Uranium series disequilibrium in the Opalinus Clay – A way to assess the effective diffusion coefficient for ^{234}U

M. PEKALA, J.D. KRAMERS AND H.N. WABER

Institute of Geological Sciences, University of Berne, Switzerland (pekala@geo.unibe.ch, kramers@geo.unibe.ch, waber@geo.unibe.ch)

The Opalinus Clay formation (OPA) in northern Switzerland is considered as a potential host rock for a deep nuclear waste repository. In such a very low permeability, diffusion dominated system the effective diffusion coefficient is a key question for the long-term safety assessments. We present the behaviour of some long-lived uranium series radionuclides in the OPA as well as a potential way of evaluating the effective, site-specific diffusion coefficient.

We studied samples of the OPA by sequential leaching with aqua regia and HF+$HClO_4$ as major final steps. The latter fraction contained most U, with a low Th/U ratio and (^{234}U/^{238}U) below equilibrium. We consider this to reflect submicron zircon grains. Pre-HF-$HClO_4$ leachates have (^{234}U/^{238}U) excess. Bulk rock (^{234}U/^{238}U) vary between 0.85 and 1.07. In the reducing pore water environment of the OPA ^{234}U is mobile due to such phenomena as alpha recoil [1], preferential leaching from radiation damaged sites [2] and oxidation of U to hexavalent state through nuclear decay [3]. The main reservoir for U are zircon grains that serve as constant rate suppliers of high solubility hexavalent ^{234}U to the pore water where it is slowly and mainly diffusively transported. A distinct anticorrelation between the concentrations of U and the (^{234}U/^{238}U) activity ratios is seen. This suggests that ^{234}U moves from regions of higher uranium concentrations towards those of lower concentrations. This fact along with sharp U concentration gradients implies very slow self-redistribution of U accross the OPA. The U concentration – (^{234}U/^{238}U) anticorrelation puts limits on the effectiveness of diffusion relative to supply.

A mathematical model that simulates the main processes responsible for U migration in the OPA is proposed. This model makes it possible to evaluate the effective diffusion coefficient for ^{234}U in that formation.

References

[1] Kigoshi K., (1971), Science 156, 932-934.
[2] Cherdyntsev V., (1955), Trans. 3rd Sess. Commision for Determining the Absolute Age of Geol. Formations, 175-182.
[3] Rosholt J. et al, (1963), Science 139, 224-226.

Thermochemical and experimental stability of synthetic La-bearing minerals as analogues to nuclear-waste forms

E. JANOTS[1], F. BRUNET[1], B. GOFFÉ[1] AND C. POINSSOT[2]

[1]Lab. de Géologie, ENS-CNRS, Paris, France (goffe@geologie.ens.fr)
[2]DEN/DPC/SECR, CEA, Saclay, France

Among the crystalline nuclear waste-forms suitable for retaining radionuclides from high-level waste, two mineral structures adopted by rare-earth-elements-bearing minerals in nature, are proposed: the monazite and the apatite structures. Nevertheless, the thermochemical properties required to predict the solubility of the corresponding mineral analogues at various pressures and temperatures remain poorly known (*i.e.* formation enthalpy, third-law entropy, heat capacity, volume). Therefore, these thermochemical data were measured for one phase of each group synthesized in the La_2O_3-CaO-SiO_2-P_2O_5-H_2O system: monazite, $LaPO_4$, and La-britholite, a silicate-apatite, $Ca_2La_3(SiO_4)_3OH$. Formation enthalpies were derived from high-temperature drop-solution calorimetry using lead borate at 975 K as solvent (Bochum, Germany). Third-law entropy value was retrieved from low-temperature heat capacities measured on monazite with an adiabatic calorimeter (LCP, Orsay) in the 30-300 K range. Heat capacities (Cp) in the 143-723 K ranges were determined from differential scanning calorimetry (Kiel, Germany). Calorimetric results were combined to thermochemical data of REE aqueous species and minerals to study the solubility of monazite and silicate apatite. In order to test these thermochemical calculations, high-temperature reactivity experiments (thermal gradient, 320–400 °C over 15 cm) were undertaken under hydrothermal conditions in presence of clays and concrete to simulate the near field. After two to eight months, monazite and silicate apatite were preserved with only a few evidence of partial destabilisation. In similar conditions, these minerals are much more stable than another synthetic phase proposed as ceramic for radionuclide storage, the thorium phosphate diphosphate, $Th_4(PO_4)_4P_2O_7$, which reacts with cement to form hydroxylapatite and thorianite (ThO_2). In conclusion, monazite appears as an excellent waste form for actinides in term of chemical durability whereas silicate apatite could be largely stabilised by high temperatures and basic calcium-rich solutions.