

Ph.D. defense

Institut de Chimie Séparative de Marcoule / CEA Marcoule
(UMR 5257, CEA, CNRS, Université Montpellier 2, ENSCM)

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will present her Ph.D. dissertation

Etude de la solubilité et des cinétiques de dissolution des phosphates et des vanadates d'uranium: implications pour l'amont du cycle électronucléaire

The defense will take place on **Friday, December 6, 2013 at 2:00 pm**
in the ICSM Auditorium

In the current context of restart of the nuclear energy, the needs in uranium are expected to increase significantly. Moreover, in a perspective of sustainable development, the exploitation, the treatment and the purification of uranium ores need to be optimized. It is thus necessary to determine reliable thermodynamic data (and especially solubility constants) for the systems of interest, especially uranium(VI) phosphates and vanadates. In this aim, a multiparametric study of the dissolution of meta-torbernite $\text{Cu}_{0.8}(\text{H}_3\text{O})_{0.2}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, meta-autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$, meta-ankoleïte $\text{K}_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ and carnotite $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ was undertaken.

First, analogues of these four minerals were synthesized, based only on dry chemistry process for carnotite or on wet chemistry methods for the phosphate phases. They were then extensively characterized (in terms of structure, microstructure and chemical composition). It particularly highlighted the similar structures of such compounds. The anionic groups (PO_4^{3-} or $\text{V}_2\text{O}_8^{6-}$) and uranyl form parallel layers between which counter cations (Cu^{2+} , Ca^{2+} or K^+) and water molecules are inserted. However, the counter cations present in the interlayer space of the three phosphate phases present different lability. The synthetic phases were also compared to their natural analogues, except for meta-ankoleïte, which allowed us to point out significant differences in the composition (presence of impurities in natural samples) and the morphology (grain size).

The dissolution of these phases was then studied from a kinetic and thermodynamic point of view, through leaching tests in static and dynamic conditions, in various acid media (sulfuric, nitric and hydrochloric) and at different temperatures. In these conditions, the dissolution of meta-autunite was found to be incongruent due to the precipitation of uranyl phosphate then avoiding the determination of solubility constants. Similarly, the dissolution of meta-ankoleïte was preceded by a cation exchange step between K^+ and H_3O^+ leading to the formation of $(\text{H}_3\text{O})_{2x}\text{K}_{2x-2}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ ($0 < x < 2$) solid solutions, whose solubility constant have been evaluated. Finally, meta-torbernite and carnotite presented congruent dissolutions, which allowed for the determination of thermodynamic data of interest such as solubility products and standard enthalpy, Gibbs free energy and entropy associated with the dissolution reaction ($\Delta_r H^0$, $\Delta_r G^0$, and $\Delta_r S^0$) and formation of each phase ($\Delta_f H^0$, $\Delta_f G^0$, and $\Delta_f S^0$).

The results obtained evidenced very low and similar solubility constants for the three phosphate phases studied ($10^{-53} < K_{s,0}^0 < 10^{-45}$). Such small variation directly came from the closely related crystal structures previously described. In addition, the difference in composition of the sheets between phosphate and vanadate phases led to greater stability of carnotite ($K_{s,0}^0 = 10^{-63}$) compared to phosphates phases. The solubility values derived from this study for phosphates and vanadates uranium(VI) allowed estimating values for similar phases. These data were also used in a geochemical model for the prediction of neoformed phases in a real case (water of a lake near an uranium deposit).

