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CHEMICAL TECHNOLOGY DIVISION

# CERIUM-PROMOTED DISSOLUTION OF $PuO_2$ AND $PuO_2$--$UO_2$ IN NITRIC ACID

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ABSTRACT

Several experiments were run to determine the feasibility of using cerium as an alternative to fluoride in promoting rapid dissolution of difficultly soluble $PuO_2$ in nitric acid. Results show that $Ce^{4+}$, but not $Ce^{3+}$, promotes dissolution with a maximum rate in boiling 4 $\underline{M}$ $HNO_3$. Other strong oxidants, including ozone, permanganate, and persulfate, were tested but were shown to be ineffective. During dissolution, the $Ce^{4+}$ is reduced to $Ce^{3+}$, which must be reoxidized electrolytically or with ozone. Ruthenium also reduces the $Ce^{4+}$ catalytically, being oxidized to the volatile $RuO_4$. Thus successful application to dissolution of irradiated fuel residues would require modification of the equipment or procedures in such a way as to encourage complete volatilization of ruthenium from the dissolver system. However, application of this method to the treatment of plutonium appears promising.

## 1. INTRODUCTION

In the advanced reactor technology, mixed plutonia-urania (nominally 20 to 25% $PuO_2$--balance $UO_2$) fuels will probably be used initially in liquid metal cooled fast breeder reactors (LMFBRs). After irradiation, the fuel elements will undergo a mechanical subdivision followed by complete dissolution in nitric acid prior to a Purex solvent extraction reprocessing step. $PuO_2$ dissolves in $HNO_3$ at an extremely slow rate; solid solutions of $PuO_2$--$UO_2$ dissolve much faster. Among the factors affecting the formation of solid solutions and hence the ease of dissolution are: (1) the method of fuel fabrication (i.e., whether mechanically blended oxides, co-precipitated oxides, or sol gel oxides), (2) the degree of sintering and temperature prior to irradiation, and (3) the irradiation level. Studies at ORNL have shown that the combination of high burnup levels and high temperatures prevailing in most parts of the fuel elements can produce a homogeneous solid solution and thus, in general, more readily soluble material. However, at the cooler outer portions of the fuel rods, initial nonhomogeneity of the fuel oxides may result in material that is difficult to dissolve ("difficultly soluble material.") As a result of this and possibly other factors, after dissolution of most of the spent fuel elements, residues composed of difficultly soluble $PuO_2$, with small amounts of $UO_2$, and more refractory fission-product metals, such as ruthenium, are obtained. Dissolution of these residues at a practicably fast rate requires the presence of small amounts of a dissolution promotor such as fluoride. The effectiveness of fluoride has been known for a long time, but if it is not subsequently complexed or

removed, it has the disadvantage of causing rapid equipment corrosion and complicating the ultimate disposal of Purex process wastes.

Other studies offering possible alternatives[1-3] have shown that cerium (some of which is already present as a fission product) may be useful as a promotor for dissolution in dilute nitric acid (Sect. 6). Besides the advantage of not being a foreign material, cerium does not complex components in the process streams and may be less corrosive than fluoride. For processing LMFBR fuels, the use of a promotor would be restricted to a small, secondary dissolver for completely dissolving the difficultly soluble residues. The output stream from this dissolver would then be combined with that from the primary dissolver prior to solvent extraction.

This report describes the results of recent tests made at ORNL (1) to define the process variables affecting dissolution of $PuO_2$ using cerium, and (2) to evaluate this promotor for use in reprocessing LMFBR fuels and/or processing nonirradiated scrap materials containing $PuO_2$. Application in the latter situation appears most promising. Application to irradiated LMFBR processing, however, would depend on developing a practicable way, if possible, of quantitatively removing ruthenium prior to or during the dissolution step.

Most of the results described in this report have been previously reported in progress reports.[1]

## 2. REAGENTS AND EXPERIMENTAL PROCEDURE

Most of the dissolution tests were made using a composite batch of $PuO_2$ microspheres composed of several batches originally prepared at ORNL. This batch of microspheres was prepared by the sol-gel technique,

steam dried at 150 to 200°C with 1-hr holds at 250 and 400°C, followed by steam calcining at 1150°C. Final densification was made in argon-4% hydrogen with a 2-hr hold at 800°C and a 4-hr hold at 1150°C. For better size-uniformity, the spheres were screened with -80 + 100 mesh screens (149- to 177-μ) and composited for use. Some typical (average of several different batches) physical and chemical properties are the following:

Bulk density, g/cc: 11.0 (about 95% of the theoretical value of 11.6 g/cc).

Pore volume, cc/g: 0.0023.

Surface area, $m^2$/g: 0.0120.

Oxygen, wt %: 12.0 (11.8 theoretical).

Carbon, ppm: 77.

Other chemical impurities in the original $Pu(NO_3)_4$ solution used to make the microspheres included very small amounts of iron, vanadium, and uranium. The effect of these impurities on dissolution was assumed to be negligible. Studies with dissolution of pellets made by Uriarte and Rainey[2b] showed that the oxide density is a very important factor affecting the dissolution rate with the rate increasing with decreasing density. This relationship must also be true for the very dense microspheres because their dissolution in nitric acid without a promotor was very slow ($<10^{-4}$ mg $cm^{-2}min^{-1}$).

A three-necked Pyrex flask fitted with a reflux condenser, thermometer, and sampling tube with a porous frit filter was used for these tests. A weighed (1-g) representative sample of the microspheres when added to 150 ml of boiling acid was taken as the initial time; filtered duplicate samples of the solution were then taken at appropriate time

intervals. The average values of the duplicate determinations of the
gross alpha activities were subsequently plotted versus the dissolution
time on linear scales. In most cases, straight lines could be drawn
through the points with only a small scatter, indicating that the
dissolution rate dA/dt, where A = activity of plutonium in solution,
was constant during the time span of the experiment. Also, since
<20% of the original amount of $PuO_2$ was dissolved (wich much less
than this in most cases), the change in surface area during the dissolu-
tion could be neglected for purposes of calculating the instantaneous
dissolution rate (IDR). Under these conditions, the IDR was defined
and calculated by the following equation:

$$\text{IDR (mg Pu cm}^{-2} \text{ min}^{-1}) = \frac{mv}{swa} = 1.2 \times 10^{-8} \, m \, , \tag{1}$$

where (under standardized conditions)

m = slope of line,

v = dissolver solution volume (150 ml),

s = initial specific surface area (0.012 $m^2$/g),

w = weight of sample taken (about 1 g),

a = specific activity of the plutonium (analytically determined to
be 1.03 x $10^8$ counts per minute per milligram of plutonium).

The IDR in terms of mg of $PuO_2$ $cm^{-2}min^{-1}$ would be obtained by
dividing Eq. (1) by 0.882; the IDRs reported, however, are in milligrams
of plutonium per square centimeter per minute. Although some of the plots
extrapolated to the origin as they should, many intercepted the ordinate
or abscissa near the origin. Two conceivable situations considered to
explain this intercept with the ordinate include (1) the presence of a

small amount of "fines" (smaller size particles that might have adhered
to larger particles and thus have escaped separation in the screening
procedure) that would be expected to have a faster dissolution rate
because of the much greater total surface than the original microspheres,
and (2) the inclusion of $^{241}$Am alpha activity in the gross alpha determina-
tions. Neither of these conditions, however, were shown to account for
the ordinate intercept problem. In tests of the first case, a 1-g
sample of $PuO_2$ microspheres was pre-dissolved in boiling 8 $\underline{M}$ $HNO_3$ for
1 hr to completely dissolve any fines that might have been present.
The remaining larger particles were then subjected to the standard
dissolution procedure. The slope of the curve and the IDR with and without
pre-dissolution, however, were essentially the same.

In the second case involving $^{241}$Am, it was shown in one dissolution
test that when gross alpha activities and the alpha activivites of plutonium
only (excluding Am activity) were plotted, the resultant straight lines
had the same extrapolated intercept with the ordinate. Also,
the differences between the two slopes was exactly equal to the differences
in specific activities, resulting in identical calculated IDR values
(Fig. 1). For simplicity's sake, we continued to use the gross alpha
activities and corresponding specific activity in all calculations
rather than using the plutonium-alpha determinations.

Although the intercept problem was not solved, the slopes of the
lines should still represent correctly the change in activity with
respect to time, dA/dt, on which the IDR calculations are based.
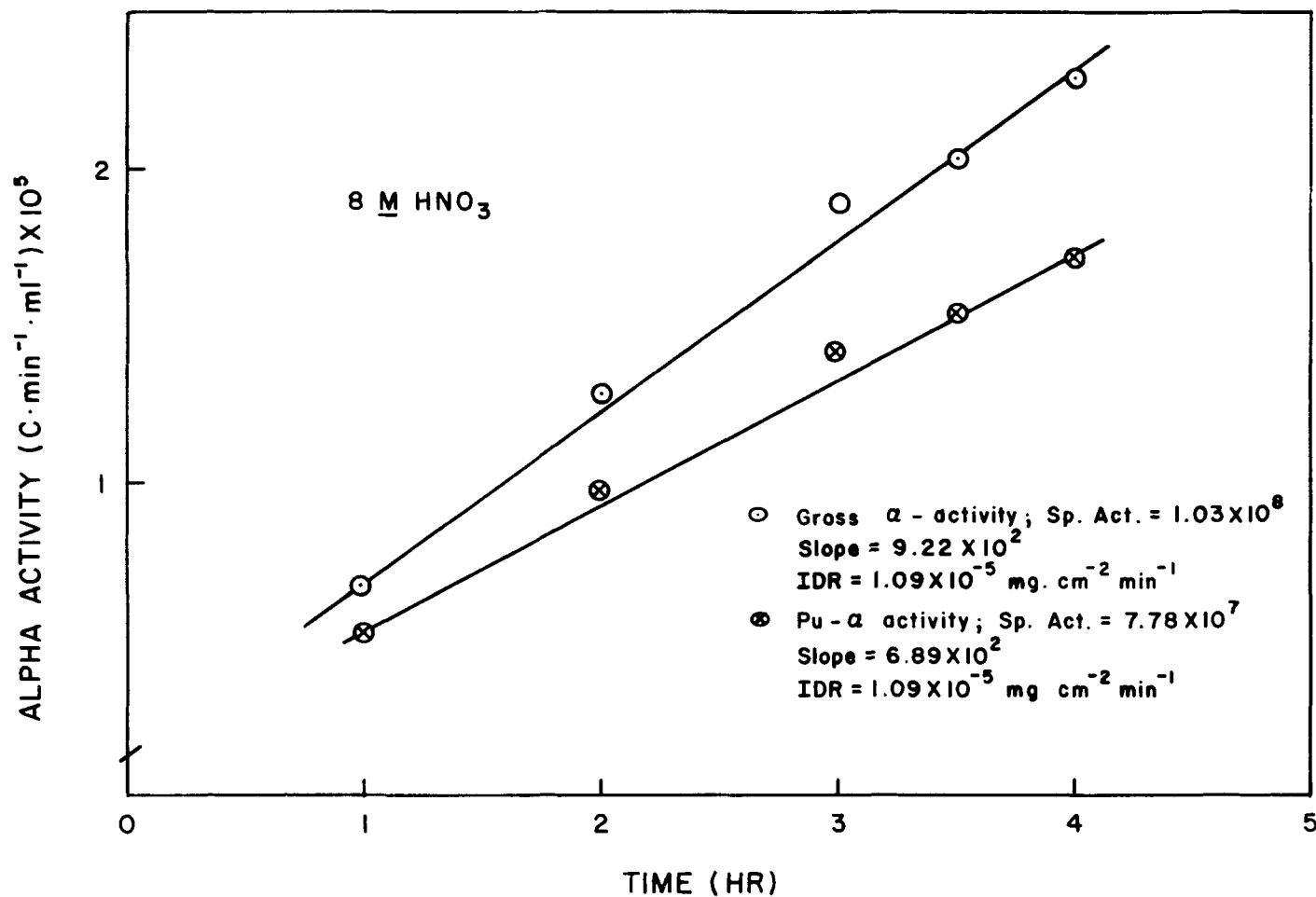
Fig. 1. Dissolution of PuO₂ microspheres in 8M̲ HNO₃ - Comparison of IDR's based on gross alpha and plutonium alpha activities.

## 3. TESTS WITH UNIRRADIATED $PuO_2$ MICROSPHERES

### 3.1 Dissolution in Nitric Acid

Without the presence of a dissolution promotor such as fluoride or cerium, high-fired $PuO_2$ (even in its most soluble form) is only very slowly ($<10^{-4}$ mg $cm^{-2}min^{-1}$) soluble in nitric acid solutions. Many previous studies have shown the dissolution rate depends markedly on the physical state of the $PuO_2$ oxide, particularly as this is determined by the preparation method. As an example, the present tests using very dense $PuO_2$ microspheres resulted in quite different dissolution properties in nitric acid than previous tests by Uriarte and Rainey[2b] with $PuO_2$ fuel pellets. In their studies, the dissolution rate increased with the fourth power of the $HNO_3$ concentration between 7 and 14 M $HNO_3$. By contrast, with the microspheres, an increase in the nitric acid concentration between 2 and 16 M resulted in only a relatively small increase in the dissolution rate (Fig. 2). The reason for this large difference in acid solubility between the two forms of oxides is not known, but it may involve the difference in oxide densities.

Figure 2 further indicates that with the microspheres similar results were obtained with increasing nitric acid solutions (initially containing 0.1 M $Ce^{3+}$).

### 3.2 Effect of $Ce^{3+}$ on Dissolution in Nitric Acid

The addition of either $Ce^{3+}$ or $Ce^{4+}$ has been reported to promote dissolution of $PuO_2$ in azeotropic nitric acid.[3] These results were confirmed in tests using both $PuO_2$ microspheres and residues left after initial dissolution of $UO_2$-$PuO_2$ mixed oxides. The present tests, however, indicate that the promotion effect in concentrated $HNO_3$ was probably due to
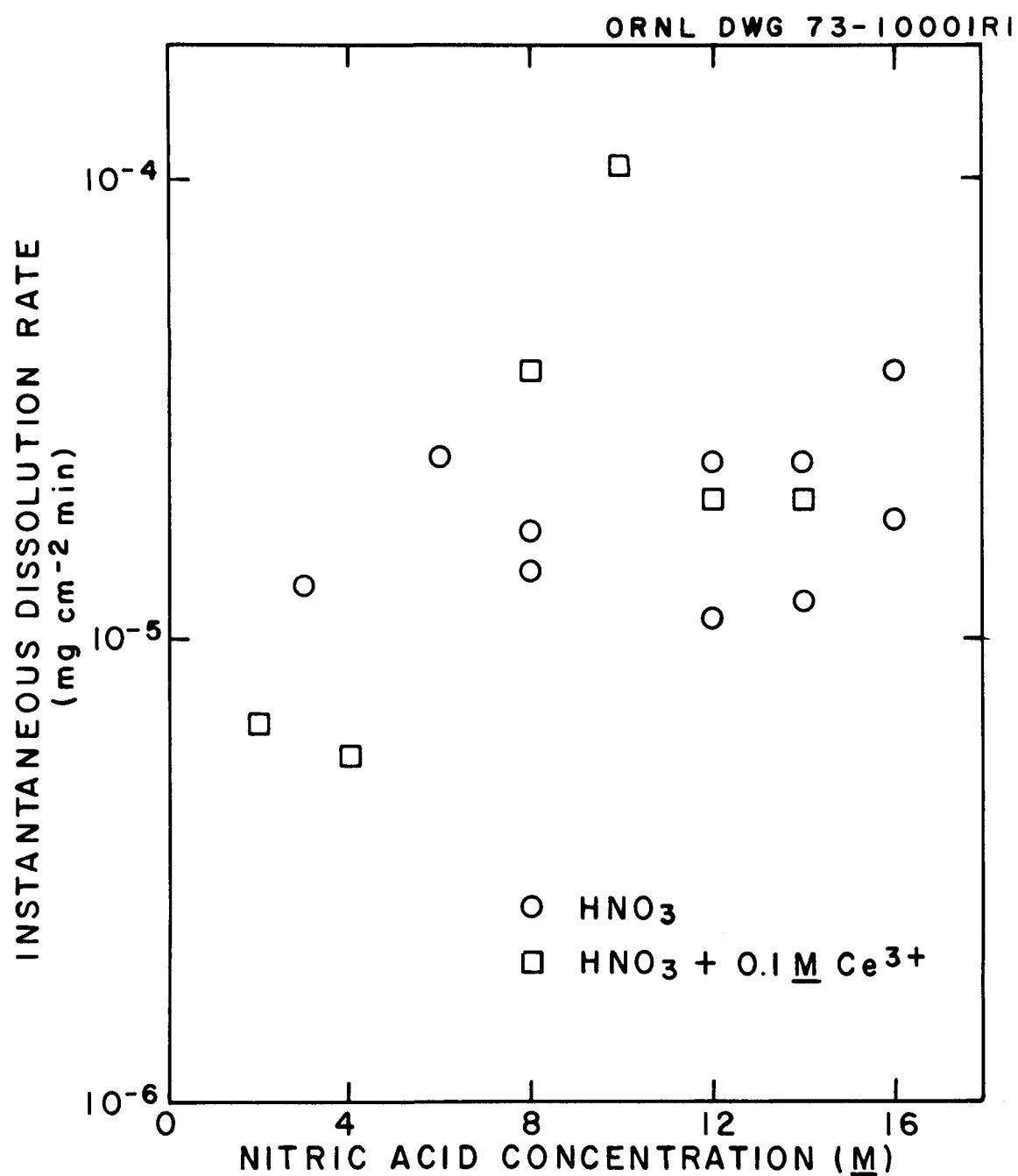
Fig. 2. Effect of nitric acid concentration and the presence of Ce³⁺ on the plutonium dissolution rate.

oxidation of a portion of the $Ce^{3+}$ to $Ce^{4+}$ by the boiling $HNO_3$, rather than to the $Ce^{3+}$ per se. The equilibrium amount of cerium oxidized was determined in separate tests to be only 1.3% in 5 hr with boiling 12 $\underline{M}$ $HNO_3$ and 35% in 5 hr with boiling 16 $\underline{M}$ $HNO_3$. These results qualitatively explain why dissolution promotion initially with 0.1 $\underline{M}$ $Ce^{3+}$ did not occur even up to 14 $\underline{M}$ $HNO_3$ using the microspheres; 16 $\underline{M}$ $HNO_3$ with $Ce^{3+}$ was not run but would not be expected to result in appreciable promotion of the microsphere dissolution because the equilibrium fraction of $Ce^{4+}$ would be too low. However, for the much more easily soluble residues remaining after pre-dissolving mixed $PuO_2$-$UO_2$ oxide as unirradiated pellets in 8 $\underline{M}$ $HNO_3$, much smaller amounts of $Ce^{4+}$ promoted dissolution in $HNO_3$, even as dilute as 8 $\underline{M}$ (see Sect. 4.).

### 3.3 Effect of $Ce^{4+}$ on Dissolution in Nitric Acid

In sharp contrast to results with $Ce^{3+}$, the presence of $Ce^{4+}$ in $HNO_3$ increases the IDR over that for $HNO_3$ alone by several orders of magnitude. The mechanism responsible for this promotion of the dissolution rate by $Ce^{4+}$ was not determined in these studies. The quantitative oxidation of $Pu^{4+}$ by the $Ce^{4+}$ readily occurs and may increase the promotion although it may not be a necessary part of the mechanism. That this $Pu^{4+}$ oxidation may not be necessary is confirmed by results of recent tests made by Tallent with $ThO_2$ whose dissolution rate in nitric acid was promoted to a small degree by $Ce^{4+}$; this result suggests by analogy that oxidation may not be necessary in dissolution of $PuO_2$ and $UO_2$. However, oxidation

may enhance the promotion effect for $PuO_2$ dissolution in the following way. The ionic diameter of the $Ce^{4+}$ cation is very close to that of $Pu^{4+}$ (0.90 $\overset{o}{A}$ vs 0.92 $\overset{o}{A}$),[4] whereas both $Ce^{3+}$ and $PuO_2^{2+}$ have greater ionic diameters. With this situation, it can be postulated that the mechanism involves simple replacement of $Pu^{4+}$ with $Ce^{4+}$ in the crystal lattice, oxidation of $Pu^{4+}$ to $PuO_2^{2+}$ which then breaks open the surface lattice as these larger ions are released into the solution. Further work is needed to determine the mechanism of dissolution. Our primary purpose in this study was to develop a process to ensure total dissolution in a practical time interval. For this, knowledge of the effect on dissolution of the process variables, including the $Ce^{4+}$ and $HNO_3$ concentrations, temperature, etc. are essential. Results of our tests to determine these effects are described below.

### 3.3.1 Effect of nitric acid concentration on dissolution with $Ce^{4+}$

In the presence of $Ce^{4+}$, the effect of changing the initial $HNO_3$ concentration is very large. Batch tests showed that between 2 and 4 $\underline{M}$ $HNO_3$, the IDR increased and then rapidly decreased as the acidity increased from 4 to 16 $\underline{M}$, resulting in a maximum rate at about 4 $\underline{M}$ $HNO_3$ (Fig. 3). Thus at 4 $\underline{M}$ $HNO_3$ with 0.1 $\underline{M}$ $Ce^{4+}$, the IDR ($3.3 \times 10^{-2}$ mg $cm^{-2}min^{-1}$) was about a factor of 200 greater than that at 16 $\underline{M}$ $HNO_3$ ($1.6 \times 10^{-4}$ mg $cm^{-2}min^{-1}$). Even at 16 $\underline{M}$ $HNO_3$, (with 0.1 $\underline{M}$ $Ce^{4+}$), the IDR is about a factor of 5 greater than that for 16 $\underline{M}$ $HNO_3$ when used alone (about $3 \times 10^{-5}$ mg $cm^{-2}min^{-1}$). The reason for the maximum at 4 $\underline{M}$ $HNO_3$ is unknown but must occur as a result of two opposing factors affecting the dissolution rate. Again, further work designed to understand the mechanism involved is desirable.

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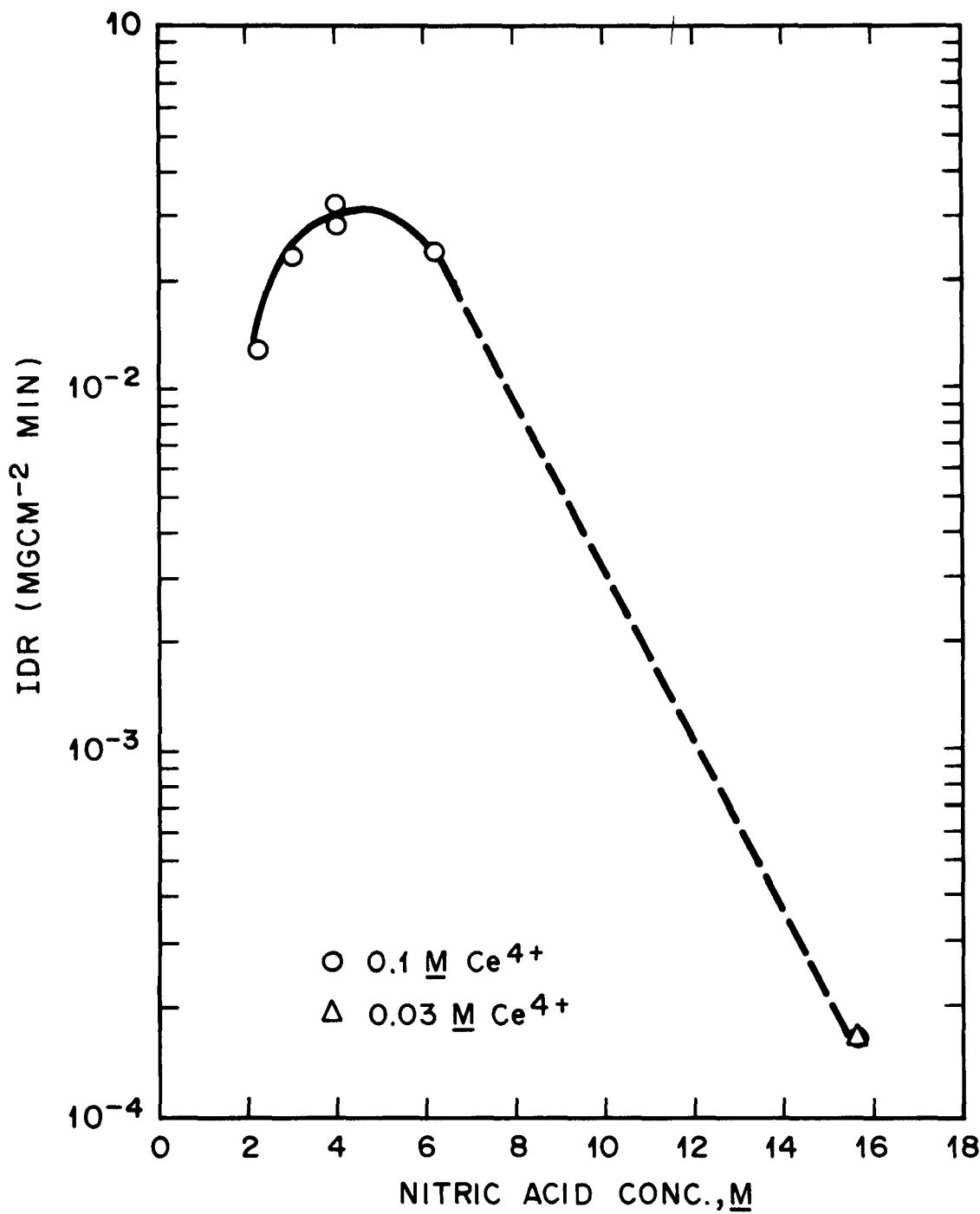


Fig. 3. IDR of PuO$_2$ at various concentration of HNO$_3$ containing Ce$^{4+}$ at boiling temperatures.
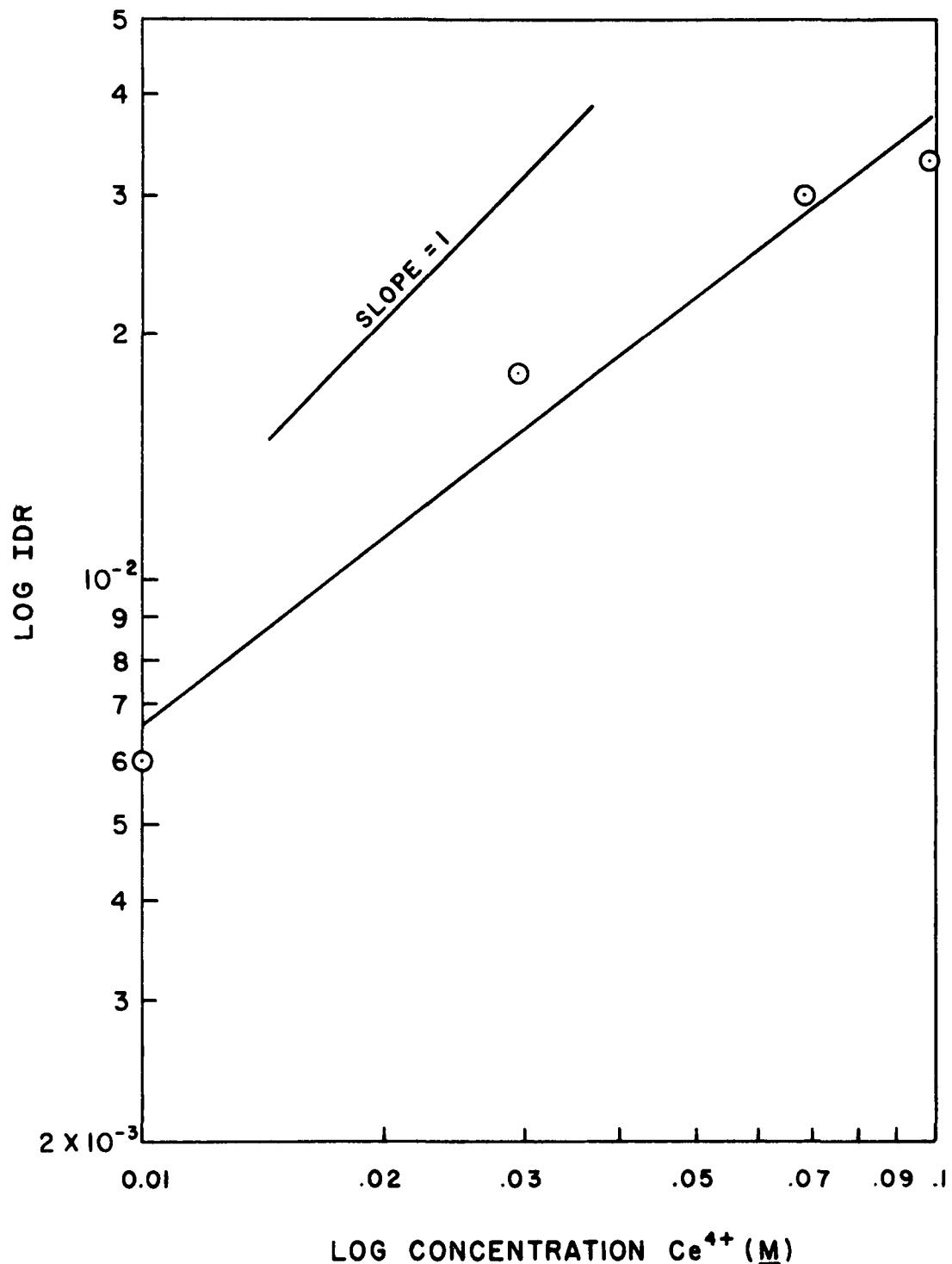
Fig. 4. Instantaneous dissolution rate as a function of the initial Ce$^{4+}$ concentration in 4$\underline{M}$ HNO$_3$.

## 3.3.2 Instantaneous dissolution rate as a function of $Ce^{4+}$ concentration

Consistent with the law of Mass Action for a component in a chemical system, an increase in the $Ce^{4+}$ concentration increases the rate of reaction (dissolution assuming the redox reaction of Sect. 3.3.4 is a necessary part of the mechanism). This increase is mainly proportional to the initial $Ce^{4+}$ concentration for the low $Ce^{4+}$ concentration but less than proportional at higher concentration. A log-log plot of the IDR vs the $Ce^4$ concentration gives a slope = 1 for the data at the lower concentration (Fig. 4). This suggests that the order of reaction with respect to $Ce^{4+}$, at least at low concentrations, is one and thus could involve the formation of $PuO_2^+$ in the dissolution mechanism. If present, the $PuO_2^+$ would rapidly disproportionate to $Pu^{4+}$ and $PuO_2^{2+}$. At the higher concentration, the dissolution rate may be limited by a factor or factors related to the limited surface area of the solid (Fig. 5), which would account for the decrease in the rate at higher $Ce^{4+}$ concentrations.

In any case, these results suggest that in any practical application, a relatively low steady-state concentration of $Ce^{4+}$ would be used; however, see Sect. 3.3.4 for the importance of a high $Ce^{4+}/Ce^{3+}$ ratio.

## 3.3.3 Effect of temperature on the instantaneous dissolution rate

As might be expected, the rate of dissolution increases with increasing temperature. As a result, the boiling temperature is recommended for process uses. When the log of IDR is plotted versus the reciprocal of the absolute temperature, $1/T$, a least-squares fit straight line was drawn (Fig. 5).
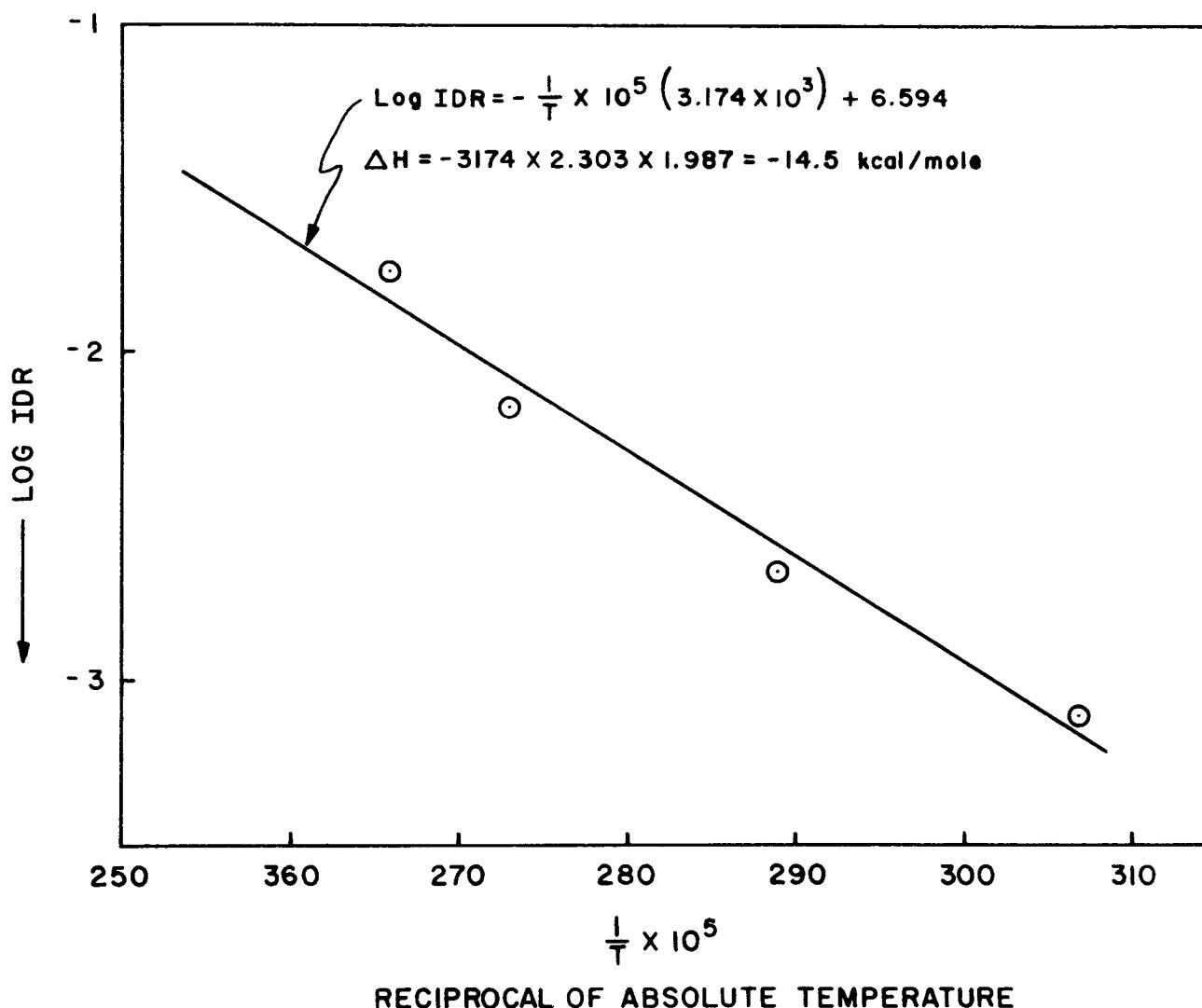
Fig. 5. Instantaneous dissolution rate as a function of temperature (4$\underline{M}$ HNO$_3$ - 0.1$\underline{M}$ Ce$^{4+}$).

The equation of this line is

$$\log IDR = - 3.174 \times 10^8 + 6.594, \tag{2}$$

from which a value of -14.5 kcal/mol was calculated for the activation

energy. This value agrees closely with that obtained from dissolution

of $PuO_2$ in $HNO_3$-HF and in HI which suggests that there may be a fundamen-

tal, basic mechanism common to all of these dissolvents.[5]

### 3.3.4 Plutonium-cerium valence changes during dissolution

The valence changes of plutonium and cerium during an extended

dissolution of $PuO_2$ microspheres in 4 $\underline{M}$ $HNO_3$--0.03 $\underline{M}$ $Ce^{4+}$ were followed

spectrophotometrically. The tests showed that the $Ce^{4+}$ oxidized the

$Pu^{4+}$ to $Pu^{6+}$ ($PuO_2^{2+}$) as the $PuO_2$ was dissolved, with the stoichiometric

amount of 2 moles of $Ce^{4+}$ per mole of $Pu^{4+}$ being required. However,

Fig. 6 shows that the dissolution rate was high only as long as the

$Ce^{4+}$ concentration was greater than the $Ce^{3+}$ concentration ($Ce^{4+}/Ce^{3+} >1$)

for the microspheres. These results indicate that the $Ce^{4+}/Ce^{3+}$ ratio,

as well as the $Ce^{4+}$ concentration, is an important rate-determining

factor. This was confirmed by results of a second series of batch tests

in which the initial ratio of $Ce^{4+}/Ce^{3+}$ was varied by holding the initial

concentration of $Ce^{4+}$ constant at 0.03 $\underline{M}$ and varying the $Ce^{3+}$ concentra-

tion over the range of 0 to 0.12 $\underline{M}$. At the lowest $Ce^{4+}/Ce^{3+}$ ratio of

0.25, the IDR for $PuO_2$ microspheres was lower by a factor of about 28

than that where initially no $Ce^{3+}$ was present. These results show that,

for an efficient dissolution rate, the ratio of $Ce^{4+}/Ce^{3+}$ should be kept

high by continuous reoxidation of $Ce^{3+}$ to $Ce^{4+}$. This most likely would

be accomplished in a small secondary dissolver in a circuit with oxida-

tion by ozone or an electrolytic oxidation cell.

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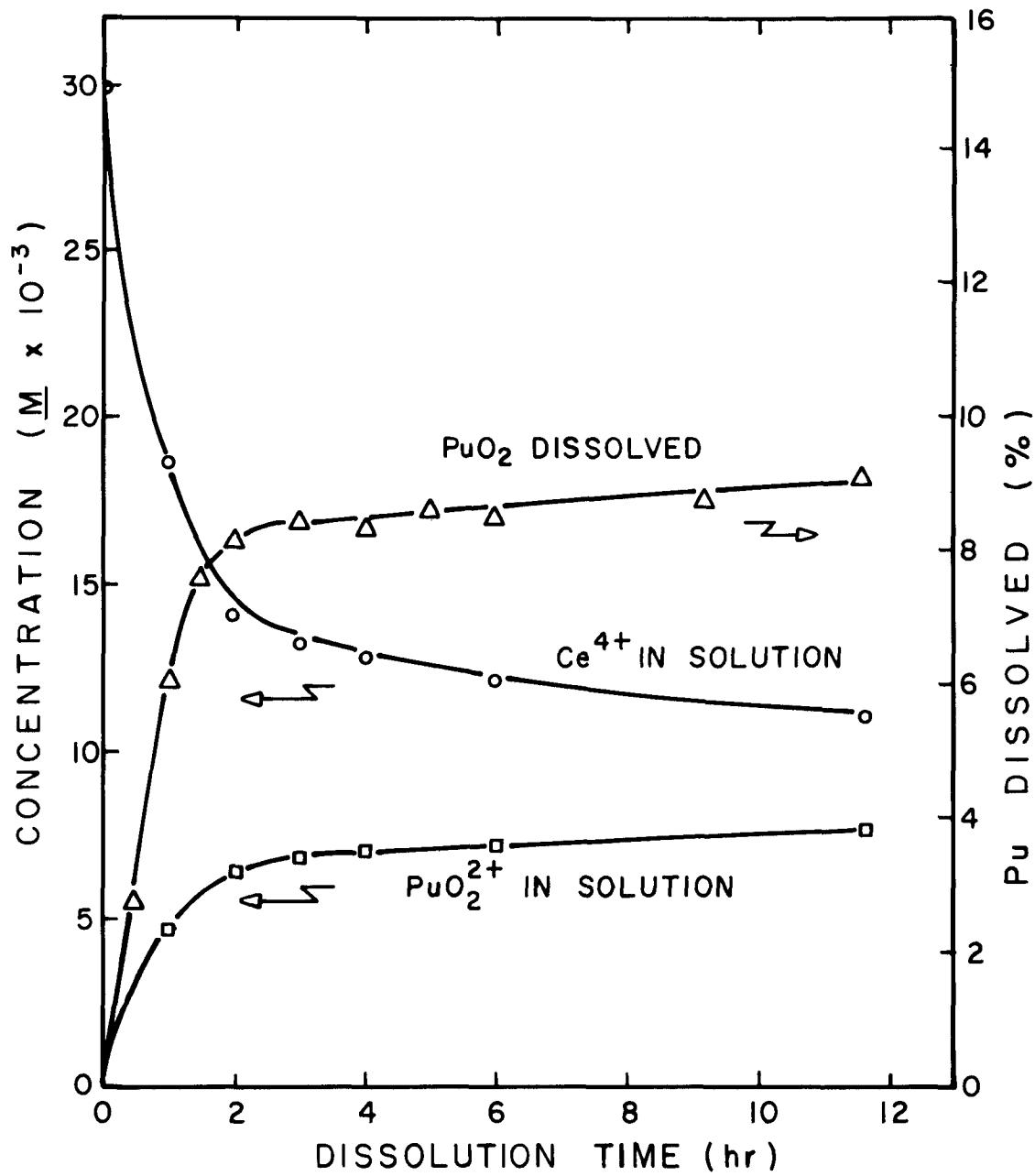


Fig. 6. Changes in $Ce^{4+}$ and $Pu_2^{2+}$ concentrations with dissolution
time. Conditions: 3 g of $PuO_2$ dissolved in 150 ml of boiling 4 $\underline{M}$
$HNO_3$--0.03 $\underline{M}$ $(NH_4)_2Ce(NO_3)_6$.

### 3.3.5 Solution potential as an indicator of dissolver effectiveness

The fact that the $Ce^{4+}/Ce^{3+}$ ratio appears to be important for efficient dissolution suggests that the electrical potential, as a measure of this redox ratio, may be a good indicator of dissolver effectiveness (at least with cerium). As an example, in the dissolution tests discussed in Sect. 3.3.4, the potentials decreased from a value of about 1.45 V for a 0.03 $\underline{M}$ $Ce^{4+}$ solution containing no $Ce^{3+}$ to 1.34 V for a 0.03 $\underline{M}$ $Ce^{4+}$--0.12 $\underline{M}$ $Ce^{3+}$ solution (Fig. 7). Over this range of $Ce^{4+}/Ce^{3+}$ ratios, the IDR decreased by about a factor of 28. These results suggested that a potential of at least 1.38 V would be needed for a practicable dissolution rate for $PuO_2$ microspheres. This potential corresponds to an approximate $Ce^{4+}/Ce^{3+}$ ratio of 1 in 4 $\underline{M}$ $HNO_3$ and shows that a lower ratio, competition by $Ce^{3+}$ with $Ce^{4+}$ is too high for effective attack of the $PuO_2$. The effect with actual difficultly soluble fuel residues qualitatively should be the same although the minimum effective potential may be lower.

### 3.4 Tests with Other Oxidants

### 3.4.1 Peroxydisulfate and others

We have also tried to correlate the potential of a $4\underline{M}$ $HNO_3$ dissolver solution containing the strong oxidant, persulfate (catalyzed with $Ag^+$), with its possible ability to enhance the dissolution rate. The potential of a freshly made 4 $\underline{M}$ $HNO_3$--0.03 $\underline{M}$ $S_2O_8^{2-}$ solution was measured to be about 1.2 V; the IDR with the $PuO_2$ microspheres in 4 $\underline{M}$ $HNO_3$--0.1 $\underline{M}$ $S_2O_2^{2-}$ (0.01 $\underline{M}$ $Ag^+$) was only about 1.4 mg $cm^{-2}$ $min^{-1}$, or no higher than that for 4 $\underline{M}$ $HNO_3$ alone. The standard oxidation potential of $S_2O_8^{2-}$
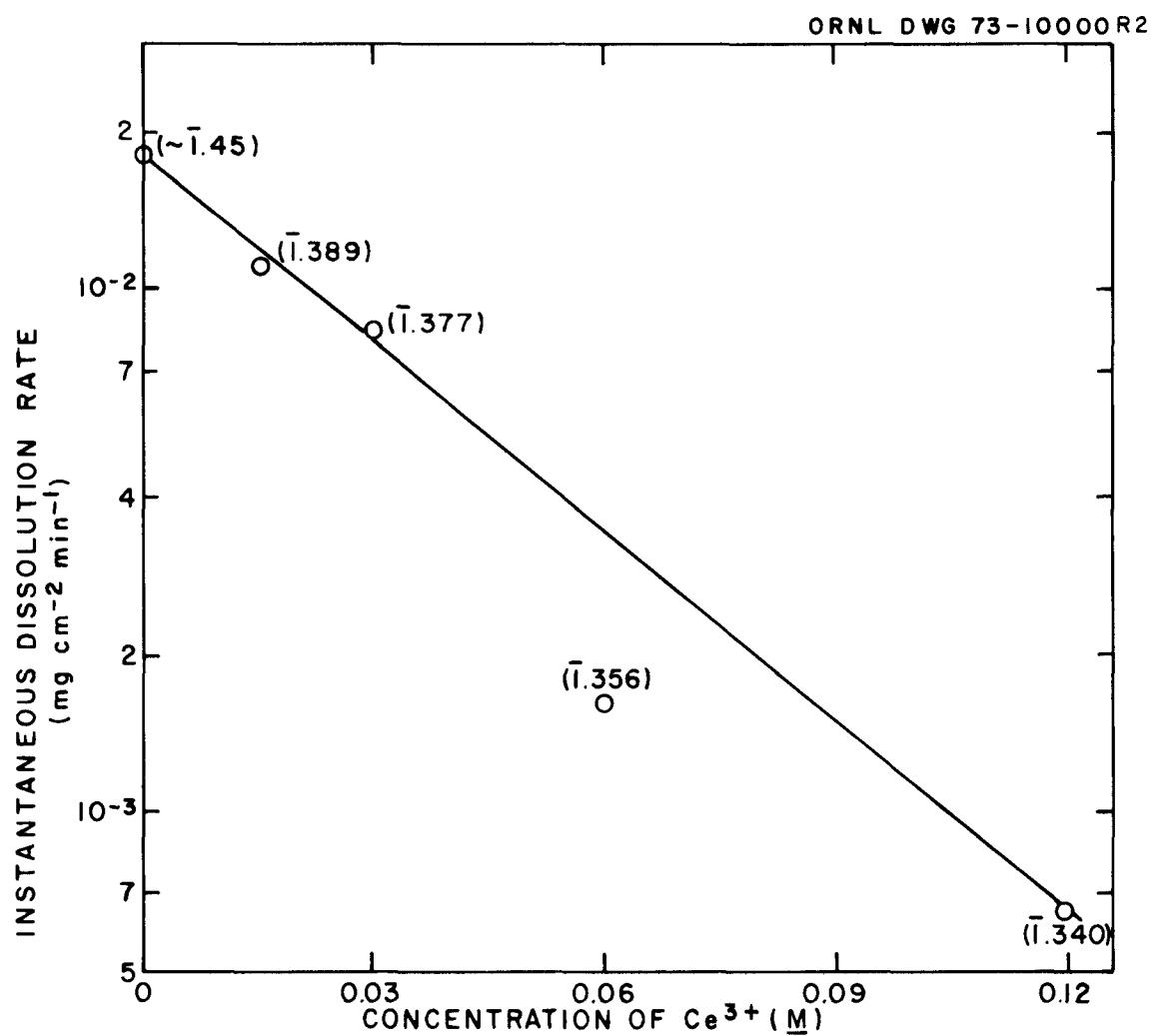
Fig. 7. Effect of $Ce^{3+}$ concentration on the instantaneous dissolution
rate of $PuO_2$ microspheres in boiling 4 M $HNO_3$ containing 0.03 M $Ce^{4+}$.
The numbers in parentheses show the solution emf (platinum vs saturated
calomel) at 25°C.

shows it is a stronger oxidant than $Ce^{4+}-Ce^{3+}$. (This can be demonstrated in a 4 $\underline{M}$ $HNO_3$ solution at room temperature by the fact that $Ce^{3+}$, in the presence of $S_2O_8^{2-}$, is partially oxidized to $Ce^{4+}$, as evidenced by the solution turning yellow.) The low potential and failure of the silver-catalyzed persulfate to increase the dissolution rate could possibly be due to the chemical instability of $S_2O_8^{2-}$ in hot acidic solutions. Even at room temperature, a solution of $S_2O_8^{2-}$ in a 4 $\underline{M}$ $HNO_3$ after standing overnight had a potential of about 1.13 V, compared to 1.20 V for a freshly made solution; this decrease in potential also indicated instability.

Other oxidants in 4 $\underline{M}$ $HNO_3$, such as 0.1 $\underline{M}$ permanganate and 0.1 $\underline{M}$ dichromate, were ineffective as dissolution promotors (IDR's were $< 10^{-4}$ mg $cm^{-2}min^{-1}$). A comparison of their standard electrode potential shows that dichromate is a weaker oxidant than persulfate while permanganate is stronger, but both of these oxidants have a high enough standard oxidation potential to oxidize $Pu^{4+}$ to $PuO_2^{2+}$.

The failure of these very strong oxidants to enhance dissolution indicates again that the oxidation of $Pu^{4+}$ to $PuO_2^{2+}$ is not the complete mechanism of promotion and may, in fact, be only incidental.

### 3.4.2  Ozonized-oxygen

To further test the premise that ability to oxidize $Pu^{4+}$ to $PuO_2^{2+}$ alone is the basic mechanism for dissolution promotion, the strong oxidant, ozone, was tested. Uriarte and Rainey observed a small beneficial effect using ozone to dissolve $PuO_2$ pellets in 2 $\underline{M}$ $HNO_3$, but not at a higher concentration (7-14 $\underline{M}$).[2b] Our tests however, with ozone

using 2, 4, and 6 $\underline{M}$ $HNO_3$ showed no significant increase in the

dissolution rate for $PuO_2$ microspheres over that for nitric

acid alone.  In these tests, 200 ml of ozonized-oxygen per minute was

bubbled through the solution while the $PuO_2$ microspheres were stirred.

The temperature of the solution was maintained at 87°C.  The rate of

oxidation with ozone in this manner undoubtedly would be limited by

its low solubility in solution at atmospheric pressure.  Because of

this, we could not be sure that ozone would fail to promote dissolution

under more favorable conditions.  Future tests should be made at greater

than atmospheric pressure to make the test conclusive.

Use of ozone at atmospheric pressure to oxidize $Ce^{3+}$ to $Ce^{4+}$ in

solution resulted in effective dissolution promotion.  For example,

ozone was bubbled through an 8 $\underline{M}$ $HNO_3$ solution containing 0.2 $\underline{M}$ $Ce^{3+}$

for about 12 hr, resulting in conversion of all the $Ce^{3+}$ to $Ce^{4+}$.  In

a subsequent dissolution test, ozone was bubbled through a 2 $\underline{M}$ $HNO_3$

dissolver solution initially containing 0.05 $\underline{M}$ $Ce^{3+}$ and $PuO_2$ micro-

spheres.  Over a 3-hr interval, the dissolution rate continuously

increased as the $Ce^{3+}$ was oxidized to $Ce^{4+}$.  This result shows the

necessity of having cerium present for promotion of dissolution by

oxidation and also basically demonstrates how ozone could be used as

an oxidizing agent for continuous $Ce^{4+}$ regeneration during the dissolution.

### 3.5  Total Dissolution Tests

Several extended tests were made (1) to determine if the rate might

change significantly during total dissolution, and (2) to be sure that

the promotion effect of the $Ce^{4+}$ did not suddenly cease for some reason

(e.g., as has been reported in catalyzed reactions in which the catalyst is poisoned). In these tests, approximately 1-g samples of the microspheres were dissolved in an initial volume of 150 ml of 4 $\underline{M}$ $HNO_3$--0.1 $\underline{M}$ $Ce^{4+}$ while numerous solution samples were taken over a total time period of 18 hr. The accumulated total plutonium in solution was calculated for each sample time increment, with which a graph of the logarithm of the undissolved fraction of $PuO_2$ was plotted as a function of the dissolution time (Fig. 8). The final residue remaining after 18 hr was filtered and then dissolved completely in 8 $\underline{M}$ $HNO_3$--0.1 $\underline{M}$ HF. Analysis of this solution showed it represented 10% of the original weight of the microspheres. Although there was appreciable scatter, a straight line could be drawn through the points, which can be interpreted to mean that the dissolution rate was essentially first order with respect to undissolved plutonium during at least 90% of dissolution. A second test gave similar results. The calculated mole ratio in these tests was approximately four or about twice the stoichiometric amount of $Ce^{4+}$ necessary to oxidize all of the $Pu^{4+}$ to $PuO_2^{2+}$. Spectrophotometric examinations of the final dissolver solution showed that all of the plutonium in solution was $Pu^{6+}$ ($PuO_2^{2+}$). This result, in addition to the results reported in the previous tests (Sect. 3.3.4), shows that the reaction in solutions during dissolution can be represented by the equation expected for this redox system:

$$2Ce^{4+} + Pu^{4+} + 2H_2O = PuO_2^{2+} + 2Ce^{3+} + 4H^+. \tag{3}$$
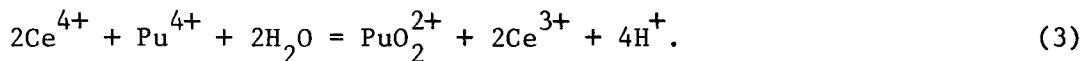
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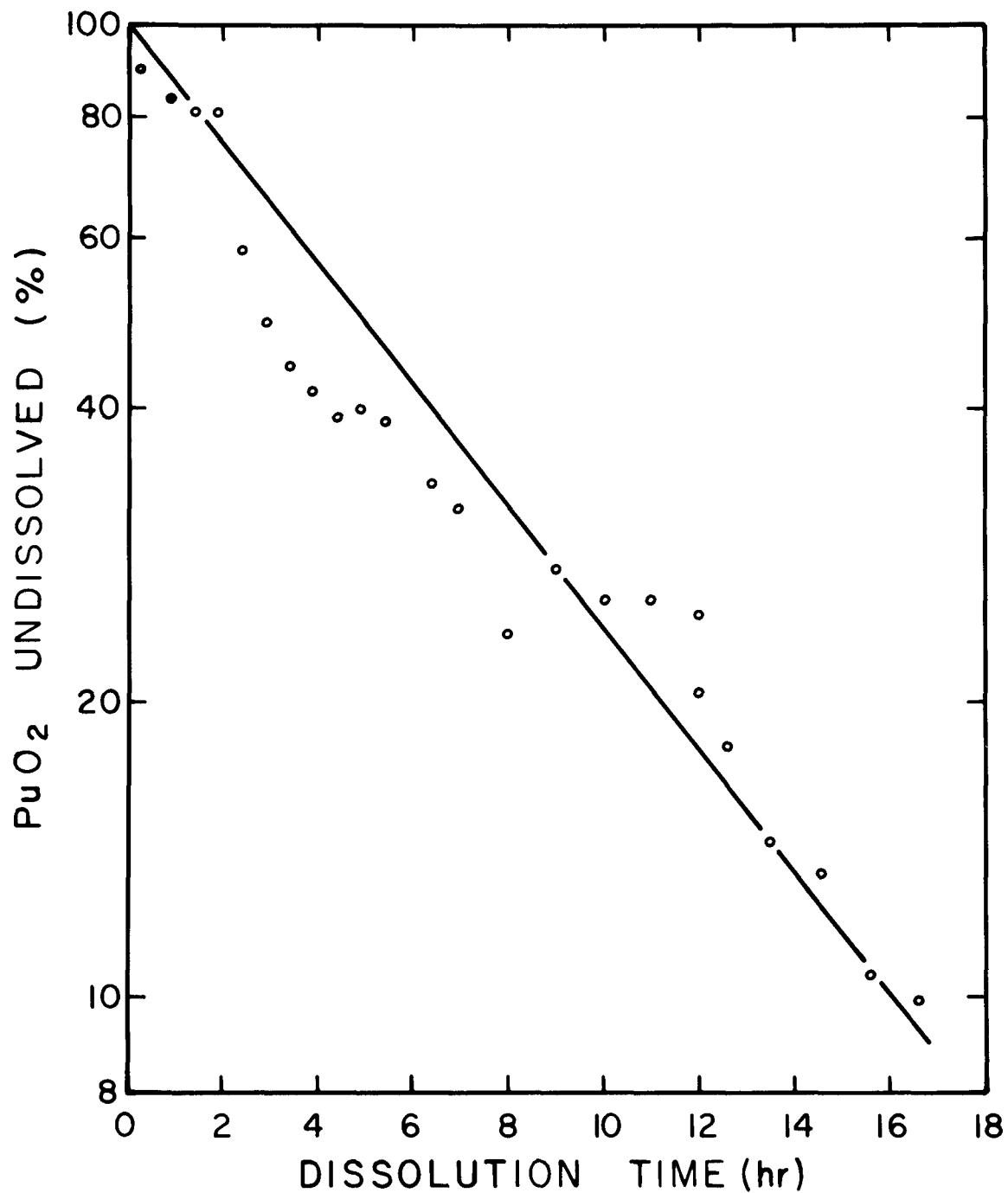


Fig. 8. Rate of dissolution of $PuO_2$ microspheres. Conditions: 1 g of $PuO_2$ dissolved in 150 ml of boiling 4 $\underline{M}$ $HNO_3$--0.1 $\underline{M}$ $(NH_4)_2Ce(NO_3)_6$.

At the conclusion of each test, the calculated mole ratio of $Ce^{4+}/Ce^{3+}$ was about 1, or at about the minimum ratio as shown previously for effective dissolution of these microspheres.

## 4. TESTS WITH UNIRRADIATED $PuO_2$-$UO_2$ PELLET RESIDUES

Additional dissolution tests were made using the residue that remained after dissolving a batch of unirradiated nonhomogeneous 75% $UO_2$--25% $PuO_2$ fuel pellets for 6 hr in boiling 10 $\underline{M}$ $HNO_3$. The residue, which contained about 15% of the original plutonium before dissolution, had an approximate composition of 75% $PuO_2$--25% $UO_2$. Samples of this residue were then tested by dissolution in the various solutions shown in Table 1, and the comparative dissolution rate was calculated in mg of plutonium per minute per gram of residue or in the percent of plutonium dissolved.

These residues, because of their different physical properties (which included a greater surface area and a lower density), were more easily dissolved than the microspheres. However, consistent with the results of the microsphere tests, the general order of promotion effectiveness, as measured by the rate of dissolution, was HF > $Ce^{4+}$ > $Ce^{3+}$ > $HNO_3$ alone. For example, dissolution with 8.4 $\underline{M}$ $HNO_3$--0.05 HF resulted in 100% solubility of the plutonium within 0.5 hr while with 4.2 $\underline{M}$ $HNO_3$--0.05 $\underline{M}$ $Ce^{4+}$, 100% dissolution required 1.5 hr (Table 1). In other tests, comparison of the rate with and without $Ce^{3+}$ initially present shows that with $Ce^{3+}$ the rates are a factor of 4 to 5 greater in 12 and 16 $\underline{M}$ $HNO_3$ than in the same concentrations of $HNO_3$ alone. The small amounts of $Ce^{4+}$ formed with these $HNO_3$ concentrations (as shown in Sect. 3.2) undoubtedly promoted the dissolution; however,

Table 1. Dissolution of Unirradiated $PuO_2-UO_2$ Pellet Residues

| Dissolver solution | Time (hr) | Dissolution rate (mg/min/g residue) | Plutonium dissolved (%) |
|---|---|---|---|
| 12 $\underline{M}$ $HNO_3$ | – | 0.105 | – |
| 12 $\underline{M}$ $HNO_3$--0.05 $\underline{M}$ $Ce^{3+}$ | – | 0.480 | – |
| 16 $\underline{M}$ $HNO_3$ | – | 0.164 | – |
| 16 $\underline{M}$ $HNO_3$--0.05 $\underline{M}$ $Ce^{3+}$ | | 0.704 | – |
| 8.4 $\underline{M}$ $HNO_3$--0.05 $\underline{M}$ HF | 0.5 | | 100 |
| 4.2 $\underline{M}$ $HNO_3$--0.05 $\underline{M}$ $Ce^{4+}$ | 1.5 | | 100 |
| 8.2 $\underline{M}$ $HNO_3$--0.03 $\underline{M}$ $Ce^{3+}$ | 3.5 | 0.140 | 4.6 |
| 8.6 $\underline{M}$ $HNO_3$ | 3.5 | 0.0737 | 2.0 |

comparison of these results with those for dissolution of the $PuO_2$ microspheres shows that the soluble residues require a much lower ratio of $Ce^{4+}/Ce^{3+}$ than that required for promotion of the microspheres. In the tests with 8 $\underline{M}$ $HNO_3$ (both with and without 0.03 $\underline{M}$ $Ce^{3+}$), the factor of about 2 in the dissolution rate (in 3.5 hr) may not be significant.

The difference between the use of $Ce^{3+}$ vs $Ce^{4+}$ was confirmed by J. H. Goode[1g] in another series of tests with unirradiated, but heat-treated, $UO_2$-$PuO_2$ pellet residues. Samples of these plutonium-rich residues were leached three times, for a total of 10 hr, in 4 $\underline{M}$ $HNO_3$-- 0.05 $\underline{M}$ $Ce^{4+}$ or 4 $\underline{M}$ $HNO_3$--0.05 $\underline{M}$ $Ce^{3+}$. In 4 hr with the $Ce^{4+}$, only 0.014% of the total plutonium remained undissolved, while with the $Ce^{3+}$, about 2% remained undissolved. At the end of 10 hr (with $Ce^{4+}$) no residue was found; but with $Ce^{3+}$, 0.12% (Fig. 9) of the total plutonium remained undissolved.

Since boron may be used as an internal neutron poison in the dissolution step in the process for these fuels, another set of dissolution tests was made to determine if the presence of this material might either affect the dissolution rate and/or cause precipitation. In these tests, 0.3 $\underline{M}$ boron (added as $H_3BO_3$) was used during the initial dissolution of easily soluble oxides in unirradiated pellets (75% $UO_2$-- 25% $PuO_2$) in 4 $\underline{M}$ $HNO_3$--0.05 $\underline{M}$ $Ce^{4+}$. The dissolution rate of plutonium was not affected; however, the dissolution rate for uranium was about a factor of 2.5 greater with boron than without (Table 2). No evidence exists that indicates the formation of insoluble boron complexes under these conditions.
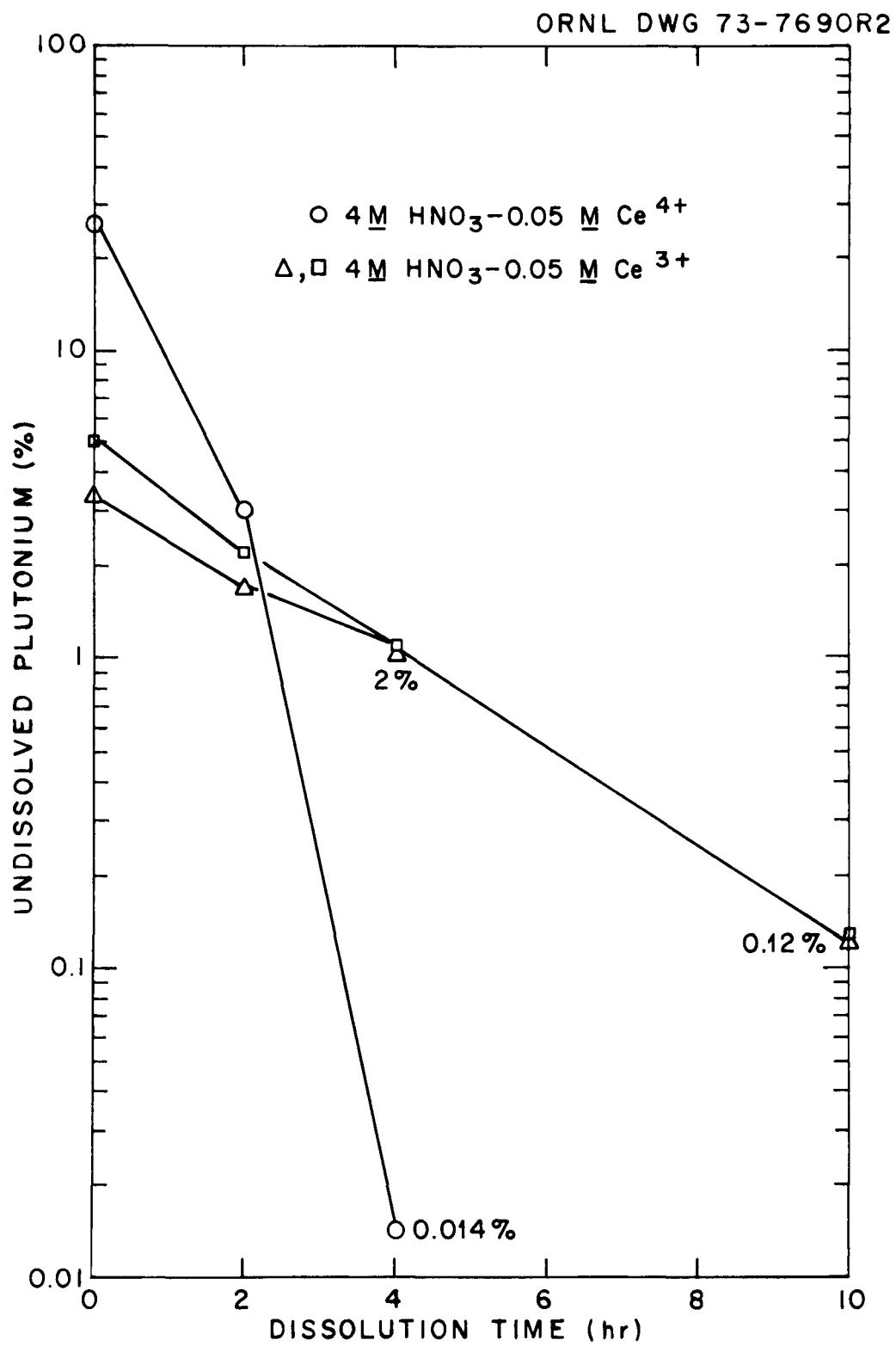
Fig. 9. Dissolution of $PuO_2$ residues from pellets.

Table 2. Effect of boric acid on dissolution of $UO_2$ and $PuO_2$ in unirradiated fuel pellets

| Additive | Dissolution rate (mg/min/g residue) | |
|----------|-------------------------------------|---|
| | Uranium | Plutonium |
| None | 0.14 | 5.72 |
| 0.3 $\underline{M}$ $H_3BO_3$ | 0.32 | 5.93 |

4.1 Precipitation of Plutonium from Dissolver Solutions

In some of the dissolution tests, small amounts of a dark precipitate formed. Subsequent tests with varying plutonium and $HNO_3$ concentrations indicated insoluble plutonium compounds were being formed primarily at an acidity of 1 $\underline{M}$ $HNO_3$. Other tests involving extended dissolution in 4 $\underline{M}$ $HNO_3$ with 0.1 $\underline{M}$ $Ce^{4+}$ produced by (1) ozone oxidation of $Ce^{3+}$ (no precipitation), and by (2) addition of $(NH_4)_2Ce(NO_3)_6$ (precipitation) indicated that $NH_4^+$ ion, but not the $Ce^{4+}$ ion, is involved in the precipitated compound of plutonium. These results suggest that >1 $\underline{M}$ $HNO_3$ should be used, particularly if $(NH_4)_2Ce(NO_3)_6$ is used as a source of $Ce^{4+}$.

5. EFFECT OF RUTHENIUM ON $Ce^{4+}$-PROMOTED $PuO_2$ DISSOLUTION

In contrast to the results of tests with unirradiated $PuO_2$, the use of $Ce^{4+}$ in dissolution tests with irradiated fuels containing $PuO_2$ (Sect. 7.) were not successful in most cases. In these latter tests, it was clear that failure was due to the rapid reduction of the $Ce^{4+}$ to $Ce^{3+}$, which had been previously shown to be ineffective. In a search for the cause of the reduction (besides that due to possible radiolytic

reduction), we considered the effect of the major nitric acid-insoluble fission products on the reduction of $Ce^{4+}$. Of these (molybdenum, noble metals, and ruthenium) the last fission product, ruthenium, appeared to be a likely possibility. Subsequent tests made with nonradioactive ruthenium showed that this fission product was probably responsible for total $Ce^{4+}$ reduction and hence failure of the irradiated fuel residue tests; tests with molybdenum and a representative noble metal were negative.

In the tests, 60 mg of ruthenium metal was first plated on a platinum wire gauze by electrolytic reduction of a solution of $RuCl_3$ in dilute $H_2SO_4$. Introduction of the ruthenium-plated gauze into 300 ml of 0.051 $\underline{M}$ solution of $Ce^{4+}$ in 4 $\underline{M}$ $HNO_3$ (subsequently heated to about 88°C) resulted in evolution of a gas (most likely $O_2$) and a change in the color of the solution from yellow-orange to green. Subsequent titration of the solution showed that 89% of the original amount of $Ce^{4+}$ had been reduced. When a portion of this solution was then heated to boiling in a reflux condenser (while being sparged with argon gas), a black material formed both in the solution and on the inner condenser walls, indicating volatility. This insoluble black material (probably $RuO_2$) resulted from decomposition of volatile $RuO_4$. Part of this material subsequently dropped back into the boiling solution to be reoxidized. The ease of decomposition of the $RuO_4$ was also demonstrated by the formation of the black $RuO_2$ on the underside of a cover glass over a portion of the solution which had not been heated but which had remained at room temperature. A sample of the remaining solution after about 0.5 hr of refluxing was titrated and shown to contain <1% of the original amount of $Ce^{4+}$.

The probable reactions that occurred can be represented by the equations:

$$Ru + 8Ce^{4+} + 4H_2O = 8Ce^{3+} + RuO_4\uparrow + 8H^+, \qquad (4)$$

$$RuO_4 = RuO_2 + O_2, \qquad (5)$$

$$RuO_2 + 4Ce^{4+} + 2H_2O = 4Ce^{3+} + RuO_4\uparrow + 4H^+. \qquad (6)$$
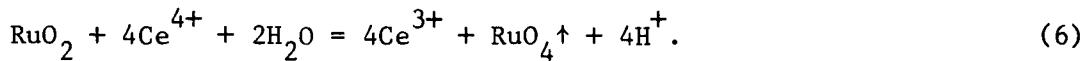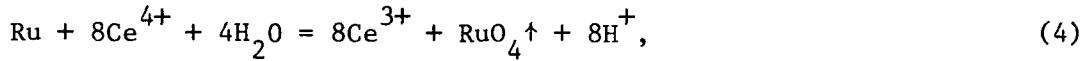
With these types of reactions, a cyclic mechanism is possible whereby ruthenium can be alternately oxidized and reduced, resulting in a continuous catalytic reduction of all $Ce^{4+}$ by only a very small amount of ruthenium. That this kind of catalytic mechanism was probably occurring in these tests is supported by the fact that the final $Ce^{4+}$ concentration in the solution was much lower than the theoretical concentration of 0.0352 $\underline{N}$ calculated by assuming the reaction shown in Eq. (4). These results also explain why all of the $Ce^{4+}$ was reduced in dissolution tests with residues from irradiated fuel pellets but why no problem occurred in tests using unirradiated $PuO_2$ (where fission product ruthenium was not present). See Sect. 3.

These results lead to the conclusion that the use of $Ce^{4+}$ as a dissolution promotor for difficultly soluble irradiated fuel residues would not be feasible unless some way could be found to remove all of the ruthenium prior to or during the dissolution. Application of this method, however, to unirradiated scrap $PuO_2$, in which no ruthenium would be present, appears to be promising.

## 6. CORROSION TESTS

Specimens of stainless steels, titanium, and tantalum were exposed to boiling 4 $\underline{M}$ $HNO_3$--0.1 $\underline{M}$ $Ce^{4+}$ dissolver solutions to determine the corrosion rates. Both 304 and 316 stainless steels were attacked, resulting in the reduction of the $Ce^{4+}$ to $Ce^{3+}$; consequently, frequent replacement of the solution was necessary. The calculated corrosion rates were in the range 6 to 11 mils/month. Other workers also have observed rapid corrosion of stainless steel in $Ce^{4+}$ solutions.[3,6] Titanium and tantalum showed no evidence of attack (no loss in weight or visible surface changes) over a total exposure period of 34 days. In these tests, the solutions were kept at the boiling temperature about 25% of the time. These results definitely show that stainless steel containment equipment would be unsuitable, but the titanium or tantalum would be satisfactory.

## 7. DISSOLUTION TESTS WITH IRRADIATED $UO_2$-$PuO_2$

In these tests made by J. H. Goode, the oxide used was an 80% $UO_2$--20% $PuO_2$ fuel from a NUMEC fuel rod irradiated in EBR-2 to about 33,000 MWd/ton. The oxide was a mechanically blended (ball-milled for 2 hr) mixture of coprecipitated $(U_{0.5}$--$Pu_{0.5})O_2$ with $UO_2$. The mixture was pressed and sintered into pellets of 91.7% theoretical density. The sintering cycle consisted of 4 hr of heating, 4 hr of firing at 1625°C, and 4 hr of cooling in a $N_2$--6% $H_2$ atmosphere. Dissolution tests made over a period of 8 hr showed there was essentially no difference in dissolution rate using both 8 and 10 $\underline{M}$ $HNO_3$ alone or with 0.05 $\underline{M}$ $Ce^{3+}$

(Fig. 10). With a similar batch of oxide, but unirradiated, dissolution

in 8 $\underline{M}$ $HNO_3$ alone always resulted in a much higher fraction of undissolved

plutonium than was the case with irradiated fuel. Similar dissolution

results for the $UO_2$ are shown in Fig. 11. Thus these results confirm

that $Ce^{3+}$ in dilute $HNO_3$ (e.g., <12 $\underline{M}$) does not promote dissolution,

but irradiation obviously greatly improves the dissolution rate.
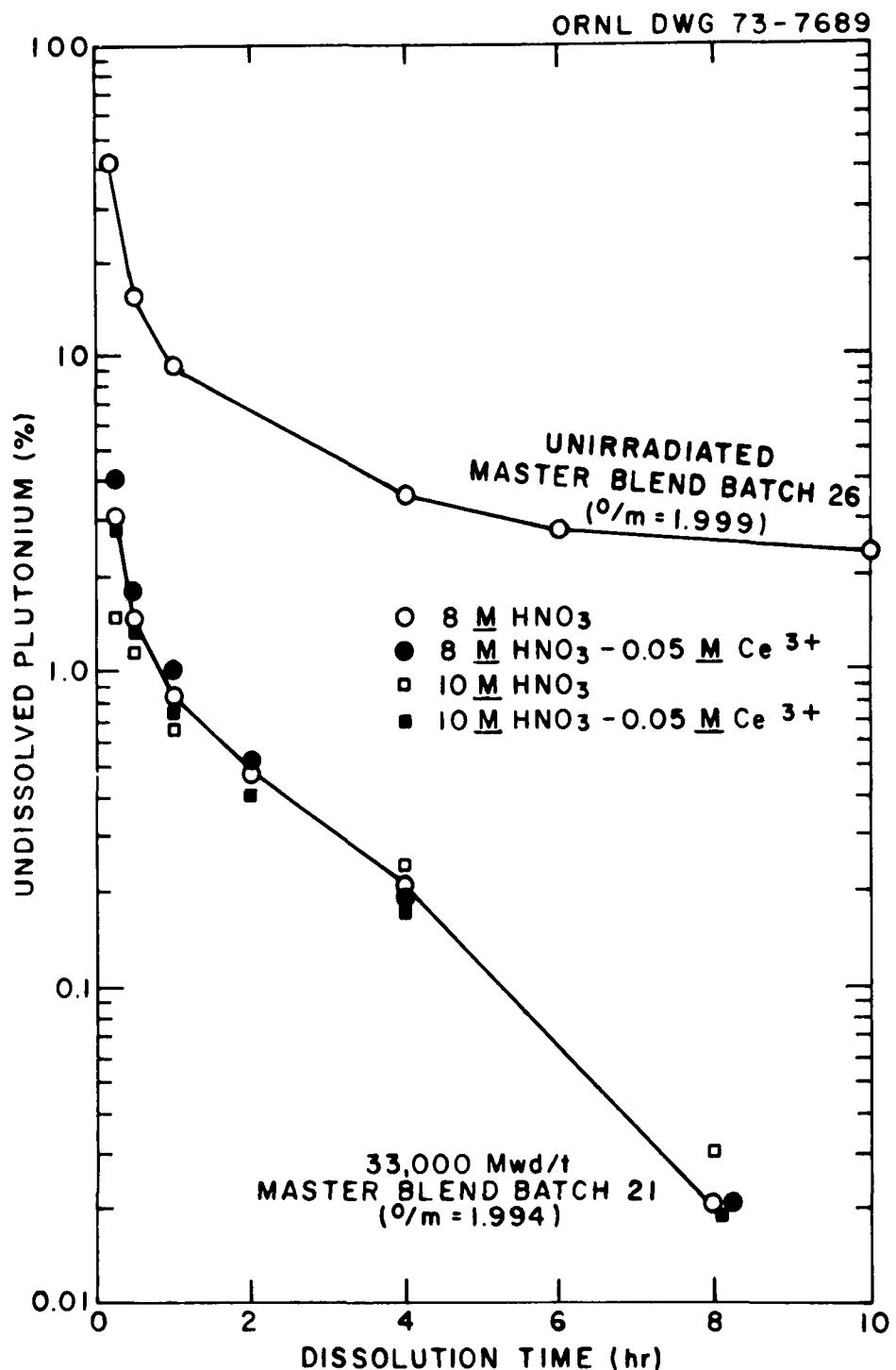
Fig. 10. Dissolution of plutonium from NUMEC "master-blend" 80% $UO_2$--20% $PuO_2$ with nitric acid and nitric acid containing $Ce^{3+}$.
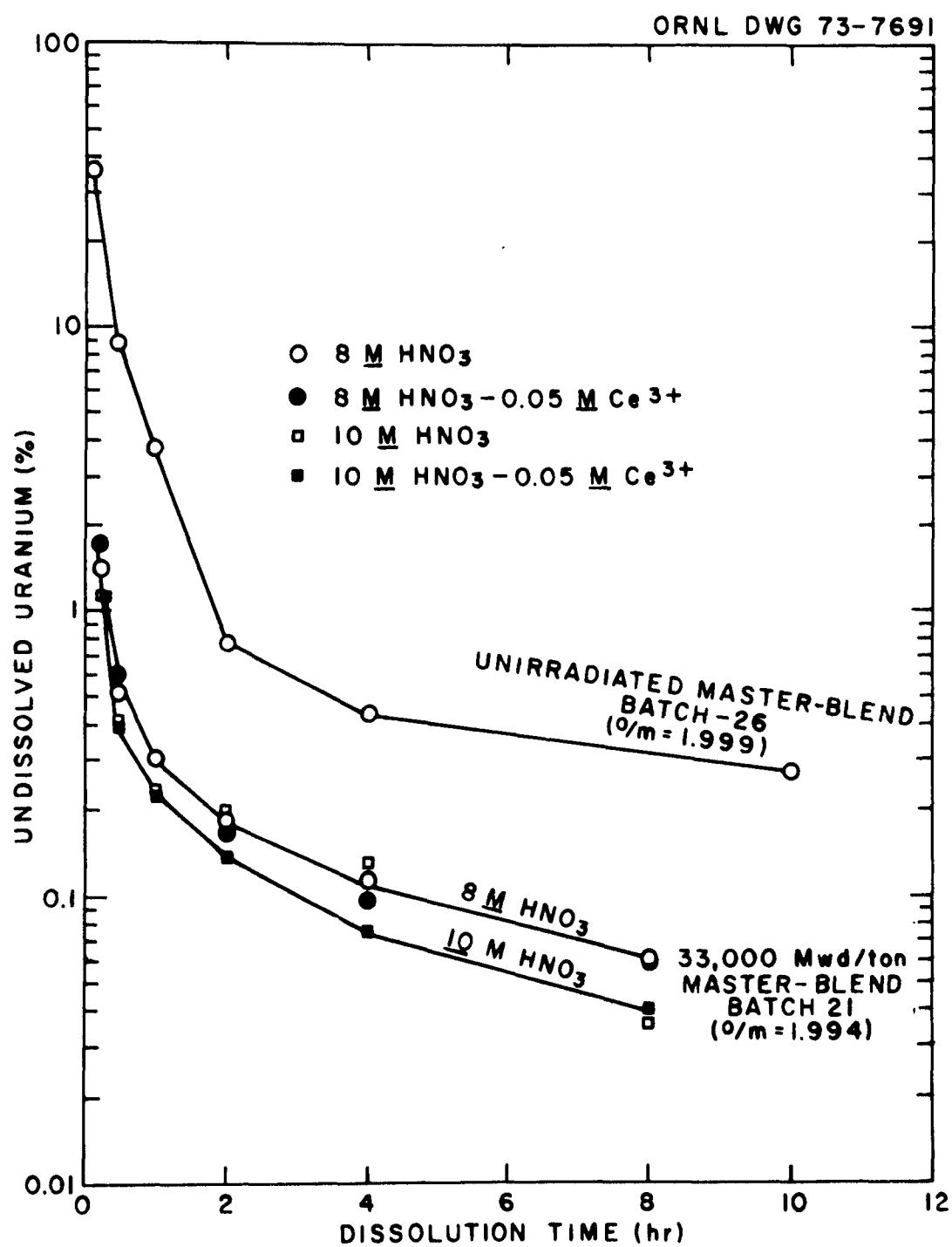
Fig. 11.  Dissolution of uranium from NUMEC "master-blend" 80% $UO_2$--20% $PuO_2$ with nitric acid and nitric acid containing $Ce^{3+}$.

## 8. ACKNOWLEDGMENTS

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