



MODELING GAS – WATER - ROCK REACTIONS INSIDE A PACKED - OFF SAMPLING INTERVAL IN THE OPALINUS CLAY (SWITZERLAND)

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Geochemical modeling of gas-water-rock reactions was performed based on kinetic and equilibrium approaches. The objective was to explain the differences in the chemical composition of two seep waters (A2-18 and A2-37) sampled from the same sealed section of borehole BWS-A2. Both samples were obtained in two different campaigns belonging to phase 3 (1998) and phase 4 (1999) of the Mont Terri Project in Switzerland, respectively. Besides of analytical uncertainties, discrepancies between both sampling campaigns refer to pH, sulphate content, alkalinity and pCO₂ measurements.

The borehole BWS-A2, of 20 m length, was drilled with compressed air flush, and it was instrumented for water sampling with a double packer system sealing off the lower side of a selected interval. The sampling interval, located above the last packer, at the end of the borehole, was N₂-flushed to remove the drilling air and to avoid some inlet of external air. The borehole instrumentation was left to collect water for periods of several months in order to obtain enough volume of water for in situ measurements and chemical analyses. For a period of two-three years, the flow rate calculated was in the range of 0-20 mL/day.

It was supposed that during the time between the two sampling periods the gas-phase filling the packered interval could cause a set of interactions among gas-water-solid phases. As a consequence, the seep water sampled seems to be not fully representative of the clayey media. If the purge by N₂(g) was complete and all the air which initially occupied the chamber was displaced, a gas-water equilibrium will take place between the dissolved CO₂(g) in the pore water and the gaseous phase in the chamber, which is totally composed of N₂(g). This equilibrium can trigger the water-rock reactions which control the CO₂(g) dissolved in the pore water, mainly represented by the water-calcite reaction. In this paper, geochemical modeling techniques were used to evaluate, both by equilibrium and kinetic approaches, the scope of these water-rock reactions during the period in which the two water sampling took place.

If the purge by N₂(g) was not complete, part of the air will stay in the gaseous phase of the chamber. Thus, the oxidation of the water will be added to the above mentioned processes. This oxidation can also trigger the water-rock reactions which determine the pore water redox state, mainly represented by the water-pyrite and water-Fe(OH)₃(a) reactions. Again, the scope of these water-rock reactions during the two sampling periods was evaluated by equilibrium and kinetic approaches.

In both cases transport by diffusion in the clayey media was included. The results indicated that despite the strong dependence of the rate of pyrite oxidation on the specific surface area, the time period between the two sampling campaigns is enough to water-rock reactions reach equilibrium. The equilibrium and kinetic approaches proposed reproduces fairly well the pore

water composition of the BWS-A2-37 sample and the processes occurred in the packered interval.

The calculations were done using the PHREEQC geochemical computer program (Parkhurst & Appelo 1999) and the Nagra/PSI thermochemical database, modified for PHREEQC (Pearson & Waber 1999).

Parkhurst D.L., Appelo C.A.J. (1999): PHREEQC (v.2): a computer program for speciation, reaction-path, 1D transport, and inverse geochemical calculations. USGS, Water-Resources Investigation Report.

Pearson F.J., Waber H.N. (1999): Nagra/PSI Thermochemical database: Preparation of a version for PHREEQC. Villingen, PSI, Switzerland, TN 44-99-01, 18pp.

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