

Reactive Chemical Transport

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1. Introduction

Heat and mass transport and the interactions of fluid with the earth's crust are of interest for many reasons. For example economic geologists are interested in where conditions are appropriate for ore deposition, geothermal field developers are interested in the chemical composition of the fluid they plan to produce and how it may change. Contaminant transport is of interest to those charged with ensuring a potable water supply.

For many years it has been possible to compute the transport of heat and mass within the earth using simulators such as TOUGH2. Also speciation codes are well developed and used as a matter of course by geochemists to unravel the intricacies of the chemistry of fluids within the earth. Recently there has been a growing interest in combined these two disciplines to allow the modelling of reactive chemical transport in porous media. Some recent workers in the area are Lichtner (1992), Steffel and Lasaga (1995) Friedly (1989), Friedly and Rubin (1992), White (1995), Lichtner and Seth (1996) and Bear and Niato (1995).

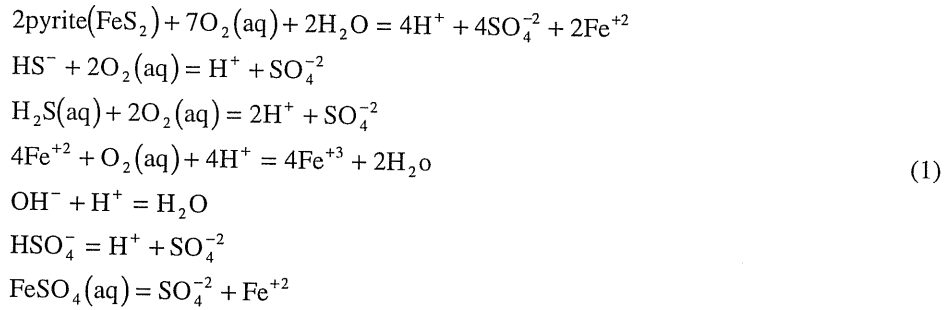
In this paper we will present an outline of modelling pyrite dissolution using Chem TOUGH2 (White 1995). Pyrite oxidation, dissolution and precipitation play an important role in the supergene enrichment of porphyry copper deposits. This process takes place when oxygen-rich water infiltrates into pyrite bearing geologic media. The pyrite is initially oxidised, with the oxidation products being in the aqueous phase. These products are transported in the aqueous phase and may precipitate when chemical or other conditions change. The importance of these processes has been known for some time (see, for example Emmons 1918, Locke 1926, Bateman 1950). Auge and Brimhall (1989) modelled the supergene enrichment of a porphyry copper deposit. Their work modelled the chemistry of the system in some detail, but the discretization of the domain used for transport calculations was quite coarse.

We consider a number of increasingly complex models of pyrite dissolution. All of these consider the reaction of oxygen-rich infiltration water with rock containing the mineral pyrite. Water in equilibrium with atmospheric oxygen has a dissolved oxygen concentration of 1.265×10^{-4} mol/l at 25° C, and we use this value for water entering the system.

2. Hydrodynamic and chemical parameters

In the first example we model a one-dimensional horizontal porous column 0.5 m long with a cross-sectional area of 1 m^2 which contains the mineral pyrite; at the left boundary infiltration water is injected at 2.31×10^{-4} kg/sec and is withdrawn from the right boundary at the same rate. Porosity of the column is 0.4 which, with the prescribed injection rate, leads to a pore velocity of 0.05 m/day. The column is discretized into 10 grid blocks, each with a length of 0.05 m.

The dissolved oxygen carried by infiltration water reacts with pyrite which dissolves. Oxidation and dissolution of pyrite results in redistribution of aqueous species. We considered that the system is made up of the following species: H^+ , H_2O , $\text{O}_2(\text{aq})$, SO_4^{2-} , Fe^{+2} , OH^- , HSO_4^- , $\text{FeSO}_4(\text{aq})$, HS^- , $\text{H}_2\text{S}(\text{aq})$, Fe^{+3} and FeS_2 (Pyrite). For this example we force the system to contain single phase liquid only (i.e. no gas phase). The boundary infiltration solution has a dissolved oxygen concentration of 1.265×10^{-4} mol/l which is a strongly oxidising condition. This amount of oxygen is equivalent to a gaseous oxygen pressure of .1 bar (assuming a fugacity coefficient of 1.0). The reactions taking place between the species in solution are



2.1 Results

The infiltration water, having a large amount of dissolved oxygen, causes pyrite oxidation and dissolution. The $\text{O}_2(\text{aq})$ is consumed almost completely (the dissolved O_2 concentration after reaction is 6.763×10^{-69} mol/l). Dissolution of one mole of pyrite consumes 3.5 moles of aqueous O_2 , and creates 2 moles of H^+ , 2 moles of SO_4^{-2} and 1 mole of Fe^{+2} . Consequently, total dissolved S and Fe concentrations increase and pH decreases.

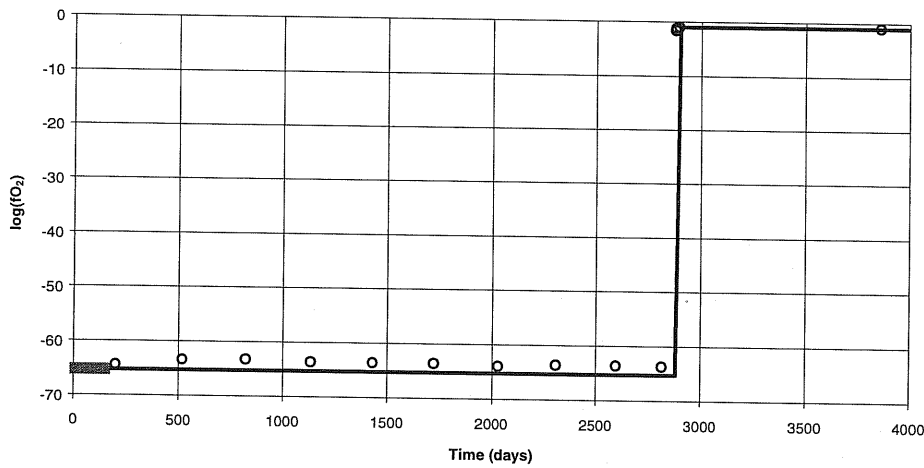


Figure 1: log of oxygen fugacity vrs grid pore volume (= time in days) at the center of the first grid block.

3. Two-phase simulations

The following two examples consider oxidation of pyrite in the vadose zone. Both examples use the same geometry shown in Figure 5. We model flows in a vertical column with a cross-sectional area of 1m^2 and a length of 150 meters. At the top is air at 25°C and 1 bar, the bottom has a liquid saturation of 1.0 and a pressure of 10.5 bars.

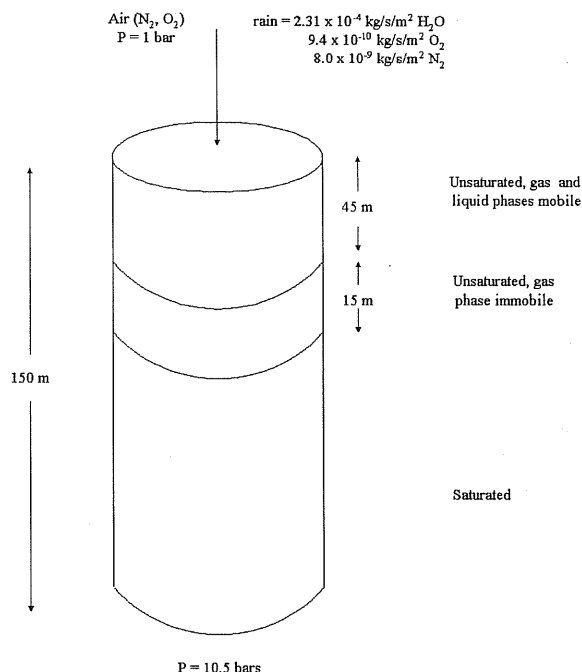
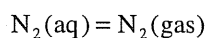
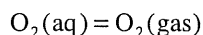


Figure 2: Schematic representation of unsaturated column.

The initial temperature is 25° C throughout the column. The initial conditions for pressure and saturation are the steady-state values calculated when chemical reactions are ignored. The column is unsaturated to a depth of 70 meters, below this the column is fully saturated. Water saturated in oxygen and nitrogen is injected into the block at the top of the column at a rate of $2.31 \times 10^{-4} \text{ kg/s}$. We have used the relative permeability and capillary pressure functions of Van Genuchten (1980). With the parameters chosen for relative permeability the gas phase becomes immobile at a liquid saturation of about 0.8. This means that gas is mobile in the top three elements of the column, immobile in the fourth element and not present below that. For these examples involving transport in both the aqueous and gas phases, the chemistry is more complicated than given Equation 1 and we must include reactions between aqueous and gaseous oxygen and between aqueous and gaseous nitrogen.



While nitrogen does not react with any of the other species we must include it to obtain the correct pressures in the gas phase. As in the horizontal case we consider two examples, in the first all reactions are considered to be in equilibrium, in the second the pyrite oxidation reaction is treated as a kinetic reaction. Oxygen concentration as a function of depth for the equilibrium case is shown in Figure 11. This figure presents an interesting contrast to the fully saturated case shown in Figure 1b. In areas where the gas phase is mobile, the pyrite dissolves at an almost uniform rate, with oxygen flowing from the surface in the gas phase, dissolving in the oxygen depleted liquid and reacting with the pyrite. Figure 11 shows the top three elements with a high dissolved oxygen concentration as all the pyrite originally in these elements has been removed. This figure represents the situation after 5200 days which is insufficient time for the oxygen in the water injected into element 1 to have dissolved this volume of pyrite. Therefore transport of oxygen in the gas phase makes a significant difference to the rate at which pyrite is removed. In the fourth block, where the gas phase is not mobile, once the small amount of oxygen initially present has been consumed no further reaction takes place until all the pyrite has been consumed from the element above. Then the water flowing into element four will be saturated in oxygen, and the oxidation front will move through the saturated portion of the column as it did in the fully saturated horizontal example.

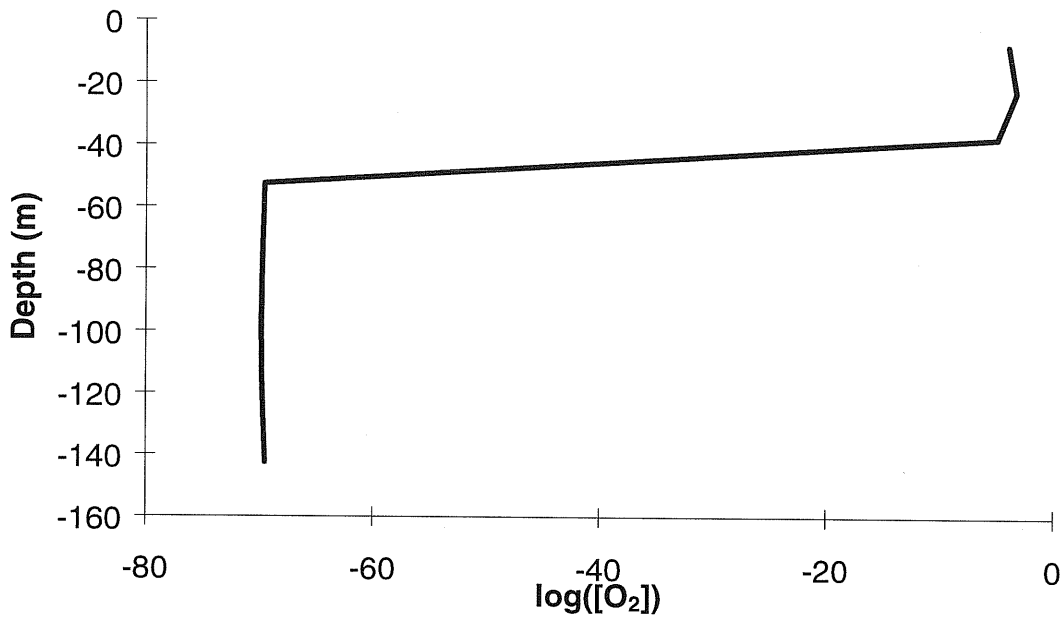


Figure 3: Aqueous phase oxygen concentration in vertical column assuming equilibrium chemistry.

3.1 Kinetic Reaction Rate

We assume a pyrite dissolution is described by a kinetic reaction of the form

$$\frac{dC_{\text{pyrite}}}{dt} = \alpha f(S)C_{\text{pyrite}} \quad (4)$$

From Welch *et al.* (1980) we estimate $\alpha = -1.8 \times 10^{-5} \text{ sec}^{-1}$ at a liquid saturation of 0.5. The reaction rate is a strong function of saturation (see Figure 16 of Welch *et al.*) and $f(S)$ is a function of liquid saturation approximated from the data of Welch *et al.* (1980).

Obviously the reaction rate will also be modified by the amount of oxygen present in the aqueous phase. The expression given in Equation (4) is modified so that in a given time the reaction cannot consume more oxygen than is available at the beginning of that time plus any that is transported into an element during that time.

In Figure 12 we show the oxygen concentration as a function of depth assuming kinetic control for pyrite oxidation. Oxygen concentration is highest in the three elements nearest the surface. Once the gas phase is immobile or disappears, oxygen concentration drops approximately linearly with depth. It is interesting to note that only a small portion of the oxygen is consumed and the water flowing out the bottom of the model still contains about 90% of the oxygen that is present in the surface elements. This contrasts with the equilibrium case where all the oxygen is consumed in the unsaturated zone or when the pyrite there is depleted in the first element containing pyrite.

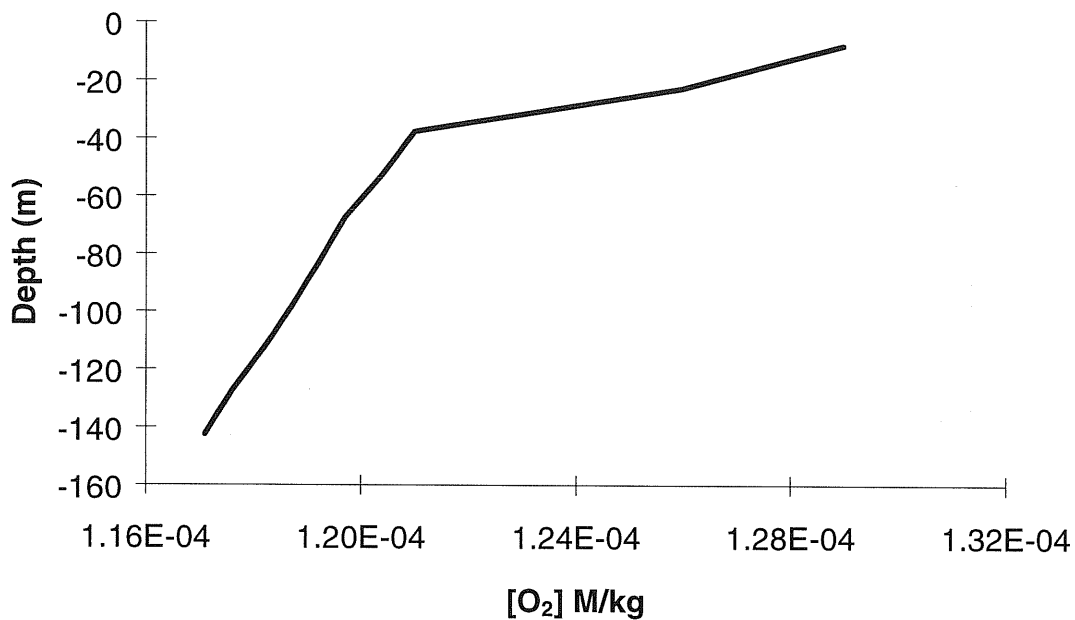


Figure 12: Aqueous phase oxygen concentration in vertical column assuming non-equilibrium pyrite dissolution.

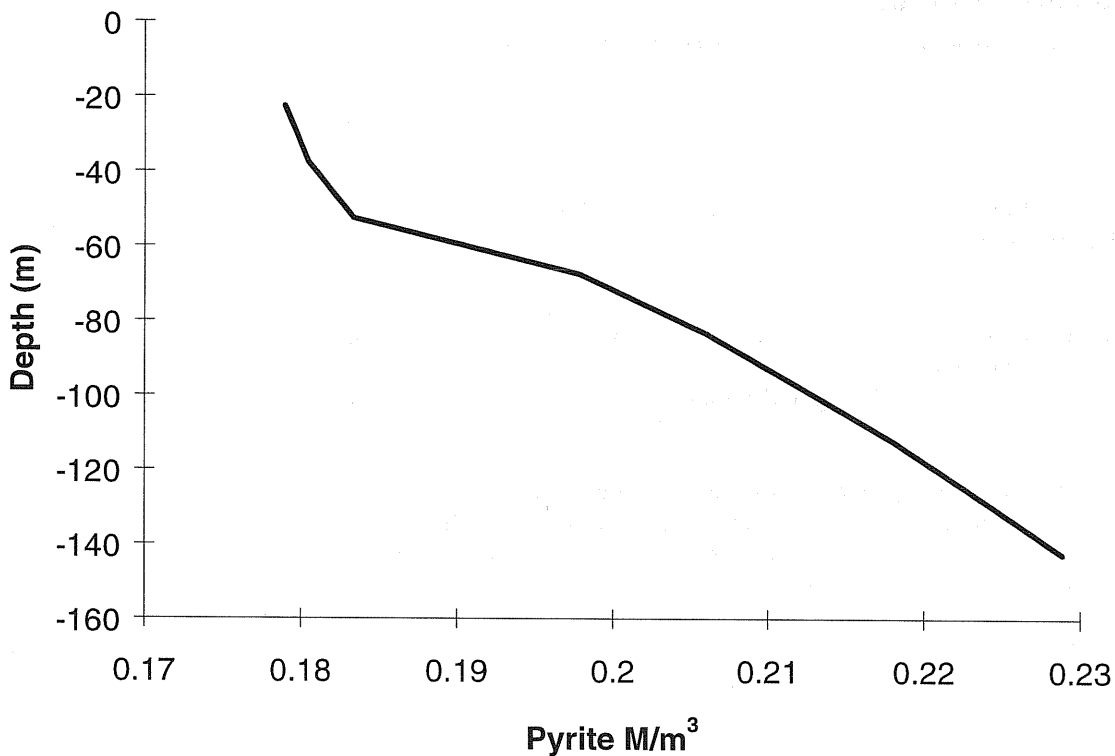


Figure 4: Pyrite concentration in vertical column assuming non-equilibrium pyrite dissolution.

4. Conclusions

We have modelled pyrite dissolution, where it is possible to calculate analytic properties of the modelled system (such as oxidation front speed), this has been done and compared with the numerical results. Good agreement with the numerical results was found.

Simulation of a vertical column containing a saturated zone confirms the importance of processes taking place in this zone to explaining the rate of pyrite removal. Pyrite will be oxidised from the rock over the whole of the vadose zone where the gas phase is mobile. This results in a much greater flux of pyrite oxidation products out of the column modelled than would be found for a fully saturated column.

When pyrite oxidation is treated as a kinetic reaction, the reaction may take place not only in the unsaturated zone but also to a considerable depth in the saturated zone. In the system modelled, only about 10% of the available oxygen was consumed by a depth of 160 meters. The kinetic reaction rate used in this modelling is an approximation to the true rate, and we have ignored the effect of pH on reaction rate and also treated the effect of oxygen concentration in a crude manner. However we believe sufficient detail has been included to reproduce the important effects of kinetic pyrite oxidation in a partially saturated column.

5. References

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