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## Neptunium (V) oxidation by nitrous acid in nitric acid

Colin Gregson<sup>a</sup>, Colin Boxall<sup>b</sup>, Michael Carrott<sup>a</sup>, Scott Edwards<sup>b</sup>, Mark Sarsfield<sup>a</sup>,  
Robin Taylor<sup>a\*</sup>, David Woodhead<sup>a</sup><sup>a</sup>National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, Cumbria, CA20 1PG, UK<sup>b</sup>Engineering Department, Lancaster University, Lancaster, Lancashire, LA1 4YW, UK

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### Abstract

To support the development of an Advanced PUREX process that fully recovers neptunium with uranium and plutonium for recycle, an enhanced understanding of neptunium behaviour in nitric acid and tributyl phosphate phases is essential. The most important reaction affecting neptunium extraction in the PUREX process is the oxidation of Np(V) by nitric acid. This paper reports new data on Np(V) oxidation in nitric acid under conditions relevant to the development of a flowsheet for the primary extraction / scrub contactor in an Advanced PUREX process.

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*Keywords:* neptunium, PUREX, nitrous acid, oxidation

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### 1. Introduction

Recovery and recycling of the minor actinides (Np, Am, Cm), either to reduce the long term radiotoxicity of radioactive wastes or to reduce the heat burden on the geological repository, is a key objective of sustainable nuclear fuel cycles<sup>1</sup>. <sup>237</sup>Np is a long lived radionuclide ( $t_{1/2} = 2.1E6$  years) that is present in significant quantities

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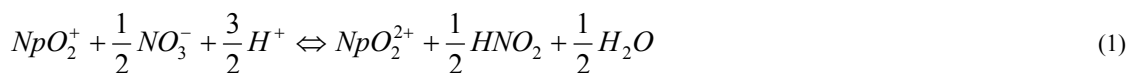
\* Corresponding author. Tel.: +44-19467-79266; fax: +44-19467-79266.

E-mail address: [robin.j.taylor@nnl.co.uk](mailto:robin.j.taylor@nnl.co.uk).

in spent nuclear fuels and due to the stability of the pentavalent neptunyl ion ( $\text{NpO}_2^+$ ) it can be mobilised in the environment<sup>2</sup>. As well as waste management benefits, improved management of Np can reduce the complexity and hence costs of reprocessing<sup>3</sup>. It is generally believed that Np can be quite easily recovered by relatively simple modifications to the well established PUREX process, which is used for the commercial scale reprocessing of spent nuclear fuels<sup>4,5</sup> but this requires complete extraction of Np in the first solvent extraction contactor. This is not achieved in current reprocessing flowsheets, which split Np between solvent product and aqueous raffinate in this contactor<sup>4</sup>.

The cause of this splitting between aqueous and solvent streams is due to the very low extractability of Np(V) compared to high extractability of Np(VI) into 30 % TBP (tributyl phosphate) together with the equilibrium established between Np(V) and Np(VI) in nitric acid and the kinetics of the forward and reverse reactions<sup>6</sup>. To support development of a “neptunium extraction” flowsheet enhanced understanding of the oxidation of Np(V) in 1-phase and 2-phase solutions is required under conditions relevant to the process. Here we report studies of Np(V) oxidation in the isolated nitric acid phase under such conditions.

Oxidation of Np(V) in nitric acid is described by equation (1) below. As is typical of oxidation reactions of actinide ions in nitric acid<sup>7</sup>, the redox reaction is autocatalysed by nitrous acid but, as  $\text{HNO}_2$  is also a product of the reaction, its build up thermodynamically inhibits the forward reaction. This leads to a complex system that has been studied by a number of researchers<sup>7-12</sup> but the reported rate equations vary significantly. The kinetics of the reverse reaction have also been recently re-evaluated<sup>13</sup>.



## 2. Experimental Methods

Experiments were carried out in two blocks of work labelled (R1) and (G2). Initially <sup>237</sup>Np stock solutions were electrochemically conditioned in  $\text{HNO}_3$  solutions at 0.7 V for Np(V) and 1.2 V for Np(VI) generation (vs. Ag/AgCl) using a platinum gauze working electrode with Ar sparging. Confirmation of conditioning to the required oxidation state was by Electronic Absorption Spectroscopy (EAS) using a Perkin-Elmer Lambda-19 or -900 UV/vis/NIR spectrometer. Electro-conditioning was carried out each day prior to experimental work to ensure Np was maintained at the required oxidation state. Various strength fresh solutions of  $\text{NaNO}_2$  in 0.01 M NaOH were prepared daily for kinetic experiments. This minimised losses of  $\text{HNO}_2$  through decomposition whilst ensuring that low added volumes minimised dilutions of experimental working solutions.

EAS (Perkin Elmer Lambda-19, dual-beam scanning spectrometer fitted with Hellma NIR fibre optic connections to a remote optical cell holder in a designated fumehood) was used to monitor progress of oxidation-reduction reactions. The single phase studies were conducted in a capped 1 cm pathlength cuvette (Perkin Elmer Supracil Quartz NIR cuvette). For temperature controlled experiments, a 1 cm path length cell holder (World Precision Instrument; Cat no. CUV-UV) with the capability for connection to a heater/chiller re-circulating unit was employed. The temperature of the solution within the cell was measured using a type K connector bead wire temperature probe connected to a temperature meter and the temperature of the heater/chiller re-circulating unit adjusted to allow for any heat loss from the apparatus. Each solution was equilibrated at the required temperature for at least 3 minutes prior to starting the kinetic studies.

Standard methods were followed, as used extensively for studying redox kinetics of actinide ions by spectrophotometry. Taking the G2 series of experiments as typical: 1.92 ml of  $\text{HNO}_3$  at the required acidity was placed into a capped quartz cuvette (1 cm pathlength) and allowed to reach the required temperature. The detector was zeroed upon achieving a steady temperature against a reference  $\text{HNO}_3$  solution of the same concentration. 80  $\mu\text{l}$  of the Np stock (2.7 g/L) was then placed into the cuvette, stoppered, mixed and placed back into the heated cell holder. The electronic absorption spectrum was recorded and the initial absorbance calculated

from the difference between the Np(V) peak,  $\lambda_{\max} = 980$  nm, and a suitable baseline reference point. Data are plotted as Relative Absorbance at 980 nm vs. time curves after correction for the baseline absorbance at 900 nm. Linear calibration curves using background subtractions at 900 and 1010 nm confirmed adherence to the Beer Lambert law across the Np(V) concentration range 0.02 – 0.2 g/L at ambient temperature and at 50 °C for 3 and 5 M HNO<sub>3</sub> solutions ( $R^2 > 0.99$ ). HNO<sub>3</sub> stock solutions were degassed with Ar to suppress residual HNO<sub>2</sub> and for the calibrations only HNO<sub>2</sub> was further excluded from the 5 M acid and 50 °C solutions by the addition of 0.03 M sulphamic acid. Calculated extinction coefficients suggested that the 980 nm peak was not fully resolved with the instrument parameters used (ambient temperature:  $\epsilon = 171 \pm 3$ ,  $150 \pm 3$  and at 50 °C:  $\epsilon = 210 \pm 7$ ,  $160 \pm 3$  l mol<sup>-1</sup> cm<sup>-1</sup> in 3 and 5 M HNO<sub>3</sub> solutions respectively *cf.* literature values of  $\epsilon \approx 275$  and  $248$  l mol<sup>-1</sup> cm<sup>-1</sup> in 4 M HNO<sub>3</sub> at 22 and 50 °C estimated from reference spectra given by Friedman and Toth<sup>14</sup>).

An aliquot of NaNO<sub>2</sub> solution (typically 40  $\mu$ l) was then added to the cell and the spectra recorded periodically. In some experiments further additions of sodium nitrite were added to extend oxidation / reduction reactions or change the equilibrium position. The R1 series of experiments followed very similar procedures except these were performed at 22 °C only. Experimental conditions covered the temperature range 22-60 °C, nitric acid concentrations 2.9-5.0 M and nitrite (NaNO<sub>2</sub>) concentrations range of  $1 \times 10^{-5}$ - $1 \times 10^{-2}$  M (plus experiments without added NaNO<sub>2</sub>). Np concentrations were  $\sim 0.1$  g/l in all experiments.

### 3. Results and discussion

The parameters that affect Np(V) oxidation are nitric acid concentration, temperature and nitrous acid concentration. The effects of HNO<sub>3</sub> concentration (selected data at 50 °C) are illustrated in Fig. 1. It is seen, particularly at the higher temperatures, that increasing acidity increases the extent of oxidation, as expected from Eq. (1). The rate of oxidation also increases with HNO<sub>3</sub> concentration, this is in agreement with literature reports<sup>9-10</sup>. The effect of temperature on the oxidation of Np(V) is illustrated in Fig. 2. It is apparent that the equilibrium favours Np(VI) at elevated temperatures, in accordance with a reported endothermicity ( $\Delta H = 16.5$  kJ mol<sup>-1</sup>)<sup>11</sup> and, as to be expected, the rate of oxidation increases with increasing temperature ( $E_a$  reported between 50.24 and 84.15 kJ mol<sup>-1</sup>)<sup>7,10,12</sup>. At the lower temperatures there appears to be an induction period as is commonly found in HNO<sub>3</sub> oxidations of actinide ions in which HNO<sub>2</sub> accumulates as a reaction product and catalyses the reaction (see e.g.<sup>7,15</sup>). At 50 °C this induction period is absent presumably due to the larger concentrations of HNO<sub>2</sub> initially present at the higher temperature.

The effects of nitrous acid, added as sodium nitrite, are more complex. With no additional nitrite the data (not illustrated) showed no oxidation of Np(V) at 4 M HNO<sub>3</sub> or below between 22 and 50 °C. At 5 M HNO<sub>3</sub> a slow oxidation occurs at 50 °C, which accelerates at 60 °C, appearing to be autocatalytic presumably due to the accumulation of HNO<sub>2</sub>. This is a common feature of reactions in HNO<sub>3</sub><sup>7</sup>. The effects of increasing HNO<sub>2</sub> concentration at 5 M HNO<sub>3</sub> and 50 °C are illustrated in Fig. 3. With similar experiments at 3 M HNO<sub>3</sub> and 22 °C there seemed to be little effect of adding HNO<sub>2</sub> although the 0.01 M addition stabilised Np(V) (Fig. 3). The effect of HNO<sub>2</sub> on the thermodynamics and kinetics of Np(V) oxidation is evident under conditions of 50 °C and 5 M HNO<sub>3</sub>. Increasing HNO<sub>2</sub> from  $1 \times 10^{-4}$  to 0.01 M leads to higher concentrations of Np(V) at the steady state, *i.e.* an equilibrium position favouring Np(V) as expected from Eq. (1). The experiment at  $1 \times 10^{-5}$  M HNO<sub>2</sub> has not reached an equilibrium position but presumably would adhere to the observed trend if left sufficiently long enough. An experiment at 0.1 M NaNO<sub>2</sub> is not shown but follows the trend – this experiment was affected by visible loss of NO<sub>x</sub> on addition of NaNO<sub>2</sub>. In accordance with Eq. (1), once the steady state has been reached, the equilibrium position can be changed in favour of Np(V) by a further addition of NaNO<sub>2</sub> (Fig. 4). The kinetic effect, however, is more complex. Oxidation is slow at  $[\text{HNO}_2]_{\text{ini}} \leq 1 \times 10^{-5}$  M. Between  $1 \times 10^{-5}$  and  $1 \times 10^{-4}$  M HNO<sub>2</sub>, there is a dramatic enhancement of the rate of oxidation (Fig. 3). Increasing initial HNO<sub>2</sub> concentration to  $1 \times 10^{-3}$  leads to a smaller increase in rate and there is no further measurable increase in rate at 0.01 M initial HNO<sub>2</sub>.

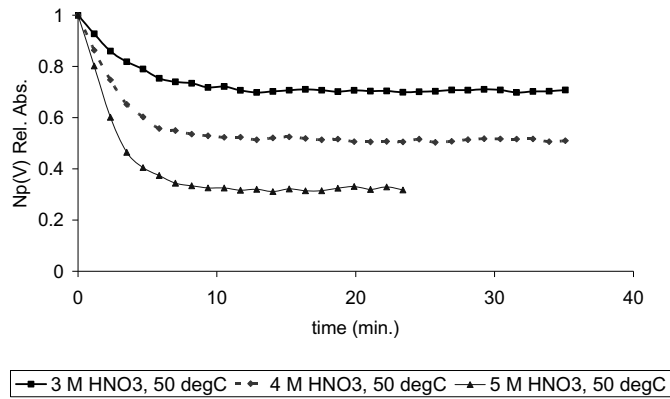


Fig. 1. Effect of [HNO<sub>3</sub>] on Np(V) oxidation at T = 50 °C with 1 mM NaNO<sub>2</sub> additions

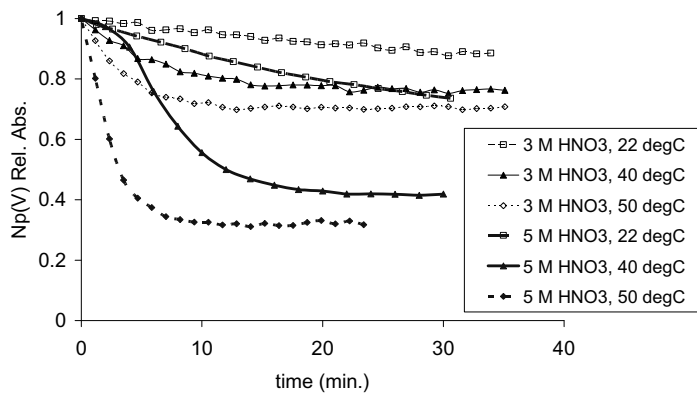


Fig. 2. Effect of temperature on Np(V) oxidation at 3 and 5 M HNO<sub>3</sub> with 1 mM NaNO<sub>2</sub> additions

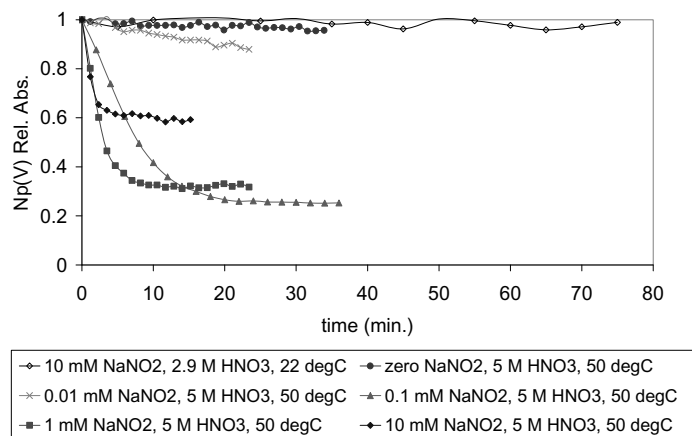


Fig. 3. Effects of initial added nitrite on Np(V) oxidation at 22 °C, 2.9 M HNO<sub>3</sub> and 50 °C, 5 M HNO<sub>3</sub>

The thermodynamic position of the Np(V)/(VI) equilibrium is illustrated by Fig. 4 in which a pair of corresponding experiments in 5 M HNO<sub>3</sub> at 50 °C are shown. It can be seen that starting with either Np(V) or Np(VI) and 1x10<sup>-3</sup> M NaNO<sub>2</sub> leads to the same equilibrium concentration of Np(V) within the same timescale. As with the Np(V) experiment in Fig. 4, in which a second addition of NaNO<sub>2</sub> led to further Np(V) oxidation, it can be seen in Fig. 5 that a further addition of NaNO<sub>2</sub> to the Np(VI) experiment leads to further Np(VI) reduction and a new equilibrium ratio of Np(V) to Np(VI). That is, in a single aqueous phase, the Np(V):Np(VI) equilibrium is dependent on the HNO<sub>2</sub> to HNO<sub>3</sub> ratio, as expected from Eq. (1).

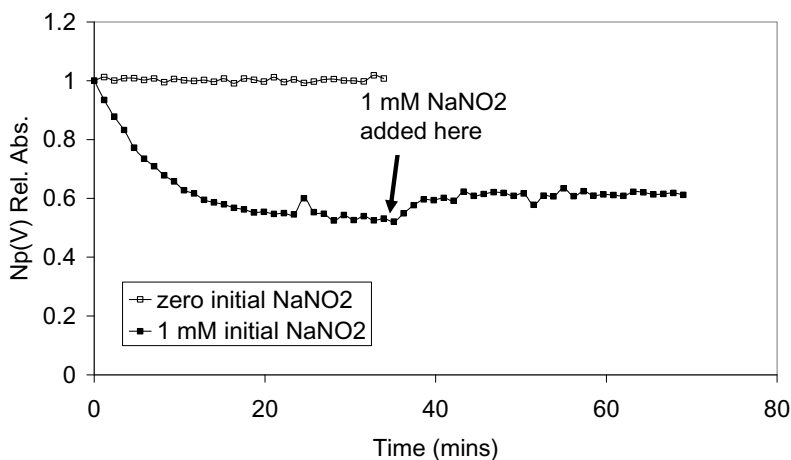


Fig. 4. Np(V) oxidation in 4 M HNO<sub>3</sub> at 40 °C with and without initial added NaNO<sub>2</sub>, also showing effects of adding a second aliquot of NaNO<sub>2</sub>

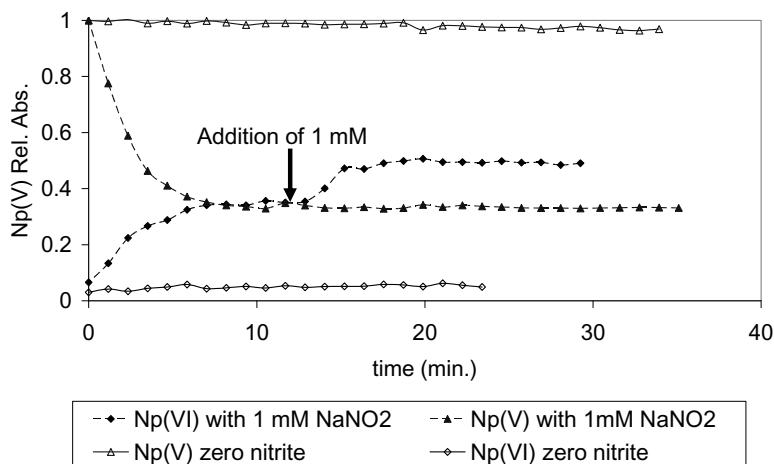


Fig. 5. Reduction of Np(VI) and oxidation of Np(V) in 5 M HNO<sub>3</sub> at 50 °C with and without NaNO<sub>2</sub>, also showing effects of adding a second aliquot of NaNO<sub>2</sub>

#### 4. Conclusions

In summary, in the isolated aqueous phase the equilibrium position of Np(V) oxidation or Np(VI) reduction by HNO<sub>3</sub> is established by the HNO<sub>3</sub>:HNO<sub>2</sub> ratio and temperature consistent with the equilibrium reaction (1) and reported endothermicity of the reaction. It is found that higher HNO<sub>3</sub> concentrations, lower HNO<sub>2</sub> concentrations and elevated temperatures increase the steady state concentration of Np(VI). However, at HNO<sub>2</sub> concentrations below 1x10<sup>-4</sup> M this equilibrium is not easily reached (long timescales), as HNO<sub>2</sub> is required to catalyse the oxidation of Np(V). In 5 M HNO<sub>3</sub>, a maximum rate of oxidation appears to be reached at ~1x10<sup>-3</sup> M initial HNO<sub>2</sub> concentration at 50 °C. Note, however, that the Np(V) oxidation reaction is sensitive to conditions, and these experiments were carried out in unstirred stoppered cuvettes with a small headspace above the solution. Future reports will extend these studies to open stirred and 2-phase (aqueous/organic) systems which present more complex situations.

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#### References

- 1 Warin, D. Future nuclear fuel cycles: Prospect and challenges for actinide recycling. *IOP Conference Series: Materials Science and Engineering* **9**, 012063 (2010).
- 2 Thompson, R. C. Neptunium: The Neglected Actinide: A Review of the Biological and Environmental Literature. *Radiation Research* **90**, 1-32 (1982).
- 3 Taylor, R. J., Dennis, I. S., Wallwork, A. L. Neptunium control in an advanced Purex process. *Nuclear Energy* **36**, 39-46 (1997).
- 4 Lecomte, M. E. in *Nuclear Energy Division Monograph* (ed J.-F. Parisot) (CEA Saclay, Paris, 2008).
- 5 Fox, O. D., Jones, C. J., Birkett, J. E., Carrott, M. J., Crooks, G., Maher, C. J., Roube, C. V., Taylor, R. J. in *Separations for the Nuclear Fuel Cycle in the 21<sup>st</sup> Century* Vol. 933 *ACS Symposium Series* (ed G. J. Lumetta, Nash, K. L., Clark, S. B., Friese, J. I.) Ch. 6, 89-102 (American Chemical Society, 2006).
- 6 Drake, V. A. in *Science and technology of tributyl phosphate* Vol. III. Applications of tributyl phosphate in nuclear fuel reprocessing (ed W. W. Schulz, Burger, L. L., Navratil, J. D., Bender, K. P.) 123-146 (CRC Press Inc., 1990).
- 7 Koltunov, V. S. *The kinetics of the actinide reactions*. (Atomizdat, 1974).
- 8 Tochiyama, O., Nakamura, Y., Katayama, Y., Inoue, Y. Equilibrium of Nitrous Acid-Catalyzed Oxidation of Neptunium in Nitric Acid-TBP Extraction System. *Journal of Nuclear Science and Technology* **32**, 50-59 (1995).
- 9 Tochiyama, O., Nakamura, Y., Hirota M., Inoue, Y. Kinetics of Nitrous Acid-Catalyzed Oxidation of Neptunium in Nitric Acid-TBP Extraction System. *Journal of Nuclear Science and Technology* **32**, 118-124 (1995).
- 10 Siddall, T. H. & Dukes, E. K. Kinetics of HNO<sub>2</sub> Catalyzed Oxidation of Neptunium(V) by Aqueous Solutions of Nitric Acid. *Journal of the American Chemical Society* **81**, 790-794 (1959).
- 11 Gourisse, D. Oxydation du neptunium(V) par les solutions aqueuses d'acide nitrique en presence d'acide nitreux. *Journal of Inorganic and Nuclear Chemistry* **33**, 831-837 (1971).
- 12 Moulin, J. P. Oxidation – reduction kinetics of neptunium in nitric acid solution. (Fontenay-aux-Roses, France, 1978).
- 13 Precek, M., Paulenova, A. Kinetics of reduction of hexavalent neptunium by nitrous acid in solutions of nitric acid. *Journal of Radioanalytical and Nuclear Chemistry* **286**, 771-776 (2010).
- 14 Friedman, H. A. & Toth, L. M. Absorption spectra of Np(III), (IV), (V) and (VI) in nitric acid solution. *Journal of Inorganic and Nuclear Chemistry* **42**, 1347-1349 (1980).
- 15 Koltunov, V. S., Taylor, R. J., Marchenko, V. I., Dvoeglazov, K. N., Savilova, O. A., May, I. The oxidation of U(IV) by nitric acid in 30% tri-butyl phosphate solutions. *Radiochimica Acta* **86**, 41-49 (1999).