Holger Ott

CO$_2$-BRINE PRIMARY DISPLACEMENT IN SALINE AQUIFERS
Experiments, Simulations and Concepts

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Gutachter:

Univ.-Prof. Dr. Janos Urai

Prof. Dr.-Ing. Michael Kersten

Prof. Dr.-Ing. Rainer Helmig

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Summary

The geological storage of carbon dioxide is a promising method to reduce greenhouse gas emissions to the atmosphere and to meet demanding climate targets. It is also a key enabler for the upstream industry when large amounts of CO$_2$ are produced in hydrocarbon production operations and a disposal concept is required. The most promising geological reservoirs for CO$_2$ storage are depleted hydrocarbon fields and deep saline aquifers. While depleted fields are usually well characterized and have proven seals, saline aquifers are generally more abundant, with a higher total storage capacity. The present habilitation treatise addresses key aspects of CO$_2$ injection and plume migration in saline aquifers, with the presented results being partly applicable to storage in depleted hydrocarbon fields.

CO$_2$ storage research is focused on storage capacity and storage safety. Several threats have been identified concerning the injection process, e.g. firstly, the migration of the CO$_2$ plume potentially leaving the characterized zone of the reservoir to a potential leakage zone and, secondly, the long-term fate of the CO$_2$ in the reservoir – how safe is CO$_2$ storage? The involved time scales range from immediately after injection up to several decades for the primary plume migration. The ultimate trapping processes might take place over centuries and even millennia. This document presents results of experimental research and numerical modeling addressing the early phase of geological storage, i.e., aspects of injectivity, plume migration and early trapping. The document is meant to provide guidance for further experimental investigations, including data interpretation by numerical modeling. We further aim to identify displacement mechanisms and their effects on plume migration, and to provide simple rules for an upfront investigation on the basis of a limited set of data and before extensive reservoir modeling is performed.

**CO$_2$-brine displacement** The basis of predicting CO$_2$-plume migration and initial pore space utilization in aquifers is (1) the microscopic displacement efficiency – how well CO$_2$ displaces brine in the pore space – and (2) the macroscopic sweep efficiency describing the macroscopic movement of the plume. Both are determined by relative-permeability and capillary-pressure saturation functions. Here, through time-lapse computed tomography of unsteady-state injection experiments, we present the first results on CO$_2$-flood front propagation, mimicking the actual field displacement process. Through numerical history matching, we derived relative permeability and capillary pressure. Two series of experiments on two distinctively different rock types are discussed – the first one is a rel-
atively homogeneous mono-modal sandstone and the other one a heterogeneous bi-modal carbonate.

The comparison revealed two major differences. The most distinguishing property is the presence of micro-porosity in the carbonate that requires unrealistically high flow rates to be invaded by the injected CO$_2$. The result is a smaller displacement efficiency leading to a smaller CO$_2$ saturation in micro-porous carbonates according to the ratio of macro-to total-porosity. Potential consequences for storage operations are a respectively lower storage density and a longer CO$_2$ migration distance in the carbonate reservoir.

Secondly, comparative studies of CO$_2$-brine and decane-brine displacements showed the sensitivity of CO$_2$-brine displacement to clay minerals. CO$_2$ floods in clay-rich sandstone showed substantially higher fluid mobilities than the case where clays were deactivated or the invading fluid is decane instead of CO$_2$. We attribute this difference to clay-CO$_2$ interactions in clay-rich sandstone. The study indicates that clays might cause larger differences in CO$_2$-brine relative permeability than the pore architecture does and hence clays deserve a special attention.

The effect of rock heterogeneity on the measurement has been touched on – capillary heterogeneity is responsible for a strongly dispersed flood front. In the carbonate case relative permeability became scale-dependent. There, the concept of displacement and sweep efficiency collide at the experimental scale, with consequences for predicting relative permeability. Further work needs to be done to understand (1) whether the obtained functions are representative for the next larger scale, and if the sample volume is not representative, (2) how to effectively include core-scale capillary heterogeneity into the description of flow in carbonates. In short, there is currently a lack of understanding regarding characterizing capillary heterogeneity.

**Viscous stability and sweep** With the generally lower viscosity of supercritical CO$_2$, CO$_2$-brine displacement is potentially unstable in the sense of viscous fingering. With the obtained relative permeability as a starting point, a numerical modeling study has been performed to determine the viscous displacement stability on experimental and field scales. It is known that the mobility ratio of the displaced to the displacing fluid is a scaling group controlling viscous displacement stability. However, there are several different definitions of “the fluid mobility ratio” in porous media flow. Through “numerical experiments” we identified the shock-front mobility ratio as the one which describes the onset of viscous fingering and discarded others. In addition, capillarity is known to stabilize flow. Experimental-scale simulations revealed that core floods are subject to stable displacement due to the stabilization of the displacement by capillary dispersion. However, on the field scale, CO$_2$-brine displacement can be unstable. As scaling groups we identified the macroscopic capillary number – the viscous to capillary forces – with the associated length scale being the scale of observation in relation to the fingering pattern and the capillary dispersion zone. As gravity becomes important, the upward migration of CO$_2$ stabilizes the flood front at the bottom of the reservoir and destabilizes it at the top. The result is a suppressed finger-
ing pattern and the formation of a dominant “gravity finger”. This is controlled by the relative significance of gravitational and viscous forces – i.e. the gravity number. In an unstable and gravity-dominated situation, gravity overrun might be self-accelerating. The presence of micro porosity might be able to suppress the gravity fingering in a situation where the aquifer exceeds a critical height, so that micro-pores can be occupied by the pressure applied via gravity.

**Injectivity and well bore integrity** Scaling in the region of CO₂-injection wells is generally considered a threat for CO₂ injection operations. There have been several field-scale simulation studies on scaling, but these studies made assumptions about the relationship between porosity reduction due to scaling and permeability. The present thesis provides the first systematic study on solute transport and the effect of salt precipitation on injectivity. In a nutshell, the effect of scaling appeared to be less of an issue in sandstone reservoirs with a relatively simple pore architecture, but might become a serious threat for complex carbonates; the micro porosity was found to play the key role – the studies in this thesis uncovered a novel mechanism that ultimately transports salt in the CO₂-conductive macro pores, where it may dramatically reduce the permeability around the injector. Permeability reduction of up to three orders of magnitude have been found, with the potential to be higher. The effect – an inverse wicking effect – has been described by a capillary equilibration process that occurs at very low brine saturations and therefore, high capillary pressure gradients are only reached in drying processes. The studies revealed that the exact pore structure determines the timescales and the magnitude of this effect. Further research is needed to identify the exact properties that set the timescale and the magnitude of permeability reduction. The identified mechanisms might also play an important role for injectivity in fractured reservoirs and have triggered ongoing research in this area.

On the other hand, the injection of CO₂ (or acid and other acid-forming agents) into water-bearing formations leads to dissolution of soluble minerals comprising reservoirs. This also increases the uncertainty in predicting injectivity and the reliability of geologic CO₂ sequestration. Depending on the reactive-flow regime, different dissolution patterns occur, with different implications for operations: improved injectivity and directional flow due to wormholes formation, well stability issues in the case of compact dissolution, and potential subsidence if dissolution is homogeneous. In single-phase reactive transport, the identification of the dissolution regimes and the controlling scaling groups have been investigated already, but are still the subject of current research. Through time-lapse computerized tomography we investigate the propagation of dissolution structures and the fluid flow therein. The thesis presents the first dynamic data and the first attempt to extend the discussion to two-phase reactive transport. In a comparative study, CO₂ has been included as a second fluid phase and it has been demonstrated that the dissolution regime can change. The typical scaling parameters – the Pécel et and Damköhler numbers, comparing advective- to diffusive-transport rates and reaction rates to advective-transport rates – appeared not to be sufficient to describe carbonate dissolution; the capillarity of
the evolving dissolution structure needs to be considered in order to describe dissolution in carbonate reservoirs due to CO$_2$ injection. The results presented here open up a new topic that requires extensive investigation.

**Pore-scale displacements and trapping** After injection stopped and during secondary plume migration, the CO$_2$ phase might become disconnected into clusters, leading to capillary trapping of CO$_2$. The mobility of the CO$_2$ phase is then governed by the “microscopic” topology of these fluid clusters, i.e. the clusters, their size and cluster-size distributions (shape and orientation might also play a role) are fundamental for predicting the efficiency of capillary trapping. It has been suggested previously that the balance between viscous and capillary forces – the capillary number – governs the mobilization of non-wetting fluid clusters.

We present studies of pore-scale displacement processes that became feasible with the development of synchrotron-based fast X-ray micro computed tomography, as described in this work. In model experiments, we determined cluster size distributions after injection stopped and during imbibition. Using the fast imaging approach in combination with direct pore-scale simulations, we provide a modified capillary number and clear definitions for the parameters entering the expression. In the meantime, such experiments have been performed with CO$_2$-brine at realistic sequestration conditions (Imperial College London), confirming the results and the concept of the critical capillary number. The feasibility of dynamic pore-scale imaging is a step change, and the details provided triggered new advances in pore-scale modeling. It also created a new stimulus for the upscaling of two-phase flow from the pore scale to the continuum scale.

In summary, through state-of-the-art flow experiments and numerical simulations, important issues of CO$_2$-injection operations have been addressed concerning injectivity, CO$_2$-plume migration/storage capacity and capillary trapping. We linked our research to the field scale through numerical simulations and the identification and refinement of scaling groups describing the characteristics of macroscopic flow properties. Finally, we opened up new topics and research activities by identifying new flow mechanisms pointing to hitherto undiscovered threats for CO$_2$ storage.
Chapter 1

Introduction

The challenge  Currently, more than 80% of the world’s primary energy supply is based on fossil fuels, i.e. on the combustion of coal, oil and gas. There are two major issues in conjunction with fossil fuel combustion. First, the earth’s fossil fuel reserves are finite, with a currently estimated remainder of \(\sim 110\) years for coal, \(\sim 50\) years for oil, \(\sim 60\) years for natural gas, assuming the present day’s consumption level in the future [US Energy Information Administration, 2014] – a scenario that is not very likely in view of the current growth rate of the total energy consumption. Second, the combustion of fossil fuels releases carbon dioxide and is to a large extent responsible for the increase of the atmospheric CO\(_2\) concentrations [IPCC, 2005]. It has been estimated that fossil fuels account for about 75% of the current anthropogenic CO\(_2\) emissions [IPCC, 2005]. There is a general agreement that the current level of CO\(_2\) emissions is unsustainable and that a key element for greenhouse gas reduction is linked to primary energy production.

Energy industries and public organizations simulate future energy scenarios based on statistical data and including different future energy policies to understand and predict future developments of the energy market. Fig. 1.1 shows the result of an energy scenario considered by Shell. There are two obvious trends: firstly, the overall energy demand is increasing in the period up to 2050, and secondly, the total demand for fossil fuels will reach a maximum – at around 2040 in the Shell scenario – and declines thereafter, while alternative energy forms increase in their importance. However, despite this trend, the share of fossil fuels is predicted to still be very high in 2050, decreasing from above 80% today to about 70% in 2050. A high share of fossil fuels in the energy mix is a characteristic of the energy scenarios of different organizations [Shell, 2013, International Energy Agency, 2014, IPCC, 2014] and reflects the inertia in the energy market with respect to existing infrastructure and investments. This is important to recognize, since the speed of restructuring the energy sector is not necessarily determined by the speed of technology development of e.g. alternative energy technologies, but rather by the inertia of the energy system caused by capacity, existing plants and infrastructure versus investment in new technology and in the distribution network.

In conclusion, it is very likely that the world will depend in the coming decades on fossil fuels. In addition to our strong emphasis on developing a renewable-energy future,
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Figure 1.1: Projected global energy demand to 2050 in million barrels of oil equivalent a day. Source: Shell analysis [Shell, 2013].

the world should pay attention to mitigation of the consequences of fossil fuel consumption.

**Driving forces for CCS**  The transition to a sustainable energy future requires reduction of anthropogenic greenhouse-gas emissions. There are various ways: the most obvious ones are on the consumer side and are energy saving by reducing consumption and by increasing energy efficiency. On the energy production side, renewable energies are promising, with an increasing share of the total primary energy production.

However, as outlined above, the share of fossil fuels in primary energy production is dominating and is predicted to dominate the next decades. Carbon Capture and Storage (CCS) could play a vital role to mitigate greenhouse gas emissions to the atmosphere. And this was indeed the purpose as CCS first became a topic of interest in the 1990s. CCS was considered as a technology that (1) was transitional, (2) could be deployed quicker than renewables, and (3) would be cheaper than renewables. As time progressed, CCS has been seen in a different light. In modern energy scenarios CCS appears as technology that can be combined with central biomass combustion or gasification to provide negative-CO$_2$ pathways to create a negative offset for continued distributed use of oil and gas in sectors where this is hard to replace. Secondly, pre-combustion capture that produces hydrogen that can be flexibly used for low-carbon power generation becomes a key enabler at the system level.

The combination of CCS and biomass combustion (BECCS) not only reduces emissions and hence slows down the CO$_2$ accumulation in the atmosphere, but has the potential to
actively reduce the atmospheric CO₂ concentration [Benson, 2014]. Demanding mitigation scenarios aim for atmospheric concentrations of 450 to 550 ppm CO₂eq (CO₂ equivalent) in 2100 with a temporary overshoot. Overshooting scenarios – in contrast to long-term accumulating scenarios – typically rely on the widespread deployment of BECCS and afforestation in the second half of the century [IPCC, 2014]. The availability and scale of CCS, BECCS and other mitigation technologies are uncertain and are associated with challenges and risks. However, many climate models could not achieve atmospheric concentration levels of about 450 ppm CO₂eq if additional mitigation is considerably delayed or in the absence or limited availability of key technologies, such as bioenergy, CCS, and their combination (BECCS) [IPCC, 2014].

The required magnitude of emission reduction is large. It has been shown that the cumulative carbon emission between 2011 and 2050 needs to be limited to 1100 Gt of CO₂ in order to limit global warming to 2°C throughout the 21st century [Meinshausen et al., 2009, McGlade and Ekins, 2015]. The present estimates of the global fossil fuel resources are that they contain \( \sim 3 \times \) more carbon [Raupach et al., 2014, McGlade and Ekins, 2015], corresponding to \( \sim 3300 \) Gt of CO₂. On the other hand, the total ongoing and projected CCS operations add up to 9.1 Gt in total up to 2100 [Global CCS Institute, 2015]. This number is of a different magnitude than the challenge, and the current efforts are probably not ambitious enough.

**Carbon Capture and Storage** What is Carbon Capture and Storage (CCS)? CCS describes a set of technologies to separate CO₂ from the exhaust of large emitters – the so-called point sources – and to store it in the subsurface on geological time scales. Typical point sources are fossil-fueled power plants and other CO₂-intensive industries such as the cement and the steel industry [MIT, 2015]. CCS is also a key enabler for the upstream industry, when large amounts of CO₂ are produced in hydrocarbon production operations and a disposal concept is required. Only large point sources currently allow for effective CO₂ capture and transport.

There are different pathways for carbon capture depending on the nature of the emitter. The most common one is the so-called post-combustion capture technology that separates CO₂ from the exhaust stream after combustion. The advantage is that post-combustion capture is an add-on technology, with which existing plants or works can be retrofitted. More sophisticated techniques are available, which are part of the process and hence part of the plant or work. The most common ones are pre-combustion capture and oxyfuel combustion. Current developments are focused on cost reduction (the costs for power generation with CCS are \( \sim 1.5 \) to \( 2 \times \) the costs without CCS [IPCC, 2005]), reduction of the energy demand (15–30% of the generated power) and optimization of integration with power generation processes or other applications.

The pure and compressed CO₂ stream is then transported via pipelines – and in exceptional cases by ship – to a storage site. While cost efficiency is the main issue for CO₂ capture and transport, subsurface storage is focused on storage capacity, performance and safety. There are many suitable types of reservoir: CO₂ can be stored in geological forma-
Figure 1.2: Options for storing CO₂ in deep underground geological formations [IPCC, 2005]. The common options are: (1) storage in depleted oil and gas reservoirs, (2) the use of CO₂ for enhanced oil recovery, (3) storage in deep saline aquifers, and (4) storage in deep unmineable coal seams or use of CO₂ for enhanced coalbed methane recovery.
tions including oil and gas reservoirs, unmineable coal seams and deep saline formations. When selecting a reservoir, there are several aspects to be considered: (1) the reservoir should be in proximity to the point source, (2) the storage capacity and the injectivity should be high enough to maintain a high injection rate over the lifetime of the emitting plant and (3) the reservoir must be well characterized and the injection and storage processes must be well understood to ensure safe storage.

The storage options are schematically shown in Figure 1.2. Currently, the most promising geological reservoirs are depleted hydrocarbon fields and deep saline aquifers. Depleted fields are usually well characterized and have proven seals. The infrastructure such as injection wells and pipelines are already in place, which might reduce costs. Saline aquifers, on the other hand, are generally more abundant – more likely to be in proximity to a point source – with a much higher total storage capacity.

In the ideal case, CCS can be combined with hydrocarbon production. CO₂ can be injected for enhanced oil recovery or enhanced coalbed methane (CBM) recovery. However, CO₂ utilization for hydrocarbon recovery is likely to remain a niche given the volume of CO₂ required to be sequestered.

Subsurface processes
For geological storage, CO₂ is injected into porous (sedimentary) rock formations deep underground. The fluids in deep formations are typically at high pressure and temperature conditions that can be estimated by assuming a geothermal gradient (here we assume 30°C temperature increase per km depth) and a hydrostatic pressure (∼100 bar per km). However, many reservoirs do not follow these rules. To penetrate the formation, CO₂ must be injected at a higher pressure than the initial fluid pressure in the reservoir in order to displace the fluids that are initially in place.

The target reservoirs are usually at a depth of more than 800 m, because assuming the above discussed pressure and temperature gradients, CO₂ is supercritical at these depths as indicated in Figure 1.3. Being in the supercritical phase is beneficial for CO₂ storage; in the SC phase, CO₂ has the density of a liquid, but the viscosity of a gas. A low viscosity is of advantage for pressure response during injection, and the high density ensures a high storage density, i.e. a high utilization of the total pore space for storage. However, the density of CO₂ under reservoir conditions is still smaller than the density of the initial brine, causing the CO₂ to migrate upward, which is the reason – disregarding pure hydrodynamic trapping as suggested by [Bachu et al., 1994] – why for CO₂ storage an upper sealing barrier is needed to prevent CO₂ from coming back to the surface.

There is no “typical architecture” of a reservoir. However, an illustrative example is an anticlinal structure with a series of permeable and impermeable layers, where the permeable layers could serve as CO₂ storage or CO₂ reservoirs and a series of impermeable layers on top would form the seal. Typically, shales or salt layers (evaporates) above a certain thickness and with a certain quality are considered as seals. Such layers are not strictly impermeable, but the permeability is many orders of magnitude smaller than the permeability of the reservoir (nD vs. D), such that penetration happens only over geological time scales. Characteristic properties of the seal layers are the capillary entry pressure, above which
non-wetting CO$_2$ may enter the otherwise water-saturated seal (for shales), and the so-called fracturing pressure above which the seal becomes fractured. Both pressures are linked to the injection pressure, which should always stay within a safety margin below the pressure that would harm the seal. The reservoir, on the other hand, should ideally have a high permeability to allow for high injection rates at a moderate response of the injection pressure, compatible with the safety margin of the capillary entry pressure and the fracturing pressure of the cap rock.

CO$_2$ and water or brine are mutually soluble but immiscible and hence CO$_2$-brine displacement is subject to two-phase (general multi-phase) flow. In contrast to the injection of a miscible fluid, immiscible displacement is never complete, i.e. just a fraction of the pore space is invaded by CO$_2$. In reservoir engineering this is called the microscopic displacement efficiency and for a practical purpose this is described by Darcy’s law (extended to two-phase flow) including relative-permeability and capillary-pressure saturation functions. In simple cases, the saturation profiles and the microscopic displacement efficiency can be derived analytically [Buckley and Leverett, 1942, Lake, 1989].

On a macroscopic scale, i.e. field scale, the displacement efficiency is hampered by gravity, leading to a gravity-driven override of the CO$_2$ and hence bypassing of the pore space in the lower part of the reservoir. Also rock heterogeneity, i.e. layering, and viscous instabilities can lead to channeling and fingering, with the result that rock matrix
**isotropic reservoir**

**unisotropic reservoir**

Displacement under dipping angle $\alpha$, gravity and heterogeneity

**Figure 1.4:** Schematic of primary plume migration and effects of gravity, fluid mobility ratio and heterogeneity on sweep efficiency and plume shape.
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Figure 1.5: Left: schematic of secondary plume migration in an anticline structure after injection has stopped. Right: schematic of CO$_2$ trapping mechanisms through time from [IPCC, 2005].

is macroscopically bypassed. These situations are sketched in Figure 1.4. The total pore space utilized for CO$_2$ storage, $\phi_U$, can be computed from the porosity $\phi$, the displacement efficiency $E_D$ and the volumetric sweep efficiency, $E_V$, by $\phi_U = \phi \cdot E_D \cdot E_V$, with the range of $E_D$ and $E_U$ being between 0 and 1. It becomes obvious that only a fraction of the pore space is actually used for storage of SC CO$_2$. This has consequences: (1) with a low pore space utilization, the CO$_2$ plume expands much further into the reservoir than in case of high $E_D$ and $E_V$. The plume is more difficult to control and might spread into areas of the reservoir that are not well characterized. On the other hand, a low $\phi_U$ means a larger fraction of remaining water in proximity to the CO$_2$ phase. This proximity facilitates secondary trapping processes and therefore leads to faster sequestration of the free CO$_2$ phase.

The primary displacement processes as discussed so far are setting the scene for later processes leading to a redistribution and to trapping of CO$_2$ in the reservoir. In the post-injection period, the plume still migrates due to gravity differences, which is illustrated in Figure 1.5. During secondary migration, the plume might disconnect from the injection well, since there is no supply any more. At this point, water starts to imbibe, i.e. to displace CO$_2$, and since water tends to wet the rock’s internal surface, it disconnects the CO$_2$ phase on the pore scale and forms clusters and bubbles. This is the so-called capillary trapping, which is the first trapping mechanism that kicks in after the stratigraphic trapping.

CO$_2$ and brine are immiscible, but mutually soluble. The dissolution process starts immediately as the CO$_2$ comes in contact with brine, but depending on distances and contact areas, dissolution acts over a long time scale. The dispersed CO$_2$ phase partly
dissolves in the brine phase and since CO$_2$-saturated brine has a higher density than fresh brine, CO$_2$ is effectively removed from the seal and sinks in dissolved form towards the bottom of the reservoir, while the fresh brine is moving upward, eventually contacting the CO$_2$ plume. This forms brine convection cycles that effectively distribute and immobilize the CO$_2$. Dissolved CO$_2$ forms carbonic acid, reacting with the rock-forming minerals. Over even longer time scales it is generally assumed CO$_2$ will react with the formation (rock-fluid system) to form new solids – this is called mineral trapping and is the ultimate form of trapping since CO$_2$ turns into rock matrix – although the time scale and magnitude of mineral trapping is poorly understood and difficult to determine in the lab.

The time scales over which the different trapping mechanisms act are schematically shown in the right-hand image of Figure 1.5. However, this is not a universal plot, as the actual time scales depend on many factors such as the capacity and the activity (brine flux) of the aquifer, the reservoir geometry and the exact injection process, which determines the distribution of the CO$_2$ in the reservoir. The question of how fast and to what extent CO$_2$ is captured by the formation (dissolved or reacted) and to what extent the CO$_2$ remains in supercritical phase can be estimated by numerical field simulations of the injection and the post injection period. How the CO$_2$-fate plot in Figure 1.5 changes for different scenarios, has nicely been shown in a case study by [Snippe and Tucker, 2014].

This work  The present habilitation treatise addresses key aspects of CO$_2$ injection and plume migration in saline aquifers through experimental research and numerical modeling. The focus is on the early phase of geological storage, i.e., aspects of injectivity, plume migration and early trapping of CO$_2$. The treatise uncovers threats, describes procedures and provides guidance for further experimental investigations including data interpretation by numerical modeling. We further identify displacement mechanisms and their impact on CO$_2$-injection operations, and provide simple rules for an upfront judgment and risk assessment on the basis of a limited set of data and before extensive reservoir modeling is performed. The treatise is cumulative, with each section consisting of a publication with a common structure including an introduction and a summary. The sections are combined into chapters as described in the following:

Chapter 2 is concerned with CO$_2$-brine immiscible displacement and focused on relative permeability and capillary pressure saturation functions. We present the first detailed time-lapse data on CO$_2$ flood front propagation, revealing valuable details of the displacement process. Through comparative studies on distinctively different rock types using CO$_2$-brine and decane-brine as model fluids, variations in relative permeability are explained by the architecture of the pore system, rock heterogeneity and by the role of clay minerals for fluid mobility.

On the basis of experimentally determined relative permeability and capillary pressure saturation functions, numerical-simulation studies have been performed to characterize the criteria for displacement stability during CO$_2$-brine primary drainage. The validity of experimental results have been proven and a systematic upscaling to the field scale has been
done providing stability criteria including mobility, capillarity and gravity. The results are discussed in Chapter 3.

Pore-scale processes in drainage and imbibition are discussed in Chapter 4. The aim of the section is to understand macroscopic flow properties on a fundamental basis, which became feasible with the utilization of fast X-ray micro computed tomography, which is described in this chapter. We investigate pore-size distributions after injection stopped and during imbibition. Using the fast imaging approach in combination with direct pore-scale simulations, we provide a sound definition of the capillary number and the parameters entering the expression. The study results in an important criterion describing the mobilization or trapping of non-wetting phase clusters, i.e. the security of the CO₂ capillary trapping process.

In Chapter 5 and Chapter 6, selected aspects are discussed that turned out to be uncertainties for predicting injectivity and well bore integrity. Chapter 5 describes the impact of formation drying due to CO₂ injection and the scaling involved. We quantify the impact of salt precipitation on permeability for sandstone, dolomite field samples and a limestone. In experimental and numerical investigations, we determine macroscopic and microscopic solute transport and the exact location of precipitation. On the basis of the microscopic data, we develop a model explaining the macroscopic observations.

Chapter 6 is concerned with carbonate dissolution. I describe the formation of dissolution structures and the impact that dissolution structures – e.g. wormholes – have on fluid flow and mechanical rock properties. We present the first dynamic data on wormhole growth and fluid flow therein by means of time-lapse computed tomography, and the first investigation of CO₂-brine reactive transport in two-phase flow.

Finally, in Appendix A, I give details of experimental setups and experimental procedures as used for this work.
Chapter 2

CO₂-Brine Primary Drainage

2.1 CO₂–brine displacement and mass-transfer in sandstone

The process of displacement and mass transfer between CO₂ and brine, which are relevant for the prediction of plume migration and pore-space utilization during CO₂ injection in saline aquifers, were studied by conducting unsteady-state core flood experiments in nearly homogeneous Berea sandstone rock. Mutually saturated and unsaturated CO₂ and brine phases were injected in the rock under realistic sequestration conditions.

Relative permeability and capillary pressure curves were extracted by history matching the unsteady state experiments conducted with mutually saturated CO₂ and brine. As a reference and for comparison, decane–brine primary drainage was conducted on the same sample. The CO₂–brine relative permeability was found to be different from the decane–brine relative permeability (which had been validated against steady-state experiments on twin-samples), reflecting the change in the wetting state from water-wet decane–brine/Berea to the rather intermediate-wet behavior of CO₂–brine/Berea, which is in agreement with literature data on contact-angles for the two cases. However, the CO₂ brine data are somewhat different from data on the same rock type as reported by [Perrin and Benson, 2010] which is likely a consequence of sample heterogeneity.

Aspects of the mass transfer between the CO₂ and the brine phase were studied by drainage and imbibition with unsaturated phases. When comparing saturated and unsaturated CO₂–brine primary drainage, the mass transfer due to mutual solubility leads to two effects: (1) evaporation near the inlet due to water dissolving in CO₂ and (2) a diminished displacement of brine by CO₂ due to CO₂ dissolving in brine. In addition, an imbibition experiment was conducted where unsaturated brine was injected into rock filled with mutually saturated CO₂ and brine phase at near-residual CO₂ saturation. After the CO₂-saturated brine had been miscibly displaced by unsaturated brine, dissolution of the trapped CO₂ in the injected brine was subsequently observed. These experiments represent the transition from residual trapping to solubility trapping and indicate the time and length scales involved.
2.1.1 Introduction

Geological sequestration of carbon dioxide (CO$_2$), originating from sources like fossil-fueled power plants and contaminated gas production, is presently seen as a large scale disposal option to reduce greenhouse-gas emission [IPCC, 2005]. Deep saline aquifers and depleted oil and gas fields are potential candidates for CO$_2$ subsurface deposits [IPCC, 2005, Bachu et al., 1994, Bachu and Gunter, 2004]. Trapping mechanisms and the degree of trapping are important factors for assessing the storage capacity for sequestration in formation rock [Suekane et al., 2008].

The migration of the CO$_2$ plume and the pore-space utilization by capillary trapping are two aspects of the displacement process in the subsurface that are relevant for assessing the safety aspects of geological sequestration [Esposito and Benson, 2010]. Single phase fluid flow in porous media, in general, is described by the porosity ($\phi$) and permeability ($K$) of the formation rock, and the fluid viscosity. When considering multiphase flow (immiscible displacement), e.g. the CO$_2$ – brine system, relative permeability ($k_r$) and capillary pressure ($p_c$) saturation functions are important factors as well. The latter two parameters largely influence the plume migration [Egermann et al., 2006], the CO$_2$ saturation of the pore space, and the residually trapped volume after re-imbibition of the aquifer.

Then availability of relative permeability data for CO$_2$–brine drainage is currently seen as one of the critical subsurface issues in CO$_2$ storage [Imbus et al., 2006]. In petroleum engineering, these parameters are commonly measured in either steady state (SS) or unsteady state (USS) core flood experiments. While these measurements already require substantial resources (rock samples, instrumentation, time), the special requirements of CO$_2$ in particular set high demands on materials and experimental procedures [Bennion and Bachu, 2005]. As a consequence, there have so far been only a few attempts to determine data such as the relative permeability of CO$_2$–brine systems.

Systematic studies were conducted by [Bennion and Bachu, 2005, Bennion and Bachu, 2008] who determined CO$_2$–brine and H$_2$S–brine relative permeability in sandstone and carbonate samples from the Wabamun and Zama area in central Alberta, Canada. Drainage and imbibition experiments were carried out in the unsteady state with mutually saturated fluid phases on representative single cores or multiple plug stacks. The relative permeability curves were extracted from the total brine and CO$_2$ flow rates and the pressure drop during the core flood. Since no in-situ saturation monitoring e.g. by imaging was used, i.e. no in-situ saturation profiles in the sample were accessible, the CO$_2$ endpoint relative permeability and the capillary end effect were determined by multi-rate end point floods. Relative permeability saturation functions were determined from production data and pressure drop over the core using numerical regression methods [Bennion and Bachu, 2005]. The residual fluid saturations were determined ex-situ by Dean-Stark extraction after depressurization.

[Egermann et al., 2006] also used unsteady-state core flooding experiments to determine relative permeability data for homogeneous limestone rock with the aim of using that data for an integrated modeling approach.

[Perrin et al., 2009, Perrin and Benson, 2010, Kuo et al., 2010] measured CO$_2$–brine
relative permeability on Berea sandstone and on a sample originating from a storage site in south-west Australia in steady-state (SS) experiments. All samples had a substantial degree of heterogeneity. The authors studied the influence of that heterogeneity on fluid flow and CO$_2$ distribution in the core. Furthermore, both experiments showed a flow rate dependence of the relative permeability curves obtained.

In this study, we report on unsteady state (USS) experiments combined with x-ray computed tomography (CT) to determine relative permeability $k_r$ and capillary pressure $p_c$ for primary drainage of brine by supercritical CO$_2$ in a nearly homogeneous Berea sandstone at conditions representative for a realistic field case. Berea sandstone is an outcrop rock which is widely used as a model and reference rock. We use the USS method because it has a large degree of analogy with the actual field process for CO$_2$ injection. USS experiments typically cover the range where fluids are mobile; this is also the range that is relevant for plume migration in the field.

**Experiments conducted in this study**

A set of four different unsteady-state experiments were conducted on the same Berea sample starting with a primary drainage experiment where brine is displaced by decane. This experiment served as a reference experiment. On a very similar Berea rock sample from the same block, steady-state experiments were conducted using decane–brine/glycol for comparison with the unsteady-state data.

In the second experiment, brine not equilibrated with CO$_2$ (referred to as unsaturated brine) was displaced by supercritical CO$_2$ not equilibrated with brine (referred to as unsaturated CO$_2$) and the effects of mass transfer between the non-equilibrated phases were observed. With respect to CO$_2$ injection in the field, this case is representative for the flood front where fluids have not yet fully equilibrated.

In experiment three, saturated brine was displaced by saturated CO$_2$. Here, no mass transfer between the fluids is expected and the data is directly compared with the decane–brine reference case. With respect to CO$_2$ injection in the field, this case is representative for regions where fluids are already fully equilibrated, e.g. behind the flood front and in the center of the plume.

Experiment four started at the end of experiment three: unsaturated brine was injected in order to “simulate” the re-imbibition of the aquifer after CO$_2$ injection was stopped.

The experiments conducted in this study are listed in Table 2.1.

### 2.1.2 Material & methods

**Flow setup**

A cylindrical rock sample (“core”) contained in a metal sleeve with a Teflon liner is enclosed in a (x-ray transparent) carbon fiber epoxy core holder [Coenen, 2009]. The core was oriented in the horizontal direction (same as main flow direction in the field). Fluids were
Table 2.1: Overview of the experiments, flow velocity and capillary numbers $N_{\text{cap}}$.

<table>
<thead>
<tr>
<th>exp</th>
<th>system parameters</th>
<th>flow velocity (ft/day)</th>
<th>$N_{\text{cap}}$ ($\times 10^{-8}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>drainage</td>
<td>1 decane $\rightarrow$ brine</td>
<td>1.2</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>decane $\rightarrow$ brine/glycol (SS)</td>
<td>1.8-88</td>
<td>29 - 1469</td>
</tr>
<tr>
<td></td>
<td>2 unsaturated: CO$_2$ $\rightarrow$ brine</td>
<td>2.3</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>3 saturated: CO$_2$ $\rightarrow$ brine</td>
<td>2.0</td>
<td>0.79</td>
</tr>
<tr>
<td>imbibition</td>
<td>4 unsat. brine $\rightarrow$ trapped CO$_2$</td>
<td>1.2</td>
<td>9.3</td>
</tr>
</tbody>
</table>

![Figure 2.1: Experimental setup.](image)

N-decane, CO$_2$ and brine are injected at a constant rate into the core via a high pressure syringe pump (Teledyne ISCO, Lincoln NE, USA). During the experiment, the pumps were held at room temperature ($25^\circ$C). The injected fluids are heated to experimental temperature ($45^\circ$C) in the injection lines. The mutual solubility limit of CO$_2$ and brine at both thermodynamic conditions deviate by less than 1% [Shell Global Solutions, 2008]. At the outlet, a constant pressure is maintained either by a dual cylinder piston pump (Quizix, Vindum Engineering, INC., San Ramon CA, USA) or two Tescom back pressure controllers which are operated in series. All seals were made from Teflon, highly fluorinated rubber or Viton-A (hardness: shore 90) to avoid the risk of explosive decompression of CO$_2$. 
Table 2.2: Data on the Berea core.

<table>
<thead>
<tr>
<th>Type</th>
<th>Berea sandstone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>14.97 cm</td>
</tr>
<tr>
<td>Diameter</td>
<td>7.57 cm</td>
</tr>
<tr>
<td>Average porosity</td>
<td>22.3 %</td>
</tr>
<tr>
<td>Pore volume</td>
<td>149.81 ml</td>
</tr>
<tr>
<td>Permeability (brine)</td>
<td>380 mD</td>
</tr>
</tbody>
</table>

Injection rates ranged between 0.25 and 0.5 ml/min which corresponds to flow velocities of 1.2-2.3 foot/day which are often considered to be typical field flow rates (can be estimated from Fig. 3-17 in [Lake, 1989]). The associated capillary numbers \( N_{\text{cap}} = \mu v/\sigma \approx 10^{-8} - 10^{-7} \) (\( \mu \) is the viscosity of the displacing fluid, \( v \) the velocity, the interfacial tension \( \sigma \) for decane–brine is 47.9 mN/m and for \( \text{CO}_2 \)-brine around 30 mN/m, see [Chalbaud et al., 2010, Hebach et al., 2002, Hebach et al., 2005, Yang et al., 2005]) are well on the plateau of typical capillary desaturation curves [Lake, 1989]. The amount of fluid injected into the core was limited by the volume of the injection pump (500 ml) and the amount required to fill flow lines and stabilize flow rate and back pressure at the beginning of each experiment.

Fluid saturations and their spatial distribution in the core were determined by x-ray computed tomography [Vinegar and Wellington, 1987, Perrin and Benson, 2010] using a medical CT scanner (Siemens Somatom Volume Zoom spiral scanner). The x-ray source was operated at 120 kV and 80 mA. Scans were performed at a resolution of 0.5 mm. For reconstruction, the B45s filter was used. Image analysis and visualization was performed with ImageJ (National Institute of Health) and Avizo (Visualization Sciences Group). Fluid saturations were determined by [Vinegar and Wellington, 1987, Perrin et al., 2009]

\[
S_{nw} = \frac{CT_{\text{exp}} - CT_w}{CT_{nw} - CT_w} = a \cdot (CT_{\text{exp}} - CT_w)
\]

where \( CT_w \) and \( CT_{nw} \) are the CT numbers of the wetting and the non-wetting phase, respectively. \( a = 1/(CT_{nw} - CT_w) \) is the “calibration” factor that relates a difference between actual CT scan \( CT_{\text{exp}} \) and the reference \( CT_w \), taken at the beginning of the experiment at \( S_w = 1 \), to the actual saturation of the non-wetting phase \( S_{nw} \).

The effluent density was monitored with a density meter (Proline Promass 83A, Endress+Hauser AG, Reinach, Switzerland) at a temperature of 45°C. All experiments were conducted at a pore pressure of 100 bar and a temperature of 45°C in the core.

**Rock**

Flow experiments were performed in a cylindrical core of Berea sandstone outcrop rock in the horizontal direction as indicated in Fig. 5.1. Properties and dimensions of the core are listed in Tab. 2.2. The core had not been fired, i.e. the clays were not destroyed.

The same core was used for multiple experiments. Before each experiment, the core was cleaned with multiple pore volumes of isopropanol. After cleaning, before and after
each experiment, the initial saturations of the core were monitored by CT scanning and the permeability was compared to the brine permeability to ensure that the core was not damaged. No clay swelling or fines migration was observed.

Visually, the core was completely homogeneous and no layering was visible as shown in Fig. 2.2(A). The porosity profile along the core determined by CT (not shown) was homogeneous without clear features or trends. In a CT cross section (dry scan), after maximizing the contrast, bedding planes became visible (Fig. 2.2B). Also the middle section of the core appeared somewhat more porous (i.e. likely more permeable) than the top and the bottom layer (line T–B). This porosity (and permeability) contrast is only very subtle and at the boundary of the sensitivity of the CT scanner. This very small porosity and permeability difference was, however, sufficient for the CO$_2$ front to propagate faster in the central streak than at the top and bottom (Fig. 2.2C) as experiment 3 (described later) shows. This very minor heterogeneity, as will be shown later, only has very little impact on the data interpretation. Therefore, the first approach for the data analysis by numerical modeling is a homogeneous model for porosity, permeability and saturation functions. For comparison, a model with a more permeable layer in the center will be considered as well.

**Liquids**

CO$_2$ (99.7% purity, Linde) is a supercritical liquid at the experimental conditions with a density of 0.41 g/cm$^3$ [Span and Wagner, 1996] and viscosity of 0.033 cP at 45°C and 100 bar [Fenghour et al., 1998].

n-decane (99.5% purity, Sigma-Aldrich) is a liquid phase at the experimental conditions with a density of 0.720 g/cm$^3$ and viscosity of 0.75 cP at 45°C and 100 bar [Shell Global Solutions, 2008].
Isopropanol (min. 99.8% purity, Sigma-Aldrich) was used for cleaning the core between experiments. Brine was made from demineralized water. In order to increase the x-ray contrast between brine and the other liquids, the brine was doped with 2 wt% of cesium chloride (CsCl, 99.9% purity, Sigma-Aldrich). The brine viscosity is approximately 0.67 cP at 45°C and 100 bar.

Mathematical model

The flow experiments were interpreted by means of numerical modeling using the Shell in-house reservoir simulator MoReS [Regtien et al., 1995]. The numerical model consisted of a 2-dimensional domain with 50 horizontal and 100 vertical grid blocks. The numerical model is based on 2-phase Darcy flow and solves the following set of equations

\[
\phi \frac{\partial S_i}{\partial t} + \nabla \cdot \vec{v}_i = 0
\]

(2.2)

\[
\vec{v}_i = \frac{k_{r,i}}{\mu_i} K (\nabla p_i - \rho_i g)
\]

(2.3)

where the wetting phase (water or brine, \(i = w\)) and the non-wetting phase (CO\(_2\) or decane, \(i = nw\)) saturation satisfy \(S_w + S_{nw} = 1\). Eqn. A.1 describes the mass balance for water and CO\(_2\). For simplicity, incompressibility \(\nabla \cdot (\vec{v}_{nw} + \vec{v}_w) = 0\) is assumed and the formalism only holds in the absence of mass transfer between the phases. The flux of the phases \(\vec{v}_i\) is described by Darcy’s law extended to 2-phase flow (Eq. A.2). \(\phi\) is the porosity and \(K\) the (absolute) permeability of the rock, \(\mu_i\) and \(\rho_i\) are the viscosities and densities of the fluids. Gravity is taken into account in the simulations where the gravity constant \(g\) acts perpendicular to the horizontal flow.

In the model, relative permeability was described with an extended Corey model [Corey, 1954, Brooks and Corey, 1964]

\[
k_{r,w} = k_{r,w}(S_{nw,r}) \left(\frac{S_w - S_{wc}}{1 - S_{wc} - S_{nw,r}}\right)^{n_w}
\]

(2.4)

\[
k_{r,nw} = k_{r,nw}(S_{wc}) \left(\frac{1 - S_w - S_{nw,r}}{1 - S_{wc} - S_{nw,r}}\right)^{n_{nw}}
\]

(2.5)

where \(S_{w,c}\) and \(S_{nw,r}\) are the residual wetting and non-wetting phase saturations, respectively, and \(k_{r,nw}(S_{wc})\) and \(k_{r,w}(S_{nw,r})\) are the corresponding relative permeability endpoints. The ratio of relative permeability over viscosity is often referred to as mobility. The mobility ratio

\[
M = \frac{k_{r,nw} \mu_w}{k_{r,w} \mu_{nw}}
\]

(2.6)

of the displacing over the displaced fluid is a critical parameter for the microscopic displacement efficiency [Dake, 1978].
The pressure difference between the wetting and non-wetting phases is the capillary pressure, \(p_c = p_{nw} - p_w\) which is a function of \(S_w\). The capillary pressure – saturation function \(p_c(S_w)\) is determined from the experimental data as described in more detail in the next section. In addition, \(p_c(S_w)\) of a similar Berea rock sample from the same block was determined in the centrifuge with decane-brine (drainage) and then scaled for the respective interfacial tension \(\sigma\). For the numerical modeling in MoReS a cubic interpolation was used.

Typical boundary conditions for experiments are a constant rate on the injection side and constant pressure and \(p_c = 0\) on the outflow side.

**Common experimental techniques**

Common experimental techniques to determine relative permeability are the unsteady-state and the steady-state techniques which are briefly discussed in the following section. Both techniques involve numerical simulations based on the mathematical model from the previous section for state-of-the-art data analysis.

**Unsteady-state technique**  The experiments 1-3 in this study were conducted using the unsteady-state technique, a technique that was also used in several other studies to determine CO\(_2\)-brine drainage relative permeability [Bennion and Bachu, 2005, Bennion and Bachu, 2006b, Bennion and Bachu, 2006c, Bennion and Bachu, 2006a, Bennion and Bachu, 2007, Bennion and Bachu, 2008, Shi et al., 2009]. In unsteady-state drainage experiments, the rock is initially saturated with brine (wetting phase), i.e. the initial \(S_w = 1\), which is then displaced by a non-wetting phase (decane or CO\(_2\)). Here the initial \(S_w = 1\) implies that the residual non-wetting phase saturation \(S_{nw,r} = 0\) and the endpoint brine relative permeability \(k_{r,w}(S_w = 1) = 1\) (since the sample is fully saturated with brine, the brine permeability is the absolute permeability of the rock). Unsteady-state experiments are dynamic measurements, meaning that saturations in the core \((S_w)\) and pressure drop \(dp\) over the core are time dependent. This type of measurement is very similar to a field CO\(_2\) injection process.

For negligible capillary pressure and negligible gravity effects, which are often achieved by conducting unsteady-state experiments at high flow rates, and in homogeneous rock, a sharp front is formed between the injected and displaced phases where the saturation of the injected phase increases rapidly from zero to a finite height (“shock”, [Buckley and Leverett, 1942]). During the displacement, this front travels from inlet to outlet. The flow behind the shock front is subject to fractional flow (see e.g. [Dake, 1978, Lake, 1989]) and can be used to determine relative permeability [Johnson et al., 1959]. Capillary pressure \(p_c \neq 0\) (at low flow rates as in this study, even small \(p_c\) can become relevant depending on \(N_{cap}\)) and heterogeneity broaden the saturation range of the technique as shown by [Goodfield et al., 2000].

In our study, saturation profiles \(S_w(x, t)\) are smooth with an elongated tongue over a saturation range of approximately \(0.4 \leq S_w \leq 1.0\). This range is also relevant for assessing field processes like plume migration in sandstone rock. The unsteady-state flooding technique typically cannot access the range of very low water saturations.
2.1. CO$_2$–BRINE DISPLACEMENT IN SANDSTONE

Unsteady-state experiments in this study  In this study, the data was analyzed by means of the numerical simulation and a best match between model and experiment was obtained by adjusting relative permeability $k_r(S_w)$ and capillary pressure $p_c(S_w)$ (“history match”). Experimental data used for the matching are the production data, the pressure drop $dp$ over the core and the spatial saturation profiles $S_w(x,t)$ along the core which are all sensitive to both $k_r(S_w)$ and $p_c(S_w)$. The saturation profile at the end of the experiment, which remained almost constant over time, is subject to the capillary end-effect (which is a consequence of a $p_c = 0$ boundary condition at the outlet, see [Huang and Honarpour, 1996]) and was used to determine $p_c(S_w)$ using an initial guess value for $k_r$. In the next step, the production curve was used to refine $k_r(S_w)$. The resulting saturation profiles $S_w(x,t)$ and pressure drop over the core $dp$ serve as checks because they are sensitive to both $k_r$ and $p_c$. The procedure which is sketched in Fig. 2.3 is iterated manually several times, refining $k_r(S_w)$ and $p_c(S_w)$ to obtain a best match.

Often the results of the numerical match are not entirely consistent with all experimental data and the resulting $k_r$ and $p_c$ are adjusted to obtain the best compromise. In our matching strategy, highest priority was given to achieving a best match of the production curve. Deviations between experimental data and the numerical model can originate from experimental artifacts caused by the setup (e.g. offsets and multiphase flow effects in the production line and the pressure transducer) but also from incorrect input information for the absolute permeability of the core and for fluid viscosities and densities.

Steady-state technique  In several publications [Perrin and Benson, 2010,Krause et al., 2009,Kuo et al., 2010], CO$_2$ drainage relative permeability values $k_{r,nw}$ and $k_{r,w}$ were determined by steady-state measurements. In the steady-state technique, wetting and non-wetting phase are co-injected simultaneously. The saturation in the core is controlled by the ratio between wetting and non-wetting phase injection, i.e. the fractional flow

![Figure 2.3: Strategy for history matching of unsteady-state experiments](image-url)
28

CHAPTER 2. CO\textsubscript{2}-BRINE PRIMARY DRAINAGE

\[ f_w = v_w / (v_w + v_{nw}) \]. A steady-state drainage experiment starts with \( S_w = 1 \) flowing only water, i.e. a fractional flow \( f_w = 1 \). By increasing the non-wetting phase injected fraction to a finite amount, i.e. \( f_w < 1 \), the non-wetting phase starts entering the rock. This “steady-state” is in fact a set of complex flow patterns. In two-dimensional micromodels, connected pathway flow at high, ganglion dynamics at intermediate and drop traffic at low non-wetting phase saturations were observed [Avraam and Payatakes, 1995, Tsakiroglou et al., 2007]. This means that in primary drainage, the first regime below \( f_w = 1 \), i.e. low non-wetting phase saturation, is not a regime of connected pathway flow but consists of drop traffic or ganglion dynamics or, in simple terms, drainage and imbibition processes occur simultaneously.

By lowering \( f_w \) step by step, the saturation in the core further decreases. For each fractional flow \( f_w \) step, fluids are co-injected until saturations and pressure drop remain constant over time (“steady-state”). The relative permeability \( k_{r,i} \) of each phase is determined from the flow rate \( v_i \) and the pressure drop \( dp_i \) using Eq. A.2. In theory (after infinitely long times) saturations as low as the residual wetting phase saturation \( S_{w,c} \) can be reached, but in practice only a remaining wetting-phase saturation is reached and the true residual wetting phase saturation \( S_{w,c} \) is usually determined by a centrifuge method [Kokkedee et al., 1996].

In order to diminish the influence of the capillary end-effect on the measurement of \( k_r \), saturation \( S_w \) and pressure drop \( dp \) are often measured only over the central section of the core at some distance from inlet and outlet [Kokkedee et al., 1996]. Another strategy is to use numerical simulations including capillary pressure \( p_c(S_w) \) that describe the end-effect as well, similar to the approach with the unsteady-state experiments.

In this study and for comparison only, relative permeability values \( k_{r,nw} \) and \( k_{r,w} \) of a similar Berea rock sample were measured by the steady-state technique with x-ray saturation measurement [Kokkedee et al., 1996] where decane displaced a NH\textsubscript{4}Cl brine–glycol mixture (1:1). Only \( S_w \) and \( dp \) from the central section of the core were used for the data analysis. A steady-state is reached when pressure drop \( dp \) and the resistivity over the central part of the core are stable. For the data shown here, for all steady-state points the resistivity remained stable within 1%. With respect to the pressure drop \( dp \), the first steady-state data point had stabilized after a time period of 6 days at a fractional flow of \( f_w = 0.98 \) reaching \( S_{nw} \approx 0.25 \). For the following 5 data points \( dp \) might not have fully stabilized but the estimated error lies with the typical error range for steady-state measurements which is indicated as a single error cross in Fig. 2.5. All following data points had reached a stable \( dp \) at steady-state. Within the indicated error range, the \( k_r \) data obtained from the numerical match of the decane-brine unsteady-state experiment (see Fig. 2.5) shows good agreement with the steady-state \( k_r \) data.

Effects of heterogeneity Homogeneous rock samples and cores can be described by one single set of \( \phi, K, k_r(S_w) \) and \( p_c(S_w) \) parameters. By homogeneous we mean that the parameters vary spatially within the limits of the experimental error and/or their explicit description leads to e.g. an unsteady-state production curve that is similar to a
homogeneous description. In our case, as we will conclude, the rock is sufficiently well described as homogeneous in almost all aspects.

For substantial sample heterogeneity, however, the interpretation of experimental data becomes much more difficult and monitoring of the spatial saturation distribution e.g. by CT scanning is crucial. In unsteady-state experiments, for instance, the point of breakthrough is influenced by capillary effects (elongated saturation profile) and by channeling in more permeable streaks. Without knowledge of both terms, the data cannot be interpreted correctly.

But sample heterogeneity also plays a role in the interpretation of steady-state experiments. The Benson group (see e.g. [Kuo et al., 2010]) report their first steady-state data point below $S_{nw} = 1$ in primary drainage as $S_{nw} \approx 0.95$, i.e. $S_{nw} \approx 0.05$. That value is relatively low compared to values of $S_{nw} = 0.15 \ldots 0.25$ reported by [Valvatne et al., 2004, Wang et al., 2006] and $S_{nw} \approx 0.25$ for the steady-state primary drainage experiment in Berea mentioned above. The low value of $S_{nw} \approx 0.05$ is most likely caused by the substantial sample heterogeneity in that study. When heterogeneous samples are described with one single set of parameters, the resulting $\phi$ and $K$ are average values and the $k_r(S_w)$ and $p_c(S_w)$ are called pseudo functions. However, if the (true) scale of heterogeneity (in the field), is larger than the sample size, these pseudo $k_r(S_w)$ and $p_c(S_w)$ depend explicitly on the sample size.

In order to avoid using pseudo-functions, one can attempt to determine the porosity distribution of the sample e.g. by CT scanning and then describe the sample with spatially dependent $\phi(\vec{x})$, $K(\vec{x})$, $k_r(S_w, \vec{x})$ and $p_c(S_w, \vec{x})$ using correlations for $K(\phi)$ and $p_c(K, \phi)$ as in the studies by [Krause et al., 2009] and [Kuo et al., 2010].

From a practical point of view, one may also attempt to map the heterogeneities in the rock with a small set of “rock types”, e.g. one for high-porosity and one for low-porosity layers and also use these values for the later upscaling to the field scale. The latter approach will be used in this study to test how sensitive the homogeneous model is to a minor degree of heterogeneity (similar to the one in our Berea core).

2.1.3 Results

N-decane displacing brine: drainage

Experiment 1 starts at 100% brine saturation. Then n-decane is injected at 0.25 ml/min (capillary number $N_{\text{cap}} \approx 6.5 \times 10^{-8}$) immiscibly displacing the brine (drainage) at 45°C and 100 bar.

In Fig. 2.4A, the production from CT and density data and in Fig. 2.4B the pressure drop $dp$ along the core are displayed. The saturation profiles along the core are displayed in Fig. 2.4C. The conversion factor from CT numbers to saturation $a$ from Eq. A.8 was determined such that the production before breakthrough follows the decane injection line (Fig. 2.4A). The results of the 2-dimensional numerical model are superimposed as well in all panels.

The (primary) drainage relative permeability ($k_{r,w}(S_w)$, $k_{r,nw}(S_w)$) and capillary pres-
Figure 2.4: Experiment 1 – n-decane displacing brine at 0.25 ml/min. Brine production (A), pressure drop $dp$ over the core (B) using the same legend as panel A and saturation profiles along the core (C). Results of the numerical modeling ($k_r$ and $p_c$ in Fig. 2.5) are included as well.
2.1. **CO$_2$–BRINE DISPLACEMENT IN SANDSTONE**

sure $p_c(S_w)$ saturation functions, used in the numerical simulation to match the production curves from Fig. 2.4A, are displayed in Fig. 2.5.

The pressure drop $dp$ also shows reasonable agreement with the history match. Besides the fluctuations there are, however, deviations like the individual “steps” in $dp$ and the pressure decline after breakthrough (determined from the “kink” in the production curve in panel A) which both may be an experimental artifact caused by the flow setup. $dp$ was not measured directly across the core, i.e. no pressure taps were used. Instead, $dp$ was measured over the core including end pieces, flow lines and fittings. Note that at the low values of $dp$ typically encountered in this study, multiphase flow effects in the flow lines start becoming relevant. But important features like the point of breakthrough and the general trends like the $dp$ increase before and decrease after breakthrough are correctly described. One could, in principle, increase the flow rate to diminish the experimental artifacts on $dp$ but then the flow rates would be larger than typical field flow rates.

The saturation profiles in Fig. 2.4C exhibit two end-effects at the inlet and outlet. The capillary end-effect [Huang and Honarpour, 1996] at the outlet is typical for drainage in a strongly water-wet core and correctly described by the numerical simulation. The inlet effect [Dong and Dullien, 1997, Chen and Wood, 2001] is caused by a combination of capillary pressure and relative permeability and is not described correctly by the numerical model with the chosen parameters. The saturation profiles and the capillary end-effect at the outlet (Fig. 2.4C) are very sensitive to $p_c(S_w)$.

The Corey parameters in this study are listed in Tab. 3.1. Since experiment 1 is primary drainage, $S_{nw,r} = 0$ and $k_{r,nw}(S_{wc}) = 1.0$. The steady-state data suggests that $S_{w,c} = 0.2$. Our best match with the numerical model was obtained for $k_{r,nw}(S_{wc}) = 0.5$, $k_{r,w}(S_{nw,r}) = 1.0$, $n_w = 4.5$, $n_{nw} = 2.8$. These parameters provide an excellent fit to our experimental production curve from Fig. 2.4A and the saturation profile (Fig. 2.4C). A set of saturation profiles from the numerical model are superimposed on the experimental data on panel C. A set of selected profiles of the “best match” model during the injection are superimposed as solid orange lines. For comparison, the results of the same numerical model in 3D (using 52 x 10 x 10 grid blocks) are shown as dotted orange lines. Due to geometrical effects, their profiles are slightly more stretched. The saturation profile at 2.5 PV injected is displayed as blue lines but is difficult to see in the figure because it closely matches the experimental data.

Steady-state $k_r$ data (drainage, glycol+3% NH$_4$Cl–decane at room temperature) and centrifuge $p_c$ data (drainage, decane–brine) on different samples from the same Berea block are superimposed for comparison.

The steady state data were measured in drainage at near ambient conditions ($T = 22^\circ$C, $p=7$ bar) using an ethylene glycol / 3% NH$_4$Cl-brine mixture (1:1) as wetting phase to increase viscosity and displacement efficiency and n-decane as non wetting phase. The total flow rate was 2 ml/min with a sample cross section of 4.75 cm$^2$, resulting in a capillary number range of $2.9 \times 10^{-7}$ at low $S_{nw}$ and $1.5 \times 10^{-5}$ at high $S_{nw}$. The steady-state $k_r$ data is in reasonable agreement with the best match for experiment 1. A Corey-fit to the steady-state data yields $n_w = 4.2$ and $n_{nw} = 2.92$. The agreement between the steady-state $k_r$ data and our best unsteady-state match is reasonably good, bearing in mind the relatively...
Figure 2.5: Primary drainage relative permeability $k_r$ (top, with logarithmic scaling on inset) and capillary pressure $p_c$ (bottom) saturation functions used for the numerical simulation of experiment 1. Steady-state $k_r$ data and centrifuge $p_c$ data on a similar Berea rock are superimposed (filled symbols) for comparison.
2.1. CO$_2$–BRINE DISPLACEMENT IN SANDSTONE

Figure 2.6: Displacement patterns (central cut along core axis) in experiment 1 (Berea core, decane displacing brine at 0.25 ml/min): experiment (left) vs. numerical model (right). The model consists of 3 layers where a central layer has slightly higher permeability (420 mD compared to 380 mD bulk permeability) and a slightly lower capillary pressure. The displacement is stable but the front is somewhat corrugated (see Fig. 2.6). It is not exactly a shock front, and in a homogeneous 2D model (not shown) the displacement front is almost perpendicular to the flow direction with only very minor effects of gravity over-run. The corrugated front observed in the experiment may be described better with a 3-layer model where a central layer has slightly higher permeability (420 mD compared to 380 mD bulk permeability) and a slightly lower capillary pressure (same $k_r$).

Unsaturated CO$_2$ displacing unsaturated brine: drainage

In experiment 2, unsaturated CO$_2$ was injected at 100 bar and 45 °C into the Berea core with unsaturated brine at a rate of 0.48 ml/min (capillary number $N_{cap} \approx 0.88 \times 10^{-8}$). The back pressure was regulated by the 2 Tescom controllers.

small sensitivity for $k_{r,nw}(S_{wc})$. The parameters for all considered models are listed in Tab. 3.1.

The displacement is stable but the front is somewhat corrugated (see Fig. 2.6). It is not exactly a shock front, and in a homogeneous 2D model (not shown) the displacement front is almost perpendicular to the flow direction with only very minor effects of gravity over-run. The corrugated front observed in the experiment may be described better with a 3-layer model where a central layer has slightly higher permeability (420 mD compared to 380 mD bulk permeability) and a slightly lower capillary pressure (same $k_r$).
In Fig. 2.7A, the production from CT and density data is plotted. Data from experiments 1 and 3 and the corresponding modeling curves are plotted for comparison only. Experiment 2 was not explicitly modeled because our numerical model describes only the displacement but not the mass transfer between the unsaturated phases. A more detailed interpretation of experiment 2 will be given in section 2.1.3 where it is quantitatively compared with experiment 3 with saturated phases, i.e. they are only subject to displacement which is fully described by our numerical model.

The pressure drop over the core and the effluent density of experiment 2 are displayed in Fig. 2.7B. The saturation profiles along the core are displayed in Fig. 2.7C. The conversion factor from CT numbers to saturation was adapted from experiment 3 which was not affected by mass transfer effects (see Fig. 2.9A). The profiles (both model and experiment) show a very extended tongue which is caused by a combination of gravity over-run and capillarity $p_c(S_w)$.

In Fig. 2.8, the 3D saturation patterns during the injection are displayed. The rock matrix is visible as semi-transparent background. The brine is displaced by CO$_2$ in the rock and approximately 50% brine saturation remains.

In experiment 2, the flood front appeared to have a larger protrusion in the center plane of the core than in experiment 1. That is presumably caused by channeling in more permeable zones which becomes more dominant in a low-viscous displacing phase. A strong gravity over-run of CO$_2$, which is responsible for the early breakthrough, is observed at the top.

**Saturated CO$_2$ displacing saturated brine: drainage**

In experiment 3, experiment 2 is repeated but with mutually saturated fluid phases at a CO$_2$ injection rate of 0.43 ml/min (capillary number $N_{cap} \approx 0.79 \times 10^{-8}$) at 45°C. The back pressure was controlled by a Quizix pump to 100 bar (which discharges against the Tescom controllers which are set to 90 bar).

In Fig. 2.9A, the production from CT and density data is plotted. The pressure drop over the core and the effluent density are displayed in Fig. 2.9B. The saturation profiles along the core are displayed in Fig. 2.9C. The conversion factor from CT numbers to saturation was chosen such that the production before breakthrough follows the CO$_2$ injection line (Fig. 2.9A).

In Fig. 2.10, the 3D saturation patterns during the injection are displayed. The rock matrix is visible as semi-transparent background. The brine is immiscibly displaced by CO$_2$ in the rock.

Experiment 3, where saturated brine is displaced by saturated CO$_2$, shows differences from experiment 2 with respect to the production curves (Fig. 2.9A) and saturation profiles (Fig. 2.9C). In the experiment with saturated phases, there is no dry-out which is visible in the saturation profile at the inlet (compare Figs. 2.7C and 2.9C) and also in the production curve.

In the following we focus on differences between the displacement of CO$_2$–brine (exp. 2,3) compared to decane–brine (exp. 1) and address in particular the question whether the
Figure 2.7: Experiment 2 – unsaturated CO₂ displacing unsaturated 2% CsCl brine at 0.48 ml/min. Brine production (A), pressure drop $dp$ over the core and effluent density (B) and saturation profiles along the core (C). Data from experiments 1 and 3 are superimposed for comparison.
Figure 2.8: Experiment 2: 3D saturation patterns (CO\textsubscript{2} in red/yellow). The rock matrix is visible as semi-transparent background. The displacement shows gravity over-run of CO\textsubscript{2}. 
Figure 2.9: Experiment 3 – saturated CO$_2$ displacing saturated 2% CsCl brine at 0.43 ml/min. Brine production (A), pressure drop $dp$ over the core and effluent density (B) and saturation profiles along the core (C). The data from the unsaturated experiment 2 (Fig. 2.7A) is added (black line in panel A) for comparison. The numerical simulation models “best match”, “sens1”, “sens2” and the numerical model of experiment 1 are shown for comparison (parameters are listed in Tab. 3.1). For better visibility, a magnification of the brine production data is displayed in the inset in panel A.
Figure 2.10: Experiment 3: 3D saturation patterns (CO$_2$ in red/yellow). The rock matrix is visible as semi-transparent background. The displacement shows gravity over-run of CO$_2$. 
relative permeabilities $k_{r,i}(S_w)$ are different for the two cases. Even though the production curves from decane–brine and CO$_2$–brine are not dramatically different (see e.g. Fig. 2.7A), one has to bear in mind that the viscosity ratio of displacing and displaced fluid is smaller by a factor of 24 for CO$_2$–brine compared to decane–brine. Since the viscosity ratio is a factor in the mobility ratio $M$ (Eq. 3.2) which is the non-dimensional scaling group for displacement, i.e. similar production curves result from similar mobility ratios (for the same $p_c$), a factor 24 smaller viscosity ratio is expected to have a major impact on the production curve. The fact that the production curves are not very different indicates that the $k_{r,i}(S_w)$ values, which are also a factor in the mobility ratio $M$, have to compensate for the different viscosity ratio, i.e. are different for CO$_2$–brine than for decane–brine. The approximate differences are computed from history matches given further below. In addition, the interfacial tension for CO$_2$–brine (30 mN/m, see [Chalbaud et al., 2010, Hebach et al., 2002, Hebach et al., 2005, Yang et al., 2005]) is smaller than for decane–brine (47.9 mN/m). Therefore, the capillary pressure $p_c$ from experiment 1 was scaled by a factor of $30/47.9 = 0.39$ (solid line in Fig. 2.11) according to the relationship

$$p_{c,2} = \frac{\sigma_2}{\sigma_1} p_{c,1}$$

(2.7)

where the indices 1 and 2 denote the system of decane–brine and CO$_2$–brine, respectively. Note that due to the cubic interpolation scheme of the numerical simulation software (MoReS) this constant factor is not maintained over the whole saturation range.

The production curve in the saturated CO$_2$–brine experiment is described well by the Corey exponents $n_w = 2.5$ and $n_{nw} = 3.7$ (“best match” for experiment 3) which are substantially different from experiment 1 in which $n_w = 4.5$ and $n_{nw} = 2.8$. The relative permeability in the experiments are summarized in Table 3.1. $k_r (k_{r,CO_2}(S_{w,c}) = 0.5)$ and $p_c$ used for the “best match” are also displayed in Fig. 2.11. The $k_{r,CO_2}$ endpoint of 0.5 was chosen as an initial estimate because the literature data [Perrin and Benson, 2010, Perrin et al., 2009] suggests that $0.1 < k_{r,CO_2}(S_{w,c}) < 0.6$.

For comparison and as a sensitivity test, it was attempted to model experiments 3 with the same numerical model as experiment 1 using the same relative permeability and capillary pressure (see Fig. 2.5) but using CO$_2$ viscosity and density instead of the values for decane. The production curves in experiment 2 and 3 (Figs. 2.7A and 2.9A) are not described very well by the relative permeability functions from decane–brine in experiment 1 (the production is under-estimated, see Fig. 2.9A). In order to further test the sensitivity of the technique, the CO$_2$ model’s “best match” was varied by increasing $n_w$ from 2.5 to 3.0 and keeping all other parameters fixed. The production curve shows a somewhat lower production compared to the experimental data, indicating that $n_w = 3.0$ is a worse match than $n_w = 2.5$. This illustrates that the technique is sensitive to changes in the Corey exponents by approximately 0.5 when all other parameters are kept fixed, i.e. error bars are approximately ±0.25. The sensitivity to variations of two parameters at the same time, e.g. $n_w$ and $p_c$, was not investigated.

At this point we have to bear in mind that any match still contains uncertainty, i.e. the model shows minor deviations from some parts of the experimental data (production curve,
Figure 2.11: Drainage relative permeability $k_r$ (top, with logarithmic scaling on inset) and capillary pressure $p_c$ (bottom) saturation functions used for the numerical simulation of experiment 3 (saturated CO$_2$–brine). The decane–brine data from experiment 1 (dotted lines) and steady-state relative permeability (filled symbols) from Fig. 2.5 are included for comparison. Relative permeability data for CO$_2$-brine in Berea rock from [Perrin and Benson, 2010, Perrin et al., 2009] are added as red and blue open symbols and another sandstone sample [Perrin and Benson, 2010] as black crosses to the $k_r$ plot.
2.1. $\text{CO}_2$–brine displacement in sandstone

Table 2.3: Overview of relative permeability (Corey parameters, see Eq. 3.10 and 3.11) resulting from the numerical interpretation of the experiments.

<table>
<thead>
<tr>
<th>Exp. label</th>
<th>$S_w,c$</th>
<th>$S_{nw,r}$</th>
<th>$k_{r, nw}(S_{w,c})$</th>
<th>$k_{r, w}(S_{nw,r})$</th>
<th>$n_w$</th>
<th>$n_{nw}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>decane-brine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 best</td>
<td>0.2</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
<td>4.5</td>
<td>2.8</td>
</tr>
<tr>
<td>1 SS</td>
<td>0.22</td>
<td>0.0</td>
<td>0.42</td>
<td>1.06</td>
<td>4.2</td>
<td>2.92</td>
</tr>
<tr>
<td>CO$_2$-brine (saturated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 best</td>
<td>0.2</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
<td>2.5</td>
<td>3.7</td>
</tr>
<tr>
<td>3 sens1</td>
<td>0.2</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
<td>3.0</td>
<td>3.7</td>
</tr>
<tr>
<td>3 sens2</td>
<td>same as “best”, $p_c = p_c^{best} \cdot \cos 40^\circ$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Saturation profiles, and pressure drop) caused by experimental artifacts or other reasons which are not fully understood. In any match, these deviations can be compensated to some extent by both $k_r$ and $p_c$ in a non-unique way which limits the sensitivity of the technique. At the moment it is not fully understood where exactly the boundaries are.

When only the Corey exponents from the best matches are compared, the most obvious difference between experiment 1 and 3 is that for decane–brine $n_w > n_{nw}$, and for CO$_2$–brine $n_w < n_{nw}$. Judging from the Corey exponents only, the decane–brine exponents $n_w = 4.5$ and $n_{nw} = 2.8$ (or $n_w = 4.2$ and $n_{nw} = 2.52$ from steady-state) indicate a water-wet situation. The CO$_2$–brine situation with $n_w = 2.5$ and $n_{nw} = 3.7$ seems to be more intermediate-wet (but still on the water-wet side). Different wetting properties of decane and CO$_2$ are in agreement with contact angle data in literature. The contact angle of decane / brine on clean quartz is zero degrees [Xie et al., 1997, Memnella et al., 1995] which means that brine is fully wetting and decane is fully non-wetting. CO$_2$, on the other hand, is known to be partially wetting e.g. clay minerals present in sandstone rock are reported to be wetted by CO$_2$ [Chiquet, 2006, Chalbaud et al., 2010]. Contact angles of 35° for quartz [Chiquet et al., 2007] and 55° for limestone rock [Chalbaud et al., 2010] are reported.

As a further sensitivity test, the model “sens2” was adapted from the “best match” keeping all parameters fixed by scaling the capillary pressure with $\cos 40^\circ$ to check the sensitivity on a change of contact angle. The results of the “sens2” model are superimposed on Fig. 2.9 with good matches for the production curve and the saturation profile at 2.5 PV but with a clear discrepancy for the pressure drop $dp$.

Relative permeability data for CO$_2$-brine in Berea rock ($K = 301$ mD and $\phi = 0.22$ at 3 ml/min and 16°C, $K = 430$ mD, $\phi = 0.203$, at 1.2 + 2.6 ml/min and 50°C) from [Perrin and Benson, 2010, Perrin et al., 2009], obtained from steady-state measurements, are added as red and blue symbols to the $k_r$ plot in Fig. 2.11. It seems that the data from these steady-state measurements are closer to the decane-brine data in our study than the saturated CO$_2$-brine data, i.e. they reflect a more water-wet situation. The steady-state data from [Perrin and Benson, 2010, Perrin et al., 2009] for Berea rock, which was measured at substantially larger capillary numbers ($N_{\text{cap}} \approx 2 \times 10^{-5}$ [Perrin et al., 2009, Perrin and Benson, 2010]), show unusually large $S_{w,c} \approx 0.62$ and rather low $S_{nw} \approx 0.05$ for the first steady-state data point. In addition, samples used by the Benson group were fired
Figure 2.12: Brine saturation profiles for the unsaturated case (experiment 2) subtracted from the saturated case (experiment 3) for 6 different injected PV. Negative values correspond to lower water saturations in the unsaturated case compared to the saturated case.

Unsaturated vs. saturated fluids The production curves in experiment 2 (unsaturated phases) and experiment 3 (saturated phases) reach very similar final plateau values. Evaporation effects are relatively small, and on an overall mass balance, are negligible as shown by the following solubility data: at a pressure of 100 bar and between 22 and 45 °C, the solubility of water in CO$_2$ is approximately 0.416 mol-%, which corresponds to 0.18 wt-% or 0.08 vol-% [Marini, 2007; Spycher et al., 2003; Spycher and Pruess, 2005; Shell Global Solutions, 2008]. Injection of 5.5 PV of unsaturated CO$_2$ corresponds to 825 ml which can dissolve 0.74 ml of water, which has an overall negligible effect on the mass balance. Only in cases where larger amounts of CO$_2$ are injected is the mass balance affected [Yan and Stenby, 2009; Ott et al., 2010].

There are, however, differences in the saturation profiles between unsaturated (Fig. 2.7C) and saturated phases (Fig. 2.9C). In order to directly compare the profiles for the two situations, in Fig. 2.12 the differential brine saturation profiles are displayed for saturated and unsaturated experiments at the same injected PV.

The dominating features in Fig. 2.12 are the “dip” at $x \approx 1$ cm with negative brine saturation values and a positive offset in the differences between 0 and 1 PV injected CO$_2$. With respect to the “dip”, negative values indicate a lower water saturation in the unsaturated case compared to the saturated case. The volume of the dip corresponds to
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approximately 1.1 ml of brine, i.e. in the unsaturated case there is 1.1 ml less brine at the inlet than in the saturated case. Using the solubility of 0.08 vol-% of H$_2$O in CO$_2$, after 2.23 PV injection approximately 0.3 ml of water would have dissolved, which is of the same order of magnitude as the dip volume. Therefore evaporation is a possible explanation for the dip. CsCl enrichment right at the inlet ($0 \leq x \leq 1$ cm) may explain why saturation values are increasing again toward the inlet because enriched CsCl causes a larger CT attenuation which is incorrectly interpreted as brine saturation.

The positive offset at 0.5 PV is a consequence of the CO$_2$ solubility in water which is 1.79 mol-% corresponding to 9 vol-% of the respective CO$_2$ phase [Span and Wagner, 1996, Marini, 2007, Spycher et al., 2003, Spycher and Pruess, 2005]. For larger injected PV > 1.0 the production (and saturations) are similar in saturated and unsaturated cases. But in the interval $0 \leq$ PV injected $\leq 1.0$ the brine production of the unsaturated case falls below the production of the saturated case as illustrated in Fig. 2.13. In this interval the brine in the core is presumably not yet fully saturated by CO$_2$. As a consequence, 0.09 PV of the injected CO$_2$ did not displace the brine but dissolved in it, i.e. as a first order approximation 0.09 PV less brine is produced. The offset of the profile at 0.5 PV in Fig. 2.12 outside of the dip is approximately 0.098 PV which is very similar to the estimation of 0.09 PV from dissolution effects. The effect is maximum at the point of breakthrough of experiment 3 with unsaturated CO$_2$. Upon further injection of CO$_2$, the brine gets more and more saturated but also increasingly displaced reaching similar saturations as in the saturated

Figure 2.13: Brine production for experiment 3 (saturated) and experiment 2 (unsaturated). The difference in production between experiment 3 and 2 has a maximum at the breakthrough of experiment 3.
case. Secondary effects may be related to viscosity and density effects (e.g. the density of CO$_2$ saturated brine is approximately 9% larger than that of unsaturated brine) that affect displacement as well.

Due to limitations in the applied numerical model, i.e. mass transfer was not modeled explicitly, determination of the evaporation kinetics is beyond the scope of this work.

**Channeling in a more permeable layer** While an overall good agreement between the production curves of the numerical model and the experiment is observed, there are some discrepancies with respect to the fluid distributions in the rock. In the experiment, at early times the CO$_2$ predominantly flows in the middle of the rock and later gravity over-run dominates. In a homogeneous model, gravity over-run of CO$_2$ is the dominating mechanism at all times.

Even though the permeability distribution of the rock is not exactly known, we found evidence for a slightly more permeable layer in the middle of the core (see Fig. 2.2). Therefore, a more permeable layer in the center was introduced into the model to account for the channeling observed in the experimental data. By channeling we mean that the displacement front is influenced by the rock structure, e.g. a variation in permeability, which is often accompanied by variation in capillary pressure and relative permeability. Note that channeling is different from viscous fingering. Viscous fingering is a viscous instability [Saffman and Taylor, 1958] which can occur at mobility ratios $M > 1$ at the flow front. [Daripa and Pasa, 2008] have shown that capillary pressure $p_c$ stabilizes the front. A systematic modeling study (data not shown here) has shown that the displacement is stable for the magnitude of $p_c$ in Figs. 2.5 and 2.11. When scaling the $p_c$ with the interfacial tension $\sigma$ according to Eq. 2.7 viscous fingering is observed for $\sigma \leq 0.1$ mN/m but no fingering is observed for $\sigma \geq 1$ mN/m, i.e. on the experimental scale the displacement is clearly stable for CO$_2$-brine with $\sigma \approx 30$ mN/m.

In Fig. 2.14, the spatial distribution of CO$_2$ from the experiment (left) is directly compared to the numerical simulation with a more permeable streak in the center (middle) and with a more permeable layer and lower $p_c$ layer (right). A more permeable layer alone did not improve the match of the model because it does not produce any channeling in the more permeable middle streak. So far, the same $p_c(S_w)$ function was assumed for the whole core irrespective of permeability variation. A more-permeable channel, however, is expected to have a smaller capillary entry pressure (see Eq. 2.8). This would imply that particularly in immiscible displacement, the non-wetting displacing phase can enter that channel more easily and will largely impact the saturation distribution. A similar conclusion was drawn by [Kuo et al., 2010].

In a modified model, the central layer was assigned a higher permeability $K$ and a lower $p_c$. This follows the principle of the Leverett-J scaling

$$p_c(S_w) = J(S_w) \sigma \cos \theta \sqrt{\phi / K}$$  \hspace{1cm} (2.8)

where the $J(S_w)$ is the Leverett-J function specific for the rock type [Lake, 1989]. Keeping all other parameters constant, a larger $K$ leads to a smaller $p_c$. [Krause et al., 2009] and [Kuo
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Figure 2.14: Displacement patterns (central cut along core axis) in experiment 3 (saturated \( \text{CO}_2 \) displacing saturated brine at 0.43 ml/min): experiment (left) vs. numerical model (middle + right). A model with permeability heterogeneity only (middle) does not fully describe the experimentally observed saturation profiles. Adding a small heterogeneity in \( p_c \) leads to a much closer match (right).
et al., 2010] followed a similar approach by modeling a more complex porosity, permeability and capillary pressure distribution for a rock sample with substantially larger heterogeneity. In our case, the central layer was assigned a permeability of 420 mD while the matrix permeability remained 380 mD. Therefore, compared to the matrix $p_c$, the more permeable layer has a $p_c^{\text{high}} = \sqrt{380/420} p_c \approx 0.95 p_c$. In our model, we used the IFT-scaled $p_c$ and the $k_r$ from Fig. 2.11 for the matrix and lowered the $p_c$ for the more-permeable layer by a factor of 0.95 compared to the matrix $p_c$.

The results of the model are added to Figs. 2.9A-C and 2.14. This model appears to be the best match with respect to production data, pressure drop, saturation profile and spatial fluid distribution. The two-layer model is also compatible with the decane–brine experiment 2 (see Figs. 2.4A-B and 2.6).

**Unsaturated brine displacing saturated CO$_2$ (at near-residual saturated brine): imbibition**

In experiment 4, unsaturated brine was injected into the Berea core saturated with brine and CO$_2$ at a flow rate of 0.25 ml/min. The initial state of experiment 4 is the final state of experiment 3 but at the end of the CO$_2$ injection in experiment 3, fluid redistribution (in particular from the end-effect) caused changes in the spatial saturation distribution before experiment 4 started.

During experiment 4, the average CO$_2$ saturation in the core decreases over time as displayed in Fig. 2.15A. The initial CO$_2$ saturation is, in principle, still mobile, i.e. subject to immiscible displacement. In the following we will discuss that the reduction of CO$_2$ saturation is caused by both the displacement and the dissolution of CO$_2$ in the injected (unsaturated) brine, with dissolution being the dominant mechanism.

The CT data is sensitive to the total in-situ CO$_2$ saturation, i.e. captures displaced and dissolved CO$_2$. The downward spikes in the density data in Fig. 2.15B are indicative for the displaced CO$_2$ only and have been used to estimate the immiscibly displaced CO$_2$. In panel A, both data sets are directly compared. The difference indicates that a substantial amount of CO$_2$ is dissolved and subsequently miscibly displaced in the brine phase. The solubility of CO$_2$ in water is 1.79 mol-% corresponding to 9 vol-% of the respective CO$_2$ phase [Span and Wagner, 1996, Marini, 2007, Spycher et al., 2003, Spycher and Pruess, 2005] which is substantial. Injection of 3.4 PV of unsaturated brine could dissolve 0.31 PV (48 ml) of the CO$_2$ phase. In the experiment, the CO$_2$ saturation decreases from 0.41 PV to 0.22 PV which is a decrease of 0.19 PV. This is of the same order of magnitude as would be expected from solubility only.

The pressure drop over the core and the effluent density are displayed in Fig. 2.15B. At the point in time when the pressure drop substantially decreases, the first increase in brine saturation at the inlet is observed. This is the onset of CO$_2$ dissolution. The dissolution is a reduction in CO$_2$ saturation, i.e. an increase in brine saturation, which means an increase in brine (relative) permeability, and since the experiment is run at constant rate, a decrease in pressure drop.

The saturation profiles along the core are displayed in Fig. 2.15C. At the inlet, a clear
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Figure 2.15: Experiment 4 – unsaturated brine injected into the core at the end of experiment 3 with trapped CO$_2$ at 0.25 ml/min. Average CO$_2$ saturation in the (whole) core on panel (A), pressure drop $dp$ over the core (left axis) and effluent density (right axis) on panel (B) and saturation profiles along the core on panel (C).
decrease in CO₂ saturation is observed which is caused by the dissolution of CO₂ in unsaturated brine. In Fig. 2.16, the 3D saturation patterns during the injection are displayed. The rock matrix is visible as semi-transparent background.

Over time, trapped CO₂ partitions (dissolves) into brine. The injected unsaturated brine *miscibly* displaces the CO₂ saturated brine in the core.

### 2.1.4 Summary and conclusions

Experiments in this study were conducted on a Berea rock sample that had only very low heterogeneity and was sufficiently well described with a homogeneous numerical model. A sensitivity test showed that the degree of heterogeneity in this sample has only very little impact on the resulting relative permeability.

The different experiments and the most important results and learnings are summarized in Fig. 2.17.

Three drainage experiments were conducted with brine and a model fluid (decane), and with unsaturated and mutually saturated CO₂–brine. In addition, an imbibition experiment was conducted where unsaturated brine was injected into saturated brine and near-residual CO₂.

The unsteady-state drainage experiments were analyzed by “history matching” with a numerical model. For the decane-brine experiments, the relative permeability and capillary pressure obtained were in good agreement with steady-state and centrifuge measurements, respectively, performed on twin samples.

The saturated CO₂–brine drainage experiment was conducted with equilibrated phases such that mass transfer between the phases during the experiment is prevented. The relative permeability obtained is clearly different than the one from the decane–brine experiment. The differences are attributed to a different wetting behavior of CO₂–brine which is more intermediate-wet compared to a water-wet situation for decane-brine, an observation which is supported by contact angle data from literature. This finding indicates that with respect to wettability it does matter whether experiments are conducted with CO₂ or with model fluids provided that a model fluid is found that exhibits similar wetting properties.

When comparing saturated with unsaturated CO₂–brine drainage experiments, solubility and mass transfer from brine to CO₂ and from CO₂ to brine were observed. The first case, water dissolving in CO₂ (solubility approx. 0.08 vol-%), leads to *evaporation* at a 2-3 cm wide zone at the inlet, i.e. the length scale $l_{\text{evap}}$ of water transfer at the respective flux is much smaller than the sample length. The decrease of water saturation in the evaporation zone estimated from CT data is larger but of a comparable order of magnitude to estimations from solubility data.

The second effect, CO₂ dissolution in brine (solubility approx. 9 vol-% in the CO₂ phase), leads to a diminished displacement of brine by CO₂ which is most pronounced at the point of breakthrough. The magnitude of the effect is close to predictions from solubility data. This effect influences the saturation profiles from inlet to outlet, meaning that the length scale of the effect $l_{\text{diss}}$ is larger than the length of the core $l_{\text{core}}$ and also much larger than $l_{\text{evap}}$, i.e. $l_{\text{diss}} > l_{\text{core}} > l_{\text{evap}}$. These findings may matter in cases where
Figure 2.16: Experiment 4 (unsaturated brine injected into Berea core with trapped CO$_2$ at 0.25 ml/min): 3D saturation patterns (increase in brine saturation in blue). CO$_2$ is displaced and dissolved by the unsaturated brine and as a consequence, the brine saturation increases.
Figure 2.17: Overview of the experiments conducted in this study and the aspects on which they are focusing.

Phase equilibration effects are relevant but for numerical modeling, a discretization coarser than $l_{\text{evap}}$ and $l_{\text{diss}}$ is used.

Imbibition of unsaturated brine into the rock sample at near-residual (trapped) CO$_2$ and CO$_2$ saturated brine shows first the miscible displacement of saturated by unsaturated brine and then a dissolution of the CO$_2$ phase. This experiment represents the transition from residual trapping to solubility trapping.

2.2 CO$_2$–brine displacement in heterogeneous carbonates

The displacement of brine by CO$_2$ is an important process controlling plume migration and initial pore-space utilization in geological CO$_2$ storage. We present CO$_2$-brine unsteady-state core flood experiments to characterize CO$_2$-brine primary displacement in Estaillades limestone, a model system for dual-porosity carbonates. We analyze the experiments by means of numerical simulations assuming 2-D homogeneous rock and parameterized $k_r(S_w)$ relationships. Assisted history matching methodologies were used to find the $k_r(S_w)$ parameters which minimize a mismatch function, giving the best match to the experimental data. We refer the results to the microscopic rock structure and we discuss the limits of applicability. Larger-scale heterogeneity was considered as intrinsic to arrive at a practical and upscaled description of the displacement process. Heterogeneity is discussed by comparing the results to classical relative permeability measurements on samples with a $24 \times$ smaller volume, which are less affected by heterogeneity. We found that larger-scale heterogeneity results in lower fluid-phase mobilities.
2.2. CO₂–BRINE DISPLACEMENT IN CARBONATES

2.2.1 Introduction

CO₂-plume migration in deep saline aquifers and the initial utilization of the pore space for CO₂ storage is to a large extent governed by CO₂-brine immiscible displacement as determined by relative permeability ($k_r(S_W)$) and capillary pressure ($p_C(S_W)$) saturation functions. These functions describe the microscopic displacement efficiency as well as the macroscopic bypassing by channeling and/or viscous fingering. Hence the characterization of the primary drainage process is essential for predicting the plume migration and the efficiency of storage. The determination of $k_r(S_W)$ requires relatively homogeneous core material due to the assumptions made in the interpretation of the experimental data and since upscaled rock properties need to be derived to be used in numerical simulations. Carbonates, however, are often heterogeneous on various length scales. While heterogeneity refers usually to the spatial variation of porosity and/or permeability, multiphase flow is mainly sensitive to the associated capillary heterogeneity [Berg et al., 2013a] to which we refer in the following.

CO₂-brine displacement in sandstones has been studied extensively, including for sandstones with different levels of sample heterogeneity [Bennion and Bachu, 2008, Perrin and Benson, 2010, Shi et al., 2011, Ott et al., 2011a, Krevor et al., 2012, Akbarabadi and Piri, 2013, Pini and Benson, 2013b, Berg et al., 2013a, Ruprecht et al., 2014]. Despite the difficulties that CO₂-brine displacement implies – i.e. high viscosity ratio, the resulting low displacement efficiency, moderate to high density ratio, chemical reactivity – public data on the same rock type – e.g. Berea sandstone – turned out to be comparable taking different sample-preparation methods and different levels of heterogeneity into account [Berg et al., 2013a, Perrin and Benson, 2010]. Also the difference between CO₂-brine and decane-brine displacements can be traced back to wetting properties related to clay minerals [Berg et al., 2013a]. In sandstones with simple pore architectures, $k_r(S_W)$ can usually be described by a minimum set of parameters (usually the Corey relative permeability model [Brooks and Corey, 1964] is used – e.g. [Shi et al., 2011, Berg et al., 2013a]). Due to multi-scale heterogeneity, the situation turns out to be more demanding for carbonates. While microscopic heterogeneity usually determines the shape of $k_r(S_W)$, larger-scale heterogeneity that is statistically not represented in the respective sample volume affects the investigation and makes the result scale-dependent – i.e. dependent on the size of the sample and dependent on the exact location of sampling.

In this paper we present an investigation into CO₂-brine primary drainage in dual-porosity limestone. We performed larger-scale CO₂-brine and decane-brine unsteady-state (USS) displacement experiments and decane-brine steady-state (SS) and USS relative-permeability experiments on samples of smaller volume. We history match the USS displacement data with a 2-D simulation model to derive $k_r(S_W)$. We account for the microscopic pore structure by using different relative permeability parameterizations, with varying degrees of complexity. Macroscopic heterogeneity is not explicitly taken into account, instead it is investigated by comparison to classical relative permeability experiments performed on smaller samples that we consider to be homogeneous. The comparison with results from single-porosity sandstone gives insight into the peculiarities of the CO₂-brine
displacement process in carbonates. With the present work we also want to open a discussion on how to deal with heterogeneity in CO$_2$-brine displacement and how to reliably and practically derive meaningful parameters for field-scale simulations.

### 2.2.2 Rock type, fluids & saturation window

The experiments were performed on Estaillades limestone, which is an outcrop rock with pure calcite mineralogy. The rock type is used as a model system for dual-porosity carbonates. The average porosity is $\sim$0.28 and the average permeability is $\sim$220 mD with a sample-to-sample variation of $\sim$10\% for porosity and $\sim$30\% for permeability. Compared to earlier studies on sandstone [Ott et al., 2011a, Berg et al., 2013a], Estaillades has a bimodal pore structure with inter-granular macro-porosity and micro-porous grains as shown in the $\mu$CT cross-section in Fig. 2.18 (b). In the following we refer to macro-porosity as the porosity that is resolved in $\mu$CT scanning; the micro-porosity is not resolved and is represented in the gray-scale behavior in the images (Fig. 2.18 (b) and (c)). The $\mu$CT-determined ratio of macro- to total-porosity is $\phi_{\text{macro}}/\phi \sim 0.58$ and is also reflected in the pore throat size distribution obtained from the Mercury Injection Capillary Pressure (MICP) measurement in Fig. 5.11; the $\mu$CT and MICP data are directly compared to data obtained from Berea sandstone to relate this study to a reference case (Fig. 2.18 (a) and 5.11). Meso- and micro-porous volumes are also present in Berea, but to a minor extent and without such clear separation of pore sizes as for Estaillades.

The separation of pore space has implications for CO$_2$-brine displacement and for two-phase flow in general. In earlier studies it has been shown that for Estaillades only 42\% ($S_{\text{CO2}} = 0.42$) of the brine can be displaced by CO$_2$ injection at high flow rates representative for near-well bore conditions [Ott et al., 2014b]. This corresponds to about 73\% of the macro-porosity being invaded. The respective $\mu$CT cross-sections are shown in Fig. 2.18. Image (b) represents the dry state and (c) shows the same cross-section after injection of...
2.2. CO$_2$–BRINE DISPLACEMENT IN CARBONATES

100 pore volumes of CO$_2$ at a capillary number of $Ca \sim 6 \times 10^{-7}$ (the present experiments were performed at $Ca \sim 5 \times 10^{-8}$ for USS decane-brine and $\sim 6 \times 10^{-9}$ for USS CO$_2$-brine). Note that the reverse contrast between solid and micro-porous grains in Fig. 2.18 (c) is due to the saturation of the micro pores by highly x-ray-absorbing brine. We consider the CO$_2$ saturation window of 40 to 50% of the pore space as the maximum that can be reached by USS or SS experiments on these samples under laboratory conditions, which are representative of field conditions. The relevance of this window for field application is discussed further below.

2.2.3 CO$_2$-brine displacement

USS experiments were performed on samples with dimensions 7.5 cm in diameter and 15 cm in length. The cores were initially saturated with brine, which was then displaced by the non-wetting CO$_2$ phase. Two types of experiments were performed: the actual CO$_2$-brine primary drainage experiment, and, on the same rock samples, experiments using decane as the displacing phase, which allows comparison with standard SCAL (Special Core Analysis) experiments and serves as a base case. From these core floods primary drainage relative permeability can be inferred.

As can be seen from Fig. 2.20, the rock type is not only heterogeneous at the pore scale (see Fig. 2.18), but also at a scale that is not statistically represented in the volumes of the larger-scale samples. Fig. 2.20 shows the porosity profile of three samples studied in this work. The lower rows show the CO$_2$ saturation profile under flow conditions at the end of the CO$_2$-brine displacement experiments as 1-D and 3-D saturation profiles. The porosity profiles were derived from CT scans. The samples show different degrees of porosity heterogeneity, with a general porosity variation of about 0.05 in porosity units. It is interesting that there is no obvious correlation between the porosity profiles and the CO$_2$
saturation profiles at the end of the respective CO₂ flood (taking the capillary end-effect into account), as reported earlier on a heterogeneous sandstone by [Perrin and Benson, 2010]. In conclusion, we found that the porosity profiles do not have a strong influence on the saturations resulting from the two-phase displacement. This means that whether or not a sample can be considered to be homogeneous can only be decided after the experiment.

The USS experiments were performed at a pressure of 100 bar and a temperature of 50°C, corresponding to an aquifer depth of about 1000 m. The experimental setup and the procedures we follow in this study have been reported by Berg and Ott [Berg et al., 2013a, Ott et al., 2013]. The procedure in brief: after a tracer test, the core was pre-saturated with CsCl-doped brine (S_W =1). For a decane-brine displacement experiment, decane was injected in the brine-saturated core with a constant flow rate of 0.25 ml/min. Subsequently, the core was cleaned and S_W =1 was reestablished as preparation for the following CO₂ experiment. In order to avoid CO₂-dissolution and chemical rock-fluid interaction during the CO₂-brine displacement, the brine was equilibrated with CO₂ and the rock’s mineral phase at experimental conditions. Thereafter, water-saturated CO₂ was injected at a rate of 0.44 ml/min, immiscibly displacing the brine phase. During the experiments, the pressure drop, ΔP, and the 3-D CT (computer tomography) density profiles were monitored as a function of time, reflecting the fluid saturation changes. The cumulative brine production was additionally and independently measured.

Data of a decane-brine (upper row) and a CO₂-brine (lower row) coreflood are shown in
2.2. CO₂–BRINE DISPLACEMENT IN CARBONATES

Figure 2.21: CT time sequences of the decane-brine (top) and the CO₂-brine experiments. The decane and CO₂ saturation distributions are in orange and the initial rock fluid system is displayed as semitransparent background. Note that the threshold setting for the saturation is comparable, but arbitrary to highlight heterogeneity in the saturation distribution.

Fig. 2.21. Both experiments were subsequently performed on the same rock sample under the same conditions. We focused on the third sample in Fig. 2.20, which we consider to be more homogeneous than the others. The heterogeneity has been judged on the basis of the final CO₂ saturation profile in Fig. 2.20 rather than on porosity data and the single-phase tracer test. Fig. 2.22 shows the data recorded during the experiment – ΔP (left), the brine-production curves (middle), and the decane/CO₂ saturation profiles at three different time steps (right). The data show the quantitative difference between decane-brine and CO₂-brine displacements, reflecting the differences in fluid viscosity, density, interfacial tension (IFT), and relative fluid permeability, $k_r(S_W)$. While viscosities, densities and IFT are known, we derive $k_r(S_W)$ by means of numerical simulations, which is the subject of the following section. Despite the differences in the final CO₂-saturation profiles, we consider the extracted $k_r(S_W)$ as representative for the larger-scale experiments, since the sample-to-sample variability of the total brine production and ΔP are relatively small. The final production- and ΔP-plateau heights are indicated in Fig. 2.22, and show standard deviations, which are larger, but in the same order as the experimental error bars of the individual experiments listed in Tab. 2.4.

2.2.4 Data interpretation

The data from coreflood experiments is analyzed to determine the $k_r(S_W)$ relationship by using analytical expressions or through simulations where the flow equations are solved numerically. We interpreted our experimental data with the aid of coreflood simulations. Core flood simulations have traditionally involved a manual tuning of parameters in order to achieve a match to the observed experimental data. More recently tools have emerged that partially automate this process: so-called assisted history matching tools. More commonly used in field-scale reservoir simulation (e.g. [Oliver and Chen, 2011, Oliver et al., 2008, Rwechungura et al., 2011]), such approaches have also been applied to coreflood simulation [Kerig and Watson, 1987, Loeve et al., 2011, Okabe, 2005, Wang et al., 2006].
Figure 2.22: Data from the larger-scale experiments compared to simulated data from the assisted history matching study for the decane-brine experiment (upper panels) and CO$_2$-brine experiment (lower panels). The results obtained from different relative-permeability models are displayed as lines with a color code. The integrated brine production (middle panels) is given in units of the total pore volume (PV). The orange stars in the lower-right and lower-middle panels indicate the average $\Delta P$- and production-plateau values of the three larger-scale CO$_2$-brine displacement experiments.
We used a Shell proprietary stochastic uncertainty management tool and reservoir simulator [Por et al., 1989] to interpret our experimental dataset. Here we describe the methodology used and present the results of the matching exercise.

Coreflood model & measured data

2-D horizontal models of the core, discretized into 465 grid cells (31 in the X-direction, of which 2 columns of grid cells are for the inlet/outlet and 29 for the core, and 15 in the Z-direction) were used. To aid numerical stability and to better resolve inlet and outlet effects, the first (and last) four columns of core cells were 0.1, 0.2, 0.4, and 0.8 times the length of the central cell, with the smallest cells being located at the ends of the core. The inlet and outlet cells were 0.001 times the length of the central core cell. Constant values of porosity (0.297) and permeability (260 mD) were assigned to all core cells. The inlet cells were assigned a constant flux boundary condition to represent the CO$_2$ injection rate, and outlet cells were connected to a production well operated at a constant pressure constraint, replicating the experimental conditions. For the decane-brine simulations a simple black-oil PVT description was used and for the CO$_2$-brine simulations a Cubic plus Association Equation of State was used to model partitioning of the CO$_2$ and H$_2$O between the supercritical CO$_2$ phase and the aqueous phase. To rule out uncertainties regarding the saturation state of the injected CO$_2$, we modeled both dry and pre-equilibrated CO$_2$ injections. The best agreement was found with the equilibrated phase simulations; only these results will be shown and discussed here.

Capillary forces were accounted for, with the capillary pressure curve being scaled from mercury-air data, accounting for changes in interfacial tension. The objective was to determine the relative permeabilities and as such these were parameterized and varied as described below.

From the measured water production and differential pressure data we selected a limited number of points to act as the observed data in the assisted history matching exercise (herein referred to as observables), thus simplifying the matching process. Two data points were selected from both the water production and differential pressure dataset. These points were chosen so that the late time and breakthrough behaviors were captured (Table 2.4). By selecting two points each from the production and pressure data these data sources carry equal weighting (note it is possible for the user to define a weighting per observable, all weights were set to unity). The standard deviations were based on pump and gauge accuracy.

Assisted history matching methodology

The assisted history matching approach consists of four main elements: a parameterization of the functions of interest (in this case relative permeability); a sampling of the parameter space using experimental design methods; the creation and quality control of a proxy model; and the subsequent interrogation of the proxy model to identify best matches to the observed experimental data.
Relative permeability parameterization

Assisted history matching works by varying input parameters in order to achieve a match between simulated and observed data. In the case of this coreflood experiment it is the relationship between relative permeability and saturation, which is unknown and which must be varied in order to get an acceptable match. To simplify this process three parameterized functions were investigated [Brooks and Corey, 1964, Lomeland et al., 2005, Masalmeh et al., 2007], as summarized in Table 2.5. Working with parameterized functions can limit the number of simulations necessary to build a good quality proxy model. However, the disadvantage is that the shapes of the resulting relative permeability curves are constrained by the functional form of the equations.

Each variable parameter was assigned a range and a probability distribution. We used uniform distributions for all parameters. The minimum and maximum values of the parameters are summarized in Table 2.6. These ranges were assigned based on an understanding of typical relative permeability behavior, or in the case of the empirical matching parameters of [Lomeland et al., 2005] on the guidance given in the original publication. Typically these ranges were wide enough to allow a satisfactory match to be achieved. However, in the case of the wetting phase Corey exponents our initial ranges proved inadequate and a match was not achieved. We had to subsequently re-visit our initial range and expand it. This explains the high maximum wetting phase Corey exponents used (Table 2.6). As we will discuss later, the sharp fall-off in wetting phase relative permeability – which required these high Corey exponents – is a characteristic of the system investigated.

Experimental design

With the parameters and their ranges stipulated, it is possible to explore the resulting parameter space by running coreflood simulations with different combinations of parameter values. To do this efficiently, experimental design methods were used. We first ran a tornado design, where parameters were systematically varied one at a time to either their minimum or maximum values, while keeping the remaining parameters at their base values. The resulting tornado plots (not shown) were used to understand which parameters are well constrained by the measured data. We then ran a Box-Behnken design [Box and Behnken, 1960] in addition to a space-filling and a latin-hypercube [McKay et al., 1979] design. The Box-Behnken and space-filling designs were used to construct our proxy model (see below), while the latin-hypercube design was used to subsequently test the quality of the proxy model.

The proxy model

Our observables were selected from the measured water production and pressure difference experimental measurements. Based on the outputs of the simulations (generated for parameter values coming from experimental design), a proxy model was generated for each of the observable points in Table 2.4. The proxy is described by a second order polynomial which is a function of the unknown parameters. The advantage of the proxy model is that
Table 2.4: Summary of the observed data used in the assisted history matching process. The early time observations coincide with the breakthrough time (pressure difference data) or approximately with a leveling off in the water production data. All observed data points are assigned equal weighting.

<table>
<thead>
<tr>
<th></th>
<th>Decane-Brine</th>
<th>CO$_2$-Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Early Time</td>
<td>Late Time</td>
</tr>
<tr>
<td>Time (hours)</td>
<td>7.63</td>
<td>21.4</td>
</tr>
<tr>
<td>Water Produced (mL)</td>
<td>48.24±1</td>
<td>48.48±1</td>
</tr>
<tr>
<td>Time (hours)</td>
<td>2.60</td>
<td>21.04</td>
</tr>
<tr>
<td>Pressure Difference (bar)</td>
<td>0.126±5%</td>
<td>0.105±5%</td>
</tr>
</tbody>
</table>

it allows a computationally cheap evaluation (estimation) of the simulated observable, and hence a faster history matching process. Our proxy models were generated based on the results of the Box-Behnken and space-filling design. We subsequently checked the quality of the model by comparing it against the results of the latin-hypercube design, our quality criteria being that the simulated observable values should be within ±10% of the value approximated by the proxy.

**Best match identification**

Having created and checked our proxy model, we then interrogated it in order to find the best matches to our measurements. This was done by minimizing the mismatch function:

$$V = \sum_{i=1}^{N_{obs}} w_i (d_i - y_i)^2,$$

where $V$ is the mismatch function, $w_i$ the weight, $d_i$ the observed data, and $y_i$ the simulated value. First we sampled the proxy surfaces one thousand times with a Monte Carlo approach, the best four matches from which were added to our proxy, which was then recomputed. We then sampled a further one thousand times with a Markov chain Monte Carlo approach [Andrieu et al., 2003]. Based on this sampling, the parameter values for the four best match cases were simulated in our simulation model to confirm the quality of these best match cases.

**Best match cases**

Table 2.7 summarizes the best match cases identified from the workflow described above, while Fig. 2.22 compares the simulated water production, pressure drop, and saturation profile responses to the measured data. The best match to the decane-brine dataset was achieved with the LET and Corey parameterizations and the best match to the CO$_2$-brine dataset was achieved with the Corey parameterization. Table 2.8 summarizes the parameter values for the best match cases, and the respective relative permeability curves are shown further below in section 2.2.6.
Table 2.5: Summary of the parameterized functions of relative permeability investigated in this study.

* In our analysis we used a fixed \( S_{wc} \) of 0.2 in all cases. It should be noted that the shape of the relative permeability curves below a water saturation of 0.6 does not affect the history match as saturations in this range were not reached in the experiments.

† The normalized water saturation \( (S_w)_n \) in the LET model is given by:

\[
(S_w)_n = \frac{(S_w - S_{wc})}{1 - S_{wc}} - S_{nwr},
\]

which for primary drainage can be simplified as

\[
(S_w)_n = \frac{S_w - S_{wi}}{1 - S_{wi}}.
\]

‡ The relative permeability equations are formulated for the primary drainage flow sequence and hence may differ slightly from those given in the original references. Differences are due to the omission of the wetting phase end point relative permeability from the wetting phase equations. Since the primary drainage flow sequence is considered this end point relative permeability is equal to unity.

| Model Reference | Primary Drainage Equation Primary Drainage Equation No of Variables* |
|-----------------|---------------------------------------------------------------|-------------------|
| Corey           | \( k_{rw} = (S_w - S_{wc})^{n_w} \)                         | \( k_{rw} = k_{rw}^{n_w}(1 - S_{wc})^{-n_w} \) | 3 |
| [Brooks and Corey, 1964] | | |
| Mod. Corey      | \( k_{rw} = \frac{(S_w - S_{wc})^{n_w}}{1 + c_w \left( \frac{S_w - S_{wc}}{1 - S_{wc}} \right)} \) | \( k_{rw} = k_{rw}^{n_w}(1 - S_{wc})^{-n_w} \) | 4 |
| [Masalmeh et al., 2007] | | |
| LET †           | \( k_{rw} = \frac{(S_w - S_{wc})^{n_w}}{S_{wc}^{n_w} + E_w^{n_w}(1 - S_{nw})^{n_w}} \) | \( k_{rw} = \frac{(1 - S_{wn})^{k_w}}{(1 - S_{wn})^{k_w} + E_w^{k_w}S_{wn}^{k_w}} \) | 7 |
| [Lomeland et al., 2005] | | |

Table 2.6: Summary of the parameter ranges used in the assisted history matching study.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Decane-Brine</th>
<th>CO2-Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>min base max</td>
<td>min base max</td>
</tr>
<tr>
<td>Corey</td>
<td>( n_w )</td>
<td>2.0 15.0 20.0</td>
<td>5.0 20.0 30.0</td>
</tr>
<tr>
<td></td>
<td>( n_{nw} )</td>
<td>1.0 1.75 2.5</td>
<td>1.5 1.9 3.5</td>
</tr>
<tr>
<td></td>
<td>( k_w )</td>
<td>0.5 0.7 0.9</td>
<td>0.3 0.6 0.9</td>
</tr>
<tr>
<td></td>
<td>( k_{rw} )</td>
<td>0.0 0.001 0.001</td>
<td>0.0 0.001 0.001</td>
</tr>
<tr>
<td>Mod. Corey</td>
<td>( n_w )</td>
<td>2.0 15.0 20.0</td>
<td>5.0 20.0 30.0</td>
</tr>
<tr>
<td></td>
<td>( n_{nw} )</td>
<td>1.0 1.75 2.5</td>
<td>1.5 1.9 3.5</td>
</tr>
<tr>
<td></td>
<td>( k_w )</td>
<td>0.5 0.7 0.9</td>
<td>0.3 0.6 0.9</td>
</tr>
<tr>
<td></td>
<td>( k_{rw} )</td>
<td>0.0 0.001 0.001</td>
<td>0.0 0.001 0.001</td>
</tr>
<tr>
<td>LED</td>
<td>( k_{rw} )</td>
<td>0.5 0.7 0.9</td>
<td>0.5 0.7 0.9</td>
</tr>
<tr>
<td></td>
<td>( L_w )</td>
<td>10.0 15.0 30.0</td>
<td>10.0 15.0 30.0</td>
</tr>
<tr>
<td></td>
<td>( E_w )</td>
<td>0.1 1.0 10.0</td>
<td>0.1 1.0 10.0</td>
</tr>
<tr>
<td></td>
<td>( T_w )</td>
<td>0.5 1.0 2.0</td>
<td>0.5 1.0 2.0</td>
</tr>
<tr>
<td></td>
<td>( L_{nw} )</td>
<td>1.5 2.0 2.5</td>
<td>1.5 2.0 2.5</td>
</tr>
<tr>
<td></td>
<td>( E_{nw} )</td>
<td>0.5 1.0 2.0</td>
<td>0.5 1.0 2.0</td>
</tr>
<tr>
<td></td>
<td>( T_{nw} )</td>
<td>0.5 1.0 2.0</td>
<td>0.5 1.0 2.0</td>
</tr>
</tbody>
</table>
2.2. CO₂–BRINE DISPLACEMENT IN CARBONATES

Table 2.7: Summary of the root-mean-square-errors (RMSE) between measured observable points and simulated responses for the parameterizations resulting from the history matching exercise.

<table>
<thead>
<tr>
<th>Model</th>
<th>Decane-Brine RMSE</th>
<th>CO₂-Brine RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corey</td>
<td>1.42</td>
<td>1.09</td>
</tr>
<tr>
<td>Modified Corey</td>
<td>1.51</td>
<td>1.35</td>
</tr>
<tr>
<td>LET</td>
<td>1.37</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Table 2.8: Summary of the best match relative permeability parameter values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Decane: LET</th>
<th>CO₂: Mod. Corey</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{rnw}$</td>
<td>0.734</td>
<td>0.802</td>
</tr>
<tr>
<td>$r_{nw}$</td>
<td>12.9</td>
<td>17.3</td>
</tr>
<tr>
<td>$E_{nw}$</td>
<td>4.3</td>
<td>3.13</td>
</tr>
<tr>
<td>$T_{nw}$</td>
<td>1.21</td>
<td>0.80</td>
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<tr>
<td>$F_{W}$</td>
<td>2.23</td>
<td>1.57</td>
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<tr>
<td>$n_{w}$</td>
<td>0.802</td>
<td>17.3</td>
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<tr>
<td>$n_{nw}$</td>
<td>3.13</td>
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2.2.5 Standard relative permeability

As we aim to characterize the CO₂-brine displacement in heterogeneous rock, we compare the larger-scale displacement experiments with standard relative permeability on smaller rock samples that we consider to be homogeneous. For this purpose, we performed standard steady-state experiments on samples with a tested volume 24× smaller than for the larger-scale displacement experiments; the sample dimensions were 3.8 cm diameter and 5 cm length, with the length over which we evaluate the saturation profile and measure $\Delta P$ being the central 2.5 cm. The classical SS approach allows for a direct interpretation by Darcy’s law, with no numerical interpretation step involved; since we consider $\Delta P$ and saturations over the central part of the sample, excluding the inlet and outlet ends, we have confidence in analyzing the data with the multiphase Darcy equation. The multiphase Darcy equation assumes that capillary pressure is negligible and by making our measurements away from the inlet/outlet ends where capillary end effects can play an important role we attempt to better honor the assumptions behind the multiphase Darcy equation. In contrast to the USS displacement process, in SS, both fluid phases are injected simultaneously stepwise, increasing the fractional flow ($F_{W}$) and keeping the total flow rate constant. For the experiments we used decane as non-wetting and brine as the wetting fluid phase, and hence the results are directly comparable to the larger-scale decane-brine displacement experiment described above.

Fig. 2.23 shows raw data and the results of the SS experiments. The top panel shows the flow rates of decane and brine and the respective pressure drop $\Delta P$. $\Delta P$ was measured over the entire core and over a smaller distance in the inside, for which we consider the saturation profile to be homogeneous. The saturation profiles in SS at different fractional flows $F_{W}$ are shown in the middle panel of Fig. 2.23. With increasing decane flow rate, brine saturation of up to 0.45 were reached. This is higher than the saturation reached in the USS experiment due to the higher decane-flow velocities at the end of the SS flood, i.e. the higher capillary number.

The resulting $k_r(S_W)$ curves are shown in the lower panel of Fig. 2.23. The measure-
CHAPTER 2. CO$_2$-BRINE PRIMARY DRAINAGE

Figure 2.23: Data and results of SS experiments. Top panel: flow rates and pressure drop $\Delta P$ as a function of injected fluid in pore volumes (PV). Note that the lower $\Delta P$ is measured over a shorter distance inside the core to avoid end effects. Middle: brine saturation profiles at different fractional flow, $F_W$. The vertical lines indicate the distance over which $\Delta P$ was measured. Lower panel: $k_r(S_W)$ derived from two different SS experiments. The data set has been complemented by decane-brine USS experiments as described in the text. USS and USS pp refers to the unsteady-state method and the porous plate method, respectively.
ments show a variation that we attribute to the variation of sample properties due to heterogeneity. Both SS datasets show comparable brine $k_r(S_W)$ branches, but deviate in decane relative permeability. Despite the spread, the SS $k_r(S_W)$ are consistently higher than the one obtained from the larger-scale USS experiments. To prove the validity of the SS results for describing an USS displacement, we carried out an USS experiment under the same conditions with the same sample size as the SS experiments were performed. The obtained USS relative permeability data are shown in the same panel of Fig. 2.23. A good agreement between the SS and USS data has been found within a reasonable sample-to-sample variation. The blue and the red lines are Corey functions, which serve as guide to the eye and for comparison to the larger-scale experiments in Fig. 2.25.

In the coreflood experiments so far, the viscous forces were not sufficient to extend the saturation window into the range of micro-porosity. To extend the decane relative permeability to larger decane saturations, effective permeability measurements have been performed on samples that were drained by means of the porous plate method [Pentland et al., 2011]. The results complement the SS and USS curves in Fig. 2.23 to lower water saturations. The data verifies the high decane mobility at the end of the SS corefloods and shows that the micro-porosity does not add to the non-wetting phase conductivity.

### 2.2.6 Discussion

We performed experiments on larger-scale rock samples, from which we have chosen the most homogeneous one for further investigation using numerical modeling. The selection has been done in order to describe the corefloods in a homogeneous model by the smallest possible number of parameters. The selection circumvents the explicit description of core-scale heterogeneity that would effectively lead to a downscaling of the problem. The heterogeneity has been judged on the basis of the final CO$_2$ saturation profile rather than on porosity data and the single-phase tracer test only, as discussed in the context of Fig. 2.20. However, despite the different CO$_2$-saturation profiles, we consider the extracted $k_r(S_W)$ as representative for the larger-scale experiments, since the sample-to-sample variability of the total brine-production-plateau and the $\Delta P$-plateau heights are relatively small as indicated in Fig. 2.22.

These experiments provide valuable insight in the fundamental CO$_2$-brine displacement and are close to the actual field displacement process. However, the determination of $k_r(S_W)$ is non-trivial. The typically sharp transition from brine production before breakthrough to predominantly CO$_2$ or decane production provides a limited dataset to which simulation models can be constrained. Furthermore, a limited accessible saturation range, in the present case $0.6 < S_W < 1.0$, is investigated due to the presence of micro-porosity with a total volume fraction of 40 to 50% of the pore space. Our interpretation is that the non-wetting phase only invaded the larger pores in this dual-porosity carbonate rock; the sub-micron pores were not invaded. The relevance of the resulting small saturation window for CO$_2$-brine plume migration will be discussed further below.

Additional information before and after breakthrough is obtained by in-situ saturation monitoring. The flood front propagation and the final saturation profile were used as
independent benchmarks for the simulations. The comparison of experimental results and simulations as shown in Fig. 2.22 is reasonable considering the simplifications applied in the simulation model, especially at early and late time (first and last scan in the right panels).

The resulting relative permeability functions are shown in Fig. 2.24. We plot the best fit of each of the applied parameterizations for comparison. The decane-brine results are shown in the left panels and the CO$_2$-brine results in the middle. The respective lower panel shows the same datasets on a logarithmic scale. The best fit of the decane-brine was obtained by LET parameterization and the CO$_2$-brine system was best described by the Corey description with the parameters provided in Table 2.8; both datasets are compared in the right panels. We observe that both the wetting and the non-wetting phase $k_r(S_W)$ in the CO$_2$-brine system tend to be smaller than those in the decane-brine system at comparable water saturations. For the non-wetting phase, this is consistent with previous studies on Berea sandstone (see [Berg et al., 2013a], and the references given in [Benson et al., 2013]). However, for the wetting phase, a previous study on the same rock using the same experimental and analysis methods showed the water relative permeability to be higher in the CO$_2$-brine system than in the decane-brine system [Berg et al., 2013a]. A compilation of data from different studies showed the opposite trend [Benson et al., 2013], but fluids and sample preparation methods differed in the compared studies.

In the left panels of Fig. 2.25 the results from the decane-brine USS experiment are compared to the results obtained from the steady-state approach. Using both SS datasets to describe the larger-scale USS coreflood through simulations failed. The obtained pressure drop and production curve are shown in the respective panels in Fig. 2.22. The main difference between the SS and USS is the relatively sharp drop of the brine branch in USS compared to SS. Furthermore, in SS a larger saturation window has been achieved. The reason is the increasingly larger advective force that was applied in SS to displace the brine phase; while in SS the flow rates of the individual phases vary by one to two orders of magnitude changing the capillary number respectively, the capillary number is constant in the larger-scale USS experiment. In the present case, the USS flow rate (corresponding to a velocity of 1 ft/day ($\approx 3.5 \times 10^{-6}$ m/s)) was comparable to the lowest decane flow rate in SS. Note that a systematic change of the capillary number could influence the shape of the relative permeability curve in cases where strong capillary heterogeneity is present.

In the middle panels of Fig. 2.25, the decane-brine USS displacement data are compared to equivalent data from Berea sandstone. Berea is a sandstone with an essentially monomodal pore architecture. For Estaillades, the available saturation window is about half of the one of Berea, which is due to the presence of micro-porosity in the limestone. However, after scaling the saturation axis to the Estaillades macro-porosity ($\phi_{macro} \rightarrow \phi_{total}$), the relative permeability curves are surprisingly comparable, despite the different architectures of the pore systems of both rock types (compare Fig. 2.18 (a) and (b)). This means that we would expect a similar displacement efficiency for both rock types if we consider the macro-pore space only.

This is not the case for the CO$_2$-brine displacement as shown in the right panels of Fig. 2.25. Applying the same scaling of the saturation axis to the CO$_2$-brine system results
Figure 2.24: The best match relative permeability relationships resulting from the assisted history matching exercise. The left panels show the decane-brine relative permeabilities, the middle panels the CO$_2$-brine relative permeabilities, and the right panels show a comparison of the best fits (lowest RMSE, Table 2.7).
Figure 2.25: Comparison of the upscaled $k_r(S_W)$ functions to results of standard $k_r(S_W)$ experiments and earlier results on Berea sandstone. Left panels: comparison of $k_r(S_W)$ obtained from larger-scale (LS – bold lines) and smaller-scale (thin lines – see Fig. 2.23) decane-brine corefloods. Middle and right panels: comparison of data obtained from Estaillades limestone and Berea sandstone for decane-brine experiments (middle) and CO$_2$-brine experiments (right). For the scaled $k_r(S_W)$ functions, the macro-porous volume of Estaillades has been scaled to the total pore volume of Berea. The scaled functions are shown as dotted lines in the respective panels.
in a noticeable difference of relative permeability in both rock types. Especially the brine-mobility is much higher in Berea sandstone compared to Estaillades. Since CO$_2$-brine and decane brine displacement in Estaillades results in comparable relative permeability saturation functions, the reason is most likely the different wetting behavior of CO$_2$ and decane in Berea as found in [Berg et al., 2013a], which has been attributed to the presence of clay minerals. We therefore attribute the main difference between the scaled Estaillades and the Berea relative permeability curves to CO$_2$-clay interactions.

The role of micro-porosity

The data discussed so far show that the micro-porosity is not invaded even at high flow rates representative for near-well-bore conditions and the CO$_2$-saturation window investigated by the experiments is 0 < $S_{nw}$ < 0.4 (< 0.5 for higher capillary numbers). The resulting questions are: 1. When will the micro porosity be invaded by viscous flow in laboratory experiments? and 2. Under which conditions is this saturation window sufficient to describe field-scale displacements? We now consider each of these questions in turn.

In the laboratory and the subsurface, CO$_2$ invades the micro-porous region if the viscous force overcomes capillary forces, i.e. the capillary entry pressure that can be estimated from the pore-throat radii $r$ by $p_C = 2\sigma/r$, with $\sigma$ being the interfacial tension. In water-wet well-separated bi-modal pore size carbonate rocks we assume that the macro-porosity is invaded prior to an invasion of the micro-porosity. This assumption is based on the simple capillary entry criterion, which is inversely proportional to pore-throat radius. Once the macro-porosity is completely filled with CO$_2$ the micro-porous carbonate grains may become isolated from one another, meaning that the wetting aqueous phase is no longer extensively inter-connected. Since CO$_2$ forms a connected phase [Ott et al., 2014b], we estimate the viscous pressure drop acting on the brine phase trapped within a single micro-porous grain by Darcy’s law; $\Delta P_{visc} = l_{grain} \cdot \mu \cdot \nu_{Darcy} / K$. Hence CO$_2$ overcomes the capillary entry pressure if

$$\frac{l_{grain} \cdot \mu \cdot \nu_{Darcy}}{K} \geq \frac{2\sigma}{r},$$

with $l_{grain}$ being the characteristic length of micro-porous grains estimated from $\mu$CT scans, $\mu$ being the CO$_2$ viscosity, $K$ the permeability and $\nu_{Darcy}$ the CO$_2$ velocity, i.e. the macroscopic capillary number $Ca_{macro} \geq 1$ (see e.g. [Armstrong et al., 2014]). Using relevant parameter ranges for CO$_2$ storage,$^1$ the mean micro-porosity pore-throat radius $r = 0.7$ $\mu$m and the permeability $K = 220$ mD, we estimate $\nu_{Darcy}$ to be in the order of meters per second, which is three to four orders of magnitude higher than the highest expected field velocities. Even in case the micro-porous system would be interconnected throughout the sample, the viscous force at relevant flow rates would not suffice. We speculate that relevant viscous forces are not sufficient to desaturate micro-porosity.

On the field scale, micro-porosity can be invaded when gravitational forces cause the capillary entry threshold to be exceeded. The gravitational pressure that is required can

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$^1$The following ranges of parameters were used: $\sigma = 30-40$ mN/m; $l_{grain} = 100-1000$ $\mu$m (from $\mu$CT scans); $\rho = 300-500$ kg/m$^3$. 
be estimated by

\[ \Delta \rho gh \geq \frac{2\sigma}{r}, \]  

(2.11)

where \( \Delta \rho \) is the difference of both fluid densities, \( g \) the gravitational constant, and \( h \) the column height. For the micro-porosity pore-throat radius range of 0.1 to 1 µm and the relevant ranges of \( \Delta \rho \) and \( \sigma \), minimum column heights of 12 m (for \( r = 1 \mu m \)) to 250 m (for \( r = 0.1 \mu m \)) are required for the CO\(_2\) to enter the micro-porosity. It seems feasible that such CO\(_2\) column heights might be expected during storage operations, resulting eventually in a higher CO\(_2\) saturation at the top of the reservoir. Since the micro pores do not contribute to the CO\(_2\) mobility, micro-porosity might act as a reservoir and might mitigate gravity overrun of the CO\(_2\) plume.

2.2.7 Summary & conclusions

We investigated multi-phase flow in heterogeneous and dual-porosity carbonate rock in order to understand effects of microscopic and macroscopic heterogeneity on CO\(_2\)-brine displacement and eventually on CO\(_2\) plume migration in carbonate aquifers. For this, a series of coreflood experiments were performed with CO\(_2\)-brine and decane-brine as fluid combinations. Decane-brine was used as water-wet reference case and for comparison to standard SCAL (Special Core Analysis). SCAL was performed on small samples that we consider to be homogeneous, i.e. the derived curves are considered to be true \( k_r(S_W) \) functions. The actual displacement experiments were performed on larger-scale rock samples with a volume 24× larger than that of the SCAL samples. From a series of three, we selected one coreflood sequence, which showed the least impact of heterogeneity on the CO\(_2\) saturation profiles.

Upscaled relative permeability saturation functions were derived by history matching the larger-scale displacement experiments in an 2-D-homogeneous numerical model. The simplest parameterization of relative permeability – the Corey model – gave an adequate description of the carbonate studied. This is likely because only the macro-porosity was invaded by CO\(_2\), and a potential discontinuity in the relative permeability saturation functions is outside the range of these experiments. In situations where there is less separation (in terms of pore size) between macro- and micro-porosity, and the micro-porosity is part of the CO\(_2\) conducting system, more complex relative permeability parameterizations may be required to describe the behavior.

The comparison of the upscaled and the true relative permeability curves reveals the influence of heterogeneity on the displacement. Heterogeneity results in lower fluid-phase mobilities – i.e. lower relative permeability functions were observed. This is reasonable, since bypassing leads to a larger fraction of effectively immobile brine and to a effectively lower total cross-section for CO\(_2\) or decane flow. An interesting point is that despite bypassing, the production from the larger-scale sample is higher than predicted for the homogeneous situation. The reason might be the higher local flow rates as a result of the reduced flow cross-section, which might lead to a locally higher displacement efficiency.
A comparison to single-porosity Berea sandstone [Berg et al., 2013a] revealed two major differences. The most distinguishing property between Berea and the dual-porosity carbonate is the presence of micro-porosity that requires unrealistically high flow rates to be invaded by the respective non-wetting phase. The result is a smaller achievable saturation window in Estaillades according to the ratio of macro- to total-porosity. By scaling the saturation window of the macro-porous volume of Estaillades to the total pore volume of Berea, we directly compare the relative permeability curves of the CO$_2$-conducting pore system of both rock types. While for the decane-brine system the displacement in both rock types is comparable, we find substantially lower fluid mobilities in Berea for the CO$_2$-brine system. In conjunction with the interpretation in [Berg et al., 2013a], we attribute this difference mainly to clay–CO$_2$ interactions in clay-rich Berea sandstone.

It has been shown that the micro-porous sub-volume cannot be invaded under realistic viscous flow conditions, but invasion can occur if gravity dominates. From the pore-throat distribution we derived column heights between 12 and 250 m that are required to drain the micro pores by gravity. However, in the experiments it has been shown that the micro-porous volume does not add to the decane and accordingly to the CO$_2$ mobility, which means that the micro-porosity above the minimum column height, at which point it starts be become drained, serves only as a reservoir. This might have consequences for CO$_2$-plume migration. Micro-porosity above the minimum column height might mitigate fluid-density-driven gravity overrun.

Further work needs to be done to understand (1) whether or not the obtained relative permeability saturation function is representative of the next larger-scale (related to heterogeneity), and if not, (2) how to effectively include the core-scale (capillary) heterogeneity into the picture. (3) If we effectively downscale the system by including heterogeneities, how to upscale it again in order to derive a useful function for reservoir-scale simulations? These are questions we would like to address to the community.

**Nomenclature**

- $k_{rw}$ = wetting phase relative permeability
- $k_{rnw}$ = non-wetting phase relative permeability
- $S_w$ = wetting phase saturation
- $S_{wn}$ = normalized wetting phase saturation
- $S_{wc}$ = connate (irreducible) wetting phase saturation
- $S_{nwr}$ = residual non-wetting phase saturation (after imbibition)
- $n_w$ = wetting phase Corey exponent
- $n_{nw}$ = non-wetting phase Corey exponent
- $c_w$ = empirical fitting parameter used when modifying the Corey functions
• $k_{r_{nw}}^{w}$ = non-wetting phase relative permeability at connate (irreducible) wetting phase saturation (also known as the non-wetting phase end point relative permeability)

• $L_{nw}^{w}$ = empirical parameter of the LET model for the wetting phase

• $L_{nw}^{w}$ = empirical parameter of the LET model for the non-wetting phase

• $E_{nw}^{w}$ = empirical parameter of the LET model for the wetting phase

• $E_{nw}^{w}$ = empirical parameter of the LET model for the non-wetting phase

• $T_{nw}^{w}$ = empirical parameter of the LET model for the wetting phase

• $T_{nw}^{w}$ = empirical parameter of the LET model for the non-wetting phase.
Chapter 3

Displacement Stability and Plume Migration

3.1 Stability of CO$_2$-brine immiscible displacement in sandstone

The viscous stability of the primary drainage process is of major interest for the injection of carbon dioxide (CO$_2$) in saline aquifers, since it determines the spread of the CO$_2$ plume in the target aquifer and consequently the initial utilization of the pore space for CO$_2$ storage. In order to analyze the stability of the displacement process, the relative permeability saturation functions must be known; these are usually derived by experiments under conditions representative for the field. It is therefore very important to characterize the flood front stability, not only on the field scale but also on the experimental scale, in order to judge the validity of the experimental results as a precondition for reliable field simulations.

Here we investigate the onset of viscous fingering, thereby studying under what conditions CO$_2$–brine displacement remains stable. We discuss the role of relative permeability and the stabilizing effect of capillary pressure at different length scales by means of numerical simulations. The results allow us to assess different definitions of the mobility ratio and establish criteria for judging the stability of the displacement process. We further show that in cases where gravitational forces are important, the gravity tongue dominates the fingering pattern, and unstable situations can occur where stability would be predicted, by considering viscous and capillary forces only.

In the literature various criteria for the onset of instability have been proposed, but these are inconsistent or inconclusive. Our intention is to bring order into this discussion. In the present study we validate or refute stability criteria by numerical modeling and show that the shock–front mobility ratio correctly describes the onset of fingering. The application of our findings is not limited to CO$_2$–brine displacement. The criteria for stability can be applied to most two-phase flow problems in reservoir engineering in general ranging from water flooding to low interfacial tension surfactant flooding.
3.1.1 Introduction

The injection of carbon dioxide (CO\textsubscript{2}) in deep saline aquifers and depleted oil and gas fields is widely discussed in the context of CO\textsubscript{2} sequestration for carbon capture and storage (CCS) [IPCC, 2005, Bachu et al., 1994, Bachu and Gunter, 2004]. Key questions relate to how much CO\textsubscript{2} can be stored in the respective geological formation, which is typically only a small fraction of the total available pore space of the sedimentary rock formation, and the exact spread of the CO\textsubscript{2} plume, which needs to be controlled to ensure safe and permanent storage. Both questions are closely related to the primary CO\textsubscript{2} plume migration which is – in the case of CO\textsubscript{2} injection in saline aquifers – a primary drainage process of immiscible fluids if the fluids are mutually saturated. Besides porosity ($\phi$), the absolute permeability ($K$) of the formation rock and the fluid viscosities ($\mu$), capillary pressure, $p_c$, and in particular the relative permeability, $k_r$, of the CO\textsubscript{2}–brine system are the key parameters used to describe the propagation of the CO\textsubscript{2} injection front in the porous rock and to assess the CO\textsubscript{2} storage capacity [Egermann et al., 2006]; $k_r$ and $p_c$ directly determine the local pore space occupation (displacement efficiency) and the macroscopic bypassing (sweep efficiency) by channeling or by viscous instabilities [Garcia and Pruess, 2003] of the displacement process. While both mechanisms – channeling and viscous fingering – cause bypassing on a macroscopic scale, channeling is the consequence of spatial variation of the abovementioned rock properties. Therefore, the saturation distribution can in principle be correctly described by numerical models if the spatial variation is known. Viscous fingering, in contrast, is the consequence of a hydrodynamic instability and can occur even in completely homogeneous rock. It strongly depends on the individual reservoir whether channeling or viscous fingering is the dominating effect, and therefore no general statement can be made about the relative importance of either mechanism. However, the two mechanisms are likely to have a combined effect and could amplify each other, leading to a severe reduction of the macroscopic formation volume that is available for CO\textsubscript{2} storage, and to an uncontrolled spread of the CO\textsubscript{2} plume. This would adversely affect CO\textsubscript{2} sequestration.

Since even subtle changes in relative permeability – as we will show in this paper – may have a strong effect on the displacement process, a reliable experimental determination of $k_r$ is of major interest. For the CO\textsubscript{2}–brine system, in several studies the relative permeability $k_r$ was determined by using the unsteady-state (USS) technique [Bennion and Bachu, 2005, Bennion and Bachu, 2008, Egermann et al., 2006, Berg et al., 2013a, Ott et al., 2011a] where CO\textsubscript{2} is injected into a brine-saturated rock sample (“core”), displacing the brine. In several studies the $k_r$ data are determined by semi-analytical or numerical interpretation of the brine production and pressure drop $dp$ over the core, and implicitly, stable displacement is assumed but not independently verified, e.g. by CT scanning during the displacement process as in [Perrin and Benson, 2010] and [Berg et al., 2013a]. A priori it is not evident that the displacement of brine by supercritical CO\textsubscript{2} is actually stable. For all conditions relevant to CO\textsubscript{2} sequestration under which experiments are typically conducted, the viscosity of the injected supercritical CO\textsubscript{2} is lower than that of the displaced brine, which raises the question whether the displacement is stable or affected by viscous
3.1. STABILITY OF CO$_2$-BRINE DISPLACEMENT IN SANDSTONE

fingering [Saffman and Taylor, 1958, Chuoke et al., 1959]. When relative permeability is determined from an unstable unsteady-state experiment subject to viscous fingering by an interpretation that implicitly assumes stable displacement, the resulting $k_r(S_w)$ and $p_c(S_w)$ would not have general validity but would only be *pseudo* functions, i.e. volume-averaged effective properties limited to the specific sample size and saturation distribution in the experiment. Therefore the question about the stability of the CO$_2$–brine displacement in unsteady-state experiments is very important for assessing the validity of the CO$_2$–brine relative permeability data obtained.

In the present work we investigate the viscous stability on an experimental scale in a linear geometry as typical for core flood experiments. As a base case we focus on the experimental data published in [Berg et al., 2013a]; this experiment was performed at a pressure and temperature of 100 bar and 45°C corresponding to an aquifer depth of about 1000 m, at which the viscosities are $\mu_{\text{CO}_2} = 0.0338$ cP, $\mu_{\text{brine}} = 0.674$ cP, i.e. the viscosity ratio is 1:20. Starting from this base case we map the parameter space relevant for CO$_2$ sequestration.

We treat CO$_2$–brine as immiscible and do not consider the mutual solubility of CO$_2$ and brine. This is justifiable because mutual solubility only plays a role close to the injection point (where the CO$_2$ is not yet water saturated) and close to the CO$_2$ flood front (where the brine might be under-saturated with respect to CO$_2$). Field simulations show that in the region ahead of the CO$_2$ flood front, the brine phase is CO$_2$-saturated by diffusive transport. Hence, CO$_2$–brine displacement is essentially an immiscible displacement with maximum interfacial tension (IFT). The continuing loss of CO$_2$, which has been quantified in [Berg et al., 2013a], leads to a slightly diminished displacement.

We start by briefly reviewing the stability criteria established in literature for immiscible displacement in porous media flows. In the absence of capillarity and gravity effects, the mobility ratio is the key parameter for the assessment of displacement stability. We focus on different definitions of the shock-front mobility ratio; the shock front is accepted as the appropriate criterion for viscous fingering nucleation [Hagoort, 1974, Riaz and Tchelepi, 2004, Riaz and Tchelepi, 2006]. The end-point mobility ratio is not compatible with the results of the present study.

We use the shock-front mobility ratio as a criterion to assess whether in the absence of capillarity and gravity an experimental condition would be stable or unstable. We identify the appropriate definition of shock-front mobility ratio and we establish stability maps as a function of relative permeability by means of 2D and 3D numerical simulations. Capillary pressure, however, is known to stabilize immiscible displacement [Hagoort, 1974, Parlange and Hill, 1976], in particular the shorter wavelengths i.e. on a short length scale [Yortsos and Hickernell, 1989, Daripa and Pasa, 2008, Babchin et al., 2008]. First the shock-front mobility ratio is used as a criterion to assess whether in the absence of capillarity an experimental condition would be stable or unstable. Then by two-dimensional numerical simulations, for the unstable configuration in the absence of capillarity, the capillary pressure is systematically increased to determine the stability limit for the given experimental scale.

As discussed in [Yortsos and Hickernell, 1989], [Daripa and Pasa, 2008] and [Babchin...
et al., 2008], capillarity stabilizes only perturbations on short length scales. On larger length scales that are relevant for the field, the displacement could actually still be unstable. We investigate the field case by upscaling the analysis conducted for the length scale of laboratory experiments to field relevant length scales.

Gravity is able to influence the displacement stability significantly and can destabilize the flow even if the no-gravity case suggests stable displacement. We take gravity into account and discuss the significance of gravitational forces with respect to viscous and capillary forces.

3.1.2 Stability of immiscible displacement in porous media

In immiscible displacement in porous media, an unstable flood front can be observed when the displacing phase has a larger mobility than the displaced phase, which can result in fingering of the displacing phase. The source of the instability is the viscous pressure gradient which leads to a steeper pressure gradient of the displaced phase ahead of the finger, which lets the finger grow as shown by the analytical model by [van Wunnik and Wit, 1989]. The phenomenon can be observed both in miscible and immiscible displacement in porous media [Van Meurs, 1957, Saffman and Taylor, 1958]. Due to hydrodynamic similarity the phenomenon is often studied in planar geometries such as Hele-Shaw cells [Homsy, 1987, Feder, 1998]. Immiscible and miscible fingering differ by the counteracting mechanism to the viscous-driven instability. For immiscible situations it is the capillarity that opposes fingering, whereas for miscible situations it is hydrodynamic dispersion that homogenizes concentration or saturation gradients caused by the fingering.

In this paper we consider only the immiscible displacement of brine by CO$_2$ in porous rock and do not consider the miscible displacement of CO$_2$–oil [Gardner and Ypma, 1984], for example. Immiscible viscous fingering has been observed and analyzed by [Chuoke et al., 1959] and [Saffman and Taylor, 1958] by using linear stability analysis, but experimental evidence was published earlier by [Engelberts and Klinkenberg, 1951], who gave a name to the phenomenon. In the early work by [Chuoke et al., 1959] and [Saffman and Taylor, 1958], the stability is assessed for an initially sharp front between displacing and displaced phases motivated by the Buckley–Leverett shock front ( [Buckley and Leverett, 1942]).

Immiscible displacement in porous media

The basis is the formulation of two-phase flow by a phenomenological two-phase extension of Darcy’s law [Darcy, 1856] where the specific flux of phase $\alpha$ ($\alpha = w$ for the wetting phase, i.e. brine and $\alpha = nw$ for the non-wetting phase, i.e. CO$_2$) is described as

$$
\mathbf{v}_\alpha = -\frac{k_{r,\alpha}}{\mu_\alpha} K \cdot (\nabla p_\alpha - \rho_\alpha g),
$$

(3.1)

$K$ is the absolute permeability tensor and $g$ is the gravity vector. $S_w$ and $S_{nw}$ are the saturations of the wetting and non-wetting phases with $S_w + S_{nw} = 1$. $p_{nw}$ and $p_w$ are the pressure of the non-wetting and wetting phases, respectively, where the difference is
3.1. STABILITY OF CO$_2$-BRINE DISPLACEMENT IN SANDSTONE

Figure 3.1: Shock front for immiscible displacement (primary drainage) with and without capillary pressure, adapted from [Lake, 1989].

defined as capillary pressure $p_c = p_{nw} - p_w$. $k_{r,\alpha}$ is the saturation-dependent two-phase relative permeability of the $\alpha$-phase. The ratio of relative permeability to viscosity is often referred to as mobility. The mobility ratio

$$M = \frac{k_{r,nw}/\mu_{nw}}{k_{r,w}/\mu_w}$$  \hspace{1cm} (3.2)

of the displacing to displaced fluid phase is a critical parameter for the microscopic displacement efficiency and the further stability analysis.

The one-dimensional unsteady-state displacement can be treated analytically by reformulating Eqn. 3.1 and the continuity equation for the fractional flow of the wetting and non-wetting phases, which is often referred to as the “Buckley–Leverett problem” [Buckley and Leverett, 1942]. For $p_c = 0$ the displacing phase propagates with a shock front as sketched in Fig. 3.1, which is often the base state for stability considerations.

In fact, the stability analysis is often not performed for an actual porous-media flow but for the planar Hele-Shaw geometry with continuous fluid phases. This situation is formally analogous to two-phase flow in a porous medium [Feder, 1998] with one important difference: the treatment of capillarity. In the Hele-Shaw cell, capillarity occurs through the interfacial tension and the Laplace pressure at curved interfaces which separates the continuous liquid phases. In a porous medium, capillarity leads to a diffusive front with a smooth saturation profile as shown in Fig. 3.1, where both phases co-exist on a microscopic scale.

Results of the linear stability analysis

The starting point for the stability analysis is a straight interface between the displaced and displacing phase. This is then perturbed, and the wavelength and growth rate of
the perturbation are analyzed. For immiscible viscous fingering, perturbations with a wavelength $\lambda$ larger than a critical wavelength $\lambda_c$ can grow. In Hele-Shaw cells $\lambda_c$ can be analytically calculated [Saffman and Taylor, 1958, Chuoke et al., 1959, Hagoort, 1974, Feder, 1998] using linear stability analysis

$$\lambda > \lambda_c = 2\pi \frac{\sigma}{\sqrt{\frac{\mu_2}{k_2} - \frac{\mu_1}{k_1} (u - u_c)}}$$

(3.3)

where $\sigma$ is the interfacial tension between the two phases, $\mu_1$ and $\mu_2$ their viscosities, $k_1 = k_2 = k$ the permeability of the Hele-Shaw cell, $u$ the flow velocity and $u_c$ the critical velocity [Feder, 1998]. For horizontal configurations $u_c = 0$. For vertical configurations $u_c = g \cdot (\rho_1 - \rho_2)/(\mu_2/k_2 - \mu_1/k_1)$. The wavelength with the fastest growth rate is $\lambda_{\text{max}} = \sqrt{3} \cdot \lambda_c$ [Feder, 1998].

For horizontal flow, which is the situation considered here, the displacement is unstable when the expression in the square root of Eqn. 3.3 is positive, i.e. the mobility of the displacing phase is larger than that of the displaced phase, i.e.

$$M = \frac{\mu_2/k_2}{\mu_1/k_1} > 1$$

(3.4)

where “1” and “2” refer to the saturation endpoints far ahead and behind the displacement front, respectively.

This stability criterion can be directly translated to porous media flows [Feder, 1998] but one has to keep in mind that this analogy is inconsistent in the sense that a shock-front profile with $p_c = 0$ serves as the base state. On the other hand, the restoring force is described as effective interfacial tension (see [Chuoke et al., 1959]) which represents capillarity with $p_c > 0$. Setting both $p_c$ and effective interfacial tension consistently to zero would rule out capillary forces as a restoring force, which would then be replaced by other mechanisms such as dispersion similar to the case of miscible fingering (see [Tan and Homsy, 1986]).

Note that the linear stability analysis is only valid for small fingering amplitudes and is therefore only valid for the initial growth regime of the fingers. The analytical model by [van Wunnik and Wit, 1989], where the fingers are approximated as half-ellipses, predicts exponential growth for small fingers and linear growth for large fingers. For large amplitudes, the non-linear interactions between the fingers are reported as the dominant factors [Riaz and Tchelepi, 2006].

### Influence of capillarity on the stability

Several attempts have been made to extend that description to actual porous media with capillarity. [Chuoke et al., 1959] substituted the microscopic interfacial tension $\sigma$ with an “upscaled” macroscopic parameter to assess the stability of the displacement and fingering wavelength in porous media with capillarity. [Hagoort, 1974] followed the approach by [Chuoke et al., 1959] but introduced a criterion based on the dissipation of viscous energy...
and conversion into capillary energy to determine stability. [Wang et al., 1998] (including the correction in [Javaux et al., 2005]) used the results of the stability analysis by [Chuoke et al., 1959] and introduced a critical gravity-viscous velocity similar to $u_c$ and a capillary velocity, which are used to determine criteria for the onset of unstable flow. The capillary velocity is used to account for capillary effects, which have been seen by many researchers to suppress viscous fingering [Parlange and Hill, 1976, Wang et al., 1998]. It is important to note that these approaches are all based on the stability analysis by [Chuoke et al., 1959] where a simplified definition of the base state is used which does not account for capillary dispersion of the shock front as sketched in Fig. 3.1.

Despite the formal similarity of the two-phase flow in a Hele-Shaw cell and a porous medium [Feder, 1998], the situation in a porous medium is certainly different. While in a Hele-Shaw cell, at any given location, either one or the other liquid phase is present but phases do not co-exist, in the continuum description of multiphase flow in a porous medium the two phases co-exist at the same location in space [Yortsos and Hickernell, 1989, Daripa and Pasa, 2008] which is parameterized via the saturation of the wetting phase $S_w$. As a consequence, in two-phase flow in porous media, capillarity manifests not only an effective interfacial tension between microscopic fluid-fluid interfaces, but $p_c \neq 0$ also causes a dispersion of the Buckley–Leverett shock front (“capillary dispersion”, [Jerauld et al., 1984]) as sketched in Fig. 3.1, which in a consistent description should then serve as the base state for the stability analysis. A stability analysis which is based on a full description of porous media flows in one dimension, including capillarity, is reported by [Jerauld et al., 1984], [Yortsos and Hickernell, 1989], [King and Dunayevsky, 1989], [Barenblatt et al., 1974], [Riaz and Tchelepi, 2004], [Riaz and Tchelepi, 2006], [Riaz et al., 2007], [Babchin et al., 2008], and [Daripa and Pasa, 2008]. One of the key findings is that capillary pressure acts in particular on the short wavelength perturbations in a stabilizing way. Analytical approximations by [Yortsos and Hickernell, 1989] and [Babchin et al., 2008] have shown that the instability growth rate consists of two terms where the first term is a purely viscous term and scales with wave number $|k|$ and the second term contains the capillarity and scales with $k^2$. In a typical situation, the first term is positive and the second term is negative, which leads to a parabolic form of the growth rate which is positive for small wavenumbers $k$, i.e. long wavelengths, and becomes negative for larger $k$, i.e. shorter wavelengths. Capillarity acts in a similar way as dispersion (sometimes termed “capillary dispersion”; see [Jerauld et al., 1984, Riaz and Tchelepi, 2004]), transforming a sharp shock front into a diffuse zone with an elongated tail. As a consequence, the mobility contrast between displacing and displaced fluid decreases and the instability is suppressed in a similar way, as dispersion is the counteracting mechanism to fingering in miscible displacement [Homsy, 1987]. Capillarity basically suppresses fingering on the same length scale as the shock front is dispersed, i.e. it is entirely a matter of scale. In fact, it is actually the ratio of viscous to capillary forces that determines how sharp the shock front is and whether fingering is suppressed or not. Core flooding experiments conducted at low flow rates are often capillary dominated while core flooding experiments at large flow rates and flow on the field scale are typically viscous dominated. The ratio of viscous to capillary forces on a Darcy flow scale is expressed by the macroscopic capillary number [Anton and Hilfer,
Therefore [Riaz and Tchelepi, 2004] scaled length by the capillary number, which accounts for this balance between viscous and capillary forces.

In the limit of no gravity and no capillarity, [Yortsos and Hickernell, 1989] recover the mobility ratio stability criteria from [Saffman and Taylor, 1958], but it is worth noting that [Yortsos and Hickernell, 1989] and [Babchin et al., 2008] use the endpoint mobility ratio. [Riaz and Tchelepi, 2004,Riaz and Tchelepi, 2006] and [Riaz et al., 2007] conduct a similar stability analysis but use the shock-front mobility ratio as a criterion.

### Endpoint vs. shock-front mobility ratio

Several authors argue that the relative permeability endpoints should be used to assess stability (see e.g. [Jerauld et al., 1984,Yortsos and Hickernell, 1989,Babchin et al., 2008,Barenblatt et al., 1990b,Barenblatt et al., 1974]). In the limit of no gravity and no capillarity, in Eqn. 5.15 in [Yortsos and Hickernell, 1989], instability is found for an endpoint mobility ratio

\[
M_e = \frac{k_{r,2}(x \to -\infty)/\mu_2}{k_{r,1}(x \to +\infty)/\mu_1} > 1
\]

where “1” and “2” refer to the displaced and displacing phase. \(x \to -\infty\) refers to a saturation where the displacing phase has reached its maximum saturation. In analogy, \(x \to +\infty\) refers to a saturation where the displaced phase has reached its maximum saturation. In other words, relative permeability of displacing and displaced phases is evaluated at the respective residual saturation. The criterion from Eqn. 3.5 is actually identical to the criterion for instability in Eqn. 18 in [Babchin et al., 2008]. For the endpoint mobility ratio the relative permeability of the displacing phase is evaluated at a location far upstream, and the relative permeability of the displaced phase is evaluated at a location far downstream. As a consequence, the criterion for the onset of instability does not depend on the concrete form of the relative permeability-saturation function like the Corey exponents, but only on the endpoint values at residual saturations. By now it has been generally accepted that instead of the endpoint mobility ratio the shock-front mobility ratio should be used [Hagoort, 1974,Riaz and Tchelepi, 2004,Riaz and Tchelepi, 2006,Riaz et al., 2007,Buchgraber et al., 2011,Tang and Kovscek, 2011] as shown in the sketch in Fig. 3.2 where \(S_{\text{shock}}\) is the saturation at the shock front. [Riaz and Tchelepi, 2006] find that the concrete form of the relative permeability function has a large influence on the onset of instability. A simple form of the shock-front mobility ratio can be written in analogy to Eqn. 3.4 as

\[
M_s = \frac{k_{r,2}(S_{\text{shock}})/\mu_2}{k_{r,1}(x \to +\infty)/\mu_1} > 1
\]

Both criteria, \(M_e\) and \(M_s\), are identical for the approximation of a step profile as it would occur for capillary numbers \(N_{\text{cap}} \to \infty\). The main difference between the \(M_e > 1\) and the \(M_s > 1\) criteria is that the endpoint mobility ratio \(M_e\) indicates instability for far more situations than the shock-front mobility ratio \(M_s\). Consider a situation where both relative permeability endpoints = 1. Then \(M_s > 1\) for any situation where the viscosity
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Figure 3.2: Immiscible displacement of brine by CO$_2$: In order to assess the stability of the displacement, the mobilities ($k_r/\mu$) of CO$_2$ and brine have to be evaluated on the left and right side of the shock front, respectively.

ratio $\mu_1/\mu_2 > 1$. But as will be shown in the following sections, for a large range of viscosity ratios $> 1$ instability occurs only for a very limited set of Corey exponents. In other words, $M_e > 1$ predicts instability for cases that are actually stable.

In the literature, some authors also use the total mobility of both phases combined as a criterion for the onset of instability. [Jerauld et al., 1984] employ the total-mobility ratio far ahead and behind the shock front as a criterion for stability. [Hagoort, 1974] uses the total-mobility ratio at the shock front in analogy to Eqn. 3.6:

$$M^T,H_s = \frac{k_{r,2}(S_{\text{shock}})/\mu_2 + k_{r,1}(S_{\text{shock}})/\mu_1}{k_{r,2}(x \to +\infty)/\mu_2 + k_{r,1}(x \to +\infty)/\mu_1} > 1,$$  \hspace{1cm} (3.7)

considering both fluid phases on both sides of the shock front, respectively. Another form of the total shock-front mobility ratio is introduced by [Riaz and Tchelepi, 2006]:

$$\lambda_T = M_e k_{r,2} + k_{r,1}$$ \hspace{1cm} (3.8)

with the criterion for instability:

$$M^{T,R}_s = \frac{\lambda_T(S_{\text{shock}})}{\lambda_T(x \to +\infty)} > 1.$$ \hspace{1cm} (3.9)

Both criteria, $M^{T,H}_s$ and $M^{T,R}_s$, coincide for both relative permeability endpoints $= 1$. 

3.1.3 Relative permeability for CO$_2$–brine

In this work the extended Corey model [Corey, 1954, Brooks and Corey, 1964] is used to parameterize the relative permeability functions with an analytical representation

\[
k_{r,w} = k_{r,w}(S_{nw,r}) \left( \frac{S_w - S_{wc}}{1 - S_{wc} - S_{nw,r}} \right)^{n_w}
\]

\[
k_{r,nw} = k_{r,nw}(S_{wc}) \left( \frac{1 - S_w - S_{nw,r}}{1 - S_{wc} - S_{nw,r}} \right)^{n_{nw}}
\]

where $S_{w,c}$ and $S_{nw,r}$ are the residual wetting and non-wetting phase saturations, respectively, and $k_{r,nw}(S_{wc})$ and $k_{r,w}(S_{nw,r})$ are the corresponding relative permeability endpoints. In the case discussed here, CO$_2$ is the non-wetting phase. CO$_2$ and brine are immiscible but there is mutual solubility [Marini, 2007, Berg et al., 2013a]. In this study, for the sake of simplicity, both fluid phases are assumed to be mutually saturated.

Relative permeability is a parameter that is typically specific for the individual rock–fluid system. In the literature, several independent measurements of relative permeability for the CO$_2$–brine combination are reported. [Bennion and Bachu, 2005, Bennion and Bachu, 2008] determined CO$_2$–brine relative permeability in Canadian sandstone and carbonate samples for drainage and imbibition from unsteady-state experiments with mutually saturated fluid phases. The relative permeability curves were extracted from the total brine and CO$_2$ flow rates and the pressure drop during the core flood. [Egermann et al., 2006] also determine relative permeability from unsteady-state core flooding experiments conducted in homogeneous limestone rock. [Perrin et al., 2009], [Perrin and Benson, 2010] and [Kuo et al., 2010] used the steady-state technique to determine the CO$_2$–brine relative permeability in Berea sandstone and sandstone rock from south-west Australia, but limitations due to large sample heterogeneity were encountered.

In a previous study [Berg et al., 2013a] we determined the relative permeability and capillary pressure for supercritical CO$_2$ displacing brine (primary drainage) in Berea sandstone rock. The unsteady-state experiment was analyzed by history matching the production data and saturation profiles obtained from CT scanning. In Fig. 3.3 the resulting $k_r$ and $p_c$ data are shown. We also show the result of a reference experiment where n-decane displaces brine under comparable conditions, which was independently verified from standard measurements on twin samples. For comparison we added the Berea data (same rock type) from [Perrin et al., 2009] and [Perrin and Benson, 2010] to the plot. The associated Corey parameters are listed in Table 3.1 and serve together with the $p_c$ data in Fig. 3.3 as the base case for the further stability assessment.

3.1.4 Stability of CO$_2$–brine primary drainage for $p_c = 0$

As discussed in section 3.1.2, the appropriate criterion for the onset of unstable displacement is the shock-front mobility ratio where $k_{r,CO_2}$ and $k_{r,brine}$ are evaluated on the shock front as shown in Fig. 3.2:
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Figure 3.3: Primary drainage relative permeability $k_r$ (left, with logarithmic scaling on inset) and capillary pressure ($p_c$, right) saturation functions for CO₂–brine in Berea sandstone rock from [Berg et al., 2013a]. Unsteady-state and steady-state data (dotted lines and open symbols, respectively) for decane–brine are included for comparison. Relative permeability data for CO₂–brine in Berea rock from [Perrin and Benson, 2010] and [Perrin et al., 2009] are added (filled symbols) to the $k_r$ plot.

$$M_s = \frac{k_{r,CO_2}(S_{shock})/\mu_{CO_2}}{k_{r,brine}(S_w = 1)/\mu_{brine}} > 1.$$  \hspace{2cm} (3.12)

The height of the shock front and hence $M_s$ can be determined by means of Buckley–Leverett calculations at $p_c = 0$.

Taking the experiment with the mutually saturated CO₂–brine in [Berg et al., 2013a], the viscosities are $\mu_{CO_2} = 0.0338$ cP, $\mu_{brine} = 0.674$ cP. The relative permeability data are listed in Table 3.1. The resulting breakthrough saturation of CO₂ is 0.36, and the CO₂ relative permeability at breakthrough is only 0.05. As a consequence, the mobility ratio is 1.06, which is larger than 1, meaning that the displacement is marginally unstable. In principle, the stability is sensitive to the following groups of parameters:

- Viscosity ratio. In most of the cases $\mu_{brine}/\mu_{CO_2} = 20$ is considered to represent the conditions of CO₂–brine at $T = 45^\circ$C and $P = 100$ bar, which is a realistic field case [Berg et al., 2013a]. Calculations at viscosity ratios of 10 and 40 show the sensitivity in a viscosity range that is realistic for sequestration projects.

- Corey exponents. In the case discussed here, they are systematically varied over a range representative for a broad range of rock–fluid properties i.e. different rock types and different wetting conditions.

- Relative permeability endpoints and residual saturations. The case discussed in the present paper is the primary drainage, which defines $S_{CO_2,r} = 0$ and $k_{r,brine}(S_w = 1) = 1$. The connate water saturation is kept fixed at $S_{wc} = 0.2$ (see Table 3.1), and
Figure 3.4: Shock-front mobility ratio $M_s$ for primary drainage and $p_c = 0$, calculated by the Buckley–Leverett formalism, as a function of the Corey exponents $n_{CO_2}$ and $n_{brine}$. For the calculations and numerical simulations the following parameters were used: $\mu_{brine}/\mu_{CO_2} = 20$, $S_{wc} = 0.2$ (compare Table 3.1), $S_{CO_2,r} = 0$ and $k_{r,brine}(S_w = 1) = 1$. On the left hand side, $k_{r,CO_2}(S_w = S_{wc}) = 1$ is chosen as an exemplary situation which is then further discussed in the paper. On the right hand side, $k_{r,CO_2}(S_w = S_{wc}) = 0.5$, which is the experimental situation. The Corey exponents for experiments (1) and (3) in Table 3.1 are indicated in the plot. The boundary between stable and unstable displacement is indicated as a red line. The dots and circles (a) to (d) represent numerical simulations discussed in more detail in section 3.1.4.

Stability map as a function of Corey exponents

In Fig. 3.4 the shock-front mobility ratio $M_s$ is plotted as a function of the Corey exponents $n_{CO_2}$ and $n_{brine}$ corresponding to $n_{nw}$ and $n_w$ in Eqn. 3.11 and 3.10. In Fig. 3.5 the shock-front mobility ratio criterion $M_s > 1$ from Eqn. 3.6 is directly compared to the shock-front total-mobility ratio criteria $M_s^{T,H} > 1$ (Eqn. 3.7) and $M_s^{T,R} > 1$ (Eqn. 3.9), which coincide in the given case ($k_{r,CO_2}(S_w = S_{wc}) = 1$). The stability assessments from the numerical simulations match the $M_s > 1$ criterion much closer and are not at all in agreement with the $M_s^{T} > 1$ criterion.
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<table>
<thead>
<tr>
<th>Shock front mobility ratio $M_s$ (left)</th>
<th>Shock front total mobility ratio $M^T_s$ (right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>stable</td>
<td>unstable</td>
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</tbody>
</table>

Figure 3.5: Shock-front mobility ratio $M_s$ (left) and shock-front total-mobility ratio $M^T_s$ for primary drainage at $p_c = 0$. The data are plotted as a function of the Corey exponents $n_{CO_2}$ and $n_{brine}$ for $\mu_{brine}/\mu_{CO_2} = 20$. The stability assessment from the numerical simulations match the $M_s > 1$ criterion on the left (identical to the left side of Fig. 3.4) much more closely and are not at all in agreement with the $M^T_s > 1$ criterion on the right side.

Influence of the viscosity ratio

In Fig. 3.6 the stability lines ($M_s = 1$) from Fig. 3.4 are plotted for three different viscosity ratios: 1:10, 1:20 (as in Fig. 3.4) and 1:40 for the two endpoints $k_{r,CO_2}(S_w = S_{wc}) = 1.0$ and 0.5. As a general trend one can observe that the region of unstable displacement expands when the viscosity ratio and the relative permeability endpoint for CO$_2$ are increased. The two effects can compensate each other, i.e. the stability lines for $\mu_{brine}/\mu_{CO_2} = 10$ and $k_{r,CO_2}(S_{wc}) = 1$ are identical to $\mu_{brine}/\mu_{CO_2} = 20$ and $k_{r,CO_2}(S_{wc}) = 0.5$, which is a result of the way in which the two parameters are entered into the fractional flow equation. Furthermore, it is evident that there is a critical viscosity ratio (dependent on $k_{r,CO_2}(S_{wc})$) below which no instability is possible ($M < 1$) in the range of Corey exponents $2 \leq n \leq 5$. When the viscosities are identical ($\mu_{CO_2} = \mu_{brine}$) and if both endpoints are unity, the shock-front mobility ratio is always $M < 1$, i.e. the displacement is always stable, and the lowest viscosity ratio at which $M \geq 1$ is seen is $\mu_{brine}/\mu_{CO_2} \approx 8$.

In Fig. 3.7 fingering for viscosity ratios of 1:20, 1:40 and 1:100 are displayed at $p_c = 0$. The larger the viscosity ratio, the smaller the wavelength (which is in agreement with Eqn. 3.3) and the more elongated the fingers, which is a consequence of a larger growth rate (see [Riaz and Tchelepi, 2004], for example).
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Figure 3.6: Stability lines ($M_s = 1$) for primary drainage and $p_c = 0$, plotted as a function of the Corey exponents $n_{CO_2}$ and $n_{brine}$. $k_{r,CO_2}(S_w = S_{wc}) = 1.0$ on the left and 0.5 on the right for viscosity ratios 1:10, 1:20 and 1:40, respectively.

Figure 3.7: Fingering pattern for viscosity ratios 1:20, 1:40 and 1:100 and $p_c = 0$. 
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Comparison to numerical simulations

In the following, a set of numerical simulations based on Eqn. 3.1 and the continuity equation is conducted to verify the stability map displayed in Fig. 3.4. For the sake of simplicity, relative permeability endpoints are taken to be $k_{r,\text{brine}}(S_w = 1) = k_{r,\text{CO}_2}(S_w = S_{wc}) = 1.0$ (left hand side of Fig. 3.4). The simulations are based on the flow geometry from the experiment reported in [Berg et al., 2013a], which is sketched in Fig. 3.8. Details of the experimental setup and the experimental conditions and protocols for the CO$_2$–brine primary drainage are reported in [Berg et al., 2013a].

The simulations were conducted with the Shell proprietary reservoir simulator MoRES [Regtien et al., 1995], which is a fully implicit finite volume Darcy flow simulator. A porous media representative for Berea sandstone with a porosity of 25% and permeability $K = 100 \pm 2$ mD was considered. In order to allow for finger nucleation inside the rock and to avoid artifacts at the inlet face, a 4 mD random permeability variation was superimposed on the 100 mD base permeability as a multi-spectral stimulation. The random field is initialized at each simulation run, i.e. at each run a different random field was used.

Except where explicitly noted otherwise, in all simulations a two-dimensional numerical grid was used with 50 grid blocks in flow direction (15 cm total length) and 100 grid blocks perpendicular (7.5 cm total width) in order to resolve the fingers. To resolve fingers of smaller wavelength, a finer grid was used. We ensured a proper grid resolution by simulating some critical cases with grid sizes refined by factors of $2 \times 2$ and $4 \times 4$. We additionally resolved the finger width in distinctly unstable cases and approached the stability border from that basis, which allowed the finger width to tend to expand (as can be seen from Eqn. 3.3), and ensured that the grid resolution was sufficient. The injection rate was 0.25 ml/min, which corresponds approximately to a linear flow velocity of 0.85 ft/day, which is a typical linear flow velocity for field conditions. The viscosity ratio is $\mu_{\text{brine}}/\mu_{\text{CO}_2} = 20$. In order to focus on the viscous fingering instability, all gravity effects are suppressed at first by using an (artificial) density difference $\Delta \rho = 0$.

A set of simulation results is shown in Fig. 3.9 where the saturation patterns during the displacement for different relative permeability values are displayed. For $p_c = 0$, where $n_{\text{CO}_2} = 2.5$, $n_{\text{brine}} = 4.5$ (a), the displacement is stable. There are some very minor

![Figure 3.8: Flow geometry and boundary conditions for the simulation domain.](image-url)
fluctuations at the shock front but they do not grow, at least not over an experimental time scale. In case (b) for $n_{\text{CO}_2} = 3.5$, $n_{\text{brine}} = 2.0$ the displacement is unstable. The fluctuations at the shock front grow to individual fingers which are fully resolved by the numerical grid. In Fig. 3.10 the growth of the fingers in situation (b) is shown in a time series after injection of 0.15, 0.25 and 0.35 PV in direct comparison to a stable front propagation.

The results of the simulations shown in Figs. 3.9 and 3.10 are in line with the stability line in Fig. 3.4. The stability line was then tracked more closely with additional numerical simulations which are not individually shown, but their outcomes, i.e. whether the displacement is stable or unstable, are marked up as circles in Fig. 3.4. In some cases it could not be clearly determined whether the displacement was stable or not on an experimental time scale, due to the generally low growth rate close to the stability line. Those cases were marked as “unclear.” Overall the stability observed in the numerical simulations is in reasonable agreement with the red stability line which supports the shock-front mobility ratio criterion $M_s > 1$.

In panel (c) of Fig. 3.9, a simulation is shown of a condition which, according to the diagram in Fig. 3.4, is stable. The displacement is indeed stable. The front is corrugated and shows some fluctuations, but these do not grow (at least not on the respective time scale). This confirms the stability condition from Eqn. 3.12 that is derived from the condition that fluctuations at the interface do not grow.

There are, however, some situations with $M < 1$ which appear as unstable in the
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Figure 3.10: Time series of finger growth for the unstable situation (b) at the top and the stable situation (a) from Fig. 3.9 at the bottom.

Numerical simulations, but the stability map in Fig. 3.4 suggests stability. The reason is not fully clear. One of the possible reasons is that it is not that straightforward to determine the stability from a numerical simulation. Close to the stability limit the fingering growth rate is very small and the displacement front can become corrugated by channeling or dispersion caused by the ±2% random permeability variation, given that over the simulated length scale in flow direction it is not always clear whether those structures grow or if the amplitude of the perturbations stays constant. The other possible reason is that in numerical simulations the shock front is somewhat smooth as a consequence of numerics and not infinitely sharp as the shock-front mobility ratio assumes. That is illustrated in Fig. 3.11 where for a stable situation the saturation profiles from a 2D numerical simulation with and without \( p_c \) are compared with the 1D Buckley–Leverett profile [Dake, 1978].

Simulations in 3D

So far all simulations have been performed in two dimensions in the \( x - z \) plane (see Fig. 3.8), which for neutrally buoyant fluids, as we assumed them to be for the sake of simplicity, is equivalent to the \( y - z \) plane. In Fig. 3.12 a 3D simulation with \( 50 \times 100 \times 100 \) grid blocks is displayed. The fingers at the displacement front (transition from green to red) can be clearly seen. This confirms that the fingering is not an effect of a two-dimensional simulation domain but is equivalent to that in 3D. Due to the high computational cost of 3D simulations, most of the simulation work in this paper was performed in 2D.

3.1.5 Influence of \( p_c > 0 \) on stability

One has to keep in mind that these Buckley–Leverett estimates for fluid mobilities do not take capillary pressure into account, even though capillarity is known to suppress fingering [Parlange and Hill, 1976], in particular for short wavelengths [Daripa and Pasa,
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Figure 3.11: Saturation profiles from a 1D Buckley–Leverett calculation ($p_c = 0$), a MoReS simulation for $p_c = 0$ and a MoReS simulation with the $p_c$ from Fig. 3.3 for $n_w = 4.5$, $n_{CO_2} = 3.0$ and $k_r$ endpoints = 1.

Figure 3.12: Fingering for the conditions from Fig. 3.9(b) ($p_c = 0$) in a 3D simulation using a grid of $50 \times 100 \times 100$ grid blocks representing $15 \times 7.5 \times 7.5$ cm.
3.1. STABILITY OF CO$_2$-BRINE DISPLACEMENT IN SANDSTONE

Unstable displacement is observed with $p_c = 0$ (situation b in Fig. 3.4). When the interfacial tension is increased from $\sigma = 0.0$ mN/m to 0.01 mN/m and 0.05 mN/m, the displacement remains unstable but the fingering wavelength increases greatly in line with Eqn. 3.3. The situation is only marginally stable at $\sigma = 0.1$ mN/m and stable at $\sigma = 1$ mN/m and larger.

Figure 3.13: Transition from unstable to stable displacement with increasing $p_c$: MoReS model for $K = 100 \pm 2$ mD, density difference $\Delta \rho = 0$, $\mu_{\text{brine}}/\mu_{\text{CO}_2} \approx 20$ at a flow rate of 0.25 ml/min and $n_{\text{CO}_2} = 3.5$, $n_{\text{brine}} = 2.0$. Unstable displacement is observed with $p_c = 0$ (situation b in Fig. 3.4). When the interfacial tension is increased from $\sigma = 0.0$ mN/m to 0.01 mN/m and 0.05 mN/m, the displacement remains unstable but the fingering wavelength increases greatly in line with Eqn. 3.3. The situation is only marginally stable at $\sigma = 0.1$ mN/m and stable at $\sigma = 1$ mN/m and larger.

Stabilization by $p_c > 0$ on an experimental scale

This stabilizing effect is demonstrated in numerical simulations of the unstable situation (b) from Fig. 3.9. In order to study from which $p_c > 0$ value onward an unstable displacement turns stable, in Fig. 3.13 we successively turn on $p_c$. As a basis for $p_c(S_w)$ we use the data

2008, Babchin et al., 2008]. This is relevant for the experiments discussed here because the wavelengths for perturbation are restricted to the width of the confining geometry which is just a few centimeters, which means that capillarity can effectively stabilize the short wavelengths. The question is, then, what happens for long wavelengths and which stability criteria apply e.g. on the field scale for realistic CO$_2$–brine capillary pressure. In the following, an answer to this question is sought by means of numerical simulations using a fine grid with $100 \times 200$ grid blocks in flow and transversal directions, respectively.
for decane/brine from Fig. 3.3 and then scale it by interfacial tension $\sigma$ according to

$$p_c(\sigma) = \frac{\sigma}{\sigma_{\text{ref}}} p_{c,\text{ref}}$$

(3.13)

where $p_{c,\text{ref}}$ is the capillary pressure measured at a reference interfacial tension $\sigma_{\text{ref}}$ which here is 47.9 mN/m for decane–brine [Berg et al., 2013a]. Unstable displacement is observed with $p_c = 0$ (situation b in Fig. 3.4 and 3.9). When the interfacial tension is increased from $\sigma = 0.0$ mN/m to 0.01 mN/m and 0.05 mN/m, the displacement remains unstable but the fingering wavelength increases greatly in line with Eqn. 3.3. The situation is only marginally stable at $\sigma = 0.1$ mN/m, i.e. the approximate point of transition from stable to unstable displacement. For $\sigma = 1$ mN/m and larger the displacement is stable, i.e. the displacement is stable for a realistic $p_c$ ($\sigma = 30$ mN/m) and on an experimental length scale.

### 3.1.6 Effect of gravity

When considering the actual densities of CO$_2$ and brine with $\rho_{\text{CO}_2} = 0.41$ g/cm$^3$ and $\rho_{\text{brine}} = 1.0$ g/cm$^3$ for the conditions reported in [Berg et al., 2013a], dramatic changes in the vertical and horizontal saturation profiles develop during the displacement as shown in Fig. 3.14. Gravitational forces have to be considered in relation to viscous forces and for $p_c > 0$ also in relation to capillary forces [Kopp et al., 2009]. Gravity in general leads to an over-run of the less dense CO$_2$ phase. Fig. 3.14 shows an unstable (top) and a stable (bottom) situation (with the stability evaluated in the absence of gravity) without and with gravity on the left and right, respectively. If gravity is significant, the gravity tongue is the dominating feature as a consequence of an interplay between gravitational and viscous forces. Gravity leads to an upward migration of CO$_2$, and hence to a higher shock front at the top of the simulation domain, whereas the saturation profile in the middle is very similar to the no-gravity case as compared in Fig. 3.15. At the bottom the flow is rather stabilized due to CO$_2$ depletion. As a result, in the already unstable case ($n_{\text{brine}} = 2.0$ and $n_{\text{CO}_2} = 4.5$), the presence of gravity leads to a further increase of instability and a domination of the gravity tongue because it is the feature with the largest shock-front height and hence has the largest growth rate. This increased shock-front height at the top can lead to an unstable situation even if the relative permeability parameters for the no-gravity case suggest stable displacement (compare bottom row for $n_{\text{brine}} = 4.5$ and $n_{\text{CO}_2} = 2.0$). Here the simple 1D Buckley–Leverett shock-front argument is no longer valid.

The relative significance of gravitational to viscous forces can be expressed by the gravity number, which [Anton and Hilfer, 1999] and [Riaz and Tchelepi, 2004] defined as:

$$N_{\text{grav}} = \frac{K g \Delta \rho}{\mu v}$$

(3.14)

where $K$ is the permeability, $\Delta \rho$ is the fluid–density contrast ($\rho_{\text{brine}} - \rho_{\text{CO}_2}$), $\mu = \mu_{\text{CO}_2}$ is the viscosity of the displacing fluid, and $v$ is the linear flow velocity. For the case
3.1. Stability of CO₂-Brine Displacement in Sandstone

Figure 3.14: Unstable (top) and stable (bottom) displacement in absence of gravity (left) and with the influence of gravity on the saturation profiles (right) for $p_c = 0$, $k_{r,CO_2}(S_{w,c}) = 0.5$ and a viscosity ratio of 1:20.

Figure 3.15: CO₂ saturation profiles along the lines indicated in Fig. 3.14.
CHAPTER 3. DISPLACEMENT STABILITY AND PLUME MIGRATION

Figure 3.16: Displacement with the influence of gravity for different injection rates resulting in $N_{\text{grav}} = 10$ (left), 1 (middle) and 0.1 (right) for $p_c = 0$, $k_{r,CO_2}(S_{w,c}) = 1$ and a viscosity ratio of 1:20.

displayed in Fig. 3.14, $N_{\text{grav}} \approx 16$ and hence the system is gravity dominated. Fig. 3.16 shows the displacement at higher flow velocities – i.e. at lower $N_{\text{grav}}$ ($N_{\text{grav}} = 10$, 1 and 0.1) to visualize the transition from a gravity to a viscous dominated flood. While for $N_{\text{grav}} \gg 1$ gravity overrun is dominant, for $N_{\text{grav}} \ll 1$ gravity can be ignored and individual fingers are formed. For $N_{\text{grav}} \approx 1$, the gravitational and viscous forces are comparable and characteristic features of both regimes are visible in the saturation profile.

In the 3D simulations displayed in Fig. 3.17 the interplay of gravity and capillary forces were studied. The left image represents the unstable case (b) in Fig. 3.9 and 3.12 with $p_c = 0$. The dominating feature is the distinct gravity tongue. The tongue shows a very minor degree of corrugation which is also much less pronounced than the fingers observed in Fig. 3.12. For a realistic capillary pressure (corresponding to $\sigma = 30$ mN/m) the displacement becomes stable and the gravity tongue disappears. The impact of gravity is only visible in a tilted front.

3.1.7 Effect of increasing length scales on the stability in the presence of $p_c > 0$

Fig. 3.13 demonstrates how on a short length scale representative for core-flood experiments, $p_c > 0$ stabilizes displacement. In the case of CO$_2$–brine primary drainage with interfacial tension of approx. 30 mN/m, the corresponding capillary pressure will always lead to stability. But as pointed out by [Yortsos and Hickernell, 1989], [Daripa and Pasa, 2008] and [Babchin et al., 2008], capillarity stabilizes only on short-length scales. The question is, then, at exactly which length scale does a displacement become unstable at a given $p_c$.

Fig. 3.18 shows an unstable situation for $p_c = 0$ ($n_w = 2.0$, $n_{CO_2} = 3.5$, both $k_r$ endpoints = 1). $p_c$ is systematically increased by scaling with interfacial tension according to Eqn. 3.13. Once the displacement appears stable at the given length scale, the length scale of the simulation domain is increased until the instability is observed again. The linear flow velocity is kept constant at 1 ft/day. In that way, the capillary pressure is increased from zero to the value found for CO$_2$–brine at an interfacial tension of 30 mN/m, and unstable displacement is found on a transversal length scale of 45 m and above which
3.1. **STABILITY OF CO₂-BRINE DISPLACEMENT IN SANDSTONE**

![Diagram of CO₂ and H₂O with gravity tongue](image)

**Figure 3.17:** Gravity over-run in the cylindrical geometry of the core flooding experiment for \( n_w = 2.0, n_{CO₂} = 3.5, k_{r,CO₂}(S_{wr,c}) = 0.5 \) endpoint and a viscosity ratio of 1:20. \( p_c = 0 \) (left) and \( p_c > 0 \) from Fig. 3.3. A realistic capillary pressure \( (p_c > 0) \) suppresses the gravity tongue.

is then relevant for typical field cases.

The result in Fig. 3.18 is actually not too surprising when considering that the onset of the instability is expected to scale with the capillary number. [Riaz and Tchelepi, 2004] included the capillary number in the length scale but [Riaz and Tchelepi, 2006] kept it as an explicit parameter. The relevant capillary number to describe the onset of fingering is the macroscopic capillary number which [Hilfer and Øren, 1996] defined as

\[
N_{cap}^M = \frac{\mu v L}{p_c K}
\]  

(3.15)

where \( \mu = \mu_{CO₂} \) is the viscosity of the displacing fluid, \( v \) is the linear flow velocity and \( K \) the permeability, and \( L \) is a characteristic length scale in flow direction.

Take for instance \( L \) as the scale of observation, which also sets the pressure gradient, then \( N_{cap}^M \) can also be understood as the ratio of the scale of observation over the width of the capillary smear-out \( \Delta x \) (compare Fig. 3.11).

Note that the arguments above describe the onset of the fingering, i.e. small fingering amplitudes (in this regime the growth rate is exponential and linear stability analysis applies). For larger fingers the amplitude is governed by the growth rate of the finger tip and the rate at which they merge in the back by capillary dispersion [van Wunnik and Wit, 1989]. In this regime the finger amplitude becomes a characteristic length defining...

---

\(^1\)We rewrite \( N_{cap}^M \) as \( N_{cap}^M = L/\Delta x \) with \( \Delta x = K p_c/(\mu v) \) being the width of the capillary smear-out. This can be expressed as \( \Delta x = D_c/v \) with \( D_c = K p_c/\mu \) which can be seen as an order of magnitude approximation for capillary dispersivity.
Figure 3.18: Increasing $p_c$ leads to stabilization only on short length scales, for a condition that is unstable on short length scales for $p_c = 0$ is also unstable on large length scales for $p_c > 0$. The linear flow velocity is kept constant at $v = 2.96 \times 10^{-6}$ m/s.
3.1. STABILITY OF CO$_2$-BRINE DISPLACEMENT IN SANDSTONE

Figure 3.19: Unstable and stable displacement on a centimeter length scale at $p_c = 0$ is reproduced on a 50–100 m length scale for $p_c > 0$.

the length of the shock-front smear-out, which is no longer defined by capillary dispersion only.

$P_c$ is a characteristic value of the capillary pressure. [Anton and Hilfer, 1999] used $p_c = p_c((S_{wc} - S_{nw,r} + 1)/2)$, which is $\approx 0.04$ bar in the present case (see Fig. 3.3). In Table 3.2, $N_M^{cap}$ is listed for the conditions from the matrix in Fig. 3.18 as a function of interfacial tension (which is used to scale capillary pressure according to Eqn. 3.13) and length scale for a linear flow velocity of $2.96 \times 10^{-6}$ m/s. The situations that were found to be stable are marked in bold. Stability is consistent for $N_M^{cap} < 1$, whereas unstable displacement was found for $N_M^{cap} > 1$.

In other words, there is a linear scaling with capillary pressure and length scale, i.e. there is a similarity in $p_c/L$ which supports the approach by [Riaz and Tchelepi, 2004] to scale length by the macroscopic capillary number.

The remaining question is whether the similarity is complete, i.e. whether on large length scales a similar stability diagram as in Fig. 3.4 applies. In Fig. 3.19 it is demonstrated that in two exemplary cases, stability and instability based on the shock-front mobility ratio are also reproduced on a large length for $p_c > 0$.

The stability based on simulation results from Fig. 3.19 and additional simulations not shown are added to the shock-front stability map displayed in Fig. 3.20, but this time based on the field length scale ($90 \times 45$ m) and a realistic $p_c > 0$ for a set of $n_{w}$ and $n_{CO_2}$. The results are very similar to those in Fig. 3.4 based on the centimeter length scale and $p_c = 0$. 

---

Table 3.2: Summary of conditions from Fig. 3.18 as a function of interfacial tension (used to scale capillary pressure according to Eqn. 3.13) and length scale for a linear flow velocity of $2.96 \times 10^{-6}$ m/s.
3.1.8 Discussion and conclusions

Stability of core flooding experiments

From the stabilizing effect of $p_c$ shown in Fig. 3.13 one can conclude that any CO$_2$–brine core-flood experiment conducted on the length scale of a few centimeters at realistic interfacial tensions in the range of 20–40 mN/m will be stable. In particular, in the CO$_2$–brine experiment reported in [Berg et al., 2013a] (see Table 3.1 and Fig. 3.3) which motivated the stability analysis here, the displacement is stable.

The corrugation of the displacement front in [Berg et al., 2013a] is therefore not a result of fingering in the sense of a viscous instability but is caused by other effects where heterogeneity is the most likely cause. A sensitivity study in [Berg et al., 2013a] by numerical simulation (where $\phi$, $K$ and $p_c$ can be varied independently) demonstrates that neither porosity nor permeability heterogeneity alone can cause the patterns observed, but that it is rather an effect of $p_c$ variation ($p_c$ heterogeneity) in combination with the unfavorably high viscosity ratio. A similar situation was presumably encountered in [Tang and Kovscek, 2011], who studied forced imbibition with large mobility ratios into Berea Sandstone which is – except for the reversal of wetting and non-wetting phases – a comparable situation with the study in [Berg et al., 2013a].

Figure 3.20: Shock-front stability map similar to that in Fig. 3.4 and results of numerical simulations for the 90 × 45 m length scale and $p_c$ from Fig. 3.3, i.e. an interfacial tension of 30 mN/m.
3.1. **STABILITY OF CO₂-BRINE DISPLACEMENT IN SANDSTONE**

![Figure 3.21: Displacement for the CO₂–brine primary drainage with relative permeability and capillary pressure shown in Fig. 3.3 and parameters listed in Table 3.1.](image)

**Stability criteria in general**

From the stability considerations supported by numerical simulations we find with gravity neglected (or neutrally buoyant fluids) the following criteria for instability:

- shock-front mobility ratio $M_s > 1$ and
- macroscopic capillary number $N_{\text{cap}}^M > 1$.

This generally also holds in cases where gravitational forces are relevant, but gravity must be taken into account for calculations of the shock-front mobility ratio $M_s$ and the macroscopic capillary number $N_{\text{cap}}^M$, i.e. the simple 1D Buckley–Leverett shock-front argument is no longer valid. We find gravity to be relevant for $N_{\text{grav}} \geq 1$.

**Concrete case for CO₂–brine on experimental and field scale**

After the discussion of stability in general on multiple length scales including $p_c$, and the insight that the stability criteria articulated by [Yortsos and Hickernell, 1989], [Babchin et al., 2008] and [Daripa and Pasa, 2008] may not be reproduced by numerical simulations, we return to the concrete case of CO₂–brine primary drainage. The relative permeability and capillary pressure functions are shown in Fig. 3.3 and the respective parameters are listed in Table 3.1. Simulation results shown in Fig. 3.21 indicate that even though the shock-front mobility criterion suggests stability (see Figs. 3.4 and 3.20), the displacement may actually be unstable both on the experimental scale for $p_c = 0$ and on the field scale for $p_c > 0$. The case is not as clear as the situation in Fig. 3.10, for example, but the corrugation of the front is persistent and growing.

The strongest fingering is expected for $n_{\text{brine}} = 2.0$ and $n_{\text{CO₂}} = 3.5$ for an endpoint of 1. Simulation results for these conditions and also for an endpoint of 0.5 for comparison are shown in Fig. 3.22. Here a scale of $180 \times 90$ m was chosen using a grid of $200 \times 400$ grid blocks.

On that scale fingering is really a macroscopic effect. For $k_{r,\text{CO₂}}(S_{wc}) = 1$ the largest fingers have a length of 18 m and a width of 4 m. A strong bypassing of rock matrix can be expected for a radial injection geometry where the distance between the fingers (and hence the bypassing) increases with time.
**Figure 3.22:** Fingering for $n_{\text{brine}} = 2.0$ and $n_{\text{CO}_2} = 3.5$ on a scale of $180 \times 90$ m (using a grid of $200 \times 400$ grid blocks) for a relative permeability endpoint of 1 on the left and 0.5 on the right.

For $N_{\text{grav}} >>> 1$, the dominating feature is the gravity over-run of the less-dense CO$_2$ as shown in Fig. 3.23. No fingering is observed (either in the horizontal or vertical direction) but the gravity tongue grows in an unstable way. On large length scales, unlike on the scale of the core flooding experiments shown in Fig. 3.17, capillarity $p'_c > 0$ does not suppress the gravity tongue.

This demonstrates that even if the CO$_2$–brine system is just moderately unstable in the porous medium – the mobility ratio is always $< 1.5$ and hence the instability is moderate – there might be a substantial bypassing of rock matrix that diminishes the sweep efficiency and hence the storage capacity of the reservoir. This can be expected when gravity effects are significant ($N_{\text{grav}} \geq 1$), leading to a gravity over-run and a main CO$_2$ pathway below the seal.

Next to viscous instability, heterogeneity plays a major role with respect to plume migration and bypassing. We want to point out that it strongly depends on the individual reservoir whether channeling (heterogeneity related) or viscous fingering is a dominating effect, and that no general statement about the importance of one or the other can be given. However, both channeling and viscous fingering are coupled: Take for example the gravity tongue, which is related to a special kind of heterogeneity – the cap rock. In the unstable case, gravity overrun is a self amplifying process in contrast to the only moderate gravity effect during a stable displacement. Along that line, heterogeneity related channeling might be amplified if the displacement is unstable and, hence, it is important to determine the displacement stability even in cases of heterogeneous reservoirs.
3.1. STABILITY OF CO$_2$-BRINE DISPLACEMENT IN SANDSTONE

Figure 3.23: 3D simulation for $n_{\text{brine}} = 2.0$ and $n_{\text{CO}_2} = 3.5$ on a scale of $90 \times 45 \times 45$ m for a relative permeability endpoint of 1.0, viscosity ratio 1:20, gravity and $p_c > 0$ from Fig. 3.3. The dominating feature is the gravity tongue.

Table 3.1: Overview of relative permeability (Corey parameters, see Eqn. 3.10 and 3.11) resulting from the numerical interpretation of the experiments in [Berg et al., 2013a].

<table>
<thead>
<tr>
<th>Exp. label</th>
<th>$S_{w,c}$</th>
<th>$S_{nw,r}$</th>
<th>$k_{r,nw}(S_{w,c})$</th>
<th>$k_{r,w}(S_{nw,r})$</th>
<th>$n_w$</th>
<th>$n_{nw}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$–brine (saturated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 best</td>
<td>0.2</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
<td>2.5</td>
<td>3.7</td>
</tr>
<tr>
<td>decane–brine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 USS</td>
<td>0.2</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
<td>4.5</td>
<td>2.8</td>
</tr>
<tr>
<td>1 SS</td>
<td>0.22</td>
<td>0.0</td>
<td>0.42</td>
<td>1.06</td>
<td>4.2</td>
<td>2.92</td>
</tr>
</tbody>
</table>

Table 3.2: Macroscopic capillary number $N_{\text{cap}}^M$ as a function interfacial tension and length scale for a linear flow velocity of $v = 2.96 \times 10^{-6}$ m/s. Stable displacement (according to Fig. 3.18) is marked in bold.

<table>
<thead>
<tr>
<th>L (m)</th>
<th>0.15</th>
<th>0.6</th>
<th>30</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>IFT (mN/m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
<tr>
<td>0.2</td>
<td><strong>0.35</strong></td>
<td>1.41</td>
<td>70.42</td>
<td>211.25</td>
</tr>
<tr>
<td>10.0</td>
<td><strong>0.007</strong></td>
<td><strong>0.028</strong></td>
<td>1.408</td>
<td>4.225</td>
</tr>
<tr>
<td>30.0</td>
<td><strong>0.002</strong></td>
<td><strong>0.009</strong></td>
<td><strong>0.469</strong></td>
<td>1.408</td>
</tr>
</tbody>
</table>
Chapter 4

Pore-Scale Processes

4.1 Real-time imaging of Haines jumps in porous media flow

Newly developed high-speed, synchrotron-based X-ray computed micro-tomography enabled us, for the first time, to directly image pore-scale displacement events in porous rock in real-time. Common approaches for modeling macroscopic fluid behavior are phenomenological, have many shortcomings and lack consistent links to elementary pore-scale displacement processes, such as Haines jumps and snap-off. Unlike the common singular pore jump paradigm based on observations of restricted artificial capillaries, we found Haines jumps typically cascade through 10–20 geometrically defined pores per event, accounting for 64% of the energy dissipation. Real-time imaging provided a more detailed fundamental understanding of the elementary processes in porous media, such as hysteresis, snap-off and non-wetting phase entrainment, and it opens the way for a rigorous process for upscaling based on thermodynamic models.

4.1.1 Introduction

There are a number of important processes in nature and technology that present particularly complex problems for our understanding of the non-steady flow of multiple immiscible phases in porous structures. In sedimentary rocks, these processes include carbon and nutrient cycling in the critical zone, the spread and long-term fate of sequestered carbon dioxide [Iglauer et al., 2011, Matter and Kelemen, 2009], the mobilization of trapped hydrocarbon phases in enhanced oil recovery [Lake, 1989], and drying processes [Xu et al., 2008], and also include mass transfer porous catalysts [Kiwi-Minsker and Renken, 2005] and membrane-based fuel cells [You and Liu, 2002]. The most widely accepted criterion for partitioning the pore space of porous materials is based on a cellular, equivalent-capillary conceptualization of individual pores, in which individual pore bodies are divided by openings or constrictions, and, when delineated this way, contribute to a characteristic pore-size distribution. This concept is most relevant to the hydraulic behavior of two-phase immis-
cible fluids such as water and air in (porous) soils. A particularly intricate characteristic of such flows are the Haines jumps [Haines, 1930], events showing a sudden drop in capillary pressure when the non-wetting phase (e.g., air, oil, mercury) passes from a pore neck into a wider pore body displacing the wetting phase (e.g., water), which were first recognized more than 80 years ago. This effect was studied in detail by high-resolution monitoring of capillary pressure fluctuations in very slow rate-controlled mercury porosimetry experiments [Yuan and Swanson, 1989] using the term “subison” to classify the events. The pore openings control the matrix pressure, $p$, at which pores empty, while the wider pore bodies control the pressure at which pores fill. For example, as soil dries and $p$ decreases, water gradually retreats as the air–water interface (meniscus) becomes more curved. At the narrowest part of the filled pore opening, the meniscus can no longer gradually increase its curvature, so it suddenly retreats to the next narrow capillary constriction, emptying the pore instantaneously through this capillary. An analogous phenomenon occurs during when the wetting phase front advances during wetting or imbibition. When the wetting layers in a narrow restriction between two pores touch and coalesce an instability occurs, called snap-off [Roof, 1970], which leads to a disconnection and (capillary) trapping of the non-wetting phase. This phenomenon ultimately leads to hysteretic behavior in water retention curves, which is well-known in soil science [Nimmo, 2004], and also impacts oil recovery efficiency [Lake, 1989] and mass transfer in porous catalysts and membrane-based fuel cells. Measuring Haines jump pore volumes provides important information on residual non-wetting phase saturation [Yuan and Swanson, 1989] because the Haines jump pore system volume distribution represents, in principle, the size distribution of the residual non-wetting phase (e.g., oil or air) ganglia.

### 4.1.2 The filling of pore space

Pore-space filling in a typical fluid displacement event is controlled by the geometry of the pore itself and by the fluid distribution in the adjacent pore network, i.e., how much fluid volume is “buffered” in the menisci and available for spontaneous local rearrangement [Yuan and Swanson, 1989]. When the associated intrinsic relaxation time-scale is comparable to the time-scale for the general advancement of fluid front propagation or an externally imposed main flow rate [Mohanty et al., 1987], the fluid configuration is not in capillary equilibrium [Barenblatt et al., 2003], leading to the well-known rate-dependency of the flow parameters [Mohanty et al., 1987, Barenblatt et al., 2003], which is not captured by the commonly used two-phase extended Darcy description [Barenblatt et al., 1990a, Niessner et al., 2011].

These rapid pore-scale events are essential to the upscaling of multiphase flow because they make up a significant fraction of the energy dissipation within the system [Morrow, 1970, Seth and Morrow, 2007] and contribute to relative permeability [Niessner et al., 2011] and to macroscopic non-equilibrium effects [Barenblatt et al., 2003]. An estimate of the Helmholtz free energy balance [Morrow, 1970], $\Delta F$, of the Haines jumps, using:
\[ \Delta F = -S \Delta T - \sum_{\alpha=1}^{2} p_{\alpha} \Delta V_{\alpha} + \sigma_{1,2} \Delta A_{1,2} \] 

(4.1)

can now be made on the basis of the pressure-volume work, \(-p \Delta V\), and changes in interfacial energy, \(\sigma_{1,2} \Delta A_{1,2}\), where \(\sigma_{1,2}\) is the interfacial tension and \(\Delta A_{1,2}\) is the change in interfacial area between the two fluid phases. The reliable parameterization of this fundamental equation presents the non-trivial problem of determining the characteristic volume, \(\Delta V\), and the change in interfacial area, \(\Delta A\), of the Haines jump events. These parameters are not necessarily equal to the averages determined from the pore-size distribution because typically only fractions of the connected pore space is subject to Haines jump hysteresis.

To date, the experimental quantification of pore-scale displacement dynamics has been based on constricted glass capillaries, artificial micro-models [Lenormand et al., 1983], glass bead packs [Moebius and Or, 2012], and other model systems [Unsal et al., 2009] that allow in-situ optical access [Xu et al., 2008]. However, these systems differ from most natural systems in dimensionality [Adler, 1988], flow regime [Moebius and Or, 2012], and the degree to which displacement events contribute to energy dissipation [Morrow, 1970, Seth and Morrow, 2007]. Consequently, the contribution of pore-scale events to fluid displacement has often been underestimated. In classical pore-network modeling inspired by two-dimensional micro-models, the relative permeability, \(k_{r,\alpha}\), is computed from the connected phase flow only, which leads to notable differences from the use of direct hydrodynamic approaches [Sheng et al., 2011]. Concepts derived from these model systems may therefore not always be applicable to natural rock, in which direct optical observation of these events is not possible because of the opacity of the minerals.

An objective of these models is to predict the state of the residual non-wetting phase (“oil”) correctly, following displacement by the wetting phase (“water”) in a porous medium. To make such a prediction, it is important to know how the pressure field affects the number and sequence of non-steady pore-scale events, given an initial condition and the pore structure. However, it is not yet known whether more than one jump can take place simultaneously. Clearly, the jumping process causes an unsteady pressure field near the microscopic water/oil interface for which Darcy’s law is no longer applicable. The externally imposed displacement rate determines the number of such jumps per cross-sectional area unit and unit of time, but the ratio of the number of simultaneous to the number of successive jumps is unknown, and this is essential to provide a correct displacement length scale per unit time [Mohanty et al., 1987] and to predict the amount and structure of the residual non-wetting phase. Multiphase hydrodynamic simulations are increasingly capable of modeling relevant system sizes, and could correctly account for the discrete pore-scale event contributions, and could therefore provide a means of consistently upscaling to the macroscopic scale. There simulations require adequate direct observation experimental validation.

Three decades ago, Shell scientists adopted a medical computed tomography (CT) scanner for use with geological samples [Hurst, 1984, Vinegar and Wellington, 1987, Wellington and Vinegar, 1987]. Computed tomography techniques have gradually matured since then,
and are now capable of a spatial resolution ("µ-CT") suitable for mesh computational fluid dynamics (CFD), with the now visible complex pore space [Coles et al., 1998a, Wildenschild et al., 2001, Wildenschild et al., 2002, Sukop et al., 2008, Scheel et al., 2008, Youssef et al., 2009, Iglauer et al., 2011, Silin et al., 2011, Armstrong and Wildenschild, 2012, Myers et al., 2011, Setiawan et al., 2012]. However, the temporal resolution of µ-CT needed to be improved to visualize the relevant pore-scale processes. This work presented here makes a contribution to a key aspect of pore-scale visualization. This is the first time that pore-scale displacement events in natural sandstone have been directly visualized at a time resolution matching their actual occurrence using dynamic micro X-ray CT. This method could previously only be used at time resolutions that were some orders of magnitude too low (typical scanning times at synchrotron beamlines were of the order of one hour [Wildenschild et al., 2001] in 2001 and 5 min in 2011 [Armstrong and Wildenschild, 2012]) compared with the intervals between individual pore-scale displacements, which are in the order of seconds [DiCarlo et al., 2003], and the intrinsic time-scales for relaxation and fluid re-arrangement. Therefore the method could only be used to investigate quasi-static situations where flow had been stopped before taking a scan to avoid fluid motion and blurring effects during scanning. But after stopping flow, i.e. pressure gradients ceased, fluids had re-arranged to a static capillary equilibrium. Hence when resuming flow, pore scale fluid distributions are typically different than at the moment the flow was stopped.

Here we report for the first time dynamic imaging of pore scale displacement, by using fast synchrotron-based µ-CT [Mokso et al., 2011] different from the previously discussed quasi-static imaging, because flow, pressure gradients, and the visco-capillary balance are always maintained (also during the imaging). By comparison with pressure data which is recorded at sub-second time resolution we will demonstrate later that a temporal resolution of 10-30 s is actually sufficient for capturing pore scale fluid distributions of uninterrupted Haines jump sequences. Using this method at ms exposure time for each projection [Mokso et al., 2011] (see Materials and Methods section), we were able to create a time series of visualized individual pore filling events under drainage conditions, with oil displacing the water that was initially present in the rock, as shown in Figs. 4.1–4.3.

4.1.3 Snap-off during imbibition

Fig. 4.5 shows an example of imbibition, in which the wetting phase invades the pore space and “snaps off” [Roof, 1970], causing the non-wetting phase to form isolated clusters at narrow pore throats (rotated view Fig. 4.5-3a). This constitutes irreducible non-wetting phase saturation. The competition between the wetting water phase at the pore throats choking the oil neck and the advancing oil head menisci jumping past the pore throats tends to favor the latter at increasing imbibition rates.

4.1.4 Cooperative pore filling events

We now consider the details of the drainage process, in which the non-wetting oil, injected at a constant rate, displaces the water initially present in the rock. The injection pressure,
4.1. REAL-TIME IMAGING OF HAINES JUMPS IN POROUS MEDIA FLOW

$p$, generally increases steadily, as shown in Fig. 4.4, as a consequence of the non-wetting oil phase being forced into the water-wet rock [Lake, 1989]. However, a more detailed view shows that this continuous increase is modulated by many small non-steady fluctuations (Fig. 4.4 inset), as has already been observed in rate-dependent high-resolution mercury porosimetry [Yuan and Swanson, 1989]. This is because, once $p$ exceeds the capillary entry pressure of a pore throat (see Fig. 4.2), the accessible pore body volume, $\Delta V$, is rapidly filled [Mohanty et al., 1987, DiCarlo et al., 2003]. These pore-filling events (like in Figs. 4.1 and 4.2) can be seen as discrete (negative) pressure jumps in $p$ (note, however, that synchronization between images and pressure curves are hampered by the fact, that events documented in the pressure data may have occurred also outside of the field of view which covers only approximately one quarter of the sample). During a jump, capillary driving forces accelerate the meniscus, which is opposed by inertial forces and the viscous resistance in the bulk fluid and rough boundary layers at the pore walls. The inertial forces are initially larger than the viscous forces, i.e., the ratio of the Reynolds and the capillary number [Mohanty et al., 1987] far exceeds 1, i.e., $Re/Ca$ $\approx$ $\sigma r_p/\mu^2$ $>>$ 1. In our study $Re/Ca$ $\approx$ 2 · $10^3$ (for $r_p$ = 100 $\mu$m). So the fluid motion was capillary-inertial controlled and the jump time was estimated to be proportional to the mass of the accelerated fluid [Mohanty et al., 1987], i.e., as an order of magnitude estimate, $\Delta t \propto (r_p^3/\sigma)^{1/2} \approx$ 1 ms, which is consistent with acoustic measurements reported by DiCarlo et al. [DiCarlo et al., 2003]. From the example shown in Fig. 4.2 the rate of such a pore-filling event could be estimated as $\Delta V/\Delta t = 5.9$ nL/1 ms = 5900 nL/s, which far exceeds the feed flow rate of 5.8 nL/s. The fluid volume, $\Delta V$, required to fill a pore body is mainly supplied by fluid re-arrangement [Morrow, 1970, Yuan and Swanson, 1989] from liquid-liquid menisci in pore throats, i.e., via the relaxation from a more to a less convex shape, accompanied by a rapid decrease in (capillary) pressure, $\Delta p$, and the dissipation of (elastic) energy. Continuous injection resupplies the volume $\Delta V$, building up the liquid-liquid menisci curvature and the pressure again. Finally, the pressure exceeds its magnitude before the filling event, at which point another Haines jump occurs [Yuan and Swanson, 1989].

In this way, the irreversible instantaneous pressure jumps and overall reversible continuous increases [Morrow, 1970] allow fluid-displacement-based partitioning of the pore space [Yuan and Swanson, 1989]. Real-time imaging, however, showed that displacement-based partitioning differs from a purely geometrical definition of pore throats and pore bodies. The $\Delta V$ event size distribution for the majority of filling events involved pores that are up to a factor of ten larger than individual geometrically defined pores (using the pore size distribution from the imaging data shown in Fig. 4.4 panel 3, for comparison, the biggest pores have a radius of $\approx$ 100 $\mu$m and a volume of 14 nL). Such major filling events may therefore be seen to be cooperative, involving many individual pores. They occur frequently, rather than being exceptional, as the event size histogram in Fig. 4.4 clearly shows. The examples shown in Figs. 4.1 and 4.3, with $\Delta V = 34$ nL (including about 20 individual pores), agree with the Haines jump statistics obtained from pressure data (Fig. 4.4), making it clear that an imaging interval of a few seconds ensures that jumps are not missed. As evident from the pressure data in Fig. 4.4 which is sampled at a sub-second time resolution, pore scale displacement events occur every dozens of seconds in the whole...
sample, typically not at the exact location but at different locations at the (disperse) flow front. Therefore we found a time resolution between 10 and 30 s is actually sufficient to capture differences in fluid front configurations in dynamic flow experiments.

### 4.1.5 Energy dissipation and upscaling

In a Haines jump, the elastic energy initially contained in the liquid-liquid menisci is converted into kinetic energy, with substantial inertial contributions from the high Reynolds number [Moebius and Or, 2012], and finally dissipated. Our data (Fig. 4.4) revealed that only 39% of the displaced volume occurs through the filling of pore throats by reversible laminar flow (rison events, [Yuan and Swanson, 1989]), while 61% occurs via rapid irreversible events (subison events, [Yuan and Swanson, 1989]), which dissipated 64% of the total work of drainage, $W = \int -p dV$, confirming previous reports on Berea sandstone [Seth and Morrow, 2007].

Measurements of the external pressure, $p$, required to quantify the externally performed work, can be complemented by in-situ estimation of the phase pressures, which is feasible in principle but the method is currently still under development [Armstrong et al., 2012]. This approach also includes the disconnected non-wetting phase clusters, through the measurement of the curvature in the liquid-liquid menisci by image analysis and by calculating the pressure using the Laplace equation. Apart from the pressure-volume work, for an energy balance as formulated in Eq. 4.1, the newly created interface and the associated interfacial energy must also be considered. In the event shown in Fig. 4.2, the interfacial area, including the area where thin water films separate oil and water-wet rock, is $\Delta A_{1,2} = 5.7 \cdot 10^{-7}$ m$^2$. This corresponds to an interfacial energy, for this specific event, of 36% of the displacement pressure-volume work. The remainder is dissipated, as accounted for in Eq. 4.1 by the entropy term $-S\Delta T$. The associated increase in temperature, $\Delta T$, is small (a few mK) and is equilibrated quickly because of the relatively large heat capacities and thermal conductivities of the surrounding liquids and solids [Morrow, 1970].

Most of the approaches used to upscale from the pore to the macro scale, particularly numerical upscaling, use a volume average, but it is not clear how big the averaging volume should be, i.e., how big the two-phase representative elementary volume (REV) [Bear, 1972] is. Georgiadis et al. [Georgiadis et al., 2011a] showed (based on the discontinuous non-wetting phase cluster size distribution) that for two-phase flow the averaging volume is substantially larger than the single-phase REV. In addition to the fluid (cluster) distribution, it may be important to consider the distance over which Haines jump pressure pulses (Fig. 4.4) can propagate, and over what volume they can be averaged, that the macroscopic two-phase properties (evaluated using the average pressure drop) are independent on averaging volume.

Niessner et al. [Niessner et al., 2011] have shown that pore scale dissipative displacement events are important contributors to macroscopic transport coefficients, leading to rate dependency. By following an argument based on reversibility and dissipation of drainage work in the framework of a thermodynamically based approach [Hassanizadeh and Gray, 1993], it has been shown that relative permeability in the traditional two-phase Darcy
formulation [Lake, 1989] has contributions originating from hydraulic conductivity and from dissipative pore-scale events. This leads to a saturation gradient and, implicitly, a rate dependency for the relative permeability [Niessner et al., 2011], which has been observed many times (e.g., [Boom et al., 1995]). The consequence of this is that commonly used steady-state (no saturation gradient) and unsteady-state (large saturation gradient caused by the Buckley-Leverett shock front [Buckley and Leverett, 1942]) techniques for measuring relative permeability give different results (e.g., [Tsakiroglou et al., 2004]).

### 4.1.6 Methods and materials

A cylindrical sample of Berea sandstone [Churcher et al., 1991] (4 mm diameter and 10 mm length, approximately three times the representative elementary volume REV [Bear, 1972], with open porosity $\approx 19.9\%$ and permeability $\approx 700$ mD = $0.7 \mu m^2$ measured on a twin sample) was tightly fitted inside a polycarbonate cylinder and initially saturated with water (with 40 wt-% of CsCl, to increase the X-ray contrast) with a free water level 1 mm above the top of the sample. A micro piston-pump integrated into the sample holder (our own design) is the key to conducting experiments without displacement artifacts caused by the bending of external flow lines during rotation during X-ray tomography or when opening and closing of the valves. For drainage experiments, n-decane was injected from bottom to top at a constant flow rate of $0.35 \mu l/min$, corresponding to a linear flow velocity of $1.54 \mu m/s$ (0.4 ft/day) and a (microscopic) capillary number, $Ca$, of $4 \cdot 10^{-8}$ (at an interfacial tension of 35 mN/m determined by the pendant drop method), which is representative of typical (field-relevant) visco-capillary flow regimes [Lake, 1989]. A piezoresistive miniature pressure sensor (Keller 2Mi, Keller AG für Druckmesstechnik, Winterthur, Switzerland) recorded the injection pressure (at a rate of 3 Hz), which for the open outlet configuration, approximately corresponded to the pressure drop over the sample plus the ambient pressure. The X-ray tomography experiments were performed at the TOMCAT beamline at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland. The sample was exposed to a parallel beam of monochromatic synchrotron X-ray radiation at 21.25 keV. The transmitted X-rays were converted into visible light by a 100 $\mu m$ thick cerium-doped lutetium aluminum garnet (LAG) scintillator and projected at $3.7 \times$ magnification onto a high-speed CMOS camera (PCO dimax, PCO AG, Kelheim, Germany) with 1440 $\times$ 896 pixels, leading to an effective voxel width of 3 $\mu m$ and a field of view covering approximately a quarter of the sample, starting at 2 mm from the bottom of the sample. A sample–detector distance of 80 mm gave a small amount of edge-enhancement in the images. Each tomogram was computed from 1401 projections (12 ms exposure time) over $180^\circ$ rotation (leading to a total acquisition time of 16.8 s) by a gridded Fourier transform-based reconstruction-algorithm [Marone et al., 2008] with a Parzen filter. The projections for seven tomograms were recorded in series, limited only by the camera memory (36 GB). The reconstructed volumes were filtered with a $3 \times 3 \times 3$ median filter, segmented with local connectivity-based thresholding, and further processed and visualized using Avizo (Visualization Sciences Group, Mérignac, France). The pore size distribution was determined with GeoDict (Fraunhofer ITWM, Kaiserslautern, Germany), using a maximum sphere
algorithm. The pressure data were analyzed using Matlab (MathWorks Inc., Natick, MA, USA).

Overall 4 experiments were performed which showed similar behavior, and in each experiment events of comparable magnitude were similar, but only the data with best quality after image processing has been selected for this publication.

4.2 Non-wetting-phase cluster-size distribution

We investigated the size and length distribution of the non-wetting phase residual clusters in a sintered glass-bead porous medium at two-phase flow conditions, by means of micro-CT imaging with pore scale resolution. Cluster size distribution functions and cluster volumes were obtained by image analysis for a range of injected pore volumes under both imbibition and drainage conditions; the field of view was larger than the porosity-based representative elementary volume (REV). We did not attempt to make a definition for a two-phase REV
Figure 4.2: Images (1) and (2): Oil filling event in a single pore during drainage, with $\Delta V = 5.9 \text{ nL}$ (subset of Fig. 4.1, transition from time step 2 to 3). Image (3): A cross-section at the toroidal pore throat with the water wetting films and the oil neck after the transition from step (1) to (2). The rough wall causes draping menisci (collars not visible because of remaining spatial resolution limitations) essential for the presence of pressure connections for the wetting water.
but used the non-wetting phase cluster size distribution as an indicator. Most of the non-wetting phase total volume was found to be contained in clusters that were one to two orders of magnitude larger than the porosity-based REV. The largest observed clusters in fact ranged in volume from 65% to 99% of the entire non-wetting phase in the field of view. As a consequence, the largest clusters observed were statistically not represented, and were smaller than the estimated maximum cluster length. The results indicate that the two-phase REV is larger than the field of view attainable by micro CT scanning, at a resolution which allows for the accurate determination of cluster connectivity.

4.2.1 Introduction

Multiphase flow in porous media is highly relevant to geology, hydro-geology, and petroleum engineering disciplines. This is usually described on a macroscopic level with continuum mechanics approaches, which are often based on empirical observations such as the two-phase extension of Darcy’s law [Darcy, 1856, Hassanizadeh and Gray, 1993, Kalaydjian, 1987, Bear, 1972, Lake, 1989], which lacks a fundamental basis [Niessner et al., 2011]. Most approaches in porous media flow depend on indirect and/or macroscopic observations. These macroscopic flow properties, however, are ultimately defined by microscopic processes, i.e. fluid flow at the pore scale (see e.g. [Das and Hassanizadeh, 2005]). There is therefore significant interest in the direct observation of the pore scale fluid behavior, aimed at determining how macroscopic properties depend on the pore scale distribution of the associated fluid phases, and defining a representative elementary volume (REV) for two-phase flow, important for numerical simulations and experimental imaging techniques.
Figure 4.4: Image (1): Pressure drop, $p$, for a sequence of seven scans showing individual pore-filling events (entire drainage experiment in inset). Image (2): $\Delta p$ and $\Delta V$ size distributions, with an inset showing the pore size distribution (PSD).
Figure 4.5: Sequence of snap-off events (time steps (1)-(3)) during imbibition ($\Delta t = 16.8$ s) occurring at the narrowest pore throats (red arrows) leading to the trapping of oil (rotated view 3a, blue arrow).
4.2. NON-WETTING-PHASE CLUSTER-SIZE DISTRIBUTION

Over the past decade, µCT (synchrotron-based and bench-top instruments) has become a frequently used technique to study porous media and geological samples [Spanne et al., 1994, Coenen et al., 2004, Olafuyi et al., 2006, Berg et al., 2013b]. Together with nuclear resonance (MRI) and acoustic techniques, X-ray based tomography is one of the few non-destructive techniques that give detailed insight into the structure of porous media over length-scales ranging down to a few hundred nanometers [Feser et al., 2008, Sisk et al., 2010]. The resolution of MRI depends primarily on the strength of the applied magnetic field gradient and can theoretically be increased to the wave length of the scattering vector. Currently, the MRI voxel resolution is limited to around $0.05 \times 0.05 \times 1 \text{ mm}$, which is not sufficient to image on a pore scale. At the pore scale, µCT images of real rocks have been used to construct 3D networks for modeling of fluid flow by pore-network modeling [Blunt et al., 2002], but also for direct modeling of fluid flow in the pore space, by e.g. Lattice Boltzmann [Okabe and Blunt, 2004] or Stokes flow [Mostaghimi et al., 2010] methods.

A fundamental understanding of fluid flow in porous media, and the verification of pore scale modeling, however, requires direct observation of different fluid phases in the pore space. Currently, the state of the art method is imaging of static fluid distributions at pore scale, which is not entirely new. The study by Coles et al. [Coles et al., 1998a, Coles et al., 1998b] in 1998 combined synchrotron-based pore scale imaging of oil and water, coupled to numerical simulations with a Lattice Boltzmann code. Since 1998, a rapid development in micro computed tomography has made the quality and spatial resolution of the 1998 synchrotron’s capabilities currently available for laboratory use with bench-top µCT scanners.

Youssef et al. [Youssef et al., 2009, Youssef et al., 2010] conducted a µCT study on Fontainebleau sandstone at spatial resolutions of 10 and 5 µm while conducting a two-phase flow experiment. The trapped non-wetting phase distribution was imaged as a function of interfacial tension. The observation represents capillary desaturation, i.e. the decrease of the residual non-wetting phase saturation with increasing capillary number ($Ca > 10^{-5}$), which is the principle often employed in enhanced oil recovery (EOR) processes. Somewhat similar studies were conducted by the ANU group [Kumar et al., 2009a, Kumar et al., 2009b], who investigated the spatial distribution of a residual gas phase in Fontainebleau sandstone, and by Iglauer et al. [Iglauer et al., 2010] who studied Clashach and Doddington sandstones, following an oil-brine drainage-imbibition sequence. The observations were similar, and qualitatively confirm earlier observations in 2D micromodels [Avraam and Payntakes, 1995] showing that over substantial saturation ranges, the non-wetting phase does not flow as a continuous phase, but as ganglia. The size distribution functions show that these ganglia are not restricted to the pore scale but can extend over many pores ranging up to the length-scale of the sample. This is an interesting finding, in particular relating to the fundamental concept of the representative elementary volume (REV) as introduced by J. Bear in 1972 [Bear, 1972] (see also [Nordahl and Ringrose, 2008]). In porous media flow, the transition from pore scale physics to continuum mechanics is performed by averaging over an REV. This concept is based on the observation that in homogeneous rocks, at a certain length-scale and above, average properties such as the porosity of a sample become independent of the averaging volume. While this concept may apply in single-phase flow,
it is not clear if it holds for multiphase flow, as clusters may span over many length-scales.

Interfacial properties of fluids in porous media flow largely determine macroscopic properties; their effect is commonly not taken into account explicitly, but lumped together with other pore scale properties. Recent work on linking between pore- and core-scale observations [Porter et al., 2010, Wildenschild et al., 2011, Armstrong et al., 2012] indicates that advances in imaging techniques and analysis allows for explicit accounting of local pore scale such effects.

In the present study we investigated the development of \( n \)-decane clusters in a glass-bead porous medium by means of \( \mu \)CT imaging with pore scale resolution. We obtained cluster size distribution functions and cluster volumes by image analysis, for a range of injected pore volumes, under both imbibition and drainage conditions; the field of view was larger than the porosity-based REV. Porous glass was used as a model rock with well-defined surface properties and suitable pore size for \( \mu \)CT imaging. \( n \)-decane was used as a model for the non-wetting phase, and the \( n \)-decane-brine interfacial tension \( \gamma \) was varied by surfactant addition over a range of values representative for \( \text{CO}_2 \)-brine systems [Georgiadis et al., 2010a, Georgiadis et al., 2010b, Georgiadis et al., 2011b, Li et al., 2012a, Li et al., 2012b]. The focus of the study was the detailed cluster analysis and the comparison of single-phase REV with the characteristic cluster dimension and saturation distribution in both drainage and imbibition.
4.2. NON-WETTING-PHASE CLUSTER-SIZE DISTRIBUTION

4.2.2 Materials and methods

Porous medium and \( \mu \)CT imaging

The flow experiments were carried out using a sintered glass-bead sample (core) with 10 mm diameter and a length of 20 mm. The porosity and permeability of the sample was experimentally determined at \( \phi = 0.318 \) and \( K = 20 - 24 \) D, respectively. We embedded the core in a polycarbonate core holder by a shrinking process for a tight fit to avoid fluid bypassing. A vertical flow geometry was used with fluid injection from top to bottom. The fluids were injected by means of two high-precision displacement pumps (Quizix), one dedicated to the \( n \)-decane and the other to the brine phase. The connections from the injection pumps to the core holder and the production vessel were made of flexible PTFE tubing allowing a full 360° rotation of the core as necessary for the tomographic scans. All wetted parts were thoroughly cleaned by sonication in isopropanol (purity > 99.5 %) to guarantee well defined interfacial properties during the experiments.

The core holder was placed in a \( \mu \)CT scanner (ProCon X-Ray) for in-situ imaging of the pore space and the fluid distribution in the pores during the core flood. The scanner was operated at 100 kV and 60 \( \mu \)A, which gave a good contrast between the fluids and porous medium of the given relatively large sample size. We performed \( \mu \)CT scans at a resolution of 4.2 \( \mu \)m (voxel size) for characterization of the pore space and at 11.5 \( \mu \)m during two-phase flow experiments. Fig. 4.6 shows a high-resolution \( \mu \)CT cross section of the porous glass sample on the left. At 4.2 \( \mu \)m resolution the grain and pore space are resolved in great detail. This detail is lost by increasing the voxel size to 11.5 \( \mu \)m, but a larger field of view is gained, which is essential for two-phase flow experiments as will be discussed further in the following section. The compromise between high spatial resolution and large field of view is adjusted as long as the ability to determine whether the pore space or fluid clusters are connected or not is maintained, information which is used in the present study.

**Figure 4.7:** High resolution image of the porous glass sample (left) and the respective pore space (right) rendered with Avizo®.
A 3D sub volume of the porous glass at high resolution (left side) and the extracted pore space (right side) are shown in Fig. 4.7; individual pores are colored differently. In further characterizing the porous medium, and subsequently the fluid distribution in the pore space, several steps of data analysis were involved. In general the following steps were required: reconstruction of the tomographic image, image filtering, segmentation of pore space and fluid phases, skeletonization, and network extraction or statistical cluster analysis. Depending on the experiment and application, not all steps are required. For the high resolution scan of the present study the pore space was segmented by a water shading algorithm (Avizo®). For the flooding-resolution scans the raw images acquired were filtered by an FFT bandpass filter, and segmented by thresholding using Li’s method (ImageJ) as further outlined below.

In Fig. 4.8 the pore radius distribution (computed with the Avizo® XSkeleton package, which is a skeletonization package that uses an Euclidean distance map and thinning) as extracted from the flooding-, and the high-resolution scans of the dry sample are displayed. The distributions are quite similar, with the flooding-resolution distribution being slightly broader, validating the workflow (scan settings and image analysis) for the flooding-resolution scans.

Based on the segmented pore space, we estimated the permeability using a single-phase flow numerical simulation, and compared the results to the experimentally determined permeability. We computed the apparent permeability (Avizo® plugin) by simulating a flow experiment in a specific spatial direction by attaching inlet and outlet distribution elements. The simulation used a finite volume scheme to simulate Stokes flow and was performed on the segmented pore structure on a length-scale larger than the porosity-
Figure 4.9: Snapshot of a single-phase stokes flow simulation in a segmented volume larger than the single-phase REV. Red lines represent the flow lines. The injection is from right to left.
CHAPTER 4. PORE-SCALE PROCESSES

Figure 4.10: Upper row: \( \mu \)CT cross section in the dry state (flooding-resolution, under vacuum) Lower row: \( \mu \)CT cross section of the sample saturated with \( n \)-decane-brine (same slice). From left to right: raw images, images after FFT filtering and images after segmentation. In the upper right, segmented images of the pore space and the fluid phase are superimposed. The lower right image shows the 3D visualization of the fluid phases: brine in blue and \( n \)-decane in white

based REV (discussed below). A snapshot of the simulation is displayed in Fig. 4.9 where the flow was from right to left, by applying a pressure drop of 0.3 bar, and using a fluid of 1 cP viscosity. The apparent permeability was computed at 15.5 D, which is in the same permeability range as, and hence in agreement with, the experimental results of \( K = 20 - 24 \) D, measured on larger samples. Potential reasons for the difference between simulated and experimental values could be sample heterogeneity – medical CT scans of the sintered glass-bead showed porosity variations in the order of 10–20 % on a larger length-scale, which can lead to a large permeability variation at the smaller length-scale. This would be in addition to uncertainties in the image analysis, e.g. filtering and thresholding.

Two-phase flow experiments

During the core flood experiments, non-wetting and wetting fluid phases were injected in different sequences. \( n \)-decane (purity > 99 %) was used as the non-wetting phase. The aqueous phase (wetting phase) used was de-mineralized water with 4 wt-% CsCl (purity > 99 %) doping for enhancing the fluid-fluid \( \mu \)CT contrast. The surfactant docecyl trimethyl ammonium bromide (DTAB, purity > 99 %) was introduced into the aqueous phase for selected experiments at concentrations ranging both above and below the critical micelle concentration. The addition of DTAB allowed a lowering of the interfacial tension, repre-
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Figure 4.11: 3D fluid saturations during drainage. The images are recorded with 11.5 $\mu$m/voxel. The length of the base line corresponds to 7.6 mm. Clearly visible is the growth of the $n$-decane clusters (white). The image on the top right shows the $n$-decane clusters individually colored after injection of 1 PV $n$-decane (the image is rotated with respect to the image on the left).

Senting changes equivalent to those that would occur in the CO$_2$-brine system over different thermodynamic conditions [Georgiadis et al., 2010b, Georgiadis et al., 2010a, Georgiadis et al., 2011a, Li et al., 2012a, Li et al., 2012b], but without influencing other fluid properties such as density and viscosity. The $n$-decane-DTAB-brine interfacial tension was measured using the du Nouy Ring method.

Prior to every experiment, the glass-bead core was cleaned by flooding at least 200 PV (pore volumes) of isopropanol, and was subsequently dried under vacuum. Before fluid injection, the core was scanned in a dry state. Subsequently, the sample was saturated with brine and/or $n$-decane under initial vacuum condition and finally flooded at 0.5 MPa pore pressure. All ensuing flooding experiments were performed at a constant flow rate of 1 ml/min, with a back pressure of 0.2 MPa. During the $\mu$CT scans injection was ceased and the inlet and outlet valves were closed. $\mu$CT scans at three different positions along the core were then conducted, each requiring approximately 20 min to complete. Following the completion of the scans for all three positions, injection continued until a different PV value was obtained and $\mu$CT scans were repeated.
4.2.3 Experimental results

Image processing

During the core flood experiments, \( \mu \)CT scans were recorded at flooding-resolution. The raw images acquired were filtered to reduce noise and then segmented to extract the pore space and fluid saturation. The data processing steps are shown in Fig. 4.10. The upper row shows a \( \mu \)CT cross section of the sample under vacuum; from left to right: raw image, FFT filtered image with the upper and lower threshold being set at 5 and 640 voxels, respectively, and image segmented by Li thresholding using ImageJ. The 3D pore space was derived from the segmented vacuum data sets, giving a porosity of 0.327, which is in good agreement with the experimentally measured porosity of 0.318. This, together with the well reproduced permeability and pore radius distribution (as discussed above), validated the image filtering and thresholding applied. The lower row of Fig. 4.10 shows the same cross section after injection of 1 PV of \( n \)-decane in the initially brine-saturated sample (primary drainage). To achieve a good X-ray contrast, the brine phase was doped with CsCl at a concentration where the contrast between glass-beads and brine is minimized, achieving a clear contrast between the glass-brine initial system and the injected \( n \)-decane system. As a consequence, the non-wetting phase volume can be directly derived by segmentation with a single threshold. The non-wetting phase clusters in this work were all derived from the segmentation of the \( \mu \)CT data taken at the respective saturation states. The cross section of the pore space combined with the extracted non-wetting phase distribution and a 3D representation of both fluid phases (with the porous medium being transparent) are shown in the rightmost images in Fig. 4.10.

Cluster analysis

A range of flooding experiments were conducted by varying (a) the flooding sequence to establish the initial saturation and (b) the concentration of DTAB to adjust the interfacial tension corresponding to capillary numbers (\( Ca \)) ranging from \( 10^{-5} \) to \( 10^{-4} \). The non-wetting phase saturations obtained for different capillary numbers are within a range in which the residual saturation starts to become a function of \( Ca \) (see capillary de-saturation curve [Lake, 1989]).

For the experiments I (\( \gamma = 50.5 \) mN/m), IV (\( \gamma = 8.6 \) mN/m) and VI (\( \gamma = 27.2 \) mN/m) the core was pre-saturated with brine and subsequently drained with 200 PV \( n \)-decane (primary drainage) before the imbibition was started. In experiments II (\( \gamma = 50.5 \) mN/m), III (\( \gamma = 8.6 \) mN/m) and V (\( \gamma = 27.2 \) mN/m) the sample was initially pre-saturated with \( n \)-decane and brine was injected thereafter. \( \mu \)CT scans were taken from the respective initial state and after injection of volumes as indicated in the respective Figures (in PV).

In Fig. 4.11, the 3D fluid distribution derived from the segmented images during drainage is shown. The brine is displayed in blue and the \( n \)-decane in white, showing the growth of the \( n \)-decane clusters as a function of injected volume. The flow direction is from top to bottom. After the injection of 1 PV, clusters of different sizes spanning across multiple pores are clearly visible. The image on the right shows the same distribution,
Figure 4.12: Top: Normalized volume distribution of the non-wetting phase ($n$-decane) clusters. Bottom: Pore radius distribution compared to the cluster length distribution. Data of different pore volumes of injected $n$-decane during drainage and imbibition are plotted.
but with the individual clusters colored differently, visualizing clusters of different sizes (rotated view). The larger clusters show a disk-like shape with the truncated length along the flow direction. The continued injection leads to a clear increase of \textit{n}-decane saturation.

Of particular interest is the size and the volume of the various trapped clusters. Their volume and length distributions are shown in Fig. 4.12 on a double logarithmic scale. The cluster volume distribution shows more scatter than the length distribution, following a power-law behavior in accordance with invasion percolation theory \cite{Wilkinson_1986, Blunt_1992} given by the form

\[ N(s) \propto s^{-\tau}, \quad (4.2) \]

where \( N(s) \) is the number frequency of cluster size \( s \). An exponent \( \tau = 2.189 \) has been found by Monte Carlo simulation on different lattices \cite{Lorenz_and_Ziff_1998}, which best agrees with most of the cluster size distribution obtained. Deviation from the power-law behavior were observed for large clusters, a fact associated with clusters growing at values away from the percolation threshold \cite{Lorenz_and_Ziff_1998}. A power-law with exponent \( \tau = 2.189 \) is also plotted in Fig. 4.12 showing agreement with the results obtained in the present study, but also the range where the larger cluster distribution deviates. Comparable observations were made by Iglauer et al., who obtained an exponent \( \tau = 2.05 \) for \((n\text{-octane + brine})\) system in water-wet sandstone \cite{Iglauer_et_al_2010}, and \( \tau = 2.12 \) for \((n\text{-decane + brine})\) system in oil-wet sandstone \cite{Iglauer_et_al_2012}. Pentland et al. \cite{Pentland_et_al_2012} found exponents ranging from (2.004 to 2.0137) for CO\textsubscript{2} trapped phases in brine-saturated glass- and sand-packs, at reservoir conditions. It should be noted that the total volume of the largest clusters may be underestimated due to possible truncation associated with field of view limitations.

The cluster length distribution, shown in the lower part of Fig. 4.12, corresponds to the diagonal length of the cluster bounding box. The data appear less scattered than the volume distribution, and both show characteristics of a power-law behavior. In order to put the cluster lengths into perspective, the pore radius distribution and the single-phase porosity-based REV are also displayed. Even the smaller clusters are clearly dispersed over several pore lengths, and apparently there are clusters extending even far beyond the porosity-based REV, which raises the question about the two-phase flow; an inherent attribute of the micro-CT analysis arises from the fact that the REV for two-phase flow is larger than the field of view (see discussion in Sections C and E).

Fig. 4.12 clearly shows that the cluster size does show a power-law distribution only for the smaller clusters but deviates from the power-law distribution at larger cluster sizes. Since data for a larger field of view are inaccessible without losing resolution (required to determine the connectivity of clusters), we can only speculate whether for a larger field of view the power-law range would increase or even span the whole dynamic range and thus indicate a two-phase REV. Instead we rather concentrate on some implications on the non-power-law tail of the cluster size distribution and the computation of the power-law exponent. Since \( N(s) \) displayed in Fig. 4.12 spans more than three orders of magnitude, in a power-law fit the much larger \( N(s) \) for the smaller \( s \) would have a much higher weight.
Figure 4.13: Normalized cluster-volume (top), and cumulative distribution (bottom) for different regions of interest. Computed exponent $\tau = 2.10$ (thick red line) derived by maximum likelihood (max. L.) estimator for power-law determination using the Matlab® script from [Clauset et al., 2009, Virkar and Clauset, 2012].
in a least square fit. Therefore, commonly the $M(s)$ distribution, given by the form

\[ M(s) = \sum_{s' = s}^{\infty} s'N(s') \propto s^{2-\tau}, \]  

(4.3)

is used [Iglauer et al., 2010] because $M(s)$ varies by less than one order of magnitude. Computing the $M(s)$ according to Equation 4.3, however, implicitly assumes that $N(s)$ has the form of a power-law distribution over the whole range, which is not the case. When computing the $M(s)$ the sum also includes the non-power-law tail with a non-negligible weight. That is illustrated for one data set taken as example (1 PV, drainage) displayed in Fig. 4.13. In the top panel we show the $N(s)$ distribution, and a power-law superimposed at an exponent of $\tau = 1.95$ that visually fits the data over the largest range. The $M(s)$ distribution computed over the whole range displayed in the bottom panel is well fitted with an exponent of $\tau = 2.23$, which is still compatible with the $N(s)$ data but not an optimum fit any more. Truncating the $N(s)$ distribution when computing the $M(s)$, cutting off the non-power-law tail (vertical line in top panel), leads then to a very different $M(s)$ fitted with $\tau = 2.34$, which clearly shows that the non-power-law tail has a large influence on the $M(s)$ and the fitting exponent. It therefore becomes questionable whether fitting the $M(s)$ for a distribution with non-power-law tails leads to reliable results.

Apart from that, already the binning when computing the $N(s)$ histogram has an influence on the power-law exponent. The maximum likelihood estimator [Clauset et al., 2009, Virkar and Clauset, 2012] is a direct method that does not rely on binning or the computation of $N(s)$ and $M(s)$. The associated power-law computed using the Matlab®
4.2. NON-WETTING-PHASE CLUSTER-SIZE DISTRIBUTION

script from [Clauset et al., 2009, Virkar and Clauset, 2012] for the cumulative distribution $M(s)$ displayed in Fig. 4.13 is shown with a red continuous line. The power-law exponent estimated in this way is $\tau = 2.10$, which shows very good agreement with the data. We performed this data analysis for all data sets in our study and display the resulting exponents in Fig. 4.14. The exponents obtained had a standard deviation of 0.11, which is in the same range as the exponents between 1.95 and 2.2. All are somewhat compatible with the $N(s)$ data in Fig. 4.13 and present an estimate of the uncertainty in the data. Within this uncertainty, no clear trends are visible and overall the data is, within its uncertainty, compatible with a percolation model that predicts exponents of $\tau = 2.189$.

In Fig. 4.15 the volume of the largest cluster is plotted versus the total non-wetting phase saturation. For both drainage and imbibition, the data follow a similar trend. The volume of the largest cluster grows monotonically with the non-wetting phase saturation and shows relative values between 65 to 99%, i.e. the majority of the non-wetting phase is contained in the largest cluster, in agreement with similar findings in the literature [Prodanovic et al., 2006, Prodanovic et al., 2007]. This is significant as the largest clusters in a porous medium bear the highest potential of being mobilised. Induced pressure gradients created by viscous forces during flow will act along the length of a large cluster more effectively compared to smaller ones, thus potentially rendering more mobile the majority of the non-wetting trapped phase. The lower graph of Fig. 4.15 shows the behavior of the six largest clusters in drainage and imbibition as a function of the non-wetting phase saturation. When the non-wetting phase saturation is increased (drainage), the largest cluster grows at the expense of smaller clusters. A similar behavior, but in the reverse direction, is observed during imbibition. When the non-wetting phase saturation is decreased (imbibition), the largest cluster breaks apart and fragments into smaller clusters.

Cluster length estimation from Ca

In the course of this study we observed clusters with lengths over the range of several millimeters, i.e. range of the dimension of the experiment (10 mm). An interesting question is whether or not the observed cutoff is a property of the finite size of the experiment (sample and field of view), as we would expect for a true power-law behavior suggesting clusters on all length-scales, or whether there is a maximum cluster size that cannot be exceeded independent of the size of the experiment. Both cases lead to a dilemma, since a further increase of sample and field of view would lead to a decrease of CT resolution, and consequently to the inability to decide whether an observed cluster is actually connected or not.

According to Hilfer & ren [Hilfer and Øren, 1996], a maximum cluster length can be estimated via the macroscopic capillary number $Ca$, defined as the ratio between the viscous $F_{visc} = A_{cl} \Delta P = A_{cl} l_{cl} \mu_w \nu_{Darcy} / K$ and capillary $F_{cap} = A_{cl} P_b$ forces, given by the form

$$ Ca = \frac{l_{cl} \mu_w \nu_{Darcy}}{KP_b}, $$

(4.4)
Figure 4.15: Cluster volume development during drainage and imbibition. Top: volume of the largest $n$-decane cluster over the total $n$-decane volume in the field of view. Bottom: length of the 6 largest clusters as a function of brine saturation for different drainage and imbibition cycles.
where $A_{cl}$ is the cluster cross-sectional area, $l_{cl}$ the cluster length along the viscous pressure drop, $K$ the permeability, $\mu_w$ the viscosity of the aqueous phase, $\nu_{Darcy}$ the Darcy velocity, and $P_b$ the breakthrough pressure from the capillary pressure curve, defined as $P_b = P_c(S_w = S_b)$. Unlike the microscopic capillary number, $Ca$ depends explicitly on the length-scale, i.e. on the cluster size. For a mobile cluster the viscous forces would overcome capillary forces, thus $Ca \geq 1$. By rearranging the terms in this inequality the maximum cluster length $l_{cl,max}$ may be determined by the form

$$l_{cl,max} \leq \frac{P_b K}{\mu_w \nu_{Darcy}}. \quad (4.5)$$

The maximum cluster size is estimated to be in the order of 0.2 m and thus one order of magnitude larger than the total size of the experiment for this specific porous medium, i.e. the larger clusters are likely to be truncated by the size of the experiment.

**Representative elementary volume**

As illustrated in Fig. 4.12 and Fig. 4.15, there are only few large non-wetting phase clusters in the field of view with a size in the order of the experimental dimensions (or even larger). This fact raises immediately the question of how representative this particular field of view is for the representation of a two-phase system. In Fig. 4.16, the porosity and the total non-wetting phase saturation are shown as a function of the averaging window. The porosity data indicate an REV around 2–3 mm (the high resolution scan gives about 2 mm), but at this length-scale the saturation still increases substantially, indicating that a two-phase REV is substantially larger – also consistent with the observations in Sec. 4.2.3 and 4.2.3.
This is best illustrated in Fig. 4.11, where the non-wetting phase saturation is obviously determined by only a few large clusters in the field of view. Since we have established from the porosity that our field of view covered more than twice the length of the REV, we should be able to take 8 subsamples and find the same saturation value. But as is obvious from Fig. 4.11, this depends entirely on the sampling. For 5 PV injected, for instance, when a sample cube with half length from the upper left corner at the front is selected, a high non-wetting phase saturation is obtained. However, if the same volume is sampled from the upper right corner at the back, a very low non-wetting phase saturation is found, which is reflected in the increase of the saturation in Fig. 4.16 beyond the porosity-based REV. While the porosity becomes almost constant for averaging windows that are approximately half the field of view, the saturation still shows a large variation. This means in practice that a two-phase REV can be much larger than a single-phase porosity-based REV.

This links to the observed cluster size distribution both in this work (Fig. 4.12, 4.13) and in the literature [Wilkinson, 1986, Blunt et al., 1992, Iglauer et al., 2010, Iglauer et al., 2012, Pentland et al., 2012] with regard to the apparent power-law distribution and the non-power-law tail for large clusters. According to a power-law distribution of cluster number $N(s) \propto s^{-\tau}$, it should follow that the cluster volume must scale as $sN(s) \propto s^{1-\tau}$. This means that the volume fraction of the largest clusters ($s \to \infty$) should vanish ($s^{1-\tau} \to 0$) for percolation exponents \( \tau \). In other words, even though percolation does not provide an upper bound for large clusters, a two-phase REV may still be defined due to the ever-insignificant contribution of large clusters to saturation, should a power-law hold throughout [Blunt, 2013]. Yet observed cluster size distributions with non-power-law tails are found in porous media flow, which further appear to depend on the morphology of the pore space; media with low pore-throat/pore-body aspect ratios seem to have more clear non-power-law tails than sandstone rock [Blunt, 2013], as seen in the present work. This signifies that large clusters become significant and do in fact affect the two-phase REV.

**Influence of surfactant**

For some experiments we added surfactant (DTAB) to the brine phase in order to reduce the interfacial tension and as a consequence to increase the capillary number $Ca$. $Ca$ has been varied from $10^{-5}$ to $10^{-4}$ over the range of capillary de-saturation. The capillary de-saturation curve [Lake, 1989] as well as the experimental non-wetting phase saturations after 1, 5 and 30 PV of brine imbibition are plotted in Fig. 4.17. The data are from two types of experiment, the first starting at initial brine saturation followed by a primary drainage of 200 PV $n$-decane and a subsequent imbibition process, and the second starting at a 100% $n$-decane saturated core (no initial brine) followed by brine imbibition.

The non-wetting phase saturations for the two different initial states show a similar behavior and follow approximately the trend of the capillary de-saturation curve. The absolute saturation of the brine – $n$-decane pre-saturated experiments tended however to be larger, compatible with the de-saturation curve scaled by a factor of $5/3$. The absolute observed non-wetting phase saturation might be a property of the individual sample and the finite volume injected, i.e. true residual saturation is not yet reached.
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Figure 4.17: Influence of interfacial tension on the total non-wetting phase saturation after imbibition of 1, 5 and 30 PV. The data is plotted as a function of the capillary number varied by the interfacial tension between both fluid phases. The red and black symbols represent different flooding sequences: black circles: n-decane (pre-saturation) – brine, red squares: brine (pre-saturation) – n-decane – brine. The capillary de-saturation curve (black) [Lake, 1989] and the same curve scales (red) are plotted for comparison.

The data of the individual experiments show a large scatter which only is partly related to the additional displacement by the injection of more brine. The scatter could be mainly related to the fact that the field of view is not sufficient to measure macroscopic saturations (see REV discussion in the section below). The total measured saturation depends on whether the large clusters have moved into or out of the field of view in the specific measurement.

4.2.4 Summary and Conclusions

We performed two-phase flow experiments in a porous medium to investigate the non-wetting phase distribution during drainage and imbibition on the pore scale. The distribution was imaged by in-situ μCT scanning with a pore scale resolution and a maximized field of view. Large non-wetting phase clusters have been observed, dispersed from the size of a single pore to the size of several hundred pore volumes and pore lengths. The maximum cluster size has been estimated to be much larger than the obtainable field of view, compatible with the experimental data. The cluster size distribution shows a signature of a power-law behavior between 10 and 100 μm with an experimental cutoff thereafter. The consequence of the experimental cutoff is that the largest clusters are statistically not well represented, which is a principal problem. However, the largest clusters contain the majority of the total non-wetting phase, with the volume of the largest cluster observed varying from 65% up to 99% of the total non-wetting phase volume. This seems to be
currently a limitation of $\mu$CT scanning, which is the preferred if not only method to image fluid distributions in 3D porous media; physically relevant clusters are only deficiently represented, while clusters that are statistically well represented are physically less relevant. The question of what constitutes a representative elementary volume of two-phase flow is not only relevant for the scale of experiment and imaging, but also for numerical modeling of pore scale processes, since the respective volumes at a sufficient resolution require a yet/not always feasible computational power.

4.3 Critical capillary number

For subsurface flow, the correct definition for the balance of viscous and capillary forces, the so-called capillary number ($Ca$), which predicts the mobilization of nonwetting phase, has been a long-standing controversy. The most common microscopic definition results in nonwetting phase mobilization at $Ca \sim 10^{-5}$, which is counterintuitive. Rather, mobilization should occur at $Ca \geq 1$. As demonstrated herein, by using fast synchrotron-based X-ray computed microtomography and averaging of thereby accessible pore-scale parameters to macroscale values, a macroscale $Ca$ definition is validated and shown to correctly describe mobilization at $Ca \sim 1$. The presented methodology provides a connection between desaturation and pore-scale fluid topology and gives insight into when and how $Ca$ changes with system size. The broader implication implies that it makes a difference whether desaturation is driven by an increase in flow rate or viscosity or decrease in interfacial tension since $Ca$ incorporates nonwetting phase cluster length, which is process-dependent.

4.3.1 Introduction

The macroscopic flow of immiscible phases in porous rock is determined by complex microscopic processes where, over large saturation ranges, the displacement of the nonwetting phase (typically air, a contaminant phase, crude oil, natural gas, or CO$_2$) is governed by the dynamics of individual disconnected ganglia at the interplay between capillary and viscous forces [Avraam and Payatakes, 1995]. The reduction of nonwetting phase saturation (desaturation) where capillary-trapped nonwetting phase is mobilized by either an increase in viscous forces or reduction in capillary forces is a typical application in contaminant hydrology, and the production of oil and gas has been studied extensively since the 1970s (e.g. [Täber, 1969, Yadav and Mason, 1983, Chatzis et al., 1983]) and more recently (e.g. [Prodanovic et al., 2007]). At the microscopic or pore-scale, where fluid topology is explicitly resolved, a balance of viscous to capillary forces (referred to as capillary number, $Ca$) can be derived from the fundamental equations of motion. However, the appropriate formulation of these forces at the macroscale is unclear since complex pore-scale fluid topologies are not resolved on the macroscale. Therefore, a wide range of dimensionless scaling groups has been proposed, attempting to define the ratio between viscous and capillary forces, as reported in [Dullien, 1979] and references therein. This overabundance of scaling groups provides neither a universal nor a straightforward approach to consis-
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tent predictions of nonwetting phase mobilization, which is essential for the evaluation
and/or parameterization of many subsurface engineering applications, such as enhanced
oil recovery, CO$_2$ sequestration, and nonaqueousphase liquid remediation.

In discussing multiphase porous media flow the respective flow regimes are denoted as
either capillary dominated with constant residual nonwetting phase saturation or viscous
dominated with mobilized residual nonwetting phase, depending on the microscopic capil-
lar number. Through a dimensional analysis of pore-scale Stokes flow, as in [Hilfer and
Øren, 1996], the microscopic capillary number is defined as

\[
Ca_{\text{micro}} = \frac{\mu_w u_w}{\gamma_{wnw}}
\]

where $\mu_w$ (Pa·s) is the viscosity, $u_w$ (m/s) is the velocity of the wetting phase, and $\gamma_{wnw}$
(N/m) is the interfacial tension between the wetting and nonwetting phases. When $Ca_{\text{micro}}$
is compared to experimental data, mobilization of the residual trapped nonwetting phase
is found to occur at $Ca_{\text{micro}}$ between $10^{-5}$ and $10^{-7}$ (e.g. [Dullien, 1979]). Unfortunately,
the result obtained this way is unique to the tested rock type, nonpredictive, and coun-
terintuitive since mobilization would be expected at a ratio of viscous to capillary forces
of 1. The inconsistency arises from the definition of $Ca_{\text{micro}}$ in equation 4.6, which is ac-
tually an interfacial definition balancing the viscous stress at a liquid-liquid interface to
the interfacial stresses at the (same) interface, often used as a scaling group in free surface
flows [Leal, 2007]. In this definition, the nonwetting phase would become mobilized by the
viscous shear forces imposed on it by the wetting phase flow field, acting on the interface
over the same length scale as the capillary forces. However, for desaturation, mobilization
of the trapped nonwetting ganglia, which can extend over many pores ranging up to and
potentially greater than millimeters [Georgiadis et al., 2013], occurs because of the viscous
shear over the whole cluster interface, which is equivalent to the viscous pressure drop
created by the flow field of the wetting phase, and capillary forces act over the length scale
of a pore throat which is typically on the order of a few micrometers. In other words, the
definition of $Ca_{\text{micro}}$ assumes that viscous and capillary forces act over the same length
scale and omits the configuration of the trapped nonwetting phase topology. A similar
problem arises with defining capillary pressure at the macroscale. Capillary pressure is the
difference in pressure across an interface at the pore scale. However, larger scale models
require capillary pressure to be defined as an averaged up-scaled parameter, where informa-
tion on fluid topology and information on phase connectivity are lost during the averaging
procedure.

A criterion for desaturation that accounts for nonwetting phase and pore-space topology
was originally defined by [Melrose and Brandner, 1974] by incorporating Darcy’s law into
equation 4.8, which resulted in

\[
Ca_{\text{critical}} = \frac{k_{rw} K}{\phi \gamma_{wnw}} \frac{\Delta P}{\ell_{cl}}
\]

where $K$ (m$^2$) is the absolute permeability, $\phi$ is the porosity, $k_{rw}$ (0 to 1) is the relative
permeability to water, $\Delta P$ (Pa) is the pressure difference across a given oil cluster, and
$l_{cl}$ (m) is the cluster length. More recently, [Hilfer and Øren, 1996] arrived at a similar formulation by connecting the microscopic and macroscopic pictures through a rigorous dimensional analysis. From this scaling analysis of the macroscopic Darcy-type flow equations a macroscale capillary number was defined as

$$Ca_{\text{macro}} = \frac{l_{cl} \mu_w V_{\text{Darcy}}}{KP_b}$$  \hspace{1cm} (4.8)

where $l_{cl}$ (m) is the cluster length along a viscous pressure drop, $\mu_w$ (Pa·s) is the viscosity, $V_{\text{Darcy}}$ (m/s) is the Darcy velocity of the wetting phase, $K$ (m$^2$) is the absolute permeability, and $P_b$ (Pa) is the capillary pressure at breakthrough. Embedded in both of these definitions (equations 4.7 and 4.8) is a ratio of two length scales, one being cluster length (equations 4.7 and 4.8) and the other a characteristic pore-size length scale defined through either permeability (equation 4.7) or capillary pressure and permeability (equation 4.8). This approach accommodates both the microscopic structure of the rock and the trapped nonwetting phase ganglia. However, strictly speaking, cluster length ($L$ or $l_{cl}$) is not a macroscale parameter since the macroscale picture does not include individual clusters, and thus, the capillary number definitions in equations 4.7 and 4.8 combine microscale and macroscale parameters. A clearer approach to defining the viscous pressure gradient would incorporate cluster length at the microscale and then an averaged length parameter at the macroscale, which would represent the lower spatial limit of the macroscale. [Anton and Hilfer, 1999] attempted to demonstrate the onset of capillary desaturation at $Ca_{\text{macro}} \sim 1$ by using previously published literature data. However, only a few data sets were available in the literature and none of the publications contained all of the necessary parameters. In particular, cluster length data were inaccessible since it is not a macroscopically resolved parameter (because pore-scale resolution data are required) and $P_b$ was deduced through a Leverett-J correlation. Second, apparently equation 4.8 assumes $k_{rw} \sim 1$ and thus omits relative permeability from the formulation, which is contrary to equation 4.7 as reported in [Melrose and Brandner, 1974].

Recently, the pore-scale parameters required to evaluate earlier capillary number definitions have become available from a single experimental dataset, meaning that no additional correlations or supplemental experiments are required. Today, evaluation is possible by using fast synchrotron-based X-ray computed microtomography ($\mu$CT), which provides information on pore-scale fluid distributions during multiphase flow in porous rock under dynamic conditions [Berg et al., 2013b]. By using this novel imaging approach, in combination with advanced image analysis techniques and direct pore-scale simulations, we provide clear definitions for the parameters in equation 4.8 and we validate a slightly modified version of the macroscale capillary number presented by [Hilfer and Øren, 1996] that includes relative permeability, as suggested by [Melrose and Brandner, 1974]. Through these efforts, we gained new insights onto how the relevant parameters evolve during capillary desaturation revealing the scale dependencies of $Ca_{\text{macro}}$ and highlighting many important practical implications to consider when designing core-flooding experiments.
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4.3.2 Experimental Methods

The flow cell used in this project was designed specifically for fast \( \mu \)CT, detailed description of which has been previously published by [Berg et al., 2013b] and [Georgiadis et al., 2013]. A cylindrical sample (diameter = 4 mm, length = 10 mm) of sintered glass (Robuglas\textsuperscript{R}, \( \phi = 31.8\% \), \( K = 8.9 \times 10^{-12} \text{ m}^2 \)) was used for the desaturation experiment. The \( \mu \)CT data were collected at the TOMCAT beamline (Paul Scherrer Institute, Swiss Light Source) and the system settings are presented by [Berg et al., 2013b] and provided in the supporting information. Fast scan mode settings allowed for continuous data readout at a temporal resolution of 30 s and a 2.2 \( \mu \text{m/pixel} \) spatial resolution, whereas the high-quality mode allowed for the same spatial resolution at a temporal resolution of 2.5 min. Initial oil saturation was established by pumping three pore volumes of the wetting phase, doped with CsCl at a one to six weight ratio for X-ray contrast, through a decane-saturated sample (constant flux = 0.1 \( \mu \text{L/min} \)). After this, the desaturation experiment was initiated and cluster distributions were imaged with fast \( \mu \)CT, flow rate was increased in a stepwise manner starting at 0.1 \( \mu \text{L/min} \) and finishing at 1000 \( \mu \text{L/min} \). Between steps, after three pore volumes were pumped, the sample was allowed 10 min to equilibrate (under a no-flow condition), and then a high-quality scan was collected.

4.3.3 Averaging Methods

In this work, for the cluster length (\( l_{cl} \)), capillary pressure (\( P_b \)), and permeability (\( K \)) values used in equation 4.8, macroscopic averages are defined, such that, a clear link between pore-scale and macroscale properties is established. For the presented experiment, the term macroscale defines the bulk observable system, which due to experimental limitations, in terms of X-ray beam width, resulted in a 4 \( \times \) 4 \( \times \) 3 mm volume.

In the following analysis, pore-scale cluster length and pore-scale capillary pressure are measured from the segmented \( \mu \)CT data and then averaged to obtain the macroscale equivalent. For clarity, microscale variables are denoted with a subscript (e.g., \( P_c \)), whereas macroscale variables are denoted with a superscript (e.g., \( P^c \)). Average cluster length (\( l^{cl} \)) was calculated by considering the saturation weighted average for each cluster

\[
l^{cl} = \frac{\sum S_c l_{cl}}{\sum S_c}
\]

(4.9)

where \( S_c \) is the corresponding saturation for a given cluster per sample volume and \( l_{cl} \) is the diagonal length, over a bounding box, for a given cluster. For information on measuring cluster length we refer to [Georgiadis et al., 2013]. Simple voxel counting was used to measure fluid saturation (i.e., wetting phase and residual nonwetting phase saturations, \( S^w \) and \( S^{nw} \), respectively), which is used extensively in the literature. Average capillary pressure (\( P^c \)) was calculated by using the measured average mean interfacial curvature (\( K^a \)) of the analyzed nonwetting phase clusters as input to the Young-Laplace equation. To calculate \( K^a \), the surface area weight average for each cluster was considered.
\[ K^w = \frac{\sum a_{nw}k_c}{\sum a_{nw}} \]  

(4.10)

where \( a_{nw} \) is the fluid/fluid interfacial area of a given cluster per sample volume and \( k_c \) is the mean curvature over the fluid/fluid interface of an individual cluster. Additionally, the specific interfacial area per total volume is defined as

\[ a^{nw} = \sum a_{nw}. \]  

(4.11)

For the measurement of interfacial curvature we refer to [Armstrong et al., 2012], and for the measurement of interfacial area we refer to [Porter and Wildenschild, 2010]. With this approach, we assume that clusters in the pore-space span the pore body and are pinned near the pore neck entry regions and thus, this measurement is an estimate of the average entry capillary pressures that are relevant to a given system of nonwetting phase clusters.

The coupling of fast \( \mu \)CT data with direct pore-scale flow simulations was used to determine the effective relative permeability \( (K_{rw}) \) of the wetting phase (i.e., \( K_{rw} = k_{rw}K \)), which was used to replace \( K \) in equation 3.15 since as proposed in equation 4.7 the effective relative permeability for the wetting phase (i.e., \( k_{rw}K \)) should be used. The governing equations for the pore-scale flow simulator are presented in [Demianov et al., 2011], and a detailed description of boundary conditions and how the analysis results were used is provided in the supporting information. Overall, the approach taken assumes that the fast \( \mu \)CT data captures quasi-static snapshots of the nonwetting phase configuration during the flow experiment. In this way, single phase flow simulations were conducted on the segmented pore-scale images and both grain and nonwetting phase pixels were set as no-flow boundaries. This provided the microscopic flow field and hence wetting phase relative permeability during desaturation.

Combining these components led to a new capillary number definition:

\[ Ca^{macro} = \frac{l^d \mu^w V^{Darcy}}{K_{rw} P_c} \]  

(4.12)

where \( l^d \) (m) is defined in equation 4.9, \( \mu^w \) (Pa·s) is the wetting-phase viscosity, \( V^{Darcy} \) (m/s) is the Darcy velocity, \( K_{rw} \) (m\(^2\)) is the relative permeability of the wetting phase as suggested by [Melrose and Brandner, 1974], and \( P_c \) (Pa) is defined through equations 4.10 and 4.11. The \( Ca^{macro} \) defined in equation 4.12 is only a slightly modified version of equation 4.8, but now the parameter definitions are explicitly defined.

### 4.3.4 Results

The capillary desaturation data are displayed in Figure 4.18, which compares residual oil saturation to \( Ca^{micro} \) from equation 4.6, \( Ca^{macro} \) from equation 4.8 with parameter values proposed by [Hilfer and Øren, 1996], and \( Ca^{macro} \) from equation 4.8 with averaged parameter values from equations 4.9 and 4.10 and pore-scale simulations. For the microscale capillary number approach, desaturation occurs at \( Ca^{micro} << 1 \). For the [Hilfer and Øren,
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Figure 4.18: (top left) Capillary desaturation data for the Robuglas sample. (top right) A visual representation of a disconnected cluster. (bottom) Images collected during desaturation (black = solid, white = wetting phase, green = nonwetting phase). With time 0 corresponding to flow initiated at 0.1 $\mu$L/min. Images 1 through 5 were collected at 28 min (0.1 $\mu$L/min), 35 min (1.0 $\mu$L/min), 42 min (10.0 $\mu$L/min), 44.1 min (100.0 $\mu$L/min), and 46.2 min (1000 $\mu$L/min), respectively.
1996] approach, we used the absolute permeability (8.9 × 10^{-12} \text{ m}^2) and capillary pressure at breakthrough (2718 Pa) values collected on a core sample of Robuglas and a cluster length (10 mm) similar to the sample size. This shifted the desaturation data to larger capillary numbers. However, desaturation still occurs at $Ca^{macro} < 1$, and thus, neither approach properly represented the viscous and capillary forces. The correct representation of viscous and capillary forces was achieved by averaging the microscopic parameters from the pore-scale images to calculate $Ca^{macro}$, for which desaturation is observed at $Ca^{macro} \sim 1$. These results demonstrate that the overall formulation for $Ca^{macro}$ and the defined averaged parameters are correct since the proper ratio between viscous and capillary forces is demonstrated when $l^{cl}$, $P_c$, and $K^{rw}$ are used. Interesting to note, when $K^{rw}$ is accounted for during desaturation then $Ca^{macro}$ remains at $\sim 1$, which is because of the nonlinear response between wetting phase flux and the pressure drop that is observed. A more general observation comes from the reality that the desaturation curve is very sharp at $Ca^{macro} \sim 1$, which implies that once desaturation is initiated by increasing flow rate the system tends to an equilibrium state where $Ca^{macro} \sim 1$. The results suggest that the largest clusters are either broken apart by snap-off processes into smaller clusters or are mobilized and recovered from the column.

To further explain why the parameter values proposed by [Hilfer and Øren, 1996] result in desaturation at $Ca^{macro} < 1$ and why the newly proposed parameters (i.e., $l^{cl}$, $P_c$, and $K^{rw}$) result in a desaturation curve that is very sharp at $Ca^{macro} \sim 1$, we present the measured parameter results in Figure 4.19. As shown in Figure 4.19a, $a^{nw}$ consistently decreases during the desaturation process, whereas $P_c$ consistently increases and is significantly less than the value of capillary pressure at breakthrough (2718 Pa) measured for the Robuglas sample. Figure 4.19b reports $l^{cl}$ during desaturation, which displays a slight reduction in cluster length during the desaturation process. However, this measurement is likely dominated by sample size, which is discussed later. The wetting phase relative permeability, shown in Figure 4.19c, shows a rapid increase in permeability as flow rate increases, which then stabilizes with multiple pore volumes injected and is also significantly less than the absolute permeability (8.9 × 10^{-12} \text{ m}^2) measured for the Robuglas sample. In Figure 4.19, changes in $K^{rw}$ appear rather abrupt since these are dynamic “unsteady” measurements, rather than the more commonly reported “steady state” values, since relative permeability is measured during the desaturation process. For example, two significantly different $K^{rw}$ values are measured for $S^w \sim 0.7$, which suggests that $K^{rw}$ is not just a function of $S^w$ and rather that the pore-scale spatial arrangement of the nonwetting phase is also a defining factor. Overall, the parameter values suggested by [Hilfer and Øren, 1996] result in the over approximation of permeability and capillary pressure and do not account for the implicit dependencies of the parameters during desaturation.

Why is there a plateau region in Figure 4.18 at low capillary number? In the experiment, as observable in Figure 4.19b, the maximum cluster length follows the scale of the maximum distance across the measured field of view. In other words, the correct $Ca^{macro}$ could not be calculated for the lower flow rates, since field of view limitations restricted the cluster length measurement. For the presented results the field of view and system boundary are of the same order of magnitude, which results in an adequate estimation of the average
Figure 4.19: (a) Average interfacial curvature and average capillary pressure values during capillary desaturation. (b) Measured and estimated average cluster length during capillary desaturation. (c) Relative permeability values simulated from the pore-scale images. (d) A visual representation of disconnected clusters. Symbol 1 represents the end point of the desaturation process shown in Figure (d).
cluster length. Nonetheless, this is a typical problem with $\mu$CT since the field of view required to observe larger clusters is coupled with the resolution required to determine connectivity. However, if we assume that $Ca^{macro}$ is the correct scaling group and that at equilibrium $Ca^{macro} = 1$ (as demonstrated in Figure 4.18), then we can estimate the maximum average cluster length for the tested flow rates. The results of this analysis are displayed in Figure 4.19b, which reveals that average cluster length is greater than the system boundary for most of the tested flow rates. This demonstrates that if sample size was increased, then desaturation may occur at a lower flow rate, and thus, the lowest flow rate would have resulted in $Ca^{macro} \sim 1$. In general, this could be the case for any capillary desaturation data that results in a plateau region at low flow rates. The traditional counter argument to explain the plateau region is simply that for low flow rates, the viscous pressure gradient is not large enough to mobilize the largest possible cluster, which is true. However, this argument assumes that the system is large enough to contain the largest possible cluster and thus is a representative volume. System size limitations must be considered as a possibility for the plateau region for two reasons: the data in Figure 4.19d, representing a field relevant flow rate ($Ca_{micro} = 10^{-7}$), demonstrate that the maximum average cluster length could be $\geq 3.5$ cm, and the asymptotic limit of the maximum possible cluster length as flow rate decreases and sample size increases is currently unclear. Of course, the spatial correlation length of the pore neck sizes that dictate the critical point for snap off must be large so that a large cluster, as estimated by $Ca^{macro} = 1$, can exist. However, this situation is very likely to occur in reservoirs where a less permeable layer exists within a highly permeable zone, see [Wang et al., 2012].

From consideration of the proposed method, practical insights are gained to better predict and measure $P^c$, $l^{cl}$, and $K^{rw}$ during desaturation. For example, capillary pressure (at breakthrough) for the Robuglas sample, measured from mercury intrusion data and scaled via a Leverett-J function, was significantly greater than $P^c$ measured from the porescale images. This suggests that capillary pressure (at breakthrough) does not properly represent a system of disconnected nonwetting phase clusters after forced imbibition. A more suitable value could likely be estimated through a $\mu$CT pore morphology analysis of pore neck and body sizes. Second, absolute permeability does not properly represent a porous system at residual oil saturation because the microscopic flow field is influenced to a substantial extent by trapped nonwetting phase clusters, as shown in Figure 4.19c and suggested by [Melrose and Brandner, 1974]. A more appropriate approach is to use $K^{rw}$ (at residual oil saturation) when calculating $Ca^{macro}$. Lastly, to avoid the system boundary effect, it should be considered that for a typical Bentheimer sandstone ($P^c = 10,000$ Pa, $K^{rw} = 1.6 \times 10^{-15}$ m$^2$) under water flood ($Ca_{micro} = 10^{-8}$ to $10^{-6}$) that $l^{cl}$ could range from 0.5 up to 5.4 cm, similar lengths are estimated by [Wang et al., 2012]. With these suggested modifications, a critical capillary number would be predictable for a given situation (and system size) using rather standard laboratory procedures.
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4.3.5 Conclusions

By using the proposed averaging approach of porescale experimental measurements of cluster length, capillary pressure, and relative permeability, we validated the capillary number definition presented in this work as equation 4.12. Providing clear definitions of the macroscale parameters in terms of the equivalent microscale parameters demonstrated the mobilization of nonwetting phase at $Ca_{\text{macro}} \sim 1$. This analysis yields insights into when and how $Ca_{\text{macro}}$ scales with system size and presents a practical approach to predicting nonwetting phase mobilization for a given system. Overall, the comparison of microscopic and macroscopic parameters indicates that cluster length is potentially a lower boundary for the definition of the macroscopic scale, which could be as large as 5.4 cm for a typical sandstone at $Ca_{\text{micro}} = 10^{-8}$. These results warrant further investigation since the extent to which length scale dependency impacts laboratory measurements is presently unclear. Additionally, the validation of $Ca_{\text{macro}}$ has more general and broader implications. For example, according to $Ca_{\text{micro}}$ increasing flow rate or viscosity and/or decreasing interfacial tension would reach the same desaturation. However, this can no longer be considered true since we have demonstrated that $Ca_{\text{micro}}$ is not the correct scaling group but instead $Ca_{\text{macro}}$, which depends on the parameters $P^c$, $l^c$, and $K^{rw}$ that are in turn functions of the process-dependent microscopic fluid configuration. Therefore, this work is a starting point to study the process-dependencies of capillary desaturation.
Chapter 5

Mass Transfer and Dryout

5.1 Capillary-driven flow and salt precipitation in unimodal sandstone

Drying and salt precipitation in geological formations can have serious consequences for upstream operations in terms of injectivity and productivity. Here we investigate the consequences of supercritical CO$_2$ injection in sandstones. The reported findings are directly relevant for CO$_2$ sequestration and acid-gas injection operations, but might also be of interest to a broader community dealing with drying and capillary phenomena.

By injecting dry supercritical CO$_2$ into brine-saturated sandstone, we investigate the drying process and the associated precipitation of salts in a capillary-pressure-dominated flow regime. Precipitation patterns were recorded during the drying process by means of µCT scanning. The experimental results and numerical simulations show that under a critical flow rate salt precipitates with an inhomogeneous spatial distribution because of brine and solutes being transported in counter-current flow upstream where salt eventually precipitates. A substantial impairment of the absolute permeability has been found, but despite high local salt accumulation, the effective CO$_2$ permeability increased during all experiments. This phenomenon is a result of the observed microscopic precipitation pattern and eventually the resulting $K(\phi)$ relationship.

The findings in this paper are related to unimodal sandstone. In a companion paper [Ott et al., 2015c] we present data on the distinctly different consequences of salt precipitation in dual- or multi-porosity rocks.

5.1.1 Introduction

Drying of porous media is an important topic in many industrial processes, in soil science and for upstream operations such as gas injection and production into and from geological formation. Drying of saline formations will cause precipitation of salt initially dissolved in the brine. This can negatively affect the performance of injection and production wells and can even lead to well clogging, which is a serious risk for such operations. In this
paper we consider large-scale geological storage of CO$_2$, originating from anthropogenic sources like fossil-fueled power plants or contaminated gas production, in order to reduce CO$_2$ emissions. Deep saline aquifers and depleted oil and gas fields are potential subsurface deposits for that purpose [IPCC, 2005, Bachu and Gunter, 2004].

If dry or under-saturated, supercritical (SC) CO$_2$ is injected into water-bearing geological formations like saline aquifers, water is removed either by viscous displacement of the aqueous phase or by evaporation/dissolution of water in CO$_2$ and subsequent advection in the injected CO$_2$-rich phase. Both mechanisms act in parallel, but while advection of the aqueous phase decreases with increasing CO$_2$ saturation (diminished mobility), evaporation becomes increasingly important as the aqueous phase becomes immobile. Below residual water saturation, only evaporation takes place and the formation dries out if no additional source of water is available. If water evaporates, the salts originally present in the water are left behind. In highly saline formations, the amount of salt that potentially precipitates per unit volume can be quite substantial. The volumes depend on brine salinity, and the transport of solutes and water in the reservoir. Since fluid saturations and flow rates close to the well bore cover a large range as functions of space and time, there are no easy answers to the questions whether, where and how salt precipitates and how precipitation affects injectivity. The questions that need to be addressed are about the mechanisms of solute transport on a macroscopic scale that determine the macroscopic distribution of salt, and the salt distribution on a pore scale that determines how the permeability is affected as function of porosity reduction.

Even though salt precipitation in the vicinity of gas production wells are generally considered as issue, there are not many studies published referring to well data. The frequently cited paper is that of [Kleinitz et al., 2001]. Probably due to the limited number of industrial-scale CO$_2$ sequestration projects, there are no well data available referring to salt precipitation during CO$_2$ injection.

The lack of well studies renders a proper problem statement difficult and we rely on numerical simulations and analytical models that are available in literature. Here, we only aim to highlight a few key studies on precipitation due to CO$_2$ injection relating to the problem discussed in this paper: In a series of publications, Pruess et al. presented numerical simulations of CO$_2$ injection in saline aquifers, investigating the fundamental aspects of formation dry-out and salt precipitation [Pruess and García, 2002, Pruess and Müller, 2009]. The simulations were performed with a single injection well in idealized 1D and 2D radial geometries. The authors observed that precipitation occurs only in a narrow dry-out zone confined to a few meters around the injection well. The solid salt saturation in this zone has been found to be constant independent of the injection rate. 2D radial simulations were carried out to explore gravity effects. In contrast to the 1D-radial scenario, gravity in combination with capillary-driven flow lead to more heterogeneous precipitation, with a maximum observed solid-salt saturation of more than 20%.

[Giorgis et al., 2007] performed field-scale simulation in radial geometry. The authors found that the amount of precipitate depends on brine mobility and can be high if there is a capillary-gradient driven brine flow in the direction of the well bore. The authors have further shown that the injection rate is an important factor in controlling precipitation
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process and in avoiding or allowing complete clogging of the formation. In their simulations, solid salt saturations of locally more than 60% have been reached.

However, field-scale simulations require input on flow physics and thermodynamics such as the $K(\phi)$ relationship and the mass transfer rates between the fluid phases. As we will show in this paper and in [Ott et al., 2015c], these parameters are of microscopic origin and need to be determined by laboratory experiments. The quality of the input is critical for reliable simulations as several studies suggest that a modest change in porosity might lead to a serious reduction in permeability. The respective literature is diverse in mechanisms and there are not many studies dealing with fluid-transport induced porosity changes. The discussed mechanisms range from the porosity variation due to lithology/rock type [Pape et al., 1999, Ehrenberg and Nadeau, 2005] via mechanical compaction [Wyble, 1958, Schutjens et al., 2004] to silica dissolution and precipitation in geothermal systems in single-phase flow [Xu et al., 2004b] to drying processes, i.e. in two-phase flow as discussed in the present paper. Even if usually described by power laws, it cannot be expected that the $K(\phi)$ relationships resulting from different mechanisms are comparable – i.e. process-independent – and generally applicable.

There are only a few studies on flow-through drying available, which are relevant for CO$_2$ storage. Zuluaga et al. investigated vaporization and salt precipitation in sand packs and sandstone for gas production wells [Zuluaga and Monsalve, 2001, Zuluaga et al., 2001]. At the GHGT-10 in Amsterdam 2010, two experimental studies on dry CO$_2$ injection have been presented. The experiments have been performed in sandstone in realistic storage conditions addressing capillary-driven solute transport, the condition of counter current flow [Ott et al., 2011b], and a permeability porosity relationship [Bacci et al., 2011]. Recently, [Peyssona et al., 2014] and [Andre et al., 2014] investigated the drying process by nitrogen injection in sandstone. The data have been used to benchmark a numerical simulation tool for field-scale modeling of CO$_2$ injection. [Ott et al., 2011b] pointed out that modeling of vaporization by an equilibrium approach is not sufficient to describe core flood experiments. [Roels et al., 2014] performed core flood experiments and succeeded in the description of the saturation profiles by a kinetic approach.

In this paper we show results of core-flood experiments that were presented at the SCA conference in Halifax and at the GHGT10 in Amsterdam in 2010 [Ott et al., 2010, Ott et al., 2011b]. The experiments were performed to investigate the drying process and the impact of salt precipitation on flow, i.e. the salt distribution and the $K(\phi)$ relationship. For this we injected dry SC CO$_2$ in brine-saturated siliciclastic sandstone. The experiments were carried out at flow rates realistic for near-well-bore flow and at realistic thermodynamic conditions. During injection, spatial and time evolution of saturation changes were monitored by means of micro computed tomography ($\mu$CT). The results in this paper are based on a number of experiments showing precipitation profiles with different degrees of heterogeneity on a macroscopic scale. For quantification we discuss two of these experiments showing the largest and the smallest spatial variation of salt saturation after dry-out. We refer to the cases as the heterogeneous and the homogeneous case, respectively. We explain the mechanisms that lead to the observed heterogeneous distribution of the precipitate by means of numerical simulations.
In addition to the saturation profiles, changes in absolute permeability and effective CO\textsubscript{2} permeability were monitored. From this data, we extract the permeability/porosity relationship ($K(\phi)$). We explain the observed mild permeability reduction by the microscopic distribution of the salt with respect to the observed CO\textsubscript{2} flow channels. Furthermore, we discuss the results in terms of precipitation in single-phase and two-phase flow situations.

### 5.1.2 Materials & methods

The experiments were carried out in a core flood setup designed for flooding with volatile and reactive fluids as sketched in Figure 5.1. A detailed description of the unit can be found elsewhere [Ott et al., 2012]. In the following, only a brief description of the elements will be given that are of relevance for the experiments here presented.

The flow experiments were performed in vertical geometry, with fluids being injected from top to bottom. The samples were embedded in polycarbonate and placed in a carbon-fiber based core holder – both are materials with low X-ray attenuation coefficients. The core holder is placed in a $\mu$CT scanner for in-situ 3D imaging of the rock-fluid system. CT imaging allows to determine fluid saturations and changes of the rock matrix due to salt precipitation. The unit is equipped with two feed sections for liquids and liquefied gas injection. The CO\textsubscript{2} feed pump was held at 3°C during the experiments – liquid CO\textsubscript{2} was injected and heated to experimental temperature and to the respective SC state in the injection lines. The density difference has been taken into account for the indicated flow rates. From flow rates and the differential pressure measurement ($\Delta P$), the absolute ($K$) and effective permeability ($K \times k_{rel}$) were derived on line.

The experiments were performed on Berea sandstone with an average permeability of 500 mD and 22% porosity. The samples were drilled from the same block and were small in cross section and volume (1 cm diameter and 5 cm length) to obtain representative flow rates and to reduce the experimental time to complete dry-out. The mineralogy of Berea is dominated by quartz with some K-feldspar, kaolinite, and minor amounts of other clay minerals as determined by eSEM/EDX. The rock samples were pre-saturated with NaCl-based high-salinity brine: 20 wt% NaCl and 2 wt% CsCl. The CsCl was added as a contrast agent as its X-ray absorption coefficient is high, leading to a high X-ray absorption contrast in $\mu$CT between the aqueous and the CO\textsubscript{2}-rich phase. The injected CO\textsubscript{2} was of high purity and essentially dry (strongly under-saturated with respect to water), not least because of the strong difference between water saturation limits at conditions in the lq.-CO\textsubscript{2} cylinder and at experimental condition of 100 bar pressure and 45°C temperature.

We observe the spatial distribution of the precipitated-salt phase by means of $\mu$CT imaging. Computer tomography is based on X-ray absorption determined by material-specific linear attenuation coefficients ($\mu$), which are directly represented as gray values of the voxels in the reconstructed image [Wellington and Vinegar, 1987, Vinegar and Wellington, 1987]. For saturation calculations we made use of tabulated mass-absorption coefficients $\mu/\rho$ [Hubbell, 1969], fluid densities $\rho$ [Pruess and Spycher, 2007, Span and Wagner, 1996], and the density of the solid-salt phase [Lide, 2003]. $\mu/\rho$ for the injected and produced fluids and their constituents are shown in Figure 5.2 and phase densities are listed
Figure 5.1: Schematic of the experimental setup. More details are provided in [Ott et al., 2012].
Figure 5.2: Top: X-ray mass-absorption coefficients of the relevant fluids and salts as function of photon energy. The vertical line indicates the calibrated effective photon energy that has been used to calculate the salt saturation by Eq. 5.2. Bottom: Relative absorption coefficients of the brine phase as function of CsCl concentration. The data has been used to determine the effective photon energy $h\nu=63$ keV.
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Table 5.1: Densities at 100 bar and 45°C and mass-attenuation coefficients for converting saturation profiles according to Equation 5.2; * = dry, ** = water saturated, † = with, and ‡ = without CsCl, § = in the presence of CO₂ ‡‡ = before CO₂-breakthrough. §: the deviation from the literature value can be explained by a ≈2K lower temperature in the external density meter.

<table>
<thead>
<tr>
<th></th>
<th>ρCO₂ [kg/m³]</th>
<th>ρbrine [kg/m³]</th>
<th>ρsalt [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>585** → 565**§</td>
<td>1140†‡‡ (±2)</td>
<td>–</td>
</tr>
<tr>
<td>Literature</td>
<td>499*, 517***</td>
<td>1140†, 1172†‡‡</td>
<td>2170 (NaCl), 3988 (CsCl), 2264 (mNaCl/mCsCl = 10)</td>
</tr>
<tr>
<td>Used</td>
<td>500</td>
<td>1140</td>
<td>2247 (mNaCl/mCsCl = 12.3)</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th></th>
<th>(µ/ρ)CO₂ [cm²/g]</th>
<th>(µ/ρ)brine [cm²/g]</th>
<th>(µ/ρ)salt [cm²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Used</td>
<td>0.185</td>
<td>0.33</td>
<td>0.85 (mNaCl/mCsCl = 10)</td>
</tr>
</tbody>
</table>

Due to the higher solubility limit of CsCl, we expect that salt precipitates in a ratio different from the initial ratio mNaCl/mCsCl =10, because CsCl might stay longer in solution and might be preferentially removed by the displacement process. To estimate CsCl depletion, we performed simulations (not shown) with the experimental brine composition. The simulations were performed as outlined in Section 5.1.4, but using ToughReact [Xu et al., 2004a] as simulation tool. NaCl and CsCl precipitation was handled in equilibrium using the ToughReact data base for NaCl and the CsCl-solubility data reported in [Lide, 2003]. The simulations result in mNaCl/mCsCl =12.3 and a respectively corrected scaling factor for saturation conversion according to Equation 5.2.

5.1.3 Longitudinal precipitation profile

For each experiment a dry and clean rock sample was mounted into the core holder and subsequently pressurized and heated under N₂ flow to 45(±1)°C/100 bar (downstream side), corresponding to the thermodynamic conditions of a saline aquifer at a depth of about 1000 m. To quantitatively determine saturations, reference scans at 100% CO₂ saturation and 100% brine saturation were recorded. For that purpose, nitrogen was displaced by
SC CO\(_2\) (miscible displacement) until 100% CO\(_2\) saturation was reached, as checked by the density of the produced fluid. Subsequently, the core was slowly depressurized and evacuated to allow brine saturation without trapping CO\(_2\). The core was then saturated with brine and subsequently pressurized. All the reference scans were taken at experimental temperature and pressure. During the experiment, dry SC CO\(_2\) was injected at a constant rate into the brine-saturated core. The injection rate at experimental condition was 2.2 ml/min (later 4.4 ml/min) corresponding to realistic near-well-bore flow rates. During the first 40 minutes brine and CO\(_2\) were produced and, in the following period, only a CO\(_2\)-rich phase with no further brine production. At that point, substantial drying by evaporation started, with a differential fluid pressure of about 600 mbar, decreasing to a lower final value of 460 mbar after about 8.5 h of CO\(_2\) flooding as later discussed in Figure 5.8.

Figure 5.3 shows the integrated µCT-response profiles along the flow direction at different experimental time steps. The profiles are already converted to saturations by eliminating the rock matrix. The CO\(_2\) saturation is represented with a scale ranging from 100% brine saturation (\(S_{CO2} = 0\)) to 100% CO\(_2\) saturation (\(S_{CO2} = 1\)). The saturations have been calculated from integrated CT profiles \(I(t)\) by:

\[
S_{CO2} = \frac{I_{brine} - I(t)}{I_{brine} - I_{CO2}} \quad (5.1)
\]

whereas \(I_{brine}\) and \(I_{CO2}\) represent the density profiles of the reference scans at 100% brine and 100% CO\(_2\) saturation, respectively. The first CT scan was started after 0.4 h of CO\(_2\) flooding. The saturation profile is flat, with an average CO\(_2\) saturation of about 0.5 (blue symbols). The displacement was still advection-dominated. Salt precipitation due to evaporation can be ignored and so the system was in a two-phase regime (CO\(_2\)-brine), for which \(S_{CO2}\) is a good scale.

Subsequently the X-ray absorption decreases with time, in line with an increase in CO\(_2\) saturation. If salt did not precipitate, flat density profiles would be expected, determined by the advection and evaporation of the brine phase. However, while the lightest component in this experiment (CO\(_2\)) was injected, a dip occurred at a position of about 2.5 mm, corresponding to a density increase – salt precipitates! The dip grew for about 9.5 h. After 10 h. (red symbols) the shape of the profile, including all features, did not change further for another 6 h of CO\(_2\) flooding. This is a clear indication that the sample is dry – no water evaporates and no salt is precipitating any more. We assume that at that point in time, the rock sample contained solid salt and CO\(_2\), which again is a two-phase system. This allows the CT response for the red profile (dry state) to be rescaled to solid salt saturation by:

\[
S_{salt} = (1 - S_{CO2}) \cdot \frac{\mu_{brine} - \mu_{CO2}}{\mu_{salt} - \mu_{CO2}}, \quad (5.2)
\]

where the \(\mu\)s denote the respective attenuation coefficients, derived from the mass-attenuation coefficients (\(\mu/\rho\)) and the respective phase densities \(\rho\), listed in Table 5.1, by \(\mu = (\mu/\rho) \rho\).

The mean value of solid-salt saturation was determined as 4.1(±0.2)%\(^1\). However, locally the saturation is as high as 18%. The mean value of 4.1% corresponds to evaporation

\(^1\)The saturation determination is mainly sensitive to the uncertainty in the dopant concentration, which
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Figure 5.3: $\mu$CT data recorded during the experiment. Top: Time series of normalized difference images projected onto the vertical sample axis in flow direction. The profiles represent changes of a three-phase system: brine/CO$_2$/salt. The saturation scales on the left and right correspond to the respective two-phase system at the beginning of the experiment and at the end: CO$_2$/brine and CO$_2$/salt, respectively.
of 41(±2)% of the total water – the immobile water fraction. From this, the average degree of water saturation in the produced CO$_2$ has been estimated to be about 35(±2)% using the saturation limit of water in CO$_2$ (≈ 0.00145 wt.%, [Pruess and Spycher, 2007, Span and Wagner, 1996]), the injection rate and the experimental time to dry-out. From this we estimate the length scale of the evaporation zone to be in the order of 0.3 to 1 m, which evidently is controlled by evaporation kinetics and the flow rate of the CO$_2$-rich phase. A numerical estimation of the length of the evaporation zone will be given in Section 5.1.5.

The observed salt accumulation, which is locally much higher than the salt originally present in the brine in the same respective volume, is explained by a capillary-driven counter-current flow, as discussed further in the next section. However, after doubling the flow rate to 4.4 ml/min, a homogeneous precipitation pattern has been observed. Both precipitation patterns are shown in the lower panel of Figure 5.3. An explanation of this effect will be given by numerical simulations in the next section. There it turns out that there is a critical flow rate above which salt precipitates homogeneously. It needs to be mentioned, that we did not observe a well defined critical flow rate, which is – as we believe – a result of the (relatively small) sample to sample variation of capillary properties. What we can state at this point is that the critical velocity for the given rock type and thermodynamic condition is in the range of the flow rates reported here.

### 5.1.4 Numerical modeling of the longitudinal profile

For an understanding of the fundamental mechanism behind the observed precipitation patterns, we performed numerical simulations with TOUGH2 [Pruess and Spycher, 2007], which is a multiphase/multi-component reservoir simulator. In combination with the fluid property module ECO2N that describes the thermodynamics of H$_2$O/NaCl/CO$_2$ systems, TOUGH2 has been used to model CO$_2$ injection in saline aquifers [Pruess and Spycher, 2007]. The present experiments were modeled in a simple vertical 1D geometry using the experimental dimensions. The first grid block was assigned as the injection point at a constant CO$_2$-injection rate. The constant pressure boundary condition was realized by setting the volume factor of the last grid block to infinite. The rock-fluid properties $K$, $k_{rel}$ and $p_C$ were derived from experiments performed on the same rock type with the same fluid configuration [Perrin and Benson, 2010, Berg et al., 2013a].

The upper panel of Figure 5.4 shows longitudinal CO$_2$-saturation profiles profile (in the direction of injection) simulated with a CO$_2$-injection rate of $3 \times 10^{-5}$ kg/s for several time steps (black lines). At the given injection rate, the shock front passes the core within might be affected by depletion as discussed in Section 5.1.2. The given errors result form the estimated error of the NaCl/CsCl ratio of (12.3)$\pm$1.

2Experimental capillary pressure ($p_C(S_W)$) and relative permeability saturation functions ($k_r(S_W)$) were approximated by the van Genuchten models [van Genuchten, 1980] available in TOUGH2. We performed the simulations using the following parameter set: $\lambda =0.48$, $S_{lr} =0.079$, $S_{ls} =1$, $1/P_0 = 3.5 \times 10^{-4}$ and $P_{max} = 10^9$ for $p_C(S_W)$ and $\lambda =0.7$, $S_{lr} =0.15$, $S_{ls} =1$ and $S_{gr} =10^{-3}$ for $k_r(S_W)$. Furthermore, $K =500$ mD, $P_m =100$ bar, $T =45^\circ$C (isothermal) and $X_{NaCl} = 0.24$ (initial brine salinity in wt%) were used.
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Figure 5.4: TOUGH2 simulations of core-flood experiments. Upper panel: CO$_2$-saturation profiles during CO$_2$ injection into a brine-saturated rock sample at a rate of $3 \times 10^{-5}$ kg/s and at different time steps (lines and filled squares). Also shown are the final states of simulations at higher injection rates as indicated in the figure (open symbols). The middle and lower panels show the respective brine and solid-salt saturation profiles.
Figure 5.5: $H_2O$ fluxes in selected grid blocks (gb) as a function of time. Squares represent the $H_2O$ flux in the aqueous phase and circles represent the $H_2O$ flux in the $CO_2$-rich phase due to evaporation and subsequent advection. Note that the aqueous phase changes the flow direction as indicated by the arrows.

seconds, followed by a continuous saturation change after breakthrough. After about 0.3 h, a dip in the $CO_2$ saturation close to the injection point occurs. This is attributed to a saturation change due to salt precipitation as displayed in the lower panel. With advancing time, a precipitation front slowly moves from the injection point downstream, accumulating salt on its way. After 3.3 h of $CO_2$ flooding, the solid-salt saturation exceeds 0.9 and the simulation stops; in the next time step the salt saturation would reach 1. Permeability changes are not taken into account, but a blockage of pore space will obviously lead to clogging. At that point more salt is precipitated than was originally present in the respective brine volume, which requires transport of salt in the upstream direction to the point of dry-out, as also observed experimentally.

In the same panels in Figure 5.4, simulations at higher and lower injection rates are displayed in their respective final states after dry-out. At higher injection rates the location of precipitation shifts away from the injection point toward a larger saturation gradient (as a result of the capillary end effect). Apparently, if the viscose force increases, a stronger saturation gradient is needed to reach the condition that leads to local precipitation. At lower flow rates, back flow seems to be even stronger, with the salt precipitating directly at the inlet with the time till clogging being longer.

More insight is provided by the fluid transport as displayed in Figure 5.5. The effective water fluxes in individual cells at the point of local precipitation (closed symbols) and at the outlet (open symbols) are plotted against time. The streams are split into water flux in the $CO_2$-rich phase (blue circles) and in the aqueous phase (black squares). The red
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Line marks the total water flux at the outlet. The water flux in the CO₂-rich phase is determined by the water content and the flow rate. It stays constant over a long period of time, according to the saturation limit. The water transport in the aqueous phase is very strong during the first few seconds but declines rapidly according to the mobility ratio of the fluid phases. The aqueous phase becomes immobile and the water transport is determined by evaporation and subsequent advection in the CO₂-rich phase. After a certain time, capillary pressure dominates the aqueous-phase transport, leading to a capillary-driven back flow into the zone of evaporation – counter current to the injected CO₂. Back flow, however, allows local accumulation of salt beyond the brine’s original local salt content. The point at which the major part of the salt precipitates is the point at which the ‘evaporation front’ no longer moves. Here, the negative water flux in the brine phase compensates for the positive water flux in the CO₂-rich phase (see Figure 5.5) and we can formulate a condition for local precipitation to occur if:

\[ q_{SC} \cdot \rho_{SC} \cdot X_{H_2O,SC} = q_{aq} \cdot \rho_{aq} \cdot X_{H_2O,aq}, \tag{5.3} \]

where \( q_{SC} \) and \( q_{aq} \) are the volumetric fluxes of the CO₂-rich phase and the aqueous phase, \( \rho_{SC} \) and \( \rho_{aq} \) are the phase densities, and \( X_{H_2O,SC} \) and \( X_{H_2O,aq} \) are the mass fractions of water in both phases, respectively.

The simulations demonstrate and explain the effect observed in the experiment. However, there are substantial differences between experiments and simulations related to saturation gradients. In the simulation, the gradient is dominated by the capillary end-effect and is therefore a geometrical property. In the experiment, however, the end effect is suppressed (as observed in the CT profiles) by capillary back flow, i.e. capillary redistribution; in contrast to the simulation, water evaporates over the entire core length and, hence, the induced back flow equalizes the brine saturation, suppressing the end effect. This is a result of evaporation kinetics, which is not accounted for in the simulations with TOUGH2 (or in any other simulator which does not take evaporation kinetics into account). Hence the saturation gradient that leads to local precipitation is not quantitatively modeled. Second, there is only a finite brine volume in the experiment, due to the finite sample size. This leads potentially to an underestimation of salt saturation as a result of depletion effects in experiments with a finite volume, which can be shown by simulations with a finite sample volumes (data not shown here).

The critical flow rate, above which a homogeneous precipitation pattern is observed in the experiment (i.e. at which the advective flux prevents capillary-driven back flow), is equivalent to the rate in the simulations at which the precipitation peak moves away form the inlet to the next point with a higher saturation gradient were the downstream flux of water in CO₂ is again compensated by counter-current flow of the aqueous phase. Such a shift is not observed for the flat saturation profiles in the experiments, since the constant saturation gradient cannot counteract the advective force at flow rates above the critical. A flat saturation profile is expected in the field. However, in radial flow geometry, where the advective force decreases with distance, the condition of local precipitation can be reached at a certain distance even with a flow rate above the critical close to the injection point.
CHAPTER 5. MASS TRANSFER AND DRYOUT

5.1.5 The zone of attraction: Kinetic model

In the simulations presented so far the produced CO\textsubscript{2} was fully water-saturated as result of the equilibrium approach of the evaporation model. However, from the experiments in Section 5.1.3 we determined the average water saturation of the produced CO\textsubscript{2} stream to be about 35\% of the solubility limit for the respective experimental conditions. The reason for the partial saturation is the finite contact area between the injected CO\textsubscript{2} stream and the brine in the rock and the finite evaporation rate, which is not taken into account (overestimated) in the equilibrium model. On the basis of the average water content of the produced CO\textsubscript{2}, we estimated the zone in which evaporation takes place to be in the order of 0.3 to 1 m in linear geometry – in any case longer than the experimental length scale. In this zone, the water saturation gradient \((dS_W/dx)\) is modified from the gradient expected from viscous displacement only and capillary-driven back flow can occur. The evaporation zone is therefore the zone over which counter current solute transport can potentially occur – we therefore call it zone of attraction.

In this section we present an estimation of the zone dimension in linear geometry by numerical simulations. We use a kinetic approach as reported by [Roels et al., 2014] and model the zone of attraction for different injection rates between 0.01 and 100 ml/min/cm\textsuperscript{2} (2 \times 10\textsuperscript{-6} and 0.1 m/s). We use rock-fluid parameters – relative permeability and capillary pressure saturation functions – obtained for CO\textsubscript{2}-brine displacement in the same rock type (Berea sandstone: [Ott et al., 2011a, Berg et al., 2013a]), for the same fluid combination and thermodynamic condition.

We model evaporation and flow only and we do not take the feedback of precipitation on permeability and capillarity into account. We determine the overall evaporation rate \(- A \times r_{\text{evap}}\), with \(A\) being the CO\textsubscript{2}-brine contact area and \(r_{\text{evap}}\) the evaporation rate – by matching the average water concentration in the produced CO\textsubscript{2} stream to the experimentally obtained value at the respective distance. Subsequently, simulations were performed with experimental input data on a semi-infinite simulation domain. From the simulation data we determined the distance, \(l_{\text{evap}}\), over which evaporation takes place – i.e. the distance that is needed to reach water saturation limit in CO\textsubscript{2} under the respective conditions.

Figure 5.6 shows the water saturation profiles in the CO\textsubscript{2} stream for different injection rates. Each simulation shows the typical increase of the water saturation in the CO\textsubscript{2} phase \((X_{H2O,SC})\) with distance from the injector till equilibrium concentration \((X_{\text{sat}})\) is reached. The data show an increasing extend of the zone of attraction with increasing injection rate. The lower panel shows the derived \(l_{\text{evap}}\) as a function of CO\textsubscript{2} injection rate. The experimentally estimated data are included in the plot. For the defined range of injection rates, evaporation zones in the order of \(l_{\text{evap}} = 3 \times 10^{-3}\) to above 10 m were found with a linear dependence on the injection rate. For the conditions at which the experiments were carried out, the zone of attraction has been simulated to be 0.4 m.

The presented kinetic simulations give valuable information about the size of the zone affected by salt precipitation and the distances over which solutes can be transported counter current in direction of the injector. This served the reservoir engineer as input for
Figure 5.6: Zone of potential attraction. Upper panel: Water saturation in the CO$_2$-rich phase as function of distance from the injection point. The profiles for different injection rates are shown simulated in a linear flow geometry. Lower panel: The zone of attraction as a function of injection rate. The filled symbols are obtained from experiments.
Figure 5.7: \( \mu \)CT data recorded with pseudo pore-scale resolution during \( \text{CO}_2 \) flooding. Top row: cross-sectional difference images showing the solid salt saturation in the region of local precipitation between 0 and 0.5 cm from the inlet (image c at maximum salt saturation) Lower image: 3D representation of the salt distribution at 0.25 cm from the inlet (orange-red). The initial \( \text{CO}_2 \) percolation pattern (after 0.4 h) is added at the right front corner of the 3D volume.

5.1.6 Effects on permeability: \( K(\phi) \) relationship

Up to this point we have discussed the longitudinal solute transport and the resulting precipitation profiles. However, the important question is related to the effect of precipitation – i.e. porosity reduction – on permeability and eventually on injectivity. While porosity reduction is measured by \( \mu \)CT, changes of permeability are reflected in the pressure drop \( \Delta P \).

The upper panel of Figure 5.8 shows the pressure drop over the core length during flooding (black line). \( \Delta P \) essentially decreases during the experiment. The onset of capillary back flow is visible as a small dip, with a subsequent \( \Delta P \) increase due to substantial local precipitation. But despite this porosity reduction, the effective permeability of the \( \text{CO}_2 \)-rich phase increased during the experiment, which means that relative permeability effects compensate for the absolute permeability (\( K \)) reduction. A \( \Delta P \) curve of a comparable experiment that showed a homogeneous precipitation pattern with about the same
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Figure 5.8: Top: Pressure drop $\Delta P$ over the core during CO$_2$ injection. Two cases are shown: (1) the local precipitation case as discussed in the text (black line), and (2) $\Delta P$ recorded during homogeneous precipitation for comparison (red line). The open symbols represent the development of the local precipitate (salt saturation in arbitrary units) in Figure 5.3. Bottom: $K(\Phi)$ relationships describing the experimental observations.
average porosity reduction is shown in the same plot (red line). The experiment was terminated after about 7 h and shows a smaller final reduction of \( K \) as in the heterogeneous case. From the final porosity profiles of both experiments as shown in Figure 5.3 and the respective pressure drop, we determine a \( K(\Phi) \) relationship for the dry state by using the correlation proposed by [Verma and Pruess, 1988]:

\[
\frac{K - K_C}{K_0 - K_C} = \left( \frac{\Phi - \Phi_C}{1 - \Phi_C} \right)^\tau,
\]

with \( K_C \) being the lowest value to which \( K \) can be reduced by precipitation. While \( K_C \) is a robust outcome, the exponent \( \tau \) and the critical porosity \( \Phi_C \) are not uniquely defined by the data set alone. However, the two extremes, \( \Phi_C = 0 \) and \( \Phi_C = 0.8 \), give similar results (with the exponent fitted to the data) as shown in the lower panel of Figure 5.8 such that either result can be used for a practical purpose in the relevant porosity range \( \Phi = \phi/\phi_0 = 1 \) to 0.8. As we will argue below, the maximum salt saturation is equal to the residual brine saturation \( S_{salt,max} = S_{W,res} \) and therefore \( \Phi_C = 1 - S_{W,res} = 0.8 \). With this we are able to determine the remaining fitting parameter \( \tau \), resulting in the parameter set: \( K_C/K_0 = 3.5 \cdot 10^{-3}, \Phi_C = 0.8 \) and \( \tau = 10.1 \).

\( K_C \) is likely to be a result of the observed precipitation pattern as shown in Figure 5.7 a–e. The images shows \( \mu \)CT cross sections (top row) and a 3D image of the data already presented in Figure 5.3 and were recorded with 24 \( \mu \)m voxel size (pseudo pore-scale resolution), which is a compromise between spatial resolution and a proper field of view with an improved time resolution (shorter total scanning time). The images range from close to the inlet (a) to about 0.5 cm into the sample (e) and show the solid-salt contribution of the dry sample. Conspicuously, the salt precipitates in spots on different length scales, ranging from a mm-scale to a sub-mm or even a micrometer-scale. A 3D representation of the solid salt distribution is shown in the lower part of Figure 5.7 in orange, while the early \( \text{CO}_2 \) percolation pattern is given in the right front corner of the 3D graph in blue. Both patterns occupy complementary space and overlap by less than 5 \% of the common cross section. This indicates that salt precipitates in the vicinity of the initially \( \text{CO}_2 \) occupied volume, leaving the initial \( \text{CO}_2 \)-pathways essentially open.

The data presented so far together with a couple of simple arguments allow us to construct a mind model – illustrated in Figure 5.22 – that supports and summarizes the findings of this work:

1. Viscous brine displacement and water evaporation act in parallel, but were found to be dominant on different time scales. While residual brine saturation is usually reached after injection of a few pore volumes, complete dry-out was reached after hundreds of pore volumes of injected \( \text{CO}_2 \). There is essentially no viscous brine displacement during dry-out.

2. The structure of the residually trapped brine phase is determined by capillary forces.

3. After reaching the solubility limit, salt precipitates in the brine phase, and hence in the volume occupied by the residual brine, \( S_{W,res} \).
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Figure 5.9: Top row: schematic view of the different flow regimes that determine the precipitation pattern and are characterized by the flow rate with respect to a critical flow rate \( q_{cr} \). Bottom row: schematic cross-sectional capillary-driven brine transport as described in the text.

4. The brine-saturated volume retracts during evaporation, leaving the precipitated salt behind.

5. There is no transport mechanism of liquid water vapor across the CO\(_2\)-brine interface and hence no transport mechanism of salt into the into the CO\(_2\) flow channels – the flow channels serve for water vapor transport, but stay open since salt precipitates in the residual brine phase.

6. Because of the well separated time scales of viscous displacement and evaporation, the maximum pore volume that can be filled by precipitate is the volume corresponding to the residual brine saturation, \( S_{W,res} \). We conclude: \( S_{salt,max} = S_{W,res} \). In Berea sandstone we typically find \( S_{W,res} \approx 0.2 \), which corresponds to the maximum observed salt accumulation in the present study.

5.1.7 Summary and conclusions

In summary, we investigated consequences of dry-zone formation in the vicinity of gas injection and production wells. In core flood experiments we injected dry SC CO\(_2\) into brine-saturated sandstone samples and reached complete dry-out. During the floods we measured effective permeability and fluid and salt saturations.

We found that time scales of viscous displacement and drying are practically well separates. Two mechanisms turned out to be of importance: (1) macroscopic solute transport due to capillary pressure gradients, which determines the macroscopic salt distribution, and
(2) the pore-scale arrangement of fluid phases during viscous displacement and the drying process. Such local effects determine effective permeability, the porosity-permeability relationship and probably the maximum possible saturation of salt in the pore space.

The principal mechanism of solute transport and the condition under which local precipitation occurs have been investigated by experiments and numerical simulations. The results are schematically displayed in Figure 5.9. We identified the origin of a critical flow rate above which salt precipitates homogeneously on a macroscopic scale. Below the critical flow rate, capillary-induced backflow of the remaining brine phase transports solutes in the direction of the injection point, where salt eventually precipitates. We further identified the length scale over which solutes can potentially be transported as a function of injection rate. The zone of attraction has been found to be 0.4 m for the described experimental situation and can reach several meters depending on the flow rate. Due to counter current flow, the amount of precipitate per unit volume can exceed the volume of salt originally dissolved in the brine in the respective volume.

From the presented experiments we calculated the permeability-porosity relationship, $K(\phi)$, describing the effect of precipitation in sandstone under the respective flow conditions. Despite the observed strong reductions of absolute permeability, the effective CO$_2$ permeability increased during the experiment in all cases. This relatively mild impact of precipitation on the sample permeability can be attributed to the observed local precipitation pattern; salt precipitates in the brine phase and hence in the vicinity of CO$_2$-conducting channels, leaving these channels essentially open.

The results of the study are of direct relevance for the risk assessment of injection operations, and are of practical used for injectivity modeling. For the prediction of macroscopic salt transport and the resulting porosity reductions, injection rates and effective evaporation rates need to be taken into account. The dimension of the affected zone has been estimated to be in the order of several centimeters to meters, which is valuable input for an adequate gridding around gas injectors and producers in reservoir modeling. For similar rock types, the respective permeability reduction can be modeled by the obtained $K(\phi)$ relationship.

Salt precipitation in similar rock types will lead to an absolute-permeability reduction, but to an improving effective permeability during the injection process. For that reason, we expect a relatively mild impact of salt precipitation on injectivity compared to the case of multi-modal carbonates as investigated in a companion paper by [Ott et al., 2015c].

5.2 The effect of salt precipitation in multi-porosity rocks

Drying of geological formations and the respective precipitation of salts can lead to serious consequences for upstream operations in terms of injectivity/productivity. We investigate the consequences of formation dry-out due to the injection of under-saturated supercritical fluid into a Middle-East dolomite formation for sequestration and enhanced oil recovery
operations. Compared to earlier reported results on sandstone, the experiments presented here show a more complex behavior with a much larger effect of porosity reduction on permeability. The permeability reduction is explained by the capillary-driven flow from the micro to the macro-porous regions on the rock’s pore scale at low brine saturations. This is in contrast to the solute transport behavior during dry-out of soils in ‘pass-by’ geometry where typically transport from macro- to micro-porous areas are found. The comparison of both rock types gives insight into the qualitatively different impact of salt precipitation on injectivity in multi- and single-porosity systems. The results might be of interest not only for gas injection and production like CO$_2$ sequestration and EOR operations, but in general for drying processes of porous media if more than one porosity class is included – e.g. drying of soils.

5.2.1 Introduction

The injection of dry or under-saturated gases or supercritical (SC) fluids into water-bearing formations might lead to a formation dry-out in the vicinity of injection wells [Pruess and García, 2002, Fuller et al., 2006, Giorgis et al., 2007, Hurter et al., 2007]. The dry-out is caused by the evaporation/dissolution of formation water into the injected fluid and the subsequent transport of dissolved water into the formation. Dry-out results in precipitation of solutes of the formation water and consequently in a reduction of the rock’s pore space and eventually to a reduction of permeability at the injection well. In the worst case there is even a total loss of injectivity [Pruess and García, 2002]. This is considered to be a substantial risk for injection operations for geological CO$_2$ storage and/or CO$_2$/acid gas injection for enhanced oil recovery (EOR). Mitigation methods such as fresh water injection to upfront lower salt concentrations are considered [Pruess and Müller, 2009], but are costly and not always possible or favorable for the respective injection operation. Consequently, an assessment of the risk of injectivity reduction is paramount for gas injection operations.

The extent of the dry zone and the average porosity reduction can reliably be modeled by numerical simulations [Pruess and García, 2002, Fuller et al., 2006]. The quality of the prediction depends thereby on the macroscopic mass balance and hence on the quality of the thermodynamic data. The associated reduction of permeability, however, is rather of microscopic origin and depends on the exact location of the precipitate. It therefore depends critically on the individual rock type and on local flow regimes. Pore-scale precipitation can not yet reliably be modeled by digital rock physics and is therefore largely subject to experimental research. However, there are only a few experimental attempts to investigate salt precipitation in flow through drying.

Zuluaga et al. investigated vaporization and salt precipitation in sand packs and sandstone for gas production wells [Zuluaga and Monsalve, 2001, Zuluaga et al., 2001]. At the GHGT-10 in Amsterdam 2010, two experimental studies on dry CO$_2$ injection have been presented. The experiments have been performed in sandstone in realistic storage conditions addressing capillary-driven solute transport, the condition of counter current flow [Ott et al., 2011b], and a permeability porosity relationship [Bacci et al., 2011]. Recently, [Peyssona et al., 2014] and [Andre et al., 2014] investigated the drying process by
nitrogen injection in sandstone. The data have been used to benchmark a numerical simulation tool for field-scale modeling of CO\textsubscript{2} injection. [Ott et al., 2011b] pointed out that modeling of vaporization by an equilibrium approach is not sufficient to describe core flood experiments. [Roels et al., 2014] performed core flood experiments and succeeded in the description of the saturation profiles by a kinetic approach.

Here we present the first study of flow through drying and salt precipitation in more complex carbonate rocks. We compare the behavior with the more simple sandstone case published in a companion paper [Ott et al., 2015b]. There, we determined capillary-driven solute transport in a model sandstone leading to homogeneous and heterogeneous salt distribution on a macroscopic scale depending on the injection rate. We quantified the porosity-permeability relationship and referred the observations to peculiarities of a primary drainage process. Our interpretation is based on the simple mono-modal pore structure of the rock. The carbonates investigated in the present paper show a distinctly different behavior that we attribute to the dual- or multi-modal pore structure as reflected in MICP (mercury injection capillary pressure). Such multi-pore-size systems have up to now not been considered in flow through geometry, but are discussed in literature for flow over geometry [Coussot, 2000, Lehmann and Or, 2009, Nachshon et al., 2011].

Typical examples refer to convective drying of soils by a gas flow (wind) over a free soil surface. In contrast to flow through drying, flow-over drying causes a capillary-driven transport perpendicular to the convective gas stream direction [Coussot, 2000, Lehmann and Or, 2009]. This might have some analogy to – e.g. – the flow through fractures with an interaction of the gas flux in the fracture and the drying rock matrix (see e.g. [Weisbrod et al., 2000]), or, as we find in the current paper, to the flow in a ‘macro’-porous system extracting water from micro-porous regions.

For drying in flow-over geometry, gravity plays an important role. Typically three drying regimes are observed [Coussot, 2000, Chauvet et al., 2009]. At early times the porous medium is saturated and drying takes place as for an open fluid surface. In the course of evaporation the surface gets desaturated, but capillary forces supply fluids against gravity to the surface – this is the so-called constant-rate regime, even if typically the rate is not constant, but slowly linearly decreasing as gravitational forces counteract capillary forces due to saturation differences – this is referred to as film thinning. If the depth of the de-saturation zone becomes too large, capillary forces cannot sustain water supply to the surface against gravity. At this point the water disconnects from the surface and the drying rate slows down from a linear ($d \propto t$) to a square-root-type of behavior ($d \propto \sqrt{t}$) after a more complex transition period [Chauvet et al., 2009]. In this so-called falling-rate period, the water transport to the surface is dominated by vapor diffusion.

If the aqueous phase is saline, the dry-out regimes and kinetics are modified. Salt leads to a continuous gradual reduction of the evaporation rate due to the increasing osmotic potential [Salhotra et al., 1985, Nachshon et al., 2011], in contrast to the constant rate for the deionized-water case. In a later stage, as the solubility limit is reached, salt precipitates, which leads to a decrease of evaporation rate due to reduction of hydraulic connectivity to the surface by the precipitate [Chen, 1992, Shimojima et al., 1996, Fujimaki et al., 2006, Nachshon et al., 2011].
5.2. SALT PRECIPITATION IN MULTI-POREITY ROCKS

In a dual porosity system with – ideally – vertically continuous and connected macro and micro-porous regions, the micro porosity acts like a wick [Nachshon et al., 2011]. Without being in capillary contact, both subsystems would act according to the behavior of the simple pore system as described above. If both subsystems are connected – i.e. are in capillary equilibrium – evaporation from the micro-porous system is compensated by capillary-induced flow from the macro- to the micro-porous system. This leads to an effectively higher ‘drying rate’ of the macro-porous system by flow [Lehmann and Or, 2009, Nachshon et al., 2011]. As a consequence, salt precipitates preferentially at the top surface of the fine textured material – i.e. the micro porosity – with the coarse textures regions sustain a high gas permeability [Nachshon et al., 2011]. The capillary entry pressures of both subsystems were identified as controlling parameters.

The data presented in this paper is part of a study performed to assess the risk of injectivity loss for miscible gas injection EOR project. The target is a Middle-East dolomite reservoir with a multi-porosity rock matrix. The reservoir is at residual brine saturation ($S_W \approx 0.15$), with the NaCl-dominated brine being at the saturation limit (about 280g/L). In the experiments we investigate the impact of salt precipitation by injecting dry SC-CO$_2$ into rock samples with different degrees of heterogeneity, at different water saturations, $S_W$, and with decane as proxy for the hydrocarbon phase. The experimental conditions are chosen to match key parameters for precipitation in the field as scaled from the field thermodynamic conditions and fluid properties. CO$_2$ was injected at residual water saturation to mimic the actual field scenario, and in 100% brine/water-saturated samples as worst-case scenario. The latter case is more extensively discussed in the present paper and is relevant for geological CO$_2$ storage in complex carbonate aquifers. The results of this study have been presented at the GHGT-11 in Kyoto 2012 [Otte et al., 2013] and are directly comparable to an earlier study on a well-sorted sandstone [Ott et al., 2015b], and hence allow the study of salt precipitation in multi-porosity versus single-porosity systems.

5.2.2 Salt precipitation in well-sorted sandstone

In a companion paper, we discuss salt precipitation in Berea sandstone [Ott et al., 2015b], which we briefly recap in this section. By a combination of experiments and numerical simulations it has been shown that there are different precipitation regimes depending on the CO$_2$ injection rate, as illustrated in Figure 5.9; above a critical volumetric flow rate $q_{cr}$, a dry-out front propagates uniformly in flow direction and salt precipitates accordingly in a uniform way. Below $q_{cr}$, the water saturation gradient resulting from evaporation is strong enough to induce a capillary-driven back flow and solute transport in the direction of the injection point. This is because substantially more water dissolves/evaporates close to the point of injection than further downstream. The brine solutes are transported to the point of injection and precipitate there. As a consequence, it is possible to precipitate locally more salt than originally dissolved in the brine phase within the same volume. As $q_{cr}$ is reached, the dry-out front stops, since the water transport upstream, induced by capillary forces, matches the water transport downstream in the CO$_2$-rich phase (vapor transport). Salt precipitates at the spot where this condition is met – with a high change of pore space
plugging. At this point the critical volumetric flow rate \( q_{cr} \) can be determined from the mass balance by:

\[
q_{SC} \cdot \rho_{SC} \cdot X_{H2O,SC} = q_{aq} \cdot \rho_{aq} \cdot X_{H2O,aq},
\]

where \( q_{SC} \) and \( q_{aq} \) are the volumetric flow rates of the CO\(_2\)-rich phase and the aqueous phase, \( \rho_{SC} \) and \( \rho_{aq} \) are the phase densities, and \( X_{H2O,SC} \) and \( X_{H2O,aq} \) are the mass fractions of water in both phases, respectively.

The capillary-driven brine/salt transport explains qualitatively the experimentally observed solid-salt saturation in the longitudinal direction [Ott et al., 2015b]. However, it does not explain the pressure data, and respectively the observed effective permeability during dry-out. In general, the effective permeability – \( K_{eff,CO_2} = K \cdot k_{r,CO_2} \) – changes due to the reduction of the absolute permeability \( K \) as consequence of salt precipitation, and due to relative permeability, \( k_{r,CO_2} \), because of fluid saturation changes during dry-out. Further below in Figure 5.12 we show experimental pressure data during dry-CO\(_2\) injection in Berea sandstone. The data are recorded under \( q_{SC} > q_{cr} \) conditions, showing a homogeneous precipitation profile. The pressure drop decreases over the experimental time according to an increasing effective permeability, with a substantial mean solid-salt saturation of about 4.5% of the pore space. Even in a case with a local pore space occupation as high as 20%, the effective permeability improved during the experiment. The experimental results suggest salt precipitation in the vicinity of the CO\(_2\)-percolation pathways, leaving the cross-sectional area of these pathways essentially open, which is illustrated further below in Figure 5.22.

The sandstone example illustrates that capillary- rather than viscous-driven transport plays the key role at low \( S_W \) as typical for dry-out situations. We therefore expect that differences in pore architecture as reflected in MICP lead to different transport mechanisms and to a different response on salt precipitation.

### 5.2.3 Multi-porosity Dolomite samples

The experiments were performed on dolomite-based reservoir rock samples with 3 to 15 wt\% anhydrite and some halite. The sample porosity varies between 0.05–0.22 and the permeability ranges between 1–300 mD.

The rock matrix shows a high degree of heterogeneity. Figure 5.10 shows images of a typical sample with heterogeneity on the sample scale (photo and CT scan) and on the micro scale (SEM image): heterogeneous structures are observed on all scales, resulting in a true multi-porosity system. MICP (mercury injection capillary pressure) curves of all samples used in the present study are shown in Figure 5.11. The data reflect the multi-porosity nature of the samples and the sample-to-sample variation. Berea data (red) is plotted for comparison.

SC CO\(_2\)/AG is known to flow predominantly in regions of lowest entry pressure associated with highest permeability [Berg et al., 2013a]. Consequently, high-permeability samples (30–300mD) were selected for this study, with the porosity in the range between 0.13–0.19. The sample dimensions were 1 inch \( \phi \times 5 \) cm (7cm for samples 3). Table 1 pro-
Figure 5.10: Photo, CT scan and SEM image of a Middle-East rock sample (sample 10).
Figure 5.11: Mercury-air capillary pressure (MICP) curves of different rock samples used in the present study. The images (Figure 5.10) and MICP curves show the multi-porosity character of the rock matrix and the heterogeneity of the formation with a strong sample to sample variation. Sample numbers are indicated in the plot (compare Table 1).

vides an overview of the studied samples and the flooding sequence as discussed further below.

5.2.4 Flow experiments

The experiments were carried out in a core flood setup designed for flooding with volatile and reactive fluids. A detailed description of the unit can be found elsewhere [Ott et al., 2012]. The flow geometry was vertical, with fluids being injected from top to bottom. µCT scanning was used to identify potential local salt accumulations at the inlet of the core as reported in [Ott et al., 2015b] – in this study, however, we did not find any indication of local salt accumulation. Fluid densities of the injected and produced fluids were recorded and effective permeability ($K \cdot k_{rel}$) was measured on-line by the differential pressure $\Delta P$ at constant flow rate. Before and after the experiments we performed a multi-rate permeability ($K$) measurement with CO$_2$ at experimental conditions.

The experiments were performed with a generic set of fluids: SC-CO$_2$ as acid-gas phase, decane as proxy for the hydrocarbon phase, and NaCl brines instead of the NaCl-dominated reservoir brine. The experimental conditions were $P$ = 110 bar and $T$ = 110°C and the CO$_2$ injection rate was 1.12 ml/min/cm$^2$, chosen to match the relevant field conditions as briefly outlined in the following; based on previous experiments in sandstone, capillarity and the timescale of dry-out are key for the distribution of precipitates in the rock, and
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Table 5.2: Samples and flooding sequences of the individual experiments. (cf) stands for centrifuge saturation resulting in a decane saturation at connate water. * estimated form production data. † refers to the maximum observed reduction during the CO\textsubscript{2} flood. \(S_{W,ini}\) refers to the brine saturation before the CO\textsubscript{2} flood.

<table>
<thead>
<tr>
<th>Exp. sample</th>
<th>K (mD)</th>
<th>(\phi)</th>
<th>flooding sequence</th>
<th>salinity %(wt% NaCl)</th>
<th>(S_{W,ini})</th>
<th>(K_{fin})</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>B Berea</td>
<td>500</td>
<td>0.22</td>
<td>brine-CO\textsubscript{2}</td>
<td>20</td>
<td>1</td>
<td>–</td>
<td>100 bar, 45°C; Fig. 5.12, top</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>61</td>
<td>water-CO\textsubscript{2}</td>
<td>0</td>
<td>1</td>
<td>–</td>
<td>Fig. 5.15</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>61</td>
<td>brine-CO\textsubscript{2}</td>
<td>6</td>
<td>1</td>
<td>76</td>
<td>Fig. 5.15</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>97</td>
<td>water-CO\textsubscript{2}</td>
<td>0</td>
<td>1</td>
<td>–</td>
<td>Fig. 5.12, top</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>97</td>
<td>brine-CO\textsubscript{2}</td>
<td>6</td>
<td>1</td>
<td>320, 1240†</td>
<td>Fig. 5.12, top</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>97</td>
<td>brine-decane-CO\textsubscript{2}</td>
<td>12</td>
<td>0.5±0.1*</td>
<td>1560†</td>
<td>Fig. 5.12, top</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>34</td>
<td>water-CO\textsubscript{2}</td>
<td>0</td>
<td>1</td>
<td>–</td>
<td>not shown</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>34</td>
<td>brine-CO\textsubscript{2}</td>
<td>6</td>
<td>1</td>
<td>250</td>
<td>Fig. 5.12, bottom</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>34</td>
<td>brine-decane (cf)-CO\textsubscript{2}</td>
<td>28</td>
<td>0.12</td>
<td>–</td>
<td>Fig. 5.12, bottom</td>
</tr>
<tr>
<td>9</td>
<td>14</td>
<td>307</td>
<td>brine-decane (cf)-CO\textsubscript{2}</td>
<td>28</td>
<td>0.23</td>
<td>–</td>
<td>not shown</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>33</td>
<td>brine-decane (cf)-CO\textsubscript{2}</td>
<td>28</td>
<td>0.18</td>
<td>–</td>
<td>not shown</td>
</tr>
</tbody>
</table>

Consequently for the permeability behavior. Capillarity determines the solute transport at low \(S_{W}\) as discussed above and was matched in the present case by matching the capillary number, \(N_{cap} = \frac{u\mu}{\sigma}\), with \(u\) and \(\mu\) being the linear velocity of the injected fluid and its viscosity, and \(\sigma\) the respective CO\textsubscript{2}/AG-brine interfacial tension. \(\sigma\) of the CO\textsubscript{2}-brine system match over a wide \(P\) and \(T\) range \(\sigma_{model} \approx \sigma_{exp}\), and hence, \(N_{cap}\) can be adjusted by \(\frac{q_{exp}}{q_{field}} \approx \frac{\mu_{field}}{\mu_{exp}}\). The timescale of dry-out determines the crystallization process and is caused by the water transport in the injected fluid phase, which is determined by the solubility limit of water in the injected fluid phase \((\rho \cdot X)\) and the injection rate \(q\). We scale the rate by \(q_{exp} \cdot \rho_{CO\textsubscript{2}} \cdot X_{H_2O,CO\textsubscript{2}} \approx q_{field} \cdot \rho_{AG} \cdot X_{H_2O,AG}\). Under experimental conditions, the water content in the CO\textsubscript{2} phase is \(\rho_{CO\textsubscript{2}} \cdot X_{H_2O,CO\textsubscript{2}} \approx 2\cdot10^{-3}\) g/ml. The amount of precipitate depends on the immobile brine fraction that finally gets dissolved in the CO\textsubscript{2}-rich phase. It was kept constant for all experiments by adjusting the brine salinity as further discussed in the text. In situ CT imaging shows overall a complex pattern due to the complex rock structure, but no indication of salt accumulation due to macroscopic capillary-driven back flow was observed as in the sandstone case for \(q > q_{cr}\).

We firstly discuss CO\textsubscript{2} flow experiments at \(S_{W}=1\) initial brine saturation. The results allow a direct comparison with the earlier experiments on sandstone. In subsequent experiments we introduced in two further steps a hydrocarbon phase as discussed in more detail below. The initial salinity has been chosen in all cases such that the same amount of salt precipitates in the samples, which requires an estimation of the immobile brine fraction by \(k_r(S_{W})\); this approach is valid, since viscous displacement (which does not lead to precipitation) and water evaporation (leading to solute enrichment and eventually to salt precipitation) are acting predominantly on different time scales: minutes for viscous displacement versus hours for evaporation and precipitation [Ott et al., 2015b].

CO\textsubscript{2}-injection experiments at 100% initial brine saturation were performed on three
Figure 5.12: Pressure drop ($\Delta P$) over the core during CO$_2$ injection. Upper panel: Experiment on Berea sandstone (black) and a dolomite field sample (red), pre-saturated with an aqueous phase; in the first experiment with water (open squares), in a second experiment with brine (filled squares) and in the third experiment with brine and a subsequent decane flood (red line). Lower panel: Experiments on a dolomite sample at 100% brine saturation (filled symbols) and pre-saturated with decane at residual water saturation.
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different samples (Exp. 2, 4 and 7). As base case we performed experiments on the same samples in advance, but initially saturated with pure water to separate relative permeability effects from effects of precipitation on the effective permeability (Exp. 1, 3 and 6). Results are shown in the upper panel of Figure 5.12 (Exp. 3 and 4). The base case (pure water experiment) shows, as expected, an increasing $K_{\text{eff}}$ (decreasing $\Delta P$) over time until the experiment was terminated after injection of 150 PV and about 9 hours. The experiment was repeated on the same rock sample and under the same conditions, but with the sample being saturated with brine instead of water. The brine salinity was 6 wt%, corresponding to about 1/4 th of the field value assuming that about 50–60% of the total water evaporates (compared to 15% in the field). About 2.5 hours after the experiment was started, $\Delta P$ starts to deviate substantially from the base case, which we interpret as the onset of precipitation with the brine salinity reaching the saturation limit. From then on $\Delta P$ increases steadily until a maximum is reached after about 8 hours of CO$_2$ injection (130 PV injected), which we interpret as the point at which the sample is dry. $K_{\text{eff}}$ improves in the following, which is likely due to the extraction of salt-bound water reducing the total volume of the precipitate. The permeability reduction observed in this experiment is more than two orders of magnitude (factor of about 350 in $K_{\text{eff}}$ compared to the base case). In all cases (Exp. 2, 4 and 7) we found permeability reductions of one to three orders of magnitude, probably depending on the exact rock structure (heterogeneity). Permeability changes are reported in Table 5.2.

In the next step we went closer to the field case (Exp. 5). The sample was presaturated with brine (12 wt% NaCl) and subsequently flooded with decane to displace brine without drying effect (water is not soluble in decane). After injection of 40 PV of decane, dry CO$_2$ was injected, leading to a miscible displacement of the oil phase and to immiscible displacement of the brine phase and finally to evaporation of water. The difference compared to the aqueous experiments is that the brine phase has a reduced mobility after decane injection compared to the pure aqueous experiment. However, this experiment also showed a reduction of permeability by more than two orders of magnitude (a factor of about 250 – data not shown), comparable to the pure aqueous case. How comparable both experiments are is not clear, since we doubled the brine-salt concentration in anticipation of a much better brine displacement by decane than by CO$_2$, resulting in a lower water saturation and mobility.

In the final step we prepared samples ex-situ by initial water/brine saturation and a subsequent decane primary drainage in a centrifuge in order to get the aqueous phase saturation down to true residual saturation as in the field case (Exp. 8-10). The obtained brine saturations are reported in Table 5.2 and are in alignment with residual saturation reported from the from the field. This procedure results in an immobile water/brine phase in the sense of viscous displacement. The ex-situ prepared samples were mounted in the core-flooding unit and then further flooded with decane and subsequently with SC CO$_2$.

$^3$The permeability is strictly speaking an effective permeability, since it still shows a slight variation at the end of the drying process. It appears that well after CO$_2$ breakthrough $K_{\text{eff}} \sim K_{\text{abs}}$ and hence $\Delta K \sim \Delta K_{\text{eff}}$. 


under otherwise the same conditions as in previous experiments. The brine salinity was close to the saturation value (28 wt% NaCl). The bottom panel of Figure 5.12 shows $\Delta P$ during the experiments (Exp. 7 and 8). Only a minor change of effective permeability was observed (in the order of equipment sensitivity), while the respective aqueous experiment (100% initial brine saturation) on the same sample showed a steady state after about 10 hours (220 PV injected), with a 110-fold reduction of permeability in line with the results observed in the previous aqueous experiments. The result at residual brine saturation was reproduced in Exp. 9 and 10 on samples with different degrees of heterogeneity.

### 5.2.5 Conceptual model

There is a clear qualitative difference between well-sorted sandstone and multi-porosity dolomite in the response to dry-out, and apparently, this difference is caused by the nature of the microscopic pore structure of the rock types. In the following we develop a conceptual model, which captures the main mechanism behind the observed behavior. The model is simple, but has some strength; it is clear, it explains the experimental data with a minimum set of assumptions for both rock types and it delivers a first concept for numerical upscaling and modeling of dry-out in multi porosity systems.

For CO$_2$-brine systems, CO$_2$ can be assumed to be the non-wetting phase, which enters first the low-$p_C$ regions of the rock, generating preferred CO$_2$-flow pathways. We can further assume that these pathways are associated with the macro-porous subsystem. Since we observe a high permeability reduction, we have to assume transport of salt from the micro-porous system to the macro pores in which CO$_2$ flows. Therefore, micro porosity might serve as a brine reservoir and accordingly as a salt supply for the macro system in contrast to the sandstone case without such a supply. Both subsystems will tend toward a capillary equilibrium at all time. Consequently, the difference in capillary pressure resulting from the selective displacement is a potential transport mechanism of brine and respectively of the solutes between both pore subsystems. This might lead to a higher salt accumulation in the macro-porous system where the CO$_2$ is predominantly flowing and a reduction of permeability, $K$, therein. However, this is counterintuitive considering the dry-out of soils discussed above (see Chapter 5.2.1), where generally a brine transport in the opposite direction is observed.

For the simulations we use the Shell in-house reservoir simulator, MoReS. With the
presented model we do not aim to describe the experiments quantitatively in detail, but rather wish to explain the underlying behavior and to attribute it to fundamental rock properties; despite the complex nature of the rock, for clarity and simplicity we consider a dual-porosity system. The model assumes the two subsystems as two separate porous domains in capillary contact with each other (see Figure 5.13). Since we do not observe a macroscopic solute transport, we can simulate the principal behavior already in a zero-dimensional (0D) system, resulting in a simulation domain consisting of two grid blocks only, one for each subsystem. The boundary conditions were realized through connections to “wells” on both ends of the grid blocks. The inlet slice has a constant rate boundary condition (through connection to an “injector well” running at constant volume rate, thus modeling the fixed flow rate from the pump). The output slice is given a constant pressure (through a “production well” running at constant pressure, thus modeling the back regulated pressure).

Key parameters characterizing the properties of both subsystems are (1) the permeability and (2) the capillary pressure, $p_C(S_W)$. We assign a realistic permeability to the macro-porous system, and make for simplicity the micro-porous volume essentially impermeable in the direction of injection, which is a good approximation, since low-viscous and non-wetting CO$_2$ will essentially flow in the pore space with the lowest capillary pressure [Berg et al., 2013a, Ott et al., 2014a, Ott et al., 2015a]. The magnitude of capillary pressure for both subsystems was estimated from the MICP data as shown in Figure 5.11. The upper panel of Figure 5.14 shows $p_C(S_W)$ for both subsystems as applied in the simulations; both saturation functions are the same and individually typical for unimodal pore systems, but to describe the micro-pore system we scaled the respective curve by a factor of 8.

The same relative permeability saturation function $k_r(S_W)$ was assigned to both subsystems. $k_r(S_W)$ was determined from a fit to the experimental data from the dry-out of the water-saturated sample (shown in Figure 5.15), where ΔP variation is determined by relative permeability only, excluding effects of salt precipitation. The reduction due to the precipitation-induced porosity change is modeled by introducing a $K(\phi)$ relationship as proposed by [Verma and Pruess, 1988]:

$$\frac{K}{K_0} = \left( \frac{\Phi - \Phi_C}{1 - \Phi_C} \right)^\tau,$$

with $K_0$ being the initial absolute permeability, $\Phi = \phi/\phi_0$ being the actual porosity ($\phi$) normalized to the initial porosity $\phi_0$ and $\Phi_C$ being the normalized critical porosity at which the permeability vanishes. The function can be fitted to experimental data by the exponent $\tau$ and $\Phi_C$. We used a sharp $K(\phi)$ function with a loss of permeability at a solid-salt saturation of about 10% of the pore volume as shown in the bottom panel of Figure 5.14. We ignore a critical permeability $K_C$ [Ott et al., 2015b] for simplicity.

The thermodynamic model is a Cubic Plus Association (CPA) model, implemented in Shell in-house reservoir simulator. CPA is an extension of traditional cubic equation of state, with an association term that takes care of the strong H$_2$O intermolecular forces.
Figure 5.14: Left: capillary pressure curve $p_C(S_W)$ and the same curve scaled by a factor of 8. These curves are used for the simulations, representing $p_C(S_W)$ of the macro- and micro-porous subsystems, respectively. The red curve shows the approximate total $p_C$ curve composed from the one of the micro and macro porosity domains with the respective volumetric ratio of both porosity values (25% macro porosity case). The arrows indicate a saturation difference between both subsystems in capillary equilibrium. Right: $K(\phi)$ relationship after Verma & Pruess and as used in the simulations (effectively applied to the macro-porous subsystem).
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Figure 5.15: Pressure difference $\Delta P$ measured across a carbonate rock during CO$_2$ injection. The sample was first water-saturated (Exp. 1: black symbols) and later brine-saturated (Exp. 2: red symbol). The lines show the respective simulations as described in the text.

(polar effects, hydrogen bonding) in the liquid phase. The model is capable of accurately describing mutual H$_2$O-CO$_2$ solubilities including the effect of salinity on the mutual solubilities.

Figure 5.15 shows simulation results in comparison to experiment 1 and 2. Note that we do not aim for a quantitative description, but are after the mechanism and an order of magnitude match. The experimental $\Delta P$ has been matched with the discussed $K(\phi)$ by variation of the volumetric ratio of the macro porosity to the total porosity of the simulation domain as explained further below. Both sets of experimental data are well described by the same model, assuming a dry-out of a pure water phase for the base case and a brine phase with the salinity of the actual experiment. In this case we find an absolute permeability reduction by a factor of about 20. It is important to note that the step-like function of the base case (pure-water) with the long-lasting plateau and rapid decline cannot be described assuming a simple (unimodal) porosity structure (see also Figure 5.16).

In the following we would like to highlight some of the relevant properties of the model. The simulated $\Delta P$ is most sensitive to (1) the $K(\phi)$ relationship with which the effect of salt precipitation on injectivity is introduced, and (2) the ratio of the macro-porosity to the total porosity. Of fundamental interest are the borderline cases of single-porosity and dual-porosity systems.

The top panel of Figure 5.16 shows simulations of CO$_2$ floods with 25% macro porosity (dual-porosity system) and 99% macro porosity (single-porosity system), using otherwise the same model and parameters (in particular the total porosity). We simulated the base
Figure 5.16: $\Delta P$ during dry-out of a single-porosity and dual-porosity system (top panel). The simulation domain was initially saturated with water (black lines) for the base case without salt precipitation, and with brine (red lines). Bottom: $\Delta P$ of the brine pre-saturated system for different volumes of macro porosity $V_{mac}/V_{total}$. 
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case with pure water, showing only the effect of relative permeability, and the actual dry-out of a brine phase under simulation settings that were otherwise the same. The single porosity case mainly differs from the dual or multi-porosity case with respect to the dry-out time, and – more importantly – in the degree of permeability reduction. The single porosity case shows a shorter time until a steady state (full dry-out) is reached. This is due to the water/brine storage property of the micro porosity leading to a more gradual release of water to the CO$_2$ phase in case of dual porosity. As the lower panel of Figure 5.16 shows, a gradual change of the volume fraction of the macro-porous system, $V_{mac}/V_{total}$, gradually changes both properties, the permeability reduction and the delay time.

In contrast to the dual-porosity case, which shows a clear impairment of injectivity, the single-porosity case shows an effective permeability, which improved from the initial to the final state of the CO$_2$ flood. But the model shows a dip in the $\Delta P$ curve caused by the relative permeability effect setting in faster than precipitation occurs. The Berea experimental data does not show such a dip, but a steadily decreasing $\Delta P$ as shown in Figure 5.12. This difference between experiment and the simulation can be explained by the salt concentration of the brine, which was close to the saturation limit in the Berea experiment, in contrast to the dilute brine used in the respective present simulation and in the carbonate experiments. As a consequence, in the simulation more time is needed to reach the salt saturation limit, and hence precipitation occurs at a time where $k_r$ has already increased $K_{eff,CO_2}$.

Figure 5.17 shows the simulated porosity reduction due to salt precipitation (top) and water respectively brine saturation, $S_W$ (bottom), for both the single-porosity and dual-porosity case. A rapid de-saturation to a value close to residual brine/water saturation is observed in the macro-porous system, while the de-saturation in the micro-porosity follows a rather linear trend, caused by the constant CO$_2$-injection rate and the associated constant water transport by evaporation and transport into and in the CO$_2$ phase in the macro-porous system. Since the CO$_2$ phase flows only in the macro-porous system, the behavior of $S_W$ reflects the brine transport from the micro to the macro-porous system. The same simulation with pure water leads to a qualitatively similar picture, but with a shorter dry-out time due to the solubility limit of water in the CO$_2$-rich phase for different salinities and with a full dry-out of the macro system after about 6 hours. An interesting behavior shows the porosity as a function of time. The salt, originating mainly from the micro-porous system, precipitated only in the macro-porous system with no precipitation in the micro porosity.

5.2.6 Summary and interpretation

We investigated the impact of salt precipitation on injectivity during acid-gas/CO$_2$ injection in dolomite-based reservoir rock by means of core flood experiments. The effect on injectivity has been found to depend on the mobility of the brine phase, with a potentially high impairment at high water saturations, i.e. at high mobility; salt precipitation in the investigated field samples led to a strong decrease of permeability in cases where the brine phase was above residual saturation, i.e. with a mobile brine phase. Which means that if
Figure 5.17: Simulation results for the dual-porosity system. Top: water- (thin lines) and brine- (thick lines) saturation (respectively $1 - S_{CO2}$) in the macro- (black) and micro- (blue) porous subsystem. Bottom: porosity reduction in the macro- (black) and micro- (blue) porous subsystem due to salt precipitation. The phase density corresponds to the density of dry salt.
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the initial $S_W$ is above residual water saturation there is a potential risk of injectivity loss. At residual saturation, as in the present field case, i.e. with an immobile brine phase, the effective permeability is not affected; from these experiments we expect no risk of injectivity loss for the current EOR project. However, sequestration in an aquifer of similar rock structure would be at risk.

The pure aqueous case study (at $S_{W, initial} = 1$) can directly be compared to the earlier study on the more simple unimodal sandstone. The observed behavior in dolomite is in strong contrast to the behavior that has been observed in sandstone, where the effective permeability improved during injection (relative permeability effect vs. effect of precipitation). The strong impact on the permeability is apparently caused by the multi-porosity nature of the dolomite rock matrix. The underlying mechanism has been identified by numerical simulations of single and dual-porosity systems, and the experimental observations have been qualitatively (semi-quantitatively) reproduced. Figure 5.22 illustrates and summarizes the underlying mechanisms for the sandstone and the carbonate, respectively.

Figure 5.22 (top: sandstone case) shows a schematic view on the pore scale of a simple sandstone. After drainage, the brine phase is at residual saturation and essentially immobile since bound by capillary forces. During the evaporation phase, water is removed and the residual brine phase further retracts. Salt predominantly precipitates in the brine phase and hence does not hinder the CO$_2$ flow.

We find a similar situation during advection and the early evaporation phase for the dolomite case. This is schematically shown in Figure 5.22 (bottom: carbonate case): the residual water phase retracts due to evaporation of water. However, the brine-saturated micro-porous system stays in contact with dry CO$_2$ and water evaporates at the interface (scenario (a) – evaporation phase). Before the entry pressure of the micro-porous system is reached, the micro-porous regions are recharged by the residually trapped phase in the macro-porous subsystem. De-saturation of the micro-porous subsystem starts if $p_C$ in the macro system is equal to the one of the micro system, i.e. as the macro system is largely desaturated (scenario (b)). This is the time where the micro system desaturates, to a minor fraction by evaporation, but mainly by a capillary-driven flow from the micro to the macro system where the water evaporates in the subsequent step and the salt precipitates.

In the dual-porosity model, the micro-porous volume acts as a brine reservoir gradually supplying brine and salt respectively to the CO$_2$-conducting macro-porous system. Solid salt has been found to precipitate only in the porosity class conducting the CO$_2$. With a given $K(\phi)$ relationship the volumetric ratio of macro to micro-porosity determines the degree of permeability reduction, explaining the improving effective permeability in simple sandstone and the strong reduction in the dolomite-based multi-porosity reservoir rock. This effect is amplified by the effectively reduced CO$_2$-conductive cross-section due to the presence of the micro-porous subsystem.

At this point, we are able to draw the analogy between drying in flow over geometry and flow through drying of multi-porosity rocks: the macro-porous domain is the CO$_2$ conducting pore system in analogy to the open space above drying rock or soil. The micro-porous domain stays in contact with the macro pores and undergoes a ‘pass-by’ drying in analogy to the ‘flow over’ geometry. However, in contrast to the open space, we can assign
a capillary pressure curve to the macro-porous system which triggers in the final stage of drying a flow from the micro- to the macro-porous subsystem which causes the salt to precipitate in the CO$_2$ conducting system.

5.3 Microscale solute transport and precipitation

Formation drying and salt precipitation due to gas injection or production can have serious consequences for upstream operations in terms of injectivity and productivity. Recently, evidence has been found that the complexity of the pore space and microscopic capillary-driven solute transport plays a key role in the relationship between permeability and porosity. In this study, we investigate drying and salt precipitation due to supercritical CO$_2$ injection in single-porosity and multiporosity systems under near well-bore conditions. We image fluid saturation states and salt deposition by means of microcomputerized tomography scanning during desaturation. We observe capillary-driven transport of brine and the respective solutes on the pore scale. Solute transport between porosity classes determines the distribution of the deposits in the pore space and the permeability porosity relationships—$K(\phi)$—for flow-through drying.

5.3.1 Introduction

Drying of porous media is an important subject in many natural and industrial processes. During drying, water evaporates into a convective gas stream and the salts, originally dissolved in the brine, precipitate after reaching the solubility limit. It is known that salt precipitation can cause damage in historic monuments and buildings [see, e.g., [Goudies and Viles, 1997]; [Shahidzadeh-Bonn et al., 2010]; [Flatt et al., 2014]], controls water loss from land surfaces [Chen, 1992, Scanlon et al., 1997, Nachshon et al., 2011], and can lead to injectivity loss for gas production and injection operations like, e.g., for CO$_2$ storage [Pruess and García, 2002, Fuller et al., 2006, Giorgis et al., 2007] as the present work refers to. All these topics have the fundamental solute transport mechanisms in common, which makes it worthwhile to discuss solute transport and salt precipitation in porous media across disciplines. For the more general discussion, we refer to gas as the drying agent and to CO$_2$ in the more specific sections.

In contrast to most hydrogeological problems and oil and gas production scenarios, where flow is driven by viscous forces, in the drying regime brine saturations ($S_W$) are generally low and the brine phase is bound by capillary forces and hence largely immobile. In this regime, flow and solute transport is determined by capillary- and osmotic-driven processes. Resulting capillary pressure gradients are responsible for macroscopic solute transport, which determines the macroscopic distribution of the final salt deposit, and hence the porosity profile as a function of space, $\phi(x)$ [Giorgis et al., 2007, Ott et al., 2011b]. However, as we will discuss in this paper, the associated permeability reduction and hence the $K(\phi)$ relationship is of microscopic origin and is determined by microscopic solute transport and eventually the exact microscopic distribution of the precipitate in the
5.3. MICROSCALE SOLUTE TRANSPORT AND PRECIPITATION

Recent studies have highlighted the role of heterogeneity in the microscopic texture in controlling the water evaporation rate and the exact location of deposition (Ott et al., 2011b, Ott et al., 2013; Roels et al., 2014; Shokri, 2014). Recent evidence suggests that heterogeneity in the microscopically textured regions plays a fundamental role in controlling the water evaporation rate and the exact location of deposition (Lehmann and Or, 2009; Nachshon et al., 2011; Ott et al., 2013) in both flow-over and flow-through geometries. For the flow-over case, ideally vertically continuous and connected macroporous and microporous regions, the microporosity acts like a wick (Nachshon et al., 2011). Without being in capillary contact, both subsystems would act according to the behavior of monomodal pore systems (described by Cousot, 2000 and Chauvet et al., 2009). If both subsystems are connected, i.e., aiming for capillary equilibrium, evaporation from the microporous system is compensated for by capillary-induced flow from the macroporous to the microporous system. Capillary-driven solute transport would as well be observed if the pore architecture were the same but the wettability of adjacent regions would be different. This issue has been recently discussed in Shokri and Or, 2013. For essentially water-wet systems, capillary pressure contrast leads to an effectively higher “drying rate” of the macroporous system by flow (Lehmann and Or, 2009, Nachshon et al., 2011). As a consequence, salt precipitates preferentially in the fine-textured regions, i.e., the microporosity, while the coarse-textured regions sustain a high gas permeability (Nachshon et al., 2011). This is seemingly in contradiction to observations in flow-through geometry by Ott et al., 2013 as discussed in the following.

Ott et al., 2013 found for different pore systems a qualitatively different response of permeability to salt precipitation due to CO₂ injection. The effective permeability, \( K_{\text{eff}} = k_{\text{rel}}(S_W) \times K \), increased during flow-through drying for a simple (essentially monomodal) sandstone, which implies that the relative gas permeability saturation function \( k_{\text{rel}}(S_W) \) increases due to drying—a reduction in water saturation—more rapidly than the decrease in absolute permeability \( K = K(\phi) \) due to salt precipitation. This limits the effect of salt precipitation on injectivity. It was suggested that salt does not precipitate in the CO₂ conducting channels and therefore does not contribute to a reduction in \( K_{\text{eff}} \) (Ott et al., 2011b, Ott et al., 2013). However, for carbonates with a more complex pore architecture, \( K_{\text{eff}} \) decreased by orders of magnitude under comparable conditions (Ott et al., 2013). This result is in contrast to the sandstone case and can only be explained by precipitation of salt in the CO₂ conducting pore volume, which requires an active brine transport mechanism from smaller pores into the CO₂ conducting macroporosity.

With this study, we present direct observations of solute transport and precipitation in the rock’s pore space during drying processes. The objective is to understand the distinctly different impact of salt precipitation on the injectivity in simple sandstone and in carbonates with a more complex pore architecture in flow-through geometry. For the carbonate case, we observe the brine transport from macroporous to the microporous regions suggested previously (Lehmann and Or, 2009, Nachshon et al., 2011) and in a later stage a novel and seemingly counterintuitive reverse process, with brine flow into the larger pores. We explain both in a model of capillary equilibration processes. The data are directly relevant for the risk assessment of CO₂ storage operations with respect to injectivity, but the observed transport mechanisms are of general interest for other situations where salt precipitation occurs.
5.3.2 Microscale experiments

We performed small-scale core flood experiments and used microcomputerized tomography (µCT) as an analytical tool for in situ pore-scale imaging of fluid phases and salt deposits. The samples were small in diameter (4 mm diameter and 20 mm length) in order to image at 2 µm voxel size and were mounted in a core holder; the assembly is reported in [Andrew et al., 2014]. The core holder was vertically placed in a µCT scanner. CO₂ was injected from top to bottom using two displacement pumps operating in a constant pressure mode at the inlet and at constant retraction rate at the outlet.

The experiments were performed on Berea sandstone and Estaillades limestone. The two rock types are comparable in permeability and porosity—φ ≈ 0.22 versus 0.3 and K ≈ 500 versus 200 mD for Berea and Estaillades—but represent a monomodal and a bimodal pore system, respectively. The rock characteristics are represented in the MICP (Mercury Injection Capillary Pressure) data shown in Figure 5.18. The limestone shows a characteristic step in the MICP corresponding to the invasion of the microporous volume, which is reflected in the two-peak structure in the pore-throat-size distribution. In this paper we refer to macroporosity as porosity that can be resolved by µCT scanning at the given resolution and to microporosity as porosity that we cannot resolve but that is visible in the gray scale behavior. Both samples show also porosity with pore sizes in between micro and macro, which we refer to as mesoporosity.

The rock samples were scanned in the dry state and subsequently saturated with KI-based brine by flooding with about 100 PV (pore volumes) at T = 50°C and ambient pressure. We subsequently pressurized the fluid to 10 MPa and continued flooding for another few PV in order to remove dissolved air. We performed a µCT scan to verify full brine saturation (S_W = 1). Thereafter, supercritical (SC) CO₂ was injected at a flow rate of 0.12 mL/min (∼2 PV/min) representing realistic field rates near injection wells. We performed another µCT scan after injection of 100 PV CO₂. At this stage, there is typically no longer any viscous brine displacement and the cumulative water loss by evaporation is still negligible due to the low solubility of water in CO₂. In the following, we refer to this state as after drainage. The scan after drainage is the second reference point for data evaluation. From then on we continuously scanned the region of interest (∼2 mm diameter and 2 mm length in the center of the sample) under flow conditions with a time resolution of about 45 min. Continuous scanning allows the detection of any change in the rock-fluid system. We define the time at which the µCT-determined sample state does not change any more as the time at which the sample is dry; the corresponding scan is used as third reference point for evaluation of the precipitated salt phase. We refer to this state as after dry out.

Figure 5.19 shows representative µCT cross sections recorded during the experiment on Berea sandstone. Figure 5.19a shows the typical rock structure in the dry state with macroporosity and mesoporous regions associated with feldspar and clay minerals, while Figure 5.19b shows the same image after drainage. Nonwetting CO₂ invades the pore space with the lowest entry pressure—the macroporosity. Finally, Figure 5.19c is an image after dry out about 10 h after drainage started. The locations of salt depositions are visible as...
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Figure 5.18: (left) Mercury Injection Capillary Pressure (MICP, micrometrics) curves of Berea sandstone and Estaillades limestone. (right) Pore-throat-size distributions of both rock types obtained from the MICP data. The blue and orange lines indicate the voxel size and the estimated physical resolution of the \( \mu \)CT scans.

bright spots. Salt precipitates essentially in the mesoporous regions that contained water at the end of drainage.

The data allow for two-phase segmentation of the volumes with the lowest X-ray attenuation (dark areas), corresponding to the macropore space in Figure 5.19a and the CO\(_2\)-saturated pore space in Figures 5.19b and 5.19c. The volumes were filtered (nonlocal means filter, Avizo fire, VSG) to reduce the noise level and registered (3-D image registration, Avizo fire, VSG) to account for small sample displacements during the experiment. We segmented by interactive thresholding (Avizo fire, VSG) and calculated the differences between the segmented macropore space and the segmented CO\(_2\)-saturated volumes in Figures 5.19b and 5.19c to extract the complementary brine and salt occupied macropore space after drainage and after dry out, respectively. Figures 5.19d and 5.19e show the segmented fluid phase after drainage. In Figure 5.19e, we additionally plot the salt phase in the macro pores after drying. It is evident that salt precipitated where the brine phase was after drainage. This is further illustrated in the 3-D images in the lower part of Figure 5.19, where the initial CO\(_2\) percolation pathway and the total volume in which salt precipitated are shown. Both occupy complementary regions of the pore space.

We performed the same experiment under the same conditions on Estaillades limestone. Figure 5.20a shows \( \mu \)CT cross sections of the initially dry rock, the same cross section after brine saturation (\( S_W = 1 \)) Figure 5.20b and after drainage Figure 5.20c. Figures 5.20d and 5.20e were obtained during dry out after \( \approx 24 \) h and after \( \approx 7 \) d of CO\(_2\) flooding, corresponding to about 3,000 and 20,000 PV CO\(_2\).

Due to the high X-ray absorption coefficient of iodine, gray-scale changes are determined
Figure 5.19: Microcomputerized tomography cross sections of Berea sandstone at different experimental stages: (a) in the dry state, (b) after presaturation and subsequent CO$_2$ drainage, and (c) after the experiment in the dry state. (d) The dry scan superimposed with the segmented brine phase after drainage (blue). (e) The complementary CO$_2$-occupied volume (orange) and the salt (green) in the macropores at a later experimental stage. (f) Segmented 3-D µCT volumes of the CO$_2$ percolation pathway after drainage, (g) the final precipitate, and (h) the both phases combined.
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Figure 5.20: Microcomputerized tomography cross sections of Estaillades limestone at different experimental stages. (a) Initially dry sample, (b) after brine saturation, (c) after drainage, (d) after 24 h, and (e) after 7 days of CO₂ injection. (f and g) Zoom-ins of Figures 5.20d and 5.20e with the superimposed positive (enrichment) and negative (depletion) differences to the respective earlier time step. (c*) The 3-D CO₂ distribution after drainage.
by salt migration only – i.e. solute transport – and other contributions can be neglected. In the following we speak of \textit{depletion} when the gray-scale value decreases and of \textit{enrichment} when the gray-scale value increases, corresponding to decreasing and increasing iodine concentration.

The early stage of the limestone (Estaillades) experiment shows similarities with the sandstone scenario: nonwetting CO$_2$ invades the macroporous regions. The remaining brine stays in the mesoporosity and in the microporous grains, as evidenced by the inverted gray scale contrast between solid and microporous grains compared to the dry scan. From Figures 5.20c and 5.20d we observe two trends: first, a salt depletion of the mesoporous regions and secondly, a salt enrichment in the microporous grains. To visualize the locations of depletion and enrichment, $\mu$CT images taken at different experimental times were subtracted. Before, contrast variation have been eliminated by linearly scaling the images, with the solid grains and the CO$_2$ phase occupied volumes as reference points on the gray scale. Figure 5.20f highlights the changes from Figures 5.20c to 5.20d; the orange/red color indicates depletion, while green/blue indicates enrichment of salt. There is obvious solute transport from the macroporous to the microporous system.

In a later stage of the experiment the trend is reversed. Between Figures 5.20d and 5.20e there is a weak depletion of the microporous area which indicates reverse flow and which is shown in the same color coding in Figure 5.20g. It should be noted that the differences in Figures 5.20f and 5.20g are thresholded to highlight the locations of depletion and enrichment and not to quantify the concentrations. In the later stage there is a clear indication of solute transport from the microporous to the macroporous subsystem, which is counterintuitive and has not been observed before. Salt accumulates in the macropores potentially affecting the CO$_2$ transport.

5.3.3 Interpretation and model

The data presented so far, together with a couple of simple arguments, allow the construction of a model that supports the findings of earlier work [Ott et al., 2010, Ott et al., 2013]. We describe the model on basis of capillary equilibration as illustrated in Figure 5.21 and the diagrams in Figure 5.22, illustrating the flow and evaporation processes in a time sequence. We first discuss the monomodal sandstone case, which we describe with a single capillary pressure-saturation curve $p_C(S_W)$.

During the injection process, viscous brine displacement and water evaporation have been found to be dominant at different time scales. While residual brine saturation ($p_C(A)$ in Figure 5.21) is usually reached after injection of a few PV, complete dry-out ($p_C(B)$) was reached after several hundred PV of injected gas. There is practically no viscous brine displacement during the drying process and precipitation, and the structure of the residually trapped brine phase is determined by capillary forces. After reaching the solubility limit, salt precipitates in the brine phase, and hence in the volume occupied by brine (Figure 5.22b). The brine-saturated volume retracts during evaporation, leaving the previously precipitated salt behind. During drainage there is no mechanism of brine transport and hence of solute transport into the gas-conducting volume. As a result, the effective
Figure 5.21: (top) The $p_C(S_W)$ curve of a simple sandstone (derived from MICP of Berea sandstone). (A) to (B) denote the $p_C$ ($p_C(A)$ and $p_C(B)$) and saturation change in the drying phase. (bottom) Constructed $p_C(S_W)$ curve of a dual-porosity system. The blue and red curves show decomposition into the macroporous and the microporous subsystem, respectively. (A) to (E) refer to capillary pressure levels during desaturation—$p_C(A)$ to $p_C(E)$ in the text.
permeability \( (K_{\text{eff, CO2}} = K \times k_{r, \text{CO2}}) \) can only increase over time, irrespective of absolute permeability reduction. Because of the separation of time scales of viscous displacement and evaporation, the maximum pore volume that can be filled by precipitate is the volume corresponding to the residual brine saturation after drainage, \( S_{W, \text{res}} \) (illustrated in Figure 5.22b). We conclude that \( S_{\text{salt, max}} = S_{W, \text{res}} \). In Berea sandstone \( S_{W, \text{res}} \) is \( \approx 0.2 \), which corresponds to the maximum observed salt accumulation due to capillary-driven countercurrent flow as reported in [Ott et al., 2011b].

These mechanisms hold as well for the more complex pore structure of carbonates. However, microporosity leads to additional effects influencing the location at which salt finally precipitates, and eventually the \( K(\phi) \) relationship. While the monomodal sandstone case is described with a single \( p_C \) curve, we decompose the bimodal limestone in macro- and microporous volumes with two individual \( p_C \) curves, as illustrated in Figure 5.21 (bottom). Both subsystems are assumed to be in contact with each other and are in capillary equilibrium during desaturation. The equilibrium states are represented by horizontal lines in Figure 5.21 and are denoted by (A) to (E), \( p_C(A) \) to \( p_C(E) \), respectively.

During primary drainage, gas invades only the macroporous system characterized by the lowest entry pressure (at \( p_C(A) \) in Figure 5.21) and the microporous volumes serve as brine reservoirs. If a microporous grain stays in contact with both, the residual brine phase of the macropores (mesopores) and the gas phase (at \( p_C(B) \)), the volume of water that evaporates gets refilled by the brine phase of the macroporous (mesoporous) system as illustrated in Figure 5.22c. Evaporation and refill lead to an effective increase of brine salinity in the micropores. This is by analogy to the dual-porosity effect in soils with brine transport from the macroporous to the microporous subsystem. Thus, it links to well-known physics but does not explain the earlier observation of \( K_{\text{eff}} \) reduction, which would require solute transport in the opposite direction, from the microporous regions to the gas-conducting channels. By further depletion of the macroporous (mesoporous) system, the brine supply to the microporous grains is no longer sufficient to prevent drying, and gas invades the microporous regions at \( p_C(C) \), which is illustrated in Figure 5.22d. This is equivalent to overcoming the entry pressure to the microporous system, but by water evaporation and not by viscous brine displacement. After exceeding the capillary entry pressure of the micropores, the brine flow is reversed; a small saturation change in the macropores \( \Delta S_{W, \text{macro}} \) (from \( p_C(D) \) to \( p_C(E) \); see Figure 5.21) will lead to a large saturation change \( \Delta S_{W, \text{micro}} \) associated with a substantial brine flow from the micro to the macroporous system to reach capillary equilibrium. A desaturation of the micropores by brine flow—and not by water vapor—leads to an effective solute transport to the gas-flow channels (the macroporous system) where salt precipitates. This finally leads to the very effective reduction of absolute and effective permeability \( (K \) and \( K_{\text{eff}}) \) compared to the rather mild impact observed in single modal sandstone.

5.3.4 Summary and outlook

We have presented a comparative study of flow-through drying in simple and complex, i.e., monomodal and bimodal—pore space. Microcomputerized tomography scanning has
Figure 5.22: (a–e) Microscopic model of solute transport and salt precipitation for the sandstone case (top row) and the carbonate case. The intergranular porosity refers to macroporosity and the intragranular porosity to microporosity. The letters (A) to (E) refer to the respective capillary pressure levels in Figure 5.21.
been used to observe capillary-driven solute transport and salt precipitation directly and in situ. During the drying process, different transport regimes have been identified: (1) evaporation of a capillary-bound brine phase, (2) capillary equilibration by brine flow from the macroporous to the microporous subsystem and—seemingly counterintuitive—capillary equilibration by flow from the microporous to the macroporous subsystem and hence into the gas-transporting channels. The latter mechanism has been identified to reduce the effective permeability. We explained the findings by a simple model of capillary equilibration. The model qualitatively describes observations in earlier studies which show that for complex pore architectures there is a risk for injectivity loss during gas injection operations.

While the study explains the principal solute transport mechanisms, the observed time scales of drying are not captured in the model. The time scales are likely to be controlled by the exact configuration of the contact areas between the macroporous and microporous subsystems and the contact area with the drying agent. Potential sealing effects at boundaries that prevent further solute transport are also not yet understood and need further investigation.
Chapter 6

Structure Formation in Limestone

6.1 Wormhole formation and compact dissolution in single- and two-phase CO$_2$-brine injection

Injection of acids and CO$_2$ into geologic formations leads to dissolution of soluble minerals comprising reservoir rocks. This increases the uncertainty in predicting the security and injectivity of geologic CO$_2$ storage. Here, through time-lapse computed tomography of injection experiments, we present the first dynamic data on wormhole formation and the fluid flow therein. We show that the dissolution during single-phase flow produces wormholes, as found previously, but that two-phase flow during CO$_2$-brine injection leads to compact dissolution. The latter is explained by CO$_2$ preferentially occupying wormhole seeds, which prevents their growth as CO$_2$ is less reactive than acidic brine. On the other hand, the wormhole seeds continue to grow under single-phase flows with only acidic fluid. The results also suggest that initial Péclet and Damköhler numbers for the single-phase flow process would fail to describe the dynamic process of whether compact or wormhole dissolution would ensue.

6.1.1 Introduction

The chemical interactions of injected CO$_2$ with the initial rock-fluid system of a target reservoir for geological CO$_2$ storage implies uncertainties with respect to CO$_2$-plume migration [Egermann et al., 2010] and mechanical rock integrity [Bemer and Lombard, 2010]. In particular, the high reaction rate of carbonic acid with carbonate minerals leads to very localized dissolution patterns that are typically beyond the resolution of field-scale modeling and are therefore not captured.

From work on well stimulation, we know that the injection of acids into carbonate rocks can lead to the formation of highly conductive flow channels, i.e. wormholes (WH) [Fredd, 2001, Hill and Schechter, 2001, Robert and Crowe, 2001]. These channels significantly enhance the flow of reservoir fluids, since fluid conductivity in WH is usually orders of magnitude higher than that of the unaltered or surrounding rock matrix. Therefore matrix
acidizing often successfully improves well productivity when the formation around the well bore is tight or damaged. The dissolution regimes can be characterized by Péclet ($Pe$) and Damköhler ($Da$) numbers, being the ratios of advective to diffusive transport rates – $Pe = ul/D$ with $u$ being the fluid velocity, $l$ representing the pore-length scale, and $D$ being the diffusion constant – and the ratio of the overall dissolution rate to the advective transport rate – $Da = kl/u$, with $k$ being the overall reaction rate. For $Pe$ and $Da$ numbers well above $10^{-2}$ a dominant WH dissolution regime is expected [Golfier et al., 2002].

In contrast to well-stimulation operations in which dissolution patterns can be ‘engineered’ and optimized, the formation of dissolution patterns is rather a concern for CO$_2$ storage projects, since flow rates and reaction rates are given and are not ‘designed’. The consequences are not easy to predict and depend on the precise knowledge of flow regimes and their development in the reservoir. Wormholing – for instance – might lead to highly directional (channelized) flow of injected fluids and to bypassing of rock matrix and hence to poor utilization of the pore space for CO$_2$ storage. In contrast to wormhole formation, compact dissolution will not affect the fluid-flow field but the mechanical integrity of the well. Homogeneous dissolution modifies fluid flow in the far field and might lead to subsidence.

At first sight, there are similarities between acidizing for well stimulation and CO$_2$ injection, since carbonate dissolution rates of both HCl solutions (typically used for acidizing) and carbonic acid – resulting from CO$_2$ injection – are higher than typical fluid transport rates in the field. This means that we could resort to the rich knowledge in chemical- and petroleum-engineering literature. However, the situation is more complex for CO$_2$ injection than for matrix acidizing. CO$_2$ does not directly react with rock-forming minerals, and hence it is not the acid that is injected, but the acid-forming agent. While there are single-phase flow domains (e.g. ahead of the CO$_2$ front), carbonic acid forms in general under two-phase flow conditions in parallel with reactions of acidic brine with the rock matrix. This has consequences: (1) Acid-forming agents can penetrate significantly deeper into the reservoir than acidic brine, since injected acidic brine gets consumed (buffered) by carbonate dissolution on the way into the reservoir. (2) For CO$_2$ storage, significantly greater quantities of CO$_2$ are injected over a much longer time scale than acid for well stimulation purposes – up to hundreds of cubic meters for acid stimulation [Robert and Crowe, 2001] to millions of cubic meters of liquid CO$_2$ for industrial-scale CCS projects [IPCC, 2005]. (3) The injected CO$_2$ phase is immiscible with the formation brine, lowering the mobility of the aqueous phase. This leads to a saturation-dependent (volumetric phase saturation) flow velocity of the aqueous phase and hence to saturation-dependent $Pe$ and $Da$ numbers. As we will argue in this paper, the description of dissolution regimes by $Pe$ and $Da$ numbers might not be sufficient, and an extension to two-phase flow properties might be required.

While numerous experimental and modeling studies have been performed for single-phase reactive transport (RT) [Daccord et al., 1993a, Fredd and Fogler, 1999], there are no studies on characterizing two-phase flow in dissolution structures and the formation of dissolution patterns under two-phase-flow conditions. Also, valuable insights in single-phase RT are reported in the CO$_2$-storage related literature [Svec and Grigg, 2001, Izgéc
et al., 2008, Egermann et al., 2010, Gharbi et al., 2013, Lamy-Chappuis et al., 2014, Vialle et al., 2014], but multi-phase aspects are still missing.

Here we present the first dynamic data on wormhole formation and the single- and two-phase flow therein. We also present the first attempt to extend structure formation by carbonate dissolution to the two-phase-flow regime, as it is relevant for CO$_2$ injection operations. We investigate the evolving dissolution patterns at reservoir conditions using time-lapse computerized tomography, and analyze the growth and structure of the resulting dissolution patterns and fluid-saturation changes. We conclude that a description of dissolution regimes by $Pe$ and $Da$ numbers only is not sufficient to describe evolving structures in two-phase flow, and outline the consequences of dissolution for CO$_2$-storage operations in carbonates.

6.1.2 Displacements and formation of dissolution structures

In order to study the formation of dissolution structures and the influence of these structures on fluid displacements we performed a series of reactive and non-reactive core flood experiments. The strategy is to perform non-reactive single- and two-phase flow experiments in order to characterize the flow properties in unaltered rock, followed by a reactive flow experiment, in which the rock structure is altered according to the flow regime. We then repeat the initial non-reactive experiments to test the influence that dissolution has on fluid displacements.

A typical experimental sequence is shown in Fig. 6.1; the experiments (a) to (e) were carried out in a sequence and on the same rock sample. Estaillades limestone has been chosen for the study, which is a commonly used outcrop carbonate [Blunt, 2013, Ott et al., 2014a, Ott et al., 2015a, Vialle et al., 2014] with an average porosity $\phi \approx 0.3$ and permeability $K \approx 200$ mD. The sample size was 7.5 cm diameter $\times$ 15 cm length. Estaillades has a nearly pure calcite mineralogy. All experiments were performed at 100 bar and 50°C, corresponding to an aquifer at a depth of about 1000 m. At these conditions, CO$_2$ is in the supercritical (SC) state. As aqueous phase, we used an NaCl-based brine (3wt% NaCl) and CsCl-doped brine (9wt%) in order to increase the x-ray absorption contrast between displacing and displaced fluids. The floods have been performed in horizontal geometry. We follow the displacement processes by means of medical computerized tomography (CT), which is sensitive to material density and x-ray absorption contrasts in the rock-fluid system. In addition we measure the pressure drop over the core. A detailed description of the setup and the following experimental procedures can be found in the supporting information.

Non-reactive displacement experiments The top row in Fig. 6.1(a) shows a time series during a single-phase displacement experiment using an X-ray tracer. CsCl-doped brine was injected into a core pre-saturated with undoped brine at a rate of 1 ml/min. The tracer concentration was recorded by CT scanning and is displayed in orange in Fig. 6.1(a), while the initial rock-fluid system is shown as a semi-transparent background. The images show the tracer front propagating nearly piston-like through the core as a function of
injected fluid volume in units of the rock’s total pore volume (PV). The flood front is slightly corrugated due to the intrinsic permeability variation of the rock sample. The relative tracer concentration reaches about 90% after injection of about 1 PV and a final value of 97%, i.e. a nearly complete displacement, as shown by the tracer-based (CT response) production curve in the middle panel of Fig. 6.2.

Subsequently, we performed a primary drainage experiment by injecting CO$_2$ at a rate of 0.44 ml/min. CO$_2$ is soluble in the brine phase and forms carbonic acid, which dissolves carbonate minerals. In order to test true immiscible displacement in the unaltered rock, the fluid phases were equilibrated with each other and with the rock-forming minerals. This prevents any fluid-fluid and rock-fluid mass transfer during the displacement experiment. Details are discussed in the supporting information. Fig. 6.1(b) shows the CT difference images during CO$_2$-brine displacement at different time steps (in PV). Orange represents in this case the CO$_2$-saturated volume. While experiment (a) is sensitive to the heterogeneity of the permeability field, CO$_2$ primary drainage reacts on local variations of capillary pressure and hence gives information about $p_C$ heterogeneity [Pini et al., 2012, Pini and Benson, 2013a, Berg et al., 2013a]. From the saturation profiles and the pressure drop, primary-drainage relative-permeability and capillary-pressure saturation functions, $k_r(S_W)$ and $p_C(S_W)$, can be derived [Berg et al., 2013a, Ott et al., 2015a]. The brine production curve in the middle panel of Fig. 6.2 shows the early CO$_2$ breakthrough and a relatively low average CO$_2$ saturation plateau of about 0.2. The characteristic is attributed to the relatively large fraction of micro-porosity that cannot be entered by the non-wetting CO$_2$ and the generally low displacement efficiency of CO$_2$-brine displacements [Berg et al., 2013a, Ott et al., 2015a].

**Single-phase reactive transport and dissolution structure** After having characterized single- and two-phase flow in the unaltered rock (experiments (a) and (b)), we performed a reactive experiment in single-phase flow. Brine was equilibrated with CO$_2$ at (near) experimental conditions, forming carbonic acid. The CO$_2$-saturated brine was then injected at a rate of $\sim$1 ml/min into an initially brine-saturated core, leading to $Pe \sim 0.6$ and $Da \sim 180$. In contrast to experiment (a) and (b), the injected fluid was initially not in chemical equilibrium with the rock matrix. Fig. 6.1(c) shows the dissolved rock matrix as a function of time in units of injected brine volume. The initial rock-fluid system is displayed semi-transparently while the dissolved rock volume is visualized in orange. Initially, several seed holes form, growing into the rock sample and reaching a certain length until they start competing with each other. Eventually, a single wormhole (WH) dominates the dissolution pattern and starts forming branches. By using time-lapse CT scanning, dynamic data on the WH growth can be derived. The top panel of Fig. 6.2 shows the length of the three longest WH as a function of time (in PV). The growth rate of the dominant WH is essentially constant while the others stop growing, which will be discussed further below. We stopped flooding as the dominant WH reached $\sim 80\%$ of the sample length.

Fig. 6.3 shows the detailed structure of the WH that shows a ramified and complex structure. Daccord and Lenormand were the first to describe such a dissolution pattern in
6.1. SINGLE- AND TWO-PHASE RT

terms of fractals [Daccord and Lenormand, 1987] – i.e. self-similar geometric patterns. A fractal system is characterized by its dimension, \( \alpha \), which describes the fractal length of a WH (\( l \)) by \( l = L^\alpha \), with \( L \) being the shortest length, i.e. the penetration depth of the WH. For the present case, we derive \( \alpha \sim 1.89 \). This value is higher than, but comparable to, values of \( \sim 1.6 \) derived for plaster of Paris systems studied by Daccord. Interestingly, despite the strong variation of the actual number of WH and branches, the total hydraulic cross-section is rather constant across the sample. Its value is in the order of \( 10^{-5} \) m\(^2\), which is large compared to the rock’s permeability, which is in the order of \( 10^{-13} \) m\(^2\), leading to the observed high conductivity and to bypassing of the remaining rock matrix, as will be discussed further below.

On a larger scale, the WH density will determine flow properties. For well stimulation, the density is often predefined by the well perforation. However, there might be an intrinsic length scale making up the density of WH if there is no constraint. It is assumed that the WH density is determined by the competition for injected fluid. The largest WH typically shows the largest diameter and the most favorable pressure field, resulting in a more rapid growth at the expense of shorter WH that eventually stop growing [Hoefner and Fogler, 1988]. Numerical simulations show that WH interact with each other, i.e. reducing each other’s flow rate. It was suggested that WH compete when the distance between neighboring WH (\( d \)) comes in the order of, or is less than, the length of the WH (\( L \)), i.e. \( L/d \sim 1 \) [Hoefner and Fogler, 1988, Buijse, 1997]. Even with the relatively large sample, the cross-sectional area is too small to accommodate enough WH to be representative and therefore there is only limited information about the WH density in this experiment. However, the data in Figs. 6.1(c) and 6.2 (upper panel) show this competition. Ignoring the branching, there are three dominant WH with a similar length up to about half of the experimental time, after which only one is growing further and the others stop growing. The ratio \( L/d \) to the longest WH is 0.9 and 1.7 for the second and third longest WH, respectively. This result is in line with the statements of Hoefner and Fogler (1988) and Buijse (1997) about WH competition [Hoefner and Fogler, 1988, Buijse, 1997].

Non-reactive fluid displacements in the altered rock After the WH had formed, we repeated the initial flooding sequence – the single-phase tracer test and the injection of \( \text{SC CO}_2 \) – using a similar experimental protocol as above and as outlined in the supporting information. Figs. 6.1(d) and (e) show saturation profiles during the floods after WH formation. Both are directly comparable to the initial floods in Figs. 6.1(a) and (b), respectively. In both cases, the injected fluid mainly flows through the WH, bypassing the remaining rock matrix and spreading in the highly ramified ‘crown’ and through the ‘tip’ of the WH, leading to fluid displacement in radial and downstream directions, respectively. We attribute the radial displacement to fluid ‘loss’ or leakage to the surrounding rock matrix. In a reactive case, leakage widens the WH system rather than it increases its length. It therefore has a strong influence on the growth rate, the maximum length and the structure of the WH [Fredd, 2001, Hill and Schechter, 2001].

The 3D images in Figs. 6.1(d) and (e) reveal some interesting features: the radial loss
Figure 6.1: CT difference images of a series of core-flood experiments in Estaillades limestone. The data were measured during a flooding sequence in the same sample. Visualized in orange: aqueous tracer concentration in single-phase flow experiments (a) and (d), SC–CO$_2$ saturation in primary drainage experiments (b) and (e), and dissolved rock matrix during reactive transport in experiment (c). (a) and (b) were performed before the reactive experiment (c), and experiments (d) and (e) were performed after (c).
Figure 6.2: Top: dynamic data of WH formation as shown in Fig. 6.1(c); pressure drop during the experiment and length of the three most mature wormholes as a function of injected fluid volume. Middle panel: brine production curves from experiments (a), (b), (d) and (e) as shown in Fig. 6.1. Bottom panel: fluid leak-off rates during experiments (d) and (e) at 4, 7 and 10 cm from the inlet as also indicated in Fig. 6.3, representing the single WH and the ramified structure.
is strong at positions of high ramification (‘the crown’) and high WH density (at the inlet). In these regions the high number of holes and the small distances between individual holes allow for an effective fluid distribution in radial direction. The loss is less pronounced at the position of a single channel (position (A) in Fig. 6.3). Fig. 6.2 (middle) shows the brine production curves of experiments (d) and (e) and compares them to the production curves obtained from the floods of the unaltered rock (a) and (b). In both cases, the displaced brine volumes fall behind the production from the undisturbed sample. The derivative of the tracer concentration and the CO\textsubscript{2} saturation at different positions along the core, i.e. the rate of radial loss, is shown in Fig. 6.2(bottom). The positions measured from the inlet face were chosen to represent the fluid loss of the single WH (4 cm), the ramified ‘crown’ (10 cm) and a position in between (7 cm). For single-phase flow (d), we expect a constant rate of loss, since the brine-brine displacement at constant flow rate corresponds to a steady-state displacement. This is observed at the position of the single WH. The loss rate at the position of the crown is initially high, but is strongly declining in time. This is because the tracer distributes efficiently through the ramified structure but the integrated tracer concentration reaches a saturation value due to the finite cross-sectional area over which we integrate (an effect of confinement). The true fluid loss rate is the initially high rate at the beginning of the flood. The CO\textsubscript{2}-loss during the drainage experiment (e) is generally lower than the brine loss in experiment (d). It shows generally, and especially at the position of the crown, a rate that starts from zero going through a maximum and then back to zero again. The occurrence of the maximum can be understood in terms of differential pressure; CO\textsubscript{2} penetrates the matrix after overcoming the entry pressure, before which the rate of loss is zero. After penetrating the matrix, the respective differential pressure increases with penetration depth, which slows down the rate. This effect will limit the radial loss of CO\textsubscript{2} and brine in a drainage situation. An interesting observation is that at positions of high ramification we reach a higher average CO\textsubscript{2} saturation than in the undisturbed matrix, while at positions of a single WH, the CO\textsubscript{2} saturation falls much behind the undisturbed case. In other words, the degree of ramification is a control parameter of the degree of bypassing. However, the radial loss seems not to widen the individual channels, but rather to increase the ramification. This indicates that the fluids flow through the tips of the individual branches, rather than through their side walls. Our conclusion is that a high fluid loss and a high degree of ramification – i.e. a high fractal dimension – go hand in hand, but the question of cause and effect remains.

**Two-phase reactive transport experiment** We repeat the reactive transport experiment under the same conditions and with the same brine-flow rate, but in contrast experiment (c) in Fig. 6.1(c), we co-inject CO\textsubscript{2} at the same flow rate. Since we do not expect direct reaction between CO\textsubscript{2} and the rock matrix, and since the (reactive) brine injection rate is the same, the global \( Pe \) and \( Da \) numbers are the same for both RT experiments. The final dissolution structure is shown on the right of Fig. 6.3. The structure is localized at the bottom inlet side and is best described as compact dissolution, in contrast to the single-phase RT experiment, which shows a clear wormholing. We attribute the fact that
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Figure 6.3: Left: detailed view on the dissolution pattern as result of the experiment in Fig. 6.1 (c). \( L \) represents the penetration depth of the WH and \( d \) the distance between two WH. The positions (A), (B) and (C) refer to the positions for which the radial loss rates in Fig. 6.2 are shown. Right: the final dissolution pattern of an experiment performed on the same rock type and under the same conditions, but co-injecting \( \text{CO}_2 \) and brine as described in the text.

The bottom is dissolved to gravity differences of saturated brine, initial brine and \( \text{CO}_2 \) \( (\rho_{\text{sat. brine}} > \rho_{\text{brine}} > \rho_{\text{CO}_2}) \) and the horizontal flow geometry. An ex-situ permeability measurement showed that the permeability of the rock matrix remained unchanged, which confirms the local nature of the dissolution process.

The mechanism that leads to compact dissolution in two-phase flow can be inferred from the experiment in Fig. 6.1(e); the injected non-wetting \( \text{CO}_2 \) prefers to occupy the volumes with the lowest \( p_C \), i.e. the wormholes. In a two-phase flow situation, \( \text{CO}_2 \) occupies the WH seeds freshly created by the flow of acidic brine, with the result that the seeds – once created – stop growing. This is because the \( \text{CO}_2 \) flow in the seeds is non-reactive. The difference between single-phase and two-phase RT is illustrated in Fig. 6.4. While for the single-phase flow situation the WH seeds accept more acidic fluid and grow – which is a permeability-related argument – in two-phase flow, non-reactive \( \text{CO}_2 \) prevents the seeds from growing – which is a capillarity-related argument – and new seeds will be created by the brine flow that will be stopped again. The process results in an apparent compact dissolution pattern as illustrated in the lower row in Fig. 6.4.

6.1.3 Summary and outlook

We have presented a study on \( \text{CO}_2 \)-brine reactive transport in limestone. In a number of experiments (not all are shown) we observed localized dissolution structures that generally
increased heterogeneity and fluid bypassing in single- and two-phase flow. Through time-lapse computerized tomography we characterized the development of dissolution structures and the single- and two-phase flow therein. The hydraulic conductivity, the sweep efficiency and the leak-off rate have been investigated and related to the structural properties of the dissolution structure.

Despite the general description of dissolution regimes by \( Pe \) and \( Da \) numbers, we observed two different dissolution regimes in single- and two-phase RT at the same global \( Pe \) and \( Da \) numbers; while we observed the expected wormholing in single-phase flow, the co-injection of CO\(_2\) and brine led to a compact dissolution at the injection side. This might have direct consequences for the performance of injection wells; while wormholes generally increase injectivity, compact dissolution might cause problems for the mechanical well bore stability.

We propose to extend the discussion of carbonate dissolution in the present context to two-phase flow. This extends the parameter space from the typical \( Pe \) and \( Da \) numbers to capillarity heterogeneity of both the rock matrix and the evolving dissolution structure. By including the dissolution structure in its own formation, a feedback mechanism is created, leading to a more complex phase diagram of dissolution regimes as introduced for single-phase RT in [Golfier et al., 2002].
6.2 Modification of mechanical rock properties due to calcite dissolution

Mechanical rock properties such as stiffness and strength vary with the natural variation of porosity [Bemer et al., 2004]. Since rock dissolution generally enhances porosity, we expect that those parameters will be affected by CO$_2$ injection as has been shown before [Egermann et al., 2010]. This implies consequences for formation stability near the well bore and in the far field. In order to predict pore collapse and subsidence for the individual rock type and flow regime, we performed reactive experiments as discussed above, but in a triaxial compaction cell with in-situ monitoring of mechanical rock properties such as elasticity, acoustic velocities and point of failure.

While wormholing occurs in dynamic situations, we expect homogeneous dissolution to occur over longer time scales in the far field, either under “no-flow conditions” or close to chemical equilibrium. Homogeneous dissolution might lead to a stronger change of the mechanical rock properties and therefore we focus in the following on the comparison of both extreme dissolution regimes, following a study by IFP for the homogeneous dissolution [Egermann et al., 2010, Bemer and Lombard, 2010].

Due to the generally high reaction rate of carbonic acid with calcite, it is difficult to reach a homogeneous dissolution by means of CO$_2$ injection on a laboratory time scale, since the acid reacts already with the carbonates at the inlet face of the sample. For that reason, we used a retarded acid (RA) approach as developed in IFP to reach a more homogeneous dissolution pattern [Bemer and Lombard, 2010]. The RA aqueous solution we used is inactive at ambient temperatures and therefore does not react with the rock. Once injected into the core, the acid is activated under no-flow conditions by increasing the temperature, forming formic acid. The activated acid then dissolves the rock matrix until the solution is buffered. The buffered solution is subsequently removed by water injection. To continue dissolution, we repeat the treatment and we assume the dissolved rock volume to be proportional to the number of retarded acid treatments (RATs). Figure 6.5 shows the dissolution patterns after three (i) and six (j) RATs. Image 6.5(i) suggests that channels are forming due to the treatment similar to the WH formation discussed before. However, in case of the RAT, the contrast of the CT images is strongly enhanced compared to image 6.5(k) in order to visualize the non-ideal part of the dissolution structure. The cause of the weak channels that have been formed during the RATs is probably related to the easier access of the RA solution in the high-permeability pathways where leaching takes place more efficiently by giving the inactive solution only a finite time for diffusion. We observe strong differences in the flow patterns (data not shown here) and in the rock mechanical parameters (discussed in the following), showing that the RA procedure was successfully applied. The results are directly compared to results of experiments on twin samples in which we inject CO$_2$-saturated brine at $Pe \sim 0.15$, leading to WH formation [Golfier et al., 2002] as shown in Figure 6.5(k).

Figure 6.6 presents data obtained for both dissolution regimes [Eide, 2012]. The left panel shows the normalized Young’s modulus as a function of porosity change, reflecting
Figure 6.5: CT difference images of dissolution patterns in Euville limestone that have been formed after 3 (i) and 6 (j) retarded acid treatments and during injection of CO$_2$-saturated brine (k). Note that the CT contrast of (i) and (j) is strongly enhanced compared to the contrast of image (k). The initial rock-fluid system is displayed as a semi-transparent background.

Figure 6.6: Left: Young’s modulus as a function of porosity change for both heterogeneous (wormholing due to CO$_2$-saturated brine injection) and homogeneous (RAT) dissolution patterns. Right: Failure envelope of samples treated with RA and untreated samples (reference data).
the change of the rock’s elastic properties. Interestingly, we observe only a minor impact of dissolution on the mechanical stiffness during wormhole formation. In contrast to this, the experiments showing a more homogeneous dissolution pattern as achieved by RATs exhibit a strong linear decay of elasticity. Despite the data scatter of the individual experiments, Young’s modulus follows a clear trend and shows a qualitatively different behavior than in the experiments leading to WHs.

Young’s modulus and acoustic velocities (not shown) decrease more strongly than predicted by a natural porosity trend [Eide, 2012]. This indicates the local nature of the wormholing, which does not affect the rock matrix away from the WH. In contrast, the homogeneous dissolution is likely to affect the grain-grain contacts and hence the mechanical rock properties.

In addition, the RATs might affect the rock strength. We performed failure tests of treated (after 6 treatments) and unaltered (reference) samples. The right panel of Figure 6.6 shows the respective Mohr-Coulomb failure lines. The failure envelope of the treated samples falls below that of the reference samples, suggesting that homogeneous dissolution weakens the rock. The data shows a significant decrease in the friction angle. The change in the cohesion (ordinate axis intercept) is within the error bars and hence not significant.
Appendix A

Experimental Capability

A.1 Core-flood experiment for transport of reactive fluids in rocks

Investigation of the transport of reactive fluids in porous rocks is an intriguing but challenging task and relevant in several areas of science and engineering such as geology, hydrogeology and petroleum engineering. We designed and constructed an experimental setup to investigate physical and chemical processes caused by the flow of reactive and volatile fluids such as supercritical CO\textsubscript{2} and/or H\textsubscript{2}S in geological formations. Potential applications are geological sequestration of CO\textsubscript{2} in the frame of carbon capture and storage (CCS) and acid-gas injection (AGI) for sulfur disposal and/or enhanced oil recovery (EOR). The present paper outlines the design criteria and the realization of reactive transport experiments on the laboratory scale. We focus on the spatial and time evolution of rock and fluid composition as a result of chemical rock fluid interaction and the coupling of chemistry and fluid flow in porous rocks.

A.1.1 Introduction

There is a growing need to understand the consequences of acid-forming fluid injection in geological formations. Prominent examples are the injection of carbon dioxide (CO\textsubscript{2}) for reduction of anthropogenic greenhouse-gas emissions [IPCC, 2005], and the re-injection of contaminants – mainly hydrogen sulfide (H\textsubscript{2}S) and CO\textsubscript{2} – from sour-gas production for disposal (acid gas injection – AGI) and/or enhanced oil recovery (EOR) [Bachu and Gunter, 2004]. Deep saline aquifers and depleted hydrocarbon fields are potential subsurface deposits for these substances [IPCC, 2005, Bachu et al., 1994, Bachu and Gunter, 2004].

These geological formations contain fluids in the rock’s pore space, mainly brine and hydrocarbons that are initially in chemical and physical equilibrium with the formation rock. By the injection of CO\textsubscript{2} and/or H\textsubscript{2}S, these reservoir fluids are partly displaced. CO\textsubscript{2} and H\textsubscript{2}S, however, interact chemically with water-bearing rock leading to dissolution
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and precipitation of minerals [Gaus et al., 2008, Marini, 2007]. This in turn affects the fluid flow in the subsurface and the rock’s mechanical strength, creating uncertainties for sequestration [Gaus et al., 2008] and EOR projects.

Reactive transport modeling is normally used to predict the fate of the injected fluid in the reservoir. Reliable modeling, however, requires experimental data for calibration and – more importantly – to understand the fundamental couplings between subsurface chemistry and fluid flow. The experimental investigation of these couplings are the subject of the present paper, but first we discuss some basics of fluid flow and the transport of reactive fluids in porous rocks.

Flow equations

For a single fluid phase and in the case of miscible displacement, fluid flow can be described through Darcy’s law [Dake, 1978, Lake, 1989] by the porosity ($\phi$) and permeability ($K$) of the formation rock, and the fluid viscosity ($\mu$). When considering two-phase flow (immiscible displacement), usually one fluid phase is wetting ($w$) to the rock’s internal surface and one is non-wetting ($nw$). The presence of two or more fluid phases usually diminishes the mobilities of the individual phase. This can be described by the concept of relative permeability for the individual fluid phase ($k_r(S_w)$) and the capillary pressure ($p_c(S_w)$) saturation functions, where $S_w$ is the wetting phase saturation (occupied pore-space fraction). The respective process of immiscible displacement is described by the following equations [Dake, 1978, Lake, 1989]:

$$\phi \frac{\partial S_i}{\partial t} + \nabla \cdot \vec{v}_i = 0 \quad (A.1)$$

$$\vec{v}_i = -\frac{k_r,i}{\mu_i} K (\nabla p_i - \rho_i \vec{g}) \quad (A.2)$$

where Equation A.1 is the mass balance for phase $i$, with $S_i$ and $\vec{v}_i$ being the respective phase saturation and flux (discharge per unit area). The flux of the phases $\vec{v}_i$ is described by Darcy’s law extended to 2-phase flow (Equation A.2), with $\mu_i$ and $\rho_i$ being the respective fluid viscosity and density, $p_i$ the phase pressure, and $g$ the gravity constant. The saturations must satisfy $S_w + S_{nw} = 1$. The pressure difference between the non-wetting and wetting phases is the capillary pressure, $p_c = p_{nw} - p_w$, which is also a function of fluid saturation ($p_c(S_w)$).

For the CO$_2$/brine combination, brine is usually the wetting phase ($i = w$) and CO$_2$ non-wetting ($i = nw$). The compressibility of CO$_2$ is often relevant, but is ignored here.

Core-flood experiments

Experimentally, fluid flow in porous rocks is commonly investigated by core-flood experiments. These experiments are widely used in petroleum engineering to investigate miscible and immiscible fluid displacement and to understand subsurface flow in order to maximize
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Oil recovery [Tiab and Donaldson, 2004]. For immiscible displacement (for fluid combinations such as oil/brine and also CO$_2$(H$_2$S)/brine), measurements of the phase-saturation profiles (pore space occupation) and the respective differential fluid pressures are required to determine the basic fluid flow parameters as defined above. Typically, phase saturations are monitored by 2D X-ray or neutron radiography or 3D computer tomography (CT) [Wang et al., 1984, Vinegar and Wellington, 1987] and additionally by monitoring the fluxes of the injected and produced fluids (production curve).

These experiments are usually performed under controlled thermodynamic conditions and special care is needed with fluid combinations like CO$_2$/brine, which are mutually soluble and reactive to the rock matrix (initial rock/fluid system). When considering fluid flow only, equilibration of rock and fluid phases is important in order to avoid physical and chemical mass transfer between the individual phases during the flood experiment that would lead to systematic errors [Bennion and Bachu, 2005, Bennion and Bachu, 2008, Berg et al., 2013a]. Mass transfer between phases, however, lies within the scope of reactive transport as discussed further below.

Only a few core-flood experiments conducted to obtain the fluid flow properties of CO$_2$/brine and H$_2$S/brine systems have been reported. [Bennion and Bachu, 2005, Bennion and Bachu, 2008] investigated CO$_2$/brine and H$_2$S/brine relative permeability on sandstone and carbonates typical for the Wabamun and Zama areas in central Alberta, Canada. [Perrin et al., 2009] and [Berg et al., 2013a] determined CO$_2$/brine relative permeability in Berea sandstone. Residual trapping of CO$_2$ in Berea sandstone was investigated by [Suekane et al., 2008], and the influence of rock heterogeneities on fluid flow and CO$_2$ distribution in Berea and in a sample originating from a sequestration site in South-West Australia were investigated by [Perrin et al., 2009, Perrin and Benson, 2010]. Some of the studies showed that imaging of saturation profiles [Perrin et al., 2009, Perrin and Benson, 2010, Berg et al., 2013a] and fluid/fluid equilibrium [Suekane et al., 2008, Berg et al., 2013a] is crucial for data interpretation.

Chemical rock/fluid interaction and reactive transport

Chemical rock/fluid interaction on the other hand is typically investigated in stirred batch experiments, [Marini, 2007] under controlled transport conditions such as with the rotating-disc technique [Sjöberg and Rickard, 1983, Marini, 2007] or in a flow-through reactor under laminar flow conditions [Compton et al., 1989, Marini, 2007]. Control of the geometry, transport and mineral surface area is essential to derive accurate equilibrium and rate constants of the chemical processes and to identify reaction mechanisms.

In this study, we are interested in investigating how transport phenomena and simultaneous reaction chemistry are coupled. On a fundamental level, the transport of reactants and reaction products defines local concentrations and is hence a thermodynamic driving force for chemical reactions. In a simple picture, reactive transport is controlled by the ratio of characteristic fluid residence time and a characteristic reaction time: $\tau_{res}/\tau_{react}$ [Steefel and Maher, 2009]. The transport mechanisms responsible for the residence times are advection (Equation A.1) and molecular diffusion, and hence reactive transport is described
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Figure A.1: Effects of the Péclet (left) and Damköhler (right) numbers on the concentration profile. The data were calculated on the basis of Equation A.4. The flow direction is from left to right.

by the advection-diffusion-reaction (ADR) equation.

A simple but illustrative case is the 1D single-phase flow with constant fluid flow properties and a first-order dissolution or precipitation reaction that can be described by a single chemical component of concentration $C$. The ADR equation becomes [Steefel and Maher, 2009]:

$$\phi \frac{\partial C}{\partial t} = -\phi v \frac{\partial C}{\partial x} + \phi D \frac{\partial^2 C}{\partial x^2} + A k (1 - \frac{C}{C_{eq}}) \quad (A.3)$$

where $v$ is the Darcy velocity, $D$ the diffusion coefficient, $A$ the reactive surface area, $k$ the rate constant and $C_{eq}$ the solubility limit of the mineral. ADR equations like Equation A.3 can be expressed in dimensionless scaling groups that characterize reactive transport regimes by comparing typical time scales: expressed in rates, the Damköhler number $- Da = A k l / (\phi v C_{eq})$ -- and the Péclet-Damköhler number $- PeDa = A k l^2 / (\phi D C_{eq})$ -- are the ratios of typical rates of reaction versus rates of advection and diffusion, respectively. The Péclet number $-Pe = vl / D$ -- describes advection to diffusion, where $l$ is a typical length scale. Equation A.3 becomes in a dimensionless form [Steefel and Maher, 2009]:

$$\frac{\partial C'}{\partial t'} = \frac{\partial^2 C'}{\partial x'^2} - Pe \frac{\partial C'}{\partial x'} - Pe Da C' \quad (A.4)$$

with $t'$, $x'$ and $C'$ being non-dimensional forms of time, space and concentration. Figure A.1 shows how the $Pe$ and $Da$ numbers in Equation A.4 influence solute transport. The influence of the $Pe$ number on the shape of the concentration profiles is illustrated on the left side: diffusion broadens the otherwise sharp flood front (homogeneous medium) – the lower the Péclet number the stronger the diffusive broadening. For large Péclet numbers ($Pe \gg 1$) advective transport dominates diffusion. A similar behavior shows the system
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Figure A.2: Coupling between fluid flow and chemical rock/fluid interaction in porous rock.

as a function of $Da$ numbers as shown on the right side of Figure A.1. For $Da >> 1$, reactions are fast compared to transport, leading to a sharp reaction front. Small $Da$ numbers lead to a relatively homogeneous concentration profile.

In the case of two-phase (or multi-phase) flow, the mobility of a fluid phase is diminished by the presence of the second fluid phase (relative permeability in Equation A.2), strongly influencing transport properties. Furthermore, with the resulting capillary pressure the capillary number $N_C = \frac{\mu v}{\sigma}$ comes into play comparing viscous to capillary forces [Lake, 1989], i.e. the relative importance of viscous and capillary transport, where $\sigma$ is the interfacial tension between the two fluids. Especially at low water saturations or at high saturation gradients capillary pressure might strongly influence transport properties and hence reactive transport.

So far (Equation A.3 only), no account has been taken of the feedback of chemical reactions on fluid flow, i.e. how physical properties of a formation rock evolve as a result of chemical reactions. For this coupling, experimental research plays a key role, since minor changes of porosity due to dissolution or precipitation reactions might have a major impact on fluid flow (i.e. $K$, $p_c$, and $k_r$) caused by structural changes, mainly on pore scale, for which the typical continuum description fails. This feedback loop is schematically shown in Figure A.2. One of the primary goals of reactive transport research is to investigate these couplings and, for example, to establish relationships between permeability and porosity $K(\phi)$.

The evolution of permeability as a result of mineral dissolution (porosity change) has been extensively studied in the context of well stimulation by acidification [Bazin, 1998]; acidic brine is injected into carbonate reservoirs to improve oil and gas production. Different dissolution regimes have been identified depending on the overall reaction charac-
Figure A.3: Single-phase flow dissolution regimes (schematic) as function of Péclet and Damköhler numbers.

characteristics, i.e. whether the overall reaction is mass transport limited or surface reaction limited [Daccord et al., 1993b, Daccord et al., 1993c]. It is now well accepted that compact dissolution (sharp dissolution front at the inlet – diffusion predominant) and a branch-type dissolution (wormhole pattern – advection predominant) are observed in transport limited systems, while uniform dissolution is observed if systems are surface reaction limited [Schechter and Gidley, 1969, Daccord et al., 1993b, Daccord et al., 1993c]. This is schematically shown in Figure A.3 where the dissolution regimes are assigned to $Pe$ and $PeDa$ numbers [Egermann et al., 2005b].

These studies refer to single phase flow, but CO$_2$ and acid gas injection largely entails multi-phase flow. Reactive transport in multi-phase flow is qualitatively different and has not yet been systematically investigated. Solute transport is governed by the mobility of the individual fluid phases, which might be very low in the presence of a second immiscible fluid phase compared to single phase flow. Wetting properties and fluid-phase connectivity might also play a major role for the effective reactive mineral surface area and the mass transfer between fluid phases that potentially limit effective reaction rates.

Only a few reactive transport experiments including CO$_2$ have been performed and/or published; core-flood experiments in sandstone with injection of carbonated brine were performed by [Ross et al., 1982] and in carbonates with injection of supercritical CO$_2$ by [Svec and Grigg, 2001, Grigg and Svec, 2003, Egermann et al., 2005a]. [Izgec et al., 2008] presented the results of CT monitored experiments to analyze permeability and porosity changes to characterize relevant chemical reactions associated with injection and storage of CO$_2$ in carbonate formations. Both have been reported, improvement and impairment of permeability, depending on the process and the flow regime.

This paper

With the experimental setup presented here, we focus on the coupling between chemical rock/fluid interaction and fluid flow. In contrast to the studies discussed above, we in-
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Figure A.4: Examples II A and II B: geometries and conditions. AQ stands for aqueous, USS for unsteady state and SS for steady state experiments.

corporate elements of both areas, core flooding and chemical rock/fluid interaction. The work includes 3D imaging for in-situ monitoring of the rock/fluid system by micro CT (µCT) scanning, differential-pressure and fluid density measurements in conjunction with fluid phase separation and subsequent chemical analysis of the fluids.

The paper is organized as follows: in Section A.1.2 the design specifications are discussed with the aid of two specific cases addressing fluid flow (A.1.2 A) and reactive transport (A.1.2 B). The principal experimental design with a detailed description of some elements and procedures is given in Section A.1.3. Finally we provide exemplary experimental results in Section A.1.4, referring to the discussions in Sections A.1.1 and A.1.2.

A.1.2 Design specifications

Despite the huge variation of geological formations, fluids, injection rates and geometries, leading to very different scenarios, an estimation of time and length scales of physical and chemical effects is crucial for a proper experimental design. In the following we present two examples that we consider useful as they provide a range of parameters used for the experimental design.

Fluid flow and mass transfer

In the following we consult a numerical simulation, given by [Pruess and Spycher, 2007] to determine the physical requirements with respect to experimental flow rates and time resolution. Pruess simulates CO₂ injection in a saline aquifer that has a porosity of 0.12, a permeability of 100 mD and a brine salinity of 15 wt%. The situation is sketched in Figure A.4. The aquifer is 100 m thick and at a depth of 1200 m, resulting in a formation temperature (T) and fluid pressure (P) of T = 45°C and P = 120 bar. At these conditions, CO₂ is in the supercritical (SC) state. The injection rate is 100 kg/s corresponding to the CO₂ production of a 288-MWe (megawatt electric) coal-fired power plant [Pruess and García, 2002]. The data were simulated using Tough2 with the equation of state module ECO2N, designed to describe multi-phase flow for mixtures of water, NaCl and CO₂ [Pruess
Figure A.5: Schematic H$_2$O/CO$_2$ phase diagram as function of mass fraction (X CO$_2$). At low and high CO$_2$ mass fractions single phases are present, with a two-phase region of mutually saturated fluids in between.

and Spycher, 2007]. The model considers fluid flow and phase behavior, but chemical rock/fluid interaction is not taken into account.

During injection a mixing zone wherein both the aqueous phase and the CO$_2$-rich phase exist together is formed, and this region or front travels radially away from the injector. In this zone, the injected dry CO$_2$ comes in contact with the formation brine, and water evaporates into the CO$_2$ rich phase and CO$_2$ dissolves in the aqueous phase. Above and below certain mass fractions (solubility limits) the resulting fluid will be single phase as indicated in Figure A.5 – an aqueous phase and a CO$_2$-rich phase respectively. An extended two-phase-flow region exists in between, where both phases coexist and are mutually saturated. In this region, the fluids can be considered as immiscible.

The simulation has been performed in 1D radial geometry. Results are shown in Figure A.6; the upper panel shows the CO$_2$ saturation as a function of $R^2/t$, where $R$ is the radial distance from the injector and $t$ is the time starting at the beginning of the injection operation. $R^2/t$ is a similarity variable accounting for the symmetry of the model. The plot shows three characteristic regions separated by sharp boundaries. From right to left there is the CO$_2$ shock front penetrating into the aquifer with an initial shock-front height (CO$_2$ saturation) of about 0.2 in pore volumes (PV). Behind the front in the upstream direction there is the zone of two-phase flow with increasing CO$_2$ saturation followed by a dry zone close to the injection well. This dry-out occurs in a clear window at a defined distance and time, with the clarity explained by a self-focusing effect [Pruess and Spycher, 2007]. In this window the salt of the brine phase precipitates leading in the present case to a solid-salt saturation of about 4% of the pore space as drawn in the upper panel of Figure A.6.

During the injection period, the flux of the injected fluid varies markedly in space and time over several orders of magnitude as a result of the radial injection geometry as displayed in the middle panel of Figure A.6. Resulting experimental flow rates range from about 10 to $10^{-5}$ ml/cm$^2$/min. The range of injection rates also determines typical velocities such as the velocities of the flood front and the dry-out front (lower panel in Figure A.6), which again vary over several orders of magnitude for the same reason. In the
Figure A.6: CO$_2$ injection in radial geometry [Pruess and Spycher, 2007]. Upper panel: CO$_2$ saturation (black, open squares) and solid-salt saturation (blue, closed circles) as a function of $R^2/t$ during injection of dry CO$_2$ in a brine-saturated formation. In the middle: flux of the CO$_2$-rich and the aqueous phase as function of $R^2/t$. The red line shows the geometrical decay. Lower panel: velocities of the flood front and the dry-out front over the injection period.
present case, velocities are determined by the flux and the saturation (shock front), and by the flux and the saturation limit of water in \( \text{CO}_2 \) (dry-out front). The lower panel of Figure A.6 shows the velocities of both fronts as a function of time, which is linked to the radial distance \( R \) through \( R^2/t \).

The fluxes are considered and manifested in the experiment by the choice of the injection pumps and sample cross-sections. The velocities define the time resolution required for, e.g., imaging of features. Fast features such as the flood front propagation can normally not be captured by the imaging technique chosen here, but is rather important for, e.g., determination of relative permeability and viscous stability of the displacement process [Ott et al., 2011a, Berg et al., 2013a]. For reactive transport we expect rather slow effects on the time scale of the dry-out (A.1.2, A.1.4) and of potential chemical reactions (A.1.2, A.1.4).

**Reactive transport**

Chemical rock/fluid interaction is considered to take place in the aqueous phase. The injected fluid, e.g. SC \( \text{CO}_2 \) or \( \text{H}_2\text{S} \), partly dissolves in the formation water and drives the rock/fluid system to depart from equilibrium, e.g. through lowering of the \( p\text{H} \). This causes minerals to dissolve and other minerals to precipitate changing the composition of the rock and the fluids, and the fluid dynamics. The variety of fluids and rock-forming minerals and their reactive surface areas (\( A \)) leads to a wide range of reaction rates and reaction mechanisms that cannot be discussed in detail here.

Instead we show an illustrative example of structure formation by rock dissolution due to the injection of \( \text{CO}_2 \) in limestone. The example demonstrates the benefit of combining a core-flood experiment with imaging and chemical fluid analysis. The set of reactions that leads to calcite dissolution by \( \text{CO}_2 \) injection is:

\[
\begin{align*}
\text{CO}_2(g) & \rightleftharpoons \text{CO}_2(aq) \quad (A.5) \\
\text{CO}_2(aq) + \text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad (A.6) \\
\text{CaCO}_3(\text{Calcite}) + \text{H}^+ & \rightleftharpoons \text{HCO}_3^- + \text{Ca}^{2+} \quad (A.7)
\end{align*}
\]

\( \text{CO}_2 \) dissolves and dissociates in the brine forming a weak acid according to Equations A.5 and A.6. Its \( p\text{H} \) is reduced with respect to the initial brine, which causes calcite to dissolve according to Equation A.7. Calcite dissolution is usually very fast, resulting in a generally high Péclet-Damköhler number (\( PeDa \)) and hence in a transport limited system. According to Figure A.3, calcite dissolution will not be homogeneous, and depending on the Péclet number (\( Pe \)) compact dissolution or wormhole formation is expected.

In the present example \( \text{CO}_2 \) saturated brine was injected into an Euville limestone (outcrop) at a pore pressure of 75 bar and a temperature of 35°C. The rock had in the initial state a permeability of 80 mD and a porosity of 0.15 and was initially brine saturated. During the experiment, \( \text{CO}_2 \) saturated brine was injected with a Darcy velocity of about \( 10^{-6} \text{m/s} \) displacing the initial brine. The flow rate results in \( Pe \approx 150 \), i.e. \( Pe >> 1 \) – the system is advection dominated. In conjunction with the high \( PeDa \) number we expect the regime to be where wormholing is the dominant dissolution mechanism.
Figure A.7: CT imaging of wormholing. The data were recorded with a medical CT scanner at a spatial resolution of 0.5 mm. Top: CT cross-sections before (left) and after (right) flooding with CO$_2$ saturated brine. Bottom: 3D reconstruction of the macroscopic pore space after the experiment showing vugs and wormholes.
Figure A.7 shows CT cross-sections before and after the experiment with a spatial resolution of about 0.5 mm (medical CT scanning). Clearly visible are large holes in the post-experimental scan that developed in the course of the experiment. A 3D image of the pore space of larger features such as vugs and wormholes is displayed in the lower part of Figure A.7. The observed pattern shows clearly that several cross-connecting wormholes were formed at the inlet. Two major wormholes developed into the sample, connecting at a certain distance to form a single one, which grew through the sample, shortcutting the rock matrix for fluid transport. The absolute permeability increased significantly during the experiment from the initial 80 mD to 13 D at the end of the experiment. After breakthrough, the Ca$^{2+}$ concentration decreased from its saturation limit by about 30%, which indicates a transition from a clearly transport limited system ($Da$ in the order of $10^6$) to a reaction limited system. In view of the definition of the $Da$ number, this change can be expressed as a reduction of the effective reactive surface area. Assuming that the change from a transport to a reaction limitation lies at $Da \approx 1$, the change in effective surface area is in the order of $10^6$, an effect related to the bypassing of the rock matrix through the wormhole – i.e. calcite dissolution further to wormhole formation is substantially diminished.

A closer view to the modified rock structure with the wormhole and its environment is provided in Figure A.8. The images are recorded by µCT scanning with a voxel size of 5 µm showing the rock structure on a pore scale. The images show the merging of two wormholes similar to the structure in Figure A.7, but this time on a pore scale beyond the resolution of the medical CT scan in Figure A.7. Figures A.8 and A.7 illustrate that similar dissolution patterns and mechanisms can occur on various length scales ranging in the given example from a centimeter to a micrometer scale, a range that needs to be covered by the potential imaging method. The surroundings of the wormhole do not seem to be greatly affected by dissolution since the grains are still angular and fossils are still intact as in the initial rock structure. Reactions seem to be limited to the surface area of the wormhole with negligible reactive transport through the rock matrix.

Major questions to be resolved are the growth rate and density of wormholes and the relationship, if any, between porosity (dissolved volume) and permeability ($K(\phi)$). What is the influence of a wormhole pattern on two- (or multi-) phase flow $k_r(\phi)$, $p_c(\phi)$, and under what conditions do wormholes form in two-phase flow? Can such a system be described by Darcy flow at all? What is the maximum formation damage with different processes such as drainage (displacement of less than one PV of brine – limited solute transport) and imbibition (displacement of less than one PV of CO$_2$ – limited acid formation) conditions?

### A.1.3 Design of the experimental unit

**Overview**

The core-flood experiment we present here is designed to inject reactive and volatile fluids in otherwise saturated rock samples in order to investigate the effects of chemical rock/fluid interaction on fluid flow. The design follows the basic principle of conventional core-flood experiments for multi-phase flow in porous media as applied in the oil and gas industry to...
Figure A.8: µCT images of Euville limestone after flooding with CO$_2$ saturated brine. The cross-sections on top show details of how two wormholes are connected and the near environment of wormholes. Bottom: 3D representation without (left) and with (right) the wormhole emphasized (in light blue).
quantify oil recovery and to develop production strategies [Tiab and Donaldson, 2004, Vinegar and Wellington, 1987]. Here, this principle is further developed for the characterization of reactive transport. A schematic of the experimental setup with its principal components is given in Figure A.9 and the more detailed Process Engineering Flow Scheme (PEFS) is shown in Figure A.10. The PEFS is simplified for a better understanding and only the elements that are important for further discussion are highlighted and labeled.

### Table A.1: Analytical methods versus measurement.

<table>
<thead>
<tr>
<th>Label in Figure A.10</th>
<th>Analytical method</th>
<th>Measurement/procedure</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI/TI</td>
<td>P &amp; T indicator</td>
<td>experimental P &amp; T</td>
<td>thermodynamic conditions</td>
</tr>
<tr>
<td>PDI</td>
<td>pressure transducer</td>
<td>differential pressure dp</td>
<td></td>
</tr>
<tr>
<td>P 1-4</td>
<td>pump control</td>
<td>volumetric flow rate</td>
<td>mass balance &amp; flux v</td>
</tr>
<tr>
<td>QI</td>
<td>Coriolis flow meter</td>
<td>fluid density $p_f(t)$</td>
<td>fluid state &amp; mass balance</td>
</tr>
<tr>
<td>µCT</td>
<td>µCT scanner</td>
<td>matrix density $\rho_m$, $\phi(x,t)$, $S_i(x,t)$</td>
<td>rock matrix &amp; saturation profile</td>
</tr>
<tr>
<td>S1/2</td>
<td>high &amp; low P/T separator</td>
<td>phase separation at experimental &amp; near ambient conditions</td>
<td>fluid phase separation &amp; fluid production</td>
</tr>
<tr>
<td>GC/MS</td>
<td>gas chromatograph &amp; mass spectrometer</td>
<td>in-line chemical gas composition</td>
<td>identification of reactions, rates &amp; mass balance</td>
</tr>
<tr>
<td>HV2/1 &amp; V2/3</td>
<td>gas sampling options</td>
<td>gas sampling &amp; precipitation</td>
<td>ex-situ analysis</td>
</tr>
<tr>
<td>ST</td>
<td>liquid sample taker</td>
<td>liquid sampling</td>
<td>ex-situ analysis</td>
</tr>
</tbody>
</table>

The central part of the experiment is the core holder (pressure vessel), which contains the cylindrical rock sample and allows for fluid injection into the rock (see A.1.3). The core holder is placed in a µCT scanner for in-situ high-resolution 3D-imaging of the rock matrix and the fluid distribution in it. The rock sample can be pressurized and heated to reasonable high fluid pressure ($P$) and temperature ($T$) to mimic subsurface processes. In the present design the maximum operation pressure and temperature is $P = 150$ bar and $T = 150^\circ C$, such that $\text{H}_2\text{S}/\text{CO}_2$ mixtures, including the end members, are in the supercritical phase [Bierlein and Kay, 1953, Carroll, 2002]. Higher $P$ and $T$ can in principle be reached. The limiting element is the core holder, since no compromises have been made regarding the x-ray properties of the materials to reach optimal CT quality.

During the experiments fluids are injected into the otherwise fluid-saturated rock sample. For preparation of the initial rock/fluid state and the actual injection process the setup is equipped with two feed sections, the liquid feed section for flooding with true liquids and the AG-feed section to supply liquefied gases/SC fluids. Both feed sections are interconnected for fluid mixing and fluid/fluid equilibration. Furthermore, fluids can be recirculated through the rock to establish, e.g., an equilibrium between the rock and the initial fluid as in the undisturbed field. A poorly prepared initial state possibly leads to time-dependent changes that are not induced by the injection fluid and, hence, to artifacts in the measurement. As well as the initial rock/fluid system, it is often required to prepare the injection fluid, such as mixing of miscible fluids (e.g. $\text{CO}_2/\text{H}_2\text{S}$) or equilibration of immiscible but mutually soluble fluids (see the $\text{CO}_2$/brine example above). The respective procedures are discussed in A.1.3.

During the experiment, the fluid saturation in the rock is monitored by µCT imaging (spatially resolved) and by the fluid production (integrated). From the fluid saturation or
Figure A.9: Schematic of the experimental setup. More details are provided in Figure A.10.
**Figure A.10:** PEFS diagram of the experimental setup. The flow diagram is simplified for ease of understanding, and discussed in the text.
the saturation profile in combination with the injection rates and a differential pressure measurement ($dp$), fluid flow parameters can be derived (Table A.1 provides an overview of the various analytical methods and measurements versus the purpose of the measurement). We opted for a vertical flow direction to avoid gravity effects (fluid over or underrun) due to the density contrast between the injected and the initial fluid. The setup has been designed for top-down or bottom-up injection. This is essential to reach a gravity-stable displacement for different viscosity and density contrasts.

If the injected fluid reacts with the initial rock/fluid system, the structure and the chemical composition of the rock matrix will change. µCT scanning provides density profiles of the sample and hence access to structural and – to a certain extent – compositional changes of the matrix.

Chemical interaction also changes the composition of the involved fluids manifested in the composition of the produced fluids compared to the initial and injected fluids. We combined the classical design of a core-flood experiment with in-line fluid analysis and sampling options as shown in Figures A.9 and A.10; the produced fluids undergo a two-step phase separation to separate, e.g., an aqueous phase from a $\mathrm{CO}_2/\mathrm{H}_2\mathrm{S}$ phase. The separation is followed by in-line chemical gas analysis by gas chromatography and sampling options for both phases for continuative ex-situ analysis. Phase separation, chemical analysis and sampling options are discussed in A.1.3 and are summarized in Table A.1.

Special attention was payed to the corrosivity and toxicity of the involved fluids. Highly saline brines and $\mathrm{H}_2\mathrm{S}/\mathrm{CO}_2$ in the presence of water are highly corrosive. Therefore the major part of flow loop components are manufactured from Hastelloy C276, which is a highly corrosion-resistant Ni, Mo and Cr-base alloy. Due to the toxicity of, e.g., $\mathrm{H}_2\mathrm{S}$ a nitrogen purge is foreseen; it must be ensured that all parts of the setup can be purged to permit the safe dismantling of components after experiments. Concentrations of critical

**Figure A.11:** Photos of the experimental setup. A) core-flood experiment including µCT scanner in the chemical safety cabinet, B) core holder in the sample manipulation stage of the µCT scanner, C) system components: injection pumps and Coriolis mass-flow meters, D) fluid analysis: separation vessels and liquid sampler.
constituents in the purging stream are controlled via the in-line gas chromatograph (GC). Furthermore, there must be a controlled and safe release of effluent streams such as the production stream, streams from pressure relief valves and purging streams. These streams are led via a stack line to an incinerator for combustion. In the case of an unintended release of H$_2$S the whole experimental setup is placed in a ventilated cabinet with the exhaust flow led through a ZnO filter (scrubber) in order to avoid emission of H$_2$S gas into the environment and to prevent exposure to the operator.

Core holder and $\mu$CT scanner

The core holder is placed in the sample manipulation stage of the $\mu$CT scanner. The scanner design is such that X-ray-source and detector positions are adjustable, but fixed during the experiment, while the sample rotates and translates along the vertical sample axis. The overall demands on the core holder and the sample manipulation stage are: (1) operation at high pressures and temperatures with volatile and corrosive fluids, (2) favorable X-ray properties to allow for optimal CT quality, (3) slim design for a reasonably high geometrical CT resolution and (4) high mechanical stability and accuracy of the sample movements.

Core holder design  The core holder is depicted in Figure A.12 and Figure A.11 B). The fluids are injected with a certain injection rate along the cylindrical axis driven by a pressure gradient over the sample that is defined by the injection rate at a given sample permeability and fluid configuration. To avoid fluid bypassing the rock matrix, the sample is wrapped in a sleeve tightly fitted to the sample by an external confinement pressure (CP) higher than the internal fluid pressure $P$. The CP is applied hydraulically by oil (sleeve oil) in the annular space between the sleeve and the outer pressure vessel (jacket). The sleeve oil is heated to experimental temperature and circulated through the core holder to heat the sample and to compensate for the heat loss to the outside (the sleeve-oil loop is not shown in Figure A.10).

On the injection side, there are two concentric feed lines to co-inject two fluids phases. For a proper fluid distribution over the entire sample cross-section, the injection lines feed via a plunger with a cross-sectional channel pattern into the core. Optionally, a high-permeable porous disc can be placed in between the plunger and the sample for a better fluid distribution as indicated in Figure A.12 B). The same arrangement is used at the outlet, but with a single line for fluid production. The whole interior of the core holder is centered by the end-flanges and stabilized by the CP (see Figure A.12 B)).

Materials surrounding the sample – the core holder – influence the CT-image quality since all materials are X-ray absorbing. The photoelectric absorption coefficient varies with atomic number $Z$ by approximately $Z^4$ [Als-Nielsen and McMorrow, 2000]. This means that a proper core holder design requires light materials (low mass density and low-$Z$ materials) to minimize X-ray absorption, but on the other hand the material must resist the required pressure and temperature regime. Furthermore, laboratory X-ray sources are usually polychromatic and materials in general do not absorb all X-ray energies in the same way; preferably, the low-energy part of the X-ray spectrum is absorbed more, leading
Figure A.12: A) 3D, and B) 2D CAD drawing of the core holder. C) shows details of the swivel construction in two sectional views.
to a change of the X-ray characteristics by passing through the core holder. Thus, the surrounding materials not only attenuate the X-ray beam, but also influence the achievable CT contrast [Kak and Stanley, 2000], and lead to artifacts. Materials therefore deserve special attention.

Figure A.12 B) shows the sectional drawing of the core holder. We find along the X-Y line from the center of rotation to the outside: (1) rock sample; (2) sleeve: the choice of the sleeve material depends on the injected fluid. Viton (elastic sleeve) or Teflon (shrink sleeve) based materials are suitable. The issue with elastomers is the possible diffusion of CO$_2$ into the sleeve leading to loss of experimental fluid into the circulating confinement fluid, and to potential damage of the sleeve material during decompression after the experiment. Composites like thin welded metal sleeves with Teflon liner appear to be a good choice. However, metal sleeves may influence the CT performance. (3) annular space for oil circulation to apply confinement pressure and sample heating; (4) layered pressure vessel (jacket) with an aluminum liner, a Glass-Cyanate-Ester layer and finally the Carbon-Cyanate-Ester outer wall.

The layered jacked combines optimal X-ray penetration properties with the respective mechanical and thermal strength. The desired properties are mainly those of the Carbon-Cyanate-Ester material. The aluminum liner is necessary for manufacturing reasons and will attenuate the X-ray beam more than the other components and is subject to beam hardening as discussed above.

**µCT scanning**  X-ray Computerized Tomography (CT) is a non-destructive analytical technique providing 3D reconstructed images of X-ray absorbing samples [Kak and Stanley, 2000]. A reconstruction algorithm calculates the images from the X-ray attenuation projection data. In the present design we opted for a micro-CT scanner. The principle of micro CT (µCT) is comparable to medical CT scanning, but with a higher spatial resolution [Coenen et al., 2004, Bauget et al., 2005] and, in the present design, with more freedom for signal optimization at the expense of the high degree of standardization and the good time resolution of a medical CT scanner.

The µCT scanner is custom-designed based on the CT compact model of PROCON X-RAY, Germany. The core holder is placed in the sample manipulation stage between the X-ray source and the opposite positioned detector. During a scan the sample is irradiated with a conical X-ray beam, which becomes attenuated by the sample. The transmitted X-ray intensity is projected onto the 2D multichannel detector. The projection pattern is characteristic for the mineral and fluid distribution in the sample, and the projections over an angular range of 360° provide the data for the 3D reconstruction of the scanned object.

For high mechanical stability, the scanner components are built on a granite foundation. The position of the X-ray tube and the detector position are adjustable along the source – sample-rotation-axis – detector line providing the degrees of freedom to choose the field of view, to tune spatial resolution and to optimize the signal-to-noise ratio. The core holder can be displaced vertically for imaging of long cores up to a length of 0.5 m by batch or helical scanning.
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The scanner is equipped with a Microfocus X-ray source from Hamamatsu. With the minimum focal spot size of 5 \( \mu \text{m} \) (at 4 W), the source is a compromise in spatial imaging resolution, but allows very stable continuous operation even at the maximum output power of 39 W (at 40 \( \mu \text{m} \)); this is a firm requirement, as an experiment could last as long as a few weeks. The range of spot sizes allows optimization between spatial resolution and photon flux (corresponding to time resolution). A Hamamatsu flat-panel sensor is used for X-ray detection. The detector has an active area is 12 \( \times \) 12 cm with a pixel size of 50 \( \times \) 50 \( \mu \text{m} \), a high readout speed and a high dynamic range. The detector pixels can be merged to 2 \( \times \) 2, 4 \( \times \) 4, etc. With the given minimum focal spot size and the relatively large sample sizes, a reasonable spatial-resolution limit (voxel size) of 5–8 \( \mu \text{m} \) can be reached.

During a scan, the core holder rotates and translates while fluids are injected i.e. with connected flow lines. For translations of up to 0.5 m (= maximum sample length) guided flexible hoses (sleeve oil) and Hastelloy-metal capillaries of sufficient length are used as flow lines. The sample rotation is realized by swivels on the injection and the production side allowing for sample rotation without curling the flow lines i.e. without angle dependent forces counteracting the rotation. The swivel construction is displayed in Figure A.12 A) and C). Each swivel consists of two concentric cylinders with the feed lines connected to the outer cylinder that is fixed with respect to the scanner. The fluids are guided from the tubing via separate annular channels to the respective injection line. These channels are sealed from each other and from the outside by O-rings (Viton H NBR) allowing for a “sealed” rotation of the inner cylinder with respect to the outer.

Fluid feed – preparation and injection

The setup is equipped with two feed sections, one for liquids, i.e. in a liquid state at ambient condition, and a second for supply liquefied gases and SC fluids (see Figure A.10). Both feed sections are interconnected for maximum flexibility in fluid preparation and core flooding as discussed in the following. A separate port for gas cylinders allows for pe-saturation with gases (“gas cylinder” in Figure A.10).

The liquid-feed section is equipped with two single-stroke pumps (ISCO pumps P3/4 in Figures A.10 and A.13) with a capacity of 500 ml each. The range of flow rates is 0.001 to 122 ml/min with a displacement resolution of 13 nl. The pumps are switched to either operate separately or combined as a two-stroke pump (see Figure A.10) for continuous recirculation of fluids. Pumps, feed lines and valves are made out of Hastelloy C276 for corrosion reasons. The pumps are loaded via vessel V1 (Figure A.10). Loading at elevated temperatures is foreseen in order to avoid precipitation in case of highly saline brines.

The acid-gas feed unit is designed to supply liquefied gases and supercritical liquids by means of two 500 ml ISCO pumps (P1/2 in Figure A.10 and A.13) that can be filled from liquefied-gas cylinders. The pumps can be operated at experimental temperature, but in order to avoid a gas cap during the filling procedure and/or to increase the total loaded mass, the pumps can be cooled as well. Both pumps can be operated separately, but also together by pumping two fluids through a static mixer (M) in order to flood with mixtures of miscible fluids, such as H\(_2\)S and CO\(_2\), with a ratio defined on a volumetric basis.
For some applications it is necessary to equilibrate fluid phases as exemplarily discussed for CO\textsubscript{2}/brine systems in A.1.2. A rapid equilibration is reached by co-flooding both fluids through a static mixer. For that purpose, both feed units are interconnected as illustrated in Figure A.13. Brine can be transferred via the cross-connection from the liquid-feed to the acid-gas-feed section. From there it can be co-flooded with CO\textsubscript{2} through the static mixer (M) back to the liquid feed (P3/P4). The fluid phases separate in the pumps by gravity and can subsequently be split on a volumetric basis to a CO\textsubscript{2}-rich phase and an aqueous phase in P1 and P2, respectively. This procedure can be repeated till mutual phase saturation is ensured with both fluid phases in separate pumps. Volume changes of the individual phases and the total volume need to be taken into account for a proper phase split. The change in the total volume can also be used to precisely monitor the equilibration process; equilibration is reached if the total cumulative volume (sum of the individual pump fillings) reached a constant value – for CO\textsubscript{2}/brine, equilibrium is reached after 2 to 3 cycles (present design). Equilibration of H\textsubscript{2}S/CO\textsubscript{2} mixtures with brine requires an additional mixing step of CO\textsubscript{2} with H\textsubscript{2}S prior phase equilibration.

**Fluid analysis and sampling**

A comprehensive fluid analysis of a multi-phase system requires in the first instance a separation of the produced fluids and a subsequent compositional analysis of the individual fluid phases. To detect small changes, not only the produced fluids, but also the initial fluids (produced during pre-saturation) and the injection fluids need to be analyzed as reference cases. The core can be bypassed such that the injection fluid can be analyzed in the same way as the produced fluids.

The analytical section is shown in the lower part of Figure A.10. The available options
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are listed in Table A.1 and are: (1) fluid density and mass flow in the acid-gas feed line and in the production line measured by Coriolis mass flow meters, (2) two-step gas/liquid phase separation, (3) online chemical gas analysis of the separated gas streams using gas chromatography (GC) and mass spectroscopy (MS), (4) gas sampling by gas bags, and sampling by precipitation of gas constituents for ex-situ isotopic composition determination, (5) automated sampling of liquid phases for subsequent ex-situ analysis.

In-line fluid analysis required departure from conventional back pressure systems. In conventional core-flood experiments the back pressure is often realized by setting the injection pump to a constant flow rate and by collecting the produced fluids in a receiving pump set to constant pressure mode; the receiving pump sets the base pressure while the injection rate and the sample permeability determine the differential pressure over the core, which is typically much smaller than the base pressure. The present unit provides this option by using, e.g., P1/2 for injection and P3/4 as receiving pumps, which is in some cases very useful, but it does not allow for time-resolved in-line fluid analysis and sampling, since the fluids accumulate in the pump during production. For continuous (time-resolved) fluid analysis, the fluids are produced into a high \( P/T \) vessel (S1), which is under a constant nitrogen purge. The nitrogen purge has three functions: firstly, together with the pressure-controlled valve (PCV in Figure A.10), it maintains a constant fluid pressure (back-pressure control). Secondly, by mixing with nitrogen in a defined ratio, the produced SC fluids make a transition to the gaseous phase, which allows for effective phase separation by gravity between the light gas phase and the heavier liquid phase. The transition to the gaseous state and, hence, an efficient working phase separation requires us to choose the nitrogen flux according to the \( \text{CO}_2/\text{H}_2\text{S} \) injection rate and the respective pressure and temperature. The resulting gas stream is led either to the GC/MS for online gas analysis or to the sampling unit. Thirdly, the nitrogen purge flows are used as internal standards for the GC analysis and the mass balance.

If the accumulated liquid (brine in the present example) in S1 reaches a defined level, it will be emptied via a level controlled needle valve (LCV in Figure A.10) to a second separation vessel (S2). S2 works with the same principle as S1, but at near-ambient condition. The accumulated liquid will degas according to the change of gas solubility caused by the change of the thermodynamic condition. Also S2 is purged by a defined nitrogen flux carrying the recovered gas to the GC/MS for compositional analysis or for gas sampling. The remaining and degassed liquid phase is sampled to an array of bottles by an automatic sample taker for external chemical and physical analysis.

Besides the above-mentioned GC/MS analysis, it might be worthwhile determining the isotopic composition of the gas. In the case of less toxic gases such as \( \text{CO}_2 \), the gas can regularly be sampled in gasbags via the manual valves HV1 or HV2 (Figure A.10). The situation is more complicated in the case of toxic gases such as \( \text{H}_2\text{S} \) as transport of \( \text{H}_2\text{S} \)-containing gasbags implies a risk. In this case the gas can be bubbled through an aqueous solution in the vessels V2 and V3 to retrieve the respective elements in other compounds by precipitation, e.g., precipitation of sulfur in an \( \text{AgNO}_3 \) solution forming a \( \text{Ag}_2\text{S} \) deposit by the reaction:

\[
2\text{Ag}^+ + 2\text{NO}_3^- + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} (\text{deposit}) + 2\text{H}^+ + 2\text{NO}_3^- - \quad \text{the deposit is easy to handle and can be shipped for isotopic analysis.}
\]
A.1.4 Experimental Results

The aim of this section is to demonstrate feasibility and experimental procedures. The two examples that are presented in the following address physical and chemical aspects of formation dry-out near the injection well [Ott et al., 2010] as outlined in Section A.1.2. At first, we show \(\mu\)CT data of the dry-out process and the associated precipitation of salts; we injected SC CO\(_2\) in brine-saturated siliciclastic sandstone, a rock/fluid combination that we considered as non-reactive. The aim of the experiment is to characterize the spatial distribution of the precipitated-salt phase by \(\mu\)CT scanning and set it in relation to the associated permeability change.

Once a formation is dry it is supposed to be chemically stable, since in reactive transport modeling only aqueous chemistry is considered. In the second example we show that this is not necessarily true. We injected SC H\(_2\)S into “dry” limestone. By “dry” we mean that the sample is as dry as achievable by extensive dry inert-gas injection under in-situ conditions, i.e. in the absence of an aqueous phase. The chemical activity under these non-aqueous (but not anhydrous) conditions is demonstrated by means of in-line fluid analysis.

**SC CO\(_2\) injection: Dry-out and salt precipitation**

This section is referred to Chapter 5.

**Injection of SC H\(_2\)S in dry limestone**

The experiment was performed on limestone (Euville, outcrop) with a permeability of 170 mD and a porosity of 16\%. The mineralogy was calcite with 2\% clay minerals and sample dimension was 1 inch diameter \(\times\) 9 cm. To mimic the dry state, the sample had been dried at 90\(^\circ\)C in a vacuum oven and was subsequently mounted in the core holder. Once there, it was pressurized by dry nitrogen to 110 bar pore pressure, and heated up to 110\(^\circ\)C under nitrogen flow of about 2 normal-liters/h. To eliminate residual moisture, the sample was flooded under these conditions for about 60 h. Only pure Nitrogen was detected in the GC signal of the gas produced from the rock sample.

During the experiment, pure SC H\(_2\)S was injected at a constant injection rate of 2.5 ml/min at experimental condition. Figure A.14 shows the density of the produced fluid (upper panel) and the response of the gas chromatograph (lower panel). At the beginning, the fluid density is close to 100 kg/m\(^3\), corresponding to the value of nitrogen at the respective condition. With a delay of about 17 min (after starting the pumps), the fluid density starts to increase gradually due to breakthrough of the injected SC fluid and reaches a constant value after about 50 min.

The GC signal showed peaks that were identified as N\(_2\), CO\(_2\), and H\(_2\)S. The GC response is shown in the lower panel of Figure A.14, representing the integrated peak intensity as function of time. Up to 13 minutes only pure nitrogen was detected. From 13 minutes onward CO\(_2\) appeared in the chromatogram and at 23 minutes a pronounced H\(_2\)S signal appeared in the GC while the CO\(_2\) peak reached its maximum. About 50 minutes after the start of the experiment, the GC signals reached steady state where they remained to
Figure A.14: Upper panel: Density of the produced fluid as function of time. The horizontal lines represent calculated values [Shell Global Solutions, 2008]. Lower panel: GC response (integrated peak intensities) in the same time interval. The CO$_2$ concentration is given in mol % with respect to H$_2$S flux in the fully saturated state (after about 30 min).
APPENDIX A. EXPERIMENTAL CAPABILITY

the end of the experiment. Nitrogen gas was produced as result of miscible displacement by supercritical H$_2$S. The flood front is indicated by the decrease in the N$_2$ signal and the simultaneous increase in the H$_2$S signal in the chromatograph. In this early period, where H$_2$S is starting to displace N$_2$, the input H$_2$S is apparently consumed by a chemical reaction with the calcite where the detected reaction product is CO$_2$; we hypothesize that this is why CO$_2$ is detected in the GC data before H$_2$S. After about 32 minutes the effluent gas density reaches a step corresponding to anhydrous H$_2$S and shortly thereafter the effluent gas density increases to a value corresponding to water-saturated H$_2$S. While the gas density is increasing the fraction of CO$_2$ is decreasing.

The nature of the chemical reaction between calcite and H$_2$S at the earliest times of the experiment is difficult to discern – is this a gas solid reaction or does the calcite retain trace moisture despite the drying procedures employed? In either case, the H$_2$S consuming – CO$_2$ generating reaction gains in rate until another governing variable dominates the system. The steady state evolution of water-saturated H$_2$S requires a source of water that appears to be the calcite rock itself, and apparently, an aqueous phase is formed in the sample since the saturation limit of water in H$_2$S is reached. Working with this hypothesis we may infer that water inhibits the reaction of calcite with H$_2$S in agreement with the fall off of CO$_2$ production, in the early stages, from the calcite core sample. However, the inhibition by water is not complete, hence a steady state production of water (in the SC H$_2$S phase) and CO$_2$ is observed over long experiment times.

We conclude that water and CO$_2$ are reaction products of H$_2$S injected into limestone. The initial reaction is likely to be induced by water but does not take place in an aqueous phase. The fluid flow characteristic changes from single-phase to two-phase flow with a reduction in the effective permeability. The moderate reduction is likely caused by a combination of mineral dissolution (permeability increase) and relative permeability (permeability decrease).

A.1.5 Conclusion

The experimental setup as presented in this paper has been designed and constructed to perform core-flood experiments with toxic, corrosive and volatile fluids such as SC CO$_2$ and SC H$_2$S. The design provides the flexibility to cover a wide range of reactive transport issues as crucial to early de-risk CO$_2$ sequestration, acid-gas injection and EOR projects.

With this paper we address the importance of initial chemical and phase equilibria for reactive transport. Furthermore, we demonstrate that the novel combination of a core-flood experiment with a $\mu$CT scanner gives extra information compared to the use of conventional (medical) CT scanning, which might be crucial for understanding processes on multiple length scales. A novel back-pressure system allows for on-line and time-resolved chemical fluid analysis and various sampling options. This, together with fluid-saturation control and differential pressure measurements, gives access to complex couplings of fluid flow and chemistry.
A.2. EXPERIMENTAL SEQUENCE

A.2 Supporting Information for ‘Wormhole formation and compact dissolution in single- and two-phase CO$_2$-brine injection’

This document provides details of the experimental setup and procedures.

**Experimental setup** A sketch of the experimental setup is shown in Fig. A.15. A cylindrical rock sample (the core) contained in a metal sleeve with a Teflon liner is enclosed in an X-ray transparent carbon fiber epoxy core holder. The orientation of the core and the main flow direction is horizontal. Fluids are injected through a distribution plate and a highly-permeable porous metal disk into the inlet face of the cylindrical sample. The same configuration was used on the production side. The annulus between the sleeve and core holder is pressurized to a pressure well above the intended pore (injection) pressure in the core in order to press the sleeve on the core and avoid bypassing of injected fluids. With a pore pressure of 100 bar, we chose the confinement pressure to be 150 bar.

The present study required the pre-conditioning of the initial and injection fluids. We used a stirred reactor to equilibrate CO$_2$ and brine in order to avoid fluid-fluid mass transfer due to their mutual solubility during the displacement experiment. To further prevent chemical interaction between the CO$_2$-saturated brine and the rock we equilibrated the fluids with the rock-forming minerals. This was done by introducing crushed rock material into the stirred reactor. After equilibration, the fluid phases separate by gravity in the reactor and are transferred to separate injection pumps (pump 1 and 2 in Fig. A.15 – Teledyne ISCO, Lincoln NE, USA).

Fluids were injected at experimental temperature and pressure and at constant injection rates. At the outlet, a constant pressure is maintained either by a dual cylinder piston pump (Quizix, Vindum Engineering, INC., San Ramon CA, USA) or two Tescom back pressure controllers operating in series. All seals are made from Teflon, highly fluorinated rubber or Viton-A (hardness: shore 90) to avoid the risk of explosive decompression if exposed to CO$_2$. During the floods, all elements of the flow loop were held at experimental pressure and temperature to maintain the equilibrium state of the injected fluid.

Fluid saturations and their spatial distribution in the core were determined by X-ray computed tomography [Vinegar and Wellington, 1987, Perrin and Benson, 2010, Berg et al., 2013a] using a medical CT scanner (Siemens Somatom Volume Zoom spiral scanner). The X-ray source was operated at 120 kV and 80 mA. Scans were performed at a resolution of 0.5 mm. For reconstruction, the B45s filter was used. Image analysis and visualization were performed with *ImageJ* (National Institute of Health) and *Avizo* (Visualization Sciences Group). Fluid saturations were determined by [Vinegar and Wellington, 1987, Perrin et al., 2009, Berg et al., 2013a]

\[
S_{nw} = \frac{CT_{\text{exp}} - CT_{\text{brine}}}{CT_{\text{CO}_2} - CT_{\text{brine}}} = \alpha \cdot (CT_{\text{exp}} - CT_{\text{brine}}),
\]

where $CT_{\text{brine}}$ and $CT_{\text{CO}_2}$ are the CT numbers of the wetting- and the non-wetting-phase
saturated sample, respectively. \( \alpha = 1/(\text{CT}_{\text{CO}_2} - \text{CT}_{\text{brine}}) \) is the calibration factor that relates a difference between actual CT scan (\( \text{CT}_{\text{exp}} \)) and the reference \( \text{CT}_{\text{brine}} \), taken at the beginning of the experiment at \( S_W = 1 \), to the actual saturation of \( \text{CO}_2 \). \( \alpha \) can also independently be determined from experimental data by a volumetric argument; the injected fluid volume must be equal to the CT-determined displaced fluid volume before breakthrough.

**Flooding sequence and experimental procedures** In order to study the formation of dissolution structures and the influence of these structures on fluid displacements we performed a series of reactive and non-reactive core flood experiments. The procedure is to perform non-reactive single- and two-phase flow experiments in order to characterize the flow properties in the unaltered rock. This is followed by a reactive flow experiment, which alters the rock structure according to the flow regime. Subsequently, we repeat the initial non-reactive experiments to test the influence that dissolution has on fluid displacements.

The ‘ideal’ experimental sequence is described here and refers to the results shown in Fig. 1 of the main manuscript; the experiments (a) to (e) were carried out in a sequence and on the same rock sample. The fluids used in this study and their composition are summarized in Table A.2.

The sequence started with a clean and dry rock sample mounted in the coreholder, which was already under confinement pressure and connected to the flow lines. In this state a reference CT scan was taken – the dry scan. From the dry scan we derive the porosity profile. The experiments were performed at 100 bar (back pressure) and 50°C – the experimental conditions.

- **Pre-saturation**: for pre-conditioning, brine was injected under vacuum, i.e. with a vacuum line attached to the outflow. As the sample was saturated, the pore pressure and the temperature were subsequently increased to experimental conditions. Further brine injection ensured that dissolved gases were removed from the core. The brine
permeability was derived from a multi-rate permeability measurement, and a CT scan taken at 100% brine saturation served as a reference scan.

- **Experiment (a):** We first performed a dispersion test by injecting brine doped with an X-ray tracer that had been equilibrated with CO$_2$ and the rock-forming minerals (doped buffered brine). The injection rate was 1 ml/min. The brine-brine displacement is miscible and the flood was used to quantify rock heterogeneity with respect to permeability. The flood pre-conditioned the sample for experiment (b).

- **Experiment (b):** CO$_2$ was injected at a rate of 0.44 ml/min, immiscibly displacing initial brine. CO$_2$ is soluble in the brine phase and forms carbonic acid, which dissolves carbonate minerals. In order to test true immiscible displacement without altering the rock, the fluid phases were equilibrated with each other and with the rock-forming minerals prior to injection. The equilibration and injection of the initial brine phase had already been done in the course of experiment (a), and the equilibrated CO$_2$ phase was injected. From the data relative permeability and capillary heterogeneity could be derived [Berg et al., 2013a, Ott et al., 2015a].

- **Core cleaning:** A cleaning step was then required to re-establish initial conditions with $S_W = 1$. The core was cleaned by depressurizing to atmospheric pressure and flushing the core with several pore volumes of fresh brine. We pressurized the core again and continued flushing, which effectively removed residual CO$_2$, which went in solution.

- **Experiment (c):** For the reactive transport experiment, brine had been equilibrated with CO$_2$, but not – as in (a) – with the rock-forming minerals. The acidic brine (carbonic acid) was injected with a flow rate of $\sim$1 ml/min, displacing the initial brine and dissolving the rock matrix. We stopped the RT experiment as the dissolution structure – the wormhole – reached about 80% of the length of the core. At the end of experiment (c) the core was still at $S_W = 1$ without dopant.

- **Experiment (d):** For characterization of single-phase fluid displacement in the altered rock, we repeated the non-reactive tracer test as in (a), but this time testing the heterogeneity of the leached rock.

- **Core cleaning:** Due to the pronounced bypassing in (d) a cleaning step was required to establish the initial saturation state without dopant gradients. Salts were removed by flooding with demineralized water at high flow rates (5 to 10 ml/min) for several hours. Subsequently we depressurized the core and extracted the water by applying vacuum. The core was re-saturated under vacuum with doped buffered brine, then pressurized. We continued flooding in order to remove potentially dissolved gas from the system.

- **Experiment (e):** Similar to experiment (b), water-saturated CO$_2$ was injected to investigate CO$_2$-brine immiscible displacement in the edged rock.
Table A.2: Fluids used in this study. The fluids were equilibrated at experimental conditions: $P = 100$ bar and $T = 50^\circ$C. INIF denotes initial and INJF denotes injection fluid.

<table>
<thead>
<tr>
<th>Fluid composition</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>brine 3wt% NaCl</td>
<td>(a), (c), (d) INIF</td>
</tr>
<tr>
<td>doped brine 9wt% CsCl</td>
<td>–</td>
</tr>
<tr>
<td>buffered doped brine doped brine equilibrated with CO$_2$ and the rock’s minerals</td>
<td>(a) INJF, (b), (e) INIF</td>
</tr>
<tr>
<td>CO$_2$ saturated brine</td>
<td>(c) INJF</td>
</tr>
<tr>
<td>water-saturated CO$_2$ CO$_2$ equilibrated with water (brine phase)</td>
<td>(b), (e) INJF</td>
</tr>
</tbody>
</table>

The two-phase flow reactive transport experiment (Fig. 3 in the main manuscript) was performed in the same way as experiment (c), but under co-injection of brine and CO$_2$ at 1 ml/m injection rate, respectively.

**Estimation of $Pe$ and $Da$ numbers** The dissolution regimes can be characterized by Péclet ($Pe$) and Damköhler ($Da$) numbers, being the ratios of advective to diffusive transport rates – $Pe = ul/D$ with $u$ being the fluid velocity, $l$ representing the pore-length scale, and $D$ being the diffusion constant – and the ratio of the overall dissolution rate to the advective transport rate – $Da = kl/u$, with $k$ being the overall reaction rate in units of 1/s.

We relate $Pe$ and $Da$ numbers to the macro-porous subsystem, which we expect to dominate fluid conduction [Ott et al., 2014a, Ott et al., 2015a]. As length scale $l$ we take the mean pore size of the macro-porous system of $l = 2 \times 10^{-5}$ m. From the porosity of the macro-porous system and the injection rate we determined the fluid velocity to $2.2 \times 10^{-5}$ m/s. With a diffusion constant of $D = 7.5 \times 10^{-10}$ m$^2$/s (see e.g. [Luquot and Gouze, 2009]) we calculate $Pe = ul/D \sim 0.6$.

We use an overall reaction rate of CO$_2$-saturated brine with calcite of $\sim 0.00064$ mol/m$^2$/s [Peng, 2015]. By estimating the relevant surface area from spherical pores with 20 μm diameter and by using a value of $\sim 36$ mol/m$^3$ (simulated with PHREEQC V 3.1.1 with Pitzer database at experimental condition) for the saturation concentration of dissolved calcite ions, we estimate the time scale of reaction to $t_R = 1/k \sim 0.18$ s. In contrast, the time scale of transport is $t_T = l/u \sim 0.9$. The time scales result in $Da = t_T/t_R \sim 5$. 


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The research presented in this thesis has been performed in the Rock & Fluid Physics Team in Shell Projects & Technology, Rijswijk and at the Shell Technology Center Amsterdam, in the Netherlands. In my role I have been responsible for the experimental research on geological gas (CO$_2$/acid gas) storage and unconventional gas production.

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During this time, I had the pleasure and privilege to collaborate closely with several colleagues and friends. My particular thanks go to Sjaam Oedai and Kees de Klo, with whom I conducted numerous experiments. Some of the pore-scale experiments were performed together with Ph.D. students from Imperial College London, namely Dr. Apostolos Georgiadis and Dr. Andrew Matthew, who brought in all their passion and pushed the envelope. Dr. Ryan Armstrong (The University of New South Wales, Australia) and Saskia Roels (Delft University, Netherlands) are gratefully acknowledged for their contributions and for all the valuable discussions.

A special thanks goes to Dr. Steffen Berg. I gratefully acknowledge his support in the discussion of new ideas and old results as well as in the experiments, which largely contributed to the success of this work. In a special venture we explored the feasibility of applying fast X-ray micro tomography to fluid displacements in rocks under the direction of Steffen. These experiments were made possible by close collaboration with Mainz University and the staff at the TOMCAT beamline at the Swiss Light Source in Villigen, Switzerland, who are acknowledged at this point.

Finally, my sincere thanks to all members of the Rock & Fluid Physics Team for the countless discussions, their great work and for the always friendly atmosphere, in which this work could thrive. Working in this great team transformed me in no time from a physicist to a geoscientist.

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Dr. Christopher Pentland from the Containment Team in Shell and their support with regards to numerical simulations, and also Dr. Henning Peters, with whom I collaborated on a different topic regarding geochemistry, and who is always open for good discussions.

My affiliation to Imperial College London and my involvement in the QCCSRC (Qatar Carbonates and Carbon Storage Research Centre) helped me to broaden my expertise in geological carbon storage and in porous media flow. For the opportunity to spend some of my time as a Reader in London I am grateful to Prof. Geoffrey Maitland (Managing Director QCCSRC), Dr. Jeroen Regtien (at that time VP Hydrocarbon Recovery in Shell) and Justin Freeman (Program Manager Rock & Fluid Science).

All these people made this time a real pleasure – thank you!
Contributions to this Work

The major part of the present habilitation treatise has been performed in the context of my role as project leader and principal investigator for the experimental research on geological gas storage and unconventional gas production at Shell. The present treatise is based on the following publications in the order of appearance in the document. * denotes the corresponding author:


Various people contributed to the work as reflected in the author lists of the publications. In the following I will describe the main contributions of the author and others to individual chapters.

In Chapter 2 we investigate CO₂-brine primary drainage in sandstone [1] and carbonates [2]. Both studies have been performed under the author’s direction. The experiments were performed with the great help of Sjaam Oedai and important contributions were made by Dr. Steffen Berg (conceptual) [1] and Dr. Christopher H. Pentland (history matching) [2].

In Chapter 3 an extensive stability analysis has been performed on basis of the experimental data in Chapter 2. The results were published in article [3]. Dr. Steffen Berg and the author evenly contributed to the work and the publication.

Chapter 4 presents an experimental study on pore-scale displacement processes in drainage and imbibition. The initial study was performed as a student project (Dr. Apostolos Georgiadis) under the author’s direction [5]. The author contributed to the following studies [4,6] with respect to the experimental design, execution and conceptually. The studies [4,6] were directed by Dr. Steffen Berg and Dr. Ryan Armstrong.

In Chapter 5 fluid-fluid mass transfer and dryout is discussed. The work has been performed under the direction of the author and is published in articles [7-9]. The experiments have been performed with the help of Kees de Kloe and as a student project involving Matthew Andrew. Dr. Jeoren Snippe contributed in a conceptual way and provided modeling support.

Chapter 6 presents a study on reactive transport and structure formation in single- and two-phase flow [10]. The experiments were performed under the author’s direction with the help of Sjaam Oedai. The data on the mechanical rock properties [11] were measured by Kristian Eide and Arjan van der Linden.

The experimental capability as presented in the Appendix A and as published in [12] has been developed under the author’s direction. This would not have been possible without the expert experimental support team of Shell, which I would like to acknowledge at this point.