# Studies of the interactions of nitrous acid in the redox system of neptunium in nitric acid solutions

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### Abstract

Investigation of the various interactions of nitrous acid in nitric acid solutions is necessary to advance understanding about the complications of extraction of neptunium in advanced reprocessing schemes like UREX and TRUEX, because HNO<sub>2</sub> plays a key role in the redox speciation of neptunium in the nitric acid solutions. Investigations of the kinetics of reversible reduction of extractable neptunium(VI) to non-extractable neptunium(V) show close to first order dependences in both reactants and an inverse first order with respect to hydrogen ion concentration. Production of nitrous acid by gamma radiolysis has been found to be proportional to the nitric acid concentration. The reaction of nitrous acid with hydrogen peroxide which is a simultaneous radiolytic product was found to proceed very fast in nitric acid solutions. Scavenging of nitrous acid by N-methylurea led to complete reduction of neptunium(VI) to neptunium(IV) in 4 M HNO<sub>3</sub> solutions irradiated by a gamma dose of 60 kGy, most probably due to the radiolytically produced hydrogen peroxide which was not eliminated by nitrous acid.

## Introduction

Extraction of hexavalent and tetravalent actinides with tributyl phosphate (TBP) from nitric acid solutions is the most widely used industrial process for the reprocessing of used nuclear fuel (UNF) and is the basis for the development of advanced reprocessing schemes like UREX and TRUEX. An unresolved issue of UNF reprocessing is the management of neptunium in the extraction system because of its not clearly defined redox speciation. Neptunium is present in both pentavalent (V) and hexavalent (VI) oxidation states that differ greatly in their extractability to the organic phase (hexavalent state being very well extracted by TBP, whereas pentavalent neptunium is almost not extracted). As a result, neptunium is distributed in both organic and aqueous streams of the separation process. In different studies we have investigated in nitric acid solutions the kinetics of reduction of neptunium(VI) by HNO<sub>2</sub> in HNO<sub>3</sub>, radiolytic production of HNO<sub>2</sub> and its reaction with a simultaneous radiolytic product H<sub>2</sub>O<sub>2</sub> and the effect of HNO<sub>2</sub> scavenging by methylurea on the final speciation of irradiated neptunium solutions in nitric acid.

#### Reaction of nitrous acid with neptunium in nitric acid solutions

Nitrous acid, a key redox controlling factor, is always present in these systems, as it forms during the dissolution of UNF and by the radiolysis of nitric acid. Low linear energy transfer radiation like  $\beta$  and  $\gamma$  have radiation yields of HNO<sub>2</sub> around 0.25 mM/kGy in 1 M HNO<sub>3</sub>, and the radiation yields of  $\alpha$  particles are approximately two times lower [1]. Nitrous acid HNO<sub>2</sub> is relatively well extracted by TBP (log  $D \approx 1$ ) and is therefore distributed from the source raffinate solution into further stages of the separation system [2]. The influence of nitrous acid on the redox state of neptunium is complex. If HNO<sub>2</sub> is present in a small concentration, it primarily acts as a catalyst of the oxidation of Np(V) by nitric acid. This reaction is an autocatalytic process, as additional HNO<sub>2</sub> is produced. However, if neptunium is initially present primarily in the hexavalent state, large concentrations of HNO<sub>2</sub> lead to reduction back to the pentavalent state. Both reactions give rise to an acidity-dependent equilibrium:

$$NpO_{2}^{+} + \frac{3}{2}H^{+} + \frac{1}{2}NO_{3}^{-} \underbrace{\operatorname{catal.HNO_{2}}}_{\text{catal.HNO_{2}}} NpO_{2}^{2+} + \frac{1}{2}HNO_{2} + \frac{1}{2}H_{2}O$$
(1)

The reaction equilibrium can be characterised by an apparent equilibrium constant  $K_{aux}$  from measured concentrations of Np(VI), Np(V), nitric acid and nitrous acid in equilibrium: . - -

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$$K_{app} = \frac{[Np(VI)][HNO_2]^{1/2}}{[Np(V)][HNO_3]^2}$$
(1)

This constant and its dependence on ionic strength, acidity and temperature has been measured by many authors [3-7]. The reported value varies between  $K_{app} = 3 \times 10^{-4} - 2 \times 10^{-3}$ . Some of the authors have also investigated the kinetics of oxidation of Np(V) by HNO<sub>3</sub> [3-5,8], using both the spectrophotometry and solvent extraction methods. The analysis of the system proved to be quite complex and the reported forms of the rate law and its associated rate constants vary greatly among the authors.

The rapid reduction of Np(VI) to Np(V) by the addition of nitrite to solutions of 1 M HNO<sub>3</sub> was observed already during the initial studies on the redox properties of neptunium performed during the Manhattan Project by Magnusson, et al. [9]. Since then, the kinetics of reduction of Np(VI) by HNO<sub>2</sub> has attracted just a little interest. To our best knowledge, only two in-depth studies about this issue have been undertaken [10-12].

Shilin and Nazarov [10] studied the Np(VI) reduction kinetics in the nitric acid/nitrate system in an excess of HNO<sub>2</sub> as an apparent first order reaction with respect to the concentration of Np(VI). A comparative study between the rates of oxidation of HNO<sub>2</sub> by Np(VI) and Am(VI) in a non-complexing perchlorate (ClO) system has been done by a spectrophotometric stopped-flow method by Woods, et al. [11]. These researchers have utilised both first- and second-order kinetic relations to describe the progress of the reaction.

In order to clarify discrepancies in the values of activation energy and dependencies of the reaction rate on the concentration of  $HNO_2$  and hydrogen ion, reported by Woods, *et al.* [11] and Koltunov and Marchenko [12], we have investigated the kinetics of the reaction using UV-VIS-NIR spectrophotometry in a stirred cell by the method of initial reaction rates. The new results along with the experimental conditions are compared in Table 1 with the previously published results.

Experimental conditions	Rate equation and kinetic parameters		
Na/HNO <sub>3</sub> solutions $C_{HNO3} = 0.18-3.0 \text{ M}$	<b>Error! Objects cannot be created from editing field codes.</b> $k_1 = 0.97 \text{ s}^{-1}, k_2 = 15.5 \text{ M}^{-0.5} \text{s}^{-1}$ (at 20°C, $\mu = 3 \text{ M}$ ) $E_{A1} = (62.4 \pm 1.3) \text{ kJ/mol}, E_{A2} = (64.9 \pm 1.5) \text{ kJ/mol}$		
Na/HClO <sub>4</sub> solutions $c_{HClO4} = 0.1-1.0 \text{ M}$	<b>Error! Objects cannot be created from editing field codes.</b> $k_1 = 2.01 \pm 0.45 \text{ M}^{-1}\text{s}^{-1}$ and $k_2 = 1.56 \pm 0.07 \text{ s}^{-1}$ (at 25°C, $\mu = 1 \text{ M}$ ) $E_{A1} = (51.5 \pm 2.4) \text{ kJ/mol}$ , $E_{A2} = (70.0 \pm 4.4) \text{ kJ/mol}$	[11]	
Li/HNO <sub>3</sub> solutions $C_{HNO3} = 0.75-4.0 \text{ M}$	Error! Objects cannot be created from editing field codes. $\vec{k} = (0.159 \pm 0.014) \text{ M}^{-0.2} \text{s}^{-1} \text{ (at } 20^{\circ}\text{C}, \mu = 4 \text{ M})$ $E_A = (57.3 \pm 1.6) \text{ kJ/mol}$	[13]	

Table 1: Comparison of experimental results of studies of reduction of Np(VI) by HNO<sub>2</sub>

For the reduction of Np(VI) by nitrous acid in a nitrate medium, the results of our investigations of the reaction orders with respect to concentrations of Np(VI),  $HNO_2$  and H<sup>+</sup> agree reasonably well with the previous investigations in the nitrate environment [10]. However, a significant difference was determined in the exact form of the rate law. As opposed to previous findings, no notable dependence on the  $NO_3^-$  concentration was observed. The value of 57.3 kJ/mol determined for the activation energy is slightly different, but agrees well with the apparent value determined for the reaction in 1 M HClO<sub>4</sub> environment [11].

# Radiolytic production of HNO<sub>2</sub> in nitric acid solutions and its reaction with H<sub>2</sub>O<sub>2</sub>

Radiolysis of aqueous solutions of nitric acid mainly produces gaseous compounds such as  $H_2$ ,  $O_2$ , and  $N_2$  while producing significant amounts of HNO<sub>2</sub> and  $H_2O_2$ . The latter two are mutually reactive:

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O \tag{3}$$

Hydrogen peroxide is not present in solutions after irradiation if the radiolytic production of  $HNO_2$  was significantly higher. This happens in solutions with  $HNO_3$  concentration greater than approximately 0.5 M (= 0.5 mol/dm<sup>3</sup>). Production of  $HNO_2$  is proportional to the concentration of nitrate anion [14].

In a simple experiment, we irradiated solutions containing different  $HNO_3$  concentrations for several days in a <sup>60</sup>Co irradiator (at dose rate 0.45 kGy/h) and concentrations of  $HNO_2$  were determined by absorption spectroscopy in the wavelength range of 350-390 nm. Production of  $HNO_2$  increases with dose and with the initial concentration of  $HNO_3$ , and evidently, a significant amount (mM) of  $HNO_2$  can be produced and affect the chemistry of Np in extraction systems. However, due to either the instability of  $HNO_2$  in nitric acid or its interaction with radiolysis products, the rate of  $HNO_2$  production at higher doses (>30 kGy) decreases. After 61 kGy dose, the 1, 2, 3, 4, 5, 6, 7 and 8 M  $HNO_3$  solutions contained 0.8, 1.6, 2.7, 3.0, 4.2, 5.2, 5.6, and 6.3 mM  $HNO_2$ , respectively.

The rate of reaction (3) is strongly dependent on acidity of the solution and tends to proceed very rapidly below pH = 1. Only a few studies have been performed in these higher acid concentrations [15] and no studies so far have addressed the higher concentrations of nitric acid (only the effect of up to 0.1 M nitrate anions were investigated [16]). Kinetic observations (recorded using stopped-flow absorption spectrophotometry  $OLIS^{TM}$  RSM 1000) have shown that the reaction proceeds through a very rapid formation of a UV-absorbing intermediate, which has been previously identified as peroxonitrous acid HOONO. The intermediate consequently

undergoes a somewhat slower decay into the products. The observed reactions behave according to the following simplified reaction scheme:

$$HNO_2 + H_2O_2 \rightarrow HOONO + H_2O \tag{4}$$

$$HOONO \rightarrow + HNO_3$$
 (5)

The shape of the absorption spectrum of HOONO between 330 and 480 nm has been determined from spectra recorded in later stages of reactions with excess  $H_2O_2$  when all  $HNO_2$  has already reacted. Using previously obtained spectrum of  $HNO_2$ , the values of molar absorption coefficients vs. wavelength were consequently quantified by parameterised subtraction from reaction spectra recorded at the beginning of the reaction where very little HOONO had time to decay. The final spectra of HOONO and  $HNO_2$  presented in Figure 1 were used for deconvolution of all spectra recorded during a particular kinetic run in order to determine the time-dependent concentrations of reactants. As can be seen in Figure 2, the reaction curves were then successfully fitted by a numeric model based on reactions (4) and (5).

# Figure 1: Absorption spectra of nitrous acid (HNO<sub>2</sub>) and peroxonitrous acids (HOONO) used for fitting kinetic data

Baseline subtracted for the 1 M total nitrate absorbance, temperature 2.5°C





Symbols represent actual concentrations determined from deconvolution of stopped-flow spectra, lines represent the fit of the numeric model based on the two consecutive reactions (4) and (5)



So far, our experiments in the nitrate system generally confirm the experimental findings of Benton and Moore performed in the perchlorate system [15] – the reaction of formation of peroxonitrous acid was determined to be of first order with respect to both  $HNO_2$  and  $H_2O_2$ . The

dependence on hydrogen ion concentration also appears to be close to first order, the value of the apparent second-order rate constant increasing from 590  $M^{-1}s^{-1}$  in 0.25 M HNO<sub>3</sub> to 2 050  $M^{-1}s^{-1}$  in 1.0 M nitric acid (at 1 M total nitrate and 2.5°C). The decomposition of peroxonitrous acid progresses by a simple first order decay process; an incomplete first-order dependence was identified with values of the apparent first-order rate constant increasing linearly from 0.22 to 0.62 s<sup>-1</sup> with the change from 0.25 to 1.0 M HNO<sub>3</sub>. These findings are also in agreement with the results determined in perchlorate system. Increase of the total nitrate concentration to 4 M seemed to produce reaction rates almost 10 times higher reaction rates, prompting future investigation of the behaviour of the reaction in the nitrate system.

### Gamma irradiation of Np solutions in HNO<sub>3</sub> with methylurea as scavenger for HNO<sub>2</sub>

Solutions of 1.3 mM neptunium [initial redox speciation was 5% Np(V) and 95% Np(VI)] in 4 M HNO<sub>3</sub>, containing 50 and 100 mM N-methylurea were subjected to integral doses of gamma radiation of 20, 40 and 60 kGy, and compared with their reference sample (a non-irradiated portion of the same solution, stored aside during the irradiation process). Redox speciation of samples was determined spectrophotometrically by fitting to reference spectra [17]. Analysis of the reference samples, presented in Table 2, showed that a very slow reduction of Np(VI) into Np(V) in 4 M HNO<sub>3</sub> occurs even without the influence of irradiation. After ~7 days, the initial ratio of Np(VI):Np(V) dropped from ~95:5 to ~75:25; however, the extent of Np(VI) reduction is clearly not significant enough to explain the changes taking place during irradiation. This slow reaction is also not likely to be of importance in the shorter time scales of real reprocessing conditions.

Dose (kGy)	100 mM methylurea (irradiated)			100 mM methylurea (non-irradiated reference)		
	Np(IV)	Np(V)	Np(VI)	Np(IV)	Np(V)	Np(VI)
0	0%	0%	0%	0%	6%	94%
20	43%	57%	0%	0%	17%	83%
40	94%	6%	0%	0%	21%	79%
60	91%	9%	0%	0%	24%	76%

Table 2: Effect of 100 mM methylurea on the redox speciation of neptunium in irradiated and non-irradiated 4 M HNO<sub>3</sub> solutions in presence of methylurea

Previous experiments with irradiation of a solution of 2 mM Np in 4 M nitric acid and no additives led to a final 50% reduction of Np(VI) to Np(V). Reduction of Np(VI) was actually enhanced by the presence of higher concentrations of MU and progressed during the radiation exposure, resulting with Np(IV) as the dominant redox state of neptunium. The reduction reaction was faster for the samples with initial concentration of 100 mM MU than with 50 mM MU; upon a dose of 40 kGy, the ratio of Np(IV):Np(V) reached approximately 10:1, and additional 20 kGy did not show any significant change. This is likely caused by scavenging of the nitrous acid by MU, which permits an increase of  $H_2O_2$  concentration. Hence, high concentrations of MU did not prevent Np(VI) reduction; however, this could have a positive practical implication when Np(IV) is the desired extraction species. Nonetheless, application of MU has to be experimentally verified since the scavenging of HNO<sub>2</sub> by MU appears to significantly alter the redox processes during nitric acid radiolysis.

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