ESTIMATING THE STABILITIES OF
AQUEOUS ACTINIDE COMPLEXES WITH SULFOXYANIONS

V. Phrommavanh, M. Descostes, P. Vitorge, C. Beaucaire, J.P. Gaudet*

*Service d'Etude du Comportement des Radionucléides,
Commissariat à l'Energie Atomique, F-91191 Gif-sur-Yvette*
*Laboratoire d'étude des Transferts en Hydrologie et Environnement,
ENSHMG, F-38041 Grenoble*

Stable aqueous sulfur species are mainly sulfide (H_2S) and sulfate (SO_4^{2-}) ions. However, several sulfoxyanions may be detected as metastable anions in natural environment, as typically thiosulfate ($S_2O_3^{2-}$) and sulfite (SO_3^{2-}) ions [1]. In natural systems, uranium speciation and migration are mainly governed by carbonate complexes in non reducing conditions. Whereas sulfate is already known as a complexing agent of actinides, data relating to $U-SO_3^{2-}$ and $U-S_2O_3^{2-}$ complexes have only been proposed for U(VI) [2] , but are usually not included in thermodynamic databases [3]. Therefore, it appears to be relevant to determine complexation constants of actinides with sulfur ligands, for RN migration studies, concerning nuclear waste disposal as well as migration behaviour in the geosphere.

In the present study, values have been estimated for the first complexing constants of $U^{(IV, VI)}-SO_3^{2-}$ and $U^{(IV, VI)}-S_2O_3^{2-}$ systems by using analogy with other metallic hard cations of alkali, alkaline-earth and lanthanide metals, and ions of transition and metalloid metals. First, a linear correlation has been observed between $\lg \beta_1$ ($M^{m+};L^{n-}$) and the first protonation constant, pKa, of hard anionic ligands for $L^{n-} = F^-$, SO_4^{2-} ; OH^-, CO_3^{2-}, Cl^-…

Published complexing constants for U(VI)–$S_2O_3^{2-}$ and SO_3^{2-} are on the correlation line, and can be used for other actinides such as NpO_2^{2+} and PuO_2^{2+}. Actinide(IV) complexes are predicted to be more stable than actinide(VI) complexes by 3 and 6 orders of magnitude for $S_2O_3^{2-}$ and SO_3^{2-} respectively. If confirmed, these values suggest to consider $S_2O_3^{2-}$ and SO_3^{2-} for U environmental speciation, typically at Uraninite and Pyrite interfaces, and for their dissolution.

[1] Beaucaire C. et *al* (1987) : Redox chemistry of uranium and iron, radium geochemistry, and uranium isotopes in the groundwaters of the Lodève Basin, Massif Central, France. *Applied Geochemistry* **2** , 417-426.
[2] Guillaumont R. et *al.* (2003) : Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. NEA-TDB, OECD, Amsterdam.
[3] Hummel W. et *al.* (2002) : Chemical Thermodynamic Data Base 01/01, Nagra/PSI, Universal Publishers, USA.