Why are reactive transport simulations computationally expensive and what can we do about it?

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Reactive transport simulations require chemical equilibrium and kinetic calculations in every cell or node of the mesh, at every time step. These calculations can be responsible for most of the computational costs in the simulation, with a detailed chemical system, containing many phases and species, easily accounting for over 90% of all calculation costs. There are many reasons for this, three major ones being: *(i)* thermodynamic models for non-ideal phases need to be evaluated many times to calculate chemical properties of species and phases (e.g., species activities); *(ii)* the chemical equilibrium calculations, in which non-linear algebraic equations are solved iteratively, may require many iterations to converge; *(iii)* the chemical kinetic calculations may require relatively short time steps to ensure numerical stability and accuracy. All these three major reasons are intrinsically connected, since small time steps, due to kinetic constraints, results in many more chemical equilibrium calculations being performed, which in turn results in numerous more evaluations of thermodynamic models.

We present computational methods for chemical equilibrium and kinetic calculations that can potentially speed up reactive transport simulations. For equilibrium calculations, two methods are presented: a *Gibbs energy minimization* (GEM) method and an *extended law of mass action* (xLMA) method. Both algorithms are based on the use of Newton's method to solve the non-linear equilibrium equations in few iterations, either using exact or approximate partial molar derivatives of the species activities, which can play a major role in achieving faster convergence rates. For kinetic calculations, we present a method that uses exact partial molar derivatives of the reaction rates in an implicit time integration scheme. This improves numerical stability and permits the use of larger time steps, which are adaptively determined over time. Finally, we remark that even advances in numerical methods for equilibrium and kinetic calculations are not enough for significant speed-up of reactive transport simulations, and we discuss alternatives that could be explored, not only from a computational perspective, using parallel computing (CPUs and GPUs), but also from a mathematical perspective, using equilibrium approximations solely based on algebraic considerations.