

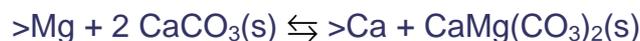
Modelling the speciation of sorbed species on clayey materials

Descostes M., Vitorge P.
michael.descostes AT cea.fr

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Calculating the migration of radionuclides in pore waters is essential for the performance assessments of underground radioactive waste disposals. A key problem is the retention of radionuclides on mineral surfaces. Aqueous chemical speciation of radionuclides is important since complexation is in competition with retention effects. On the other hand the aqueous speciation of the major elements is also important because major cations are known to be in competition with radionuclides for sorption sites. In granitic formations, the understanding of the water/rock system is well established (Grimaud et al., 1990). The numerous dissolved species are actually well constrained, since almost each element is controlled by a mineral phase, which diminishes considerably the degrees of freedom. Halogen elements are usually considered as free elements, *i.e.* their concentrations are not constrained by the precipitation of a mineral phase. The same approach has been developed for clayey formations, but it was concluded that geochemical modelling might also have to take into account ion exchange reactions at the clay mineral surface (Beaucaire et al., 2000). Nevertheless, the lack of experimental data -and above all the low water contents of such rocks- lead scientists to extrapolate experimental data from leaching experiments before further modelling (Bradbury and Baeyens, 1998; Gaucher et al., 2002; Motellier et al., 2002).

We used a homogeneous set of data from Motellier et al. (2002) already interpreted in terms of ionic exchange constants $K_{ex,i}$, number of exchange sites of capacity CEC_i on the COx argillite. Typically Cl⁻ was considered as a free element (determined by leaching experiments), whereas the concentrations of elements Al, Si, Na, K, Ca, Mg were constrained by saturation with a mineral phase, and by ionic exchange reactions. The inorganic C content was fixed. pH was obtained from the electroneutrality condition. However there are still uncertainties concerning each modelling parameter: (i) sulfate content might have been overestimated as a result of pyrite oxidative dissolution (Descostes, 2001), which (ii) would also induce acidification, calcite and dolomite dissolutions and overestimation of aqueous bicarbonate; (iii) CO₂ degassing would also induce an overestimation of calcium and magnesium contents; (iv) ion exchange models. These uncertainties can be dramatic specially, when using the electroneutrality condition. To circumvent the electroneutrality difficulty we performed a parametric study (pH and P_{CO₂}) on the COx argillite. This modelling was carried out taking into account 3 ionic exchange sites, Ca²⁺ and Mg²⁺ contents imposed by calcite and dolomite solubilities, [HCO₃⁻]=10⁻⁴ mol.L⁻¹. Ca²⁺ and Mg²⁺ are the main sorbed cations at the clayey mineral surface. The proportion of each sorbed cation tends to change with pH (sorbed species Y^{Z+} are noted >Y): >H is predominant in acidic condition, whereas >Na and >K increase with pH. The ratio of sorbed Ca and Mg is constant since it is regulated by the following equilibrium:



In the full paper we will discuss the influence of major cations of groundwaters on the saturation of each site for different clayey materials. The speciation of the clayey

mineral is focussed on, since radioactive ions are expected to be sorbed on this material through ionic exchanges with the major ions.