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Existence and Uniqueness of a Global Solution for Reactive Transport with Mineral Precipitation-Dissolution and Aquatic Reactions in Porous Media

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Abstract

We consider a macroscopic (averaged) model of transport and reaction in the porous subsurface. The model consists of PDEs for the concentrations of the mobile (dissolved) species and of ODEs for the immobile (mineral) species. For the reactions we assume the kinetic mass action law. The constant activity of the mineral species leads to set-valued rate functions or complementarity conditions coupled to the PDEs and ODEs. In this paper we first prove the equivalence of several formulations in a weak sense. Then we prove the existence and the uniqueness of a global solution for a multi-species multi-reaction setting with the method of a priori estimates. Besides the mineral precipitation-dissolution reactions the model also allows for aqueous reactions, i.e., reactions among the mobile species. Both in the mineral precipitation–dissolution rates and in the aqueous reaction rates we consider polynomial nonlinearities of arbitrarily high order.

Key words. Existence of global solution, reactive transport in porous media, kinetic mineral precipitation-dissolution, complementarity problems, law of mass action

AMS subject classifications. 35A01, 35D35, 35Q86

1 Introduction

Let us consider a macroscopic model of reactive transport in a porous medium that is filled or partially filled by a fluid. We assume to have several chemical species dissolved in the fluid. The evolution of the concentrations of these species is described by advection-diffusion-dispersion-reaction equations, i.e., by partial differential equations (PDEs). Besides, we assume that there are a number of minerals which are part

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of the soil matrix, i.e., of the skeleton of the porous medium. In an averaged sense, the concentrations of these immobile mineral species are described by ordinary differential equations (ODEs). There are reactions taking place among the mobile species and among mobile and immobile species. The latter describe the precipitation and the dissolution of minerals. The reactions are modeled with the law of mass action, a highly nonlinear kinetic rate law. A special difficulty arises, since the mathematical description of mineral precipitation-dissolution contains the Heaviside "function" (see [10, 19, 20, 21]), or a complementarity condition (see [11, Sec. 4.6]), or an ODE with a discontinuous rate function (see [2, 6]).

Models of reactive transport in porous media play an important role especially in the computational geosciences; during many decades many numerical codes were developed to solve reactive transport problems in porous media numerically. Extensions of these numerical models to mineral precipitation-dissolution reactions and the related complementarity conditions can be handled well by semismooth Newton methods [3, 13], for instance.

However, as soon as it comes to a mathematical analysis of the model equations, the literature becomes scarcer. For mass-action reactive transport models *without* immobile species, with all species dissolved in the fluid, proofs of the existence of a global solution, i.e., a solution on arbitrarily large time intervals, can be found in [12], based on a Lyapunov functional representing the Gibbs free energy, or in [16], based on a maximum principle, or, even for species-dependent diffusion, in [4], or, circumventing the question of L^∞-boundedness by considering so-called renormalized solutions, in [5]. The main challenge in these considerations is the strong nonlinearity of the rate terms.

One direction to extend these results from the situation where all species are mobile to a situation where some species are immobile is the consideration of sorption reactions. For example, in [1] a pore scale model with sorption reactions at the walls of the pores is considered; existence of a global solution is shown. However, it is well known that such a model with smooth rates is not suited to describe the precipitation-dissolution of minerals.

For the mineral precipitation-dissolution model we are considering here, we have to take into account non-smooth or set-valued reactions. In the literature one can find some works dealing with this problem. In [9] the existence for the case of one single kinetic reaction between one mobile and one mineral species (and no other chemical reaction) is proven. In [21] and [14] a model on the pore scale is considered, where the precipitation-dissolution process is descibed by an ODE on the interface between pore space and soil matrix, and a corresponding boundary condition for the mobile species. For this model the existence of a global solution is proven, and via homogenization techniques and two-scale convergence an existence result for the macro-scale problem follows. However, it still covers only the case with one mineral and without any aqueous reactions.

In [2] a macro-scale model is considered, and existence of a solution is shown by proving convergence of a finite volume scheme. However, also this model does not contain any aqueous reactions, i.e., reactions among the mobile species, and only one single kinetic mineral reaction.

In this article techniques from [9], [11], and [21] will be adapted and extended to prove the existence and uniqueness of a rather general formulation of the macro-scale problem. Our model includes an arbitrary number of kinetic reactions among the mobile species and an arbitrary number of kinetic mineral reactions. Comparing our model to the existing literature, let us emphasize that the aqueous reaction rates and the precipitation rates and the dissolution rates may contain polynomial terms of arbitrary order. Since we go beyond the setting of one mobile and one immobile species, the question arises which assumptions have to be posed on the stoichiometric matrices occuring in our multi-species model. It turns out that a condition on the stoichiometric matrix is required, but this condition is fulfilled for typical reaction networks. In fact, at least as far as the aquatic reactions are concerned, our condition is even milder than the typical assumption of mass conservation (conservation of the number of atoms), which is heavily exploited e.g. in [4]. Like most models used for numerical simulations of reactive transport in porous media, we assume a species-independent diffusion for our analysis. Our focus lies on the handling of the complementarity condition and in a mild condition on the stoichiometry in a multi-species multi-reaction setting. Let us mention that we neither use a discrete scheme nor a micro-scale model as an intermediate step on the way to establish existence of a global solution.

This article consists of two parts. In Sec. 2 and 3 we introduce different formulations of reactions with minerals and show that they are equivalent in a weak sense. We use a simple situation of just one mineral and two dissolved species, but the considerations remain valid for larger systems. From these equivalent formulation we choose the Heaviside formulation for the second part of the paper, which consists of Secs. 4 to 6. In Sec. 4 we present our general multi-species multi-reaction model. In Sec. 5 we present our main result, which is the proof of existence of a solution on arbitrarily large time intervals without 'blow ups', i.e., the solution remains bounded in L^∞. In Sec. 6 we prove that the solution is unique.

2 Formulations of Kinetic Mineral Reactions

In this section we consider a model problem with two mobile species A, B, one immobile species $\overline{\mathrm{C}}$, and one kinetic mineral reaction

$$n\mathrm{A} + m\mathrm{B} \leftrightarrow \overline{\mathrm{C}}$$

with stoichiometric coefficients $m, n \in \mathbb{N}$. Let c_1, c_2 be the concentrations of the mobile species (in mole per fluid volume), $\theta \in (0,1)$ the water content (water volume per total volume), $\bar{c}$ the concentration of the mineral (in mole per total mass of the porous skeleton) and ρ the bulk density (mass of the porous skeleton per total volume) For the three unknowns $c_1, c_2, \bar{c}$ we get the two partial differential equations

$$\begin{aligned} \partial_t(\theta c_1) + Lc_1 &= -n\rho\partial_t\bar{c} \\ \partial_t(\theta c_2) + Lc_2 &= -m\rho\partial_t\bar{c} \end{aligned}$$

expressing the mass balance. Here, L is a transport operator which may cover advection (with respect to a given flow field), molecular diffusion, and dispersion. We assume that the precipitation rate r_p is given by law of mass action with so-called ideal activity coefficients,

$$r_p(c_1, c_2) = k_p c_1^n c_2^m , \tag{1}$$

and that the mineral has a so-called constant activity, i.e., the dissolution rate r_d is a constant k_d independent of $\bar{c}$, if the mineral is present,

$$r_d = k_d, \text{ if } \bar{c} > 0 ,$$

$k_p, k_d > 0$. For the equation describing the concentration of the mineral being subject to precipitation and dissolution, the formulation $\rho\partial_t\bar{c} = \theta(r_p(c_1, c_2) - k_d)$ is only reasonable as long as $\bar{c} > 0$. In order to cover also the situation of a total dissolution of the mineral in some parts of the domain there are different formulations used in the literature:

Formulation with set-valued rate function

In [10, 19, 20, 21] a formulation with a set-valued rate function

$$\begin{aligned} \rho\partial_t\bar{c} &= \theta(r_p(c_1, c_2) - k_d w) \\ w &\in H(\bar{c}) \end{aligned} \tag{2}$$

is used where H is the set-valued Heaviside "function"

$$H(u) = \begin{cases} \{1\} & \text{for } u > 0 \\ [0, 1] & \text{for } u = 0 \\ \{0\} & \text{for } u < 0 . \end{cases} \tag{3}$$

Formulation with complementarity condition

Like in the equilibrium case [3, 13] it is also possible to formulate this kinetic mineral problem as a complementarity condition (see [11, Sec. 4.6])

$$\begin{aligned} \bar{c}\,(\rho\partial_t\bar{c} - \theta(r_p(c_1, c_2) - k_d)) &= 0 \\ \bar{c} \geq 0,\ \rho\partial_t\bar{c} - \theta(r_p(c_1, c_2) - k_d) &\geq 0 . \end{aligned} \tag{4}$$

Formulation with discontinuous rate function

Formulations with discontinuous rate functions are used as well. In [6] the following formulation with a case distinction can be found:

$$\rho\partial_t\bar{c} = \begin{cases} \theta(r_p(c_1, c_2) - k_d) & \text{for } (\bar{c} > 0) \vee (r_p(c_1, c_2) - k_d > 0) \\ 0 & \text{for } (\bar{c} = 0) \wedge (r_p(c_1, c_2) - k_d \leq 0) \end{cases} \tag{5}$$

Let us compare this with the formulation used in [2] which reads

$$\rho\partial_t\bar{c} = \theta(F^+(c_1, c_2) - \text{sign}^+(\bar{c})F^-(c_1, c_2)) \tag{6}$$

with

$$F(c_1, c_2) := r_p(c_1, c_2) - k_d .$$

Here we have used the following notation:

$$x^+ := \max\{0, x\}, \qquad x^- := (-x)^+,$$

$$\operatorname{sign}(x) := \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x = 0 \\ -1 & \text{for } x < 0 \end{cases}, \qquad \operatorname{sign}^+(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x \leq 0 \,. \end{cases}$$

It holds $x = x^+ - x^-$.

The two formulations with the discontinuous rates (5) and (6) are identical for $\bar{c} \geq 0$. This can be seen in the following way: For $t \in (0, T)$ such that $\bar{c}(t) > 0$ we have $\operatorname{sign}^+(\bar{c}(t)) = 1$ and so the right-hand side of (6) becomes $\theta F(c_1(t), c_2(t))$. This coincides with (5). For $t \in (0, T)$ such that $\bar{c}(t) = 0$ we have $\operatorname{sign}^+(\bar{c}(t)) = 0$ and so the right-hand side of (6) becomes $\theta F^+(c_1(t), c_2(t))$, i.e., the right-hand side is $\theta F(c_1(t), c_2(t))$ for $F(c_1(t), c_2(t)) > 0$ and 0 for $F(c_1(t), c_2(t)) \leq 0$. This also coincides with (5). For $\bar{c} < 0$ (5) is not defined.

3 Equivalence of the Different Formulations

3.1 States of equilibrium

In the following it is always assumed that $r_p(c_1, c_2)$ is nonnegative (e.g., by assuming (1) and $c_{1,2} \geq 0$).

We observe that the formulation with the set-valued rate function (2) is constructed in such a way that the states of equilibrium are

$$((r_p(c_1, c_2) = k_d) \wedge (\bar{c} > 0)) \vee ((r_p(c_1, c_2) \leq k_d) \wedge (\bar{c} = 0)) \tag{7}$$

(see [10]). Formally the formulation with the set-valued rate function has the additional state of equilibrium $((r_p(c_1, c_2) = 0) \wedge (\bar{c} < 0))$.

The formulation with the complementarity condition (4) leads to the states of equilibrium

$$\begin{aligned} \bar{c}\,(r_p(c_1, c_2) - k_d) &= 0 \\ \bar{c} \geq 0,\ -(r_p(c_1, c_2) - k_d) &\geq 0\,. \end{aligned}$$

It is obvious that these states of equilibrium are the same as (7).

And the formulation with the discontinuous rate function (6) leads to the states of equilibrium

$$F^+(c_1, c_2) - \operatorname{sign}^+(\bar{c}) F^-(c_1, c_2) = 0\,.$$

For $\bar{c} > 0$ we have $\operatorname{sign}^+(\bar{c}) = 1$ and so we get $F(c_1, c_2) = 0$. With the definition of F it follows that $r_p(c_1, c_2) = k_d$. For $\bar{c} = 0$ we have $\operatorname{sign}^+(\bar{c}) = 0$. This yields $F^+(c_1, c_2) = 0$, which is equivalent to $F(c_1, c_2) \leq 0$. Plugging in the definition of F leads to $r_p(c_1, c_2) \leq k_d$. So for nonnegative mineral concentration $\bar{c}$ the states of equilibrium are exactly (7). For $\bar{c} < 0$ there are the states of equilibrium $r_p(c_1, c_2) \leq k_d$.

3.2 Pointwise considerations

The different formulations for the kinetic mineral problem are not pointwise equivalent. As a consequence, solutions of the formulation with the set-valued rate function are not always solutions of the formulation with the discontinuous rate function. For example, if travelling wave solutions of the formulation with the set-valued rate function, which are piecewise continuously differentiable with right-continuous derivative are considered, like it is done in [19], then these solutions are not solutions to the formulation with the discontinuous rate function.

This can be seen in the following way: A travelling wave solution is a function of the variable $\eta := x - at$ with the wave speed $a > 0$. Let η_d be a point of discontinuity of $\partial_t \bar{c}$ with $\bar{c}(\eta) = 0$ for $\eta \leq \eta_d$ and $r_p(\eta_d) < k_d$. Such points η_d exist in travelling wave solutions (see [10, Sec. 3] for travelling wave solutions). Because of $\bar{c}(\eta) = 0$ for $\eta \leq \eta_d$ it holds $\partial_t \bar{c}(\eta) = 0$ for $\eta < \eta_d$. As $\partial_t \bar{c}$ is continuous from the right $\partial_t \bar{c}(\eta_d) = \lim_{\eta \searrow \eta_d} \partial_t \bar{c}$. This limit is not zero because we have assumed that $\partial_t \bar{c}$ is discontinuous at η_d. But (5) yields $\partial_t \bar{c}(\eta_d) = 0$ because of $\bar{c}(\eta_d) = 0$. So the travelling wave solution of the formulations with the set-valued rate function is not a solution of the formulation with the discontinuous rate function.

However, if we consider weak solutions we will see that the three formulations are equivalent.

3.3 Weak solutions

We assume that the concentrations of the mobile species $c_1, c_2 : \Omega \times [0,T]$ are given such that $r_p(c_1, c_2) \in L^\infty(0,T)$ for $x \in \Omega$. In this section we study weak solutions of the three different formulations. A weak solution of the set-valued formulation is (compare [2]), for a given $x \in \Omega$, a pair of functions $(\bar{c}, w) \in H^1(0,T) \times L^\infty(0,T)$ which fulfills

$$\int_0^T (\rho \partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d w))\phi \, dt = 0 \qquad \forall \phi \in H_0^1(0,T) \tag{8}$$

$$w \in H(\bar{c}) \qquad \text{a.e. in } (0,T) \tag{9}$$

$$\bar{c}(0) = \bar{c}_0 \,. \tag{10}$$

In case of the complementarity formulation, $\bar{c} \in H^1(0,T)$ is a weak solution if

$$\bar{c}\,(\rho \partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d)) = 0 \qquad \text{a.e. in } (0,T) \tag{11}$$

$$\bar{c} \geq 0 \qquad \text{in } (0,T) \tag{12}$$

$$\rho \partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d) \geq 0 \qquad \text{a.e. in } (0,T) \tag{13}$$

$$\bar{c}(0) = \bar{c}_0 \,. \tag{14}$$

And using the formulation with a discontinuous rate function, $\bar{c} \in H^1(0,T)$ is a weak solution if

$$\int_0^T (\rho \partial_t \bar{c} - \theta(F^+(c_1, c_2) - \mathrm{sign}^+(\bar{c}) F^-(c_1, c_2)))\phi \, dt = 0 \quad \forall \phi \in H_0^1(0,T) \tag{15}$$

$$\bar{c}(0) = \bar{c}_0 \,. \tag{16}$$

Lemma 1 *A weak solution $\bar{c}$ of the formulation with the set-valued rate function, (8)-(10), is nonnegative if the initial value $\bar{c}_0$ is nonnegative.*

Proof. Using
$$\phi(s) = \begin{cases} -\bar{c}^-(s) & \text{for } s \le t \\ 0 & \text{for } s > t \end{cases}$$
for $t \in (0,T)$ as test function in (8) yields
$$\int_0^t \rho\, \partial_t \bar{c}(-\bar{c}^-) = \int_0^t \theta\,(\underbrace{r_p(c_1,c_2)}_{\ge 0} - k_d w)(\underbrace{-\bar{c}^-}_{\le 0})\, ds \le \int_0^t \theta k_d w \bar{c}^- \,.$$
Because of
$$\int_0^t \partial_t \bar{c}(-\bar{c}^-)\, ds = \frac{1}{2}\int_0^t \partial_t (\bar{c}^-)^2\, ds = \frac{1}{2}(\bar{c}^-(t))^2 - \frac{1}{2}(\bar{c}^-(0))^2$$
we obtain the estimate
$$\frac{1}{2}\rho\,(\bar{c}^-(t))^2 \le \int_0^t \theta k_d w \bar{c}^-\, ds + \frac{1}{2}\rho\,(\bar{c}^-(0))^2 \,.$$
The first term on the right-hand side is zero because one of the factors w, $\bar{c}^-$ is zero a.e. due to (9) and the second term is zero due to the assumption that $\bar{c}_0$ is nonnegative. Hence, $\bar{c}^-$ is the zero function. That concludes the proof. □

Let us state the following well-known Lemma (for a proof, see, e.g., Lemma 7.7 in [8], which is based on Stampacchia's theorem).

Lemma 2 *Let $u \in H^1(\Omega)$. Then $Du = 0$ a.e. on every subset of Ω where u is constant.*

To prove the following two theorems we apply similar strategies as in [2, Proposition 3.4] where the equivalence of the formulation with a discontinuous rate function to a formulation similar to a complementarity condition is shown.

Theorem 3 *The formulation with the set-valued rate function, (8)-(10), and the formulation with the complementarity condition, (11)-(14), are equivalent.*

Proof. "$\Leftarrow$": Let $\bar{c} \in H^1(0,T)$ be a weak solution of the complementarity formulation (11)-(14). First we define the set $A := \{t \in (0,T) |\, \bar{c}(t) = 0\}$ and its complement $\bar{A} := \{t \in (0,T) |\, \bar{c}(t) > 0\}$. We set
$$w = \begin{cases} \frac{1}{k_d} r_p(c_1,c_2) & \text{on } A \\ 1 & \text{on } \bar{A}\,. \end{cases}$$

Because of (12) we can split the integral in (8) in an integral over A and an integral over $\bar{A}$:
$$\int_0^T (\rho\partial_t \bar{c} - \theta(r_p(c_1,c_2) - k_d w))\phi\, dt$$
$$= \int_A (\rho\partial_t \bar{c} - \theta(\underbrace{r_p(c_1,c_2) - r_p(c_1,c_2)}_{=0}))\phi\, dt + \int_{\bar{A}} (\rho\partial_t \bar{c} - \theta(r_p(c_1,c_2) - k_d))\phi\, dt$$

By Lemma 2, on A we have $\partial_t \bar{c} = 0$ a.e. and so the first integral vanishes. Because of the complementarity condition (11) $\rho\partial_t \bar{c} - \theta(k_p r(c_1, c_2) - k_d)$ is zero a.e. on $\bar{A}$ and so the second integral vanishes, too. That proves (8).

Using again that $\partial_t \bar{c} = 0$ a.e. on A by Lemma 2 we obtain from (13) that

$$\begin{aligned} 0 - \theta(r_p(c_1, c_2) - k_d) &\geq 0 \qquad \text{a.e. on } A \\ \Leftrightarrow \frac{1}{k_d} r_p(c_1, c_2) &\leq 1 \qquad \text{a.e. on } A\,. \end{aligned}$$

That proves (9).

"$\Rightarrow$": Let $(\bar{c}, w) \in H^1(0,T) \times L^\infty(0,T)$ be a weak solution of the formulation with the set-valued rate function (8)-(10). According to Lemma 1 $\bar{c}$ is nonnegative. So the inequality (12) is valid. From (8) it follows

$$\begin{aligned} \rho\partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d w) &= 0 \qquad \text{a.e. in } (0,T) \\ \Leftrightarrow \rho\partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d) &= \theta k_d \underbrace{(1 - w)}_{\geq 0} \qquad \text{a.e. in } (0,T)\,. \end{aligned}$$

$1 - w$ is nonnegative a.e. due to (9). That proves (13). Furthermore we get with the relation above

$$\bar{c}\,(\rho\partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d)) = \bar{c}\,\theta k_d(1 - w) = 0 \qquad \text{a.e. in } (0,T)\,.$$

The product on the right-hand side is zero a.e. because $\bar{c}$ is nonnegative and so one of the factors $\bar{c}$, $1 - w$ is zero a.e. due to (9). This proves (11). □

Theorem 4 *The formulation with the discontinuous rate function (15)-(16) and the formulation with the complementarity condition (11)-(14) are equivalent.*

Proof. "$\Leftarrow$": Let $\bar{c} \in H^1(0,T)$ be a weak solution of the complementarity formulation (11)-(14). First we define the set $A := \{t \in (0,T) |\, \bar{c}(t) = 0\}$ and its complement $\bar{A} := \{t \in (0,T) |\, \bar{c}(t) > 0\}$. It holds

$$F^+(c_1, c_2) - \text{sign}^+(\bar{c}) F^-(c_1, c_2) = \begin{cases} F^+(c_1, c_2) & \text{on } A \\ F(c_1, c_2) & \text{on } \bar{A}\,. \end{cases}$$

Because of (12) we can split the integral in (15) in an integral over A and an integral over $\bar{A}$:

$$\begin{aligned} &\int_0^T (\rho\partial_t \bar{c} - \theta(F^+(c_1, c_2) - \text{sign}^+(\bar{c}) F^-(c_1, c_2)))\phi \, dt \\ &= \int_A (\rho\partial_t \bar{c} - \theta F^+(c_1, c_2))\phi \, dt + \int_{\bar{A}} (\rho\partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d))\phi \, dt \end{aligned} \tag{17}$$

Because of the complementarity condition (11), $\rho\partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d)$ is zero a.e. in $\bar{A}$ and so the second integral vanishes.

By Lemma 2 we have $\partial_t \bar{c} = 0$ on A a.e. Using this it follows from (13) that

$$\begin{aligned} 0 - \theta F(c_1, c_2) &\geq 0 \qquad \text{a.e. on } A \\ \Leftrightarrow F(c_1, c_2) &\leq 0 \qquad \text{a.e. on } A \\ \Rightarrow F^+(c_1, c_2) &= 0 \qquad \text{a.e. on } A\,. \end{aligned}$$

So the first integral in (17) vanishes, too. That proves (15).

"$\Rightarrow$": Let $\bar{c}$ be a weak solution of the formulation with the discontinuous rate function (15)-(16). If for $t \in (0, T)$ it holds $\bar{c}(t) \leq 0$ then it follows that a.e.

$$\begin{aligned} \rho \partial_t \bar{c}(t) &= \theta(F^+(c_1(t), c_2(t)) - \underbrace{\text{sign}^+(\bar{c}(t))}_{=0} F^-(c_1(t), c_2(t))) \\ &= \theta F^+(c_1(t), c_2(t)) \geq 0\,. \end{aligned}$$

If $\bar{c}_0 \geq 0$ it follows that $\bar{c}$ is nonnegative. That proves (12).

Due to (15) and the definition of F we have a.e. in $(0, T)$

$$\begin{aligned} &\rho \partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d) \\ &\quad = \theta(F^+(c_1, c_2) - \text{sign}^+(\bar{c}) F^-(c_1, c_2)) - \theta(F^+(c_1, c_2) - F^-(c_1, c_2)) \\ &\quad = \theta(\underbrace{1 - \text{sign}^+(\bar{c})}_{\geq 0}) \underbrace{F^-(c_1, c_2)}_{\geq 0} \geq 0\,. \end{aligned}$$

That proves (13). Furthermore using this identity we get

$$\int_0^T \bar{c}\,(\rho \partial_t \bar{c} - \theta(r_p(c_1, c_2) - k_d))\phi\, dt = \int_0^T \bar{c}\,\theta(1 - \text{sign}^+(\bar{c})) F^-(c_1, c_2)\phi\, dt\,.$$

One of the factors $\bar{c}$, $1 - \text{sign}^+(\bar{c})$ is always zero because for $t \in (0, T)$ such that $\bar{c}(t) > 0$ it holds $\text{sign}^+(\bar{c}(t)) = 1$. So the integral on the right-hand side vanishes. That proves (11). □

4 A multi-species multi-reaction model

Let us consider a more general setting where we have $I \in \mathbb{N}$ mobile species X_i und $J_{mob} \in \mathbb{N}$ kinetic reactions among the mobile species, as well as J_{min} mineral species $X_{min,j}$ and mineral reactions. The vector of the mobile species concentrations is denoted by $\boldsymbol{c} = (c_1, ..., c_I)^T$ and the vector of the mineral species concentrations by $\bar{\boldsymbol{c}}_{min} = (\bar{c}_1, ..., \bar{c}_{J_{min}})^T$. From the three formulations of the precipitation-dissolution rates which we found equivalent in Sec. 3, we choose the formulation with the Heaviside function. The goal is to prove the existence of a global solution. The reactions can be expressed as

$$\underline{\sigma}_{1,j} X_1 + ... + \underline{\sigma}_{I,j} X_I \longleftrightarrow \overline{\sigma}_{1,j} X_1 + ... + \overline{\sigma}_{I,j} X_I\,, \quad j = 1, ..., J_{mob}, \qquad (18)$$

$$\underline{\tau}_{1,j} X_1 + ... + \underline{\tau}_{I,j} X_I \longleftrightarrow \overline{\tau}_{1,j} X_1 + ... + \overline{\tau}_{I,j} X_I + X_{min,j}\,, \quad j = 1, ..., J_{min} \quad (19)$$

We assume that all the stoichiometric coefficients $\underline{\sigma}_{ij}, \overline{\sigma}_{ij}, \underline{\tau}_{ij}, \overline{\tau}_{ij}$ are nonnegative, and that $\overline{\sigma}_{ij}\underline{\sigma}_{ij} = 0$ and $\overline{\tau}_{ij}\underline{\tau}_{ij} = 0$ for all i, j, and we set $s_{ij} := \overline{\sigma}_{ij} - \underline{\sigma}_{ij}$, $s_{min,ij} := \overline{\tau}_{ij} - \underline{\tau}_{ij}$, $\boldsymbol{S}_{mob} := (s_{ij}) \in \mathbb{R}^{I,J_{mob}}$, $\boldsymbol{S}_{min} := (s_{min,ij}) \in \mathbb{R}^{I,J_{min}}$. Let Ω be a bounded domain in $\mathbb{R}^n$, $Q_T := \Omega \times (0,T)$, $S_T := \partial\Omega \times (0,T)$, with $T > 0$ arbitrarily large. Let us define the spaces

$$\begin{aligned} W_p^{2,1}(Q_T) &= \{v \in L^p(Q_T) \,|\, \partial_t v \in L^p(Q_T), \nabla_x v \in L^p(Q_T)^n, \nabla_x^2 v \in L^p(Q_T)^{n^2}\}, \\ \mathcal{L}(Q_T) &= \{v \in L^\infty(Q_T) \,|\, \partial_t v \in L^\infty(Q_T)\}, \\ \mathcal{C}(\overline{Q}_T) &= \{v \in C(\overline{Q}_T) \,|\, \partial_t v \in C(\overline{Q}_T)\}. \end{aligned} \tag{20}$$

We are looking for a tuple $(\boldsymbol{c}, \bar{\boldsymbol{c}}_{min}, \boldsymbol{w}) \in W_p^{2,1}(Q_T)^I \times \mathcal{L}(Q_T)^{J_{min}} \times L^\infty(Q_T)^{J_{min}}$ with

$$\partial_t \boldsymbol{c} + L\boldsymbol{c} = \boldsymbol{S}_{mob}\boldsymbol{r}_{mob}(\boldsymbol{c}) + \boldsymbol{S}_{min}\boldsymbol{r}_{min}(\boldsymbol{c}, \boldsymbol{w}) \quad \text{on } Q_T \tag{21}$$
$$\partial_t \bar{\boldsymbol{c}}_{min} = \boldsymbol{r}_{min}(\boldsymbol{c}, \boldsymbol{w}) \quad \text{on } Q_T \tag{22}$$
$$\boldsymbol{c}(\cdot, 0) = \boldsymbol{c}_0 \quad \text{on } \overline{\Omega} \tag{23}$$
$$\boldsymbol{w} \in H(\bar{\boldsymbol{c}}_{min}) \quad \text{on } Q_T \tag{24}$$
$$\bar{\boldsymbol{c}}_{min}(\cdot, 0) = \bar{\boldsymbol{c}}_{min,0} \quad \text{on } \overline{\Omega} \tag{25}$$
$$d\partial_{\boldsymbol{\nu}}\boldsymbol{c} = \beta(\boldsymbol{c} - \boldsymbol{c}^*) \quad \text{on } S_T\,. \tag{26}$$

In this formulation we have the linear transport operator $Lu_i := -\nabla\cdot(d\nabla u_i) + \boldsymbol{q}\cdot\nabla u_i$, and (with a slight abuse of notation) $Lu = (Lu_1, ..., Lu_I)$; the inclusion with the set-valued Heaviside "function" (cf. (3)) is meant componentwise $w_j \in H(\bar{c}_{min,j})$, $j = 1, ..., J_{min}$, and the rates $\boldsymbol{r}_{mob}$ for the J_{mob} reactions among the mobile species according to law of mass action

$$r_{mob,j}(\boldsymbol{c}) = k_{f,j} \prod_{\substack{i=1 \\ s_{ij}<0}}^{I} c_i^{-s_{ij}} - k_{b,j} \prod_{\substack{i=1 \\ s_{ij}>0}}^{I} c_i^{+s_{ij}}\,, j = 1, ..., J_{mob}\,. \tag{27}$$

Furthermore we have the J_{min} mineral reaction rates $\boldsymbol{r}_{min}$ that are of the form

$$r_{min,j}(\boldsymbol{c}, \boldsymbol{w}) = k_{p,j} \prod_{\substack{i=1 \\ s_{min,ij}<0}}^{I} c_i^{-s_{min,ij}} - k_{d,j} \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} c_i^{s_{min,ij}}\, w_j \tag{28}$$

(see some remarks on the modeling of the precipitation-dissolution rates at the end of the section).

The problem (21)-(28) is denoted **(*P*)**. The boundary conditions include the cases (i) flux boundary conditions ($\beta = \boldsymbol{q}\cdot\boldsymbol{\nu} \le 0$ on the inflow boundary) and (ii) homogeneous Neumann boundary conditions ($\beta = 0$) (compare [9, (2.10)]).

To prove an a priori estimate with help of the maximum principle the following assumption is needed:

Assumptions 5 *There is a vector $\boldsymbol{s}^\perp \in \mathbb{R}^I$ with only strictly positive entries which is perpendicular to all those columns of the matrix $\boldsymbol{S} = (\boldsymbol{S}_{mob}|\boldsymbol{S}_{min})$ which have at least one strictly positive entry.*

Let us discuss whether this assumption is justified and which situations are covered by this assumption.

If a particle of every species consists of a positive number of atoms (a reasonable assumption), then taking $(\boldsymbol{s}^{\perp})_i$ as the number of atoms of which a particle of species i consists yields a positive vector $\boldsymbol{s}^{\perp}$ which is orthogonal to all columns of $\boldsymbol{S}_{mob}$, since the orthogonality represents the conservation of the number of atoms in the reactions (18). When additionally all entries of $\boldsymbol{S}_{min}$ are nonpositive, i.e., in the reaction equation (19) of each mineral reaction no mobile species are on the same side as the mineral (i.e., $\overline{\tau}_{i,j} = 0$), then the assumption is always fulfilled.

Note that this (i.e., every mobile particle consists of a positive number of atoms, and the aqueous reactions conserve the number of atoms, and there is no reaction with mineral and mobile species on the same side) is sufficient, but not necessary for the assumption to hold: Sometimes species which are present in abundance and have an almost constant concentration, such as, e.g., water, are taken out of the system in order to reduce the size. A reaction $\mathrm{OH}^- + \mathrm{H_3O}^+ \leftrightarrow 2\,\mathrm{H_2O}$ would be modelled by the rate $r_j = k_{f,j} c_{[OH^-]} c_{[H_3O^+]} - \tilde{k}_{b,j}$ with $\tilde{k}_{b,j}$ being the product of $k_{b,j}$ and $c^2_{[H_2O]}$ (assumed to be constant). Although there is no conservation of atoms in this model (hydroxide and oxonium react to 'nothing' by this rate r_j), the corresponding column in $\boldsymbol{S}_{mob}$ has only nonpositive entries (-1,-1,0) which means that Assumption 5 is still not violated. And also precipitation-dissolution reactions with non-mineral species on the right-hand side of the reaction do not necessarily lead to a violation of Assumption 5.

Furthermore the following assumptions on the data of the problem are needed (compare [9, Assumption 2.2]):

Assumptions 6

1. $d > \delta = \text{const} > 0$
2. $d, \partial_{x_k} d \in C^{\alpha,\alpha/2}(\overline{Q}_T)$ $(k = 1,\ldots,n)$, $\boldsymbol{q} \in C^{\alpha,\alpha/2}(\overline{Q}_T)^n$ *for some* $\alpha \in (0,1)$
3. $p > (n+2)/2$, $p \geq 2$, $p \neq n+2$, *and* $c_{0,i} \in W_p^{2-2/p}(\Omega)$; $c_{0,i}$ *is continuously differentiable in a neighborhood of* $\partial\Omega$ $(i = 1,\ldots,I)$
4. $\bar{c}_{min,0,j} \in C^{\alpha}(\overline{\Omega})$ $(j = 1,\ldots,J_{min})$
5. $c_i^* \in W^{1-1/p,(1-1/p)/2}(S_T) \cap C(\overline{S}_T)$ $(i = 1,\ldots,I)$
6. $\beta \in C^{1-1/p+\epsilon,(1-1/p+\epsilon)/2}(\overline{S}_T)$ *for some* $\epsilon > 0$, $\beta \leq 0$
7. *If* $p > 3$: $\partial_{\boldsymbol{\nu}} c_{0,i} = \beta(\cdot,0)(c_{0,i} - c_i^*(\cdot,0))$ *on* $\partial\Omega$ $(i = 1,\ldots,I)$
8. $\partial\Omega \in C^{2+\alpha}$
9. $\boldsymbol{c}_0, \bar{\boldsymbol{c}}_{min,0}, \boldsymbol{c}^* \geq 0$

Discussion of the model and possible future extensions. Note that for model $(\boldsymbol{P})$ to be valid, in particular eq. (28), we have assumed that on the microscale the different minerals precitipate on distinguished sites. Hence, the different mineral reactions do *not* interfere with one another in the sense that one mineral might precipitate on top of another mineral, obstructing a possible dissolution of the latter. Let us mention that, not so much for analysis, but at least for numerical computations, also models which take into account a variation of the reactive surface are sometimes used. For our analysis we do not consider a variability of the surface. However, it seems that our analysis in the Secs. 5-6 (existence and uniqueness of solutions) could be extended to a model with a surface factor $A_j(\bar{\boldsymbol{c}}_{min})$ which is nonnegative, locally Lipschitz, and bounded, in front of the term (28). For A_j being non-Lipschitz (e.g., at the boundary of the positive cone $(\mathbb{R}^+)^{J_{min}}$, if ball-shaped mineral structures are considered instead of flat layers), however, non-uniqueness of solutions could be expected.

5 Existence of a Global Solution

The objective of this section is to prove the existence of a global nonnegative solution of problem **(*P*)** defined in Sec. 4. To this end, let us consider a modified problem **(*P*$^+$)** which is identical to **(*P*)**, up to a replacement of the rate functions $\boldsymbol{r}_{mob}(\boldsymbol{c})$ by $\boldsymbol{r}_{mob}(\boldsymbol{c}^+)$ and the rates $\boldsymbol{r}_{min}(\boldsymbol{c}, \bar{\boldsymbol{c}}_{min})$ replaced by $\boldsymbol{r}_{min}(\boldsymbol{c}^+, \bar{\boldsymbol{c}}_{min})$. Additionally we define the regularized problem

$$\begin{aligned}
\partial_t \boldsymbol{c} + L\boldsymbol{c} &= \boldsymbol{S}_{mob}\boldsymbol{r}_{mob}(\boldsymbol{c}^+) + \boldsymbol{S}_{min}\boldsymbol{r}_{\varepsilon,min}(\boldsymbol{c}^+, \bar{\boldsymbol{c}}_{min}) && \text{on } Q_T && (29)\\
\partial_t \bar{\boldsymbol{c}}_{min} &= \boldsymbol{r}_{\varepsilon,min}(\boldsymbol{c}^+, \bar{\boldsymbol{c}}_{min}) && \text{on } Q_T && (30)\\
\boldsymbol{c}(\cdot, 0) &= \boldsymbol{c}_0 && \text{on } \overline{\Omega} && (31)\\
\bar{\boldsymbol{c}}_{min}(\cdot, 0) &= \bar{\boldsymbol{c}}_{min,0} && \text{on } \overline{\Omega} && (32)\\
d\,\partial_{\boldsymbol{\nu}} \boldsymbol{c} &= \beta\,(\boldsymbol{c} - \boldsymbol{c}^*) && \text{on } S_T && (33)
\end{aligned}$$

with the regularized rate functions

$$r_{\varepsilon,min,j}(\boldsymbol{c}^+, \bar{\boldsymbol{c}}_{min}) = k_{p,j} \prod_{\substack{i=1\\ s_{min,ij}<0}}^{I} (c_i^+)^{-s_{min,ij}} - k_{d,j} \prod_{\substack{i=1\\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} H_\varepsilon(\bar{c}_{min,j}) \quad (34)$$

where H_ε is the regularized Heaviside function

$$H_\varepsilon(s) := \begin{cases} 1 & \text{for } s \geq \varepsilon \\ s/\varepsilon & \text{for } 0 < s < \varepsilon \\ 0 & \text{for } s \leq 0 \end{cases}$$

with $\varepsilon > 0$. We are looking for solutions $(\boldsymbol{c}, \bar{\boldsymbol{c}}_{min}) \in W_p^{2,1}(Q_T)^I \times \mathcal{C}(\overline{Q}_T)^{J_{min}}$. This problem is denoted by **(*P*$_\varepsilon^+$)**.

Let us state that our solution space $W_p^{2,1}(Q_T)$, for $p > (n+2)/2$ (compare Assumption 6 pt. 3), is continuously embedded in an anisotropic Hölder space. In fact,

$$W_p^{2,1}(Q_T) \hookrightarrow C^{\alpha,\alpha/2}(\overline{Q}_T) \quad \text{for} \quad 0 < \alpha \leq 2 - \frac{n+2}{p} \quad (35)$$

(e.g. [23, Thm. 1.4.1]). In particular, the compact embedding

$$W_p^{2,1}(Q_T) \hookrightarrow\hookrightarrow C(\overline{Q}_T) \quad (36)$$

follows for $p > (n+2)/2$.

5.1 Nonnegativity

Lemma 7 *Let* $(\boldsymbol{c}, \bar{\boldsymbol{c}}_{min}) \in W_p^{2,1}(Q_T)^I \times \mathcal{C}(\overline{Q}_T)^{J_{min}}$ *be a solution of problem* $(\boldsymbol{P_\varepsilon^+})$. *Then* $\boldsymbol{c}$ *is nonnegative.*

Proof. Let $\Omega_i^- = \Omega_i^-(t)$ be the support of $c_i^-(\cdot, t)$. Testing the i-th PDE with $-c_i^-$ and an integration by parts of the diffusion term yields

$$\begin{aligned}
\frac{1}{2}\partial_t \int_{\Omega_i^-} |c_i^-|^2\, d\boldsymbol{x} + \int_{\Omega_i^-} (d|\nabla c_i^-|^2 + \boldsymbol{q}\cdot\nabla c_i^-\, c_i^-)\, d\boldsymbol{x} - \int_{\partial\Omega} \beta\,(c_i^- + c_i^*) c_i^-\, do \\
= \; -\sum_{j=1}^{J_{mob}} s_{ij} \int_{\Omega_i^-} \left(k_{f,j} \prod_{\substack{k=1\\ s_{kj}<0}}^{I} (c_k^+)^{-s_{kj}} - k_{b,j} \prod_{\substack{k=1\\ s_{kj}>0}}^{I} (c_k^+)^{s_{kj}} \right) c_i^-\, d\boldsymbol{x} \\
-\sum_{j=1}^{J_{min}} s_{min,ij}\, \cdot \\
\cdot \int_{\Omega_i^-} \left(k_{p,j} \prod_{\substack{k=1\\ s_{min,kj}<0}}^{I} (c_k^+)^{-s_{min,kj}} - k_{d,j} \prod_{\substack{k=1\\ s_{min,kj}>0}}^{I} (c_k^+)^{s_{min,kj}} H_\varepsilon(\bar{c}_{min,j}) \right) c_i^-\, d\boldsymbol{x}. \quad (37)
\end{aligned}$$

We know that $c_i^+ \equiv 0$ on the domain of integration Ω_i^-. Using this we get for those j with $s_{ij} > 0$ in the first sum (note that c_i^+ is one of the factors of the second product for these j)

$$\begin{aligned}
-s_{ij} \int_{\Omega_i^-} \left(k_{f,j} \prod_{\substack{k=1\\ s_{kj}<0}}^{I} (c_k^+)^{-s_{kj}} - k_{b,j} \prod_{\substack{k=1\\ s_{kj}>0}}^{I} (c_k^+)^{s_{kj}} \right) c_i^-\, d\boldsymbol{x} \\
= \; -s_{ij} \int_{\Omega_i^-} \left(k_{f,j} \prod_{\substack{k=1\\ s_{kj}<0}}^{I} (c_k^+)^{-s_{kj}} \right) c_i^-\, d\boldsymbol{x} \le 0\,.
\end{aligned}$$

Analogously we obtain for those j with $s_{ij} < 0$ that the term is nonpositive. In the same way we show that the terms in the second sum in (37) is nonpositive, too. So we get

$$\frac{1}{2}\partial_t \int_{\Omega_i^-} |c_i^-|^2\, d\boldsymbol{x} + \int_{\Omega_i^-} (d|\nabla c_i^-|^2 + \boldsymbol{q}\cdot\nabla c_i^-\, c_i^-)\, d\boldsymbol{x} \le 0$$

where also $\beta \le 0$ (cf. Assumption 6) was used. Using Young's inequality it follows

$$\frac{1}{2}\partial_t \int_{\Omega_i^-} |c_i^-|^2\, d\boldsymbol{x} + \int_{\Omega_i^-} d|\nabla c_i^-|^2\, d\boldsymbol{x} \le \frac{Q^2}{2\delta} \int_{\Omega_i^-} |c_i^-|^2\, d\boldsymbol{x} + \frac{\delta}{2} \int_{\Omega_i^-} |\nabla c_i^-|^2\, d\boldsymbol{x}$$

with $Q := \|\boldsymbol{q}\|_{L^\infty(Q_T)^n}$. Absorbing the term with $\delta/2$ on the left hand side gives (note that $d > \delta$, see Assumptions 6 (i))

$$\partial_t \int_{\Omega_i^-} |c_i^-|^2\, d\boldsymbol{x} + \int_{\Omega_i^-} d|\nabla c_i^-|^2\, d\boldsymbol{x} \le \frac{Q^2}{\delta} \int_{\Omega_i^-} |c_i^-|^2\, d\boldsymbol{x}\,.$$

In particular,

$$\partial_t \int_{\Omega_i^-} |c_i^-|^2 \, d\boldsymbol{x} \le \frac{Q^2}{\delta} \int_{\Omega_i^-} |c_i^-|^2 \, d\boldsymbol{x} \, .$$

Because of the assumption that the initial values are nonnegative (Assumptions 6 (ix)) it follows that $\int_{\Omega_i^-} |c_i^-|^2 \, d\boldsymbol{x} \equiv 0$ for all $t \ge 0$ and hence it holds $c_i \ge 0$ a.e. in Q_T. □

Lemma 8 *Let $(\boldsymbol{c}, \bar{\boldsymbol{c}}_{min})$ be a solution of problem $(\boldsymbol{P}_{\boldsymbol{\varepsilon}}^{+})$. Then $\bar{\boldsymbol{c}}_{min}$ is nonnegative.*

Proof. We multiply the j-th ODE by $-\bar{c}_{min,j}^-$ and integrate from 0 to t to obtain

$$\int_0^t \partial_t \bar{c}_{min,j}(-\bar{c}_{min,j}^-) \, ds =$$
$$\int_0^t \Bigg(\underbrace{k_{p,j} \prod_{\substack{i=1 \\ s_{min,ij}<0}}^{I} (c_i^+)^{-s_{min,ij}}}_{\ge 0} - k_{d,j} \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} H_\varepsilon(\bar{c}_{min,j}) \Bigg) \underbrace{(-\bar{c}_{min,j}^-)}_{\le 0} \, ds$$

a.e. on Ω. Because of

$$\int_0^t \partial_t \bar{c}_{min,j}(-\bar{c}_{min,j}^-) \, ds = \frac{1}{2} \int_0^t \partial_t |\bar{c}_{min,j}^-|^2 \, ds = \frac{1}{2} |\bar{c}_{min,j}^-(\cdot,t)|^2 - \frac{1}{2} |\bar{c}_{min,j}^-(\cdot,0)|^2$$

we get the estimate

$$\frac{1}{2} |\bar{c}_{min,j}^-(\cdot,t)|^2 \le \int_0^t k_{d,j} \prod_{\substack{i=1 \\ S_{1,min,ij}>0}}^{I} (c_i^+)^{S_{1,min,ij}} H_\varepsilon(\bar{c}_{min,j}) \bar{c}_{min,j}^- \, ds + \frac{1}{2} |\bar{c}_{min,j}^-(\cdot,0)|^2 = 0.$$

The first summand on the right-hand side is zero because one of the factors $H_\varepsilon(\bar{c}_{min,j})$, $\bar{c}_{min,j}^-$ is zero a.e. due to the definition of H_ε, and the second one is zero due to the assumption that the initial value $\bar{c}_{min,0,j}$ is nonnegative (Assumptions 6 (ix)). □

Remark 9 *The assertions of the previous two lemmas are also true for the problem $(\boldsymbol{P}^{+})$.*

Proof. Just replace "$H_\varepsilon(\bar{c}_{min,j})$" by "$w_j$" in the previous two proofs. □

We want to prove the existence of a global solution of the modified and regularized problem with help of Schaefer's fixed point theorem (see [17] or [8, Thrm. 10.3]).

5.2 The Fixed Point Operator

We define the fixed point operator $\mathcal{Z}$:

$$\begin{aligned} \mathcal{Z} : W_p^{2,1}(Q_T)^I &\longrightarrow W_p^{2,1}(Q_T)^I \\ \hat{\boldsymbol{c}} &\longmapsto \boldsymbol{c} = \mathcal{Z}(\hat{\boldsymbol{c}}) \end{aligned}$$

with $p > (n+2)/2$ and $\boldsymbol{c}$ being the solution of the problem

$$\begin{array}{rcll} \partial_t \boldsymbol{c} + L\boldsymbol{c} &=& \boldsymbol{S}_{mob}\boldsymbol{r}_{mob}(\hat{\boldsymbol{c}}^+) + \boldsymbol{S}_{min}\boldsymbol{r}_{\varepsilon,min}(\hat{\boldsymbol{c}}^+, \bar{\boldsymbol{c}}_{min}) & \text{on } Q_T \\ \partial_t \bar{\boldsymbol{c}}_{min} &=& \boldsymbol{r}_{\varepsilon,min}(\hat{\boldsymbol{c}}^+, \bar{\boldsymbol{c}}_{min}) & \text{on } Q_T \\ \boldsymbol{c}(\cdot,0) &=& \boldsymbol{c}_0 & \text{on } \overline{\Omega} \\ \bar{\boldsymbol{c}}_{min}(\cdot,0) &=& \bar{\boldsymbol{c}}_{min,0} & \text{on } \overline{\Omega} \\ d\partial_{\boldsymbol{\nu}}\boldsymbol{c} &=& \beta(\boldsymbol{c}-\boldsymbol{c}^*) & \text{on } S_T\,. \end{array} \qquad (38)$$

Lemma 10 *The fixed point operator $\mathcal{Z}$ is well-defined.*

Proof. Some ideas of this proof are adapted from the argumentation in [11, page 104]. First we will show that a solution $\bar{\boldsymbol{c}}_{min}$ of the ODE subsystem exists and that this solution is in $C(\overline{Q}_T)^{J_{min}}$. From the embedding (36) the continuity of $\hat{\boldsymbol{c}}$ follows. So for fixed $\boldsymbol{x} \in \overline{\Omega}$ the right-hand side $\boldsymbol{r}_{\varepsilon,min}(\hat{\boldsymbol{c}}^+(\boldsymbol{x},t), \bar{\boldsymbol{c}}_{min})$ (see (34) for the definition of $\boldsymbol{r}_{\varepsilon,min}$) as a function of t and $\bar{\boldsymbol{c}}_{min}$ is continuous in t. The Lipschitz continuity of H_ε yields that $\boldsymbol{r}_{\varepsilon,min}(\hat{\boldsymbol{c}}^+(\boldsymbol{x},t), \bar{\boldsymbol{c}}_{min})$ is Lipschitz continuous in $\bar{\boldsymbol{c}}_{min}$ with a Lipschitz constant independent of $\boldsymbol{x}$ and t:

$$\begin{array}{l} |r_{\varepsilon,min,j}(\hat{\boldsymbol{c}}^+(\boldsymbol{x},t), y) - r_{\varepsilon,min,j}(\hat{\boldsymbol{c}}^+(\boldsymbol{x},t), \tilde{y})| \\ \qquad = \left| k_{d,j} \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} \left(\hat{c}_i^+(\boldsymbol{x},t)\right)^{s_{min,ij}} \right| |H_\varepsilon(y) - H_\varepsilon(\tilde{y})| \\ \qquad \leq C_M L_\varepsilon |y - \tilde{y}| \end{array}$$

with M a bound for the $C(\overline{Q}_T)^I$-norm of $\hat{\boldsymbol{c}}$, C_M a constant depending on M and on the exponents $s_{min,i,j}$, and L_ε the Lipschitz constant of H_ε. Such a bound $M < \infty$ exists because of $\hat{\boldsymbol{c}} \in C^{\alpha,\alpha/2}(\overline{Q}_T)^I \subset C(\overline{Q}_T)^I$. So the Picard-Lindelöf theorem proves that $\bar{\boldsymbol{c}}_{min}$ exists on the whole interval $[0,T]$, i.e., $\bar{\boldsymbol{c}}_{min}(\boldsymbol{x},\cdot) \in C([0,T])^{J_{min}}$ for fixed $\boldsymbol{x} \in \overline{\Omega}$.

To complete the proof that $\bar{\boldsymbol{c}}_{min} \in C(\overline{Q}_T)^{J_{min}}$ we will show that $\bar{\boldsymbol{c}}_{min}$ is Hölder continuous in $\boldsymbol{x}$, uniformly in $\overline{Q}_T$. Let $y \in C^1([0,T])$ be the solution of [1]

$$\begin{array}{rcl} y' &=& r_{\varepsilon,min,j}(\hat{\boldsymbol{c}}^+(\boldsymbol{x},\cdot), y) \\ y(0) &=& \bar{c}_{min,0,j}(\boldsymbol{x}) \end{array}$$

and $\tilde{y} \in C^1([0,T])$ be the solution of

$$\begin{array}{rcl} \tilde{y}' &=& r_{\varepsilon,min,j}(\hat{\boldsymbol{c}}^+(\tilde{\boldsymbol{x}},\cdot), \tilde{y}) \\ \tilde{y}(0) &=& \bar{c}_{min,0,j}(\tilde{\boldsymbol{x}})\,. \end{array}$$

As $\bar{c}_{min,0,j}$ is Hölder continuous (see Assumptions 6 (iv)) we know that

$$|\bar{c}_{min,0,j}(\boldsymbol{x}) - \bar{c}_{min,0,j}(\tilde{\boldsymbol{x}})| \leq K_1 |\boldsymbol{x} - \tilde{\boldsymbol{x}}|^\alpha\,.$$

[1] Note that we omitted the irrelevant arguments of $r_{\varepsilon,min,j}$, cf. (34), for the sake of simplicity.

Because of the Hölder continuity of $\hat{\boldsymbol{c}}$ we know that (remember that the product of two functions that are Hölder continuous with exponent α is also Hölder continuous with exponent α)

$$|r_{\varepsilon,min,j}(\hat{\boldsymbol{c}}^+(\boldsymbol{x},t),y) - r_{\varepsilon,min,j}(\hat{\boldsymbol{c}}^+(\tilde{\boldsymbol{x}},t),y)| \le K_2|\boldsymbol{x}-\tilde{\boldsymbol{x}}|^\alpha \quad \forall t\in[0,T]\,.$$

With well-known results from the theory of ODEs, e.g., [22, § 12, Thrm. V],

$$|y(t)-\tilde{y}(t)| \le \max\{K_1,K_2\}\Big(e^{LT}+\frac{1}{L}(e^{LT}-1)\Big)|\boldsymbol{x}-\tilde{\boldsymbol{x}}|^\alpha \quad \forall t\in[0,T]$$

with $L = C_M L_\varepsilon$ being a Lipschitz constant of $\boldsymbol{r}_{\varepsilon,min}(\hat{\boldsymbol{c}}^+(\boldsymbol{x},t),\cdot)$, and therefore $\bar{\boldsymbol{c}}_{min}$ is Hölder continuous in $\boldsymbol{x}$, uniformly on $\overline{Q}_T$:

$$|\bar{c}_{min,j}(\boldsymbol{x},t) - \bar{c}_{min,j}(\tilde{\boldsymbol{x}},t)| \le \max\{K_1,K_2\}\Big(e^{LT}+\frac{1}{L}(e^{LT}-1)\Big)|\boldsymbol{x}-\tilde{\boldsymbol{x}}|^\alpha \quad \forall t\in[0,T]$$

The right-hand side of the ODE subsystem $\boldsymbol{r}_{\varepsilon,min}(\hat{\boldsymbol{c}}^+,\bar{\boldsymbol{c}}_{min})$ is an element of $C(\overline{Q}_T)^{J_{min}}$. So we obtain

$$\bar{\boldsymbol{c}}_{min} \in \mathcal{C}(\overline{Q}_T)^{J_{min}}$$

(cf. (20)).

Now we consider the PDE subsystem. The right-hand side of it, $\boldsymbol{S}_{mob}\boldsymbol{r}_{mob}(\hat{\boldsymbol{c}}^+) + \boldsymbol{S}_{min}\boldsymbol{r}_{\varepsilon,min}(\hat{\boldsymbol{c}}^+,\bar{\boldsymbol{c}}_{min})$, is an element of $C(\overline{Q}_T)^I$. It follows that the right-hand side is an element of $L^q(Q_T)^I$ for all $1 \le q \le \infty$. Using the linear parabolic theory (compare [15, IV, 9]), we get a solution of the PDE subsystem $\boldsymbol{c} \in W_p^{2,1}(Q_T)^I$. □

5.3 A Priori Estimates

Since we are going to apply Schaefer's fixed point theorem (cf. [17], [8, Thrm. 10.3]) we have to construct a bound holding for arbitrary solutions $\boldsymbol{c} \in W_p^{2,1}(Q_T)^I$ of the equation

$$\boldsymbol{c} = \lambda\mathcal{Z}(\boldsymbol{c})$$

with $\lambda \in [0,1]$. So we have to find a bound for the solutions $(\boldsymbol{c},\bar{\boldsymbol{c}}_{min})$ of

$$\begin{aligned}
\partial_t\boldsymbol{c} + L\boldsymbol{c} &= \lambda\,(\boldsymbol{S}_{mob}\boldsymbol{r}_{mob}(\boldsymbol{c}^+) + \boldsymbol{S}_{min}\boldsymbol{r}_{\varepsilon,min}(\boldsymbol{c}^+,\bar{\boldsymbol{c}}_{min})) && \text{on } Q_T\\
\partial_t\bar{\boldsymbol{c}}_{min} &= \boldsymbol{r}_{\varepsilon,min}(\boldsymbol{c}^+,\bar{\boldsymbol{c}}_{min}) && \text{on } Q_T\\
\boldsymbol{c}(\cdot,0) &= \lambda\boldsymbol{c}_0 && \text{on } \overline{\Omega}\\
\bar{\boldsymbol{c}}_{min}(\cdot,0) &= \bar{\boldsymbol{c}}_{min,0} && \text{on } \overline{\Omega}\\
d\partial_{\boldsymbol{\nu}}\boldsymbol{c} &= \beta(\boldsymbol{c}-\lambda\boldsymbol{c}^*) && \text{on } S_T.
\end{aligned} \tag{39}$$

To derive the required a priori estimate we want to use the maximum principle (e.g. [15, I, Thm. 2.2/2.3]), which is also used in [9, Sec. 3]. In the following we will construct an upper bound $\tilde{\eta}$ for the mobile concentrations c_i with help of the maximum principle. The function $\tilde{\eta}$ will be the solution of a PDE, and again using the maximum principle one can show that there is a bound for the $C(\overline{Q}_T)$-norm of $\tilde{\eta}$ which only depends on the data and which is independent of the solution. As $\tilde{\eta}$

is an upper bound for every c_i we have found a bound for the $C(\overline{Q}_T)^I$-norm of $\boldsymbol{c}$. Then it follows from the linear parabolic theory that there is also a bound for the $W_p^{2,1}(Q_T)^I$-norm for arbitrary solutions. For applying the maximum principle it is needed that the solution of the PDE is a classical solution. To show this the existence theorem from [7, Chap. 5, p. 147, Cor. 2] will be used.

Let $\tilde{\eta}$ be the solution of

$$\begin{array}{rcll} \partial_t\tilde{\eta} + L\tilde{\eta} &=& \lambda\left(\boldsymbol{s}^\perp\cdot(\boldsymbol{S}_{mob}^-(-\boldsymbol{k}_b^-)) + \boldsymbol{s}^\perp\cdot(\boldsymbol{S}_{min}^-(-\boldsymbol{k}_d^-))\right) & \text{on } Q_T \\ \tilde{\eta}(\cdot,0) &=& \lambda\boldsymbol{s}^\perp\cdot\boldsymbol{c}_0 & \text{on } \overline{\Omega} \\ d\partial_{\boldsymbol{\nu}}\tilde{\eta} &=& \beta(\tilde{\eta} - \lambda\boldsymbol{s}^\perp\cdot\boldsymbol{c}^*) & \text{on } S_T \end{array} \tag{40}$$

where $\boldsymbol{S}_{mob}^-$ and $\boldsymbol{S}_{min}^-$ are the submatrices of $\boldsymbol{S}_{mob}$ and $\boldsymbol{S}_{min}$, respectively, that contain all columns with only nonpositive entries. The vectors $\boldsymbol{k}_b^-$ and $\boldsymbol{k}_d^-$ contain all reaction constants $k_{b,j}$ and $k_{d,j}$, respectively, that correspond to a column of $\boldsymbol{S}$ with only nonpositive entries. $\tilde{\eta}$ is the solution of a parabolic PDE with constant right-hand side. According to [7, Chap. 5, p. 147, Cor. 2] a classical solution exists.

To apply the existence theorem from [7] to the PDE subsystem of (39) we have to show that the right-hand side is Hölder continuous in $\boldsymbol{x}$, uniformly in $\overline{Q}_T$. From the embedding (35) we know that $\boldsymbol{c}$ is Hölder continuous. In the proof of Lemma 10 we have already shown that $\bar{\boldsymbol{c}}_{min}$ is Hölder continuous in $\boldsymbol{x}$, uniformly in $\overline{Q}_T$. Hence the requirements of the existence theorem [7, Chap. 5, p. 147, Cor. 2] are fulfilled. So we obtain that $\boldsymbol{c}$ is a classical solution of the PDE subsystem.

As next step we examine the function

$$u := \boldsymbol{s}^\perp\cdot\boldsymbol{c} - \tilde{\eta}\,.$$

By taking linear combinations of the PDEs in (39) and substracting the PDE in (40) one can see that u is a solution of (remember that $\boldsymbol{s}^\perp$ is perpendicular to all columns of $\boldsymbol{S}$ except of those with only nonpositive entries)

$$\begin{array}{rcll} \partial_t u + Lu &=& \lambda\boldsymbol{s}^\perp\cdot\big(\boldsymbol{S}_{mob}\boldsymbol{r}_{mob}(\boldsymbol{c}^+) + \boldsymbol{S}_{mob}^-\boldsymbol{k}_b^- & \\ && \quad + \boldsymbol{S}_{min}\boldsymbol{r}_{\varepsilon,min}(\boldsymbol{c}^+,\bar{\boldsymbol{c}}_{min}) + \boldsymbol{S}_{min}^-\boldsymbol{k}_d^-\big) & \\ &=& \lambda\boldsymbol{s}^\perp\cdot\big(\boldsymbol{S}_{mob}^-(\boldsymbol{r}_{mob}^-(\boldsymbol{c}^+) + \boldsymbol{k}_b^-) & \\ && \quad + \boldsymbol{S}_{min}^-(\boldsymbol{r}_{\varepsilon,min}^-(\boldsymbol{c}^+,\bar{\boldsymbol{c}}_{min}) + \boldsymbol{k}_d^-)\big) & \text{on } Q_T \\ u(\cdot,0) &=& 0 & \text{on } \overline{\Omega} \\ d\partial_{\boldsymbol{\nu}}u &=& \beta u & \text{on } S_T \end{array} \tag{41}$$

where $\boldsymbol{r}_{mob}^-$ and $\boldsymbol{r}_{\varepsilon,min}^-$ contain all reaction rates $r_{mob,j}$ and $r_{\varepsilon,min,j}$, respectively, that correspond to a column of $\boldsymbol{S}$ with only nonpositive entries. Because of this all components of $\boldsymbol{r}_{mob}^-$ have the form, cf. (27),

$$r_{mob,j}^-(\boldsymbol{c}^+) = k_{f,j}\prod_{\substack{i=1\\ s_{ij}^-<0}}^{I}(c_i^+)^{-s_{ij}^-} - k_{b,j}$$

and one sees immediately that all components of the vector $(\boldsymbol{r}_{mob}^-(\boldsymbol{c}^+) + \boldsymbol{k}_b^-)$ are nonnegative. Analogously, considering the components of $\boldsymbol{r}_{\varepsilon,min}^-$ one knows that the second product in (34) is empty. So every component of the vector $(\boldsymbol{r}^-_{\varepsilon,min}(\boldsymbol{c}^+,\bar{\boldsymbol{c}}_{min})+\boldsymbol{k}^-_d)$ is of the form

$$k_{p,j}\prod_{\substack{i=1\\ s^-_{min,ij}<0}}^{I}(c_i^+)^{-s^-_{min,ij}}+k_{d,j}(1-H_\varepsilon(\bar{c}_{min,j}))\,.$$

Because of $H_\varepsilon \leq 1$ it follows that all components of $(\boldsymbol{r}^-_{\varepsilon,min}(\boldsymbol{c}^+,\bar{\boldsymbol{c}}_{min})+\boldsymbol{k}^-_d)$ are nonnegative. Furthermore by definition all components of $\boldsymbol{s}^\perp$ are positive and all entries of $\boldsymbol{S}^-_{mob}$ and $\boldsymbol{S}^-_{min}$ are nonpositive. Altogether we get that the right-hand side of the PDE for u is nonpositive. So applying the maximum principle[2] (compare [15, I, Thm. 2.2/2.3]) yields

$$\sup_{Q_T} u \leq 0\,.$$

As all components of $\boldsymbol{s}^\perp$ are positive and all mobile concentrations are nonnegative (see Lemma 7) it follows

$$c_i \leq \frac{1}{s_i^\perp}\tilde{\eta} \qquad \forall i=1,\ldots,I\,.$$

Hence, $\max_i \frac{1}{s_i^\perp}\tilde{\eta}$ is an upper bound for the mobile concentrations.

Function $\tilde{\eta}$ is the solution of (40). Applying the maximum principle [15, I, Thm. 2.3] to it gives

$$\sup_{Q_T}|\tilde{\eta}| \leq K_1$$

with a constant K_1 only depending on the data β, $\boldsymbol{c}^*$, $\boldsymbol{c}_0$, $\boldsymbol{s}^\perp$, $\boldsymbol{S}^-_{mob}\boldsymbol{k}^-_b$, $\boldsymbol{S}^-_{min}\boldsymbol{k}^-_d$, d, $\|\boldsymbol{q}\|_{C(\overline{Q}_T)^n}$, T, and Ω, but obviously independent of ε. So we have found a bound for the $C(\overline{Q}_T)^I$-norm of $\boldsymbol{c}$ for an arbitrary solution of (39). It follows that the $C(\overline{Q}_T)^I$-norm of the right-hand side of the PDE in (39) is bounded by a constant K_2 only depending on K_1, $\boldsymbol{S}$, and the reaction constants $k_{f,j}$, $k_{b,j}$, $k_{p,j}$, $k_{d,j}$. In particular, every $L^q(Q_T)^I$-norm $(1 \leq q \leq \infty)$ of the right-hand side is bounded independent of the solution $(\boldsymbol{c},\bar{\boldsymbol{c}}_{min})$. Then with the linear parabolic theory (compare [18, Thm. 17], [15, IV, 9]) it follows

$$\|\boldsymbol{c}\|_{W_p^{2,1}(Q_T)^I} \leq K_3 \tag{42}$$

with a constant K_3 depending on the data, but independent of ε and the solution $(\boldsymbol{c},\bar{\boldsymbol{c}}_{min})$.

5.4 Compactness

Theorem 11 *The operator $\mathcal{Z}$ is continuous and compact.*

Proof. Let $(\hat{\boldsymbol{c}}^n)$ be a sequence bounded in $W_p^{2,1}(Q_T)^I$. Due to the compact embedding (35) there is a subsequence, again denoted by $(\hat{\boldsymbol{c}}^n)$, which is convergent in

[2]See Appendix A for a detailed description of the application of the maximum principle

$C(\overline{Q}_T)^I$. Let M be a bound in $C(\overline{Q}_T)^I$. Let $(\boldsymbol{c}^n, \bar{\boldsymbol{c}}^n_{min})$ be the sequence of solutions of (38). We have to prove that $(\boldsymbol{c}^n)$ converges in $C(\overline{Q}_T)^I$. First we consider the ODE subproblem

$$\begin{aligned} \partial_t \bar{\boldsymbol{c}}^n_{min} &= \boldsymbol{r}_{\varepsilon,min}\big((\hat{\boldsymbol{c}}^n)^+, \bar{\boldsymbol{c}}^n_{min}\big) && \text{on } Q_T \\ \bar{\boldsymbol{c}}^n_{min}(\cdot,0) &= \bar{\boldsymbol{c}}_{min,0} && \text{on } \overline{\Omega} \end{aligned}$$

in order to show that $(\bar{\boldsymbol{c}}^n_{min})$ is a Cauchy sequence in $C(\overline{Q}_T)^{J_{min}}$. To this end, let $l, m \in \mathbb{N}$ and let $y \in C^1([0,T])$ be the solution of [3]

$$\begin{aligned} y' &= r_{\varepsilon,min,j}\big((\hat{\boldsymbol{c}}^l)^+(\boldsymbol{x},\cdot), y\big) \\ y(0) &= \bar{\boldsymbol{c}}_{min,0,j} \end{aligned}$$

and $\tilde{y}$ be the solution of

$$\begin{aligned} \tilde{y}' &= r_{\varepsilon,min,j}\big((\hat{\boldsymbol{c}}^m)^+(\boldsymbol{x},\cdot), \tilde{y}\big) \\ \tilde{y}(0) &= \bar{\boldsymbol{c}}_{min,0,j}\,. \end{aligned}$$

Let us define

$$r_{1,j}(\boldsymbol{c}^+) = k_{p,j} \prod_{\substack{i=1 \\ s_{min,ij}<0}}^{I} (c_i^+)^{-s_{min,ij}}, \quad r_{2,j}(\boldsymbol{c}^+) = k_{d,j} \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}}.$$

As both functions $r_{1,j}, r_{2,j} : \mathbb{R}^I \to \mathbb{R}$ are uniformly continuous on a ball of radius M around $0 \in \mathbb{R}^I$ it holds

$$\begin{aligned} &\big|r_{\varepsilon,min,j}\big((\hat{\boldsymbol{c}}^l)^+(\boldsymbol{x},t), y\big) - r_{\varepsilon,min,j}\big((\hat{\boldsymbol{c}}^m)^+(\boldsymbol{x},t), y\big)\big| \\ &\quad\le \big|r_{1,j}\big((\hat{\boldsymbol{c}}^l)^+(\boldsymbol{x},t)\big) - r_{1,j}\big((\hat{\boldsymbol{c}}^m)^+(\boldsymbol{x},t)\big)\big| \\ &\qquad + \big|r_{2,j}\big((\hat{\boldsymbol{c}}^l)^+(\boldsymbol{x},t)\big) - r_{2,j}\big((\hat{\boldsymbol{c}}^m)^+(\boldsymbol{x},t)\big)\big| \underbrace{|H_\varepsilon(y)|}_{\le 1} \\ &\quad\le \omega_{r_{1,j}}(|\hat{\boldsymbol{c}}^l(\boldsymbol{x},t) - \hat{\boldsymbol{c}}^m(\boldsymbol{x},t)|) + \omega_{r_{2,j}}(|\hat{\boldsymbol{c}}^l(\boldsymbol{x},t) - \hat{\boldsymbol{c}}^m(\boldsymbol{x},t)|) \end{aligned}$$

with ω_f the modulus of continuity of a function f.

The Lipschitz constant L of $r_{\varepsilon,min,j}((\hat{\boldsymbol{c}}^n)^+(\boldsymbol{x},t),\cdot)$ is $C_M L_\varepsilon$ with L_ε the Lipschitz constant of H_ε (see proof of Lemma 10). So we get, e.g. with [22, § 12, Thrm. V], for all $t \in [0,T]$

$$|y(t) - \tilde{y}(t)| \le \frac{\omega_{r_{1,j}}(|\hat{\boldsymbol{c}}^l(\boldsymbol{x},t) - \hat{\boldsymbol{c}}^m(\boldsymbol{x},t)|) + \omega_{r_{2,j}}(|\hat{\boldsymbol{c}}^l(\boldsymbol{x},t) - \hat{\boldsymbol{c}}^m(\boldsymbol{x},t)|)}{L}(e^{LT} - 1)\,.$$

It follows that

$$|\bar{c}^l_{min,j}(\boldsymbol{x},t) - \bar{c}^m_{min,j}(\boldsymbol{x},t)| \le \frac{\omega_{r_{1,j}}(h) + \omega_{r_{2,j}}(h)}{L}(e^{LT} - 1) \quad \forall t \in [0,T]\,,\ \forall \boldsymbol{x} \in \Omega$$

[3]Again we omitted the irrelevant arguments of $r_{\varepsilon,min,j}$, cf. (34), for the sake of simplicity.

with $h := \|\hat{\boldsymbol{c}}^l - \hat{\boldsymbol{c}}^m\|_{C(\overline{Q}_T)^I}$. Hence, $(\bar{\boldsymbol{c}}^n_{min})$ converges in $C(\overline{Q}_T)^{J_{min}}$.

Therefore the right-hand side of the PDE system

$$\partial_t \boldsymbol{c}^n + L\boldsymbol{c}^n = \boldsymbol{S}_{mob}\boldsymbol{r}_{mob}((\hat{\boldsymbol{c}}^n)^+) + \boldsymbol{S}_{min}\boldsymbol{r}_{\varepsilon,min}((\hat{\boldsymbol{c}}^n)^+, \bar{\boldsymbol{c}}^n_{min})$$

converges in $C(\overline{Q}_T)^I$. In particular, the right-hand side converges in $L^q(Q_T)^I$ for all $1 \le q \le \infty$. From the linear parabolic theory we know that the sequence of solutions $(\boldsymbol{c}^n)$ then converges in $W^{2,1}_p(Q_T)^I$, $(n+2)/2 < p < \infty$. □

Theorem 12 *Problem* $(\boldsymbol{P}^+_{\boldsymbol{\varepsilon}})$ *has a nonnegative solution.*

Proof. We apply Schaefer's fixed point theorem ([17], [8, Thrm. 10.3]) to the operator $\mathcal{Z}$, using the a priori estimate (42) and Theorem 11, to obtain a solution of $(\boldsymbol{P}^+_{\boldsymbol{\varepsilon}})$. For the nonnegativity we refer to the Lemmas 7, 8. □

5.5 Passing to the Limit

In order to prove the existence of a solution of problem $(\boldsymbol{P})$ we are going to show that a sequence of solutions of $(\boldsymbol{P}^+_{\boldsymbol{\varepsilon}})$ converges (in some sense) and that the limit is a solution of $(\boldsymbol{P}^+)$ and of $(\boldsymbol{P})$. We state the main result:

Theorem 13 *Problem* $(\boldsymbol{P})$ *has a nonnegative solution.*

Proof. We are going to show that the tuple $(\boldsymbol{c}_\varepsilon, \bar{\boldsymbol{c}}_{\varepsilon,min}, \boldsymbol{w}_\varepsilon)$ with $(\boldsymbol{c}_\varepsilon, \bar{\boldsymbol{c}}_{\varepsilon,min})$ being a solution of $(\boldsymbol{P}^+_{\boldsymbol{\varepsilon}})$ (cf. Theorem 12) and $\boldsymbol{w}_\varepsilon := H_\varepsilon(\bar{\boldsymbol{c}}_{\varepsilon,min})$ converges (in some sense) for $\varepsilon \searrow 0$ to a tuple $(\boldsymbol{c}, \bar{\boldsymbol{c}}_{min}, \boldsymbol{w}) \in W^{2,1}_p(Q_T)^I \times \mathcal{L}(Q_T)^{J_{min}} \times L^\infty(Q_T)^{J_{min}}$ which fulfills

$$\begin{aligned}
\partial_t \boldsymbol{c} + L\boldsymbol{c} &= \boldsymbol{S}_{mob}\boldsymbol{r}_{mob}(\boldsymbol{c}^+) + \boldsymbol{S}_{min}\tilde{\boldsymbol{r}}_{min}(\boldsymbol{c}^+, \boldsymbol{w}) && \text{on } Q_T && (43)\\
\partial_t \bar{\boldsymbol{c}}_{min} &= \tilde{\boldsymbol{r}}_{min}(\boldsymbol{c}^+, \boldsymbol{w}) && \text{on } Q_T && (44)\\
\boldsymbol{w} &\in H(\bar{\boldsymbol{c}}_{min}) && \text{on } Q_T && (45)\\
\boldsymbol{c}(\cdot, 0) &= \boldsymbol{c}_0 && \text{on } \overline{\Omega} && (46)\\
\bar{\boldsymbol{c}}_{min}(\cdot, 0) &= \bar{\boldsymbol{c}}_{min,0} && \text{on } \overline{\Omega} && (47)\\
d\,\partial_{\boldsymbol{\nu}} \boldsymbol{c} &= \beta(\boldsymbol{c} - \boldsymbol{c}^*) && \text{on } S_T && (48)
\end{aligned}$$

with

$$\tilde{r}_{min,j}(\boldsymbol{c}^+, \boldsymbol{w}) = k_{p,j} \prod_{\substack{i=1 \\ s_{min,ij}<0}}^{I} (c_i^+)^{-s_{min,ij}} - k_{d,j} \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_j \,.$$

From the a priori estimate (42) we know that the $W^{2,1}_p(Q_T)^I$-norm of $\boldsymbol{c}_\varepsilon$ is bounded with a bound independent of ε. From the embedding (36) we obtain that $\boldsymbol{c}_\varepsilon$ is also bounded in the $C(\overline{Q}_T)^I$-norm independent of ε.

Using the two obvious estimates

$$\partial_t \bar{c}_{\varepsilon,min,j} = r_{\varepsilon,min,j}(\boldsymbol{c}^+, \bar{\boldsymbol{c}}_{\varepsilon,min}) \begin{cases} \leq k_{p,j} \prod\limits_{\substack{i=1 \\ s_{min,ij}<0}}^{I} (c_i^+)^{-s_{min,ij}} \\ \geq -k_{d,j} \prod\limits_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} \end{cases}$$

we get that $\partial_t \bar{c}_{\varepsilon,min,j}$ is bounded in the $L^\infty(Q_T)$-norm. Since $\bar{\boldsymbol{c}}_{min,0} \in C^\alpha(\overline{\Omega})^{J_{min}}$, also $\bar{c}_{\varepsilon,min,j}$ is bounded in the $L^\infty(Q_T)$-norm independent of ε. Because of the definition of $\boldsymbol{w}_\varepsilon$ we have $0 \leq w_{\varepsilon,j} \leq 1$.

By passing to a subsequence, if necessary, we see that:

$$\begin{array}{rcll} \boldsymbol{c}_\varepsilon & \longrightarrow & \boldsymbol{c} & \text{weakly in } W_p^{2,1}(Q_T)^I \\ \boldsymbol{c}_\varepsilon & \longrightarrow & \boldsymbol{c} & \text{strongly in } C(\overline{Q}_T)^I \\ \bar{c}_{\varepsilon,min,j} & \longrightarrow & \bar{c}_{min,j} & \text{weakly-star in } L^\infty(Q_T) \quad (j = 1, \ldots, J_{min}) \\ \partial_t \bar{c}_{\varepsilon,min,j} & \longrightarrow & \partial_t \bar{c}_{min,j} & \text{weakly-star in } L^\infty(Q_T) \quad (j = 1, \ldots, J_{min}) \\ w_{\varepsilon,j} & \longrightarrow & w_j & \text{weakly-star in } L^\infty(Q_T) \quad (j = 1, \ldots, J_{min}) \end{array}$$

By passing to the limit $\varepsilon \searrow 0$ in (29)-(33) it is obvious that the limits fulfill the equations (43)-(48) except (45). To show that also (45) is met we adapt some ideas of the proof of [21, Thm. 2.21]. First we introduce

$$\underline{\bar{c}}_{min,j}(\boldsymbol{x}, t) := \liminf_{\varepsilon \searrow 0} \bar{c}_{\varepsilon,min,j}(\boldsymbol{x}, t) \geq 0 \qquad \text{a.e. in } Q_T$$

and decompose $Q_T = S_{j,1} \cup S_{j,2}$, where (in the almost everywhere sense)

$$S_{j,1} = \{\underline{\bar{c}}_{min,j} > 0\} \text{ and } S_{j,2} = \{\underline{\bar{c}}_{min,j} = 0\}\,.$$

In order to prove (45) we are going to show that $\bar{c}_{min,j} > 0$ and $w_j = 1$ in $S_{j,1}$, while $\bar{c}_{min,j} = 0$ and $w_j \in [0, 1]$ in $S_{j,2}$:

Because of $\bar{c}_{min,j} \geq \underline{\bar{c}}_{min,j}$ it follows that $\bar{c}_{min,j} > 0$ in $S_{j,1}$. Then for $(\boldsymbol{x}, t) \in S_{j,1}$ we choose $\mu > 0$ sufficiently small such that $\underline{\bar{c}}_{min,j}(\boldsymbol{x}, t) > 2\mu > 0$. So we have $\bar{c}_{\varepsilon,min,j}(\boldsymbol{x}, t) > \mu$ and, by definition of w_ε, $w_\varepsilon(\boldsymbol{x}, t) = 1$ for all ε small enough. Hence it holds $w(\boldsymbol{x}, t) = 1$.

Now we exclude that $\bar{c}_{min,j} > 0$ in $S_{j,2}$. As $\boldsymbol{c}$ is bounded in $L^\infty(Q_T)^I$ we have

$$\int_0^t \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_{\varepsilon,j} \, ds \to \int_0^t \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_j \, ds$$

weakly-star in $L^\infty(Q_T)$. It follows

$$\liminf_{\varepsilon \searrow 0} \int_0^t \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_{\varepsilon,j} \, ds \leq \int_0^t \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_j \, ds \quad \text{a.e. in } Q_T\,.$$

Using (30) and (44) that are valid a.e. in Q_T, and integrating in time gives a.e. in Q_T

$$\begin{aligned}
\bar{c}_{\varepsilon,min,j} &= \bar{c}_{min,0,j} + \int_0^t \tilde{r}_{min,j}(\boldsymbol{c}_\varepsilon^+, \boldsymbol{w}_\varepsilon)\, ds \\
&= \bar{c}_{min,j} + \int_0^t \tilde{r}_{min,j}(\boldsymbol{c}_\varepsilon^+, \boldsymbol{w}_\varepsilon)\, ds - \int_0^t \tilde{r}_{min,j}(\boldsymbol{c}^+, \boldsymbol{w})\, ds \\
&= \bar{c}_{min,j} + \int_0^t k_{p,j} \Bigg(\prod_{\substack{i=1 \\ s_{min,ij}<0}}^{I} (c_{\varepsilon,i}^+)^{-s_{min,ij}} - \prod_{\substack{i=1 \\ s_{min,ij}<0}}^{I} (c_i^+)^{-s_{min,ij}} \Bigg) ds \\
&\quad - \int_0^t k_{d,j} \Bigg(\prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_{\varepsilon,i}^+)^{s_{min,ij}} w_{\varepsilon,j} - \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_{\varepsilon,j} \Bigg) ds \\
&\quad - \int_0^t k_{d,j} \Bigg(\prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_{\varepsilon,j} - \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_j \Bigg) ds\,.
\end{aligned}$$

As $\boldsymbol{c}_\varepsilon$ converges pointwisely and $w_{\varepsilon.j}$ is bounded in $L^\infty(Q_T)$ we know that the first and the second of the three integrals converge to zero for $\varepsilon \searrow 0$. Hence, by considering the above identity on $S_{j,2}$ and by taking the $\liminf_{\varepsilon\searrow 0}$ of it we obtain

$$\begin{aligned}
0 &= \bar{c}_{min,j} - k_{d,j} \liminf_{\varepsilon\searrow 0} \int_0^t \Bigg(\prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_{\varepsilon,j} - \prod_{\substack{i=1 \\ s_{min,ij}>0}}^{I} (c_i^+)^{s_{min,ij}} w_j \Bigg) ds \\
&\geq \bar{c}_{min,j} \qquad \text{a.e. in } S_2\,,
\end{aligned}$$

where we have used $w_{\varepsilon,j} - w_j \leq 0$ in the last step. Hence, $\bar{c}_{min,j} = 0$ in $S_{j,2}$. The assertion $0 \leq w \leq 1$ is valid because $0 \leq w_\varepsilon \leq 1$ for all ε.

Hence, we have proven the existence of a solution of (43)-(48), i.e., of problem $(\boldsymbol{P}^+)$. With Remark 9 this is also a solution of problem $(\boldsymbol{P})$. □

6 Uniqueness

In order to prove uniqueness of a solution of problem $(\boldsymbol{P})$ we proceed as follows. For two solutions given, we first estimate the difference of the minerals in terms of the difference of the mobile species by using the ODEs, and then, by using the PDEs, integrated in time, we show that the difference between the mobile species can at most increase exponentially in time, from which uniquess of the solution follows.

In this chapter we additionally assume that $\boldsymbol{q}, d, \beta$ do not depend on time. Then the following theorem holds.

Theorem 14 *Let* $(\boldsymbol{c}_1, \bar{\boldsymbol{c}}_{1,min}, \boldsymbol{w}_1), (\boldsymbol{c}_2, \bar{\boldsymbol{c}}_{2,min}, \boldsymbol{w}_2) \in W_p^{2,1}(Q_T)^I \times \mathcal{L}(Q_T)^{J_{min}} \times L^\infty(Q_T)^{J_{min}}$ *be two solutions of problem* $(\boldsymbol{P})$*. Then* $\boldsymbol{c}_1 = \boldsymbol{c}_2$ *and* $\bar{\boldsymbol{c}}_{1,min} = \bar{\boldsymbol{c}}_{2,min}$ *holds.*

Proof. From Theorem 13 we know that there is a nonnegative solution of problem $(\boldsymbol{P})$. So, let $(\boldsymbol{c}_1, \bar{\boldsymbol{c}}_{1,min}, \boldsymbol{w}_1)$ be a nonnegative solution and let us asume that $(\boldsymbol{c}_2, \bar{\boldsymbol{c}}_{2,min}, \boldsymbol{w}_2)$ is any other solution. Let us consider the differences

$$\boldsymbol{u} = \boldsymbol{c}_2 - \boldsymbol{c}_1\,, \quad \boldsymbol{v} = \bar{\boldsymbol{c}}_{2,min} - \bar{\boldsymbol{c}}_{1,min}$$

and, for the sake of brevity, let us define

$$\rho_{prec,j}(z) = k_{p,j} \prod_{\substack{i=1\\ s_{min,ij}<0}}^{I} z_i^{-s_{min,ij}}\,, \quad \rho_{diss,j}(z) = k_{d,j} \prod_{\substack{i=1\\ s_{min,ij}>0}}^{I} z_i^{s_{min,ij}}$$

for $z \in \mathbb{R}^{J_{min}}$, $j = 1, ..., J_{min}$ (compare to (28)). We use (22) for $\bar{\boldsymbol{c}}_{1,min}$ and for $\bar{\boldsymbol{c}}_{2,min}$ to obtain

$$\begin{aligned}\partial_t v_i &= \rho_{prec,i}(\boldsymbol{c}_2) - \rho_{prec,i}(\boldsymbol{c}_1) - [\rho_{diss,i}(\boldsymbol{c}_2) w_{2,i} - \rho_{diss,i}(\boldsymbol{c}_1) w_{1,i}]\\ &= \rho_{prec,i}(\boldsymbol{c}_2) - \rho_{prec,i}(\boldsymbol{c}_1) - [\rho_{diss,i}(\boldsymbol{c}_2) - \rho_{diss,i}(\boldsymbol{c}_1)] w_{2,i}\\ &\qquad - \rho_{diss,i}(\boldsymbol{c}_1)(w_{2,i} - w_{1,i})\end{aligned}$$

We multiply by v_i and integrate over $[0,t]\times\Omega$. Then we exploit that $-\rho_{diss,i}(\boldsymbol{c}_1)(w_{2,i} - w_{1,i})(\bar{c}_{2,min,i} - \bar{c}_{1,min,i}) \le 0$ (which is true because of the nonnegativity of $\boldsymbol{c}_1$ and the monotonicity of $\bar{c}_{j,min,i} \mapsto w_{j,i} \in H(\bar{c}_{j,min,i})$, $j = 1, 2$). We also use that $w_{2,i}$ is bounded by 1 and that $\boldsymbol{c}_1, \boldsymbol{c}_2$ are bounded in $L^\infty(Q_T)^I$ which allows us to introduce a Lipschitz constant L (depending on the $L^\infty(Q_T)^I$-norm of $\boldsymbol{c}_1, \boldsymbol{c}_2$) for the polynomials $\rho_{prec,i}, \rho_{diss,i}$. We obtain

$$\frac{1}{2}\|v_i(t)\|^2 \le 2L \int_0^t \|\boldsymbol{u}(s)\| \|v_i(s)\|\, ds$$

for $t \in (0,T]$, where $\|\cdot\| = \|\cdot\|_{L^2(\Omega)}$. We sum up over $i = 1, ..., J_{min}$ and use Young's inequality to get

$$\frac{1}{2}\|\boldsymbol{v}(t)\|^2 \le L^2 J_{min} \int_0^t \|\boldsymbol{u}\|^2\, ds + \int_0^t \|\boldsymbol{v}\|^2\, ds\,.$$

From Gronwall's inequality we obtain

$$\|\boldsymbol{v}(t)\|^2 \le C_{vu}^2 \int_0^t \|\boldsymbol{u}(s)\|^2\, ds \tag{49}$$

for all $t \in [0,T]$ with $C_{vu} = \sqrt{2J_{min}}L\, e^T$.

Now we consider the PDEs (21) for $\boldsymbol{c}_1$ and for $\boldsymbol{c}_2$ and obtain

$$\partial_t u_i - \nabla\cdot(d\nabla u_i) + \boldsymbol{q}\cdot\nabla u_i = [S_{mob}(\boldsymbol{r}_{mob}(\boldsymbol{c}_2) - \boldsymbol{r}_{mob}(\boldsymbol{c}_1))]_i + [S_{min}\partial_t \boldsymbol{v}]_i\,.$$

For a given $t \in (0,T]$, we multiply by a function $\varphi_i \in H^1(\Omega)$ and integrate over $[0,t]\times\Omega$, and use integration by parts for the diffusion term:

$$\begin{aligned}&(u_i(t), \varphi_i) + (\int_0^t d\,\nabla u_i(s)\, ds, \nabla\varphi_i) - \int_{\partial\Omega}\int_0^t d\nabla u_i(s)\cdot n\, ds\, \varphi_i\, do\\ &= \int_0^t ([\boldsymbol{\rho}_{mob}(\boldsymbol{c}_2(s)) - \boldsymbol{\rho}_{mob}(\boldsymbol{c}_1(s))]_i, \varphi_i)\, ds + ([S_{min}\boldsymbol{v}(t)]_i, \varphi_i) - (\int_0^t \boldsymbol{q}\cdot\nabla u_i(s)\, ds, \varphi_i)\end{aligned}$$

where $(\cdot,\cdot)$ denotes the $L^2(\Omega)$ scalar product and $\boldsymbol{\rho}_{mob}(\boldsymbol{c}) = S_{mob}\boldsymbol{r}_{mob}(\boldsymbol{c})$. For $t \in (0,T]$, let us choose $\varphi_i := u_i(t)$. We further exploit the boundedness of $\boldsymbol{c}_1, \boldsymbol{c}_2$ in $L^\infty(Q_T)$, the boundary condition (26), and the assumption that $\boldsymbol{q}$ and β do not depend on time:

$$\begin{aligned}&\|u_i(t)\|^2 + \Big(\int_0^t d\nabla u_i(s)\,ds, \nabla u_i(t)\Big) - \int_{\partial\Omega}\beta\int_0^t u_i(s)\,ds\,u_i(t)\,do\\ &\quad\le L\int_0^t\int_\Omega |\boldsymbol{u}(s)|\,|u_i(t)|\,dx\,ds + C_S\|\boldsymbol{v}(t)\|\|u_i(t)\| + \|\boldsymbol{q}\cdot\int_0^t \nabla u_i(s)\,ds\|\,\|u_i(t)\|\end{aligned}$$

Using $\int_0^t\int_\Omega |\boldsymbol{u}(s)|\,|u_i(t)|\,dx\,ds \le \int_0^t \|\boldsymbol{u}(s)\|\,\|u_i(t)\|\,ds \le \sqrt{t}(\int_0^t \|\boldsymbol{u}(s)\|^2 ds)^{\frac12}\|u_i(t)\|$ and (49), it follows that

$$\begin{aligned}&\|u_i(t)\|^2 + \Big(\int_0^t d\nabla u_i(s)\,ds, \nabla u_i(t)\Big) - \int_{\partial\Omega}\beta\int_0^t u_i(s)\,ds\,u_i(t)\,do\\ &\quad\le (L\sqrt{T} + C_S C_{vu})\Big(\int_0^t \|\boldsymbol{u}(s)\|^2 ds\Big)^{\frac12}\|u_i(t)\| + C_q\,\|\int_0^t \nabla u_i(s)\,ds\|\,\|u_i(t)\|\\ &\quad\le (L\sqrt{T}+C_S C_{vu})^2\int_0^t \|\boldsymbol{u}(s)\|^2 ds + \frac12\|u_i(t)\|^2 + \frac{C_q^2}{\delta}\|\int_0^t d^{\frac12}\nabla u_i(s)\,ds\|^2\end{aligned}$$

where we have used Young's inequality $Cab \le C^2a^2 + \frac{b^2}{4}$ on both terms in the last step. We sum up over i and have

$$\begin{aligned}&\frac12\|\boldsymbol{u}(t)\|^2 + \sum_{i=1}^I\Big(\int_0^t d\nabla u_i(s)\,ds, \nabla u_i(t)\Big) - \int_{\partial\Omega}\beta\int_0^t u_i(s)\,ds\,u_i(t)\,do\\ &\quad\le I(L\sqrt{T}+C_S C_{vu})^2\int_0^t \|\boldsymbol{u}(s)\|^2 ds + \frac{C_q^2}{\delta}\sum_{i=1}^I\|\int_0^t d^{\frac12}\nabla u_i(s)\,ds\|^2\,.\end{aligned}\tag{50}$$

Setting $E(t) := \int_0^t \|\boldsymbol{u}(s)\|^2 ds + \sum_{i=1}^I \|d^{\frac12}\int_0^t \nabla u_i(s)\,ds\|^2 - \int_{\partial\Omega}\beta\left(\int_0^t u_i(s)\,ds\right)^2 do$, the left-hand side of (50) is equal to $\frac12 E'(t)$, and the right-hand side of (50) can be estimated by a constant times $E(t)$ (remember that $\beta \le 0$). So, the above inequality reads

$$E'(t) \le C\,E(t)\,,$$

with $E(0) = 0$. Hence, $E(t) = 0$ and finally $\boldsymbol{u} = \boldsymbol{0}$ follows on $[0,T]$. Due to (49) also $\boldsymbol{v} = \boldsymbol{0}$ follows. □

7 Conclusion

In this article we first proved that some formulations for precipitation-dissolution of minerals are equivalent. Then we proved the existence of global solutions for a macro-scale multicomponent reactive-transport model for reactions with minerals. The model we have considered goes beyond what has been investigated in the past (cf. Sec. 1). Instead of one mineral and two mobile species we considered an arbitrary number, and besides the mineral reactions, we also allowed for reactions among the mobile species, and, most important, the aqueous and the precipitation and the dissolution reaction rates are allowed to have arbitrarily high polynomial order with respect to the mobile species concentrations. The main challenges were the set-valued shape of the dissolution rates and the high nonlinearity of all the rate terms. We used a Lipschitz regularization and the method of a priori estimates in combination with a maximum principle. The proof of global existence comes together with an $L^\infty((0,\infty)\times\Omega)$-estimate for the solution. A certain assumption on the stoichiometric matrix is required. However, we think that this is a rather mild restriction, in particular for mass conservative reactive systems.

A Applying the Maximum Principle

In [15, I, Thm. 2.2/2.3] the boundary conditions are of the form

$$\Big(\sum_{i=1}^{n} b_i(\boldsymbol{x},t)\partial_i u + b(\boldsymbol{x},t)u\Big)\Big|_{S_T} = \psi(\boldsymbol{s},t)\,.$$

Using the boundary conditions of Section 5 we have

$$b_i = d\nu_i\,, \qquad b = -\beta\,.$$

One assumption of [15, I, Thm. 2.2] is $b|_{S_T} > 0$, which is not fulfilled for $\beta = 0$. In [15, I, Thm. 2.3] there is the assumption $b|_{S_T} \geq -b_0$ with $b_0 = \text{const} \geq 0$, which is fulfilled for $\beta = 0$. However, in [15, I, Thm. 2.3] the assertion is simplified and depends on $|f|$ while in [15, I, Thm. 2.2] the assertion depends only on $\max f$. The problem is that we only know that $f \leq 0$, but we do not know a lower bound for f. So we have to look inside the proof of [15, I, Thm. 2.3]. The proof of [15, I, Thm. 2.3] is done by applying [15, I, Thm. 2.2] to the function $w(\boldsymbol{x},t) := u(\boldsymbol{x},t)\varphi(\boldsymbol{x})$ with $\varphi \in O^2(\overline{\Omega})$ ($O^2(\overline{\Omega})$ is the set of all continuous functions in $\overline{\Omega}$ having continuous derivatives in $\overline{\Omega}$ up to order 1, with the derivatives of order 1 having a first differential at each point of $\overline{\Omega}$ and the derivatives of order 2 being bounded in $\overline{\Omega}$) a function that satisfies

$$\min_{\Omega}\varphi(\boldsymbol{x}) \geq \frac{1}{2}\,, \qquad \varphi|_{\partial\Omega} = 1\,, \qquad -\partial_{\boldsymbol{\nu}}\varphi|_{\partial\Omega} = m$$

where $m = \text{const} > b_0/\delta$ with δ out of Assumptions 6 (i). So we get for any $t_1 \in [0,T]$

$$w(\boldsymbol{x},t_1) \leq \inf_{\lambda > a_0} \max\left\{0; \max_{S_{t_1}} \frac{\psi\varphi e^{\lambda(t_1-t)}}{b - b_i\frac{\partial_i\varphi}{\varphi}}; e^{\lambda t_1}\max_{\Omega} w(\boldsymbol{x},0); \frac{1}{\lambda - a_0}\max_{Q_{t_1}} f e^{\lambda(t_1-t)}\right\}$$

with $a_0 = \max_{Q_T}(-a(\boldsymbol{x},t))$ where a is the 0th order coefficient of the PDE.

Now let u be the solution of (41). Because of the boundary condition $d\partial_{\boldsymbol{\nu}}u = \beta u$ on S_T it holds $\psi \equiv 0$, because of the initial condition $u(\cdot,0) = 0$ on $\overline{\Omega}$ it holds

$w(\boldsymbol{x}, 0) = 0$ for all $\boldsymbol{x} \in \Omega$ and as there is no 0th order term in the PDE we have $a_0 = 0$. This yields

$$w(\boldsymbol{x}, t_1) \leq \inf_{\lambda>0} \max \left\{ 0; \frac{1}{\lambda} \max_{Q_{t_1}} f e^{\lambda(t_1 - t)} \right\} .$$

As the right-hand side f of the PDE for u is nonpositive it follows $w(\boldsymbol{x}, t_1) \leq 0$. Because of $\varphi \geq 1/2$ this yields

$$u(\boldsymbol{x}, t) \leq 0 .$$

This is the assertion needed to derive the a priori estimate.

References

[1] D. Bothe, M. Köhne, S. Maier, and J. Saal, *Global solutions for a class of heterogeneous catalysis models*. arXiv:1510.06195v1 [math.AP] 21 Oct 2015, http://arxiv.org/pdf/1510.06195.pdf, accepted for publication in J. Math. Anal. Appl.

[2] N. Bouillard, R. Eymard, R. Herbin, and Ph. Montarnal, *Diffusion with dissolution and precipitation in a porous medium: Mathematical analysis and numerical approximation of a simplified model*, ESAIM: Mathematical Modelling and Numerical Analysis, 41 (2007), pp. 975–1000.

[3] H. Buchholzer, C. Kanzow, P. Knabner, and S. Kräutle, *The semismooth newton method for the solution of reactive transport problems including mineral precipitation-dissolution reactions*, Comput. Optim. Appl., 50 (2011), pp. 193–221.

[4] J. Cañizo, L. Desvillettes, and K. Fellner, *Improved duality estimates and applications to reaction-diffusion equations*, Comm. Part. Diff. Equ., 39 (2014), pp. 1185–1204.

[5] J. Fischer, *Global existence of renormalized solutions to entropy-dissipating reaction–diffusion systems*, J. Arch Rational Mech Anal, 218 (2015), p. 553587. doi:10.1007/s00205-015-0866-x.

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

[7] A. Friedman, *Partial differential equations of parabolic type*, Prentice-Hall, Englewood Cliffs, NJ, 1964.

[8] D. Gilbarg and N. Trudinger, *Elliptic partial differential equations of second order*, Springer, 1977.

[9] P. Knabner, *A free boundary problem arising from the leaching of saline soils*, SIAM Journal on Mathematical Analysis, 17 (1986), pp. 610–625.

[10] P. Knabner, C.J. van Duijn, and S. Hengst, *An analysis of crystal dissolution fronts in flows through porous media. part 1: Compatible boundary conditions*, Advances in Water Resources, 18 (1995), pp. 171–185.

[11] S. Kräutle, *General multi-species reactive transport problems in porous media: efficient numerical approaches and existence of global solutions*, habilitation thesis, University Erlangen–Nuremberg, 2008. http://www.mso.math.fau.de/applied-mathematics-1/research/publications/theses/.

[12] ———, *Existence of global solutions of multicomponent reactive transport problems with mass action kinetics in porous media*, J. Appl. Ana. Comp., 1 (2011), pp. 497–515.

[13] ———, *The semismooth newton method for multicomponent reactive transport with minerals*, Advances Water Res., 34 (2011), pp. 137–151.

[14] K. Kumar, M. Neuss-Radu, and I.S. Pop, *Homogenization of a pore scale model for precipitation and dissolution in porous media*. arXiv:1401.7025v1 [math.AP] 27 Jan 2014, http://arxiv.org/pdf/1401.7025.pdf.

[15] O.A. Ladyzenskaja, V.A. Solonnikov, and N.N. Uralceva, *Linear and Quasi-linear Equations of Parabolic Type*, vol. 23 of Translations of Mathematical Monographs, American Mathematical Society, 1968.

[16] M. Mincheva and D. Siegel, *Stability of mass action reaction-diffusion systems*, Nonlinear Analysis, 56 (2004), pp. 1105–1131.

[17] H. Schaefer, *Über die Methode der a priori-Schranken*, Math. Annalen, 129 (1955), pp. 415–416.

[18] V.A. Solonnikov, *A priori estimates for second-order parabolic equations*, Trudy Mat. Inst. Steklov, 70 (1964), pp. 133–212. *Amer. Math. Soc. Transl. Ser. 2*, 65:51-138, 1967.

[19] C.J. van Duijn and P. Knabner, *Travelling wave behaviour of crystal dissolution in porous media flow*, European Journal on Applied Mathematics, 8 (1997), p. 455 ff.

[20] C.J. van Duijn, P. Knabner, and R.J. Schotting, *An analysis of crystal dissolution fronts in flows through porous media part 2: Incompatible boundary conditions*, Advances in Water Resources, 22 (1998), pp. 1–16.

[21] C.J. van Duijn and I.S. Pop, *Crystal dissolution and precipitation in porous media: Pore scale analysis*, J. Reine Angew. Math., 577 (2004), pp. 171–211.

[22] W. Walter, *Ordinary differential equations*, Springer, New York, 1998.

[23] Zhuoqun Wu, Jingxue Yin, and Chunpeng Wang, *Elliptic & parabolic equations*, World Scientific, Singapore, 2006.

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