

Kinetics and thermodynamics of the dissolution of $\text{Th}_{1-x}\text{M}_x\text{O}_2$ solid solutions (M = U, Pu)

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Abstract - Kinetics of the dissolution of $\text{Th}_{1-x}\text{M}_x\text{O}_2$ (M = U, Pu) solid solutions was investigated as a function of several chemical parameters such as pH, substitution ratio, temperature, ionic strength, and electrolyte. Several compositions of $\text{Th}_{1-x}\text{U}_x\text{O}_2$ and $\text{Th}_{1-x}\text{Pu}_x\text{O}_2$ were synthesized and characterized before and after leaching by using several methods such as XRD, EXAFS, BET, PIXE, SEM, and XPS. Leaching tests were performed in nitric, hydrochloric or sulfuric media and groundwater. The normalized dissolution rates were evaluated for $\text{Th}_{1-x}\text{U}_x\text{O}_2$, and $\text{Th}_{0.88}\text{Pu}_{0.12}\text{O}_2$ leading to the determination of the partial order related to the proton concentration, n , and to the corresponding normalized dissolution rate constant at $\text{pH} = 0$, k'_T . While for Th enriched solids, the solid solutions $\text{Th}_{1-x}\text{U}_x\text{O}_2$ have the same dissolution behaviour than ThO_2 with a partial order $n \sim 0.3$, in the case of uranium enriched solids, $\text{Th}_{1-x}\text{U}_x\text{O}_2$ has the same dissolution behaviour than UO_2 with a partial order of $n \geq 1$, indicating that uranium oxidation rate becomes the limiting step of the dissolution process.

The stoichiometry of the release of both actinides (U or Pu, Th) was verified until the precipitation of thorium occurred in the leachate for $\text{pH} > 2$, while uranium was released in the solution as an uranyl form. For uranium enriched solid solutions, thermodynamic equilibrium was reached after 100 days, and solubility constant of secondary phase was determined. In the case of $\text{Th}_{1-x}\text{Pu}_x\text{O}_2$, the dissolution behaviour is similar to that of ThO_2 , but only kinetic aspect of the dissolution can be studied. From the analysis of XPS and EXAFS data on leached and unleached $\text{Th}_{1-x}\text{U}_x\text{O}_2$ samples, the dissolution mechanism of solid solutions was explained and will be discussed. The role of the electrolytes on the dissolution of the solid solutions is discussed. Kinetics parameters of dissolution are also given in groundwater and in neutral media.