Habilitation thesis

Convergent mass conservative schemes for flow and reactive solute transport in variably saturated porous media

Florin Adrian Radu

Friedrich-Alexander University of Erlangen-Nuremberg
Department of Mathematics

May 2013

Mentors of the habilitation procedure at the Friedrich-Alexander University of Erlangen-Nuremberg:

Prof. Dr. Peter Knabner, Department of Mathematics, University of Erlangen-Nuremberg.

Prof. Dr. Sabine Attinger, Helmholtz Center for Environmental Research Leipzig and University of Jena.

Prof. Dr. Eberhard Bänsch, Department of Mathematics, University of Erlangen-Nuremberg.

Contents

Chapter 1

Introduction

Flow and transport in porous media have plenty of real world applications, like e.g. water and soil pollution, CO_2 storage, oil recovery, nuclear waste management, drug delivery systems, and cancer research. The use of computers for solving problems such as those mentioned above is standard today. More and more decisions, some of them with possibly dramatic consequences for human beings and the environment, are based on predictions made with the help of computer programs. Nevertheless, for reliable predictions one needs adequate mathematical models and solvers, benchmarks and experiments for calibration of the models and an interdisciplinary team to interpret the results. We especially enhance the need for powerful (mass-conservative) discretizations (which can capture the important features of the problem, like a complicate computational domain, heterogeneous media, sharp interfaces or reactive fronts...) and robust and efficient linear and nonlinear solvers. This work contributes on the development, understanding and analyzing of numerical schemes for reactive flow and transport in porous media.

The need for mass conservative numerical schemes for simulating flow in porous media is well recognized in water research [22, 55]. Therefore numerical schemes based on FVM (finite volume method) and MFEM (mixed finite element method) are the first choices. Besides, the MFEM has the advantage of furnishing an accurate flux directly as an intrinsic part of the solution. Moreover, the flux is continuous over the edges (faces) of the finite element meshes. This is an enormous advantage when the water flux is also needed for the simulation of reactive contaminant transport in the soil (see [15, 16, 72]). We further refer to [55, 23, 32, 37] for the advantages of MFEM over other methods for heterogeneous media. In this thesis, we consider mainly numerical schemes based on MFEM, more exactly on the lowest order Raviart-Thomas elements [P1], [P3]-[P9]. The backward Euler method is used for the temporal discretization. Paper [P2] is considering a MPFA discretization (multipoint flux approximation method) which is variant of the MFEM.

The set-up and especially the analysis of numerical schemes for flow and transport in porous media is a very challenging task. The reasons for this are mainly:

- Nonlinearity of the equations
- Degeneracy of the flow equation
- Coupling of flow and transport
- Coefficient functions are not Lipschitz-, but just Hölder-continuous.

A description of the models used for flow and reactive transport in porous media is given in the corresponding sections together with a brief state of the art concerning discretization possibilities and their analysis. We will distinguish between discretization error and linearization error. The discretization error refers to the error of the spatial and temporal discretization, by assuming that the nonlinear systems are solved exactly in each time step. The aim is to provide order of convergence estimates for the discretization error. The linearization error is referred to the error induced due to the linearization schemes applied to solve the nonlinear systems at each time step. We will consider general saturated/unsaturated flow as well as strictly unsaturated flow and reactive flow transport with equilibrium or non-equilibrium sorption. The sorption isotherm is considered to be of Freundlich-type, which is modeled by a Hölder- but not Lipschitz-continuous function. Due to this a regularization step is necessary when applying Newton method for linearization.

The main contribution of this thesis are:

- We proved the convergence for a mixed finite element discretization of Richards' equation in a very general framework: slow and fast diffusion being allowed. No unrealistic regularity assumption were assumed. Order of convergence estimates are derived.
- We proved the convergence for a multipoint flux approximation discretization (O-method) for the Richards equation for saturated/unsaturated flow. Order of convergence estimates are obtained.
- We have shown the optimal convergence for a mixed finite element scheme for Richards' equation for strictly unsaturated flow (nonlinear parabolic equation).
- We proved the convergence for a MFEM scheme for reactive solute transport with equilibrium or non-equilibrium sorption in porous media. The proof takes in account the low regularity of the flow equation. The order of convergence depends naturally on the accuracy of the numerical scheme for the flow equation.
- We set up Newton schemes for solute transport with equilibrium or non-equilibrium sorption. We derived *a priori* constraints on the discretization parameters to ensure their (quadratic) convergence. These constraints are of a relevant interest for practical use.

- We provided a comprehensive comparative study on numerical diffusion for different discretization schemes for solute transport in porous media. The study included Galerkin finite element-, FVM- and MFEM-schemes, higher order schemes in space or time, and upwind schemes. The study can be used by researchers to test their codes and/or new numerical schemes.

- We developed a more robust mixed hybrid finite element scheme for solute transport and an upwind variant of it. The schemes are more suitable for convection-dominated problems.

- We provided a mass conservative scheme for concrete carbonation. The scheme is based on the MFEM. The model for concrete carbonation is a fully coupled flow and reactive transport system. Error estimates are derived for some particular cases.

The thesis is structured as follows. In Section 1.1 are listed the notations and abbreviations used throughout this work. There are eight journal papers which are discussed in Chapters 2 and 3. A list of the papers is given in Section 1.2. Chapter 2 concerns flow in porous media. In its first section the general framework is presented: the equations, the state of the art and outline our contribution. The Sections 2.1-2.3 are then concrete describing the first three papers, which are all concerning flow in porous media. Each paper is described by a short introduction, presentation of the numerical scheme considered their and the assumptions made on the data and by giving the main results. Following the same line, Chapter 3 is considering reactive solute transport and the Sections 3.1-3.5 are describing the remaining papers. Chapter 4 gives the conclusions and outlook.

1.1 Notations.

Throughout this thesis we use common notations in the functional analysis. We denote by Ω a bounded, open domain in $\mathbb{R}^d$ (d denotes the spatial dimension) with a Lipschitz-continuous boundary $\partial\Omega$. By $\langle\cdot,\cdot\rangle$ we mean the inner product on $L^2(\Omega)$, or the duality pairing between $H_0^1(\Omega)$ and $H^{-1}(\Omega)$. Further, $\|\cdot\|$ and $\|\cdot\|_1$ stand for the norms in $L^2(\Omega)$ and $H^1(\Omega)$, respectively. The functions in $H(\mathrm{div};\Omega)$ are vector valued, having a L^2 divergence. We denote by $T<\infty$ a finite end time and let $N\geq 1$ be an integer giving the time step $\tau = T/N$, and $t^k = k\tau$ for $k\in\{1,\ldots,N\}$. We further denote by $\epsilon > 0$ a small regularization parameter.

Furthermore, we let $\mathcal{T}_h$ be a regular decomposition of Ω into closed d-simplices; h stands for the mesh-size (see [24]). Here we assume $\overline{\Omega} = \cup_{T\in\mathcal{T}_h} T$, hence Ω is polygonal. In this way the errors caused by an approximation of a non-polygonal domain are avoided; we mention [58] for a detailed analysis. We will use the discrete

subspaces $W_h \subset L^2(\Omega)$ and $V_h \subset H(\mathrm{div};\Omega)$ defined as

$$\begin{aligned} W_h &:= \{p \in L^2(\Omega) |\ p \text{ is constant on each element } T \in \mathcal{T}_h\}, \\ V_h &:= \{\mathbf{q} \in H(\mathrm{div};\Omega) |\ \mathbf{q}_{|T} = \mathbf{a} + b\mathbf{x} \ \text{ for all } T \in \mathcal{T}_h\}. \end{aligned} \tag{1.1}$$

In other words, W_h denotes the space of piecewise constant functions, while V_h is the RT_0 space (see [18]). Notice that $\nabla \cdot \mathbf{q} \in W_h$ for any $\mathbf{q} \in V_h$.

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

$$P_h : L^2(\Omega) \to W_h, \quad \langle P_h w - w, w_h \rangle = 0, \tag{1.2}$$

for all $w_h \in W_h$. Furthermore, a projector Π_h can be defined on $(H^1(\Omega))^d$ (see [18, p. 131]) such that

$$\Pi_h : (H^1(\Omega))^d \to V_h, \quad \langle \nabla \cdot (\Pi_h \mathbf{v} - \mathbf{v}), w_h \rangle = 0, \tag{1.3}$$

for all $w_h \in W_h$. Following [66], p. 237, this operator can be extended to $H(\mathrm{div};\Omega)$. For the above operators there holds

$$\|w - P_h w\| \ \leq \ Ch\|w\|_1, \tag{1.4}$$

$$\|\mathbf{v} - \Pi_h \mathbf{v}\| \ \leq \ Ch\|\mathbf{v}\|_1, \tag{1.5}$$

for any $w \in H^1(\Omega)$ and $\mathbf{v} \in (H^1(\Omega))^d$. Throughout this work we mean by C a positive constant, not depending on the unknowns or the discretization parameters, e.g. the mesh diameter h, the time step size τ and the regularization parameter ϵ.

1.1.1 Abbreviations

The following abbreviations will be used throughout this thesis.

MFEM = Mixed Finite Element Method
MHFEM = Mixed Hybrid Finite Element Method
FEM = (Galerkin) Finite Element Method
FVM = Finite Volume Method
RT$_0$ = Raviart-Thomas lowest order finite elements
BDM$_1$ = Brezzi-Douglas-Marini lowest order finite elements

1.2 List of the papers

The following papers are the subject of this thesis.

[P1] **F. A. Radu**, I. S. Pop and P. Knabner, Error estimates for a mixed finite element discretization of some degenerate parabolic equations. **Numer. Math.** 109 (2), 2008, pp. 285-311.

[P2] R. A. Klausen, **F. A. Radu** and G. T. Eigestad, Convergence of MPFA on triangulations and for Richards' equation. **Int. J. for Numer. Meth. Fluids** 58 (12), 2008, pp. 1327-1351.

[P3] **F. A. Radu** and W. Wang, Convergence analysis for a mixed finite element scheme for flow in strictly unsaturated porous media. **Nonlinear Analysis Serie B: Real World Applications**, DOI:10.1016/j.nonrwa.2011.05.003, 2011.

[P4] **F. A. Radu**, I. S. Pop and S. Attinger, Analysis of an Euler implicit - mixed finite element scheme for reactive solute transport in porous media. **Num. Meth. for Partial Diff. Eqs.** 26 (2), 2010, pp. 320-344.

[P5] **F. A. Radu** and I. S. Pop, Newton method for reactive solute transport with equilibrium sorption in porous media. **J. Comput. and Appl. Math.** 234 (7), 2010, pp. 2118-2127.

[P6] **F. A. Radu** and I. S. Pop, Mixed finite element discretization and Newton iteration for a reactive contaminant transport model with non-equilibrium sorption: convergence analysis and error estimates. **Comput. Geosci.** 15 (3), 2011, pp. 431-450.

[P7] **F. A. Radu**, N. Suciu, J. Hoffmann, A. Vogel, O. Kolditz, C.H. Park and S. Attinger, Accuracy of numerical simulations of contaminant transport in heterogeneous aquifers: a comparative study. **Adv. Water Resour.** 34 (1), 2011, pp. 47-61.

[P8] **F. A. Radu**, A. Muntean, I. S. Pop, N. Suciu and O. Kolditz, A mixed finite element discretization scheme for concrete carbonization in unsaturated porous media. **J. Comput. and Appl. Math.** 246, 2013, pp. 74-85.

1.2.1 Role of co-authors

I am the first author in seven of the eight papers in this thesis. I was the driving-force for all these papers and I did the main part of the work. At one of the papers I am the second author. In that paper I did the work concerning the convergence of the scheme for Richards equation, which is the relevant part for this thesis. I acknowledge the contribution of all co-authors: I. S. Pop, P. Knabner, S. Attinger, N. Suciu, R. Klausen, A. Muntean, G. T. Eigestad, W. Wang, J. Hoffmann, A. Vogel, and O. Kolditz. The papers and implicit this thesis are of higher quality due to them.

Chapter 2

Flow in porous media

In this section we consider flow in saturated/unsaturated porous media. We present the mathematical model and some numerical schemes together with convergence results. The papers associated to this section are [P1]-[P3]. A short description of each of them is given in Sections 2.1 - 2.3.

The water flow in porous media is mathematically described by the Richards equation, a nonlinear, possibly degenerate, parabolic partial differential equation. In the pressure formulation, the Richards equation [17] is expressed as

$$\partial_t \Theta(\psi) - \nabla \cdot (K(\Theta(\psi))\nabla(\psi + z)) = 0 \quad \text{ in } (0,T) \times \Omega. \tag{2.1}$$

Here ψ denotes the pressure head, Θ the volumetric water content, K the hydraulic conductivity and z the height against the gravitational direction. The Richards equation results from the Darcy law

$$\mathbf{q} = -K(\Theta(\psi))\nabla(\psi + z), \tag{2.2}$$

and the mass balance equation for water, which is assumed incompressible

$$\partial_t \Theta(\psi) + \nabla \cdot \mathbf{q} = 0. \tag{2.3}$$

Equations (2.2) - (2.3) are completed by initial and boundary conditions

$$\psi(t=0) = \psi_I \quad \text{in} \quad \Omega, \qquad \text{and } \psi = 0 \quad \text{on} \quad (0,T) \times \partial\Omega. \tag{2.4}$$

We consider only homogeneous Dirichlet boundary conditions, but the results presented in this work can be easily extended to more general types. Based on experimental results, different functional relationships have been proposed for describing the dependency between K, Θ and ψ (see e. g. [17]), yielding the nonlinear model (2.1). In this sense we mention the model proposed by van Genuchten - Mualem [89, 56], where

$$\begin{aligned} &\Theta(\psi) = \Theta_R + (\Theta_S - \Theta_R)\theta(\psi), \qquad \theta(\psi) = \left(1 + (-\alpha\psi)^{\frac{1}{1-m}}\right)^{-m}, \\ &K(\theta) = K_S \theta^{\frac{1}{2}} \left[1 - \left(1 - \theta^{\frac{1}{m}}\right)^m\right]^2. \end{aligned} \tag{2.5}$$

whenever the flow is unsaturated ($\psi < 0$). Here $\Theta_R, \Theta_S, K_S > 0$, $\alpha > 0$ and $m \in (0,1)$ are medium dependent parameters. For the fully saturated regime ($\psi \geq 0$) we have $\Theta = \Theta_S$ and $K = K_s$. Notice that in the present setting the Richards equation degenerates whenever ψ goes to $-\infty$, implying that both $\Theta'(\psi)$ and $K(\Theta(\psi))$ are approaching 0, or in the fully saturated regime ($\psi \geq 0$), when $\Theta'(\psi) = 0$. The regions of degeneracy depend on the saturation of the medium; therefore these regions are not known *a priori* and may vary in time and space.

The set-up and especially the analysis of numerical schemes for the Richards equation are very challenging tasks. A classical method to deal with this is to apply the Kirchhoff transformation, see e.g. [4]. The main benefit of applying the Kirchhoff transformation is that the two nonlinearities in (2.1) are combined in just one which makes the analysis easier.

The Kirchhoff transformation is given by

$$\begin{aligned} \mathcal{K} : \mathbb{R} &\longrightarrow \mathbb{R} \\ \psi &\longmapsto \int_0^{\psi} K(\Theta(s))\, ds. \end{aligned} \tag{2.6}$$

Notice that the hydraulic conductivity K can only vanish in the completely unsaturated case, when $\Theta = 0$. Hence $K(\Theta(s)) > 0$ whenever $\Theta > 0$, so the transformation is bijective. With

$$\begin{aligned} u &:= \mathcal{K}(\psi), \\ b(u) &:= \Theta \circ \mathcal{K}^{-1}(u), \\ k(b(u)) &:= K \circ \Theta \circ \mathcal{K}^{-1}(u), \end{aligned} \tag{2.7}$$

we can bring equation (2.1) to

$$\partial_t b(u) - \nabla \cdot (\nabla u + k(b(u))\, \mathbf{e_z}) = 0, \tag{2.8}$$

where $\mathbf{e_z}$ denotes the vertical unit vector. $b(\cdot)$ is assumed to be monotone increasing and only Hölder-continuous (not Lipschitz-continuous). Therefore two types of degeneracy are allowed: for some $\overline{u} \in \mathbb{R} \bigcup \{\pm\infty\}$ the following situations may occur:

a) $u \to \overline{u}$ implies $b'(u) \to 0$: the *fast diffusion* case,

b) $u \to \overline{u}$ implies $b'(u) \to \infty$: the *slow diffusion* case.

In particular, the vanishing of $b'(\cdot)$ may occur on intervals.

Among the papers where numerical schemes are set and analyzed for equations like the Richards equation with the Kirchhoff transformation we mention: [8, 68, 81] for MFEM, [92] for an expanded MFEM, [34] for FVM, [35] for a combined MFEM-FVM and [58, 62, 65] for the Galerkin FEM. The discretization in time is done by using the backward Euler method. The convergence for Galerkin FEM schemes for Richards equation has been proved in [5, 58] for saturated/unsaturated flow. The authors in [8] provided a proof for the MFEM scheme for Richards equation and saturated/unsaturated flow by using the Kirchhoff transformation. To obtain order of

convergence estimates by using [8] one needed additional, non-realistic regularity assumptions for the solution of Richards' equation. This has been improved in [68], where order of convergence estimates are shown for saturated/unsaturated flow (fast diffusion case). For strictly unsaturated flow, when Richards' equation is regular, we mention [6] for the convergence of Galerkin FEM. The convergence for the MFEM scheme in cases of both slow and fast diffusion was still missing, as well as the convergence for the MFEM in the strictly unsaturated case. A still open problem is the convergence of the MFEM scheme without using Kirchhoff's transformation for saturated/unsaturated flow.

In [P1] we prove the convergence for the MFEM-scheme in a very general framework, see short description below (Section 2.1). Furthermore, in [P2] we give a proof also for the convergence of a MPFA-scheme for Richards' equation. The convergence is shown for saturated/unsaturated flow, but only fast diffusion case (i.e. $b'(\cdot)$ is Lipschitz-continuous). The analysis can be but extended to include also the slow diffusion case (i.e. $b'(\cdot)$ is only Hölder continuous). A short description of the paper is given in Section 2.2.

All the schemes above involve the Kirchhoff transformation. Nevertheless, many researchers are using the Richards equation without involving the Kirchhoff transformation. Although the use of the Kirchhoff transformation at the continuous level gives an equivalent equation, at the discrete level the schemes are not equivalent anymore. This makes it very difficult to transfer the error estimates obtained for the scheme with Kirchhoff's transformation to the one without it. For the general case, saturated/unsaturated flow there is no convergence proof for MFEM scheme for the Richards equation that does not involve a Kirchhoff transformation. For Galerkin FEM we mention [5] for the saturated/unsaturated flow and [6] for the strictly unsaturated flow regime. We give in [P3] a proof for the convergence of the MFEM for strictly unsaturated flow. A short description of the results of [P3] is given in Section 2.3.

The nonlinear systems at each time step are commonly solved by different methods: the quadratic convergent Newton method, robust first-order linearization schemes, e. g. [63, 93], or the Jäger-Kačur scheme [38, 39]. The convergence of the Newton method applied to systems provided by a MFEM for an elliptic problem is studied in [60] and for degenerate parabolic equations in [69, 73, 74].

2.1 Convergence of the MFEM-scheme for variably saturated flow: [P1]

In [P1] we prove the convergence of the MFEM (RT_0), Euler implicit scheme for Richards' equation in a general framework. It continues the work in [68], where the ideas in [8, 81] are combined with the techniques for degenerate parabolic equations that are developed in [58]. The order of convergence estimates in [68] are obtained for a Lipschitz-continuous nonlinearity $b(\cdot)$. An essential point of the proof in [68] is the

equivalence between the mixed and conformal formulations, for both the continuous and the time discrete problems.

In [P1] we only assume the Hölder continuity of $b(\cdot)$. Therefore both degeneracies mentioned before are allowed. This applies in particular to the Richards equation (2.1) and extends the results presented in [68, 81]. Although the equivalence to a conformal formulation remains valid in this general framework, it is used now only for the regularity of the solution. We exploit in [P1] the possibility to have L^2 test functions in the mass conservation equation, which is a particular feature of the RT_0 elements. This leads to a simplified convergence proof for the semidiscrete scheme, avoiding the techniques involving the Green operator used in [58, 62, 65, 68]. Notice also that in this work we do not assume $b(u) \in L^\infty(0,T;L^\infty(\Omega))$, as commonly done in the literature (see e. g. [8, 92]). Another advantage of the present approach is that the convergence in the non-degenerate case, as well as in the fast diffusion case where $b(\cdot)$ is Lipschitz-continuous, can be obtained directly as particular cases of the current results. We also mention that in many papers a regularized problem is considered as an intermediate step in obtaining the convergence results, where an adaption rule between the regularization and the discretization parameters is required. Here we avoid such a regularization step and make the result more transparent.

Fully discrete mixed variational formulation. Let $n = 1, \ldots, N$ and u_h^{n-1} be given. Find $(u_h^n, \mathbf{q}_h^n) \in W_h \times V_h$ such that

$$\langle b(u_h^n) - b(u_h^{n-1}), w_h\rangle + \tau\langle \nabla\cdot \mathbf{q}_h^n, w_h\rangle = 0, \tag{2.9}$$

$$\langle \mathbf{q}_h^n, \mathbf{v}_h\rangle - \langle u_h^n, \nabla\cdot \mathbf{v}_h\rangle + \langle k(b(u_h^n))\mathbf{e_z}, \mathbf{v}_h\rangle = 0, \tag{2.10}$$

for all $w_h \in W_h$ and $\mathbf{v}_h \in V_h$. Initially we take a $p_h^0 \in W_h$ such that it satisfies the condition $b(p_h^0) = P_h b(u_I)$ on any $T \in \mathcal{T}_h$. The discrete scheme is implemented in the software package UG [13].

Assumptions. The following assumptions are made on the domain, coefficient functions and regularity of solution.

(P1-A1) $\Omega \subset \mathbb{R}^d$ is open, bounded and has a Lipschitz-continuous boundary.

(P1-A2) $b(\cdot) \in C^{0,\alpha}$ is non-decreasing and Hölder continuous: there exists an $\alpha \in (0,1]$ and $C_b > 0$ so that $|b(u_1) - b(u_2)| \le C_b|u_1 - u_2|^\alpha$ for all $u_1, u_2 \in \mathbb{R}$. For simplicity we assume $b(\cdot)$ continuously differentiable almost everywhere.

(P1-A3) $k(b(\cdot))$ is continuous and bounded and satisfies for all $u_1, u_2 \in \mathbb{R}$, $|\, k(b(u_2)) - k(b(u_1))\,|^2 \le C_k(b(u_2) - b(u_1))(u_2 - u_1)$.

(P1-A4) The initial data satisfies $u_I \in L^2(\Omega)$.

(P1-A5) $\mathbf{q}^n \in H^1(\Omega)^d$ for all $n = 1, \ldots, N$ and $\displaystyle\sum_{n=1}^{N} \tau\|\mathbf{q}^n\|_1^2 \le C\tau^{-\frac{2(1-\alpha)}{1+\alpha}}$, where $\mathbf{q}^n$

is the solution of semi-discrete (discrete in time) variational problems as defined in [P1], p. 292.

Remark 2.1.1 *When the coefficient functions are given by the Genuchten-Mualem model [89, 56], the assumption (P1-A2) holds with* $\alpha = 2m/(3m+2)$ *(so* $b(\cdot)$ *is not Lipschitz-continuous!), whereas (P1-A3) is satisfied whenever* $m \in [2/3, 1)$*. For the porous medium equation (P1-A2) is satisfied with* $\alpha = 1/m$*.*

Remark 2.1.2 *Assumption* (P1-A5) *is automatically fulfilled in the case of one spatial dimension, when the spaces* $H(\mathrm{div};\Omega)$ *and* $H^1(\Omega)$ *coincide. In the multi dimensional case and in the absence of convection, one can also show that* (P1-A5) *holds true.*

Order of convergence estimates. The main result of [P1] is the following theorem, which gives the convergence of the MFEM scheme for Richards' equation and saturated/unsaturated flow (both slow and fast diffusion cases are allowed).

Theorem 2.1.1 *Assuming (P1-A1)-(P1-A5), for any* $K = 1, \dots, N$ *we have*

$$\sum_{n=1}^{K} \int_{t_{n-1}}^{t_n} \|b(u(t)) - b(u_h^n))\|_{L^{1+\frac{1}{\alpha}}(\Omega)}^{1+\frac{1}{\alpha}} dt + \left\| \sum_{n=1}^{K} \int_{t_{n-1}}^{t_n} (u(t) - u_h^n) dt \right\|^2 + \left\| \sum_{n=1}^{K} \int_{t_{n-1}}^{t_n} (\mathbf{q}(t) - \mathbf{q}_h^n) dt \right\|^2 \leq C\Big(\tau + h^2 \tau^{-\frac{2(1-\alpha)}{1+\alpha}}\Big). \tag{2.11}$$

Remark 2.1.3 *If we allow above only the slow diffusion case, i.e.* $b' \geq C_{inf} > 0$ *we obtain*

$$\sum_{n=1}^{K} \int_{t_{n-1}}^{t_n} \|b(u(t)) - b(u_h^n))\|_{L^{1+\frac{1}{\alpha}}(\Omega)}^{1+\frac{1}{\alpha}} dt + \left\| \sum_{n=1}^{K} \int_{t_{n-1}}^{t_n} (u(t) - u_h^n) dt \right\|^2 + \left\| \sum_{n=1}^{K} \int_{t_{n-1}}^{t_n} (\mathbf{q}(t) - \mathbf{q}_h^n) dt \right\|^2 \leq C\Big(\tau^2 + h^2 \tau^{-\frac{2(1-\alpha)}{1+\alpha}}\Big).$$

For $\tau = h^{\frac{1+\alpha}{2}}$ *this gives a convergence of order* $h^{1+\alpha}$*.*

Numerical experiments are presented in [P1] to sustain the theoretical results.

2.2 Convergence of the MPFA-scheme for variably saturated flow: [P2]

The MPFA method (see [1] for the description of the method) can be seen as modified MFEM, when the Raviart-Thomas space V_h is replaced by the broken Raviart-Thomas

space $\mathcal{RT}_h^{1/2}$ (see [P2] p. 1331 for the definition) and the scalar product $\langle \mathbf{q}, \mathbf{v} \rangle$ is computed by a quadrature formula, with the resulting discrete scalar product being denoted by $a_h(\cdot,\cdot) : \mathcal{RT}_h^{1/2} \times \mathcal{RT}_h^{1/2} \to \mathbb{R}$. The corresponding finite element space $\mathcal{RT}_h^{1/2}$ is still in $H(\mathrm{div};\Omega)$, giving the continuity of the fluxes over edges. The canonical degrees of freedom for the space $\mathcal{RT}_h^{1/2}$ are $\mathbf{v} \cdot \mathbf{n}$ of each half edge, with $\mathbf{n}$ denoting the outer normal. The definition of a_h depends on the chosen MPFA variant. We refer to [43] for MPFA on quadrilateral grids and to [P2] for triangular grids.

Fully discrete MPFA variational formulation. Let $n = 1, \ldots, N$ and u_h^{n-1} be given. Find $(u_h^n, \mathbf{q_h^n}) \in W_h \times \mathcal{RT}_h^{1/2}$ such that

$$\langle b(u_h^n), w_h \rangle + \tau \langle \sum_{j=1}^{n} \nabla \cdot \mathbf{q_h^j}, w_h \rangle = \langle b(u_h^0), w_h \rangle, \tag{2.12}$$

$$a_h(\mathbf{q_h^n}, \mathbf{v_h}) - \langle u_h^n, \nabla \cdot \mathbf{v_h} \rangle + a_h(k(b(u_h^n))\mathbf{e_z}, \mathbf{v_h}) = 0, \tag{2.13}$$

for all $w_h \in W_h$ and $\mathbf{v_h} \in \mathcal{RT}_h^{1/2}$.

Assumptions. Assumptions (P2-A1), (P2-A3) and (P2-A4) are the same as in Section 2.1 above. (P1-A2) and (P1-A5) are now replaced by

(P2-A2) $b(\cdot) \in C^1$ is non-decreasing and Lipschitz-continuous.

(P2-A5) $\mathbf{q^n} \in H^1(\Omega)^d$ for all $n \in \{1, \ldots, N\}$.

Order of convergence estimates. We prove in [P2] the convergence of the MPFA schemes for Richards' equation, for both quadrilateral and triangular grids. Saturated/unsaturated flow is allowed (fast diffusion case), so the equation is degenerate. The main result of [P2] is the following theorem.

Theorem 2.2.1 *Assuming (P2-A1)-(P2-A5), for any $K = 1, \ldots, N$ there holds*

$$\left\| \sum_{n=1}^{K} \int_{t_{n-1}}^{t_n} (u(t) - u_h^n)\, dt \right\|^2 + \left\| \sum_{n=1}^{K} \int_{t_{n-1}}^{t_n} (\mathbf{q}(t) - \mathbf{q}_h^n) dt \right\|^2 \leq C(\tau + h^2). \tag{2.14}$$

The paper [P2] is concluded by numerical experiments.

2.3 Convergence of the MFEM-scheme for strictly unsaturated flow: [P3]

In [P3] we prove the optimal convergence of a MFEM-scheme for the Richards equation (2.1) for strictly unsaturated flow. This time we do not make use of the Kirchhoff transformation. The proof combines the techniques used in [6] with the specific ones for MFEM (as presented in [6, 68, 70]).

Fully discrete mixed variational formulation. Let $n \in \{1, \ldots, N\}$ and $\psi_h^{n-1} \in W_h$ be given. Find $(\psi_h^n, \mathbf{q}_h^n) \in W_h \times V_h$ such that

$$\langle \frac{\Theta(\psi_h^n) - \Theta(\psi_h^{n-1})}{\tau}, w_h \rangle + \langle \nabla \cdot \mathbf{q}_h^n, w_h \rangle = 0, \tag{2.15}$$

$$\langle k^{-1}(\Theta(\psi_h^n))\mathbf{q}_h^n, \mathbf{v}_h \rangle - \langle \psi_h^n, \nabla \cdot \mathbf{v}_h \rangle + \langle \mathbf{e_z}, \mathbf{v}_h \rangle = 0, \tag{2.16}$$

for all $w_h \in W_h$ and $\mathbf{v}_h \in V_h$. We take at time $t = 0$: $\psi_h^0 = P_h \psi_I$. The discrete scheme is implemented in the software package UG [13].

Assumptions. The following assumptions are defining the framework of paper [P3].

(P3-A1) There exists some constants $\Theta_S, \Theta_R, L_\Theta, l_\Theta, L_{\Theta'} \in \mathbb{R}$ such that there holds for all $x \in \mathbb{R}$

$$0 < \Theta_R \leq \Theta(x) < \Theta_S \leq 1$$

and

$$0 < l_\Theta \leq \Theta'(x) \leq L_\Theta < \infty,$$

and $|\Theta''(x)| \leq L_{\Theta'}$.

(P3-A2) There exists some constants $K_0, K_1 \in \mathbb{R}$ such that there holds for all $x \in \mathbb{R}$

$$0 < K_0 \leq K(x) \leq K_1 < \infty.$$

Moreover, $K(\cdot)$ is assumed to be Lipschitz-continuous.

(P3-A3) The initial function ψ_I is essentially bounded; furthermore, $\psi_I \in H^1(\Omega)$.

(P3-A4) The solution of the continuous problem $(\psi, \mathbf{q})$ has the following regularity: $\partial_t \Theta(\psi) \in L^2(0, T; H^1(\Omega))$, $\partial_{tt} \Theta(\psi) \in L^2(0, T; L^2(\Omega))$, $\psi \in L^\infty(0, T; H^1(\Omega))$, $\partial_t \psi \in L^\infty((0, T) \times \Omega) \cap L^2(0, T; H^1(\Omega))$, and $\mathbf{q} \in L^\infty(0, T; (H^1(\Omega))^d) \cap (L^\infty((0, T) \times \Omega))^d$.

A very important tool in the proof of the convergence of the scheme (2.15) – (2.16) is given by the following lemma, which was first first presented in [5]. The proof, which is elementary, can be also found in [6], p. 1685.

Lemma 2.3.1 *Let u^n, v^n be real numbers, $n \in \{1, \ldots N\}$. Suppose that $|u^n - u^{n-1}| \leq C_u \tau$ and $\Theta : \mathbb{R} \to \mathbb{R}$ is such that $0 \leq \Theta' \leq C_{\Theta'} < \infty$ and $|\Theta''| \leq C_{\Theta''}$. Then*

$$\frac{\Theta(u^n) - \Theta(v^n) - \Theta(u^{n-1}) + \Theta(v^{n-1})}{\tau}(u^n - v^n)$$
$$= \frac{\displaystyle\int_{v^n}^{u^n} \Theta(\mu) - \Theta(v^n) d\mu - \int_{v^{n-1}}^{u^{n-1}} \Theta(\mu) - \Theta(v^{n-1}) d\mu}{\tau} - E,$$

where

$$E \leq C\{(u^n - v^n)^2 + (u^{n-1} - v^{n-1})^2 + \tau^2\},$$

for some C depending on $C_u, C_{\Theta'}$ and $C_{\Theta''}$.

Corollary 2.3.1 *Assuming that Θ and ψ satisfy (P3-A1) and (P3-A4), there holds*

$$\sum_{n=1}^{N} \langle \frac{\Theta(\psi(t^n)) - \Theta(\psi(t^{n-1}) - \Theta(\psi_h^n) + \Theta(\psi_h^{n-1})}{\tau}, \psi(t^n) - \psi_h^n \rangle$$
$$\geq C_1 \frac{\|\psi(t^N) - \psi_h^N\|^2}{\tau} - C_2 \frac{\|\psi_I - P_h\psi_I\|^2}{\tau} - C_3 \sum_{n=1}^{N} \|\psi(t^n) - \psi_h^n\|^2 - C_4\tau, \tag{2.17}$$

with C_1, C_2, C_3 and C_4 strict positive constants, not depending on the discretization parameters h or τ.

Order of convergence estimates. The following optimal order of convergence estimates are proved in [P3].

Theorem 2.3.1 *Assuming that (P3-A1)-(P3-A4) hold, we have for any $K = 1, \ldots, N$*

$$\|\psi(t^K) - \psi_h^K\|^2 + \sum_{n=1}^{K} \tau \|\mathbf{q}(t^n) - \mathbf{q}_h^n\|^2 \leq C(\tau^2 + h^2), \tag{2.18}$$

with the constant C not depending on discretization's parameters τ and h.

Numerical simulations of Richards' equation with the scheme (2.15)-(2.16) are presented in [P3]. Examples with known analytical solution are used. The numerical results clearly sustain the optimal convergence of the scheme.

Chapter 3

Reactive solute transport in porous media

In this chapter we consider multicomponent, reactive transport in saturated/unsaturated porous media. The first part of the chapter is devoted to the description of the problem, of the state of the art in the field and a brief overview over our contribution. Then each of the papers of the thesis concerning this topic, i.e. [P4]-[P8] will be detailed summarized.

A mathematical model for transport and reaction of N_S species including the effects of advection, dispersion, sorption and degradation is described by the set of equations

$$\partial_t(\Theta c_i) + \rho_b \partial_t s_i - \nabla \cdot (\mathbf{D_i} \nabla c_i - \mathbf{Q} c_i) = -\Theta R_i \quad \text{in } (0,T) \times \Omega\,, \tag{3.1}$$

with $i \in \{1, \ldots, N_S\}$, where c_i, s_i denote the concentration of the dissolved and the adsorbed species, respectively, $\mathbf{D_i}$ is the diffusion-dispersion coefficient, ρ_b [ML^{-3}] is the bulk density and R_i denotes the reaction rate of the ith species. The water content Θ and the water flux $\mathbf{Q}$ are determinated by solving the Richards equation (2.1). For the sake of simplicity we consider only homogeneous Dirichlet boundary conditions in the sequel. For other types of boundary conditions we refer to [67]. Additionally we formulate a mass balance for the ith microbial or other immobile species, $i \in \{N_S + 1, \ldots, N_S + M\}$, that are only subject to reactions:

$$\partial_t c_i + k_{di} c_i = R_i\,. \tag{3.2}$$

Here k_{di} denotes the decay rate of species i. Equations (3.1) and (3.2) have to be supplemented with initial conditions $c_i(x,0) = c_{i0}(x)$ for $x \in \Omega$, $i \in \{1, \ldots, N_S+M\}$.

The sorption may be of equilibrium or kinetic (non-equilibrium) type

$$s_i = \phi(c_i) \text{ or } \partial_t \mathrm{s_i} = \mathrm{k_i}(\phi(\mathrm{c_i}) - \mathrm{s_i})\,, \tag{3.3}$$

with ϕ being an arbitrary sorption isotherm and k_i a rate parameter. The sorption isotherm ϕ can be linear, of Freundlich, Langmuir or Freundlich-Langmuir type, see

e.g. [67] or a form free function resulting from an experimental study or a parameter identification process. Of a special interest from the mathematical point of view, and also for this thesis, is the Freundlich type isotherm: $\phi(x) = x^\alpha$, with $\alpha \in (0, 1)$. In this case the sorption isotherm is only Hölder continuous (not Lipschitz-continuous) and this makes the design and analysis of efficient numerical schemes for equations (3.1) - (3.3) more challenging. The Freundlich isotherm has an infinite derivative in zero, therefore one needs a regularization in order to can apply the Newton method for linearization.

Several papers are considering numerical schemes for transport equations. We mention [11, 12, 15] for a conformal FEM discretization, [44, 59] for finite volume schemes, and [79, 80] for discontinuous Galerkin methods. Furthermore, the method of characteristics is studied in [40] and a characteristic - mixed method in [7], upwind MFEM are considered in [26, 27], whereas combined finite volume-mixed hybrid finite elements are employed in [35]. Typically either a constant Θ is assumed, which corresponds to a saturated flow (see [11, 12, 26, 35]), or a Θ that does not depend on time (see [7, 79, 80]). Another possible simplification is to incorporate the term $c\partial_t\Theta$ in the reactive term $r(\cdot)$ and to assume that the resulting rate remains Lipschitz-continuous [15]. In the general case of a saturated-unsaturated flow this assumption is not satisfied since the factor $\partial_t\Theta(\psi)$ needs not to be essentially bounded.

An interesting situation is considered in [27], where the term $c\partial_t\Theta$ is replaced by Ac, with A a positive constant. Error estimates are obtained without using the Gronwall lemma. A similar situation appears in [35] where the divergence of the water flux is assumed non-negative: $\nabla \cdot \mathbf{Q} = r \geq 0$. However, in a general saturated-unsaturated porous media flow such an assumption is not necessary true and we do not assume it here either.

All the papers above are considering the discretization error and assume that the nonlinear systems at each time step are solved exactly, which is in practice not the case. 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 [63, 93]), or the Jäger-Kačur scheme [38, 39]. The convergence of the Newton method applied to the system provided by a MFEM discretization of an elliptic problem is studied in [60]. Concerning the systems provided by the MFEM discretization of degenerate parabolic equations we mention [63] for a robust linear scheme and [69] for the Newton method.

We present in [67, 71] a numerical scheme based on MFEM for the spatial discretization and backward Euler for the temporal discretization. The Raviart-Thomas lowest order elements are used. The scheme is analyzed for one component reactive transport in porous media in [P4], where order of convergence estimates are derived. The order of convergence naturally depends on the accuracy of the numerical scheme for the flow equation. The low regularity of the flow equation was considered in the analysis. The analysis is continued in [P5] and [P6], where also the linearization error is considered. The Newton method, which is locally but quadratic convergent is

used. A regularization step is necessary when dealing with non-Lipschitz-continuous sorption isotherms. The main benefit of the type of analysis performed in [P5, P6] is that *a priori* constraints on the discretization parameters are derived to ensure the convergence of the whole scheme (including the quadratic convergence of the Newton method). An important hint for the proof was to use that the starting choice for the Newton iteration is the solution at the last time step, which can not be 'too far away' from the actual solution (which is shown by *a priori* estimates).

In [P7] we studied the numerical diffusion for different discretization schemes for transport problems. We considered Galerkin FEM, MFEM and FVM, including higher order Galerkin FEM and FVM, and higher order temporal discretization. Also upwind schemes were considered. A systematic study was performed using both an academical example and a realistic case one. Although the problem of numerical diffusion is well-recognized, such a comparative study was missing in the literature. The results in [P7] can be used by researchers to test new numerical schemes and/or codes.

It is well-known that for convection-dominated problems one needs stabilization techniques to avoid an unphysical solutions. Although there is a rich literature on stabilization methods for Galerkin FEM, see e.g. [48], much less is done for MFEM. The implementation of MFEM schemes is done in most cases by hybridizing, so MHFEM schemes are arising [18]. The Lagrange multipliers are used in MHFEM schemes to enforce the continuity of the fluxes over the edges (sides) of the triangulations. They are furnishing a second order approximation for the concentration [18]. Based on this, we proposed in [P7] a more robust MHFEM for RT_0, and an upwind variant of it, where the Lagrange multipliers are used to discretize the convective term. The same idea is used in [20] for the BDM_1 and tested for various examples. The numerical tests have shown that the new scheme for BDM_1 is now optimal, which is not the case for the classical BDM_1 scheme [28]. The convergence for the upwind MHFEM scheme for lowest-order Raviart-Thomas elements has been analyzed in [21]. The analysis for the new scheme for BDM_1 is ongoing.

Further, fully coupled flow and reactive transport was considered in the frame of concrete carbonation in [P8]. There are plenty of papers concerning analysis of discretization methods for flow [8, 68, 70, 81, 92, 42, 34, 35, 58, 62, 93, 5, 6] and reactive solute transport in porous media [7, 11, 12, 15, 31, 2, 35, 36, 39, 38, 54, 71, 72, 73, 79], but none of them is considering the fully coupled situation (when the flow is affected by the transport). In [P8] we consider a model where water is produced by the reaction and there is a variable porosity, which gives a back-coupling of the transport to flow equation. We proposed a semi-implicit MFEM scheme for the discretization and performed analysis for the strictly unsaturated flow case and a constant porosity. The model for concrete carbonation presented in [P8] can be seen as a special case of dissolution-precipitation models.

We consider also more general dissolution-precipitation models, as in [46, 88, 87], where these processes are modeled by a multi-valued function. As basis model we considered the one in [46]. We set and analyzed a Galerking FEM formulation for this

model in [49] and for a MFEM formulation in [50]. The convergence of the schemes was proved in both cases by compactness arguments. More exactly, we first proved stability estimates in L^2, then used the Eberlein-Smuljan theorem to get the weak convergence and finally apply the Fréchet-Kolmogorov theorem to get the convergence for a sub-sequence. A special effort had to be invested in proving the translation estimates which are needed in the Fréchet-Kolmogorov theorem. Nevertheless, the papers [49, 50] are not part of this thesis.

3.1 Convergence analysis of a MFEM scheme for transport problems: [P4]

In paper [P4] we consider one component solute transport equation without sorption:

$$\partial_t(\Theta(\psi)c) - \nabla \cdot (D\nabla c - \mathbf{Q}c) = \Theta(\psi)r(c) \quad \text{in } (0,T)\times\Omega, \tag{3.4}$$

with c denoting the concentration of the solute, D the diffusion-dispersion coefficient and $r(\cdot)$ a non-linear reaction term. The initial condition is given by $c(t=0) = c_I$ and $\psi(t=0) = \psi_I$. The water content Θ and water flux $\mathbf{Q}$ are obtained by solving the Richards equation (2.1). In [P4] we analyze the discretization error for a MFEM scheme. The discretization in time is done by using the backward Euler method. The aim of paper [P4] is to prove order of convergence estimates in a very general framework, and especially by considering the low regularity of the flow equation. Moreover, we take in account that the Richards equation is also solved numerically, so approximations Θ_h and $\mathbf{Q}_h$ of the water content and water flux have to be considered. In spite of a rich literature regarding convergence of discretization schemes for transport equation, see e.g. [7, 11, 12, 15, 26, 27, 35, 40, 44, 59, 79, 80] and the brief description in section above, the analysis for the MFEM scheme for the transport equation in this general framework was still missing. For the proofs we employ techniques that are similar to those used in [8, 68, 81].

Fully discrete MFEM scheme. Let $n \in \{1,\dots,N\}$, and $\Theta(\psi_h^n)$, $\Theta(\psi_h^{n-1})$, $\mathbf{Q}_h^n$, as well as c_h^{n-1} be given. Find $(c_h^n, \mathbf{q}_h^n) \in W_h \times V_h$ such that

$$\langle \Theta(\psi_h^n)c_h^n - \Theta(\psi_h^{n-1})c_h^{n-1}, w_h\rangle + \tau\langle \nabla\cdot\mathbf{q}_h^n, w_h\rangle = \tau\langle \Theta(\psi_h^n)r(c_h^n), w_h\rangle, \tag{3.5}$$

$$\langle \mathbf{q}_h^n, \mathbf{v}_h\rangle - \langle c_h^n, \nabla\cdot\mathbf{v}_h\rangle - \langle c_h^n\mathbf{Q}_h^n, \mathbf{v}_h\rangle = 0, \tag{3.6}$$

for all $w_h \in W_h$ and $\mathbf{v}_h \in V_h$. Initially we take $c_h^0 = \dfrac{P_h(\Theta(\psi_I)c_I)}{P_h(\Theta(\psi_I))}$. The discrete scheme is implemented in the software package UG [13].

Remark 3.1.1 *The existence and uniqueness of the problem above is proved in [P4], p. 329 (in [P4], p. 326 is also proved the existence and uniqueness for the continuous variational formulation of equation (3.4), which is not given here).*

Assumptions. The following assumptions are made on coefficient functions and regularity of solution.

(P4-A1) The rate function $r : \mathbb{R} \to \mathbb{R}$ is Lipschitz-continuous with the constant L_r; furthermore, $r(c) = 0$ for all $c \leq 0$.

(P4-A2) The diffusion coefficient D does not depend on ψ or $\mathbf{Q}$. For simplicity, let $D = 1$.

(P4-A3) $1 \geq \Theta_S \geq \Theta(x) \geq \Theta_R > 0$, $\forall\, x \in \mathbb{R}$.

(P4-A4) The initial concentration c_I is essentially bounded and positive; furthermore, $\Psi_I \in L^2(\Omega)$.

(P4-A5) $\mathbf{Q} \in L^\infty((0,T) \times \Omega) \cap L^2(0,T; H^1(\Omega))$.

(P4-A5′) $\mathbf{Q}_h^n \in L^\infty(\Omega)$ for all $n \in \{1, \ldots, N\}$.

Remark 3.1.2 *For the ease of presentation we take $D = 1$. The extension to a positive definite tensor is immediate.*

Remark 3.1.3 *In (P4-A3) we assume that $\Theta(\cdot)$ is uniformly bounded by a strictly positive constant. Since Θ stands for the water content, the boundedness of $\Theta(\cdot)$ is a reasonable assumption. However, by taking the lower bound strictly positive we disregard the case of a completely dry (fully unsaturated) medium. For commonly used porous media models (see e.g. [17]) such an assumption holds, for example, in the case of a homogeneous medium if the initial and boundary saturation (where prescribed) also exceed the lower limit. Furthermore, (A5) also implies that $\partial_t \Theta(\psi) \in L^2((0,T) \times \Omega)$. Since $\Theta(\psi)$ is essentially bounded, we immediately obtain $\Theta(\psi) \in C([0,T]; L^2(\Omega))$.*

Remark 3.1.4 *(P4-A5) is also assumed in recent papers referring to the discretization of porous media flow models (see also [15, 35]). Previous results are under stronger assumptions: a constant divergence of the flux ([79, 80, 27]), a constant sign for the water flux ([26]), or a a constant water flux [11, 12, 31].*

Theorem 3.1.1 *Assuming that (P4-A1)-(P4-A5′) hold true we have*

$$\begin{aligned}\sum_{n=1}^{N} \int_{t_{n-1}}^{t_n} \|c(t) - c_h^n\|^2 \, dt + \left\| \sum_{n=1}^{N} \int_{t_{n-1}}^{t_n} \mathbf{q}(t) - \mathbf{q}_h^n \, dt \right\|^2 &\leq C \left\{ \tau^2 + h^2 \right. \\ + \sum_{n=1}^{N} \tau \|\Theta(\psi(t_n)) - \Theta(\psi_h^n)\|^2 &+ \int_{t_{n-1}}^{t_n} \|\Theta(\psi) - \Theta(\psi_h^n)\|^2 \, dt \\ + \sum_{n=1}^{N} \tau \left\| \frac{1}{\tau} \int_{t_{n-1}}^{t_n} \mathbf{Q}(t) dt - \mathbf{Q}_h^n \right\|^2 &\left. \right\}. \end{aligned} \tag{3.7}$$

We clearly see in the theorem above that the order of convergence depends on the accuracy of the scheme for water flow. In particular, this implies that it does not make much sense to use a higher order finite element scheme for the transport equation when the flow is discretized by a lower order scheme. Numerical results are presented in [P4] to confirm the theoretical estimates. We especially have there an example where one obviously see the influence of the accuracy of the flow scheme in the transport. We also mention that the results in Theorem 3.1.1 are optimal.

3.2 Newton method for reactive solute transport with equilibrium sorption in porous media: [P5]

In this paper we consider again one component reactive transport with equilibrium sorption in porous media. The paper is a continuation of [P4] and [71]. The mathematical model is given by (the notations are the same as in previous section):

$$\partial_t(\Theta(\psi)c) + \rho_b\partial_t\phi(c) - \nabla\cdot(D\nabla c - \mathbf{Q}c) = \Theta(\psi)r(c) \quad \text{in } (0,T)\times\Omega. \tag{3.8}$$

For sorption we consider in [P5] two situations: Lipschitz-continuous isotherms, as well as the commonly used Freundlich-type isotherm

$$\phi(c) = c^\alpha, \quad \text{with } \alpha \in (0,1]. \tag{3.9}$$

In the latter case, i.e. $\alpha \in (0,1)$, the derivative of $\phi(\cdot)$ is singular at $c=0$, so $\phi(\cdot)$ is not Lipschitz-continuous. In the summary of [P4] below we treat only the intersting case, i.e. $\alpha \in (0,1)$. To apply the Newton method for Freundlich type isotherms we then employ a regularization step. The reaction rate is assumed Lipschitz-continuous.

The fully discrete MFEM variational formulation for equation (3.8) reads as:

Fully discrete scheme. Let $\Theta(\psi_h^n), \Theta(\psi_h^{n-1}), c_h^{n-1} \in W_h$ and $\mathbf{Q}_h^n \in V_h$ be given. Find $(c_h^n, \mathbf{q}_h^n) \in W_h \times V_h$ such that for all $w_h \in W_h$ there holds

$$\begin{aligned}\langle\Theta(\psi_h^n)c_h^n - \Theta(\psi_h^{n-1})c_h^{n-1}, w_h\rangle + \rho_b\langle\phi(c_h^n) - \phi(c_h^{n-1}), w_h\rangle \\ +\tau\langle\nabla\cdot\mathbf{q}_h^n, w_h\rangle = \tau\langle\Theta(\psi_h^n)r(c_h^n), w_h\rangle,\end{aligned} \tag{3.10}$$

and for all $\mathbf{v}_h \in V_h$ we have

$$\langle\mathbf{q}_h^n, \mathbf{v}_h\rangle - \langle c_h^n, \nabla\cdot\mathbf{v}_h\rangle - \langle c_h^n\mathbf{Q}_h^n, \mathbf{v}_h\rangle = 0. \tag{3.11}$$

Having in mind that we want to use the Newton method for linearization we introduce a regularized sorption isotherm ϕ_ϵ defined by

$$\phi_\epsilon(x) = \begin{cases} \phi(x) & \text{if } x \notin [0,\epsilon], \\ (\alpha-1)\epsilon^{\alpha-2}x^2 + (2-\alpha)\epsilon^{\alpha-1}x & \text{if } x \in [0,\epsilon]. \end{cases}$$

Lemma 3.2.1 *The regularized sorption isotherm is nondecreasing. Further, $\phi_\epsilon(\cdot)$ and $\phi'_\epsilon(\cdot)$ are Lipschitz-continuous on $[0,\infty)$ with the Lipschitz constants $L_{\phi_\epsilon} = \alpha\epsilon^{\alpha-1}$, respectively $L_{\phi'_\epsilon} = \alpha(1-\alpha)\epsilon^{\alpha-2}$. Finally, we have*

$$0 \le \phi_\epsilon(x) - \phi(x) \le (1-\alpha)\epsilon^\alpha \tag{3.12}$$

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

The regularized fully discrete MFEM scheme becomes now:

Fully discrete regularized scheme. Given $\Theta(\psi_h^n), \Theta(\psi_h^{n-1}), c_h^{n-1,reg} \in W_h$ and $\mathbf{Q}_h^n \in V_h$, find $(c_h^{n,reg}, \mathbf{q}_h^{n,reg}) \in W_h \times V_h$ such that for all $w_h \in W_h$ there holds

$$\begin{aligned}\langle \Theta(\psi_h^n)c_h^{n,reg} - \Theta(\psi_h^{n-1})c_h^{n-1,reg}, w_h\rangle + \rho_b\langle \phi_\epsilon(c_h^{n,reg}) - \phi_\epsilon(c_h^{n-1,reg}), w_h\rangle \\ +\tau\langle \nabla\cdot\mathbf{q}_h^{n,reg}, w_h\rangle = \tau\langle \Theta(\psi_h^n) r(c_h^{n,reg}), w_h\rangle,\end{aligned} \tag{3.13}$$

and for all $\mathbf{v}_h \in V_h$ we have

$$\langle \mathbf{q}_h^{n,reg}, \mathbf{v}_h\rangle - \langle c_h^{n,reg}, \nabla\cdot\mathbf{v}_h\rangle - \langle c_h^{n,reg}\mathbf{Q}_h^n, \mathbf{v}_h\rangle = 0. \tag{3.14}$$

We choose $c_h^{0,reg}$ such that there holds $\Theta(\psi_h^0)c_h^0 + \phi(c_h^0) = \Theta(\psi_h^0)c_h^{0,reg} + \phi_\epsilon(c_h^{0,reg})$.

We can now formulate the Newton method for the nonlinear system given by (3.13)-(3.14).

The Newton method. Let $c_h^{n,i-1}$ be given, $i \ge 1$. Find $(c_h^{n,i}, \mathbf{q}_h^{n,i}) \in W_h \times V_h$ such that for all $w_h \in W_h$ there holds

$$\begin{aligned}\langle \Theta(\psi_h^n)c_h^{n,i}, w_h\rangle + \rho_b\langle \phi_\epsilon(c_h^{n,i-1}) + \phi'_\epsilon(c_h^{n,i-1})(c_h^{n,i} - c_h^{n,i-1}) - \phi_\epsilon(c_h^{n-1,reg}), w_h\rangle \\ +\tau\langle \nabla\cdot\mathbf{q}_h^{n,i}, w_h\rangle = \langle \Theta(\psi_h^{n-1})c_h^{n-1,reg}, w_h\rangle \\ +\tau\langle \Theta(\psi_h^n) r(c_h^{n,i-1}) + \Theta(\psi_h^n) r'(c_h^{n,i-1})(c_h^{n,i} - c_h^{n,i-1}), w_h\rangle,\end{aligned} \tag{3.15}$$

and for all $\mathbf{v}_h \in V_h$ we have

$$\langle \mathbf{q}_h^{n,i}, \mathbf{v}_h\rangle - \langle c_h^{n,i}, \nabla\cdot\mathbf{v}_h\rangle - \langle c_h^{n,i}\mathbf{Q}_h^n, \mathbf{v}\rangle = 0. \tag{3.16}$$

Assumptions. The following assumptions are necessary to prove the convergence of the proposed scheme.

(P5-A1) The rate function $r : \mathbb{R} \to \mathbb{R}$ is differentiable with $r'(\cdot)$ bounded and Lipschitz-continuous. Furthermore, $r(c) = 0$ for all $c \le 0$.

(P5-A2) $1 \ge \Theta_S \ge \Theta(x) \ge \Theta_R > 0$, $\forall\, x \in \mathbb{R}$.

(P5-A3) The initial c_I is essentially bounded and positive; furthermore, $\Psi_I \in L^2(\Omega)$.

(P5-A4) $\mathbf{Q} \in L^\infty((0,T)\times\Omega) \cap L^2((0,T); H^1(\Omega))$ and $\mathbf{Q}_h^n \in L^\infty(\Omega)$ for all $n \in \{1,\dots,N\}$.

(P5-A5) The sorption isotherm $\phi(\cdot)$ is non-decreasing, non-negative and Hölder continuous with an exponent $\alpha \in (0,1]$, i. e. $|\phi(a)-\phi(b)| \le C|a-b|^\alpha \quad \forall\, a,b \in \mathbb{R}$. Moreover, $\phi(c)=0$ if $c \le 0$.

(P5-A6) Let $\Omega_\epsilon^{n,h} := \{T \in \mathcal{T}_h \,|\, 0 < c_{h|T}^n < \epsilon\}$. We assume that

$$\sum_{n=1}^{N} \sigma(\Omega_\epsilon^{n,h}) \le C\tau^p \epsilon^q h^l. \tag{3.17}$$

Remark 3.2.1 *The inequality in (P5-A6) above holds obviously for $p=-1, q=0, l=0$. Such an inequality is assumed in [12] for the continuous case, where $p=0, q=1, l=0$; furthermore, a similar situation is considered in [57] for phase transition problems. Here we consider a general context and derive the convergence condition in terms of p, q and l, where $p \le 0$, $q \ge 0$, and $l \ge 0$.*

The analysis in [P5] can be summarized in the following three theorems (the first one is quantifying the discretization error, the second estimates the error caused by the regularization and the last one concerns the convergence of the Newton method).

Theorem 3.2.1 *Assuming (P5-A1)–(P5-A5) there holds*

$$\sum_{n=1}^{N} \int_{t_{n-1}}^{t_n} \|c(t)-c_h^n\|^2\,dt + \left\| \sum_{n=1}^{N} \int_{t_{n-1}}^{t_n} \mathbf{q}-\mathbf{q}_h^n\,dt \right\|^2 \le C \left\{ \tau^{\frac{4\alpha}{1+\alpha}} + h^{1+\alpha} + \sum_{n=1}^{N} \frac{1}{\tau} \left\| \int_{t_{n-1}}^{t_n} \mathbf{Q}-\mathbf{Q}_h^n\,dt \right\|^2 + \tau \|\Theta(\psi(t_n))-\Theta(\psi_h^n)\|^2 + \int_{t_{n-1}}^{t_n} \|\Theta(\psi)-\Theta(\psi_h^n)\|^2\,dt \right\}. \tag{3.18}$$

Theorem 3.2.2 *Assuming (P5-A1)–(P5-A5) there holds*

$$\sum_{n=1}^{N} \|c_h^n - c_h^{n,reg}\|^2 + \sum_{n=1}^{N} \langle \phi_\epsilon(c_h^n)-\phi_\epsilon(c_h^{n,reg}), c_h^n - c_h^{n,reg}\rangle + \tau \sum_{n=1}^{N} \|\mathbf{q}_h^n - \mathbf{q}_h^{n,reg}\|^2 \le C\epsilon^{1+\alpha}\tau^p\epsilon^q h^l. \tag{3.19}$$

Theorem 3.2.3 *Assuming (P5-A1)–(P5-A5) there holds*

$$\|c_h^{n,i} - c_h^{n,reg}\|^2 + \langle \phi_\epsilon'(c_h^{n,i-1})(c_h^{n,i} - c_h^{n,reg}), c_h^{n,i} - c_h^{n,reg}\rangle + \tau \|\mathbf{q}_h^{n,i} - \mathbf{q}_h^{n,reg}\|^2 \le C(\tau + L_{\phi_\epsilon'}^2) h^{-d} \|c_h^{n,i-1} - c_h^{n,reg}\|^4. \tag{3.20}$$

The quadratically convergence is ensured if we have (P5-A1)-(P5-A6) and

$$C\tau^{1+p}\epsilon^{3\alpha+q-3}h^{l-d} < 1. \tag{3.21}$$

In other words, if either $1+p>0$, or $3\alpha+q>3$, or $l>d$, one can correlate the discretization parameters to ensure the quadratic convergence of the Newton scheme, as well as the convergence of the regularization scheme. The sufficient condition (3.21) can be used to tune *a priori* the discretization parameters in order to ensure the proper convergence of the scheme. The paper [P5] is concluded by relevant numerical experiments.

3.3 Convergence analysis for a MFEM scheme with Newton iterations for transport with non-equilibrium sorption: [P6]

In paper [P6] we consider one component reactive transport with non-equilibrium sorption in saturated porous media. The paper [P6] extends the work done in [P5], where equilibrium sorption was considered. The mathematically model is given by:

$$\Theta_S\partial_t c + \rho_b\partial_t s - \nabla\cdot(D\Theta_S\nabla c - c\mathbf{Q}) = \Theta_S r(c) \quad \text{in} \quad (0,\mathrm{T})\times\Omega, \tag{3.22}$$

$$\partial_t s = k_s(\phi(c)-s) \quad \text{in} \quad (0,\mathrm{T})\times\Omega \tag{3.23}$$

The notations are the one introduced in the beginning of this chapter. The sorption isotherm is again of Freundlich type, see (3.9). A regularization step is needed in order to apply the Newton method. In paper [P6] we analyze the discretization and the linearization method together. We derive a sufficient condition on the discretisation parameters (time step size τ, mesh diameter h and regularization parameter ϵ) for the convergence of both methods, including the quadratic convergence of the Newton method.

We begin by stating the fully discrete mixed variational formulation for (3.22) – (3.23):

Fully discrete scheme. Let $n\in\{1,\dots,N\}$ and $(c_h^{n-1},s_h^{n-1})\in W_h\times V_h$ be given. Find $(c_h^n,\mathbf{q}_h^n,s_h^n)\in W_h\times V_h\times W_h$ so that for all $t\in(0,T]$ we have

$$\langle c_h^n - c_h^{n-1}, w_h\rangle + \rho_b\langle s_h^n - s_h^{n-1}, w_h\rangle + \tau\langle\nabla\cdot\mathbf{q}_h^n, w_h\rangle = \tau\langle r(c_h^n), w_h\rangle \tag{3.24}$$

$$\langle\mathbf{q}_h^n,\mathbf{v}_h\rangle - \langle c_h^n,\nabla\cdot\mathbf{v}_h\rangle - \langle c_h^n\mathbf{Q}_h,\mathbf{v}_h\rangle = 0 \tag{3.25}$$

$$\langle s_h^n - s_h^{n-1}, w_h\rangle = \tau k_s(\langle\phi_\epsilon(c_h^n),w_h\rangle - \langle s_h^n, w_h\rangle), \tag{3.26}$$

for all $w_h\in W_h$ and $\mathbf{v}_h\in V_h$. We take at time $t=0$: $c_h^0 = P_h c_I$ and $s_h^0 = P_h s_I$.

To solve the nonlinear system (3.24) –(3.26) we use the Newton method, which is locally quadratic convergent:

Newton iterations. Let $n \in \{1, \dots, N\}$ 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 $(c_h^{n,i}, \mathbf{q}_h^{n,i}, s_h^{n,i}) \in W_h \times V_h \times W_h$ such that

$$\begin{aligned} \langle c_h^{n,i} - c_h^{n-1}, w_h \rangle + \rho_b \langle s_h^{n,i} - s_h^{n-1}, w_h \rangle + \tau \langle \nabla \cdot \mathbf{q}_h^{n,i}, w_h \rangle \\ = \tau \langle r(c_h^{n,i-1}) + r'(c_h^{n,i-1})(c_h^{n,i} - c_h^{n,i-1}), w_h \rangle \end{aligned} \tag{3.27}$$

for all $w_h \in W_h$,

$$\langle \mathbf{q}_h^{n,i}, \mathbf{v}_h \rangle - \langle c_h^{n,i}, \nabla \cdot \mathbf{v}_h \rangle - \langle c_h^{n,i} \mathbf{Q}_h, \mathbf{v}_h \rangle = 0 \tag{3.28}$$

for all $\mathbf{v}_h \in V_h$ and

$$\langle s_h^{n,i} - s_h^{n-1}, w_h \rangle = \tau k_s (\langle \phi_\epsilon(c_h^{n,i-1}) + \phi_\epsilon'(c_h^{n,i-1})(c_h^{n,i} - c_h^{n,i-1}), w_h \rangle - \langle s_h^{n,i}, w_h \rangle), \tag{3.29}$$

for all $w_h \in W_h$.

To fix the notations: $n \in \{1, \dots, N\}$ always indexes the time step, while i is used to index the iteration. Accordingly, $\{c_h^n, \mathbf{q_h^n}, s_h^n\}$ denotes the solution of (3.24)–(3.26) at the n^{th} time step and $\{c_h^{n,i}, \mathbf{q}_h^{n,i}, s_h^{n,i}\}$ 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

$$\|c^n - c_h^n\| + \|\mathbf{q}^n - \mathbf{q}_h^n\| + \|s^n - s_h^n\| \overset{\epsilon,\tau,h \to 0}{\to} 0, \tag{3.30}$$

and

$$\|c_h^n - c_h^{n,i}\| + \|\mathbf{q}_h^n - \mathbf{q}_h^{n,i}\| + \|s_h^n - s_h^{n,i}\| \overset{i \to \infty}{\to} 0 \tag{3.31}$$

quadratically. This will be achieved for a sufficiently small time step τ. A sufficient condition on the discretization parameters ϵ, τ, h is derived to ensure both convergences stated above.

Assumptions. The frame of paper [P5] is given by the following assumptions.

(P6-A1) The rate function $r : \mathbb{R} \to \mathbb{R}$ is differentiable with $r'(\cdot)$ bounded and Lipschitz-continuous. Furthermore, $r(c) = 0$ for all $c \leq 0$.

(P6-A2) The initial c_I, s_I are essentially bounded and positive.

(P6-A3) The water flux and its numerical approximation are essentially bounded, $\mathbf{Q}, \mathbf{Q}_h \in L^\infty(\Omega)$.

(P6-A4) The sorption isotherm $\phi(\cdot)$ is non-decreasing, non-negative 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 $c \leq 0$.

(P6-A5) For the solution of continuous problem (see [P6], p. 434) we have $c \in L^\infty((0,T)\times\Omega)$, while $\partial_t c$ and $\partial_t s$ are Hölder continuous in t with exponent $\alpha/2$ and α respectively. Furthermore, there holds

$$\sum_{n=1}^{N} \tau \|\mathbf{q}(t_n)\|^2 \le C. \tag{3.32}$$

Remark 3.3.1 *The regularity assumed in (P6-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 [45] Chapter II.4, if the initial and boundary data are compatible and sufficiently smooth we have $c \in C^{2+\alpha,1+\alpha/2}(\Omega\times(0,T))$ and $s \in C^{\alpha,1+\alpha}(\Omega\times(0,T))$. Furthermore, Proposition 1 in [P6], p. 437 justifies (3.32) in the one dimensional case, when $H(\mathrm{div};\Omega) = H^1(\Omega)$. 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 non-realistic - the rates r and ϕ are extended by 0 in the negative part.*

The main results of [P6] are given in the theorems below.

Theorem 3.3.1 *Assuming (P6-A1) – (P6-A5), we have*

$$\begin{aligned}\|P_h c(t_N) - c_h^N\|^2 + \sum_{n=1}^{N} \tau \|\phi(c(t_n)) - \phi(c_h^n)\|^{\frac{1+\alpha}{\alpha}}_{L^{\frac{1+\alpha}{\alpha}}(\Omega)} + \sum_{n=1}^{N} \tau \|P_h c(t_n) - c_h^n\|^2 \\ + \sum_{n=1}^{N} \tau \|\mathbf{q}(t_n) - \mathbf{q}_h^n\|^2 \le C(h^{1+\alpha} + \tau^\alpha + \epsilon^{1+\alpha}).\end{aligned} \tag{3.33}$$

and

$$\begin{aligned}\|P_h s(t_N) - s_h^N\|^2 + \sum_{n=1}^{N} \tau \|P_h s(t_n) - s_h^n\|^2 \le \\ C(\tau^{\frac{2\alpha r}{1-\alpha}} + \tau^{-r}(h^{1+\alpha} + \tau^\alpha + \epsilon^{1+\alpha})).\end{aligned} \tag{3.34}$$

for any $r \in \mathbb{R}$.

Remark 3.3.2 *In Theorem 3.3.1 we show that the numerical solution converges to the continuous solution if the nonlinear system (3.24)–(3.26) is solved exactly. This guarantees that the numerical scheme provides a good approximation of the solution if the mesh size, as well as the time step and the regularization parameter are small enough, while the nonlinear system is solved exactly.*

Remark 3.3.3 *If the sorption $\phi(\cdot)$ and its derivative are Lipschitz-continuous (thus*

$\alpha = 1$), a slightly modified proof leads to optimal error estimates

$$\begin{aligned}\|P_h c(t_N) - c_h^N\|^2 + \sum_{n=1}^{N} \tau \|\phi(c(t_n)) - \phi(c_h^n)\|^2 + \sum_{n=1}^{N} \tau \|P_h c(t_n) - c_h^n\|^2 \\ + \sum_{n=1}^{N} \tau \|\mathbf{q}(t_n) - \mathbf{q}_h^n\|^2 \leq C(h^2 + \tau^2).\end{aligned} \tag{3.35}$$

Remark 3.3.4 *Similar results can be obtained in the strictly unsaturated flow regime, or for a steady unsaturated flow, where Θ is time independent (as assumed for example in [12, 25]).*

The next theorem shows the local quadratic convergence of the Newton method as given in (3.27) – (3.29).

Theorem 3.3.2 *Assuming (P6-A1) – (P6-A4), for sufficiently small τ we have*

$$\|c_h^n - c_h^{n,i}\|^2 + \tau \|\mathbf{q}_h^n - \mathbf{q}^{n,i}\|^2 \leq C\tau^2 (L_{r'}^2 + L_{\phi_\epsilon'}^2) h^{-d} \|c_h^n - c_h^{n,i-1}\|^4 \tag{3.36}$$

and

$$\|s_h^n - s_h^{n,i}\|^2 \leq C\tau^2 (L_{\phi_\epsilon'}^2 + \tau^2 L_{\phi_\epsilon}^2 (L_{r'}^2 + L_{\phi_\epsilon'}^2)) h^{-d} \|c_h^n - c_h^{n,i-1}\|^4. \tag{3.37}$$

$L_{r'}$ and $L_{\phi_\epsilon'}$ are denoting the Lipschitz constants for the functions $r'(\cdot)$ and $\phi_\epsilon'(\cdot)$, respectively. We derive a sufficient condition, guaranteeing the convergence of the scheme, see (3.39) below. This means that by a suitable choice of the time step (depending on the mesh size and regularization parameter) one ensures the quadratic convergence of the Newton method and the convergence of the approximation solution to the continuous one. On the other hand, it is easy to find parameters violating this condition, for which the Newton scheme diverges. From (3.36) we have that the quadratic convergence of the Newton scheme is ensured by

$$C\tau^2 \epsilon^{2\alpha - 4} h^{-d} \|c_h^n - c_h^{n-1}\|^2 \leq 1. \tag{3.38}$$

With the stability estimate

$$\sum_{n=1}^{N} \|c_h^n - c_h^{n-1}\|^2 \leq C \frac{\tau}{\epsilon^{2(1-\alpha)}}$$

proved in Proposition 2 in [P6], p. 439 this condition becomes

$$C\tau^3 \epsilon^{4\alpha - 6} h^{-d} \leq 1. \tag{3.39}$$

Using (3.39) and Theorem 3.3.1, 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 [P6]. Referring to [3], where the Newton-error is controlled adaptively with respect to the total error, condition (3.39) can provide useful information for the initial tuning of the discretization parameters for adaptive methods.

Remark 3.3.5 *The condition (3.39) is derived under pessimistic conditions. In this sense we mention the stability estimates in Theorem 3.3.2, bounding to the sum* $\sum_{n=1}^{N} \|c_h^n - c_h^{n-1}\|^2$. *We used to obtain (3.39) the bound for the whole sum for bounding just one term* $\|c_h^n - c_h^{n-1}\|^2$, *which means a clear room for improvements. In case all the terms have similar orders, this would provide* $\|c_h^n - c_h^{n-1}\|^2 \leq C(\tau^2\epsilon^{2\alpha-2})$, *implying*

$$C\tau^4\epsilon^{4\alpha-6}h^{-d} \leq 1. \tag{3.40}$$

In the performed numerical calculations, (3.40) was always enough for quadratic convergence.

The paper [P6] is concluded by numerical experiments showing the quadratic convergence of the Newton method.

3.4 A new MHFEM for convection-diffusion problems and a study on the numerical diffusion for different schemes for transport problems: [P7]

While the papers [P1]-[P6] have all focused on convergence proofs for the different numerical schemes considered, the paper [P7] is devoted to quantifying the numerical diffusion for an one component transport problem and various discretization schemes. Numerical diffusion is a very important artifact that may lead to erroneous solutions and therefore to false prognoses [15, 51, 52, 59]. Although this is well recognized, it does not exist any systematical study to quantify the numerical diffusion for the most used discretization schemes. We propose in [P7] a systematic comparative study of the numerical diffusivity of various numerical schemes, including higher order in space and time, upwind schemes, finite element, finite volume and mixed finite elements. The method we use to quantify the numerical diffusion for discretization schemes for the transport equation is very simple to implement and therefore very attractive from a practical view. The results obtained can be used by researchers as a reference (benchmark) to test their numerical schemes or stabilization techniques.

The second objective of [P7] is to present a new MHFEM method, and an upwind variant of it, which are more robust for convection-dominated problems. Although for Galerkin finite elements many stabilization methods are proposed and analyzed in the literature, see e.g. the overview paper [48], there is not much done in the field of MHFEM. We shortly describe below the new method (for more details we refer to [P7] and [71]). The results regarding numerical diffusion are presented afterwards.

We consider again a MFEM - Euler implicit discretization of an one component transport problem without sorption or reaction:

Fully discrete MFEM scheme. For $n = 1, \ldots, N$ let $\Theta_h^n, \Theta_h^{n-1}, \mathbf{Q_h^n}, c_h^{n-1}$ be given and find $(c_h^n, \mathbf{q_h^n}) \in W_h \times V_h$ such that there holds

$$\langle \Theta_h^n c_h^n - \Theta_h^{n-1} c_h^{n-1}, w_h \rangle + \tau \langle \nabla \cdot \mathbf{q_h^n}, w_h \rangle = 0, \tag{3.41}$$

$$\langle \mathbf{D}^{-1} \mathbf{q_h^n}, \mathbf{v}_h \rangle - \langle \mathbf{D}^{-1} \mathbf{Q_h^n}\, c_h^n, \mathbf{v}_h \rangle - \langle c_h^n, \nabla \cdot \mathbf{v}_h \rangle = 0, \tag{3.42}$$

for all $w_h \in W_h$ and $\mathbf{v_h} \in V_h$. The water content Θ_h^n and water flux $\mathbf{Q_h^n}$ above are obtained by using also a MFEM scheme (2.15)–(2.16).

Unfortunately, the MFEM formulation (3.41)–(3.42) leads to a linear system of equations with an indefinite matrix such that standard iterative solvers cannot be applied. To overcome this difficulty, one often uses a hybridization technique (see [18]). Its basic idea is to relax firstly the continuity constraint of the normal components of the fluxes over inter-element faces that is implied by $\mathbf{v} \in H(\mathrm{div}; \Omega)$. The continuity constraint is then ensured by means of an additional variational equation involving Lagrange multipliers. Precisely, the space V_h is replaced by

$$\tilde{V}_h := \{\mathbf{q} \in L^2(\Omega) | \mathbf{q}_{|T}(\mathbf{x}) = \mathbf{a} + b\mathbf{x}, \mathbf{a} \in \mathbb{R}^d, b \in \mathbb{R} \ \text{ for all } T \in \mathcal{T}_h\}.$$

We consider below only the 2D case, i. e. $d = 2$, but the extension to 3D is straightforward. The discrete space for the Lagrange multiplier is defined by

$$\Lambda_{h,0} = \{\lambda \in L^2(\mathcal{E}_h) \mid \lambda_{|E} = \text{constant on E } \forall \mathrm{E} \in \mathcal{E}_\mathrm{h} \text{ and } \lambda_{|\mathrm{E}} = 0 \ \forall \mathrm{E} \in \partial\Omega\}.$$

We denoted above by $\mathcal{E}_h$ the set of edges of the triangulation $\mathcal{T}_h$. The fully discrete mixed hybrid variational formulation of the overall system (3.41)–(3.42) then reads as follows:

Fully discrete MHFEM scheme. For $n = 1, \ldots, N$ let $\Theta_h^n, \Theta_h^{n-1}, \mathbf{Q_h^n}, c_h^{n-1}$ be given and find $(c_h^n, \lambda_h^n, \mathbf{q_h^n}) \in W_h \times \Lambda_{h,0} \times \tilde{V}_h$ such that there holds

$$\langle \Theta_h^n c_h^n - \Theta_h^{n-1} c_h^{n-1}, w_h \rangle + \tau \langle \nabla \cdot \mathbf{q_h^n}, w_h \rangle = 0, \tag{3.43}$$

$$\langle \mathbf{D}^{-1} \mathbf{q_h^n}, \mathbf{v}_h \rangle - \langle c_h^n, \nabla \cdot \mathbf{v}_h \rangle + \sum_{T \in \mathcal{T}_h} \langle \lambda_h^n, \mathbf{v}_h \cdot \mathbf{n} \rangle_{\partial T} = \langle \mathbf{D}^{-1} \mathbf{Q_h^n}\, c_h^n, \mathbf{v}_h \rangle, \tag{3.44}$$

$$\sum_{T \in \mathcal{T}_h} \langle \mu_h, \mathbf{q_h^n} \cdot \mathbf{n} \rangle_{\partial T} = 0 \tag{3.45}$$

for all $w_h \in W_h$, $\mathbf{v}_h \in \tilde{V}_h$, $\mu_h \in \Lambda_{h,0}$.

Let now Θ_T^n and c_T^n denote the water content and concentration, respectively, on the element (triangle in our case) T, $\{q_{TE}^n\}_{E \subset T}$, $\{Q_{TE}^n\}_{E \subset T}$ the components of the flux of contaminant and water, respectively, in the local Raviart-Thomas space basis $\{\mathbf{w}_{TE}\}_{E \subset T}(\mathbf{x}) = \frac{\mathbf{x} - \mathbf{x}_E}{d\,|T|}$ (cf. [18]), $B_{TEE'} := \displaystyle\int_T (\mathbf{D^{-1}} \mathbf{w}_{TE'}) \cdot \mathbf{w}_{TE}\, d\mathbf{x}$, and λ_E^n be the constant Lagrange multiplier on the edge E. We denote by $|T| := \int_T d\mathbf{x}$ the area

(volume) of element T and by $\mathbf{x}_E$ the corner of T which is not on E. We obtain from (3.43)–(3.45) the following system of nonlinear equations:

Mass conservation equation:

$$\Theta_T^n c_T^n - \Theta_T^{n-1} c_T^{n-1} + \frac{\tau}{|T|} \sum_{E \subset T} q_{TE}^n = 0 \qquad \forall\, T \in \mathcal{T}_h\,. \tag{3.46}$$

Equation for the flux:

$$\sum_{E' \subset T} B_{TEE'} q_{TE'}^n = \sum_{E' \subset T} B_{TEE'} Q_{TE'}^n c_T^n + c_T^n - \lambda_E^n \qquad \forall\, T \in \mathcal{T}_h, E \subset T\,. \tag{3.47}$$

Continuity of the flux over edges:

$$\sum_{T \supset E} q_{TE}^n = 0 \quad \forall\, E \in \mathcal{E}_h^I\,. \tag{3.48}$$

The system of equations (3.46)–(3.48) gives the **classical MHFEM scheme** for solute transport in porous media. A **new MHFEM scheme** is obtained by using the Lagrange multipliers, instead of the piecewise constant concentrations, for discretizing the convective term in (3.4). This approach is based on the observation that the Lagrange multipliers furnish a second order approximation of the concentration [15, 18]. Moreover, in the linear case, the Lagrange multiplier on edge E between two triangles T and T' is approximately the average between c_T and $c_{T'}$. The idea is now to discretize the convection term by multiplying the component of the water flux over edge E, i.e. Q_{TE} by λ_E instead c_T, which seems to be more naturally. The same idea was similarly used in [91]. Instead of (3.47), this yields

$$\sum_{E' \subset T} B_{TEE'} q_{TE'}^n = \sum_{E' \subset T} B_{TEE'} Q_{TE'}^n \lambda_{E'}^n + c_T^n - \lambda_E^n \qquad \forall\, T \in \mathcal{T}_h, E \subset T. \tag{3.49}$$

The equations (3.46) and (3.48) remain unchanged. The **new MHFEM scheme** (referred to as MHFEM 1 from now on) is given by (3.46), (3.48) and (3.49). Numerical results show that the MHFEM 1 scheme is much more robust for convection-dominated problems and has the same convergence properties as the classical scheme.

We also propose a **full upwind MHFEM scheme** (referred to as MHFEM 2 from now on) given by (3.46), (3.48) and

$$\sum_{E' \subset T} B_{TEE'} q_{TE'}^n = \sum_{E' \subset T} B_{TEE'} Q_{TE'}^n \alpha_{E'} + c_T^n - \lambda_E^n \qquad \forall\, T \in \mathcal{T}_h, E \subset T. \tag{3.50}$$

with

$$\alpha_E = \begin{cases} c_T^n, & if\ Q_{TE}^n \geq 0 \\ 2\lambda_E^n - c_T^n, & \text{otherwise} \end{cases}\,.$$

The idea is the following: Q_{TE} is the normal component of the flux (velocity) over the edge E between two elements (triangles) T and T', as one looks from the center of T. If this component is positive, we take $\alpha_E = c_T$ the (local) concentration on T, if not we take $\alpha_E = 2\lambda_E - c_T \approx c_{T'}$ the concentration on T'. This is the reason we call it an *upwind scheme*. The MHFEM 2 scheme is suitable for highly convection-dominated problems. We also refer to [19] where our MHFEM 2 scheme was tested for multicomponent reactive transport, example from [15, 59]. The problem there is highly convection-dominated. It was found that the new scheme has less numerical diffusion as a stabilized linear FVM scheme or the SUPG stabilized scheme for linear Galerkin finite elements, see [P7].

Remark 3.4.1 *The convergence of the new schemes was analyzed in [21]. We have shown that the schemes have the same convergence order like the classical scheme. The proof is based on techniques from [29, 30].*

Remark 3.4.2 *We applied the same idea of using the Lagrange multipliers when discretizing the convection term also for the BDM$_1$ (Brezzi-Douglas-Marini lowest order elements) and also for nonlinear problems in [20, 14]. We again remarked that the new scheme is more robust as the classical one. Moreover, the new scheme for BDM$_1$ has now an optimal order of convergence, which is not the case for the classical BDM$_1$ scheme (see [28]).*

As previously mentioned, the main aim of [P7] is to quantify the numerical diffusion of different discretization methods: FEM, FVM and MHFEM when they are applied to advective-diffusive transport of a solute in porous media. We start with linear and quadratic Galerking finite elements with or without upwinding. As next, FVM, including higher order ones are involved. We then consider local mass conservative MHFEM schemes, based on RT$_0$. For the temporal discretization we consider two implicit schemes: backward Euler and BDF(2) (second order backward differentiation formula). As mentioned before, a systematic comparative study of the numerical diffusivity of these methods was missing in the literature at that time. We formulate two tests:

- A problem with an analytical solution: a two-dimensional Gauss bell. We vary the Péclet number (by changing the magnitude of water velocity and/or the diameter of the mesh) to see its influence on numerical diffusion.
- A realistic solute transport problem in a heterogeneous soil. The hydraulic conductivity is stochastically generated (log-normal distributed). The water flux is obtained by solving the flow equation.

We quantify the artificial diffusion by numerically computing the slope of the central second spatial moment of the solute concentration. In the first example we deal

with a deterministic problem and it can be elementarily shown, that, for a big-enough domain, the half-slope of the second moment gives exactly the diffusion coefficient. For the second example, where we conduct stochastic simulations, the ensemble dispersion coefficients are estimated by the half-slope of the second moments of the ensemble mean concentration (see e.g. [41, 9, 85]). The ensemble dispersion coefficients can be derived theoretically by homogenization methods or by stochastic upscaling (see e.g. [10, 9, 85, 84]). For the purposes of this study, we also estimated the ensemble dispersion coefficients through numerical simulations with the Global Random Walk (GRW) algorithm, a superposition of Particle Tracking procedures, free of numerical diffusion, which yields highly accurate results by managing very large numbers of particles [90, 82, 83]. The deviation from such reference estimates of the numerically computed half-slope of the second moment of the mean concentration is then used to characterize the numerical diffusion of the methods evaluated, see [P7] for details.

The conclusions of our tests in [P7] are summarized below.

- The numerical diffusion increases with the Péclet number for all discretization schemes under consideration. When dealing with a convection-dominated-problem one has two possibilities to obtain accurate solutions: (1) to decrease the size of the discretization parameters (time step and mesh diameter) till the numerical oscillations disappear or (2) apply certain stabilization techniques. The first method can be very time costly; the second one may have too much numerical diffusion. The compromise normally is to find a balance of the two methods.

- The local Péclet number is not always (or not alone) relevant for estimating numerical diffusion. The results show that for the same local Péclet number but on different meshes and different convective fluxes the schemes are also showing different numerical diffusion (for the same type of problem).

- Higher order FVM schemes in space show just a bit lower numerical diffusion for homogeneous problems, whereas the quadratic FEM produces almost the same results like the linear FEM. The higher order method in time, i.e. BDF(2) was clearly improving the backward Euler method for both FEM and FVM. The cost for better accuracy is a larger computational expense. For more realistic problems (i.e. heterogeneity in parameter distribution) the differences between lower and higher order schemes are negligible but the computational cost are much higher for higher order schemes.

3.5 Fully coupled flow and transport: [P8]

As mentioned before, there is a rich literature on numerical methods for flow [8, 68, 70, 81, 92, 42, 34, 35, 58, 62, 93, 5, 6] and reactive solute transport in porous media

[7, 11, 12, 15, 31, 2, 35, 36, 39, 38, 54, 71, 72, 73, 79], but none of them is considering the fully coupled situation (when the flow is affected by the transport). Moreover, the analysis of the schemes for transport in porous media considers mostly a saturated flow regime and the water flux to be given analytically, e.g. [11, 12]. A MFEM based discretization for flow and transport in variably saturated porous media is analyzed in [P4] by taking explicitly into account the low regularity of the solution of Richards' equation.

The paper [P8] is considering fully coupled flow and reactive transport. The reactive transport is influencing now the flow by two means: on the one hand water is produced by the reaction and therefore the mass balance equation is changed and on the other hand the porosity of the porous medium is varaiable because of dissolution and precipitation processes. The changes in porosity affect also the permeability of the medium, and we may even have pore clogging.

Concrete carbonation is one of the most important processes limiting the service life of reinforced concrete. Due to carbonation, the pH of reinforced concrete drops below the passivization threshold of steel and this affects the strength of the concrete structure, with possible dramatic consequences. As common applications of reinforced concrete we mention buildings, bridges or dams (among many others). The process of concrete carbonation is given by

$$\tilde{\mathrm{A}}(\mathrm{g} \to \mathrm{aq}) + \tilde{\mathrm{B}}(\mathrm{s} \to \mathrm{aq}) \to \tilde{\mathrm{C}}(\mathrm{aq} \to \mathrm{s}) + \mathrm{H_2O}, \tag{3.51}$$

where $\tilde{\mathrm{A}}$, $\tilde{\mathrm{B}}$, and $\tilde{\mathrm{C}}$ are $\mathrm{CO_2}$, $\mathrm{Ca(OH)_2}$, and respectively, $\mathrm{CaCO_3}$. The equation (3.51) summarizes the following: gaseous CO_2 penetrates a non-saturated porous medium via the air phase of its pore space and quickly dissolves in the pore water where CO_2 reacts very fast with calcium hydroxide $Ca(OH)_2$. Then $Ca(OH)_2$ becomes available from the solid matrix by a dissolution mechanism. The reaction produces calcium carbonate $CaCO_3$ which precipitates to the porous matrix.

By considering Henry-type transfer at air-liquid interface, we derive the following mathematical model.

$$\begin{aligned}
(\phi\phi_w)_t + \nabla\cdot\mathbf{q} &= \frac{\phi\phi_w}{\rho} rAB, && (3.52)\\
\mathbf{q} &= -K_S\phi k(\phi_w)\nabla(p+z), && (3.53)\\
(\phi\phi_w A)_t + \nabla\cdot(-D_A\phi\phi_w\nabla A + \mathbf{q}A) &= -P(H\phi\phi_w A - \phi\phi_g a) - r\phi\phi_w m_A AB, && (3.54)\\
(\phi\phi_g a)_t + \nabla\cdot(-D_a\phi\phi_g\nabla a) &= P(H\phi\phi_w A - \phi\phi_g a), && (3.55)\\
(\phi\phi_w B)_t + \nabla\cdot(-D_B\phi\phi_w\nabla B + \mathbf{q}B) &= f_{\mathrm{Diss}}\phi\phi_w - r\phi\phi_w m_B AB, && (3.56)\\
(\phi_s b)_t &= -f_{\mathrm{Diss}}\phi_s, && (3.57)\\
(\phi\phi_w C)_t + \nabla\cdot(-D_C\phi\phi_w\nabla C + \mathbf{q}C) &= -f_{\mathrm{Prec}}\phi\phi_w + r\phi\phi_w m_C AB, && (3.58)\\
(\phi_s c)_t &= f_{\mathrm{Prec}}\phi_s, && (3.59)\\
\phi_t &= s(\phi-\delta)\frac{1-\phi}{Z_\phi+(1-\phi)}(\phi_w f_{\mathrm{Diss}} - \phi_w f_{\mathrm{Prec}}), && (3.60)
\end{aligned}$$

where a, A, b, B, c, and C the molar concentrations of the species $\tilde{\mathrm{A}}(\mathrm{g})$, $\tilde{\mathrm{A}}(\mathrm{aq})$, $\tilde{\mathrm{B}}(\mathrm{s})$, $\tilde{\mathrm{B}}(\mathrm{aq})$, $\tilde{\mathrm{C}}(\mathrm{s})$, and $\tilde{\mathrm{C}}(\mathrm{aq})$, ρ is the density of water, $\delta > 0$ and $Z_\phi > 0$ are two regularization parameters and $f_{\mathrm{Diss}} = S_{\mathrm{Diss}}(B_{eq} - B)$ and $f_{\mathrm{Prec}} = S_{\mathrm{Prec}}(C - C_{eq})$. Further, ϕ is the porosity, ϕ_w, ϕ_s, ϕ_g the volume fractions of water, solid and gas, respectively, K_S the saturated hydraulic conductivity, D_X the diffusion coefficient of the species X, m_X the molar mass of the species X, P is a mass-transfer coefficient, which is in most cases unknown and needs to be identified for instance via a homogenization approach, and H is the Henry constant. The water fraction $\phi_w(\cdot)$ and hydraulic conductivity $k(\cdot)$ are given in terms of the van Genuchten-Mualem parametrization [89, 56]. Initial and boundary conditions complete the model. We point out also that the hydraulic conductivity depends on porosity, so pore clogging will induce a zero conductivity. In this case the flow equation degenerates. In [P8] we assumed that the hydraulic conductivity depends linearly on porosity.

The model (3.52) – (3.60) can be further simplified by assuming that the mass transfer across liquid-air interfaces is very fast, i.e. $P \to \infty$ enforcing that

$$H\phi_w A \approx \phi_g a. \tag{3.61}$$

By this (3.55) decouples from the rest of the system and can be therefore ignored in what follows. We remark that also the equations (3.57) and (3.59) are decoupled from the rest of the system and will be not considered in the next. Consequently, we solve the equations for the water flow (3.52)-(3.53), for A, B and C (3.54), (3.56) and (3.58) and for the porosity (3.60). We discretize the resulting system of equations by using again the MFEM, RT_0 in space and a semi-implicit Euler scheme in time. The following discrete schemes was obtained:

Fully discrete scheme. Let $n \in \{1, \dots, N\}$, and $p_h^{n-1}, A_h^{n-1}, B_h^{n-1}, C_h^{n-1}, \phi_h^{n-1}$ be given. Find $p_h^n, A_h^n, B_h^n, C_h^n, \phi_h^n \in W_h$ and $\mathbf{q}_h^n, \mathbf{q}_{A_h}^n, \mathbf{q}_{B_h}^n, \mathbf{q}_{C_h}^n \in V_h$ such that for all $w_h \in W_h$ and $\mathbf{v}_h \in V_h$ there holds

$$\langle \phi_h^n {\phi_w}_h^n - \phi_h^{n-1} {\phi_w}_h^{n-1}, w_h\rangle + \tau\langle \nabla\cdot \mathbf{q}_h^n, w_h\rangle = \tau\langle \frac{r}{\rho}\phi_h^{n-1}{\phi_w}_h^{n-1} A_h^{n-1} B_h^{n-1}, w_h\rangle, \tag{3.62}$$

$$\langle K^{-1}(\phi_h^n {\phi_w}_h^n)\mathbf{q}_h^n, \mathbf{v}_h\rangle - \langle p_h^n, \nabla\cdot\mathbf{v}_h\rangle + \langle \nabla z, \mathbf{v}_h\rangle = 0, \tag{3.63}$$

and

$$\langle \phi_h^n {\phi_w}_h^n A_h^n - \phi_h^{n-1}{\phi_w}_h^{n-1} A_h^{n-1}, w_h\rangle + \tau\langle \nabla\cdot \mathbf{q}_{A_h}^n, w_h\rangle = \tau\langle -m_A r \phi_h^n {\phi_w}_h^n A_h^n B_h^n, w_h\rangle, \tag{3.64}$$

$$\langle \frac{1}{D_A \phi_h^n {\phi_w}_h^n}\mathbf{q}_{A_h}^n, \mathbf{v}_h\rangle - \langle A_h^n, \nabla\cdot\mathbf{v}_h\rangle - \langle A_h^n \mathbf{q}_h^n, \mathbf{v}_h\rangle = 0, \tag{3.65}$$

$$\begin{aligned}\langle\phi_h^n{\phi_{w_h}}^n B_h^n - \phi_h^{n-1}{\phi_{w_h}}^{n-1}B_h^{n-1}, w_h\rangle + \tau\langle\nabla\cdot\mathbf{q}_{B_h}^n, w_h\rangle &= -\tau\langle m_B r\phi_h^n{\phi_{w_h}}^n A_h^n B_h^n, w_h\rangle \\ &\quad +\tau\langle\phi_h^n{\phi_{w_h}}^n {f_{\mathrm{Diss}}}_h^n, w_h\rangle, \quad (3.66)\end{aligned}$$

$$\langle\frac{1}{D_B\phi_h^n{\phi_{w_h}}^n}\mathbf{q}_{B_h}^n, \mathbf{v}_h\rangle - \langle B_h^n, \nabla\cdot\mathbf{v}_h\rangle - \langle B_h^n\mathbf{q}_h^n, \mathbf{v}_h\rangle = 0, \quad (3.67)$$

$$\begin{aligned}\langle\phi_h^n{\phi_{w_h}}^n C_h^n - \phi_h^{n-1}{\phi_{w_h}}^{n-1}C_h^{n-1}, w_h\rangle + \tau\langle\nabla\cdot\mathbf{q}_{C_h}^n, w_h\rangle &= \tau\langle m_C r\phi_h^n{\phi_{w_h}}^n A_h^n B_h^n, w_h\rangle \\ &\quad -\tau\langle\phi_h^n{\phi_{w_h}}^n {f_{\mathrm{Prec}}}_h^n, w_h\rangle \quad (3.68)\end{aligned}$$

$$\langle\frac{1}{D_C\phi_h^n{\phi_{w_h}}^n}\mathbf{q}_{C_h}^n, \mathbf{v}_h\rangle - \langle C_h^n, \nabla\cdot\mathbf{v}_h\rangle - \langle C_h^n\mathbf{q}_h^n, \mathbf{v}_h\rangle = 0, \quad (3.69)$$

and

$$\langle\phi_h^n - \phi_h^{n-1}, w_h\rangle = \tau s\langle\frac{(\phi_h^{n-1}-\delta)(1-\phi_h^{n-1})}{Z_\phi + (1-\phi_h^{n-1})}({\phi_{w_h}}^{n-1}{f_{\mathrm{Diss}}}_h^{n-1} - {\phi_{w_h}}^{n-1}{f_{\mathrm{Prec}}}_h^{n-1}), w_h\rangle, \quad (3.70)$$

where ${\phi_{w_h}}^k := \phi_w(p_h^k)$, ${f_{\mathrm{Diss}}}_h^k = S_{\mathrm{Diss}}(B_{eq} - B_h^k)$ and ${f_{\mathrm{Prec}}}_h^k = S_{Prec}(C_h^k - C_{eq})$, $k = 0, \ldots, N$.

Initially we take $\phi_h^0 = P_h\phi_I$, p_h^0 so that the following hold true: $\phi_h^0{\phi_{w_h}}^0 = P_h(\phi_I\phi_{w,I})$ and $A_h^0 = \frac{P_h(\phi_I\phi_{w,I}A_I)}{\phi_h^0{\phi_{w_h}}^0}$, $B_h^0 = \frac{P_h(\phi_I\phi_{w,I}B_I)}{\phi_h^0{\phi_{w_h}}^0}$ and $C_h^0 = \frac{P_h(\phi_I\phi_{w,I}C_I)}{\phi_h^0{\phi_{w_h}}^0}$. The particular form of the initial data is allowed by the lower bound on $\phi\phi_w$ and was used in the proof of Theorem 3.5.1 below. The discrete scheme is implemented in the software package UG [13].

Throughout paper [P8] we make use of the following assumptions.

(P8-A1) The conductivity function $k : [0,1] \to \mathbb{R}$ is strictly increasing, positive and Lipschitz-continuous.

(P8-A2) The initial concentrations A_I, B_I, and C_I are bounded and non-negative. The initial pressure p_I is bounded.

(P8-A3) For both continuous and discrete cases there holds $1 \geq \phi\phi_w \geq \beta > 0$, and ϕ_w is Lipschitz-continuous.

(P8-A4) $\mathbf{q}, \mathbf{q}_A, \mathbf{q}_B, \mathbf{q}_C \in L^\infty(J\times Y)\cap L^2(J; H^1(Y))$ and $\partial_t p, \partial_t A, \partial_t B, \partial_t C \in L^\infty(J\times Y)$.

(P8-A5) The reaction rates are Lipschitz-continuous.

The convergence of the scheme presented in (3.62)-(3.70) can be shown for constant porosity (i.e. $s = 0$) and strictly unsaturated flow (when $\phi_w' > 0$) or fully saturated flow (when $\phi_w = \phi_{w,\max}$ everywhere). We give below the convergence result for the unsaturated case, for the saturated case as well as other details we refer to [P8].

Theorem 3.5.1 *(Strictly unsaturated flow) Let $s = 0$. Assuming (P8-A1) – (P8-A5), there holds*

$$\begin{aligned}
&\|p(T) - p_h^n\|^2 + \sum_{n=1}^{N} \tau \|\mathbf{q}^n - \mathbf{q}_h^n\|^2 + \sum_{n=1}^{N} \tau \|A^n - A_h^n\|^2 \\
&+ \sum_{n=1}^{N} \tau \|B^n - B_h^n\|^2 + \sum_{n=1}^{N} \tau \|C^n - C_h^n\|^2 + \sum_{n=1}^{N} \tau \|\mathbf{q}_A{}^n - \mathbf{q}_{A_h}^n\|^2 \\
&+ \sum_{n=1}^{N} \tau \|\mathbf{q}_B{}^n - \mathbf{q}_{B_h}^n\|^2 + \sum_{n=1}^{N} \tau \|\mathbf{q}_C{}^n - \mathbf{q}_{C_h}^n\|^2 \leq c(\tau^2 + h^2).
\end{aligned} \tag{3.71}$$

The proof of Theorem 3.5.1 is based on techniques from [6] and [72]. The results above can be extended to the case with a variable porosity at least for the non-degenerate case (no pore clogging and strictly unsaturated flow). The general, degenerate case needs further investigations.

The paper [P8] is concluded by numerical experiments: one academical example to check the convergence also numerically and one example with real case parameters. In the former we considered fully coupled nonlinear flow and transport, but a constant porosity and strictly unsaturated flow conditions. In this regime we were able to derive an analytical solution for the problem and test the convergence of the MFEM approximations. The observed order of convergence sustains the theoretical results. The latter experiment was conducted in the general case: saturated/unsaturated flow and a variable porosity. Realistic parameters have been chosen. The preliminary results have shown no significant differences between the model with and without a variable porosity. Further tests will follow.

Chapter 4

Conclusions and Outlook

We considered in this thesis flow and reactive solute transport with sorption in porous media. We concentrated on numerical methods for solving these problems and their analysis. Most of the proposed schemes are based on MFEM, lowest-order Raviart-Thomas elements. We set and proved the convergence for a MFEM scheme for the Richards equation in the strictly unsaturated flow case. For the saturated/unsaturated case, when Richards' equation becomes degenerate, we used the Kirchhoff transformation. We proved the convergence of the resulting scheme in a very general framework: both slow and fast diffusion being allowed. We proved also the convergence for a MPFA scheme (O-method) for unsaturated/saturated flow, this time but only fast diffusion being allowed. The convergence proof will be extended to include the slow diffusion case and the MPFA L-method. The convergence for the MFEM scheme without Kirchhoff's transformation and saturated/unsaturated flow is still an open problem. There are two possibilities to close this gap: quantify the differences between the schemes with and without the Kirchhoff transformation at the discrete level (at the continuous level the schemes are equivalent) or capture the interfaces between the saturated and unsaturated regions as lower dimensional manifolds and prove the convergence on each side (where the equation is regular). This will be the subject of a further research.

A MFEM scheme for reactive transport in saturated/unsaturated porous media was then presented and analyzed. The analysis considers the low regularity of the solution of the flow equation and, moreover, includes that the flow equation is solved also numerically. Error estimates have been proven. The order of convergence for the MFEM scheme for the transport equation depends as expected on the accuracy of numerical scheme for the flow equation.

The nonlinear systems arising after the MFEM discretization are solved by a Newton method. For this a regularization step was considered. The convergence of the schemes is analyzed for transport with equilibrium or non-equilibrium sorption. *A priori* constrains on the discretization parameters are derived to ensure the quadratic convergence of the Newton scheme and of the MFEM scheme. These constraints are

of a relevant practical interest, because they enable the *a priori* tunning of the discretization parameters (time step size, mesh diameter and regularization parameter) to ensure the convergence of the scheme.

We also analyzed the numerical diffusion for different discretization schemes for the transport equation, including higher order schemes in space (FVM and FEM) and in time. We concluded that for realistic problems all the schemes perform similar with respect to numerical diffusion as long as upwind was not used. We especially did not see any significant improvement when using the higher order schemes for numerical diffusion. The upwind schemes have shown, as expected, high numerical diffusion. For convection-dominated problems we proposed to new MHFEM schemes. The upwind MHFEM have shown less numerical diffusion as the FEM upwind schemes.

Finally we considered fully coupled flow and reactive solute transport: not only that the transport is affected by the flow, but also the flow is influenced by the transport. Concrete carbonation was the underlying application for such reactive flows. Water is now produced by the reaction and besides we have a variable porosity, so the flow and transport equations are fully coupled. A semi-implicit MFEM was proposed and analyzed for the strictly unsaturated flow case and a constant porosity. This analysis can be extended more or less straightforward to the case with variable porosity as long as the equations remain regular (no degeneracies). The degenerate cases (saturated/unsaturated flow, pore clogging) are the subject of a further analysis.

In the future we will also analyze other type of reactive flow couplings, e. g. when the water content is concentration depend as in the case of surfactant transport. Also more general dissolution-precipitation models (where a multi-valued function is involved for describing the dissolution/precipitation) will be considered and analyzed. For these type of models the convergence is normally shown by compactness arguments (Fréchet-Kolmogorov theorem). The existing works for saturated flow should now be extended to saturated/unsaturated flow. Another long term project will be to consider heat conduction in porous media in the view of application to geo-thermal energy. In that case we have a fully coupled flow-transport-heat system.

Bibliography

[1] I. AAVATSMARK, *An introduction to multipoint flux approximations for quadrilateral grids*, Comput. Geosci. 6 (2002), pp. 404-432.

[2] L. EL ALAOUI, *An adaptive finite volume box scheme for solving a class of nonlinear parabolic equations*, Applied Mathematics Letters 22 (2009), pp. 291–296.

[3] L. EL ALAOUI, A. ERN AND M. VOHRALIK, *Guaranteed and robust a posteriori error estimates and balancing discretization and linearization errors for monotone nonlinear problems*, HAL Preprint 00410471, 2009.

[4] H. W. ALT AND S. LUCKHAUS, *Quasilinear elliptic-parabolic differential equations*, Math. Z., 183 (1983), pp. 311–341.

[5] T. ARBOGAST, *An error analysis for Galerkin approximations to an equation of mixed elliptic-parabolic type*, Technical Report TR90-33, Department of Computational and Applied Mathematics, Rice University, Houston, TX, 1990.

[6] T. ARBOGAST, M. OBEYESEKERE AND M. F. WHEELER, *Numerical methods for the simulation of flow in root-soil systems*, SIAM J. Num. Anal. 30 (1993), pp. 1677-1702.

[7] T. ARBOGAST AND M. F. WHEELER, *A characteristics-mixed finite-element method for advection-dominated transport problems*, SIAM J. Numer. Anal. 33 (1995), pp. 402–424.

[8] T. ARBOGAST, M. F. WHEELER AND N. Y. ZHANG, *A nonlinear mixed finite element method for a degenerate parabolic equation arising in flow in porous media*, SIAM J. Numer. Anal. 33 (1996), pp. 1669–1687.

[9] S. ATTINGER, M. DENTZ, H. KINZELBACH AND W. KINZELBACH, *Temporal behavior of a solute cloud in a chemically heterogeneous porous medium*, J. Fluid Mech. 386 (1999), pp. 77-104.

[10] S. ATTINGER, J. EBERHARD AND N. NEUSS, *Filtering procedures for flow in heterogeneous porous media: numerical results*, Comput. Visual. Sci. 5 (2002), pp. 67-72.

[11] J. W. BARRETT AND P. KNABNER, *Finite Element Approximation of the Transport of Reactive Solutes in Porous Media. Part 1: Error Estimates for Nonequilibrium Adsorption Processes*, SIAM J. Numer. Anal. 34 (1997), pp. 201–227.

[12] J. W. BARRETT AND P. KNABNER, *Finite Element Approximation of the Transport of Reactive Solutes in Porous Media. Part II: Error Estimates for Equilibrium Adsorption Processes*, SIAM J. Numer. Anal. 34 (1997), pp. 455–479.

[13] P. BASTIAN, K. BIRKEN, K. JOHANSSEN, S. LANG, N. NEUSS, H. RENTZ-REICHERT AND C. WIENERS, *UG–a flexible toolbox for solving partial differential equations*, Comput. Visualiz. Sci. 1 (1997), pp. 27–40.

[14] M. BAUSE, F. BRUNNER, F. A. RADU AND P. KNABNER, *An improved optimal order mixed finite element method for semilinear transport problems.*. In Numerical Mathematics and Advanced Applications. A. Cangiani et al. (editors), Springer, 2013, pp. 247–256.

[15] M. BAUSE AND P. KNABNER, *Numerical simulation of contaminant biodegradation by higher order methods and adaptive time stepping*, Comput. Visualiz. Sci. 7 (2004), pp. 61–78.

[16] M. BAUSE, *Higher and lowest order mixed finite element approximation of subsurface flow problems with solutions of weak regularity*, Adv. Water Resour. 31 (2007), pp. 370-382.

[17] J. BEAR AND Y. BACHMAT, *Introduction to Modelling of Transport Phenomena in Porous Media*, Kluwer Academic, Dordrecht, The Netherlands, 1991.

[18] F. BREZZI AND M. FORTIN, *Mixed and Hybrid Finite Element Methods*, Springer-Verlag, New York, 1991.

[19] F. BRUNNER, *Hybrid gemischte Finite Elemente fuer Systeme von Transportreaktionsgleichungen in poroesen Medien: Algorithmische Umsetzung und Simulation von 2D-Szenarien*, Diplom-Thesis, University of Erlangen, 2010.

[20] F. BRUNNER, F. A. RADU, M. BAUSE AND P. KNABNER, *Optimal order convergence of a modified BDM1 mixed finite element scheme for reactive transport in porous media.*, Adv. Water Resour. 35 (2012), pp. 163–171.

[21] F. BRUNNER, F. A. RADU AND P. KNABNER, *Analysis of an upwind-mixed hybrid finite element method for transport problems*, Preprint IAM Erlangen, No. 364, 2013.

[22] M. CELIA, E. BOULOUTAS AND R. ZARBA, *A General Mass Conservative Numerical Solution for the Unsaturated Flow Equation*, Water Resour. Res. 26 (1990), pp. 1483–1496.

[23] G. CHAVENT, G. COHEN AND J. JAFFRE, *Discontinuous upwinding and mixed finite elements for two-phase flows in reservoir simulation*, Comput. Methods Appl. Mech. Eng. 47 (1984), pp. 93–118.

[24] P. G. CIARLET, *The Finite Element Method for Elliptic Problems*, North–Holland, Amsterdam, 1978.

[25] C. DAWSON, C.J. VAN DUIJN AND M.F. WHEELER, *Characteristic-Galerkin Methods for Contaminant Transport with Nonequilibrium Adsorption Kinetics*, SIAM J. Numer. Anal. 31 (1994), pp. 982–999.

[26] C. DAWSON, *Analysis of an upwind-mixed finite element method for nonlinear contaminant transport equations*, SIAM J. Numer. Anal. 35 (1998), pp. 1709–1724.

[27] C. DAWSON AND V. AIZINGER, *Upwind-mixed methods for transport equations*, Comput. Geosci. 3 (1999), pp. 93-110.

[28] A. DEMLOW, *Suboptimal and Optimal Convergence in Mixed Finite Element Methods*, SIAM J. Numer. Anal. 39 (2002), pp. 1938–1953.

[29] J. DOUGLAS, JR. AND J. E. ROBERTS, *Mixed finite element methods for second order elliptic problems*, Math. Aplic. Comp. 1 (1982), pp. 91–103.

[30] J. DOUGLAS, JR. AND J. E. ROBERTS, *Global Estimates for Mixed Methods for Second Order Elliptic Equations*, Math. of Comp. 44 (1985), pp. 39–52.

[31] C.J. VAN DUIJN AND P. KNABNER, *Solute transport in porous media with equilibrium and nonequilibrium multiple-site adsorption: travelling waves*, J. Reine Angew. Math. 415 (1991), pp. 1–49.

[32] L. J. DURLOFSKY, *Accuracy of mixed and control volume finite element approximations to Darcy velocity and related quantities*, Water Resour. Res. 30 (1994), pp. 965–973.

[33] L. C. EVANS, *Partial Differential Equations, American Mathematical Society*, Providence, 1998.

[34] R. EYMARD, M. GUTNIC AND D. HILLHORST, *The finite volume method for Richards equation*, Comput. Geosci. 3 (1999), pp. 256–294.

[35] R. EYMARD, D. HILHORST AND M. VOHRALÍK, *A combined finite volume-nonconforming/mixed-hybrid finite element scheme for degenerate parabolic problems*, Numer. Math. 105 (2006), pp. 73–131.

[36] K. B. FADIMBA, *A linearization of a backward Euler scheme for a class of degenerate nonlinear advectiondiffusion equations*, Nonlinear Analysis 63 (2005), pp. 1097–1106.

[37] R. HUBER AND R. HELMIG, *Multiphase flow in heterogeneous porous media: A classical finite element method versus an implicit pressure-explicit saturation based mixed finite element finite volume approach*, Int. J. Numer. Methods Fluids 29 (1999), pp. 899-920.

[38] W. JÄGER AND J. KAČUR, *Solution of doubly nonlinear and degenerate parabolic problems by relaxation schemes*, M^2AN Math. Model. Numer. Anal. 29 (1995), pp. 605-627.

[39] J. KAČUR, *Solution to strongly nonlinear parabolic problems by a linear approximation scheme*, IMA J. Num. Anal. 19 (1995), pp. 119-145.

[40] J. KAČUR AND R. VAN KEER, *Solution of contaminant transport with adsorption in porous media by the method of characteristics*, M2AN 35 (2001) pp. 981-1006.

[41] P. K. KITANIDIS, *Prediction by the method of moments of transport in a heterogeneous formation*, Journal of Hydrology 102 (1988), pp. 453-473.

[42] R. A. KLAUSEN, F. A. RADU AND G. T. EIGESTAD, *Convergence of MPFA on triangulations and for Richards' equation*, Int. J. for Numer. Meth. Fluids 58 (2008), pp. 1327–1351.

[43] R. A. KLAUSEN AND R. WINTHER, *Convergence of multi point flux approximations on quadrilateral grids*, Numer. Methods for PDE's, 22 (2006), pp. 1438–1454.

[44] R. KLÖFKORN, D. KRÖNER AND M. OHLBERGER, *Local adaptive methods for convection dominated problems*, Internat. J. Numer. Methods in Fluids 40 (2002), pp. 79–91.

[45] P. KNABNER, *Mathematische Modelle für Transport und Sorption gelöster Stoffe in porösen Medien*, Methoden und Verfahren der mathematischen Physik, Band 36, Verlag Peter Lang, Frankfurt/Main, 1990.

[46] 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*, Adv. Water Resour. 18 (1995), pp. 171–185.

[47] P. KNABNER, A. PRECHTEL, S. BITTERLICH, R. ISA-TERAN AND E. SCHNEID, *Influence of Surfactants on Spreading of Contaminants and Soil Remediation*, in Mathematics - Key Technology for the Future, Jäger W. and Krebs H.-J. (editors), Springer-Verlag, 2003, pp. 152–161.

[48] P. KNOBLOCH AND L. TOBISKA, *On the stability of finite-element discretizations of convection-diffusion-reaction equations*, IMA J. Numer. Anal. 31 (2011), pp. 147–164.

[49] K. KUMAR, I. S. POP AND F. A. RADU, *Convergence analysis for a conformal discretization of a model for precipitation and dissolution in porous media*, Preprint CASA 8-20 (2012), TU Eindhoven, The Netherlands.

[50] K. KUMAR, I. S. POP AND F. A. RADU, *Convergence analysis of mixed numerical schemes for reactive in a porous medium*, Preprint CASA 12-20 (2012), TU Eindhoven, The Netherlands.

[51] R. B. LANTZ, *Quantitative evaluation of numerical diffusion (truncation error)*, SPE Journal 11 (1971), pp. 315-320.

[52] R. LAVAL, B. R. HODGES AND J. IMBERGER, *Reducing numerical diffusion effect with pycnocline filter*, Journal of Hydraulic Engineering 129 (2003), pp. 215-224.

[53] S. A. MEIER, M.A. PETER, A. MUNTEAN AND M. BÖHM, *Dynamics of the internal reaction layer arising during carbonation of concrete*, Chemical Engineering Science 62 (2007), pp. 1125-1137.

[54] S. MICHELETTI, R. SACCO AND F. SALERI, *On Some Mixed Finite Element Methods with Numerical Integration*, SIAM J. Sci. Comput. 23 (2001), pp. 245–270.

[55] R. MOSE, P. SIEGEL, P. ACKERER AND G. CHAVENT, *Application of the mixed hybrid finite element approximation in a groundwater flow model: Luxury or necessity ?*, Water Resour. Res. 30 (1994), pp. 3001–3012.

[56] Y. MUALEM, *A new model for predicting hydraulic conductivity of unsaturated porous media*, Water Resour. Res. 12 (1976), pp. 513-522.

[57] R.H. NOCHETTO, *Error estimates for two-phase Stefan problems in several space variables I: linear boundary conditions*, Calcolo 22 (1985), pp. 501-534.

[58] R. H. NOCHETTO AND C. VERDI, *Approximation of degenerate parabolic problems using numerical integration*, SIAM J. Numer. Anal. 25 (1988), pp. 784–814.

[59] M. OHLBERGER AND C. ROHDE, *Adaptive finite volume approximations of weakly coupled convection dominated problems*, IMA J. Numer. Anal. 22 (2002), pp. 253-280.

[60] E.J. PARK, *Mixed finite elements for nonlinear second-order elliptic problems*, SIAM J. Numer. Anal. 32 (1995), pp. 865–885.

[61] M. A. PETER, A. MUNTEAN, S. A. MEIER AND M. BÖHM, *Competition of several carbonation reactions in concrete: A parametric study*, Cement and Concrete Research 38 (2008), pp. 1385–1393.

[62] I. S. POP, *Error estimates for a time discretization method for the Richards' equation*, Comput. Geosci. 6 (2002), pp. 141–160.

[63] I. S. POP, F. A. RADU AND P. KNABNER, *Mixed finite elements for the Richards' equation: linearization procedure*, J. Comput. Appl. Math. 168 (2004), pp. 365–373.

[64] I. S. POP, M. SEPULVEDA, F. A. RADU AND O. P. VERA VILLAGRAN, *Error estimates for the finite volume discretization for the porous medium equation*, J. Comput. Appl. Math. 234 (2010), pp. 2135–2142.

[65] I. S. POP AND W. A. YONG, *A numerical approach to degenerate parabolic equations*, Numer. Math. 92 (2002), pp. 357–381.

[66] A. QUARTERONI AND A. VALLI, *Numerical approximations of partial differential equations*, Springer-Verlag, 1994.

[67] F. A. RADU, *Mixed finite element discretization of Richards' equation: error analysis and application to realistic infiltration problems*, PhD Thesis, University of Erlangen–Nürnberg, 2004.

[68] F. A. RADU, I. S. POP AND P. KNABNER, *Order of convergence estimates for an Euler implicit, mixed finite element discretization of Richards' equation*, SIAM J. Numer. Anal. 42 (2004), pp. 1452–1478.

[69] F. A. RADU, I. S. POP AND P. KNABNER, *On the convergence of the Newton method for the mixed finite element discretization of a class of degenerate parabolic equation*, Numerical Mathematics and Advanced Applications, A. Bermudez de Castro et al. (editors), Springer Verlag, 2006, pp. 1194–1200.

[70] F. A. RADU, I. S. POP AND P. KNABNER, *Error estimates for a mixed finite element discretization of some degenerate parabolic equations*, Numer. Math. 109 (2008), pp. 285–311.

[71] F. A. RADU, M. BAUSE, A. PRECHTEL AND S. ATTINGER, *A mixed hybrid finite element discretization scheme for reactive transport in porous media*, Numerical Mathematics and Advanced Applications, K. Kunisch, G. Of and O. Steinbach (editors), Springer Verlag, 2008, pp. 513–520.

[72] F. A. RADU, I. S. POP AND S. ATTINGER, *Analysis of an Euler implicit - mixed finite element scheme for reactive solute transport in porous media*, Num. Meth. for Partial Diff. Eqs. 26 (2010), pp. 320–344.

[73] F. A. RADU AND I. S. POP, *Newton method for reactive solute transport with equilibrium sorption in porous media*, J. Comput. Appl. Math. 234 (2010), pp. 2118–2127.

[74] F. A. RADU AND I. S. POP, *Mixed finite element discretization and Newton iteration for a reactive contaminant transport model with nonequilibrium sorption: convergence analysis and error estimates*, Comput. Geosci. 15 (2011), pp. 431–450.

[75] F. A. RADU, A. MUNTEAN, I. S. POP, N. SUCIU AND O. KOLDITZ, *A mixed finite element discretization scheme for a concrete carbonation model with concentration-dependent porosity*, J. Comput. Appl. Math. 246 (2013), pp. 74-85.

[76] F. A. RADU AND N. SUCIU, *Stochastic simulations based on mixed finite elements for solute transport in groundwater*, PAMM 9 (2009), pp. 19–22.

[77] F. A. RADU, N. SUCIU, J. HOFFMANN, A. VOGEL, O. KOLDITZ, C-H. PARK AND S. ATTINGER, *Accuracy of numerical simulations of contaminant transport in heterogeneous aquifers: a comparative study*, Adv. Water Resour. 34 (2011), pp. 47–61.

[78] F. A. RADU AND W. WANG, *Convergence analysis for a mixed finite element scheme for flow in strictly unsaturated porous media*, Nonlin. Anal. Serie B: Real World Appl., DOI:10.1016/j.nonrwa.2011.05.003, 2011.

[79] B. RIVIERE AND M. F. WHEELER, *Discontinuous Galerkin methods for flow and transport problems in porous media*, Communications in numerical methods in engineering 18 (2002), pp. 63–68.

[80] B. RIVIERE AND M. F. WHEELER, *Non conforming methods for transport with nonlinear reaction*, Contemporany mathematics 295 (2002), pp. 421-432.

[81] E. SCHNEID, P. KNABNER AND F. A. RADU, *A priori error estimates for a mixed finite element discretization of the Richards' equation*, Numer. Math. 98 (2004), pp. 353–370.

[82] N. SUCIU, C. VAMOŞ, J. VANDERBORGHT, H. HARDELAUF AND H. VEREECKEN, *Numerical investigations on ergodicity of solute transport in heterogeneous aquifers*, Water Resour. Res. 42 (2006), W04409, DOI:10.1029/2007WR004546.

[83] N. SUCIU, C. VAMOŞ AND J. EBERHARD *Evaluation of the first-order approximations for transport in heterogeneous media*, Water Resour. Res. 42 (2006), W11504, doi:10.1029/2005WR004714.

[84] N. SUCIU, *Spatially inhomogeneous transition probabilities as memory effects for diffusion in statistically homogeneous random velocity fields*, Physical Review E 81 (2010), 056301, DOI:10.1103/PhysRevE.81.056301.

[85] N. SUCIU, C. VAMOŞ, F. A. RADU, H. VEREECKEN AND P. KNABNER, *Persistent memory of diffusing particles*, Phys. Rev. E 80 (2009), pp. 061134-1–061134-12.

[86] N. SUCIU, F. A. RADU, A. PRECHTEL, F. BRUNNER AND P. KNABNER, *Coupled finite element - global random walk approach to advection-dominated transport in porous media with random hydraulic conductivity*, J. Comput. and Appl. Math. 2012, DOI: http://dx.doi.org/10.1016/j.cam.2012.06.027.

[87] C.J. VAN DUIJN AND P. KNABNER, *Solute transport in porous media with equilibrium and nonequilibrium multiple-site adsorption: travelling waves*, J. Reine Angew. Math. 415 (1991), pp. 1–49.

[88] C.J. VAN DUIJN AND P. KNABNER, *Travelling wave behaviour of crystal dissolution in porous media flow*, European J. Appl. Math. 8 (1997), pp. 49–72.

[89] M. VAN GENUCHTEN, *A closed-form equation for predicting the hydraulic conductivity of unsaturated soils*, Soil Sci. Soc. Am. 44 (1980), pp. 892-898.

[90] C. VAMOŞ, N. SUCIU AND H. VEREECKEN, *Generalized random walk algorithm for the numerical modeling of complex diffusion processes*, J. Comput. Phys. 186 (2003), pp. 527–544.

[91] M. VOHRALIK, *A posteriori error estimates for lowest-order mixed finite element discretizations of convection-diffusion-reaction equations*, SIAM J. Numer. Anal. 45 (2007), pp. 1570–1599.

[92] C. WOODWARD AND C. DAWSON, *Analysis of expanded mixed finite element methods for a nonlinear parabolic equation modeling flow into variably saturated porous media*, SIAM J. Numer. Anal. 37 (2000), pp. 701-724.

[93] W. A. YONG AND I. S. POP, *A numerical approach to porous medium equations*, Numer. Math. 92 (2002), pp. 357-381.