Redox chemistry of Pu and Np under alkaline to hyperalkaline pH conditions

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Aqueous actinide chemistry is a relevant, multifold and scientifically challenging research field of inorganic chemistry. In the context of nuclear waste disposal, actinides represent the main contributors to the radiotoxic inventory in a repository. Because of their specific electronic configuration, several oxidation states of actinides (+III to +VII) can exist in aqueous solution. This imposes specific chemical behaviour evolving as function of the boundary redox conditions. It is essential to continuously reduce experimental and systematic uncertainties, fill existing gaps in thermodynamic databases and improve knowledge and available data for relevant (geo)chemical systems.

This presentation focuses on plutonium and neptunium studies, highlighting the experimental and conceptual approach employed by KIT–INE for investigating aquatic actinide chemistry and thermodynamics. Based upon experimental studies to identify and quanitfy actinide redox transformation processes, systematic series of solubility experiments with relevant actinide solid phases are performed in dilute to concentrated saline systems. Solubility experiments are analysed with several complementary advanced analytical techniques available at KIT–INE, e.g. EXAFS, (synchrotron-based) in-situ XRD, TRLFS, TEM, among others. Comparisons with data for other actinides are systematically evaluated in order to analyse consistency within the actinide series.

Selected examples from recent research performed at KIT-INE will be presented and discussed in this contribution:

- Redox chemistry of Pu and Np under alkaline to hyperalkaline pH conditions,
- Np(VI) and Pu(VI) solubility in alkaline NaCl media: analogies with U(VI),
- Formation of Np(VII) under hyperalkaline oxidizing conditions.

All studies included in this presentation aim at deriving comprehensive thermodynamic models of the investigated systems, which can be implemented in thermodynamic databases.