Is it possible to provide simple solutions for evaluating reaction rates in multiespecies reactive transport problems?

Xavier Sánchez-Vila[1], A. Guadagnini[2], J. Carrera[3], M. De Simoni[2], L. Donado[1,4], M. Dentz[1], D. Fernandez-Garcia[1], M. Saaltink[1]

[1]Department of Geotechnical Engineering and Geosciences, Technical University of Catalonia, UPC, Barcelona, Spain
[2]Dipartimento di Ingegneria Idraulica, Ambientale, Infrastrutture Viarie, Rilevamento, Politecnico di Milano, Milano, Italy.
[3]Institut de Ciències de la Terra Jaume Almera, CSIC, Barcelona, Spain
[4]School of Civil Engineering, Industrial University of Santander, Bucaramanga, Colombia

ABSTRACT

Chemical reactions are driven by disequilibrium, which in several reactive transport problems is caused by mixing. Therefore, quantification of the mixing rate is essential for evaluating the fate of solutes in natural systems, such as rivers and aquifers. Traditionally reactions rates are computed numerically by means of mass balances once the concentrations of the aqueous and mineral species are computed by means of a multicomponent reactive transport code.

We propose a global paradigm that focus on the direct evaluation of reaction rates. The idea consists on decoupling as possible the transport and the reactive processes, by means of defining a combination of aqueous species that are not affected by a given reaction. As an example, in the case of precipitation, there is a stoichiometric relationship between the moles of the different species that are removed from the system, and thus it is possible to define a vector of some given quantities, termed components in the geochemistry literature, that are not affected by reactions. In short, we define a number of conservative species that are governed by the transport equation used to model conservative quantities. The second problem becomes now how to write the reaction rates as a function of the conservative quantities, a problem that has been widely tackled in the literature for decades by means of speciation codes.

As a consequence, we are able to solve a multicomponent reactive transport problem, which can mostly be solved only numerically, by means of solving two independent problems, one of transport of one or more conservative species, and one of speciation. Each one of these problems is simpler than that of the full problem, and so, in some cases, it is possible to obtain closed-form solutions for particular setups.

We review a number of practical solution for problems of increasing complexity. First, we illustrate the full benefits of the methodology by starting with a simple precipitation problem where the governing reaction

$$Ca^{2+} + SO_4^{2-} \rightleftarrows CaSO_{4s} \Rightarrow \left[Ca^{2+} \right] \cdot \left[SO_4^{2-} \right] = K_{eq}$$
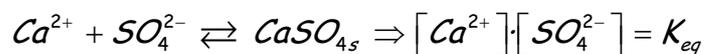
can be assumed in equilibrium at all points (instantaneous equilibrium). In this case the component can be defined

$$u = \left[Ca^{2+} \right] - \left[SO_4^{2-} \right] = c_1 - c_2 \quad \text{(new notation)}$$

It can be easily seen that u is a conservative quantity, and thus satisfies a conservative transport equation with the corresponding boundary and initial conditions. Once u is obtained, the speciation step provides the reaction rate, r, directly (without the need to solve for the actual concentrations of the two aqueous species) by means of an explicit expression. This expression would depend on the choice for the transport equation we are actually using. The simplest one would be considering that transport is governed by an advection-dispersion (or diffusion) equation, characterized by a local dispersion tensor $\mathbf{D}$. The corresponding expression becomes

$$r = \phi \frac{\partial^2 c_2}{\partial u^2} \left[\nabla u^T \cdot \mathbf{D} \cdot \nabla u \right] \tag{1}$$

where ϕ is porosity, the term in brackets corresponds to a measure of dilution, and there is a speciation term explicitly given by $\partial^2 c_2 / \partial u^2 = 2K \left(u^2 + 4K \right)^{-3/2}$.

Notice that whenever the solution for u can be obtained analytically, it is also possible to write the exact local expression for the reaction rate at any point in space and time by means of (1).

It is also possible to apply this method whenever the transport of conservative species is governed by an effective dynamics equation with a term accounting for physical heterogeneity. Then, the reaction rate is given by adding an additional term to (1) which explicitly includes the memory function.

We can take an alternative approach to consider reactive transport in heterogeneous media. Since (1) is valid locally, u can be treated as a Random Space Function, thus making r another SRF. The issue of upscaling and effective properties can then be addressed for simple flow configurations such as a stratified media, where it can be shown analytically that an equivalent hydraulic conductivity value can be defined, that being much lower than the equivalent value corresponding to flow.

Last, we study the case where equilibrium is not reached instantaneously, but rather by means of an equation involving the Damköhler number (Da), which measures the ratio between the reaction and the diffusion characteristics times. In such a case it is not possible to write an explicit expression for r, but rather the reaction rate can be obtained from the solution of a highly non-linear partial differential equation, which needs to be solved numerically. Only for large Da values it is possible to write the solution by means of a truncated Taylor's expansion, where each of the terms can be written explicitly in terms of u and Da .

In summary, it is possible to provide simple solutions to quite complicated problems, which opens the possibility of exploring analytically the parameters controlling multicomponent reactive transport. This can then be used to stablish a number of benchmark problems that can be tested against analtytical solutions rather than test them against numerical solutions as it has been, and still is, routinely done nowadays.