REDOX REACTIONS OF NEPTUNIUM WITH NITROUS ACID AND ACETOHYDROXAMIC ACID UNDER RADIOLYSIS CONDITIONS

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Abstract

Nitrous acid (HNO_2) is an important redox-active compound significantly influencing the extraction behavior of neptunium and plutonium during separation processes. Nitrous acid, present in high content in the aqueous phase, acts as a stabilizer of extractable tetravalent plutonium; it has a catalytic effect on the rate of oxidation of Np(V) by HNO_3, but on the other hand, it also leads to the reduction of a significant portion of neptunium to its non-extractable pentavalent state. Redox behavior of neptunium in gamma-irradiated nitric acid of 0.5 M – 4 M concentration and radiolytic production of HNO_2 was investigated spectrophotometrically.

Nitrous acid was found to be well extracted (log D ≈ 1). The equilibrium between Np(V) and Np(VI) was achieved regardless of the initial fractions of the oxidation states Np(V):Np(VI), which varied from 5:95 to 45:55, and the final redox speciation of neptunium was found to be controlled primarily by the radiolytically produced nitrous acid. The radiolytic yields of HNO_2 in the aqueous phase were found significantly lower than in the organic phase – which is a result of much smaller presence in the organic phase of nitrite-scavenging intermediate species produced by the radiolysis of water (such as the hydroxyl radical or hydrogen peroxide).

Nitrous acid is also scavenged by acetohydroxamic acid (AHA, $CH_3CO\text{-}NHOH$) that was proposed as a salt-free stripping reagent to advanced PUREX process (UREX) to effectively separate neptunium and plutonium from uranium product. While rapidly reducing Np(VI) and Pu(VI), and forming un-extractable complexes with Np(IV) and Pu(IV), AHA doesn't affect the extraction of uranium. However, investigation of the redox stability of Np(V) in solutions of AHA-HNO_3 has revealed that after several hours, once all AHA is hydrolyzed into hydroxylamine, nitrous acid generated by autocatalytic reaction of hydroxylamine with nitric acid causes a sudden reoxidation of Np(V) to Np(VI). This effect prevents utilization of AHA as a long-term holding reductant for neptunium and plutonium and can complicate reprocessing operations.