Radiolytically Generated Hydrogen and Oxygen from Plutonium Nitrate Solutions

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Received January 27, 1993

Hydrogen and oxygen gases radiolytically generated in a nitrate system by α-radiation were investigated. The following points were elucidated:

1. Plutonium (IV) is involved in the G-value for hydrogen generation. The difference in G-values in 244Cm-HNO₃ solution and Pu(IV)-HNO₃ solution can be explained by the presence of Pu.

2. No significant effect of the difference of oxidation states, Pu(IV)/Pu(VI), resulting from heating solution on the hydrogen generation was observed.

3. Radiolytic evolution of hydrogen in plutonium nitrate solutions depends upon a height of the solution in a vessel, although this dependence is apparently less than that observed under γ-radiation.

4. The effect of the solution height would be explained by a reaction between OH and H₂ because the effect can be approximately described by concentrations of undissociated HNO₃ and Pu(IV), which are thought to be primary scavengers of OH radicals.

5. The G-value for oxygen generation in plutonium nitrate solutions was roughly in accord with that observed in the 244Cm/210Po-HNO₃ system.

KEYWORDS: hydrogen, oxygen, G value, alpha particles, alpha sources, radiolysis, radiation chemistry, plutonium nitrates, nuclear fuel reprocessing

I. INTRODUCTION

Knowledge of the α-radiolysis of solutions containing plutonium nitrate (PuN) is of importance for a safety verification of a Pu storage. The hydrogen generation by the γ-radiolysis and that observed in nuclear fuel reprocessed waste solutions were summarized(10), whereas, the hydrogen generation by the α-radiolysis in nitric acid solutions was investigated with Pu(IV)-(2)-(4), 244Cm(2) and 210Po(19). Bibler et al. (4) pointed out that the G-values of hydrogen, G(H₂), with 244Cm/210Po were consistently higher than that with Pu, but a further discussion was not given. On the other hand, Bibler et al. also studied the mechanism of oxygen generation in the α-radiolysis. He presented a view divergent from the previous suggestion that the effect of Pu on the oxygen generation, namely, the Pu-catalyzed decomposition of hydrogen peroxide stated by Kazanjian et al. (3), was incorrect. We have reinvestigated the radiolytic evolution of H₂/O₂ gases, specially focussing on the effect of Pu concentration on the α-radiolysis.

Many studies of the γ-radiolysis of neutral and acidic aqueous nitrate solutions have been reported(1)-(8). Becker et al. reported that hydrogen release rates in highly β-, γ-radioactive waste solutions were considerably lower than those in laboratory experiments due to differences in the height of the solutions(6). This effect may be due primarily to the reaction between molecular hydrogen and OH radicals(19). It is expected that less effect of solution height is observed in the α-radiolysis because of lower OH radical density than that in the γ-radiolysis. No information is available about the effect of solution height in the α-radiolysis.
about the effect in PuN solutions has been, however, reported. In the present work, the effect of solution height on the hydrogen generation in PuN solutions was also investigated.

II. EXPERIMENTAL

1. Reagents

Plutonium solutions used in these experiments were prepared from the PuN solutions recovered at the Tokai Reprocessing plant and also from high purity metal (NBL 126>99.9%). The PuN was purified by an anion exchange method in nitrate form. The concentrations of foreign elements were less than 10 ppm. Two different isotopic compositions of Pu used, shown in Table 1, were obtained from four repeated determinations by mass spectrometry after the purification of the Pu by the anion exchange method. Other reagents were of analytical reagent grade. The concentrations of Ar, H₂ and O₂ gases used were 99.999%, 100 ppm (in Ar balance gas) and 100 ppm (in Ar balance gas), respectively.

2. Method

A carefully studied procedure and repeated measurements were used. A 40.0 ml sample of PuN solution was placed in a stainless steel cylindrical reaction vessel (3.6 cmØ). The PuN solutions degassed by bubbling Ar gas for 30 min were allowed to stand for 12 h in the vessel after the system was closed. The Ar gas with generated gases in the gas phase was displaced by new Ar gas after starting vibration of the vessel. The vibrator (50 Hz) attached to the outside of the vessel was confirmed to be effective for complete removal of bubbles attached to the inner surface of the vessel. The gases generated in the gas phase were circulated with Ar in a closed line by a pump once every 30 min, when the concentrations of H₂/O₂ gases were measured by a gas chromatograph (Shimadzu Model GC-14A) with a column (Molecular Sieve 5A) and a detector of TCD (Thermal Conductivity Detector). The amount of gases was calculated using the concentration, the volume of the circulation system and the gas pressure. The effect of temperature was corrected when the solutions were heated. The measured values, which showed a linear relationship between the amount of generated gas and irradiated time, were adopted for results. A slight amount of oxygen contributed by air was corrected using the initial value of oxygen contained in the Ar carrier gas. The reliability of the circulation system was confirmed with standard H₂ and O₂ gases. The G-values of H₂/O₂ shown in this paper refer to the apparent G-values calculated from the gases passing into the gas phase. The G(H₂) from identical independent experiments varied less than 5%, whereas those for oxygen varied less than 10%. The solutions were not agitated except for the above vibration, because poor reproducibility was observed when the solutions were agitated and also exact expression for the agitation seems to be difficult.

III. RESULTS AND DISCUSSION

1. Effect of Pu on Hydrogen Generation

The effect of the presence of cations on the hydrogen generation in water was reported, where the decrease of G(H₂) results from reactions between cations and eaq. The predominant reaction for the hydrogen generation in an acidic solution is H⁺H². Pu(IV) is expected to be involved in the hydrogen generation as shown in the following reaction, although Kazanjian et al. stated that Pu did not participate chemically in the radiation induced reactions for the hydrogen generation.

\[
\text{H} + \text{Pu(IV)} \rightarrow \text{Pu(III)} + \text{H}^+. \quad (1)
\]

In the presence of nitric acid or nitrate ion, the following reaction of H with NO₃⁻ can also competitively occur with a recom-
The combination reaction of $H$:
\[ H + NO_3^- \rightarrow NO_3^- + OH^- \]
\[ (2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+) \]  
(2)

The values for $G(H_2)$ in nitric acid solutions containing Pu are plotted in Fig. 1 as a function of nitrate concentration because the nitrate must be the predominant anion in the given system. The above $G$-values plotted are the average of five independently determined data points, which agreed within 6%. Published values with $^{244}$Cm\(^{4+}\) are also plotted. The results at higher concentrations of Pu are in agreement with the published values \(^{3}(1)\). The curves/plots, however, indicated that $G(H_2)$ at lower concentration of Pu came closer to the values in $^{244}$Cm. In addition, the low concentration of Pu did not decrease $G(H_2)$ as much as the higher concentration did. Assuming that $G(H_2)$ at 0 M Pu corresponds to that in $^{244}$Cm, $G(H_2)$ at a certain concentration of nitrate (4.2 M) was plotted in Fig. 2 against $[Pu(M)]^{1/3}$, which suggests that Pu(IV) acts as a scavenger of H out of spur, in much the same manner in which NO obeys the same theoretical curve. The fraction of undissociated HNO3, which does not act as a H scavenger, increases with increasing nitric acid concentration\(^{14}\). Hence, the plots of the $G$-values against nitrate concentration as shown in Fig. 1 does not provide exact comparisons of $G(H_2)$ since the concentration of nitrate as a NO\(_3^-\) form is not the same in all cases. Two kinds of PuN solutions having different Pu concentrations but the same radioactivity for both $\alpha$ and $\beta$ emission were prepared in order to accurately confirm the effect of Pu concentration. The results shown in Table 2 imply that the significant effect of Pu(IV) on $G(H_2)$ appears to be certain.

\[ \text{Total nitrate concentrations of solutions are } \bullet: 1.7 \text{ M, } \circ: 4.2 \text{ M and } \blacktriangle: 4.8 \text{ M.} \]

\[ \text{Fig. 2 Relationship between } G(H_2) \text{ and Pu(IV) concentration} \]

\[ \text{Table 2 Effect of Pu(IV) on hydrogen generation} \]

<table>
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<tr>
<th>Sample(^t)</th>
<th>No. 1</th>
<th>No. 2</th>
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</thead>
<tbody>
<tr>
<td>Concentration of Pu(IV) (g/l)</td>
<td>18.5</td>
<td>37.1</td>
</tr>
<tr>
<td>Absorption rate of $\alpha/\beta$ energy (W/l)</td>
<td>0.172/0.222</td>
<td>0.172/0.222</td>
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<tr>
<td>$G(H_2)$(^{**})</td>
<td>0.23 ± 0.01</td>
<td>0.20 ± 0.01</td>
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\(^t\) Isotopic compositions of sample Nos. 1 and 2 were identical to those shown in Table 1. The concentration of HNO\(_3\) and total nitrate were 1.30 and 1.72 M, respectively, for both the samples. The difference in [NO\(_3^-\)] was adjusted by the addition of NaNO\(_3\).

\(^{**}\) Mean value ± av. dev. for 6 repeated determinations.

Pu (VI) generated by heating solutions is said to possibly result in a positive influence on the hydrogen generation probably accompanied by its reduction, although no evidence has been reported. At a high concentration of Pu(VI), the reduction of PuO\(_2\)^{2+} by a reaction with radiolytically generated...
H$_2$O$_2$(19) would increase the hydrogen generation, because the rate of reaction between H and H$_2$O$_2$ which interferes with the hydrogen generation would be reduced. Rabideau et al., however, stated that the concentration of H$_2$O$_2$ decreased with increasing temperature(20). This implies that the decrease in the concentration of H$_2$O$_2$, not Pu(VI), may increase the hydrogen generation. The effect of heating on $G$(H$_2$) was investigated by either keeping the temperature of PuN solution at 70° or cooling it from 70° to 25°. In the latter case, the fraction of Pu(VI) was decreased from 45% to less than a few percent. (The rest of the fraction was Pu(IV).) No significant difference was observed in $G$(H$_2$) regardless of the heating as shown in Table 3. This result indicates either that the above effect can be negligible or that other reactions giving a negative bias are involved. The reaction between PuO$_2^{2+}$ and H would, for instance, occur(19), which reduces the hydrogen generation. The chemical reduction of Pu(VI) by H$_2$ may also be involved at low concentration of nitric acid(17).

Table 3 Effect of heating solution on hydrogen generation*1

<table>
<thead>
<tr>
<th>$G$(H$_2$) at 25°</th>
<th>$G$(H$_2$) at 70°*2</th>
<th>$G$(H$_2$) at 70°*3</th>
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<td>0.36±0.01</td>
<td>0.36±0.01</td>
<td>0.35±0.01</td>
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</table>

*1 Concentrations of Pu and HNO$_3$ were 10.0g/l and 0.6M, respectively. Pu(VI) was confirmed to be 45% of total Pu at 70°. The value shown is mean ±av. dev. for 4 repeated determinations.
*2 Temperature of solution was kept at 70°.
*3 Solution was cooled from 70° to 25°.

2. Dependence of Hydrogen Released on Height of Solution

It has been proposed that the effect of the height of solution on hydrogen released is due to the following reaction(1):

$$\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}.$$  (3)

Assuming that the above explanation is true, the effect under $\alpha$-radiation is expected to be less than that under $\beta/\gamma$-radiation because apparent $G$(OH) under $\alpha$-radiation observed out of tracks is small relative to that under $\beta/\gamma$-radiation(18). On the other hand, a certain fraction of OH would be scavenged by Pu in solutions(15), so that the concentration of Pu also may be involved in the effect of the height of solution. The $G$-values of molecular hydrogen ($G$(H$_2$)) on varying the solution height were investigated, where the volume of solution remained unchanged (40 ml). Specht et al. suggested that the corrosion products of stainless steel catalyzed the recombination of H$_2$ with O$_2$(14). The $G$-value for the same solution height with additional thin stainless steel foil soaked was investigated. No significant difference was found, which implies that the stainless steel did not significantly work as a catalyst in this experiment. Values for $G$(H$_2$) as a function of the solution height are shown in Fig. 3, where the $G$-values decrease almost linearly with a small slope. It is obvious that two PuN solutions having the same concentration of Pu but different concentrations of nitric acid showed a significant difference in the effect of the solution height.

![Graph showing dependence of $G$(H$_2$) on height of solution](image)

It is probable that this is due to the difference in the concentration of undissociated nitric acid known to be an OH scavenger(15), which should decrease the reaction (3). It was also confirmed that the effect of solution height under $\alpha$-radiation was apparently less than that under $\gamma$-radiation. These results can also
be considered evidence for the validity of the above explanation for the effect of the solution height. The dependence of the effect of solution height on Pu was investigated at the same concentration of OH radicals. Two PuN solutions having the same concentration of α/β emitters but different concentrations of Pu (shown in Table 2) were used. A small but significant contribution of Pu to the decrease in the effect of solution height was found as shown in Fig. 4. This may be in accord with the conclusion that Pu (IV) scavenges OH as stated in the previous study(13). Assuming that the effect of the solution height is due only to the reaction (3), $G(H_2)$, the $G$-value for a height of $h$ is described by

$$G(H_2)_h = G(H_2)_0 - G(H_2)_d,$$

where $G(H_2)_0$ and $G(H_2)_d$ are the $G$-values at a position having no effect of solution height (4 cm for this experiment) and that of decomposed $H_2$ by reaction (3), respectively. Thus, divided by $G(H_2)_0$,

$$G(H_2)_h/G(H_2)_0 = 1 - G(H_2)_d/G(H_2)_0,$$

$G(H_2)_d$ is described by $G(OH) \cdot W$, where $W$ is the fraction of the reaction between OH and $H_2$ in all the reactions scavenging OH

$$G(H_2)_h/G(H_2)_0 = 1 - G(OH) \cdot W/G(H_2)_0.$$  

The OH radicals in this system would primarily react with undissociated HNO₃ and Pu(IV), referring to the previous work(13):

$$G(H_2)_h/G(H_2)_0 = 1 - G(OH)/G(H_2)_0 \cdot k_{H_2}[H_2]/(k_{HNO_3}[HNO_3] + k_{Pu}[Pu] + k_{H_2}[H_2])$$

$$= 1 - G(OH)/G(H_2)_0 \cdot k_{H_2}[H_2]/(k_{HNO_3}[HNO_3] + k_{Pu}[Pu]),$$

where $k_{H_2}$, $k_{HNO_3}$ and $k_{Pu}$ are bimolecular rate constants of the reactions of OH-$H_2$, OH-HNO₃ and OH-Pu, respectively; $[H_2]$ represents the apparent concentration of $H_2$ involving the effect of the shape of the same volume of solution on the hydrogen generation. $[H_2]$ can be regarded to be approximately proportional to $G(H_2)_0 \cdot h$ because $G(H_2)_h$ almost linearly decreases with increasing $h$ as shown in Fig. 4. Since $G(OH)$ is constant in the given solutions,

$$G(H_2)_h/G(H_2)_0 = 1 - K \cdot h/(k_{HNO_3}[HNO_3] + k_{Pu}[Pu]) \cdot (4)$$

It was found that a good fit can be obtained for both the straight lines shown in Fig. 3 when a certain value was taken for the constant $K$ in Eq. (4), where $k_{HNO_3}$ and $k_{Pu}$ are, respectively, $1 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}(18)$ and $2 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ that was obtained from the result of the previous report(13). It was also confirmed that Eq. (4) with the same value for $K$ fairly satisfied the straight lines shown in Fig. 4. These imply that Eq. (4) would be an approximate expression for the effect of solution height in PuN solutions.

3. $G(O_2)$ for PuN Solution

Both Kazanjian et al.(3) and Sheppard(2) showed that $G(O_2)$ decreased continuously with increasing nitric acid concentration up to 10 M. That was explained by the following Pu-catalytic reaction that was predominant among the reactions producing oxygen(3):

$$2H_2O_2 \rightarrow O_2 + 2H_2O,$$

$G(O_2)$ decreased with increasing $NO_3^-$ because nitrous acid, the main radiolysis product of HNO₃, rapidly reacted with $H_2O_2$. Bibler,
however, showed apparently inconsistent results, namely that \( G(O_2) \) increased with increasing \( NO_3^- \), based on the following predominant reaction:

\[
NO_3^- \xrightarrow{\alpha} NO_2^- + O (O + O \rightarrow O_2).
\]  

(6)

He suggested that the difference was due to the fact that a sizeable fraction of gases can remain in solution because of the absence of agitation of the solution. He also indicated that the direct decomposition of HNO_3 was not occurring in the \( \alpha \)-radiolysis. Although the gas generated was collected without agitation of the solution except for vibrating the solution in this work, good agreement with other literature results was observed in the hydrogen generation as shown previously. Figure 5 shows \( G(O_2) \) plotted against \( NO_3^- \) obtained with a relatively high concentration of Pu (100~210 g/l) where literature data are also plotted. It was found that our results nearly agreed with the \( G(O_2) \) observed with \( ^{244}\text{Cm} \) or \( ^{244}\text{Cm} + ^{239}\text{Pu}(4) \) and that of \( ^{210}\text{Po}(5) \).

The results shown in Fig. 5 agreed with the literature data in spite of the fact that the concentrations of \( NO_3^- \) and HNO_3 varied widely, which suggests the presence of both reactions (6) and (7). Although no explanation for the disagreement in \( G(O_2) \) between the previous published literature(2)(3) and Bibler's(4) has been offered here, the trend that \( G(O_2) \) increases with increasing nitrate concentration, which Bibler also showed, is concluded to be correct.

### IV. CONCLUSION

Radiolytic generation of \( H_2 \) and \( O_2 \) gases in PuN solutions were studied.

(1) Plutonium (IV) is found to be involved in the \( G \)-value for the hydrogen generation, which can explain the difference in \( G \)-values in a \( ^{244}\text{Cm} \)-HNO_3 solution and a Pu(IV)-HNO_3 solution.

(2) Heating PuN solutions, by which Pu(VI) was formed, showed no significant difference in the hydrogen generation.

(3) The dependence of radiolytic evolution of hydrogen upon the height of the solution in a vessel is apparently found to be less than that observed under \( \gamma \)-radiation.

(4) The reaction between OH and \( H_2 \) may explain the effect of solution height on the hydrogen generation because the effect would be approximately described with the concentrations of principal OH scavengers, namely undissociated HNO_3 and Pu(IV).

(5) It was reconfirmed that \( G(O_2) \) increased with increasing \( NO_3^- \), which approximately agreed with \( G(O_2) \) observed in nitrate solutions containing \( ^{244}\text{Cm}/^{210}\text{Po} \).

### ACKNOWLEDGMENT

The authors wish to express here great appreciation to Dr. S. Matsuoka, Japan Nuclear Fuel Co., Ltd. for his kind suggestions.

### REFERENCES


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Errata (Vol. 30, No. 7 (1993))

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