# AN EVALUATION OF GEOCHEMICAL MODELS OF BENTONITE PORE WATER EVOLUTION

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The understanding of the evolution of bentonite pore water composition with time underpins many EBS issues, such as: buffer erosion; canister corrosion; radionuclide solubility, sorption, diffusion; and plays a vital, if indirect, role in safety assessment. Models of bentonite-water interactions usually consider cation exchange, clay edge surface reactions, and the hydrolysis of calcite, gypsum, and quartz. Clay hydrolysis is usually ignored, which means that clay is assumed to be preserved indefinitely, even over million-year timescales. Unfortunately, this is contrary to evidence from natural systems, which indicates that smectites may be destroyed over safety-relevant timescales (e.g. Savage *et al.*, in press). Here, we present an alternative model that incorporates clay hydrolysis reactions, and which has been tested against laboratory data where Eh and pH have been measured directly in compacted bentonite.

Simulations of 'end-point' pH measurements in batch bentonite-water slurry experiments showed different pH values according to the complexity of the system studied. The most complete system investigated (clay hydrolysis + cation exchange + trace mineral solubility + clay edge reactions) revealed pH values were a strong function of $CO_{2(g)}$ partial pressure, with pH increasing with decreasing $pCO_2$ (log $pCO_2$ values from -3.5 to -7.5 bars produced pH values from 7.9 to 9.6). A slightly less complex system excluding clay mineral hydrolysis produced essentially identical pH values ranging across the same values of $pCO_2$. Therefore these 'end-point' calculations showed that the inclusion of clay mineral hydrolysis has an insignificant impact upon calculated pore fluid pH.

Other simulations investigating disequilibrium between clay and pore fluid in lab squeezing cell tests (Muurinen & Carlsson, 2007) with water (pH = 9.0) or a 1M NaOH solution (pH = 12.1) ignored the presence of trace minerals, clay cation exchange, and clay edge reactions in the interests of focusing upon the effects of clay hydrolysis. Simulations carried out for 100 days (experimental time scale) showed that smectite remained far from equilibrium throughout, and that accompanying changes in pH due to smectite hydrolysis were trivial. This confirmed that on the timescale of the experiments, clay hydrolysis is insignificant in modifying pore fluid composition. Extending the time to that required for clay equilibration necessitated 7 and 65 years for pure water and 1M NaOH, respectively, and again produced relatively minor changes in pH (decreasing by 0.1-0.2 pH units). However, if the (equilibrium) precipitation of secondary minerals was included, then not only was the equilibration period extended dramatically (7 to 360 years for pure water; 65 to 2600 years for 1 M NaOH), but changes in pH were significant (9.0 to 8.6 for pure water; 12.1 to 9.0 for 1 M NaOH). Repetition of these calculations using an alternative method of estimating smectite $\_G_f^0$ (Vieillard, 2000) replacing the Polymerisation model (Mattigod & Sposito, 1978) increased the equilibration time for reaction with 1M NaOH to 5000 years, highlighting the effects of the uncertainty in thermodynamic data for smectite.

Calculations were also carried out to study both the time- and space-dependent variations in pore fluid composition during in-diffusion experiments conducted for over 600 days (again from Muurinen & Carlsson, 2007), initially with pure water and 'spiked' after 271 days with a Na-Ca-OH-Cl solution (pH = 11.7). Here, the sensitivity of the results to both variations in a number of parameters/conditions (porosity, reaction rate of secondary minerals, degree of mixing of the external fluid reservoirs, effective diffusion
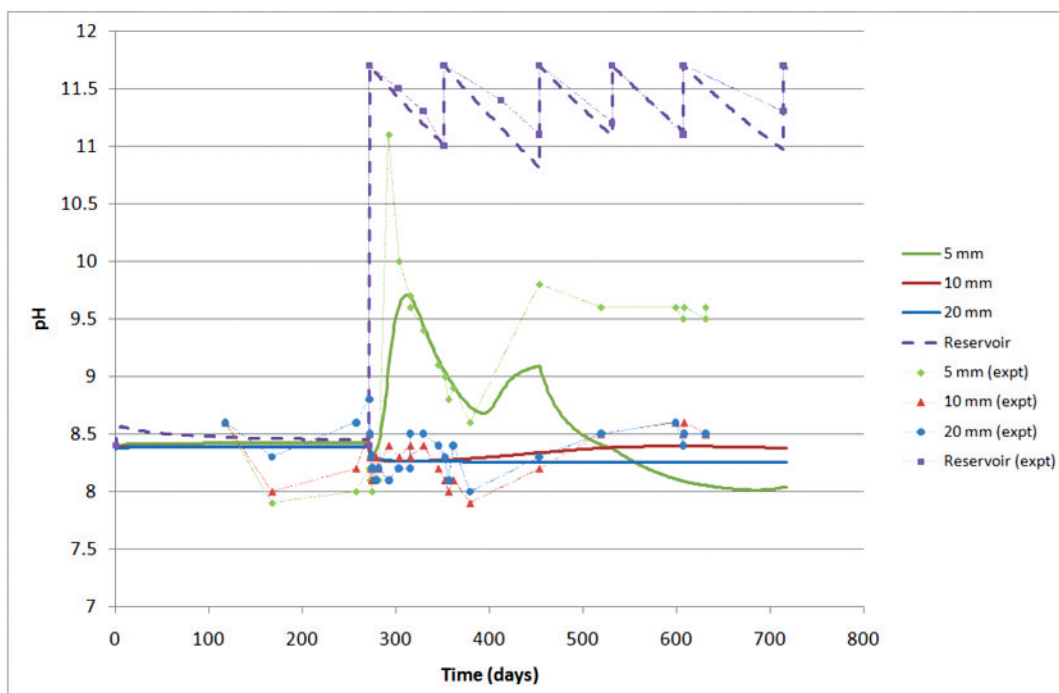
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**Figure 1:** The evolution of pH with time and depth for an in-diffusion experiment reported by Muurinen and Carlsson (2007). The model includes smectite hydrolysis, secondary mineral precipitation, surface complexation, and a less well-mixed reservoir. Experimental data are shown as points.

coefficient) and the inclusion of key processes (clay hydrolysis, secondary mineral precipitation, ion exchange, clay edge reactions) were investigated. This showed that there were closer fits to data at shallow depths in the bentonite than those at greater depth (Figure 1), suggesting that there was a process missing in the simulations (Donnan exclusion?) which inhibited diffusion of solutes to greater depths in the experiments.

In conclusion, the modelling does not support the view that because smectite dissolution is slow, it is a process of minor importance in the geochemical evolution of the EBS. The effects of smectite dissolution on the chemistry of bentonite pore waters would be essentially undetectable over time scales of a few years, but when both reaction kinetics and precipitation of secondary phases are included in the simulations, significant changes in solution chemistry and mineralogy are predicted to occur over time scales that are relevant to EBS evolution (hundreds to thousands of years). The simulations are of a scoping nature and do not fully account for uncertainties related to the variable chemistry of the smectite clays, the nature of porosity in compacted clays, the reactive surface area of smectite, and the thermodynamic properties of clay minerals. Studies of natural systems could provide a new perspective on these uncertainties, and provide approaches that could be used to resolve them.

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