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by

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Abstract We present a computational numerical scheme for reactive contaminant transport with non-equilibrium sorption in porous media. The mass conservative scheme is based on Euler implicit, mixed finite elements (MFE) and Newton method. We consider the case of a Freundlich type sorption. In this case the sorption isotherm is not Lipschitz, but just Hölder continuous. To deal with this, we perform a regularization step. The convergence of the scheme is analysed. An explicit order of convergence depending only on the regularization parameter, the time step and the mesh size is derived. We give also a sufficient condition for the quadratic convergence of the Newton method. Finally relevant numerical results are presented.

1 Introduction

Water pollution is a grave problem nowadays. Questions like how dangerous a contaminated site is, whether natural attenuation can occur, which processes are dominant and whether an active remediation is necessary become relevant for decisions on what we have to do in order to properly protect ourselves and the next generations, as well as the environment. To answer these questions, predictions based on mathematical modelling and numerical simulations are needed, requiring efficient and reliable numerical codes. Besides modern discretization tools and efficient linear and nonlinear solvers, it is very important that the implemented model allows to simulate realistic, complicated scenarios. The model must include: flow in saturated/unsaturated, heterogeneous soils and multicomponent advective-diffusive-reactive transport with sorption.

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in porous media. We especially emphasize that a reliable simulation tool must comprehend the effects of sorption on the transport of contaminants in soil, see e.g. [36,37]. In this paper we present and analyze a mass conservative numerical scheme to efficiently simulate reactive solute transport with non-equilibrium sorption in aquifers. Here we continue the work in [32,33], where the case of equilibrium sorption was treated.

A general mathematical model for reactive solute transport with non-equilibrium sorption is

\[ \Theta_S \partial_t c + \rho_h \partial_t s - \nabla \cdot (D \Theta_S \nabla c - c \mathbf{Q}) = \Theta_S r(c) \quad \text{in } J \times \Omega, \quad (1) \]

\[ \partial_t s = k_s (\phi(c) - s) \quad \text{in } J \times \Omega, \quad (2) \]

with \( c(t, \mathbf{x}) \) denoting the concentration of the dissolved species, \( s(t, \mathbf{x}) \) the concentration of the adsorbed species, \( D \) the constant diffusion coefficient (we take for simplicity \( D = 1 \)), \( r(\cdot) \) a reaction rate and \( k_s \) the Damkohler number assumed also of moderate order. We further assume that the water content \( \Theta_S \) is constant, as encountered for example in the saturated flow regime, where \( \Theta_S = 1 \), \( J \subset \mathbb{R}^d \) denotes the computational domain, \( d \) the space dimension and \( J = (0, T) \) the time interval, \( T \) being some finite end time. Further, \( \phi(\cdot) \) is a sorption isotherm, with a possible unbounded derivative. This choice covers the realistic, practical case of a Freundlich type isotherm, e.g. \( \phi(x) = x^\alpha \), with \( \alpha \in (0, 1] \). Initial \( c(0, \mathbf{x}) = c_f(\mathbf{x}), s(0, \mathbf{x}) = s_f(\mathbf{x}) \) and homogeneous Dirichlet boundary conditions complete the model. The homogeneous Dirichlet boundary conditions were chosen just for the sake of simplicity, all the results presented in this paper can be extended to more general boundary conditions. The water flux \( \mathbf{Q}(\mathbf{x}) \) solves

\[ \nabla \cdot \mathbf{Q} = 0, \quad (3) \]

\[ \mathbf{Q} = -K_S \nabla (\psi + z), \quad (4) \]

in \( \Omega \), with \( \psi(\mathbf{x}) \) being the pressure head, \( K_S \) the hydraulic conductivity and \( z \) the height against the gravitational direction. We consider here only the case of fully saturated flow, but the scheme is implemented for the general saturated/unsaturated flow case. Furthermore, the analysis presented in the next section can be extended also to strictly unsaturated flow (see also [32]).

In this paper we present an Euler-implicit, mixed finite element scheme for the system (1) – (2). The sorption isotherm is assumed monotone and Hölder continuous. Choosing for a mixed finite element discretization ensures the local mass conservation. Because the model is degenerate, its solution lacks regularity, therefore we only consider the lowest order Raviart-Thomas finite elements. The nonlinear problems arising at each time step are solved by a Newton method. To this aim, we discretize a regularized approximation of the original model. We provide error estimates for the fully discrete solution and derive an explicit condition for the convergence of the scheme, in terms of the discretization and the regularization parameters. This condition allows to control a priori the time step, the regularization parameter and the mesh diameter, so that an optimal convergence is achieved. We use the solution of the previous time step \( n - 1 \) as the starting choice for the Newton iteration at the current step \( n \). In this way the initial error can be quantified due to a stability estimate, and an explicit constraint on the discretization parameters can be derived to ensure the certain quadratic convergence of the Newton method. This a priori knowledge is very important for practical computation because a suitable choice of the parameters saves a lot of computation.
time. In this sense we mention [14], proposing an adaptive method that takes into account the error made in each Newton step with respect to the total error, resulting into a very fast method.

In spite of the rich literature on numerical methods for solute transport in porous media (like [2, 5–8, 13, 15–20, 23, 24, 30, 32–35]), only a few are considering nonlinear sorption. We refer to [5, 6] and [13] for conforming finite element discretization. There both the cases of non-equilibrium and equilibrium sorption are considered. The water flow is assumed saturated, with the flux Q being given analytically. A similar situation is also considered in [11]. We also refer to [16] for a combined finite volume-finite element scheme for transport with equilibrium sorption. The mixed finite element discretization for equilibrium sorption is considered in [12] and [32]. The latter also considered saturated/unsaturated flow, taking explicitly into account the low regularity of the solution to the Richards equation. The resulting estimates depend on the accuracy of the scheme for the water flow. In all this works the nonlinear systems arising at each time step are supposed to be solved exactly. The degeneracy related with a Freundlich type isotherm makes solving these systems a complicated task. The resulting fully discrete nonlinear problems are commonly solved by different methods: the Newton scheme, which is locally quadratic convergent, some robust first-order linearization schemes (see [26, 38]), or the Jäger-Kačur scheme [23, 19]. The convergence of the Newton method applied to the system provided by a MFE discretization of an elliptic problem is studied in [25]. Concerning the systems provided by the MFE discretization of degenerate parabolic equations we mention [26] for a robust linear scheme and [29, 33] for the Newton method.

The followings are the novel aspects in this paper:

- We analyze a mixed finite element scheme for solute transport in porous media with non-equilibrium sorption.
- We study the convergence of the Newton scheme solving the nonlinear systems arising at each time step.
- We derive explicit, sufficient conditions on the three parameters (the time step, the mesh diameter and the regularization parameter) ensuring the optimal convergence of the scheme.

The paper is structured as follows: in the next section the discretization scheme is presented. The main results concerning the convergence of the scheme are given and discussed. In Section 3 we present stability estimates and the proofs of the theorems stated in the preceding section. Two numerical studies: an example with an analytical solution and a realistic infiltration problem are given in Section 4. In the last section we present concluding remarks.

2 Discretization and main results

Throughout this paper we use common notations in the functional analysis. By $\langle \cdot, \cdot \rangle$ we mean the inner product on $L^2(\Omega)$. Further, $\|\cdot\|$ and $\|\cdot\|_{L^p(\Omega)}$ stand for the norms in $L^2(\Omega)$ and $L^p(\Omega)$ respectively. The functions in $H(\text{div}, \Omega)$ are vector valued, having a $L^2$ divergence. $\|\cdot\|$ stands for the norm in $H^1(\Omega)$. $C$ denotes a positive constant, not depending on the unknowns or the discretization parameters. $L_f$ the Lipschitz constant of a Lipschitz continuous function $f(\cdot)$. 
For the discretization in time we let $N \in \mathbb{N}$ be strictly positive, and define the time step $\tau = T/N$, as well as $t_n = n\tau$ ($n \in \{1, 2, \ldots, N\}$). Furthermore, $T_h$ is a regular decomposition of $\Omega \subset \mathbb{R}^d$ into closed $d$-simplices; $h$ stands for the mesh diameter. Here we assume $\mathcal{T} = \bigcup_{T \in T_h} T$, hence $\Omega$ is polygonal. Correspondingly, we define the discrete subspaces $W_h \subset L^2(\Omega)$ and $V_h \subset H(\text{div}; \Omega)$:

$$
W_h := \{ p \in L^2(\Omega) \mid p \text{ is constant on each element } T \in T_h \},
$$

and

$$
V_h := \{ q \in H(\text{div}; \Omega) \mid q|_T = a + bx \text{ for all } T \in T_h \}.
$$

In other words, $W_h$ denotes the space of piecewise constant functions, while $V_h$ is the $RT_0$ space (see [10]).

In what follows we make use of the usual $L^2$ projector:

$$
P_h : L^2(\Omega) \to W_h, \quad \langle P_h w - w; w_h \rangle = 0,
$$

for all $w_h \in W_h$. Furthermore, a projector $\Pi_h$ can be defined on $(H^1(\Omega))^d$ (see [10, p. 131]) such that

$$
\Pi_h : (H^1(\Omega))^d \to V_h, \quad \langle \nabla \cdot (\Pi_h \mathbf{v} - \mathbf{v}); w_h \rangle = 0,
$$

for all $w_h \in V_h$. Following [27], p. 237, this operator can be extended to $H(\text{div}; \Omega)$. For the above operators there holds

$$
\| w - P_h w \| \leq Ch \| w \|_1, \quad \| \mathbf{v} - \Pi_h \mathbf{v} \| \leq Ch \| \mathbf{v} \|_1
$$

for any $w \in H^1(\Omega)$ and $\mathbf{v} \in (H^1(\Omega))^d$.

Mixed finite elements are applied for solving the flow problem (3) - (4) numerically. One has (see [28, 31] for details)

$$
\| \psi - \psi_h \| + \| \mathbf{Q} - \mathbf{Q}_h \| + \| \nabla \cdot (\mathbf{Q} - \mathbf{Q}_h) \| \leq Ch,
$$

where $(\psi, \mathbf{Q}) \subset L^2(\Omega) \times H(\text{div}; \Omega)$ and $(\psi_h, \mathbf{Q}_h) \subset W_h \times V_h$ denote the continuous and discrete solutions respectively. For error estimates for MFE schemes for unsaturated/saturated flow we refer to [3, 28, 31] and for strictly saturated flow to [3]; a brief review can be found in [32]. We mention that the ideas in the analysis carried out in this paper can also be applied for the conformal, mixed or finite volume discretization of the groundwater flow, as long as they provide estimates like (10), and the assumption (A3) made below holds.

The Newton iteration considered here requires that the derivatives of the nonlinear functions are bounded away from 0 and infinity. Therefore we perform a regularization step. For simplicity only the regularization isothersm for the Friedrichs isothersm $\phi(x) = [x]^\alpha_-$ is given, where $\alpha \in (0, 1]$ and $[x]^+_{\alpha}$ stands for the positive cut of $x$. A generalization to other isothersms is straightforward.

$$
\phi_\alpha(x) = \begin{cases} 
\phi(x) & \text{if } x \not\in [0, \varepsilon], \\
(\alpha - 1)x^{\alpha - 2}x^2 + (2 - \alpha)x^{\alpha - 1} & \text{if } x \in [0, \varepsilon].
\end{cases}
$$

Some properties of $\phi_\alpha$ are given in the following lemma. Its proof is elementary.
Lemma 1 The regularized sorption isotherm is nondecreasing. Further, \( \phi_i(\cdot) \) and \( \phi'_i(\cdot) \) are Lipschitz continuous on \([0, \infty)\) with the Lipschitz constants \( L_{\phi_i} = e^{\alpha-1} \), respectively. Finally, we have

\[
0 \leq \phi(x) - \phi_i(x) \leq (1 - \alpha)e^\alpha
\]  

if \( x \in (0, \epsilon) \), whereas \( \phi(x) = \phi_i(x) \) whenever \( x \notin (0, \epsilon) \).

To write (1) - (2) in a mixed form we define the contaminant flux \( q = -\nabla c + \epsilon Q \). In this way the reactive solute transport problem is formulated as

**Problem 1** (continuous mixed variational formulation)

Find \((c, q, s) \in H^1(J; L^2(\Omega)) \times L^2(J; H(div; \Omega)) \times H^1(J; L^2(\Omega))\), with \( c_{|t=0} = c_I \) and \( s_{|t=0} = s_I \) so that for all \( t \in J \) we have

\[
\langle \partial_t c, w \rangle + \rho_b \langle \partial_\tau s, w \rangle + \langle \nabla \cdot q, w \rangle = \langle r(c), w \rangle 
\]

(13)

\[
\langle q, v \rangle - \langle c, \nabla \cdot v \rangle - \langle \epsilon Q, v \rangle = 0
\]

(14)

\[
\langle \partial_t s, w \rangle = \kappa_s \langle \phi(c), w \rangle - \langle s, w \rangle,
\]

(15)

for all \( w \in L^2(\Omega) \) and \( v \in H(div; \Omega) \).

Throughout this paper we make use of the following assumptions:

(A1) The rate function \( r: \mathbb{R} \rightarrow \mathbb{R} \) is differentiable with \( r' \) bounded and Lipschitz continuous. Furthermore, \( r(c) = 0 \) for all \( c \leq 0 \).

(A2) The initial \( c_I, s_I \) are essentially bounded and positive.

(A3) The water flux and its numerical approximation are essentially bounded, \( Q, Q_h \in L^\infty(\Omega) \).

(A4) The sorption isotherm \( \phi(\cdot) \) is nondecreasing, nonnegative and Hölder continuous with an exponent \( \alpha \in (0, 1] \), i.e. \( |\phi(a) - \phi(b)| \leq C|a - b|^\alpha \) for all \( a, b \in \mathbb{R} \). Moreover, \( \phi(c) = 0 \) if \( c \leq 0 \).

(A5) For the solution of Problem 1 we have \( c \in L^\infty(J \times \Omega) \), while \( \partial_t c \) and \( \partial_t s \) are Hölder continuous in \( t \) with exponent \( \alpha/2 \) and \( \alpha \) respectively. Furthermore, there holds

\[
\sum_{n=1}^N \tau \|q(t_n)\|^2 \leq C.
\]

Remark 1 The regularity assumed in (A5) for \( \partial_t c \) and \( \partial_t s \) is the maximal regularity one can expect for transport problems with non-equilibrium sorption, when the sorption isotherm is of Freundlich type. According to [21] Chapter II.4, if the initial and boundary data are compatible and sufficiently smooth we have \( c \in C^{2+\alpha, 1+\alpha/2}(\Omega \times J) \) and \( s \in C^{\alpha, 1+\alpha}(\Omega \times J) \). Furthermore, Proposition 1 below justifies (16) in the one dimensional case, when \( H(div; \Omega) = H^1(\Omega) \). For the essential bounds of \( c \) one only needs to assume that the data are essentially bounded. Furthermore, to avoid negative values for \( c \) and \( s \) - which are unrealistic - the rates \( r \) and \( \phi \) are extended by 0 in the negative part.

We now state the fully discrete mixed variational formulation for (1) - (2):
**Problem 2** (fully discrete variational formulation)

Let \( n \in \{1, \ldots, N\} \) and \((c_h^{n-1}, s_h^{n-1}) \in W_h \times V_h\) be given. Find \((c_h^n, q_h^n, s_h^n) \in W_h \times V_h \times W_h\) so that for all \( t \in J \) we have

\[
\langle c_h^n - c_h^{n-1}, w_h \rangle + \rho_h \langle q_h^n - s_h^{n-1}, w_h \rangle + \tau \langle \nabla \cdot q_h^n, w_h \rangle = \tau(r(c_h^n) - \phi', c_h^n, w_h) \\
\langle q_h^n, v_h \rangle - \langle c_h^n, \nabla \cdot v_h \rangle - \langle q_h^n, v_h \rangle - \langle c_h^n Q_h, v_h \rangle = 0 \\
\langle s_h^n - s_h^{n-1}, w_h \rangle = \tau \kappa_s(\langle \phi(c_h^n), w_h \rangle - \langle s_h^n, w_h \rangle),
\] (17)

for all \( w_h \in W_h \) and \( v_h \in V_h\). We take at time \( t = 0: c_h^0 = P_h c_I \) and \( s_h^0 = P_h s_I\).

The system (17)–(19) is nonlinear. To solve it we consider a Newton method, which is locally quadratic convergent:

**Problem 3** (Newton iterations)

Let \( n \in \{1, \ldots, N\} \) and \((c_h^{n-1}, s_h^{n-1}) \in W_h \times V_h\) be given and let \( c_h^{n,0} = c_h^{n-1}, s_h^{n,0} = s_h^{n-1}\). For \( i \geq 1 \) find \((c_h^{n,i}, q_h^{n,i}, s_h^{n,i}) \in W_h \times V_h \times W_h\) such that

\[
\langle c_h^{n,i} - c_h^{n-1}, w_h \rangle + \rho_h \langle q_h^{n,i} - s_h^{n-1}, w_h \rangle + \tau \langle \nabla \cdot q_h^{n,i}, w_h \rangle = \tau(r(c_h^{n,i-1}) + \phi'(c_h^{n,i-1})(c_h^{n,i} - c_h^{n,i-1}), w_h) \\
\langle q_h^{n,i}, v_h \rangle - \langle c_h^{n,i}, \nabla \cdot v_h \rangle - \langle q_h^{n,i}, v_h \rangle - \langle c_h^{n,i} Q_h, v_h \rangle = 0 \\
\langle s_h^{n,i} - s_h^{n-1}, w_h \rangle = \tau \kappa_s(\langle \phi(c_h^{n,i-1}) + \phi'(c_h^{n,i-1})(c_h^{n,i} - c_h^{n,i-1}), w_h \rangle - \langle s_h^{n,i}, w_h \rangle),
\] (20)

for all \( w_h \in W_h \),

\[
\langle q_h^{n,i}, v_h \rangle - \langle c_h^{n,i}, \nabla \cdot v_h \rangle - \langle q_h^{n,i}, v_h \rangle = 0
\] (21)

for all \( v_h \in V_h \) and

\[
\langle s_h^{n,i} - s_h^{n-1}, w_h \rangle = \tau \kappa_s(\langle \phi(c_h^{n,i-1}) + \phi'(c_h^{n,i-1})(c_h^{n,i} - c_h^{n,i-1}), w_h \rangle - \langle s_h^{n,i}, w_h \rangle),
\] (22)

for all \( w_h \in W_h \).

To fix the notations: \( n \in \{1, \ldots, N\} \) always indexes the time step, while \( i \) is used to index the iteration. Accordingly, \((c_h^{n}, q_h^{n}, s_h^{n})\) denotes the solution of Problem 2 at the \( n^{th} \) time step and \((c_h^{n,i}, q_h^{n,i}, s_h^{n,i})\) stands for the solution triple at iteration \( i \geq 1 \). The iteration process starts with \( c_h^{n,0} = c_h^{n-1}, s_h^{n,0} = s_h^{n-1}\). In proving the convergence of the scheme it is sufficient to show that

\[
\|c_h^n - c_h^n\| + \|q_h^n - q_h^n\| + \|s_h^n - s_h^n\| \xrightarrow{i\tau h \to 0} 0,
\] (23)

whereas

\[
\|c_h^n - c_h^{n,i}\| + \|q_h^n - q_h^{n,i}\| + \|s_h^n - s_h^{n,i}\| \xrightarrow{i \to \infty} 0
\] (24)

quadratically. This will be achieved for a sufficiently small time step \( \tau \). A sufficient condition on the discretization parameters \( \epsilon, \tau, h \) is derived to ensure both convergences stated above. The main results in this paper are

- Theorem 1 showing the convergence (23).
- Theorem 2 showing the quadratic convergence (24).
- An explicit condition on \( \tau, \epsilon \) and \( h \) to ensure the convergences above.

The proofs are given in Section 3.
Theorem 1 Assuming (A1) - (A5), we have
\[
\| P_h c(t_N) - c_h^n \|_2^2 + \sum_{n=1}^{N} \tau \| \phi(c(t_n)) - \phi(c_h^n) \|_{L^{1+\alpha}}^2 + \sum_{n=1}^{N} \tau \| P_h c(t_n) - c_h^n \|_2^2 \\
+ \sum_{n=1}^{N} \tau \| q(t_n) - q_h^n \|_2^2 \leq C(h^{1+\alpha} + \tau^\alpha + \epsilon^{1+\alpha}).
\] (25)
and
\[
\| P_h s(t_N) - s_h^n \|_2^2 + \sum_{n=1}^{N} \tau \| P_h s(t_n) - s_h^n \|_2^2 \leq C(\tau^{\frac{1+\alpha}{\alpha}} + \tau^{-r} (h^{1+\alpha} + \tau^\alpha + \epsilon^{1+\alpha})).
\] (26)
for any $r \in \mathbb{R}$.

Remark 2 If the sorption $\phi(\cdot)$ and its derivative are Lipschitz continuous (thus $\alpha = 1$), a slightly modified proof leads to optimal error estimates
\[
\| P_h c(t_N) - c_h^n \|_2^2 + \sum_{n=1}^{N} \tau \| \phi(c(t_n)) - \phi(c_h^n) \|_2^2 + \sum_{n=1}^{N} \tau \| P_h c(t_n) - c_h^n \|_2^2 \\
+ \sum_{n=1}^{N} \tau \| q(t_n) - q_h^n \|_2^2 \leq C(h^2 + \tau^2).
\] (27)

Remark 3 Similar results can be obtained in the strictly unsaturated flow regime, or for a steady unsaturated flow, where $\Theta$ is time independent (as assumed for example in [6, 11]).

Theorem 2 Assuming (A1) - (A4), for sufficiently small $\tau$ we have
\[
\| c_h^n - c_h^{n,i} \|_2^2 + \tau \| q_h^n - q_h^{n,i} \|_2^2 \leq C \tau^2 (L^2_{\phi'} + L^2_{\phi}) h^{-d} \| c_h^n - c_h^{n,i-1} \|_4^2
\] (28)
and
\[
\| s_h^n - s_h^{n,i} \|_2^2 \leq C \tau^2 (L^2_{\phi'} + \tau^2 L^2_{\phi} (L^2_{\phi'} + L^2_{\phi})) h^{-d} \| c_h^n - c_h^{n,i-1} \|_4^2.
\] (29)

From (28) we can derive sufficient condition for the quadratic convergence of the Newton scheme
\[
C \tau^3 \epsilon^{2,\alpha-1} h^{-d} \| c_h^n - c_h^{n-1} \|_2^2 \leq 1.
\] (30)

With the stability estimate
\[
\sum_{n=1}^{N} \| c_h^n - c_h^{n-1} \|_2^2 \leq C \frac{\tau^2}{\epsilon^{2(1-\alpha)}}
\]
proved in Proposition 2, this condition becomes
\[
C \tau^3 \epsilon^{2,\alpha-1} h^{-d} \leq 1.
\] (31)

Using (31) and Theorem 1, one can choose a priori the time step, the regularization parameter and the mesh size in such a way that the optimal convergence is guaranteed. In this sense numerical examples are provided in Section 4. Referring to [14], where the Newton-error is controlled adaptively with respect to the total error, condition (31) can provide useful information for the initial tuning of the discretization parameters for adaptive methods.
Remark 4 The condition (31) is derived under pessimistic conditions. In this sense we mention the the stability estimates in Theorem 2, bounding to the sum \(\sum_{n=1}^{N} \|e_{h}^{n} - e_{h}^{n-1}\|^{2}\), wherefrom one term, \(\|e_{h}^{n} - e_{h}^{n-1}\|^{2}\) is used to derive (31) from (30). In case all the terms have similar orders, this would provide \(\|e_{h}^{n} - e_{h}^{n-1}\|^{2} \leq C(\tau^{2} h^{2\alpha - 2})\), implying
\[
C\tau^{4} e^{\delta_{h} - \delta_{h} - d} \leq 1. \tag{32}
\]
In the numerical calculations presented at the end, (32) was always enough for the quadratic convergence.

3 Stability and convergence results

In this section we derive stability estimates for both continuous, as well as discrete problems 1 and 2, and prove the \textit{a priori} error estimates stated in Theorem 1. Then we prove Theorem 2), showing the convergence of the Newton method. We start with preliminary results and notations:

\[
\begin{align*}
{f}^{n} & = f(t_{n}), \quad \tau^{n} = \frac{1}{\tau} \int_{t_{n}}^{t_{n+1}} f(t)dt, \\
\epsilon_{h}^{n} & = \epsilon_{h}^{n}, \\
\epsilon_{n}^{k} & = \epsilon_{h}^{n} - \epsilon_{h}^{n}, \\
e_{n}^{i} & = \epsilon_{h}^{n} - \epsilon_{h}^{n}. \\
\end{align*}
\]

We recall that \(n \in \{1, \ldots, N\}\) is indexing the time step, while \(i\) is used for the iteration. Accordingly, \(\{\epsilon_{h}^{n}, q_{h}^{n,1}, s_{h}^{n}\}\) stands for the solution of Problem 2 at the \(n^{th}\) time step, whereas \(\{\epsilon_{h}^{n,1}, q_{h}^{n,1}, s_{h}^{n,1}\}\) is the \(i^{th}\) iteration \((i \geq 1)\) in the Newton scheme. The iteration process starts with \(\epsilon_{h}^{0} = \epsilon_{h}^{n-1}\) and \(s_{h}^{0} = s_{h}^{n-1}\).

Next we use the following elementary lemmas (see [22], p. 350 for the proof of the first one; for the second one is elementary):

Lemma 2 Let \(f : \mathbb{R} \rightarrow \mathbb{R}\) differentiable with \(f'()\) Lipschitz continuous. Then there holds
\[
|f(x) - f(y) - f'(y)(x - y)|^2 \leq \frac{L}{2} |x - y|^2, \quad \forall x, y \in \mathbb{R}. \tag{33}
\]

Lemma 3 For any set of \(m\)-dimensional real vectors \(a^{k}, b^{k} \in \mathbb{R}^{m}\) \((k \in \{0, \ldots, N\}, m \geq 1)\) the following identities are valid
\[
\begin{align*}
\sum_{n=1}^{N} (a^{n} - a^{n-1}, b^{n}) & = \sum_{n=1}^{N} (a^{n}, b^{n}) - (a^{0}, b^{0}), \\
\sum_{n=1}^{N} (\sum a^{k}, a^{n}) & = \frac{1}{2} \sum_{n=1}^{N} \|a^{n}\|^2 + \frac{1}{2} \sum_{n=1}^{N} \|a^{n}\|^2, \\
\sum_{n=1}^{N} (a^{n} - a^{n-1}, a^{n}) & = \frac{1}{2} \|a^{n}\|^2 + \frac{1}{2} \sum_{n=1}^{N} \|a^{n} - a^{n-1}\|^2 - \frac{1}{2} \|a^{0}\|^2. \tag{34} \tag{35} \tag{36}
\end{align*}
\]
The following inequalities will be used sever times below: the inequality of means
\[ ab \leq \frac{1}{2}a^2 + \frac{\delta}{2}b^2, \quad \text{for any } a, b \in \mathbb{R} \text{ and } \delta > 0, \] (37)
and the Young inequality
\[ ab \leq \frac{p^a}{p} + \frac{q^b}{q} \quad \text{for any } a, b > 0 \text{ and } p, q \in (1, \infty) \text{ such that } \frac{1}{p} + \frac{1}{q} = 1. \] (38)

We also need the following technical Lemma

**Lemma 4** Let \( \alpha \in (0, 1) \) and \( f_n \in L^{\frac{1+\alpha}{\alpha}}(\Omega) \), \( n \in \{1, \ldots, N\} \) such that there holds
\[ \sum_{n=1}^{N} \tau \| f_n \|_{L^{\frac{1+\alpha}{\alpha}}(\Omega)} \leq A. \] (39)

For all \( r \in \mathbb{R} \) we have
\[ \sum_{n=1}^{N} \tau \| f_n \|^2 \leq C(\tau \sum_{n=1}^{N} \| f_n \|_{L^{\frac{1+\alpha}{\alpha}}(\Omega)}^r + \tau^{-r}A). \] (40)

**Proof.** Since \( \Omega \) is bounded, \( L^{\frac{1+\alpha}{\alpha}}(\Omega) \subset L^2(\Omega) \) (\( \alpha < 1 \)), and \( \| f_n \| \leq C \| f_n \|_{L^{\frac{1+\alpha}{\alpha}}(\Omega)} \)
for all \( n \in \{1, \ldots, N\} \), where \( C > 0 \) only depends on \( \Omega \). Then the Young inequality (38) gives
\[ \sum_{n=1}^{N} \tau \| f_n \|^2 \leq C \tau^{-r} \sum_{n=1}^{N} \tau^r \| f_n \|_{L^{\frac{1+\alpha}{\alpha}}(\Omega)} \]
\[ \leq C \sum_{n=1}^{N} \frac{\tau^{p+1-r}}{p} + \sum_{n=1}^{N} \frac{\tau^{1-r}}{q} \| f_n \|_{L^{\frac{1+\alpha}{\alpha}}(\Omega)}^2 \] (41)
for all \( r \in \mathbb{R} \), and \( p, q > 0 \) with \( \frac{1}{p} + \frac{1}{q} = 1 \). Taking \( p = \frac{1+\alpha}{1-\alpha} \) and \( q = \frac{1+\alpha}{2\alpha} \), from (41) and (39) we get (40).

### 3.1 Stability estimates

We start with the stability estimates for Problem 1. These are similar to the standard energy estimates for parabolic problems, but restricted to the times \( t_1, \ldots, t_N \).

**Proposition 1** Assuming (A1)–(A5) there holds
\[ \sum_{n=1}^{N} \tau \| e^n \|^2 + \sum_{n=1}^{N} \langle \phi(e^n), e^n \rangle + \sum_{n=1}^{N} \tau \| q^n \|^2 \leq C, \] (42)
\[ \| s^N \|^2 + \sum_{n=1}^{N} \| s^n - s^{n-1} \|^2 + \sum_{n=1}^{N} \tau \| s^n \|^2 \leq C, \] (43)
\[ \sum_{n=1}^{N} \| e^n - e^{n-1} \|^2 \leq C \tau, \] (44)
\[ \sum_{n=1}^{N} \tau \| \nabla \cdot q^n \|^2 \leq C. \] (45)
Proof. We take \( w = c^n \) in (13), \( v = r \) in (14) and \( w = -\rho \phi c^n \) in (15) to obtain
\[
(\partial_t c, c^n) + \rho \partial_t s, c^n) + (\nabla \cdot q^n, c^n) = (r(c^n), c^n),
\]
\[
\|q^n\|^2 - (c^n, \nabla \cdot q^n) - (c^n Q, q^n) = 0,
\]
\[
-\rho \partial_t \phi c^n) = -\rho \phi c^n) = -\rho \phi c^n) = (\phi c^n), c^n) - (s^n, c^n).
\]
Adding the three equalities above, summing up the result from \( n = 1 \) to \( N \), and multiplying by \( \tau \) gives
\[
\sum_{n=1}^N (c^n - c^{n-1}, c^n) + \sum_{n=1}^N \tau \|q^n\|^2 + \sum_{n=1}^N \rho \phi \partial_t \phi c^n) - \sum_{n=1}^N k_3 \rho \phi (s^n, c^n)
\]
\[
= \sum_{n=1}^N (c^n - c^{n-1} - \tau \partial_t c, c^n) + \sum_{n=1}^N \tau r(c^n), c^n) + \sum_{n=1}^N \tau (c^n Q, q^n).
\]
We now take \( w = k_3 \tau^2 \sum_{n=1}^N c^n \) in (13), sum up (14) for \( n \) to \( N \) and take in the result \( v = k_3 \tau^2 q^n \) to obtain
\[
k_3 \tau ((c^n - c^{n-1}), c^n) + k_3 \tau (\tau \partial_t c - (c^n - c^{n-1}), c^n) + k_3 \tau^2 (\nabla \cdot q^n, c^n)
\]
\[
+ k_3 \rho \phi \tau ((s^n - s^{n-1}), c^n) + k_3 \rho \phi \tau (\tau \partial_t s - (s^n - s^{n-1}), c^n) = k_3 \tau^2 (r(c^n), c^n), c^n),
\]
and
\[
k_3 \tau^2 ((q^n, c^n) - k_3 \tau^2 (\sum_{n=1}^N c^n, c^n)) = k_3 \tau^2 (Q \sum_{n=1}^N c^n, c^n).
\]
Adding (50) and (51), summing up from \( n = 1 \) to \( N \) and using Lemma 3 yields
\[
\sum_{n=1}^N k_3 \tau^2 \|q^n\|^2 + \sum_{n=1}^N \frac{1}{\tau} (c^n - c^{n-1} - \tau \partial_t c, c^n) + \sum_{n=1}^N \tau r(c^n), c^n)
\]
\[
+ \sum_{n=1}^N (s^n - s^{n-1} - \tau \partial_t s, c^n) + \sum_{n=1}^N k_3 \tau^2 (r(c^n), c^n)
\]
\[
+ \sum_{n=1}^N k_3 \tau^2 (Q \sum_{n=1}^N c^n, c^n).
\]
From (49) and (52), by Lemma 3, the Cauchy-Schwarz inequality and (37) one gets
\[
\|c^n\|^2 + \sum_{n=1}^N \tau \|c^n\|^2 + \sum_{n=1}^N \tau \|q^n\|^2 + \sum_{n=1}^N \tau (\phi(c^n), c^n)
\]
\[
\leq C (\|q\|^2 + \|s\|^2 + \sum_{n=1}^N \frac{1}{\tau} (c^n - c^{n-1} - \tau \partial_t c)^2 + \sum_{n=1}^N \tau r(c^n), c^n)
\]
\[
+ C (\sum_{n=1}^N \tau \|Q c^n\|^2 + \sum_{n=1}^N \frac{1}{\tau} (s^n - s^{n-1} - \tau \partial_t s)^2 + \sum_{n=1}^N \tau \|c^n\|^2).
\]
Since \( c_I, s_I \) and \( Q \) are bounded, the Lipschitz continuity of \( r(\cdot) \), the Hölder continuity of \( \partial_t c \) and \( \partial_t s \) with respect to time, as well as the Gronwall Lemma give

\[
\|c^N\|^2 + \sum_{n=1}^{N} \tau \|c^n\|^2 + \sum_{n=1}^{N} \tau (\phi(c^n), c^n) + \sum_{n=1}^{N} \tau \|q^n\|^2 \leq C. \tag{54}
\]

For more details on bounding the terms involving the time derivative we refer to the proof of Theorem 1, estimates (85), (87) and (88), dealing with similar terms. Further, from (14) one immediately obtains

\[
\sum_{n=1}^{N} \tau \|\nabla c^n\|^2 \leq C \sum_{n=1}^{N} \tau \|q^n\|^2 + \sum_{n=1}^{N} \tau \|Qq^n\|^2. \tag{55}
\]

Then (42) is follows from (A3), the Poincare inequality, (54) and (55).

To prove (43), we test in (15) by \( w = \tau s^n \) and sum up from \( n = 1 \) to \( N \) to obtain

\[
\sum_{n=1}^{N} \langle s^n - s^{n-1}, s^n \rangle + \sum_{n=1}^{N} k_s \tau \|s^n\|^2 = \sum_{n=1}^{N} \langle s^n - s^{n-1} - \tau \partial_t s, s^n \rangle + \sum_{n=1}^{N} k_s \tau (\phi(c^n), s^n). \tag{56}
\]

Using (A2), Lemma 3, the Hölder continuity of \( \partial_t s \) and \( \phi \), as well as the boundedness of \( c^n \) (see (A5)), (56) gives the estimate (43).

To show (44) we take \( w = c^n - c^{n-1} \) in (13), \( v = \tau q_n \) in (14) written for \( t = t_n \) as well as for \( t = t_{n-1} \), and \( w = -\rho_k(c^n - c^{n-1}) \) in (15) to obtain

\[
(\partial_t c, c^n - c^{n-1}) + \rho_k(\partial_t s, c^n - c^{n-1}) + \langle \nabla \cdot q^n, c^n - c^{n-1} \rangle = \langle r(c^n), c^n - c^{n-1} \rangle,
\]

\[
\langle q^n - q^{n-1}, q^n \rangle - \langle c^n - c^{n-1}, \nabla \cdot q^n \rangle - \langle (c^n - c^{n-1}) Q, q^n \rangle = 0,
\]

\[
-\rho_k(\partial_t s, c^n - c^{n-1}) + \rho_k k_s (\phi(c^n), c^n - c^{n-1}) = \rho_k k_s (s^n, c^n - c^{n-1}).
\]

Adding the above, summing up from \( n = 1 \) to \( N \), multiplying by \( \tau \) and using Lemma 3 leads to

\[
\sum_{n=1}^{N} \|c^n - c^{n-1}\|^2 + \frac{\tau}{2} \|q^n\|^2 + \sum_{n=1}^{N} \frac{\tau}{2} \|q^n - q^{n-1}\|^2
\]

\[
= \sum_{n=1}^{N} \langle c^n - c^{n-1} - \tau \partial_t c, c^n - c^{n-1} \rangle + \frac{\tau}{2} \|q^n\|^2 + \sum_{n=1}^{N} \tau (r(c^n), c^n - c^{n-1})
\]

\[
+ \sum_{n=1}^{N} \tau \langle (c^n - c^{n-1}) Q, q^n \rangle + \tau \sum_{n=1}^{N} \rho_k k_s (\phi(c^n), c^n - c^{n-1})
\]

\[
+ \sum_{n=1}^{N} \rho_k k_s (s^n, c^n - c^{n-1}).
\tag{57}
\]

Using the Hölder continuity of \( \partial_t c \) an \( \phi \), the Lipschitz continuity of \( r \), the boundedness of \( Q \) and \( c^n \) and the stability estimate (43) we obtain (44).

For proving (15), by (13) and (15) one gets

\[
\sum_{n=1}^{N} \|\nabla \cdot q^n\|^2 \leq C \sum_{n=1}^{N} \tau c^n - c^{n-1} - \tau \partial_t c \|c^n\|^2 + \sum_{n=1}^{N} \frac{\tau}{2} \|c^n - c^{n-1}\|^2
\]

\[
+ C \sum_{n=1}^{N} \tau \|\phi(c^n)\|^2 + \sum_{n=1}^{N} \tau \|r(c^n)\|^2 + \sum_{n=1}^{N} \tau \|s^n\|^2. \tag{58}
\]
From (58), proceeding as for (44) and using the stability estimates obtained before one obtains (45).

We continue with the stability estimates for the solution of Problem 2.

**Proposition 2**  Assuming (A1)–(A4) there holds

\[
\|c_h^n\| + \sum_{n=1}^N \tau \|c_h^n\| + \sum_{n=1}^N \|c_h^n - c_h^{n-1}\|^2 + \sum_{n=1}^N \tau \phi_i(c_h^n, c_h^n) + \sum_{n=1}^N \tau \|q_h^n\|^2 \leq C \tag{60}
\]

and

\[
\|s_h^n\| + \sum_{n=1}^N \tau \|s_h^n\|^2 + \sum_{n=1}^N \|s_h^n - s_h^{n-1}\|^2 \leq C e^{2\alpha - 2} - 2, \tag{60}
\]

\[
\sum_{n=1}^N \|c_h^n - c_h^{n-1}\|^2 + \tau \|q_h^n\|^2 + \sum_{n=1}^N \|q_h^n - q_h^{n-1}\|^2 \leq C (\tau + e^{2\alpha - 2}). \tag{61}
\]

**Proof.** We take \(w_h = c_h^n\) in (17), \(v_h = \tau q_h^n\) in (18) and \(w_h = -\rho c_h^n\) in (19) to obtain

\[
\langle c_h^n - c_h^{n-1}, c_h^n \rangle + \rho \langle s_h^n - s_h^{n-1}, c_h^n \rangle + \tau (\nabla \cdot q_h^n, c_h^n) = \tau r(c_h^n, c_h^n) \tag{62}
\]

\[
\tau \|q_h^n\|^2 - \tau \langle c_h^n, \nabla \cdot q_h^n \rangle - \tau \langle q_h^n, q_h^n \rangle = 0 \tag{63}
\]

\[-\rho \tau (s_h^n - s_h^{n-1}, c_h^n) + \rho \tau k_s(\phi_i(c_h^n, c_h^n)) = \rho \tau k_s(s_h^n, c_h^n). \tag{64}
\]

Adding (62), (63) and (64) and summing up the result from \(n = 1\) to \(N\) we get

\[
\sum_{n=1}^N \langle c_h^n - c_h^{n-1}, c_h^n \rangle + \sum_{n=1}^N \tau \|q_h^n\|^2 + \sum_{n=1}^N \rho \tau k_s(\phi_i(c_h^n, c_h^n))
\]

\[
= \sum_{n=1}^N \tau r(c_h^n, c_h^n) + \sum_{n=1}^N \tau \langle q_h^n, q_h^n \rangle + \sum_{n=1}^N \rho \tau k_s(s_h^n, c_h^n). \tag{65}
\]

Testing with \(v_h = k_s \tau \sum_{k=n}^N c_h^k\) in (17) and summing up from \(n = 1\) to \(N\) gives

\[
k_s \tau \sum_{k=n}^N \langle c_h^k - c_h^{k-1}, c_h^k \rangle + \sum_{k=n}^N \rho k_s \tau \langle s_h^k - s_h^{k-1}, c_h^k \rangle + \sum_{k=n}^N \rho k_s \tau \langle \nabla \cdot q_h^k, c_h^k \rangle
\]

\[
+ \sum_{n=1}^N \rho k_s \tau ^2 \langle \nabla \cdot q_h^n, \sum_{k=n}^N c_h^k \rangle = \sum_{n=1}^N \rho k_s \tau ^2 \langle r(c_h^n), \sum_{k=n}^N c_h^k \rangle. \tag{66}
\]

Further, we write (18) for \(n = k\), sum up from \(k = n\) to \(N\), test the result by \(\tau ^2 k_s q_h^n\) and finally sum up from \(n = 1\) to \(N\) to get

\[
\sum_{n=1}^N \tau ^2 k_s \langle \sum_{k=n}^N q_h^k, q_h^n \rangle - \sum_{n=1}^N \tau ^2 k_s \langle \sum_{k=n}^N c_h^k, \nabla \cdot q_h^n \rangle = \sum_{n=1}^N \tau ^2 k_s \langle q_h^n, \sum_{k=n}^N c_h^k, q_h^n \rangle \tag{67}
\]
We add (65), (66) and (67), and use Lemma 3 to obtain

\[
\frac{1}{2} \| \phi_h^n - \phi_h^{n-1} \|^2 + \frac{1}{2} \sum_{n=1}^{N} \| \phi_h^n - \phi_h^{n-1} \|^2 + \sum_{n=1}^{N} \tau \| S_h^n \|^2 + \sum_{n=1}^{N} \rho_h \tau k_s \langle \phi_h^n, \phi_h^n - \phi_h^{n-1} \rangle \\
\leq \frac{1}{2} \| \phi_h^n - \phi_h^{n-1} \|^2 + \sum_{n=1}^{N} \tau \langle r(c_h^n), \phi_h^n \rangle + \sum_{n=1}^{N} \tau \langle c_h^n, \phi_h^n + \rho_h \tau k_s \phi_h^n - \phi_h^n \rangle \\
+ \tau \langle c_h^n, \sum_{n=1}^{N} \phi_h^n - \sum_{n=1}^{N} \phi_h^{n-1} \rangle + \sum_{n=1}^{N} \tau^2 \rho_h \tau k_s \langle \sum_{n=1}^{N} \phi_h^n, \phi_h^n - \phi_h^{n-1} \rangle.
\]

(68)

Using (A1), (A2), (A3), the Cauchy-Schwarz inequality and (37) and finally the Gronwall Lemma, (39) follows from (68).

To prove (60) we test in (19) with \( w_h = s_h^n \), sum the result up from \( n = 1 \) to \( N \) and use Lemma 3 and the Cauchy-Schwarz inequality, as well as (37) to obtain

\[
\| s_h^n \|^2 + \sum_{n=1}^{N} \| s_h^n - s_h^{n-1} \|^2 + \sum_{n=1}^{N} \tau \| s_h^n \|^2 \leq C \| s_h^n \|^2 + C \sum_{n=1}^{N} \tau \| \phi_h^n \|^2.
\]

(69)

(60) follows immediately by (A2), (59), and the Lipschitz continuity of \( \phi_i \).

For (61) we subtract (18) at \( t = t_{n-1} \) from (18) at \( t = t_n \), take in the result \( v_h = \tau q_h^n \) and add the resulting to (17) tested by \( w_h = c_h^n - c_h^{n-1} \). This gives

\[
\| c_h^n - c_h^{n-1} \|^2 + \rho_h \langle s_h^n - s_h^{n-1}, c_h^n - c_h^{n-1} \rangle + \tau \langle q_h^n - q_h^{n-1}, q_h^n \rangle \\
= \tau \langle r(c_h^n), c_h^n - c_h^{n-1} \rangle + \tau \langle q_h^n, c_h^n - c_h^{n-1} \rangle.
\]

(70)

Taking \( w_h = -\rho_h (c_h^n - c_h^{n-1}) \) in (19), adding the result to (70) and summing up for \( n = 1, \ldots, N \), by Lemma 3 we obtain

\[
\sum_{n=1}^{N} \| c_h^n - c_h^{n-1} \|^2 + \frac{1}{2} \tau \| q_h^n \|^2 - \frac{1}{2} \tau \| q_h^{n-1} \|^2 + \frac{1}{2} \sum_{n=1}^{N} \tau \| q_h^n - q_h^{n-1} \|^2 \\
= \sum_{n=1}^{N} \rho_h \tau k_s \langle \phi_h^n, c_h^n - c_h^{n-1} \rangle + \sum_{n=1}^{N} \rho_h \tau k_s \langle s_h^n, c_h^n - c_h^{n-1} \rangle \\
+ \sum_{n=1}^{N} \tau \langle r(c_h^n), c_h^n - c_h^{n-1} \rangle + \tau \langle q_h^n, c_h^n - c_h^{n-1} \rangle.
\]

(71)

From equation (71), recalling (A3) one immediately gets

\[
\sum_{n=1}^{N} \| c_h^n - c_h^{n-1} \|^2 + \tau \| q_h^n \|^2 + \tau \| q_h^{n-1} \|^2 \\
\leq \tau C \| q_h^n \|^2 + C \sum_{n=1}^{N} \tau \| \phi_h^n \|^2 + C \sum_{n=1}^{N} \tau^2 \| s_h^n \|^2 + C \sum_{n=1}^{N} \tau^2 \| q_h^n \|^2 + C \sum_{n=1}^{N} \tau \| q_h^n \|^2.
\]

(72)

By the Lipschitz continuity of \( r(\cdot) \) and \( \phi_i \), using (70) and (60), (61) follows by the Gronwall Lemma.
3.2 \textit{A priori} error estimates

In this section we prove the \textit{a priori} error estimates stated in Section 2.

\textbf{Theorem 1} Assuming (A1) – (A4), we have

\[
\|e^*_n\| + \sum_{n=1}^{N} \|e^*_n - e^*_n - 1\| + \sum_{n=1}^{N} \|e^*_n - e^*_n\| \leq \frac{C(h^{1+\alpha} + \tau\alpha + \epsilon^{1+\alpha})}{L^{1+\alpha}} + \sum_{n=1}^{N} \|e^*_n\|^{2},
\]

and, for all \( r \in \mathbb{R}, \)

\[
\|P_h s(t_N) - s_h^N\|^2 + \sum_{n=1}^{N} \|P_h s(t_n) - s_h^N\|^2 \leq C(h^{1+\alpha} + \tau\alpha + \epsilon^{1+\alpha}).
\]

\textbf{Proof.} We combine the ideas in [6, 11] with the ones in [32, 33]. Considering Problem 1 at \( t = t_n, \) we subtract (17) from (13), (18) from (14) and (19) from (15), and use the properties of the projectors \( P_h \) and \( \Pi_h \) to obtain

\[
\langle \tau_1 c - (c^*_h - c^*_h - 1), w_h \rangle + \rho_\delta \tau_1 s - (s^*_h - s^*_h - 1), w_h \rangle + \tau \langle \nabla \cdot \Pi_h e^*_n, w_h \rangle = \tau \langle r(c^*_n) - r(c^*_n), w_h \rangle
\]

\[
\langle e^*_n, v_h \rangle - \langle \nabla \cdot P_h e^*_n, v_h \rangle - \langle e^*_n Q_h, v_h \rangle = 0
\]

\[
\tau \langle \tau_1 s - (s^*_h - s^*_h - 1), w_h \rangle + k_\delta \tau \langle e^*_n, w_h \rangle = k_\delta \tau \langle \phi(c^*_n) - \phi(c^*_n), w_h \rangle.
\]

For all \( w_h \in W_h \) and \( v_h \in V_h. \) We take now \( w_h = e^*_n \in W_h \) in (75), \( v_h = \tau \Pi_h e^*_n \in V_h \) in (76) and \( w_h = -\rho_\delta e^*_n \in W_h \) in (77) to get

\[
\langle \tau_1 c - (c^*_h - c^*_h - 1), e^*_n \rangle + \rho_\delta \tau \langle \tau_1 s - (s^*_h - s^*_h - 1), e^*_n \rangle
\]

\[
+ \tau \langle \nabla \cdot \Pi_h e^*_n, e^*_n \rangle = \tau \langle r(c^*_n) - r(c^*_n), e^*_n \rangle
\]

\[
\tau \langle e^*_n, \Pi_h e^*_n \rangle - \tau \langle e^*_n \nabla \cdot P_h e^*_n, e^*_n \rangle - \tau \langle e^*_n Q_h, \Pi_h e^*_n \rangle = 0
\]

\[
- \rho_\delta \tau \langle \tau_1 s - (s^*_h - s^*_h - 1), e^*_n \rangle + \rho_\delta k_\delta \tau \langle e^*_n, e^*_n \rangle = - \rho_\delta k_\delta \tau \langle \phi(c^*_n) - \phi(c^*_n), e^*_n \rangle.
\]

Furthermore, we take \( w_h = k_\delta \tau \sum_{k=1}^{N} e^*_n \in W_h \) in (75) and obtain

\[
k_\delta \tau \langle \tau_1 c - (c^*_h - c^*_h - 1), \sum_{k=1}^{N} e^*_n \rangle + k_\delta \rho_\delta \tau \langle \tau_1 s - (s^*_h - s^*_h - 1), \sum_{k=1}^{N} e^*_n \rangle
\]

\[
+ k_\delta \tau^2 \langle \nabla \cdot \Pi_h e^*_n, \sum_{k=1}^{N} e^*_n \rangle = k_\delta \tau^2 \langle r(c^*_n) - r(c^*_n), \sum_{k=1}^{N} e^*_n \rangle.
\]
Writing (76) for \( n = k \), summing it up from \( k = n \) to \( N \) and taking \( \varphi_h = k_s \tau^2 \Pi h \mathbf{q}^n \) in the result leads to
\[
k_s \tau^2 \left( \sum_{k=n}^{N} e_k^h \Pi h e_k^n \right) - k_s \tau^2 \left( \sum_{k=n}^{N} e_k^c, \nabla : \Pi h e_k^n \right) = k_s \tau^2 \left( \sum_{k=n}^{N} \left( c_k^h \mathbf{Q} - c_k^h \mathbf{Q}_h \right), \Pi h e_k^n \right) = 0. \tag{82}
\]
We sum up (78) to (82) for \( n = 1 \) to \( N \), ad the result and use Lemma 3, as well as the property \( \langle e_0^n, e_0^n \rangle = 0 \) for all \( n \in \{1, \ldots, N\} \) to obtain
\[
\sum_{n=1}^{N} \left( \tau \partial_t c - \left( c^n_n - c_{n-1}^n \right), e^n_c \right) + \sum_{n=1}^{N} k_s \tau \left( \tau \partial_t c - \left( c^n_n - c_{n-1}^n \right) \right, \sum_{k=n}^{N} e_k^c \right) + \sum_{n=1}^{N} k_s \tau \left( \phi \left( c^n_u \right) - \phi \left( c^n_h \right), e^n_c \right) \\
= \sum_{n=1}^{N} \tau \left( r \left( c^n_h \right), e^n_c \right) + \sum_{n=1}^{N} k_s \tau \left( r \left( c^n_h \right), e^n_c \right) + \sum_{n=1}^{N} k_s \tau \left( r \left( c^n_h \right), e^n_c \right) + \sum_{n=1}^{N} k_s \tau \left( \sum_{k=n}^{N} \left( c_k^h \mathbf{Q} - c_k^h \mathbf{Q}_h \right), \Pi h e_k^n \right) \]}

We denote the ten terms in the above by \( T_1, \ldots, T_{10} \) and proceed by estimating each of them separately. Using Lemma 3, since \( e_0^c = 0 \) we have
\[
T_1 = \sum_{n=1}^{N} \left( \tau \partial_t c - \left( c^n_n - c_{n-1}^n \right), e^n_c \right) \\
= \sum_{n=1}^{N} \left( \tau \partial_t c - \left( c^n_n - c_{n-1}^n \right), e^n_c \right) + \sum_{n=1}^{N} \left( e^n_c - e_{n-1}^n, e^n_c \right) \\
= T_{11} + \frac{1}{2} \| e^n_c \|^2 + \frac{1}{2} \sum_{n=1}^{N} \| e^n_c - e_{n-1}^n \|^2. \tag{84}
\]

Since \( \partial_t c \) is Hölder continuous with exponent \( \alpha/2 \) (see (A5)), the Cauchy-Schwarz inequality and (37) give
\[
|T_{11}| \leq \sum_{n=1}^{N} \frac{1}{2} \int_{\Omega} \left( \int_{t_{n-1}}^{t_n} (\partial_t c(t)) - \partial_t c(s) \right) ds^2 \, dx + \sum_{n=1}^{N} \frac{\tau}{2} \| e^n_c \|^2 \\
\leq C \tau^\alpha + \sum_{n=1}^{N} \frac{\tau}{2} \| e^n_c \|^2. \tag{85}
\]

To estimate \( T_2 \) we use Lemma 3 and obtain
\[
T_2 = \sum_{n=1}^{N} k_s \tau \left( \partial_t c - \left( c^n_n - c_{n-1}^n \right), e^n_c \right) + \sum_{n=1}^{N} k_s \tau \left( \partial_t c - \left( c^n_n - c_{n-1}^n \right), e^n_c \right) \\
= T_{21} + \sum_{n=1}^{N} k_s \tau \| e^n_c \|^2. \tag{86}
\]
As for $T_{21}$, for $T_{21}$ we have

$$|T_{21}| \leq \frac{1}{2r} \sum_{n=1}^{N} \| \tau \partial \psi - (c^n - c^{n-1}) \|^2 + \frac{r^2}{2} \sum_{n=1}^{N} \sum_{k=0}^{N} e_k^n \|^2$$

$$\leq C(r^2 + \sum_{n=1}^{N} \tau \| e^n \|^2). \tag{87}$$

For $T_3$ we recall that $\partial \psi$ is Hölder continuous with exponent $\alpha$. This gives

$$T_3 = \tau \sum_{n=1}^{N} k \rho_k (\tau \partial \psi - (s^n - s^{n-1}), \sum_{k=0}^{N} e_k^n) \leq \sum_{n=1}^{N} \frac{k \rho_k}{2r} \| \tau \partial \psi - (s^n - s^{n-1}) \|^2 + C \sum_{n=1}^{N} \tau \| e^n \|^2$$

$$\leq C(r^{2\alpha} + \sum_{n=1}^{N} \tau \| e^n \|^2). \tag{88}$$

Further,

$$T_4 = \sum_{n=1}^{N} \tau \langle e^n\psi, \Pi_ne^n\psi \rangle = \sum_{n=1}^{N} \tau \langle e^n\psi, \Pi_ne^n\psi - e^n\psi \rangle + \sum_{n=1}^{N} \tau \| e^n\psi \|^2$$

$$= T_{41} + \sum_{n=1}^{N} \tau \| e^n\psi \|^2. \tag{89}$$

Using the inequalities (9) and (37), by and (A5) - and more precisely (16) - one has

$$|T_{41}| \leq \frac{\delta_{41}}{2} \sum_{n=1}^{N} \tau \| e^n\psi \|^2 + \frac{1}{2\delta_{41}} \sum_{n=1}^{N} \tau \| q^n - \Pi_nq^n \|^2$$

$$\leq \frac{\delta_{41}}{2} \sum_{n=1}^{N} \tau \| e^n\psi \|^2 + C \frac{1}{2\delta_{41}} \sum_{n=1}^{N} \tau h^2 \| q^n \|^2$$

$$\leq \frac{\delta_{41}}{2} \sum_{n=1}^{N} \tau \| e^n\psi \|^2 + Ch^2, \tag{90}$$

for any $\delta_{41} > 0$.

By Lemma 3, for $T_5$ we have

$$T_5 = \sum_{n=1}^{N} k_3 r^2 \left( \sum_{k=0}^{N} e_k^n, \Pi_ne_k^n \right)$$

$$= \sum_{n=1}^{N} k_3 r^2 \left( \sum_{k=0}^{N} e_k^n, e_k^n \right) + \sum_{n=1}^{N} k_3 r^2 \left( \sum_{k=0}^{N} e_k^n, \Pi_ne_k^n - e_k^n \right)$$

$$= \frac{k_3 r^2}{2} \sum_{n=1}^{N} \| e^n \|^2 + \frac{k_3 r^2}{2} \sum_{n=1}^{N} \| e^n \|^2 + T_{51}. \tag{91}$$
As for $T_{11}$ we immediately get

$$|T_{51}| \leq \frac{\delta_{h1}}{2} \sum_{n=1}^{N} \frac{\| \sum_{k=n}^{n+1} e_k^n \|^2}{\tau} + \frac{\tau}{2 \delta_{h1}} \sum_{n=1}^{N} \| q^n - \Pi_k q^n \|^2$$

$$\leq \frac{\delta_{h1} T^2}{2} \sum_{n=1}^{N} \| e_k^n \|^2 + \text{Ch}^2. \quad (92)$$

Since $\phi(\cdot)$ is monotone and Hölder continuous,

$$T_0 = \sum_{n=1}^{N} k_s \rho \tau (\phi(c^n) - \phi(c_h^n), e^n)$$

$$= \sum_{n=1}^{N} k_s \rho \tau (\phi(c^n) - \phi(c_h^n), e^n) + \sum_{n=1}^{N} k_s \rho \tau (\phi(c_h^n) - \phi(c_h^n), e^n)$$

$$= \sum_{n=1}^{N} k_s \rho \tau (\phi(c^n) - \phi(c_h^n), e^n) + \sum_{n=1}^{N} k_s \rho \tau (\phi(c^n) - \phi(c_h^n), e^n)$$

$$+ \sum_{n=1}^{N} k_s \rho \tau (\phi(c^n) - \phi(c_h^n), e^n)$$

$$\geq \sum_{n=1}^{N} C \tau \| \phi(c^n) - \phi(c_h^n) \|^{\frac{1+\alpha}{1-\alpha}} + T_{01} + T_{02}. \quad (93)$$

The Young inequality, the imbedding $L^2(\Omega) \subseteq L^{1+\alpha}(\Omega)$, the stability estimates in Proposition 1 and the estimate (8) imply

$$|T_{01}| \leq \frac{\alpha \delta_{h1}}{1+\alpha} \sum_{n=1}^{N} \| \phi(c^n) - \phi(c_h^n) \|^{\frac{1+\alpha}{1-\alpha}} + \frac{\tau}{1+\alpha} \sum_{n=1}^{N} \| P_k c^n - e^n \|^{1+\alpha}$$

$$\leq \frac{\alpha \delta_{h1}}{1+\alpha} \sum_{n=1}^{N} \| \phi(c^n) - \phi(c_h^n) \|^{\frac{1+\alpha}{1-\alpha}} + C(h^{1+\alpha} + \tau^2 + \text{Ch}^2). \quad (94)$$

for any $\delta_{h1} > 0$. To estimate $T_{02}$ we use Lemma 1 and the positivity of the concentrations:

$$T_{02} = \sum_{n=1}^{N} k_s \rho \tau (\phi(c_h^n) - \phi(c_h^n), P_k c^n) - \sum_{n=1}^{N} k_s \rho \tau (\phi(c^n) - \phi(c_h^n), e^n)$$

$$\geq -C e^{1+\alpha}. \quad (95)$$
The estimates for the next terms are based on the Lipschitz continuity of the degradation rate \( r(\cdot). \) We use Proposition 1 and (8),

\[
T_7 = \sum_{n=1}^{N} \tau (r(c^n) - r(c_h^n, \epsilon^n)) \\
\leq \sum_{n=1}^{N} \tau L_r \|c^n - c_h^n\| \|\epsilon^n\| \\
\leq \sum_{n=1}^{N} \frac{\tau L_r}{2} \|c^n - P_h c^n\|^2 + \sum_{n=1}^{N} \frac{3\tau L_r}{2} \|\epsilon^n\|^2 \\
\leq Ch^2 + \sum_{n=1}^{N} \frac{3\tau L_r}{2} \|\epsilon^n\|^2. \tag{96}
\]

Similarly,

\[
T_8 = \sum_{n=1}^{N} k_s \tau^2 (r(c^n) - r(c_h^n)) + \sum_{k=n}^{N} \epsilon_h^n \\
\leq C(h^2 + \sum_{n=1}^{N} \tau \|\epsilon^n\|^2). \tag{97}
\]

To estimate \( T_9 \) we use (A3), the estimates in Proposition 1, as well as in (10), (8) and (9), the essential boundedness of \( c, \) and the inequality (37)

\[
T_9 = \sum_{n=1}^{N} k_s \tau (c^n Q - \epsilon_h^n Q_h, P_h \epsilon^n) \\
= \sum_{n=1}^{N} k_s \tau (c^n Q - \epsilon_h^n Q_h, P_h \epsilon^n) + \sum_{n=1}^{N} k_s \tau ((c^n - \epsilon_h^n) Q_h, P_h \epsilon^n) \\
\leq C\|Q - \epsilon_h\|^2 + \delta_0 \sum_{n=1}^{N} \tau \|\epsilon_h^n\|^2 + \delta_0 \sum_{n=1}^{N} \tau \|q^n - P_h q^n\|^2 \\
+C\tau \sum_{n=1}^{N} \|c^n\|^2 + C\tau \sum_{n=1}^{N} \|c^n - P_h c^n\|^2 \\
\leq Ch^2 + \delta_0 \sum_{n=1}^{N} \tau \|\epsilon_h^n\|^2 + C \sum_{n=1}^{N} \tau \|\epsilon^n\|^2. \tag{98}
\]

Similarly, the last term gives

\[
T_{10} = \sum_{n=1}^{N} k_s \tau^2 (\sum_{k=n}^{N} (c^n Q - \epsilon_h^n Q_h, P_h \epsilon_h^n) \\
\leq Ch^2 + \delta_{10} \sum_{n=1}^{N} \tau \|\epsilon_h^n\|^2 + C \sum_{n=1}^{N} \tau \|\epsilon^n\|^2. \tag{100}
\]
From (83) – (100) we immediately obtain
\[
\|e^N_t\|^2 + \sum_{n=1}^N \|e^n_t - e^{n-1}_t\|^2 + \sum_{n=1}^N \tau \|\phi(e^n_t) - \phi(e^n_h)\|^2 \quad \leq \quad \frac{1}{\tau^{1+\alpha}} \frac{h^{1+\alpha}}{\Gamma(\alpha+1)} + \sum_{n=1}^N \tau \|e^n_e\|^2 + \sum_{n=1}^N \tau \|e^n_q\|^2.
\]
(101)

The first estimate in Theorem 1 is obtained by applying the discrete Gronwall Lemma.
To prove the inequality (20) we take \(w_h = e^n_h\) in (77) and obtain
\[
\langle \tau \partial_t s - (s^n_h - s^{n-1}_h), e^n_h + k_h \tau \|e^n\|^2 = k_h \tau (\phi(e^n) - \phi(e^n_h)), \quad (102)
\]
giving
\[
\langle \tau \partial_t s - (s^n - s^{n-1}), e^n \rangle + (e^n - e^{n-1}_e, e^n_e) + k_h \tau \|e^n\|^2 \leq \frac{k_h}{2} \tau \|\phi(e^n) - \phi(e^n_h)\|^2 + \frac{k_h}{2} \tau \|e^n_e\|^2.
\]
(103)

Summing up the above for \(n = 1, \ldots, N\), since \(e^0 = 0\) we use Lemma 3 and (37) to obtain
\[
\frac{1}{2} \|e^n\|^2 + \frac{1}{2} \sum_{n=1}^N \|e^n - e^{n-1}\|^2 + \sum_{n=1}^N \frac{k_h}{2} \tau \|e^n\|^2 \leq C \sum_{n=1}^N \frac{1}{\tau} \langle \partial_t s - (s^n - s^{n-1}), e^n \rangle + \|\phi(e^n) - \phi(e^n_h)\|^2 + C \sum_{n=1}^N \tau \|\phi(e^n) - \phi(e^n_h)\|^2.
\]
(104)

Since \(\partial_t s\) is Hölder continuous, the first term on the right hand in (104) is bounded by \(C \tau^{2\alpha}\). For the last term we use (25) and Lemma 4, yielding
\[
\sum_{n=1}^N \tau \|\phi(e^n) - \phi(e^n_h)\|^2 \leq 2 \sum_{n=1}^N \tau \|\phi(e^n) - \phi(e^n_h)\|^2 + 2 \sum_{n=1}^N \tau \|\phi(e^n_h) - \phi(e^n)\|^2 \leq C(\tau^{2\alpha} + \tau^{-\alpha} (h^2 + h^{1+\alpha} + \tau^2 + \tau^{2\alpha} + \tau \frac{\tau^{1+\alpha}}{\Gamma(\alpha+1)} + \epsilon^{1+\alpha}) + \epsilon^{2\alpha}).
\]

Now (26) follows from (104) – (105) in a straightforward manner. \(\blacksquare\)

3.3 Convergence of the Newton method

The quadratic convergence of the Newton scheme (21)-(22) is proven in the following

**Theorem 2** Assuming (A1) – (A4), if \(\tau\) is small enough we have
\[
\|e^N_t\|^2 + \tau \|e^N_q\|^2 \leq C \tau^2 (L^2_{r^2} + L^2_{q^2}) \|e^N_t\|^2 \quad (105)
\]
and
\[
\|e^N_t\|^2 \leq C \tau^2 (L^2_{r^2} + \tau^2 L^2_{q^2} (L^2_{r^2} + L^2_{q^2})) \|e^N_t\|^2 \quad (106)
\]
Proof. From (19) we have
\[
\langle \phi_h^n, w_h \rangle = \frac{\tau k_h}{1 + \tau k_h} \langle \phi_t(c_h^n), w_h \rangle + \frac{1}{1 + \tau k_h} \langle \phi_t(c_h^{n-1}), w_h \rangle
\]  \hspace{1cm} (107)
for all \( w_h \in W_h \). Using this in (17) gives
\[
\langle c_h^n - c_h^{n-1}, w_h \rangle + \frac{\rho \tau k_h^2}{1 + \tau k_h} \langle \phi_t(c_h^n) - \phi_t(c_h^{n-1}), w_h \rangle + \frac{\tau}{1 + \tau k_h} \langle \nabla \cdot q_h^n, w_h \rangle = \tau (r(c_h^n) - r(c_h^{n-1})),
\]  \hspace{1cm} (108)
for all \( w_h \in W_h \). Similarly, by (20) and (22),
\[
\langle c_h^{n,i} - c_h^{n,i-1}, w_h \rangle + \frac{\rho \tau k_h^2}{1 + \tau k_h} \langle \phi_t(c_h^{n,i}) - \phi_t(c_h^{n,i-1}), w_h \rangle + \tau (r(c_h^{n,i}) - r(c_h^{n,i-1})),
\]  \hspace{1cm} (109)
Subtracting (109) and (21) from (108) and (18) respectively leads to
\[
\langle c_h^{n,i} - c_h^{n,i-1}, w_h \rangle + \frac{\rho \tau k_h^2}{1 + \tau k_h} \langle \phi_t(c_h^{n,i}) - \phi_t(c_h^{n,i-1}), w_h \rangle + \tau (\nabla \cdot q_h^{n,i}, w_h) = \tau (r(c_h^{n,i}) - r(c_h^{n,i-1})),
\]  \hspace{1cm} (110)
for all \( w_h \in W_h \), and
\[
\langle e_h^{n,i}, v_h \rangle = \langle e_h^{n,i}, \nabla \cdot v_h \rangle = 0,
\]  \hspace{1cm} (111)
for all \( v_h \in V_h \). Taking \( w_h = e_h^{n,i} \in W_h \) in (110) and \( v_h = \tau q_h^{n,i} \in V_h \) in (111), adding the resulting yields yields
\[
\| e_h^{n,i} \|^2 + \frac{\rho \tau k_h^2}{1 + \tau k_h} \| \phi_t(c_h^{n,i}) - \phi_t(c_h^{n,i-1}), e_h^{n,i} \|^2 + \tau \| e_h^{n,i} \|^2
\]  \hspace{1cm} (112)
Since \( r'(\cdot) \) is bounded, whereas and \( |Q_h| \leq M_Q \) (see (A1) and (A3)), using the inequality (37) in the above furnishes
\[
\| e_h^{n,i} \|^2 + \frac{\rho \tau k_h^2}{1 + \tau k_h} \| \phi_t(c_h^{n,i}) - \phi_t(c_h^{n,i-1}), e_h^{n,i} \|^2 + \tau \| e_h^{n,i} \|^2
\]  \hspace{1cm} (113)
We denote the first and the last terms on the right by \( T_{N1} \) and \( T_{N2} \) and proceed by estimating them separately. For \( T_{N1} \) we use Lemmas 1 and 2, the assumption (A1) and the inequality (37):
\[
T_{N1} \leq C \tau \int_\Omega L_0 \| e_h^{n,i} \|^2 dx
\]  \hspace{1cm} (114)
Analogously, there holds

$$T_{N2} \leq C r_t^2 L_t^2 \|e^{n,i-1}\|_{L^4(D)}^2 + \frac{1}{4} \|e^{n,i}\|^2. \quad (115)$$

From (113)-(115), using also that $\phi' \geq 0$ we immediately obtain

$$\frac{\tau}{2} \|\phi'_n\|^2 + \frac{T}{2} \|\phi'_n\|^2 \leq \tau(L_t + M Q/2)\|\phi^n_{i-1}\|^2 + C \tau^2 (L_t^2 + L_t^2)\|\phi^n_{i-1}\|^2 \|e^{n,i-1}\|_{L^4(D)}. \quad (116)$$

The result (28) follows now by using the inverse estimate (see e.g [9])

$$\|e^{i-1}\|_{L^4(D)} \leq C^h^{-d/4}\|e^{i-1}\|. \quad (117)$$

Finally, for proving the inequality (29) we use (19) and (22) and obtain

$$\langle e^n_{x,i}, w_h \rangle = \frac{\tau h_n}{1+\tau h_n} (\phi_i(c^n_h) - \phi_i(c^{n,i-1}_h) - \phi'_i(c^n_{i-1}_h)(c^n_{i-1}_h - c^{n,i-1}_h), w_h) \quad (118)$$

for all $w_h \in W_h$. Taking $w_h = e^n_{x,i}$ and using Lemma 2 gives

$$\|e^{n,i}_x\| \leq C (\tau L_{\phi'_i} \|\phi^n_{i-1}\|^2 + L_{\phi'_i} \|e^{n,i}_x\|^2), \quad (119)$$

which, together with (28), leads to (29).

4 Numerical Results

In this section we present two numerical tests that verify the theoretical findings in the preceding section. The first is a problem of academic nature, admitting an analytical solution. The second is a realistic infiltration problem. Specifically, we solve (1) - (2) with a source term $f(\cdot)$ and a Freundlich type sorption isotherm $\phi(x) = x^\alpha$:

$$\Theta_S \partial_t c + \rho_b \partial_t s - \nabla \cdot (D \Theta_S \nabla c - c Q) = \Theta_S r(c) + f \quad \text{in } J \times \Omega, \quad (119)$$

$$\partial_t s = k_s(c^\alpha - s) \quad \text{in } J \times \Omega. \quad (120)$$

In the first example the water flux is constant, whereas in the second example it is obtained by solving the flow equations (3) - (4).

**Example 1.** We solve the problem above in the unit square $\Omega = [0, 1] \times [0, 1]$. We set $\Theta_S = 1$, $\rho_b = 1$, $D = 1$, $k_s = 1$ and take a constant water flux $Q = (Q_1, Q_2)^T$. Here $r(c) = -0.1c$. With

$$f(t, x, y) = \frac{\alpha^{1/\alpha-1}}{\alpha} x(1-x)y(1-y) + [x(1-x)y(1-y)]^\alpha (1-e^{-t})$$

$$+ 2[x(1-x) + y(1-y)]t^{1/\alpha} + [Q_1(1-2x)y(1-y) + Q_2(1-2y)x(1-x)]t^{1/\alpha}$$

$$+ 0.1x(1-x)y(1-y)t^{1/\alpha},$$

and suitable initial and boundary conditions, (119)-(120) admit the analytical solution

$$c(t, x, y) = t^{1/\alpha} x(1-x)y(1-y), \quad \text{and} \quad (121)$$

$$s(t, x, y) = [x(1-x)y(1-y)]^\alpha (t - (1-e^{-t})). \quad (122)$$
The final time is $T = 1$, and the water flux $\mathbf{Q} = (0.01, 0.01)^T$. Inspired by Theorem 1 we compute the errors

$$E_{c, q} = \sum_{n=1}^{N} \tau \| P_h c(t_n) - c^n_h \|^2 + \sum_{n=1}^{N} \tau \| q(t_n) - q^n_h \|^2,$$

and

$$E_s = \sum_{n=1}^{N} \tau \| P_h s(t_n) - s^n_h \|^2.$$

In all simulations we take $\epsilon = h$. We perform computations with $\alpha = 0.75$, $\alpha = 0.5$ and $\alpha = 0.25$. In view of Theorem 2, more exactly condition (31), taking $\tau = h^2$ ensures the quadratic convergence of the Newton method for the first two values of $\alpha$. The results are presented in Tables 1 and 2. The initial spatial grid has a mesh diameter $h = 0.2$, and is refined uniformly by halving $h$. The other parameters, $\tau$ and $\epsilon$, are changed accordingly.

The theoretical estimates in Theorem 1 predict an order of convergence of $\gamma_c = 2\alpha$ for $E_{c, q}$, so the error reduction should be of at least $2^{2\alpha}$. This is exceeded for the case $\alpha = 0.75$, where $\gamma_c = 2$ is obtained. For $\alpha = 0.5$ we observe an order of $\gamma_c = 1.7$ for $E_{c, q}$ since this error is reduced by a factor of $3.24 = 2^{1.7}$. Again, this is beyond the theoretically predicted order of $2\alpha = 1$. One of the reasons for this superconvergence is in the assumption on $\partial_t c$, namely its Hölder continuity with an exponent $\alpha/2$. This affects the theoretical estimates directly. With respect to $E_s$, in all cases we obtained an order of convergence $\gamma_s$ - and therefore a reduction factor of $2^{\alpha}$ - that is much smaller, in agreement with the estimates in Theorem 1. We mention that for all the simulations maximal three Newton iterations were needed per time step, and the convergence was quadratic (as expected).

For the case $\alpha = 0.25$ we took again $\tau = h^2$, which violates the condition (31). However, this choice is still in agreement with the framework of Remark 4. Again, the Newton method converges quadratically. Since the Hölder exponent is now smaller, a significant decrease in the convergence order of the discretization error is expected. Table 3 confirms these expectations.

**Table 1** Numerical results for Example 1 with $\tau = h^2 = r^2$ and $\alpha = 0.75$.

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<th>$E_{c, q}$</th>
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<th>$E_s$</th>
<th>$\gamma_s$</th>
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</tr>
</tbody>
</table>

**Example 2.** In the second example we consider the infiltration of benzene in a saturated, heterogeneous soil. A sketch of this situation is displayed in Figure 1. The units are milligram, meter and day, and will be not written explicitly further. The entire computational domain is $\Omega = [0, 2] \times [0, 3]$, and includes two subdomains, $\Omega_1 = [0.2, 1.2] \times [2, 2.7]$ and $\Omega_2 = [1.3, 1.7] \times [0.8, 1.8]$, having a much smaller permeability. The final time is $T = 1$. The water flux $\mathbf{Q}$ is obtained by solving (1) - (2) in the same domain. The boundary and initial conditions, as well as the absolute permeabilities
Table 2  Numerical results for Example 1 with $\tau = h^2 = \varepsilon^2$ and $\alpha = 0.5$.

<table>
<thead>
<tr>
<th>$h$</th>
<th>$E_{\text{err}}$</th>
<th>$\gamma_c$</th>
<th>$E_{\alpha}$</th>
<th>$\gamma_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.789692e-04</td>
<td>2.866419e-04</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.653120e-05</td>
<td>1.732716e-04</td>
<td>0.90</td>
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</tr>
<tr>
<td>3</td>
<td>1.652990e-05</td>
<td>1.662176e-04</td>
<td>0.96</td>
<td></td>
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<tr>
<td>4</td>
<td>5.130814e-06</td>
<td>3.790851e-05</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.566592e-06</td>
<td>1.413045e-05</td>
<td>1.38</td>
<td></td>
</tr>
</tbody>
</table>

Table 3  Numerical results for Example 1 with $\tau = h^2 = \varepsilon^2$ and $\alpha = 0.25$.

<table>
<thead>
<tr>
<th>$h$</th>
<th>$E_{\text{err}}$</th>
<th>$\gamma_c$</th>
<th>$E_{\alpha}$</th>
<th>$\gamma_s$</th>
</tr>
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<tbody>
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<td>1</td>
<td>5.832920e-04</td>
<td>2.864994e-03</td>
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<tr>
<td>2</td>
<td>2.933227e-04</td>
<td>2.003572e-03</td>
<td>0.50</td>
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<tr>
<td>3</td>
<td>1.420611e-04</td>
<td>1.659036e-03</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.243242e-05</td>
<td>7.589515e-04</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.410411e-05</td>
<td>4.171508e-04</td>
<td>0.84</td>
<td></td>
</tr>
</tbody>
</table>

are given in Figure 1. The other parameters involved are $\Theta_S = 0.5$, $\rho_b = 1$ and $D = 1$.

The source term $f$ in (119) is zero, and for the reaction term we have $r(c) = -0.2c$.

Fig. 1  Computational domain for simulating benzene infiltration in a heterogeneous, saturated soil.

The first set of computations are for $h = \varepsilon = 0.05$ and $\alpha = 0.5$. According to (31), a
time step of order $h^2$ ensures the optimal convergence of the Newton scheme. Therefore
we took $\tau = 0.0025$. Figures 2 and 3 present $c$ and $s$, the dissolved, respectively adsorbed
benzene concentration profiles, at different times. As follows from Table 4 presenting
the total residual, the iteration converges quadratically.

The second set of calculations is carried out again starting with $h = \varepsilon = 0.05$, but now $\alpha = 0.25$. According to (31), a time step of order $h^{2.5}$ is needed to ensure
the optimal convergence of the Newton method. Therefore we took $\tau = 0.0015385$. As before, the Newton method converges quadratically, see Table 5. The dissolved benzene concentration profiles are quite similar to the ones in the previous case, therefore no additional plots are included. However, as can be clearly noticed when comparing
Figures 3 and 4, much more contaminant is adsorbed in the second case, for a lower value of $\alpha$. Then the adsorption rate is much higher for small values of $c$.

**Fig. 2** Benzene concentration profiles at $T = 0.025$, $T = 0.05$ and $T = 1$ (days), for $\alpha = 0.5$.

**Fig. 3** Adsorbed benzene concentration profiles at $T = 0.025$, $T = 0.05$ and $T = 1$ (days), for $\alpha = 0.5$.

**Table 4** Convergence of the Newton method for the Example 2, with $\alpha = 0.5$, $\epsilon = h = 0.05$, $\tau = 0.0025$.

<table>
<thead>
<tr>
<th>$T$</th>
<th>0.025</th>
<th>0.05</th>
<th>0.125</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{A}$</td>
<td>2.4750291e-01</td>
<td>1.5146763e-01</td>
<td>3.1237680e-02</td>
<td>1.5634855e-03</td>
<td>9.7716344e-04</td>
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<tr>
<td></td>
<td>2.3360443e-03</td>
<td>1.4145270e-03</td>
<td>2.3762921e-04</td>
<td>6.1729415e-06</td>
<td>6.8882752e-06</td>
</tr>
<tr>
<td></td>
<td>1.3700470e-07</td>
<td>9.6783616e-08</td>
<td>9.1480894e-09</td>
<td>5.5553846e-11</td>
<td>6.7827843e-10</td>
</tr>
<tr>
<td>$\bar{A}$</td>
<td>7.3949556e-11</td>
<td>6.1280302e-12</td>
<td>5.3960197e-13</td>
<td>4.8980074e-14</td>
<td>4.5463232e-15</td>
</tr>
</tbody>
</table>
Table 5  Convergence of the Newton method for the Example 2, with $\alpha = 0.25$, $\epsilon = h = 0.05$, $\tau = 0.0015385$.

<table>
<thead>
<tr>
<th>$T = 0.025$</th>
<th>$T = 0.05$</th>
<th>$T = 0.125$</th>
<th>$T = 0.5$</th>
<th>$T = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.19223874e-01</td>
<td>1.46725172e-01</td>
<td>2.95117813e-02</td>
<td>1.83180986e-03</td>
<td>1.13442203e-03</td>
</tr>
<tr>
<td>1.86833098e-03</td>
<td>1.29220266e-03</td>
<td>1.77148099e-04</td>
<td>1.73196465e-05</td>
<td>1.05359396e-05</td>
</tr>
<tr>
<td>5.430407e-08</td>
<td>4.56556246e-08</td>
<td>4.45309269e-09</td>
<td>9.878094e-10</td>
<td>5.4116583e-10</td>
</tr>
</tbody>
</table>

Fig. 4 Adsorbed benzene concentration profiles at $T = 0.025$, $T = 0.05$ and $T = 1$ (days), for $\alpha = 0.25$.

5 Conclusions

We analyzed a mass conservative scheme for solute transport with non-equilibrium sorption in porous media. The time discretization is Euler implicit, and mixed finite elements are employed for the spatial one. At each time step, the emerging nonlinear algebraic systems are solved by a Newton method. A Hölder continuous sorption isotherm is assumed, which makes the analysis very challenging. This type of sorption corresponds to the real, practical situations (like Freundlich isotherms) and weakens the commonly assumed Lipschitz continuity. Stability and a priori error estimates are shown, guaranteeing the convergence of the scheme. The order of convergence depends only on the discretization parameters. Moreover, a sufficient condition for the quadratic convergence of the Newton scheme is obtained. Especially this condition provides useful information for the practical calculations, by indicating a priori how to control the discretization parameters. This saves a lot of computational time. To sustain the theoretical results, two numerical examples have been presented. The first one is an academic example having an analytical solution, and the second represents a realistic scenario. The theoretical estimates are not necessary sharp but rather pessimistic, the practice showing a better convergence behavior. However, the calculations reveal a clear dependence of the convergence orders by the Hölder exponent, in the sense that values close to 0 have a negative influence.

Based on the theoretical results and the numerical experiments, we conclude that the presented mass conservative numerical scheme is effective and can be employed for reliable and efficient simulations of multicomponent, reactive transport with sorption in porous media.
Acknowledgments

Part of the work of ISP was supported by the German Research Foundation (DFG), within the Cluster of Excellence in Simulation Technology (EXC 310/1) at the University of Stuttgart. This support is gratefully acknowledged.

References

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