ROBERT ANNEWANDTER

DISCRETE FRACTURE AND MATRIX SIMULATION OF CO2-BRINE MIGRATION, HYSTERESIS EFFECT AND CAPILLARY TRAPPING IN FRACTURED GEOLOGICAL FORMATIONS
DISCRETE FRACTURE AND MATRIX SIMULATION OF CO\textsubscript{2}-BRINE MIGRATION, HYSTERESIS EFFECT AND CAPILLARY TRAPPING IN FRACTURED GEOLOGICAL FORMATIONS

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Robert Annewandter: *Discrete Fracture and Matrix Simulation of CO2-Brine Migration, Hysteresis Effect and Capillary Trapping in Fractured Geological Formations*, PhD-Thesis
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**IN:** Edinburgh, Scotland

Oct 2014
DECLARATION

Put your declaration here.

Edinburgh, Scotland, Oct 2014

__________________________
Robert Annewandter
Dedicated to my mother Loreto Annewandter and the memory of my father of Engelbert Annewandter.
I was in New York in the 30’s. I had a box seat at the depression. I can assure you it was a very educational experience. We shut the country down because of monetary reasons. We had manpower and abundant raw materials. Yet we shut the country down. We’re doing the same kind of thing now but with a different material outlook. We are not in the position we were in 1929-30 with regard to the future. Then the physical system was ready to roll. This time it’s not.

We are in a crisis in the evolution of human society. It’s unique to both human and geologic history. It has never happened before and it can’t possibly happen again. You can only use oil once. You can only use metals once. Soon all the oil is going to be burned and all the metals mined and scattered.

— Marion King Hubbert (October 5, 1903 - October 11, 1989)
Injection of supercritical CO$_2$ allows us to sequester an important component of the greenhouse gases in the subsurface to reduce emissions of CO$_2$ in the energy sector. In light of global environmental change, it is of utmost importance to reliably predict the fate and containment of injected CO$_2$ at geological time scales. Therefore, modelling of the CO$_2$ plume migration and its containment within geological carbon storage repositories helps to uncover and understand challenges arising during injection and post-injection phase.

Discrete fracture and matrix (DFM) simulations have emerged as a powerful technology to analyse the fundamental flow and transport properties in naturally fractured reservoirs and bridge gaps between geosciences and reservoir engineering: they help to validate upscaling workflows, improve the analysis of pressure transients from well-tests, and allow to explore how uncertainties in fracture network properties impact hydrocarbon recovery. The key difference between DFM simulations and traditional dual-porosity approaches is that the structurally complex fracture geometries are explicitly discretised as 2D surfaces in a 3D reservoir model, hence provides a more geologically realistic representation of the fracture patterns and rock matrix as compared to dual-porosity models.

Here I extend the DFM simulation workflow to account for capillary trapping of CO$_2$ in fractured porous media. Fluid flow is described by a fully compositional model including an equation of state for CO$_2$–H$_2$O–NaCl fluids. The governing equations are discretised in space using unstructured and mixed-dimensional finite element - finite volume techniques. An Operator splitting approach is used to decouple capillary diffusion from the mass balance equation. For the first time, relative permeability hysteresis within the DFM method has been performed.
I demonstrate how my new DFM approach can be applied to simulate CO$_2$ injection and trapping of CO$_2$ in fractured geological formations with geologically realistic fracture networks. I show how matrix diffusion and capillary forces influence the rate at which CO$_2$ is trapped in the rock matrix.
ACKNOWLEDGMENTS

Finally, a long, challenging journey comes to an end. I like to thank those people who made the past years a wonderful experience!

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I am also very grateful for the support of my other supervisor Ian Main, who kept my interest for rock deformations burning! I enjoyed very much working with him during my two consultancies and to become a better writer. Thanks for showing me, that an academic career can go along with a music one! Whenever I make it back to Edinburgh during the festival month of August, I will check out the royal oak.

Grateful thanks also goes to Jens Birkholzer at the Earth Science Division of LBNL for providing me TOUGH2-ECO2M and to share his time with me through fruitful discussions which helped to improve the understanding of capillary trapping in fractured media despite his busy schedule. Without his support, I would never have enjoyed the inspiring environment in the Bay Area.

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There are many PhD mates who made my office life in Edinburgh such an enriching experience through discussions about reservoir physics, politics, religion, culture, office policies, and just the general non-sense of life. I like to first thank you John Mills for the many coffee discussions we shared together about research questions at the smallest scale, institute politics, private life issues. I missed the Old-Town coffee walks and talks since you left. I found a friend in you and what started in the early autumn in Beijing will hopefully last over our whole life time!

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Without the support of my mother, I never would have been able to finish this PhD. I dedicate this work to her.

So long, and thanks again for the fish!

Sophie, you know..!
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THERMODYNAMIC

\[ \Omega^\ast \] Collision Integral 36
\( \beta \) Pressure Coefficient of Pure Water 34
\( \beta_{aq} \) Pressure Coefficient for Pure Water 34
\( \beta^E \) Excess Pressure Coefficient at NaCl Saturation 34
\( \beta^* \) Reduced Pressure Coefficient 35
\( \gamma^* \) Activity Coefficient of CO\(_2\) 25
\( \Delta \mu_{ca} \) Excess Property of the Viscosity of the Carbonic Phase 36
\( \Delta \mu^c_{ca} \) Critical Enhancement of the Viscosity of the Carbonic Phase 36
\( \zeta \) Third-Order Interaction Parameter 25
\( \theta \) Temperature in Degree Celsius 17
\( \lambda \) Second-Order Interaction Parameter 25
\( \mu_{ij} \) Chemical Potential of Species \( j \) in Phase \( i \) 14
\( \mu_{aq} \) Viscosity of the Aqueous Phase 33
\( \mu^0_{aq} \) Zero-Pressure Viscosity of the Aqueous Phase 34
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\( \varphi_j \) Fugacity Coefficient of Species \( j \) in the Carbonic Phase 12
\( \rho_{aq,\text{sat}} \) Density of the CO\(_2\)-Saturated Aqueous Phase 32
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INTRODUCTION

Geological Carbon Storage (GCS) is one possible mean of reducing greenhouse gas emissions (IPCC, 2005). Numerous studies have been carried out to understand how CO₂ migrates in geological formations such as depleted oil and gas reservoirs (Liu et al., 2012) or saline aquifers (e.g. (Bachu, 2000; Bickle, 2009; Szulczewski et al., 2012), Fig. 1.1).

However, geological formations often contain natural fractures, which can comprise high-permeability pathways for fluid flow. CO₂ migration and trapping in naturally fractured geological formations is not yet extensively studied and new approaches to robustly upscale this behaviour for large-scale reservoir simulations are largely missing. The overarching aim of this thesis is hence to develop high-resolution numerical techniques that enable us to study CO₂ migration and trapping in fractured geological formations that contain geometrically realistic fracture networks. Such fracture networks can be readily sources from outcrop analogues of subsurface formations. The numerical techniques can then be used to study CO₂ migration and trapping in model geometries of fractured geological formations at the grid-block and inter-well scale. Results from the high-resolution simulations would eventually allow us to formulate new correlations and upscaling procedures that enable us to model CO₂ migration and trapping through fractured porous media without resolving the fractures directly.

Thermodynamic of H₂O-NaCl-CO₂ Mixtures

Modelling the long term behaviour of GCS repositories requires calculation of thermodynamic properties of CO₂-H₂O-NaCl mixtures and their phase compositions relevant to the temperature and pressure regime occurring at depth considered. Assuming a geothermal gradient of 35°C/km, a hydrostatic pressure gradient of 105 bar/km and surface temperature of 15°C the temperature and pressure range likely to occur for GCS
Cubic equations in volume are simple enough to be used in numerical models where pressure and temperature are primary variables, yet provide enough accuracy over $p - T$ ranges relevant for GCS. A very common equation of state for CO$_2$–H$_2$O–NaCl systems was developed by Spycher et al. (2003), which I also use in the thesis. It is a Redlich-Kwong equation of state for CO$_2$–H$_2$O systems which was combined with mixing rules in terms of the equation’s intermolecular attraction $a_{\text{mix}}$ and repulsion parameters $b_{\text{mix}}$, and assuming vanishing H$_2$O concentration levels in the carbonic phase when applying the mixing rules. Mixing rules state how $a_{\text{mix}}$ and $b_{\text{mix}}$ depend on the composition. Both attraction and repulsion parameter for the pure carbonic phase ($a_{\text{CO}_2}$ and $b_{\text{CO}_2}$), the repulsion parameter for the pure aqueous phase ($b_{\text{H}_2\text{O}}$), and the CO$_2$–H$_2$O binary interaction parameter ($a_{\text{CO}_2-\text{H}_2\text{O}}$) were fitted against experimental data accumulated in their publication and against reference data from Span and Wagner (1996) for pure carbonic phases, an approach first exploited by King et al. (1992). The carbonic attraction parameter $a_{\text{CO}_2}$ is assumed to vary linearly with temperature. Because H$_2$O is infinitely diluted in the carbonic phase when applying the mixing rules the parameter $a_{\text{H}_2\text{O}}$ is not needed. Thus, as will be shown later, phase mole fractions can be calculated directly.

**Figure 1.1**: Estimation of US-wide storage capacity from 20 arrays of injection wells in 11 aquifers (Szulczewski et al., 2012).
without iteration.

*Capillary Effects in Fractured Reservoirs and Trapping of CO₂*

Many reservoirs around the world exhibit fractures, i.e. macroscopic planar discontinuities which were formed due to deformation or physical diagenesis (*Nelson, 2001*). Particularly the Middle East carbonates could be an important area for GCS combined with enhanced oil recovery but there are other regions where fractures could have formed, for example the North Sea due to glacial loading and unloading (*Wiprut and Zoback, 2000; Grollimund and Zoback, 2000*).

Fractures may have been initially open given brittle failure, or exist as a band of highly deformed country rock if they were exposed to ductile failure. These discontinuities almost always affect fluid flow as they can introduce strong anisotropy in permeability either through open or cemented fractures. There are some indications which shows links between the stress field in the North Sea and post glacial lithospheric flexure as a result of deglaciation.

![Figure 1.2](image)

*Figure 1.2:* Outcrop images of a fractured carbonate formation in Oman (Courtesy of Patrick Corbett, Institute of Petroleum Engineering, Heriot-Watt University) and fractured sandstones in Torridon, Scotland (Courtesy of Robert Annewandter, Institute of Petroleum Engineering, Heriot-Watt University). Both outcrops can be viewed as analogues for geological subsurface formations offshore Oman and Scotland. Note that most of the fractures are bed-bound, i.e. they terminate at the boundaries between comparatively thin sedimentary beds.
Capillary trapping of CO$_2$ is viewed as one of the key processes that sequesters CO$_2$ in the subsurface (MacMinn et al., 2011). Capillary trapping occurs when brine re-imbibes, either after CO$_2$ injection has stopped or when a chase-brine is injected into the reservoir (Qi et al., 2009a). While trapping of a gas phase has been studied extensively in geological formations (Land, 1968; Killough, 1976; Jackson et al., 2003; Spiteri et al., 2005; Juanes et al., 2006; Saadatpoor et al., 2009; Shamshiri and Jafarpour, 2012), trapping of a gas phase in fractured formations is less well studied. Hence a key focus of this thesis is to develop numerical techniques that enable us to study CO$_2$ trapping in realistically fractured geological formations.

**Dual-Porosity/Dual-Permeability Problem**

Common approaches for simulation of fluid flow and transport in naturally fractured reservoirs are dual porosity models (Barenblatt et al., 1960; Warren and Root, 1963) with extension to multiphase-flow (Kazemi et al., 1976; Gilman and Kazemi, 1988, 1983). The dual porosity model assumes that advection takes place in the mobile fracture domain, whereas the immobile matrix domain only allows for diffusion. The dual-permeability model relaxes this assumption and also allows for viscous displacement in the rock matrix. A transfer function connects both domains across their interface and describes the physics of fluid exchange between them (Babadagli et al., 2009; Balogun et al., 2009; Ramirez et al., 2009; Al-Kobaisi et al., 2009; Abushaikha and Gosselin, 2008; Lu et al., 2008). The transfer function accounts for gravitational and capillary forces, fluid diffusion and expansion. Viscous forces in the matrix are assumed to be negligibly small in a dual porosity model. A shape factor describes the geometry of the rock and defines the area over which fluid exchange between fractures and matrix can occur. (Lim and Aziz, 1995; Rangel-German and Kovscek, 2006; Hassanzadeh and Pooladi-Darvish, 2006; Gong et al., 2008).

It is well-known that the dual-porosity/permeability model is a highly idealised representation of a fractured geological formation. Hence the dual-porosity/permeability model may not represent flow in the fractures and transfer of fluids between fractures and matrix correctly. It neglects complex geological heterogeneities which are below the scale of a single reservoir simulation grid block but which are known to control recovery behaviour (Tecklenburg et al., 2013; Geiger et al., 2013; Ahmed Elfeel et al., 2013a,b; Maier
et al., 2013). Hence a key focus of this thesis is to develop numerical techniques that enable us to study CO₂ trapping in realistically fractured geological formations so as to better understand the limitations of dual-porosity and dual-permeability formulations when modelling CO₂ migration and trapping in fractured geological formations. However, comparisons between the developed methods and the dual-porosity/permeability models are not the focus of this thesis.

Discrete Fracture-Matrix Simulation

The key difference between Discrete Fracture-Matrix (DFM) simulations and traditional dual-continuum approaches is that the structurally complex fracture geometries are explicitly discretised as lower-dimensional surfaces in reservoir models, which hence comprises a geologically realistic representation of the fracture patterns and rock matrix. By numerically studying the physics of fluid flow in naturally fractured reservoirs (NFR), fine grid DFM allows to describe and quantify the complex emergent flow behaviour resulting from numerous matrix-fracture interactions, ultimately enabling us to formulate upscaling strategies and new correlations that capture the flow behaviour at the grid-block scale in large-scale reservoir simulation. Examples of DFM simulations include, but are not limited to, quantifying anomalous heat and solute transport in fractured geological formations (Geiger et al., 2010; Geiger and Emmanuel, 2010) or improved dual-
porosity formulations using non-local matrix diffusion (Tecklenburg et al., 2013; Geiger et al., 2013). For a recent overview of DFM simulation applications see Geiger and Matthai (2012).

The DFM simulation is characterised by (1) explicitly representing material discontinuities such as fractures, joints and faults as well as complex geologic structures by an unstructured mesh, (2) reducing computational cost by capturing discontinuities as lower dimensional manifolds.

DFM methods utilise unstructured grids which allows to capture complex geologic structures as opposed to traditional structured mesh with corner node type grids used traditionally in reservoir simulation. Even when local grid refinement is applied for Cartesian grids, they suffer to some degree alignment issues when complex geologic structures are captured. Combination of different mesh types (tetrahedral, prism and hexahedral, lowerdimensional triangles, quadrilaterals and line elements) will result in reduced CPU time and memory requirements as the number of nodes and elements is decreased compared to single type discretisations. A wide range of numerical methods exist for DFM methods, including finite element methods (Huyakorn et al., 1983; Baca et al., 1984; Kim and Deo, 2000; Granet et al., 2001; Juanes et al., 2002; Karimi-Fard and Firoozabadi, 2003; Chambon et al., 2010; Zhang et al., 2013), finite volume methods (Verma and Aziz, 1997; Bourbiaux et al., 1999; Karimi-Fard et al., 2004; Montagudo and Firoozabadi, 2004; Reichenberger et al., 2006; Belayneh et al., 2006; Montagudo and Firoozabadi, 2007a; Sahimi et al., 2010; Sandve et al., 2012, 2014), a combination of both (Therrien and Sudicky, 1996; Bastian et al., 2004; Geiger et al., 2004; Matthai et al., 2007; Paluszny et al., 2007; Coumou et al., 2008a; Geiger-Bosching et al., 2009a; Paluszny and Matthai, 2010; Agar et al., 2010; Blessent et al., 2013), mixed element methods (Martin et al., 2005), and a discontinuous Galerkin finite element method (Hoteit and Firoozabadi, 2005a; Moortgat and Firoozabadi, 2013a).

While DFM simulations are mature, they are not computationally efficient enough to allow full-field reservoir simulations. Attempts have been made to speed-up computation using domain decomposition and parallelisation (Coumou et al., 2009, 2008b; Geiger-Bosching et al., 2009b). Although such techniques allow to reduce simulation run time,
DFM simulations still cannot compete with traditional reservoir simulation techniques because of the large number of elements needed to resolve the complex geometries as well as the wide range in element sizes that impose restrictions on the time-step size, even if implicit methods with non-linear solvers are used (Maier et al., 2013).

Recently, DFM models for anisotropic and fractured porous media with control-volume discretisations using multipoint flux approximation (MPFA) were developed to explicitly account for fractures (Sandve et al., 2012). MPFA methods were designed to give a correct discretisation, when flow equations were described in general nonorthogonal grids or in the principal directions of the permeability tensor (Aavatsmark, 2002). MPFA methods approximate the flux between neighbouring elements by introducing a transmissibility calculated at the interface between the elements. The extension to multidimensional problems is carried out by introducing transmissibility coefficients which constitutes a positive definite transmissibility tensor. Traditionally the transmissibility is evaluated as a harmonic average between the two neighbouring elements, to respect continuity of flux and potential. The harmonic average takes the permeability and potential either side of the interface into account, and assumes linearity in their values on the interface. Sandve et al. (2012) introduces hybrid cells for lower-dimensional fractures with hybrid faces between fracture-fracture and fracture-matrix connections. Continuity points on the hybrid faces are chosen by selecting the hybrid face centroids and connected to the cell centroids carrying out a O-method. The hybrid method assumes that the fracture aperture is sufficiently small, i.e. much smaller than the corresponding cell length. The hybrid DFM method leads to better conditioned discretisation matrix and therefore im-

![Figure 1.4: Finite element finite volume discretisation of a fractured, porous medium as realised in discrete fracture and matrix models (Geiger and Matthai, 2012).](image-url)
proves simulation time significantly. As a last remark, the finite element - finite volume discretisation within the DFM method used in this thesis does not use transmissibilities and therefore is not related to the MPFA method.

Aim of Thesis

Although the DFM approach has been applied to a range of flow problems, it has rarely been used to study the migration and trapping of CO₂ in fractured formations (Moortgat and Firoozabadi, 2013b). As noted above, fractures are ubiquitous in geological formations and will impact the rate of CO₂ migration and the way CO₂ is trapped. I have therefore extended an existing finite element - finite volume algorithm (Geiger et al., 2009) to model CO₂-brine migration in fractured geological formation, including the trapping of CO₂ in the rock matrix due to capillary forces. I use a modified non-iterative Redlich-Kwong equation of state to calculate the mutual solubilities of H₂O and CO₂ in CO₂–H₂O–NaCl fluids. Fracture apertures and resulting fracture permeabilities are modelled using a simple relationship controlled by rock normal and shear loading. The governing equations are discretised in space using unstructured and mixed-dimensional finite element - finite volume techniques. I carry out implementations using the Complex System Modelling Platform (CSMP++), an unstructured finite element - finite volume simulator for modelling fluid flow in complex geological structures (Matthäi et al., 2007)

I demonstrate how the new DFM approach can be applied to simulate CO₂ injection and trapping of CO₂ in fractured geological formations with geologically realistic fracture networks to analyse how matrix and fracture properties, as well as capillary forces influence the rate at which CO₂ is trapped in the rock matrix

Thesis Structure

bThe thesis is structured as follows: In Chap. 2, I will discuss a thermodynamic model for CO₂–H₂O–NaCl mixtures. In Chap. 3, I develop a strategy to simulate compress-
ible, multi-component multi-phase flow and transport in the presence of capillary forces. In Chap. 4, I will develop the numerical formulation for the finite element-finite volume method based on the operator-splitting method developed in Chap. 3. In Chap. 5, I will present three benchmark cases to demonstrate the correctness of the decoupled implementation developed before. In Chap. 6, I will demonstrate the numerical method developed to investigate capillary trapping of CO$_2$ on four idealised model geometries containing fractures. In Chap. 7, I will revisit the experimental setup from the previous chapter with the only difference: enabling non-wetting relative permeability hysteresis. In Chap. 8, the four model geometries used in the two chapters before are substituted by an outcrop analogue which contains a realistic fracture network. In Chap. 9, I will revisit the previous experimental setup and enable similar to Chap. 7, the non-wetting relative permeability hysteresis. I finish with conclusion (Chap. 10) and recommendations for future work (Chap. 11).
A possible mitigation strategy for global environmental change driven by the generation of greenhouse gases, mainly carbon dioxide, requires sequestering of carbon dioxide in man-made geologic repositories and the long-term prediction of its behaviour to ensure its containment. At depth of geologic relevant CO$_2$ storage, pressure, temperature and composition ($p - T - x$) properties of CO$_2$–HO$_2$–NaCl mixtures in equilibrium need to be calculated sufficiently accurate to describe flow and transport characteristics reliably (Fig. 2.1). The focus of this chapter is to present an equation of state for mixtures which strives to balance accuracy and computational cost. The equation of state allows to calculate fugacity coefficients. Fugacity coefficients are a measure for the difference of a real liquid or real gas behaviour from the ideal liquid or ideal gas behaviour. These coefficients allow to calculate mutual solubilities of pure H$_2$O and CO$_2$ in thermodynamic equilibrium for a partially given thermodynamic state ($p, T$), that is, the accurate partitioning of H$_2$O and CO$_2$ between aqueous and carbonic phase. Henry law constants enable the extension to non-ideal aqueous solutions, i.e. these constants account for the presence of chloride salt in the aqueous phase. More precisely, modification of the activity coefficient used in calculating fugacity coefficients captures the effect of chloride salt. After determining the thermodynamic state ($p, T, x$) the calculation of thermophysical properties, such as phase densities, phase viscosities and phase compressibilities, becomes possible while accounting for component dissolution.

Mutual solubilities for initially pure H$_2$O and CO$_2$ mixtures can be calculated by solving iteratively an equation of state for the molar volume of CO$_2$ and H$_2$O, together with the fugacities $\phi_{ij}$ of both species $j \in \{\text{CO}_2, \text{H}_2\text{O}\}$ in both, the carbonic and aqueous phase (denoted by $i$). However, a computationally inexpensive way to calculate mutual solubilities of pure H$_2$O and CO$_2$ mixtures is achieved by using a non-iterative modified...
Redlich-Kwong equation of state (Spycher et al., 2003; Sprecher and Pruess, 2005). The approach used therein is to reduce the application of the equation of state to the carbonic phase to calculate mutual solubilities, i.e. molar phase mass fractions $x_{ij}$ of component $j$ in phase $i$, for both the carbonic and aqueous phase. Correlations between the thermodynamic state $(p, T, x)$ and thermophysical properties are needed to model flow and transport of CO$_2$ in an H$_2$O-filled storage repository. For brevity, I will present these correlations briefly and refer to the respective publications. For an introduction into the molecular thermodynamics of fluid-phase equilibria, see Prausnitz et al. (1999), which is used throughout this chapter.

This chapter provides a collection of already published research by others. It does not present any new knowledge nor does it present any work I have done. However, the equation of state, subsequent calculation of mutual solubilities of HO$_2$ and CO$_2$ and calculations of thermophysical properties were not implemented in the research code CSMP++ used in this work until now, and are essential to study multi-phase, multi-compositional flow and transport characteristics of fluids, which are constituted by CO$_2$–HO$_2$–NaCl mixtures.

The chapter is structured as follows: First, the non-iterative modified Redlich-Kwong equation of state is presented along with needed non-mixing rules (Sec. 2.1). It provides the molar volume of the carbonic phase necessarily to calculate fugacity coefficients. Next, the calculation of fugacity coefficients $\varphi_j$ is presented from which molar phase mass fractions $x_{ij}$ of CO$_2$–H$_2$O mixtures can be calculated (Sec. 2.2). Then, the extension to CO$_2$–H$_2$O–NaCl mixtures is presented introducing an activity coefficient formulation for NaCl solutions (Sec. 2.3). The chapter is completed by correlations of thermophysical properties to the thermodynamic state $(p, T, x)$ (Sec. 2.4).

The term component and species will be used in this chapter synonymously. Since the latter term is more common in the literature of thermodynamics of mixtures considered here, the preference is using the term species over component. However, in subsequent chapters I revert back to the term component.
As a last remark on phase indices: the index \( ca \) denotes the carbonic phase, the index \( aq \) denotes the aqueous phase. The phase state is denoted by \( (l) \) for liquid, \( (g) \) for gaseous, and \( (sc) \) for super-critical. Solid phase states \( (s) \) are not considered in this chapter. Since the focus in this chapter is on thermodynamics of mixtures, wettabilities are not considered in this chapter, hence the index \( n \) or \( w \) is not used here. However, from Chap. 3 on, phase index \( n \) and \( w \) will denote the carbonic and the aqueous phase. The component (species) index CO\(_2\) and H\(_2\)O will be used consistently throughout all chapters.

**Figure 2.1:** P-T projection of the CO\(_2\)–H\(_2\)O phase diagram. The lower dotted line indicates typical equilibrium subsurface conditions with a geothermal gradient of 35°C km\(^{-1}\), a hydrostatic pressure gradient of 10.5 MPa km\(^{-1}\), and mean surface temperature of 20°C and mean surface pressure of 100 kPa. The upper dashed line indicates maximum injection pressures with a geothermal gradient of 25°C km\(^{-1}\), maximum injection pressure gradient of 16 MPa m\(^{-1}\), mean surface temperature of 15°C, and assuming thermal equilibrium. The solid lines are three-phase coexistence curves with the critical point at their intersection. The circles denoted literature data, with open ones used in this work to validate phase mass fractions \( X_{ij} \) of CO\(_2\) in the aqueous phase and H\(_2\)O in the carbonic phase. The figure is an unmodified version from *Spycher et al. (2003)*.

### 2.1 Equation of State and Mixing Rules for H\(_2\)O-CO\(_2\) Mixtures

The Redlich-Kwong equation of state for mixtures takes the form (*Prausnitz et al., 1999*)

\[
p = \left( \frac{RT}{V_m - b_{mix}} \right) - \left( \frac{a_{mix}}{\sqrt{T} V (V_m - b_{mix})} \right),
\]

(2.1)
where \( V_m \) is the molar volume [cm\(^3\)] of the carbonic phase at pressure \( p \) [Pa] and temperature \( T \) [K], parameter \( a_{\text{mix}} \) [bar cm\(^6\) K\(^{0.5}\) mol\(^{-2}\)] and \( b_{\text{mix}} \) [cm\(^3\) mol\(^{-1}\)] accounts for intermolecular attraction and repulsion, and \( R \) [J mol\(^{-1}\) K\(^{-1}\)] is the gas constant. The mixtures parameter \( a_{\text{mix}} \) and \( b_{\text{mix}} \) are calculated by a standard mixing rule with vanishing mole fraction of \( H_2O \) in the carbonic phase \( (x_{ca,H_2O} = 0) \)

\[
a_{\text{mix}} = \sum_{j=1}^{n_c} \sum_{k=1}^{n_c} x_{ca,j} x_{ca,k} a_{jk}
= x_{ca,H_2O}^2 a_{H_2O} + 2x_{ca,H_2O} x_{ca,CO_2} a_{H_2O-CO_2} + x_{ca,CO_2} a_{CO_2}
= a_{CO_2}
\]

and

\[
b_{\text{mix}} = \sum_{j=1}^{n_c} x_{ca,j} b_j
= x_{ca,H_2O} b_{H_2O} + x_{ca,CO_2} b_{CO_2}
= b_{CO_2},
\]

where \( x_{ca,j} \) is mole fraction of component \( j \) in the carbonic phase [-], \( x_{ca,H_2O} \) is the mole fraction of \( H_2O \) in the carbonic phase [-], \( a_{H_2O} \) is the intermolecular attraction parameter for \( H_2O \), \( x_{ca,CO_2} \) is the mole fraction of \( CO_2 \) in the carbonic phase [-], \( a_{CO_2-H_2O} \) is the intermolecular attraction parameter for the \( CO_2-H_2O \) mixture, and \( b_{CO_2} \) the intermolecular repulsion parameter for \( CO_2 \).

Despite the disappearing interaction term \( a_{CO_2-H_2O} \), the strongly non-ideal mixing behaviour, i.e. the deviance from ideal fluids or ideal gases behaviour, is captured when calculating the fugacity coefficients \( \varphi_j \) for component \( j \) in the carbonic phase through the interaction parameters \( a_{ij} \) and \( b_j \). The Redlich-Kwong equation of state is a cubic equation in terms of volume and recasting yields

\[
0 = V_m^3 - \left( \frac{RT}{p} \right) V_m^2 - \left( \frac{RT b_{\text{mix}}}{p \sqrt{T}} - \frac{a_{\text{mix}}}{p} + b_{\text{mix}}^2 \right) V_m + \left( \frac{a_{\text{mix}} b_{\text{mix}}}{p \sqrt{T}} \right),
\]

which can be solved directly by the method of \textit{Nickalls} (1993). This method links the algebraic solution of a cubic equation to its geometric property. The solution \( V_m \) is used in computing \( \varphi_j \). Any cubic equation can produce up to three solutions when the system
is below the critical point in $pV$-space, thus capturing the transition from a liquid to
gaseous carbonic phase state accompanied by discontinuous volume change. The stable
volume value at a given pressure and temperature is obtained by calculating the work
in the $pV$-space (Fig. 2.2). The volume of the gas phase is given by the maximum root,
the minimum root gives the volume of the liquid phase. When phase transition occurs
the work along an isobar is equal to the work along an isothermal. Now using the work
definition $W = \int p \, dV$ and integrating along isobars and isothermals gives

$$\left. W \right|_{\text{isob}} = p \left( V_{\text{gas}} - V_{\text{liquid}} \right)$$

and

$$\left. W \right|_{\text{isoth}} = RT \ln \left( \frac{V_{\text{gas}} - b_{\text{mix}}}{V_{\text{liquid}} - b_{\text{mix}}} \right) + \frac{a_{\text{mix}}}{\sqrt{T} \, b_{\text{mix}}} \ln \left( \frac{V_{\text{gas}} + b_{\text{mix}}}{V_{\text{liquid}} + b_{\text{mix}}} \right) \left( \frac{V_{\text{liquid}}}{V_{\text{gas}}} \right).$$

The isobar starts at $V_{\text{liquid}}$ and goes to $V_{\text{gas}}$ along a path parallel to the $V$-coordinate.
The isothermal follows a curved path given by the equation of state (Eq. 2.1). Its implicit
form can be derived by differentiating the equation of state between $V_{\text{liquid}}$ to $V_{\text{gas}}$. The
stable phase can be inferred by comparing the work spent: if

$$\left( W \right|_{\text{isoth}} - \left. W \right|_{\text{isob}} > 0,$$

the stable phase’s volume is the maximum root, i.e. is the gaseous phase, otherwise
the minimum root, i.e. the liquid phase. When the volumes are equal, both phases are
stable and the maximum root is selected.
2.2 FUGACITY COEFFICIENTS OF CO₂—H₂O MIXTURES

A homogeneous system has uniform properties within its boundaries, i.e. a phase. A heterogeneous closed system comprises two or more phases, and each phase can be considered an open system within the overall closed system. If the system is closed, it does not exchange mass with its environment but may exchange energy. Phase equilibrium is achieved if equilibrium is achieved for each of the following three processes (Prausnitz et al., 1999):

- Heat transfer between any two phases within the heterogeneous system \((T)\),
- Displacement of a phase boundary \((p)\),
- Mass transfer of any component in the system across a phase boundary \((\mu_{ij})\).

Therefore, given an equilibrium state for a closed heterogeneous system with \(n_p\) phases and \(n_c\) species or components, the intense quantities phase temperature \(T_i\), phase pressure \(p_i\), and chemical potentials \(\mu_{ij}\) \([\text{kJ mol}^{-1}]\), with \(i \in n_p, j \in n_c\), are equal across all phases (for fixed \(j\)). A link between the abstract concept of chemical potential and the real world is established by introducing fugacities which can be directly measured. The chemical potential of component \(j\) is directly related logarithmically to the component’s
2.2 Fugacity Coefficients of CO$_2$–H$_2$O Mixtures

Fugacity $f_j$ [-] which accounts for non-ideality of mixtures due to molecular considerations (Prausnitz et al., 1999). The fugacity of a component in a mixture of ideal gases is equal to the partial pressure of that component. Fugacity can be regarded as a “corrected pressure”. It manifests the deviance of a substance from a phase. It is expressed relative to a standard state $f_j^0$ [-] in which the component acts as an ideal gas at the same temperature and composition but varying pressure or density. The reference state is usually set to a fixed value at 1 bar. All systems approach ideal-gas behaviour at very low pressure, therefore fugacity is defined by

$$\lim_{p \to 0} \frac{f_j}{x_j p} \to 1.$$  \hfill (2.8)

The ratio $a_j = f_j/f_j^0$ is called activity of component $j$ [-], and is a measure of the effective concentration of a species in a mixture. If the carbonic and the aqueous phase are at equilibrium, the chemical potential for each species (component) are equal. The respective reactions and associated equilibrium constants $K_{H_2O}$ and $K_{CO_2(g)}$ are written as

$$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g) : \quad K_{H_2O} = \frac{f_{H_2O(g)}}{a_{H_2O(l)}}$$ \hfill (2.9)

$$\text{CO}_2(l) \rightleftharpoons \text{CO}_2(g) : \quad K_{CO_2(g)} = \frac{f_{CO_2(g)}}{a_{CO_2(l)}}$$ \hfill (2.10)

where $f_j(g)$ are the fugacities of the components in the carbonic phase [-], $a_{H_2O(l)}$ is the activity of H$_2$O in the aqueous phase [-], $a_{CO_2(aq)}$ is the activity in the aqueous phase [-] and the equilibrium constants $K_j$ are related to the standard change of reaction in Gibb’s free energy $\Delta G^0$ by

$$\Delta G^0 = -RT \ln K.$$ \hfill (2.11)

The fugacity for the carbonic phase is given by

$$f_j = \varphi_j x_{ca,j} p_{tot}$$ \hfill (2.12)
The total pressure $p_{\text{tot}}$ [Pa] is the sum over all partial pressures in the carbonic phase. Hence, one obtains

$$K_{\text{H}_2\text{O}} = \frac{\varphi_{\text{H}_2\text{O}} x_{\text{ca.H}_2\text{O}} p_{\text{tot}}}{a_{\text{H}_2\text{O}(l)}}$$
(2.13)

$$K_{\text{CO}_2(g)} = \frac{\varphi_{\text{CO}_2} x_{\text{ca.CO}_2} p_{\text{tot}}}{a_{\text{CO}_2(aq)}}.$$  
(2.14)

Since the values of $K_{\text{H}_2\text{O}}$ and $K_{\text{CO}_2(g)}$ depends on temperature and pressure, the temperature variation is taken into account by expressing $K_j$ as polynomial function of temperature at the reference pressure of one bar, and the aqueous saturation pressure above 100 °C. The pressure correction is approximated by an exponential function, called the Poynting correction (Prausnitz et al., 1999). Pressure correction takes the form

$$K\big|_{(T,p)} = K\big|_{(T,p^0)}^0 \exp\left(\frac{(p - p^0) \bar{v}_j}{RT}\right),$$  
(2.15)

where $\bar{v}_j$ is the average partial molar volume of the pure condensed species $j$ [cm$^3$ mol$^{-1}$] over the pressure interval $p$ to $p^0$, with $\bar{v}_{\text{H}_2\text{O}} = 18.1$ cm$^3$ mol$^{-1}$, $\bar{v}_{\text{CO}_2(g)} = 32.6$ cm$^3$ mol$^{-1}$, $\bar{v}_{\text{CO}_2(aq)} = 32.0$ cm$^3$ mol$^{-1}$, and $p^0$ is the reference pressure as taken as 1 bar. Additionally, to account for phase transition of CO$_2$ as free-energy is released, another equilibrium constant $K_{\text{CO}_2(0)}$ is considered. $K_{\text{CO}_2(g)}$ substitutes $K_{\text{CO}_2(l)}$ when the following conditions are met: (1) temperature is above 31 °C and (2) calculated volume of the compressed gas phase is above 94 cm$^3$/mol. The polynomial functions of the equilibrium constants $K_j^0$ at standard state can then be calculated following Sprecher et al. (2003)

$$\log K_{\text{CO}_2(g)}^0 = 1.189 + 1.304 \times 10^{-2} \theta - 5.446 \times 10^{-5} \theta^2$$

$$\log K_{\text{CO}_2(l)}^0 = 1.169 + 1.358 \times 10^{-2} \theta - 5.380 \times 10^{-5} \theta^2$$
(2.16)

$$\log K_{\text{H}_2\text{O}}^0 = -2.209 + 3.097 \times 10^{-2} \theta - 1.098 \times 10^{-4} \theta^2 + 2.048 \times 10^{-7} \theta^3,$$
Table 2.1: Parameter for the Redlich-Kwong equation of state

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{\text{CO}_2}$</td>
<td>$7.54 \times 10^7 - 4.13 \times 10^4 \times T(K)$</td>
<td></td>
</tr>
<tr>
<td>$b_{\text{CO}_2}$</td>
<td>27.80</td>
<td>cm³/mol</td>
</tr>
<tr>
<td>$b_{\text{H}_2\text{O}}$</td>
<td>18.18</td>
<td>cm³/mol</td>
</tr>
<tr>
<td>$a_{\text{H}_2\text{O}-\text{CO}_2}$</td>
<td>$7.89 \times 10^7$</td>
<td>bar cm⁶ K⁰.⁵ mol⁻²</td>
</tr>
</tbody>
</table>

where $\theta$ is the temperature in °C. Finally, the fugacity coefficients $\phi_{\text{H}_2\text{O}}$ and $\phi_{\text{CO}_2}$ can be expressed in terms of molar volume $v$ according to Prausnitz et al. (1999). For a mixture it is

$$\ln(\phi_j) = \ln\left(\frac{V}{V - b_{\text{mix}}}\right) + \left(\frac{b_j}{V - b_{\text{mix}}}\right)$$

$$- \left(\frac{2 \sum_{ij} x_{ca,j} a_{ij}}{R \sqrt{T^3 b_{\text{mix}}}}\right) \ln\left(\frac{V + b_{\text{mix}}}{V}\right)$$

$$+ \left(\frac{a_{\text{mix}} b_j}{R \sqrt{T^3 b_{\text{mix}}}}\right) \left[\ln\left(\frac{V + b_{\text{mix}}}{V}\right) + \left(\frac{b_{\text{mix}}}{V + b_{\text{mix}}}\right)\right]$$

$$- \ln\left(\frac{PV}{RT}\right). \quad (2.17)$$

Assuming infinite dilution of H₂O in the carbonic phase, i.e. $x_{ca,\text{H}_2\text{O}} = 0$ and $x_{ca,\text{CO}_2} = 1$ in the mixing rules (Eq. 2.2 & Eq. 2.3), the interaction parameters $a_{\text{mix}}$ and $b_{\text{mix}}$ simplify to $a_{\text{mix}} = a_{\text{CO}_2}$ and $b_{\text{mix}} = b_{\text{CO}_2}$. This results in a non-iterative, direct computation of $\phi_j$ (Spycher et al., 2003). The parameter $a_{\text{H}_2\text{O}}$ is not needed (King et al., 1992). The water mole fraction in the gaseous carbonic phase $x_{ca,\text{H}_2\text{O}}$ including the correction to $K_{\text{H}_2\text{O}}$ is written as

$$x_{ca,\text{H}_2\text{O}} = \frac{K_{\text{H}_2\text{O}}^{0} a_{\text{H}_2\text{O}}}{\phi_{\text{H}_2\text{O}} p_{\text{tot}}} \exp \left(\frac{(p - p^0) \bar{v}_{\text{H}_2\text{O}}}{RT}\right). \quad (2.18)$$

Since the pressure and temperature range considered here are sufficiently small, we can apply Raoult’s law to set the water activity $a_{\text{H}_2\text{O}}$ equal to its mole fraction in the water phase $x_{\text{aq,H}_2\text{O}}$, which leads for this binary-mixture to

$$x_{ca,\text{H}_2\text{O}} = \frac{K_{\text{H}_2\text{O}}^{0} \left(1 - x_{\text{aq,CO}_2}\right)}{\phi_{\text{H}_2\text{O}} p_{\text{tot}}} \exp \left(\frac{(p - p^0) \bar{v}_{\text{H}_2\text{O}}}{RT}\right). \quad (2.19)$$
The mole fraction of CO$_2$ in the aqueous phase $x_{aq,CO_2}$ is calculated analogously by

$$ x_{aq,CO_2} = \frac{(1 - x_{ca,H_2O}) \varphi_{CO_2} p_{tot}}{K^0_{CO_2(g)}} \exp \left( \frac{(p - p^0) \bar{v}_{CO_2}}{RT} \right). $$

(2.20)

By setting

$$ A = \frac{K^0_{H_2O}}{\varphi_{H_2O} p_{tot}} \exp \left( \frac{(p - p^0) \bar{v}_{H_2O}}{RT} \right) $$

(2.21)

$$ B = \frac{\varphi_{CO_2} p_{tot}}{K^0_{CO_2(g)}} \exp \left( \frac{(p - p^0) \bar{v}_{CO_2}}{RT} \right) $$

(2.22)

the respective mole fractions can be directly computed without iterations using

$$ x_{ca,H_2O} = \frac{1 - B}{1/A - B} $$

(2.23)

$$ x_{aq,CO_2} = B(1 - x_{ca,H_2O}) $$

(2.24)

$$ x_{ca,CO_2} = 1 - x_{ca,H_2O} $$

(2.25)

$$ x_{aq,H_2O} = 1 - x_{aq,CO_2}. $$

(2.26)

The calculation of $x_i$ the phase mole fraction of component $j$ in phase $i$ for H$_2$O–CO$_2$ mixtures is now complete.

Plots for the mole fractions $x_{aq,CO_2}$ and $x_{ca,H_2O}$ are shown in Fig. 2.3 to Fig. 2.14 and are plotted against experimental data (Wiebe and Gaddy, 1939, 1940, 1941; Tödheide and Franck, 1963; Takenouchi and Kennedy, 1964; Greenwood and Barnes, 1966; Coan and King Jr, 1971; Gillespie and Wilson, 1982; Briones et al., 1987; Song and Kobayashi, 1987; Müller et al., 1988; D’Souza et al., 1988; Sako et al., 1991; King et al., 1992; Dohrn et al., 1993; Jackson et al., 1995; Teng et al., 1997; Bamberger et al., 2000; Rosenbauer et al., 2001). The data from Tödheide and Franck (1963) in Fig. 2.14 were reported with a low precision of ±1 mol%. For a discussion of the experimental errors of the experimental data used, the reader is referred to the discussion section of Sprecher et al. (2003).
2.2 Fugacity Coefficients of CO₂ - H₂O Mixtures

Figure 2.3: Concentration of CO₂ in aqueous phase at 15°C with data from King et al. (1992), Teng et al. (1997) and Gillespie and Wilson (1982).

Figure 2.4: Concentration of H₂O in carbonic phase at 15°C with data from King et al. (1992), Gillespie and Wilson (1982) and Song and Kobayashi (1987).
2.2 FUGACITY COEFFICIENTS OF $\text{CO}_2$ – $\text{H}_2\text{O}$ MIXTURES

Figure 2.5: Concentration of $\text{CO}_2$ in aqueous phase at 25 °C with data from King et al. (1992), Wiebe and Gaddy (1940), and Gillespie and Wilson (1982).

Figure 2.6: Concentration of $\text{H}_2\text{O}$ in carbonic phase at 25 °C with data from King et al. (1992), Wiebe and Gaddy (1940), Coan and King Jr (1971), Gillespie and Wilson (1982), and Song and Kobayashi (1987).
2.2 FUGACITY COEFFICIENTS OF CO₂–H₂O MIXTURES

Figure 2.7: Concentration of CO₂ in aqueous phase at 31 °C with data from Wiebe and Gaddy (1940) and Gillespie and Wilson (1982).

Figure 2.8: Concentration of H₂O in carbonic phase at 31 °C with data from Wiebe and Gaddy (1941), Gillespie and Wilson (1982), and Song and Kobayashi (1987).
Figure 2.9: Concentration of CO$_2$ in aqueous phase at 50 °C with data from Wiebe and Gaddy (1939), Tödheide and Franck (1963), Briones et al. (1987), D’Souza et al. (1988), Dohrn et al. (1993), and Bamberger et al. (2000).

Figure 2.10: Concentration of H$_2$O in carbonic phase at 50 °C with data from Wiebe and Gaddy (1941), Wiebe and Gaddy (1939), Coan and King Jr (1971), Tödheide and Franck (1963), Jackson et al. (1995), Briones et al. (1987), D’Souza et al. (1988), Dohrn et al. (1993), and Bamberger et al. (2000).
2.2 FUGACITY COEFFICIENTS OF CO₂—H₂O MIXTURES

Figure 2.11: Concentration of CO₂ in aqueous phase at 80 °C with data from Bamberger et al. (2000).

Figure 2.12: Concentration of H₂O in carbonic phase at 80 °C with data from Bamberger et al. (2000).
2.2 FUGACITY COEFFICIENTS OF CO₂—H₂O MIXTURES

Figure 2.13: Concentration of CO₂ in aqueous phase at 100 °C with data from Wiebe and Gaddy (1939), Tödheide and Franck (1963), and Müller et al. (1988).

Figure 2.14: Concentration of H₂O in carbonic phase at 100 °C with data from Coan and King Jr (1971), Tödheide and Franck (1963), and Müller et al. (1988).
2.3 EXTENSION TO CO$_2$–HO$_2$–NACL MIXTURES

*Duan and Sun* (2003) derived an activity coefficient formulation based on a Pitzer ion-interaction model (a fifth-order virial expansion of Gibbs excess energy), combined with an equilibrium equation of state. The activity coefficient formulation was chosen by *Spycher and Pruess* (2005) for the extension of (*Spycher et al.*, 2003) to account for salt-out effects. *Duan and Sun* (2003) fitted their formulation to a large number of experimental data on solubility for pure water and electrolyte solutions in terms of pressure and temperature. It is valid for aqueous NaCl solutions in the temperature range from 273 to 533 K, for pressures from 0 to 2000 bar, and for a NaCl ionic strength up to 4.5 m. Their model introduces a general formulation of the activity coefficient $\gamma^*$ [-] of CO$_2$ in terms of dissolved salt ions $m_j$ [mol kg$^{-1}$] in molality scale by means of virial expansion of the excess Gibb’s energy for cations and anions

$$\ln(\gamma^* ) = 2\lambda (m_{Na} + m_K + m_{Ca} + m_{Mg})$$

$$+ \zeta m_{Cl} (m_{Na} + m_K + m_{Ca} + m_{Mg})$$

$$- 0.07m_{SO_4},$$

(2.27)

which is simplified for NaCl solutions by writing

$$\ln \gamma^* = 2\lambda m_{Na} + \zeta m_{Cl} m_{Na}.$$  

(2.28)

The molality scale is more practical over the mole fraction scale as it is independent of CO$_2$ solubility. The second-order and third-order interaction parameters $\lambda$ and $\zeta$ are given by

$$\text{Par}(T, p) = c_1 + c_2 T + \frac{c_3}{T} + \frac{c_4 p}{T} + \frac{c_5 p}{630 - T} + c_6 T \ln p,$$

(2.29)

in which *Par* stands for the respective parameter, T is temperature in Kelvin, p is pressure in bar. The values for coefficients $c_1$ – $c_6$ are given in table 2.2.
Since $\gamma^*$ is not a true activity coefficient, i. e. it does not depend on salt concentration whilst deviating from unity at non-zero concentration of the dissolved CO$_2$, it is related to the CO$_2$ solubility by

$$m_{\text{CO}_2} = m_{\text{CO}_2}^0 / \gamma^*$$

(2.30)

where $m_{\text{CO}_2}^0$ is the aqueous CO$_2$ molality in pure water [mol kg$^{-1}$] at $T$ and $p$ calculated from Eq. 2.24, and $m_{\text{CO}_2}$ is the aqueous CO$_2$ molality [mol kg$^{-1}$] in a saline solution. Eq. 2.30 allows to calculate the mole fraction of CO$_2$ in the aqueous phase

$$x_{\text{aq,CO}_2} = \frac{m_{\text{CO}_2}}{m_{\text{CO}_2} + 55.508 + \nu m_s}$$

(2.31)

where $m_s$ is the salt molality, and $\nu$ is the stochiometric number of ions in the dissolved salt, here $\nu = 2$. Using

$$x_{\text{salt}} = \frac{\nu m_s}{55.508 + \nu m_s + m_{\text{CO}_2}}$$

(2.32)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>$\lambda_{\text{CO}_2-\text{Na}}$</th>
<th>$\zeta_{\text{CO}_2-\text{Na-Cl}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>-0.411 370 585</td>
<td>3.363 897 23 × 10$^{-4}$</td>
</tr>
<tr>
<td>$c_2$</td>
<td>6.076 320 13 × 10$^{-10}$</td>
<td>1.982 989 80 × 10$^{-2}$</td>
</tr>
<tr>
<td>$c_3$</td>
<td>97.534 770 8</td>
<td>0</td>
</tr>
<tr>
<td>$c_4$</td>
<td>-0.023 762 246 9</td>
<td>2.122 220 83 × 10$^{-3}$</td>
</tr>
<tr>
<td>$c_5$</td>
<td>0.017 065 623 6</td>
<td>-5.248 733 03 × 10$^{-3}$</td>
</tr>
<tr>
<td>$c_6$</td>
<td>1.413 358 34 × 10$^{-5}$</td>
<td>0</td>
</tr>
</tbody>
</table>
will finally give for the component mole fractions $x_j$ in phase $i$ and for equilibrium rates $K_j$

\[
x_{\text{aq,H}_2\text{O}} = 1 - x_{\text{aq,CO}_2} - x_{\text{aq,NaCl}} \quad (2.33)
\]

\[
x_{\text{ca,H}_2\text{O}} = \frac{\kappa_{\text{H}_2\text{O}} 0 (1 - x_{\text{aq,CO}_2} - x_{\text{aq,NaCl}})}{\varphi_{\text{H}_2\text{O}} p} \exp \left( \frac{(p - p^0) V_{\text{H}_2\text{O}}}{RT} \right) \quad (2.34)
\]

\[
x_{\text{ca,CO}_2} = 1 - x_{\text{ca,H}_2\text{O}} \quad (2.35)
\]

\[
K_{\text{CO}_2} = \frac{x_{\text{ca,CO}_2}}{x_{\text{aq,H}_2\text{O}}} \quad (2.36)
\]

\[
K_{\text{H}_2\text{O}} = \frac{x_{\text{ca,H}_2\text{O}}}{x_{\text{aq,H}_2\text{O}}} \quad (2.37)
\]

Finally, mutual solubility of H$_2$O and CO$_2$ in CO$_2$–H$_2$O–NaCl mixtures are now possible to determine by calculating the phase mole fraction $x_j$ of component $j$ in phase $i$ for CO$_2$–H$_2$O mixtures by using Eq. 2.31, Eq. 2.33, Eq. 2.34, and Eq. 2.35.
Figure 2.15: Concentration of CO$_2$ in aqueous phase with dissolved NaCl at 30 °C.

Figure 2.16: Concentration of H$_2$O in carbonic phase with dissolved NaCl at 30 °C
Figure 2.17: Concentration of CO$_2$ in aqueous phase with dissolved NaCl at 60 °C.

Figure 2.18: Concentration of H$_2$O in carbonic phase with dissolved NaCl at 60 °C
Figure 2.19: Concentration of CO$_2$ in aqueous phase with dissolved NaCl at 90 °C

Figure 2.20: Concentration of H$_2$O in carbonic phase with dissolved NaCl at 90 °C
2.4 THERMOPHYSICAL PROPERTIES OF FLOW AND TRANSPORT PARAMETERS

Simulation of compressible multi-phase multi component flow and transport requires data on thermophysical properties. The previous section Sec. 2.3 enabled to calculate phase composition in terms of phase mole fraction $x_{ij}$ of component $j$ in phase $i$ for $\text{CO}_2-\text{H}_2\text{O}-\text{NaCl}$ mixtures by using Eq. 2.31, Eq. 2.33, Eq. 2.34, and Eq. 2.35. Further data is needed on phase densities, phase compressibilities and phase viscosities. As this section merely is a collection of experimental work by others, the reader is referred to the original publications. As far as possible, all symbols and units used therein have been adopted unchanged, as measurements were taken in non-SI units. The straight-forward adoption leads to the unfortunate situation that the same symbol can have different meaning in different context. However, the situation only applies to this section and following chapters use a consistent nomenclature. Within the research code CSMP++ used in this work values were transferred internally into SI units.

2.4.1 Phase Densities

The aqueous phase density is calculated using the correlation of *Rowe and Chou* (1970) and given by

\[
\frac{1}{\rho_{aq}} = \left( a_1 - a_2 \pi - a_3 \pi^2 + a_4 X_{aq,NaCl} + a_5 X_{aq,NaCl}^2 - a_6 \pi X_{aq,NaCl} 
- a_7 \pi X_{aq,NaCl}^2 - 0.5 a_8 \pi^2 X_{aq,NaCl} \right) \times 10^{-3}
\]  

(2.38)
where pressure $\pi$ [kgf/cm$^2$] is in cgs units, $X_{aq,NaCl}$ is the mass fraction of NaCl in the aqueous phase [-], and the temperature $T$ [K] dependent coefficients $a_1, \ldots, a_8$ are calculated as

$$a_1 = 5.916365 - 0.01035794 T + 0.9270048 \times 10^{-5} T^2 - \frac{1127.522}{T} + \frac{100674.1}{T^2}$$

$$a_2 = 0.520491 \times 10^{-2} - 0.10482101 \times 10^{-4} T + 0.8328532 \times 10^{-8} T^2 - \frac{1.1702939}{T} + \frac{102.2783}{T^2}$$

$$a_3 = 0.118547 \times 10^{-7} - 0.6599143 \times 10^{-10} T$$

$$a_4 = -2.5166 + 0.011176 T - 0.170522 \times 10^{-4} T^2$$

$$a_5 = 2.84851 - 0.0154305 T + 0.223982 \times 10^{-4} T^2$$

$$a_6 = -0.0014814 + 0.829636 \times 10^{-5} T - 0.12469 \times 10^{-7} T^2$$

$$a_7 = 0.0027141 - 0.15391 \times 10^{-4} T + 0.22655 \times 10^{-8} T^2$$

$$a_8 = 0.62158 \times 10^{-6} - 0.40075 \times 10^{-8} T + 0.65972 \times 10^{-11} T^2.$$

(2.39)

The calculation is valid for the temperature range 0-175 °C, for the pressure range 0-350 kg cm$^{-2}$, and NaCl-concentration range 0 weight % to 25 weight %. The density of the CO$_2$-saturated aqueous phase $\rho_{aq, sat}$ [m$^3$ kg$^{-1}$] is calculated by using the correlation

Garcia (2001)

$$\rho_{aq, sat} = \frac{1 + \frac{M_{CO_2}}{M_{H_2O}} X_{aq, CO_2}}{\frac{V_\phi}{M_{H_2O}} X_{aq, H_2O} + \frac{1}{\rho_{aq}}}$$

(2.40)

where $M_{H_2O}$ and $M_{CO_2}$ are the molecular weight of the solvent H$_2$O and of the solute CO$_2$ [kg mol$^{-1}$], $X_{aq, H_2O}$ and $X_{aq, CO_2}$ are the respective phase mole fraction, and $V_\phi$ [cm$^3$ mol$^{-1}$] is the partial molar volume of CO$_2$ in water as a function of temperature. It is calculated by

$$V_\phi = 37.51 - 9.585 \times 10^{-2} \theta + 8.740 \times 10^{-4} \theta^2 - 5.044 \times 10^{-7} \theta^3.$$

(2.41)
where $\theta$ is the temperature in °C. For the carbonic phase density it is assumed that there is no H$_2$O dissolved. This allows to calculate the density from the molar volume $V_m$ knowing the molecular weight of CO$_2$

$$
\rho_{ca} = \frac{M_{CO_2}}{V_m}.
$$

(2.42)

### 2.4.2 Phase Compressibility

The aqueous phase compressibility $c_{aq}$ [kPa$^{-1}$] is given by the correlation of Rowe and Chou (1970) as

$$
c_{aq}(p) = \frac{\rho_{aq}(p) - \rho_{aq}^0}{\rho_{aq}(p)(p - p^0)}
$$

(2.43)

where $\rho_{aq}^0$ is the aqueous phase density [kg m$^{-3}$] at reference pressure $p^0 = 101.325$ kPa and $\rho_{aq}(p)$ the aqueous phase density at pressure $p$ [bar]. The carbonic phase compressibility $c_{ca}$ [bar$^{-1}$] can be derived from the equation of state Eq. 2.1 by differentiation with respect to volume (Mathias et al., 2008)

$$
c_{ca} = -\frac{1}{V_m} \frac{dV}{dp},
$$

(2.44)

with

$$
\frac{dp}{dV} = -\frac{RT}{(V_m - b_{CO_2})^2} + \frac{a_{CO_2}(2V_m + b_{CO_2})}{\sqrt{T}V_m^2(V_m + b_{CO_2})}.
$$

(2.45)

### 2.4.3 Phase Viscosities

**Viscosity of the Aqueous Phase** The viscosity for aqueous NaCl solutions $\mu_{aq}$ [$\mu$Pa s] can be calculated using the correlation by Kestin et al. (1978a,b, 1981) neglecting the effect of dissolved CO$_2$ as proposed by Sayegh and Najman (1987), Enick and Klara (1992) and Batzle and Wang (1992). The correlation is

$$
\mu_{aq} = \mu_{aq}^0(\theta, b_{NaCl})(1 + \beta(\theta, b_{NaCl})p),
$$

(2.46)
where \( \mu_0^{\text{aq}}(\theta, b_{\text{NaCl}}) \) is the zero-pressure viscosity of pure water at the limit of zero concentration [\( \mu \text{Pa s} \)] and \( \beta(\theta, b_{\text{NaCl}}) \) a pressure coefficient [\( \text{Pa}^{-1} \)], \( \theta \) the temperature [\( ^\circ \text{C} \)] and \( b_{\text{NaCl}} \) the salt molality [\( \text{mol kg}^{-1} \)]. The former is calculated by introducing the relative viscosity \( \mu_{\text{aq}, r}^{0}(\theta, b_{\text{NaCl}}) [-] \)

\[
\mu_{\text{aq}, r}^{0}(\theta, b_{\text{NaCl}}) = \frac{\mu_{\text{aq}}^{0}(\theta, b_{\text{NaCl}})}{\mu_{\text{aq}}^{0}(\theta, 0)}, \quad (2.47)
\]

where \( \mu_{\text{aq}}^{0}(\theta, 0) \) is the viscosity of water at low pressure given by

\[
\log \left( \frac{\mu_{\text{aq}}^{0}(\theta, 0)}{\mu_{\text{aq}}^{0}(20 ^\circ \text{C}, 0)} \right) = \frac{1}{96 - \theta} \sum_{i=1}^{4} c_i (20 + \theta)^i, \quad (2.48)
\]

with constant \( \mu_{\text{aq}}^{0}(20 ^\circ \text{C}, 0) = 1002.0 \mu \text{Pa s} \). The relative viscosity \( \mu_{\text{aq}, r}^{0}(\theta, b_{\text{NaCl}}) \) is given by

\[
\log \left( \frac{\mu_{\text{aq}, r}^{0}(\theta, b_{\text{NaCl}})}{\mu_{\text{aq}}^{0}(20 ^\circ \text{C}, 0)} \right) = A(b_{\text{NaCl}}) + B(b_{\text{NaCl}}) \log \left( \frac{\mu_{\text{aq}}^{0}(\theta, 0)}{\mu_{\text{aq}}^{0}(20 ^\circ \text{C}, 0)} \right) \quad (2.49)
\]

\[
A(b_{\text{NaCl}}) = \sum_{i=1}^{3} a_i (b_{\text{NaCl}})^i, \quad (2.50)
\]

\[
B(b_{\text{NaCl}}) = \sum_{i=1}^{3} b_i (b_{\text{NaCl}})^i. \quad (2.51)
\]

The pressure coefficient \( \beta \) in Eq. 2.46 is determined by

\[
\beta(\theta, b_{\text{NaCl}}) = \beta_{\text{s}}^{\text{E}}(\theta, b_{\text{NaCl}}) \beta^*(b_{\text{NaCl}}) - \beta_{\text{aq}}(\theta), \quad (2.52)
\]

where \( \beta_{\text{aq}} \) [\( \text{GPa}^{-1} \)] is the pressure coefficient for pure water given by

\[
\beta_{\text{aq}}(\theta) = \sum_{i=0}^{4} d_i \theta^i, \quad (2.53)
\]

and \( \beta_{\text{s}}^{\text{E}} \) is the excess pressure coefficient [\( \text{GPa}^{-1} \)] at saturated NaCl-concentration \( b_{\text{NaCl}}^{\text{satt}} \) [\( \text{mol kg}^{-1} \)] calculated by

\[
\beta_{\text{s}}^{\text{E}}(\theta) = 0.545 + \left( (0.28 \times 10^{-2}) \theta - \beta_{\text{aq}}(\theta) \right). \quad (2.54)
\]
The value of the reduced pressure coefficient $\beta^*$ [-] is calculated in terms of the reduced NaCl-concentration $b^*_{\text{NaCl}}$ [-] through

$$\beta^*(b^*_{\text{NaCl}}) = 2.5 b^*_{\text{NaCl}} - 2.0 b^2_{\text{NaCl}} + 0.5 b^3_{\text{NaCl}}, \quad (2.55)$$

with the reduced NaCl-concentration $b^*_{\text{NaCl}}$ calculated by

$$b^*_{\text{NaCl}} = b_{\text{NaCl}} / b_{\text{NaCl}}^{\text{sat}}, \quad (2.56)$$

and the saturated NaCl-concentration $b_{\text{NaCl}}^{\text{sat}}$ calculated by

$$b_{\text{NaCl}}^{\text{sat}}(\theta) = \sum_{i=0}^{2} e_i \theta^i. \quad (2.57)$$

The viscosity correlation is valid for the temperature range 20–150 °C, for the pressure range 0.1 to 30 MPa and for the concentration range 0 to 5.4 m. The viscosity varies only weakly with pressure.

**Viscosity of the Carbonic Phase**  Viscosity calculations for CO$_2$ are based on gas kinetic theory (Kestin *et al.*, 1972; Trengove and Wakeham, 1987) where collisions between molecules determine the bulk properties of a substance. The intermolecular forces between pairs of molecules undergoing collisions can be captured by a potential $U$ which accounts for shape, orientation and separation. For example, the viscosity $\mu$ can be described following Trengove and Wakeham (1987)

$$\mu = \frac{5 \sqrt{mkT / \pi}}{15 \sigma^2 \Omega_{\mu}^*(T^*)}, \quad (2.58)$$
where $m$ [kg mol$^{-1}$] is the molecular mass of the molecule of interest, $T$ the absolute temperature [K] and $k$ the Boltzmann’s constant [J K$^{-1}$], $\sigma$ a length scaling parameter [nm], and $\Omega^*$ a functional of the pair potential for the interaction between molecules, sometimes referred to as collision integrals. Vesovic et al. (1990) have replaced $\Omega^*$ by the effective cross section $\Theta$ to arrive at a more compact notation at the zero density limit. Here we use Vesovic et al. (1990) and Fenghour et al. (1998) to implement CO$_2$ viscosity calculation into CSMP++, assuming the gas phase consists of pure CO$_2$. The correlations are valid for the temperature range 0-1500 K and for the pressure range 0 MPa to 100 MPa. The total viscosity of CO$_2$ is then expressed as a sum of three independent contributions

$$
\mu_{ca}(\rho, T) = \mu_{ca}^0(T) + \Delta \mu_{ca}(\rho, T) + \Delta \mu_{ca}^\mu(\rho),
$$

(2.59)

where $\mu_{ca}^0$ is the viscosity [µPa s] in the limit of zero density with vanishing two-body molecular interactions, the last term $\Delta \mu_{ca}^\mu$ is the critical enhancement [µPa s] accounting for long-range fluctuations at the CO$_2$’s critical point, and $\Delta \mu_{ca}$ is the excess property [µPa s] including all other effects at elevated densities (i.e. many-body collisions, molecular-velocity correlations, and collisional transfer). The first term, the zero-density viscosity $\mu_{ca}^0(T)$, is given by

$$
\frac{1}{\Theta_{\mu}^* (T^*)} = 1.00697 \sqrt{T} \quad (2.60)
$$

$$
\ln \Theta_{\mu}^* (T^*) = \sum_{i=0}^{4} a_i (\ln T^*)^i \quad (2.61)
$$

$$
T^* = kT / \epsilon \quad (2.62)
$$

$$
\frac{\epsilon}{k} = 251.196 \text{ K}, \quad (2.63)
$$

where $\mu_{ca,0}$ is valid for a temperature range of 200-1500 K, $\Theta_{\mu}^*$ the reduced effective cross section [-], $T^*$ the reduced temperature [-], and $\epsilon/k$ the energy scaling parameter,
Table 2.4: Coefficients for the calculation of carbonic viscosity $\mu_{ca}$

<table>
<thead>
<tr>
<th>Index</th>
<th>$a_i$</th>
<th>$d_i$</th>
<th>$e_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.235156</td>
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<td></td>
</tr>
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<td>1</td>
<td>-0.491266</td>
<td>0.4071119 × 10^{-2}</td>
<td>5.5934 × 10^{-3}</td>
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<td>5.21155 × 10^{-2}</td>
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<td>6.1757 × 10^{-5}</td>
</tr>
<tr>
<td>3</td>
<td>5.347906 × 10^{-2}</td>
<td>0.2411697 × 10^{-16}</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>-1.537102 × 10^{-2}</td>
<td>0.2971072 × 10^{-22}</td>
<td>2.6430 × 10^{-11}</td>
</tr>
<tr>
<td>5</td>
<td>-0.1627888 × 10^{-22}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and coefficients $a_i$ given in Tab. 2.4. The excess viscosity $\Delta \mu_{ca}$ and the critical enhancement $\Delta \mu_{ca,c}$ are given by

\[
\Delta \mu_{ca}(\rho, T) = d_1 \rho + d_2 \rho^2 + \frac{d_3 \rho^6}{T^3} + d_4 \rho^8 + \frac{d_5 \rho^8}{T^4}
\] (2.64)

\[
\Delta \mu_{ca,c}(\rho) = \sum_{i=1}^{4} e_i \rho^i,
\] (2.65)

with coefficients $d_i, e_i$ shown in Tab. 2.4.

Plots of phase densities (Fig. 2.21 & Fig. 2.22), phase viscosities (Fig. 2.23 & Fig. 2.24), and phase compressibilities (Fig. 2.25 & Fig. 2.26) in terms of pressure for different temperature are provided. Thermophysical properties of the carbonic close to the critical temperature of CO$_2$ at 31 °C are denoted by blue lines and exhibit discontinuities when pressure rises above the critical pressure of 73 bar as phase transition from gaseous to liquid CO$_2$ occurs.
2.4 THERMOPHYSICAL PROPERTIES OF FLOW AND TRANSPORT PARAMETERS

Figure 2.21: Density of aqueous phase at different temperature (blue: 30°C, green: 60°C, red: 90°C).

Figure 2.22: Density of carbonic phase at different temperature (blue: 30°C, green: 60°C, red: 90°C). The discontinuity due in the blue line is due to phase transition of CO₂ from gaseous to liquid CO₂ occurs as CO₂ is not yet in a super critical state (above 31°C).
2.4 THERMOPHYSICAL PROPERTIES OF FLOW AND TRANSPORT PARAMETERS

**Figure 2.23:** Viscosity of aqueous phase at different temperature (blue: 30 °C, green: 60 °C, red: 90 °C).

**Figure 2.24:** Viscosity of carbonic phase at different temperature (blue: 30 °C, green: 60 °C, red: 90 °C). The discontinuity due in the blue line is due to phase transition of CO$_2$ from gaseous to liquid CO$_2$ occurs as CO$_2$ is not yet in a super critical state (above 31 °C).
2.4 THERMOPHYSICAL PROPERTIES OF FLOW AND TRANSPORT PARAMETERS

Figure 2.25: Compressibility of aqueous phase at different temperature (blue: 30°C, green: 60°C, red: 90°C).

Figure 2.26: Compressibility of carbonic phase at different temperature (blue: 30°C, green: 60°C, red: 90°C). The discontinuity due in the blue line is due to phase transition of CO₂ from gaseous to liquid CO₂ occurs as CO₂ is not yet in a super critical state (above 31°C).
This chapter provides the mathematical background of compressible, multi-component (compositional), multi-phase flow and transport with focus on devising a global pressure formulation. A global pressure formulation weakens the coupling between the mass balance equation and the pressure equation, which is suitable for operator-splitting methods within a finite element - finite volume discretisation of these equations. Migration and trapping of CO\textsubscript{2} can be significantly influenced when hysteresis is accounted for. Therefore, this chapter also provides relationships on non-wetting relative permeability hysteresis which constitutes the trapping model. Furthermore, it provides relationships between the ambient stress field at depth and fracture apertures realised through simple geomechanics. First, an introduction into the governing equations for compressible, compositional, multiphase flow and transport is presented (Sec. 3.1). Then, a global pressure formulation for the governing equations is devised (Sec. 3.2). Thereafter, the interface condition between fracture and matrix in the presence of capillary pressure are given based on the extended pressure condition (Sec. 3.3). Since saturation is not a conserved quantity, as mass transfer across the phase interface can take place, a saturation split is presented (Sec. 3.4). A trapping model based on non-wetting relative permeability hysteresis is introduced (Sec. 3.5). Fracture apertures are calculated by a simple geomechanical model, which accounts for stress at depth (Sec. 3.6) and is based on the Linear Elastic Fracture Model (Sec. 3.7). This chapter is closed by a brief summary of the governing equation and primary variables used (Sec. 3.8).

Throughout this chapter, I assume that the aqueous phase is the wetting phase, whereas the carbonic phase is the non-wetting phase.
3.1 GOVERNING EQUATIONS

Let a porous medium $\Omega$ be a bounded open domain in $\mathbb{R}^d, d \leq 3$ with boundary $\partial \Omega$ and outer unit normal $\mathbf{n}_{\partial \Omega}$. Unlike in immiscible two-phase flow, saturation is not a conserved quantity because mass transfer of $\text{CO}_2$ and $\text{H}_2\text{O}$ across the phase boundaries takes place. However, mass conservation across phases is still preserved. Flow of a slightly compressible isothermal fluid in fractured media with component transfer across the phase interface is described by a mass balance equation and and Darcy’s law for each fluid with thermophysical properties fully dependent on pressure, temperature and salinity. The mass balance equation for a compositional system with given component mass density $M_j$ is

$$\partial_t M_j(\mathbf{x}) = - \text{div} F_j(\mathbf{x}) + q_j, \quad j \in \{\text{H}_2\text{O}, \text{CO}_2\}. \quad (3.1)$$

The mass accumulation term or component mass density $M_j$ of component $j$ is

$$M_j = \phi(\mathbf{x}) \sum_{i}^{n_p} S_i X_{ij} \rho_i \quad i \in \{w, n\} \quad j \in \{\text{H}_2\text{O}, \text{CO}_2\} \quad (3.2)$$

summed over all $n_p$ phases of component $j$ and the flux function is

$$F_j = \sum_{i}^{n_p} X_{ij} \rho_i \mathbf{v}_i(\mathbf{x}), \quad (3.3)$$

where $\phi[-]$ is the porosity, $\rho_i [\text{kg/m}^2]$ the phase density, is $X_{ij}[-]$ is the phase mass fraction, and the phase saturations $S_i[-]$ are assumed to completely fill the pore space

$$\sum_{i=1}^{n_p} S_i = 1 \quad i \in \{w, n\} \quad (3.4)$$

and phase mass fractions add up to unity

$$\sum_{j=1}^{n_p} X_{ij} = 1 \quad i \text{ fixed,} \quad j \in \{\text{H}_2\text{O}, \text{CO}_2\}. \quad (3.5)$$
The mass balance equation requires a velocity field which we take from Darcy’s law. Originally it was developed for laminar single-phase flow in a porous media, but has been extended to account for multi-phase flow by introducing bounded relative permeability functions $k_{ri} : [S_{nr}, 1 - S_{wr}] \rightarrow [0, 1]$ with residual saturations $S_{nr}$ and $S_{wr}$.

$$v_i(x) = -\sum_{t} \frac{k_{ri}}{\mu_i} \mathbf{K}(x) \left( \text{grad} \, p_i - \rho_i \mathbf{g} \right) \quad i \in \{w, n\},$$  \hspace{1cm} (3.6)

where $v_i [m^3/m^2/s]$ is the volumetric phase velocity, also known as the Darcy velocity or specific discharge, $\mathbf{K}(x)$ is the locally varying permeability tensor field $[m^2]$, $\mu_i$ the phase viscosity $[Pa \, s]$, $p_i$ the phase pressure $[Pa]$ and $\mathbf{g}$ is the gravitational acceleration vector $[m/s^2]$. It represents a momentum balance equation (Hubbert, 1956; Whitaker, 1986). Inserting Eq. 3.6 into Eq. 3.1 leads to a generalised form of a compositional two-phase model

$$\partial_t M_j = \text{div} \left( X_{ij} \rho_i \mathbf{K} \left( \frac{k_{ri}}{\mu_i} \left( \text{grad} \, p_i - \rho_i \mathbf{g} \right) \right) \right) + q_j \quad i \in \{w, n\} \quad \text{and} \quad j \in \{H_2O, CO_2\}.$$  \hspace{1cm} (3.7)

Boundary and initial conditions are given on pairwise disjunct sets $\partial \Omega_D \cap \partial \Omega_D \cap \Omega = \emptyset$ such that

$$p_i(x,t) = p_d(x,t) \quad \forall x \in \partial \Omega_D \quad (3.8)$$

$$M_j(x,t) = M_{j,d}(x,t) \quad \forall x \in \partial \Omega_D \quad (3.9)$$

$$(X_{ij} \rho_i v_i, n_{\partial \Omega}) = V(x,t) \quad \forall x \in \partial \Omega_N \quad (3.10)$$

and

$$p_i(x,0) = p_0(x) \quad \forall x \in \Omega \quad (3.11)$$

$$M_j(x,0) = M_{j,0}(x) \quad \forall x \in \Omega \quad (3.12)$$

3.2 Global Pressure Formulation

When compared to phase formulation of the pressure equation (Helmig and Huber, 1998; Helmig et al., 2010), global pressure formulation (Chavent, 1976; Kružkov and Sukorjanskii,
...are more efficient from a computational point of view (Binning and Celia, 1999), because the partial differential equations describing fluid pressure and mass distributions resemble governing equations of single-phase flow (Chen and Ewing, 1997b). Using the phase formulation, boundary conditions can be specified easier and are therefore commonly used in the hydrology community, whereas global pressure formulation are widely used in the petroleum industry due to their numerical efficiency. The existence of a compressible global pressure formulation fully equivalent to the two-pressure approach has been claimed recently (di Chiara Roupert et al., 2010; Amaziane et al., 2011) with application to an immiscible, compressible, two-phase system including capillary forces (Amaziane et al., 2012). The global pressure formulation weakens the non-linear character of the coupling between the mass balance and the pressure equation due to the presence of the total mobility and fractional flow functions. Operator-splitting methods such as the finite element - finite volume method presented here can exploit the weakening to avoid costly iterative methods such as the Newton-Raphson method (Helmig et al., 2010).

I follow the global pressure formulation and devise a global pressure formulation for compressible fluids from the compositional mass balance equation (Eq. 3.1) assuming laminar flow so Darcy’s law can be used to specify the flux function (Eq. 3.3). Furthermore differences in phase pressures arising from capillary pressure are neglected when thermodynamic properties such as phase densities, viscosities and compressibilities are used (Fritz, 2010). The work of Galusinski and Saad (2009) gives a mathematical proof which justifies this approach for small capillary pressures if the weak formulation of the pressure equation is rewritten to include capillary pressure dependence in the thermo-physical properties. The global pressure formulation requires the definition of a global pressure which provides mean values between the wetting and non-wetting phase pressure and is smoother than any of the phase pressures in the presence of capillary forces. This formulation provides a total velocity field which together with fractional flow functions are used in the mass balance equation. If slightly compressible fluids, i.e. $\partial_t \rho_i \neq 0$, are accounted for, quadratic terms in velocities appear both in the pressure and in the mass balance equation. If an explicit temporal discretisation such as the forward Euler
method is applied to the mass balance equation, the quadratic terms will impose severe restrictions on the time stepping. This restriction motivates a further operator-splitting presented later (see Sec. 4.2).

For an isothermal system the temporal change for the mass accumulation term Eq. 3.2 is

$$\partial_t (\phi S_i X_{ij} \rho_i) = \rho_i S_i X_{ij} \frac{\partial \phi}{\partial t} + \phi \rho_i X_{ij} \frac{\partial S_i}{\partial t} \frac{\partial p_i}{\partial t} + \phi \rho_i S_i \frac{\partial X_{ij}}{\partial t} \frac{\partial p_i}{\partial t} + \phi S_i X_{ij} \frac{\partial \rho_i}{\partial t} \frac{\partial p_i}{\partial t}$$

$$= S_i X_{ij} \rho_i \frac{\partial \phi}{\partial t} + \left( S_i X_{ij} \frac{\partial \rho_i}{\partial p_i} + \phi X_{ij} \rho_i \frac{\partial S_i}{\partial p_i} + \phi S_i \rho_i \frac{\partial X_{ij}}{\partial p_i} \right) \frac{\partial p_i}{\partial t}. \quad (3.13)$$

Division by phase densities $\rho_i$ and subsequent summation over all phases $i$ and components $j$ yields

$$\sum_{ij}^{n_p, n_c} \frac{1}{\rho_i} \partial_t (\phi S_i X_{ij} \rho_i) = \frac{\partial \phi}{\partial t} + \sum_{ij}^{n_p, n_c} \left( \phi S_i X_{ij} \frac{1}{\rho_i} \frac{\partial \rho_i}{\partial p_i} \right) \frac{\partial p_i}{\partial t} +$$

$$\sum_{ij}^{n_p, n_c} \left( \phi X_{ij} \frac{\partial S_i}{\partial p_i} + \phi S_i \frac{\partial X_{ij}}{\partial p_i} \right) \frac{\partial p_i}{\partial t}. \quad (3.14)$$

To resolve those terms in Eq. 3.14, which includes derivatives in $S_i$ and $X_{ij}$, note that a change in phase $i$ induces a change in all other phases $k \leq n_p$, with $k \neq i$. Together with Eq. 3.4 and Eq. 3.5 following identity holds

$$S_i + \sum_{k=1}^{n_p} S_k = 1 \quad (3.15)$$

$$\Rightarrow \quad S_i + \Delta S_i + \sum_{k=1}^{n_p} S_k + \Delta S_k = 1 \quad (3.16)$$

$$\Rightarrow \quad \Delta S_i = -\sum_{k=1}^{n_p} \Delta S_k. \quad (3.17)$$

This argument can be applied analogously to $X_{ij}$ as well. It states that any change in $S_i$ or $X_{ij}$ is compensated by the sum of changes of all other phases or components.
Hence, those sums in Eq. 3.14 with derivatives in in \( S_i \) or \( X_\phi \) evaluate to zero. Further exploitation of Eq. 3.4 and Eq. 3.5 then yields

\[
\sum_{ij}^{n_p,n_c} \frac{1}{\rho_i} \partial_t (\phi S_i X_\phi \rho_i) = \frac{\partial \phi}{\partial t} + \sum_i^{n_p} \left( \phi S_i \frac{1}{\rho_i} \frac{\partial \rho_i}{\partial p_i} \right) \frac{\partial p_i}{\partial t}. \tag{3.18}
\]

I assume, that changes in pore space are induced by changes in partial pressures \( p_i \), and are described by the rock compressibility \( \beta_r \), such that

\[
\frac{\partial \phi}{\partial t} = \sum_i^{n_p} \frac{\partial (\phi \beta_r)}{\partial p_i} \frac{\partial p_i}{\partial t} \tag{3.19}
\]

\[
= \beta_r \frac{\partial p_i}{\partial t}, \tag{3.20}
\]

where \( \phi \) = 1 - \( \phi \) is the fractional space occupied by rock. Therefore, the temporal partial derivation term \( \partial_t (\phi S_i X_\phi \rho_i) \) in Eq. 3.13 finally simplifies to

\[
\sum_{ij}^{n_p,n_c} \frac{1}{\rho_i} \partial_t (\phi S_i X_\phi \rho_i) = \sum_i^{n_p} \left( (1 - \phi) \beta_r + \phi \beta_i \right) \frac{\partial p_i}{\partial t}, \tag{3.21}
\]

where \( \frac{1}{\rho_i} \frac{\partial \rho_i}{\partial p_i} = \beta_i \) is the phase compressibility.

Applying the product rule to the flux term on the right-hand side of Eq. 3.1 yields

\[
\text{div} \left( X_\phi \rho_i \mathbf{v}_i \right) = \rho_i \mathbf{v}_i \text{grad} X_\phi + X_\phi \mathbf{v}_i \text{grad} \rho_i + X_\phi \rho_i \text{div} \mathbf{v}_i. \tag{3.22}
\]

Division by phase densities \( \rho_i \), subsequent summation over all phases \( i \) and components \( j \), and further exploitation of the argument presented in Eq. 3.15 to Eq. 3.17 leads to

\[
\sum_j^{n_c} \text{grad} X_\phi = 0, \quad \text{and it follows}
\]

\[
\sum_{ij}^{n_p,n_c} \frac{1}{\rho_i} \text{div} \left( X_i \rho_i \mathbf{v}_i \right) = \sum_i^{n_p} \mathbf{v}_i \rho_i \text{grad} \rho_i + \sum_i^{n_p} \text{div} \mathbf{v}_i. \tag{3.23}
\]

Substituting the temporal derivation term (Eq. 3.18) for the mass accumulation term (Eq. 3.2), and respectively the spatial derivation term (Eq. 3.23) for the flux function
(Eq. 3.3), one arrives at the pressure equation derived from the mass balance equation (Eq. 3.1). The pressure equation is

$$\sum_{ij} \left( (1-\phi)\beta_r + \phi S_i \beta_i \right) \frac{\partial p_i}{\partial t} = -\sum_i n_c \text{div} v_i + \sum_i \frac{n_c}{f_i} \text{grad} p_i + \sum_{ij} \frac{n_c}{f_i} q_j.$$  \hspace{1cm} (3.24)

Here, the phase compressibilities depend on the thermophysical state $\beta_i = \beta_i(p, T)$, but the rock compressibility $\beta_r [Pa^{-1}]$ is assumed to be constant for a given rock type.

Phase mobilities $\lambda_i : [S_{wr}, 1 - S_{nr}] \rightarrow [0, \infty), \lambda_i = \frac{k_i}{\mu_i}$ are introduced, such that $\lambda_w(S_{wr}) = 0$ and $\lambda_n(1 - S_{nr}) = 0$, with $\lambda_i$ monotone Lipschitz functions (Cancès, 2009). The total mobility is $\lambda_t = \lambda_w + \lambda_n$. This enables us to define fractional flows $f_i : [0, 1] \rightarrow [0, 1]$ as

$$f_i = \frac{\lambda_i}{\lambda_t}$$  \hspace{1cm} (3.25)

where $f_n + f_w = 1$ (Chen and Huan, 2005). Note that non-linear fractional flow functions have usually S-shape form with the property that for $\lim S_w \rightarrow 1$ its derivative is $f_w'(S_w) = 0$. It is also possible to define fractional flow function in terms of the fluid flow functions $q_i$. Based on this definition the fractional flows allows to incorporate not only viscous, but also capillary and gravitational/density forces. The introduction of the global pressure $p$ aims to yield a smoother pressure field within the domain $\Omega$. With means of fractional flow functions such that $\text{grad} p = \sum_i n p_i \text{grad} p_i$ (Chavent and Jaffre, 1986) the global pressure can be defined as

$$p = \frac{1}{2}(p_w + p_n) - \int_{S_c} f(S_w) \left( f_1(S_w) - \frac{1}{2} \right) \frac{dp_c(S_w)}{d\xi} \, d\xi$$  \hspace{1cm} (3.26)

$$= p_w + p_c(S_w) - \int_{S_c} f_w(S_w) \frac{dp_c(S_w)}{d\xi} \, d\xi$$  \hspace{1cm} (3.27)

with $p_c(S_c) = 0$. The global pressure is not a meaningful physical variable and can not be measured directly. The equation implies that the pressure at which the fluid flows is equal to the sum of the phase flows. Different definitions of the global pressure exist based on the non-wetting phase pressure (Bastian, 1999), the arithmetic mean pressure (Durlofsky, 1993; Huber and Helmig, 1999; Nayagum et al., 2004), or a mobility weighted
3.2 Global Pressure Formulation

Note that in Eq. 3.26 and Eq. 3.27, capillary pressure is assumed to be homogeneous, i.e. a function of the wetting saturation only. A global pressure formulation allows to express the total velocity field without explicit capillary pressure term, i.e. it models a single phase fluid such that

\[ v_t = -\lambda_t K (\text{grad} \ p - G) \]  

(3.28)

with \( G = \sum_{i=1}^{n} f_i \rho_i \). Phase velocities can be expressed in terms of total velocity (see Eq. 3.37 and Eq. 3.38). First note that the capillary pressure links the phase pressures. Often it is assumed to be dependent on the wetting saturation only with \( p_c : [S_{wr}, 1 - S_{nr}] \rightarrow [0, \infty) \) a decreasing continuously differentiable function and defined as

\[ p_n - p_w = p_c(S_w). \]  

(3.29)

As outlined in the introduction of this chapter referring to work of Fritz (2010) and Galusinski and Saad (2009), I assume that phase pressure differences due to capillary pressures are small compared to reservoir conditions. Hence, changes in thermophysical properties due to changes in phase pressures are assumed to vary only in terms of a global pressure \( p \), so that the pressure equation can be reformulated in terms of the global pressure \( p \). With \( \sum_{i}^{n_p} v_i = v_t \), Eq. 3.24 becomes

\[ \sum_{i}^{n_p} \left( (1 - \phi) \beta_t + \phi S_i \beta_i \right) \frac{\partial p}{\partial t} = - \text{div} v_t + \sum_{i}^{n_p} \frac{f_i}{\rho_i} v_i \text{grad} \rho_i + \sum_{j}^{n_c} q_j \rho_i \]  

(3.30)

\[ = - \text{div} v_t + \sum_{i}^{n_p} f_i v_i \beta_i \text{grad} p + \sum_{i}^{n_c} q_i \]  

(3.31)

where \( \frac{1}{\rho_i} \nabla \rho_i = \frac{1}{\rho_i} \frac{\partial \rho_i}{\partial p} \nabla p = \beta_i \nabla p \), and \( \sum_{j}^{n_c} \frac{q_j}{\rho_i} = q_i \), the volumetric injection rate of phase \( i \). Note that the second term on the right-hand side is quadratic in velocity. Sometimes these quadratic terms are neglected, when compressibilities during pressure changes are very small, \( \beta(\Delta p) \ll 1 \) (see Durlofsky (1993) for an exemplary calculation).
Defining the total compressibility \( \beta_t = \sum_{p} ((1 - \phi) \beta_r + \phi S_i \beta_i) \), expressing total velocity in terms of the global pressure, further rearrangement yields

\[
\beta_t \partial_t p = \text{div} (\lambda_t K \text{grad} p) - (\lambda_w \beta_w + \lambda_n \beta_n) K \text{grad} p \text{grad} p
\]

\[
- \text{div} (\lambda_t K G) - (\lambda_w \beta_w + \lambda_n \beta_n) K G \text{grad} p + \sum_i q_i. \tag{3.32}
\]

Reformulating the mass balance equation Eq. 3.1 by using Eq. 3.3, Eq. 3.6, Eq. 3.29, Eq. 3.28, and Eq. 3.25, yields a phase velocity and phase pressure free formulation

\[
\partial_t M_j = - \text{div} \left( \sum_i \rho_i \lambda_i \partial_t V_i f_i \right) + \lambda_t \lambda_n \lambda_w K (\text{grad} p - \rho_w g) + q_j \quad k \in \{w, n\}, k \neq i. \tag{3.33}
\]

The phase velocities can be now expressed in terms of the wetting phase pressure \( p_w \)

\[
v_w = -\lambda_w K (\text{grad} p_w - \rho_w g) \tag{3.34}
\]

\[
v_n = -\lambda_n K (\text{grad} p_w + \text{grad} p_c - \rho_n g) \tag{3.35}
\]

Solving Eq. 3.35 for \( K \text{grad} p_w \) and inserting it into Eq. 3.34 gives

\[
v_w = -\lambda_w \left( -\frac{v_n}{\lambda_n} - \lambda_w K \text{grad} p_c + \lambda_w K \rho_n g \right) + \lambda_w K \rho_w g
\]

\[
= \frac{\lambda_w}{\lambda_t} v_n + \lambda_w K \text{grad} p_c + \lambda_w K (\rho_w - \rho_n) g \tag{3.36}
\]

Expressing the wetting phase velocity by \( v_w = v_t - v_n \) and analogue derivation of the non-wetting phase velocity leads to

\[
v_w = \frac{\lambda_w}{\lambda_t} v_t + \frac{\lambda_w \lambda_n}{\lambda_t} K (\text{grad} p_c + (\rho_w - \rho_n) g) \tag{3.37}
\]

\[
v_n = \frac{\lambda_n}{\lambda_t} v_t - \frac{\lambda_w \lambda_n}{\lambda_t} K (\text{grad} p_c + (\rho_w - \rho_n) g). \tag{3.38}
\]

3.3 TWO-PHASE FLOW IN HETEROGENEOUS MEDIA

Multi-phase flow including capillary effects in heterogeneous porous medium is closed by constitutive relationships which link saturation levels to capillary pressure and rel-
ative permeabilities. The latter describes the impediment of a phase by another one present. In reservoirs commonly used relationships are the van Genuchten and the Brooks-Corey models. Using the effective saturation $S_e$ defined as

$$S_e = \frac{S_w - S_{rw}}{1 - S_{rw} - S_{nr}},$$

we can write for the Van Genuchten model

$$k_{rw} = \sqrt{S_e} \left(1 - \left(1 - S_e^{1/m}\right)^{2m}\right)$$

$$k_{rn} = \left(1 - S_e\right)^{1/3} \left(1 - S_e^{3/2}\right)^{2m}$$

$$P_c = \frac{1}{\alpha} \left(S_e^{-1/m} - 1\right)^{-1/n}$$

$$P'_c = -\frac{1}{\alpha n m} \frac{1}{\left(1 - S_{rw} - S_{rn}\right)} \left(S_e^{-1/m} - 1\right)^{(1/n-1)} \left(S_e^{-1/m} - 1\right)^{-(1/n+1)},$$

Figure 3.1: The left figure shows a comparison of relative permeability curves $k_{ri}$ for a Brooks-Corey type (blue lines) and Van Genuchten type (red lines) model. The right figure shows their associated capillary diffusivities and capillary pressure derivative. The derivative of the capillary pressure function is scaled with permeability to allow direct comparison to the capillary diffusivity $D^{cap}$. Model parameters are $p_d = 2.0$ kPa, $\lambda = 2$, $m = 0.722$, $\mu_w = 5.97778 \times 10^{-4}$ Pa s, and $\mu_n = 5.433230 \times 10^{-5}$ Pa s.
and the Brooks-Corey Model

\[ k_{rw} = S_c^{(2+3)/\lambda} \]

\[ k_{rn} = (1 - S_c)^2 (1 - S_c)^{(2+3)/\lambda} \]

\[ P_c = p_d S_e^{-1/\lambda} \]

\[ P'_c = -\frac{p_d}{\lambda (1 - S_{rw} - S_{rn})} S_e^{-(1/\lambda + 1)} \]

where \( p_d \) is the capillary entry pressure and \( \lambda \) quantifying the pore size distribution. Both are fitting parameters tuned to experiments but for our purposes we fix them to constant values (see chapter Sec. 2.1). The entry pressure \( p_d \) has to be exceeded to start displacement of the wetting phase in the largest pore available at any phase saturation interface available.

In general, the capillary pressure is proportional to \( \sqrt{\phi/K} \), a quantity associated to the mean pore diameter, This relation is described by the Leverett J-function \( J(S_w) \), which enables the rescaling of \( p_c \) in a given lithology

\[ p_n - p_w = p_c(x, S_w, p_i, T) = \sigma(p_i, T) \sqrt{\frac{\phi(x)}{K(x)}} J(S_w) \]

where \( \sigma = \sigma(p_i, T) \) is the interfacial tension at the pore level. Capillary pressure for both, the Van Genuchten and the Brooks-Corey model can be described in terms of the Leverett J-relationship where \( 1/\alpha \) and \( p_d \) quantify the coefficient of \( J \). The capillary pressure for \( S_w \to 1 \) can be either \( p_c = 0 \) or \( p_c = p_d < \infty \). The Van Genuchten type model belong to the former and Brooks-Corey type to the latter case.

Consider a material discontinuity at \( x = 0 \) with domains denoted by I for \( x < 0 \) and II for \( x > 0 \) with different capillary pressure curves either side at \( x = 0 \) (Fig. 3.2), both initially filled with a wetting fluid. If there are entry pressures present with \( p_{d,I} < p_{d,II} \) then for the lower capillary pressure curve \( p_{c,I} < p_{c,II} \) there exists a threshold saturation \( S^* \) such that

\[ S^* = p_{c,I}^{-1}(p_{d,II}) = p_{c,II}^{-1}(p_{c,I}(1)) \]

where \( p_{c,I}^{-1} \) is the inverse function. The existence of the threshold saturation derives directly from the capillary pressure continuity condition which requires \( p_{c,I} = p_{c,II} \) with
$S_{w,I} \neq S_{w,II}$, sometimes denoted as the extended pressure condition \citep{VanDuijn1995}. More generally the condition reads to

$$
\begin{align*}
    p_{c,I} &= p_{c,II} \quad \text{if } S_{w,I} \leq S^* \\
    S_{w,I} &= 1 \quad \text{if } S^* < S_{w,I} \leq 1.
\end{align*}
$$

\begin{equation}
(3.50)
\end{equation}

For values $S_w > S^*$, the capillary pressure is discontinuous as the non-wetting saturation $S_{n,II}$ in domain II is immobile or vanishes, i.e. $S_{n,II} \leq S_{n,II}$. Hence the non-wetting phase pressure is undefined and a capillary pressure becomes physically meaningless, therefore discontinuous. As a consequence, the non-wetting phase can be immobilised by spatially varying capillary entry pressures. It follows for the saturation at the discontinuity

$$
S_{w,II} = \begin{cases} 
1 & \text{if } S^* < S_{w,I} \leq 1 \\
\frac{1}{p_{c,II}^{-1}(p_{c,I}(S_{w,I}))} & \text{if } S_{w,I} \leq S^*
\end{cases}
$$

\begin{equation}
(3.51)
\end{equation}

Depending on the flow direction, there can be a temporarily build up of the non-wetting saturation before a material heterogeneity.

(I) Brooks-Corey Type with $p_d \neq 0$

(II) Van Genuchten Type with $p_d = 0$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.2}
\caption{Illustration of the extended pressure condition on capillary pressure curves as a function of model parameters for the Brooks-Corey and Van Genuchten model. A material discontinuity exists at $x = 0$ separating two domains denoted by I for $x < 0$ and II for $x > 0$ with different capillary pressure curves either side. Phase viscosities are, $\mu_w = 5.97778 \times 10^{-4}$ Pa s, and $\mu_n = 5.433230 \times 10^{-5}$ Pa s.}
\end{figure}
Figure 3.3: Comparison of capillary pressure curves between a typical rock and an open fracture. The capillary pressure curve of the fracture is calculated with the Young-Laplace equation (Eq. 3.52) as a function of apertures $a_f$. Note that capillary pressures for fractures are very small compared to the entry pressure and hence can be chosen to be set to zero. Model parameters are $p_d = 2.0 \text{kPa}$, $\lambda = 2$, $m = 0.722$, $\mu_w = 5.97778 \times 10^{-4} \text{Pa s}$, and $\mu_n = 5.433230 \times 10^{-5} \text{Pa s}$. For the Young-Laplace equation an interfacial tension of $\sigma = 35 \times 10^{-6} \text{N m}^{-1}$ is used for a CO$_2$–H$_2$O system. The contact angle is $\theta = 20^\circ$.

Explicit representation of fractures embedded in a porous media introduces material discontinuities. For these discontinuities, capillary forces can be neglecting if fractures are assumed to be open, or the capillary model applied is inherited from the surrounding rock matrix with adjusted entry pressures and mean pore distributions if fractures are assumed to be filled. The presence of filled or open fractures depends on the geomechanical history of the lithology in question. If fractures are assumed to be open, the capillary pressure can be approximated by the Young-Laplace equation. It describes the capillary pressure in a sufficiently narrow tube model with a circular cross section of radius $r = a_f/2$, and fracture aperture $a$. The equation is

$$p_c = \frac{2\sigma \cos \theta}{r}$$ (3.52)

where $\theta$ is the contact angle [rad]. The interfacial tension between two phases is $\sigma$ [mN m$^{-1}$], and is a function of temperature, pressure and composition of each phase. If fracture apertures are sufficiently open, the capillary pressure in fractures can be well
below the entry pressure of the rock matrix (see Fig. 3.3). Hence, flow across the fracture-matrix interface only occurs, if capillary pressure will become continuous across it.

3.4 SATURATION SPLIT

Saturation is not a conserved quantity and needs to be calculated from the component mass $M_j$. This is done by using the Lever-Rule (Cheng and Wang, 1996; Pruess and Spycher, 2007). The CO$_2$ mass can be expressed either by summing dissolved and pure CO$_2$ components over all phases or by measuring the mass fraction of CO$_2$ associated with the total mass. Assuming, that the carbonic phase is the non-wetting phase, we have

$$M_{CO_2} = \sum_{j} \rho_i S_i X_i,CO_2$$

$$= \rho_w S_w X_{w,CO_2} + \rho_n (1 - S_w) X_{n,CO_2}$$

$$= S_w (\rho_w X_{w,CO_2} - \rho_n X_{n,CO_2}) + \rho_n X_{n,CO_2}$$

$$= S_w \rho_w X_{w,CO_2} - S_w \rho_n X_{n,CO_2} + \rho_n X_{n,CO_2}$$  (3.53)

and to account for the mass fraction of CO$_2$ contributing to the total mass we introduce

$$X_{CO_2} = \frac{M_{CO_2}}{M_{CO_2} + M_{H_2O}}$$  (3.54)

to get

$$M_{CO_2} = X_{CO_2} M_{tot}$$

$$= X_{CO_2} \sum_{j} \rho_i S_i$$

$$= \left( S_w \rho_w + (1 - S_w) \rho_n \right) X_{CO_2}$$

$$= S_w \rho_w X_{CO_2} + \rho_n X_{CO_2} - S_w \rho_n X_{CO_2}$$  (3.55)

Combining Eq. 3.53 with Eq. 3.55 and some rearranging yields

$$S_w \left( \rho_w (X_{w,CO_2} - X_{CO_2}) + \rho_n (X_{CO_2} - X_{n,CO_2}) \right) = \rho_n (X_{n,CO_2} - X_{CO_2}).$$  (3.56)
Hence, we arrive at the saturation split

\[ S_w = \frac{\rho_w (X_{w,CO_2} - X_{CO_2})}{\rho_n (X_{n,CO_2} - X_n) + \rho_w (X_{w,CO_2} - X_{CO_2})} \] (3.57)

The phase mass fractions \( X_{ij} = X_{ij}(p, T) \) are calculated from Eq. 2.23 to Eq. 2.26 using the modified Redlich-Kwong equation of state and fugacity coefficients. The mass fraction of \( CO_2, X_{CO_2} \), is calculated in the advection step (Sec. 4.5) after the FV-advection takes place.

### 3.5 Trapping Model for Wetting Rocks

Rock wettability is a prime factor in controlling multiphase flow and phase trapping (Kovscek et al., 1993). It dictates how a non-wetting fluid propagates through a porous media. Smaller pores are occupied by the wetting fluid, thus rendering smallest pores hydrodynamically most resistive. The non-wetting fluid chooses channels of least resistivity and distributes itself to the largest pore channels. Wettability can be broadly divided into three categories: strongly water-wet, strongly oil-wet (here carbonic-wet) and intermediate/mixed wet. For polished smoothed representative rock surfaces the most widely used measure for wettability is the contact angle. Water-wet surfaces exhibit contact angles of 0°C whereas oil-wet has an angle of 180°C.

**Observations** Both the primary drainage capillary pressure and the hysteresis in the \( CO_2 \) saturation influences its trapping behaviour (Pentland et al., 2011). The primary drainage capillary pressure is influenced by the threshold pressure needed to enter the rock and can control the containment of \( CO_2 \) within a storage repository when combined with low permeability barriers. The hysteresis is a function of the initial \( CO_2 \) saturation, sometimes referred to as the trapping curve, and controls the amount of \( CO_2 \) rendered discontinuous and immobile, thus trapped. Hence, both processes control how far the \( CO_2 \) plume can migrate and will affect injection strategies designed to be safe, especially if heterogeneities such as fractures are present.
Effective trapping can be achieved by means of smart injection for which a chasing water/brine injection follows the CO$_2$ injection causing imbibition at the trailing edge of the CO$_2$ plume. It requires the CO$_2$ phase to be non-wetting within the rock during both drainage and imbibition. However, there are indications that during imbibition the CO$_2$ phase can become neutral wetting (Plug and Bruining, 2007; Chiquet et al., 2007; Dickson et al., 2006; Yang et al., 2008). Others found lower contact angles on mica, quartz and caprock surfaces (Espinoza and Santamarina, 2010; Tonnet et al., 2013; Farokhpoor et al., 2013; Saraji et al., 2013). Yet the review by Naylor et al. (2011) and experimental work by Pentland et al. (2011) suggest that supercritical CO$_2$ is the non-wetting phase.

Trapping Physics

Hysteresis expresses the history and saturation path dependence of relative permeabilities and capillary pressure. It is caused by differences in contact angle between imbibition and drainage, i.e. the advancing wetting contact angle is larger than the receding contact angle because of chemical heterogeneities within the pore space and/or geometric variation of pore shape and surface roughness. Another contribution comes from the immobilisation of the non-wetting phase causing it to be disconnected in terms of blobs or ganglias in the presence of a complex pore topology.

At pore-scale level solid grains are naturally water-wet because of their chemical composition. The pore space is irregularly shaped, cornered and interconnected to various degrees. During drainage, CO$_2$ cannot enter a single pore until a threshold pressure is exceeded, the capillary entry pressure (Kovscek et al., 1993). The entry pressure depends on the geometry and the interfacial tension. As CO$_2$ enters the pore forming a continuously connected cluster throughout the rock, it displaces brine form the central portion and leaves brine in the corner. A protective thick water film can cover surfaces within the pore and eventually will collapse upon further increase of CO$_2$ with accompanying increase in capillary pressure. Areas free of water films are exposed to CO$_2$ and wettability changes can occur due to asphaltene-adsorption creating mixed-wet situations. The smallest pores stay completely filled with brine, CO$_2$ enters the largest pores first and thick-film breakage with subsequent wettability changes occur for intermediate-sized pores when a capillary pressure exceeds a critical value. The largest pores remain water-wet.
Upon imbibition water-wet pores refill immediately as long as there exists a capillary connection to a brine supply. As the capillary pressure fall within a pore, water-filled corners eventually connect and will separate CO₂ drops from the continuous cluster. This is known as snap-off effect. Isolated CO₂ drops do not communicate with the cluster anymore. Even if small pressure gradients are applied, they are immobilised due to pore constrictions and remain as residual CO₂. A secondary drainage can reconnect distributed CO₂ drops provided the entry pressure is exceeded.

**Trapping Model**

Empiric trapping models have been developed to quantify the behaviour of fluid flow during imbibition and drainage in terms of capillary pressure and relative permeability curves. For water-wet rock snap-off of CO₂ during imbibition is the dominant physical mechanism of displacement leading to trapping and relative permeability hysteresis with a stronger impact on non-wetting rather than on wetting relative permeabilities. Trapping models relate the trapped saturation of non-wetting fluid $S_{nt}$ to the initial non-wetting saturation at flow reversal $S_{ni}$ with most hysteretic relative permeability models based on the Land trapping model (Land, 1968; Killough, 1976; Carlson, 1981; Lenhard and Parker, 1987; Jerauld and Salter, 1990; Jerauld, 1997; Larsen and Skauge, 1998; Blunt, 2000). This relationship is computed by

$$S_{nt} = \frac{S_{ni}}{1 + CS_{ni}}$$

(3.58)

with the Land trapping coefficient $C$ determined experimentally by bounding drainage and imbibition relative permeability curves

$$C = \frac{1}{S_{nt,\text{max}}} - \frac{1}{S_{n,\text{max}}},$$

(3.59)

where $S_{nt,\text{max}}$ is the maximum trapped non-wetting saturation associated with the bounding imbibition curve at the maximum non-wetting saturation $S_{n,\text{max}}$. Both quantities as well as the bounding curves are illustrated in Fig. 3.4 and as mentioned are experimentally determined. Experimental data are required to determine these bounding curves. Intermediate scanning curves interpolate relative permeabilities between imbibition and

drainage cycles. For flow-reversals at $S_n \leq S_{n,max}$ the Killough-method (Killough, 1976) provides relative permeabilities along these scanning curves. Scanning curves are paths produced by drainage and imbibition cycles in $S - k_r$ space. To construct these scanning curves, normed saturations $S_{n,norm}$ are determined by

$$S_{n,norm} = S_{nt,max} + \frac{(S_n - S_{nt}) (S_{ni,max} - S_{nt,max})}{S_{ni} - S_{nt}} \tag{3.60}$$

for which relative permeabilities are calculated by

$$k_{imb}^{\text{rn}} (S_n) = k_{imb}^{\text{rn}} (S_{n,norm}) \frac{k_{drn}^{\text{rn}} (S_{ni})}{k_{drn}^{\text{rn}} (S_{n,max})} \tag{3.61}$$

The bounding curves determined from an experiment on a rock sample are denoted by $k_{drn}^{\text{rn}}$ and $k_{imb}^{\text{rn}}$. We assume reversibility of the flow cycles, i.e. new scanning curves are not generated when secondary drainage occurs, and $k_{imb}^{\text{rn}} = k_{drn}^{\text{rn}}$ holds for $S_{nr} \leq S_n \leq S_{ni}$.

The non-wetting flowing saturation $S_{nf}$ is

$$S_{nf} = \frac{1}{2} \left( (S_n - S_{nt}) + \sqrt{(S_n - S_{nt})^2 + \frac{1}{4} (S_n - S_{nt})} \right) \tag{3.62}$$
3.6 Stress magnitudes at depth

Stress acts over a given area as a force, and is defined as a symmetric second-rank tensor which describes the density of forces acting on all surfaces passing through a given point (Pollard and Fletcher, 2005; Zoback, 2007)

\[
S = \begin{bmatrix}
S_{11} & S_{12} & S_{13} \\
S_{21} & S_{22} & S_{23} \\
S_{31} & S_{32} & S_{33}
\end{bmatrix}
\] (3.63)

The first index of each stress component refers to the direction of a given force acting on a given point, the second index refers to the face of the unit upon which the stress component acts. Since the matrix is symmetric, the stress state at depth can be described by three stress magnitudes and three angles which define the orientation of the stress coordinate system with respect to a reference coordinate system. By convention com-
pressive stress is positive, since in-situ stress at greater depths are always compressive.

Tensor transformations are useful to diagonalise stress tensors which helps to describe the in-situ state of stress at depths in terms of the principal stress’s. The transformation is defined by

\[
S' = A^T S A
\]  

(3.64)

with

\[
A = \begin{bmatrix}
a_{11} & a_{12} & a_{13} \\
a_{21} & a_{22} & a_{23} \\
a_{31} & a_{32} & a_{33}
\end{bmatrix}
\]  

(3.65)

and \(a_{ij}\) the direction cosines. In the associated principal coordinate system the stress field is completely described by the three principal stresses \(S_1 \geq S_2 \geq S_3\). They are the eigenvalues of the stress tensor where the principal stress direction corresponds to its eigenvectors

\[
S = \begin{bmatrix}
S_1 & 0 & 0 \\
0 & S_2 & 0 \\
0 & 0 & S_3
\end{bmatrix}
\]  

(3.66)

The principal coordinate system gives a description of \(S\) in which shear stress vanishes. Assuming that one principal stress is generally normal to the earth’s surface and the two other principal stresses acting in a horizontal plane at any depth, only four parameters are needed to fully describe the state of stress: \(S_v\), the vertical stress corresponding to the weight of the overburden; \(S_{H_{\text{max}}}\), the maximum principal horizontal stress; and \(S_{h_{\text{min}}}\), the minimum horizontal stress, plus the azimuth of the maximum horizontal compression \(S_{H_{\text{max}}}\), which gives a stress orientation. The effective stress \(\sigma\) takes into
account pore pressure and since liquids can not maintain shear forces, its definition in
the more compact tensor index notation is

\[ \sigma_{ij} = S_{ij} - \delta_{ij} P_p, \quad (3.67) \]

with normal components \( \sigma_i \) and shear components \( \sigma_{ij} \) with \( i \neq j \). At depth \( z \), \( S_v \) is

\[ S_v = \rho_w g z_w + \int_{z_w}^{z} \rho_r(z) g dz, \quad (3.68) \]

where \( \rho_w [\text{g/m}^3] \) is the density of water, \( z_w [\text{m}] \) is the water depth and \( g \) the gravitational acceleration.
3.6 Stress Magnitudes at Depth

Figure 3.5: Variation of stress magnitudes with depth in normal, strike-slip and reverse faulting stress regimes for hydrostatic (a–c) and overpressure conditions (d–f) after (Zoback, 2007).

An assumption in modelling fracture networks is to fix the fracture aperture to a constant value. Here we use another method where the aperture varies spatially according to the ambient stress field and along the fracture, that is the shear and normal stress component resolved on the fracture will impact its opening and its hydraulic properties. A linear elastic fracture model has been presented in Pollard and Segall (1987), and applied to fracture pattern in sandstone in the Garden Area of the Arches National Park (U.S.A.) to interpret conditions responsible for secondary fractures and identify rules for interpreting them (Cruikshank et al., 1991). In 2D-simulations only mode I and mode II fractures are possible.

The width $W$ (or aperture) of the fracture is calculated from

$$W(x^*) = 2(\sigma_{yy} + p_p) \frac{1 - \nu}{G} \sqrt{\ell^2 - x^{*2}}, \quad (3.69)$$

with $\sigma_{yy}$ the normal stress resolved on the fracture, $p_p$ the pore pressure, $\nu$ the Poisson’s ratio, $G$ the shear modulus, $\ell$ the fractures half-length and $x^*$ the x-coordinate with the centre of coordinate located at the fracture’s barycentre and its principal axis align parallel and normal to the fractures orientation. Shear displacement $U$ is calculated from

$$U(x^*) = 2\sigma_{xy} \left( \frac{1 - \nu}{G} \right) \sqrt{\ell^2 - x^{*2}}, \quad (3.70)$$

where $\sigma_{xy}$ is the shear stress resolved on the fracture. The Linear Elastic Fracture Model (LEFM) yields

$$a = \min (W, U, 10 \mu m), \quad (3.71)$$

where $a = 10 \mu m$ serves as an lower aperture bound (Min et al., 2004). The parallel plate approach calculates the fracture permeability from its aperture and is

$$k_f = \frac{a^2}{12} \quad (3.72)$$
Both equations Eq. 3.69 and Eq. 3.70 are formulated for a single-phase fluid. The transition to multi-phase fluids is established by introducing the equivalent pressure \( p_E \) (Coussy, 2004), which accounts for the interface energy in the free energy of the system. It leads to a thermodynamically consistent and mathematically well-posed description of the multiphase fluid response to solid deformations (Kim et al., 2013). The equivalent pressure \( p_E \) substitutes the pore pressure \( p_p \) in Eq. 3.69 and Eq. 3.70. It is defined by

\[
p_E = \sum_{i=1}^{n_p} S_i p_i - U,
\]

where \( U \) is the interfacial energy computed from the capillary pressure relations (Kim et al., 2013; Jha and Juanes, 2014), and is calculated for a two-phase fluid by

\[
U = \int_{S_2} p_c(S) S.
\]

The link between pore pressure \( p_p \), the phase pressure \( p_i \) and the global pressure \( p \) is now established through Eq. 3.26 or Eq. 3.27.

---

**Figure 3.6:** Fracture aperture determined by the Linear Elastic Fracture Method which scales the permeability along the fracture, i.e. fractures are closed at the tip and maximal open in their centre. Local coordinate system chosen to be centred about the fracture centre, with the \( x^* \)-axis pointing along the fracture. The length of the fracture is \( \ell \). Normal stress component acting on fracture is \( \sigma_{yy} \), shear stress component is \( \sigma_{yx} \). The fracture aperture \( a_f \) is calculated in mode I (Fig. 3.71).

---

### 3.8 Model Equations and Primary Variables

I close this chapter by briefly listing the governing equations and the primary variables. There are two governing equations, the pressure diffusion equation and the mass trans-
port equation, with primary variables in \( p \) and \( M_j \). The pressure diffusion equation is solved in \( p \) and is

\[
\beta_t \frac{\partial p}{\partial t} = \text{div} (\lambda_t \mathbf{K} \text{grad} p) - (\lambda_w \beta_w + \lambda_n \beta_n) \mathbf{K} \text{grad} p \text{grad} p \\
- \text{div} (\lambda_t \mathbf{K} \mathbf{G}) - (\lambda_w \beta_w + \lambda_n \beta_n) \mathbf{K} \mathbf{G} \text{grad} p + \sum_i^n q_i. \tag{3.75}
\]

The pressure diffusion equation will be solved by a finite element method (Sec. 4.2), assuming for the sake of simplicity that near-wellbore can be disregarded. Therefore, the quadratic terms in \( \nabla p \) will be neglected. Note, that when flow velocities in fractures are sufficiently high, neglecting these quadratic terms introduces an error, which quantification is not subject of this thesis. Furthermore, if gravity is neglected, the pressure diffusion equation reduces to

\[
\beta_t \frac{\partial p}{\partial t} = \text{div} (\lambda_t \mathbf{K} \text{grad} p) + \sum_i^n q_i. \tag{3.76}
\]

The governing transport equation is

\[
\frac{\partial t} M_j = - \text{div} \left( \sum_i^n \rho_i X_{ij} f_i v_t + \mathbf{K} \frac{\lambda_w \lambda_n}{\lambda_w + \lambda_n} \text{grad} p_c \right) \\
- \text{div} \left( \sum_i^n \mathbf{K} \frac{\lambda_w \lambda_n}{\lambda_w + \lambda_n} (\rho_k - \rho_i) g \right) + q_j \\
+ k \in \{w, n\}, k \neq i, \tag{3.77}
\]

which, if gravity is neglected, simplifies to

\[
\frac{\partial t} M_j = - \text{div} \left( \sum_i^n \rho_i X_{ij} f_i v_t + \mathbf{K} \frac{\lambda_w \lambda_n}{\lambda_w + \lambda_n} \text{grad} p_c \right) + q_j. \tag{3.78}
\]

In Sec. 4.6, a primary variable switch from \( M_j \) to \( S_i \) will be executed to enable decoupling between the mass advective and the capillary diffusion term in above transport equation.
This chapter provides the numerical formulation of the mathematical model of compressible, compositional multiphase flow and transport (Chap. 3). First an introduction into a combined finite element - finite volume method is presented (Sec. 4.1). It is followed by a motivation why a decoupled numerical formulation of the governing equations has been chosen including respective numerical discretisations (FE or FV) Sec. 4.2, and sequence diagrams of their implementation (Sec. 4.4, Sec. 4.5, Sec. 4.6). An argument is presented to simplify the capillary diffusion step (Sec. 4.6). Implementation of relative permeability hysteresis (Sec. 4.7), treatment of capillary entry pressure (Sec. 4.8) and representation of lower dimensional fracture representation (Sec. 4.3) are provided. I conclude with the overall splitting (Sec. 4.10).

4.1 Finite Element-Finite Volume Method

Approaches to model multiphase flow and transport governed by partial differential equations comprises finite difference methods (Courant et al., 1928; Aziz and Settari, 1979), finite element methods (Huyakorn et al., 1983; Chavent and Jaffre, 1986; Istok, 1989; Zienkiewicz et al., 2005) and finite volume methods (LeVeque, 1992, 2002). Thomée (2001) published a review on the stability of these methods. Finite difference discretisations have the advantage of straight-forward implementation of physics and where originally based on central-difference schemes. However at higher Peclet number this scheme produces spurious, physically unrealistic oscillations which can be overcome by using very fine grid resolutions on the expense of increase computational costs. Alternatively upwind difference schemes have been developed to mitigate this problem on the expense of numerical accuracy at small Peclet numbers (Gentry et al., 1966; Barakat and Clark, 1966; Runchal and Wolfshtein, 1969). Hybrid schemes where developed blending upstream
schemes with central difference schemes (Spalding, 1972), but which only work well for near steady-state situations with flow aligned to grid lines or with no strong cross flow gradients (Raithby, 1976), introducing numerical diffusion otherwise rendering the solution of partial differential equations discretised inaccurate. Additionally, finite difference methods ideally require the computational mesh to be parallel to Cartesian coordinate axes limiting their application to regularly shaped domains. Therefore, complex geometries are difficult to implement because calculations of gradients requires the interface to be perpendicular to the connecting line between two adjacent nodes, i.e. a Voronoi-type partition of the mesh is required making it difficult to construct meshes respecting complex geometries or material boundaries.

Gradient calculations in standard finite element discretisations do not require the interface between nodes to be normal to the connecting line. Instead gradients are calculated by means of the finite element interpolation functions. Hence, finite element methods enjoy a greater degree of flexibility to capture structurally complex geometries (Sheu, 2002, 2014) whilst providing a sufficiently accurate velocity field for advection. However, standard finite element discretisations for advection-diffusion type problems suffer from the same problems that afflict central difference schemes, and upwind-type finite element formulations have been proposed (Heinrich et al., 1977; Huyakorn, 1977; Heinrich and Zienkiewicz, 1977; Hughes et al., 1979) with extensions to streamlines (Brooks and Hughes, 1982).

The combination of finite element discretisation with finite volume discretisation has become popular for modelling flow and transport problems (Durlofsky, 1993; Huber and Helmig, 1999, 2000; Geiger et al., 2004; Hoteit and Firoozabadi, 2005b; Reichenberger et al., 2006; Montagudo and Firoozabadi, 2007b; Couniou et al., 2008b; Lupi et al., 2010; Zaretskiy et al., 2010; Agar et al., 2010; Moortgat and Firoozabadi, 2013a; Schmid et al., 2013; Weis et al., 2012; Paluszny and Zimmerman, 2013; Schmid et al., 2013). This combination of discretisation techniques derives from a control volume based finite element method pioneered by Baliga (1978), Baliga and Patankar (1980), and Baliga and Patankar (1983) for modelling convection-diffusion problems of a scalar quantity in the presence of fluid flow. The reason for its popularity stems from flexibility to adapt to structurally complex domains whilst being locally conservative. The flexibility is provided by the finite-element grid on which a dual finite-volume grid is superimposed (Fig. 4.2). The conservation property
is achieved when a velocity field is continuous on a finite element, i.e. it ensures flux continuity across finite volume faces, and therefore advection across the finite volume faces is guaranteed to be locally conservative. This combination has the advantage that if an operator-splitting is applied to a coupled set of partial differential equation, it leads to a sequential approach in which the best discretisation method can be used for the appropriate subproblem, i.e. the finite element for the calculation of diffusion type problems and its associated velocity field, the finite volume discretisation for advective type problems such as mass transport. The velocity field is used in the mass balance equation during the transport step. In reservoir modelling the FEFV method is suitable for implicit pressure-explicit saturation or concentration schemes (IMPES/IMPEC) where the pressure field is solved by an implicit finite element method whereas the saturations or concentrations are treated with an explicit finite volume method. Usually an iterative procedure is required to resolve non-linearities introduced by mobility and capillary functions. The aforementioned FEFV method effectively decouples the pressure diffusion from the mass balance equation, avoiding the need to use non-linear iteration procedure such as the Newton-Raphson method (Geiger et al., 2004).

Within the finite element discretisation, only the dependent variable is resolved on the nodes whereas diffusion equation parameters are linearly interpolated at the barycentre of finite elements (Fig. 4.1 and Fig. 4.6). The velocity field is linearly interpolated on the barycentre of the finite element and held constant across it with equal velocities on each facet within a given finite element. For the finite volume discretisation the dependent variable also lives on the nodes but advection equation parameters are taken from the upwind node (Fig. 4.4).

Alternatives to the finite element finite volume method are mixed finite element methods and discontinuous Galerkin finite element-finite volume methods. Mixed finite element method solve the velocity field equation together with the pressure diffusion equation and therefore produce accurate velocity fields whereas in the finite element-finite volume method presented here the velocities are calculated in a post-process step. Discontinuous Galerkin finite element-finite volume methods are best suited if dependent variables can be discontinuous due to abrupt changes in permeabilities and poros-
ities within the domain, e.g. when including capillary forces in highly heterogeneous geologic models.

Finite element discretisation of partial differential equation leads to a linear system of algebraic equations of the form

\[ Au = f \]  \hspace{1cm} (4.1)

with \( A \) a matrix describing the advection-diffusion problem and \( u \) the vector of unknowns with size of \( N \). Because of the locality of basic physical laws \( A \) is very sparsely populated typical which size is \( O(N) \). Geological model’s grid size can be \( O(10^7) - O(10^8) \), and the size of industrial models is typically \( O(10^7) - O(10^8) \), which imposes challenges on the computational requirements (Gerritsen and Durlofsky, 2005). Ideally computational time to solve linear systems is \( O(N) \). However, for standard solvers, solving Eq. 4.1 can become difficult and extremely time consuming: for direct solver both memory requirements and computational complexity growth rates are \( O(N^2) \) or higher, making iterative solvers often the only choice in practice because their memory requirement is \( O(N) \), but computational work is still \( W(N) = O(N^\alpha) \) with \( \alpha > 1 \). For complex subsurface problems new solver strategies are required with numerical work scaling linearly with \( N \). These solver are called scalable. This situation lead ultimately to the development of algebraic multigrid solver which have become a well established tool to solve partial differential equations in the reservoir modelling community because of its numerical efficiency and its scalability (Fraunhofer Institute SCAI, 2012; Stüben, 2007). This enables the simulation of flow and transport problems with large numbers of unknowns (Lupi et al., 2010; Zaretskiy et al., 2010; Weis et al., 2012; Schmid et al., 2013).

I implemented the mathematical model presented Chap. 3 into the standard Galerkin finite-element upstream-weighted node-centered finite volume method into the C++ library Complex System Modelling Platform, CSMP++ (Matthäi et al., 2004; Paluszny et al., 2007) which is developed within a multi-institutional collaboration to model multiphase flow problems in fractured reservoirs. My implementation also includes the thermody-
4.2 Decoupled formulation

There are two reasons why a decoupled formulation is desired. First, the system of partial differential equations comprising the essentially hyperbolic mass balance equation (Eq. 3.1) of advection-diffusion type and the parabolic pressure equation (Eq. 3.24) form a non-linearly coupled system of equation in the presence of capillary forces. It requires an iteration methods such as the Newton-Raphson method to solve the pressure and mass balance equation simultaneously, preferably with a backward Euler method (implicit method) which can impose severe memory requirements. A global pressure formulation (Sec. 3.2) reduces the coupling between the pressure and mass balance equation by introducing saturation dependent mobilities and capillary pressure functions. Therefore, costly iteration methods can be avoided.

Second, a decoupled formulation enables the application of operator-splitting techniques to use the optimal numerical discretisation for the partial differential equations sequentially. The reservoir modelling community commonly uses an explicit time stepping scheme (a forward Euler method) applied to the mass balance equation within a solving strategy known as the implicit pressure-explicit saturation/concentration/mass method (IMPES/IMPEC/IMPEM). If an explicit time stepping scheme is applied to the mass balance equation with capillary forces present and with $\Delta x$ the smallest spatial discretisation, the Courant-Friedrich-Levy criterion will impose severe time stepping restrictions as the diffusive part requires $\Delta t = O(\Delta x^2)$, whereas for the advective part $\Delta t = O(\Delta x)$. However, further operator splitting applied to the mass balance equation can mitigate these restrictions by exploiting the saturation dependency of the capillary pressure to decouple the diffusive term from the advective term (Nayagum et al., 2004; Schmid et al., 2013). This splitting allows to use an implicit or semi-implicit Euler method for the diffusive term whilst still using an explicit Euler method for the advective term.

The pressure equation Eq. 3.32 is solved by an semi-implicit standard Galerkin finite-element method. Semi-implicit refers to the time level at which the total mobility lives.
Whilst an implicit method solves the equation with both the dependent variable and
the total mobility at the next time level \( t + \Delta t \), the semi-implicit takes the total mobility
from the previous time step \( t \). An explicit method computes values at the next time
level \( t + \Delta t \) with values only from the previous time step. The mass balance equation
Eq. 3.33 is split into an advective and diffusive part. The advective part is solved by an
explicit upstream-weighted, node-centered finite-volume method and the diffusive part
by a semi-implicit standard Galerkin finite element method. The capillary diffusivity
\( D_{\text{cap}} \) is taken from the previous timestep. A Godunov operator split (Godunov, 1959) is
applied and produces following system of equation:

\[
\text{(FE)} \quad \beta_i \partial_t p = \text{div} (\lambda_i \mathbf{K} \text{grad } p) - \text{div} (\lambda_i \mathbf{K} \mathbf{G}) + \sum_{i} n_i q_i, \quad (4.2)
\]

\[
\text{(FV)} \quad \partial_t M_j = - \text{div} \left( \sum_{i} \mathbf{v}_i \rho_i X_{ij} \right) + q_j, \quad (4.3)
\]

\[
\text{(FE)} \quad \partial_t M_j = - \text{div} \left( \sum_{i} \rho_i X_{ij} \mathbf{K} \frac{\lambda_\text{w} \lambda_n}{\lambda_\text{w} + \lambda_n} \frac{dp_{\text{c}}}{ds_i} \text{grad } S_i \right). \quad (4.4)
\]

Note that the Godunov splitting is first-order accurate in time. Strang splitting (Strang,
1968) can reduce the splitting order yielding a second-order accuracy. Splitting-order is
not the focus in this work and the reader is referred to Tang and Teng (1995); Langseth
et al. (1996); Tang (1998) for detailed discussion. The capillary diffusion step (Eq. 4.4) is
cast into a saturation based formulation, effectively carrying out a variable switch (see
Sec. 4.6) for which a fixpoint iteration, the Picard-iteration, is carried out to reduce the
error in the capillary diffusivity. The Picard iteration is easy to implement but has slower
convergence behaviour compared to the Newton-Raphson method which requires the
calculation of a Jacobian.

4.3 DISCRETISATION OF LOWER DIMENSIONAL FRACTURES

Fractures are commonly represented as lower-dimensional entities to reduce computa-
tional cost. An early application by Kiraly (1979) used a finite element method with
lower dimensional fractures for a steady-state ground water flow in a highly discon-
tinuous karstic/fractured hydrogeological system. Fundamentally, in finite element cal-
culations the (contravariant) nodal basis functions \( \Phi = (\Phi^1, \ldots, \Phi^n)^T \) live on the local
coordinate system \( s^k \in \mathbb{R}^n \), but transformation to the global coordinate system \( x^k \in M \), with \( M \) a manifold, requires the transformation matrix \( \frac{\partial x}{\partial s} \) to be square, which implies that local and global coordinate system must be of same dimension. However, lower dimensional manifolds can be embedded in a global coordinate system when the differential operator is described in curvilinear co-ordinate system (Perrochet, 1995). Here, the gradient is expressed as a tensor product of the covariant base and the contravariant components of the gradient by using the contravariant metric tensor. This very general differential-geometric approach has been extended to integration on manifolds as required for finite-element calculations (Juanes et al., 2002) by calculating a Jacobian for mapping between manifolds of different dimensions. As a consequence the lower dimensional differential volumes of fractures need to be multiplied by their cross-sectional area, i.e. their aperture. Hence, high-aspect ratio fractures are avoided and which leads to more efficient computing (Paluszny et al., 2007) as small time steps in explicit discretisation schemes and are avoided and the number of nodes further reduced.

We divide the computational domain \( \Omega \subset \mathbb{R}^d \) in two subdomains \( \Omega_m \subset \mathbb{R}^d \) and \( \Omega_f \subset \mathbb{R}^{d-1} \) with \( \Omega_m \cap \Omega_f = \emptyset \), where the two subdomains represents the matrix and the fracture. Let \( \Omega_f = \{ f_1, \ldots, f_{n_f} \} \subset \mathbb{R}^{d-1} \) with varying aperture \( a_f \). Then

\[
\Omega = \Omega_m \cup a_f \cdot \Omega_f. \tag{4.5}
\]

Fractures are assumed to be open, and hence the porosity is set to \( \phi_f = 1 \). We weigh permeability \( K_f(x) \) and fracture porosity \( \phi_f \) with the aperture \( a_f \) to respect the cubic law in numerical discretisations (Witherspoon et al., 1980). We solve the pressure diffusion, advection and capillary diffusion equation on both \( \Omega_m \) and \( \Omega_f \). For \( G \) representing dependent variables \( p, S_i \) or \( M_j \) the integration over the computational domain is given by

\[
\int_G d\Omega = \int_{\Omega_m} G d\Omega_m + a_f \int_{\Omega_f} G d\Omega_f. \tag{4.6}
\]

Discretisation of the domain is achieved by constrained conforming Delauny triangles with a dual node-centred FV grid for which the barycentre of element \( (e) \) is connected to the mid-side points of its edges. I develop the weak formulation by holding \( K, \phi_m, \phi_f \)
and $\phi_f$ piecewise constant on the elements and interpolate $\lambda_t$, $\beta_t$, $D_{\text{cap}}$, and $\bar{\lambda}$ at the barycentre.

## 4.4 Pressure Diffusion Equation

Contrary to the finite difference method, the finite element method requires a more sophisticated level of mathematical understanding but in return complex irregular structures and unstructured geometries are easily accommodated. It seeks to find an approximate solution to a boundary value problem for a given partial differential equation. As opposed to finite difference methods it does not require orthogonal Cartesian coordinates to have the problems formulated in. Neumann boundary conditions are naturally incorporated into the finite element method. Finite element formulation exist for simple flow problems (Zienkiewicz and Cheung, 1965; Oden and Wellford, 1972; Chung, 1978; Baker, 1983), Upwind Petrov-Galerkin methods (Heinrich et al., 1977; Hughes and Brooks, 1982; Hughes et al., 1986), Taylor-Galerkin methods (Donea, 1984; Löhner et al., 1985), and hp-adaptive methods (Oden and Demkowicz, 1991), discontinuous Galerkin methods (Oden et al., 1998). In all these methods the basis functions is equal to the weighting function. If they differ the resultant methods are known as the weighted residual methods, such as the spectral element method, the least square method, and the finite point method.

For an introductions into the finite element theory applied to computational fluid dynamics the reader is referred to Istok (1989) or Chung (2002). A brief overview is provided here for completeness which closely follows Chung (2002). Note that as opposed to finite volume methods, which are locally conservative, finite element methods are only globally conservative, because it seeks to approximate the solution of a dependent variable of a partial differential equation by linear combination of shape functions. Let a partition of a domain $\Omega$ be given by

$$\Omega = \bigcup_{e=1}^{n_e} \Omega_e$$

(4.7)
then the global node index is denoted by $Z_\alpha$ and the local node index by $z_n$ and they are related through the boolean matrix

$$
\Delta_{n\alpha}^{(e)} = \begin{cases} 
1 & \text{if local node } n \text{ corresponds to global node } \alpha \\
0 & \text{otherwise}
\end{cases}
$$

through

$$
Z_\alpha = \Delta_{n\alpha}^{(e)} z_n^{(e)}.
$$

(4.9)

Introducing local shape functions $\Phi_n^{(e)}(x)$ with $n \in \{1, \ldots, n_{n(e)}\}$ and $n_{n(e)}$ number of nodes of element $e$, allows to linearly approximate a variable $u$ within an element $e$ such that

$$
u^{(e)}(x) = \Phi_n^{(e)}(x) u_n^{(e)},
$$

(4.10)

if $\Phi_n^{(e)}(x)$ has the properties

$$
0 \leq \Phi_n^{(e)} \leq 1
$$

(4.11)

$$
\sum_{n=1}^{n_{n(e)}} \Phi_n^{(e)} = 1
$$

(4.12)

$$
\Phi_n^{(e)}(z_m) = \delta_{nm}
$$

(4.13)

and $\delta_{nm}$ the Kronecker symbol. The global function $u$ can then be written as a union over all local elements

$$
u = \bigcup_{e=1}^E u^{(e)}
$$

(4.14)

$$
= \bigcup_{e=1}^E \Phi_n^{(e)}(x) u_n^{(e)}
$$

(4.15)

$$
= \bigcup_{e=1}^E \Phi_n^{(e)}(x) \Delta_{n\alpha}^{(e)} u_\alpha,
$$

(4.16)
and in short

\[ u = \Phi_\alpha u_\alpha. \quad (4.17) \]

with \( \Phi_\alpha \) the global basis function

\[ \Phi_\alpha = \bigcup_{e=1}^{E} \Phi_{\alpha}(e) \Delta_{n\alpha}^{(e)} \quad (4.18) \]

and

\[ \Phi_\alpha(Z_\beta) = \delta_{\alpha\beta}. \quad (4.19) \]

Now a weak formulation of a differential equation can be found by a weighted residual method which seeks to minimise the residual \( R \) of the governing differential equation by forming a subspace spanned by test functions or weighting functions \( W_\alpha \), and projecting the residual orthogonally onto this subspace by an inner product yet to define. The residual \( R \) is a measure of the induced error arising from the used approximation. The error \( e \) under a \( p \)-norm between the global solution \( u \) and its approximation \( \hat{u} \) is given by

\[ R = u - \hat{u} = ||e||_p, \quad (4.20) \]

usually with \( p = 1 \) the \( L_1 \)-norm or with \( p = 2 \) the \( L_2 \)-norm. The inner product \( (\cdot, \cdot) : U \times V \to \mathbb{R} \) between a weighting function \( W_\alpha \) and the residual \( R \) is

\[ (W_\alpha, R) = \int_{\Omega} W_\alpha R \, dx = 0. \quad (4.21) \]

The method of weighted residual seeks to minimise the residual \( R \) in Eq. 4.21 as a weighted average over the domain \( \Omega \). If weighting functions are substituted by interpol-
4.4 Pressure Diffusion Equation

Ation functions, \( W_\alpha = \Phi_\alpha \), the scheme is the Galerkin method. Its inner product with the pressure equation (Eq. 4.2) yields

\[
(\Phi_\alpha, R) = \int_\Omega \Phi_\alpha (\beta_i \partial_i \hat{p} - \text{div} (\hat{\lambda}_t \text{grad} \hat{p}) + \text{div} (\hat{\lambda} \text{K} \hat{G}) - \hat{q}) \, dx = 0,
\]

and with \( p = \Phi_\alpha p_\alpha \) and integration by parts, the weak formulation of Eq. 4.2 is

\[
\int_\Omega \Phi_\alpha (\hat{\beta}_i \partial_i \hat{p}) \Phi_{\hat{\beta}} \, dx = \int_\Omega \partial_x \Phi_\alpha (\hat{\lambda}_t \text{K} p_\alpha) \partial_x \Phi_{\hat{\beta}} \, dx
\]

\[
- \int_\Omega \Phi_\alpha \left( \hat{\lambda}_t \text{K} \sum_{f_i} f_i \rho_i \text{g} \right) \, dx
\]

\[
+ \int_\Omega \Phi_\alpha \hat{q} \, df + \int_{\partial \Omega} \Omega_a (\partial_x \hat{p}, n) \, dx.
\]

Casting the weak formulation into a linear system of equation and applying a semi-implicit Euler method yields

\[
\left( \frac{1}{\Delta t} \left[ A^p_{\alpha \hat{\beta}} \right] + \left[ K^p_{\alpha \hat{\beta}} \right] \right) p^{t+\Delta t} = \frac{1}{\Delta t} \left[ A^p_{\alpha \hat{\beta}} \right] p^t + \left[ F^p_\alpha \right] + \left[ G^p_\alpha \right]
\]

with the mass matrix \( A^p_{\alpha \hat{\beta}} \), the stiffness matrix \( K^p_{\alpha \hat{\beta}} \), the source vector \( F^p_\alpha \), and the Neumann boundary vector \( G^p_\alpha \) defined by

\[
A^p_{\alpha \hat{\beta}} = \int_\Omega \Phi_\alpha \beta_i \Phi_{\hat{\beta}} \, dx
\]

\[
K^p_{\alpha \hat{\beta}} = \int_\Omega \partial_x \Phi_\alpha \lambda_t \text{K} \partial_x \Phi_{\hat{\beta}} \, dx
\]

\[
F^p_\alpha = \int_\Omega \Phi_\alpha \hat{q} \, dx - \int_\Omega \Phi_\alpha \left( \lambda_t \text{K} \sum_{f_i} f_i \rho_i \text{g} \right) \, dx
\]

\[
G^p_\alpha = \int_{\partial \Omega} \Phi_\alpha \left( \partial_x \hat{p}, n \right) \, dx
\]

allows to apply algebraic multigrid solvers to invert the linear system, because the matrices \( A^p_{\alpha \hat{\beta}} \) and \( K^p_{\alpha \hat{\beta}} \) are symmetric, positive definite and sparsely populated matrices, which makes the linear system therefore uniquely solvable. Total mobilities \( \lambda_t \) and total compressibilities \( \beta_t \) used in Eq. 4.27 and Eq. 4.28 are held constant on the element. They are calculated at the element’s barycentre by interpolating their dependent variables to
After the pressure equation has been solved, the velocity field is computed piecewise constant on the elements in a post-process step. Differentiation of the pressure field for element \((e)\) for each node \(n \in \{1, \ldots, n_{n(e)}\}\) on the element

\[
v_t = - \sum_{n \in e} K^{(e)} \lambda_t^{(e)} p_n^{(e)} \partial_x \Phi_n^{(e)},
\]

(4.31)

where derivatives of \(\Phi_n^{(e)}\) constitutes the matrix elements of \(\partial_x \Phi_n^{(e)}\) which has size of \(n_{n(e)} \times \text{dim}(\Omega)\). The element permeabilities \(K^{(e)}\) and element total mobilities \(\lambda_t^{(e)}\) are assumed to be piecewise constant.

**Figure 4.1:** Sequence diagram of the pressure diffusion step. The sequence evolution is from top to down. The blue shaded area marks the finite element method and the dependent variable \(p\) is denoted in bold (Eq. 4.26)). The total mobility \(\lambda_t\) and total compressibility \(\beta_t\) are used to populate the matrices in Eq. 4.27 and Eq. 4.28 are calculated at element’s barycentre and held constant across the element. The calculation requires their dependent variables to be interpolated at the element’s barycentre. The solution is obtained by using a the algebraic multigrid solver SAMG (see Sec. 4.1). In a post process step the total velocity \(v_t\) is calculated from Eq. 4.31 and is constant cross the element. The pressure diffusion step is completed by calculations of the thermophysical properties (see Chap. 2) on the nodes.
4.5 MASS ADVECTION

The finite volume formulation here follows the work of Baliga (1978); Baliga and Patankar (1980) and Baliga and Patankar (1983). For an introduction into finite volume methods for hyperbolic problems read LeVeque (2002). This section formulates the explicit finite volume discretisation of Eq. 4.3 and introduces time-stepping procedure different from the classical CFL-criterion.

According to the Gauss-Ostrogradsky’’s-theorem (Gauss, 1813; Ostrogradsky, 1965) an n-dimensional integration over an divergence field is equivalent to an integration over the closed (n-1) dimensional surface of the associated vector field through the surface. This feature is exploited in the finite volume discretisation. The advective sub-problem Eq. 4.3 represents a conservation law and therefore the theorem can be applied. The vector field is given by the velocity field \( \mathbf{v} \) and the (n-1) dimensional surface is represented

![Figure 4.2: Finite element-finite volume mesh with conforming Delaunay triangle (dashed line) and dual node-centered finite-volume grid (solid line). A lower-dimensional fracture is represented by the red line. A finite element is partitioned into sectors by the facets forming the finite volume. Pressure values are node-centered at \( x_i \) and linearly interpolated across the finite element. Velocities are interpolated at the element’s barycentre and held constant across it. Hence, fluxes across the facets are continuous, which is exploited in the finite-volume method (e.g. in Eq. 4.35). The outward pointing normal of facet \( j \) is denoted by \( \mathbf{n}_j \). Permeability and porosity values are defined on the element \( e_i \) and piece wise constant over all elements. Cartoon is modified after Schmid et al. (2013).](image_url)

*Sometimes the Gauss-Ostrogradsky’s-theorem is known as the divergence theorem. For a historical note see Katz (1979)*
by the node-centered finite volume’s enclosing facets (see Fig. 4.3). Application of the Gauss-Ostrogradsky’s-theorem yields

\[
\partial_t M_j = - \text{div} \left( \sum_{i=1}^{n_p} v_i \rho_i X_{ij} \right) + q_j
\]  

(4.32)

\[
\int_\Omega \partial_t M_j \, dx = - \int_\Omega \text{div} \left( \sum_{i=1}^{n_p} v_i \rho_i X_{ij} \right) \, dx + \int_\Omega q_j \, dx
\]

(4.33)

\[
= - \sum_{i=1}^{n_p} \int_{\partial \Omega} (v_i, n) \rho_i X_{ij} \, dx + \int_\Omega q_j \, dx
\]

(4.34)

Note that swapping integration and summation is possible when functions are smooth, which is always the case for physical systems. Forward Euler method and finite volume discretisation for nodes \( \alpha \in \{1, \ldots, n_n\} \) with the fluxes across the facets taken from the upstream node yields

\[
[M_{\alpha,j}]_{t+\Delta t} = [M_{\alpha,j}]_t - \frac{\Delta t}{V_\alpha} \sum_{i, \beta} H_{\alpha \beta,i} A_{\alpha \beta} \left[ \rho_{\alpha,i} X_{\alpha,i} f_{\alpha,i} \right] (n_{\alpha \beta}, [v_t])^t
\]

\[
- \frac{\Delta t}{V_\alpha} \sum_{i, \beta} (1 - H_{\alpha \beta,i}) A_{\alpha \beta} \left[ \rho_{\beta,i} X_{\beta,i} f_{\beta,i} \right] (n_{\alpha \beta}, [v_t])^t
\]

\[
+ \Delta t [q_{a,j}]^t,
\]

(4.35)

where \( V_\alpha \) is the volume of the finite volume around node \( \alpha \), \( A_{\alpha \beta} \) is the area of the facet shared between node \( \alpha \) and adjacent node \( \beta \), \( n_{\alpha \beta} \) the outward pointing normal vector on \( A_{\alpha \beta} \), \( v_t \) is the total velocity, \( f_i \) the fractional flow function of phase \( i \), and \( q^t_j \) the source of component \( j \). The scalar product is denoted by \( (\cdot, \cdot) : \mathbb{R}^d \times \mathbb{R}^d \to \mathbb{R} \) and \( H_{\beta,i} \) is the Heaviside function defined by

\[
H_{\alpha \beta,i} = \begin{cases} 
1 & \text{if } f_{\beta,i}(n_{\alpha \beta}, v_t) > 0 \\
0 & \text{otherwise},
\end{cases}
\]  

(4.36)

which picks the upstream node value of \( \rho_{i,i} X_{ij} \) and \( f_i \). If \( A_\beta \) is a facets on a 1-dimensional fracture element, then \( A_\beta = 1 \).

The Courant-Friedrich-Levy (CFL) criterion (Courant et al., 1928) usually gives the maximum permissible time step in explicit time stepping schemes. Grid discretisations of
fractures can lead to very small volumes, and therefore can impose severe time-stepping restrictions. Hence a more robust time-stepping method is needed to circumvent the severe restrictions arising from the CFL-criterion. A mass-based criterion relaxes the time stepping criterion as carried out by Weis et al. (2014). They used an explicit finite volume discretisation for the advective term when modelling highly compressible fluids with a control volume-finite element method. In their work the time step $\Delta t$ is calculated based on both the mass available in a finite volume and the outgoing flux, ensuring that within the calculated time step $\Delta t$ the finite volume can not be emptied by fluxes across its boundaries. They do not provide a derivation, possibly because of its simplicity. However for completeness it is provided here and formulated for compositional compressible fluids with upstream-node weighting. The required condition can be stated easily and it follows immediately

$$0 < \left[ M_{\alpha,j} \right]^t - \frac{\Delta t}{V_\alpha} \left[ F_{\alpha,j} \right]^t$$

$$\Rightarrow \quad \Delta t = \min_{\alpha} \left( \frac{\left[ M_{\alpha,j} \right]^t V_\alpha}{\left[ F_{\alpha,j} \right]^t} \right)$$

$$\left[ F_{\alpha,j} \right]^t \neq 0,$$  \hspace{1cm} (4.37)

$$\text{Figure 4.3:} \quad \text{Treatment of lower-dimensional fractures for the finite element-finite volume discretisation within the DFM method. Shown here are three finite elements (thick lines) with corresponding finite volume stencils (thin lines): two two-dimensional finite elements (triangles) representing the matrix, and one one-dimensional finite element (thick line) representing the fracture. The filled circles indicate integration points at the finite volume faces, which take their values from the upstream node. The open circles represent finite element nodes. The velocity vector (Eq. 4.31) is projected onto the barycentre of the 2D elements. The velocity vector in the fracture is aligned to its principal direction, and its location coincides with the integration point of the fracture. Note that nodes at the corner B are all identified, i.e. all three nodes exhibit the same value for the property under consideration. This identification also applies to D.}$$
where \( F_{\alpha,j} \) is the outgoing flux function for component \( j \) from control volume \( \alpha \) defined by

\[
[F_{\alpha,j}]^t = \sum_{i,\beta} H_{\alpha\beta,i} A_{\alpha\beta} \left[ \rho_{\alpha,i} x_{\alpha,i f} f_{\alpha,j} \right]^t (n_{\alpha\beta,i} [v_j]^t)
\]  

(4.39)

After the advection step a saturation split calculation is executed (Sec. 3.4) to allow the calculation of saturation dependent total mobilities \( \lambda_t \), total compressibilities \( \beta_t \) and capillary diffusivities \( D_{cap} \) required for the following capillary diffusion step presented in Sec. 4.6. The sequential diagram of the advection step is shown in Fig. 4.4 which includes the finite volume method, the saturation split and update of the aqueous wetting phase density and update of the trapping variables presented in Sec. 4.7.

![Figure 4.4: Sequence diagram of the mass advection step.](image-url)
We now devise the weak formulation for modelling the effects of capillary forces within the splitting strategy outlined in Sec. 4.2. The idea of this section is to rewrite the capillary diffusion step (Eq. 4.4) in terms of saturation which becomes the dependent variable, i.e. the primary variable is changed from $M_j$ to $S_i$. Then the weak formulation is derived by applying integration by parts and subsequent application of the product rule. The component mass $M_j$ is then recalculated from the saturation distribution. The finite element formulation presented here closely follows Sec. 4.4.

Inserting Eq. 3.2 into Eq. 4.4, dividing by $\frac{1}{\rho_i X_{ij}}$, assuming constant porosity throughout $\Omega$ and reformulating yields

$$\phi \frac{\partial t}{\partial s_i} = -\frac{1}{\rho_i X_{ij}} \text{div} \left( \rho_i X_{ij} \lambda K \frac{d\rho_c}{dS_i} \text{grad} S_i \right) - \frac{S_i}{\rho_i X_{ij}} \partial_t \left( \rho_i X_{ij} \right). \tag{4.40}$$

With basis functions $\Phi_\alpha$ introduced in Sec. 4.3

$$S_i = \Phi_\alpha S_{\alpha,i} \tag{4.41}$$

the inner product of the residual of Eq. 4.40 with basis function $\Phi_\alpha$ is

$$\int_\Omega \Phi_\alpha \phi \partial_t (S_i, \beta \Phi_\beta) \, dx = -\int_\Omega \Phi_\alpha \frac{1}{\rho_i X_{ij}} \partial_x \left( \rho_i X_{ij} \lambda k \frac{d\rho_c}{dS_i} S_{i,\beta} \partial_x \Phi_\beta \right) \, dx$$

$$-\int_\Omega \Phi_\alpha \frac{1}{\rho_i X_{ij}} \partial_t \left( \rho_i X_{ij} \right) S_{i,\beta} \Phi_\beta \, dx, \tag{4.42}$$

and applying integration by parts on the first term of the right hand side whilst respecting $\rho_i$ and $X_{ij}$ to be piecewise constant on the elements the gives

$$\int_\Omega \Phi_\alpha \phi \partial_t (S_i, \beta \Phi_\beta) \, dx = \left[ \Phi_\alpha k \lambda \frac{d\rho_c}{dS_i} S_{i,\beta} \partial_x \Phi_\beta \right]_{\partial\Omega}$$

$$- \int_\Omega \partial_x \left( \Phi_\alpha \frac{1}{\rho_i X_{ij}} \right) \rho_i X_{ij} \lambda k \frac{d\rho_c}{dS_i} S_{i,\beta} \partial_x \Phi_\beta \, dx$$

$$- \int_\Omega \Phi_\alpha \frac{1}{\rho_i X_{ij}} \partial_t \left( \rho_i X_{ij} \right) S_{i,\beta} \Phi_\beta \, dx. \tag{4.43}$$
Because a global formulation is used (Eq. 4.17), the Neumann boundary condition enforced on elements represented by the first term in brackets cancels out for adjacent elements until the global boundary \( \partial \Omega \) is reached. Applying the product rule on the second term gives

\[
\int_{\Omega} \Phi_\alpha \phi \partial_t (S_{i, \beta} \Phi_\beta) \, dx = \left[ \Phi_\alpha \bar{\lambda} K \frac{dp_c}{dS_i} S_{i, \beta} \partial_s \Phi_\beta \right]_{\partial \Omega} \\
- \int_{\Omega} \partial_s \Phi_\alpha \bar{\lambda} K \frac{dp_c}{dS_i} S_{i, \beta} \partial_s \Phi_\beta \, dx \\
- \int_{\Omega} \Phi_\alpha \partial_s \left( \frac{1}{\rho_i \bar{X}_q} \right) \frac{1}{\rho_i \bar{X}_q} \bar{\lambda} K \frac{dp_c}{dS_i} S_{i, \beta} \partial_s \Phi_\beta \, dx \\
- \int_{\Omega} \Phi_\alpha \frac{1}{\rho_i \bar{X}_q} \partial_t (\rho_i \bar{X}_q) S_{i, \beta} \Phi_\beta \, dx, 
\] (4.44)

and noting that \( \rho_i \) and \( \bar{X}_q \) are piecewise constant on elements will zero out the third right hand side term and finally gives the weak form Eq. 4.40

\[
\int_{\Omega} \Phi_\alpha \phi \partial_t (S_{i, \beta} \Phi_\beta) \, dx = \left[ \Phi_\alpha \bar{\lambda} K \frac{dp_c}{dS_i} S_{i, \beta} \partial_s \Phi_\beta \right]_{\partial \Omega} \\
- \int_{\Omega} \partial_s \Phi_\alpha \bar{\lambda} K \frac{dp_c}{dS_i} S_{i, \beta} \partial_s \Phi_\beta \, dx \\
- \int_{\Omega} \Phi_\alpha \frac{1}{\rho_i \bar{X}_q} \partial_t (\rho_i \bar{X}_q) S_{i, \beta} \Phi_\beta \, dx. 
\] (4.45)

Analogue to Eq. 4.26 a semi-implicit Euler method of the weak formulation yields a system of linear equations

\[
\left( \frac{1}{\Delta t} \left[ A_{s_{i, \beta}}^\delta \right]' + \left[ K_{s_{i, \beta}}^\delta \right]' + \left[ B_{s_{i, \beta}}^\delta \right]' \right) S_{i, \beta}^{t+\Delta t} = \frac{1}{\Delta t} \left[ A_{s_{i, \beta}}^\delta \right]' S_{i, \beta}^t + \left[ G_{s_{i, \beta}}^\delta \right]' 
\] (4.46)
Figure 4.5: Boundary condition imposed on boundary elements during the capillary diffusion step. To suppress CO$_2$ contribution from spontaneous imbibition or spurious spontaneous drainage, boundary elements carry effectively vanishing values of capillary diffusivity $D^{cap}$. Spurious spontaneous drainage is caused if a Van Genuchten $p_c$-functions is used, and the domain is initially filled with a water-wet fluid. The Van Genuchten model exhibits a steep entry slope near $S_e \to 1$ and consequently leads to very high capillary diffusivities (see also Fig. 3.1 (II) for a comparison of $D^{cap}$ when $S_e \to 1$ between the Brooks-Corey model and the Van Genuchten model).

with the mass matrix $A^{S_i}_{a\beta}$, the stiffness matrix $K^{S_i}_{a\beta}$, the compressibility matrix $B^{S_i}_{a\beta}$, and the Neumann boundary vector $G^{S_i}_a$ defined by

\begin{align}
A^{S_i}_{a\beta} &= \int_{\Omega} \Phi_a \phi \Phi_\beta \, dx, \\
K^{S_i}_{a\beta} &= \int_{\Omega} \partial_x \Phi_a \bar{\lambda} \frac{d p_c}{d S_i} \partial_x (\Phi_\beta) \, dx, \\
B^{S_i}_{a\beta} &= \int_{\Omega} \Phi_a \frac{1}{\rho_i X_{\bar{j}}} \partial_i \left( \rho_i X_{\bar{j}} \right) \Phi_\beta \, dx, \\
G^{S_i}_a &= \int_{\partial \Omega} \Phi_a \left( \partial_x \left( \bar{\lambda} \frac{d p_c}{d S_i} S_{i\beta} \right), n \right) \, dx
\end{align}

The stiffness matrix $K^{S_i}_{a\beta}$ is wrapped into a fixpoint-iteration, namely the Picard-iteration to lift its contribution to the same time level at which the saturation $S_i$ is solved. This reduces further errors introduced by the operator splitting. In this work, the iteration usually converges within two cycles. If the temporal change in phase densities are small, then $B^{S_i}_{a\beta} \approx 0$ can be assumed. This is justified in the context of this work, because the ambient pressure regime under reservoir conditions at the MPa-scale is much higher than the capillary pressure values of few kPa, hence $\partial_t (\rho_i X_{\bar{j}}) = 0$. This leads to $B^{S_i}_{a\beta} = 0$. Note that during the capillary diffusion step the global pressure does not change. For a discussion of the error introduced, the reader is referred to Chavent (2009), di Chiara Roupert et al. (2010), Amaziane et al. (2011), and Amaziane et al. (2012).
Boundary Condition  

Boundary conditions are imposed by assuming no flow across all boundaries if an injection strategy is followed. The reasoning is following: if boundary nodes act as a virtual injector, then their saturation values need to be fixed to $S_i = 1$ during the advection step if $i$ is the injecting phase. Otherwise the corresponding fractional flow function results in $f_i < 1$, effectively reducing the injection rate. Fixing the saturation this way has consequences for the capillary diffusion step (Eq. 4.5): capillary diffusivities $D_{\text{cap}} = \bar{\lambda} K \frac{d p_c}{dS}$ used for the finite element method are calculated from saturations interpolated at the element’s barycentre, and will cause a wetting phase $i$ to spontaneously imbibe, or spontaneously drain if $S_e = 1$ when Van Genuchten $p_c$-functions are used (see steep entry slope near $S_e \to 1$ in figure Fig. 3.1 (II)). Hence, additional mass is injection into the domain $\Omega$ which needs to be avoided. This is numerically realised by setting $D_{\text{cap}}$ to a very small value, typically $1 \times 10^{-23}$ to avoid degeneracy of Eq. 4.46. Additional sources are not considered, therefore $G_s^i = 0$ and mass injection is realised in the advection step only for convenience reason.

Post-Process  

If a 2-phase situation is encountered then $X_j$, the phase mass fractions of component $j$, needs to be corrected due to thermal equilibrium. The equilibrated values are calculated based on the equation of state (Eq. 2.31, Eq. 2.33 to Eq. 2.35). Reconstruction of the mass components $M_j$ is achieved by

$$M_j = \sum_{i=1}^{n_p} \left[ \rho_i X_j S_i \right]^f.$$  \hspace{1cm} (4.51)
Figure 4.6: Sequence diagram of the finite element capillary diffusion step. The sequence evolution is from top to down. The inner blue shaded area marks the finite element method and the dependent variable $S_i$ is denoted in bold. The capillary diffusivity $D^{cap}$ is calculated from phase viscosities $\mu_i$ and flowing saturation $S_i^f$ interpolated to the element’s barycentre, and corrected for elements which exhibit a node boundary to avoid spontaneous imbibition/spontaneous drainage effects (see text). The Neumann boundary vector $G_i^a$ is set to zero. The outer blue shaded area marks the Picard-iteration. Post-processing incorporates updating $X_{ij}$, the phase mass fractions of component $j$ in phase $i$, and the restoration of $M_j$ the mass component $j$. 

\[
S_i^{(t-dt)} \quad S_i^{t,k} \quad S_i \quad \mu_i \quad S_{if} \quad D^{cap} \quad M_j \quad X_{ij}
\]
4.7 Relative Permeability Hysteresis

The hysteresis affected non-wetting relative permeability are contributing to the pressure equation step (Sec. 4.4) through total mobility \( \lambda_t \), to the mass advection step (Sec. 4.5) through the fractional flow functions \( f_i \), and to the capillary diffusion step (Sec. 4.6) through reduced mobilities \( \hat{\lambda} \). This relative permeability is calculated in the post-process step of the mass advection and the capillary diffusion step. A typical non-wetting relative permeability curve respecting hysteresis effects is shown in Fig. 3.4. The trapped saturation \( S_{nt} \) considered here is identified with the residual saturation of non-wetting fluid \( S_{nr} \) for calculations of the effective saturation \( S_e \). The discretisation of Eq. 3.58, Eq. 3.59, Eq. 3.60, and Eq. 3.62 is straight-forward. The sequence is shown below.

The sequence to pick and calculate the correct relative permeability curve is shown below.

1. Initialise Trapping Variables
   - \( S_{ni,\text{max}} = 1 - S_{n,\text{irr}} \)
   - Calculate \( S_{nr,\text{max}}(S_{ni,\text{max}}, C) \) with \( C = 1 \)

2. Determine Flow Direction:
   - Primary Drainage:
     \[
     [S_n]^{t+\Delta t} > [S_{ni}]^{t+\Delta t}
     \]
   - Imbibition
     \[
     [S_n]^{t+\Delta t} < [S_{ni}]^{t+\Delta t} \land [S_n]^{t+\Delta t} < [S_n]^t
     \]
   - Subsequent Drainage
     \[
     [S_n]^{t+\Delta t} < [S_{ni}]^{t+\Delta t} \land [S_n]^{t+\Delta t} > [S_n]^t
     \]

3. If Primary Drainage
   - Set \( [S_{ni}]^{t+\Delta t} = [S_n]^{t+\Delta t} \)
   - No residual saturation: \( S_{nt} = 0 \)
   - Non-wetting saturation is flowing saturation : \( S_n = S_{nf} \)
4. If on Scanning Curve (Imbibition or Subsequent Drainage)

- Use regular non-wetting relative permeability

4.8 Capillary Entry Pressure

To simulate the extended pressure conditions at interfaces, an equivalent pressure potential approach has been adopted (Helmig and Huber, 1998). The extended pressure condition applies when a $p_c$-function is used with non-vanishing capillary entry pressure $p_d > 0$. The interface is assumed to sit between nodes, that is, it encapsulates fractures only and thus can prevent flow into the surrounding rock matrix. In this approach the non-wetting pressure potential $\psi_{n,\alpha}$ at each node $\alpha$ considers the experienced flow state at that node (see Sec. 4.7), i.e. the presence of an non-wetting phase. It is defined as

$$\psi_{n,\alpha} = \begin{cases} p_{n,\alpha} + p_{c,\alpha} - \rho_n g z_{\alpha} & \text{if } S_{n,\alpha} > S_{nt,\alpha} \\ p_{n,\alpha} + p_{d,\alpha} - \rho_n g z_{\alpha} & \text{if } S_{n,\alpha} \leq S_{nt,\alpha}. \end{cases}$$

(4.52)

If a non-wetting phase is present with $S_n > S_{nt}$, flow occurs. If the non-wetting phase is below residual saturation or zero $S_n \leq S_{nt}$, it is immobile. By comparing the pressure potential at adjacent nodes $\psi_{n,\alpha}$ and $\psi_{n,\beta}$, one can determine whether flow will occur. For a finite volume at $\alpha$, flow across the facet shared with adjacent nodes $\beta$ will happen when the non-wetting fractional flow function is not zero,

$$f_{n,\alpha\beta} = \begin{cases} f_{n,\alpha}^{up} & \text{if } (\psi_{n,\alpha}^{up} - \psi_{n,\alpha}^{down}) > 0 \\ 0 & \text{if } (\psi_{n,\alpha}^{up} - \psi_{n,\alpha}^{down}) \leq 0, \end{cases}$$

(4.53)
4.9 BREAKTHROUGH CURVES AND MASS INVENTORIES

with

\[
\psi_{n}^{\text{up}} = H_{n,\alpha\beta} \psi_{n,\alpha} + (1 - H_{n,\alpha\beta}) \psi_{n,\beta}
\]

\[
\psi_{n}^{\text{down}} = (1 - H_{n,\alpha\beta}) \psi_{n,\alpha} + H_{n,\alpha\beta} \psi_{n,\beta}
\]

and \(H_{n,\alpha\beta}\) the Heaviside function defined in Eq. 4.36.

In the operator split strategy considered here (Sec. 4.2), the capillary diffusivity \(D_{\text{cap}}\) vanishes when \(S_e \to 1\) for \(p_{c}\)-functions with \(p_{d} > 0\).

4.9 BREAKTHROUGH CURVES AND MASS INVENTORIES

Velocity-weighted breakthrough curves measure the quantity of a variable \(\varphi\) across a plane by integration over the plane through which \(\varphi\) flows and normalising by the flow. It is defined as

\[
F_{\varphi,\text{BTC}} = \sum_{e} \frac{\varphi^{(e)} v_{\text{vol}}(e) v^{(e)\#\phi}}{v_{\text{vol}}(e) v^{(e)\#\phi}}
\]

Integration of a density \(\zeta(t)\) over a domain yields the mass inventory curve for \(\zeta\) at a given time \(t\):

\[
M_{\varphi,\text{inv}}(t) = \sum_{e} \zeta(t) \ast \phi
\]

4.10 OVERALL SPLITTING SEQUENCE

Godunov operator-splitting of the mass balance equation (Eq. 3.1) and the pressure equation (Eq. 3.24) lead to a sequence of steps to execute, namely the pressure diffusion step (Eq. 4.2), advection step (Eq. 4.3), and capillary diffusion step (Eq. 4.4), which weakens the strong coupling between Eq. 3.1 and Eq. 3.24. Still, the non-linear weak coupling through total mobility, total compressibility, and capillary pressure introduces some error into the splitting procedure. We therefore use a predictor-corrector method
to reduce these splitting errors (Gresho et al., 1978). The operator-splitting sequence is shown below.

1. Initialize Model

2. Predictor Step: Save $M^t_j$ and $p^t$

3. Advection Step per Explicit FV
   - Advect $M^t_j \rightarrow M^{t+\Delta t}_j$ (Eq. 4.35)
   - Update $S_i(M^{t+\Delta t}_j)$ and $X_{ij}(M^{t+\Delta t}_j)$ by Applying Phase Split (Eq. 3.57)

4. Capillary Diffusion Step per Implicit FE
   - Update $D^\text{cap}(S_i)$
   - Capillary Diffusion of $S_i \rightarrow S^{t+\Delta t}_i$ (Eq. 4.46)
   - Update $X_{ij}(S^{t+\Delta t}_i)$ (from EOS)
   - Reconstruct $M^{t+\Delta t}_j(X^{t+\Delta t}_{ij}, S^{t+\Delta t}_i)$ (Eq. 4.51)
   - Apply Picard-iteration until Convergence: $|S^{t,k+1}_i - S^{t,k}_i| < \varepsilon$

5. Pressure Diffusion Step per Implicit FE
   - Update $\lambda_i(S^{t+\Delta t}_i), \beta_i(S^{t+\Delta t}_i)$
   - Pressure Diffusion $p^t \rightarrow p^{t+\Delta t}$ (Eq. 4.46)
   - Update $X_{ij}(p^{t+\Delta t}, T), \rho_i(p^{t+\Delta t}, T, X_{ij}), \beta_i(p^{t+\Delta t}, T), \mu_i(p^{t+\Delta t}, T)$
   - Update $v_i(p^{t+\Delta t}, \lambda_i)$ (Eq. 4.31)

6. Corrector Step: Restore $M^t_j$ and $p^t$
   - Discard $M^{t+\Delta t}_j$ and $p^{t+\Delta t}$
   - Keep $\rho_i, \beta_i, \mu_i, X_{ij}, D^\text{cap}$
   - Execute Advection Step
   - Execute Capillary Diffusion Step
   - Execute Pressure Diffusion Step

7. Proceed with Predictor Step at new Time Level $t + \Delta t$
This chapter presents the benchmarking of the decoupled finite element - finite volume method devised in Sec. 4.2 (and subsequent sections) designed to simulate compressible compositional flow and transport in fractured media when capillary forces are present. It is equipped with an modified non-iterative Redlich-Kwong equation of state (Sec. 2.1) and additional procedures to calculate thermophysical properties (Sec. 2.4) for realistic pressure and temperature regimes of CO$_2$–H$_2$O–NaCl fluids occurring during geological carbon storage. The benchmarks are designed to scrutinise the correctness of the operator-splitting strategy in combination with the equation of state and the thermophysical properties. The benchmarks are divided into three groups.

The first benchmark group (Sec. 5.1) compares numerical results against the Buckley Leverett solution to test the interplay between the thermodynamic properties (Sec. 2.4), the pressure equation (Sec. 4.4) and the finite volume transport (Sec. 4.5).

The second benchmark group (Sec. 5.2) compares numerical results of various spontaneous imbibition simulations in a homogeneous medium against the well-established fully-coupled multiphase flow and transport simulator TOUGH2 (Pruess et al., 2011) which comes with the fluid property module ECO2M (Pruess, 2013) designed for application of geologic storage of CO$_2$. It uses a integral finite difference method to discretise the its continuum equations in space (Edwards, 1972; Narasimhan and Witherpoon, 1976)*. The benchmarks test the correct implementation of the capillary diffusion outlined in Sec. 4.6. The results are also compared against the analytical McWhorter-Sunada-Schmid solution (Schmid and Geiger, 2012) for spontaneous imbibition.

The third benchmark group (Sec. 5.3) compares numerical results of combined effects of viscous and capillary forces with regard to the spreading of CO$_2$ in a fractured media containing a single through-going fracture against the finite difference fully coupled reservoir simulator ECLIPSE/300 in its CO2STORE mode. The benchmarks test the correctness of the full operator-splitting sequence (Sec. 4.10) including the pressure diff-

*Resolve literature via Pruess et al. (2011)
fusion step, the mass advection step and the capillary diffusion step together with a predictor-corrector method, the non-iterative, modified Redlich-Kwong equation of state and the calculations of thermophysical properties.

5.1 BUCKLEY-LEVERETT TEST

The Buckley-Leverett problem for incompressible and immiscible two-phase flow describes a non-linear flow problem of displacement of a phase by another invading one, and for which analytical solution has been derived (Buckley and Leverett, 1941). The original work described a problem where a completely the oil in an oil-filled medium is displaced by either water (wetting phase) or by gas (non-wetting phase) under a pressure gradient. The invading phase exhibits a discontinuity in saturation, the so-called shock front. With increase in saturation the invading fluid becomes more mobile whereas the displaced fluid becomes less mobile to the point where it almost ceases to flow. This behaviour is controlled by non-linear relative permeability curves. The non-linear nature of the relative permeabilities contributes to the creation of a rarefaction upstream behind the shock front with saturation values between the shock front saturation $S_{i,s}$ and the saturation value at the inlet boundary $S_{i,0}$. The analytical solution to the Buckley-Leverett problem is described by the mass balance equation

\[
\partial_t S_i = -\frac{q_i}{\phi A} \partial_x f_i
\]

\[
= -\frac{q_i}{\phi A} \frac{\partial f_i}{\partial S_i} \partial_x S_i
\]

(5.1)

where $S_i$ is the saturation of the displacing fluid, $A$ is the cross-sectional area, $q_i$ is the volumetric flow rate through $A$, and $f_i$ is the fractional flow function as defined by Eq. 3.25. Note that the equation describes flow in the absence of capillary and gravitational forces. The solution’s shock saturation is controlled by the viscosity ratio of the
wetting and non-wetting fluid. The solution for both phases can be computed analytically by finding the root of

\[ g_1(S_w) = f_w - (S_w - S_i) \frac{df_w}{dS_w} \]
\[ g_2(S_w) = f_n - ((1 - S_w) - S_i) \frac{df_n}{dS_n}. \]  

(5.2)

Numerical results are based on the mass balance equations Eq. 3.33 in the absence of gravitation, capillary forces, and miscibility effects. They reduce to

\[ \partial_t M_j = - \text{div} \left( \sum_i n_i \delta_{ij} \rho_i X_{ij} f_i \mathbf{v}_i \right) + q_j \]  

(5.3)

where \( \delta_{ij} \) is the Kronecker symbol.

The used grid geometry is \( 10 \text{ m} \times 1 \text{ m} \). CSMP uses a unstructured mesh with 11022 elements and 5510 nodes. The grid is shown in Fig. 5.1. Further flow parameters are given in Tab. 5.1. Note that thermodynamic properties, i.e. viscosities, are held constant.

The roots of (Eq. 5.2) are shown in Fig. 5.2 (II) and matches those obtained through the Welge tangent method (Welge, 1952; Pope, 1980) shown in Fig. 5.2 (III) for both phases as can be seen by the vertical, dashed grey lines. The non-wetting shock front saturation is \( S_{n, s} = 0.33757 \), the wetting shock front saturation is \( S_{w, s} = 0.89947 \). In Fig. 5.2 (IV) numerical results of the non-wetting phase injected at \( q = 1 \times 10^{-4} \text{ m/s} \) are compared against the analytical solution at different times. The figure shows that the rarefaction fans, the shock positions, and the shock front saturations are in good agreement with the analytical solution. Therefore, the implementation of the thermodynamic properties, the pressure equation and the finite volume transport correct.

![Figure 5.1: Unstructured FE Mesh for CSMP.](image-url)
Figure 5.2: Overview of the parameter used in the Buckley-Leverett problem. Parameter are given in Tab. 5.1. The Fig. 5.2 (I) shows the used Brooks-Corey relative permeability curves, Fig. 5.2 (II) shows the roots of Eq. 5.2 which matches well with the shock front saturation determined by the Welge tangent method in Fig. 5.2 (III). The non-wetting shock front saturation is $S_{n,w} = 0.33757$. The invading non-wetting CO$_2$ phase is injected at a rate of $q = 1 \times 10^{-4}$ m/s. Numerical results are shown in Fig. 5.2 (IV) with good agreement in rarefaction fan, shock front position and shock front saturation value.
Table 5.1: Parameter for the Buckley-Leverett benchmark.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection Rate $q$</td>
<td>$1 \times 10^{-4}$ m/s</td>
</tr>
<tr>
<td>Non-wetting Viscosity $\mu_n$</td>
<td>$5.17641 \times 10^{-5}$ Pa s</td>
</tr>
<tr>
<td>Wetting Viscosity $\mu_w$</td>
<td>$5.97778 \times 10^{-4}$ Pa s</td>
</tr>
<tr>
<td>Porosity $\phi$</td>
<td>15 %</td>
</tr>
<tr>
<td>Permeability, $k$</td>
<td>$10^{-12}$ m$^2$</td>
</tr>
<tr>
<td>Initial Wetting Saturation $S_{wi}$</td>
<td>1.0</td>
</tr>
<tr>
<td>Brooks-Corey $\lambda$</td>
<td>2</td>
</tr>
<tr>
<td>Residual Non-wetting Saturation, $S_{rn}$</td>
<td>0.0</td>
</tr>
<tr>
<td>Residual Wetting Saturation, $S_{rw}$</td>
<td>0.0</td>
</tr>
<tr>
<td>Left Boundary Condition (Saturation)</td>
<td>1.0</td>
</tr>
<tr>
<td>Model Size</td>
<td>$10$ m $\times$ $2$ m</td>
</tr>
</tbody>
</table>

5.2 COMPRESSIBLE COMPOSITIONAL FLOW IN A HOMOGENEOUS MEDIUM

The benchmarking of the operator splitting sequence alongside with the equation of state and the thermophysical properties with full pressure dependence is divided into three parts. Gravitational forces are not considered. The respective equations used are stated.

First, the pressure diffusion and the mass transport step are benchmarked to verify the correctness of viscous forces only transport of compressible compositional flow and transport problems. Results are benchmarked against the well-established fully coupled multiphase simulator TOUGH2/ECO2M. An overview of publications used to calculate thermophysical properties in CSMP ++ and TOUGH2/ECO2M are listed in Tab. 5.2.

Second, only the capillary diffusion step is benchmarked to verify the correctness of capillary forces driven fluid propagation such as spontaneous imbibition and spontaneous drainage. Spontaneous drainage occurs when the capillary pressure function exhibits a non-zero entry slope. Results are benchmarked against TOUGH2/ECO2M.

Third, the full operator splitting sequence is tested for forced drainage scenario, where both viscous and capillary forces affect the propagation of a non-wetting fluid. Results are benchmarked against TOUGH2/ECO2M and the commercial reservoir simulator ECLIPSE/300 CO2STORE.

All benchmarks assume isothermal fluid propagation within a homogeneous medium and full pressure dependence of the equation of state and calculations of thermophys-
ical properties involved. There are no gravitational forces considered, and molecular diffusion is not permitted. The same grid geometry and grid meshes are used as in the Buckley-Leverett Benchmark (Fig. 5.1 & Fig. 5.3). Two different relative permeability curves are used, associated with the Van Genuchten model (Eq. 3.40 & Eq. 3.41) and with the Brooks-Corey model (Eq. 3.44 & Eq. 3.45). The respective calculations of thermodynamical properties in TOUGH2/ECO2M and CSMP++ are listed in Tab. 5.2.

Table 5.2: Comparison of thermodynamical properties between TOUGH2/ECO2M and CSMP

<table>
<thead>
<tr>
<th>Property</th>
<th>TOUGH2/ECO2M</th>
<th>CSMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase Mass Fraction $X_{ij}$</td>
<td>Tabulated Altunin (1975) Correlation</td>
<td>Pruess &amp; Spycher (2007)</td>
</tr>
<tr>
<td>H$_2$O Viscosity $\mu_w$</td>
<td>Phillips et al. (1981)</td>
<td>Kestin et al. (1978)</td>
</tr>
<tr>
<td>CO$_2$ Viscosity $\mu_n$</td>
<td>Tabulated Altunin (1975) Correlation</td>
<td>Fenghour &amp; Wakeham (1998)</td>
</tr>
<tr>
<td>H$_2$O Density $\rho_w$</td>
<td>Batistelli et al. (1997)</td>
<td>Rowe and Chou (1970)</td>
</tr>
<tr>
<td>CO$_2$ Density $\rho_n$</td>
<td>Tabulated Altunin (1975) Correlation</td>
<td>Pruess &amp; Spycher (2007)</td>
</tr>
</tbody>
</table>

5.2.1 Viscous Flow and Transport

CO$_2$ migration due to viscous forces and in the absent of capillary and gravitational forces are tested by comparing numerical results of carbonic phase profiles. The simulation conducted in Sec. 5.1, is revisited. The model geometry used for CSMP++ is shown in Fig. 5.1, the model geometry used for TOUGH2/ECO2M is shown in Fig. 5.3. The model geometry used for TOUGH2 is structured and divided into $100 \times 51$ FV cells. At the left model boundary CO$_2$ is injected at a constant rate. The injection rate of CO$_2$ mass is $M_{\text{inj}} = 0.663 \text{kgs}^{-1}$. Fluids can leave the model geometry at the right boundary where pressure is held constant at $p_0 = 10.0 \text{MPa}$. Initial pressure and temperature used are $p_0 = 10.0 \text{MPa}$ and $40^\circ\text{C}$. The top and bottom boundaries are no flow boundaries.

Figure 5.3: Structured finite volume mesh of TOUGH2/ECO2M used for benchmarks in Sec. 5.2.
Matrix permeability is \( k_m = 1 \times 10^{-13} \text{ m}^2 \) and matrix porosity is \( \phi = 15\% \). Residual saturations are zero. Values for the relative permeability models are listed in Tab. 5.3. Gravity effects are neglected.

Numerical results are based on the mass balance equations Eq. 3.33, the pressure diffusion equation Eq. 3.32 and the Darcy velocity Eq. 3.28, in the absence of gravitation, capillary forces. They reduce to

\[
\beta_i \frac{\partial}{\partial t} p = \text{div} \left( \lambda_i K \text{grad} p \right) + \sum_i n_p q_i. \tag{5.4}
\]

\[
v_t = -\lambda_i K \text{grad} p \tag{5.5}
\]

\[
\frac{\partial}{\partial t} M_j = -\text{div} \left( \sum_i n_p \rho_i X_{ij} f_i v_t \right) + q_j. \tag{5.6}
\]

Numerical results for carbonic saturation profiles are shown in Fig. 5.4 after injection of \( \text{CO}_2 \) started. The non-wetting carbonic shock front saturation for CSMP is approximately \( S_{n,s} = 0.334 \), and for TOUGH2 approximately \( S_{n,s} = 0.333 \). The figure shows that numerical results for the rarefaction fans, the shock positions, and the shock front saturations of CSMP++ are in good agreement with numerical results of TOUGH2/ECO2M.

5.2.2 Drainage and Spontaneous Imbibition

\( \text{CO}_2 \) migration due to capillary forces and in the absent of viscous and gravitational forces are tested by comparing numerical results of carbonic phase profiles. Two situations flow directions are modelled: (a) drainage where the non-wetting carbonic phase displaces the wetting aqueous phase and, (b) counter-current spontaneous imbibition \((\text{McWhorter and Sunada, 1990; Schmid and Geiger, 2012})\), where the wetting aqueous phase is displaced by capillary drive of the carbonic phase.

The model geometries from the previous section were used with no flow boundaries at the top, right and bottom boundary. The left model boundary is open. Saturations were fixed at the left model boundary with \( S_w = 0 \) for the drainage test and \( S_w = 1 \)
Table 5.3: Overview of benchmark data used in this chapter.

<table>
<thead>
<tr>
<th>Relative Permeability Model†</th>
<th>Brooks-Corey (Eq. 3.44 &amp; Eq. 3.45)</th>
<th>( \lambda = 2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Van Genuchten (Eq. 3.40 &amp; Eq. 3.41)</td>
<td>( m = 0.772 )</td>
</tr>
<tr>
<td>Capillary Pressure Model‡</td>
<td>Van Genuchten (Eq. 3.43)</td>
<td>( m = 0.772, \alpha = 3.7 \times 10^{-4} \text{ Pa}^{-1} )</td>
</tr>
<tr>
<td>Reservoir Properties</td>
<td>Matrix Permeability</td>
<td>( k_m \in {1 \times 10^{-13} \text{ m}^2, 1 \times 10^{-13} \text{ m}^{15} } )</td>
</tr>
<tr>
<td></td>
<td>Fracture Permeability</td>
<td>( k_f = 1.0 \text{ mm} )</td>
</tr>
<tr>
<td></td>
<td>Porosity</td>
<td>( \phi = 15% )</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td>( T = 40\degree \text{ C} )</td>
</tr>
<tr>
<td></td>
<td>Residual Wetting Saturation</td>
<td>( S_{rw} = 0.10 )</td>
</tr>
<tr>
<td></td>
<td>Residual Non-Wetting Saturation</td>
<td>( S_{rn} = 0.15 )</td>
</tr>
<tr>
<td>Boundary Conditions SI</td>
<td>Wetting Saturation (Left Border)</td>
<td>( S_w = 0.85 )</td>
</tr>
<tr>
<td>Boundary Conditions FD</td>
<td>Injector</td>
<td>( q = 1 \times 10^{-4} \text{ m/s} )</td>
</tr>
<tr>
<td></td>
<td>Producer</td>
<td>( p = 100 \text{ MPa} )</td>
</tr>
<tr>
<td></td>
<td>Everywhere else</td>
<td>no flow</td>
</tr>
<tr>
<td>Mesh</td>
<td>Size</td>
<td>( 10 \text{ m} \times 2 \text{ m} )</td>
</tr>
<tr>
<td></td>
<td>CSMP Grid</td>
<td>10513 Elements, 4972 Nodes</td>
</tr>
<tr>
<td></td>
<td>TOUGH2 Grid</td>
<td>102 \times 10 Elements</td>
</tr>
</tbody>
</table>

† Fracture flow obeys linear relative permeability curves.
‡ The derivative is used according to Sec. 4.6.

Figure 5.4: Injection benchmark with viscous forces only. TOUGH2 operates at a fixed injection rate of 0.0663 kg/s. CSMP++ uses a corresponding volume flux rate based on the fixed CO2 density chosen which is spatially constant and does not change over time (see setup slide). High \((\mu, \rho)\) values lead to a slower front propagation and vice versa. Family of profiles shown at 20 and 60 mins after injection start.
for the spontaneous imbibition test. The initial saturation is set to the model \( S_w = 1 \) for the drainage test and to \( S_w = 0 \) for the imbibition test. Residual saturations are set to zero. Two different relative permeability models were used, the Brooks-Corey and the Van Genuchten relative permeability model. Parameters of the relative permeability models are listed in Tab. 5.3. Only the Van Genuchten capillary pressure model was used, because a Brooks-Corey capillary pressure model is not implemented in TOUGH2/ECO2M. Model parameters for the Van Genuchten capillary pressure model are also listed in Tab. 5.3. Note, that the Van Genuchten capillary pressure model has a steep capillary entry slope ([Fig. 3.1 (II)](#)) which leads to order of magnitudes higher values of the capillary diffusivity \( D_{\text{cap}} \) when \( S_w \to 1 \), compared to the Brooks Corey capillary pressure model. It also causes artificial spontaneous drainage when a Van Genuchten capillary pressure model is employed. The same permeability and porosity values from the previous chapter were used.

Numerical results are based on the capillary diffusion equation Eq. 4.46, in the absence of viscous and gravitational forces. The compressibility matrix \( B^S_{\alpha\beta} \) is neglected as changes in thermophysical properties due to changes in capillary pressure are assumed to be small against reservoir pressure and temperature conditions. For a discussion of the error introduced, see Chavent (2009), di Chiara Roupert et al. (2010), Amaziane et al. (2011), and Amaziane et al. (2012).

Numerical results for profiles of the carbonic phase are shown for imbibition in [Fig. 5.5](#) and for drainage in [Fig. 5.6](#). Numerical results from TOUGH2 were produced where mobilities were taken form the upwind element or averaged across adjacent elements. Numerical results of profiles of carbonic saturations during spontaneous imbibition when a Brooks-Corey relative permeability model is used are shown after 480 min and after 1920 min [Fig. 5.5 (I)](#), and after 60 and 440 min when a Van Genuchten relative permeability model is used [Fig. 5.5 (II)](#). When a Brooks-Corey relative permeability model is used. Shock front position of CSMP results are 0.40 m after 440 min and 0.75 m after 1920 min, for TOUGH2 upwind 0.50 m and 0.90 m, and for TOUGH2 average 0.45 m and 0.80 m. When imbibition is employed with the Van Genuchten relative permeability model, shock front positions are 0.35 m after 60 min and 0.74 m after 440 min, for TOUGH2
upwind 0.38 m and 0.87 m, and for TOUGH2 average 0.37 m and 0.81 m. Numerical results show that rarefactions for profiles of carbonic saturation are in good agreement between CSMP++ and TOUGH2 results.

Numerical results for profiles of carbonic saturations during drainage are shown after 20 min, after 960 min, and after 1920 min when a Brooks-Corey relative permeability model is used Fig. 5.6 (I). Shock front positions for CSMP are 0.27 m, 0.86 m and 1.19 m for the time listed before. Shock front positions for the TOUGH2 average case are 0.26 m, 0.77 m, and 1.05 m. Shock front positions for the TOUGH2 upwind case are 0.30 m, 0.82 m and 1.16 m. Shock front positions are in good agreement. Rarefactions representing CSMP++ results show crossing with rarefactions representing TOUGH2 results, indicating fair agreement. As time develops shock front positions representing TOUGH2 and CSMP++ results show divergent behaviour over time, i.e. CSMP shock front positions eventually overtake TOUGH2 front positions.

Results for profiles of carbonic saturation are shown after 80 and 240 min when a Van Genuchten relative permeability model is used Fig. 5.6 (II). Shock front positions for CSMP are hard to quantify, because no distinct shock front is established. Numerical results show that rarefactions for CSMP and TOUGH2 at a given time show some fair agreement.
5.2 Compressible Compositional Flow in a Homogeneous Medium

(I) Imbibition, Brooks-Corey $k_r$-Model

(II) Imbibition, Van Genuchten $k_r$-Model

Figure 5.5: Spontaneous imbibition benchmark, where numerical results from CSMP++ (blue lines) are compared against TOUGH2/ECO2M (uncolored lines). TOUGH2/ECO2M results are based on mobilities either upwind weighted (black line) or averaged across adjacent element (grey line). Results shown in the left figure uses the Brooks-Corey relative permeability curve (Eq. 3.44 & Eq. 3.45), and they are displayed at 480 min (solid line) and 1920 min (dashed line). Results shown in the right figure uses the Van Genuchten relative permeability curve (Eq. 3.40 & Eq. 3.41), and they are displayed at 60 min (solid line) and 440 min (dashed line). Both results uses the same capillary pressure curves from the Van Genuchten model (TOUGH2/ECO2M: Eq. 3.42, CSMP++: Eq. 3.43).

(I) Drainage, Brooks Corey $k_r$-Model

(II) Drainage, Van Genuchten $k_r$-Model

Figure 5.6: Spontaneous drainage benchmark, where numerical results from CSMP++ (blue lines) are compared against TOUGH2/ECO2M (uncolored lines). TOUGH2/ECO2M results are based on mobilities either upwind weighted (black line) or averaged across adjacent element (grey line). Results shown in the left figure uses the Brooks-Corey relative permeability curve (Eq. 3.44 & Eq. 3.45), and they are displayed at 20 min (solid line), 960 min (dashed line), and 1920 min (dotted line). Results shown in the right figure uses the Van Genuchten relative permeability curve (Eq. 3.40 & Eq. 3.41), and they are displayed at 80 min (solid line) and 240 min (dashed line). Both results uses the same capillary pressure curves from the Van Genuchten model (TOUGH2/ECO2M: Eq. 3.42, CSMP++: Eq. 3.43).

5.2.3 Forced Drainage

$\text{CO}_2$ migration due to capillary and viscous forces in the absent of gravitational forces are tested by comparing numerical results of carbonic phase profiles produced by CSMP++,
ECLIPSE/300 and TOUGH2/ECO2M. No changes were made in the model geometries. At the left model boundary CO₂ is injected at a constant rate. The injection rate of CO₂ mass is $M_{\text{inj}} = 0.663 \text{kgs}^{-1}$. Fluids can leave the model geometry at the right boundary where pressure is held constant at $p_0 = 10.0 \text{MPa}$. Initial pressure and temperature used are $p_0 = 10.0 \text{MPa}$ and $40^\circ \text{C}$. The top and bottom boundaries are no flow boundaries. Parameter of the capillary pressure and relative permeability models are listed in Tab. 5.3. Only the capillary entry pressure was changed to 2 kPa, resulting in change of a Van Genuchten model parameter to $\alpha = 5 \times 10^{-4}$. A Brooks-Corey relative permeability model was combined with an Van Genuchten capillary pressure model. Brooks-Corey relative permeability curve data and Van Genuchten capillary pressure curve data were generated in MATLAB from the respective relationships (EQ Xx) and provided to ECLIPSE/300 as input files.

Numerical results for profiles of carbonic saturations during forced drainage are shown for invading CO₂ after 3 hours, after 6 hours. The show good agreement in rarefaction. However, the front positions relative to each other for a given time increases indicating divergent behaviour. CSMP has the most advanced front position, TOUGH2 the most retarded front position.
I benchmark the displacement of H$_2$O by invading CO$_2$ in a fractured porous medium due to capillary and viscous forces against the multi-phase simulator TOUGH2/ECO2M. Two different matrix permeabilities were used while the fracture permeability was held constant.

The model geometry used has dimensions of 2mm. A 10 m long through-going fracture is located 1 meter either side of the top and bottom boundary. The fracture is explicitly represented by 2D elements. The fracture’s width is 0.01961 m. The mesh for TOUGH2 is divided into 100 $\times$ 51 FV cells Fig. 5.9. There are two variants for the CSMP mesh: (1) 100 $\times$ 51 and (2) with 100 $\times$ 102 grid points Fig. 5.8 to ensure that the fracture width is resolved by one and two finite elements. If the fracture is resolved by two finite element perpendicular to its principal axis, it ensures that phase mobilities and capillary diffusivity, which require nodal saturation input interpolated at the element’s barycentre, will not be potentially influenced by matrix element properties.
The porosity of the matrix is fixed to $\phi_m = 15\%$, the fracture is assumed to be open with a porosity of $\phi_{ch} = 100\%$. Van Genuchten relative permeabilities were employed to the matrix. A linear relative permeability model is applied to the fracture. A Van Genuchten capillary pressure model is employed for the matrix and the fracture. Van Genuchten model parameters used are shown in (Tab. 5.3). No flow boundaries are applied to the top and bottom boundary. A constant volumetric injection rate of $q = 1 \times 10^{-4}$ m/s is applied at the left influx boundary and a fixed pressure of 100 MPa at the right outflux boundary. The wetting aqueous phase was fixed along the left boundary to $S_w = 0.85$, and the initial aqueous saturation is $S_w = 0.11$. Initial pressure is 100 MPa and temperature is 40 °C.

Two different matrix permeabilities were used $k_m \in \{10^{-15}, 10^{-13}\}$ m$^2$ and fracture permeability was set constant to $k_{ch} = 10^{-11}$ m$^2$. Numerical result for profiles of carbonic saturation Fig. 5.10 6 hours after CO$_2$ injection started, indicate that show good agreement in rarefactions.

**Figure 5.8:** Unstructured FE Mesh with through-going fracture for CSMP.

**Figure 5.9:** Structured FV Mesh with through-going fracture for TOUGH2.
5.3 Compressible Compositional Flow in a Fractured Porous Medium

(I) $k_f/k_w = 100$

(II) $k_f/k_w = 10,000$

Figure 5.10: Benchmark for spontaneous imbibition between CSMP and TOUGH2. CSMP results are denoted by 1 FE/2 FE which refers to the FE-width of the permeability channel. The saturation profiles are shown for 6 hours after imbibition start. The left figure shows wetting (aqueous) saturation profiles with $k_f/k_w = 100$, the right figure with $k_f/k_w = 10,000$. With MOP$(11) = 2$ mobilities are upstream weighted and permeabilities are harmonic weighted. Reservoir porperties are given in Tab. 5.3.
I will now demonstrate the numerical method developed and discussed in the previous chapters to investigate capillary trapping of CO$_2$ in some generic and idealised models with embedded fractures. Focusing on such simple model geometries helps to reveal fluid flow behaviour originating from fracture-matrix interactions during CO$_2$-brine migration through the fractured porous medium. The examples will focus on differences between (a) the Brooks-Corey and Van Genuchten relative permeability and capillary pressure models* which impact overall fluid flow and control trapping behaviour, and (b) low and high matrix permeabilities which allow for fracture or matrix dominated flow. The fracture aperture is held constant in all examples. To further reduce the physical complexity, phase densities are held constant. Thermophysical properties used throughout this chapter are listed in Tab. 6.2. The term two-phase model, which will be used in the following, refers to the $k_r$ and $p_c$ models used.

Two sets of model geometries are used throughout Chap. 6 to Chap. 9, each of which contains four different model geometries. All eight model geometries have identical model dimensions of 90 m $\times$ 90 m. The first set of four model geometries contains idealised fracture networks with up to four fractures, and are used in Chap. 6 and in Chap. 7. A second set of four model geometries contains geologically realistic fracture networks with 784 fractures, and is used in Chap. 8 and Chap. 9.

The BC and VG model have been chosen because of their different behaviour when the effective saturation is near one, i.e. $\lim S_e \to 1$. The BC and VG model have different entry slope regions (Fig. 3.2) which affects capillary diffusion (Fig. 3.1 (II)) when the non-wetting phases enters a medium which is completely filled with the wetting (here:

*Further referred to as BC and VG model
aqueous) phase. BC-type model exhibits a capillary entry pressure and thus requires the pressure of the non-wetting fluid to locally exceed the capillary entry pressure. Therefore, the entry pressure can impose restrictions on fluid migration. This feature is completely absent for VG-typ capillary pressure models. The impact of the application of the two-phase model is studied throughout Chap. 6 to Chap. 9.

Two matrix permeabilities of $k_m = 1 \times 10^{-13} \text{ m}^2$ (100 mD) and of $k_m = 1 \times 10^{-12} \text{ m}^2$ (1000 mD) have been chosen to study fracture or matrix dominated flow. The lower value represents a siliciclastic storage formation for CO$_2$ with moderate injectivity and the higher value represents a storage formations with exceptionally good injectivity. Permeability values lower than $k_m \ll 1 \times 10^{-13} \text{ m}^2$ are not considered for storage as the poor injectivity will lead to very small injection rates to prevent fracturing of the storage formation considered. The impact of the application of two different matrix permeabilities is studied throughout Chap. 6 to Chap. 9.

The impact of the two-phase models or the matrix permeabilities chosen on storage performance are studied by two measures: the velocity-weighted break through curves of CO$_2$ at the outlet boundary (Eq. 4.56), and the mass inventory of CO$_2$ within the entire model geometry (Eq. 4.57). The break through curve of CO$_2$ measures, at which time after injection start CO$_2$ will reach the outlet model boundary, and at which quantities. When break through of CO$_2$ occurs, injected CO$_2$ will not anymore completely add to the amount of CO$_2$ present within the model geometry, therefore the increase in cumulative amounts of CO$_2$ will slow down. The mass inventory of CO$_2$ measures the amount of CO$_2$ present within the model boundary and at a given time. A decline in the mass inventory indicates that more CO$_2$ is leaving the model geometry than is entering. These two measures, velocity-weighted break through curves of CO$_2$ and mass inventory of CO$_2$, are measured throughout Chap. 6 to Chap. 9.

In this chapter I considered pressure build-up and relaxation during injection, laminar multi-phase multi-component transport without turbulences, capillary diffusion, compressible fluids, and capillary entry pressure at the fracture-matrix interface. Phase densities account for pressure, temperature and salinity, but is held constant throughout
the simulation. Effects neglected are gravity, heterogeneous capillary entry pressures, hysteresis, energy transport, near-wellbore effects, and reactive transport.

6.1 Model Setup

All model geometries have a dimension of $90 \text{ m} \times 90 \text{ m}$ and are shown in Fig. 6.1. They are assumed to represent aerial view maps, hence gravity effects are absent. Here and in the following three chapters, I assume bed-bound fractures. They comprise four models

1. with 15568 triangles and no fracture present (Fig. 6.1 (I)) (GM1),

2. with 15606 triangles and an embedded fracture with 84 line elements (Fig. 6.1 (II)) (GM2),

3. with 15623 triangles and an through-going fracture with 67 line elements (Fig. 6.1 (III)) (GM3),

4. with 15718 triangles and 4 disconnected fractures with 117 line elements (Fig. 6.1 (IV)) (GM4).

All triangles are irregular. The model without a fracture (GM1) will serve as the base case to which the models containing fractures are compared. The meshes have been generated with the commercial software ANSYS/ICEM and the underlying geometry was created with the CAD program Rhino3D.

The CO$_2$ is injected in a super-critical state at the inlet (i.e. the left model boundary) across its entire length of 90 m. The top and bottom boundaries are no flow boundaries. Fluids can exit at the outlet (i.e. the right model boundary) where the pressure is kept constant at 1.2 MPa. CO$_2$ is injected along the entire left boundary at a rate of $M_{\text{inj}} = 0.5 \text{ kgs}^{-1}$ until one pore volume of $V_{\text{PV}} = 1.215 \times 10^3 \text{ m}^2$ has been injected. A pore volume CO$_2$ equals 826 200 kg at the initial pressure and temperature conditions of 12.0 MPa and 318 K (45 °C). The volumetric injection rate that can be computed for the given CO2 mass injection rate is $V_{\text{inj}} = 7.480 \times 10^{-4} \text{ m}^3\text{s}^{-1}$. After 1 PV of CO$_2$ has been injected, water is injected for 2 pore volumes. Injecting H$_2$O, the so-called chase brine,
causes capillary trapping of CO$_2$ and hence increases storage security (Qi et al., 2009b).

The volumetric rate of injected H$_2$O is the same as the volumetric CO$_2$ injection rate to avoid sudden pressure drop due to the higher density of H$_2$O compared to CO$_2$. In all cases, CO$_2$ is injected for 19.12 d while water is injected for 38.24 d. The total simulation

![Figure 6.1](image)

**Figure 6.1:** Overview of the model geometries used. Their dimension is 90 m × 90 m. Red lines indicate fractures which are discretised by 1D line elements. Fracture permeability is $k_f = 2.1 \times 10^{-8}$ m$^2$, and matrix permeabilities are $k_m \in \{1 \times 10^{-13}$ m$^2$; $1 \times 10^{-12}$ m$^2\}$. Hence, the fracture-matrix permeability ratio is $\approx 10,000$ to $100,000$. All model geometries have an inlet along left model boundary with mass injection rate of $M_{\text{inj}} = 0.5$ kgs$^{-1}$ has been applied to the entire model boundary of 90 m. The outlet is located at the right boundary, where pressure is held constant at 12.0 MPa. The initial pressure is 12.0 MPa and the initial temperature is 318 K (45°C). The temperature remains constant throughout the simulation. No flow occurs across the top and bottom boundary.
Table 6.1: Model parameters applied to all model geometries depicted in Fig. 6.1

<table>
<thead>
<tr>
<th>Sensitivity Parameter</th>
<th>Type</th>
<th>Model Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Permeability Model†</td>
<td>Brooks-Corey (Eq 3.44 &amp; Eq 3.45)</td>
<td>$\lambda = 2, k_{rn}(1) = 0.4$</td>
</tr>
<tr>
<td></td>
<td>Van Genuchten (Eq. 3.40 &amp; Eq. 3.41)</td>
<td>$m = 0.772, k_{rn}(1) = 0.4$</td>
</tr>
<tr>
<td>Capillary Pressure Model†</td>
<td>Brooks-Corey (Eq 3.47)</td>
<td>$\lambda = 2, p_d = 2000\ Pa$</td>
</tr>
<tr>
<td></td>
<td>Van Genuchten (Eq. 3.43)</td>
<td>$m = 0.772, \alpha = \frac{1}{p_d}$</td>
</tr>
<tr>
<td>Matrix Permeability</td>
<td>Constant</td>
<td>$k_m = 1 \times 10^{-13}\ m^2$</td>
</tr>
<tr>
<td>Fracture Permeability</td>
<td>Constant</td>
<td>$k_f = 2.1 \times 10^{-8}\ m^2$</td>
</tr>
</tbody>
</table>

† For fractures linear relative permeability curves are used and capillary pressure is assumed to be zero (see Fig. 3.3).

The model is considered to be isothermal throughout the simulation and hence the temperature is fixed at 318 K (45°C). The initial pressure is 12.0 MPa, as noted above. The brine salinity is set to zero. Residual saturations for both phases are set to zero. The carbonic phase is considered to be the non-wetting phase and has endpoint relative permeability of $k_{rn}(1) = 0.4$. The aqueous phase is considered to be the wetting phase with endpoint relative permeability of $k_{rw}(1) = 1.0$. Further model parameters are listed in Tab. 6.2. The fracture permeability is calculated from the parallel plate approach (Eq. 3.72), which yields a permeability of $k_f = 2.1 \times 10^{-8}\ m^2$ for an aperture of $a = 0.5\ mm$. Fractures exhibit a linear relative permeability model with residual saturations set to zero and end point saturation of $k_{ri}(1) = 1.0$. Capillary pressure are very small according to the young equation (), and therefore set to zero. Two different matrix permeabilities are used with $k_m = 1 \times 10^{-13}\ m^2$ and $k_m = 1 \times 10^{-12}\ m^2$.

For the four model geometries GM1 to GM4, the combination of two two-phase models (BC and VG model) and two matrix permeabilities (low and high) leads to 16 different simulations.

The initial pressure and velocity fields for all cases are shown in Fig. 6.2 and Fig. 6.3 for the individual model geometries. Note that initially the model is completely filled with $H_2O$ and hence pressure and velocity fields are identical for both two-phase models. At a fixed injection rate, the pressure at the inlet can vary as the pressure gradient...
adjusts to fracture and matrix permeabilities. The pressure at the inlet is approximately 15.0 MPa, with highest values measured for GM1 at 16.5 MPa, and lowest for GM3 at 15.5 MPa if a lower matrix permeability is used. These differences in fluid pressure at the model inlet are less pronounced at higher matrix permeabilities. However, the velocity fields show, that when fractures are present, flow is fracture-dominated because the fracture velocities are more than two orders of magnitude higher than the matrix velocities. When matrix permeabilities are low, gradients in the velocity field between the fracture and matrix are higher compared to when matrix permeabilities are high.

Mass inventories (Eq. 4.57) of CO2 are shown in Fig. 6.6. These figures plot the amount of CO2 within the respective model against time and pore volume injected (Fig. 6.7). The mass inventories are shown for the individual model geometries used, so that the effect of the kr and pc models and matrix permeabilities can be compared directly. Similarly, differences in mass inventories stemming from the application of the BC and VG model are shown in absolute (Fig. 6.8) and relative values (Fig. 6.9). Relative values are calculated by subtracting BC model values by VG model values and normalising by division by the BC model values, according to

\[ \Delta M_{j,\text{rel}}(t) = \frac{M_{j}^{\text{BC}}(t) - M_{j}^{\text{VG}}(t)}{M_{j}^{\text{BC}}(t)} \quad \forall t \in [t_0, t_{\text{end}}] \]  

(6.1)

Hence, positive values indicate a surplus of CO2 for the BC model over the VG model.

Velocity-weighted breakthrough curves (Eq. 4.56) have been measured and are shown in Fig. 6.10 for the individual model geometries as well. Breakthrough times are listed in Tab. 6.3 with bar plots provided in Fig. 6.4, grouped according to the model geometries (Fig. 6.4 (II)) and compared to the base case GM1 (Fig. 6.4 (II)). Here, breakthrough time \( t_{\text{btc}} \) is defined as the time when

\[ \exists t_{\text{btc}} : M_{\text{CO}_2}(t) > 1 \text{ g.} \]  

(6.2)

In figures that show both, mass inventories and breakthrough curves, blue lines are used for results when a BC model has been employed, and green lines for results when VG model has been employed. Solid lines indicate low matrix permeabilities of
\[ k_m = 1 \times 10^{-13} \text{ m}^2 \] and dashed line high matrix permeability of \( k_m = 1 \times 10^{-12} \text{ m}^2 \).

CO\(_2\) mass distribution are shown in figure Fig. 6.11 to Fig. 6.18 and are divided into two sets. The first set of 4 figures (Fig. 6.11 to Fig. 6.14) shows CO\(_2\) mass distribution within the model geometries for \( k_m = 1 \times 10^{-13} \text{ m}^2 \). The second set of 4 figures (Fig. 6.15 to Fig. 6.18) shows CO\(_2\) mass distribution within the model geometries for \( k_m = 1 \times 10^{-12} \text{ m}^2 \). Each set shows mass distributions at two different times before and after fluid injection changed from CO\(_2\) to H\(_2\)O: before the change at day 10 and day 18, and afterwards at day 20 and day 26.

<table>
<thead>
<tr>
<th>Table 6.2: Model Geometry, Thermo- and Petrophysical Properties for Application Examples.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td>Porosity</td>
</tr>
<tr>
<td>Permeability (Fracture)( ^\dagger )</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Initial Pressure</td>
</tr>
<tr>
<td>CO(_2) Density</td>
</tr>
<tr>
<td>H(_2)O Density</td>
</tr>
<tr>
<td>Initial Aqueous Saturation</td>
</tr>
<tr>
<td>Residual Aqueous Saturation</td>
</tr>
<tr>
<td>Residual Carbonic Saturation</td>
</tr>
<tr>
<td>– Endpoint Saturation of Aqueous Phase</td>
</tr>
<tr>
<td>– Endpoint Saturation of Carbonic Phase</td>
</tr>
<tr>
<td>– Residual Aqueous Saturation</td>
</tr>
<tr>
<td>– Residual Carbonic Saturation</td>
</tr>
<tr>
<td>Inlet Boundary Condition (Saturation)</td>
</tr>
<tr>
<td>CO(_2) Injection Rate</td>
</tr>
<tr>
<td>Model Size</td>
</tr>
</tbody>
</table>

\( ^\dagger \) The permeability is calculated from parallel plate approach for an aperture of \( a_f = 0.5 \text{ mm} \).
Figure 6.2: Overview of the global pressure field for different model geometries and matrix permeabilities. Different rows correspond to the different model geometries GM1 to GM4 while different columns correspond to the different matrix permeabilities ($1 \times 10^{-13} \text{m}^2$, left; and $1 \times 10^{-12} \text{m}^2$, right).
Figure 6.3: Overview of the velocity field for different model geometries and matrix permeabilities. Different rows correspond to the different model geometries GM1 to GM4 while different columns correspond to the different matrix permeabilities ($1 \times 10^{-13}$ m$^2$, left; and $1 \times 10^{-12}$ m$^2$, right).
6.2 RESULTS

6.2.1 No Fracture Case (GM1)

Simulated mass inventory curves of CO₂ for GM1 exhibit three distinct discontinuities in the slope of mass inventories at different stages during the entire simulation (Fig. 6.6 (I)). The first discontinuity occurs approximately 9 d after injection started, and is related to the breakthrough of CO₂ at the outlet boundary between 8.54 d and 9.84 d. Breakthrough times are listed in Tab. 6.3 and breakthrough curves are shown in Fig. 6.10 (I).

(I) Breakthrough Times \( t_{btc} \)

(II) Differences of Breakthrough Times \( \Delta t_{btc} \) Compared to Base Model Geometry GM1

Figure 6.4: Overview of breakthrough times \( t_{btc} \) and the differences between GM2 to GM4 and GM1. Breakthrough time \( t_{btc} \) is defined in Eq. 6.2.

(I) The top figure shows \( t_{btc} \) for all 16 simulations for different two-phase models (blue for BC model, green for VG model) and matrix permeabilities (darker colours for low \( k_m \), lighter colour for high \( k_m \)). GM1 results exhibit largest \( t_{btc} \) whereas GM3 results exhibit smallest \( t_{btc} \) independent of matrix permeability and two-phase model. Except for GM1, higher matrix permeabilities result in higher \( t_{btc} \) independent of the two-phase model. For all \( k_m \) the BC-Model always leads to higher \( t_{btc} \) except for high \( k_m \) in GM3. However the difference is less than 0.04 d (see Tab. 6.3).

(II) The bottom figure shows the difference in \( t_{btc} \) between GM1 and other model geometries form GM2 to GM4. In all model geometries that contain fractures, \( t_{btc} \) is always smaller, i.e. by approximately 1 to 9 d compared to GM1.
Table 6.3: Values of breakthrough time $t_{\text{btc}}$ as defined by Eq. 6.2. A visual overview is provided in Fig. 6.4.

<table>
<thead>
<tr>
<th>$k_r$</th>
<th>zp-Model</th>
<th>GM1</th>
<th>GM2</th>
<th>GM3</th>
<th>GM4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>BC</td>
<td>9.7949 d</td>
<td>1.5181 d</td>
<td>0.24539 d</td>
<td>7.0187 d</td>
</tr>
<tr>
<td>High</td>
<td>BC</td>
<td>9.6032 d</td>
<td>2.0512 d</td>
<td>0.56621 d</td>
<td>7.1292 d</td>
</tr>
<tr>
<td>Low</td>
<td>VG</td>
<td>8.5815 d</td>
<td>1.2595 d</td>
<td>0.21923 d</td>
<td>6.0944 d</td>
</tr>
<tr>
<td>High</td>
<td>VG</td>
<td>8.56 d</td>
<td>1.8229 d</td>
<td>0.56297 d</td>
<td>6.3185 d</td>
</tr>
</tbody>
</table>

A second discontinuity is visible around day 19, when injection of CO$_2$ ceases and H$_2$O injection commences. A third discontinuity is visible around day 27 (BC model) and day 29 (VG). This discontinuity is caused by breakthrough of chasing H$_2$O (Fig. 6.14 (I) & Fig. 6.14 (II) and Fig. 6.18 (I) & Fig. 6.18 (II)).

Comparing simulation results for the BC to the VG models shows that using the VG model leads to lower overall amounts of CO$_2$ in the model. This lower amount is caused by the earlier breakthrough of CO$_2$, which occurs between day 8 and 9, compared to simulations using the BC model. Higher matrix permeability also cause slightly earlier CO$_2$ breakthrough and hence less CO$_2$ in the model.

6.2.2 Embedded Fracture Case (GM2)

Compared to the no fracture case (GM1), discontinuities in the slope of the mass inventory curves are less pronounced when they are directly compared for the low and high permeabilities (Fig. 6.6 (II)). Inventory curves associated with low matrix permeabilities

![Figure 6.5](image)

Figure 6.5: Overview of maximum mass of CO$_2$ for GM1 to GM4. The figure shows the maximum CO$_2$ mass for all 16 simulations for different two-phase models (purple for BC model, orange for VG model) and matrix permeability (darker colour for low $k_m$, lighter colour for high $k_m$).
show a delay for the first discontinuity in the slope associated with breakthrough of CO$_2$ after the changes observed at the same time in the 18 d (BC model) and 14 d (VG). However, for inventory curves associated with high matrix permeabilities, the first slope discontinuity is related to CO$_2$ breakthrough approximately at day 11 for the VG model and approximately at day 13 for the BC model. They occur later when directly compared to the high matrix permeability inventories of GM1 (see Tab. 6.3 for values of $t_{bte}$). For both matrix permeabilities, inventory curves also do not exhibit the third slope discontinuity associated with breakthrough of the chasing H$_2$O.

Before fluid injection changes occurs from CO$_2$ to H$_2$O at 1 PV, the difference in mass inventory curves for low-$k_m$ and high-$k_m$ cases are small until 0.5 PV (Fig. 6.8 (I)). At approximately 0.6 PV the difference for the low-$k_m$ case increases rapidly. For the high-$k_m$ case the difference increases rapidly at approximately 0.75 PV. This behaviour is also evident in the breakthrough curves in Fig. 6.10 (II) where rapid increase in the CO$_2$ concentration curves coincides with the changes observed at the same time in the differences in the mass inventory curves.

After fluid injection change from CO$_2$ to H$_2$O, inventory curves for low and high $k_m$ cases are very similar. Figures for mass distribution at day 20 and day 26 for both matrix permeabilities (Fig. 6.13 (III) & Fig. 6.13 (IV)) and (Fig. 6.17 (III) & Fig. 6.17 (IV)) show that CO$_2$ is equally distributed within the model. It indicates that matrix flow of CO$_2$ contributes significantly to breakthrough curves. Similar to GM1, the differences in the inventory curves between BC and VG models at low $k_m$ after 1.5 PV are very small. High $k_m$ indicating that matrix permeability in GM1 and GM2 has little effect on the inventory curve difference.

Breakthrough of CO$_2$ occurs earlier if a fracture is present (Fig. 6.10 (II)) because most of the flow occurs in the high-permeability fracture, and hence bypasses a significant part of the rock matrix, compared to the model GM1. Breakthrough is always earlier compared to case GM1, independently of the two-phase model or matrix permeability Fig. 6.10 (II). However, as in case GM1, CO$_2$ breakthrough is still affected by the matrix permeability and two-phase model. Higher matrix permeabilities cause CO$_2$ to break
Table 6.4: Maximum mass of CO₂.

<table>
<thead>
<tr>
<th>k&lt;sub&gt;r&lt;/sub&gt;</th>
<th>2p-Model</th>
<th>GM1</th>
<th>GM2</th>
<th>GM3</th>
<th>GM4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>BC</td>
<td>519.52 × 10³ d</td>
<td>495.94 × 10³ d</td>
<td>341.09 × 10³ d</td>
<td>507.98 × 10³ d</td>
</tr>
<tr>
<td>High</td>
<td>BC</td>
<td>517.70 × 10³ d</td>
<td>494.31 × 10³ d</td>
<td>490.65 × 10³ d</td>
<td>484.31 × 10³ d</td>
</tr>
<tr>
<td>Low</td>
<td>VG</td>
<td>487.98 × 10³ d</td>
<td>455.94 × 10³ d</td>
<td>338.35 × 10³ d</td>
<td>479.46 × 10³ d</td>
</tr>
<tr>
<td>High</td>
<td>VG</td>
<td>485.68 × 10³ d</td>
<td>474.32 × 10³ d</td>
<td>463.12 × 10³ d</td>
<td>481.14 × 10³ d</td>
</tr>
</tbody>
</table>

through after the changes observed at the same time in the 3.68 d (BC model) and 3.39 d (VG model) compared to 2.13 d (BC model) and 1.95 d (VG model) for lower matrix permeabilities. The VG model causes CO₂ to breakthrough after 1.95 d (low k<sub>r</sub>) and 3.39 d (high k<sub>r</sub>) while the BC model causes CO₂ to breakthrough after 2.13 d and 3.68 d (see Tab. 6.3 for values of t<sub>btc</sub>).

All breakthrough curves exhibit a sudden change in their slope at two different times before fluid injection changes from CO₂ to H₂O. The slope change is characterised by transition from shallow to steep slopes (Fig. 6.10 (II)). The first change is related to the breakthrough of the two-finger CO₂ plume generated by the fracture (Fig. 6.11 (III) & Fig. 6.15 (III)) and occurs 8.7 d (BC model) and 6.7 d (VG model) after injection for low k<sub>m</sub> and after 9.5 d (BC model) and 7.5 d (VG model) for high k<sub>m</sub>. The second change is due to the matrix contribution (Fig. 6.15 (III) & Fig. 6.15 (IV)) and occurs after 16.8 d (BC model) and 13.86 d (VG model) for low k<sub>m</sub> and after 12.6 d (BC model) and 10.5 d (VG model) for high k<sub>m</sub>. Breakthrough times have been obtained by visually inspecting Fig. 6.10 (II) and are therefore approximated.

6.2.3 Through-Going Fracture Case (GM3)

There are many differences between the simulation results for a through-going fracture (GM3) and the embedded fracture cases (GM2) in terms of CO₂ mass inventory. Whereas in GM1 and GM2 show a distinct discontinuity in the slope of the mass inventory curves, which can be delayed or less pronounced, this discontinuity is completely missing in GM3 for low-k<sub>m</sub>. The missing discontinuity is due to CO₂ breaking through early, that is in less than a day (see Tab. 6.3 for values of t<sub>btc</sub>). For high-k<sub>m</sub> cases the first
discontinuity in the slope is the simulation results using the corresponding two-phase model in GM2. It occurs both approximately after 18 d (BC model) and after 14 d (VG). As in case GM2, the second slope discontinuity in the mass inventory curve after 1 PV is very distinct, because no CO₂ is added to the model. As a consequence, the CO₂ mass declines within the model geometry. Furthermore, GM2 and GM3 have in common that high \( k_m \) leads to higher CO₂ masses in the model geometry, because CO₂ enters the matrix more readily. It is interesting to note, however, that the mass inventory curves for the low- and high-\( k_m \) cases in GM3 cross after approximately 37 d and 49 d. This effect is caused by the through-going fracture, which enables CO₂ to travel directly from the inlet to the outlet. Hence uptake of CO₂ into the matrix is dominated by capillary forces and therefore much slower compared to case GM2 where CO₂ needs to flow through the rock matrix before entering the fracture and after leaving the fracture, respectively (see velocity fields for high- and low- \( k_m \) cases in GM2 (Fig. 6.3 (III) & Fig. 6.3 (IV)) and GM3 (Fig. 6.3 (V) & Fig. 6.3 (VI))).

Before fluid injection change from CO₂ to H₂O occurs, the mass inventory curves related to the low-\( k_m \) case are below those in the high-\( k_m \) case (Fig. 6.8 (I)). At low \( k_m \) values capillary forces become more influential compared to viscous dominated CO₂ transport, and the steep capillary pressure entry slope of the VG model causes CO₂ to enter into the matrix. After approximately 0.75 PV the BC model exhibits higher CO₂ mass in the model geometry compared to the VG model. Shortly thereafter it exceeds CO₂ mass levels in the high-\( k_m \) case until simulation end, similarly to GM1 and GM2.

When fluid injection changes from CO₂ to H₂O, the CO₂ mass peaks. The peak CO₂ mass in GM1 is significantly lower compared to GM1 and GM2 as a consequence of the early CO₂ breakthrough. However, for a given two-phase model, the mass inventory curves for low- and high \( k_m \) get asymptotically close, as opposed to GM1 and GM2 (Fig. 6.6 (III)).

Breakthrough times \( t_{btc} \) of CO₂ occur very early after injection of CO₂ started. It is composed of fracture contribution only. For the low-\( k_m \) case CO₂ breaks through after 0.25 d (BC model) and after 0.22 Days (VG). For the high-\( k_m \) case CO₂ breaks through
after 0.64 Days (BC model) and 0.68 Days (VG model) (Tab. 6.3). Until fluid injection changes from CO$_2$ to H$_2$O the contribution to the breakthrough curve for the low-$k_m$ case is from the fracture only, whereas in the high-$k_m$ case the matrix contributes CO$_2$ to the breakthrough after approximately 17 d (BC model) and after 13 d (VG). This coincides with steep slopes in the breakthrough curves in Fig. 6.10 (III). Matrix contribution of CO$_2$ to the breakthrough curves for the low-$k_m$ case start approximately after 47 Days (BC model) and 43 Days (VG). See also CO$_2$ mass distribution at day 26 in GM3 for the low-$k_m$ (Fig. 6.14 (V) & Fig. 6.14 (VI)) and high-$k_m$ case (Fig. 6.18 (V) & Fig. 6.18 (VI)). In the former case the CO$_2$ mass covers an area away from the outlet and slowly migrates towards to the outlet. This behaviour causes the late matrix contribution of CO$_2$ to the breakthrough curve.

6.2.4 Disconnected Fracture Case (GM4)

The disconnected fracture case (GM4) shares many features with the no fracture case (GM1) and the embedded fracture case (GM2) with respect to CO$_2$ mass inventory curves. It also shares some features with the through-going fracture case (GM3) with respect to the difference in CO$_2$ mass resulting from simulations using the BC and VG model, as well as with the appearance of the first discontinuity in the slope of the mass inventory curve of CO$_2$ associated with CO$_2$ breakthrough. First, a distinct discontinuity in the slope of mass inventories coinciding with CO$_2$ breakthrough is only visible for the high-$k_m$ case in conjunction with the VG model (Fig. 6.6 (IV)). It is missing in the other three cases. Furthermore, the second slope discontinuity at 1 PV is present (Fig. 6.7 (IV)). The third slope discontinuity coinciding with H$_2$O breakthrough is missing.

The maximum mass of CO$_2$ (measured at 1 PV) are similarly high compared to GM1 and GM2, but are different in contrast to GM3 (Fig. 6.6 (IV) & Fig. 6.7 (IV)). The tail of the inventory curves (after approximately 27 d or 1.25 PV) are very close, independent of the matrix permeability for a given two-phase model, similar to GM1 and GM2 and different to GM3 (Fig. 6.6 (IV) & Fig. 6.7 (IV)). Before fluid injection change, the BC model leads to lower CO$_2$ mass until approximately 0.75 PV for the low $k_m$ case and until 0.9 PV for the high $k_m$ case (Fig. 6.8 (IV)). After 2 PV two-phase difference in CO$_2$
mass are also very close independent form $k_m$ in agreement with GM1 and GM2, but different to GM3. In between the low $k_m$ case favours the BC model in terms of mass surplus.

Breakthrough time $t_{btc}$ occurs for the low-$k_m$ case after 7.84 Days (BC model) and after 7.10 Days (VG). For the high-$k_m$ case it occurs after 8.39 Days (BC model) and after 7.66 Days. Breakthrough time occurs later than GM2 and GM1 but earlier than GM1 (see Tab. 6.3 for values of $t_{btc}$). The matrix dominates contribution of CO$_2$ to the breakthrough curve for the high-$k_m$ when using the VG model after approximately 12 d (Fig. 6.10 (IV)). This is characterised by the steep slope in breakthrough curves. The high $k_m$ VG model case has the earliest matrix contribution when compared to the other three $k_m$/two-phase model cases. The matrix contribution is latest for the low-$k_m$ case in conjunction with the BC model after approximately 26 d. The remaining two cases show matrix contribution of CO$_2$ to the breakthrough curves becoming dominant at similar times after approximately 17 d.
Figure 6.6: Evolution of the CO₂ mass inventory (Eq. 4.57) measuring the total CO₂ mass present in the model geometries GM₁ to GM₄ (Fig. 6.1).
Figure 6.7: Pore volume parametrised evolution of the CO$_2$ mass inventory (Eq. 4.57) measuring the total CO$_2$ mass present in the model geometries GM1 to GM4 (Fig. 6.1).
(I) No Fracture Case (GM1)

(II) Embedded Fracture Case (GM2)

(III) Through-Going Fracture Case (GM3)

(IV) Disconnected Fractures Case (GM4)

Figure 6.8: Evolution of differences in CO₂ mass inventories between Brooks-Corey model and Van Genuchten model for low matrix permeabilities (red line) and high matrix permeabilities (purple line) in the model geometries GM₁ to GM₄. After fluid injection change the BC model always leads to higher overall CO₂ amount in the model geometries GM₁ to GM₄ (Fig. 6.1).
Figure 6.9: Evolution of relative differences in CO₂ mass inventories between Brooks-Corey model and Van Genuchten model for low matrix permeabilities (red line) and high matrix permeabilities (purple line) in the generic model geometries GM₁ to GM₄. After fluid injection change the BC model always leads to higher overall CO₂ amount in the model geometries GM₁ to GM₄ (Fig. 6.1).
Figure 6.10: Evolution of velocity-weighted breakthrough curves (Eq. 4.56) of CO₂ mass for model geometries GM₁ to GM₄ (Fig. 6.4).
(I) Brooks-Corey Model (GM1)  (II) Van Genuchten Model (GM1)

(III) Brooks-Corey Model (GM2)  (IV) Van Genuchten Model (GM2)

(V) Brooks-Corey Model (GM3)  (VI) Van Genuchten Model (GM3)

(VII) Brooks-Corey Model (GM4)  (VIII) Van Genuchten Model (GM4)

Figure 6.11: Overview of CO₂ mass distributions after 10 d for model geometries GM₁ to GM₄ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m². Different rows correspond to the different model geometries GM₁ to GM₄ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 6.12: Overview of CO$_2$ mass distributions after 18 d for model geometries GM$_1$ to GM$_4$ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. Different rows correspond to the different model geometries GM$_1$ to GM$_4$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 6.13: Overview of CO$_2$ mass distributions after 20 d for model geometries GM$_1$ to GM$_4$ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. Different rows correspond to the different model geometries GM$_1$ to GM$_4$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
6.2 RESULTS

Figure 6.14: Overview of CO$_2$ mass distributions after 26 d model geometries GM$1$ to GM$4$ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. Different rows correspond to the different model geometries GM$1$ to GM$4$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 6.15: Overview of CO$_2$ mass distributions after 10 d for model geometries GM$_1$ to GM$_4$ (Fig. 6.1) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m$^2$. Different rows correspond to the different model geometries GM$_1$ to GM$_4$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 6.16: Overview of CO₂ mass distributions after 18 days for model geometries GM₁ to GM₄ (Fig. 6.1) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m². Different rows correspond to the different model geometries GM₁ to GM₄ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 6.17: Overview of CO$_2$ mass distributions after 20 d for model geometries GM$_1$ to GM$_4$ (Fig. 6.1) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m$^2$. Different rows correspond to the different model geometries GM$_1$ to GM$_4$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 6.18: Overview of CO$_2$ mass distributions after 26 d for model geometries GM$_1$ to GM$_4$ (Fig. 6.11) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m$^2$. Different rows correspond to the different model geometries GM$_1$ to GM$_4$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
6.3 DISCUSSION

Mass inventory curves for CO$_2$ and breakthrough curves of CO$_2$ concentration share an intimate relationship: as soon as CO$_2$ breaks through, the capacity to keep CO$_2$ within a confined volume is lost. Any CO$_2$ additionally added does not contribute significantly to further accumulation of CO$_2$ mass in this volume. In a fracture-matrix system, storage of CO$_2$ occurs mainly in the matrix, whereas fractures cause redistribution of a migrating CO$_2$ plume and therefore can cause bypassing of large matrix volumes.

Fractures in particular contribute to capillary heterogeneity, i.e. open fractures do not inherit the capillary pressure relationship from the surrounding matrix. In fractures, one either neglects capillary forces or uses a linear capillary pressure. This has dramatic effects on the migration of a non-wetting CO$_2$ migration in fractured porous media: capillary pressure in fractures can become so low that flow from the fracture into an initially water filled matrix can be impeded if a Brooks-Corey model is used. This behaviour is caused by the capillary entry pressure which needs to be exceeded in the matrix before CO$_2$ can enter the matrix. In contrast, the Van Genuchten type model has a continuous capillary pressure, the so-called entry-slope region, at $S_w = 1 - S_{nr}$, i.e. the capillary entry pressure is zero. Hence the VG model causes the the non-wetting carbonic phase to enter the initially water-filled matrix.

Two-phase models which exhibit an entry slope region in their capillary pressure curve such as the Van Genuchten model, cause a non-wetting plume to advance faster. This behaviour is induced by the infinitely steep slope when wetting saturation approaches $S_w \to 1$. Li et al. (2013) showed that in the context of buoyancy-driven migration of the CO$_2$ plume, the entry slope region can have significant effect to the extent of a CO$_2$ plume. The entry slope region causes a so-called saturation tail with very low CO$_2$ mass. This behaviour is missing in two-phase models of Brooks-Corey type which exhibit a capillary entry pressure. Therefore, the question of whether natural rock is better represented by either a Van Genuchten-type model or a Brooks-Corey-type model can impact the prediction of the performance of a geological CO$_2$ storage repository with regard to the CO$_2$ mass immobilised.
Numerical results for breakthrough curves show clearly that if a Van Genuchten model is employed, earlier breakthrough takes place (Fig. 6.10). As a consequence, Brooks-Corey model must show a surplus in CO$_2$ mass compared to the Van Genuchten model with regard to mass inventory curves of CO$_2$. Mass inventory curves for CO$_2$ show that in all model geometries the application of the Brooks-Corey model does lead to higher CO$_2$ mass (Fig. 6.6). The difference to the Van Genuchten model is up to 10% before 1 PV, and up to 80% afterwards (Fig. 6.9). The time difference in breakthrough of CO$_2$ between the VG model and the BC model leads to further mass build up when a BC model is employed (Fig. 6.8).

The model geometries represented by cases GM1 to GM4 have very different results on breakthrough curves (Fig. 6.4 (I)). Direct pressure communication through a highly conductive fracture between inlet and outlet facilitates very fast breakthrough and hence the smallest breakthrough time, because fluid flow in the fracture can be several orders of magnitude higher than in the matrix. The through-going fracture case GM2 has breakthrough times of approximately 0.23 to 0.56 d. In comparison the slowest breakthrough time occurs for the no fracture case GM1, with values ranging between 8.5 and 9.7 d. In the disconnected fracture case GM3, the distribution of fractures and their orientation forces CO$_2$ to migrate through a greater part of the matrix compared to the embedded fracture case GM2.

In terms of breakthrough times the disconnected fracture model GM4 behaves similar to the no fracture case GM1 with values ranging from approximately 6.0 d to 7.0 d. In contrast, the embedded fracture case GM2 shows similar breakthrough time behaviour as the through-going fracture case GM3 with values ranging from approximately 1.2 d to 2.1 d.

Matrix permeability variation impacts breakthrough curves of CO$_2$ and CO$_2$ mass inventory curves differently with respect to the model geometry, that is, the no fracture case GM1 sets itself apart from the cases which contain fractures GM2 to GM4. In the no fracture case, breakthrough times for low $k_m$ are marginally larger by approximately less then 0.2 % than for high $k_m$. In model geometries which contains fractures, the situation is reversed and more pronounced: the breakthrough time for high $k_m$ differ
significantly approximately of few 10% up to over 100% for the through-going fracture case GM2.

Higher matrix permeability also changes the flow ratio between fracture and matrix. Fluid velocities in the fracture become comparable to fluid velocities in the matrix as opposed to cases where matrix permeability is low. This allows CO\textsubscript{2} to migrate into and through the matrix more readily. Consequently mass inventory curves for CO\textsubscript{2} are in general higher than for low matrix permeabilities.

6.4 CONCLUSIONS

The purpose of this chapter was to demonstrate the numerical method developed and discussed in the previous chapters to investigate capillary trapping of CO\textsubscript{2} in some generic and idealised models with embedded fractures. Focusing on idealised fracture geometries establishes a fundamental understanding of CO\textsubscript{2} migration in unfractured and fractured porous medium for further studies in the following chapters. Two different two-phase models, and two different matrix permeabilities were employed to study their impact on CO\textsubscript{2} mass inventory curves and CO\textsubscript{2} breakthrough curves. The main findings are as follows:

1. In all model geometry cases breakthrough times are smallest if a Van Genuchten model is applied. This behaviour is caused by the infinitely steep \( p_{c} \) curves for high H\textsubscript{2}O saturations \( S_{w} \to 1 \) in the VG model at the advancing end of the CO\textsubscript{2} plume, which results in early breakthrough of CO\textsubscript{2} (Fig. 6.10).

2. The application of the Brooks-Corey model leads to higher CO\textsubscript{2} mass amounts in model geometries where fractures are present compared to the Van Genuchten model (Fig. 6.8).

3. Breakthrough times are lowest for the through-going fracture case (GM3) independent of matrix permeability and two-phase model (Fig. 6.4 (I) & Fig. 6.4 (II)), because the inlet and outlet boundaries are connected through a highly conductive fracture, which has fluid velocities several order of magnitudes higher than the matrix.
4. Breakthrough times are largest for the no fracture case (GM1) independent of matrix permeability and two-phase model (Fig. 6.4 (I)) because CO$_2$ can not bypass significant parts of the matrix due to the absence of highly conductive fractures.

5. For a given two-phase model, high matrix permeability leads to later breakthrough compared to low matrix permeabilities when fractures are present (Fig. 6.4 (I)), because fluid velocities in the fracture are lower compared when matrix permeability is low (Fig. 6.3).

6. The disconnected fracture case (GM4) which exhibits more fractures than the embedded fracture case (GM2) with one fracture, has later breakthrough times compared to GM2 (Fig. 6.4 (I)), because CO$_2$ is forced to migrate to greater parts of the matrix (Fig. 6.11) slowing down the advancing plume front.
Relative permeability hysteresis controls multiphase fluid flow behaviour significantly when a wetting phase traps the non-wetting phase (Juanes et al., 2006). That is, at the trailing edge of a CO\textsubscript{2} plume imbibing H\textsubscript{2}O displaces, causing the continuous CO\textsubscript{2} plume to disconnect into blobs and ganglia at pore scale. Therefore, CO\textsubscript{2} becomes immobile. Subsequently, the flowing non-wetting saturation decreases significantly and vanishes when the CO\textsubscript{2} saturation has reached residual saturation. Immobilising CO\textsubscript{2} due to imbibition is known as capillary or residual trapping. Significant capillary trapping does not occur during CO\textsubscript{2} injection, but only when CO\textsubscript{2} injection stops and is displaced by H\textsubscript{2}O. Here I study the impact of capillary trapping on mass inventories and breakthrough curves after CO\textsubscript{2} injection ceases and H\textsubscript{2}O injection commences. As outlined in the previous chapter the focus will be on differences between (a) the Brooks-Corey and Van Genuchten relative permeability and capillary pressure models which impacts overall fluid flow and controls trapping behaviour, (b) low and high matrix permeabilities which allow for fracture or matrix dominated flow.

In this chapter I considered pressure build-up and relaxation during injection, laminar multi-phase multi-component transport without turbulences, capillary diffusion, compressible fluids, capillary entry pressure at the fracture-matrix interface, and non-wetting relative permeability hysteresis. Phase densities account for pressure, temperature and salinity, but is held constant throughout the simulation. Effects neglected are gravity, heterogeneous capillary entry pressures, energy transport, near-wellbore effects, and reactive transport.
7.1 Model Setup

The experimental setup from the previous chapter is revisited, and no changes to model geometries (Fig. 6.1), boundary and initial conditions or model parameter values (Tab. 6.2 & Tab. 6.2) were applied. The only difference I consider is the enabling of non-wetting relative permeability hysteresis (NRPH). Simulating NRPH requires to determine the flow direction state (primary drainage, imbibition, secondary drainage) of a finite-volume (Sec. 4.7). If imbibition occurs, the non-wetting relative permeability (Eq. 3.61) can become zero when CO₂ is completely residual CO₂ (Eq. 3.60). When CO₂ is immobilised, evaporation of CO₂ into the fresh CO₂ unsaturated aqueous phase takes place. The evaporation takes place because an equilibrium state is assumed for the two-phase situation. Thus, the CO₂ component phase mass fractions of the aqueous phase \(X_{aq,CO₂}\) becomes non zero in Eq. 4.35. Consequently, dissolved CO₂ reduces the amount of residual or immobilised CO₂.

Mass inventories (Eq. 4.57) of CO₂ are shown in Fig. 7.3. These figures plot the amount of CO₂ within the respective model against time and pore volume injected (Fig. 7.4). The mass inventories are shown for the individual model geometries used, so that the effect of the \(k_r\) and \(p_c\) models and matrix permeabilities can be compared directly. Similarly, differences in mass inventories stemming from the application of the BC and VG model are shown in absolute (Fig. 7.5) and relative values (Fig. 7.6). Relative values are calculated by subtracting from BC model values of the VG model and subsequent division by the BC model values. Hence, positive values indicate a surplus of CO₂ for the BC model over the VG model. The maximum CO₂ mass within the model geometry is given in Tab. 7.2, and visualised in Fig. 7.2.

Velocity-weighted breakthrough curves (Eq. 4.56) have been measured and are shown in Fig. 7.7 for the individual model geometries as well. Contrary to GM1 to GM4, the breakthrough curves now measure the actual flowing part of CO₂. Hence, residual trapped CO₂ does not contribute to breakthrough curves. Breakthrough times are listed in Tab. 7.1 with bar plots provided in Fig. 7.1, grouped according to the model geomet-

\*Residual CO₂ is trapped, and carbonic saturation equals residual saturation.
ries (Fig. 6.1) and compared to the case GM1 to GM4 (Fig. 7.1 (II)). Here, breakthrough time $t_{btc}$ is defined by Eq. 6.2. An overview of breakthrough times $t_{btc}$ for all 16 simulations for GM1 HYST to GM4 HYST are presented in Fig. 7.1 (I) and their difference to GM1 to GM4 are shown in Fig. 7.1 (II). Note that HYST indicates that hysteresis was accounted for in the model geometries. Because the differences in breakthrough times between GM1 to GM4 and GM1 HYST to GM4 HYST are small, it indicates that the discussion of the results can be limited to the time after 1 PV, i.e. when injection changes from CO$_2$ to H$_2$O. Values of $t_{btc}$ for all 16 simulations are presented in Tab. 7.1.

In figures that show both, mass inventories and breakthrough curves, blue lines are used for results when a BC model have been employed, and green lines for results when VG model has been employed. Solid lines indicate low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$ and dashed line high matrix permeability of $k_m = 1 \times 10^{-12}$ m$^2$.

7.2 RESULTS

7.2.1 No Fracture Case (GM1 HYST)

Simulated mass inventory curves of CO$_2$ for GM1 HYST show no major difference on position and number of discontinuities in the slope compared to GM1 where hysteresis effect were absent (Fig. 7.3 (I).) The first changes in slope occurs after 11.23 d (BC/low $k_m$), after 10.83 d (BC/high $k_m$), after 9.37 d (VG/low $k_m$), and after 9.47 d (VG/high $k_m$). The second change occurs after fluid injection changes from CO$_2$ to H$_2$O at 19.12 days. The third slope change coincides with H$_2$O breakthrough and occurs after 23.41 d (BC/low $k_m$), 23.4 d (BC/high $k_m$) 23.3 d (VG/low $k_m$) 23.3 d (VG/high $k_m$). After H$_2$O breakthrough the CO$_2$ mass in the model geometry is significantly higher compared to GM1 because an imbibition-like process traps CO$_2$ at the trailing edge of the CO$_2$ plume.

When CO$_2$ injection stops and H$_2$O injection commences, CO$_2$ is increasingly rendered immobile. When H$_2$O breakthrough occurs the mass of immobilised CO$_2$ reaches maximum (darker colours in Fig. 7.3 (I)), and the slope of the inventory curve for the mass
of immobilised CO$_2$ changes from positive to negative. A slope discontinuity in the mass inventory curve for immobilised CO$_2$ occurs after 23.4 d (BC/low $k_m$), after 23.4 d (BC/high $k_m$), after 23.3 d (VG/low $k_m$), and after 23.3 d (VG/high $k_m$). The maximum trapped amounts of CO$_2$ are listed in Tab. 7.2. The largest maximum mass of immobilised CO$_2$ is approximately $262 \times 10^3$ kg for a VG model with low $k_m$. The smallest maximum mass of immobilised CO$_2$ is approximately $213 \times 10^3$ kg for a BC model with low $k_m$. As H$_2$O injection continues, CO$_2$ evaporation into the unsaturated aqueous

![Figure 7.1](image)

(Figure 7.1): Overview of breakthrough times $t_{btc}$ and differences between GM$_1$ to GM$_4$ and GM$_1$ HYST to GM$_4$ HYST. Breakthrough time $t_{btc}$ is defined in Eq. 6.2.

(I) The top figure shows $t_{btc}$ for all 16 simulations for different two-phase models (blue for BC model, green for VG model) and matrix permeabilities (darker colours for low $k_m$, lighter colour for high $k_m$). GM$_1$ HYST results exhibit largest $t_{btc}$ whereas GM$_3$ results exhibit smallest $t_{btc}$ independent of matrix permeability and two-phase model. Except for GM$_1$ HYST, higher matrix permeabilities result in larger $t_{btc}$ independent of the two-phase model. For all $k_m$ the BC-Model always leads to larger $t_{btc}$, except for high $k_m$ in GM$_3$ HYST. However the difference is less than 0.0007 d (see Tab. 7.1).

(II) The bottom figure shows the difference between $t_{btc}$ when hysteresis is absent to cases where hysteresis is considered. When hysteresis is modelled, the difference in $t_{btc}$ is approximately up to 1.5 d. The difference is smallest for the through-going fracture case (GM$_3$) and highest for the disconnected fracture case (GM$_4$ HYST). The no fracture case (GM$_1$ HYST) has the second largest $t_{btc}$. 
phase leads to a decrease in mass of immobilised \( \text{CO}_2 \). The time at which of maximum mass of immobilised \( \text{CO}_2 \) occurs is listed in Tab. 7.2. The smallest time when maximum mass of immobile \( \text{CO}_2 \) occurs is 23.29 d for the VG model and high \( k_m \), the largest time is 28.52 d for the BC model with high \( k_m \).

Plots showing the differences in \( \text{CO}_2 \) mass inventory resulting from using different two-phase models for GM1 and GM1 HYST are given in absolute (Fig. 7.6(I)) and relative values (Fig. 7.6(I)). They show that after injection changes from \( \text{CO}_2 \) to \( \text{H}_2\text{O} \) the VG model contains more \( \text{CO}_2 \) in the model until approximately 2.1 PV for low \( k_m \) and until approximately 1.45 PV for high \( k_m \). This is opposed to GM1 (dashed line) where the BC model contains more \( \text{CO}_2 \) in the model for the length of the simulation. Furthermore, the difference in \( \text{CO}_2 \) mass inventories between GM1 and GM1 HYST for low \( k_m \) (red solid line) exhibits oscillations in \( \text{CO}_2 \) mass starting approximately after 1.25 PV. Towards 3 PV the BC model contains more \( \text{CO}_2 \) in the model geometry independent of the matrix permeability. This behaviour was also observed in GM1.

The breakthrough curve of \( \text{CO}_2 \) in Fig. 7.7(I) exhibits a sharp drop in \( \text{CO}_2 \) mass after 23.16 days due to \( \text{H}_2\text{O} \) breakthrough. This drop occurs independent of two-phase model and matrix permeability. After the drop, breakthrough curves for the BC model are higher than for the VG model, independent of the matrix permeability. Breakthrough curves for the VG model show oscillations in \( \text{CO}_2 \) mass until the simulation finishes.

Figure 7.2: Overview of maximum \( \text{CO}_2 \) mass for GM1 HYST to GM4 HYST. The figure shows the maximum \( \text{CO}_2 \) mass for all 16 simulations for different two-phase models (purple for BC model, orange for VG model) and matrix permeability (darker colour for low \( k_m \), lighter colour for high \( k_m \)).
The periodic changes have higher amplitude for low \( k_m \). After 28 days these oscillations are visible in form of wave structures in distribution plots of the flow direction state Fig. 7.20 (II) to Fig. 7.31 (II). The wave-like structures are comprised of spatially connected secondary drainage states (green) propagating towards the outlet.

7.2.2 Embedded Fracture Case (GM2 HYST)

Simulated mass inventory curves of \( CO_2 \) for GM2 HYST (Fig. 7.3 (II)) only differ to GM2 after fluid injection changes from \( CO_2 \) to \( H_2O \). Mass inventories are significantly higher after approximately 25d independent of the two-phase model and matrix permeability used in GM2 HYST. No abrupt changes in the slope of mass inventory curves occur during the simulation except when fluid injection changes from \( CO_2 \) to \( H_2O \). A tailing in mass inventories, i.e. sustained linear trend, due to immobilised \( CO_2 \) starts after 25.5 d (BC/low \( k_m \)), after 25.6 d (BC/high \( k_m \)), after 24.7 d (VG/low \( k_m \)), and after 24.9 d (VG/high \( k_m \)). The maximum trapped amounts of \( CO_2 \) are listed in Tab. 7.2.

The largest maximum mass of immobilised \( CO_2 \) of approximately \( 233 \times 10^3 \) kg is observed when a VG model is combined with low matrix permeabilities, similar to GM1 HYST. The smallest maximum mass of immobilised \( CO_2 \) of approximately \( 208 \times 10^3 \) kg is observed for a BC model with low \( k_m \), similar to GM1 HYST. As \( H_2O \) continuous to be injected, \( CO_2 \) evaporation into the unsaturated aqueous phase leads to a decrease in immobilised \( CO_2 \) mass. The times when maximum immobilised \( CO_2 \) mass is achieved are listed in Tab. 7.3. Earliest maximum immobilisation time is 25.54 d for the VG model and low \( k_m \), largest immobilisation time is 30.88 d for the BC model with high \( k_m \). This behaviour was also observed in GM1 HYST.

Plots showing the differences in \( CO_2 \) mass inventory resulting from using different two-phase models for GM2 and GM2 HYST are given in absolute (Fig. 7.6 (II)) and relative values (Fig. 7.6 (II)). For GM2 HYST, the difference in \( CO_2 \) mass is calculated for the immobilised \( CO_2 \). They show that after injection changes from \( CO_2 \) to \( H_2O \), the VG model contains more \( CO_2 \) in the model geometry approximately until 2.2 PV for low \( k_m \) and until approximately 1.8 PV for high \( k_m \) than the BC model (solid lines). This is
opposed to GM2 (dashed line) where the BC model contains more CO$_2$ in the model for the duration of the simulation. The difference in mass inventories of CO$_2$ between GM2 and GM2 HYST (red solid line) shows oscillations in CO$_2$ mass of smaller amplitude compared to GM1 HYST. When approximately 3 PV of CO$_2$ are injected, the BC model contains more CO$_2$ in the model geometry independent of the matrix permeability. This behaviour was also observed in GM2.

Breakthrough curves of CO$_2$ in Fig. 7.7 (II) after injection changes from CO$_2$ to H$_2$O show no sudden drop in CO$_2$ mass compared to GM1 HYST. The VG model shows some mild oscillations in CO$_2$ mass that occur independent from the matrix permeability. The oscillations are caused by changes in flowing saturations as the flow direction changes spatially and temporally (Fig. 7.20 (IV) to Fig. 7.31 (IV)). The flow direction state is roughly axial symmetric. Multiple concentric elliptic-like structures comprising spatially connected drainage states (green) are visible for the duration of the simulation. Its major semi-axis is parallel to the fracture and its minor semi-axis lies on the right boundary of the model geometry.

Table 7.1: Values of breakthrough time $t_{btc}$ as defined by Eq. 6.2. A visual overview is provided in Fig. 7.1.

<table>
<thead>
<tr>
<th>$k_r$</th>
<th>2p-Model</th>
<th>GM1 HYST</th>
<th>GM2 HYST</th>
<th>GM3 HYST</th>
<th>GM4 HYST</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>d</td>
<td>d</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>Low</td>
<td>BC</td>
<td>10.78</td>
<td>2.10</td>
<td>0.35</td>
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<tr>
<td>High</td>
<td>BC</td>
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<td>0.58</td>
<td>8.63</td>
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<tr>
<td>Low</td>
<td>VG</td>
<td>9.21</td>
<td>1.64</td>
<td>0.31</td>
<td>6.85</td>
</tr>
<tr>
<td>High</td>
<td>VG</td>
<td>9.20</td>
<td>2.31</td>
<td>0.58</td>
<td>7.40</td>
</tr>
</tbody>
</table>

Table 7.2: Overview of maximum mass of immobilised CO$_2$.

<table>
<thead>
<tr>
<th>$k_r$</th>
<th>2p-Model</th>
<th>GM1 HYST</th>
<th>GM2 HYST</th>
<th>GM3 HYST</th>
<th>GM4 HYST</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>kg</td>
<td>kg</td>
<td>kg</td>
<td>kg</td>
</tr>
<tr>
<td>Low</td>
<td>BC</td>
<td>$213.55 \times 10^3$</td>
<td>$205.73 \times 10^3$</td>
<td>$148.72 \times 10^3$</td>
<td>$218.61 \times 10^3$</td>
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<tr>
<td>High</td>
<td>BC</td>
<td>$233.57 \times 10^3$</td>
<td>$208.57 \times 10^3$</td>
<td>$175.04 \times 10^3$</td>
<td>$212.81 \times 10^3$</td>
</tr>
<tr>
<td>Low</td>
<td>VG</td>
<td>$262.12 \times 10^3$</td>
<td>$233.66 \times 10^3$</td>
<td>$171.18 \times 10^3$</td>
<td>$252.45 \times 10^3$</td>
</tr>
<tr>
<td>High</td>
<td>VG</td>
<td>$250.51 \times 10^3$</td>
<td>$232.73 \times 10^3$</td>
<td>$170.10 \times 10^3$</td>
<td>$240.64 \times 10^3$</td>
</tr>
</tbody>
</table>
### Table 7.3: Time when maximum mass of immobilised CO\(_2\) occurs.

<table>
<thead>
<tr>
<th>(k_m)</th>
<th>2p-Model</th>
<th>GM(_1) HYST</th>
<th>GM(_2) HYST</th>
<th>GM(_3) HYST</th>
<th>GM(_4) HYST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low BC</td>
<td>26.20</td>
<td>29.28</td>
<td>33.26</td>
<td>28.79</td>
<td></td>
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<td>High BC</td>
<td>28.52</td>
<td>30.88</td>
<td>44.52</td>
<td>30.03</td>
<td></td>
</tr>
<tr>
<td>Low VG</td>
<td>26.13</td>
<td>25.54</td>
<td>29.43</td>
<td>24.47</td>
<td></td>
</tr>
<tr>
<td>High VG</td>
<td>23.29</td>
<td>26.37</td>
<td>35.50</td>
<td>25.08</td>
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</tr>
</tbody>
</table>

#### 7.2.3 Through-Going Fracture Case (GM\(_3\) HYST)

Simulated mass inventory curves of CO\(_2\) for GM\(_3\) HYST (Fig. 7.3 (III)) only differ to GM\(_3\) after fluid injection changes from CO\(_2\) to H\(_2\)O. Afterwards, CO\(_2\) mass inventories are observed to be always significantly higher, i.e. up to 40 % compared to GM\(_3\). This behaviour is independent of the 2-phase model and matrix permeability used in GM\(_3\) HYST. No abrupt slope changes in mass inventory curves occur during the simulation except when fluid injection changes from CO\(_2\) to H\(_2\)O. Tailing of mass inventories of CO\(_2\) due to immobilisation of CO\(_2\) occurs approximately after 25 d for low \(k_m\) and approximately after 35 d to 40 d for high \(k_m\).

The largest maximum mass of immobilised CO\(_2\) is approximately \(175 \times 10^3\) kg for a BC model with high \(k_m\). The smallest maximum mass of immobilised CO\(_2\) is approximately \(148 \times 10^3\) kg for a BC model with low \(k_m\), similar to GM\(_1\) HYST and GM\(_2\) HYST. As H\(_2\)O continuous to be injected, CO\(_2\) evaporation into the unsaturated aqueous phase leads to a decrease in immobilised CO\(_2\) mass. The times when maximum mass of immobilised CO\(_2\) occurs are listed in Tab. 7.3. The earliest time when maximum mass of immobilised CO\(_2\) occurs is 28.00 d for the VG model and for both low \(k_m\) and high \(k_m\). The largest time is 36.00 d for the BC model with high \(k_m\). This behaviour was also observed in GM\(_1\) HYST and GM\(_2\) HYST.

Plots showing the differences in CO\(_2\) mass inventory resulting from using different two-phase models for GM\(_3\) and GM\(_3\) HYST are given in absolute (Fig. 7.6 (III)) and relative values (Fig. 7.6 (III)). For GM\(_3\) HYST, the difference in CO\(_2\) mass is calculated for the immobilised CO\(_2\). They show that after injection changes from CO\(_2\) to H\(_2\)O, the
VG model contains more CO$_2$ in the model for the entire duration of simulation for low $k_m$ and until approximately 2.5 PV for high $k_m$. This is in contrast to GM2 (dashed line) where the BC model contains more CO$_2$ in the model geometry for the entire duration of the simulation. The difference in mass of immobilised CO$_2$ for low $k_m$ (solid red line) shows oscillations in CO$_2$ mass of smaller amplitude compared to GM1 HYST.

When approximately 3 PV of CO$_2$ are injected, the BC model contains more CO$_2$ in the model geometry independent of the matrix permeability. This behaviour was also observed in GM2 and GM 2 HYST.

Breakthrough curves of CO$_2$ in Fig. 7:7 (III) after injection changes from CO$_2$ to H$_2$O show a drop in CO$_2$ mass occurring after 19.84 d, because H$_2$O breaks through. Simulated breakthrough curves using the BC models show no oscillation in CO$_2$ mass afterwards. Simulated BTC curves using the VG model show some saw-tooth-like oscillations, which occur independent of the matrix permeability.

Flow direction changes spatially and temporally (Fig. 7:20 (VI) to Fig. 7:31 (VI)). The flow direction state is roughly axial symmetric. After injection changes from CO$_2$ to H$_2$O and until approximately 1.2 PV, strong high frequency fluctuations in CO$_2$ mass occur. The reason for this might be a potential incompatibility between the mass-based time increments and the implementation of the non-wetting relative permeability hysteresis. For simulations using 1D model geometries with smaller time increments, reduction in these oscillations have been observed. For sufficiently small time increments close to the CFL-criterion, these oscillations vanish.

7.2.4 Disconnecte Fracture (GM4 HYST)

Simulated mass inventory curves of CO$_2$ for GM3 HYST (Fig. 7:3 (IV)) only differ to GM3 after fluid injection changes from CO$_2$ to H$_2$O. Mass inventories are significantly high very short after fluid injection change after approximately 20 d. The effect is independent of the two-phase model and matrix permeability, and occurs earlier compared to GM2 HYST. No abrupt changes in the slope of mass inventory curves for CO$_2$ occur during the simulation except when fluid injection is changes from CO$_2$ to H$_2$O. The tail-
ing in mass inventories due to immobilised CO$_2$ occurs after 24.1 d (BC/low $k_m$), after 24.0 d (BC/high $k_m$), after 24.4 d (VG/low $k_m$), and after 26 d (VG/high $k_m$).

The maximum mass of immobilised CO$_2$ is approximately $175 \times 10^3$ kg for a BC model with high $k_m$. The minimum immobilised CO$_2$ amount is approximately $148 \times 10^3$ kg for a BC model with low $k_m$, similar to GM1 HYST and GM2 HYST. As H$_2$O continuous to be injected, CO$_2$ evaporation into the CO$_2$-undersaturated aqueous phase leads to a decrease in immobilised CO$_2$ mass. Times when maximum mass of immobilised CO$_2$ occurs are listed in Tab. 7.3. The earliest time when maximum mass occurs is 28.00 d for the VG model. This time is the same for both, low $k_m$ and high $k_m$. The largest time is 36.00 d for the BC model with high $k_m$. This behaviour was also observed in GM1 HYST and GM2 HYST.
Figure 7.3: Overview of CO₂ evolutions of CO₂ mass inventories. The mass inventories measure the mass of immobilised CO₂ (darker colours) and the total mass of CO₂ present for model geometries GM₁ to GM₄ (Fig. 6.1).
(I) Homogeneous Case (GM1 HYST), time in PV

Figure 7.4: Overview of CO₂ evolutions of CO₂ mass inventories. The mass inventories measure the mass of immobilised CO₂ (darker colours) and the total mass of CO₂ present for model geometries GM1 to GM4 (Fig. 6.1). Mass inventories are parametrised in terms of pore volume.
Figure 7.5: Evolution of differences of mass inventories of CO$_2$ between Brooks-Corey model and Van Genuchten model for low matrix permeabilities (red line) and high matrix permeabilities (purple line) for the simulation cases GM$_1$ HYST to GM$_4$ HYST. After fluid injection changes from CO$_2$ to H$_2$O, the BC model always leads to higher overall mass of CO$_2$ compared to the VG model. Model geometries for GM$_1$ HYST to GM$_4$ HYST are shown in Fig. 6.1.
Figure 7.6: Evolution of relative differences of mass inventories of CO₂ between Brooks-Corey model and Van Genuchten model for low matrix permeabilities (red line) and high matrix permeabilities (purple line) for the simulation cases GM₁ HYST to GM₄ HYST. After fluid injection changes from CO₂ to H₂O, the BC model always leads to higher overall mass of CO₂ compared to the VG model. Model geometries for GM₁ HYST to GM₄ HYST are shown in Fig. 6.1.
(I) Homogeneous (GM1 HYST)

(II) Embedded Fracture (GM2 HYST)

(III) Through-Going Fracture (GM3 HYST)

(IV) Disconnected Fractures (GM4 HYST)

Figure 7.7: Overview of breakthrough curves of CO₂ mass for GM1 HYST to GM4 HYST. Model geometries are shown in Fig. 6.1.
(I) Brooks-Corey Model (GM₁ HYST)  (II) Van Genuchten Model (GM₁ HYST)

(III) Brooks-Corey Model (GM₂ HYST)  (IV) Van Genuchten Model (GM₂ HYST)

(V) Brooks-Corey Model (GM₃ HYST)  (VI) Van Genuchten Model (GM₃ HYST)

(VII) Brooks-Corey Model (GM₄ HYST)  (VIII) Van Genuchten Model (GM₄ HYST)

Figure 7.8: Overview of CO₂ mass distributions after 18 days for model geometries GM₁ to GM₄ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13} \text{m}^2$. Different rows correspond to the different simulation cases GM₁ HYST to GM₄ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
Figure 7.9: Overview of CO$_2$ mass distributions after 20 days for model geometries GM$_1$ to GM$_4$ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. Different rows correspond to the different simulation cases GM$_1$ HYST to GM$_4$ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
Figure 7.10: Overview of CO₂ mass distributions after 22 days for model geometries GM₁ to GM₄ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-12}$ m². Different rows correspond to the different simulation cases GM₁ HYST to GM₄ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
(I) Brooks-Corey Model (GM\textsubscript{1} HYST)  (II) Van Genuchten Model (GM\textsubscript{1} HYST)

![Image](image1)

(III) Brooks-Corey Model (GM\textsubscript{2} HYST)  (IV) Van Genuchten Model (GM\textsubscript{2} HYST)

![Image](image2)

(V) Brooks-Corey Model (GM\textsubscript{3} HYST)  (VI) Van Genuchten Model (GM\textsubscript{3} HYST)

![Image](image3)

(VII) Brooks-Corey Model (GM\textsubscript{4} HYST)  (VIII) Van Genuchten Model (GM\textsubscript{4} HYST)

![Image](image4)

Figure 7.11: Overview of CO\textsubscript{2} mass distributions after 24 days for model geometries GM\textsubscript{1} to GM\textsubscript{4} (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m\textsuperscript{2}. Different rows correspond to the different simulation cases GM\textsubscript{1} HYST to GM\textsubscript{4} HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
**Figure 7.12:** Overview of CO₂ mass distributions after 26 days for model geometries GM₁ to GM₄ (Fig. 6.1) with low matrix permeabilities of \( k_m = 1 \times 10^{-13} \text{ m}^2 \). Different rows correspond to the different simulation cases GM₁ HYST to GM₄ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
Figure 7.13: Overview of CO₂ mass distributions after 28 days for model geometries GM₁ to GM₄ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m². Different rows correspond to the different simulation cases GM₁ HYST to GM₄ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
Figure 7.14: Overview of CO₂ mass distributions after 30 days for model geometries GM₁ to GM₄ (Fig. 6.1) with low matrix permeabilities of \( k_m = 1 \times 10^{-13} \text{ m}^2 \). Different rows correspond to the different simulation cases GM₁ HYST to GM₄ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
Figure 7.15: Overview of CO$_2$ mass distributions after 32 days for model geometries GM$_1$ to GM$_4$ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. Different rows correspond to the different simulation cases GM$_1$ HYST to GM$_4$ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
Figure 7.16: Overview of CO₂ mass distributions after 34 days for model geometries GM₁ to GM₄ (Fig. 6.1) with low matrix permeabilities of \( k_m = 1 \times 10^{-13} \text{ m}^2 \). Different rows correspond to the different simulation cases GM₁ HYST to GM₄ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
(I) Brooks-Corey Model (GM1 HYST)  (II) Van Genuchten Model (GM1 HYST)

(III) Brooks-Corey Model (GM2 HYST)  (IV) Van Genuchten Model (GM2 HYST)

(V) Brooks-Corey Model (GM3 HYST)  (VI) Van Genuchten Model (GM3 HYST)

(VII) Brooks-Corey Model (GM4 HYST)  (VIII) Van Genuchten Model (GM4 HYST)

Figure 7.17: Overview of CO₂ mass distributions after 36 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of \( k_m = 1 \times 10^{-13} \) m². Different rows correspond to the different simulation cases GM1 HYST to GM4 HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
Figure 7.18: Overview of CO$_2$ mass distributions after 38 days for model geometries GM$_1$ to GM$_4$ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. Different rows correspond to the different simulation cases GM$_1$ HYST to GM$_4$ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
Figure 7.19: Overview of CO₂ mass distributions after 40 days for model geometries GM₁ to GM₄ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m². Different rows correspond to the different simulation cases GM₁ HYST to GM₄ HYST while different columns correspond to the different two-phase model (BC model, left; and VG model, right). Simulations account for hysteresis effect.
Figure 7.20: Overview of flow direction state (Sec. 4.7) after 18 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of $k_m = 1 	imes 10^{-13}$ m$^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
Figure 7.21: Overview of flow direction state (Sec. 4.7) after 20 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
Figure 7.22: Overview of flow direction state (Sec. 4.7) after 22 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
Figure 7.23: Overview of flow direction state (Sec. 4.7) after 24 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
Figure 7.24: Overview of flow direction state (Sec. 4.7) after 26 days for model geometries GM₁ to GM₄ (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
(I) Brooks-Corey Model (GM₁ HYST)  (II) Van Genuchten Model (GM₁ HYST)

(III) Brooks-Corey Model (GM₂ HYST)  (IV) Van Genuchten Model (GM₂ HYST)

(V) Brooks-Corey Model (GM₃ HYST)  (VI) Van Genuchten Model (GM₃ HYST)

(VII) Brooks-Corey Model (GM₄ HYST)  (VIII) Van Genuchten Model (GM₄ HYST)

**Figure 7.25:** Overview of flow direction state (Sec. 4.7) **after 28 days** for model geometries GM₁ to GM₄ (Fig. 6.1) with **low** matrix permeabilities of $k_m = 1 \times 10^{-13}$ m². (red, imbibition; green, secondary drainage; blue, primary drainage).
Figure 7.26: Overview of flow direction state (Sec. 4.7) after 30 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13} \text{m}^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
Figure 7.27: Overview of flow direction state (Sec. 4.7) after 32 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
(I) Brooks-Corey Model (GM1 HYST)  (II) Van Genuchten Model (GM1 HYST)

(III) Brooks-Corey Model (GM2 HYST)  (IV) Van Genuchten Model (GM2 HYST)

(V) Brooks-Corey Model (GM3 HYST)  (VI) Van Genuchten Model (GM3 HYST)

(VII) Brooks-Corey Model (GM4 HYST)  (VIII) Van Genuchten Model (GM4 HYST)

Figure 7.28: Overview of flow direction state (Sec. 4.7) after 34 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
(I) Brooks-Corey Model (GM1)  (II) Van Genuchten Model (GM1 HYST)

(III) Brooks-Corey Model (GM2 HYST)  (IV) Van Genuchten Model (GM2 HYST)

(V) Brooks-Corey Model (GM3 HYST)  (VI) Van Genuchten Model (GM3 HYST)

(VII) Brooks-Corey Model (GM4 HYST)  (VIII) Van Genuchten Model (GM4 HYST)

Figure 7.29: Overview of flow direction state (Sec. 4.7) after 36 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of \( k_m = 1 \times 10^{-13} \text{ m}^2 \). (red, imbibition; green, secondary drainage; blue, primary drainage).
Figure 7.30: Overview of flow direction state (Sec. 4.7) after 38 days for model geometries GM1 to GM4 (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
(I) Brooks-Corey Model (GM\textsubscript{1} HYST)  

(II) Van Genuchten Model (GM\textsubscript{1} HYST)  

(III) Brooks-Corey Model (GM\textsubscript{2} HYST)  

(IV) Van Genuchten Model (GM\textsubscript{2} HYST)  

(V) Brooks-Corey Model (GM\textsubscript{3} HYST)  

(VI) Van Genuchten Model (GM\textsubscript{3} HYST)  

(VII) Brooks-Corey Model (GM\textsubscript{4} HYST)  

(VIII) Van Genuchten Model (GM\textsubscript{4} HYST)  

Figure 7.31: Overview of flow direction state (Sec. 4.7) after 40 days for model geometries GM\textsubscript{1} to GM\textsubscript{4} (Fig. 6.1) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. (red, imbibition; green, secondary drainage; blue, primary drainage).
Accounting for hysteresis has some effect on the breakthrough time: they are delayed by up to 1.5 d. This delay is caused by parts of the matrix switching from primary drainage to imbibition. Consequently, the relative non-wetting relative permeability curve is computed along a scanning curve resulting in reduced fractional flows. However numerical results indicate that differences in the maximum mass of CO$_2$ when hysteresis is enabled to when hysteresis is absent, are in average less then 0.001%. In other words: breakthrough curves of CO$_2$ and mass inventory curves of CO$_2$ before fluid injection changes from CO$_2$ to H$_2$O, are essentially equivalent. Hence, I focus only on numerical results after 1 PV. Findings from the previous chapter do also apply if not stated otherwise.

Mass inventory curves for CO$_2$ are parallel after 1.6 PV independent of the model geometry, the two-phase model or the matrix permeability (Fig. 7.4). This behaviour is caused by immobilisation and subsequent evaporation of CO$_2$ into the CO$_2$-undersaturated fresh aqueous phase. However, numerical results show that in contrast to mass inventory curves for CO$_2$, mass inventory curves for immobilised CO$_2$ do cross. It results in a more rapid decline of CO$_2$ mass if a VG model is employed (Fig. 7.6). Differences in mass inventories curves for immobile CO$_2$ can vary between -25 and +20 %.

There are some features shared between the cases OM1 to OM4 and OM1 HYST to OM4 HYST. Similarly to when hysteresis is absent, VG model show earlier breakthrough compared to BC model due to their entry-slope region. The entry-slope region causes the CO$_2$ plume to advance faster compared to the BC model. Mass inventories of CO$_2$ will therefore show that the BC model predict more CO$_2$ to be in the model geometries than the VG model. If hysteresis is accounted for, this situation is still true. However, mass inventories for residual trapped saturations show that the VG model lead to higher predictions in mass inventories of CO$_2$ (Fig. 7.5). This behaviour is caused by the imbibition-bound non-wetting relative permeability curve: for a given effective
saturation the VG model leads smaller numerical values than the BC model.

7.4 Conclusion

The purpose of this chapter was to investigate the impact of non-wetting relative permeability hysteresis on CO$_2$ mass inventories and CO$_2$ breakthrough curves. Hysteresis lead to residual trapping of CO$_2$, which takes place at the trailing edge of the CO$_2$ plume. Two different two-phase model were employed and two different matrix permeabilities were considered. Four simple and idealised model geometries were considered. One PV of CO$_2$ was injected, followed by the injection of 2 PV of H$_2$O.

The main findings are as follows:

1. The application of the Brooks-Corey model leads to higher masses of CO$_2$ mass in all model geometries compared to the Van Genuchten model after injection of CO$_2$ ceases and injection of H$_2$O commences (Fig. 7.5), because of early breakthrough when VG models are employed.

2. However, the Van Genuchten model predicts higher immobilised or CO$_2$ mass inventories, because the imbibition-bound non-wetting relative permeability curves for the Van Genuchten model on scanning curves are steeper than for Brooks-Corey model (Fig. 7.5). This situation results in immobilisation of CO$_2$ at higher carbonic saturations compared to the Brooks-Corey model.

3. Mass inventory curves of CO$_2$ are linear trending and parallel after 1.6 PV whilst CO$_2$ continues to evaporate into the fresh CO$_2$-undersaturated aqueous phase.
A discrete fracture-matrix method (DFM) was developed (Chap. 4) to account for capillary forces (Sec. 3.5 & Sec. 4.7). Its application to generic and idealised model geometries (Fig. 6.1) including fractures (Chap. 6 & Chap. 7) shows that mass inventories (Fig. 4.57) and breakthrough curves (Fig. 4.56) are impacted by the choice of two-phase model. in terms of maximum CO$_2$ mass (Fig. 7.2) of breakthrough time of CO$_2$ (Fig. 7.4). The effect of non-wetting relative permeability hysteresis was investigated in Chap. 7 by using an identical model setup of Chap. 6. Significant parts of the CO$_2$ was immobilised after injection changes from CO$_2$ to H$_2$O, when hysteresis was employed (Fig. 7.3).

This chapter revisits the experiments conducted in Chap. 6 and Chap. 7. There are two differences between the models considered in this chapter and those in the previous two chapters: First, the idealised model geometries are substituted by a well-known analogue; four different fracture aperture models are used. The focus will be again on quantifying differences between (a) the Brooks-Corey and Van Genuchten relative permeability and capillary pressure models* which control overall fluid flow and trapping behaviour, (b) low and high matrix permeabilities which can allow for fracture or matrix dominated flow, and (c) the impact of fracture aperture models. Thermophysical properties used throughout this chapter are identical to those listed in Tab. 6.2. The two-phase model properties are identical to those listed in Tab. 6.1.

In this chapter I considered pressure build-up and relaxation during injection, laminar multi-phase multi-component transport without turbulences, capillary diffusion, compressible fluids, and capillary entry pressure at the fracture-matrix interface. Phase

*Further referred to as BC and VG model
densities account for pressure, temperature and salinity, but is held constant throughout the simulation. Effects neglected are gravity, heterogeneous capillary entry pressures, hysteresis, energy transport, near-wellbore effects, and reactive transport.

8.1 model setup

An aerial photograph from a Devonian sandstone outcrop in the Hornelen basin in western Norway served as an analogue for the fractured geological formation Odling (1997). The model has dimensions of 90 m × 90 m. The digitised model comprises 784 single fractures. The unstructured mesh contains 85,546 elements of which 70,991 are 2D-triangles and 13,772 are 1D line elements. The remaining line elements constitute the model boundaries. All triangles are irregular. The mesh is generated with the commercial software ANSYS/ICEM and the underlying geometry was created with the CAD program Rhino3D. I assume the model to be horizontal and fractures to be bed-bound with limited vertical extend, hence I can neglect gravity effects (Fig. 8.2).

Figure 8.1: Overview of the Odling map 4 fracture network used. It dimension is 90 m × 90 m. The figure is taken from Odling (1997)
I use a different model geometry based on a digitised version of the 90 x 90 m fracture geometry mapped by (Odling, 1997). (Odling, 1997) refers to this geometry as map 4. We therefore refer to this model geometry as MAP4.

Figure 8.2: Overview of the Odling map 4 model geometry used. Its dimension is 90 m x 90 m. Fracture permeability is variable between $k_f = 2.1 \times 10^{-8}$ m$^2$, and matrix permeabilities are $k_m \in \{1 \times 10^{-13}$ m$^2; 1 \times 10^{-12}$ m$^2\}$. Hence permeability ratio is $\approx 10,000$ to $100,000$. All model geometries have an inlet at the left boundary with mass injection rate of $M_{inj} = 0.5$ kgs$^{-1}$ along the boundary length of 90 m. The outlet is located at the right boundary, where pressure is held constant at 12.0 MPa. The initial pressure is 12.0 MPa. No flow occurs across the top and bottom boundary. Apertures for cases OM1 to OM3 are assumed to be uniform and constant. Fracture aperture for OM4 are calculated using the Linear Elastic Fracture Model (Eq. 3.71) which determines the aperture from the ambient stress field. In doing so, the LEFM introduces length-correlated apertures that vary along the fracture. Fracture permeabilities in all cases are calculated from a parallel plate approach (Eq. 3.72).
The model geometries have different fracture apertures with

1. small uniform aperture of $a = 0.1 \text{ mm}$ (OM1),

2. medium uniform aperture of $a = 0.5 \text{ mm}$ (OM2),

3. high uniform aperture of $a = 1.0 \text{ mm}$ (OM3),

4. stress-correlated variable apertures (OM4).

The grid of the model geometries are shown in Fig. 8.2. Fractures with uniform aperture have apertures independent of their fracture length. For uniform fracture apertures, the parallel plate approach yields spatially constant fracture permeabilities of permeabilities of $k_f \in \{8.3 \times 10^{-10} \text{ m}^2, 2.1 \times 10^{-8} \text{ m}^2, 8.3 \times 10^{-8} \text{ m}^2 \}$. Fracture apertures for OM4 are calculated from the anisotropic ambient stress field and from rock properties typical for Sandstone using the Linear Elastic Fracture Model (LEFM, Eq. 3.71). In doing so, the LEFM introduces apertures that vary along the fracture. For the sandstone a shear modulus of $G = 1.0 \text{ GPa}$, and a Poisson’s ratio of $\nu = 0.2$ was used. All fractures are assumed to be open, hence the fracture permeabilities are calculated from the parallel plate approach (Eq. 3.72). For stress-correlated apertures, the matrix permeability serves as a lower bound, because the aperture at fracture tips becomes very small (Fig. 3.6). Therefore, fracture permeabilities equal matrix permeability if, for a given aperture, the fracture permeability becomes smaller than the matrix permeability.

The model setup is essentially identical to the one used in Sec. 6.1. However, CO$_2$ is injected for 19.12 days while water is injected for 19.12 days. The total simulation time is 38.24 days, different to the idealised fracture model geometries discussed in Chap. 6 and Chap. 7

For every model geometry, the combination of two two-phase models (BC and VG model) and two matrix permeabilities (low and high) leads to 16 different simulations.

The initial pressure and velocity fields for all cases are shown in Fig. 8.3 and Fig. 8.4 for the individual model geometries used. Note that initially the model is completely filled with H$_2$O and hence pressure and velocity fields are identical for both two-phase
models. At fixed injection rate the pressure at the inlet can vary as the pressure gradient adjust to fracture and matrix permeabilities. The pressure at the inlet for low matrix permeabilities varies from approximately between 12.5 MPa (OM3) and 15.3 MPa (OM1). For high matrix permeabilities, the inlet pressure ranges approximately 12.07 MPa (OM3) to approximately 12.43 MPa (OM1). Similar to the initial pressure distribution of GM1 to GM4 (see p. 112), the differences in initial inlet pressure are less pronounced at higher matrix permeabilities. Flow is fracture-dominated for OM1 to OM4 and independent of the matrix permeability with several order of magnitude faster flow in fractures.

Mass inventories (Eq. 4.57) of CO\textsubscript{2} are shown in Fig. 8.7. These figures plot the amount of CO\textsubscript{2} within the respective model against time and pore volume injected (Fig. 8.8). The mass inventories are shown for the individual aperture models used, so that the effect of the \(k_r\) and \(p_c\) models and matrix permeabilities can be compared directly. Similarly, differences in mass inventories stemming from the application of the BC and VG model are shown in absolute (Fig. 8.9) and relative values (Fig. 8.10). Relative values are calculated by subtracting from BC model values the VG model values and normalising by division by the BC model values. Hence, positive values indicate a surplus of CO\textsubscript{2} for the BC model over the VG model.

Velocity-weighted breakthrough curves (Eq. 4.56) have been measured and are shown in Fig. 8.11 for the individual model geometries as well. Breakthrough times \(t_{btc}\) (Eq. 6.2) are listed in Tab. 8.1 with bar plots provided in Fig. 8.5. They are grouped according to the model geometries OM1 to OM4.

In figures that show both, mass inventories and breakthrough curves, blue lines are used for results when a BC model has been employed, and green lines for results when VG model has been employed. Solid lines indicate low matrix permeabilities of \(k_m = 1 \times 10^{-13} \text{ m}^2\) and dashed line high matrix permeability of \(k_m = 1 \times 10^{-12} \text{ m}^2\).
Figure 8.3: Overview of the global pressure field for different fracture aperture models applied to the model geometry shown in Fig. 8.2 and different matrix permeabilities. Different rows correspond to the different aperture models OM1 to OM4 while different columns correspond to the different matrix permeabilities ($1 \times 10^{-13} \text{ m}^2$, left; and $1 \times 10^{-12} \text{ m}^2$, right).
Figure 8.4: Overview of the volumetric velocity field for different fracture aperture model applied to the model geometry shown in Fig. 8.2. Different rows correspond to the different aperture models OM1 to OM4 while different columns correspond to the different matrix permeabilities ($1 \times 10^{-13}$ m$^2$, left; and $1 \times 10^{-12}$ m$^2$, right).
8.2 Results

8.2.1 Small Uniform Aperture Model (OM1)

All CO₂ mass inventory curves in Fig. 8.7 (I) exhibit three abrupt slope changes, or slope discontinuities, at different stages, except for the high matrix permeability simulation that uses the VG model simulation. The three slope changes are related to breakthrough of CO₂, fluid injection changes from CO₂ to H₂O and breakthrough of H₂O. For the low matrix permeability case the first slope change occurs approximately after 9 days (BC model) and after approximately 8 d (VG model). For high \( k_m \), the slope change is after 11 d (BC model) and after 10 d (VG model). However, the CO₂ mass inventory curve of the high \( k_m \) simulation that uses the VG model simulation (green dashed line) exhibits a shape which does not follow the trend of the other three curves and also when this particular mass inventory curve is compared to the mass inventory curves of GM1 to GM4 (Fig. 6.6).

After fluid injection changes from CO₂ to H₂O, the CO₂ mass in the model geometry drops rapidly until the third slope change occurs after approximately 23 d (BC model) and 24 d (VG model) in the case of low \( k_m \). The effect is less pronounced for the high

\[
\begin{array}{c|c|c|c|c}
\text{OM Case} & \text{BC, low } k_m & \text{BC, high } k_m & \text{VG, low } k_m & \text{VG, high } k_m \\
\hline
1 & & & & \\
2 & & & & \\
3 & & & & \\
4 & & & & \\
\end{array}
\]

\( t_{\text{btc}} \) is defined in Eq. 6.2. The figure shows \( t_{\text{btc}} \) for all 16 simulations for different two-phase model (blue for BC model, green for VG model) and matrix permeabilities (darker colours for low \( k_m \), lighter colour for high \( k_m \)). OM1 results exhibit highest overall \( t_{\text{btc}} \). Lowest \( t_{\text{btc}} \) values in every fracture aperture model OM1 to OM4 are achieved with the BC model and low \( k_m \) settings. See Tab. 8.1 for values of \( t_{\text{btc}} \). Breakthrough for the high \( k_m \) VG models in OM1 and OM2 is absent, as breakthrough does not occur within given simulation time of 57 d. It indicates that the simulation setup might be misconfigured.

Figure 8.5: Overview of breakthrough times \( t_{\text{btc}} \) for the model cases OM1 to OM4. Breakthrough time \( t_{\text{btc}} \) is defined in Eq. 6.2. The figure shows \( t_{\text{btc}} \) for all 16 simulations for different two-phase model (blue for BC model, green for VG model) and matrix permeabilities (darker colours for low \( k_m \), lighter colour for high \( k_m \)). OM1 results exhibit highest overall \( t_{\text{btc}} \). Lowest \( t_{\text{btc}} \) values in every fracture aperture model OM1 to OM4 are achieved with the BC model and low \( k_m \) settings. See Tab. 8.1 for values of \( t_{\text{btc}} \). Breakthrough for the high \( k_m \) VG models in OM1 and OM2 is absent, as breakthrough does not occur within given simulation time of 57 d. It indicates that the simulation setup might be misconfigured.
Table 8.1: Values of breakthrough time $t_{brc}$ as defined by Eq. 6.2. A visual overview is provided in Fig. 8.5.

<table>
<thead>
<tr>
<th>$k_m$</th>
<th>2p-Model</th>
<th>OM1</th>
<th>OM2</th>
<th>OM3</th>
<th>OM4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>BC</td>
<td>6.06 d</td>
<td>1.41 d</td>
<td>1.15 d</td>
<td>0.81 d</td>
</tr>
<tr>
<td>Low</td>
<td>VG</td>
<td>6.25 d</td>
<td>1.61 d</td>
<td>1.31 d</td>
<td>0.89 d</td>
</tr>
<tr>
<td>High</td>
<td>BC</td>
<td>10.25 d</td>
<td>2.74 d</td>
<td>1.50 d</td>
<td>2.28 d</td>
</tr>
<tr>
<td>High</td>
<td>VG</td>
<td>-†</td>
<td>-‡</td>
<td>1.70 d</td>
<td>2.28 d</td>
</tr>
</tbody>
</table>

† No breakthrough of CO$_2$ occurs during the entire simulation. It indicates that the simulation setup might be misconfigured.

$k_m$ cases, where a slope change occurs approximately after 21 d (BC model). A slope change in the VG is barely visible.

The evolution of CO$_2$ mass differences between the BC and VG model are shown in Fig. 8.9 (I) where the red line denotes the difference in results when employing different two-phase models difference for low $k_m$ cases. The purple line denotes the difference for the high $k_m$ cases. As mentioned before, positive values indicate a surplus of CO$_2$ mass when a BC model is applied. For low $k_m$, the VG model causes a surplus in CO$_2$ mass until 1.7 PV, thereafter the BC model causes a surplus. For high $k_m$ value, the BC model causes a surplus in CO$_2$ mass within the model geometry, except for the first 0.1 PV.

Breakthrough times $t_{brc}$ (Eq. 6.2) are listed in Tab. 8.1 and visualised in Fig. 8.5. Breakthrough times for the low $k_m$ case occur at 6.06 d (BC model) and 6.25 d (VG model). For the high $k_m$ case, only in the BC model does CO$_2$ break through after 10.25 d. It is missing for the VG model. The three remaining breakthrough curves show a slope discontinuity indicating H$_2$O breakthrough after approximately 23 d or approximately between 1.2 and 1.4 PV. The earliest occurs for the high $k_m$ simulation that uses the BC model after 21.15 d. The low $k_m$ simulation that uses the BC model exhibits slope discontinuity after 21.63 d, and after 22.73 d for the low $k_m$ simulation that uses the VG model. These three values were determined by inspecting graphically when drops in CO$_2$ breakthrough curves occur.

Mass distribution for CO$_2$ in OM1 are shown 2 d, 4 d and 6 d after CO$_2$ injection start for low matrix permeabilities in Fig. 8.13 to Fig. 8.15, and for high matrix permeabilities in Fig. 8.19 to Fig. 8.21. Fracture dominant CO$_2$ transport is visible for low $k_m$ but less
Table 8.2: Overview of maximum mass of CO₂.

<table>
<thead>
<tr>
<th>( k_m )</th>
<th>2p-Model</th>
<th>OM₁</th>
<th>OM₂</th>
<th>OM₃</th>
<th>OM₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>BC</td>
<td>439.97 ( \times 10^3 )</td>
<td>283.84 ( \times 10^3 )</td>
<td>210.79 ( \times 10^3 )</td>
<td>325.20 ( \times 10^3 )</td>
</tr>
<tr>
<td>High</td>
<td>BC</td>
<td>369.80 ( \times 10^3 )</td>
<td>314.04 ( \times 10^3 )</td>
<td>248.51 ( \times 10^3 )</td>
<td>255.51 ( \times 10^3 )</td>
</tr>
<tr>
<td>Low</td>
<td>VG</td>
<td>493.34 ( \times 10^3 )</td>
<td>314.95 ( \times 10^3 )</td>
<td>211.71 ( \times 10^3 )</td>
<td>370.97 ( \times 10^3 )</td>
</tr>
<tr>
<td>High</td>
<td>VG</td>
<td>218.71 ( \times 10^3 )</td>
<td>198.80 ( \times 10^3 )</td>
<td>273.76 ( \times 10^3 )</td>
<td>435.61 ( \times 10^3 )</td>
</tr>
</tbody>
</table>

so for high \( k_m \). However, the case where a high \( k_m \) is used in conjunction with a VG Model (Fig. 8.19 (II), Fig. 8.20 (II), Fig. 8.21 (III)) shows an unusual pattern, i.e. the CO₂ plume front is irregularly shaped and exhibits approximately between 10 and 20 fingers with an amplitude if several meters. The respective BC model cases (Fig. 8.19 (I), Fig. 8.20 (I), Fig. 8.21 (I)) have realitvely uniform CO₂ plume fronts with almost absent fingering formation at the displacement front.

The low matrix permeability cases show slightly fracture dominant transport. The CO₂ plume front exhibits some degree of ramification terminated by small blobs of CO₂ at the very end of almost all tips of the CO₂ plume This behaviour occurs independently of the two-phase model used. Whereas the BC model exhibits a relatively uniform plume front with steep changes in CO₂ mass, the VG model does not. The VG model

![Figure 8.6: Overview of maximum mass of CO₂ for OM₁ to OM₄.](image)

Figure 8.6: Overview of maximum mass of CO₂ for OM₁ to OM₄. The figure shows maximum CO₂ mass for all 16 simulations for different two-phase models (purple for BC model, orange for VG model) and matrix permeability (darker colour for low \( k_m \), lighter colour for high \( k_m \)). In the individual cases OM₁ to OM₃, the VG model leads to highest maximum mass of immobilised CO₂, with an overall highest value of 111.88 \( \times 10^3 \) kg. The VG model for high \( k_m \) has overall lowest maximum mass of CO₂ of 198.80 \( \times 10^3 \) kg. For a given matrix permeability the BC model shows smaller maximum residual trapped CO₂ values compared to VG models. Simulations of OM₄ are yet not complete. Values of maximum residual trapped CO₂ are listed in Tab. 8.2.
exhibits higher CO₂ mass in matrix blocks adjacent to the inlet, i.e. close to the left model boundary. Fractures connected to the inlet have higher CO mass compared to the BC model. The BC model shows a more even lateral distribution of CO₂ behind its plume front compared to the VG model. CO₂ Bypassing of matrix blocks is more prominent for the BC model, whereas CO₂ enters the rock matrix more readily if the VG model is used due to the steep Pc/S gradient in the VG model at high water saturation (for a visualisation of the gradient, see also Fig. 3.1 (II)).

8.2.2 Medium Uniform Aperture Model (OM2)

Mass inventory curves are shown in Fig. 8.7 (II) and Fig. 8.8 (II). Slope changes are only visible in the low $k_m$ cases due to H₂O breakthrough. They occur after approximately 22 d (BC model) and 25 d (VG model). Peak CO₂ mass at 1 PV differ by less then 20% for the low $k_m$ case. Higher maximum CO₂ masses are observed for the VG model (Fig. 8.10 (I)). For the high $k_m$ case, the difference is approximately 40% with higher values for the BC model. Compared to OM1, maximum mass of CO₂ are always lower because CO₂ break through earlier. Breakthrough occurs significantly faster after 1.41 d (BC model) and after 1.61 d (VG model) for low $k_m$ case. In the high $k_m$-BC model case CO₂ breaks through after 2.74 d. Breakthrough for the high $k_m$ case using the VG model was not observed within 57 days. Hence the breakthrough time in this case is reported as zero.

Breakthrough curves show a distinct upward jump in CO₂ after fluid injection changes from CO₂ to H₂O which lasts for approximately 1 to 2 d followed by a sudden decline. The upward jump occur after 19.12 d (BC model/high $k_m$), after 19.18 d for both the VG model and the BC model for low $k_m$. The rapid decline occurs after 20.9 d (BC model/high $k_m$), after 22.37 d (VG model/low $k_m$) and after 21.45 d (BC model/low $k_m$) and are caused by the channelling of the injected H₂O which displaces CO₂ towards the outlet right model boundary. The jump height is smaller for high matrix permeability as H₂O can enter matrix blocks which attenuates the effect.
CO₂ mass distribution plots after 2 d, 4 d, and 6 d for low $k_m$ (Fig. 8.13 to Fig. 8.15 and high $k_m$ Fig. 8.19 to Fig. 8.19) reveal a distinctly different pattern in terms of CO₂ distribution within the model geometry compared to OM1. The CO₂ mass build up in matrix blocks adjacent to the inlet is confined to less fractured areas. These matrix blocks are indicated by areas of high pressure gradients and high fluid velocities away from fractures (Fig. 8.3 & Fig. 8.4). A series of connected or closely located fractures enables fracture dominated transport, hence mass build up within the model geometry is slower compared to OM1 as CO₂ can more easily leave the model geometry at the outlet. CO₂ blobs at fracture tips are bigger when matrix permeability is high and occur independently of the matrix permeability as opposed to OM1. The VG model causes more CO₂ mass build up within fractures compared to the BC model. CO₂ mass gradients are steeper adjacent to the inlet for the VG model compared to the BC model. Plume fronts exhibit shallower CO₂ mass gradient upstream for VG models compared to the BC model, independent of the matrix permeability. In the high $k_m$ case, the BC model achieves a greater areal coverage in terms of matrix blocks bypassing than the VG model. For low $k_m$, the areal coverage is similarly extensive to the BC model.

8.2.3 Large Uniform Aperture Model (OM3)

Mass inventory curves of CO₂ are shown in Fig. 8.7 (III). Only the slope changes due to fluid changes from CO₂ to H₂O and due to H₂O breakthrough are visible in all four simulations. The third slope change occurs approximately after 22 d (BC model) and 23 d (VG model) for low $k_m$, and approximately after 21 d (BC model) and after 23 d (VG model). Compared to results for the VG model, the BC model causes a higher CO₂ mass accumulation within the model geometry until fluid injection changes from CO₂ to H₂O (Fig. 8.9 (III)). After 1.2 PV the VG model shows higher CO₂ masses within the model geometry. Thereafter, the results of a simulation using the BC model show that more CO₂ mass has been accumulated. For high $k_m$ the BC model accumulates more CO₂ between 0 and 0.5 PV and again from approximately 1.2 PV on.

Breakthrough curves are shown in Fig. 8.11 (III). Breakthrough of CO₂ occurs after 1.15 d (BC model) and 1.15 d (VG model) for low $k_m$, and after 1.50 d (BC model) and
1.70 d (Tab. 8.1). The sudden increase in the CO$_2$ breakthrough curves after fluid injection changes from CO$_2$ to H$_2$O is less distinct in OM$_3$ compared to OM$_2$. In all four cases the increases in the CO$_2$ breakthrough curves occur after 19.23 d independently of matrix permeability and two-phase curve, because the injecting H$_2$O displaces CO$_2$ in the fractures. The breakthrough curves continue to rise slightly for approximately another day. Afterwards, the curves show sudden slope discontinuities. The discontinuities occur after 20.86 d (BC model) and 22.16 d (VG model) for high $k_m$, and after 21.61 d (BC model) and after 22.48 d (VG model) for low $k_m$.

CO$_2$ mass distribution plots after 2 d, 4 d, and 6 d for low $k_m$ (Fig. 8.13 to Fig. 8.15 and high $k_m$Fig. 8.19 to Fig. 8.19) show fracture dominant transport of CO$_2$. The evolution of the CO$_2$ mass after breakthrough is similar for OM$_2$ and OM$_3$. However, CO$_2$ blobs, approximately 2 to 3 metres in size, that formed at the tips of the fracture are largely absent at low $k_m$ but can be observed at high $k_m$. The difference in the mass gradients of CO$_2$ in matrix blocks adjacent to the inlet is less pronounced in OM$_3$ compared to OM$_2$. Fractures contain more CO$_2$ when the VG model is used and when the fractures are connected to the inlet. The areal coverage of the CO$_2$ filled fracture network is similar for both two-phase models for high $k_m$. This is in contrast to GM$_2$.

8.2.4 Variable Aperture via Linear Elastic Fracture Model (OM$_4$)

Mass inventory curves of CO$_2$ are shown in Fig. 8.7 (IV). Only the slope changes due to fluid changes from CO$_2$ to H$_2$O and due to H$_2$O breakthrough are visible in all four simulations. Compared to results for the BC model, the VG model leads to larger maximum mass of CO$_2$ within the model geometry until fluid injection changes from CO$_2$ to H$_2$O (Fig. 8.9 (III)).

Breakthrough curves are shown in Fig. 8.11 (III). Breakthrough of CO$_2$ occurs after 0.81 d (BC model) and 0.89 d (VG model) for low $k_m$, and after 2.28 d (BC model) and 2.28 d for high $k_m$ as shown in (Tab. 8.1). The sudden increase in the CO$_2$ breakthrough curves after fluid injection changes from CO$_2$ to H$_2$O is less pronounced in OM$_4$ compared to OM$_2$. All results show a abrupt increases in the CO$_2$ breakthrough curves occur
after 19.23 d independently of matrix permeability and two-phase curve, because the injecting H₂O displaces CO₂ in the fractures. The breakthrough curves continue to rise slightly for approximately another day. Afterwards, the curves show sudden slope discontinuities. The discontinuities occur after 20.86 d (BC model) and 22.16 d (VG model) for high \( k_m \), and after 21.61 d (BC model) and after 22.48 d (VG model) for low \( k_m \).

CO₂ mass distribution plots after 2 d, 4 d, and 6 d for low \( k_m \) (Fig. 8.13 to Fig. 8.15) and high \( k_m \) (Fig. 8.19 to Fig. 8.21) show fracture dominant transport of CO₂ compared to numerical results of OM₂ and OM₃, and CO₂ blobs are bigger with sizes of approximately 2 to 10 metres in diameter are formed at the tips of fractures independent of the matrix permeability. Greater blob sizes are caused due to CO₂ propagating through the matrix to reach another fracture, i.e. the fracture network is less connected as compared to OM₁ to OM₃. Fractures contain more CO₂ when the VG model is used and when the fractures are connected to the inlet.
(I) Small Uniform Aperture Case (OM1)

(II) Medium Uniform Aperture Case (OM2)

(III) High Uniform Aperture Case (OM3)

(IV) Stress-Correlated Variable Aperture Case (OM4)

Figure 8.7: Evolution of the CO₂ mass inventory (Eq. 4.57) measuring the total CO₂ mass present in the model geometries OM1 to OM4 (Fig. 8.2).
**Figure 8.8:** Pore volume parametrised evolution of the CO$_2$ mass inventory (Eq. 4.57) measuring the total CO$_2$ mass present in the fracture aperture models OM1 to OM4 (Fig. 8.2).
(I) Low Uniform Aperture Case (OM1)

(II) Medium Uniform Aperture Case (OM2)

(III) High Uniform Aperture Case (OM3)

(IV) Stress-Correlated Variable Aperture Case (OM4)

Figure 8.9: Evolution of differences in mass inventories of CO₂ between Brooks-Corey model and Van Genuchten model for low matrix permeabilities (red line) and high matrix permeabilities (purple line) in the model geometries OM1 to OM4. Positive values indicate that the BC model leads to higher CO₂ mass over the VG model. After fluid injection changes from CO₂ to H₂O the BC model generally leads to higher CO₂ mass in the model geometries OM1 to OM3 (Fig. 8.2). The OM4 case shows that application of the VG model leads to higher CO₂ mass over the BC model.
(I) Low Uniform Aperture Case (OM1)

(II) Medium Uniform Aperture Case (OM2)

(III) High Uniform Aperture Case (OM3)

(IV) Stress-Correlated Variable Aperture Case (OM4)

Figure 8.10: Evolution of relative differences in mass inventories of CO₂ between Brooks-Corey model and Van Genuchten model for low matrix permeabilities (red line) and high matrix permeabilities (purple line) in the model geometries OM1 to OM4. Positive values indicate that the BC model leads to higher CO₂ mass over the VG model. After fluid injection changes from CO₂ to H₂O OM1 to OM3 (Fig. 8.2). The OM4 case shows that application of the VG model leads to higher CO₂ mass over the BC model.
Figure 8.11: Evolution of velocity-weighted breakthrough curves (Eq. 4.56) of CO$_2$ mass for model geometries OM1 to OM4 (Fig. 8.2).
Figure 8.12: Evolution of velocity-weighted breakthrough curves (Eq. 4.56) of CO$_2$ mass for fracture aperture models OM1 to OM4 (Fig. 8.2). The two top figures have logarithmic x-axis scaling, the two bottom figures have linear x-axis scaling.
(I) Brooks-Corey Model (OM1)  

(II) Van Genuchten Model OM1

(III) Brooks-Corey Model (OM2)  

(IV) Van Genuchten Model (OM2)

(V) Brooks-Corey Model (OM3)  

(VI) Van Genuchten Model (OM3)

(VII) Brooks-Corey Model (OM4)  

(VIII) Van Genuchten Model (OM4)

Figure 8.13: Overview of CO₂ mass distributions after 2 days for model geometries OM1 to OM4 (Fig. 8.2) with low matrix permeabilities of \( k_m = 1 \times 10^{-13} \text{m}^2 \). Different rows correspond to the Aperture model cases OM1 to OM4 while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.14: Overview of CO₂ mass distributions after 4 days for model geometries OM₁ to OM₄ (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-12}$ m². Different rows correspond to the Aperture model cases OM₁ to OM₄ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.15: Overview of CO₂ mass distributions after 6 days for model geometries OM₁ to OM₄ (Fig. 8.2) with low matrix permeabilities of \( k_m = 1 \times 10^{-13} \) m². Different rows correspond to the Aperture model cases OM₁ to OM₄ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.16: Overview of CO$_2$ mass distributions after 18 days for model geometries OM$\text{I}$ to OM$\text{IV}$ (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. Different rows correspond to the Aperture model cases OM$\text{I}$ to OM$\text{IV}$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.17: Overview of CO$_2$ mass distributions after 22 days for model geometries OM$_1$ to OM$_4$ (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$. Different rows correspond to the Aperture model cases OM$_1$ to OM$_4$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.18: Overview of CO₂ mass distributions after 26 days for model geometries OM₁ to OM₄ (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m². Different rows correspond to the Aperture model cases OM₁ to OM₄ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.19: Overview of CO₂ mass distributions after 2 days for model geometries OM₁ to OM₄ (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m². Different rows correspond to the Aperture model cases OM₁ to OM₄ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.20: Overview of CO₂ mass distributions after 4 days for model geometries OM₁ to OM₄ (Fig. 8.2) with high matrix permeabilities of \( k_m = 1 \times 10^{-12} \text{ m}^2 \). Different rows correspond to the Aperture model cases OM₁ to OM₄ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.21: Overview of CO$_2$ mass distributions after 6 days for model geometries OM$_1$ to OM$_4$ (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m$^2$. Different rows correspond to the Aperture model cases OM$_1$ to OM$_4$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
8.2 RESULTS

Figure 8.22: Overview of CO₂ mass distributions after 18 days for model geometries OM₁ to OM₄ (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m². Different rows correspond to the Aperture model cases OM₁ to OM₄ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.23: Overview of CO₂ mass distributions after 22 days for model geometries OM₁ to OM₄ (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m². Different rows correspond to the Aperture model cases OM₁ to OM₄ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
Figure 8.24: Overview of CO$_2$ mass distributions after 26 days for model geometries OM$_1$ to OM$_4$ (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m$^2$. Different rows correspond to the Aperture model cases OM$_1$ to OM$_4$ while different columns correspond to the different two-phase model (BC model, left; and VG model, right).
8.3 Discussion

CO₂ migrating in a highly fractured porous media experiences multiple fracture-matrix interactions. These fracture-matrix interactions can lead to complicated breakthrough curve patterns. Breakthrough curves of solutes measured for fractured porous medium can show early breakthrough and long tailing (Geiger et al., 2010). Both features are caused by a range of fluid velocities in the fracture and the matrix, different possible path lengths and multirate diffusion between fracture and matrix.

Simply fractured model geometries as used in the two previous chapters showed that a Van Genuchten model always leads to earlier breakthrough (Fig. 6.10). This behaviour is caused by the steep entry-slope region the Van Genuchten capillary pressure model exhibits when \( S_w \to 1 \). However, numerical results of breakthrough curves for a highly fractured, porous medium show that the Brooks-Corey leads to earlier breakthrough (Fig. 8.11). This is facilitated by the higher cumulative path lengths of the fractures for cases OM1 to OM4 compared to the idealised examples GM2 to GM4. As path length increases the likelihood of fracture matrix interactions due to the entry-slope feature of the Van Genuchten model increases. The entry pressure of the Brooks Corey model does not allow fracture-matrix interactions as long as the capillary entry pressure in the matrix is not exceeded.

Consequently, earlier breakthrough of CO₂ for Brooks-Corey models leads to higher mass inventory curves of CO₂ for the Van Genuchten model, because when breakthrough occurs, significant mass build up ceases (Fig. 8.7). This situation is in contrast to the idealised fractured model geometries used previously.

When CO₂ transport is fracture dominated, a pronounced increase in breakthrough curves of CO₂ occurs shortly after fluid injection changes from CO₂ to H₂O. The increase is followed by a more gradual increase that lasts approximately a day, before the breakthrough curves declines sharply (Fig. 8.11). This behaviour is due to injecting H₂O displacing CO₂ in fractures towards the outlet until H₂O breaks through.
The purpose of this chapter was to investigate how capillary trapping and fracture aperture impact CO₂ migration in fractured porous media containing geologically realistic fracture patterns coming from outcrop analogue data. Therefore 16 simulations were conducted, considering different two-phase models, matrix permeabilities and fracture aperture models. The impact on CO₂ mass inventories and breakthrough curves was studied. The main findings are as follows:

1. When CO₂ transport is fracture dominated, CO₂ breakthrough occurs very early within approximately 1-2 Days (Tab. 8.1), consistent with results using generic fracture model geometries (Tab. 6.3) from Chap. 6 and Chap. 7.

2. The application of the Brooks-Corey model leads to earlier breakthrough times when directly compared to the Van Genuchten model independent of the matrix permeability (Fig. 8.5), because the entry-slope region for the Van Genuchten model allows CO₂ to enter the matrix faster as opposed to the Brooks-Corey capillary entry pressure.

3. After fluid injection changes from CO₂ to H₂O a pronounced increase in breakthrough curves occur. Within approximately a day the breakthrough curve decreases sharply. This is caused by chasing H₂O emptying the fractures towards the outlet.

4. Maximum mass of CO₂ is highest for the case with the smallest uniform fracture aperture and lowest for the case with the highest uniform fracture aperture (Fig. 8.7). This behaviour is caused by early breakthrough of CO₂.
Including trapping models in multiphase flow and transport simulations is crucial in predicting realistic amount of residual trapped, esp. if trapping occurs in highly heterogeneous media such as fractured porous rock. For the first time a Discrete Fracture-Matrix (DFM) method is used to simulate residual trapping of CO$_2$ in a realistic fractured porous rock by accounting for relative permeability hysteresis. Here I study the impact of capillary trapping on mass inventories and breakthrough curves after CO$_2$ injection ceases and H$_2$O injection commences. As outlined in the previous chapters the focus will be on differences between (a) the Brooks-Corey and Van Genuchten relative permeability and capillary pressure models* which impacts overall fluid flow and controls trapping behaviour, (b) low and high matrix permeabilities which allow for fracture or matrix dominated flow, and (c) the impact of fracture aperture models.

In this chapter I considered pressure build-up and relaxation during injection, laminar multi-phase multi-component transport without turbulences, capillary diffusion, compressible fluids, capillary entry pressure at the fracture-matrix interface, and non-wetting relative permeability hysteresis. Phase densities account for pressure, temperature and salinity, but is held constant throughout the simulation. Effects neglected are gravity, heterogeneous capillary entry pressures, energy transport, near-wellbore effects, and reactive transport.

*Further referred to as BC and VG model
9.1 MODEL SETUP

The experimental setup from the previous chapter (Chap. 8) is revisited, and no changes to aperture models (Fig. 8.2), boundary and initial conditions or model parameter values (Tab. 6.2 & Tab. 6.2) were applied. Similar to Chap. 7, the only difference is the enabling of the non-wetting relative permeability hysteresis (NRPH). The four aperture model cases in Chap. 8 reused here are referred to as OM1 HYST to OM4 HYST.

Mass inventories (Eq. 4.57) of CO$_2$ are shown in Fig. 9.3. These figures plot the amount of CO$_2$ within the respective model against time and pore volume injected (Fig. 9.4). The mass inventories are shown for the individual model geometries used, so that the effect of the $k_r$ and $p_c$ models and matrix permeabilities can be compared directly. Similarly, differences in mass inventories stemming from the application of the BC and VG model are shown in absolute (Fig. 9.5) and relative values (Fig. 9.6). Relative values are calculated by subtracting from BC model values of the VG model and subsequent division by the BC model values. Hence, positive values indicate a surplus of CO$_2$ for the BC model over the VG model. The maximum CO$_2$ mass within the model geometry is given in Tab. 9.2, and visualised in Fig. 9.2.

Velocity-weighted breakthrough curves (Eq. 4.56) have been measured and are shown in Fig. 9.7 for the individual model geometries as well. Contrary to GM1 to GM4, the breakthrough curves now measure the actual flowing part of CO$_2$. Hence, residual trapped CO$_2$ does not contribute to breakthrough curves. Breakthrough times are listed in Tab. 9.1 with bar plots provided in Fig. 9.1, grouped according to the aperture models (Fig. 8.2). Here, breakthrough time $t_{btc}$ is defined by Eq. 6.2. An overview of breakthrough times $t_{btc}$ for all 16 simulations for OM1 HYST to OM4 HYST are presented in Fig. 9.1 (I) and their difference to OM1 to OM4 are shown in Fig. 9.1 (II). It indicates that the discussion of the results can be limited to the time after 1 PV, i.e. when injection changes from CO$_2$ to H$_2$O.

In figures for both mass inventories and breakthrough curves, blue lines are used for results when a BC model have been used, and green lines for results when VG model
have been used. Solid lines indicate low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$ and dashed line high matrix permeability of $k_m = 1 \times 10^{-12}$ m$^2$.

**Figure 9.1:** Overview of breakthrough times $t_{b tc}$ of the cases OM1 HYST to OM4 HYST and their differences to OM1 to OM4 (GM1 - GM1 HYST, etc). Breakthrough time $t_{b tc}$ is defined in Eq. 5.2.

(I) The top figure shows $t_{b tc}$ for all 16 simulations for different two-phase models (blue for BC model, green for VG model) and matrix permeabilities (darker colours for low $k_m$, lighter colour for high $k_m$). Similar to Fig. 8.5, the OM1 HYST case exhibit largest $t_{b tc}$. No case has an overall smallest $t_{b tc}$. However, among the uniform aperture models OM3 HYST has smallest $t_{b tc}$ independent of matrix permeability and two-phase model, whereas OM4 Hyst exhibits largest relative difference in $t_{b tc}$. Compared to the VG model, the BC model has smaller $t_{b tc}$ for a given matrix permeability in all cases. Values of $t_{b tc}$ for OM1 HYST to OM4 HYST are listed in Tab. 9.1).

(II) The bottom figure shows $\Delta t_{b tc}$, the difference between $t_{b tc}$ when no non-wetting relative permeability hysteresis is applied, and when non-wetting relative permeability hysteresis is applied. Negative values indicate later arrival, positive values indicate earlier arrival. When hysteresis effect is accounted for, the difference in $t_{b tc}$ ranges from approximately $-0.23$ d to approximately 1.6 d. For the uniform aperture models OM1 HYST to OM3 HYST, the BC model shows larger $t_{b tc}$. For the VG model and low $k_m$ the difference $\Delta t_{b tc}$ decreases with increase in uniform aperture. For high $k_m$, the VG model has vanishing $\Delta t_{b tc}$. The VG model exhibits overall smaller $t_{b tc}$ compared to OM1 to OM4, except for OM3 and high $k_m$. 

9.2 RESULTS

9.2.1 Small Uniform Aperture Model (OM1 HYST)

Simulated mass inventory curves of CO$_2$ for OM1 HYST are shown in Fig. 9.3 (I) and in units of PV in Fig. 9.4 (I). All mass inventory curves exhibit three abrupt slope changes, or slope discontinuities, at different stages, except for the high matrix permeability/VG model simulation. The three slope changes are related to breakthrough of CO$_2$, fluid injection change and breakthrough of H$_2$O. For the low matrix permeability (low $k_m$) case the first slope change occurs approximately after 9 days (BC) and after approximately 8 Days (VG). For high $k_m$, the slope change is after 11 Days (BC) and after 10 Days (VG). However, the CO$_2$ mass inventory curve of the high $k_m$/VG model simulation (green dashed line) exhibits a shape which does not follow the trend of the other three curves and when compared with the mass inventory curves of GM1 to GM4 (Fig. 6.6).

After fluid injection change occurs, the CO$_2$ mass in the model geometry drops rapidly until the third slope change occurs after approximately 23 Days (BC) and 24 Days (VG) in the case of low $k_m$. The effect is less pronounced for the high $k_m$ cases, where a slope change occurs approximately after 21 Days (BC). A slope change in the VG is barely visible.

Plots showing the differences in CO$_2$ mass inventory resulting from using different two-phase models for OM1 and OM1 HYST are given in absolute (Fig. 9.5 (I)) and relative values (Fig. 9.6 (I)). The red line denotes the two-phase model difference for low $k_m$ cases and the purple line denotes the difference for the high $k_m$ cases. As mentioned before, positive values indicate a surplus of CO$_2$ mass when a BC model is applied. For low $k_m$ the VG model produces a surplus in CO$_2$ mass until 1.7 PV, thereafter the BC model produces a surplus. For high $k_m$ value the BC model shows a surplus in CO$_2$ mass within the model geometry, except for the first 0.1 PV.

Breakthrough times $t_{btr}$ (Eq. 6.2) are listed in Tab. 9.1 and visualised in Fig. 9.1. Breakthrough times for the low $k_m$ case occur at 6.08 d (BC) and 6.10 d (VG). For the high $k_m$ CO$_2$ breaks through after 10.32 d (BC) and after 8.84 d. Breakthrough curves are of
similar shape before CO\textsubscript{2} breaks through.

Breakthrough curves of CO\textsubscript{2} are shown in Fig. 9.7 (I) after fluid injection changed from CO\textsubscript{2} to H\textsubscript{2}O. The lines with darker colours represent simulation results with hysteresis. The lines with lighter colour represents results with absent hysteresis for comparison. H\textsubscript{2}O breakthrough causes discontinuities in the slopes of breakthrough curves with steep downward jumps. Afterwards the breakthrough curves decline over the duration of the simulation.

After fluid injection changes from CO\textsubscript{2} to H\textsubscript{2}O the CO\textsubscript{2} breakthrough curve falls rapidly in two jumps independent of matrix permeability and two-phase model. The first jump or discontinuity in the slope occurs for high $k_m$ when using a BC model after 20.68 d. It is followed by a second discontinuity after 20.97 d. Simulation results for the low $k_m$ when using a BC model shows a discontinuity after 21.16 d, followed by a second one after 21.36 d. Simulation results for the low $k_m$ when using a VG model shows a discontinuity after 21.94 d, followed by a second one after 22.17 d. Simulation results for the high $k_m$ when using a VG model shows a discontinuity after 22.3 d, followed by a second one after 22.59 d.

Aftwards, breakthrough curve, breakthrough curves follow a linear trend. The first linear trend begins after 21.44 d (high $k_m$/BC model), the second after 21.84 d (low $k_m$/BC model), the third after 23.12 d (low $k_m$/VG model), and the fourth after 23.15 d (high $k_m$/VG model).

Simulation results for breakthrough curves of CO\textsubscript{2} show that for a given two-phase model high $k_m$ lead to higher values in CO\textsubscript{2} concentration compared to low $k_m$. Breakthrough curves of CO\textsubscript{2} are getting asymptotically close for a given matrix permeability, independent of the two-phase model.

All values were determined by inspecting the breakthrough curves of CO\textsubscript{2} graphically when downward jumps in the breakthrough curves occur.

Mass distribution for CO\textsubscript{2} in OM\textsubscript{4} HYST are shown after 2 d, 4 d and 6 d after injection of CO\textsubscript{2} started for low matrix permeabilities in Fig. 9.9 to Fig. 9.11, and for high matrix permeabilities in Fig. 9.16 to Fig. 9.18.
Table 9.1: Values of breakthrough time \( t_{\text{btc}} \) as defined by Eq. 6.2. A visual overview is provided in Fig. 9.1.

<table>
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<th>( k_r )</th>
<th>2p-Model</th>
<th>OM1 HYST</th>
<th>OM2 HYST</th>
<th>OM3 HYST</th>
<th>OM4 HYST</th>
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<td>Low</td>
<td>BC</td>
<td>6.08</td>
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<tr>
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<td>VG</td>
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<td>1.31</td>
<td>0.78</td>
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<td>VG</td>
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<td>3.11</td>
<td>1.77</td>
<td>2.26</td>
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</table>

Table 9.2: Overview of maximum residual trapped CO\(_2\) mass.

<table>
<thead>
<tr>
<th>( k_r )</th>
<th>2p-Model</th>
<th>OM1 HYST</th>
<th>OM2 HYST</th>
<th>OM3 HYST</th>
<th>OM4 HYST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>BC</td>
<td>41.63 ( \times 10^3 )</td>
<td>41.83 ( \times 10^3 )</td>
<td>36.73 ( \times 10^3 )</td>
<td>41.05 ( \times 10^3 )</td>
</tr>
<tr>
<td>High</td>
<td>BC</td>
<td>74.97 ( \times 10^3 )</td>
<td>48.35 ( \times 10^3 )</td>
<td>47.58 ( \times 10^3 )</td>
<td>56.39 ( \times 10^3 )</td>
</tr>
<tr>
<td>Low</td>
<td>VG</td>
<td>60.61 ( \times 10^3 )</td>
<td>56.14 ( \times 10^3 )</td>
<td>49.12 ( \times 10^3 )</td>
<td>60.49 ( \times 10^3 )</td>
</tr>
<tr>
<td>High</td>
<td>VG</td>
<td>112.08 ( \times 10^3 )</td>
<td>62.73 ( \times 10^3 )</td>
<td>61.90 ( \times 10^3 )</td>
<td>90.21 ( \times 10^3 )</td>
</tr>
</tbody>
</table>

9.2.2 Medium Uniform Aperture Model (OM2 HYST)

Simulated mass inventory curves of CO\(_2\) for OM1 HYST are shown in Fig. 9.3 (I) and in units of PV in Fig. 9.4 (I).

Figure 9.2: Overview of maximum residual trapped CO\(_2\) mass for OM1 HYST to OM4 HYST. The figure shows maximum CO\(_2\) mass for all 16 simulations for different two-phase models (purple for BC model, orange for VG model) and matrix permeability (darker colour for low \( k_m \), lighter colour for high \( k_m \)). In the individual cases OM1 HYST to OM3 HYST, the VG model leads to highest maximum mass of immobilised CO\(_2\), with an overall highest value of 111.88 \( \times 10^3 \) kg. The BC model for low \( k_m \) has overall lowest maximum residual trapped CO\(_2\) of 47.58 \( \times 10^3 \) kg. For a given matrix permeability the BC model shows smaller maximum residual trapped CO\(_2\) values compared to VG models. Simulations of OM4 HYST are yet not complete. Values of maximum residual trapped CO\(_2\) are listed in Tab. 9.2 and their time of occurance in Tab. 9.3.
<table>
<thead>
<tr>
<th>$k_r$</th>
<th>2p-Model</th>
<th>OM1 HYST</th>
<th>OM2 HYST</th>
<th>OM3 HYST</th>
<th>OM4 HYST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low BC</td>
<td>23.43</td>
<td>23.40</td>
<td>22.99</td>
<td>25.96</td>
<td></td>
</tr>
<tr>
<td>High BC</td>
<td>53.31</td>
<td>35.30</td>
<td>27.92</td>
<td>36.04</td>
<td></td>
</tr>
<tr>
<td>Low VG</td>
<td>57.41</td>
<td>23.66</td>
<td>22.26</td>
<td>57.30</td>
<td></td>
</tr>
<tr>
<td>High VG</td>
<td>36.49</td>
<td>28.38</td>
<td>22.66</td>
<td>37.03</td>
<td></td>
</tr>
</tbody>
</table>

Plots showing the differences in CO$_2$ mass inventory resulting from using different two-phase models for OM12 and OM1 HYST are given in absolute (Fig. 9.5 (II)) and relative values (Fig. 9.6 (II)). The red line denotes the two-phase model difference for low $k_m$ cases and the purple line denotes the difference for the high $k_m$ cases.

Breakthrough times $t_{b(tc)}$ (Eq. 6.2) are listed in Tab. 9.1 and visualised in Fig. 9.1. Breakthrough times for the low $k_m$ case occur at 1.63 d (BC) and 1.59 d (VG). For the high $k_m$ CO$_2$ breaks through after 2.92 d (BC) and after 3.11 d (VG). Breakthrough curves are of similar shape before CO$_2$ breaks through.

Breakthrough curves of CO$_2$ are shown in Fig. 9.7 (II) after fluid injection changed from CO$_2$ to H$_2$O. The lines with darker colours represent simulation results with hysteresis. The lines with lighter colour represents results with absent hysteresis for comparison. H$_2$O breakthrough causes discontinuities in the slopes of breakthrough curves with steep downward jumps. Afterwards the breakthrough curves decline over the duration of the simulation.

After fluid injection changes from CO$_2$ to H$_2$O the CO$_2$ breakthrough curve falls rapidly in two jumps independent of matrix permeability and two-phase model. This behaviour was also observed in OM1 HYST. The first jump or discontinuity in the slope occurs for high $k_m$ when using a BC model after 20.52 d. It is followed by a second discontinuity after 20.74 d. Simulation results for the low $k_m$ when using a BC model shows a discontinuity after 21.05 d, followed by a second one after 21.44 d. Simulation results for the low $k_m$ when using a VG model shows a discontinuity after 21.86 d, followed by a second one after 22.08 d. Simulation results for the high $k_m$ when using a VG model shows a discontinuity after 22.3 d, followed by a second one after 22.23 d.

Afterwards, breakthrough curves follow a linear trend. The first linear trend begins after 21.29 d (high $k_m$/BC model), the second after 21.82 d (low $k_m$/BC model), the third
after 22.64 d (high \( k_m \)/VG model), and the fourth after 23.19 d (low \( k_m \)/VG model). In contrast to GM1 HYST, breakthrough curves for the BC model are close during their linear trend independent of the matrix permeability. This behaviour is less pronounced for the VG model.

Mass distribution for CO\(_2\) in OM2 HYST are shown after 2 d, 4 d and 6 d after injection of CO\(_2\) started for low matrix permeabilities in Fig. 9.9 to Fig. 9.11, and for high matrix permeabilities in Fig. 9.16 to Fig. 9.18.

9.2.3 Large Uniform Aperture Model (OM3 HYST)

Simulated mass inventory curves of CO\(_2\) for OM1 HYST are shown in Fig. 9.3 (I) and in units of PV in Fig. 9.4 (I).

Plots showing the differences in CO\(_2\) mass inventory resulting from using different two-phase models for OM12 and OM1 HYST are given in absolute (Fig. 9.5 (III)) and relative values (Fig. 9.6 (III)). The red line denotes the two-phase model difference for low \( k_m \) cases and the purple line denotes the difference for the high \( k_m \) cases.

Breakthrough times \( t_{btc} \) (Eq. 6.2) are listed in Tab. 9.1 and visualised in Fig. 9.1. Breakthrough times for the low \( k_m \) case occur at 1.36 d (BC) and 1.31 d (VG). For the high \( k_m \) CO\(_2\) breaks through after 1.71 d (BC) and after 1.77 d (VG). Breakthrough curves are of similar shape before CO\(_2\) breaks through.

Breakthrough curves of CO\(_2\) are shown in Fig. 9.7 (III) after fluid injection changed from CO\(_2\) to H\(_2\)O. The lines with darker colours represent simulation results with hysteresis. The lines with lighter colour represents results with absent hysteresis for comparison. H\(_2\)O breakthrough causes discontinuities in the slopes of breakthrough curves with steep downward jumps. Afterwards the breakthrough curves decline over the duration of the simulation.

After fluid injection changes from CO\(_2\) to H\(_2\)O the CO\(_2\) breakthrough curve falls rapidly in two jumps independent of matrix permeability and two-phase model. This behaviour was also observed in OM1 HYST. The first jump or discontinuity in the slope
occurs for high $k_m$ when using a BC model after 20.51 d. It is followed by a second discontinuity after 20.94 d. Simulation results for the low $k_m$ when using a BC model shows a discontinuity after 21.21 d, followed by a second one after 21.39 d. Simulation results for the low $k_m$ when using a VG model shows a discontinuity after 21.46 d, followed by a second one after 21.67 d. Simulation results for the high $k_m$ when using a VG model shows a discontinuity after 21.86 d, followed by a second one after 22.13 d.

Afterwards, breakthrough curves follow a linear trend. The first linear trend begins after 21.51 d (high $k_m$/BC model), the second after 22.21 d (low $k_m$/BC model), the third after 22.06 d (high $k_m$/VG model), and the fourth after 22.52 d (low $k_m$/VG model). In contrast to OM1 HYST and OM2 HYST, all breakthrough curves are close during their linear trend.

Mass distribution for CO$_2$ in OM3 HYST are shown after 0 d, 0 d and 0 d after injection of CO$_2$ started for low matrix permeabilities in Fig. 9.9 to Fig. 9.11, and for high matrix permeabilities in Fig. 9.16 to Fig. 9.18.

9.2.4  Variable Aperture Model (OM4 HYST)

Simulated mass inventory curves of CO$_2$ for OM1 HYST are shown in Fig. 9.3 (I) and in units of PV in Fig. 9.4 (I).

Plots showing the differences in CO$_2$ mass inventory resulting from using different two-phase models for OM12 and OM1 HYST are given in absolute (Fig. 9.5 (IV)) and relative values (Fig. 9.6 (IV)). The red line denotes the two-phase model difference for low $k_m$ cases and the purple line denotes the difference for the high $k_m$ cases.

Breakthrough times $t_{btc}$ (Eq. 6.2) are listed in Tab. 9.1 and visualised in Fig. 9.1. Breakthrough times for the low $k_m$ case occur at 0.91 d (BC) and 0.78 d (VG). For high $k_m$ CO$_2$ breaks through after 2.24 d (BC) and after 2.26 d (VG). Breakthrough curves are of similar shape before CO$_2$ breaks through.
Figure 9.3: Temporal evolution of the CO$_2$ mass inventory (Eq. 4.57) measuring the total CO$_2$ mass present in the model geometries GM$_1$ to GM$_4$ (Fig. 8.2)
(I) Small Uniform Aperture Case (OM1 HYST), time in PV

(II) Medium Uniform Aperture Case (OM2 HYST), time in PV

(III) Large Uniform Aperture Case (OM3 HYST), time in PV

(IV) Stress-Correlated Variable Aperture Case (OM4 HYST), time in PV

Figure 9.4: Temporal evolution of the CO$_2$ mass inventory (Eq. 4.57) measuring the total CO$_2$ mass present in the model geometries OM1 to OM4 (Fig. 8.2)
Figure 9.5: Evolution of relative differences in mass inventories of CO$_2$ between Brooks-Corey model and Van Genuchten model for low matrix permeabilities (red line) and high matrix permeabilities (purple line) in the generic model geometries GM$_1$ to GM$_4$. Positive values indicate a surplus in CO$_2$ mass when a VG model is employed. After fluid injection changes from CO$_2$ to H$_2$O, the BC model always leads to higher overall CO$_2$ amount in the model geometries OM$_1$ to OM$_4$ (Fig. 8.2).
Figure 9.6: Evolution of relative differences in mass inventories of CO₂ between Brooks-Corey model and Van Genuchten model for low matrix permeabilities (red line) and high matrix permeabilities (purple line) in the generic model geometries GM₁ to GM₄. After fluid injection changes from CO₂ to H₂O, the BC model always leads to higher overall CO₂ amount in the model geometries OM₁ to OM₄ (Fig. 8.2).
Figure 9.7: Evolution of velocity-weighted breakthrough curves (Eq. 4.56) of CO$_2$ mass for model geometries GM1 to GM4 (Fig. 8.2).
(I) BC Model (with hysteresis)

(II) VG Model (with hysteresis)

(III) BC Model (with hysteresis)

(IV) VG Model (with hysteresis)

Figure 9.8: Evolution of velocity-weighted breakthrough curves (Eq. 4.56) of CO\textsubscript{2} mass for fracture aperture models OM\textsubscript{1} HYST to OM\textsubscript{4} HYST (Fig. 8.2). The two top figures have logarithmic x-axis scaling, the two bottom figures have linear x-axis scaling.
Figure 9.9: Overview of CO₂ mass distribution after 2 days for aperture models GM₁ HYST to GM₄ HYST (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m² and non-wetting relative permeability hysteresis.
Figure 9.10: Overview of CO₂ mass distribution after 4 days for aperture models GM₁ HYST to GM₄ HYST (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13} \text{m}^2$ and non-wetting relative permeability hysteresis.
Figure 9.11: Overview of CO$_2$ mass distribution after 6 days for aperture models GM$_1$ HYST to GM$_4$ HYST (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$ and non-wetting relative permeability hysteresis.
(I) Brooks-Corey Model (OM$_1$ HYST)  
(II) Van Genuchten Model (OM$_1$ HYST)

(III) Brooks-Corey Model (OM$_2$ HYST)  
(IV) Van Genuchten Model (OM$_2$ HYST)

(V) Brooks-Corey Model (OM$_3$ HYST)  
(VI) Van Genuchten Model (OM$_3$ HYST)

(VII) Brooks-Corey Model (OM$_4$ HYST)  
(VIII) Van Genuchten Model (OM$_4$ HYST)

Figure 9.12: Overview of CO$_2$ mass distribution after 18 days for aperture models GM$_1$ HYST to GM$_4$ HYST (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$ and non-wetting relative permeability hysteresis.
Figure 9.13: Overview of CO₂ mass distribution after 20 days for aperture models GM₁ HYST to GM₄ HYST (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13} \text{m}^2$ and non-wetting relative permeability hysteresis.
Figure 9.14: Overview of CO$_2$ mass distribution after 24 days for aperture models GM1 HYST to GM4 HYST (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$ and non-wetting relative permeability hysteresis.
**Figure 9.15:** Overview of CO$_2$ mass distribution after 26 days for aperture models GM$_1$ HYST to GM$_4$ HYST (Fig. 8.2) with low matrix permeabilities of $k_m = 1 \times 10^{-13}$ m$^2$ and non-wetting relative permeability hysteresis.
Figure 9.16: Overview of CO₂ mass distribution after 2 days for aperture models GM₁ HYST to GM₄ HYST (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m² and non-wetting relative permeability hysteresis.
Figure 9.17: Overview of CO₂ mass distribution after 4 days for aperture models GM₁ HYST to GM₄ HYST (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12} \text{m}^2$ and non-wetting relative permeability hysteresis.
(I) Brooks-Corey Model (OM1 HYST)  (II) Van Genuchten Model (OM1 HYST)

(III) Brooks-Corey Model (OM2 HYST)  (IV) Van Genuchten Model (OM2 HYST)

(V) Brooks-Corey Model (OM3 HYST)  (VI) Van Genuchten Model (OM3 HYST)

(VII) Brooks-Corey Model (OM4 HYST)  (VIII) Van Genuchten Model (OM4 HYST)

**Figure 9.18:** Overview of CO$_2$ mass distribution after 6 days for aperture models GM$_1$ HYST to GM$_4$ HYST (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m$^2$ and non-wetting relative permeability hysteresis.
Figure 9.19: Overview of CO$_2$ mass distribution after 18 days for aperture models GM$1$ HYST to GM$4$ HYST (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m$^2$ and non-wetting relative permeability hysteresis.
Figure 9.20: Overview of CO₂ mass distribution after 20 days for aperture models GM₁ HYST to GM₄ HYST (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m² and non-wetting relative permeability hysteresis.
Brooks-Corey Model (OM\textsubscript{1} HYST) \hspace{2cm} Van Genuchten Model (OM\textsubscript{1} HYST)

Brooks-Corey Model (OM\textsubscript{2} HYST) \hspace{2cm} Van Genuchten Model (OM\textsubscript{2} HYST)

Brooks-Corey Model (OM\textsubscript{3} HYST) \hspace{2cm} Van Genuchten Model (OM\textsubscript{3} HYST)

Brooks-Corey Model (OM\textsubscript{4} HYST) \hspace{2cm} Van Genuchten Model (OM\textsubscript{4} HYST)

Figure 9.21: Overview of CO\textsubscript{2} mass distribution after 24 days for aperture models GM\textsubscript{1} HYST to GM\textsubscript{4} HYST (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12}$ m\textsuperscript{2} and non-wetting relative permeability hysteresis.
(I) Brooks-Corey Model (OM₁ HYST)  (II) Van Genuchten Model (OM₁ HYST)

(III) Brooks-Corey Model (OM₂ HYST)  (IV) Van Genuchten Model (OM₂ HYST)

(V) Brooks-Corey Model (OM₃ HYST)  (VI) Van Genuchten Model (OM₃ HYST)

(VII) Brooks-Corey Model (OM₄ HYST)  (VIII) Van Genuchten Model (OM₄ HYST)

Figure 9.22: Overview of CO₂ mass distribution after 28 days for aperture models GM₁ HYST to GM₄ HYST (Fig. 8.2) with high matrix permeabilities of $k_m = 1 \times 10^{-12} \text{ m}^2$ and non-wetting relative permeability hysteresis.
9.3 Conclusion

The purpose of this chapter was to investigate how a trapping model will impact the immobilisation of CO$_2$ in a highly fractured porous media. The focus was to quantify changes in mass inventory curves of CO$_2$ and breakthrough curves of CO$_2$ compared to when hysteresis is absent. The model dimensions of Chap. 6 to Chap. 9, injection rate of CO$_2$, thermophysical properties, and model parameters of the two phase flow are all identical allowing for cross chapter comparison. In this chapter 16 simulations were conducted with different matrix permeabilities, two phase models and fracture aperture models. The impact on CO$_2$ mass inventories and breakthrough curves was studied. The main findings are as follows:

1. The amount of immobilised mass of CO$_2$ is significantly lower for a highly fractured porous media compared to idealised fractured model geometries (see Fig. 9.3 & Fig. 7.3), because a larger portion of the matrix is intersected by fractures and most of the flow takes place in the fractures.

2. The Van Genuchten model leads to higher mass inventories of CO$_2$ for OM$_1$ HYST to OM$_3$ HYST for the entire duration of the simulation (Fig. 9.6 (I) & Fig. 9.6 (II)), because CO$_2$ breaks through earlier when a Brooks-Corey model is used as opposed to a Van Genuchten Model which prevents further mass build up of CO$_2$.

3. Breakthrough curves of CO$_2$ show convergent behaviour for the high uniform aperture case (OM$_3$ HYST) after H$_2$O breaks through (Fig. 9.7 (III)), because fluid migration in the model geometry dominantly takes place in fracture with little interaction with the matrix.

4. In the small uniform aperture case (OM$_1$ HYST) breakthrough curves of CO$_2$ are not affected by the choice of two-phase (Fig. 9.7 (III)), because CO$_2$ migration is matrix dominant and little fracture matrix interaction occurs.
In this thesis, I have developed a new discrete fracture matrix (DFM) method to simulate CO\textsubscript{2} injection and trapping of CO\textsubscript{2} in fractured geological formations comprising geologically realistic fracture networks to analyse how matrix and fracture properties, as well as capillary forces influence the rate at which CO\textsubscript{2} migrates through a fractured porous medium and is trapped. For the first time residual trapping of CO\textsubscript{2} in fractured rock accounting for hysteresis, has been simulated using a DFM method. Throughout, all implementations were added to the CSMP++ platform (Matthai et al., 2007).

In Chapter Chap. 2 I discussed a thermodynamic model for CO\textsubscript{2}—H\textsubscript{2}O—NaCl mixtures. It consists of:

1. A non-iterative modified Redlich Kwong equation of state to calculate the molar volume of a carbonic phase for CO\textsubscript{2}—H\textsubscript{2}O mixtures. A separate calculation for the aqueous phase is not needed if assumptions about the mixing rules are made, namely infinite dissolution of water in the carbonic phase.

2. Correlations for fugacity coefficients to calculate the mutual solubilities of pure H\textsubscript{2}O and CO\textsubscript{2} from molar volume input, i.e. molar phase mass fractions.

3. An extension to CO\textsubscript{2}—H\textsubscript{2}O—NaCl mixtures by introducing an activity coefficient formulation for NaCl solutions.

4. A collection of correlations to calculate thermophysical properties (i.e. viscosity, density, and compressibility) for CO\textsubscript{2}—H\textsubscript{2}O—NaCl mixtures.

The chapter does not add any new knowledge. However, it was required to implement these correlations because CSMP++ did not provide any means to simulate flow and transport problems for fluids composed of CO\textsubscript{2}, H\textsubscript{2}O and NaCl.
In Chap. 3 I provided the mathematical and physical background for isothermal, compressible, multi-component, multi-phase flow and transport of \( \text{CO}_2-\text{H}_2\text{O} \) fluids in the presence of capillary forces in fractured porous media. The aim is to devise a global pressure formulation for compressible fluids from the compositional mass balance equation. The benefit of a global pressure formulation lies in the decoupling of the mass balance equation and the pressure equation. An operator-splitting methods together with a finite element - finite volume discretisation exploits this decoupling. If an explicit temporal discretisation, such as the forward Euler method, is applied to the mass balance equation, the quadratic terms will impose severe restrictions on the time stepping. To account for stress-dependent fracture apertures, a simple geomechanical model based on the Linear Elastic Fracture Method was presented. Furthermore, a trapping model has been presented to account for hysteresis effects.

In Chap. 4 I developed a strategy to simulate compressible, multi-component, multi-phase flow and transport in the presence of capillary forces in fractured porous media. I devised the numerical formulation for a finite element - finite volume method based on a compressible global pressure formulation discussed in Chap. 3. It is well-known that a fully explicit time discretisation can lead to excessively small time increments if capillary forces are taken into account. This is because of the diffusive contribution in the mass balance equation coming from the capillary pressure, which requires a CFL condition of the form \( \Delta t = O(\Delta x^2) \). By splitting the mass balance equation into an advective and diffusive part where I simulate advection with explicit time-stepping and diffusion with implicit time-stepping, I was able to overcome the strict CFL condition imposed by capillary diffusion. However, the operator-splitting of the mass balance equation required a primary variable change from the mass component \( M_j \) to the phase saturation \( S_i \). The overall operator split is divided into three main parts: the pressure diffusion step, the mass advection step and the capillary diffusion step. Each step is complemented by post-processes to update saturation and mass dependent transport variables. A predictor-corrector scheme was used to increase numerical stability. Sequence diagrams show the control flow of variables for each operator step.
In Chap. 5 I presented three benchmark cases to demonstrate the correctness of the decoupled implementation developed in the previous chapters. The first benchmark is the Buckley-Leverett Problem. It tests the correctness of my algorithm in terms of modelling multi-phase flow and transport with the finite volume - finite element approach. The second case benchmarks the advective transport, spontaneous imbibition and the combination on a uniform grid against the fully coupled multiphase well-established simulator TOUGH2 and EcLipse 300. The third benchmark is identical to the previous but has a fracture embedded into the model geometry. All three benchmarks show that the algorithms discussed in the previous chapters and implemented in CSMP++ yield results that agree well with the reference solutions.

In Chap. 6 I demonstrated that the numerical method developed algorithms can be used to investigate capillary trapping of CO\textsubscript{2} on four idealised model geometries containing fractures. The dimension, thermophysical properties, initial conditions are kept for the following chapters to allow for cross comparison. The focus is on differences between (a) the Brooks-Corey and Van Genuchten relative permeability and capillary pressure models which impact overall fluid flow and control trapping behaviour, and (b) low and high matrix permeabilities which impact the amount of CO\textsubscript{2} that is migrating through the rock matrix and fractures. The impact on mass inventory curves for CO\textsubscript{2} and breakthrough curves of CO\textsubscript{2} have been studied.

In Chap. 7 I revisited the experimental setup from the previous chapter but now considered non-wetting relative permeability hysteresis. The focus is again on the difference between the Van Genuchten and the Brooks-Corey capillary pressure and relative permeability models. The impact on mass inventory curves for CO\textsubscript{2} and breakthrough curves of CO\textsubscript{2} have been studied and compared to cases where hysteresis is neglected.

In Chap. 8 the four model geometries used before were substituted by a geologically realistic fracture network mapped in an outcrop analogue. This chapter also included further sensitivity studies to analyse the impact of fracture aperture models. A uniform fracture aperture model was used with three different apertures. This was complemented by a the Linear Elastic Fracture Method (LEFM) to calculate more realistic
apertures depending on the ambient stress field. The impact on mass inventory curves for CO$_2$ and breakthrough curves of CO$_2$ have been studied.

In Chap. 9 I revisited the previous experimental setup and considered, as similar to Chap. 7, non-wetting relative permeability hysteresis. The impact on mass inventory curves for CO$_2$ and breakthrough curves of CO$_2$ has been studied and was compared to the cases where hysteresis was absent.

Main findings from Chap. 6 to Chap. 9 are as follows:

1. For the idealised model geometries that have been used in Chap. 6 and Chap. 6, the Brooks-Corey relative permeability and capillary model predicts that more CO$_2$ will be retained in the model geometry compared to the case where a Van Genuchten relative permeability and capillary pressure model is used.

2. In contrast, when the fractures network is complex, and geologically more realistic, such as in Chap. 8 and Chap. 9, a Van Genuchten model predicts that more CO$_2$ will be retained within the model geometry compared to the Brooks Corey model.

3. The model geometries representing highly fractured porous media (Chap. 8 & Chap. 9) will immobilise less CO$_2$ compared to model geometries representing simple and idealised fractured porous media. This behaviour is caused by the more extensive fracture network which fragments the entire formation and causes, as long as fracture apertures are above approximately 0.1 mm, fracture dominated flow. CO$_2$ is transferred from the fractures into the matrix only if capillary forces are strong enough and the capillary entry pressure of the matrix can be overcome if the matrix is water-wet. However, the Van Genuchten model predicts, probably physically incorrect, that the rock matrix drains spontaneously and CO$_2$ enters the rock matrix instantaneously due to the infinite slope of the capillary pressure curve at high water saturations.

With regard to the the aims presented in the introduction, I have shown that following combination can be successful implemented in an existing discrete fracture and matrix (DFM) model: (a) a global pressure formulation in the presence of capillary forces, (b) an
operator-splitting technique applied to the mass balance equation including a primary variable change, (c) the accounting for hysteresis relevant for capillary trapping, (d) for a fractured, porous media.
There are several areas where this work could be extended in the future. The four main points are:

1. **A better treatment of discontinuous capillary pressure at fracture matrix interfaces**: standard Galerkin Finite-Element Methods are not capable to capture discontinuous saturations across fracture-matrix interfaces. As a consequence, capillary entry pressures in Brooks-Corey capillary pressure models are not captured accurately. If correctly accounted for, this will lead to even more fracture dominated flow when a Brooks-Corey model is used. Several approaches exist to model discontinuous saturations ([Hoteit and Firoozabadi, 2005a; Reichenberger et al., 2006; Nick and Matthäi, 2011]).

2. **More robust time stepping for trapping models**: I have observed oscillations in breakthrough curves stemming from changes in the flow direction state, i.e. drainage and imbibition. The mass based time increment criterion (Eq. 4.38) allows for CFL overstepping by calculating a new time increment based on the mass present in a finite volume and the outgoing mass fluxes. This approach essentially computes the time increments such no finite volume will be “emptied” or contain negative masses. The trapping models however are saturation formulated and provide non-wetting relative permeabilities. If trapping is enabled, the fractional flows, which are required for the advection step, are affected. Reducing the time steps closer to the CFL criterion eliminates oscillations from breakthrough curves. This is currently done empirically and should be dealt with in a more robust manner, for example by using a-priori error estimates.

3. **Rigorous coupling of geomechanics with fluid flow**: Even though an LEFM model has been used to approximate fracture apertures, this approach is still simplistic in terms of the geomechanics. A more robust coupling of geomechanics, fracture opening/closing and fluid flow would be desirable to simulate the dynamic
changes in the aperture field because small fracture apertures can drastically change CO$_2$ migration and trapping in the rock matrix. There exists several approaches of rigorous coupling between geomechanics and multiphase flow with strong capillarity for finite element-finite volume discretisation (Kim et al., 2013; Jing et al., 2013).

4. Gravity effects to account for long-term post-injection time-scale: All simulations so far consider CO$_2$ migration in bed-bound fractures where gravity forces are negligibly small. In order to carry out simulations in 3D model geometries with the same level of detail and grid refinement that was used in 2D, parallelisation would be needed. Accounting for gravity would allow to simulate containment scenarios within Geological Carbon Storage (GCS), where density differences between the heavier CO$_2$-saturated and lighter CO$_2$-unsaturated aqueous phase leads to gravity fingering away from the caprock. This scenario becomes important at the post-injection time-scale, when migration of the buoyant CO$_2$ plume is accompanied by capillary and solubility trapping (MacMinn et al., 2011; Li et al., 2013).
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