid by reaction with a mixture of $HNO_3$ and hydrogen peroxide[2] in separate evaporators.[16] Since the reaction of HAN with $HNO_3$ proceeds autocatalytically and involves $HNO_2$ as an intermediate, it may be desirable to utilize a $NO_2$ 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[2,16,19,20] 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[16] or in a batch campaign manner. Recycle of $HNO_3$, cerium, and gadolinium to the HEPA leaching step would reduce the amounts of cerium and gadolinium rejected to the salt waste[2,16] and hence minimize the quantity of that waste.

## SUMMARY

The experimental studies carried out in this investigation included (1) the electrolytic production of Ce(IV) from Ce(III), (2) the leaching of refractory $PuO_2$ 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 $A/dm^2$ at a platinum anode. Refractory $PuO_2$ was dissolved by a 4.0 $\underline{M}$ $HNO_3$ - 0.1 $\underline{M}$ 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 $HNO_3$ - 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.

## REFERENCES

1. D. W. Tedder and J. O. Blomeke, Actinide Partitioning and Transmutation Program Progress Report for Period October 1977 to March 31, 1978, ORNL/TM-6480 (October 1978).

2. A. G. Croff, D. W. Tedder, J. P. Drago, J. O. Blomeke, and J. J. Perona, A Preliminary Assessment of Partitioning and Transmutation as a Radioactive Waste Management Concept, ORNL/TM-5808 (September 1977).

3. W. D. Bond, H. C. Claiborne, and R. E. Leuze, "Methods for Removal of Actinides from High-Level Wastes," Nucl. Technol. 24, 362 (1974).

4. W. D. Bond and R. E. Leuze, Feasibility Studies of the Partitioning of Commercial High-Level Waste Generated in Spent Fuel Reprocessing: Annual Progress Report FY-1974, ORNL-5012 (January 1975).

5. W. D. Bond and R. E. Leuze, "Removal of Actinides from High-Level Wastes Generated in the Reprocessing of Commercial Fuels," pp. 423-31 in Transplutonium Elements, W. Muller and R. Lindner (Eds.), North-Holland, Amsterdam, 1976.

6. F. M. Scheitlin and W. D. Bond, Recovery of Plutonium from HEPA Filters by Ce(IV)-Promoted Dissolution of $PuO_2$ and Recycle of the Cerium Promoter, ORNL/TM-6802 (May 1980).

7. D. E. Horner, D. J. Crouse, and J. C. Mailen, Cerium-Promoted Dissolution of $PuO_2$ and $PuO_2$-$UO_2$ in Nitric Acid, ORNL/TM-4716 (August 1977).

8. D. F. Luthy and E. L. Lewis, Decontamination of HEPA Filters, January-March 1977, MLM-2435 (September 1977).

9. D. F. Luthy and E. L. Lewis, Decontamination of HEPA Filters, April-June 1977, MLM-2445 (September 1977).

10. T. W. Newton, The Kinetics of Oxidation-Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium in Aqueous Solutions, ERDA Critical Review Series, TID-26506 (1975).

11. A. Ekstrom and A. B. McLaren, "The Kinetics and Mechanism of the Oxidation of Pu(IV) by Ce(IV) in Sulphate and Nitrate Media," J. Inorg. Nucl. Chem. 33, 3511 (1971).

12. W. W. Schulz and L. D. McIsaac, "Removal of Actinides from Nuclear Fuel Reprocessing Waste Solutions with Bidentate Organophosphorous Extractants," pp. 433-48 in *Transplutonium Elements*, W. Muller and R. Lindner (Eds.), North-Holland, Amsterdam, 1976.

13. G. F. Smith, G. Frank, and A. E. Kott, "Cerate Oxidimetry," Ind. Eng. Chem., Anal. Ed. 12, 268 (1940).

14. H. J. T. Ellingham, "Alternative Electrode Reactions. Part 1. Reactions at a Platinum Cathode in Nitric Acid Solutions," J. Chem. Soc. 1932, 1565.

15. C. A. Burchsted, A. B. Fuller, and J. E. Kahn, *Nuclear Air Cleaning Handbook*, Chap. 3, ERDA-76-21 (March 1976).

16. D. W. Tedder, B. C. Finney, and J. O. Blomeke, *Actinide Partitioning-Transmutation Program Final Report. II. Partitioning Processes for LWR Fuel Reprocessing and Refabrication Plant Wastes*, ORNL/TM-6982 (in press).

17. M. R. Bennett and A. D. Kelmers, *The Reduction of Plutonium (VI) to Plutonium (IV) in Nitric Acid by Nitric Oxide and Nitrogen Dioxide Gases*, ORNL/TM-6552 (November 1978).

18. J. M. McKibben and J. E. Bercaw, *Hydroxylamine Nitrate as a Plutonium Reductant in the Purex Solvent Extraction Process*, DP-1248 (January 1971).

19. E. J. Wheelwright and F. P. Roberts, *The Use of Alternating DTPA and NTA Cation-Exchange Flowsheets for the Simultaneous Recovery and Purification of Pm, Am, and Cm*, BNWL-1072 (July 1968).

20. J. A. Kelley, *Ion Exchange Process for Separating Americium and Curium from Irradiated Plutonium*, DP-1308 (November 1972).