Modeling biogeochemical reactive transport in a fracture zone

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Abstract – *A coupled model of groundwater flow, reactive solute transport and microbial processes for a fracture zone of the Äspö site at Sweden is presented. This is the model of the so-called Redox Zone Experiment aimed at evaluating the effects of tunnel construction on the geochemical conditions prevailing in a fracture granite. It is found that a model accounting for microbially-mediated geochemical processes is able to reproduce the unexpected measured increasing trends of dissolved sulfate and bicarbonate. The model is also useful for testing hypotheses regarding the role of microbial processes and evaluating the sensitivity of model results to changes in biochemical parameters.*

I. INTRODUCTION

The Äspö Hard Rock Laboratory (Äspö HRL) is a prototype, full-scale underground facility launched and operated by SKB (the Swedish Nuclear Waste Management Company). The main aim of the Äspö HRL is to provide an opportunity for research, development and demonstration in a realistic rock environment down to the depth planned for a future deep nuclear waste repository. The Äspö HRL is located in the southeast part of Sweden, 400 km south of Stockholm. The underground facility consists of a 3,600 m long tunnel which starts with an access ramp and runs in two spirals and turns down to a depth of 450 m under the Äspö island (Figure 1).

On March 13th 1991 the access tunnel of the Äspö HRL intersected a vertical fracture zone at a depth of 70 m below sea level. This vertical fracture zone is known within the context of the Äspö HRL as the Redox Zone (Figure 1). Prior to tunnel intersection, a borehole was drilled and sampled in order to characterize undisturbed conditions of groundwater at the tunnel position. These samples provided a reference state for comparing the subsequent evolution of groundwater conditions.

Prior to the intersection of the tunnel, the water table was located approximately 0.5 m below the topographic surface and remained close to the surface during the experiment[1]. Groundwater samples were collected in boreholes and tunnel walls during the Redox Zone Experiment. A detailed account of the Redox Zone Experiment can be found in Banwart et al. (1999)[2].

A sharp dilution front was observed in the tunnel three weeks after the start of the experiment. A dramatic decrease in Cl^- and cation concentrations was measured in samples collected from the roof of the tunnel. A short time later, dissolved Fe concentrations in tunnel inflows decreased to near zero for a period of a few weeks. This could be taken as an indication of the arrival of an oxidation front to the tunnel position[2]. However, after 50 days, significant dissolved Fe concentrations were measred at all sample locations while measured redox potentials remained within the range $-150 < Eh < -100$, thus indicating that anoxic conditions were prevailing in the fracture zone. pH remained constant near a value of 8 throughout the experiment[2]. Dilution of the saline native groundwater by fresh recharge water was the dominant process controlling the hydrochemistry evolution during the experiment. However, HCO_3^- and SO_4^{2-} concentrations increased significantly during the experiment at sampling points located at 70 m depth.

Isotopic and microbiological studies conclusively rule out SO_4^{2-} reduction during the experiment[3], and provide significant evidence supporting Fe(III) reduction as the respiration pathway for the oxidation of organic carbon in the fracture zone. Previous research at Äspö[4] also report a large increase in ^{14}C activity in both dissolved organic and inorganic carbon during the experiment, providing evidence for a source of water containing young organic carbon. There is no conclusive explanation[2] for the increase in dissolved SO_4^{2-}. Sulfur isotope data[5] show that SO_4^{2-} originating from either sea water, deeper groundwater or atmospheric deposition would not be consistent with the isotopic signature of dissolved SO_4^{2-} at sampled boreholes.

The Redox Zone Experiment carried out at the Äspö HRL provides a unique opportunity to study and model redox and other relevant geochemical, isotopic and microbiological processes, when an isolated vertical fracture zone is disturbed by the construction of a tunnel.

II. COUPLED FLOW AND REACTIVE TRANSPORT MODEL

Groundwater flow and reactive transport simulations accounting for inorganic chemical processes such as aqueous complexation, acid base reactions, redox processes, cation exchange and minerals dissolution/precipitation were performed.

Five different material zones were defined in the numerical model in order to account for spatial heterogeneity (Figure 2). There is field evidence for a decrease in fracture width in depth[6], from a nominal width of tens of meters on the ground surface to a nominal width of 1 m at a depth of 70 m. Assuming a constant hydraulic conductivity, a decrease of transmissivity with depth can be expected as a result of fracture width decreasing with depth. Results of hydraulic field tests[6] indicate that transmissivity at a depth of 45 m is larger than at a depth of 70 m, which is consistent with previous considerations. Three material zones were used to represent the transmissivity of the granite: material zone #1 which extends from the surface to a depth of 50 m, material zone #2 which covers from 50 to 150 m depth and, finally, material zone #3 which extends from 150 m to a depth of 300 m. Material zones #4 and #5 represent seafloor Baltic sea sediments and a nearby landfill, respectively (Figure 2).

Boundary conditions for groundwater flow include: impervious boundaries at both sides of the model (groundwater divides) and prescribed recharge of 30 mm/year on the upper boundary. An exception of the upper boundary is the Baltic Sea area where groundwater head is prescribed to a value of 0 m. The tunnel and the open borehole constitute inner boundaries of the model. Measured flow rates at these discharge points were prescribed.

The largest uncertainty for solute transport boundary conditions occurs at the bottom boundary. Chemical information about undisturbed saline native groundwater for the Redox Zone Experiment is available only at a depth of 70 m. In order to define the chemical composition at a depth of 300 m, an analysis of undisturbed chemical information at other locations of the Äspö site was performed. Clear relationships between concentrations and depth were found[7] which were used to generate bottom boundary conditions for the Redox Zone model.

In order to select the hydrochemical processes to be included in the reactive transport model, an analysis of chemical speciation was made with the initial waters (i.e. fresh and marine surface waters and native saline groundwater). More than 60 homogeneous reactions were finally selected including aqueous complexation, acid-base and redox processes. Moreover, 4 mineral phases were included in the reactive model as well as cation exchange between calcium and sodium. Minerals include: calcite, hematite, quartz and pyrite. Mineral selection was made on the basis of mineralogical characterization availabe at the Äspö laboratory. Details on the groundwater flow and reactive transport model can be found in Molinero (2000)[7]. Figure 3 shows the comparison of measured data and computed values of groundwater heads (at a depth of 45 m) and dissolved chlorides at tunnel surroundings.

The groundwater flow and reactive transport model is also able to reproduce accurately the recorded evolution of most dissolved species. However, numerical results underestimate measured bicarbonate and sulphate concentrations. These discrepancies may be caused by microbially-catalyzed processes.

III. COUPLED FLOW AND BIOGEOCHEMICAL REACTIVE TRANSPORT MODEL

In order to test microbial processes hypotheses, microbially-mediated processes were included within the reactive transport model using BIO-CORE[8]. These processes are fully coupled with abiotic reactions. There are firm evidences of microbial activity in the groundwater system of the Äspö site. The REX experiment[9] was launched in order to investigate in detail dissolved oxygen comsuption. This research was made by creating a controlled oxidising perturbation in a deep rock environment at the Äspö tunnel. Results of the REX experiment provided evidence for a significant microbial oxigen comsumption through the oxidation of organic carbon naturally present in groundwater[9]. There are several microbial processes taking place in the fracture zone[3]. Fermentation of Particulate Organic Carbon (POC) controlled by yeast (anaerobic rods and cocci) takes place in the shallow anaerobic zone. Dissolved oxygen coming from the surface is consumed by the aerobic metabolism near the surface. Fermentation provides the source of Dissolved Organic Carbon (DOC). In the fermentation processes, organic sulfur contained in POC could be released in the form of reduced sulfur such as HS^-. DOC and HS^- are then transported and oxidized in deeper parts containing Fe (III)-minerals. Iron-reducer microorganisms catallyze the oxidation of organic matter through the reduction of ferric minerals.

These processes can be represented by:

$$POC+H_2O \rightarrow DOC+HS^-+H^+ \quad (1)$$

$$DOC+Fe^{3+} \rightarrow HCO_3+H_2O+Fe^{2+} \quad (2)$$

$$HS^-+Fe^{3+} \rightarrow SO_4^{2-}+Fe^{2+} \quad (3)$$

In fact, not only Fe^{3+} can be employed as electron acceptor in the biodegradation of DOC. Other possible electron acceptors for the biodegradation of DOC include Mn^{4+}, Mn^{3+} and NO_3^-. Microbially-mediated processes described in Equations 1 to 3 were considered in the numerical model. It is assumed that Fe^{3+} is the only electron acceptor for the oxidation of DOC.

It is worth noting that in these microbially-mediated processes, DOC is produced by yeast metabolism from POC. At the same time DOC is also a substrate for iron-reducer microbes.

The rates of reactions (1), (2) and (3) are assumed to be controlled by Monod kinetics according to

$$R_{Yearst}=\mu_{\max yeast}C_{Yeast}\frac{C_{POC}}{K_{POC}+C_{POC}}\frac{C_{H2o}}{K_{H2o}+C_{H2o}} \quad (4)$$

$$R_{POC}=\frac{R_{Yeast}}{Y_{POC}} \quad (5)$$

and

$$R_{Fe-red}=\mu_{\max,Fe-red}C_{Fe-red}\frac{C_{DOC}}{K_{DOC}+C_{DOC}}\frac{C_{Fe^{3+}}}{K_{Fe^{3+}}+C_{Fe^{3+}}} \quad (5)$$

$$R_{DOC}=\frac{R_{Fe-red}}{Y_{DOC}} \quad (6)$$

where $\mu_{\max,yeast}$ and $\mu_{\max,Fe-red}$ are the maximum growth rate (specific rate) of yeast and iron-reducer (g of biomass/day), respectively; C is concentration measured as g biomass/L, g/L for DOC and moles/L for chemical species; K is the half-saturation constant (g/L for POC and DOC, moles/L for Fe^{3+}), R is the reaction rate, Y_{POC} and Y_{DOC} are yield coefficients of POC to yeast (g biomass/ g DOC) and DOC to iron-reducer, respectively.

Figure 4 shows a comparison of measured data and computed values of dissolved bicarbonates and sulphates. The hydrobiogeochemical model computes a dramatic increase of these two dissolved species as a result of accounting for the microbial processes described above. These calculations are in agreement with field-recorded trends. Sensitivity analyses have been carried out for several biochemical parameters. Dissolved concentrations of bicarbonate and sulphate are found to be very sensitive to changes in the values of maximum growth rate of yeast (Figure 4). Figure 4 shows computed results of the time evolution concentration of bicarbonate and sulphate after opening the tunnel, by using values of maximum growth rate for yeast ranging from 0.1547 to 0.1563 day^{-1}. Although not shown here, computed results are sensitive to half-saturation constants of microorganisms. On the

other hand, neither bicarbonate nor sulfate are sensitive to the maximum growth rate of iron-reducer. The numerical model is found to be less sensitive to other biological parameters.

IV. CONCLUSIONS

A coupled model of groundwater flow, reactive solute transport and microbial processes for the Redox fracture zone of the Äspö site at Sweden has been presented. A coupled groundwater flow and reactive transport model is able to reproduce observed drawdowns and concentrations of most dissolved species. However, it fails to explain the measured increasing trends of dissolved sulfate and bicarbonate. It has been shown that such trends can be reproduce by accounting for microbially-mediated geochemical processes. reproduce. Model sensitivity analyses indicate that concentrations of sulfate and bicarbonate are extremely sensitive to the maximum grow rate of the iron-reducer microbials.

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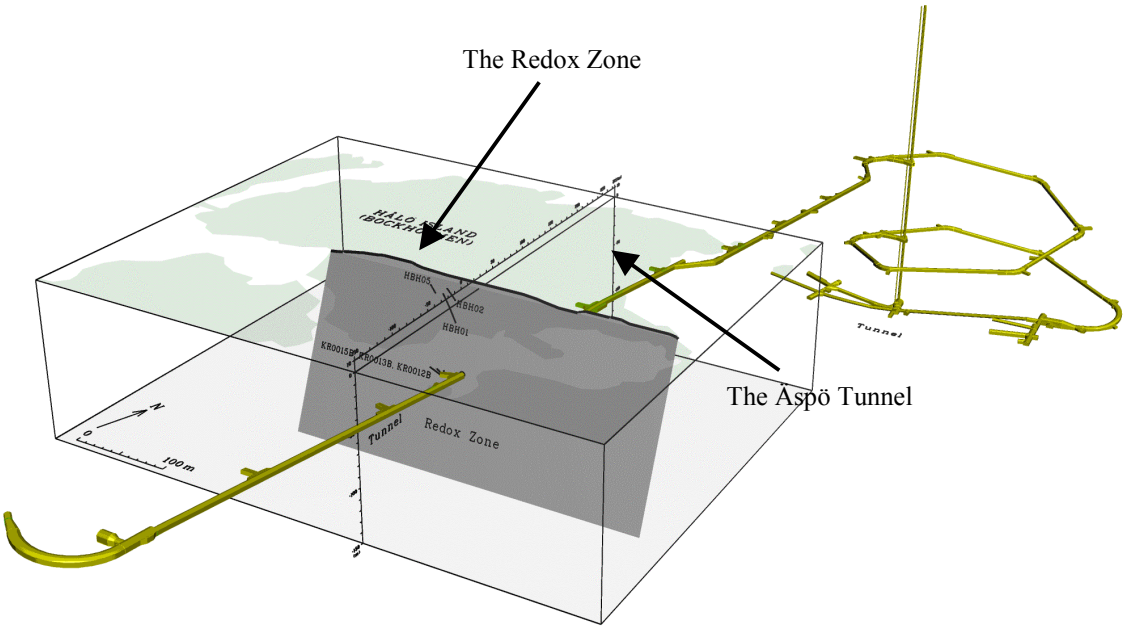

Figure 1. General layout of the Äspö HRL. The total length of the tunnel is 3,600 m. The first fracture zone intersected by the Äspö tunnel is known as the Redox Zone.

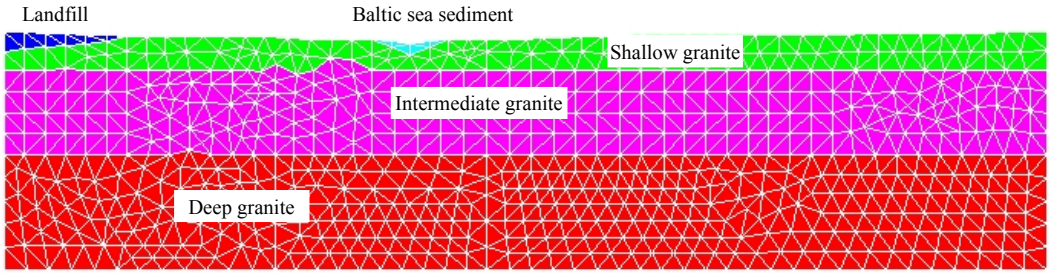

Figure 2. Finite element grid and material zones. The model domain is divided into 5 material zones according to their permeabilities.

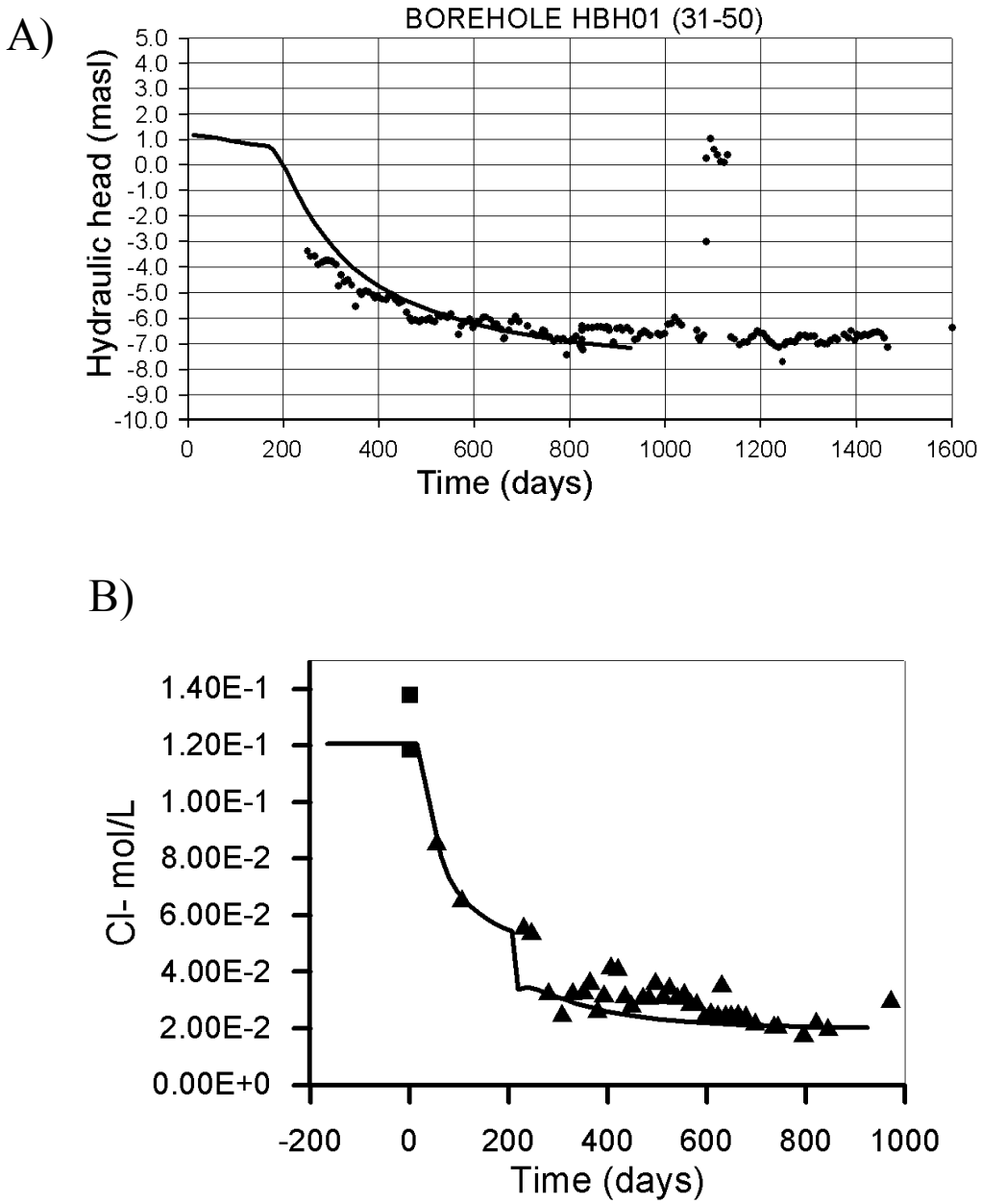

Figure 3. Computed (line) and measured (symbols) of: A) hydraulic heads (m) at a depth of 45 m, and B) chloride concentrations at the tunnel surroundings (70 m deep).

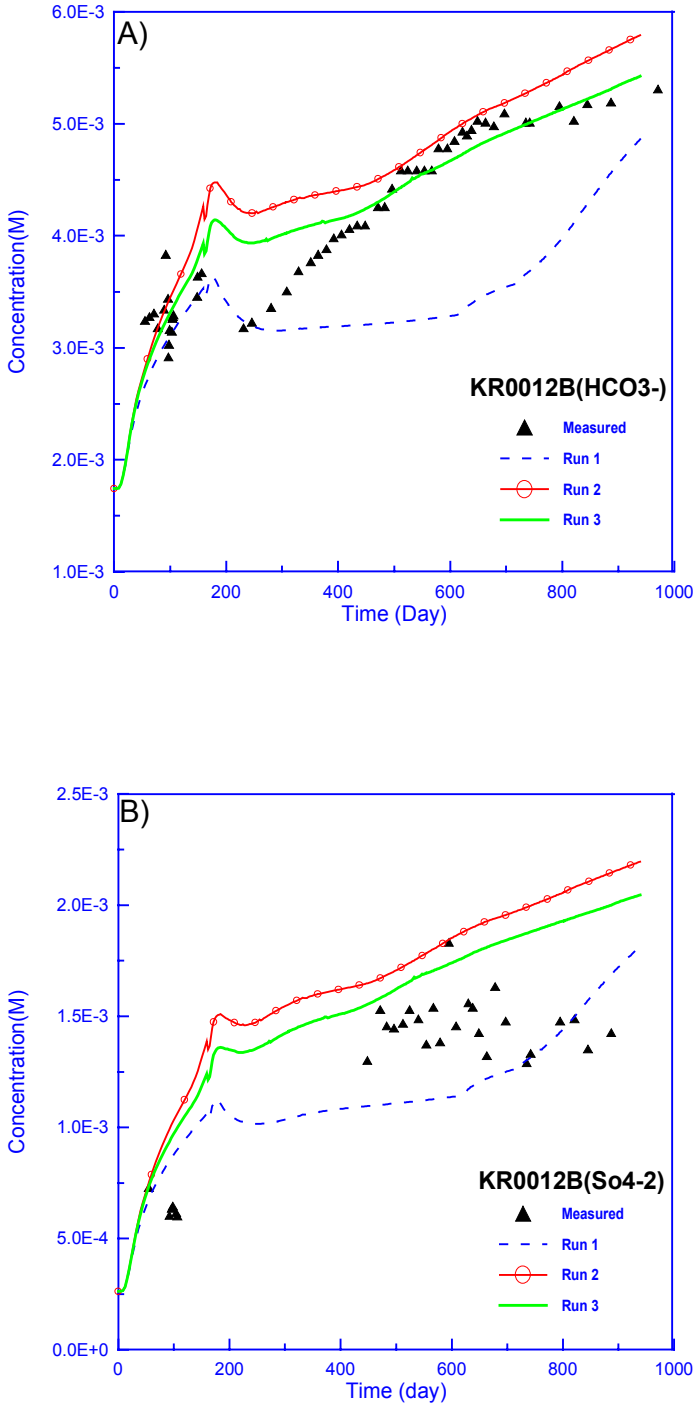

Figure 4. Measured and computed concentrations of bicarbonate (A) and sulphate (B) using different values of yeast's maximum growth rates: 0.1547 day^{-1} (Run 1), 0.1563 day^{-1} (Run 2) and 0.1555 day^{-1} (Run 3).