

Alpha radiolysis of nitric acid aqueous solution irradiated by ²³⁸Pu source

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Abstract Alpha radiolysis of nitric acid aqueous solution by a ²³⁸Pu source is investigated experimentally and theoretically. The time dependence of the nitrous acid yield on dose rate, nitric acid concentration, and nitrate ion concentration is studied. A novel kinetic model for the α -radiolysis of nitric acid aqueous solution is established, by considering the direct and indirect effects. The simulation results agree well with the experimental data, indicating the validity of our model to treat the reaction paths for generation and consumption of nitrous acid. It is shown that the redox reactions involving Pu cannot be neglected in the α -radiolysis of the solution. The results provide a better understanding of the α -ray radiolysis of aqueous nitric acid.

Keywords α -Radiolysis · Nitric acid · Plutonium · Aqueous solution · Kinetic model · Nitrous acid

1 Introduction

Nitric acid is the most common inorganic acid used in the Plutonium Uranium Recovery EXtraction (PUREX) process, under intense α , β , and γ radiations [1–4]. The

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radiolytic products of aqueous nitric acid, such as nitrous acid, hydrogen peroxide, hydrogen, and oxygen, affect the organic phase degradation, valence of actinides, corrosion of the container, and the reductants in PUREX [4, 5]. Thus, investigation on the radiolysis of nitric acid attracts increasing attention [5-10].

Experiments on radiolysis of solid nitrates were began in 1970s [11-15], and the direct radiolysis effect was proposed. For nitric acid aqueous solution, the reactions involved are more complex due to the influence of water radiolysis. The formation of gases (e.g., H_2 and O_2) in the solution was investigated [15-18]. It was proved that both the direct radiolysis of solutes and the reactions between radiolytic products and water contributed to the production of gases. However, while there are many experimental and theoretical works on y-ray radiolysis of aqueous nitric acid [7-9, 19-21], just limited investigations using an α -radiation source have been reported [16–18, 22–25], largely due to the lack of an α irradiation facility and the operation difficulties. The yield of HNO₂ was measured by Miner et al. [26] with the ²³⁸Pu microsphere as an α -radiation source. The survey on HNO₂ yield is important for understanding the mechanism of α radiolysis of aqueous nitric acid and for the application in PUREX, considering that HNO₂ can consume the reductant for Pu(III) in PUREX. However, the concentration gradient of nitric acid in Ref. [22] is too large to be applied for practical use. On the theoretical side, the redox reactions about Pu and some radiolytic products of nitric acid were proposed in Refs. [27, 28], though the primary yields of some radicals and several reactions involving nitric acid were absent. To the best of our knowledge, there is still no complete kinetic model for the α -radiolysis of aqueous nitric acid.

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In this paper, experiments on production of NO₂⁻ using ²³⁸Pu as the α -radiation source is conducted (²³⁸Pu decays, in a half-life of 87.7 years, by emitting α particles in averaged energy of 5.49 MeV). A novel complete kinetic model for α -radiolysis of aqueous nitric acid is established using MCPA FACSIMILE version 4.0 (MCPA Software Ltd., UK) [29]. FACSIMILE is a powerful modeling tool designed to efficiently solve differential equations in engineering and scientific researches and is widely used in chemical kinetic simulation [30, 31]. The experimental and simulation results should benefit for a better understanding of the radiolysis of aqueous nitric acid in our work is within the range of that in the typical PUREX process.

2 Materials and methods

2.1 Materials

The ²³⁸Pu in the form of PuO₂ powder and the deionized water (18.25 M Ω cm) were provided by China Institute of Atomic Energy. The nitric acid and sodium nitrate were analytically pure (Sinopharm Group Co. Ltd.).

2.2 Preparation of stock solution

A ²³⁸Pu solution, instead of the ²³⁸Pu microsphere [26], was employed, in consideration of radiation uniformity, convenience of dose rate determination (nearly all radiation energy was absorbed by the solution), and the less amount (just mg or less) of α emitter required for the experiments [26].

The long-term stock solution was prepared by dissolving 238 PuO₂ powder in aqueous nitric acid catalyzed by Ag⁺– Ag²⁺ cycle under constant-current electrolysis. The 238 Pu(IV)–NO₃⁻ stock solution was purified with No. 2606 anion exchange resin packed column (offered by China Institute of Atomic Energy). During the purification, Pu was adsorbed in the exchange column and the Ag⁺ remained with the solution. The Pu was eluted by 0.35 M HNO₃ solution. It is worth noting that there should be radiolytic resin products in solution, since the Pu is a strong radiation source. Thus, before the experiments, the small amount of stock solution to be used was purified again with the same method. In the second purification, the radiation source was less and the purification time was shorter, with negligible radiolytic products.

2.3 Preparation of experimental solutions

The stock solution was adjusted to desired conditions. Different dose rates were achieved by adjusting the Pu concentration, noted as c(Pu), and the variation of NO₃⁻ concentration was realized by adding sodium nitrate. The concentration of nitric acid used in the experiments was within the range of PUREX process (about 1.0–5.0 M); thus, the results are suggestive for understanding of the actual α -radiolysis of aqueous nitric acid.

2.4 Characterization

The concentration of nitrous acid was determined by spectrophotometry (SPECORD S600 Spectrophotometer, Analytik Jena AG, German), using a 1-cm quartz cuvette (YiXing JingKe Optical Instrument Co. Ltd.). Spectrophotometry was used to continuously measure the production of nitrous acid.

2.5 Kinetic model

There are many reaction paths for the α -radiolysis of aqueous nitric acid. Firstly, the radiolytic products of water react with nitric acid or nitrate ion [30]:

$$OH + HNO_3 \rightarrow NO_3 + H_2O, \quad k = 1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1},$$
(1)

$$H + NO_3^- \to HNO_3^-, \quad k = 1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}.$$
 (2)

The effect of direct radiolysis of solute also plays an important role for concentrated solution, as the solute absorbs a large fraction of the radiation energy [21]:

$$NO_3^- - \vee \vee \to NO_2^-, O(^1D), O(^3P),$$
 (3)

$$O(^{1}D) + H_{2}O \rightarrow H_{2}O_{2}, \qquad (4)$$

$$O(^{3}P) + NO_{3}^{-} \rightarrow NO_{2}^{-} + O_{2}.$$
(5)

For concentrated nitric acid solution, radiolysis of the un-dissociated nitric acid molecule should not be neglected [20, 21]:

$$HNO_3 - \forall \forall \to HNO_2, O(D), O(P),$$
(6)

$$HNO_3 - \forall \forall \to NO_3 + e_{aq} + H^+.$$
(7)

In addition, the actinides can react with radicals in aqueous nitric acid [27, 32]. The redox reactions involving actinides may also affect the generation and consumption of nitrous acid, for example [27]:

$$\frac{Pu(III) + NO_2 \rightarrow Pu(IV) + NO_2^-}{k = 2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}},$$
(8)

Therefore, in order to get an overall picture about the radiolysis of aqueous nitric acid under α -radiation, we set up a kinetic model including the primary yields of the radicals for the radiolysis of both pure water and nitric acid, and the reaction sets for the reaction between these radicals and nitric acid, water, and Pu.

The radical yields of pure water, nitric acid, and nitrate ion are essential to the simulation for α -radiolysis of nitric acid aqueous solution. The primary yields for the α -radiolysis of pure water at α -particle energy of 4.6 MeV were reported by Eriksen et al. [33]. This energy is close to the averaged α -particle energy for ²³⁸Pu (5.5 MeV), so the radical yields in Ref. [34] were used in this work with slight adjustment. Due to the rapid scavenging reaction between presolvated electron and nitrate ion, NO₃²⁻ should replace e_{aq}^{-} . Linear energy transfer (LET) effect was also considered. The radical yields for pure water are given in Table 1. The γ -radiolysis of nitric acid/nitrate ion was studied by Jiang et al. [21]. For α -radiolysis, the decomposition paths should be the same and the radical yields should be smaller. The radical yields used in this work (the right rows of Table 1) are adjusted by fitting with experimental data.

The yield of certain radical in solution is described by:

$$G_{\text{tot}}(X_i) = \sum_j G_{Y_j}(X_i) f_j, \tag{9}$$

where X_i is the *i*th radical; Y_j is the *j*th component (water, molecular nitric acid, nitrate ion, etc.) of solution; and $f_j = N_j/N_{tot}$ is the electron fraction of that component, with N_j and N_{tot} being the electron number of the corresponding component and total electron number of the solution, respectively. The absorbed energy for corresponding component ($E_j = E_{tot}f_j$) varies as the concentration of solute changes. E_{tot} represents the total energy absorbed by the solution. Thus, the primary radical yield varies as the concentrations of solutes change.

In order to build a kinetic model, the reaction sets and corresponding rate constants about water, nitric acid, and Pu are needed. The reactions between radicals produced in pure water radiolysis have been studied by many researchers. Buxton et al. [35] summarized the reactions and determined the selected values for reaction rate constants. Elliot and Bartels reported the reaction rate constants in water radiolysis with temperature from room temperature to 300 °C based on the experimental data in Chalk River Laboratory [36]. The reactions about pure water radiolysis can be obtained from the two works. There are various nitrogenous radicals and corresponding reactions in the radiolysis of nitric acid aqueous solution [34, 37–39]. In Pu + HNO₃ system, reactions involving Pu have been studied by Vladimirova [27, 28]. All the reactions and rate constants used in this model are summarized in Table 2.

The numerical calculations in the simulation for the radiolysis of aqueous nitric acid were conducted with MCPA FACSIMILE [29]. All the primary yields and reaction rate constants keep invariant, while the dose rate, pH value, and nitrate ion concentration vary.

3 Results and discussion

3.1 Time dependence of absorbance curve

The typical absorbance curve for the aqueous nitric acid solution of 238 Pu as a function of irradiation time (up to 300 min) is illustrated in the upper part of Fig. 1, with the wavelength from 340 to 500 nm. The absorbance peaks of Pu(III), Pu(IV), Pu(V), and Pu(VI) appear at 600, 476, 569, and 831 nm, respectively [40–42]. Their corresponding molar absorption coefficients are 36, 68, 20, and 158 M⁻¹ cm⁻¹, respectively. (The molar absorption coefficients of Pu vary with the HNO₃ concentration. Only typical values are shown here.) In Fig. 1, the absorbance peaks for Pu(IV) is distinct and has little variation. The peaks for Pu(V) and Pu(IV) are not observed, and that for Pu(III) is quite weak (not shown in Fig. 1). This indicates that Pu ions are mostly tetravalent during experiment.

The absorbance curve changes obviously around 371 nm, so the area near 371 nm is enlarged in the lower part of Fig. 1. One of the five absorbance peaks of nitrous acid is located at 371 nm. As the concentration of Pu(IV) is nearly invariant, the change in absorbance around 371 nm can be completely attributed to the production of nitrous

Table 1 Primary radical yields (in 100 eV^{-1}) of pure water, un-dissociated nitric acid, and nitrate ion

Radiolysis of pure water				Radiolysis of un-dissociated nitric acid		Radiolysis of nitrate ion	
Radicals	G value	Radicals	G value	Radicals	G value	Radicals	G value
$G_{ m H_2O}(m H^{\cdot})$	0.21	$G_{\mathrm{H}_{2}\mathrm{O}}(^{\cdot}\mathrm{HO}_{2})$	0.22	$G_{\mathrm{HNO}_3}(\mathrm{HNO}_2)$	0.5	$G_{\mathrm{NO}_3^-} ig(\mathrm{NO}_2^-ig)$	0.7
$G_{\mathrm{H_2O}}(\mathrm{H_2})$	1.23	$G_{\mathrm{H_2O}}(\mathrm{^{\cdot}NO_3^{2-}})$	0.2	$G_{\mathrm{HNO}_3}(^{\cdot}\mathrm{O}(\mathrm{P}))$	0.5	$G_{\mathrm{NO}_3^-}(^{\circ}\mathrm{O}(\mathrm{P}))$	0.7
$G_{\rm H_2O}(^{-}\rm OH)$	0.24						

Due to the rapid reaction between presolvated electron and nitrate ion, NO_3^{2-} is expressed instead of the hydrated electron [6]

Table 2 Reaction set and corresponding reaction constants between the nitric acid, water, Pu, and radicals

No.	Reaction	Rate constant	No.	Reaction	Rate constant
R001 [35]	$e_{aq}^- + H_2O \rightarrow H^- + OH^-$	1.9×10^{1}	R113 [46]	$OH + NO_2 \rightarrow ONOOH$	4.5×10^{9}
R002 [35]	$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-$	5.5×10^{9}	R114 [37]	$H_2O_2 + HNO_2 \rightarrow ONOOH + H_2O$	7.17×10^{5}
R003 [35]	$e_{aq}^- + H^- \rightarrow H_2 + OH^-$	2.5×10^{10}	R115 [37]	$ONOOH + H_2O \rightarrow H_2O_2 + HNO_2$	3×10^2
R004 [35]	$e_{aq}^- + OH \rightarrow OH^-$	3.0×10^{10}	R116 [39]	$ONOOH \rightarrow H^+ + NO_3^-$	0.9×10^{0}
R005 [35]	$e_{aq}^- + O^- \rightarrow 2OH^-$	2.2×10^{10}	R117 [37]	$^{\circ}H + ^{\circ}NO_2 \rightarrow H^+ + NO_2^-$	1.0×10^{10}
R006 [35]	$e_{aq}^{-} + H^{+} \rightarrow H^{-}$	2.3×10^{10}	R118 [37]	$e_{aq}^- + NO_2 \rightarrow NO_2^-$	1.0×10^{10}
R007 [35]	$e_{aq}^{-} + H_2O_2 \rightarrow OH^{-} + OH$	1.1×10^{10}	R119 [35]	$e_{aq}^{-} + NO_2^{-} \rightarrow NO_2^{2-}$	3.5×10^{9}
R008 [35]	$e_{aq}^{-} + HO_2^{-} \rightarrow 2OH^{-} + OH$	3.5×10^{9}	R120 [46]	$H + NO_2^- \rightarrow NO + OH^-$	1.6×10^{9}
R009 [35]	$e_{aq}^{-} + O_2 \rightarrow O_2^{-}$	1.9×10^{10}	R121 [35]	$OH + NO_2^{2-} \rightarrow NO_2^{-} + OH^{-}$	3.0×10^{9}
R010 [35]	$e_{aq}^{-} + O_2^{-} \rightarrow O_2^{2-}$	1.3×10^{10}	R122 [35]	$H^+ + NO_2^{2-} \rightarrow NO + OH^-$	2.0×10^{10}
R011 [35]	$H^{-} + H_2O \rightarrow H_2 + OH$	1.0×10^{1}	R123 [35]	$H_2O + NO_2^{2-} \rightarrow NO + 2OH^-$	1.0×10^{5}
R012 [35]	$H^{\cdot} + H^{\cdot} \rightarrow H_2$	7.8×10^{9}	R124 [39]	$ONOOH \rightarrow H^+ + ONOO^-$	5.0×10^{4}
R013 [35]	$H' + OH \rightarrow H_2O$	7.0×10^{9}	R125 [39]	$H^+ + ONOO^- \rightarrow ONOOH$	5.0×10^{10}
R014 [35]	$H' + OH^- \rightarrow e_{aq}^- + H_2O$	2.2×10^{7}	R126 [47]	$2HNO_2 \rightarrow NO + NO_2 + H_2O$	1.34×10^{1}
R015 [35]	$H' + H_2O_2 \rightarrow OH + H_2O$	9.0×10^{7}	R127 [47]	$NO + NO_2 + H_2O \rightarrow 2HNO_2$	1.68×10^{8}
R016 [35]	$H^{\circ} + O_2 \rightarrow HO_2^{\circ}$	2.1×10^{10}	R128 [39]	$ONOOH \rightarrow NO_2 + OH$	3.5×10^{-1}
R017 [35]	$H^{-} + HO_{2}^{-} \rightarrow H_{2}O_{2}$	1.14×10^{10}	R129 [37]	$HNO_2 + HNO_3 \rightarrow 2^{\circ}NO_2 + H_2O$	4.5×10^{-2}
R018 [35]	$OH + OH \rightarrow H_2O_2$	5.5×10^{9}	R130 [47]	$2 \text{ NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$	8.4×10^{7}
R019 [35]	$OH + O^- \rightarrow HO_2^-$	7.61×10^{9}	R131 [35]	$OH + HNO_2 \rightarrow NO_2 + H_2O$	2.6×10^{9}
R020 [35]	$OH + H_2 \rightarrow H + H_2O$	4.2×10^{7}	R132 [48]	$H + HNO_2 \rightarrow NO + H_2O$	4.5×10^{8}
R021 [35]	$OH + OH^- \rightarrow O^- + H_2O$	1.3×10^{10}	R133 [49]	$NO_3 + HNO_2 \rightarrow NO_2 + HNO_3$	2.0×10^{8}
R022 [35]	$OH + H_2O_2 \rightarrow H_2O + HO_2$	2.7×10^{7}	R134 [37]	$HNO_2 \rightarrow H^+ + NO_2^-$	4.6×10^{6}
R023 [35]	$OH + HO_2^- \rightarrow OH^- + HO_2$	7.5×10^{9}	R135 [37]	$H^+ + NO_2^- \rightarrow HNO_2$	1.0×10^{10}
R024 [35]	$OH + H_2O_2^+ \rightarrow H_3O^+ + O_2$	1.2×10^{10}	R136 [50]	$HNO_3 \rightarrow H^+ + NO_3^-$	2.0×10^{10}
R025 [35]	$OH + HO_2 \rightarrow H_2O + O_2$	6.0×10^{9}	R137 [50]	$H^+ + NO_3^- \rightarrow HNO_3$	4.4×10^{8}
R026 [35]	$OH + O_2^- \rightarrow OH^- + O_2$	8.0×10^{9}	R138 [21]	$NO_3^- + O(P) \rightarrow NO_2^- + O_2$	2.2×10^{9}
R027 [35]	$O^- + H_2O \rightarrow OH^- + OH$	1.8×10^{6}	R139 [38]	$NO_2 + HO_2 \rightarrow HNO_2 + O_2$	1.8×10^{9}
R028 [35]	$0^{-} + 0^{-} \rightarrow 0_{2}^{2-}$	9.0×10^{8}	R140 [38]	$NO_2 + O_2^- \rightarrow NO_2^- + O_2$	4.5×10^{9}
R029 [35]	$O^- + H_2 \rightarrow OH^- + H^-$	8.0×10^{7}	R141 [this work]	$NO \rightarrow NO(g)$	9.0×10^{-2}
R030 [35]	$O^{-} + H_2O_2 \rightarrow O_2^{-} + H_2O_2$	7.08×10^{8}	R141 [30]	$NO_3 + H_2O \rightarrow HNO_3 + OH$	3.0×10^{2}
R031 [35]	$O^- + HO_2^- \rightarrow O_2^- + OH^-$	4.0×10^{8}	R142 [30]	$NO_3 + H_2O_2 \rightarrow HNO_3 + HO_2$	7.1×10^{6}
R032 [35]	$O^- + O_2 \rightarrow O_3^-$	3.6×10^{9}	R143 [30]	$NO_3 + HO_2 \rightarrow HNO_3 + O_2$	3.0×10^{9}
R033 [35]	$O^- + O_2^- \rightarrow 2OH^- + O_2$	6.0×10^{8}	R201 [27]	$Pu(IV) + e_{ra}^{-} \rightarrow Pu(III)$	1.0×10^{11}
R034 [36]	$HO_2 \rightarrow O_2^{} + H^+$	6.62×10^5	R202 [27]	$Pu(IV) + H \rightarrow Pu(III) + H^+$	1.0×10^{8}
R035 [36]	$O_2^{-} + H^+ \rightarrow HO_2$	4.52×10^{10}	R203 [27]	$Pu(VI) + e_{aa}^{-} \rightarrow Pu(V)$	6.5×10^{10}
R036 [36]	$H_2O_2 \rightarrow H^+ + HO_2^-$	6.49×10^{-2}	R204 [27]	$Pu(VI) + H \rightarrow Pu(V) + H^+$	6.5×10^{7}
R037 [36]	$H^+ + HO_2 \rightarrow H_2O_2$	4.52×10^{10}	R205 [27]	$Pu(VI) + HNO_2 \rightarrow Pu(V) + NO_2 + H^+$	1×10^{-1}
R038 [36]	$H_2O_2 \rightarrow H_2O + (1/2)O_2$	8.29×10^{-8}	R206 [27]	$Pu(V) + NO_2 \rightarrow Pu(VI) + NO_2^{-1}$	1.9×10^4
R101 [35]	$NO_2^- + e^- \rightarrow NO_2^{2-}$	9.7×10^9	R207 [27]	$Pu(IV) + HNO_2 \rightarrow Pu(III) + NO_2 + H^+$	7×10^{-3}
R102 [48]	$NO_2^- + H^- \rightarrow OH^- + NO_2$	1.4×10^{6}	R208 [27]	$Pu(III) + NO_2 + H^+ \rightarrow Pu(IV) + HNO_2$	2.5×10^{3}
R103 [37]	$HNO_2 + H \rightarrow H_2 + NO_2$	1.0×10^{7}	R209 [27]	$Pu(V) + NO_2 + H^+ \rightarrow Pu(VI) + HNO_2$	1×10^9
R104 [35]	$NO_2^{2-} + H^+ \rightarrow OH^- + NO_2$	2.0×10^{10}	R210 [27]	$Pu(III) + NO_2 + H^+ \rightarrow Pu(IV) + HNO_2$	2.5×10^{8}
R105 [35]	$NO_2^{2-} + H_2O \rightarrow 2OH^- + NO_2$	5.6×10^4	R211 [27]	$Pu(IV) + NO_2 + H^+ \rightarrow Pu(V) + HNO_2$	6×10^2
R106 [35]	$NO_2^{2-} + O_2 \rightarrow NO_2^{-} + O_2^{-}$	2.4×10^{8}	R212 [27]	$Pu(V) + Pu(IV) \rightarrow Pu(VI) + Pu(III)$	1.2×10^{1}
R107 [35]	$NO_2^{2-} + OH \rightarrow NO_2^{-} + OH^{-}$	3.0×10^9	R213 [27]	$Pu(VI) + Pu(III) \rightarrow Pu(V) + Pu(IV)$	2.4×10^{10}
R108 [20]	$HNO_2 + OH \rightarrow NO_2 + H_2O$	1.4×10^8	R214 [27]	$Pu(V) + Pu(III) \rightarrow 2Pu(IV)$	3.5×10^{0}
R109 [35]	$NO_2 + OH \rightarrow NO_2 + HO_2$	2.9×10^{7}	R215 [27]	$2\operatorname{Pu}(\mathrm{IV}) \rightarrow \operatorname{Pu}(\mathrm{V}) + \operatorname{Pu}(\mathrm{III})$	3×10^{-6}
R110 [51]	$2^{\circ}NO_2 \rightarrow 2^{\circ}NO_2 \pm O_2$	7.9×10^5	R216 [27]	$2\operatorname{Pu}(V) \rightarrow \operatorname{Pu}(V) + \operatorname{Pu}(V)$	1×10^{-2}
K110 [J1]	$2100_3 \rightarrow 2100_2 + 0_2$	1.7 \ 10	1210 [2/]	$21 u(v) \rightarrow 1 u(1v) + 1 u(v1)$	1 × 10

Table 2	2 continued
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No.	Reaction	Rate constant	No.	Reaction	Rate constant
R111 [35]	$NO_2^- + OH \rightarrow NO_2 + OH^-$	9.6×10^{9}	R217 [27]	$Pu(IV) + H_2O_2 \rightarrow Pu(III) + HO_2 + H^+$	2×10^3
R112 [35]	$NO_2^- + NO_3 \rightarrow NO_2 + NO_3^-$	1.2×10^{9}	R218 [27]	$Pu(VI) + H_2O_2 \rightarrow Pu(V) + HO_2 + H^+$	3×10^{-2}

The units of reaction rate constants for second-order reactions are $M^{-1} s^{-1}$, and those of rate constants for first-order reactions are s^{-1}



Fig. 1 Evolution of absorbance curve for aqueous nitric acid solution of 238 Pu with time. c(Pu) = 1.7 g/L; $c(HNO_3) = 4.0$ M; optical path 1.0 cm

acid. The equilibrium constant for dissociation of nitrous acid is $10^{-3.27}$ M [43]. The solution is strongly acidic in experiment, with the concentration of HNO₃ ranging from 1.0 to 5.0 M. So nitrous acid hardly dissociates. The absorbance at 371 nm represents the changes in nitrous acid concentration, noted as $c(\text{HNO}_2)$. The absorbance $A = \varepsilon cl$, where ε is the molar absorption coefficient, c is the concentration, and l is the optical path. The molar absorption coefficient of nitrous acid is taken from Ref. [44]: $\varepsilon(\text{HNO}_2, 371 \text{ nm}) = 60.46 \text{ M}^{-1} \text{ cm}^{-1}$ and $\varepsilon(\text{NO}_2^{-}, 371 \text{ nm}) = 16.18 \text{ M}^{-1} \text{ cm}^{-1}$.

3.2 Valence of Pu

The simulated oxidation states of Pu as a function of irradiation time is shown in Fig. 2. It is obvious that the valences of Pu hardly change during experiment. Pu is predominantly tetravalent. This is in agreement with experimental results.

What should be emphasized is that the radiolysis behavior of aqueous nitric acid takes place as early as PuO_2 powder is suspended in stock solution (0.35 M nitric acid). However, the reactions following the complete dissolution of PuO_2 powder in aqueous nitric acid are complex and



Fig. 2 Percentages of Pu(III) and Pu(IV) versus the irradiation time, at c(Pu) = 1.7 g/L and $c(HNO_3) = 3.0$ M. The percentages of Pu(V) and Pu(VI) are not shown in the figure as they are two orders of magnitude smaller than of Pu(III)

unpredictable as the inhomogeneity of solution and impurities are involved. As shown in experiment, Pu is mainly tetravalent in the stock solution, and the valences of Pu have little change during experiment. For simplicity, Pu is assumed to be tetravalent totally. Besides, the variation instead of amount of $c(HNO_2)$ is concerned in this work. Without loss of generality, the $c(HNO_2)$ in stock solution is set to be zero in simulation.

3.3 Dose rate effect

Since the radiation energy is almost totally absorbed by the solution, the absorbed dose is proportional to the concentration of Pu. The dose rate effect on the production of nitrous acid is investigated by varying the concentration of Pu. Figure 3 shows the experimental and theoretical results of absorbance at 371 nm as a function of the irradiation time. The dose rate of solution using 1 g/L Pu as radiation source is 32.5 Gy min⁻¹. (The exact value of dose rate varies with the solution density. Such effect is taken into consideration in our calculation.)

This value is calculated from the half-life of 238 Pu (87.7 years) and the averaged energy of α particles



Fig. 3 Radiation time dependence of absorbance at 371 nm with different concentrations of 238 Pu; $c(HNO_3) = 3.0$ M; optical path 1.0 cm

(5.5 MeV) assuming that all the energy of α particles is absorbed by the solution. The calculated value has good consistency with the measured data using scintillation spectrometry within the experimental time range. The experimental method was described in our previous work [45]. Thus, the kinetic model is suitable to describe the α radiolysis of nitric acid aqueous solution using ²³⁸Pu as the radiation source. The production of nitrous acid increases with increasing dose obviously.

3.4 Variation of the concentration of nitric acid

Figure 4 shows the time dependence of absorbance at 371 nm with different concentrations of nitric acid. The calculation results fit fairly well with the experimental data. The nitrous acid production increases with the concentration of nitric acid. Together with the results about dose rate effect (shown in Fig. 3), one can see that the radical yield, instead of nitric acid concentration, is vital for the nitrous acid yield, within the range of nitric acid concentration and dose rate in this experiment. Thus, the roughly overall reaction about nitrous acid yield, namely $NO_3^- \leftrightarrow$ $NO_2^- + O'$, is far from being desired. Besides, as the nitric acid concentration rises, the electron fraction of each component varies, hence the changes in radical yield. Such change in radical yield has little effect on the nitrous acid yield, either. That can be roughly explained by the competition among the radiolysis of pure water, un-dissociated nitric acid, and nitrate ion.

3.5 Variation of concentration of nitrate ion

Both the concentrations of molecular nitric acid and nitrate ion change with $c(HNO_3)$. Figure 5 shows the



Fig. 4 Time dependence of the absorbance at 371 nm with different concentrations of nitric acid. c(Pu) = 1.7 g/L; optical path 1.0 cm

measured and simulated absorbance at 371 nm with different $c(NaNO_3)$ as a function of irradiation time, at $c(HNO_3) = 1.0$ M and c(Pu) = 2.9 g/L. The two results agree well with each other. It is seen that the yield of HNO₂ increases with $c(NO_3^-)$ slowly. Since the radiolysis of pure water produces more radicals, the increase in $c(NO_3^-)$ only increase the yield of radicals slightly. Thus, the production of HNO₂ has an unconspicuous increase with $c(NaNO_3)$ from 1.41 to 3.53 M.

3.6 Effect of redox reactions about Pu

The influences of the reactions involving Pu (R201–R218 in Table 2) on the production of HNO₂ were analyzed. In order to check the effects of R201–R218, Fig. 6a shows the simulated absorbance at 371 nm with the model



Fig. 5 Time dependence of absorbance at 371 nm with different concentrations of NaNO₃; $c(\text{HNO}_3) = 1.0 \text{ M}; c(\text{Pu}) = 2.9 \text{ g/L};$ optical path 1.0 cm

that excludes certain reactions, at $c(\text{HNO}_3) = 3.0$ M and c(Pu) = 1.7 g/L. Without all the reactions about Pu, the curve deviates significantly from the experimental data, indicating the importance of reactions involving Pu.

Then, the important reactions among all the 18 reactions involving Pu were picked up. As shown in Fig. 6a, without R217, the production of HNO_2 is much less than the experimental data and close to results without all reactions involving Pu. R217 is the vital reaction, which is expressed as:

$$Pu(IV) + H_2O_2 \to Pu(III) + HO_2 + H^+, k = 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$
(10)

Pu(IV) is reduced to Pu(III) by H_2O_2 . H_2O_2 also consumes HNO_2 rapidly through the reaction:

$$\frac{\text{HNO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{ONOOH} + \text{H}_2\text{O},}{k = 7.17 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}}$$
(11)

Thus, R217 benefits the production of HNO_2 . Pu(III) produced in R217 can be oxidized to Pu(IV) in R208:

$$\begin{aligned}
&Pu(III) + NO_2 \to Pu(IV) + NO_2^-, \\
&k = 2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}
\end{aligned} \tag{12}$$

Here NO_2 was reduced to NO_2^- . This reaction, together with its reverse reaction R207, also has obvious influence on the production of HNO₂. All the other reactions about Pu, such as the disproportionate/symproportionate reactions (R212–R216), are of either too small reactant concentrations or reaction rate constants. Their contributions are negligible (less than 0.1%) and are not plotted in Fig. 6a.

For further discussion about the effect of reactions involving Pu, $c(Pu)_{react}$ is defined as the concentration of Pu involved in the chemical reactions. The simulation results of different $c(Pu)_{react}$ are plotted in Fig. 6b, at $c(HNO_3) = 3.0$ M and c(Pu) = 1.7 g/L. The yield of



Fig. 6 a Measured and simulated absorbance at 371 nm versus irradiation time, together with the results simulated without certain redox reactions involving Pu (R201–R218 are the reactions in

HNO₂ increases with $c(Pu)_{react}$ at $c(Pu)_{react} < 0.5$ g/L and keeps nearly invariant at $c(Pu)_{react} > 0.5$ g/L. This indicates that Pu(IV) should be treated as catalyst instead of reactant/oxidant for the production of HNO₂ on the whole. Its effect can be represented roughly as:

$$H_2O_2 + NO_2 \xrightarrow{Pu(IV)} HNO_2 + HO_2.$$
(13)

Besides, the reaction rate constants of Pu depend on $c(\text{HNO}_3)$ [27, 28]. However, the rate constant for the most important reaction, $Pu(\text{IV}) + H_2O_2 \rightarrow Pu(\text{III}) + HO_2 + H^+$, is invariant with $c(\text{HNO}_3)$. Therefore, the variation of rate constants with $c(\text{HNO}_3)$ has little effect on the yield of HNO₂.

3.7 Mechanism for the production of nitrous acid

The intrinsic mechanism of nitrous acid generation and consumption was comprehensively investigated. With this model, the reaction rates for the reactions that directly generate or consume nitrous acid were calculated at $c(\text{HNO}_3) = 3.0 \text{ M}$ and c(Pu) = 1.7 g/L. The results of the six most important reactions for generation and consumption of HNO_2 are shown in Fig. 7. The rates of other reactions are more than one order of magnitudes lower than that of the selected ones. The most important reactions that contribute to generation of nitrous acid are given as below:

R127: NO + NO₂ + H₂O
$$\rightarrow$$
 2HNO₂,
 $k = 1.8 \times 10^{1} \text{ M}^{-1} \text{ s}^{-1}$
(14)

$$\begin{array}{l} \text{R130:2'NO}_2 + \text{H}_2\text{O} \to \text{HNO}_2 + \text{HNO}_3, \\ k = 8.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1} \end{array}$$
(15)

R115: ONOOH + H₂O
$$\rightarrow$$
 H₂O₂ + HNO₂,
 $k = 5.4 \times 10^{0} \text{ M}^{-1} \text{ s}^{-1}$ (16)

And the three reactions that dominate the consumption of nitrous acid are also collected here:



Table 2). **b** The simulated absorbance at 371 nm with different values of $c(Pu)_{react}$, the concentration of Pu that participates in the redox reaction. $c(HNO_3) = 3.0$ M. c(Pu) = 1.7 g/L; optical path 1.0 cm





$$\frac{\text{R126:2HNO}_2 \to \text{'NO} + \text{'NO}_2 + \text{H}_2\text{O}}{k = 1.34 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}}$$
(17)

$$\frac{\text{R129:HNO}_2 + \text{HNO}_3 \rightarrow \text{'NO}_2 + \text{'NO}_3 + 2 \text{ H}^+}{k = 4.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}}$$
(18)

$$\begin{array}{l} \text{R114:} \text{H}_2\text{O}_2 + \text{HNO}_2 \to \text{ONOOH} + \text{H}_2\text{O}, \\ k = 7.17 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \end{array}$$
(19)

The two sets of reactions are reverse reactions. It is seen that NO₂, NO and H₂O₂ are the vital intermediate products for production of HNO₂. Obviously, these reactions and intermediate productions in the PUREX process are paramount in that they actually show us how to manipulate the concentration of nitrous acid. Although the reaction constant rates in Eqs. (14)-(19) differ by seven orders of magnitude, their contribution to the generation/consumption of HNO₂ is comparable, as there is significant difference between the concentrations of reactant.

4 Conclusion

In this work, the α -radiolysis of aqueous nitric acid with ²³⁸Pu as an irradiation source is studied, and a kinetic model is established accordingly. The influence of dose rate, nitric acid concentration, and nitrate ion concentration on the yield of nitrous acid are investigated experimentally. Our results have implications for the practical reprocessing of spent fuel, as the nitric acid concentration used in the experiment purposely simulates that in PUREX process. A complete kinetic model including the indirect effect and direct effect is provided. With this model, the time dependences of the yield of nitrous acid with different dose rates, nitric acid concentrations, and nitrate ion concentrations are calculated. For each condition, the theoretical results agree well with the experimental data. Additionally, six reactions and intermediate products that dominate the generation and consumption of nitrous acid are proposed

based on this model. Moreover, the calculation results imply that the redox reactions involving Pu are important components among all the complex reactions occurred in α -radiolysis of aqueous nitric acid solution. The experimental results and kinetic model are valuable for understanding the α -radiolysis of aqueous nitric acid.

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