Kinetic Study of the Reduction of Np(VI) by Acetohydroxamic Acid in the Aqueous Solution

Dong-Yong Chung and Eil-Hee Lee

Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong-gu, Daejeon

ndychung@kaeri.re.kr

Irradiated spent nuclear fuel is reprocessed commercially by the Purex 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. 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 Purex process is important for the efficient production of purified U and Pu products.

In a nitric acid solution, Np can exist simultaneously in three stable oxidation states, Np(IV), Np(V) and Np(VI) (Np^{4+}, NpO_2^{+}, NpO_2^{2+} ions). Np(V) is almost inextractable, 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.

Formohydroxamic acid(FHA) and acetohydroxamic acid(AHA) are especially suited to the separation of Np(IV) from U(VI) by a 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. The reduction of Np(VI) by formohydroxamic acid in 2.0 M HNO_3 has been reported. A rapid reduction, taking less than a few seconds to complete, was demonstrated. The kinetics, as determined by a stopped-flow spectrophotometry, have been shown to be a first order with respect to [FHA] and [Np(VI)] with a rate constant k=1019 $M^{-1}s^{-1}$ at 22℃ and [HNO_3]=2.0 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. The rate equation for the reduction of Np(VI) to Np(V) in nitric acid aqueous solution have been determined as:

$$-\frac{d[NpO_2^{2+}]}{dt} = k[NpO_2^{2+}][AHA]$$

with k=191.2±11.2 $M^{-1}s^{-1}$ at 25℃ and [HNO_3]=1.0 M.

Comparison with other reductants available in the literature, acetohydroxamic acid is a strong agent for NpO_2^{2+}.