An analysis of crystal dissolution fronts in flows through porous media.
Part 1: Compatible boundary conditions

P. Knabner
University of Erlangen-Nürnberg, Institute of Applied Mathematics, Marientr. 3, D-91058 Erlangen, Germany

C. J. van Duijn
Delft University of Technology, Department of Mathematics, PO Box 5031, NL 2600 GA Delft, The Netherlands

&

S. Hengst
Institute for Applied Analysis and Stochastics (IAAS), Mohrenstr. 39, D-10117 Berlin, Germany

(Received 30 March 1994; accepted 18 January 1995)

Proposed in this study is 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 the situation is 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 or no dispersion, travelling waves are established under the same conditions, but with different qualitative properties.

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

1 INTRODUCTION

In this paper chemistry-affected transport processes in porous media are considered, where the transported solutes are participants in a precipitation–dissolution reaction, which in general is not in equilibrium, but is 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.

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 Pawell and Kranich and Willis and Rubin, respectively.

Further references to numerical approaches, also for more complex situations, may be found in Willis and Rubin.

Here, the same problem and model is dealt with, also allowing for non-equilibrium, but the aim is different. This work starts from a model formulation without explicit reference to free boundaries in the 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, the solutions are established analytically. The situation dealt with in this first part 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 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 Pawell and Krannich and Willis and Rubin.

Two spatially one-dimensional flow regimes, with constant water content, bulk density, pore velocity \( q \) (cm/s) and diffusion/dispersion coefficient \( D \) (cm²/s) will be analysed. The spatial domain will be represented by the whole real line, according to the goal of developing solutions which describe the behaviour for large flow domains, e.g. large soil columns. In Section 2 the following set of equations will be derived for \( u \) and \( v \) (mM/cm³), 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 \( w(\cdot) \), which is used here to take into account the nature of the dissolution reaction.

\[
\begin{align*}
\frac{\partial}{\partial t}(u + v) + q \frac{\partial}{\partial x} u - D \frac{\partial^2}{\partial x^2} u &= 0 \quad (1) \\
\frac{\partial}{\partial t} v &= k \{ g(u; c) - w K \} \quad (2) \\
0 &< w(x, t) < 1, \quad \text{and} \quad w(x, t) = 1 \quad \text{if} \quad v(x, t) > 0 \quad (3) \\
\text{for} & \quad -\infty < x < \infty, \quad t > 0
\end{align*}
\]

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

\[
\begin{align*}
\frac{\partial}{\partial t} c + q \frac{\partial}{\partial x} c - D \frac{\partial^2}{\partial x^2} c &= 0 \quad (4) \\
\text{for} & \quad -\infty < x < \infty, \quad t > 0
\end{align*}
\]

Equations (1), (2) and (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.

\[
g(u; c) = w K \quad (5)
\]

This case will be referred to as '\( k = \infty \).

If the dispersive transport is negligible compared to the advective transport, it is reasonable to let \( D \to 0 \), i.e. cancel the corresponding term in eqn (1) and eqn (4), and thus consider a hyperbolic system. This case will be referred to as '\( D = 0 \).

Two charge distributions \( c \) will be considered. The first is

\[
\text{The function } c \text{ is constant} \quad (6)
\]

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, eqn (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 large time period 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 eqns (1)–(4) this can be modelled by an initial distribution of \( c \) in form of a step function, i.e. with two levels \( c^*, c_0 > 0 \)

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

If we will restrict ourselves to the limit case \( D = 0 \), then the solution of eqn (4) is given by the piston flow profile, i.e. the function \( c \) is given by

\[
c(x, t) = c_0(x - qt) \quad (8)
\]

with \( c_0 \) as in eqn (7).

In Part 2 of the paper this situation will be analysed, if also the initial conditions for \( u \) and \( v \) are analogous step functions, i.e. the Riemann problem of eqns (1)–(4) will be considered (with \( D = 0 \)). It will turn out that the structure of solutions is more involved, exhibiting two fronts of different speeds, 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

The following precipitation–dissolution reaction in a
An analysis of crystal dissolution fronts in flows through porous media

porous medium will be discussed. 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 $M_{12}$ present (at the grain surface). Here we adopt the notation of Rubin, and relate to the reasoning of Friedly and Rubin, and Jenkins and Willis and Rubin. There may be two species $M_1, M_2$, for example ions, say $M_1$ being a cation and $M_2$ an anion. The stoichiometry of the reaction is supposed to be as follows

$$M_{12} \rightarrow nM_1 + mM_2 \tag{9}$$

Here $n, m$ denote positive numbers. If the species $M_1, M_2$ are ions, a reaction like eqn (9) leads to the electroneutrality of the fluid, if the valence of $M_1$ is $m$ and of $M_2$ is $n$. Let $c_1$ (mm/cm$^3$) be the molar concentration of $M_i$ in solution relative to the water volume, and let $c_{12}$ (mm/g) be the molar concentration of $M_{12}$ relative to the mass of the porous skeleton. By its meaning only $c_1, c_{12} \geq 0$ 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 $\rho$ (g/cm$^3$), the diffusion/dispersion tensor $D$ (cm$^2$/s) and the specific discharge vector $q^*$ (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. $\Theta$, is not affected by the reaction (9). As $M_{12}$ is spatially immobile, the conservation of the corresponding total masses leads to the partial differential equations

$$\frac{\partial}{\partial t}(\Theta c_1) + n \rho \frac{\partial}{\partial t} c_{12} - \text{div}(\Theta D \nabla c_1 - q^* c_1) = 0 \tag{10}$$
$$\frac{\partial}{\partial t}(\Theta c_2) + m \rho \frac{\partial}{\partial t} c_{12} - \text{div}(\Theta D \nabla c_2 - q^* c_2) = 0 \tag{11}$$

Here $\partial/\partial t$ denotes the partial derivative with respect to time $t(s)$, and $\text{div}, \nabla$ denotes the divergence and gradient with respect to the space coordinate $\nabla (cm)$.

Note that the ionic nature of the aqueous products is not necessary to set up eqns (10), (11) and their consequences, but only a stoichiometric relation like the one implied by eqn (9) is required. As a further example one may think of the dissociation of an organic solid in an organic solvent. Reactions like eqn (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.

Defining

$$c = m c_1 - n c_2 \tag{12}$$

then eqns (10) and (11) imply that the quantity $c$ is conserved

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

For a spatially homogeneous reaction, the continuous stirred tank reactor (CSTR) situation, 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 $c = 0$. It will be shown that for travelling wave solutions the same holds true. For the special case of anionic binary reaction, another interpretation is also possible: the valence of $M_1$ is $m\nu$ and the valence of $M_2$ is $n\nu$ with some positive integer $\nu$. If $M_1$ is a cation and $M_2$ an anion, then $\nu c$ denotes the total positive electric charge of the solute.

It is a well-known observation that we can resolve eqn (13) (with appropriate initial and boundary conditions) at least numerically and thus reduce the number of unknown functions by one, by setting

$$c_1 = \frac{1}{n} (m c_1 - c) \tag{14}$$

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

$$c_1 \geq \left( \frac{c}{m} \right) \nu \tag{15}$$

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 $r_p$ (mm/cm$^3$) denote the dissolution and precipitation rates relative to the water volume and $k^*$ (1/s) is a rate parameter then

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

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

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

This relation will be taken 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\(^{12,13}\) (i) the activity of the crystalline solid is a positive constant, say \(k_d (\text{mm/cm}^3)\), therefore
\[ r_d = k_d, \text{ if } c_{12} > 0 \] (18)
(ii) 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
\[ r_p = k_p r(c_1, c_2) \] (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
\[ r(c_1, c_2) = c_1^n c_2^m \] (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
\[ c_1^n c_2^m = K \] (21)
where \(K = k_d/k_p\). The condition due to eqn (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 eqn (17) satisfies all the properties 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
\[ 0 \leq r(c_1, c_2) \leq K \]
\[ c_{12} > 0 \Rightarrow r(c_1, c_2) = K \]
\[ r(c_1, c_2) < K \Rightarrow c_{12} = 0 \] (22)
or in more compact notation
\[ 0 \leq r(c_1, c_2) \leq K \]
\[ \left( -r(c_1, c_2) \right) c_{12} = 0 \] (23)
This can be recast in the form of eqn (17) by writing
\[ 0 \in k_p r(c_1, c_2) - k_d H(c_{12}) \]
\[ \Leftrightarrow r(c_1, c_2) \in KH(c_{12}) \] (24)
where \(H\) is the set-valued Heaviside ‘function’ (better: Heaviside graph) defined by
\[ H(u) = \begin{cases} 1 & \text{for } u > 0 \\ [0, 1] & \text{for } u = 0 \\ 0 & \text{for } u < 0 \end{cases} \] (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 eqn (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.\(^{12,13}\) Guided by this and relation (24), the following rate description is proposed
\[ \frac{\partial}{\partial t} c_{12} \in \Theta k^*(k_p r(c_1, c_2) - k_d H(c_{12})) \] (26a)
or equivalently
\[ \frac{\partial}{\partial t} r_{12} = \Theta k^*(k_p r(c_1, c_2) - k_d w) \] (26b)
where \(w \in H(c_{12})\) which means
\[ 0 \leq w \leq 1 \quad \text{and} \quad w = 1 \quad \text{for} \quad c_{12} > 0 \] (26b)
Thus eqns (10), (11), (26a,b) have been arrived at with the unknowns \(c_1, c_2, c_{12}\) or equivalently eqns (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 the precipitation rate of eqn (19) is kept, and so is the dissolution rate from eqn (18) for \(c_{12} > 0\), but a ‘fictitious’ dissolution rate \(k_d w \leq k_d\) for \(c_{12} = 0\) is allowed for. This is necessary to be compatible with (24)/(22) at equilibrium.
If we use the elimination of \(c_2\) by means of \(c\), setting
\[ g(c_1; c) := r(c_1, \frac{1}{n} (mc_1 - c)) \] (27)
and furthermore, defining
\[ u := c_1 \quad v := np / \Theta c_{12} \]
\[ q := q'/\Theta \quad k := nk^*k_p \]
\[ K := k_d/k_p \] (28)
the eqns (10), (13), (26a,b) take the form, which for one space dimension is displayed in (1)–(4).

**An alternative rate description**

Note that eqn (24) is not the only way to express eqn (22) by means of a Heaviside graph. Another equivalent form of the equilibrium conditions is given by
\[ 0 \in H(\max(c_{12}, r(c_1, c_2) - K))(k_p r(c_1, c_2) - k_d) \] (29)
This suggests, as alternative to eqn (26a,b), the rate equation
\[ \frac{\partial}{\partial t} c_{12} \in \Theta k^* H(\max(c_{12}, r(c_1, c_2) - K)) \times (k_p r(c_1, c_2) - k_d) \] (30a)
An analysis of crystal dissolution fronts in flows through porous media

or equivalently
\[ \frac{\partial}{\partial t} c_{12} = \Theta k^* w(k_p r(c_1, c_2) - k_d) \]
where \( w \in H(\max(c_{12}, r(c_1, c_2) - K)) \)

which means
\[ 0 < w < 1 \quad \text{and} \quad w = 1 \quad \text{for} \quad c_{12} > 0 \quad \text{or} \quad r(c_1, c_2) > K \]

This means that the rates of eqns (18) and (19) are kept, if a 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

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 eqns (26a,b) and eqns (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 eqns (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 a priori, 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 Friedly and Rubin is similar to eqns (30a,b), but not identical. It corresponds to eqns (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 Friedly and Rubin 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 Friedly and Rubin is required to hold everywhere, then the models are different and, for example, 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, which may be considered as linearizations of eqns (26a,b) or eqns (30a,b). We use the elimination of \( c_2 \) by means of \( c \), i.e. let \( c \) be given by eqn (13) supplemented with appropriate initial and boundary conditions. The nonlinearity in the rate eqns (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
\[ g(c_S; c) = K \]
i.e. \( c_S \) being the solubility and
\[ g(c_1; c) < K \quad \text{for} \quad 0 \leq c_1 < c_S \]
\[ g(c_1; c) > K \quad \text{for} \quad c_1 > c_S \]

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 eqns (26a,b) or (30a,b) for \( c_{12} > 0 \), i.e.
\[ \frac{\partial}{\partial t} c_{12} = \Theta k^* k_p (g(c_1; c) - g(c_S; c)) \]
\[ = \Theta k^* k_p \left( \frac{\partial}{\partial c_1} g(c_S; c)(c_1 - c_S) \right) \]
\[ + \text{higher order terms in } (c_1 - c_S) \]

This suggests the following alternative rate description for \( c_{12} > 0 \)
\[ \frac{\partial}{\partial t} c_{12} = \Theta k_L(c_1 - c_S) \]

where the rate \( k_L \) in this linearized version approximately corresponds to
\[ k_1 \sim k^* k_p \frac{\partial}{\partial c_1} g(c_S; c) \]

The rate function (34) can be found, e.g. in Snoeyink and Jenkins and Walton. For comparison one has to take into account that a batch experiment situation is considered there. For spatially constant concentrations however, eqn (10) reduces to
\[ n_p \frac{\partial}{\partial t} c_1 = -\frac{\partial}{\partial t} (\Theta c_1) \]

and thus with a water content \( \Theta \) being constant in time eqn (34) is equivalent to
\[ \frac{\partial}{\partial t} c_1 = k_L/n(c_S - c_1) \]

As above we have to also extend eqn (34) to vanishing crystal concentrations. Analogous to (26a,b) and (30a,b) we propose the two variants
\[ \frac{\partial}{\partial t} c_{12} = \Theta k_L(c_1 - H(c_{12})c_S) \]

or
\[ \frac{\partial}{\partial t} c_{12} = \Theta k_L H(\max(c_{12}, c_1 - c_S))(c_1 - c_S) \]

Mathematically, eqns (38) and (39) are special cases of (26a,b) and (30a,b), respectively, if one substitutes
\[ r(c_1, c_2) = g(c_1; c) = c_1 \]
i.e. \( K = c_S \)
and \( k^* k_p = k_L \)
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 \( q^* \) and, correspondingly, \( \Theta \) and \( D \) 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 \( q^* \) and are homogeneous orthogonal to \( q^* \) the model eqns (10), (13), (14), (26a,b) can be reduced to one space dimension, as follows. In particular, \( D = D^* \), \( q^* = q^* \) are scalar values from now on. This assumption usually is justified considering soil column experiments. 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 time periods to a fixed spatial profile, which is transported in time with a constant wave speed \( \alpha \). The mathematical model for this limited solution is a travelling wave solution, i.e. a solution of eqns (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 \( c(x, t) = c(\eta) \), the ordinary differential equations are obtained

\[
\begin{align*}
- a(\Theta c_1 + npc_{12})' - \Theta Dc_1' + q^*c_1' &= 0 \\
- a(\Theta c_2 + npc_{12})' - \Theta Dc_2' + q^*c_2' &= 0 \\
- apc_{12}'(k_p(c_1, c_2) - k_dH(c_{12})) &= 0
\end{align*}
\]

and

\[
- a(\Theta + q^*)c' - \Theta Dc'' = 0 \tag{43}
\]

for \(-\infty < \eta < \infty \). To select the solutions related to the situation described above, the following boundary conditions at \( \eta = -\infty \) and \( \eta = +\infty \) are prescribed

\[
c_i(-\infty) = c_i^*, \quad c_i(+\infty) = c_i^*, \quad i = 1, 2, \tag{44}
\]

\[
c_{12}(-\infty) = c_{12}, \quad c_{12}(+\infty) = c_{12}^*.
\]

Consider that a travelling wave solution is 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 eqns (42a,b)–(44) can be translated in \( \eta \) by an arbitrary amount to give a new solution. The one whose total mass corresponds asymptotically for large time periods to the total mass of the solution of the initial–boundary value problem will appear to be the asymptotic limit.

#### Homogeneous charge distribution as a necessary condition for travelling waves

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

\[
mc_i^* - nc_i^* = mc_{12} - nc_{12}, \tag{45}
\]

Thus eqn (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 aqueous products it also may be interpreted as a fact that the overall electric charge of the dissolution products in the invading fluid coincides with the electric charge of those in the resident fluid. If this situation does not occur, different asymptotic profiles will develop, which are the subject of Part 2 of this paper.

#### Travelling wave formulation in transformed variables, fixed wave speed

With \( c \) being a constant given by

\[
c := mc_i^* - nc_i^* \tag{46}
\]

the problem can be reduced to the variables \( u = u(\eta), v = v(\eta) \) defined in eqn (28) and \( w = w(\eta) \)

\[
\begin{align*}
- au' - m'u' - Dw' + qu' &= 0 \\
- av' &= k(g(u; c) - Kw) \tag{47}
\end{align*}
\]

\[
0 \leq w(\eta) \leq 1, \quad w(\eta) = 1, \quad \text{if} \ v(\eta) > 0 \tag{48}
\]

for \(-\infty < \eta < \infty \). The boundary conditions transform to

\[
\begin{align*}
u(-\infty) &= u^*, \quad u(+\infty) = u_* \\
v(-\infty) &= u^*, \quad v(+\infty) = v_* \tag{50}
\end{align*}
\]

where \( v^* = np/\Theta c_{12}^* \) etc. Note that \( q > 0 \) such that \( \eta = -\infty \) corresponds to upstream and \( \eta = +\infty \) to downstream. Only non-negative boundary conditions are considered and the solution is required to be non-
An analysis of crystal dissolution fronts in flows through porous media

We want the dissolved concentration and the mass flux or equivalently \( u \) and \( u' \) to be continuous, but allow for jumps in \( u' \). The eqns (47), (48) imply that it is necessary to allow also for jumps in \( u'' \) and \( w \). A jump of a function \( f \) at a point \( \eta \) by definition means that the one-sided limits \( f(\eta^-) \) and \( f(\eta^+) \) exist. The jump from right to left is then \( [f](\eta) := f(\eta^+) - f(\eta^-) \). Note that continuity of \( f \) at \( \eta \) is equivalent to \( [f](\eta) = 0 \). In the notion of the solution for eqns (47)-(49) only finitely many jumps \( \eta_j \) in \( \nu' \) (and \( w, u'' \)) are allowed for the eqns (47), (48) to hold for all \( \eta \neq \eta_j \). Consequently for all jumps \( \eta - \eta_j \) the jump relation is

\[ a[\nu'](\eta_j) = -D[a''u](\eta_j) = kK[w](\eta_j) \quad (52) \]

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

By integration, taking eqn (50) into account eqn (47) can be reduced to a first order equation. From this first order equation it is possible to conclude using eqn (50) that the limits \( \nu'(\pm \infty) \) exist and then \( \nu'(\pm \infty) = 0 \). The first order equation thus takes the form (see Proposition 1.2, Corollary 1.3 in van Duijn and Knabner for details)

\[ u' = \frac{q - a}{D}(u - u_*) - \frac{a}{D}(v - v_*) \]
\[ = \frac{q - a}{D}(u - u') - \frac{a}{D}(v - v') \quad (53) \]

From this the wave speed \( a \) is fixed to

\[ a = \frac{\Delta u}{\Delta u + \Delta v}, \text{ if } \Delta u + \Delta v \neq 0 \quad (54) \]

where \( \Delta u := u' - u_* \), \( \Delta v := v' - v_* \).

Excluding some trivial cases, it may be assumed \( \Delta u + \Delta v \neq 0 \), thus having a fixed wave speed. It will turn out that 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).

Note that all solutions \( u = u(\eta), v = v(\eta), w = w(\eta) \) of the first order system, eqns (53), (48) together with eqns (49), (50), for which \( u, v, u' \) are continuous and finitely many jumps in \( \nu' \) and \( w \) are allowed, such that \( u'' \) exists as a continuous function with finitely many jumps, the jump relations are satisfied and also the original eqn (47) holds true. Thus, an equivalent formulation has been found 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 following discussion, it is necessary to assume, for fixed \( c \)

\[ g(u; c) \text{ is strictly increasing for } u \geq \left( \frac{c}{m} \right)_+ \]
\[ g\left( \left( \frac{c}{m} \right)_+ ; c \right) = 0 \quad (55) \]

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

Condition (55) assures the unique existence of the solubility concentration \( u_0 \geq 0 \) (related to \( c \) and \( K \))

\[ g(u_0; c) = K \quad (56) \]

and \( u_0 \) monotonically depends on \( K \) (for fixed \( c \)), i.e. for increasing \( K, u_0 \) also increases. As already mentioned, a consequence of the first part of eqn (50) are the boundary conditions \( u'(\pm \infty) = 0 \). A further necessary condition for the existence of travelling wave solutions are the boundary conditions

\[ v'(\pm \infty) = 0, \quad v'(\infty) = 0 \quad (57) \]

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 with Ref. 3. for a more detailed discussion). Conditions (57) imply that \( w^* = w(\infty), w_* = w(1 \infty) \) exist and \( 0 < w_*, w^* \leq 1, \) and

\[ g(u^*, c) = Kw^* \leq K \]
\[ g(u_*, c) = Kw_* \leq K \quad (58a) \]

Due to eqns (55) and (56) it can be concluded that

\[ u^* \leq u_0 \quad \text{and} \quad v^* > 0 \Rightarrow u^* = u_0 \quad (58b) \]

These trivial waves certainly exist and will not be considered further.
Continuing our discussion, for \( v^* = v_n = 0, u^* \neq u \), it is concluded that \( a = q \) and eqn (53) reduces to \( u' = -q/Du \leq 0 \), leading to a contradiction. Therefore apart from the stationary wave the following cases fulfill the requirement of eqn (58a)

\[-v^* = v_n > 0, u^* = u_n = u_S \]

\[-v^* = v_n = 0, u^* = u_n \leq u_S \]

In these cases the wave speed is not determined. It is doubtful that, except for the stationary waves \( a = 0, u = u_S \), solutions exist, but it cannot be excluded at the moment. These cases will not be considered further. Thus the two remaining cases are: the dissolution wave

\[ v^* = 0, \quad v_n > 0 \text{ arbitrary} \]

\[ \left( \frac{c}{m^+} \right) u^* < u_n, \quad u = u_S \]

and the precipitation wave

\[ v^* > 0 \text{ arbitrary}, \quad v_n = 0 \]

\[ u^* = u_S, \quad \left( \frac{c}{m^+} \right) u_n < u < u_S \]

In the following it will be shown that precipitation waves cannot exist and that dissolution waves indeed exist. The key observation for the first statement, justified in detail in van Duijn and Knabner,\(^3\) is that both dissolution and precipitation waves can only exist for undersaturated fluids

\[ u(\eta) < u_S \text{ for } -\infty < \eta < \infty \]  

The proof goes in two steps: first it is shown that \( u(\eta) \leq u_S \) for \(-\infty < \eta < \infty\). Otherwise there would be a point \( \eta_0 \) with \( u'(\eta_0) = 0 \) and \( u(\eta_0) > u_S \). Equations (53) and (48) lead to a contradiction for both cases (59) and (60); secondly, if \( u(\eta_1) = u_S \) for some \( \eta_1 \), then \( u'(\eta_1) = 0 \) and thus from eqns (53) and (48) and from the unique solvability of the corresponding initial value problem, \( u = u_S \) and \( v = v_n \) for eqn (59), also \( v = v_n \) for eqn (60). This is in contradiction to the boundary conditions.

An immediate consequence of eqns (48) and (49) is that

\[ v'(\eta) > 0, \text{ if } v(\eta) > 0 \]  

and from this

Precipitation waves cannot exist

\[ u'(\eta) > 0 \text{ for } -\infty < \eta < \infty \]  

Hence, the only possibility left is a dissolution wave, which will be shown 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 van Duijn and Knabner,\(^3\) 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

\[ v(\eta) = 0 \text{ for } -\infty < \eta < L \]

\[ v(\eta) > 0 \text{ for } L < \eta < \infty \]

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 where relationships (52) together with (64) build the free boundary condition. The appearance of a dissolution front in the strict sense of eqn (64) is a consequence of the non-differentiable nature of the rate function due to the use of the Heaviside function. 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 Knabner\(^3\)). In other words, the solution would behave like solutions of the linear diffusion-advection equation with dominating advection. A further discussion (see van Duijn and Knabner\(^3\)) reveals

\[ u'(\eta) > 0 \text{ for } -\infty < \eta < \infty \]  

\[ u''(\eta) > 0 \text{ for } -\infty < \eta < L \]

\[ u''(\eta) < 0 \text{ for } L < \eta < \infty \]  

\[ v''(\eta) < 0 \text{ for } L < \eta < \infty \]

That is, \( u \) changes curvature at the dissolution front and this is the only position, where a jump according to eqn (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 eqns (53), (48)-(50) is equivalent to finding a number \( u^* < u_0 < u_\infty (= u_S) \) such that the solution of the initial value problem

\[ u' = \frac{q}{D}(u - u^*) - \frac{a}{D}(v - v^*) \text{ for } \eta > L \]

\[ v' = \frac{k}{a}(K - g(u_\infty; c)) \text{ for } \eta > L \]

\[ u(L) = u_0, \quad v(L) = 0 \]

fulfills

\[ u(\infty) = u_\infty, v(\infty) = v_n, v(\eta) > 0 \text{ for } \eta > L \]  

\[ u''(\eta) > 0 \text{ for } -\infty < \eta < \infty \]  

\[ u''(\eta) > 0 \text{ for } -\infty < \eta < L \]

\[ u''(\eta) < 0 \text{ for } L < \eta < \infty \]  

\[ v''(\eta) < 0 \text{ for } L < \eta < \infty \]  

\[ v'(L^+) > 0, \quad v'(L^-) = 0 \]
If such a value $u_0$ can be found then the solution of eqn (68) can be elongated to the desired solution by solving
\[
\begin{align*}
u' &= \frac{q-a}{D}(u - u^*) \quad \text{for } \eta < L \\
u(L) &= u_0
\end{align*}
\] (69)
The solution is given by
\[
\begin{align*}
u(\eta) &= (u_0 - u^*) \exp\left(\frac{q-a}{D}\eta\right) + u^* \quad \text{for } \eta \leq L
\end{align*}
\] (70)
Let $\ell$ be the straight line connecting $(u^*, v^*)$ and $(u_0, v_0)$, then according to the first equation of (68) the condition $\ell(u) = v$ describes the set of equilibrium points of the first ordinary differential equation given in (68) and for any $u' < u_0 < u_*$ we have
\[
u'(\eta) > 0, \quad \text{if } v(\eta) < \ell(u(\eta))
\] (71)
Furthermore
\[
u'(\eta) > 0, \quad \text{if } v(\eta) < u_*
\] (72)
Therefore, three cases can occur

Case A: $u$ and $v$ increase, until eventually, for some $\eta > L$, $v(\eta) = \ell(u(\eta))$, $v(\eta) < u_*$. 

Case B: $u$ and $v$ increase, until eventually, for some $\eta > L$, $u(\eta) = u_*$, $v(\eta) < \ell(u(\eta))$. 

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

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

I. $n = 0$
Select $u^* < u_0 < u_*$ small enough such that Case A occurs for $u_0 = u_0^1$. 
Select $u' < u_0 < u_*$ big enough such that Case B occurs for $u_0 = u_0^2$. 

II. $n := n + 1$, $u^{n+1} := \frac{1}{2}(u^n + u_0^n)$, compute $u$ and $v$ according to eqn (68) and $u_0 = u_0^{n+1}$ and check whether Case A or Case B occurs.
For Case A: $u^{n+1}_R, u^{n+1}_L$, for Case B: $u^{n+1}_R, u^{n+1}_L$, 
If Case C occurs or $|u^{n+1}_R - u^{n+1}_L|$ is small enough, stop, otherwise goto II.

This algorithm will at least produce sequences $u^n_L < u_0 < u^n_R$ such that $|u^n_R - u^n_L| \to 0$. The computation of $u$ and $v$ according to eqn (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 Hall and Watt) becomes decisive for the correct performance of the shooting algorithm. For the following examples the parameters still allowed the use of a method for a mildly stiff system with appropriately chosen fixed step size (see Ashour and Hanna).

### A basic numerical example

The parameters of the following basic example, called the reference case, and depicted in Fig. 1, are assembled in Table 1 and chosen analogously to the computation of Willis and Rubin, only the equilibrium case $k = \infty$ is considered, and most important, the charge distribution, $c$, of Willis and Rubin corresponds to the step function with $c^* = 2.0 \times 10^{-5}$, $c_* = 0$ rather than a constant $c = 0$. Therefore the computations of Willis and Rubin are in relation to the solutions of Part 2 of the paper and will be discussed there. $K$ is determined by $c_1^*$, $c_2^*$ and thus has to be different from Willis and Rubin, as we do not consider Debye–Hückel corrections in this computation. In Fig. 1 and all the following figures a translation is applied such that $L = 0$.

### The closed form solution for the linearized model

For the linearized model eqn (38), i.e. $g(u; c) = u$, $u^* = K$, the initial value $u_0$ from eqn (68) can be computed explicitly. Rewriting eqn (68) as the second order equation
\[
Du'' - (q-a)u' - k(u - K) = 0
\] (73)
we see that the general solution with the boundary condition $u(\infty) = u_* = u_0$ is given by
\[
u(\eta) = u_0 - (u_0 - u_*) \exp(-\lambda(\eta - L)) \quad \text{for } \eta \geq L
\] (74a)

| Table 1. Parameters of the reference case |
|-----------------|----------------|
| $\Theta$        | $0.32[-]$       |
| $\rho$          | $1.8[g/cm^3]$   |
| $q^*$           | $3.0 \times 10^{-3}[\text{cm/s}]$ |
| $\Theta D^*$    | $2.0 \times 10^{-3}[\text{cm/s}]$ |
| $M$             | $5.17, M_2 = \text{SO}_4^-$ |
| $n$             | $m = 1$         |
| $v(c_1, c_2)$   | $c_0 c_1$       |
| $c^*$           | $0$             |
| $k_1$           | $1, k_2 = 3.86884 \times 10^{-7}$ |
| $k^*$           | $-0.1, i.e. k = 0.1$ |
| $c_1^*$         | $2.0 \times 10^{-5}[\text{mm/cm}^3]$ |
| $c_2^*$         | $0[\text{mm/g}]$ |
| $c^*$           | $6.22 \times 10^{-4}$ |
| $c_2^*$         | $4.9 \times 10^{-6}$ |
with

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

and thus

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

The value $u_0$ is determined by the shooting requirement

$$\frac{k}{a} (u_s - u_0) \frac{1}{\lambda} = v(\infty) = v_*$$  \hspace{1cm} (76)$$

which gives, using eqn (54)

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

Fig. 1. The travelling wave solution for the reference parameters.

Fig. 2. The travelling wave solution for the reference case (mass action law) and the linearized model.
For the reference case, a comparison with the linearized model with $k$ chosen according to eqn (35) is shown in Fig. 2, which shows only slight variations.

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 = ∞', corresponds to the formal procedure

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

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

Travelling wave formulation

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

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

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

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

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

Reduced continuity of solutions

The travelling wave solutions for a sequence of rate parameters $k_n \to \infty$, and all other parameters and boundary conditions being the same, are expected to converge to a solution of (78)–(80). As seen later on, these limits, in general, have a jump in $v$. Therefore in the notion of travelling wave solutions for the equilibrium reaction, the continuity of $u$ only is required and finitely many jumps in $v$ are allowed 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 eqn (78). If the jumps of $Du'$ and $av$ cancel each other, then the combination

$$Du' + av \tag{81}$$

is continuous and we can interpret eqn (78) as

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

such that the jump relations are

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

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

The impossibility of precipitation waves

The discussion leading to the wave speed $a$ given by eqn (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 of having the ordinary differential eqn (48) at one's disposal (see van Duijn and Knabner, proof of Prop. 2.1). It can only be concluded that the fluid is not over-saturated. But again a precipitation wave is impossible and the dissolution wave has a simple structure leading to an explicit solution. This can be seen in the following.

In an $\eta$-interval where $v$ is positive, then from eqns (79) and (80) and the uniqueness of the solubility concentration (according to eqn (56)) we have $u = u_0$ and by eqn (53) $v = v_i$, where $v = v_i$ for a dissolution wave and $v = v'$ for a precipitation wave. Thus a wave induces a sequence of $\eta$-subintervals on which either $v = \bar{v} > 0$ or $u = u_0$ or on which $v = 0$. In the later subintervals $u$ is given explicitly by eqn (53) and the value $u = u_0$ is at the left boundary point of these subintervals.

From this we can conclude (compare van Duijn and Knabner, proof of Prop. 4.3 for dissolution waves) that precipitation waves cannot exist

$$(84)$$

A closed form solution for dissolution waves

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

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

$$u(\eta) = (u_0 - u*) \exp \left(\frac{q}{D} (\eta - L)\right) \quad \text{for} \quad \eta < L$$

$$u(\eta) = u_0 \quad \text{for} \quad \eta > L \tag{86}$$

Thus $\eta = L$ is the only point in which jumps occur, according to eqn (83), which can be made more precise by $|v| = v_i$ 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 to the free boundary condition of Willis and Rubin (p. 1563, (5d)) for this special case. As also $u(s(t), t) = u_0$, the transformation $\tilde{u} = u - u_0$ leads to the classical Stefan problem and is a special case of the transformation applied in Rubin.

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

To have a consistent modelling of the equilibrium and the non-equilibrium case, it is expected that the
solutions of eqns (47)–(50) converge to eqn (85) and (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 Fig. 1), 1, 10, 100 which clearly show a convergence from below to the equilibrium solution (85) and (86).

This observation can also be made rigorous (see van Duijn and Knabner,\(^3\) Th. 4.5). Furthermore, even the rate of convergence can be detected, which will not be shown for the linearized model by means of its closed form solution eqns (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 \( k < \infty \)

\[
k^{1/2}(u_0 - u(L)) \to \frac{(q - a)(u_0 - u)}{D^{1/2}}, \quad \text{for} \quad k \to \infty
\]

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 different initial values \( u(L) \) and \( u_0 \) at \( \eta = L \). From eqn (87) it can be seen that the same rate of convergence holds true. The result also extends to \( \eta > L \) by virtue of eqn (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**

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

\[
- au' - av' + qu' = 0
\]

\[
- av' = k(g(u,c) - Kw)
\]

\[
0 \leq w(\eta) \leq 1, \quad w(\eta) = 1, \quad \text{if} \quad v(\eta) > 0
\]

which satisfy the boundary and sign conditions (50) and (51). Analogous to \( k \to \infty \), it is expected that 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 eqns (88)–(90). As will be seen later on, these limits have in general a jump in \( u', v' \) and \( w \). Thus we require only the continuity 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

\[
\frac{\Delta v}{\Delta u}[u'] = \frac{aK}{a}[w]
\]

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

**The impossibility of precipitation waves**

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

\[
(q - a)(u - u*) = a(v - v*)
\]

i.e. the shapes of \( u \) and \( v \) are the same. The whole reasoning from eqns (57) to (62) holds true here also, 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

\[
v(\eta) = 0 \quad \text{for} \quad \eta \leq L
\]

\[
v = \frac{\Delta v}{\Delta u}(u - u*) \quad \text{for} \quad \eta > L
\]

\[
u(\eta) = u* \quad \text{for} \quad \eta \leq L
\]

\[
u' = \frac{k}{q - a}(K - g(u;c))
\]

\[
u(L) = u* \quad \text{for} \quad \eta > L
\]
An analysis of crystal dissolution fronts in flows through porous media

Fig. 4. Convergence of the travelling wave solution for \( D \to 0 \).

\( \begin{align*}
7.0 \times 10^{-4} & \\
3.0 \times 10^{-4} & \\
-15 & -10 & 0 & 5 & 10 & 15 \\
\text{eta} & \\
\text{Hyperbolic case - } u & \\
\text{D1} & \\
\text{D2} & \\
\text{D3} & \\
\text{Hyperbolic case - } v & \\
\text{D1} & \\
\text{D2} & \\
\text{D3} & \\
-15 & -10 & 0 & 5 & 10 & 15 & \text{eta} \\
\end{align*} \)

i.e. only the initial value problem in eqn (94) has to be resolved.

In particular, the jumps of eqn (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 eqns (47)–(50) to the ones of eqns (93) and (94) for \( D \to 0 \) can be clearly observed numerically (see Fig. 4, where the data of Table 1 are used with \( D = D_i \), \( i = 1, 2, 3 \), \( D_1 = 6.25 \times 10^{-4} \), \( D_2 = 2.76 \times 10^{-4} \), \( D_3 = 6.25 \times 10^{-6} \), \( D_1 \) 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 (van Duijn and Knabner\textsuperscript{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 \( D \to 0 \)

\[
1 \over D (u(L) - u^*) = \left( \frac{u_0 - u_*}{q - a} \right)^2 / \left( 4Dk \left( q - a \right)^2 + 2 \left( 1 + 4Dk \left( q - a \right)^2 \right)^{1/2} \right)
\]

\[
= \frac{(u_0 - u_*)k}{(q - a)^2}
\]

i.e. the convergence is linear in \( D \). This rate, even with the leading coefficient of eqn (95) can also be justified in general (see van Duijn and Knabner\textsuperscript{3}, Th. 5.4)) and it holds true for all arguments \( \eta \).

**CONCLUSIONS**

A model for transport and dissolution/precipitation was set up, where the kinetics of the reaction were taken into account. Contrary to other possible approaches, this model was 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.

**ACKNOWLEDGEMENT**

The authors are grateful to Prof. J. C. Friedly (Department of Chemical Engineering, University of Rochester, NY, USA) who provided us with very detailed comments and suggestions and helped us to clarify the presentation of the results.

**REFERENCES**

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. (Unpublished.)


10. Pawell, A. & Krannich, K.-D. Dissolution effect arising in transport in porous media which affect a chemical equilibrium. (Unpublished.)


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

The purpose of this Appendix is to indicate reasonable and sufficient conditions under which the function $g(x; c)$ according to eqn (27) is strictly monotone increasing in $x$ for $x > (c/m)_+$ and a fixed real number $c$, i.e. satisfies eqn (55), if the rate function is described according to the Debye–Hückel theory. The precipitation rate function $r$ from eqn (19) then takes the form (compare e.g. Garrels and Christ, Klotz and Rosenberg and Snoeyink and Jenkins)

$$r(c_1, c_2) = \gamma_1 c_1^n c_2^m (\frac{1}{n} (mx - c))^m$$

with positive integers $n$, $m$ and

$$\gamma_1 := \exp(-m^2a_1)$$

$$\gamma_2 := \exp(-n^2a_2)$$

$$a(I) := \frac{a_1}{1 + c^2a_2^2}$$

where $a_1$, $a_2$ are positive parameters, and $a(I) = \frac{1}{m^2c_1 + n^2c_2 + c}$. (A1)

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 $c$ is 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 $a_i$ in the definition of $\sigma = \sigma_0$. From eqn (14) $f(x) := g(x; c)$ takes the form

$$f(x) = \gamma_1^n \gamma_2^m (\frac{1}{n} (mx - c))^m$$

and

$$I(x) = c x + \beta, \text{ where}$$

$$\alpha := \frac{1}{2} (mn(n + m))$$

$$\beta := \frac{1}{2} (c - nc)$$

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

$$4a_2 \geq nm(n + m)a_1$$

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

Let $K > 0$ and consider the equation

$$f(x) = K \text{ or equivalently } Kg(x) = h(x)$$

where

$$g(x) := \exp(\gamma_0 f(x))$$

with

$$\gamma := mn(n + m)$$

$$h(x) := x^n (\frac{1}{n} (mx - c))^m$$

Then an equivalent formulation of the assertion is: for $K > 0$ there exists a unique solution $x = x_K > (c/m)_+$ of (A8) and the solution depends monotonically on $K$, i.e.

$$0 < K_1 < K_2 \Rightarrow x_K < x_{K_1}$$

The functions $g$, $h$ have the following properties for $x > (c/m)_+$: $g$ and $h$ are strictly monotone, increasing and smooth for $x > (c/m)_+$.

$$g((c/m)_+) = 1, \quad g(\infty) = \exp(\gamma_1/a_2)$$

$$h((c/m)_+) = 0, \quad h(\infty) = -\infty$$

$h$ is strictly convex for $x > (c/m)_+$.

Therefore the existence of a solution $x_K$ of (A8) is clear, and $h(x_K) > K$ 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 (A11) is satisfied, which can be seen as follows

\[
\begin{align*}
  h(x) &< K g(x) \quad \text{for} \quad (c/m)_+ \leq x < x_K \\
  h(x) &> K g(x) \quad \text{for} \quad x > x_K
\end{align*}
\]

(A13)

Let \( 0 < K_1 < K_2 \) and \( x_1, x_2 \) be the corresponding solutions of (A8), then by means of (A12) and (A13)

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

and

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

and thus \( x_1 < x_2 \). A sufficient condition for concavity of \( g \) (for \( x \geq (c/m)_+ \)) is given by (A7), which can be seen by direct computation

\[
g(x) = g_1(g_2(x)) \quad \text{with} \quad g_1 = \exp \quad g_2 = \gamma \sigma(I)
\]

i.e.

\[
g''(x) = g(x)(g_2'(x) + g_2''(x))
\]

\[
= g(x)((\gamma \alpha \sigma'(I))^2 + \gamma \alpha^2 \sigma''(I))
\]

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

\[
\gamma \sigma'^2(I) + \sigma''(I) = -\frac{3}{4} \frac{a_1 a_2^3}{f^{3/2}(1 + a_2 f^{1/2})^4}
\]

\[
\times \left[ f + \frac{4 a_2 - \gamma a_1}{3 a_2^2} f^{1/2} + \frac{1}{3 a_2^2} \right]
\]

(A14)

If (A7) is satisfied, then the square bracket in (A14) is strictly positive for \( x \geq (c/m)_+ \), i.e. \( f \geq 0 \), and thus \( g''(x) < 0 \).