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Neptunium Redox Chemistry in Irradiated HNO3 Solutions

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The reliable separation methods for neptunium assume the ability to maintain a preferred oxidation state. However, regardless of its initial redox speciation, a series of reactions occurs in nitric acid to create a mixture of oxidation states including Np(V), Np(VI) and sometimes Np(IV). Additionally, the irradiated solutions such as dissolved nuclear fuel contain both transient and long-lived radiolysis products which may be strongly oxidizing or reducing. Thus, irradiation may be expected to impact the chemical equilibrium and distributions of neptunium of various oxidation states.

Among the transient products of the irradiation of aqueous nitric acid are the reducing •H atom and solvated electron and the oxidizing •OH radical from water radiolysis, and the oxidizing •NO3 and •NO2 radicals from nitric acid radiolysis. Longer-lived radiolysis products include hydrogen peroxide from water radiolysis and nitrous acid from nitric acid radiolysis. While it has been known that HNO2 acts as a reducing agent toward Np(VI); the effects of the oxidizing transient species have been much less studied.

Solutions of neptunium in nitric acid irradiated with Co-60 gamma-rays were analyzed by UV/Vis spectroscopy on radiolytically-induced changes in neptunium valences, as well as the nitrous acid concentration. It was found that at low absorbed doses, the oxidizing radicals oxidized Np(V) to Np(VI). However, as the irradiation proceeded the concentration of nitrous acid became sufficient to reduce Np(VI) to Np(V), and then continued irradiation favored this reduction until an equilibrium was achieved in balance with the oxidation of Np(V) by nitric acid itself. The starting concentrations of the two neptunium valences did not affect the final equilibrium concentrations of Np(V) and Np(VI).

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