An analysis of crystal dissolution fronts in flows through porous media

Part 1: Compatible boundary conditions [1]

P. Knabner

University of Erlangen–Nürnberg, Institute of Applied Mathematics,
Martensstraße 3, D – 91058 Erlangen, Germany

C. J. van Duijn

Delft University of Technology, Department of Mathematics,
P.O. Box 5031, NL 2600 GA Delft, The Netherlands

S. Hengst

Institute for Applied Analysis and Stochastics (IAAS),
Mohrenstraße 39, D – 10117 Berlin, Germany

Key words: Transport, travelling wave, crystal dissolution, porous media, mathematical analysis.

Abstract

We propose a model for transport of solutes in a porous medium participating in a dissolution/precipitation reaction, in general not in equilibrium. For an unbounded spatial domain, travelling wave solutions exist, if and only if the charge distribution is constant and we deal with a dissolution situation. The travelling wave in fact exhibits a sharp dissolution front. The wave is given in a nearly explicit manner. Also for the limit cases of equilibrium reaction or no dispersion, travelling waves are established under the same conditions, but with different qualitative properties.

---

[1] This work was supported by EC project "Filtration and Nonlinear Diffusion Processes" (Contract No. SC 1 – 0018 – C (TT)) and Institute for Applied Analysis and Stochastics

1. INTRODUCTION

In this paper we consider chemistry–affected transport processes in porous media, where the transported solutes are participants in a precipitation–dissolution reaction, which in general is not in equilibrium, but kinetically controlled. The mineral phase, which occurs as a very thin layer on the grains of the porous medium and does not effect the pore geometry, may be present or completely dissolved, or not yet precipitated.

In [11] Rubin set up a model for the spatially one–dimensional situation on a bounded domain with specific inflow boundary and initial conditions, which lead to the evolution of a dissolution front. The initial–boundary value problem is formulated classically, i.e. with the explicit appearance of the dissolution front as a free boundary. A transformation of the problem is indicated, on which a numerical approximation scheme and a general analysis assuring existence, uniqueness and some general properties are based in [14] and [10], respectively. Further references to numerical approaches, also for more complex situations, may be found in [14].

We will deal with the same problem and model, also allowing for non–equilibrium, but our aim is different. We start from a model formulation without explicit reference to free boundaries in form of dissolution and precipitation fronts, i.e. from a "weak" or "variational" interpretation of the emerging conservation and rate equations. For two situations, characterized by an unbounded spatial domain and a specific condition in terms of the excess charge distribution, we establish the solutions analytically. For the situation dealt with in this first part, this will be travelling wave solutions, i.e. fixed profiles, which are translated in time with a constant wave speed. These solutions are given in a nearly explicit manner. All qualitative properties of the solution can be investigated in detail.

Note that the notion "(travelling) wave" is always used here in this strict sense, made more precise later on, and not in the more relaxed form as being just synonymous to "fronts", as it is usually done in the chemical engineering literature. In situations where travelling wave solutions do not exist, there may be dissolution or precipitation fronts (of nonconstant speed). Such a situation will be analysed in Part 2 of the paper. In addition, for equilibrium reactions, we refer again to [14] and [10].

We will analyse two spatially one–dimensional flow regimes, with constant water content, bulk density, pore velocity $q[cm/s]$ and diffusion/dispersion coefficient $D[cm^2/s]$. The spatial domain will be represented by the whole real line, according to the goal to develop solutions which describe the behaviour for large flow domains, e.g. large soil columns. In Section 2 we will derive the following set of equations for u and v [millimoles/cm^3], being the molar concentration of one of the participating ions in solution, say the cation, and a scaled concentration of the crystalline solid, both relative to the water volume, and a third unknown $w[-]$, which is used here to take into account the nature of the dissolution reaction.

$$\frac{\partial}{\partial t}(u+v)+q\frac{\partial}{\partial x}u-D\frac{\partial^2}{\partial x^2}u=0, \tag{1}$$

$$\frac{\partial}{\partial t}v=k\left\{g(u;c)-wK\right\}, \tag{2}$$

$$0\le w(x,t)\le 1, \quad \text{and} \quad w(x,t)=1 \qquad \text{if} \quad v(x,t)>0, \tag{3}$$

$$\text{for } -\infty<x<\infty, \quad t>0.$$

The dissolution/precipitation reaction is described by the (nonlinear) function g related to the precipitation reaction, the constant $K > 0$, being the saturation constant, and the rate parameter $k > 0$. There is a further function c appearing in (2), which may be interpreted in our special case as the (scaled) excess (positive) charge distribution. This function satisfies the linear diffusion–advection equation:

$$\frac{\partial}{\partial t}c + q\frac{\partial}{\partial x}c - D\frac{\partial^2}{\partial x^2}c = 0, \qquad \text{for } -\infty < x < \infty, \quad t > 0. \tag{4}$$

Equations (1), (2), (4) have to be supplemented by appropriate initial and/or boundary conditions. This will give c explicitly in the cases to be considered here.

Furthermore, there are several limit situations. If the rate parameter k is large compared to the parameters of the transport process, it is reasonable to use the local equilibrium assumption and to substitute the non–equilibrium description (2) by a quasistationary description, which is formally obtained by letting $k \to \infty$, i.e.

$$g(u; c) = wK. \tag{5}$$

We will refer to this case as "$k = \infty$".

If the dispersive transport is negligible compared to the advective transport, it is reasonable to let $D \searrow 0$, i.e. cancel the corresponding term in (1) and (4), and thus consider a hyperbolic system. We will refer to this case as "$D = 0$".

Two charge distributions c will be considered. The first is:

$$\text{– The function } c \text{ is constant.} \tag{6}$$

This situation will be analysed in the first part of the paper. It will turn out that for certain initial and boundary conditions, which correspond to the appearance of a dissolution front, travelling wave solutions exist. In fact, (6) is necessary for their existence. These travelling waves will be analysed, for the original problem taking non-equilibrium and dispersion into account, in Section 3, and for both limit cases in Section 4. One can interpret these solutions as the large time behaviour of the situations, where the boundary condition does not disturb the constant initial charge distribution (see Section 3 for more details). As the appearance of a dissolution front often corresponds to the injection of a fluid with a different ionic composition, the contrary, i.e. the disturbance of the initial charge distribution, may be considered to be likely. In the formulation of (1) – (4) this can be modelled by an initial distribution of c in form of a step function, i.e. with two levels $c^*, c_* > 0$:

$$c(x, 0) = c_0(x) = \begin{cases} c^* & \text{for} \quad x < 0, \\ c_* & \text{for} \quad x \geq 0. \end{cases} \tag{7}$$

We will restrict ourselves to the limit case $D = 0$, where the solution of (4) is then given by the piston flow profile, i.e. we have

– The function c is given by $\quad c(x,t) = c_0(x - qt),$ (8)
with c_0 from (7).

In Part 2 of the paper we will analyse this situation, if also the initial conditions for u and v are analogous step functions, i.e. we will consider the Riemann problem of (1) – (4) (with $D = 0$). It will turn out that the structure of solutions is more involved, exhibiting two fronts of different speed, where one is very much related to the travelling wave solutions of this Part 1.

2. Modelling of Equilibrium and Non–equilibrium Crystal Dissolution and Precipitation

Mass and Charge Conservation

We are going to discuss the following precipitation-dissolution reaction in a porous medium: We consider as solutes two species M_1, M_2, for example ions, say M_1 being a cation and M_2 an anion. In addition there may be a crystalline solid $\overline{M}_{12}$ present (at the grain surface). Here we adopt the notation of Rubin [11] and relate to the reasoning of [5], [14], [12]. M_1, M_2 may precipitate at the surface of the porous skeleton and form $\overline{M}_{12}$ and vice versa the crystalline solid may dissolve. The stoichiometry of the reaction is supposed to be as follows

$$\overline{M}_{12} \rightleftarrows nM_1 + mM_2. \tag{9}$$

Here n, m denote positive numbers. If the species M_1, M_2 are ions, a reaction like (9) leads to the electroneutrality of the fluid, if the valence of M_1 is m and of M_2 is n. Let c_i [millimoles/cm^3] be the molar concentration of M_i in solution relative to the water volume, and let c_{12} [millimoles/g] be the molar concentration of $\overline{M}_{12}$ relative to the mass of the porous skeleton. By its meaning only $c_1, c_2, c_{12} \geq 0$ are reasonable and will be considered. We want to describe the conservation equations for a general flow regime, where at the moment the dimension and geometry of the macroscopic spatial domain are unspecified. The underlying geology and water flow regime are described by the water content $\Theta[-]$, the bulk density $\varrho[g/cm^3]$, the diffusion/dispersion tensor $\underline{\underline{D}}[cm^2/s]$ and the specific discharge vector $\underline{q}^*[cm/s]$. Here we assume that the dispersive part in D is so prominent that we need not to distinguish between the different species. Furthermore, we assume that the pore geometry, i.e. Θ, is not effected by the reaction (9). As $\overline{M}_{12}$ is spatially immobile, the conservation of the corresponding total masses leads to the partial differential equations

$$\frac{\partial}{\partial t}(\Theta c_1) + n\varrho\frac{\partial}{\partial t}c_{12} - \text{ div } (\Theta\underline{\underline{D}}\nabla c_1 - \underline{q}^* c_1) = 0, \tag{10}$$

$$\frac{\partial}{\partial t}(\Theta c_2) + m\varrho\frac{\partial}{\partial t}c_{12} - \text{ div } (\Theta\underline{\underline{D}}\nabla c_2 - \underline{q}^* c_2) = 0. \tag{11}$$

Here $\frac{\partial}{\partial t}$ denotes the partial derivative with respect to time $t[s]$, and div, ∇ denote the divergence and gradient with respect to the space coordinate x[cm].

Note that the ionic nature of the aqueous products is not necessary to set up equations (10),(11) and their consequences, but only a stoichiometric relation like the one implied by

(9) is required. As a further example one may think of the dissociation of an organic solid in an organic solvent. Reactions like (9) with more than two aqueous products lead to a similar model, therefore results analogous to ours are to be expected. Unfortunately our analysis which will be presented below, relies on the reduction to two unknowns, therefore it cannot be extended directly.

If we define

$$c = mc_1 - nc_2 \tag{12}$$

then equations (10), (11) imply that the quantity c is conserved:

$$\frac{\partial}{\partial t}(\Theta c) - \text{ div } (\Theta \underline{\underline{D}} \nabla c - \underline{q}^* c) = 0. \tag{13}$$

For a spatially homogeneous reaction, the *continuous stirred tank reactor* (CSTR) situation, where all concentrations are functions of time only, this implies that c is constant, i. e. all possible values of the concentrations $c_1(t), c_2(t)$ lie in a one dimensional affine subspace of the *stoichiometric subspace* of the dissolution reaction, defined by the condition $c = 0$. We will see that for travelling wave solutions the same holds true. For the special case of a ionic binary reaction, also another interpretation is possible: Then the valence of M_1 is $m\nu$ and the valence of M_2 is $n\nu$ with some positive integer ν. If M_1 is a cation and M_2 an anion, then νc denotes the total positive electric charge of the solute.

It is a well–known observation (cf. e.g. [5]) that we can resolve equation (13) (with appropriate initial and boundary conditions) at least numerically and thus reduce the number of unknown functions by one by setting

$$c_2 = \frac{1}{n}(mc_1 - c). \tag{14}$$

The requirement $c_1 \geq 0, c_2 \geq 0$ for a solution of (10), (11) is then equivalent to

$$c_1 \geq \left(\frac{c}{m}\right)_+ \quad , \tag{15}$$

where $u_+ = u$ for $u \geq 0$ and $u_+ = 0$ for $u < 0$.

Rate description for dissolution and precipitation

Now we turn to the description of the chemical reaction. If r_d and r_p [millimoles/cm^3] denote the dissolution and precipitation rates relative to the water volume and k^* [$1/s$] a rate parameter then

$$\varrho \frac{\partial}{\partial t} c_{12} = \Theta k^* (r_p - r_d). \tag{16}$$

Note that the appearance of the factors ϱ, Θ in (16) is caused by the choice of the reference systems of r_p and r_d. In [5] e.g. r_p, r_d are related to the total volume such that Θ does not appear in (16). The following arguments hold true independent of the reference system chosen, i.e. for another reference system of r_p, r_d equation (16) has to be changed correspondingly by a factor on the right hand side and analogously all the following expressions derived from (16). For $k^* \to \infty$ equation (16) reduces at least formally to

$$r_p = r_d \tag{17}$$

We will take this relation to be a guideline for the definition of the rate functions in those cases, where they are not fixed due to other grounds. It is generally accepted that (cf. e.g. [12],[13]):

- The activity of the crystalline solid is a positive constant, say k_d [millimoles/cm^3], therefore:

$$r_d = k_d, \quad \text{if } c_{12} > 0. \tag{18}$$

- The precipitation rate is given by the *mass action law* or extensions with concentration dependent activity coefficients (e.g. given by the Debye–Hückel theory), therefore

$$r_p = k_p r(c_1, c_2), \tag{19}$$

  where r is a smooth nonnegative nonlinearity (for arguments $c_1, c_2 \geq 0$); an example is, if we assume the thermodynamically ideal mass action law

$$r(c_1, c_2) = c_1^n c_2^m. \tag{20}$$

The nonlinearity r will be discussed later on in relation to the analysis of Section 3. Thus in the presence of crystalline solid at some (x, t) we have the well–known equilibrium description by the *solubility product:*

$$\text{If } \; c_{12} > 0, \quad \text{then } \; r(c_1, c_2) = K, \tag{21}$$

where $K := k_d/k_p$. The condition $r(c_1, c_2) = K$ is called *saturation* and $r(c_1, c_2) < K$ or $> K$ *under–* and *oversaturation,* respectively. Due to (14) these (in)equalities can be reduced to a relation for c_1 alone for given c. The concentration c_1, fulfilling $r(c_1, c_2) = K$, is also called the *solubility* (for given c).

To include the case $c_{12} = 0$, we need to extend the definition of the dissolution rate. We are going to do this in such a way that the corresponding equilibrium description according to (17) satisfies all the propertis of an equilibrium situation. These properties are, for arbitrary $c_{12} \geq 0$:

- Either saturation or undersaturation holds.
- If crystalline solid is present, then saturation holds.
- Under undersaturated conditions, no crystalline solid can be present.

This is equivalent to

$$\begin{aligned} &0 \leq r(c_1, c_2) \leq K \\ &c_{12} > 0 \Rightarrow r(c_1, c_2) = K \\ &r(c_1, c_2) < K \Rightarrow c_{12} = 0 \end{aligned} \tag{22}$$

or in more compact notation

$$\begin{aligned} &0 \le r(c_1 c_2) \le K, \;\; c_{12} \ge 0 \\ &(K - r(c_1, c_2))c_{12} = 0 \end{aligned} \tag{23}$$

This can be recast in the form of (17) by writing

$$\begin{aligned} &0 \in k_p r(c_1, c_2) - k_d H(c_{12}) \\ &(\Leftrightarrow r(c_1, c_2) \in K H(c_{12})), \end{aligned} \tag{24}$$

where H is the set–valued Heaviside"function" (better: Heavisidegraph) defined by

$$H(u) = \begin{cases} \{1\} & \text{for} \;\; u > 0 \\ [0,1] & \text{for} \;\; u = 0 \\ \{0\} & \text{for} \;\; u < 0. \end{cases} \tag{25}$$

Each possible choice $H(0) = \alpha(\in[0,1])$ would fix $r(c_1, c_2) = \alpha K$ for $c_{12} = 0$. Note that in particular (21) is included in (22)-(24).

We now turn to the rate description for the non–equilibrium case. A usual requirement is that in non-equilibrium also oversaturation is possible (cf.[12],[13]). Guided by this and relation (24), we propose the following rate description

$$\varrho \, \frac{\partial}{\partial t} c_{12} \in \Theta k^* (k_p r(c_1, c_2) - k_d H(c_{12})) \tag{26a}$$

or equivalently

$$\begin{aligned} &\varrho \, \frac{\partial}{\partial t} c_{12} = \Theta k^* (k_p r(c_1, c_2) - k_d w), \\ &\text{where } w \in H(c_{12}) \;\; \text{which means} \\ &0 \le w \le 1 \quad \text{and} \quad w = 1 \quad \text{for } c_{12} > 0. \end{aligned} \tag{26b}$$

Thus we have arrived at (10), (11), (26a,b) with the unknowns c_1, c_2, c_{12} or equivalently at (10), (13), (14), (26a,b) with the unknowns c_1, c_{12}, c, supplemented with appropriate initial and boundary conditions, as a possible model for transport and non–equilibrium dissolution and precipitation.

This means that we keep the precipitation rate of (19), and also the dissolution rate from (18) for $c_{12} > 0$, but allow for a "fictious" dissolution rate $k_d w \le k_d$ for $c_{12} = 0$. This is necessary to be compatible with (24) / (22) at equilibrium.

If we use the elimination of c_2 by means of c, setting

$$g(c_1; c) := r\left(c_1, \frac{1}{n}(m c_1 - c)\right), \tag{27}$$

and furthermore, defining

$$\begin{aligned} u &:= c_1, & v &:= n\varrho/\Theta c_{12}, \\ q &:= q^*/\Theta, & k &:= n k^* k_p, \\ K &:= k_d/k_p \end{aligned} \tag{28}$$

the equations (10), (13), (26a,b) take the form, which for one space dimension is displayed in (1) – (4).

An alternative rate description

Note that (24) is not the only way to express (22) by means of a Heavisidegraph. Another equivalent form of the equilibrium conditions is given by

$$0 \in H(\max(c_{12}, r(c_1, c_2) - K))\ (k_p r(c_1, c_2) - k_d). \tag{29}$$

This suggests as alternative to (26a,b) the rate equation

$$\varrho \frac{\partial}{\partial t} c_{12} \in \Theta k^* H(\max(c_{12}, r(c_1, c_2) - K))\ (k_p r(c_1, c_2) - k_d) \tag{30a}$$

or equivalently

$$\begin{gathered} \varrho \frac{\partial}{\partial t} c_{12} = \Theta k^* w (k_p r(c_1, c_2) - k_d), \\ \text{where } w \in H(\max(c_{12}, r(c_1, c_2) - K)), \\ \text{which means} \\ 0 \le w \le 1, \quad \text{and} \\ w = 1 \quad \text{for } c_{12} > 0 \quad \text{or} \quad r(c_1, c_2) > K. \end{gathered} \tag{30b}$$

This means that the rates of (18) and (19) are kept, if crystalline solid is present or if the fluid is oversaturated. Otherwise, an overall nonpositive rate, i.e. dissolution rate, is possible.

The equivalence of the different formulations

In [3] van Duijn and Knabner establish the equivalence between these two rate descriptions. The analysis relies on an investigation of the different functions w appearing in (26a,b) and (30a,b), respectively. It turns out that they are fixed by the other unknown functions c_{12}, c_1, c_2 up to a set of "exceptional" points in space-time (rigorously, a set of Lebesgue measure 0), denoted by C. In particular, for (30a,b) the function w can only take the values 0 and 1 (on subsets determined by c_1, c_2). The topological structure of C is not clear apriori, as we want to take into account all kinds of scenarios caused by various initial and boundary conditions. In the simple one-dimensional situation of section 3 the set C will turn out to be a straight line, representing the dissolution front in space-time.

The formulation, proposed and used in [5] is similar to (30a,b), but not identical. It corresponds to (30a,b), if the set–valued function is substituted by a single–valued, discontinuous one with $H(0) = 0$. If we interpret the model of [5] in a sense that the rate is not defined at the "exceptional" points of C, i.e. in a weak sense, then also this formulation is equivalent to the two developed above. If, however, the rate function of [5] is required to hold everywhere, then the models are different and e.g. the solutions developed in Section 3 are excluded.

Linearized rate descriptions

There are still other variants of the rate function, usually to be found in the corresponding text books (see e.g. [12]), which may be considered as linearizations of (26a,b) or (30a,b). We use the elimination of c_2 by means of c, i.e. let c be given by (13) supplemented with appropriate initial and boundary conditions. The nonlinearity in the rate equation (26a,b) is then given by $g = g(c_1; c)$. For the following discussion we will assume that there is a unique $c_S = c_S(x,t) \geq 0$, satisfying

$$g(c_S; c) = K, \tag{31}$$

i.e. c_S being the solubility and

$$\begin{aligned} g(c_1; c) < K \quad &\text{for} \quad 0 \leq c_1 < c_S, \\ g(c_1; c) > K \quad &\text{for} \quad c_1 > c_S. \end{aligned} \tag{32}$$

This property is fulfilled, if g is strictly increasing in the variable c_1. In Appendix A it will be shown that this property holds true for the expressions usually taken for r.

Consider (26a,b) or (30a,b) for $c_{12} > 0$, i.e.

$$\begin{aligned} \varrho \frac{\partial}{\partial t} c_{12} &= \Theta k^* k_p (g(c_1; c) - g(c_S; c)) \\ &= \Theta k^* k_p \bigg(\frac{\partial}{\partial c_1} g(c_S; c)\ (c_1 - c_S) \\ &\quad + \text{higher order terms in} \quad (c_1 - c_S) \bigg). \end{aligned} \tag{33}$$

This suggests the following alternative rate description for $c_{12} > 0$

$$\varrho\frac{\partial}{\partial t}c_{12} = \Theta k_L(c_1 - c_S), \tag{34}$$

where the rate k_L in this linearized version approximately corresponds to

$$k_L \sim k^* k_p \frac{\partial}{\partial c_1} g(c_S; c). \tag{35}$$

The rate function (34) can be found, e.g. in [12], [13]. For comparison one has to take into account that a batch experiment situation is considered there. For spatially constant concentrations however, equation (10) reduces to

$$n\varrho\frac{\partial}{\partial t}c_{12} = -\frac{\partial}{\partial t}(\Theta c_1), \tag{36}$$

and thus with a water content Θ being constant in time equation (34) is equivalent to

$$\frac{\partial}{\partial t}c_1 = k_L/n(c_S - c_1). \tag{37}$$

As above we have to extend (34) also to vanishing crystal concentrations. Analogously to (26a,b) and (30a,b) we propose the two variants

$$\varrho\frac{\partial}{\partial t}c_{12} \in \Theta k_L(c_1 - H(c_{12})c_S) \tag{38}$$

or

$$\varrho\frac{\partial}{\partial t}c_{12} \in \Theta k_L H(\max(c_{12}, c_1 - c_S))\ (c_1 - c_S). \tag{39}$$

Mathematically, (38) and (39) are special cases of (26a,b) and (30a,b), respectively, if one substitutes

$$r(c_1, c_2) = g(c_1; c) = c_1,\ \textit{i.e.}\quad K = c_S, \quad \text{and} \quad k^* k_p = k_L. \tag{40}$$

Therefore the above discussion concerning the functions w and the equivalence of the two model formulations hold true here analogously.

3. Travelling Wave Solutions for Non–equilibrium Reactions with Dispersion

Significance and definition of travelling wave solutions

The most simple situation appears, if the underlying flow field $\underline{q}^*$ and, correspondingly, Θ and $\underline{\underline{D}}$ are constant. If the influence of boundary conditions etc. is such that fluid flow, solute transport and chemical reaction only take place in the direction of $\underline{q}^*$ and are homogeneous orthogonal to $\underline{q}^*$, we can reduce the model (10), (13), (14), (26a,b) to one space dimension, what we will do in the following. In particular, $\underline{\underline{D}} = D$, $\underline{q}^* = q^*$ are scalar values from now on. This assumption usually is justified considering soil column experiments. We will take $q^* > 0$ such that $x = -\infty$ corresponds to upstream and $x = +\infty$

to downstream. Depending on the interplay of reaction and dispersion, the concentration profiles in a *continuous feed experiment,* i.e. for a constant inflow concentration may be *self–sharpening fronts,* i.e. stabilize for large times to a fixed spatial profile, which is transported in time with a constant wave speed a. The mathematical model for this limit solution is a travelling wave solution, i.e. a solution of (10), (11), (26a,b) for one space dimension, which only depends on the variable

$$\eta = x - at. \tag{41}$$

Setting $c_i(x,t) = c_i(\eta),\ i = 1,2,\ c_{12}(x,t) = c_{12}(\eta)$, and as a consequence $c(x,t) = c(\eta)$, we obtain the ordinary differential equations

$$\begin{aligned} &-a(\Theta c_1 + n\varrho c_{12})' \ - \ \Theta D c_1'' + q^* c_1' = 0, && (42a)\\ &-a(\Theta c_2 + m\varrho c_{12})' \ - \ \Theta D c_2'' + q^* c_2' = 0, &&\\ &-a\varrho c_{12}' \in \Theta k^*(k_p r(c_1,c_2) - k_d H(c_{12})), && (42b)\end{aligned}$$

and

$$(-a\Theta + q^*)c' - \Theta D c'' = 0 \tag{43}$$

for $-\infty < \eta < \infty$. To select the solutions related to the situation described above, we have to prescribe boundary conditions at $\eta = -\infty$ and $\eta = +\infty$:

$$\begin{array}{llll} c_i(-\infty) & = c_i^*, & c_i(+\infty) & = c_{i*}, \qquad i = 1,2, \\ c_{12}(-\infty) & = c_{12}^*, & c_{12}(+\infty) & = c_{12*}. \end{array} \tag{44}$$

If we consider a travelling wave solution as the limit profile for $t \to \infty$ for a corresponding initial–boundary value problem for $x \geq 0$, then the boundary condition at $\eta = +\infty$ corresponds to the (constant) initial condition $(x > 0, t = 0)$ and the boundary condition at $\eta = -\infty$ to the (inflow) boundary condition for $x = 0,\ t > 0$. Note that any solution of (42a,b) – (44) can be translated in η by an arbitrary amount to give a new solution. The one whose total mass corresponds asymptotically for large times to the total mass of the solution of the initial–boundary value problem will appear to be the asymptotic limit.

Homogenous charge distribution as necessary condition for travelling waves

As a first observation, also the conserved concentration c fulfills boundary conditions at $\eta = \pm\infty$ due to (44) and (12), which is only possible if c is constant for all $-\infty < \eta < \infty$ or equivalently the boundary conditions of c coincide:

$$mc_1^* - nc_2^* = mc_{1*} - nc_{2*} \quad . \tag{45}$$

Thus (45) is a necessary condition for the existence of a travelling wave solution and will be assumed to hold from now on in this part of the paper. It means that all values $c_1(\eta), c_2(\eta)$ or equivalently the downstream and upstream values belong to the same affine stoichiometric subspace of the dissolution reaction. For ionic aquaeous products it also may be interpreted as the fact that the overall electric charge of the dissolution products in the invading fluid coincides with the electric charge of them in the resident fluid. If this situation does not occur, different asymptotic profiles will develop, which are the subject of Part 2 of the paper.

Travelling wave formulation in transformed variables, fixed wave speed

With c being a constant given by

$$c := mc_1^* - nc_2^* \tag{46}$$

we reduce the problem to the variables $u = u(\eta)$, $v = v(\eta)$ defined in (28) and $w = w(\eta)$:

$$-au' - av' - Du'' + qu' = 0, \tag{47}$$

$$-av' = k(g(u;c) - Kw), \tag{48}$$

$$0 \le w(\eta) \le 1, \quad w(\eta) = 1, \quad \text{if } v(\eta) > 0, \tag{49}$$

for $-\infty < \eta < \infty$.

The boundary conditions transform to

$$\begin{array}{ll} u(-\infty) = u^*, & u(+\infty) = u_*, \\ v(-\infty) = u^*, & v(+\infty) = v_*, \end{array} \tag{50}$$

where $v^* = n\varrho/\Theta c_{12}^*$ etc. Note that $q > 0$ such that $\eta = -\infty$ corresponds to upstream and $\eta = +\infty$ to downstream. We consider only nonnegative boundary conditions and require the solution to be nonnegative, which is equivalent to (see (15))

$$u \ge \left(\frac{c}{m}\right)_+, \quad v \ge 0. \tag{51}$$

We want the dissolved concentration and the mass flux or equivalently u and u' to be continuous, but allow for jumps in v'. The equations (47), (48) imply that we have to allow also for jumps in u'' and w. A jump of a function f at a point η by definition in particular means that the one-sided limits $f(\eta+), f(\eta-)$ exist. The jump from right to left is then $[f](\eta) := f(\eta+) - f(\eta-)$. Note that continuity of f at η is equivalent with $[f](\eta) = 0$. In our notion of solution for (47)-(49) we allow only for finitely many jumps η_i in v' (and w, u'') and the equations (47), (48) to hold for all $\eta \ne \eta_i$. Consequently we have for all jumps $\eta = \eta_i$ the *jump relation*

$$a[v'](\eta) = -D[u''](\eta) = kK[w](\eta) \tag{52}$$

The first equality results from the difference of the one-sided limits of equation (47), the second analogously of equation (48). At points of continuity of v', w, u'' (52) trivially holds such that all our travelling wave solutions always fulfill (52) everywhere.

By integration, taking (50) into account, equation (47) can be reduced to a first order equation. From this first order equation we can conclude using (50) that the limits $u'(\pm\infty)$ exist and then $u'(\pm\infty) = 0$. The first order equation thus takes the form (see Proposition 1.2, Corollary 1.3 in [3] for details):

$$\begin{aligned} u' &= \frac{q-a}{D}(u - u_*) - \frac{a}{D}(v - v_*) \\ &= \frac{q-a}{D}(u - u^*) - \frac{a}{D}(v - v^*). \end{aligned} \tag{53}$$

From this we conclude that the wave speed a is fixed to

$$a = \frac{\Delta u}{\Delta u + \Delta v}\, q, \quad \text{if} \quad \Delta u + \Delta v \neq 0, \tag{54}$$

where $\Delta u := u^* - u_*, \quad \Delta v := v^* - v_*$.

Excluding some trivial cases, we may assume $\Delta u + \Delta v \neq 0$, thus having a fixed wave speed. It will turn out that for the only relevant case, where a travelling wave exists is $\Delta u < 0,\ \Delta v < 0$ such that $a < q$, reflecting the retardation effect of the chemical reaction, analogous to adsorption reactions (see van Duijn and Knabner [2]).

Note that all solutions $u = u(\eta), v = v(\eta), w = w(\eta)$ of the first order system (53),(48) together with (49),(50), for which u, v, u' are continuous and finitely many jumps in v' and w are allowed, are such that u'' exists as a continuous function with finitely many jumps, the jump relations are satisfied and also the original equation (47) holds true. Thus we have found an equivalent formulation which is the basis for our theoretical consideration and our numerical approach. Therefore in particular the jump conditions are always satisfied.

The impossibility of precipitation waves

For the further discussion, we have to assume for fixed c:

$$\begin{aligned} &g(.;c) \text{ is strictly increasing for } u \geq \left(\frac{c}{m}\right)_+, \\ &g\left(\left(\frac{c}{m}\right)_+; c\right) = 0. \end{aligned} \tag{55}$$

If r is given by the mass action law according to (20), then (55) is obvious, as $c_2 \geq 0$ is guaranteed by $u \geq (c/m)_+$. For the Debye–Hückel description of r in Appendix A a reasonable sufficient condition for (55) is developed.

Condition (55) assures the unique existence of the *solubility* concentration $u_S \geq 0$ (related to c and K):

$$g(u_S; c) = K \tag{56}$$

and u_S monotonically depends on K (for fixed c), i.e. for increasing K also u_S increases.

As already mentioned, a consequence of the first part of (50) are the boundary conditions $u'(\pm\infty) = 0$. A further necessary condition for the existence of travelling wave solutions are the boundary conditions

$$v'(+\infty) = 0, v'(-\infty) = 0. \tag{57}$$

They are only fulfilled for certain combinations of boundary values u^*, v^*, u_*, v_*. In the following we work out which cases are possible (compare [3] for a more detailed discussion). Conditions (57) imply that $w^* = w(-\infty), w_* = w(+\infty)$ exist and $0 \leq w_*, w^* \leq 1$, and

$$\begin{array}{lll} g(u^*, c) = Kw^* \leq K, & \text{and} & v^* > 0 \ \Rightarrow w^* = 1 \\ g(u_*, c) = Kw_* \leq K, & \text{and} & v_* > 0 \ \Rightarrow w_* = 1 \end{array} \tag{58a}$$

Due to (55), (56) we conclude

$$\begin{array}{lll} u^* \leq u_S, & \text{and} & v^* > 0 \ \Rightarrow u^* = u_S \\ u_* \leq u_S, & \text{and} & v_* > 0 \ \Rightarrow u_* = u_S \end{array} \tag{58b}$$

Therefore $v^* > 0, v_* > 0, v^* \neq v_*$ imply $a = 0$ and thus that u is a constant, $u = u_S$. This is one case of the appearance of

- *The stationary wave* $(a = 0)$ *for a saturated fluid:*
  $u^* = u_* = u_S,\ u(\eta) = u_S$ for $-\infty < \eta < \infty$,
  $v^* \geq 0,\ v_* \geq 0$ with arbitrary $v(\eta) \geq 0$
  for $-\infty < \eta < \infty$ fulfilling these boundary conditions.

These trivial waves certainly exist and will not be considered further.
Continuing our discussion, we conclude for $v^* = v_* = 0,\ u^* \neq u_*$ that $a = q$ and (53) reduces to $u' = -q/Dv \leq 0$, leading to a contradiction. Therefore apart of the stationary wave the following cases fulfill the requirement (58a):

- $v^* = v_* > 0,\ u^* = u_* = u_S$
- $v^* = v_* = 0,\ u^* = u_* \leq u_S$

In these cases the wave speed is not determined, we doubt that except of the stationary waves $a = 0, u = u_S$ solutions exist, but we cannot exclude it at the moment. These cases will not be considered further. Thus the following two cases are left:

- *The dissolution wave:*

$$v^* = 0, \quad v_* > 0 \quad \text{arbitrary} \qquad \left(\frac{c}{m}\right)_+ \leq u^* < u_S, \quad u_* = u_S. \tag{59}$$

- *The precipitation wave:*

$$v^* > 0 \quad \text{arbitrary}, \quad v_* = 0 \qquad u^* = u_S, \quad \left(\frac{c}{m}\right)_+ \leq u_* < u_S. \tag{60}$$

In the following we will show that precipitation waves cannot exist and that dissolution waves indeed exist. The key observation for the first statement, justified in detail in [3], is:

Both dissolution and precipitation waves can only exist for undersaturated fluids:

$$u(\eta) < u_S \quad \text{for} \quad -\infty < \eta < \infty. \tag{61}$$

The proof goes in two steps: First we show that $u(\eta) \leq u_S$ for $-\infty < \eta < \infty$. Otherwise there would be a point η_0 with $u'(\eta_0) = 0$ and $u(\eta_0) > u_S$. Equations (53), (48) lead to a contradiction for both cases (59) and (60). Secondly, if $u(\eta_1) = u_S$ for some η_1, then $u'(\eta_1) = 0$ and thus from (53), (48) we conclude from the unique solvability of the corresponding initial value problem that $u = u_S$ and $v = v_*$ for (59), $v = v_*$ for (60) respectively. This is in contradiction with the boundary conditions.

An immediate consequence from (48) and (49) is:

$$v'(\eta) > 0, \quad \text{if} \quad v(\eta) > 0, \tag{62}$$

and from this:

$$\text{Precipitation waves cannot exist.} \tag{63}$$

Assume that a precipitation wave exist, then because of the boundary condition at $-\infty$ we have $v(\eta) > 0$ for small η, say $\eta \leq \eta_0$. We show that also for $\eta \geq \eta_0$ we have $v(\eta) > 0$, i. e. $v'(\eta) > 0$, in contradiction to the boundary condition at $+\infty$. If $v(\eta_3) = 0$ for some $\eta_3 > \eta_0$, then there is a minimal one of these values, $\eta = \eta_2 \leq \eta_3$, i. e. $v(\eta_2) = 0$, and an interval given by $\eta_1, \eta_0 \leq \eta_1 < \eta_2$ such that $v(\eta) > 0$ for $\eta_1 \leq \eta < \eta_2$. But thus $-v(\eta_1)/(\eta_2 - \eta_1) = v'(\tilde{\eta}) > 0$ for some $\eta_1 < \tilde{\eta} < \eta_2$, i. e. a contradiction.

Hence, the only possibility left is a dissolution wave, which we will show to exist.

The dissolution front of a dissolution wave

Due to the boundary conditions the cases $v(\eta) = 0$ for each $-\infty < \eta < \infty$ and also $v(\eta) > 0$ for each $-\infty < \eta < \infty$ are excluded (see [3], Proposition 2.3 for a full argument) such that a dissolution wave must have a dissolution front in the following sense:

There exists a number L such that

$$\begin{array}{lll} v(\eta) = 0 & \text{for} & -\infty < \eta \leq L, \\ v(\eta) > 0 & \text{for} & L < \eta < \infty. \end{array} \tag{64}$$

In the variables (x, t) this front has the position $(at + L, t)$. The line $x = s(t) = at + L$ is the free boundary of the solution, relationships (52) together with (64) build the free boundary condition. The appearance of a dissolution front in the strict sense of (64) is a consequence of the non-differentiable nature of the rate function due to the use of the Heavisidefunction. For a smooth rate function solutions would be strictly positive everywhere, even if there are fronts in the sense that the solution exhibits large gradients. (compare [9]). In other words, the solution would behave like solutions of the linear diffusion-advection equation with dominating advection. A further discussion (see [3]) reveals

$$u'(\eta) > 0 \quad \text{for} \quad -\infty < \eta < \infty, \tag{65}$$

$$\begin{array}{lll} u''(\eta) > 0 & \text{for} & -\infty < \eta < L, \\ u''(\eta) < 0 & \text{for} & L < \eta < \infty, \end{array} \tag{66}$$

$$v''(\eta) < 0 \quad \text{for} \quad L < \eta < \infty. \tag{67}$$

That is, u changes curvature at the dissolution front and this is the only position, where a jump according to (52) really occurs, and the jump is positive, as due to (67) $v'(L+) > 0$ (and $v'(L-) = 0$).

A shooting algorithm to compute a travelling wave

Due to its structure, the computation of u, v, w according to (53), (48) – (50) is equivalent to find a number $u^* < u_0 < u_* \ (= u_S)$ such that the solution of the initial value problem

$$\begin{aligned} u' &= \frac{q-a}{D}(u-u^*) - \frac{a}{D}(v-v^*) \quad \text{for} \quad \eta > L \\ v' &= \frac{k}{a}(K - g(u;c)) \qquad\qquad\qquad \text{for} \quad \eta > L \\ u(L) &= u_0, \qquad v(L) = 0 \end{aligned} \tag{68}$$

fulfills

$$u(\infty) = u_*, \ v(\infty) = v_*, \ v(\eta) > 0 \quad \text{for} \quad \eta > L.$$

If such a value u_0 can be found then the solution of (68) can be prolongated to the desired solution by solving

$$\begin{aligned} u' &= \frac{q-a}{D}(u-u^*) \qquad \text{for} \quad \eta < L \\ u(L) &= u_0. \end{aligned} \tag{69}$$

The solution is given by

$$u(\eta) = (u_0 - u^*) \exp\left(\frac{q-a}{D}\eta\right) + u^* \quad \text{for} \quad \eta \le L. \tag{70}$$

Let l be the straight line connecting (u^*, v^*) and (u_*, v_*), then according to the first equation of (68) the condition $l(u) = v$ describes the set of equilibrium points of the first ordinary differential equation given in (68) and for any $u^* < u_0 < u_*$ we have

$$u'(\eta) > 0, \qquad \text{if} \quad v(\eta) < l(u(\eta)), \tag{71}$$

Furthermore

$$v'(\eta) > 0, \qquad \text{if} \quad u(\eta) < u_*. \tag{72}$$

Therefore three cases can happen:

Case A: u, v increase, till eventually for some $\overline{\eta} > L \quad v(\overline{\eta}) = l(u(\overline{\eta})), \quad u(\overline{\eta}) < u_*$.

Case B: u, v increase, till eventually for some $\overline{\eta} > L \quad u(\overline{\eta}) = u_*, \quad v(\overline{\eta}) < l(u(\overline{\eta}))$.

Case C: Neither case A nor case B happen, such that $u(\infty) = u_*, \quad v(\infty) = v_*$, i.e. u_0 is the desired value.

As values u_0 from case A must be smaller than values from case B, the case C must occur for at least one u_0 and such a value can be found by the following *shooting algorithm.*

I. $n = 0$

Select $u^* < u_L^n < u_*$ small enough such that case A occurs for $u_0 = u_L^n$.

Select $u^* < u_R^n < u_*$ big enough such that case B occurs for $u_0 = u_R^n$.

II. $n := n+1, \quad u^{n+1} := \frac{1}{2}(u_L^n + u_R^n)$,

compute u, v according to (68) and $u_0 = u^{n+1}$ and check whether case A or case B occurs.

For case A: $u_L^{n+1} := u^{n+1}, \quad u_R^{n+1} := u_R^n$.

For case B: $u_L^{n+1} := u_L^n, \quad u_R^{n+1} := u^{n+1}$.

If case C occurs or $\left|u_R^{n+1} - u_L^{n+1}\right|$ is small enough, stop, otherwise goto II.

This algorithm will at least produce sequences $u_L^n < u_0 < u_R^n$ such that $|u_R^n - u_L^n| \to 0$.

The computation of u, v according to (68) in I. and in II. can be performed with any numerical procedure, if k and D are in the same range as the other parameters. If one also wants to compute the limit cases $k \to \infty$ or $D \to 0$ (see Section 4), the system (68) becomes very stiff, so that the use of a corresponding procedure with order and step size control as e.g. Gear's method (see e.g. [7]) becomes decisive for the correct performance of the shooting algorithm. For the following examples the parameters still allowed the use of a method for mildly stiff system with appropriately chosen fixed step size (see [1]).

A basic numerical example

The parameters of the following basic example, called the reference case and depicted in Figure 1, are assembled in Table 1 and chosen analogously to the computation of [14], p. 1568, Figure 3. The differences are the following: K is slightly larger, in [14] only the equilibrium case $k = \infty$ is considered, and most important, the charge distribution c of [14] corresponds to the step function (7) with $c^* = 2.0 * 10^{-5}, c_* = 0$ rather than a constant $c = 0$. Therefore the computations of [14] are in relation to the solutions of Part 2 of the paper and will be discussed there. K is determined by $c_{1*}, c_{2*}(= c_{1*})$ and thus has to be different from [14], as we do not consider Debye-Hckel corrections in this computation. In Figure 1 and all the following figures a translation is applied such that $L = 0$.

$$\begin{aligned}
\Theta &= 0.32[-],\ \varrho = 1.8[g/cm^3],\\
q^* &= 0.3 * 10^{-3}[cm/s],\ \Theta D = 0.2 * 10^{-3}[cm^2/s],\\
M_1 &= Sr^{2+},\ M_2 = SO_4^{2-},\\
n &= m = 1,\ r(c_1, c_2) = c_1 c_2,\\
c &= 0,\\
k_p &= 1,\ k_d = K = 3.86884 * 10^{-7},\\
k^* &= 0.1,\ \text{i.e. } k = 0.1,\\
c_1^* &= 2.0 * 10^{-5}\ [millimoles/cm^3],\\
c_{12}^* &= 0\ [millimoles/g],\\
c_{1*} &= 6.22 * 10^{-4},\\
c_{12*} &= 4.9 * 10^{-5}
\end{aligned}$$

Table 1: Parameters of the reference case.

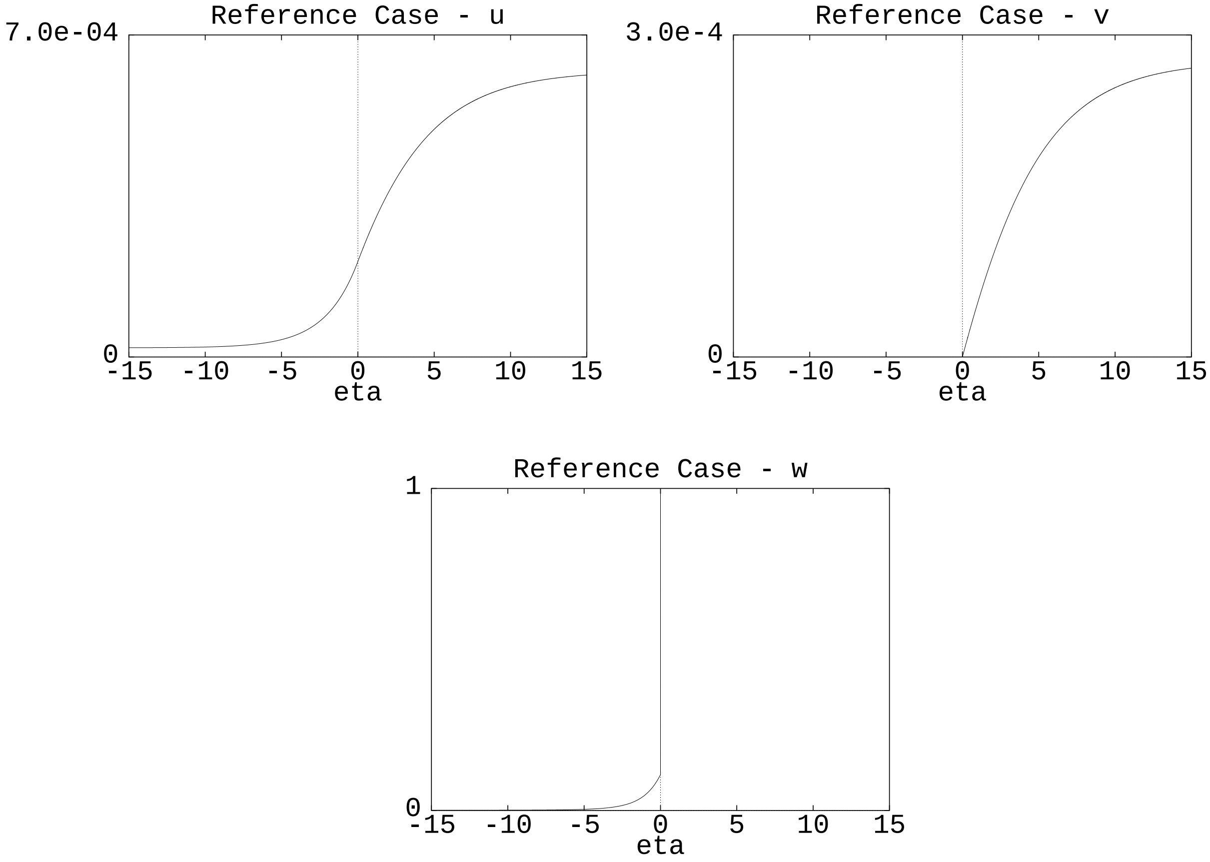


Figure 1: The travelling wave solution for the reference parameters.

The closed form solution for the linearized model

For the linearized model (38), i.e. $g(u;c) = u,\ u_S = K$, the initial value u_0 from (68) can be computed explicitly:

Rewriting (68) as the second order equation

$$Du'' - (q-a)u' - k(u-K) = 0 \tag{73}$$

we see that the general solution with the boundary condition $u(\infty) = u_* = u_S$ is given by

$$u(\eta) = u_S - (u_S - u_0)\exp(-\lambda(\eta - L)) \quad \text{for} \quad \eta \geq L, \tag{74a}$$

with

$$\lambda = \frac{q-a}{2D}\left(\left(1 + \frac{4Dk}{(q-a)^2}\right)^{1/2} - 1\right) \tag{74b}$$

and thus

$$v(\eta) = \frac{k}{a}(u_S - u_0)\frac{1}{\lambda}\left(1 - \exp(-\lambda(\eta - L))\right) \quad \text{for} \quad \eta \geq L. \tag{75}$$

The value u_0 is determined by the shooting requirement

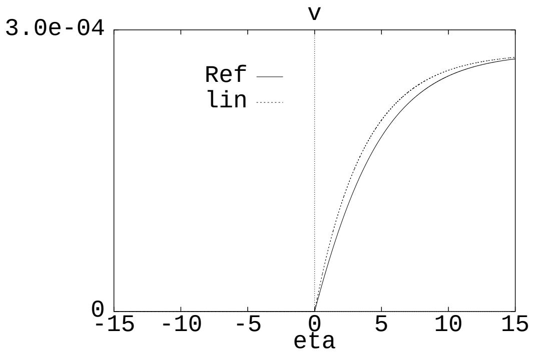
$$\frac{k}{a}(u_S - u_0)\frac{1}{\lambda} = v(\infty) \overset{!}{=} v_* \tag{76}$$

which gives using (54)

$$u_0 = u_S - \frac{2(u_S - u^*)}{1 + \left(1 + \frac{4Dk}{(q-a)^2}\right)^{1/2}}. \tag{77}$$

For the reference case, a comparison with the linearized model with k chosen according to (35) is shown in Figure 2, which shows only slight variations.

Figure 2: The travelling wave solution for the reference case (mass action law) and the linearized model.



4. TRAVELLING WAVE SOLUTIONS FOR EQUILIBRIUM REACTIONS OR NEGLIGIBLE DISPERSION

Equilibrium reactions

In Section 1 we indicated two limit cases, which we will examine in this section. The first $''k = \infty''$, corresponds to the formal procedure

$$k \to \infty, \quad K > 0 \quad \text{constant} \quad (k, K \text{ defined in (28)})$$

and substitutes in a quasistationary manner the rate equation (26a,b) by the equilibrium description (23) (or equivalently (22) or (24)).

Travelling wave formulation

The corresponding travelling wave formulation is given by (42a), (43), (44) with (42b) substituted by (23). We see that we can repeat the discussion of Section 3 leading to (45) as a necessary condition for travelling waves and the following formulation in the transformed variables:
We look for functions $u = u(\eta)$, $v = v(\eta)$ and $w = w(\eta)$ such that

$$-au' - av' - Du'' + qu' = 0, \tag{78}$$

$$g(u; c) = Kw, \tag{79}$$

$$0 \le w(\eta) \le 1, \quad w(\eta) = 1, \quad \text{if} \quad v(\eta) > 0, \tag{80}$$

for $-\infty < \eta < \infty$, which satisfy the boundary and sign conditions (50), (51).

Reduced continuity of solutions

We expect that the travelling wave solutions for a sequence of rate parameters $k_n \to \infty$, and all other parameters and boundary conditions being the same, converge to a solution of (78)-(80). As we will see later on, these limits in general have a jump in v. Therefore in our notion of travelling wave solutions for the equilibrium reaction, we only require the continuity of u and allow for finitely many jumps in v and thus v' does not exist (as a function). Similarly, we have to allow for jumps in u' and thus u'' does not exist (as a function). This requires a proper interpretation of (78): If the jumps of Du' and av cancel each other, then the combination

$$Du' + av \quad \text{is continuous} \tag{81}$$

and we can interpret (78) as

$$(Du' + av)' = (q - a)u' \tag{82}$$

such that the *jump relations* are

$$D[u'] = -a[v] = \frac{D}{q-a}\left[(Du' + av)'\right], \tag{83}$$

which follow from (81) and (82). For a more detailed analogous reasoning consult the discussion related to (52). In particular there is an equivalent formulation with equation (82) substituted by (53).

The impossibility of precipitation waves

The discussion leading to the wave speed a given by (54) and to the possible cases of dissolution or precipitation wave (59) or (60) can be repeated. The conclusion (61), that the fluid is undersaturated is not true here, since it was based on the fact to have the ordinary differential equation (48) at one's disposal (see [3], proof of Prop. 2.1). It can only be concluded that the fluid is not oversaturated. But again a precipitation wave is impossible and the dissolution wave has a simple structure leading to an explicit solution. This can be seen as follows:
In an η–interval where v is positive, then due to (79), (80) and the uniqueness of the solubility concentration (according to (56)) we have $u = u_S$ and by (53) $v = \tilde{v}$, where $\tilde{v} = v_*$ for a dissolution wave and $\tilde{v} = v^*$ for a precipitation wave. Thus a wave induces a sequence of η–subintervals on which either $v = \tilde{v} > 0$ and $u = u_S$ or on which $v = 0$. In the later subintervals u is given explicitly by (53) and the value $u = u_S$ at the left boundary point of these subintervals.

From this we can conclude (compare [3], proof of Prop. 4.3 for dissolution waves):

$$\text{Precipitation waves cannot exist.} \tag{84}$$

A closed form solution for dissolution waves

Furthermore, a dissolution wave is characterized by a dissolution front $\eta = L$ and

$$v(\eta) = 0 \quad \text{for} \quad \eta < L, \quad v(\eta) = v_* \quad \text{for} \quad \eta > L, \tag{85}$$

$$u(\eta) = (u_S - u^*)\exp\left(\frac{q-a}{D}(\eta - L)\right) + u^* \quad \text{for} \quad \eta < L, \tag{86}$$

$$u(\eta) = u_S \quad \text{for} \quad \eta \geq L.$$

Thus $\eta = L$ is the only point which jumps according to (83) occur, which can be made more precise by $[v] = v_*$ for $\eta = L$. Again it represents the free boundary $x = s(t)$ of the solution, (83) together with $v(s(t), t) = 0$ being the free boundary condition. It is identical with the free boundary condition of [14] (p. 1563, (5d)) for this special case. As also $u(s(t), t) = u_S$, the transformation $\tilde{u} = u - u_S$ leads to the classical Stefan problem and is a special case of the transformation applied in [11].

Convergence (rates) for $k \to \infty$

To have a consistent modelling of the equilibrium and the non–equilibrium case, we expect that the solutions of (47) – (50) converge to (85), (86) for $k \to \infty$ and all other parameters fixed. Figure 3 displays a sequence of numerical solutions for the data of Table 1 and $k = 0.1$, (i. e. the reference case from Figure 1), $1, 10, 100$ which clearly show a convergence from below to the equilibrium solution (85), (86).

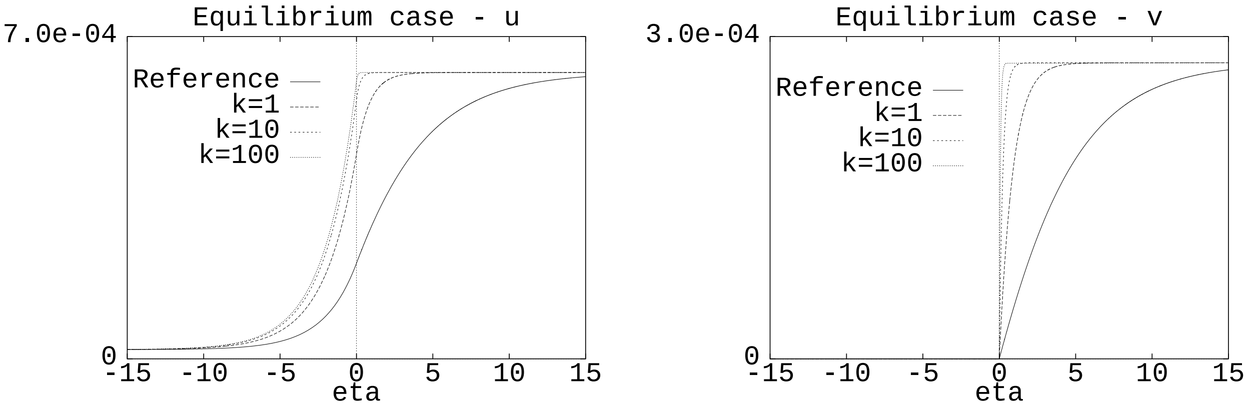


Figure 3: Convergence of the travelling wave solutions for $k \to \infty$.

This observation can also be made rigorous (see [3], Th. 4.5). Furthermore, even the rate of convergence can be detected, which we will do for the linearized model by means of its closed form solution (74a,b) – (77). The most critical point is the front $\eta = L$ due to the jump of v for $k = \infty$: From (77) we see for $k < \infty$:

$$k^{1/2}(u_S - u(L)) \to \frac{(q-a)(u_S - u^*)}{D^{1/2}}, \quad \text{for} \quad k \to \infty, \tag{87}$$

i.e. the convergence rate is $1/k^{1/2}$ and even the coefficient of the leading term is given. For $\eta < L$ we consult the explicit solutions (70) for $k < \infty$ and (86) for $k = \infty$, respectively, which have the same shapes,but the different initial values $u(L)$ and u_S at $\eta = L$. We see from (87) that the same rate of convergence holds true. The result also extends to $\eta > L$ by virtue of (74a,b).

Negligible Dispersion

The second limit case $''D = 0''$ introduced in Section 1 corresponds to the formal procedure

$$D \to 0$$

and emphasizes situations where advective or kinetic effects are much more important than dispersive ones.

Travelling wave formulation

We set $D = 0$ in (42a,b) – (44), i.e.:
We look for functions $u = u(\eta), v = v(\eta)$, and $w = w(\eta)$ such that

$$-au' - av' + qu' = 0, \tag{88}$$

$$-av' = k(g(u;c) - Kw), \tag{89}$$

$$0 \le w(\eta) \le 1, \quad w(\eta) = 1, \quad \text{if} \quad v(\eta) > 0 \tag{90}$$

which satisfy the boundary and sign conditions (50), (51). Analogously to $k \to \infty$, we expect that the travelling wave solutions for a sequence of dispersion coefficients $D \to 0$, and all other parameters and boundary conditions being the same, converges to a solution of (88)-(90). As we will see later on, these limits have in general a jump in u', v', and w. Thus we require only the continity of u, v and we allow for finitely many jumps in u', v' and w, which have to cancel each other according to the following jump relations

$$\frac{\Delta v}{\Delta u}[u'] = [v'] = \frac{kK}{a}[w] \tag{91}$$

They follow from (88), (89), as $(q-a)/a = \Delta v/\Delta u$ (defined in (54)).

The impossibility of precipitation waves

As above, we can repeat the discussion of Section 3, leading to the wave speed (54) and a system, which instead of (53) contains

$$(q-a)(u-u^*) = a(v-v^*), \tag{92}$$

i.e. the shape of u and v are the same. The whole reasoning from (57) to (62) holds true also here, even with simpler arguments. The only possible case of a dissolution wave is given in a nearly explicit form: It is given by the dissolution front $\eta = L$ and

$$v(\eta) = 0 \text{ for } \eta \le L,\ v = \frac{\Delta v}{\Delta u}(u-u^*) \quad \text{for} \quad \eta > L, \tag{93}$$

$$u(\eta) = u^* \text{ for } \eta \le L,\ u' = \frac{k}{q-a}(K - g(u;c)),\ u(L) = u^* \text{ for } \eta > L, \tag{94}$$

i.e. only the initial value problem in (94) has to be resolved.
In particular, the jumps of (91) only occur at $\eta = L$ and can be made more precise by $[w] = 1 - g(u^*;c)/K$. Again, with $v = 0$, they give the free boundary condition.

Convergence(rates) for $D \to 0$

The convergence of the solutions of (47) – (50) to the ones of (93), (94) for $D \to 0$ can be clearly observed numerically (see Figure 4, where the data of Table 1 are used with $D = Di, i = 1,2,3, D1 = 6.25 * 10^{-4}, D2 = 2.76 * 10^{-4}, D3 = 6.25 * 10^{-6}$), $D1$ is the reference case. The convergence in the u-profiles is not from one side, rather there is one intersection point of all profiles for $\eta > L$. There is a rigorous argument for this assertion [3, Prop. 4.7]. For the linearized model its closed form solution (74a,b) – (77) reveals a rate of convergence. At $\eta = L$ we have for $D \to 0$

$$\begin{aligned} \frac{1}{D}(u(L) - u^*) &= \frac{(u_S - u_*)4k}{(q-a)^2} \Bigg/ \left(\frac{4Dk}{(q-a)^2} + 2\left(1 + \frac{4Dk}{(q-a)^2}\right)^{1/2} + 2 \right) \\ &\to \frac{(u_S - u_*)k}{(q-a)^2}, \end{aligned} \tag{95}$$

i.e. the convergence is linear in D. This rate, even with the leading coefficient of (95) can also be justified in general (see [3, Th. 5.4]) and it holds true for all arguments η.

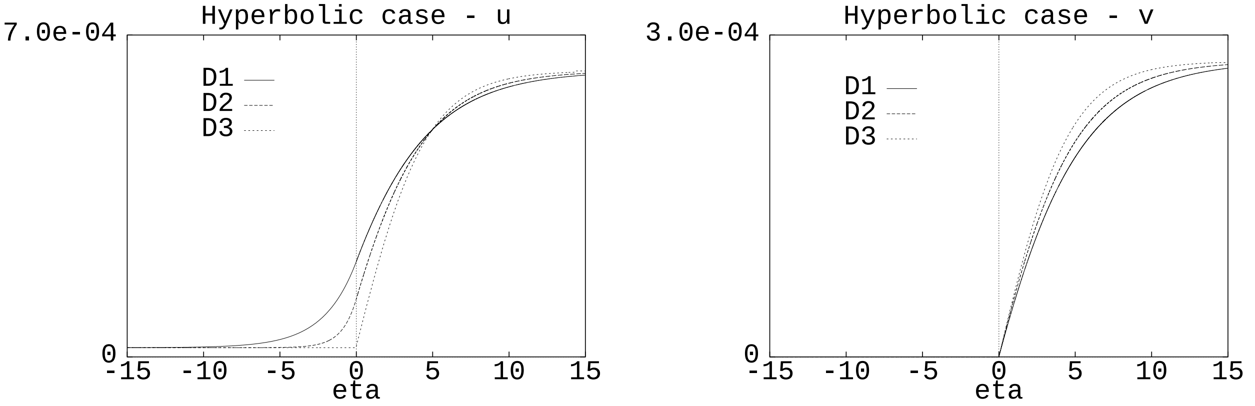


Figure 4: Convergence of the travelling wave solution for $D \to 0$.

CONCLUSIONS

We set up a model for transport and dissolution/precipitation, where the kinetics of the reaction is taken into account. Contrary to other possible approaches, our model is consistent with the corresponding model, assuming equilibrium for the reaction. The set–valuedness of the nonlinearity is one way to allow for solutions with sharp dissolution and precipitation fronts, which in fact occur. It turns out that travelling wave solutions only exist for a constant charge distribution and only as dissolution waves. These waves are given nearly explicitly: It remains to solve numerically initial value problems for ordinary differential equations, possibly within a shooting algorithm. All qualitative properties of the solutions can be investigated in detail, including the appearance of a dissolution front, the behaviour there, the convergence to limit cases of equilibrium or no dispersion, even with convergence rates. Thus these solutions enhance the understanding of the interplay advection–dispersion–dissolution–kinetics, also for more general situations, which can only be attacked numerically. In particular, they can be used to validate numerical codes for these problems.

APPENDIX A: THE RATE FUNCTION ACCORDING TO DEBYE–HÜCKEL THEORY

The purpose of this appendix is to indicate reasonable sufficient conditions under which the function $g(x;c)$ according to (27) is strictly monotone increasing in x for $x \geq (c/m)_+$ and a fixed real number c, i.e. satisfies (55), if the rate function is described according to the Debye–Hückel theory. The precipitation rate function r from (19) then takes the form (compare e.g. [12], [6], [8])

$$r(c_1, c_2) = \gamma_1^n c_1^n \gamma_2^m c_2^m \tag{A.1}$$

with positive integers n, m and

$$\begin{aligned} \gamma_1 &:= \exp(-m^2\sigma(I)) \ , \\ \gamma_2 &:= \exp(-n^2\sigma(I)) \ , \end{aligned} \tag{A.2}$$

$$\sigma(I) := \frac{a_1 I^{1/2}}{1 + a_2 I^{1/2}} \ , \tag{A.3}$$

where a_1, a_2 are positive parameters, and

$$I := \frac{1}{2}(m^2 c_1 + n^2 c_2 + \hat{c}). \tag{A.4}$$

Note that according to Section 1 we have taken the electric charges of M_1, M_2 to be $m, -n$ (or $-m, n$), respectively. The constant $\hat{c} \geq 0$ in the definition of the *ionic strength* I expresses the weighted sum of concentrations of all further species in solution, which do not take part in the dissolution/precipitation reaction. For the sake of simplicity we have taken the "effective diameters" of M_i to be the same, otherwise we would have to distinguish between different a_2^i in the definition of $\sigma = \sigma_i$. Due to (14) $f(x) := g(x; c)$ takes the form

$$f(x) = \gamma_1^n x^n \gamma_2^m \left(\frac{1}{n}(mx - c) \right)^m \tag{A.5}$$

and

$$\begin{aligned} I(x) = \alpha x + \beta, \qquad &\text{where} \\ \alpha := \frac{1}{2} m(n+m), \quad \beta := \frac{1}{2}(\hat{c} - nc).& \end{aligned} \tag{A.6}$$

As the problem is stated till now, there will be cases where f is not strictly increasing in x for $x \geq (c/m)_+$. Thus we have to impose a reasonable restriction on the parameters. We will show that it is sufficient to assume

$$4a_2 \geq nm(n+m)a_1. \tag{A.7}$$

This condition, which is invariant under linear scalings of x, c and $\hat{c}$, i.e. a change of concentration units, seems to be fulfilled in general (cf. e.g. [8]).

Let $K > 0$ and consider the equation

$$f(x) = K \qquad \text{or equivalently} \quad Kg(x) = h(x), \tag{A.8}$$

where

$$\begin{aligned} &g(x) := \exp(\gamma \sigma(I(x))), \\ &\text{with} \quad \gamma := mn(n+m), \end{aligned} \tag{A.9}$$

$$h(x) := x^n \left(\frac{1}{n}(mx - c) \right)^m. \tag{A.10}$$

Then an equivalent formulation of the assertion is:

For $K > 0$ there exists a unique solution $x = x_K \geq (c/m)_+$ of (A.8) and the solution depends monotonically on K, i.e.

$$0 < K_1 < K_2 \;\Rightarrow\; x_{K_1} < x_{K_2}. \tag{A.11}$$

The functions g, h have the following properties for $x \geq (c/m)_+$:

$$\begin{aligned} &g \text{ and } h \text{ are strictly monotone increasing and smooth for } x > (c/m)_+, \\ &g((c/m)_+) \geq 1, \quad g(\infty) = \exp(\gamma a_1/a_2), \\ &h((c/m)_+) = 0, \quad h(\infty) = \infty, \\ &h \text{ is strictly convex for } x \geq (c/m)_+. \end{aligned} \tag{A.12}$$

Therefore the existence of a solution x_K of (A.8) is clear, and $h(x_K) \geq K$ for each solution x_K. If g changes curvature, then there may be several solutions, but the solution is unique, if g is concave for $x \geq h^{-1}(K)$. In this case also (A.11) is satisfied, which can be seen as follows:

We have

$$\begin{aligned} h(x) &< Kg(x) \quad \text{for} \quad (c/m)_+ \leq x < x_K, \\ h(x) &> Kg(x) \quad \text{for} \quad x > x_K. \end{aligned} \tag{A.13}$$

Let $0 < K_1 < K_2$ and x_1, x_2 be the corresponding solutions of (A.8), then by means of (A.12), (A.13)

$$x_1 = h^{-1}(K_1 g(x_1)) < h^{-1}(K_2 g(x_1)) =: \hat{x}$$

and

$$h(\hat{x}) = K_2 g(x_1) < K_2 g(\hat{x}), \quad \text{i.e. } \hat{x} < x_2$$

and thus $x_1 < x_2$. A sufficient condition for concavity of g (for $x \geq (c/m)_+$) is given by (A.7), which can be seen by direct computation:

$$\begin{aligned} &g(x) = g_1(g_2(x)) \text{ with } g_1 = \exp,\ g_2 = \gamma\sigma(I), \text{ i.e.} \\ &g''(x) = g(x)(g_2'^2(x) + g_2''(x)) = g(x)\left((\gamma\alpha\sigma'(I))^2 + \gamma\alpha^2\sigma''(I)\right), \end{aligned}$$

i.e. the sign of $g''(x)$ is the sign of

$$\begin{aligned} &\gamma\sigma'^2(I) + \sigma''(I) = \\ &-\frac{3}{4}\,\frac{a_1 a_2^2}{I^{3/2}(1 + a_2 I^{1/2})^4}\,\left[I + \frac{4a_2 - \gamma a_1}{3a_2^2}\,I^{1/2} + \frac{1}{3a_2^2}\right]. \end{aligned} \tag{A.14}$$

If (A.7) is satisfied, then the square bracket in (A.14) is strictly positive for $x \geq (c/m)_+$, i.e. $I \geq 0$, and thus $g''(x) < 0$.

Acknowledgement:

We are grateful to Prof. J. C. Friedly (Dept. Chem. Eng., Univ. Rochester, N.Y., USA) who provided us with very detailed comments and suggestions. They helped us to clarify the presentation of the results.

REFERENCES

[1] Ashour, S. S., & Hanna, O. T., A new very simple explicit method for the integration of mildly stiff ordinary differential equations. *Computers and Chemical Engineering* 14 (1990), 267–272.

[2] van Duijn, C. J. & Knabner, P., Travelling waves in the transport of reactive solutes through porous media: Adsorption and binary ion exchange. Part 1,2. *Transport in Porous Media* 8 (1992), 167–194, 199-226.

[3] van Duijn, C. J., & Knabner, P., Travelling wave behaviour of crystal dissolution in porous media flow. Preprint No. 62, IAAS Berlin (1993), accepted for publication in *European Journal of Applied Mathematics.*

[4] van Duijn, C. J., & Knabner, P., & Schotting, R., An analysis of crystal dissolution fronts in flows through porous media. Part 2: Incompatible boundary conditions. to be submitted to *Advances in Water Resources.*

[5] Friedly, J. C., & Rubin, J., Solute transport with multiple equilibrium – controlled or kinetically controlled chemical reactions. *Water Resources Research* 28 (1992), 1935–1953.

[6] Garrels, R. M., & Christ, C. L., Solutions, Minerals and Equilibria. *Freemann, Cooper,* San Francisco, 1965.

[7] Hall, G. & Watt, J. M. (eds.), Modern numerical methods for ordinary differential equations. *Clarendon Press,* Oxford, 1976.

[8] Klotz, I. M., & Rosenberg, R. M., Chemical Thermodynamics – Basic Theory and Methods. (3rd ed.), *Benjamin,* Menlo Park, 1972.

[9] Knabner, P., Mathematische Modelle fr Transport und Sorption gelster Stoffe in porsen Medien (in German). Verlag P. Lang, Frankfurt/M.,1991.

[10] Pawell, A., & Krannich, K.–D., Dissolution effect arising in transport in porous media which affect a chemical equilibrium. *submitted to Math. Meth. Appl. Sci.*.

[11] Rubin, J., Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions. *Water Resources Research* 19 (1983), 1231–1252.

[12] Snoeyink, V. L., & Jenkins, D., Water chemistry. *J. Wiley,* New York, 1980.

[13] Walton, A. G., The formation and properties of precipitates. *Wiley – Interscience,* New York, 1967.

[14] Willis, C., & Rubin, J., Transport of reacting solutes subject to a moving dissolution boundary: Numerical methods and solutions. *Water Resources Research* 23 (1987), 1561–1574.