

APPARENT SOLUBILITY OF SILICA IN ARGILLITE PORE WATERS

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The controls of silica concentrations in argillite pore water have significant bearing on potential mineralogical transformations with temperature and due to interaction with engineered barrier materials and waste matrices. A particularly important issue are Si concentration controls with respect to the dissolution of nuclear waste glass. A detailed study of Si solubility of various constituting minerals and of Callovo-Oxfordian (COX) clay stone samples has been conducted in the frame of ANDRA's laboratory consortium on interactions in the clay/steel/glass system. Solubility experiments were conducted at pH 7-8 for 400 d at 25, 50 and 90°C for quartz, illite, MX80 bentonite and two COX samples of rather similar mineralogical composition from the C2b1 horizon. Reversibility at solubility equilibrium was checked by ³²Si addition after achievement of solubility equilibrium. Time to reach apparent equilibrium is about 100 days. Si concentrations obtained in batch experiments at low clay/water ratios (between 10 and 20 g/l) were similar to those obtained for the compact clay pore water collected by high pressure percolation experiments both at 25 and 90°C. The obtained data were also similar to Si concentrations reported for field conditions¹. It is interesting to notice that apparent equilibrium concentrations of Si for clay rock samples vary by as much as a factor of 5 for rock samples which are less than a meter apart. This indicates that Si concentrations are controlled by local solubility equilibria.

Experimental data can be described both by sorption constants and by solubility equilibrium. Rationalizing the data as sorption processes, both the number of exchanging surface sites and K_d values were obtained from isotopic exchange experiments. Such data are used in the literature to assess by modeling the effect of clay rock on nuclear waste glass dissolution. However, relative large parts (50 to 100%) of crystallographic Si surface sites participate in the exchange equilibrium for all minerals at 25°C and hence, it is more likely that the observed dynamic exchange involves a whole monolayer on the surface not only on quartz, but as well on the edge sites of illite and bentonite clay. At high temperature (90°C) the extent of Si isotopic exchange remains similar for bentonite but it increases for illite and quartz by a factor of 3 and for COX samples by as much as a factor of 10. For clay samples this cannot be described by a simple sorption constant but by solubility constraints involving surface precipitation and/or surface restructuring at edge sites. Solution concentrations of Si in case of clay rock samples are lower but close to quartz solubility at all temperatures.

Reference:

ANDRA, Callovo-Oxfordian Pore Water Geochemical Characterization PAC Experiment – Meuse/Haute Marne Underground Research Laboratory, A. Vinsot, S. Mittler, 2007