Chemically reactive multicomponent transport simulation in soil and groundwater: 1. Model development and evaluation

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Abstract  The model, REACTRAN2D, is for simulating the transport of chemically reactive components in conjunction with energy transport in groundwater systems. It is coded on the basis of two well-known models, SUTRA and MINTEQA2. On the assumption that local equilibria exist, this coupled geochemical and heat transport model is solved by a parallel and sequential iteration approach. It has been compared with HYDROGEOCHEM and limited field data. Very close matches were achieved. This model can deal with chemically reactive transport involving solid phase, aqueous phase and gas phase, therefore, having a great potential to simulate the full range of geochemical problems covered by MINTEQA2.

Keywords  Geochemical · Reaction · Transport · Modeling

Introduction

The methods for the simulation of chemically reactive multicomponent transport have attracted much interest from hydrogeologists and/or hydrogeochemists for years. So far, quite a few models have been developed, including DYNAMIX, HYDROGEOCHEM, MINTRAN, RT3D, etc. DYNAMIX (Narasimhan and others 1986) is a dynamic mixing cell model, based on a transport model TRUST and a geochemical speciation model PHREEQE, capable of handling several element problems (Narasimhan and others 1986). HYDROGEOCHEM (Yeh and Tripathi 1991) is a coupled chemically reactive transport model based on the previous model FEMWATER, a flow and transport model on both saturated and unsaturated conditions, and EQMOD, a geochemical model for aqueous complexation, precipitation–dissolution, adsorption–desorption, oxidation–reduction, ion exchange and acid-base reactions. Walter and others (1994) developed a model, MINTRAN, for multiple component reactive transport in groundwater. This model resulted from a finite element transport model (PLUME2D) and a geochemical speciation model (MINTEQA2). RT3D (Clement and others 1998) is based on MT3D (Zheng 1990), which requires USGS groundwater flow model MODFLOW to obtain groundwater flow heads. It is claimed that the present version of RT3D is sufficiently flexible for simulating various types of chemical reactions, microbial metabolisms, and microbial transport kinetics. However, primary applications studied so far are mostly related to natural attenuation of certain organic species. Restricted by MODFLOW, this model is applicable to saturated porous media only. These models are undoubtedly very useful to solve a wide range of reactive groundwater problems. However, in real environmental applications, those methods seem inadequate in terms of solving some specific environmental problems. For example, the problem of heat contamination and the influence of heat distribution on the behavior and fate of contaminants were not considered. In fact, those scenarios, which involve more complex environmental problems, are common. To take acid mine drainage contamination as an example, the heat transport and the disturbed temperature field may be of concern, given the evidence that the temperature in sulphide-containing waste rock tailings could be as high as 45 °C (Cathles and Apps 1975), even up to 80 °C (Fell and others 1993). A high temperature source may cause an uneven distribution of groundwater temperature in the nearby tailings area. The distributed rather than a constant temperature in groundwater may result in a quite different situation because chemical reactions are influenced by the ambient temperature (Freeze and cherry 1979; Stumm and Morgan 1996). The effect of temperature on chemical...
Model development

For a contaminated groundwater system, the flowing water body will carry contaminants through the transport medium, while the contaminants react with both groundwater body and possible minerals in the transport matrix. This complex procedure includes physical transport and some geochemical reactions.

For the sake of numerical solution to the fully coupled equations, some assumptions have to be given. First, chemical reactions are assumed to be sufficiently fast, relative to hydrological processes, for the local equilibria to be established throughout the solute transport domain (Rubin 1983; Yeh and Tripathi 1989; Walter and others 1994). This assumption may not be applicable to some very slow reactions such as the acid buffering reactions with non-carbonate minerals and redox reactions without acceleration, i.e. Fe$^{3+}$/Fe$^{2+}$ transfer without bacterial acceleration. Secondly, for a multi-component system, the transport of individual components or species is considered to occur independently (Rubin 1983). In other words, all individual components have identical physical transport behaviors. Finally, the energy change caused by various exothermic and endothermic chemical reactions in the groundwater environment is sufficiently small not to cause observable temperature variations in the huge groundwater and rock body. In steady, the groundwater temperature changes may only be caused by energy transport originating from a heat source (a tailings dam for example).

Chemical reaction term: derivation of the accumulation rate \( R_j \)

All possible chemical reactions cause a change of the concentration of component \( j \) during the transport. This rate is a sum of the mass accumulation from all chemical reactions expressed as:

\[
R_j = R_j^a + R_j^b + R_j^d + R_j^{ab}.
\]

where \( R_j^a \) is the rate of accumulation of the \( j \) substance due to the aqueous complexation, \( R_j^b \) is the rate of accumulation of the \( j \) substance due to adsorption-desorption, \( R_j^d \) is the rate of accumulation of the \( j \) substance due to precipitation-dissolution, \( R_j^{ab} \) is the rate of accumulation of the \( j \) substance due to redox reaction, and \( R_j^{ab} \) is the rate of accumulation of the \( j \) substance due to acid-base reaction.

Since the rate of accumulation of component \( j \) due to ion-exchange reaction, redox reaction and acid-base reaction can be described mathematically in terms of accumulation of component \( j \) due to aqueous complexation, adsorption/desorption and precipitation/dissolution reactions (Yeh and Tripathi 1989; Gao 1998), Eq. (3) can be simply re-written as:

\[
R_j = R_j^a + R_j^b + R_j^d.
\]

They can be further extended in the following expressions:

\[
R_j^a = -\frac{\partial}{\partial t} \left[ \frac{N_j}{X} \sum_{i=1}^{N_c} a_{ij}^X P_i^X \right], \quad R_j^b = -\frac{\partial}{\partial t} \left[ \frac{N_j}{S} \sum_{i=1}^{N_c} a_{ij}^S S_i \right], \quad j = 1, ..., N_c
\]

where \( a_{ij}^X \) is the stoichiometric coefficient for the total aqueous concentration of component \( j \) in complex \( X \), and \( N_c \) is the number complex for component \( j \); \( a_{ij}^S \) is the stoichiometric coefficient for the total adsorbed concentration of component \( j \) in adsorbed site \( S_i \), and \( N_i \) is the number of sorbed complexes for component \( j \); while \( a_{ij}^P \) is the stoichiometric coefficient for the total precipitated concentration of component \( j \) in precipitate \( P_i \), and \( N_p \) is the number precipitates for component \( j \).While, the concentrations, \( X \), \( S_i \), and \( P_i \) are related to the concentration of aqueous component \( j \) by means of the following ways, respectively: