

Modeling of hydro-geochemical processes in waste disposal systems with a coupled chemical reactions-transport code

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Since a few years ago, the mass transport of reactive chemical elements in waste containment systems and pollutant migration are studied with computer programs. The mathematical code STELE is an iterative model coupling a geochemical speciation code (CHIMERE) with a code simulating mass transport, fluid and heat flows (METIS). The application - NaOH injection in sandstone - presented consists in a verification of the program compared to an exact theoretical solution defined as part of the CCE CHEMVAL project.

Introduction

Pollutant migration in groundwater and geochemical behaviour of waste disposal (nuclear or heat storage) have in common that they depend upon mechanisms coupling fluid flow and the chemical reactions between dissolved species and solid matrix. In the course of the last few years, coupled chemistry-transport models have been built where chemical thermodynamic laws are introduced into the transport models. These coupled codes allows the reactivity of the solid through which the water is flowing (review in Yeh and Tripathi, 1989).

Description of STELE code

STELE used to simulate the transfer of fluid and heat is METIS (Goblet, 1981), where fluid and heat transfers are coupled by the temperature dependence of the dynamic viscosity and the mass per unit volume of fluid. Balance equations of fluid and heat are solved alternately. METIS is based on a 2-D modelling of the calculation of heat or solute transport in a saturated porous medium.

The geochemical module of STELE - CHIMERE code - is able to calculate aqueous complexation, dissolution/precipitation of solids, equilibrium of gases, ion exchange, surface adsorption and includes the two-layer model

(Coudrain-Ribstein, 1988; Madé and Jamet, 1993b). The method elaborated to clearly pose the chemical constraints and the equations of speciation and transport is based on the use of chemical components.

Application

The application is a verification test case of CCE CHEMVAL project (Read, 1991a). This concerns the injection of sodium hydroxide into an aquifer where the sole mineral represented is silica. The initial state is one of pure water at equilibrium with SiO₂. The injection of sodium hydroxide into the system displaces the equilibrium of the silica towards dissolution. The equilibria controlling the speciation of the silica in the system H₂O-SiO₂ take into account only two aqueous silica species, H₄SiO₄ and H₃SiO₄⁻. As the species (Na⁺) is known, the equation of electric neutrality is used to determine the system completely.

The analytical solution of the static system can be obtained by treating the activities as concentrations, which is permissible for weak ionic strengths. We can written:

$$[Na^+] + [H^+] = \frac{K_2 K_1}{[H^+]} + \frac{K_3}{[H^+]}$$

with K₁, K₂ and K₃, solubility constants defined more far. If we write [Na⁺] = C, the H⁺ ions concentration is defined by the positive root of this second-degree polynome, i.e.:

$$[H^+] = \frac{-C + \sqrt{C^2 + 4(K_3 + K_2 K_1)}}{2}$$

Thus, the concentrations of all the other species in the system can be obtained, i.e. for the anions OH⁻ and H₃SiO₄⁻ (Madé and Jamet, 1993a).

The equations established above are valid for all points of the study domain; the only remaining unknown is the concentration in space and time of sodium. As it is not involved in any geochemical

equilibrium, Na^+ behaves like a perfect tracer for which there is an analytical solution of the transport in certain simple flow situation (ex.: constant flow along the x axis). The solution of the problem for the two-dimensional case, is given in De Marsily (1986) by:

$$C(x, y, t) = \frac{dM}{4\pi t \sqrt{D_L D_T}} \exp\left(-\frac{(x - \frac{Ut}{\omega})^2}{\sqrt{4D_L t}} - \frac{y^2}{4D_T t}\right)$$

with $C(x, y, t)$, concentration in space and time of the perfect tracer; dM , injected mass (per m of aquifer); D_L , D_T , transverse and longitudinal dispersion coefficients; U , Darcy's velocity and ω , porosity of the formation.

—Transport parameters: U , Darcy's velocity = 0.1 m/day; D_L , longitudinal dispersion coefficient = 0.5 m²/day; D_T , transverse dispersion coefficient (for the 2D case only) = 0.1 m²/day; ω , porosity = 0.1; M , mass of the injected tracer per unit of thickness of the aquifer = 10⁻² moles/m;

—Chemical parameters: K_1 , solubility constant for chalcodony = 10^(-3.554); K_2 , silicic acid first constant = 10^(-9.77); K_3 , water dissociation constant : 10^(-13.998).

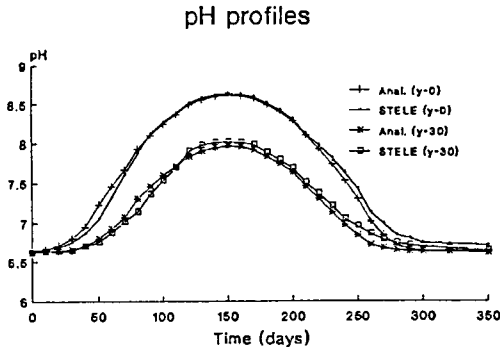


FIG. 1. Variation of pH profiles versus time at $x=150\text{m}$, $y=0\text{m}$ and at $x=150\text{m}$, $y=30\text{m}$ (simulation in 2D) compared to analytical solutions.

Conclusion

The results obtained by STELE code are in good agreement with the analytical solution. Others test cases have been simulated within the context of the CCE CHEMVAL project allowing to validate this program.

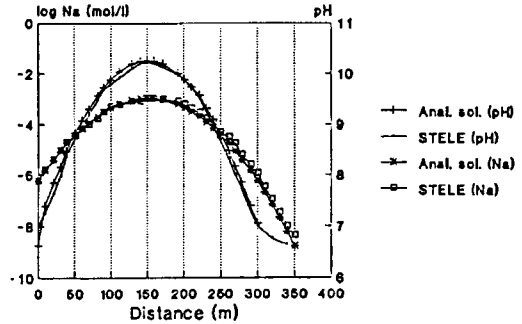


FIG. 2. Profiles of Na^+ concentration and pH calculated versus distance after a simulated time of 150 days (simulation in 1D) compared to analytical solutions.

The coupled chemical reactions-transport code STELE has been applied for the simulation of many and various natural or induced phenomena at low temperature: silicification of Fontainebleau's sandstones, calcite dissolution/precipitation, as well at highest temperature: diagenetic reactions in sedimentary basins, dissolution/precipitation of solids in induced hydrothermal systems (heat storage, nuclear waste storage...).

References

- Coudrain-Ribstein, A. (1988) Transport d'éléments et réactions géochimiques dans les aquifères. Unpublished Ph-D Thesis, Quantitative Hydrogeology, U.L.P., Strasbourg, France, 381p.
- Goblet, P. (1981) Modélisation des transferts de masse et d'énergie en aquifère. Unpublished Ph-D Thesis, Ecole des Mines de Paris, France, 199p.
- Madé, B. and Jamet, P. (1993a) CHEMVAL2 progress report. *Report Ecole Mines Paris/CIG, LHM/RD/93/38*, France, 101p.
- Madé, B. and Jamet, P. (1993b) Modeling of hydrothermal systems with coupled chemical reactions-transport code. In *Proc. 4th Intern. Symp. on Hydrothermal Reactions* (Cuney M. and Cathelineau M. eds.), Nancy, France, 139–42.
- Marsily De, G. (1986) *Quantitative hydrogeology, groundwater hydrology for engineers*. Academic Press, London, 215p.
- Read, D. (1991) CHEMVAL project. CEC report, EUR 13675 EN, 234p.
- Yeh, G.T. and Tripathi, V.S. (1989) *Water Res. Res.*, **25**, 1, 93–08.