REACTIVE TRANSPORT MODELS WITHOUT MATHEMATICAL SOLUTION

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ABSTRACT

It is well known that mathematical equations may lack a solution or have non-unique solutions. Also reactive transport models, being actually mathematical equations, can show this feature, which in practice means severe numerical problems. This paper studies non-existence and non-uniqueness of mathematical equations that represent reactive transport models. We found that there are rate laws for kinetic reactions that may lead to non-existence or non-uniqueness. Moreover, these are typical rate laws obtained from laboratory experiments. We also propose modifications to these rate laws so that they can be applied to reactive transport models without problems.

1. INTRODUCTION

Understanding groundwater quality and processes undergone by rocks in natural systems, the study of soil and groundwater contamination and the performance assessment of waste disposal facilities require quantitative analysis of the migration of reactive substances, that is, the modelling of reactive transport. Chemical reactions to be modelled can be assumed to be in equilibrium or kinetic. Obtaining data for many equilibrium reactions is usually not a problem, as large thermodynamic databases do exist. On the other hand, data for kinetic reactions are more difficult to gather because rate laws expressing the kinetic reactions have a weaker theoretical basis and can be affected by unknown or uncontrolled factors. Typically, rate laws are derived from laboratory experiments that measure reaction rates for different concentrations. Commonly, a rate constant and the order of the rate law are deduced from a plot of the logarithm of the rate versus the logarithm of the concentration.

Reactive transport models are just mathematical equations that, like any other mathematical equation, may lack a mathematical solution, have non-unique solutions or have only a solution in a domain not applicable to the variable (for instance, zero or negative concentrations). In practice non-existence and non-uniqueness mean severe numerical problems. Nevertheless, in reactive transport studies the possibility of non-existence or non-uniqueness of a solution is seldom taken into account. A reason may be that detection of non-existence or non-uniqueness is far from obvious, especially for complex models.

The objective of this paper is to first analyse the conditions under which solutions may not exist or not be unique and, second, to propose solutions. We focus on kinetic rate laws that can lead to non-existence or non-uniqueness problems when applied to reactive transport. To do so we start, in section 2, by giving two simple examples that illustrate the problem of non-existence and non-uniqueness. Then, in section 3, we give the general conditions that may

cause non-existence or non-uniqueness. Section 4 proposes some remedies to solve the problem. Finally section 5 summarizes the conclusions.

2. EXAMPLES

In general, reactive transport can be written mathematically as follows (e.g., Saaltink et al., 1998):

$$\frac{\partial \mathbf{c}}{\partial t} = \mathbf{M}L(\mathbf{c}) + \mathbf{S}_e^T \mathbf{r}_e + \mathbf{S}_k^T \mathbf{r}_k \tag{1}$$

where $\mathbf{c}$ is a vector for the concentrations of all species, where $\mathbf{M}$ is a diagonal matrix whose diagonal terms equal 1 for mobile species and 0 otherwise; $\mathbf{S}_e^T$ and $\mathbf{S}_k^T$ are the transposed equilibrium and kinetic reactions stoichiometric matrices, respectively - each row representing a reaction-; $\mathbf{r}_e$ and $\mathbf{r}_k$ are the vectors of reaction rates for equilibrium and kinetic reactions, respectively, and L is a linear transport operator accounting for advection, diffusion and dispersion. This equation has to be solved together with mass action laws for the equilibrium reactions and rate laws for the kinetic reactions. However, equation (1) may be too complicated to analyse existence or uniqueness. Therefore this paper is limited to monosolute kinetic cases without transport, that is:

$$\frac{\partial c}{\partial t} = r(c) \tag{2}$$

Nevertheless, we conjecture that conclusions on existence and uniqueness of equation (2) can be extended to equation (1).

In this section we will illustrate through two simple examples the problems on existence and uniqueness. The first example is the oxidation of pyrite controlled by oxygen. The rate of pyrite oxidation is found to be proportional more or less to the square root of the concentration of oxygen in many studies (Nicholson et al., 1988; Domènech et al., 2002; amongst others). Therefore, for a simplified monosolute case, without oxygen transport, it can be written as:

$$\frac{\partial c}{\partial t} = -kc^{1/2} \tag{3}$$

Solution of equation (3) is:

$$\begin{cases} c = \left(\sqrt{c_0} - 0.5kt \right)^2 & t < \frac{1}{k}\sqrt{c_0} \\ c = 0 & t \geq \frac{1}{k}\sqrt{c_0} \end{cases} \tag{4}$$

That is, the concentration drops parabolically to zero at a finite time and afterwards remains zero (see figure 1). Zero concentrations in the simple model of equation (3) do not give problems, but do in combinations with mass action laws, because they may necessitate a division by concentrations. Therefore, one may want to require concentrations to be larger than zero. In that case, equation (3) has no solution for $t \geq k^{-1}\sqrt{c_0}$.
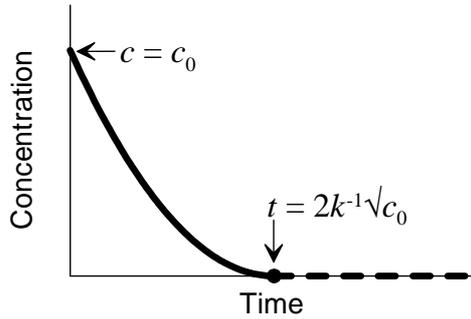
FIGURE 1. Solution of the pyrite example of equation (3). After a finite time concentrations are exactly zero.

A second example is the kinetic precipitation of a mineral in a highly supersaturated solution so that precipitation only depends on the reactive surface of the mineral. Assuming a two-thirds power-relationship between reactive surface area and concentration of the mineral (Lichtner, 1996) then, again for a simplified case without transport, the concentration of the mineral can be written as:

$$\frac{\partial c}{\partial t} = kc^{2/3} \tag{5}$$

Solution of equation (5) is:

$$c = \left(c_0^{1/3} + \frac{1}{3}kt \right)^3 \tag{6}$$

However, if the initial concentration of the mineral (c_0) is zero there is more then one solution (see figure 2):

$$\begin{cases} c = 0, & t \le t_0 \\ c = \left(\frac{1}{3}k(t-t_0) \right)^3, & t > t_0 \end{cases} \tag{7}$$

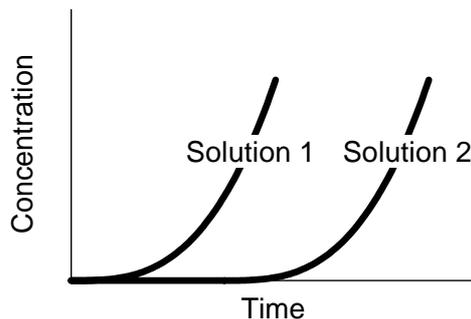where t_0 can have any positive value and is different for every solution.

FIGURE 2. Solution of the mineral precipitation example of equation (5). More then one solution exists if the initial concentration of the mineral is zero.

It can be expected that problems may arise when one tries to solve numerically these examples. For instance, in the pyrite example of equation (3) a small error may lead to negative concentrations disallowing the calculation of the rate law. When zero or negative

concentrations are avoided (e.g., by using logarithms) an iterative algorithm will not converge, because it searches something that does not exists. In realistic cases, when transport and more species and reactions are added, such problems can be expected. Unfortunately, the high degree of complexity will make it difficult to find the cause.

3. PROBLEM STATEMENT

Equation (2) is an autonomous first order ordinary differential equation. Theory on existence and uniqueness for such equations can be found in Teschl (2004, chapter 1) or any other textbook on ordinary differential equations. In general, problems occur when the function to be integrated (the reaction rate) is non differentiable at the extreme values of c. In rate laws of the form of equations (3) or (5), the derivative of the rate with respect to the concentration ($\partial r/\partial c$) goes to infinite for the concentration that gives a rate of zero. For a rate law of the type

$$r = kc^a \tag{8}$$

the derivative, $\partial r/\partial c$, goes to infinite for $c = 0$ and $r = 0$ when a is smaller then 1. Therefore, we can say that such rate laws should not be used in order to avoid problems when concentration are zero. If for some reason, one knows that concentration never tends to zero (e.g., because the initial concentration in equation (5) is larger then zero), then these rate laws do not give any problems.

If models are more complex and include transport and more then one component and reaction, a formal mathematical proof is in most cases impossible. However we expect the same problems for multisolute rate laws of the type:

$$r = k \prod_i c_i^{a_i} \tag{9}$$

with one or more exponents a_i smaller then 1. The reason is that a reaction reduces the concentration of reactants at more or less the same absolute amount (according to stoichiometry), but in relative terms it reduces low concentrations more then high concentrations. Therefore, high concentrations are more or less constant in comparison to a concentration close to zero, which converts the multisolute rate law of equation (9) into a rate law depending primarily on one concentration of the type of equation (8).

Obviously the problematic rate laws cannot represent reality, hence are wrong and should be avoided or changed in such a way that they do not give problems. We should bear in mind the way these rate laws are usually obtained. Often values for k and a_i of equation (9) are fitted to experimental data, which are within certain range. Therefore we have to modify the rate law of equations (8) or (9) in such a way that it is derivable for the concentration where $r = 0$ and that the modification only affects concentrations that are outside the range of the experiment. The next section discusses some options to do so.

4. REMEDIES

The first option to avoid infinite derivatives is multiplying equation (8) by an affinity term $\left(1 - c_{eq}^a / c^a\right)$, where c_{eq} is the concentration at thermodynamic equilibrium:

$$r = kc^a \left(1 - \frac{c_{eq}^a}{c^a}\right) = kc^a - kc_{eq}^a \tag{10}$$

This equation is derivable at $c = c_{eq}$ (where $r = 0$) and, therefore, there will be one unique solution. This rate law has a strong theoretical basis because the rate is zero at equilibrium (figure 3), which probably is the reason why the affinity term is often used. For example, Mayer et al. (2002) presented a number of generalized kinetic rate laws of which almost all included an affinity term. Values for c_{eq} are generally obtained easily from thermodynamic data. However this does not apply to mineral precipitation example of equation (5), where c_{eq} would represent some minimum mineral concentration, which also would be rather sensitive parameter. Another problem is that in some cases a value for c_{eq}, obtained from thermodynamic data, may be extremely low. For the pyrite example of equation (3), an oxygen concentration at equilibrium with pyrite is roughly 10^{-57} mol/L (supposing a pH of 3 and a Fe^{2+} and SO_4^{2-} concentration of both 10^{-3} mol/L), whereas rate laws for pyrite oxidation are measured for oxygen concentrations of around 10^{-5} - 10^{-4} mol/L. Although the derivative at this low equilibrium concentration is not exactly infinite, it may be high enough to cause numerical problems.
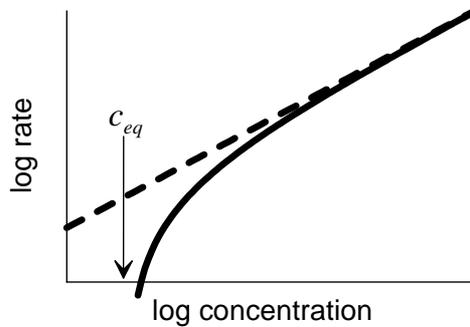

FIGURE 3. A rate law with affinity term (continuous line) according to equation (10) in comparison with the *a*-order rate law (discontinuous line) of equation (8).

A second option is to use a monod type of rate law:

$$r = \frac{r_{max} c}{k + c} \qquad (11)$$

where r_{max} is the maximum rate. It is linear for low concentrations (slope is one on a log log scale) and is constant for high concentrations (see figure 4). Therefore derivatives will never become too high, as long as r_{max} is a moderate value. This type of rate law is typically used for microbially mediated reactions, but it could be used for any reaction. However, experimental data may just not fit well on this rate law, because it not only affects the rate at low concentrations, which are the ones that give problems, but also at higher concentrations.

A better option is to only linearize an *a*-order rate law at the low concentrations without affecting it at the high concentration end (figure 5). For *a* smaller then one, this can be done by means of the following equation:

$$r = kc^a \frac{1}{\left(c / c_c\right)^{a-1} + 1} \qquad (12)$$

where c_c is the concentration where the rate law changes from first order to *a*-order. In this way, an *a*-order rate law ($a < 1$) of equation (8), which fit certain experimental data, may be substituted by equation (12) as long as c_c is much lower then the lowest experimental concentration.
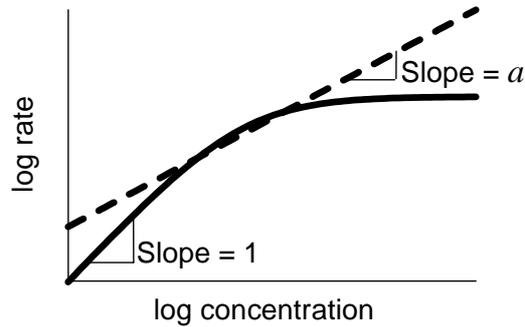
FIGURE 4. A monod rate law (continuous line) according to equation (11) in comparison with the *a*-order rate law (discontinuous line) of equation (8).
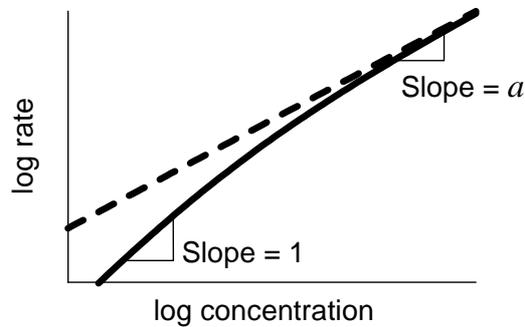

FIGURE 5. A rate law with linear part for low concentrations (continuous line) according to equation (12) in comparison with the *a*-order rate law (discontinuous line) of equation (8).

5. SUMMARY AND CONCLUSIONS

Reactive transport models can lack mathematical solutions or have non-unique solutions. In practice this means severe numerical problems. This problem particularly occurs when *a*-order kinetic rate laws are used with *a* smaller then one. This can be proved formally for monosolute models without transport. We conjecture that the same problem may exist for multisolute multireaction models with transport.

Rate laws are usually obtained by fitting an *a*-order rate law to experimental data. This permits us to modify the rate law in such a way that it is only affected at concentrations outside the range of the experimental ones. We have presented three remedies to overcome rate laws causing problems of non-existence and non-uniqueness. The first is to multiply the rate law by an affinity factor. The advantage is that often it has a good theoretical basis for thermodynamic reasons. However, in some cases it still may give numerical problems if concentrations at equilibrium are extremely low for the same thermodynamic reasons. The second option is to use a monod rate law, which will generally not give problems. Nevertheless, it affects more the fit to experimental data. A third is to linearize an *a*-order rate law only at the low concentrations. It permits the prevention of non-existence and non-uniqueness without affecting the fit too much.

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