Multispecies reactive transport under equilibrium and kinetic geochemical conditions

Leonardo David DONADO[1,2], Alberto GUADAGNINI[3], Xavier SANCHEZ-VILA[1], and Jesus CARRERA[4]

[1]Department of Geotechnical Engineering and Geosciences, Technical University of Catalonia, Jordi Girona 1-3, Building D2, 08034 Barcelona, Spain

[2]School of Civil Engineering, Industrial University of Santander. Ciudad Universitaria, Bucaramanga, Colombia.

[3]DIIAR, Politecnico di Milano, Piazza L. Da Vinci 32, 20133 Milano, Italy

[4]Institute of Earth Sciences Jaume Almera, Spanish National Research Council, CSIC. Luis Sole i Sabaris, s/n, 08028 Barcelona, Spain

Abstract

Transport of reactive species in the subsurface is driven by mixing processes. Quantification of the mixing rate is, therefore, the basis for a proper characterization of the fate of pollutants in geochemically active environments. *De Simoni et al*. [2005, 2007] have proposed a methodology conducive to the evaluation of solute concentrations and reaction rates in complex geochemical systems where homogeneous (between aqueous species) or heterogeneous (involving both aqueous species and the solid phase) reactions take place under chemical equilibrium conditions. Their main result is an exact expression for the spatial-temporal distribution of the reaction rate as a function of the spatial distribution of some conservative components (defined as stoichiometric combination of species), and a speciation term, highlighting the role of chemical reactions.

In general, geochemical processes occurring in natural aquifers following mixing of different waters can be relatively fast, so that they can be described by equilibrium models, or slow (kinetics), thus becoming a controlling factor in the evolution of the system. Whenever both types of reactions are present, the solution of the multicomponent system is extremely complex [e.g., *Steefel et al*., 2005 and references therein]. Here, we build on the methodology of *Molins et al*. [2004] and *De Simoni et al*. [2005, 2007] and present an analytical expression for computing kinetic and equilibrium reaction rates for a system characterized by the occurrence of two reactions. One of these is considerably faster than the other so that one can model them as an equilibrium and a kinetic one, respectively. The key result is that the equilibrium reaction rate is provided by the sum of two terms: one is a linear function of the kinetic reaction rate through a speciation term and the second one is proportional to the rate of mixing. The main idea is that the solution of such a complicated problem, involving a relatively high number of species, can be decoupled so that the system can be written as a succession of partial differential equations, each one incorporating the solution of the previous one. As a result, there is no need to solve a coupled system. The drawback is that at least one of the PDE's is highly non-linear. Still, in some particular simple cases the methodology allows for finding the exact solution of some reactive problems without the need to use a fully coupled reactive transport code. Thus, the methodology can be used to test numerical codes by setting benchmark problems and also to derive closed-form analytical solutions for simplified geochemical set-ups.

References.

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