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Solubility, speciation and solid phase formation of Pu(III) in dilute to concentrated carbonate-containing solutions

PHILIPP MÜLLER, DAVID FELLHAUER, DIETER SCHILD, XAVIER GAONA, KATHY DARDENNE, JÖRG ROTHE, MARCUS ALTMAIER AND HORST GECKEIS

Karlsruhe Institute of Technology

Emplacement in deep geological repositories is the internationally favored option for the final disposal of spent nuclear fuel and vitrified waste. With respect to the long-term safety assessment of repositories, the potential release of radionuclides in aqueous solutions is important. Processes such as solubility equilibria, complexation by inorganic and organic ligands, redox reactions, and interactions with mineral phases are relevant processes that influence the mobility of radionuclides and are therefore the focus of dedicated research.

Plutonium is the main transuranic element in spent nuclear fuel. Under the reducing conditions of a sealed deep geological repository, trivalent and tetravalent plutonium species are prevalent. Carbonate is a relevant ligand in environmental systems and interacts strongly with all actinide oxidation states. While the behavior of chemical analogues of Pu(III), namely Am(III), Cm(III) and Ln(III), were extensively studied in carbonate-containing solutions, there are only few investigations dedicated to Pu(III). Especially the lack of any systematic solubility study on the Pu(III)-CO_3 system currently implies uncertainties regarding the position and extension of the stability fields (Pourbaix diagrams) of Pu(III) and Pu(IV) in carbonate-containing solutions and related solubility phenomena.

In this study, the solid phase formation and solubility of $PuCO_3OH$(cr), $NaPu(CO_3)_2$(cr) and $KPu(CO_3)_2$(cr) were investigated. The transformed Pu(III)-carbonate phases were obtained by equilibration of $Pu(OH)_3$(am) in Na/K-HCO_3-CO_3-Cl solutions at T = 23 °C under argon atmosphere, and characterized by VIS/NIR, SEM/EDX, powder XRD and XAS. Subsequently, their solubility behavior was investigated using batch experiments as a function of ionic strength and pH_m (atmosphere: 99% Ar and 1% CO_2). The experimental solubility data show expected systematic dependences on pH_m and ionic strength and can be well described by the established thermodynamic model reported for the Am(III) and Cm(III) analog. The solubilities of the Pu(III)-carbonate-phases are up to 4 orders of magnitude lower than for $Pu(OH)_3$(am) which is currently often assumed as solubility-determining Pu(III) solid phase. Our results significantly extend the thermodynamic database for Pu(III) allowing more precise source term estimations for Pu under reducing repository relevant conditions.