

A two-dimensional model for non-linear ion exchange processes in acid mine drainage environments

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ABSTRACT

An accurate prediction of the transport of cations through groundwater flow system associated with acid mine drainage environments requires on a through understanding of ion exchange processes. Specifically, any change in the quantity of ferrous iron may affect the rate of pyritic oxidation and the subsequent pollution load. Furthermore, cation exchange reactions can neutralise the pH of the aqueous phase by the exchange of acidic cations such as hydrogen ions against basic cations such as calcium ions. This paper presents a two-dimensional finite volume transport model of the hydrodynamic dispersion, advection assuming non-linear ion exchange processes. Transportation of solutes is through a saturated porous medium, when the local chemical equilibrium exists at every point of the flow system. The numerical finite volume software known as PHOENICS was used to model and solve the governing equations to describe the reactive solute transport processes. The modelling predictions were first verified with results obtained by field data. It was found that the ion exchange reactions removed some ferrous iron from the solution phase due to substitution by sodium ion. The level of pH can be changed slightly by depletion of hydrogen ions in aqueous phase affected by ion exchange reactions.

INTRODUCTION

Many chemical reactions may take place during the transport of the oxidation products through the groundwater flow system. Included in these reactions are the acid neutralisation reaction, precipitation reaction, ion exchange reactions and complexation reaction. Ion exchange is a special case of competitive sorption which occurs due to the substitution of cations in solids (Reddi & Inyang, 2000). This reaction is due to the electrostatic attraction between charged cations in solution and the surface charge on clay minerals. Clay minerals have an important fixed negative surface charge (Domenico & Schwartz, 1990). Cations binding to the exchange surfaces balance the negative charges of the mineral. These cations may exchange with other cations present in the solution. Cation exchange reactions may neutralise the *pH* of the solution by the exchange of acidic cations such as

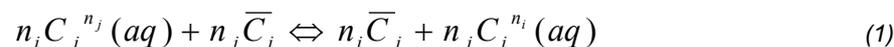
H^+ and Al^{3+} instead of basic cations such as Ca^{2+} and Mg^{2+} .

This paper presents a two-dimensional numerical finite volume model for the simulation of reactive transport of solutes incorporating non-linear ion exchange reactions commonly associated with acid mine drainage. The method presented for treating ion exchange reactions is similar to that employed by Rubin and James (1973). The ion exchange reaction is controlled by local equilibrium. This assumption is applicable only when the ion exchange processes are relatively fast in comparison with the physical transport processes (Rubin & James, 1973; Jennings *et al.*, 1982).

The accuracy of the model was verified with the analytical solution incorporating a simplified linear sorption. Furthermore, the data from a field test presented by Valocchi *et al.* (1981) and two of the five computed examples presented by Rubin & James (1973) were used to validate the numerical model for non-linear ion exchange processes. The two-dimensional model accounts for pyrite oxidation, subsequent pollutant transportation and the equilibrium-controlled ion exchange reactions from the spoil of an open cut coal mine. The mathematical equations of the model have been solved using a multi-purpose PHOENICS computational fluid dynamic software (CHAM, 2000).

ION EXCHANGE REACTIONS

The ion exchange reaction can be given as:



where,

n = valence of the ion;

C = aqueous concentration;

aq = aqueous phase;

\bar{C} = sorbed component.

The mass action equation (Fetter, 1988; and Schnoor, 1996) for the above reaction reduces to:

$$K_i^j = \left(\frac{\bar{C}_j}{C_j} \right)^{n_i} \left(\frac{C_i}{\bar{C}_i} \right)^{n_j}, \quad i \neq j \quad i, j = 1, 2, \dots, N \quad (2)$$

where,

K_i^j = ion exchange selectivity coefficient, assumed to be constant. In fact, K_i^j is not constant and is a function of the sorbed phase concentrations (Valocchi, *et al.*, 1981).

MODELLING GOVERNING EQUATIONS

The following operational partial differential equations presented by Rubin & James (1973) have been modified to model non-linear ion exchange processes numerically.

$$\left(\phi + \frac{\rho_b}{g_i} f_{ii} \right) \frac{\partial C_i}{\partial t} - \frac{\rho_b}{g_i} \sum_{j=1}^{n_c} f_{ij} \frac{\partial C_j}{\partial t} = D_x \frac{\partial^2 C_i}{\partial x^2} + D_y \frac{\partial^2 C_i}{\partial y^2} - q_j \frac{\partial C_i}{\partial x} - q_j \frac{\partial C_i}{\partial y} + q_{re} C_i \pm S$$

$$i = 1, 2, 3, \dots, n_c \quad (3)$$

In the above:

$$f_j^i = K_j^i C_i^{P_j} \bar{C}_j^{P_i} - \bar{C}_i^{P_j} C_j^{P_i} = 0 \quad (4)$$

$$g_i = 1 - \sum_{j=1}^{n_c} \frac{\partial f_j^i / \partial \bar{C}_i}{\partial f_j^i / \partial \bar{C}_j} \quad (5)$$

$$f_{ii} = \sum_{j=1}^{n_c} \frac{\partial f_j^i / \partial C_i}{\partial f_j^i / \partial \bar{C}_j} \quad (6)$$

$$f_{ij} = - \frac{\partial f_j^i / \partial C_j}{\partial f_j^i / \partial \bar{C}_j} \quad (7)$$

where,

t = time (s);

C = concentration of dissolved species (mol / m^3);

x, y = Cartesian coordinates (m);

\bar{C} = concentration of the adsorbed form of species i of dry porous medium (mol / Kg);

ρ_b = bulk density of the medium (Kg / m^3);

D_x, D_y = longitudinal and transverse dispersion coefficients respectively (m^2 / s);

q_{re} = surface recharge (m / s);

S = sink and source terms ($mol / m^3 S$);

q_j = vector components of the pore fluid specific discharge (m / s);

ϕ = porosity.

Given the appropriate initial and boundary conditions, the non-linear partial differential Equation 3 is solved for each component involved in ion exchange reactions using the finite volume method (Doulati Ardejani *et al.*, 2004).

MODEL VALIDATION

The model, it was first run as one-dimensional simulations of solute transport incorporating physical processes as well as linear and non-linear ion exchange reactions. The modelling results were in close agreement with the results obtained from the analytical equations, published numerical models and field data (Doulati Ardejani, 2003; Doulati Ardejani *et al.*, 2004; Singh & Doulati Ardejani, 2004).

MODEL PREDICTIONS

A two-dimensional simulation was performed to demonstrate the capability of the finite volume model for prediction of solute transport problems taking place in reactive porous medium. The contaminants are produced due to the pyrite oxidation reactions from spoils of an open cut coalmine. The input parameters and the chemical species are similar to those input data and chemical components used for one-dimensional simulation (Doulati Ardejani *et al.*, 2002) but slight modification was made to the influx and background chemistry of the aqueous components. Furthermore, the ions Mg^{2+} , Ca^{2+} and Na^+ are also included in the two-dimensional simulations in order to simulate the non-linear ion-exchange processes between the ions Fe^{2+} , Ca^{2+} , Mg^{2+} , and Na^+ . These chemical species with their influx and background concentrations are listed in Table 1.

Table 1. Source and background concentrations of aqueous components used for two-dimensional simulation of ion exchange process (Doulati Ardejani, 2003).

Chemical component	Source concentration mol / m^3	Background concentration mol / m^3
Fe^{2+}	5.00×10^{-1}	5.00×10^{-1}
Fe^{3+}	2.00×10^{-5}	0
SO_4^{-2}	5.00×10^1	5.00×10^1
Ca^{2+}	2.25×10^{-3}	1.64×10^{-3}
Mg^{2+}	1.24×10^{-3}	2.50×10^{-5}
Na^+	2.50×10^{-1}	3.00×10^{-1}
<i>pH</i>	4	5

A cation exchange capacity of 0.1 meq/gr was used for the simulations. The role of bacteria was not considered for this simulation. The selectivity coefficients used here are listed in Table 2.

Table 2. Ion exchange reactions and selectivity coefficients for a quaternary heterovalent ion exchange problem (Doulati Ardejani *et al.*, 2004).

Chemical reactions	Selectivity coefficient
$Mg^{2+} + 2\bar{Na} \Leftrightarrow \bar{Mg} + 2Na^+$	$K_2^1 = 0.2$
$Ca^{2+} + 2\bar{Na} \Leftrightarrow \bar{Ca} + 2Na^+$	$K_3^1 = 0.1$
$Fe^{2+} + 2\bar{Na} \Leftrightarrow \bar{Fe} + 2Na^+$	$K_4^1 = 0.5$

The two-dimensional cross-sectional dimensions are 50 m horizontally by 20 m vertically and this domain is subdivided into 40×20 control volumes of size 1.25 m horizontally \times 1 m vertically. For better representation of the problem, it was assumed that reactive pyrite was contained only in a 12.5-m-wide segment of the unsaturated zone of the spoil. Figure 1 shows the finite volume grid of the problem.

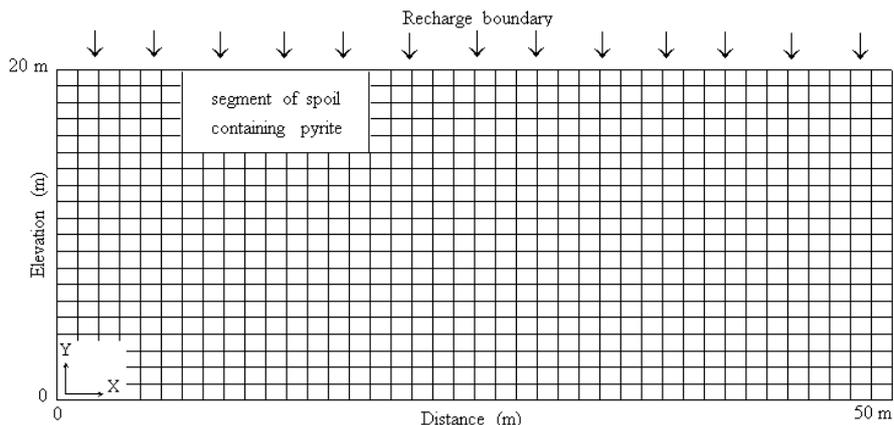


Figure 1. Two-dimensional finite volume grid.

The groundwater flow system was assumed to be steady. Gaseous diffusion was considered to be the main mechanism for the transport of oxygen through the pore spaces of spoil. The upper 4 m of the grid was assumed to be unsaturated and the remainder fully saturated with a constant porosity of 0.321. Figure 2 illustrates the velocity vectors only for the saturated zone and oxygen concentration after 5 years of simulation. Oxygen decreased in the segment where the oxidation reactions take place. Figure 3 shows the contour plots for the percent of the pyrite oxidised for a simulation time of 5 years.

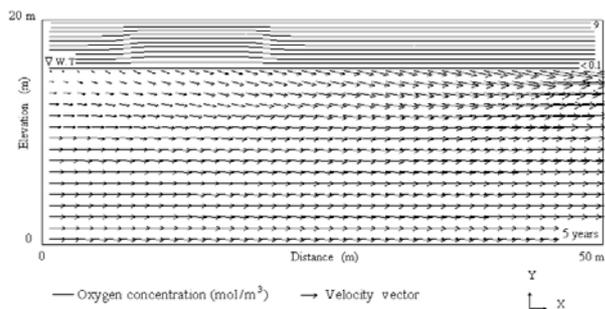


Figure 2. Velocity vectors and oxygen concentration after 5 years of simulation.

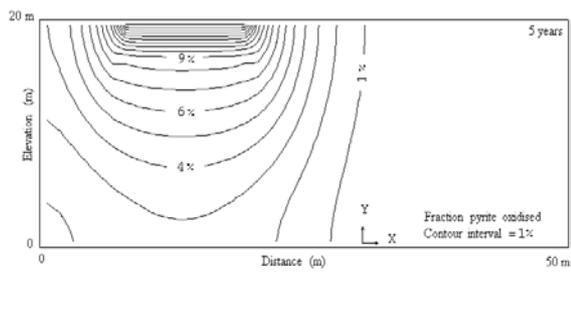


Figure 3. Modelling results for the pyrite percent oxidised within the mine spoil for a simulation time of 5 years.

As Figure 3 shows more than about 15 % of pyrite was oxidised in the section above the water table where the concentration of oxygen is high. In the zone where the oxygen decreased to less than $3 \text{ mol} / \text{m}^3$, only about 1 % of the pyrite was oxidised.

Figures 4 and 5 compare Fe^{2+} concentration for two different cases where the ion exchange reactions were incorporated and without ion exchange reactions at simulation times of 5 and 10 years.

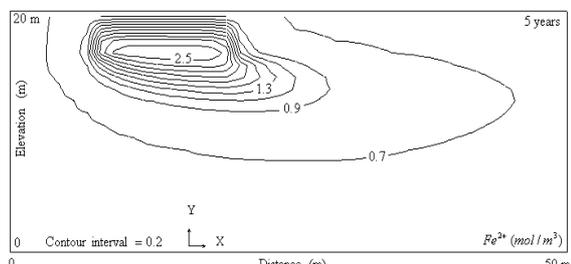
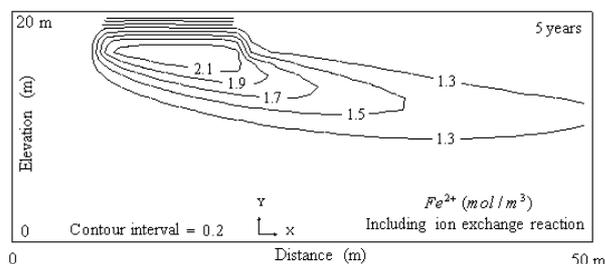


Figure 4. Fe^{2+} concentration after 5 years of simulation with (left) and without (right) ion exchange reactions.

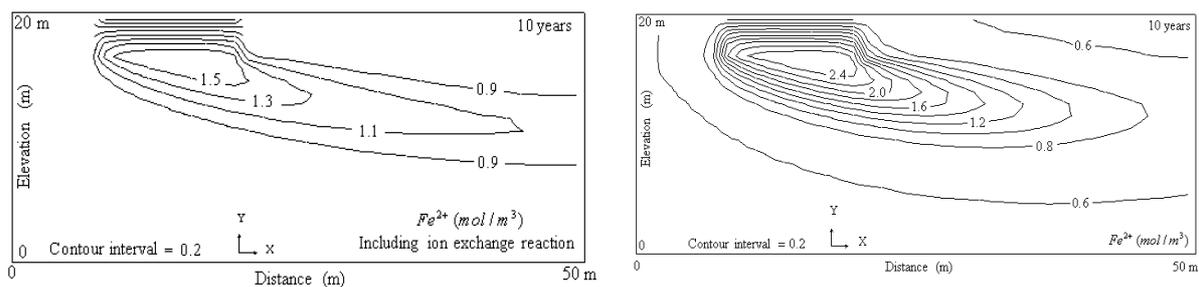


Figure 5. Fe^{2+} concentration after 10 years of simulation with (left) and without (right) ion exchange reactions.

Due to flowing groundwater, some Fe^{2+} is removed from the solution phase because of the ion exchange reactions and substitution by Na^+ . Furthermore, the ion exchange reactions caused that the Fe^{2+} plumes become sharper in the direction of groundwater movement.

The solution pH levels for a simulation time of 5 years with and without ion exchange reactions are illustrated in Figure 6. The pH dropped to less than 2.5 at the shallow unsaturated zone where the oxidation reactions take place and then spread into the saturated groundwater flow system. The value of pH increased slightly by consumption of hydrogen ions in aqueous phase affected by ion exchange reactions.

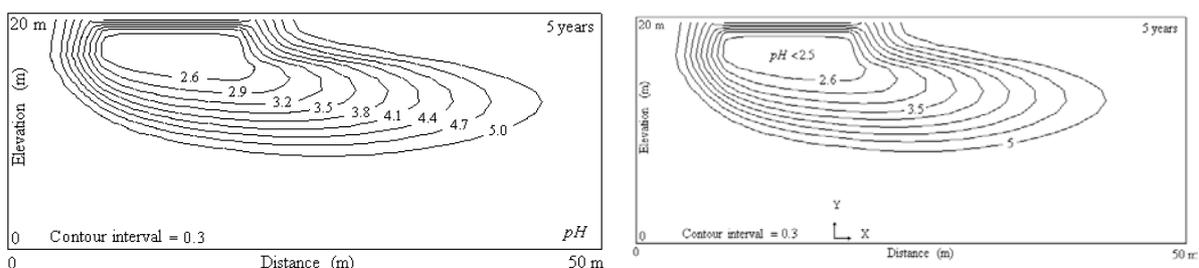


Figure 6. Solution pH after 5 years of simulation with (left) and without (right) ion exchange reactions.

Figure 7 shows the concentration of sulphate for a time period of 5 years with and without ion exchange reactions. In the unsaturated zone where oxygen is present; SO_4^{2-} increased from its background concentration (50 mol/m^3) to 54 mol/m^3 . By incorporating ion exchange reactions, some sulphate ions were removed from the solution phase due to ferrous iron removal caused by ion exchange processes.

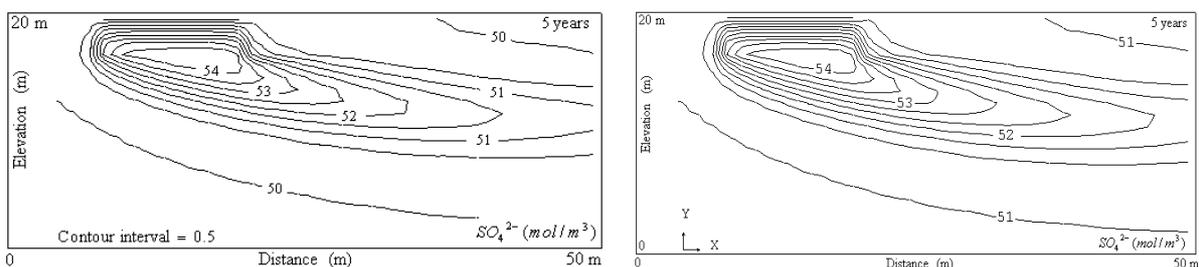


Figure 7. SO_4^{2-} concentration after 5 years of simulation with (left) and without (right) ion exchange reactions.

Figures 8 and 9 compare Fe^{3+} concentration for two different cases where the ion exchange reactions were incorporated and without ion exchange reactions at simulation times of 5 and 10 years.

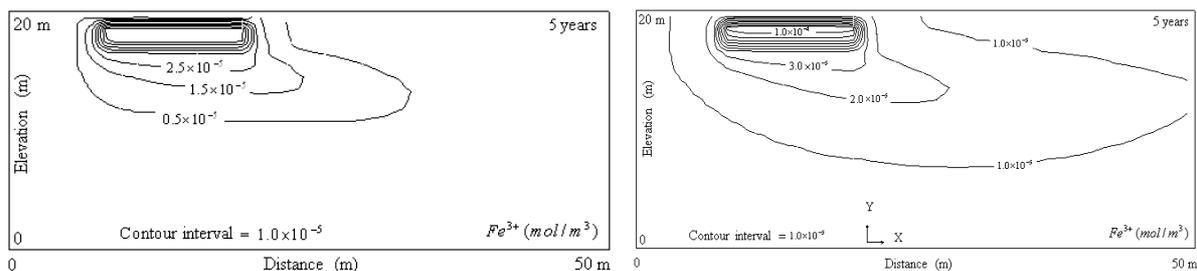


Figure 8. Fe^{3+} concentration after 5 years of simulation with (left) and without (right) ion exchange reactions.

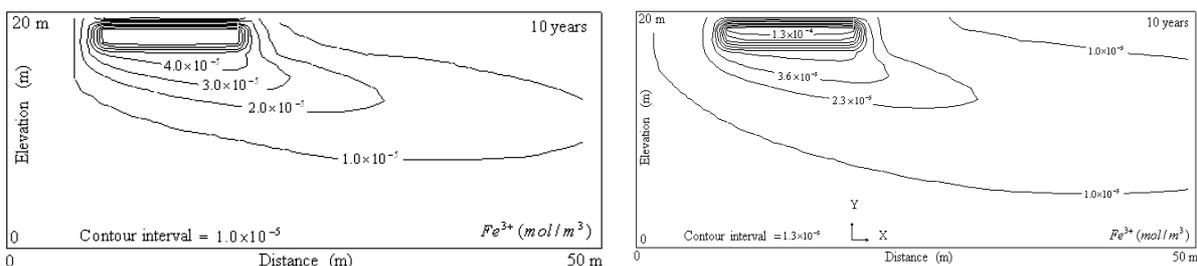
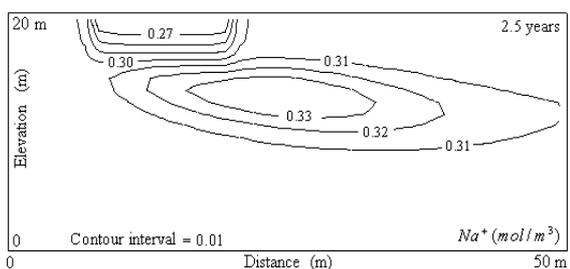
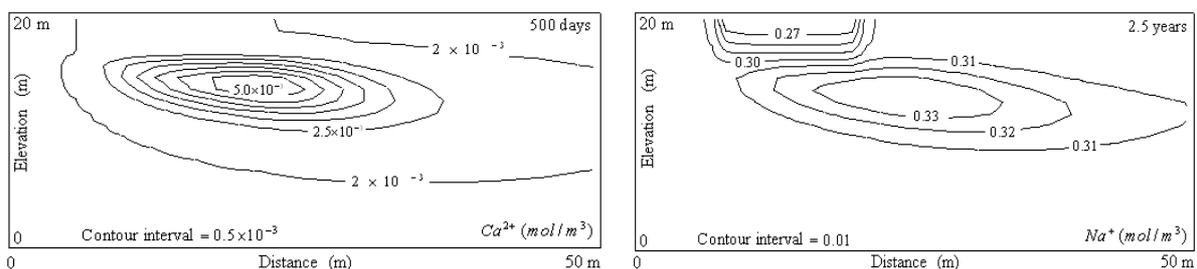


Figure 9. Fe^{3+} concentration after 10 years of simulation with (left) and without (right) ion exchange reactions.

Ferric iron precipitation reaction was not considered in this case. The ferric iron concentration are mainly limited to the unsaturated zone, but as time progresses some Fe^{3+} is being transported below the water table. By incorporating ion exchange reaction, the rate of ferric iron generation is decreased due to removal of ferrous iron affected by ion exchange reaction.

Figures 10 and 11 show the evolution of Ca^{2+} and Na^+ over 10 years of simulation. Both Ca^{2+} and Na^+ concentration plumes are affected by the exchange reaction. As Figure 10 shows, a Ca^{2+} peak occurred in the saturated zone. While time progresses, the Ca^{2+} concentration increased in value and the peak moved further down into the saturated zone as groundwater flows downward. Na^+ showed different behaviour. According to Figure 11, mostly the upper part of the Na^+ plume is affected by the exchange reaction and its concentration slightly increased in solution phase due to substitution by ferrous iron in solid phase. The lower part of the Na^+ plume reflects more the original pore water concentration while the effect of influent concentration is relatively very low.



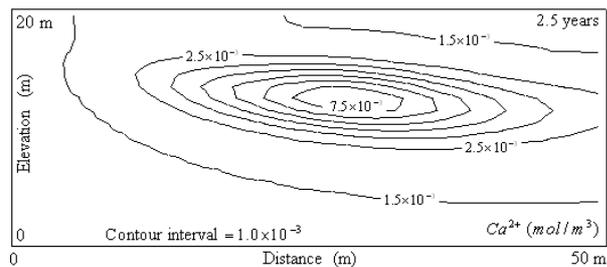


Figure 10. Ca^{2+} concentrations after 500 days, 2.5 and 10 years of simulation.

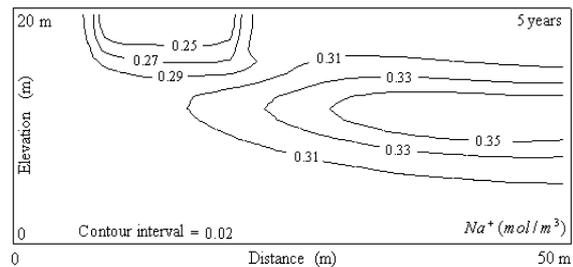
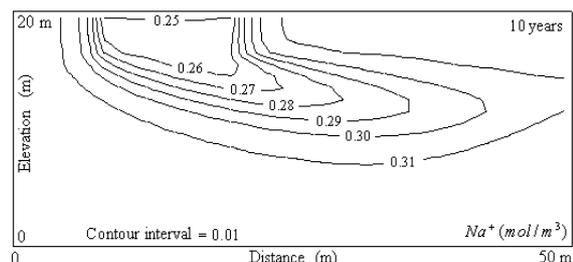
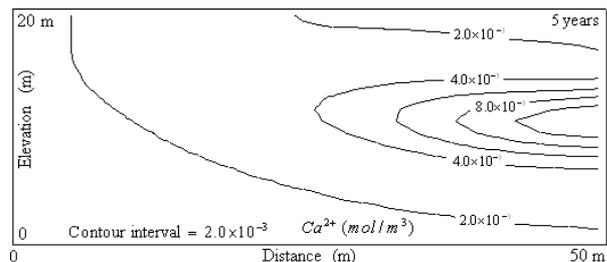


Figure 11. Na^{+} concentrations after 2.5, 5 and 10 years of simulation.



CONCLUSIONS

A two-dimensional numerical finite volume model using PHOENICS as a multi-purposes computational finite volume software has been developed to simulate the non-linear ion exchange reactions taking place in acidic mine drainage environments. An exact prediction of solute transport problems in sites where acid mine drainage is controlled by the ion exchange reactions. It was found that the ion exchange reactions removed some ferrous iron from the aqueous phase. Furthermore, the solution pH increased slightly by depletion of hydrogen ions in aqueous phase affected by ion exchange reactions. Such reactions reduce the rate of sulphate and ferric iron generation due to removal of ferrous iron participated in ion exchange reactions. Consideration of ion exchange reactions in any model related to acid mine drainage is necessary to describe the processes taking place in such environments.

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