

Modelling of ferric iron complexation and precipitation reactions associated with acid mine drainage environments

Doulati Ardejani Faramarz ^{1,2}, Singh Raghu ³, Baafi Ernest ⁴, Shafaei Sied Ziadin ^{1,2}, Marandi Amid ²

1- Faculty of Mining and Geophysics, Shahrood University of Technology, Shahrood, Iran, P.O. BOX: 36155-316.

2- Environmental Engineering Department, Iran Colour Research Centre, Shahid Afshari St Cross, East end of Shahid Hemmat Highway, 1665618481, Tehran, Iran.

3- Nottingham Centre for Geomechanics, School of Civil Engineering, University of Nottingham, UK

4- School of Civil, Mining and Environmental Engineering, Faculty of Engineering, University of Wollongong, Northfields Avenue, Wollongong, NSW 2522, Australia.

E-mail: fdoulati@shahrood.ac.ir

Keywords: complexation, precipitation, acid mine drainage, PHOENICS, CFD

ABSTRACT

Ferric iron complexation and precipitation reactions are noted to be important mechanisms affecting pyrite oxidation and subsequent pollutant generation and transportation. In particular, the ferric complexation raises the total dissolved concentration of ferric iron which affects transport of dissolved ferric iron. Total dissolved ferric iron in the aqueous phase is used to determine the rate of pyrite oxidation hence the calculation of the actual values of ferric ions is necessary. Therefore, simulation of such reactions is an interesting subject of the environmental studies. This paper attempts to describe a method for modelling of these reactions. Both reactions are assumed to be relatively fast so that local chemical equilibrium always exists at every point of the system. For modelling purpose, a multi-purpose computational fluid dynamics (CFD) package called PHOENICS incorporating a finite volume Discretisation scheme has been modified. It is found that the precipitation reaction removed ferric iron from the solution phase in the direction of the groundwater flow where the pH is above 3. The concentrations of ferric iron are mainly restricted to the unsaturated zone.

INTRODUCTION

Complexation involves reaction between simple cations (usually metallic), and anions called ligands (Reddi & Inyang, 2000). Complexation facilitates the transport of potentially toxic metals such as cadmium, chromium, copper, lead, uranium, or plutonium. Such reaction also influences some types of surface reactions. A complex is an ion that forms by combining simpler cations, anions, and sometimes molecules. The ligand includes many of the common inorganic species found in groundwater such as OH^- , Cl^- , F^- , Br^- , SO_4^{2-} , PO_4^{3-} and CO_3^{2-} .

The ligand might also comprise various organic molecules such as amino acids. It should be noted that OH^- is a very important ligand in aqueous solutions (Pankow, 1991). The simplest complexation reaction involves the combination of a metal and ligand as follows:



A more complicated case of complexation reaction is the reaction series that forms when complexes themselves combine with ligands. An example is the hydrolysis reaction of Cr^{3+} . The metal is distributed among at least three complexes. Such series involve not only hydrolysis reactions but also other ligands such as Cl^- , F^- and Br^- (Domenico & Schwartz, 1990).

Complexation reactions are important in studying the transport of metals in the subsurface. In assessing the total metal concentration in the pore fluid, the complexes must be considered in addition to the free metal ion concentration. Because of the complexation reactions the actual quantities of metal transported downstream in the pore fluid might be more than the concentrations of metal ions alone might indicate (Reddi & Inyang, 2000). Most inorganic reactions involving complexes are kinetically fast. Thus, equilibrium concepts can be used to examine these reactions quantitatively. Calculation of the distribution of metals among various complexes involves the solution of a series of mass-action equations.

Mineral precipitation and dissolution reactions are described by the mass action law for a solid and the reacting ions. The general form of the dissolution reaction of a solid is:



where,

(aq) = aqueous phase

(*s*) = solid phase

The reaction above is described by a solubility product of the form:

$$\frac{[C]^c [D]^d}{[C_c D_d]} = K_{sp} \quad (3)$$

where,

K_{sp} = solubility product which is an equilibrium constant specific to a solid.

The left-hand side of Equation 3 is called the ion activity product (IAP). For a pure solid, $[C_c D_d] = 1$.

When a system is at equilibrium, then, $K_{sp} = IAP$

If system is not at equilibrium, the degree of disequilibrium can then be given by the following expression (Walter *et al.*, 1994a, b):

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \quad (4)$$

where,

SI = saturation index.

- (i) In the case of supersaturation, $SI > 0$, the mineral tends to precipitate;
- (ii) When $SI = 0$, the mineral and the solution are in equilibrium;
- (iii) When $SI < 0$, the solution is under saturation and mineral tends to dissolve.

It should be mentioned that the dissolution and precipitation of minerals are two of the important chemical reactions in terms of their control on chemistry of groundwater that affect solute transport (Domenico & Schwartz, 1990). These processes have significant effects on the mass transfer taking place in groundwater systems (Reddi & Inyang, 2000). Dissolution reaction supplies dissolved material into the pore water whereas a precipitation process removes it from pore water (Lerman, 1979; Reddi & Inyang, 2000). Hence, these reactions must be considered in the model.

In this paper a numerical finite volume model was developed using a multi-purpose CFD package called PHOENICS (CHAM, 2000). The necessary coding was supplied to PHOENICS in FORTRAN language in order to take into consideration all extra sources and sink terms in the governing equations. All these modifications were carried out in a subroutine called GROUND and were linked to the PHOENICS solver by the PHOENICS input file called Q1.

FERRIC IRON COMPLEXATION REACTIONS

One of the most important metals, which forms relatively strong complexes with ligands of OH^- (hydroxides) and SO_4^{2-} is ferric iron. Ferric complexation raises the total dissolved concentration of Fe^{3+} a hundred to a thousand times in particular at $pH \approx 5$ (Jaynes *et al.*, 1984a). Therefore, the ferric complexation reaction is noted to be an important reaction, which affects transport of dissolved ferric iron and must be considered in the present model. Furthermore, total dissolved ferric iron in the aqueous phase is used to determine the rate of pyrite oxidation hence the calculation of the actual values of ferric ions is necessary.

Table 1 shows the ferric iron complexes, their mass action and equilibrium constants included in this model (Jaynes *et al.*, 1984a; Pankow, 1991; Walter *et al.*, 1994a, b; Stumm & Morgan, 1996; and Wunderly *et al.*, 1996).

Instantaneous equilibrium is assumed for all of these Fe^{3+} complexation reactions according to the appropriate mass action expressions. In the case of non-equilibrium, kinetic expressions may be substituted for any reaction by adding terms to the differential rather than algebraic equation set (Jennings *et al.*, 1982).

The mole balance equation for $(Fe)_T$ is:

$$(Fe)_T = \{Fe^{3+}\} + \{Fe(OH)^{2+}\} + \{Fe(OH)_2^+\} + \{Fe(OH)_3^0\} + \{Fe(OH)_4^-\} + 2\{Fe_2(OH)_2^{4+}\} + \{FeSO_4^+\} + \{Fe(SO_4)_2^-\} \quad (5)$$

Table 1. Ferric iron complexes, Log of the equilibrium constants and their mass action expressions (Jaynes et al., 1984a; Pankow, 1991; Walter et al., 1994a, b; Stumm & Morgan, 1996; and Wunderly et al., 1996).

Reaction	$\log K$	Mass action
$Fe^{3+} + H_2O \Leftrightarrow Fe(OH)^{2+} + H^+$		
$Fe^{3+} + 2H_2O \Leftrightarrow Fe(OH)_2^+ + 2H^+$	-2.2	$*K_1 = \frac{\{Fe(OH)^{2+}\}\{H^+\}}{\{Fe^{3+}\}}$
$Fe^{3+} + 3H_2O \Leftrightarrow Fe(OH)_3^0 + 3H^+$	-5.7	$*\beta_2 = \frac{\{Fe(OH)_2^+\}\{H^+\}^2}{\{Fe^{3+}\}}$
$Fe^{3+} + 4H_2O \Leftrightarrow Fe(OH)_4^- + 4H^+$	-13.6	$*\beta_3 = \frac{\{Fe(OH)_3^0\}\{H^+\}^3}{\{Fe^{3+}\}}$
$2Fe^{3+} + 2H_2O \Leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$	-21.6	$*\beta_4 = \frac{\{Fe(OH)_4^-\}\{H^+\}^4}{\{Fe^{3+}\}}$
$2Fe^{3+} + 2H_2O \Leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$	2.9	$*\beta_{22} = \frac{\{Fe_2(OH)_2^{4+}\}\{H^+\}^2}{\{Fe^{3+}\}^2}$
$Fe^{3+} + SO_4^{2-} \Leftrightarrow FeSO_4^+$	3.92	$K_1 = \frac{\{FeSO_4^+\}}{\{Fe^{3+}\}\{SO_4^{2-}\}}$
$Fe^{3+} + 2SO_4^{2-} \Leftrightarrow Fe(SO_4)_2^-$	5.42	$K_2 = \frac{\{Fe(SO_4)_2^-\}}{\{Fe^{3+}\}\{SO_4^{2-}\}^2}$

where, a factor of 2 is included in term $Fe_2(OH)_2^{4+}$ since there are two Fe^{3+} in each $Fe_2(OH)_2^{4+}$ species.

By substitution of the appropriate mass action equations, the concentrations of all complex species may be eliminated as follows:

$$(Fe)_T = \{Fe^{3+}\} + \frac{*K_1\{Fe^{3+}\}}{\{H^+\}^1} + \frac{*K_1\{Fe^{3+}\}}{\{H^+\}^2} + \frac{*K_1\{Fe^{3+}\}}{\{H^+\}^3} + \frac{*K_1\{Fe^{3+}\}}{\{H^+\}^4} + \frac{2\{Fe^{3+}\}^2*\beta_{22}}{\{H^+\}^2} + \{SO_4^{2-}\}\{Fe^{3+}\}K_1 + \{SO_4^{2-}\}^2\{Fe^{3+}\}K_2$$

(6)

where,

$*K_1$, K_1 , K_2 , $*\beta_2$, $*\beta_3$, $*\beta_4$, and $*\beta_{22}$ are the stability constants for Fe^{3+} complexes.

Equation 6 can be rearranged as follows:

$$(Fe)_T = \{Fe^{3+}\} \left\{ 1 + \frac{*K_1}{\{H^+\}^1} + \frac{*K_1}{\{H^+\}^2} + \frac{*K_1}{\{H^+\}^3} + \frac{*K_1}{\{H^+\}^4} + \frac{2\{Fe^{3+}\}*\beta_{22}}{\{H^+\}^2} + \{SO_4^{2-}\}K_1 + \{SO_4^{2-}\}^2K_2 \right\}$$

Now consider the following mass transport partial differential equation:

$$R_f \frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x_j^2} - u_j \frac{\partial C_i}{\partial x_j} + q_{re} C_i \pm S, \quad i = 1, 2, \dots, n_c$$

Substitution of Equation 7 into the mass transport equation for $C_i = Fe^{3+}$ yields:

$$L_{Fe^{3+}} \left(\{Fe^{3+}\}, \{SO_4^{2-}\} \right) \equiv R_f \frac{\partial \{Fe^{3+}\}}{\partial t} = D \frac{\partial^2 \{Fe^{3+}\}}{\partial x_j^2} - u_j \frac{\partial \{Fe^{3+}\}}{\partial x_j} + q_{re} \{Fe^{3+}\} \pm \left(\frac{1}{A} \right) (S)$$

$$- \left(\frac{1}{A} \right) \{Fe^{3+}\} \left(K_1 + K_2 \{SO_4^{2-}\} \right) \frac{\partial \{SO_4^{2-}\}}{\partial t} + \left(\frac{1}{A} \right) D \{Fe^{3+}\} \left(K_1 + K_2 \{SO_4^{2-}\} \right) \frac{\partial^2 \{SO_4^{2-}\}}{\partial x_j^2}$$

$$- \left(\frac{1}{A} \right) \{Fe^{3+}\} \left(K_1 + K_2 \{SO_4^{2-}\} \right) u_j \frac{\partial \{SO_4^{2-}\}}{\partial x_j}$$

where,

$$A = \left[1 + \frac{*K_1}{\{H^+\}^1} + \frac{*K_1}{\{H^+\}^2} + \frac{*K_1}{\{H^+\}^3} + \frac{*K_1}{\{H^+\}^4} + \frac{2\{Fe^{3+}\}*\beta_{22}}{\{H^+\}^2} + \{SO_4^{2-}\}K_1 + \{SO_4^{2-}\}^2K_2 \right]$$

Modified transport equation of SO_4^{2-}

Because the ligand SO_4^{2-} is involved in ferric complexation reaction, modification must be made to take this into account in the transport equation of SO_4^{2-} .

By assumption that the ligand SO_4^{2-} only forms complexes with ferric iron (Table 1, two last reactions), the mole balance equation for $(SO_4)_T$ will be:

$$(SO_4)_T = \{SO_4^{2-}\} + \{FeSO_4^+\} + \{Fe(SO_4)_2^-\} \quad (11)$$

Substitution of mass action equations into Equation 11 yield:

$$(SO_4)_T = \{SO_4^{2-}\} \left(1 + K_1 \{Fe^{3+}\} + K_2 \{Fe^{3+}\} \{SO_4^{2-}\}\right) \quad (12)$$

Substitution of Equation 12 into the mass transport Equation 8 gives:

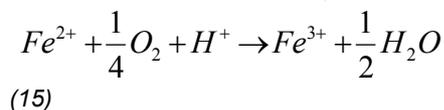
$$\begin{aligned} L_{SO_4^{2-}}(\{Fe^{3+}\}, \{SO_4^{2-}\}) &\equiv R_f \frac{\partial \{SO_4^{2-}\}}{\partial t} = D \frac{\partial^2 \{SO_4^{2-}\}}{\partial x_j^2} - u_j \frac{\partial \{SO_4^{2-}\}}{\partial x_j} + q_{re} \{SO_4^{2-}\} \pm \left(\frac{1}{C}\right) (S) \\ &- \left(\frac{1}{C}\right) \{SO_4^{2-}\} (K_1 + K_2 \{SO_4^{2-}\}) \frac{\partial \{Fe^{3+}\}}{\partial t} + \left(\frac{1}{C}\right) D \{SO_4^{2-}\} (K_1 + K_2 \{SO_4^{2-}\}) \frac{\partial^2 \{Fe^{3+}\}}{\partial x_j^2} \\ &- \left(\frac{1}{C}\right) \{SO_4^{2-}\} (K_1 + K_2 \{SO_4^{2-}\}) u_j \frac{\partial \{Fe^{3+}\}}{\partial x_j} \end{aligned} \quad (13)$$

where,

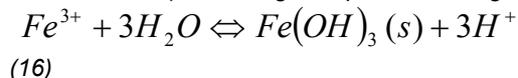
$$C = \left[1 + \{Fe^{3+}\} K_1 + \{SO_4^{2-}\} \{Fe^{3+}\} K_2\right] \quad (14)$$

FERRIC IRON PRECIPITATION REACTIONS

In open cut mine spoil the only important source of Fe^{3+} is the in situ oxidation of ferrous iron as given below:



Fe^{3+} formed by this reaction may react with pyrite to produce additional Fe^{2+} , SO_4^{2-} and H^+ . Alternatively, the Fe^{3+} released may be hydrolysed and precipitated as amorphous ferrihydrite (Jaynes *et al.*, 1984a, Walter *et al.*, 1994a, b) according to Equation 16 as given below:

**Modelling of precipitation reactions**

All reactions will be assumed to be relatively fast so that local chemical equilibrium always exists at every point of the system (Rubin & James, 1973).

The solubility product for Equation 16 may be expressed as:

$$K = [Fe^{3+}] / [H^+]^3 \quad (17)$$

where,

K = solubility product of amorphous ferrihydrite based on the stoichiometric relationship (16).

The rate of dissolution or precipitation of a solid phase can be estimated by the rate of change of concentration in pore fluid ($\partial C / \partial t$) (Lerman, 1979). Thus to incorporate an equilibrium precipitation-dissolution reaction, the following transport equations can then be written to describe the system in question:

$$\phi \frac{\partial [Fe^{3+}]}{\partial t} + \frac{\partial \bar{C}_{fh}}{\partial t} = D \frac{\partial^2 [Fe^{3+}]}{\partial x_j^2} - q_j \frac{\partial [Fe^{3+}]}{\partial x_j} \pm [Source\ terms]_{[Fe^{3+}]} \quad (18)$$

$$\phi \frac{\partial [H^+]}{\partial t} - \frac{\partial \bar{C}_{fh}}{\partial t} = D \frac{\partial^2 [H^+]}{\partial x_j^2} - q_j \frac{\partial [H^+]}{\partial x_j} \pm [Source\ terms]_{[H^+]} \quad (19)$$

where,

\bar{C}_{fh} = amount of precipitated ferrihydrite per bulk volume of solids;

ϕ = porosity;

$[]$ = concentration operator.

It is assumed that the precipitate occurs as very thin layers on non-reacting surfaces, thus not affecting the other processes or the groundwater flow (Rubin, 1983; Eriksson & Destouni, 1997).

Adding Equations 18 and 19 and rearranging the new equation gives:

$$\phi \frac{\partial [\psi]}{\partial t} = D \frac{\partial^2 [\psi]}{\partial x_j^2} - q_j \frac{\partial [\psi]}{\partial x_j} \pm [Source\ terms]_{[Fe^{3+}]} \pm [Source\ terms]_{[H^+]} \quad (20)$$

where,

$$[\psi] = [Fe^{3+}] + [H^+] \quad (21)$$

Equation 20 now can be solved by defining the appropriate initial and boundary conditions. The required $[Fe^{3+}]$ and $[H^+]$ concentrations can then be obtained from $[\psi]$ by combining and rewriting Equations 17 and 21 as follows:

$$K [H^+]^3 + [H^+] - [\psi] \quad (22)$$

$$[Fe^{3+}] = [\psi] - [H^+] \quad (23)$$

Initial and boundary conditions

The following initial and boundary conditions can be specified for problem at hand:

$$\begin{aligned} t = 0 \quad , \quad x_j \geq 0 \quad , \quad [\psi] &= [Fe^{3+}]_{init} + [H^+]_{init} \\ t \geq 0 \quad , \quad x_j = 0 \quad , \quad [\psi] &= q_{rd} \left([Fe^{3+}] + [H^+] \right)_{inflow} \\ t \geq 0 \quad , \quad x_j = \infty \quad , \quad [\psi] &= [Fe^{3+}]_{init} + [H^+]_{init} \end{aligned} \quad (24)$$

The nonlinear Equation 22 was first solved for $[H^+]$ using the Secant method (Yakowitz & Szidarovszky, 1989). The ferric iron concentrations were then calculated from Equation 23. The calculation were done with FORTRAN language and supplied in group 19 of GROUND subroutine in PHOENICS CFD package (CHAM, 2000).

MODELLING SETTING AND INPUT DATA

A one-dimensional simulation was performed to take into account the complexation reactions. The accuracy of the model was evaluated and compared with those results obtained by POLS model developed by Jaynes *et al.* (1984b). Such comparisons and model input data were previously presented in Doulati Ardejani *et al.* (2002) and Singh & Doulati Ardejani (2003).

ONE - DIMENSIONAL RESULTS

Figure 1 shows the ratio of ferric iron to ferrous iron versus time in the outlet of the spoil profile for two different cases where the complexation reactions were incorporated (upper curve) and without complexation reactions (lower curve). The complexation reactions increased the Fe^{3+} / Fe^{2+} ratio.

The normalised concentration of ferric iron as a function of depth for a reaction time of 5 years with and without complexation reactions was illustrated in Figure 2. Because of the complexation reactions more ferric iron transported downstream in the pore fluid. Therefore, although not shown here, more pyrite was oxidised due to the complexation reaction.

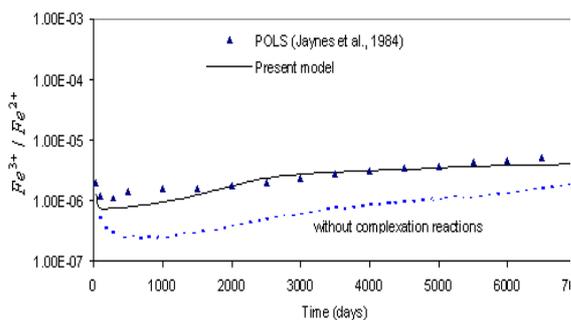


Figure 1. Fe^{3+}/Fe^{2+} in the water leaving the profile.

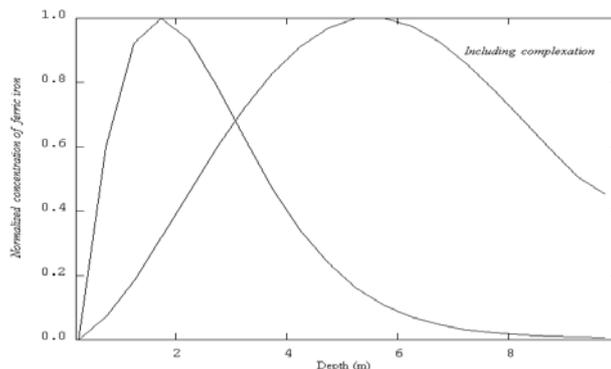


Figure 2. Normalised concentration of ferric iron vs. depth over a 5 year period with and without complexation reactions.

TWO - DIMENSIONAL RESULTS

A two-dimensional simulation was also performed to show the capability of the model for considering the effects of the ferric iron precipitation reaction. The two-dimensional cross-sectional dimensions are 50 m horizontally by 20 m vertically and this domain is discretised into 40×20 control volumes of size 1.25 m horizontally \times 1 m vertically. The groundwater flow system was assumed to be steady. An average recharge value of 0.3 m/yr was considered for the upper boundary (spoil surface). For the simulation it was assumed that reactive pyrite was contained only in a 12.5-m-wide segment of the unsaturated zone of the spoil. The spoil surface was maintained as a first-type boundary condition for oxygen equal to its atmospheric concentration (0.21 mol/mol). A zero concentration gradient boundary conditions were specified above the water table for the oxygen transport model. To avoid non-linearity problems, no ferric complexation reactions were allowed to take place. The two-dimensional results are given for oxygen concentration and the fraction of pyrite oxidised in the spoil (Figure 3).

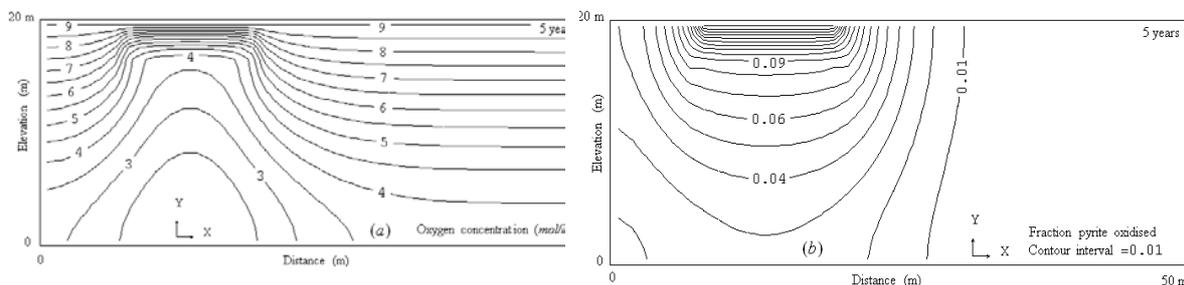


Figure 3. Two-dimensional simulation results after 5 years: (a) oxygen concentration; (b) pyrite fraction oxidised.

The depletion zone of oxygen is due to the chemical oxidation of ferrous iron as well as pyrite oxidation (Figure 3.a). As Figure 3.b shows that 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 mol/m^3 , only about 1 % of the pyrite was oxidised.

Ferric iron concentrations are shown in Figures 4 and 5 for the simulation time of 5 years and 10 years respectively. In Figures 4.b and 5.b the effects of the ferric precipitation are included. In Figure 4, because the chemical oxidation of ferrous iron is the main source of ferric iron generation no significant ferric iron was generated. As illustrated in Figures 4.b and 5.b, the precipitation reaction removed ferric iron from the solution phase in the direction of the groundwater flow where the pH is above 3. The results for the solution pH are not presented here.

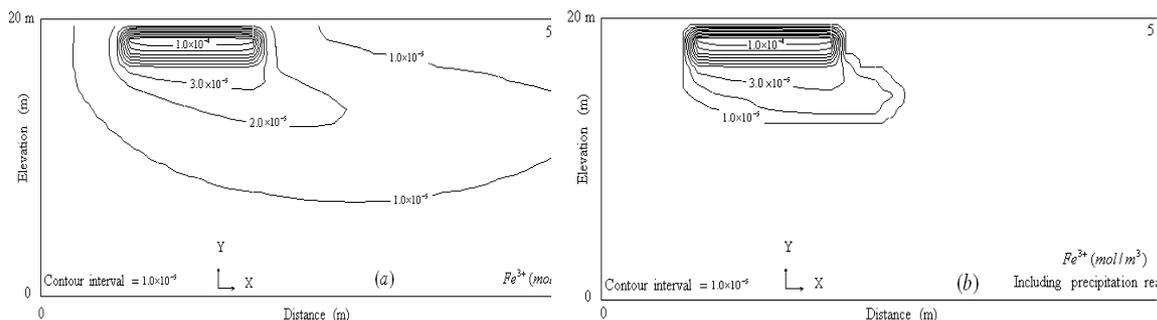


Figure 4. Fe^{3+} after 5 years of simulation: (a) without precipitation reaction; (b) including precipitation reaction.

In Figure 5, bacteria were allowed to be active. The ferric concentrations are mainly limited to the unsaturated zone, but as time progresses (Figure 5.a) some is being transported below the water table. In the case where pyrite is present below the water table, Fe^{3+} is converted back into Fe^{2+} through the Fe^{3+} -pyrite reaction. By incorporating the ferric iron precipitation reaction (Figure 5.b), aqueous ferric iron was removed from the solution phase in the saturated zone where the pH is greater than 3.5.

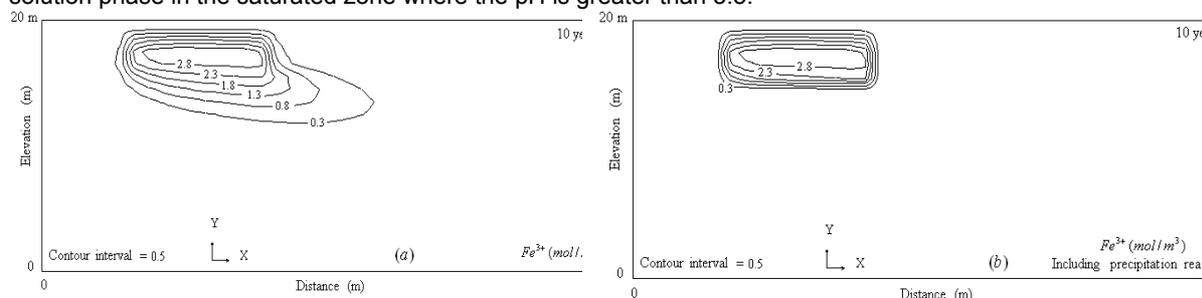


Figure 5. Fe^{3+} concentration after: (a) 10 years (without precipitation reaction); (b) 10 years (including precipitation reaction) of simulation. The role of bacteria was considered.

CONCLUSIONS

A numerical finite volume model using a multi-purposes CFD package called PHOENICS has been developed to simulate the ferric iron complexation and precipitation reactions taking place in acidic mine drainage environments. In such sites, the calculation of the actual amounts of ferric iron is important to determine the rate of pyrite oxidation and therefore the subsequent leaching generation. It was found that the complexation reactions increased the Fe^{3+} / Fe^{2+} value. The precipitation reaction removed ferric iron from the solution phase in the direction of the groundwater flow where the pH is above 3. The simulation of such reactions is an interesting subject of the environmental studies and gives realistic results and provides a better understanding of the complexity of the acidic mine drainage environments.

REFERENCES

- CHAM, 2000. The PHOENICS On-Line Information System, http://www.cham.co.uk/phoenics/d_polis/polis.htm
- Domenico, P.A. & Schwartz, F.W. 1990. *Physical and chemical hydrogeology*, 1st edition. John Wiley & Sons, Inc. New York.
- Doulati Ardejani F., et al. 2002. A numerical finite volume model for prediction of pollution potential of open cut mine backfill. EERE 2002. 6th Annual Environmental Engineering Research Event conference. Blackheath NSW, Australia, 2002., 10p.
- Eriksson, N. & Destouni, G. 1997. Combined effects of dissolution kinetics, secondary mineral precipitation, and preferential flow on copper leaching from mining waste rock. *Water Resources Research*, Vol. 33, No. 3, 471-483.
- Jaynes, D.B. et al. 1984a. Acid mine drainage from reclaimed coal strip mines, 1, Model description. *Water Resources Research*, Vol. 20, No. 2, 233-242.
- Jaynes, D.B. et al. 1984b. Acid mine drainage from reclaimed coal strip mines, 2, Simulation results of model. *Water Resources Research*, Vol. 20, No. 2, 243-250.
- Jennings, A.A. et al. 1982. Multicomponent equilibrium chemistry in groundwater quality models. *Water Resources Research*, Vol.18, No. 4, 1089-1096.

- Lerman, A. 1979. *Geochemical processes: water and sediment environments*. John Wiley. New York.
- Pankow, J.F. 1991. *Aquatic chemistry concepts*. Lewis Publishers. Chelsea, Mich.
- Reddi, L.N. & Inyang, H.I. 2000. *Geoenvironmental engineering, principles and applications*. Marcel Dekker, Inc. New York.
- Rubin, J. 1983. Transport of reacting solutes in porous media: relation between mathematical nature of problem formulation and chemical nature of reactions. *Water Resources Research*, Vol. 19, No. 5, 1231-1252.
- Rubin, J. & James, R.V. 1973. Dispersion-affected transport of reacting solutes in saturated porous media: Galerkin method applied to equilibrium-controlled exchange in unidirectional steady water flow. *Water Resources Research*, Vol. 9, No. 5, 1332-1356.
- Singh, R.N. & Doulati Ardejani, F. 2003. Evaluation of factors affecting pyrite oxidation and subsequent pollutant generation in backfilled open cut coal mines. 8th International Congress on Mine Water and the Environment, Johannesburg, South Africa, 173-186.
- Stumm, W. & Morgan, J. 1996. *Aquatic chemistry: chemical equilibria and rates in natural waters*. John Willey. New York.
- Walter, A.L. *et al.* 1994a. Modelling of multicomponent reactive transport in groundwater, 1, Model development and evaluation. *Water Resources Research*, Vol. 30, No.11, 3137-3148.
- Walter, A.L. *et al.* 1994b. Modelling of multicomponent reactive transport in groundwater, 2, Metal mobility in aquifers impacted by acidic mine tailings discharge. *Water Resources Research*, Vol. 30, No. 11, 3149-3158.
- Wunderly, M.D. *et al.* 1996. Sulfide mineral oxidation and subsequent reactive transport of oxidation products in mine tailings impoundments: A numerical model. *Water Resources Research*, Vol. 32, No. 10, 3173-3187.
- Yakowitz, S. & Szidarovszky, F. 1989. *An introduction to numerical computations*, 2nd edition. Macmillan. New York.