

The Reduction of Np(VI) by Acetohydroxamic Acid in Nitric Acid Solution

Dong Yong Chung* and Eil Hee Lee

Department of Nuclear Chemical Engineering, Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong, Daejeon 305-600, Korea. *E-mail: ndychung@kaeri.re.kr

Received June 28, 2005

Spent nuclear fuel is reprocessed commercially by the chemical process to recover U and Pu. Recently, new salt-free reagents to separate plutonium and neptunium from uranium suitable for use in a single cycle flowsheet have been developed. Acetohydroxamic acid (CH₃CONHOH) has been taken much interest in as a complexing agent capable of selective stripping of tetravalent actinides from U(VI) when actinides are present in the solvent stream of the advanced PUREX process. Additionally acetohydroxamic acid will rapidly reduce Np(VI) to inextractable Np(V) thus allowing the separation of Np from U. In this study, the rate equation for the reduction of Np(VI) to Np(V) in nitric acid aqueous solution has been determined as: $-[NpO_2^{2+}]/dt = k[NpO_2^{2+}][AHA]$ with $k = 191.2 \pm 11.2 \text{ M}^{-1}\text{s}^{-1}$ at $25 \pm 0.5 \text{ }^\circ\text{C}$ and $[\text{HNO}_3] = 1.0 \text{ M}$. Comparison with other reductants available in the literature, acetohydroxamic acid is a strong one for NpO₂²⁺.

Key Words : Neptunium(VI) reduction, Acetohydroxamic acid, Nitric acid

Introduction

Irradiated spent nuclear fuel is reprocessed commercially by the chemical process to recover the uranium and plutonium from the radioactive fission products. However, spent nuclear fuel contains minor actinides other than the useful U and Pu. Neptunium is the most prevalent of these minor actinides.¹ In current reprocessing plants Np is generally regarded as an unwanted component and both the Pu and particularly the U products have restrictive specifications for it. Therefore, its effective control in the chemical process is important for the efficient production of purified U and Pu products.²

In a nitric acid solution, Np can exist simultaneously in three stable oxidation states, Np(IV), Np(V) and Np(VI) (Np⁴⁺, NpO₂⁺, NpO₂²⁺ ions).³ Np(V) is almost inextractable,⁴ while Np(IV) and Np(VI) can be readily extracted into a TBP/n-alkane solution and this can cause problems in reprocessing, as the Np can pass into more than one product or waste stream in the Purex process. Such a contamination makes a significant contribution to the complexity of the reprocessing plants. Efficient control of Np can also increase the range of products available from the process by allowing the recovery or recycle of Np as a minor actinide.⁵

BNFL is currently undertaking an extensive research and development work both to enhance the current reprocessing technology and to develop further Advanced chemical processes. One major goal is the development of a flowsheet which will reduce both the cost and environmental impact of reprocessing in the future.⁶ Several different methods for Np routing in the process and several new salt-free reagents to separate Pu(IV) and Np(IV) from U(VI) have been reported in the literature, including the development of new salt-free reagents.⁷⁻⁹

Formohydroxamic acid (FHA) and acetohydroxamic acid (AHA) are especially suited to the separation of Np(IV)

from U(VI) by selective formation of a hydrophilic complex with Np(IV). U(VI) extraction in to 30%TBP is unaffected. Additionally these hydroxamic acids will reduce Np(VI) to inextractable Np(V), thus allowing for the separation of Np from U.¹⁰⁻¹² The reduction of Np(VI) by formohydroxamic acid in 2 M HNO₃ has been reported by Colston *et al.*¹³ A rapid reduction, taking less than a few seconds to complete, was demonstrated. The kinetics, as determined by stopped-flow spectrophotometry, have been shown to be first order with respect to [FHA] and [Np(VI)] with a rate constant $k = 1019 \text{ M}^{-1}\text{s}^{-1}$ at $22 \text{ }^\circ\text{C}$ and $[\text{HNO}_3] = 2.0 \text{ M}$. However, a rate constant for the reduction kinetics of Np(VI) by AHA has not been reported. This paper will determine the rate constant for the reduction reaction of Np(VI) to Np(V) by AHA.

Experimental Section

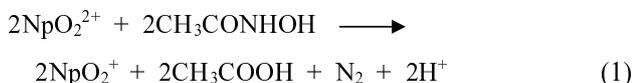
All the reagents were of an analytical grade (Aldrich and Merck) and the solutions were prepared with twice distilled water. ²³⁷Np(*t*_{1/2} = 2.14 × 10⁶ y) was supplied by AEA Technology as a 1 mCi ([Np]_{total} = 1.186 M) in a 5 mL solution volume of a 2 N HNO₃ concentration. UV-Vis-NIR spectrophotometry showed that the purchased Np was present at Np(V) and Np(VI). Np(V) in this solution can be oxidized to Np(VI) by K₂Cr₂O₇ and, after increasing the HNO₃ concentration, extracted into 30% TBP/*n*-dodecane. If an aqueous stock solution is required, the extracted Np(VI) can then be stripped back from the solvent phase into 0.01 M HNO₃ and acidity adjusted. Total concentration of Np was analysed radiometrically, and the concentration of the different Np oxidation states were determined spectrophotometrically.

Variation in the absorbance as a function of the time were recorded in a 1 cm optical cell with a cell stirring module installed in a model 8453 Hewlett-Packard UV-VIS spectro-

photometer. During the kinetic experiments the rate of decrease of the Np(VI) concentration was followed by monitoring the increase in the concentration of Np(V), which was determined from the intensity of the absorption band at 980 nm.

Results and Discussion

Hydroxamic acids, as hydrophilic complexants for tetravalent actinides, are also reducing agents, which are probably thermodynamically capable of reducing Np(VI).^{14,15} Especially, the reduction of Np(VI) to Np(V) by FHA and AHA was found to be rapid and complete. Further reduction of Np(V) to Np(IV) by FHA and AHA, as indicated by the onset potentials,¹⁰ is not expected since the hydrolysis of FHA and AHA by nitric acid is likely to be much faster than the reduction of Np(V) to Np(IV) which requires a breaking of the covalent Np-O bonds in NpO_2^{2+} . Colston *et al.*¹³ reported the reduction kinetics of Np(VI) to Np(V) by FHA in a nitric acid solution. Their results indicate that the reduction of Np(VI) by FHA is particularly fast. The stoichiometry of the Np(VI)-AHA reaction was not directly studied but, by an analogy to the stoichiometric equations of the reaction between Np(VI) and FHA, it is perhaps likely that nitrogen and acetic acid are the products of an AHA oxidation. In this case, the stoichiometry of the reduction routes might be expressed by the following equations:



The kinetic equation for the reduction of Np(VI) by AHA, as determined by Colston for the reduction by FHA, are described by:

$$-\frac{d[\text{NpO}_2^{2+}]}{dt} = k' \frac{[\text{NpO}_2^{2+}][\text{AHA}]}{[\text{H}^+]} \quad (2)$$

For the case of a constant acidity, therefore, the reduction rate is a 1st order with respect to both $[\text{NpO}_2^{2+}]$ and $[\text{AHA}]$. Therefore we can write,

$$-\frac{d[\text{NpO}_2^{2+}]}{dt} = k[\text{NpO}_2^{2+}][\text{AHA}] \quad (3)$$

As seen in Figure 1, the dependency of $\log([\text{Np(VI)}]/[\text{Np(VI)}]_0)$ on the time is a linear function, which indicates that the reaction is a first-order with respect to Np(VI). The first-order rate constant k maintains constant at a variation of the Np(VI) initial concentration. On the other hand, the reaction rate linearly increases with an increasing AHA concentration.

Noting that the amounts of N(VI) and AHA which have reacted at any time are equal and given by $[\text{Np(VI)}] = [\text{Np(VI)}]_0 - [\text{Np(V)}]$, $[\text{AHA}] = [\text{AHA}]_0 - [\text{Np(V)}]$. After an integration and rearrangement of equation (3), the final result in a number of different forms is

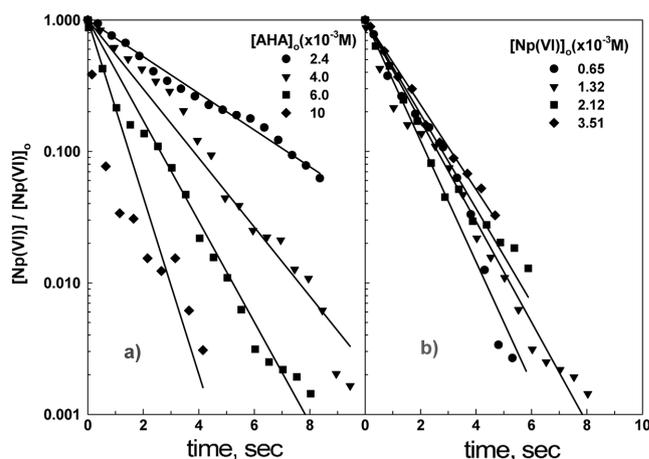


Figure 1. Plot of $[\text{Np(VI)}]/[\text{Np(VI)}]_0$ vs. time. (a) at $[\text{Np(VI)}] = 1.32 \times 10^{-3}$ M, $[\text{HNO}_3] = 1.0$ M, b) at $[\text{AHA}] = 6.0 \times 10^{-3}$ M, $[\text{HNO}_3] = 1.0$ M, 25 ± 0.5 °C

$$\frac{1}{[\text{Np(VI)}]_0 - [\text{AHA}]_0} \times \ln\left(\frac{[\text{AHA}]_0}{[\text{Np(VI)}]_0} \cdot \frac{[\text{Np(VI)}]_0 - [\text{Np(V)}]_0}{[\text{AHA}]_0 - [\text{Np(V)}]_0}\right) = kt \quad (4)$$

Hence, a plot of the left-hand side (2nd order function) versus t will give a straight line of slope k through the origin. Figure 2 shows that the experimental data is consistent with equation (4). Consequently, the values of k were determined under various $[\text{Np(VI)}]_0$ and $[\text{AHA}]_0$ conditions and are listed in Table 1. Also, since all the experiments were run at the same temperature, k has a value of $k = 191.2 \pm 11.2$ $\text{M}^{-1}\text{s}^{-1}$ at 25 ± 0.5 °C and $[\text{HNO}_3] = 1.0$ M.

Conclusions

The rate equation for the reduction of Np(VI) to Np(V) by

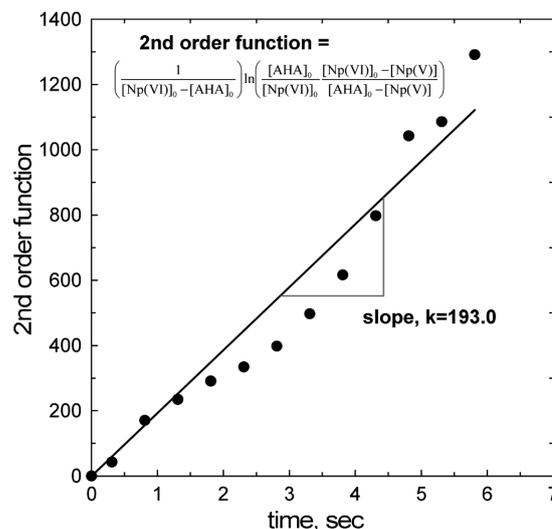


Figure 2. The 2nd order function against time for the reduction of Np(VI) by AHA at 25 ± 0.5 °C. ($[\text{Np(VI)}]_0 = 6.5 \times 10^{-4}$ M and $[\text{AHA}]_0 = 6.0 \times 10^{-3}$ M)

Table 1. Rate constants of Np(VI)-AHA reaction at $[\text{HNO}_3] = 1.0$ M and 25 ± 0.5 °C

$[\text{Np(VI)}]_0$ (M)	$[\text{AHA}]_0$ (M)	k ($\text{M}^{-1}\text{s}^{-1}$)
1.32×10^{-3}	2.4×10^{-3}	201.8
1.32×10^{-3}	4.0×10^{-3}	191.2
1.32×10^{-3}	6.0×10^{-3}	182.4
1.32×10^{-3}	1.0×10^{-2}	173.3
6.5×10^{-4}	6.0×10^{-3}	193.0
2.12×10^{-3}	6.0×10^{-3}	187.2
3.51×10^{-3}	6.0×10^{-3}	209.3
Average		191.2 ± 11.2

acetohydroxamic acid in nitric acid has been determined. The reduction of Np(VI) by AHA in nitric acid is rapid and first order with respect to both $[\text{Np(VI)}]$ and $[\text{AHA}]$. The reduction of Np(V) to Np(IV) by AHA in a nitric acid media was not found.

Acknowledgments. This work has been carried out as part of nuclear R&D program of Korea Atomic Energy Research Institute (KAERI) funded by the Ministry of Science and Technology of Korea.

References

1. Drake, V. A. *Science and Technology of Tributylphosphate*, Vol.

- III. Applications of Tributylphosphate in Nuclear Fuel Reprocessing*; Schulz, W. W.; Burger, L. L.; Navratil, J. D.; Bender, K. P., Eds.; CRC Press Inc.: Florida, 1990; pp 123-145.
2. Taylor, R. J.; Denniss, I. S.; Wallwork, A. L. *Nuclear Energy* **1997**, 36, 39.
3. Burney, G. A.; Harbour, R. M. *Radiochemistry of Neptunium*, NAS-NS-3060; US Atomic Energy Commission: 1974.
4. Kolarik, Z.; Dressler, P. *Purex Process Related Distribution Data on Np(IV,VI)*, KfK-4667; Karlsruhe, 1990.
5. Taylor, R. J.; May, I.; Wallwork, A. L.; Denniss, I. S.; Hill, N. J.; Galkin, B. Ya.; Zilberman, B. Ya.; Fedorov, Yu. S. *J. of Alloys and Compounds* **1998**, 271-273, 534.
6. Taylor, R. J.; May, I. *Separation Science and Technology* **2001**, 35, 1225.
7. Koltunov, V. S.; Taylor, R. J.; Baranov, S. M.; Mezhev, E. A.; May, I. *Radiochim. Acta* **1999**, 86, 115.
8. Koltunov, V. S.; Baranov, S. M. *Inorganica Chimica Acta* **1987**, 140, 31.
9. Taylor, R. J.; May, I.; Koltunov, V. S.; Baranov, S. M.; Marchenko, V. I.; Mezhev, E. A.; Pastuschak, V. G.; Zhuravleva, G. I.; Saviliva, O. A. *Radiochim. Acta* **1998**, 81, 149.
10. Taylor, R. J.; May, I. *Czech. J. Phys.* **1999**, 49/S1, 617.
11. Taylor, R. J. *J. of Nucl. Sci. and Tech.* **2002**, Supp.3, 886.
12. May, I.; Taylor, R. J.; Denniss, I. S.; Brown, G.; Wallwork, A. L.; Hill, N. J.; Rawson, J. M.; Less, R. *J. of Alloys and Compounds* **1998**, 275-277, 769.
13. Colston, B. J.; Choppin, G. R.; Taylor, R. J. *Radiochim. Acta* **2000**, 88, 329.
14. May, I.; Taylor, R. J.; Brown, G. *J. of Alloys and Compounds* **1998**, 271-273, 650.
15. May, I.; Taylor, R. J.; Denniss, I. S.; Brown, G.; Wallwork, A. L.; Hill, N. J.; Rawson, J. M.; Less, R. *J. of Alloys and Compounds* **1998**, 275-277, 769.