Model of geochemical interaction between water and granite

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Abstract In this contribution we simulate aqueous solution flow through a rock. The main focus was concentrated to chemical interactions between water and rock. The motivation for this work is an effort to predict the development of chemical composition of water after some anthropogenic activities. A general model of geochemical interactions between water and granite is presented. Sensitivity analysis of some components of the model was done to better understand the model.

Keywords geochemical modelling; water-rock interaction

INTRODUCTION AND BACKGROUND INFORMATION

Our aim was creating of global and real model of flow aqueous solution trough a fracture rock zone. We do this on the base of the previous work (Bruský 2008). If the model will be a really realistic one, it could be used to study of some effects in neighbourhood of a radioactive waste repository or in former uranium mine in Stráž pod Ralskem.

Our model is composed of two parts: the chemical reactive part and the transport part. In the chemical reactive part we describe chemical composition of the aqueous solution and chemical composition of reacting minerals in the rock. In this part we describe also the important chemical interactions. In the transport part we use common physical relations to define our problem.

CHEMICAL REACTIOVE PART OF THE MODEL

The major components participating in geochemical interactions between rain water and granite rock are written down in the Table 1.

Table 1 Chemical components in model.

(Ca^{2+})	(CO_2)
(H^+)	(Na_2X_2)
(OH^-)	(CaX_2)
(HCO_3^-)	(Al^{3+})
(Na^+)	(SiO_2)
(Cl^-)	(K^+)

All components are supposed to be dissolved in water and participating in chemical reactions, except of Na_2X_2 and CaX_2 that substitute the sorbed ions Na^+ and Ca^{2+} and Cl^- which does not react and is included into the model to hold electric neutrality of the solution:

$$\left(H^+\right)+\left(Na^+\right)+2\left(Ca^{2+}\right)+3\left(Al^{3+}\right)+\left(K^+\right)=\left(OH^-\right)+\left(HCO_3^-\right)+\left(Cl^-\right). \tag{1}$$

All concentrations of chemical components are expressed in terms of mol l^{-1}, i.e. the molar concentration (molarity). The concentration will be denoted by the symbol of the chemical component in brackets, for example (H^+) for molarity of H^+.

Chemical reactions

Chemical equations in the model describe interactions between the aqueous solution and the rock or chemical reactions in the aqueous solution. For our model, we suppose the normal conditions: temperature 25 °C and atmospheric pressure (1.01325×10^5 Pa). Our model is a closed system.

In our model, there are two types of chemical reactions: kinetic reactions and equilibrium reactions. Each chemical reaction tends to equilibrium and it takes some time. We classify the chemical reactions in agreement with which property is more important for us.

Kinetics reactions in our model

Each kinetic reaction r has a reaction rate $O^{(r)}$ (mol m^{-3} s^{-1}). We calculate reaction rate for the kinetic reaction from the equation:

$$O^{(r)} = k^{(r)}\, s^{(r)}\, \frac{1}{n}, \tag{2}$$

where $k^{(r)}$ (mol m^{-2} s^{-1}) is speed of releasing ions from rock to aqueous solution associated with a unit area of rock surface, $s^{(r)}$ (m) is reactive area of rock surface , i.e. the area of rock surface covered by reacting mineral in a unit volume of the rock, and n (-) is porosity of rock, i.e. the volume of pores in a unit volume of rock.

We suppose that these all variables are constant in whole modelled system for each chemical reaction r.

Relationship between reaction rate $O^{(r)}$ and kinetic reaction is given by equation:

$$O^{(r)} = \frac{1}{\nu_i^{(r)}} \frac{dm_i}{dt} \quad (\forall i). \tag{3}$$

Where m_i (mol l^{-1}) is molarity of the chemical component i, $\nu_i^{(r)}$ (-) is the stoichiometric coefficient of the chemical component i in the chemical reaction r, and t is time.

Kinetics reactions are a significant source of chemical components in the model. In our model, there are the following specific kinetic interactions between aqueous solution and rock:

- Dissolving of orthoclase in water. It is a source of potassium cation, aluminium cation, and silica, and it takes hydrogen cation. In terms of chemical equation:

  $$4\,H^+ + KAlSi_3O_8 \rightarrow K^+ + Al^{3+} + 3\,SiO_{2(aq)} + 2\,H_2O \tag{4}$$

  with the reaction rate $O^{(K^+)}$.

- Dissolving of albite. It is a source of sodium cation, aluminium cation, and silica, and it takes hydrogen cation. In terms of chemical equation:

  $$4\ H^+ + NaAlSi_3O_8 \rightarrow Na^+ + Al^{3+} + 3\ SiO_{2(aq)} + 2\ H_2O \tag{5}$$

  with the reaction rate $O^{(Na^+)}$.
- Dissolving of calciclase. It is a source of calcium cation, aluminium cation, and silica, and it takes hydrogen cation. In terms of chemical equation:

  $$8\ H^+ + CaAl_2Si_2O_8 \rightarrow Ca^{2+} + 2\ Al^{3+} + 2\ SiO_{2(aq)} + 4\ H_2O \tag{6}$$

  with the reaction rate $O^{(Ca^{2+})}$.

Equilibrium reactions in our model

Each equilibrium reaction has an equilibrium constant $K^{(r)}$ (-). The value of the equilibrium constant is computed from the Gibbs reactive isotherm using experimental or estimative standards combining Gibbs energies of reacting species.

The relationship between the equilibrium constant $K^{(r)}$ and the equilibrium reaction r is given by the equation:

$$K^{(r)} = \prod_i (\gamma_i\ m_i)^{\nu_i^{(r)}}\ , \tag{7}$$

where γ_i is activity coefficient of chemical component i (l mol^{-1}). We suppose that all activity coefficients are 1 (l mol^{-1}), because in our model, there are low concentrations of all chemical components.

Equilibrium reactions are chosen so that they describe elementary chemical actions in the modelled system:

- Dissolving of carbon dioxide in the water. This reaction is a source of a hydrogen cation and hydrogen carbonate anion. In terms of chemical equation:

  $$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{8}$$

  with the equilibrium constant $K^{(1)}$.
- Dissolving of calcite under rising of a calcium cation and a hydrogen carbonate anion. In terms of chemical equation:

  $$H^+ + CaCO_3 \leftrightarrow Ca^{2+} + HCO_3^- \tag{9}$$

  with the equilibrium constant $K^{(C)}$.
- Sodium and calcium ion exchange (sorption) on rock surface. In terms of chemical equation:

  $$CaX_2 + 2Na^+ \leftrightarrow Na_2X_2 + Ca^{2+} \tag{10}$$

  with the equilibrium constant $K^{(Sorb)}$.

- Dissociation of molecules of the water under rising of a hydrogen cation and a hydroxyl anion. In terms of chemical equation:

  $$H_2O \leftrightarrow H^+ + OH^- \qquad (11)$$

  with the equilibrium constant $K^{(H2O)}$.
- Precipitation of kaolinite taking an aluminium cation, silica, and water. In terms of chemical equation:

  $$2Al^{3+} + 2SiO_2 + 5H_2O \leftrightarrow 6H^+ + Al_2Si_2O_5(OH)_4 \qquad (12)$$

  with the equilibrium constant $K^{(7)}$.

TRANSPORT PART OF THE MODEL

Rain water is absorbed in the zone of infiltration in surface of the rock. Then the underground water moves with a natural water flow modelled by Darcy's law. Values of hydraulic conductivity, hydraulic head in zone of infiltration and hydraulic head at the spring were set so that transported solutes migrate 100 meters per year. See Figure 1.

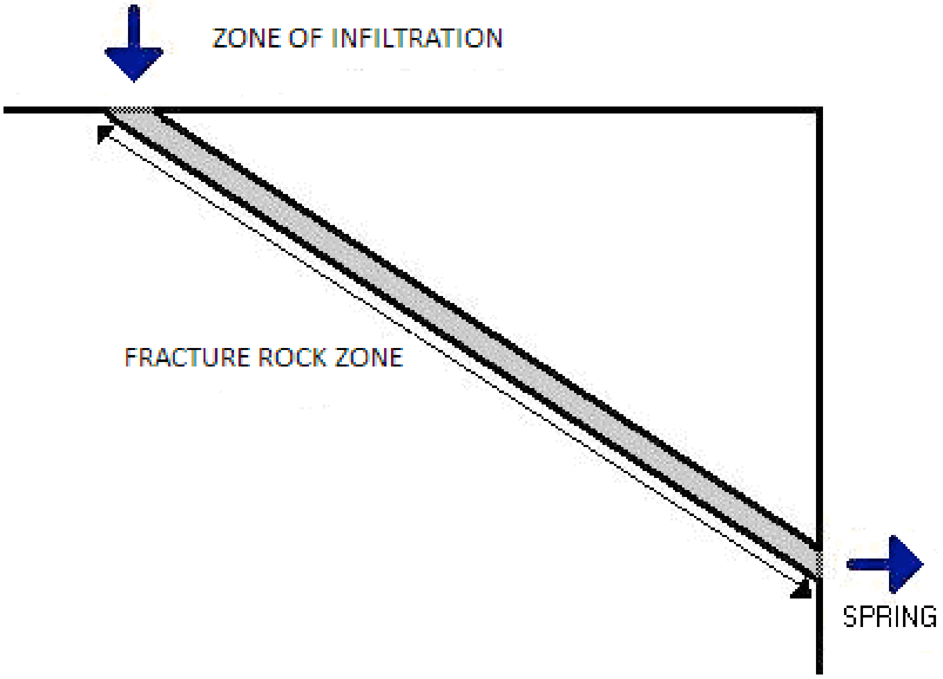

Figure 1 Scheme of our model.

The size of the fracture rock zone conducting the aqueous solution is: 500 m × 10 m × 10 m. We use a 1D model of flow along the fractured zone. The base rock is granite and it includes feldspar and clay. Due to presence of feldspar, the kinetic reactions are in progress. Due to presence of clay, sorption is in progress. The fracture rock zone is homogeneous. The Darcy's Law in our case can be written as:

$$Q = S\ K\ \frac{h_1 - h_2}{L}, \tag{13}$$

where Q is flux ($m^3\ s^{-1}$), S is area of the square cut of the zone (m^2), K is hydraulic conductivity ($m\ s^{-1}$), L is length of fracture rock zone (m), h_1 is hydraulic head in zone of infiltration (m) and h_2 hydraulic head at the spring (m).
Filtration velocity u ($m\ s^{-1}$) is given by the equation:

$$u = \frac{Q}{S}. \tag{14}$$

Average pore velocity v ($m\ s^{-1}$) is given by the equation:

$$v = \frac{u}{n}. \tag{15}$$

We suppose the steady state system (a system in dynamical balance). This supposition has two consequences: (1) sorption is in the balance and does not manifest – for this reason we omit equation of sorption from our model; (2) space and time are somehow equivalent – the residence time is proportional to the travelled distance from the infiltration zone.

SOFTWARE

We simulate our model in two computer programs. The first one is React, this is a part of the commercial software package the Geochemist's Workbench 7.0 (GWB). The second one is Semchem. This software was made at the Technical University of Liberec. It simulates batch experiments.

VALUES IN OUR MODEL

We choose the initial concentrations for our model so that they correspond to the common concentrations in rain water. The values are in Table 2.

Table 2 Initial molarities of chemical components.

Component	Molarity (mol l^{-1})	Component	Molarity (mol l^{-1})
(Ca^{2+})	3.00×10^{-3}	(Cl^-)	1.2×10^{-2}
(H^+)	2.397731×10^{-6}	(CO_2)	1.062467×10^{-5}
(OH^-)	4.170549×10^{-9}	(Al^{3+})	1×10^{-20}
(HCO_3^-)	2.397327×10^{-6}	(SiO_2)	1×10^{-20}
(Na^+)	6.00×10^{-3}	(K^+)	1×10^{-20}

We set up the same reaction rates for all kinetic reactions: $O^{(Ca2+)} = O^{(K+)} = O^{(Na+)}$ $= 5.76 \times 10^{-9}$ mol dm^{-3} day^{-1}. It was calculated according to equation (2) from the following values: $k^{(r)} = 8.64 \times 10^{-12}$ mol dm^{-2} day^{-1}, $s^{(r)} = 20$ $dm^2\ dm^{-3}$, and $n = 0.03$.

The values of the equilibrium constant are chosen according to the thermodynamic database of GWB and expert estimates of Prof. T. Pačes.

Table 3 Constants of equilibrium reactions.

Equilibrium constant (-)	
$K^{(1)}$	5.3856×10^{-7}
$K^{(C)}$	1
$K^{(H2O)}$	1×10^{-14}
$K^{(7)}$	1.0498×10^{-8}

The parameters of Darcy's law (13) are: $K = 0.1499$ m day^{-1}, $h_1 = 77.3785$ m, $h_2 = 50$ m, $L = 500$ m and S = 100 m^2. The average pore velocity $v = 100$ m year^{-1}. Aqueous solution travels trough the fracture rock zone 5 years.

SENSITIVITY ANALYSIS

We performed a sensitivity analysis on initial molarities of some chemical components (Al^{3+}, Ca^{2+}, CO_2, and HCO_3^-). We chose them according to the results of previous sensitivity analysis of a similar model, which was done in the student project (Bruský 2009). Furthermore we performed a sensitivity analysis on the equilibrium constant $K^{(C)}$ and a sensitivity analysis on rate of kinetic equations $O^{(r)}$. The sensitivity analysis shows us the changes of model behaviour due to change of some values. This can help us to better understand our model and it can help us in the future with the changes or calibration of the model on real problem. We used the software Semchem for the sensitivity analysis.

When we change the initial concentration of Al^{3+}, Ca^{2+}, and HCO_3^-, we have to keep electric balance equation (1). This can be done with the relevant change of initial molarity of Cl^-, which does not react in current model.

The following graphs reflect pH or molarity of some chemical component depending on the travelled distance from the zone of infiltration. The distance 500 meters corresponds to the residence time 5 years. Most of the graphs include a progressions jump between first and second plotted value. It is caused by equilibrium constitution between aqueous solution and rock.

Next sections are named according to parameters, for that the sensitivity analysis was performed. In the key of graphs, there are the values of analysed parameter. The violet curve (in key in the middle) is calculated from the original value of the model. For each sensitivity analysis we display the graph of pH and several other graphs displaying interesting information.

Sensitivity analysis on the initial molarity of Al^{3+}

Original initial concentration of Al^{3+} at our model is 1×10^{-20} mol l^{-1} because aluminium is not present in rain water. But aluminium concentration increases in the aqueous solution due to kinetic reactions in our model. In other similar models the concentration of Al^{3+} can be larger. We examine effect, which will bring a different initial concentration of Al^{3+}. From graphs on Figures 2 – 4 we can see that for the molarity 5×10^{-9} mol l^{-1} the result is the same as at the our model. At the molarity 5×10^{-5} mol l^{-1} the results differ.

Sensitivity analysis of Al^{3+} molarity made clear relationship between Al^{3+} and Ca^{2+}. Both chemical components are connected by their reactions because both supply H^+ to the simulated aqueous solution. From the Figure 2 we see that higher value of

Al^{3+} has large influence on pH. When Al^{3+} is in an oversupply, the equation (12) gives so much H^+, that kinetic reactions which normally take much H^+ and control progression of pH, have enough H^+ now. Supply of the H^+ is so large that the equation $Ca^{2+} + HCO_3^- \leftarrow H^+ + CaCO_3$ runs in this direction. This direction run is opposite to the one in our model. This has an effect on increase of molarity of Ca^{2+} – see Figure 3. Increase of molarity of Ca^{2+} influences the kinetic equation (6), too. Amount of H^+ will influence progression of HCO_3^- – see Figure 4 – and CO_2, they are connected with the equation (8). Both concentrations are growing even that HCO_3^- is being consumed in this reaction. Generally, HCO_3^- grows due to large donation of HCO_3^- from the equation $Ca^{2+} + HCO_3^- \leftarrow H^+ + CaCO_3$.

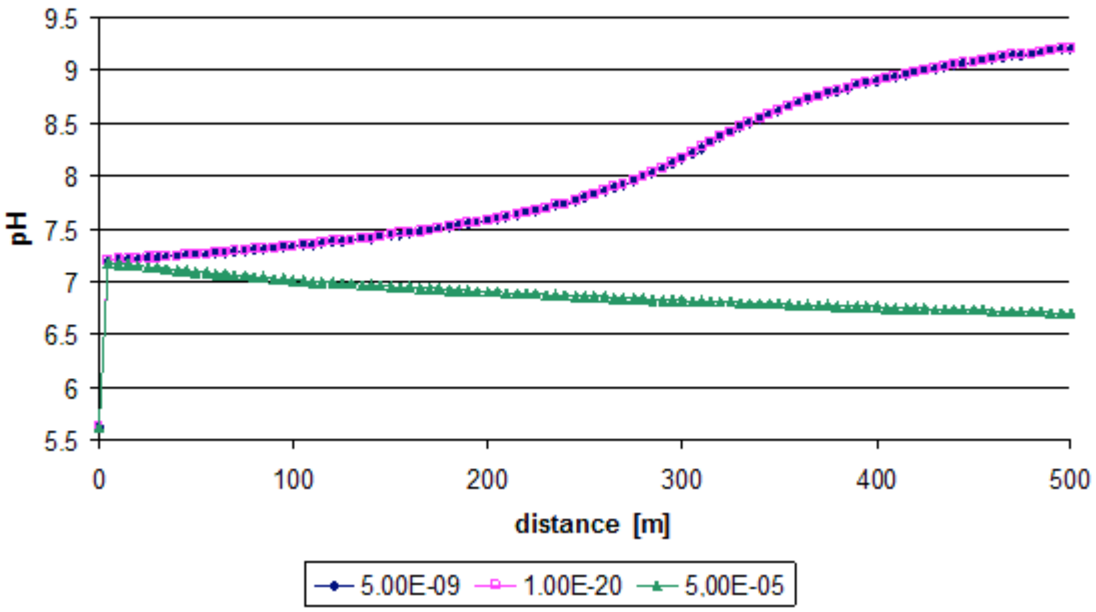

Figure 2 Progression of pH at different initial molarities of Al^{3+}.

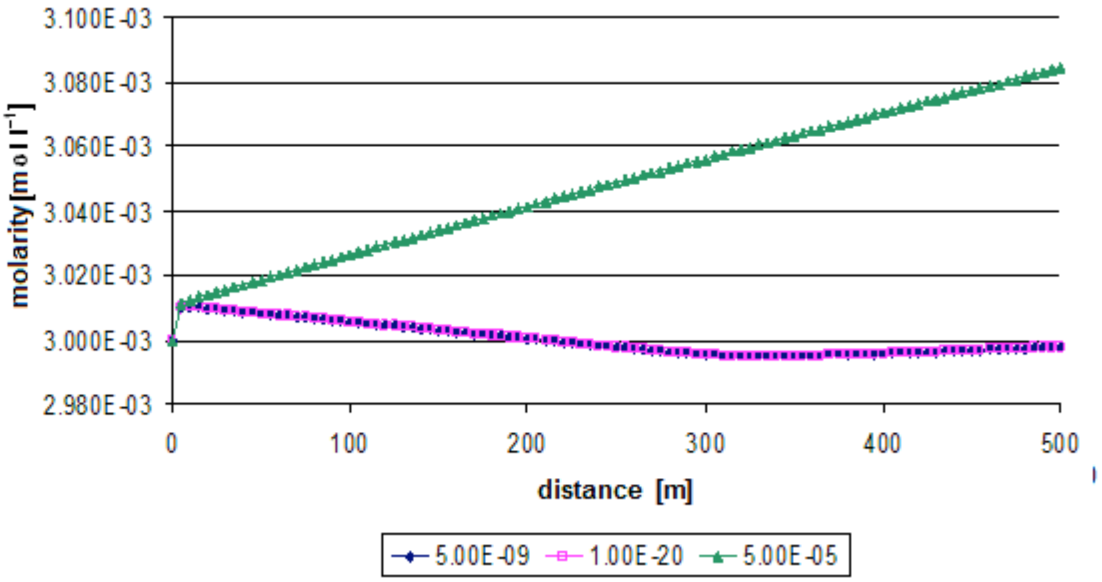

Figure 3 Progression of Ca^{2+} at different initial molarities of Al^{3+}.

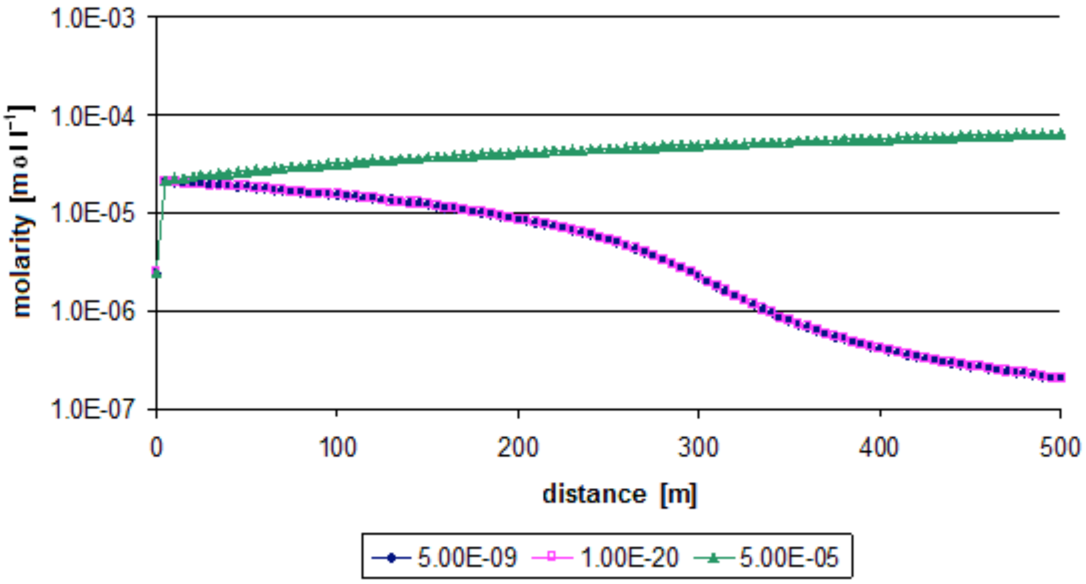

Figure 4 Progression of HCO_3^- at different initial molarities of Al^{3+}.

Sensitivity analysis on the initial molarity of Ca^{2+}

We choose the range of the initial molarities Ca^{2+} so that it corresponds to possible measured values. We pick up two values. The first one is three times lower and the second one is ten times higher than the value which we used at our model.

Figure 5 shows that the molarity of Ca^{2+} does not have (in the surveyed range) a large influence on final water pH. The initial concentration of Ca^{2+} influences progression of Al^{3+} but at the end of simulated process, values of Al^{3+} go always to the same value like at previous progression of pH – see Figure 6. That is due to withdrawal of H^+ by kinetics reactions. Higher concentration of Ca^{2+} influences also progression of HCO_3^- – see Figure 7.

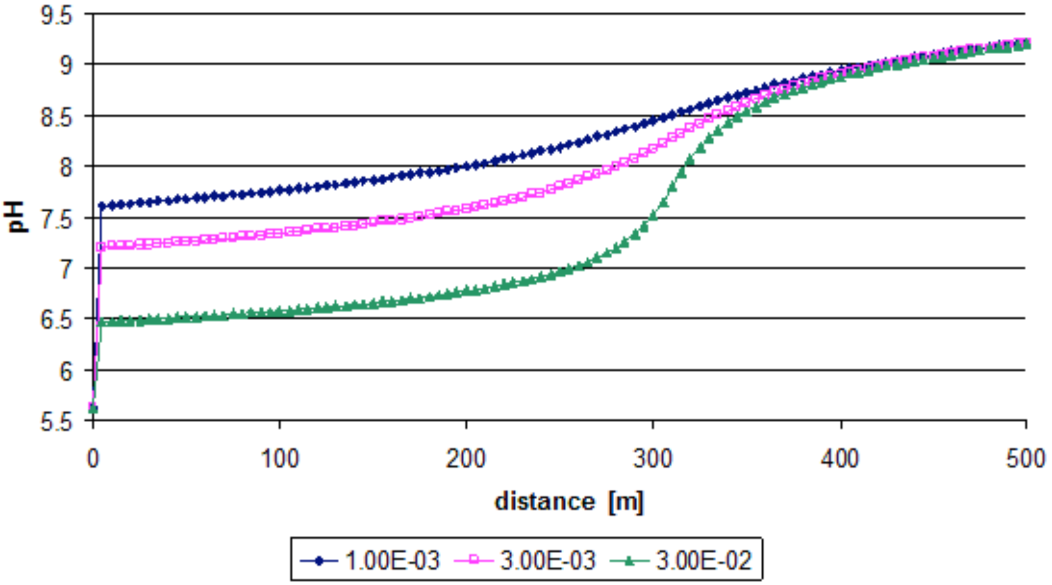

Figure 5 Progression of pH at different initial molarities of Ca^{2+}.

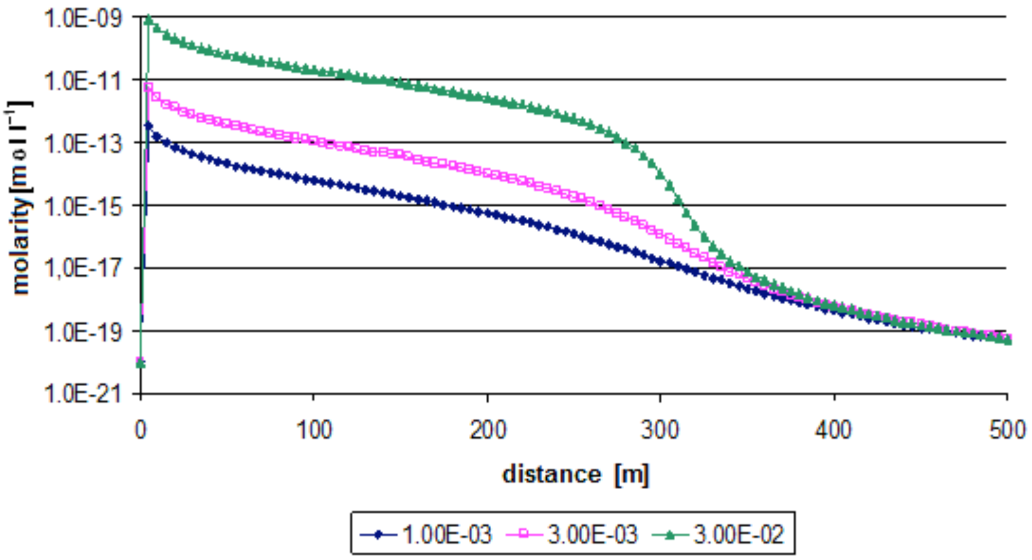

Figure 6 Progression of Al^{3+} at different initial molarities of Ca^{2+}.

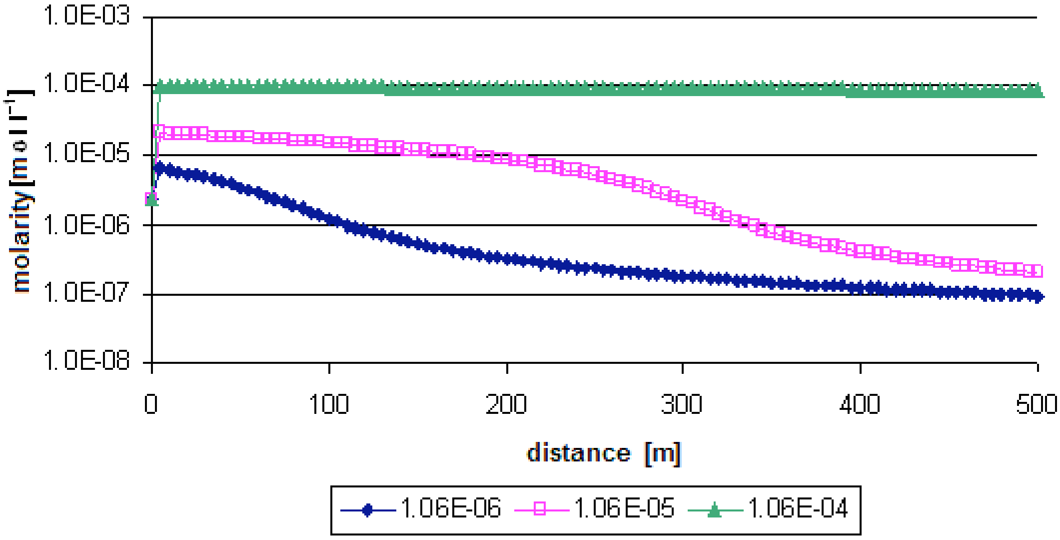

Figure 7 Progression of HCO_3^- at different initial molarities of Ca^{2+}.

Sensitivity analysis on the initial molarities of CO_2 and HCO_3^-

Tested initial concentrations of CO_2 are ten times higher and ten times lower than the value in our model.

Influence of CO_2 is given by the equation (8) which under standard conditions supplies H^+ and HCO_3^- to the model. Further HCO_3^- reacts with Ca^{2+} and supplies H^+ and $CaCO_3$ to the model, equation (9). Amount of CO_2 has great influence on concentration of H^+ – see Figure 8. Initial molarity of CO_2 influences the progression of Ca^{2+} (Figure 9) and progression of Al^{3+}.

Initial molarity of HCO_3^- has very similar influence on the model as molarity of CO_2 because CO_2 directly influences only HCO_3^-, equation (8).

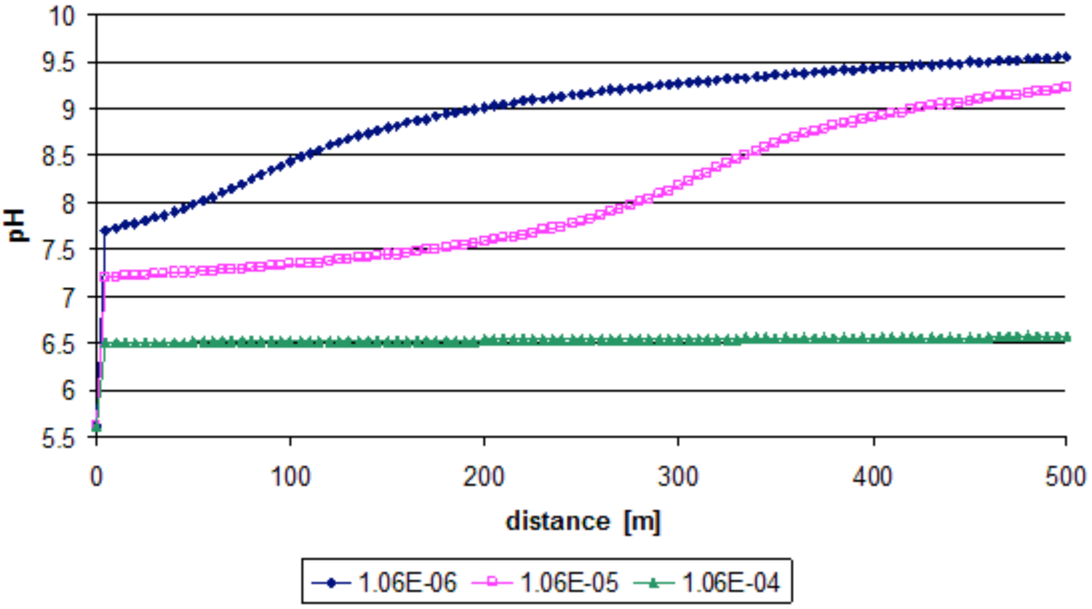

Figure 8 Progression of pH at different initial molarities of CO_2.

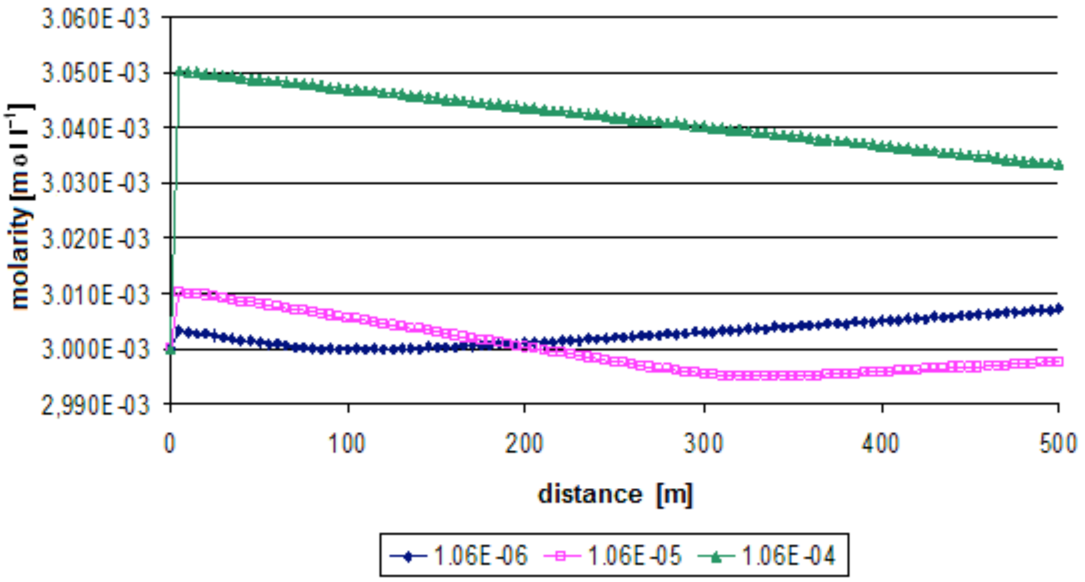

Figure 9 Progression of Ca^{2+} at different initial molarities of CO_2.

Sensitivity analysis on the equilibrium constant $K^{(C)}$

Range of surveyed values of equilibrium constant $K^{(C)}$ were chosen after our previous work on simpler models and previous work with the GWB.

Equilibrium constant $K^{(C)}$ represents this fraction: $\dfrac{\left(\mathrm{Ca}^{2+}\right)\left(\mathrm{HCO}_3^{-}\right)}{\left(\mathrm{H}^{+}\right)}$. From the Figure 10 it can be seen that values of pH are influenced by value of $K^{(C)}$ but finally pH goes to the similar value. Value of $K^{(C)}$ has great influence on concentration of Ca^{2+}, Figure 11. This affected progression of other chemical components that are connected with Ca^{2+} such as Al^{3+}, HCO_3^-, and CO_2.

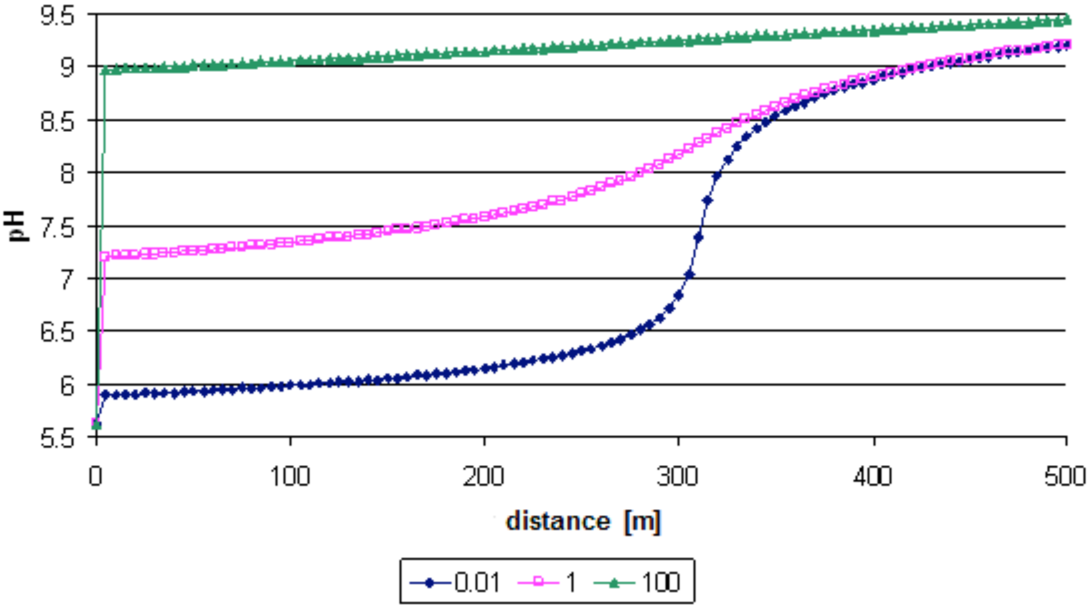

Figure 10 Progression of pH at different equilibrium constants $K^{(C)}$.

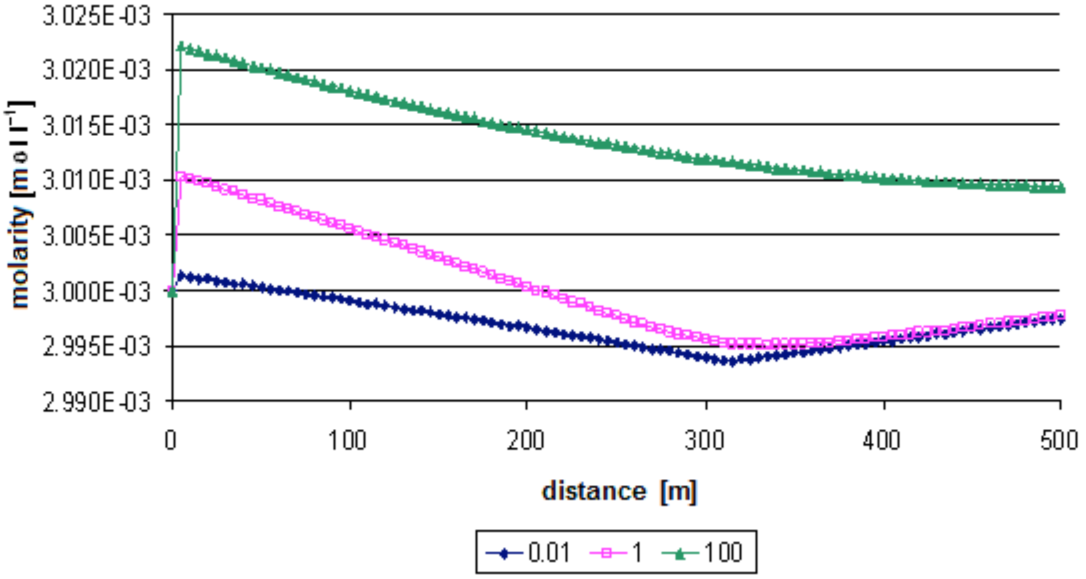

Figure 11 Progression of Ca^{2+} at different equilibrium constants $K^{(C)}$.

Sensitivity analysis on the reaction rates $O^{(r)}$

Values of reaction rates $O^{(r)}$ to the sensitive analysis were chosen so that we take value roughly twice higher and value roughly six times lower than the original one.

Figure 12 shows that the reaction rate has fundamental influence on progression of pH. This causes faster or slower consumption of H^+ and donation of other chemical components. In all figured graphs of pH in this paper, progression has form of horizontally elongated S. This form is due to consumption of H^+. Progression of pH is connected with other chemical equations donating H^+ to aqueous solution. Change in reaction rate influences directly all other processes. In the Figure 13 we can see the progression of Ca^{2+}. It is influenced by different pH in models and by different rate donating Ca^{2+} from equation (6). From Figures 13 and 14 we see connection between

Ca^{2+} and HCO_3^-: At lower concentration of HCO_3^-, $CaCO_3$ does not precipitate so much and concentration of Ca^{2+} is growing due to equation (6)

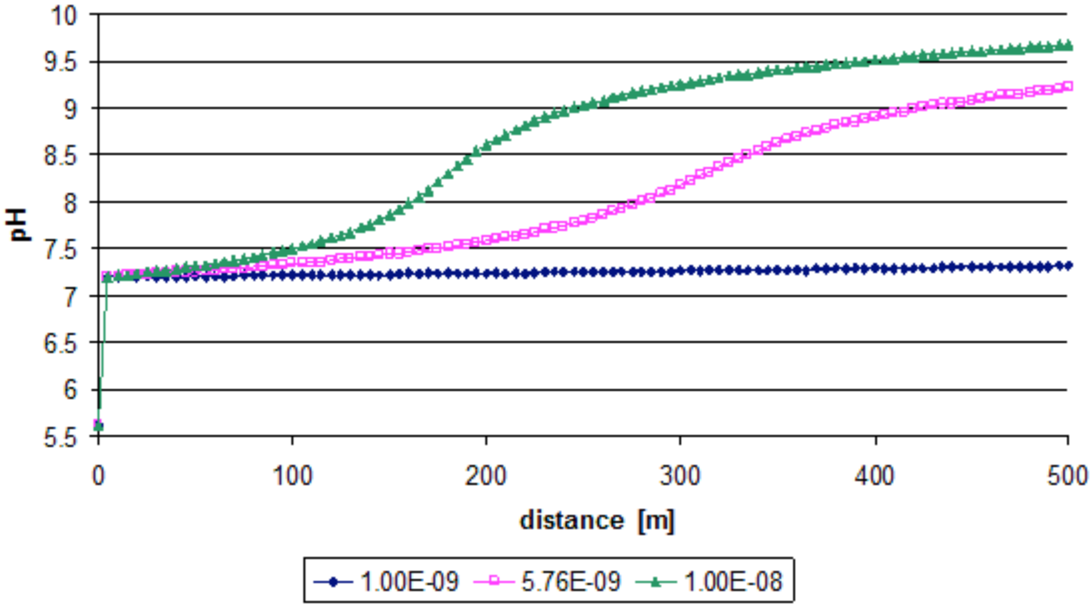

Figure 12 Progression of pH at different reaction rates $O^{(r)}$.

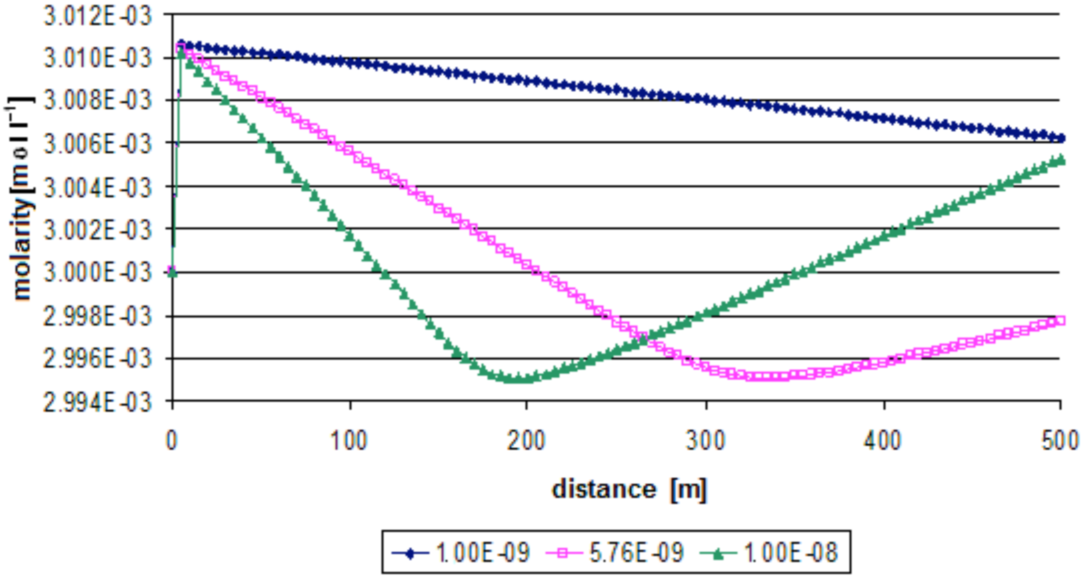

Figure 13 Progression of Ca^{2+} at different reaction rates $O^{(r)}$.

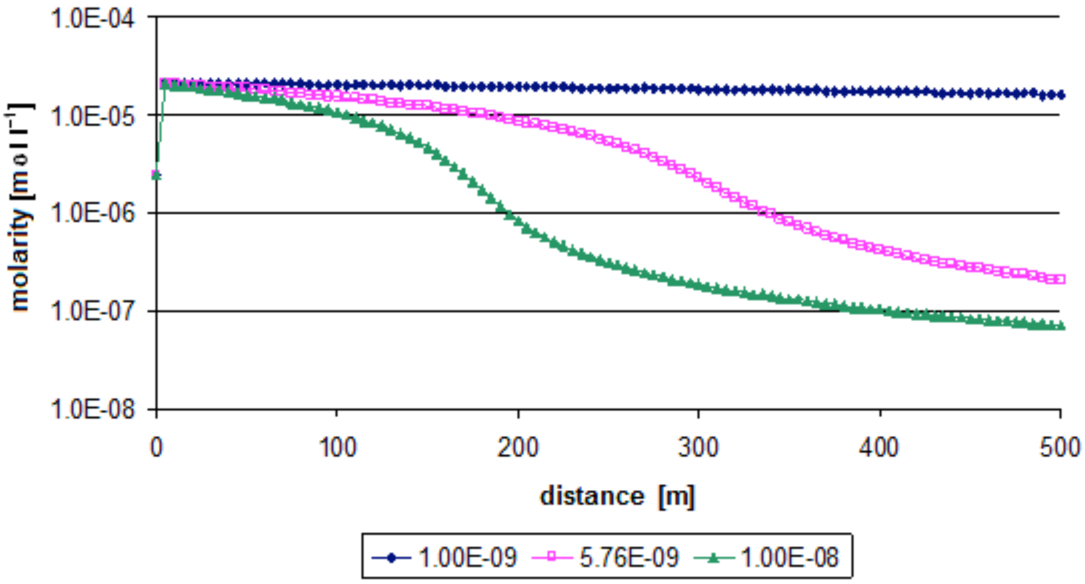

Figure 14 Progression of HCO_3^- at different reaction rates $O^{(r)}$.

CONCLUSION

We simulated the aqueous solution flow through a rock. The main focus was concentrated to chemical interactions between water and rock. A general model of geochemical interactions between water and granite is presented. Sensitivity analysis of some components of the model was done to better understand the model. In the future, the model will be compared with data from a real site and consequently applied to a real problem.

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