



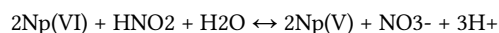
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Kinetics of reduction of hexavalent neptunium by nitrous acid in solutions of nitric acid

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Extraction of hexavalent and tetravalent actinides with tributylphosphate (TBP) from their solutions in nitric acid is the most industrially mature process for reprocessing of spent nuclear fuel and is the basis for the development of advanced reprocessing schemes like UREX and TRUEX. One of the less resolved issues is the management of neptunium in the extraction system, because of not clearly defined redox speciation. Neptunium is present in both pentavalent and hexavalent oxidation state that differ greatly in their extractability to the organic phase (hexavalent state being very well extracted by TBP, whereas pentavalent neptunium is almost not extracted). As a result, neptunium is distributed in both organic and aqueous streams of the separation process. Apparently, the most important factor determining the redox speciation of neptunium is the presence of nitrous acid that is formed during the dissolution of spent fuel and also by radiolysis. Nitrous acid HNO₂ is relatively well extracted by TBP ($\log D \approx 1$) and is therefore distributed from the source raffinate solution in further stages of the separation system [1]. If present in small quantities, it autocatalyzes the oxidation of Np(V) by nitric acid, whereas large concentration of HNO₂ leads to reduction of Np(VI) back to the pentavalent state –the kinetics of this reaction have been covered in detail by many authors [2]. The kinetics of reduction of Np(VI) by HNO₂ have so far attracted only little interest and are the subject of this study. UV-VIS-NIR absorption spectrophotometry (OceanOpticsTM) in a stirred cuvette was employed in order to study the reaction:



The reaction progress was recorded by following the absorbance at characteristic peak of Np(V) at 981nm and simultaneous observation of the broad absorption peak of HNO₂ between 350-400 nm. The reaction orders with respect to concentrations of Np(VI) and HNO₂ were found to be close to one. Increasing the concentration of nitric acid at constant ionic strength ($\mu=4\text{M H/LiNO}_3$) had a decreasing effect on the reaction rate with an order of -0.8. The dependence of the rate constant on the ionic strength and temperature will be also reported.

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