

Arbitrarily Complex Water/Water and Water/Rock Reactions with Particles

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Introduction

Previous particle-tracking (PT) algorithms for chemical reaction conceptualize each particle being composed of one species. Reactions occur by either complete or partial birth/death processes between interacting particles. We extended the method by placing any number of chemical species on each particle. The particle/particle interaction is limited to mass exchange. After exchange, reactions of any sort are carried out independently on each particle.

The original method for simulating bimolecular reactions on particles is described by [1]. It combines the probability that two particles will be co-located and the thermodynamic probability that two particles will react, given colocation: $P(\text{react}) = P(\text{react}|\text{co-location})P(\text{co-location})$. Over a timestep dt for 2 particles undergoing local Fickian diffusion, the latter colocation probability density is a Gaussian with variance $2dt(D_1+D_2)$, where D are the diffusion coefficients. The thermodynamic probability was approximated by the rate coefficient times dt . The algorithm is straightforward to extend to multiple dimensions and variable flow fields, where the performance and accuracy gains over grid-based methods can be substantial [Benson AWR]. The algorithm suffered from poor concentration resolution (order $O(1/N)$, where N is the number of particles), until the probability was shown to be equivalent to mass fraction reduction in the particles [Bolster].

In order to perform more complex reactions with particles, there are several possible tacks. One can construct any reaction as a sequence of bimolecular and monomolecular reactions, but this sequence is potentially extremely long. This method was used to simulate Monod-type biologic growth and carbon tetrachloride degradation at the Schoolcraft site in Michigan, USA [Dong]. An interesting component of that study was the separation of poor mixing effects (via the particle method) and the rate coefficient “scaling” that typically accompanies reactive transport simulation at the field-scale. In other words, the particle method used beaker-scale rates for the field-scale simulations, while previous grid-based models required empirical adjustment of reaction rates.

A newer method {Benson} places any number of species on a particle and performs any and all reactions on the particles (Fig. 1). This method recognizes that mixing is a reaction of sorts, which can be written, e.g. $pA + qA \rightarrow \frac{1}{2}(p+q)A + \frac{1}{2}(p+q)A$. Now the probability that two particles co-locate is accompanied by the mixing “reaction”. This method exactly accounts for mixing at the local scale, quite differently from random-walk dispersion. One mass transfer occurs (weighted by co-location probability), the balances of species will have changed, and levels of disequilibrium will have also changed. Based on the new mass balances, chemical reactions of any sort can be performed. The technique applies to immobile particles (with $D = 0$), and all or part of these particles may be solid species.

All of the particle-tracking and reaction (PTR) algorithms have, at their core, the ability to simulate sub-grid fluxes. The particle numbers are chosen so as to replicate the chemical heterogeneity as reflected in the auto- and cross-covariances of the chemical species. The particles exactly represent the concentration fluctuations that are ubiquitous at all scales. As the particles move, transfer mass, and react, these fluctuations interact with sub-grid velocity fluctuations (also continuously represented by particles), and solid species mass fluctuations in ways that elude representation in upscaled grid-based simulations. The novel portion of this new algorithm is the mass-transfer (mixing) between mobile and immobile particles. Once particles are moved and re-mixed based on proximity, any geochemical reaction routine can be used in massively parallel implementations. We have used phreeqcrm [Engdahl], without loss of generality, to simulate oxidized waters moving through sulfide mine waste (Fig. 2), and the benchmark

problem of high pressure CO₂ (with magnesium) injection and dissolution of calcite-bearing material, with replacement by dolomite.

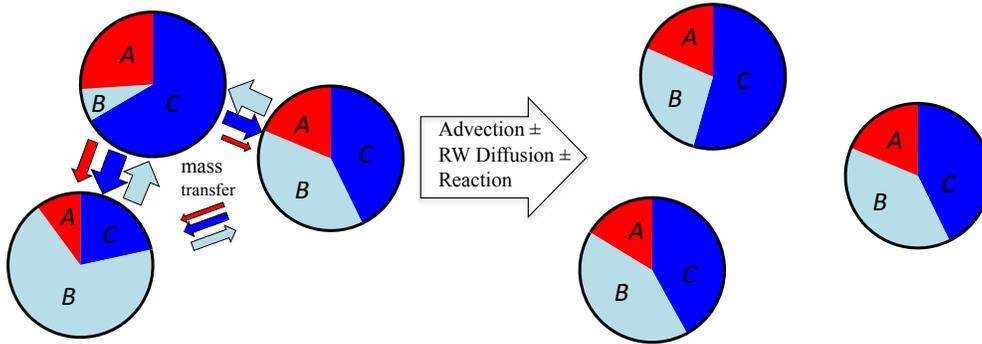


Figure 1: Schematic of multi-species PTR.

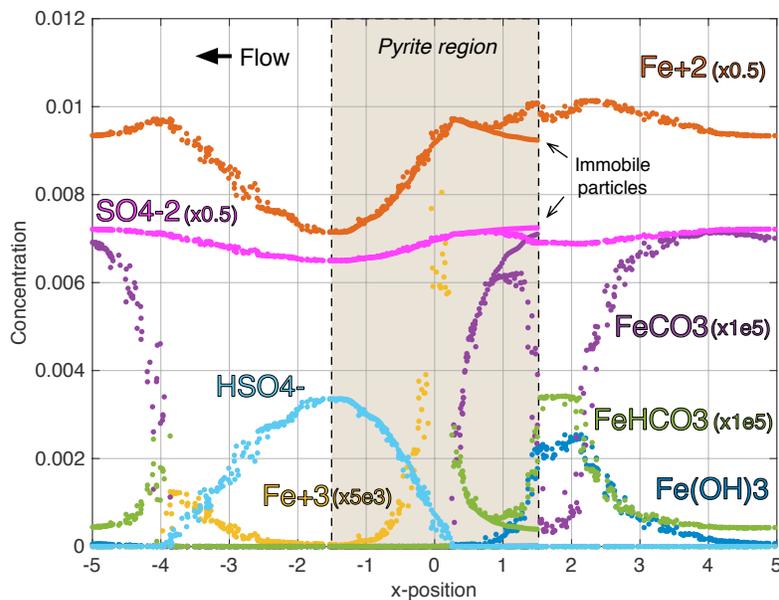


Figure 2: Distribution of species while moving through mine-waste sulfides.

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