Modeling of geohydrological processes in geological CO$_2$ storage – with focus on residual trapping

KRISTINA RASMUSSON
Abstract


Geological storage of carbon dioxide (CO\textsubscript{2}) in deep saline aquifers is one approach to mitigate release from large point sources to the atmosphere. Understanding of in-situ processes providing trapping is important to the development of realistic models and the planning of future storage projects. This thesis covers both field- and pore-scale numerical modeling studies of such geohydrological processes, with focus on residual trapping. The setting is a CO\textsubscript{2}-injection experiment at the Heletz test site, conducted within the frame of the EU FP7 MUSTANG and TRUST projects.

The objectives of the thesis are to develop and analyze alternative experimental characterization test sequences for determining in-situ residual CO\textsubscript{2} saturation (S\textsubscript{gr}), as well as to analyze the impact of the injection strategy on trapping, the effect of model assumptions (coupled wellbore-reservoir flow, geological heterogeneity, trapping model) on the predicted trapping, and to develop a pore-network model (PNM) for simulating and analyzing pore-scale mechanisms.

The results include a comparison of alternative characterization test sequences for estimating S\textsubscript{gr}. The estimates were retrieved through parameter estimation. The effect on the estimate of including various data sets was determined. A new method, using withdrawal and an indicator-tracer, for obtaining a residual zone in-situ was also introduced.

Simulations were made of the CO\textsubscript{2} partitioning between layers in a multi-layered formation, and parameters influencing this were identified. The results showed the importance of accounting for coupled wellbore-reservoir flow in simulations of such scenarios.

Simulations also showed that adding chase-fluid stages after a conventional CO\textsubscript{2} injection enhances the (residual and dissolution) trapping. Including geological heterogeneity generally decreased the estimated trapping. The choice of trapping model may largely effect the quantity of the predicted residual trapping (although most of them produced similar results). The use of an appropriate trapping model and description of geological heterogeneity for a site when simulating CO\textsubscript{2} sequestration is vital, as different assumptions may give significant discrepancies in predicted trapping.

The result also includes a PNM code, for multiphase quasi-static flow and trapping in porous materials. It was used to investigate trapping and obtain an estimated trapping (IR) curve for Heletz sandstone.

Keywords: capillary trapping, CCS, characterization test, CO\textsubscript{2}, injection design, pore-network model

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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


Reprints of Papers I, II and III were made with permission from the respective publisher. In Paper I, the author of this thesis contributed with half of the numerical modeling, half of the writing of the first draft of the paper and half of the analysis of results (the other half was made by Maria Rasmusson). In Papers II, III and IV the author developed the conceptual models, carried out the numerical modeling, analyzed the simulation results and wrote the drafts of the papers. Additionally, for Papers II and III the author made code alterations to the existing TOUGH2 numerical simulator with respective module. For Paper IV the author developed the code for the pore-network model. The co-authors of Papers I, II, III and IV have either con-
tributed with experimental data, data concerning parameter properties, provided the T2well code, provided suggestions of improvements concerning the text, layout and analysis interpretation of the manuscript or taken part in discussions concerning the content of the papers.

The following papers, although not part of this thesis, have also been produced during the author’s graduate studies:


Several conference abstracts and MUSTANG deliverables available at www.co2mustang.eu.
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1. Introduction

1.1 Background of geological CO₂ storage

Geological storage of carbon dioxide (CO₂), also referred to as geological CO₂ sequestration, is part of the carbon capture and storage (CCS) concept, where exhaust CO₂ is injected deep into the underground, thereby hindering it from reaching the atmosphere. This type of injection is made for environmental purposes. In the work of reducing greenhouse gas exhausts to the atmosphere, CCS is a complement to other emission mitigation approaches such as decreasing the fossil fuels usage, technology improvements to increase energy efficiency, switching to alternative energy sources or the use of methods to enhance natural CO₂ sinks (IPCC, 2005). The technique is suitable for mitigating CO₂ release from large point sources e.g. power plants and certain industries. The International panel on climate change (IPCC) estimates that at least 1000 GtCO₂ may be stored in deep saline formations worldwide. Oil reservoirs, gas reservoirs and coal seams also provide potential storage space; however the global capacity of these options is estimated to be lower than that of the deep saline formations (IPCC, 2005).

The first large-scale industrial CO₂ geological storage project was put into operation in 1996 at Sleipner, Utsira formation, in the North Sea. In 2016 there were 15 large-scale CCS projects with ongoing sequestration operations (Global CCS Institute, 2016), these included the four commercial-scale geological CO₂ storage projects Sleipner, Snøhvit, In Salah and Weyburn. In addition many pilot and demonstration projects for research purposes have been carried out at e.g. Frio, Ketzin and Otway (IPCC, 2005), and recently Heletz (Niemi et al., 2016), as part of the MUSTANG project to which this thesis is closely linked.

CO₂ subsurface injections have been carried out even prior to the development of CCS, although with other aims than to solely mitigate greenhouse gas emissions. Figure 1 shows a time line for the start of some application areas of CO₂ subsurface injection. In enhanced oil recovery (EOR) operations, CO₂ flooding is used to increase oil production. The CO₂ decreases the viscosity of the oil phase, thereby making it easier to displace (Jarrell et al., 2002). Another area of utility for CO₂ injection is enhanced coal bed methane (ECBM) recovery, where methane desorbs from the coal in preference for CO₂ to adsorb, so-called displacement desorption (Stevens et al., 1998).
CO₂ is also co-injected with H₂S during acid-gas disposal operations (Bachu and Gunter, 2004).

Geological CO₂ storage can therefore be seen as a new area of use for CO₂ subsurface injection with a new target; aquifers in deep saline formations. An aquifer is a geological formation that not only accommodates water but also allows large quantities of water to flow through it (Bear, 1988), or to be produced from it. In addition to these criteria the water must contain a high content of dissolved salts for the aquifer to be considered a saline aquifer.

Deep saline aquifers suitable for CO₂ geological storage need to have an appropriate thickness to reduce the spreading of the CO₂ plume and a large enough permeability and porosity to ensure an adequate injectivity. Chadwick et al. (2008) recommended a permeability above 200 mD and a porosity above 10%. The formation fluid salinity should be high enough so that the brine cannot be of better use as a water resource. The aquifer should be located at a depth of 800-2500 m, where the temperature and pressure conditions leave the CO₂ in the denser supercritical phase. The upper limit is due to the reduction of porosity and permeability usually seen at greater depth. A seal, preferable a thick, low permeable, lateral continuous caprock with a capillary entry pressure over the anticipated injection pressure, should also be present (Chadwick et al., 2008). Sedimentary basins (unlike crystalline and metamorphic ones), consisting of e.g. sandstone and carbonate, have high enough porosity and permeability to enable CO₂ sequestration and seals in the form of shale or evaporite layers are often present (Gunter et al., 2004).

In situ the geological storage of CO₂ consists of four main trapping mechanisms; structural and stratigraphical trapping, residual trapping, dissolution/solubility trapping and geochemical/mineral trapping. Structural and stratigraphical trapping is when the movement of CO₂ is obstructed due to the presence of low permeable structures or layers. Residual trapping is when CO₂ is immobilized due to capillary forces and left behind the moving...
CO₂ plume. Dissolution trapping is when CO₂ is left in dissolved form in the formation fluid. Geochemical trapping is when CO₂ chemically reacts with formation fluid and minerals resulting in precipitation of new minerals or formation of aqueous complexes (Chadwick et al., 2008). The last one is more important at long time scales. Local capillary trapping; when the heterogeneity of the rock creates locally high capillary entry pressures which hinders the buoyant migration of CO₂, has also been suggested as a trapping mechanism. This takes place within the target layer at a smaller spatial scale than structural trapping (Saadatpoor et al., 2010).

Although geological CO₂ storage operations have been ongoing for some time, there is a need for increased knowledge of what happens to the sequestered CO₂ and the formation during storage. Direct observations are complicated due to the underground location hindering accessibility and research in this area is therefore conducted through multiple approaches e.g. laboratory experiments, field experiments, study of analogous events, and analytical and numerical modeling. By comparing field or laboratory study results to simulation results, models can be validated. The validated models can then be used for planning and predictions of future sequestration projects.

1.2 The Heletz injection test site

To build confidence in geological CO₂ storage in deep saline aquifers as a viable technique to securely contain greenhouse gases, knowledge of what happens to the CO₂ once injected into the subsurface is needed. Understanding the geohydrological processes taking place is essential for creating reliable models that can be used when planning future storage projects and predicting the outcomes of different storage scenarios. This thesis was carried out within the frame of EU FP7 projects MUSTANG (www.co2mustang.eu) and TRUST (http://trust-co2.org). The MUSTANG project aimed at improving the understanding and modeling of processes occurring during geological CO₂ storage and developing improved methods for e.g. site characterization and monitoring. This included carrying out injection experiments to determine CO₂ trapping in the field. The aims of the TRUST project included improving the predictive capability of numerical models, evaluating optimal injection strategies for enhanced trapping and carrying out CO₂ injection experiments which can give insight into this. Both projects have involved field experiments at the Heletz test site. The Heletz site in the Southern Mediterranean Coastal Plain of Israel, hosts a 2 km by 4 km structure, containing Lower Cretaceous sand layers (Heletz formation of the Kurnub group) at a depth of approximately 1600 m. These layers consist of three sandstone layers (interbedded by shale), providing potential for sequestration activities. Two of these sandstone layers were ultimately selected as
target layers for the CO₂ injection experiments (Niemi et al., 2016). A map of the area is shown in Figure 2.

**Figure 2.** The location of the Heletz test site. Reprinted with permission from Elsevier, originally published in Niemi et al. (2016).

### 1.3 Objectives of this thesis

The objective of the thesis is to improve the understanding and to develop methods and numerical models to characterize as well as to simulate processes occurring during geological CO₂ storage, with particular focus on residual trapping. This thesis covers analysis of alternative characterization test designs for quantifying residual CO₂ trapping in the field, the impact of the injection strategy itself on trapping, the effect of model assumptions (such as including wellbore-reservoir flow, heterogeneity, etc.) on the predictions of trapping, but also residual trapping mechanisms at the pore-scale, using numerical modeling.

The papers of this thesis concern pre-modeling of the Heletz field test experiments or matters related to this and aimed to guide the implementation of the field experiments. Therefore all papers focus on the properties and characteristics of the Heletz site. During the projects life times and the duration of this thesis work, information and data concerning the site properties were
continuously collected, updated and incorporated in the modeling. This gave rise to some differences in assumptions between the papers.

*The specific aims of the individual papers presented in this thesis are:*

i) To analyze and develop alternative experimental field test sequences for site characterization that can be used to determine in-situ residual CO₂ saturation (*Paper I*).

ii) To investigate through numerical modeling with a coupled wellbore-reservoir flow simulator the distribution of injected CO₂ between the layers in a multi-layered aquifer. The aims are to identify parameters influencing the estimated distribution of CO₂ between the layers, evaluate the possibility to operationally modify the distribution, and to investigate the effect of neglecting the wellbore-reservoir coupling in numerical simulations (*Paper II*).

iii) To investigate through numerical simulations the effect of the trapping model, geological heterogeneity and injection strategy on the estimated residual and dissolution trapping in a CO₂ injection field experiment scenario (*Paper III*).

iv) To develop a pore-network model which can simulate multiphase flow in porous materials and to use this simulator to investigate residual trapping in Heletz sandstone as well as the mechanisms and parameters influencing the trapping (*Paper IV*).
2. Processes occurring during geological CO₂ storage

During geological CO₂ storage, the CO₂ is sequestrated deep into the subsurface. The subsurface consists of solid material, such as consolidated rock or unconsolidated sediments, with voids filled with fluids (water/brine, oil or gas). These voids are called pores and the subsurface is therefore a porous medium. The CO₂ is usually introduced into an aquifer; an originally brine-filled porous medium. At least three phases exist in such a system; the CO₂-rich phase (here referred to as gas phase), the water-rich phase (liquid or aqueous phase) and the solid phase (mineral phase). The two former phases may migrate, making this a two-phase flow system. Several components are present within the phases; CO₂, H₂O, other species (e.g. salts), and minerals.

Figure 3. a) A schematic of an injection well and target layer (to scale in the vertical direction) and some of the processes occurring during CO₂ sequestration; b) capillarity, c) viscous fingering, d) buoyancy flow, e) residual trapping (after migrating CO₂ plume), f) dissolution and convective mixing. Components in the aqueous phase may undergo g) diffusion, h) dispersion, and i) chemical reactions (mineralization).
This section contains an overview of the hydraulic, chemical, thermal and mechanical processes associated with geological CO$_2$ storage, with more weight given to the hydraulic processes as this is the focus of the thesis. Figure 3 shows some of these processes. Couplings between the different processes exist. Throughout the section attention is given to the ones of importance to hydraulic processes.

![Phase diagram for pure CO$_2$](image)

*Figure 4. Phase diagram for pure CO$_2$ showing the pressure and temperature conditions at which CO$_2$ occurs in its different phase states (solid, liquid, gaseous and supercritical phase). The sublimation line (black), saturation line (purple) and melting line (turquoise), are shown as well as the supercritical phase area. The critical point is located at T=30.98 °C and P=7.38 MPa. The figure is based on data from Span and Wagner (1996).*

Depending on the prevailing temperature and pressure conditions, the CO$_2$-rich phase itself, may exist in different states; gaseous, liquid or supercritical (Figure 4). In the supercritical state, which is the normal state for the CO$_2$-rich phase during injection, the phase exhibits a liquid-like density and a gas-like viscosity (van der Meer et al., 2009). If the temperature and pressure, or one of these, is below its critical values, CO$_2$ will be in a liquid or gaseous phase state or a two-phase mixture. Note that Figure 4 shows a phase diagram for pure CO$_2$. CO$_2$ undergoing geological storage coexists with other species and phase diagrams for more complicated systems may deviate from this case. Multi-component phase diagrams have been explored by e.g. Wendland et al. (1999), Tödheide and Franck (1963) and Sun and Dubessy (2012).
2.1 Hydraulic implications and processes

The hydraulic processes occurring during geological CO₂ storage include multiphase flow with CO₂ spreading as a free phase through capillarity, viscous fingering and buoyancy flow, volumetric displacement, as well as transport of the dissolved CO₂ and other species through diffusion, advection, convective mixing and mechanical dispersion.

**Capillarity:** Capillarity is exhibited when an interface between two phases due to intermolecular forces assumes an equilibrium shape, a process which results in capillary rise in tubes of small radii (Adamson and Gast, 1997). Two parameters that govern the capillarity of the system and therefore are of importance to the behavior of flow and trapping in multiphase systems are the interfacial tension (σ) and contact angle (θ).

When two phases (at least one being a fluid) are in contact, the molecules of each phase experience an attraction between its own molecules that are different from the attraction exhibited in between molecules of the different phases. The difference in attraction gives rise to an interfacial tension, which is equal to the amount of work needed to separate a unit area of a particular substance from another substance (Bear, 1988). Under relevant thermodynamic conditions measurements of σ_{water–CO₂} were carried out by e.g. Chiquet et al. (2007a) and Georgiadis et al. (2010), and measurements of σ_{brine–CO₂} were carried out by e.g. Yang et al. (2005), Chalbaud et al. (2006) and Bachu and Bennion (2009). The σ_{brine–CO₂} is dependent on the temperature, pressure and salinity conditions (Bennion and Bachu, 2006b), and an empirical relationship for this was presented by Bennion and Bachu (2008b).

θ is the angle between the surface of the solid and the interface of the fluids (liquid phase and gas phase), seen from the point of view of the denser fluid (Bear, 1988) and is given by Young's equation, eq. 1.

\[
\theta = \arccos \left( \frac{\sigma_{solid–gas} - \sigma_{solid–liquid}}{\sigma_{gas–liquid}} \right) \tag{1}
\]

This relates to the wettability; the tendency of a fluid to adhere to the solid surface when multiple fluid phases are present. If θ<90° the fluid is wetting the solid surface, adhering to it, while for a θ>90° the fluid is not. The fluid is under these circumstances refered to as the wetting and non-wetting fluid, respectively (Bear, 1988). A contact angle may experience hysteresis, i.e. the contact angle for a liquid advancing across a surface (θₐ) is different than the contact angle for the liquid when receding from the surface (θᵣ), with the latter being smaller than the former (Adamson and Gast, 1997). For CO₂-brine/water-sandstone systems, strongly water-wet (Krevor et al., 2012) as well as intermediate water-wet (Berg et al., 2013) conditions have been ob-
served. Studies also show that the phase state of the CO$_2$-rich phase may affect the water-wettability in certain mineral-brine/water-CO$_2$ systems (Chiquet et al., 2007b; Plug and Bruining, 2007).

The interactions between the CO$_2$-rich phase, water-rich phase and formation rock depends on the $\sigma$ and $\theta$. The capillary pressure ($P_c$), the difference in pressure between the non-wetting phase and the wetting phase, is related to the curvature of the interface of the fluids (Bear, 1988), eq. 2. As written here an assumption of circular cross-section is made. If the radius of the largest pore throat is used as $r$, eq. 2 gives the capillary entry pressure ($P_c^e$), i.e. the pressure that needs to be exceeded for a non-wetting phase to enter a certain porous medium saturated with a wetting phase.

$$P_c = (2\sigma/r) \cdot \cos \theta \quad (2)$$

**Viscous fingering:** The CO$_2$-rich phase has a lower viscosity than the water-rich phase, approximately $1/15^{th}$ that of the latter. This difference in viscosity can give rise to instability phenomena at the phase boundary during the injection of CO$_2$ into the brine, i.e. viscous fingering (Garcia and Pruess, 2008). Such interface instability can take place if the mobility ratio ($M$) between a displacing (here CO$_2$-rich phase) and a displaced (here water-rich phase) fluid exceeds 1 (Bear, 1988), eq. 3. The mobility ratio is a function of the permeability to CO$_2$ at residual water saturation ($k_{CO_2}$), the permeability to water at connate $^1$ CO$_2$ saturation ($k_{brine}$) and the viscosity ($\mu$) of respective phase. Other stability studies and suggested use of stability criteria have been presented by e.g. Berg and Ott (2012).

$$M = \frac{k_{CO_2}/\mu_{CO_2}}{k_{brine}/\mu_{brine}} \quad (3)$$

Fingering can reduce the sweep efficiency, but might also increase dissolution due to the increased contact area between the phases (Garcia and Pruess, 2008). Viscous fingering is suppressed by the occurrence of heterogeneity, gravity, capillary pressure and dispersion (Chang et al., 1994).

**Buoyancy flow:** Under the thermodynamic conditions of geological storage the density of the CO$_2$-rich phase is in the range of 290-960 kgm$^{-3}$, while the density of the water-rich phase is ca 1000 kgm$^{-3}$. The difference in density creates a buoyancy effect. The density difference ($\Delta \rho_{crit}$) needed for buoyant forces to exceed the capillary forces and thereby induce buoyant flow, eq. 4, is a function of average pore diameter ($d$), interfacial tension ($\sigma$), the gravitational constant ($g$) and plume height/diameter ($D$) (Riaz and Tchelepi, 2012).

$$\Delta \rho_{crit} = \frac{d \cdot g}{\sigma \cdot D} \quad (4)$$

---

$^1$ Lowest saturation in situ.

$^2$ Based on Span and Wagner (1996) and assuming a temperature range of 40-60 °C and a pressure range of 10-40 MPa.
Strong buoyancy forces lead to gravity override resulting in the typical CO₂-plume shape appearance with a gravity tongue. The buoyant flow may be strongly influenced by properties of the formation such as the heterogeneity of permeability and capillary pressure which induce channeling (Bryant et al., 2008).

\[ \Delta \rho_{\text{crit}} = \frac{g d \sigma}{g D^2} \]  

\( (4) \)

**Volumetric displacement:** Flow in porous media is described by the characteristic functions; the capillary pressure as a function of saturation \( (P_c - S) \) and the relative permeability as a function of saturation \( (k_r - S) \). The former relates the phase saturations to the difference in pressure between the phases and the latter relates the phase saturations to the ease of migration of the phases. These relationships govern the phase-displacement behavior during injection and storage. As the CO₂ plume migrates, drainage (non-wetting phase displacing wetting phase) occurs at the plume front and imbibition (wetting phase displacing non-wetting phase) occurs at the opposite end of the plume. If flow alternates between drainage and imbibition conditions, the characteristic functions depend not only on the prevailing saturation but also on the past saturation path, i.e. hysteresis is exhibited (Doughty, 2006; Doughty and Myer, 2009). At the start of drainage, when the porous medium is water saturated, the \( k_r \) of the water-rich phase \( (k_{rw}) \) is 1.0, while that of the CO₂-rich phase \( (k_{rg}) \) is zero. As drainage proceeds and the water saturation decreases, the magnitude of \( k_{rw} \) decreases until it reaches a value of zero, and the magnitude of \( k_{rg} \) increases until it reaches its maximum value (end-point relative permeability), which occurs at the residual water saturation \( (S_{wr}) \) (also referred to as the irreducible saturation or connate saturation). If followed by imbibition, i.e. increase of water saturations, \( k_{rw} \) increases again and \( k_{rg} \) decreases until \( k_{rg} \) reaches a value of zero which occurs at the residual gas saturation \( (S_{gr}) \). At this saturation the \( k_{rw} \) is said to have reached its end-point relative permeability. The \( S_{wr} \) and \( S_{gr} \) are the saturations at which, respective phase, becomes immobile, i.e. stops to flow (Burnside and Naylor, 2014). Several studies have measured the relative permeability of CO₂-brine/water flow during drainage and/or imbibition in sandstone, carbonate, shale and/or anhydrite (Akbarabadi and Piri, 2013; Bachu and Bennion, 2008; Bennion and Bachu, 2005, 2006a, 2007, 2008a; Berg et al., 2013; Krevor et al., 2012; Perrin and Benson, 2010; Perrin et al., 2009; Ruprecht et al., 2014; Zuo et al., 2012). Measurements of drainage capillary pressure for CO₂-brine/water in sandstone have also been carried out (Berg et al., 2013; El-Maghraby et al., 2011; Li et al., 2015; Pentland et al., 2011; Pini et al., 2012). If direct measurements are lacking, the capillary pressure function is often obtained by Mercury intrusion porosimetry, followed by conversion of the data to the CO₂-brine system.
The residual gas saturation obtained at the end of imbibition, for a porous medium that at the end of drainage had a water saturation equal to the irreducible saturation, is called the maximum residual gas saturation ($S_{gr, max}$). Hamon et al. (2001) found that the $S_{gr, max}$ in heterogeneous sandstones ranged from 0.05 to 0.85. The study also included other gases than CO$_2$. However, it is not necessary so that the irreducible water saturation is reached during a drainage event. In this case the gas saturation at the point when drainage stopped and imbibition started is referred to as the initial gas saturation ($S_{gi}$). On the pore-scale, residual trapping i.e. disconnection and immobilization of a phase occurs due to an interplay of displacement and trapping mechanisms such as piston-type displacement, snap-off and cooperative pore filling (Lenormand et al., 1983; Patzek, 2001). The magnitude of the $S_{gr}$ is dependent on the rock grain size, the porosity, the microporosity, the $S_{gi}$, the capillary number (i.e. the relative importance of viscous and capillary forces), the state of the CO$_2$-rich phase, the processes by which the CO$_2$-rich is introduced into the sandstone (as this affects the spatial saturation distribution), the wettability of the medium, the grain shape and the interfacial tension (Akbarabadi and Piri, 2013; Bennion and Bachu, 2006b; Chaudhary et al., 2013; Hamon et al., 2001; Holtz, 2002; Jerauld, 1997; Prather et al., 2016; Rahman et al., 2016; Sahimi, 2011; Suzanne et al., 2003; Zuo and Benson, 2014).

Residual CO$_2$ saturation in sandstone has been observed in the range of 0.09-0.48 in experimental studies (Akbarabadi and Piri, 2013; Andrew et al., 2014; Bennion and Bachu, 2008a; El-Maghraby et al., 2011; Iglauer et al., 2011; Krevor et al., 2012; Li et al., 2015; Pentland et al., 2011; Rahman et al., 2016; Shi et al., 2011; Suekane et al., 2008; Zuo and Benson, 2014). However, not all these studies measured the maximum residual saturation. Residual brine/water saturation in sandstone after drainage with CO$_2$ as the invading fluid has been reported in the range of 0.05-0.66 (Bennion and Bachu, 2008a; Krevor et al. 2012). Measurements of the initial and corresponding residual non-wetting phase saturation, also referred to as trapping curve or initial-residual (IR) curve, for CO$_2$-brine/water flow in sandstone have been presented by e.g. Akbarabadi and Piri (2013), El-Maghraby et al. (2011), Krevor et al. (2012), Li et al. (2015), Pentland et al. (2011) and Ruprecht et al. (2014).

Transport of dissolved CO$_2$ or other species through diffusion, advection, convective mixing and mechanical dispersion: Once dissolved in the water-rich phase the components such as CO$_2$ are transported by diffusion, advection, convective mixing and mechanical dispersion processes.

Diffusive transport strives to reduce concentration gradients. The diffusive mass flux ($J_{diff}$) in a porous media is a function of the effective diffusion coefficient ($D_{eff}^d$) and the gradient in concentration ($\nabla C$), eq. 5 (Domenico and Schwartz, 1997). $D_{eff}^d$ is in turn a function of the diffusion coefficient
in a liquid and parameters accounting for the effect of the porous media on this value.

\[ J_{\text{diff}} = -D'_d \cdot \nabla C \]  \hspace{1cm} (5)

Several relevant studies on diffusion coefficients of CO\textsubscript{2} in water (Frank et al., 1996; Thomas and Adams, 1965) and water/brine in CO\textsubscript{2} (Espinoza and Santamarina, 2010; Xu et al. 2003) have been presented. Also studies of effective diffusion coefficient of CO\textsubscript{2} in different rock types have been carried out (Busch et al., 2008; Wollenweber et al., 2010).

Transport of a dissolved component together with the formation fluid is called advection. The advective mass flux \( J_{a,\text{adv}} \) is the product of the Darcy velocity \( q \) and the concentration of the dissolved component \( C \) (Batu, 2006), eq. 6. \( q \) is a function of the hydraulic conductivity \( K \) and hydraulic gradient \( \partial h / \partial l \) (Domenico and Schwartz, 1997).

\[ J_{\text{adv}} = \frac{q}{-K(\partial h / \partial l)} \cdot C \]  \hspace{1cm} (6)

Convective mixing, also referred to as density-driven convection, CO\textsubscript{2}-solution-driven convection or density fingering, incorporates both diffusion and advection. Molecular diffusion of CO\textsubscript{2} from the CO\textsubscript{2}-rich phase to the surrounding water-rich phase affects the density of the water-rich phase. The density difference between pure water and water containing dissolved CO\textsubscript{2} can be 2-3\% (Garcia, 2001). This results in a modified density gradient in the water-rich phase, with denser CO\textsubscript{2}-containing brine overlaying lighter brine without dissolved CO\textsubscript{2}. This may in turn lead to instability and induce convection (heavier brine containing CO\textsubscript{2} sinking and being replaced by fresh brine). As convection is a much faster transport mechanism than diffusion, the dissolution of the CO\textsubscript{2}-rich phase is enhanced (Lindeberg and Wessel-Berg, 1997). Instability and convection occur if conditions are such that the Rayleigh-Darcy number\(^3\) exceeds a critical value. The magnitude of this number depends on the induced density increase, permeability, porosity, layer thickness, fluid viscosity, molecular and thermal diffusivity, and gravitational acceleration. Several of these parameters are functions of temperature, pressure and salinity. The occurrence of instability and convective mixing is also influenced by the storage depth and geothermal gradient (Rasmussen et al., 2015b).

Mechanical dispersion arises due to velocity differences between different flow paths and results in mixing. Molecular diffusion and mechanical dispersion is often combined in solute transport equations and referred to as dispersion (Domenico and Schwartz, 1997).

\(^3\) \( Ra = k_g \Delta \rho h / (\mu \varphi D) \)
2.2 Chemical implications and processes

The chemical processes occurring during geological CO\textsubscript{2} storage include component interphase mass transfer and dissolution processes, as well as CO\textsubscript{2} interactions with the mineral phase through direct interaction of free phase and via chemical processes in the aqueous phase.

*Interphase mass transfer and dissolution:* Interphase mass transfer between the CO\textsubscript{2}-rich and the water-rich phases, solubility, exsolution and desiccation processes can occur during geological CO\textsubscript{2} storage.

From a thermodynamically perspective a component \(i\), at equilibrium\(^4\) is distributed between the gas (CO\textsubscript{2}-rich) phase and the aqueous (water-rich) phase in accordance with eq. 7 (Marini, 2007). The parameters are the fugacity coefficient (\(\Gamma_{i,g}\)), the molar fraction of the component in the gas phase (\(y_{i,g}\)), the total gas pressure (\(P\)), the fugacity of the component at standard state (\(f_{i}^{\text{\text{\scriptsize 0}}}\)), the activity coefficient (\(\gamma_{i,aq}\)) and the molar fraction of the component in the aqueous phase (\(x_{i,aq}\)).

\[
\frac{\Gamma_{i,g} y_{i,g} P}{f_{i}^{\text{\text{\scriptsize 0}}}} = \gamma_{i,aq} x_{i,aq}
\]

Mass transfer of CO\textsubscript{2}, water or other components occurs across the interface of the CO\textsubscript{2}-rich and water-rich phase. The mass transfer is dependent on the component type and prevailing thermodynamic conditions (Kögel et al., 2004; Teng and Yamasaki, 1998).

A chemical description of how CO\textsubscript{2} dissolves in water is given by eq. 8 (Rochelle et al., 2004). The first step is dissolution into the formation fluid and the next ones are formation of carbonic acid and further dissociation into bicarbonate anions and carbonate anions. As CO\textsubscript{2} dissolves in the formation fluid, acidification, i.e. a decrease in pH occurs.

\[
\text{CO}_2(g) + \text{H}_2\text{O} \leftrightarrow \text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3^\circ \leftrightarrow \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+
\]

In situ, solubility is determined by the prevailing temperature, pressure, buffering minerals, contact area between phases, mixing, composition of the water-rich phase (ionic strength and ionic composition) and pH conditions (Rochelle et al., 2004; Zerai et al., 2009). More CO\textsubscript{2} can dissolve if the pressure is increased, the temperature is decreased and the ionic strength of the brine is decreased (Zerai et al., 2009). The magnitude of the salting-out effect, the decrease in solubility due to interionic interactions, also depends on

\(^4\) The chemical potential of the component in the gas phase is equal to the chemical potential of the component in the aqueous phase.
the type of ions present (Rumpf et al., 1994). A solubility model is a formula for the partition of CO$_2$ or CO$_2$/water between the phases, expressed as a function of temperature, pressure and ionic composition. Solubility models have been presented by Duan and Sun (2003), Spycher et al. (2003), Spycher and Pruess (2005) and Akinfiev and Diamond (2010).

Dissolved gases, such as CO$_2$, can exsolve from brine (i.e. CO$_2$ goes from the water-rich phase into the CO$_2$-rich phase) if transported into areas with lower gas solubility conditions, as can be the case when a large vertical displacement occurs. Exsolution results in a reduced relative permeability and potentially an increase in pore pressure (Kuo, 1997; Zuo et al., 2012). As CO$_2$ exsolves the volume of the fluids increases. Withdrawal of brine containing dissolved CO$_2$ can lead to CO$_2$ exsolution in the well. This can result in geysering as two phases with a fluctuating average mixture density, arising from the difference in flow velocity, appear (Pruess, 2008).

Injection of CO$_2$ into an aquifer may lead to water desiccation (formation dry-out), as water goes from the water-rich phase into the CO$_2$-rich phase. An effect of this is precipitation of salt originally dissolved in the brine. The precipitation can alter the porosity, permeability and injectivity of the formation (Giorgis et al., 2007; Muller et al., 2009; Pruess and Müller, 2009). However, this effect can be reduced through an appropriate choice of injection rate, use of CO$_2$ with a small water-content or carrying out fresh water pre-flushing (Muller et al., 2009).

**CO$_2$ interactions with the mineral phase through direct interaction of free phase or via chemical processes in the aqueous phase:** During geological CO$_2$ storage, reactions with formation fluids, formation rock, caprock and borehole material can occur (Rochelle et al., 2004).

Interactions occur between the CO$_2$-rich phase, containing solvated water, and rock minerals (as well as steel surfaces in wells). These interactions include mineral replacement and transformation reactions such as precipitation. There appears to be a threshold water content that has to be exceeded for reactivity to occur (McGrail et al., 2009). It has also been observed that sorption of CO$_2$ may occur on formation rock (Busch et al., 2008, 2009; Wollenweber et al., 2010).

The geochemical reactions occurring during geological CO$_2$ sequestration depend on the mineralogical composition of the reservoir and caprock, porewater composition, as well as pressure and temperature in the aquifer (Rochelle et al., 2004). For aqueous-phase mediated chemical reactions during geological CO$_2$ storage in sedimentary basins, generally silicates and Al-silicates are dissolved and carbonates (calcite, magnesite, dolomite, brucite, dawsonite), silica minerals (quartz) and clay minerals (kaolinite, smectite) are precipitated (Marini, 2007). Dissolution and precipitation reaction rates depend on the temperature, thermodynamic affinity, ionic strength and pH as well as transport in the form of diffusion and advection. Dissolution and
precipitation of carbonates occurs faster than dissolution and precipitation of silicates and oxides (Marini, 2007). Field and experimental studies of CO₂-EOR have demonstrated that acidification-induced carbonate mineral dissolution can occur at a time scale of days to years (Worden and Smith, 2004). Precipitation and dissolution reactions may result in a decreased and increased porosity of the formation, respectively (Marini, 2007; Xiao et al., 2009).

2.3 Thermal implications and processes

The geothermal gradient of a site depends on factors such as the surface temperature, basin character, heat sources, thermal conductivity and age, and ranges from below 20°Ckm⁻¹ to above 80°Ckm⁻¹ (Gunter et al., 2004). CO₂ storage operations can alter the temperature conditions in an aquifer. Potential thermal implications and processes of CO₂ sequestration include addition of heat with the injected CO₂, release of heat of CO₂ dissolution (resulting in a temperature increase), release of latent heat of water evaporation (resulting in a temperature decrease) and the Joule-Thomson effect (resulting in a temperature decrease) (André et al., 2010). The Joule-Thomson effect is temperature change due to adiabatic expansion of a real gas. This may under certain conditions occur if CO₂ is transported from a high pressure to a lower pressure environment resulting in expansion of the gas and a temperature decrease. The magnitude of the temperature change is determined by the change in pressure experienced by the CO₂, which in turn is sensitive to the injection rate, injectivity and thermal properties of the rock. If the temperature decrease is large, potential resulting effects include that residual water may freeze and thermal stresses may induce fracturing, impacting the permeability and injectivity (Oldenburg, 2007). Numerical simulation studies indicate that the Joule-Thomson effect may occur during CO₂ injection into natural gas reservoirs (Oldenburg, 2007), to some extent during CO₂ sequestration in aquifers (Bielinski et al., 2008) and if CO₂ leaks or is withdrawn up a well (with negligible heat exchange) (Pruess, 2008). Two mechanisms for heat transport in the subsurface include advective/convective heat transport and heat conduction. Advective heat transport is energy transfer with migrating fluids (Bielinski et al., 2008). Heat conduction is energy transfer through substances with the magnitude of the heat flux dependent on the thermal conductivity of the substance multiplied by the temperature gradient and occurs towards the lower temperature (Fouier’s law) (Somerton, 1992). The thermal conductivity not only depends on the properties of the rock such as the density, porosity, grains size and shape, mineral constituents and cementation (Somerton (1992), citing Scorer (1964)), but also the thermal properties of the aqueous or gas phases inside
the pores (Somerton, 1992). Thus thermal conductivity is a function of the saturation of different phases.

2.4 Mechanical implications and processes

During CO₂ injection, pressure is changed in-situ. As the pore pressure is raised, the mean effective stresses are decreased. Due to altered stress conditions, potential mechanical outcomes of geological CO₂ storage are: uplift of the ground surface, altered rock properties and mechanical failure (Rutqvist and Tsang, 2002).

Certain rock properties are stress-dependent. When sandstones are subjected to changes in stress condition an elastic volumetric response, i.e. mechanical deformation, might occur. Pressure change may result in a volume change as given by the compressibility. Compressibility can be classified as compressibility of the bulk volume due to changes in the confining pressure \( c_{bc} \) or pore pressure \( c_{pp} \), and compressibility of the pore volume due to changes in the confining pressure \( c_{\phi c} \) or pore pressure \( c_{\phi p} \) (Zimmerman, 1991). The permeability of rock is altered as stresses change. Lower effective stresses lead to an increased absolute permeability (Rutqvist and Tsang, 2002).

Withdrawal of formation fluids such as oil, gas or water may lead to ground surface subsidence (Colazas and Strehle, 1995; Zaman et al., 1995; Brighenti et al., 1995). Likewise injection operations, such as geological CO₂ sequestration, may cause small detectable changes at the ground surface. The lower effective stress leads to poro-elastic expansion of the formation rock which can induce uplift (also referred to as heave, vertical displacement or absidence) (Rutqvist and Tsang, 2002). The magnitude of the uplift is sensitive to the magnitude of the injection induced pressure increase, the volume of CO₂ and the elastic properties of the formation rocks (Rutqvist et al., 2010). At In Salah the magnitude of the surface uplift was ca 7 mm/year for the period 2003-2008 (Onuma and Ohkawa, 2009).

Potential mechanical failure include that faults and fractures may open or slip displacement (fault reactivation) may occur which can lead to induced seismicity. As CO₂ injection induces a rise in pore fluid pressure and decreases the effective stresses, the occurrence of slip is made easier (Streit and Hillis, 2004). Fractures can appear if the fluid pressure is raised above the least compressive principal stress (Rutqvist and Tsang, 2002). Methods for calculating the maximum sustainable pressure for fault slip not to occur and/or the limiting pressure for fracturing were presented by e.g. Streit and Hillis (2004) and Mathias et al. (2009). Injection-induced seismicity was observed during CO₂-EOR at the Aneth oil field, Paradox Basin, Utah (McPherson, 2009).
3. Numerical simulations – Modeling of multiphase flow and trapping in porous media

Simulation of geological CO$_2$ storage scenarios requires models that can capture the behavior of multiphase flow in porous media. A model is a simplified representation of a system and its processes, for use when making predictions. Optimally a model should be as simple as possible while still accounting for all important features that influences the accuracy of the predictions. Simplifications are made by making assumptions regarding which features are or aren’t of importance to the result and thereafter include or exclude these in the model. The needed complexity of a model depends on the subject under study. Depending on the spatial (pore or field) and temporal (minutes, days or years) scale of interest, relevant contributing processes as well as the need of including process couplings may differ.

For geological CO$_2$ storage, mineral trapping is expected to become more important, i.e. a larger part of the total trapping contribution, after hundreds to thousands of years after injection has stopped (IPCC, 2005). Also the solubility trapping and residual trapping are expected to become more important with time. These trapping mechanisms are, however, expected to initiate right from the start. It is therefore common for studies concerning short time scales (days or months) to assume that chemical reactions are limited and can be neglected. Different processes and forces (capillary, gravity and viscous forces) dominate depending on the spatial scale under consideration. For example viscosity, gravity and pressure forces are more influential on larger scales while capillary forces can govern the flow behavior on smaller scales (Eichel et al., 2005). Dimensionless numbers (Table 1) can be used to quantify the relative importance of forces, and thereby provide input on suitable simplifying assumptions for models.

This thesis covers numerical modeling of flow and trapping processes related to geological CO$_2$ storage at two different spatial scales; the field-scale by using continuum models (Papers I-III) and the pore-scale by using a discrete network model (Paper IV). Following subsections present the modeling approaches and simulators employed or developed in Papers I-IV. First, the well-known TOUGH2 model (Pruess et al., 1999) along with a number of different available features and modules used for modeling field-scale processes are briefly described. Secondly, the model used to analyze
the pore-scale processes is described. This was developed specifically for the thesis and is therefore covered in greater detail.

Table 1. Some dimensionless numbers. These are functions of the density difference between the phases (\(\Delta \rho\)), gravitational acceleration (\(g\)), interfacial tension (\(\sigma\)), dynamic viscosity (\(\mu\)), fluid velocity (\(v\)), average distance between molecules (\(\lambda\)), specific discharge (\(q\)), kinematic viscosity (\(\nu\)) and characteristic length scale (\(l\)) e.g. mean grain diameter or mean pore size.

<table>
<thead>
<tr>
<th>Name</th>
<th>Definition</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond number ((Bo))(^a)</td>
<td>(Bo = \Delta \rho \cdot g l^2 / \sigma)</td>
<td>Relative importance of gravity to capillary forces. A high value indicates that gravity is the dominating force.</td>
</tr>
<tr>
<td>Capillary number ((N_c))(^a)</td>
<td>(N_c = \mu v / \sigma)</td>
<td>Relative importance of viscous to capillary forces. (N_c&lt;&lt;1) means capillary forces dominate, i.e. a quasi-static assumption is okay.</td>
</tr>
<tr>
<td>Knudsen number ((K_n))(^c)</td>
<td>(K_n = \lambda / l)</td>
<td>For (K_n&lt;0.01) a fluid continuum assumption is okay.</td>
</tr>
<tr>
<td>Reynolds number ((Re))(^b)</td>
<td>(Re = q l / \nu)</td>
<td>Relative importance of inertial and viscous forces. In porous media (Re) should be (\leq 1) to (10) (laminar flow conditions) for Darcy’s law to be applicable.</td>
</tr>
</tbody>
</table>


3.1 Modeling of processes at the field-scale – TOUGH2 simulations

Because modeling of molecular processes for a larger spatial domain (microscopic or macroscopic scale) would be enormously demanding computationally, a continuum approach is used when modeling flow in porous media at these scales, i.e. a fluid is seen as a continuum instead of as individual molecules. By applying the continuum approach, flow in a porous medium can be formulated using partial differential equations (Bear, 1988). Continuum-models consist of mass, momentum and energy conservation equations, as well as constitutive assumptions, equation-of-state, initial conditions and boundary conditions (Bear, 1988). This subsection contains an overview of the continuum-scale simulator TOUGH2, the modules ECO2N and EOS7C, T2Well, the inverse modeling methods of iTOUGH2, the PEST protocol and some features of GSLIB used in Papers I-III for simulating and addressing various issues concerning the Heletz CO\(_2\) injection experiments.
TOUGH2; TOUGH2 (Pruess et al., 1999) can simulate isothermal or non-isothermal, multicomponent, multiphase flow in porous media. The input data for TOUGH2 includes rock properties (such as absolute permeability, porosity, characteristic functions, pore compressibility and thermal properties), initial and boundary conditions, sinks/sources and a grid description. The use of modules, e.g. ECO2N or EOS7C, provides TOUGH2 with modeling capabilities for specific purposes. A module contains the equation-of-state (EOS), which set the fluid properties (as a function of temperature, pressure and composition) and handles the phase conditions and appearance/disappearance of phases (Pruess et al., 1999).

For each grid block \((V_n)\) enclosed by a surface \((\Gamma_n)\), mass balance equations for each component and an energy balance equation are set up. For each component \((\kappa)\), the change of mass \((\frac{d}{dt}M^\kappa)\) in an element equals the sum of mass fluxes \((F^\kappa)\) across the elements surface and any sinks or sources \((q^\kappa)\) of mass in that element, eq. 9. A multiphase extension of Darcy’s law, eq. 10, is used to calculate advection. Dispersion or diffusion may be considered in each phase \((F^\kappa|_{dis})\) (Pruess et al., 1999).

\[
\frac{d}{dt} \int_{V_n} \left( \varphi \sum_\beta \rho_\beta X_\beta^\kappa \right) dV_n = \int_{\Gamma_n} \left( F^\kappa \right)_{adv} + F^\kappa|_{dis} \cdot n d\Gamma_n + \int_{V_n} q^\kappa dV_n \tag{9}
\]

With

\[
F^\kappa|_{adv} = \sum_\beta X_\beta^\kappa \left( -k \frac{k_{\kappa\beta}\rho_\beta}{\mu_\beta} (\nabla P_\beta - \rho_\beta g) \right) \tag{10}
\]

The energy balance is shown in eq. 11. Heat conduction and heat convection are accounted for by the model (Pruess et al., 1999).

\[
\frac{d}{dt} \int_{V_n} \left( (1 - \varphi) \rho_R C_R T + \varphi \sum_\beta \rho_\beta u_\beta \right) dV_n = \\
\int_{\Gamma_n} \left( -\lambda \nabla T + \sum_\beta h_\beta \left( -k \frac{k_{\kappa\beta}\rho_\beta}{\mu_\beta} (\nabla P_\beta - \rho_\beta g) \right) \right) \cdot n d\Gamma_n + \int_{V_n} q^{energy} dV_n \tag{11}
\]

Here \(\beta\) represents the phase. The parameters include porosity \((\varphi)\), saturation \((S)\), density \((\rho)\), mass fraction of component \(\kappa\) \((X^\kappa)\), grain density \((\rho_R)\), specific heat of the rock \((C_R)\), temperature \((T)\), specific internal energy \((u)\), absolute permeability \((k)\), relative permeability \((k_r)\), viscosity \((\mu)\), fluid pressure \((P)\), gravitational acceleration vector \((g)\), the normal vector on \(d\Gamma_n (n)\), thermal conductivity\(^5\) \((\lambda)\) and specific enthalpy \((h)\) (Pruess et al., 1999).

Space discretization is implemented using the integral finite difference method, while time discretization is made using first-order backward finite

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\(^5\) It is assumed that heat conductivity is dependent on the liquid saturation. The option where \(\lambda = \lambda_{dry} + S_l (\lambda_{wet} - \lambda_{dry})\) was used here.
For each time step the resulting system of equations is solved for the primary variables such as pressure, saturation/mass fractions, temperature, etc., by a Newton-Raphson iteration process (Pruess et al., 1999).

ECO2N; ECO2N (Pruess, 2005), used in Papers II and III, is a module specifically developed to simulate geological CO₂ storage in saline aquifers, i.e. H₂O-NaCl-CO₂ mixtures. Table 2 shows the components and phases considered. Concerning the aqueous phase thermophysical properties; density is modeled as a function of temperature, pressure, salinity and CO₂ content. The viscosity is a function of temperature, pressure and salinity, while neglecting any dissolved CO₂. The enthalpy of the aqueous phase is a function of temperature, pressure, CO₂ content and salinity. Concerning the CO₂ thermophysical properties; density, enthalpy and specific enthalpy calculations are based on Altunin (1975). Any water content is ignored when calculating these properties. Further details can be found in Pruess (2005).

EOS7C; EOS7C (Oldenburg et al., 2004), used in Paper I, is a module for multicomponent gas mixtures of (supercritical and subcritical) CO₂, alternatively N₂, and CH₄ in reservoirs with additional capability of handling an aqueous phase, H₂O vapor and a gas tracer. It was selected for the study in Paper I due to its capability to handle both CO₂ and a gas tracer which are needed when simulating the test sequences. Table 2 shows the components and phases considered. Concerning the CO₂ thermophysical properties; density and enthalpy are determined using an EOS. In Paper I the Peng-Robinson (Peng and Robinson, 1976) EOS was used. Viscosity is determined employing the work of Chung et al. (1988). Dissolved gas components are not taken into account when determining the liquid phase density (Oldenburg et al., 2004).
Table 2. Overview of the modules employed in the papers.

<table>
<thead>
<tr>
<th></th>
<th>ECO2N\textsuperscript{a}</th>
<th>EOS7\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Components</strong></td>
<td>Water, NaCl, CO\textsubscript{2}</td>
<td>Water, brine, non-condensible gas (CO\textsubscript{2} or N\textsubscript{2}), gas tracer, CH\textsubscript{4}, heat</td>
</tr>
<tr>
<td><strong>Phases</strong></td>
<td>Single-phase or two-phase flow;</td>
<td>Single-phase or two-phase flow;</td>
</tr>
<tr>
<td></td>
<td>-CO\textsubscript{2}-rich/gas phase</td>
<td>-Gas phase</td>
</tr>
<tr>
<td></td>
<td>-Aqueous/liquid phase</td>
<td>-Liquid phase</td>
</tr>
<tr>
<td></td>
<td>Solid phase (NaCl)</td>
<td></td>
</tr>
<tr>
<td><strong>Partitioning of CO\textsubscript{2} and water between phases</strong></td>
<td>Follows equilibrium of chemical potential. A modified version of Spycher and Pruess (2005) where an EOS employing Altunin's correlation (Altunin, 1975) is used to derive CO\textsubscript{2} molar volumes. Partitioning is dependent on temperature, pressure and salinity.</td>
<td>Follows equilibrium of chemical potential. Equilibrium constants for solubility of CO\textsubscript{2} are calculated employing Spycher et al. (2003) for determining partial molar volumes. Additionally, SUPCRT92 (Johnson et al., 1992) and the slop98 database are used for other components. Effects of salinity on gas solubility are not accounted for. Partitioning is a dependent on temperature and pressure.</td>
</tr>
<tr>
<td><strong>Salt precipitation</strong></td>
<td>Yes, equilibrium solubility dependent on the temperature.</td>
<td>No</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Pruess (2005), \textsuperscript{b}Oldenburg et al. (2004).

\textit{T2Well/ECO2N; T2Well/ECO2N (Pan et al., 2011), used in Paper II, models coupled wellbore-formation flow of CO\textsubscript{2} and saline water. The formation flow is handled as in ECO2N (see TOUGH2 section). The wellbore flow is modeled using the drift-flux model approach (extending the work of Shi et al. (2005)) and conservation equations. Exchange between the wellbore and reservoir is calculated similarly as for porous media flow, but with the node-interface distance of zero at the wellbore side. Different flow regimes can occur in the wellbore. Heat transmission between the wellbore and the surrounding formation is accounted for.}

For each wellbore grid block, a mass conservation equation for each component $\kappa$ (eq. 12, here shown for components H\textsubscript{2}O or CO\textsubscript{2}), and an energy conservation equation (eq. 13) is set up (Pan et al., 2011).

$$
\frac{\partial}{\partial t} \left( \sum_\beta \rho_\beta S_\beta X_\beta^\kappa \right) = q^\kappa + \left( -\frac{1}{A} \sum_\beta \frac{\partial (A \rho_\beta X_\beta^\kappa S_\beta u_\beta)}{\partial z} \right) \tag{12}
$$
These state that the change in mass/energy \( \frac{d}{dt} M \) equals the sum of potential sources/sinks \( q \) and the advective transport of mass/energy \( F \). In addition to the parameters already defined in the TOUGH2 section the parameters include; the wellbore cross-sectional area \( A \) and average velocity vector of the phase in the wellbore \( \mathbf{u}_\beta \). In a wellbore element the saturation of a phase is the fraction of the well cross-section area occupied by the phase. Regarding the energy, internal and kinetic energy are considered. The parameters include; internal energy per unit mass \( \beta \), velocity \( \mathbf{u} \), area-averaged thermal conductivity \( \mathbf{k} \), gravitational acceleration \( g \), inclination angle \( \theta \) and heat loss or gain per unit length of wellbore \( q'' \). Energy transport \( F_{\text{energy}} \) by thermal conduction, advection, kinetic energy, potential energy and lateral wellbore heat loss or gain is accounted for.

A drift-flux model approach is used, when solving the momentum conservation equations, to calculate flow velocities in the wellbore \( \mathbf{u}_\beta \). The drift-flux model (Zuber and Findlay, 1965) uses an empirical relationship between the gas phase velocity \( \mathbf{u}_\infty \) and the volumetric flux of the mixture \( j \), eq. 14 (Pan et al., 2011).

\[
\begin{align*}
\mathbf{u}_G &= C_0 \left( S_G \mathbf{u}_G + (1 - S_G) \mathbf{u}_L \right) + \mathbf{u}_d \\
\end{align*}
\]

The parameters include; the profile parameter \( C_0 \), volumetric flux of the mixture \( j \) and drift velocity of gas \( \mathbf{u}_d \). \( C_0 \) describes the gas saturation and velocity profiles across the wellbore cross section. \( \mathbf{u}_d \) is the difference in flow velocity of the gas phase and that of the mixture, accounting for buoyancy effects. \( C_0 \) and \( \mathbf{u}_d \) depend on the flow regime conditions in the wellbore. Using this approach the momentum equation of two-phase flow in a wellbore element, eq. 15, can be expressed using the mixture velocity \( \mathbf{u}_m \) and mixture density \( \rho_m \), which can be solved for \( \mathbf{u}_m \). \( \gamma \) takes into account slip between the phases and is a function of the gas saturation, phase densities, phase velocities, drift velocity and \( C_0 \). \( P \) is pressure, \( \Gamma \) is the cross-section's perimeter and \( f \) is the Fanning friction coefficient.

\[
\begin{align*}
\frac{d}{dt} \left( \rho_m u_m \right) + \frac{1}{A} \frac{d}{dz} \left[ A \left( \rho_m u_m^2 + \gamma \right) \right] &= - \frac{\partial P}{\partial z} - \frac{f \rho_m |u_m| u_m}{2A} - \rho_m g \cos \theta \\
\end{align*}
\]
$u_d$ is given by an empirical relationship (a function of the $C_0$, gas saturation, $\theta$, phase densities, surface tension between the phases, gravitational acceleration and the Kutateladze number). $u_m$ and $u_d$ are in turn used to determine $u_G$ and $u_L$, using eq. 16 and 17 (Pan et al., 2011).

\[ u_G = C_0 \frac{\rho_m}{(S_G c_0 \rho_G + (1-S_G c_0) \rho_L)} u_m + \frac{\rho_L}{(S_G c_0 \rho_G + (1-S_G c_0) \rho_L)} u_d \]  

(16)

\[ u_L = \frac{(1-S_G c_0) \rho_m}{(1-S_G)(S_G c_0 \rho_G + (1-S_G c_0) \rho_L)} u_m - \frac{S_G \rho_G}{(1-S_G)(S_G c_0 \rho_G + (1-S_G c_0) \rho_L)} u_d \]  

(17)

$iTOUGH2$; $iTOUGH2$ (Finsterle, 2007), used in Papers I-III, enables parameter estimation, sensitivity analysis and uncertainty propagation analysis to be carried out for TOUGH2 or other simulators.

Parameter estimation, used in Paper I, is a procedure where the model output is compared to observations and the model input that produces the least disagreement between these is sought. To quantify the misfit between observations and model output an objective function is used, specified as a norm of the weighted residuals, such as the least squares, eq. 18 (Finsterle, 2007).

\[ S = \sum_{i=1}^{m} \frac{(z_i^* - z_i)^2}{\sigma_{z_i}^2} \]  

(18)

Here $S$ is the objective function, $z_i$ is the value of the output variable of the model, $z_i^*$ is the observation/measurement, $\sigma_{z_i}^2$ is the error variance of calibration point $i$ and $m$ is the number of observations/calibration points. The difference in the parentheses constitutes the residual $(r_i)$. Another way to express eq. 18 is $S = r^T C^{-1} r$. A minimization algorithm is used to search for the minimum of the objective function (occurring when the best-estimate parameters are used as input) by systematically changing the input parameters ($p_k$, with $k$ being the number of the iteration). The search is stopped once a convergence criterion is met. The Levenberg-Marquardt minimization algorithm was used in Paper I. It is a second derivative method, i.e. the first and second derivative of the objective function with respect to the parameter vector is determined and used to find the next set of input parameters values to test ($p_{k+1} = p_k + \Delta p_k$). If this new parameter set reduces the objective function the parameter set is used as the updated $p_k$. Eq. 19 is a Taylor-series expansion of $S$ relating it to $\Delta p_k$ (Finsterle, 2007).

\[ S(p_{k+1}) \approx S(p_k) + g_k^T \Delta p_k + \frac{1}{2} \Delta p_k^T H_k \Delta p_k \]  

(19)

$g_k$ is the gradient vector and $H_k$ is the Hessian. These can be expressed as functions of the observation covariance matrix ($C_{zz}$), eq. 20, containing the
variance corresponding to the measurement error of the observations, and the Jacobian matrix ($J$), eq. 21, containing the sensitivity coefficients (Finsterle, 2007). $n$ is the number of parameters to estimate.

$$
\mathbf{C}_{zz} = \begin{bmatrix}
\sigma_{z_1}^2 & 0 & 0 & \cdots & 0 \\
0 & \sigma_{z_2}^2 & 0 & \cdots & 0 \\
0 & 0 & \sigma_{z_3}^2 & \cdots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & \cdots & \sigma_{z_m}^2 
\end{bmatrix}
$$

(eq. 20)

$$
\mathbf{J} = \begin{bmatrix}
\frac{\partial z_1}{\partial p_1} & \cdots & \frac{\partial z_1}{\partial p_n} \\
\vdots & \ddots & \vdots \\
\frac{\partial z_m}{\partial p_1} & \cdots & \frac{\partial z_m}{\partial p_n}
\end{bmatrix}
$$

(eq. 21)

For the Levenberg-Marquardt method, $\Delta \mathbf{p}_k$ is expressed as eq. 22. Where $\lambda$ is the Levenberg parameter, $\mathbf{D}_k$ is a diagonal matrix with $D_{jj} = (\mathbf{J}_k^T \mathbf{C}_{zz}^{-1} \mathbf{J}_k)^{-1}$ for $j=1,\ldots,n$, and $\mathbf{r}_k$ holds the residuals. Starting with a large value of $\lambda$ and decreasing it as the search is approaching its goal ensures a positive-definite Hessian approximation (Finsterle, 2007).

$$
\Delta \mathbf{p}_k = (\mathbf{J}_k^T \mathbf{C}_{zz}^{-1} \mathbf{J}_k + \lambda_k \mathbf{D}_k)^{-1} \mathbf{J}_k^T \mathbf{C}_{zz}^{-1} \mathbf{r}_k
$$

(eq. 22)

This procedure should lead to finding the parameter set for which the minimum of the objective function occurs – the best-estimate parameter set ($\hat{\mathbf{p}}$). The uncertainties of the estimates can be found in the covariance matrix of the estimated parameters ($\mathbf{C}_{pp}$), eq. 23. The variances of the estimated parameters are the diagonal elements of the matrix. Here $m - n$ is the degree of freedom (Finsterle, 2007).

$$
\mathbf{C}_{pp} = \frac{s_0^2}{\mathbf{r}^T \mathbf{C}_{zz}^{-1} \mathbf{r}} (\mathbf{J}^T \mathbf{C}_{zz}^{-1} \mathbf{J})^{-1}
$$

(eq. 23)

In case all but one parameter is known or uncorrelated the standard deviation of the estimated parameter is instead given by the reciprocal of the corresponding diagonal element of the matrix in eq. 24 (Finsterle, 2007).

$$
\mathbf{F} = s_0^{-2} (\mathbf{J}^T \mathbf{C}_{zz}^{-1} \mathbf{J})
$$

(eq. 24)

Sensitivity analysis provides information on the resulting change in model output variables when slightly changing the model input parameters, i.e. it
provides a measure of the influence and importance of the input parameters on the simulation results. Eq. 25 shows the scaled sensitivity coefficient matrix containing dimensionless sensitivity coefficients made comparable through scaling with the standard deviation of the observation ($\sigma_{z_i}$) and expected parameter variation ($\sigma_{p_j}$), thereby accounting for potential differences in units, etc (Finsterle, 2007).

$$\tilde{J} = \begin{bmatrix}
\frac{\partial z_1}{\partial p_1} \cdot \frac{\sigma_{p_1}}{\sigma_{z_1}} & \cdots & \frac{\partial z_1}{\partial p_n} \cdot \frac{\sigma_{p_n}}{\sigma_{z_1}} \\
\vdots & \ddots & \vdots \\
\frac{\partial z_m}{\partial p_1} \cdot \frac{\sigma_{p_1}}{\sigma_{z_m}} & \cdots & \frac{\partial z_m}{\partial p_n} \cdot \frac{\sigma_{p_n}}{\sigma_{z_m}}
\end{bmatrix}$$ (25)

Sensitivity can be quantified and explored by using $\tilde{J}$. One sensitivity measure is $b_{kj}$ (eq. 26), which provides the value of a certain data set when estimating a specific parameter ($j$) (Finsterle, 2007). Here $k \leq m$. This was used in Paper I.

$$b_{kj} = \sum_{i=1}^{m} \left| \frac{\partial z_i}{\partial p_j} \right|_{i \in k}$$ (26)

Sensitivity analysis in iTOUGH2 can also be carried out using the Morris one-at-a-time method (Finsterle and Zhang, 2011; Morris, 1991), as used in Paper II. In individual steps a parameter in the input parameter set is perturbed and the elementary effect ($EE_{ij}$), eq. 27, determined. Several paths in the parameter space with random start origin is followed to determine a large amount of $EE_{ij}$.

$$EE_{ij} = \frac{z_i(p_{1..k}+\Delta p_{j..n})-z_i(p_{1..k})}{\Delta p_j}$$ (27)

The statistics of the assembly of the calculated $EE_{ij}$ values i.e. the mean elementary effect and its variance provide information concerning importance of parameters to output, linearity of the model and/or correlations between parameters.

Uncertainty propagation analysis investigates the span of the resulting model output, i.e. uncertainty of prediction, when taking into consideration the uncertainty (probability distribution) of the input parameters. Such an analysis can be carried out, as in Paper II, using the Monte Carlo simulations method. The method consists of (i) specifying a probability distribution for each input parameter which is considered uncertain, (ii) running the forward model a large number of times, each time with an updated input parameter sets randomly sampled from the specified distributions, and finally (iii) the col-
lected output from the forward runs is analyzed statistically (Finsterle, 2007).

**PEST protocol;** iTOUGH2 in combination with the PEST protocol (Doherty, 2008; Finsterle, 2011) makes it possible to use the analysis capabilities of iTOUGH2 in cases where the forward model is an external model/simulator or alternatively a TOUGH2 code that does not exist as an iTOUGH2 version. The code provides exchange of input and output between iTOUGH2 and the forward model. The PEST protocol was used in **Paper II** to connect the ECO2N/T2Well simulator to iTOUGH2.

**GSLIB;** The Geostatistical Software Library (GSLIB) can be employed within iTOUGH2 (Deutsch and Journel, 1998; Finsterle and Kowalsky, 2007). Thereby heterogeneous spatially correlated permeability fields with individual permeability values specified for the grid blocks can be produced.

Spatial variability/correlation of a variable can be described and quantified by a variogram (Deutsch, 2002). The semivariogram gives half the averaged squared difference of values at a separation distance of \( h \) (the lag). Several options for semivariograms models which provide the spatial correlation structure exist. In **Paper III**, where the role of geological heterogeneity was specifically addressed, the exponential model was employed, eq. 28 (Deutsch and Journel, 1998). Here \( \gamma \) is the semivariogram value, \( a \) is 1/3\(^{rd} \) of the range and \( c \) is the variance contribution (sill).

\[
\gamma(h) = c \cdot \left[ 1 - \exp\left(-\frac{3h}{a}\right) \right] \tag{28}
\]

One method for creating random correlated fields is sequential Gaussian simulation (Finsterle and Kowalsky, 2007). When carrying out sequential Gaussian simulation, firstly, the univariate cumulative distribution function (CDF) for the whole field (all gridblock variable values) is determined. Then the original data is transformed to data with a standard normal CDF. Each element of the grid is in turn selected in a random order. (i) All variable values, original or simulated, at elements within a specified neighborhood from the currently selected element constitute the conditioning data. (ii) Kriging (linear regression) with the normal score variogram model is employed to provide statistics of the conditional CDF at the element. (iii) A simulated data value for the element is obtained by picking a value at random from that conditional CDF and including it in the data set. When variable values for all unsampled elements have been retrieved in this manner transformation of the data back to the original form is made (Finsterle and Kowalsky, 2007). Multiple realizations, following the geostatistics and therefore equally probable are used in stochastic simulations (Deutsch, 2002).
3.2 Modeling of processes at the pore-scale – Pore-network modeling

This section contains a description of a quasi-static pore-network model (PNM) for simulating two-phase flow, drainage and imbibition, in porous media. The simulator was specifically developed for this thesis to investigate residual CO₂ trapping during geological storage. The basic assumptions and simulation capabilities of the PNM are described below. CO₂ is in this case the non-wetting phase and brine/water is the wetting phase. Both phases are assumed to be immiscible and incompressible. Further flow is assumed to be laminar. The PNM simulator code is a Fortran code and ASCII data files are used for providing input to and output from the simulator. An overview of the code is given in Figure 5.

Figure 5. Schematic over the workflow of the PNM code.

The first part of the PNM is the input reading step. The input includes e.g. the maximum number of bodies in each dimension, a mean coordination number for the whole network (or alternatively a probability that a throat exist in a certain direction), spacing between the body centers, shape of throat and body cross sections, throat radii size distribution, body radii size
distribution, aspect ratio (ratio between the throat and body radius), interfa-
cial tension, contact angles, phase viscosities, density difference between
phases, slip conditions, imposed pressure gradient when calculating permea-
bility, solver specifications, output printing options and several seed num-
bers for different stochastic options.

A central part of the PNM is the matrix setup routine. This subroutine de-
termines the position of the bodies in the network and how they are linked
by throats. The PNM uses the method by Raoof and Hassanizadeh (2010) for
constructing multi-directional semi-regular cubic lattice networks with a
specified mean coordination number ($\bar{z}$) for the whole network, although
individual bodies have randomly assigned coordination numbers ($z$) of 0 to
26. To achieve the specified $\bar{z}$ some of the pore throats, as well as any isolated
bodies, are eliminated during the matrix setup. Figure 6 and 7 show some
different network structures which the code can create.

![Network Structures (10x10x10 Lattices)](image)

**Figure 6.** Examples of network structures (10x10x10 lattices) a) with the highest possible $z$ ($\bar{z}=26$, not including bodies at the sides), b) with connections in three predefined directions ($\bar{z}=6$, not including bodies at the sides), and c) with $\bar{z}=6$ and random throat directions.

---

6 It is also possible to create regular lattice networks with the routine.
Figure 7. Example of a network structure (20x20x20 lattice) created by the PNM with \( z = 4 \) if disregarding bodies at the sides. Throats and bodies with both circular and angular cross sections are displayed.

After the network matrix structure has been created the property setup is carried out. For each throat and body the following properties are specified; inscribed circle radius \( (r) \), shape factor \( (G) \), corner half-angles \( (\beta_l) \), and receding and advancing contact angles \( (\theta_r \text{ and } \theta_a) \). The shape factor concept (Mason and Morrow, 1991) is employed to characterize the geometry of the network elements and relate it to the drainage and imbibition displacement mechanisms. Simplified shapes are assumed for the network elements. Individual throats have equilateral triangular or circular cross sections; \( G \) is equal to \( \sqrt{3}/36 \) or \( 1/(4\pi) \), respectively. Individual bodies have square or circular cross section; \( G \) is equal to \( 1/16 \) or \( 1/(4\pi) \), respectively. The available radii distributions include e.g. the truncated log-normal distribution, the truncated Weibull distribution, bimodal versions of the two former distributions and uniform distribution with specified range. The \( \theta_r \) and \( \theta_a \) can be uniform or follow a uniform distribution. The length of each pore throat\(^7\),

\(^7\) This is equal to the distance between the centers of the connected pore bodies minus the sum of their radii.
element volumes, distances between nodes, lattice dimensions and the effective porosity are calculated at the end of this step. Effective porosity means that only throat and bodies belonging to the backbone of the network are considered, i.e. not including eliminated elements.

The next step in the PNM workflow is the simulation step. The quasi-static simulation mode starts by setting the initial conditions (full wetting phase saturation). It is assumed that flow occurs over the left (referred to as inflow side) and right (referred to as outflow side) side boundaries of the network. No flow occurs over the other sides. At the start of drainage, the bodies at the left boundary are filled by non-wetting phase, i.e. main terminal arc menisci (MTAMs) appear. The order in which network elements are invaded by non-wetting phase during drainage is determined by the throats of the network. The entry pressure \( P_{c}^e \) \( ^8 \) for invasion of a non-wetting phase into a throat with triangular cross section is calculated using eq. 29 (Øren et al., 1998; Patzek, 2001; Al-Futaisi and Patzek, 2003). \( \sigma \) is the interfacial tension and \( r \) is the throat radius.

\[
P_{c}^e = \frac{\sigma}{r} \cdot \cos \theta_r \cdot \left( 1 + \sqrt{1 - \frac{4G \cdot \sum_{i=1}^{3} \left( \frac{\cos(\theta_r + \beta_i)}{\sin \beta_i} \cos \theta_r - \frac{\pi}{2} + \theta_r + \beta_i \right)} \cos^2 \theta_r \right) \tag{29}
\]

For a throat with circular cross section, \( P_{c}^e = \left( 2.0 \cdot \frac{\sigma}{r} \right) \cdot \cos \theta_r \).

All throat entry pressures are calculated and ordered in a list of increasing entry pressure. The pressure is increased step wise during drainage, following the list. At each pressure level a search is made to find possible displacement events. The drainage simulation is stopped if i) the highest \( P_{c} \) in the list has been reached or ii) a specified initial gas saturation (\( S_{gi} \)) has been reached/exceeded.

Procedure for identifying possible drainage displacement events:
All throats connected to drained bodies are checked. If such a throat is found to be saturated with wetting phase, the \( P_{c}^e \leq P_{c} \) and a continuous wetting-phase path exists from the throat to the outflow side for the displaced wetting phase to exit the network through, then the throat undergoes drainage. Any undrained body connected to the drained throat is drained as well, as it has a lower entry pressure (>\( r \)) than the throat. The search procedure is repeated until no more events are identified at that \( P_{c} \) level.

\(^8\) Optionally a correction term to account for gravity effects (buoyancy) on \( P_{c}^e \) may be applied (see Paper IV for details).
During imbibition several displacement and trapping mechanisms are accounted for by the PNM simulator; piston-type displacement in throats, snap-off in throats, snap-off in bodies, cooperative pore body filling ($I_2-I_{p,1}$) in bodies and piston-type displacement in bodies (representing $I_1$). Figure 8 displays these mechanisms and descriptions are given in Paper IV.

**Figure 8.** Displacement and trapping mechanisms considered by the simulator; a) piston-type displacement, b) snap-off and c) cooperative pore body filling ($I_1$ and $I_2$). The figure is modified after Lenormand et al. (1983).

In Paper IV cases of spontaneous imbibition are considered. The maximum advancing contact angle at which spontaneous imbibition through piston-
type displacement ($\theta_{a,\text{max}}^{\text{pd}}$) and snap-off ($\theta_{a,\text{max}}^{\text{so}}$) can occur in are calculated with eq. 30 and 31 (Al-Futaisi and Patzek, 2003), respectively. $P_{c}^{\text{max}}$ is the highest $P_{c}$ during drainage and $n$ is the number of corners.

$$\theta_{a,\text{max}}^{\text{pd}} \approx \arccos \left( \frac{-4 \cdot G \cdot \sum_{i=1}^{n} \cos(\theta_{r} + \beta_{i})}{(r_{p} P_{c}^{\text{max}})^{2} \cos \theta_{r} + 4 \cdot n \cdot G \cdot \sin \theta_{r}} \right)$$  \hspace{1cm} (30)

$$\theta_{a,\text{max}}^{\text{so}} = \frac{\pi}{2} - \min(\beta_{i})$$  \hspace{1cm} (31)

Description of the displacement and trapping mechanisms during imbibition and determination of threshold capillary pressure

Piston-type displacement: The threshold capillary pressure for piston-type displacement ($P_{c}^{\text{e,PISTON}}$) in an element with triangular cross section is given by eq. 32 where $r_{p}$ results from iteratively solving several equations (details concerning these are given in Paper IV) (Al-Futaisi and Patzek, 2003; Patzek, 2001).

$$P_{c,\text{PISTON}} = \begin{cases} \frac{\sigma}{r_{p}}, & \theta_{a} \leq \theta_{a,\text{max}}^{\text{pd}} \text{ (spontaneous imb.)} \\ 2 \cdot \sigma \cdot \cos \theta_{a} / r, & \theta_{a,\text{max}}^{\text{pd}} < \theta_{a} < \frac{\pi}{2} + \min(\beta_{i}) \text{ (forced imb.)} \end{cases}$$  \hspace{1cm} (32)

In case of a circular cross section, the $P_{c}$ during imbibition for piston-type displacement in a throat or body is simply, $P_{c}^{\text{e}} = (2.0 \cdot \sigma / r) \cdot \cos \theta_{a}$. Here $r$ is the radius of the throat or body.

Snap-off: Snap-off is a mechanism where the wetting phase arc meniscus (AMs) swells, eventually resulting in fusion, instability and wetting phase filling the element. The threshold capillary pressure for snap-off ($P_{c}^{\text{e,SO}}$) in a triangular cross section is determined using eq. 33 (Al-Futaisi and Patzek, 2003). $r_{\text{SOij}}$ results from iteratively solving two equations (details concerning these are given in Paper IV).

$$P_{c,\text{SO}} = \begin{cases} \frac{\sigma}{\min(r_{\text{SOij}})}, & \theta_{a} < \theta_{a,\text{max}}^{\text{so}} \text{ (spontaneous imb.)} \\ 0, & \theta_{a} = \theta_{a,\text{max}}^{\text{so}} \text{ (spontaneous imb.)} \\ \frac{P_{c}^{\text{max}}}{\cos(\theta_{r} + \min(\beta_{i}))}, & \theta_{a,\text{max}}^{\text{so}} < \theta_{a} < \pi - \min(\beta_{i}) \text{ (forced imb.)} \\ \frac{P_{c}^{\text{max}}}{\cos(\theta_{r} + \min(\beta_{i}))}, & \theta_{a} \geq \pi - \min(\beta_{i}) \text{ (forced imb.)} \end{cases}$$  \hspace{1cm} (33)

The threshold capillary pressure for snap-off in a square cross section is determined using eq. 34 (Lenormand and Zarcone, 1984).
Cooperative pore body filling: The PNM takes into consideration $I_2$ to $I_{z-1}$-cooperative pore body filling events, while $I_1$ is treated as a piston-type displacement event. The threshold capillary pressure for $I_n$-cooperative pore body filling ($P_{e,n}^p$) is determined using eq. 35 and 36 (Patzek, 2001), where $n$ is the n.o. adjacent throats with non-wetting phase. In eq. 35 $r_o$ is the body radius, $W_{j-k}$ is a random number in the interval $[0,1]$, $r_{j-n}$ is the throat radius and $w^{(j-n)}$ is a parametric weight. This weight takes into account the geometry effects and the ease of occurrence of one mechanism relative to another (Patzek, 2001). Further details are given in Paper IV.

\[
\bar{R}_n = \left[ \frac{r_o + \sum_{n} \sum_{couples} W_{j-k-n}(r_{j-k} + r_{k-n})}{\sum_{n} \sum_{couples} W_{j-k-n}} \right] \cos \theta_a
\]

(35)

\[
P_{e,n}^p = \frac{2 \cdot \sigma}{\bar{R}_n} \quad \text{for} \quad \theta_a \leq \theta^{\text{pd}}_{a,max}
\]

(36)

The threshold capillary pressures, at $P_{e}^{\text{max}}$, for all piston-type displacement, snap-off and cooperative pore body filling events are calculated and ordered in a list of decreasing capillary entry pressure. Following this – the pressure is decreased step wise during imbibition. At each pressure level a search is made to find possible displacement events. During imbibition invasion of an element by wetting phase can only occur if there is a continuous non-wetting phase path from that element to the left side (original inflow side), through which displaced non-wetting phase can exit the network (a nw-escape path). Further, there must exist a continuous wetting phase path to the right side (original outflow side), providing the displacing wetting phase (a w-path). The steps below are used when simulating the wetting-phase advancement in the network at each $P_e$ level. Imbibition is finished after the lowest $P_e$ in the list has been reached and evaluated.

Procedure for identifying possible imbibition displacement events;

1. A check is made if any of the bodies on the right side (original outflow side which is assumed to be connected to a wetting-phase reservoir) should undergo piston-type displacement or cooperative pore body filling. Imbibition occurs if $P_{e}^{p} \geq P_e$ and a nw-escape path exists. In case of imbibition the wetting phase fills the body and any throats connected to the body are examined to determine if they should be subjected to piston-type displacement.

\(^9\) A modified version of the model of Blunt (1997).
2. A check is made if any snap-off event should occur in the throats. Snap-off does not occur in elements with circular cross section. Snap-off occurs if the two bodies connected to the throat contain non-wetting phase, \( P_{c,sto} \geq P_c \) and a nw-escape path as well as a w-path exist. In case of snap-off the throat is filled with wetting phase.

3. A check is made if any piston-type displacement or cooperative pore body filling event in bodies should occur. Imbibition occurs if at least one connected throat already has been invaded by wetting phase (i.e. a MTAM is present), \( P_c \geq P_c \) and a nw-escape path exists. In case of imbibition the body is filled with wetting phase and any unimibed throats connected to the body are examined to determine if they should be subjected to piston-type displacement. If at least one event occurs during step 3 the search in step 3 is restarted.

4. A check is made if any snap-off event should occur in the bodies. Snap-off does not occur in elements with circular cross section. Imbibition occurs if \( P_{c,sto} \geq P_c \), a nw-escape path exists, a w-path (facilitating corner flow) exists and all connected throats contain non-wetting phase, i.e. absence of invading interfaces. Additionally the body must not belong to the right side boundary (which is assumed to be connected to a wetting-phase reservoir). In case of imbibition the body is filled with wetting phase, and any throats connected to the body are examined to determine if they should be subjected to piston-type displacement. If an event occurs during step 4 the search is restarted from step 3.

After evaluating events at a specific \( P_c \) level, newly formed clusters are localized. For these the current \( P_c \) is the trapping \( P_c (P_c^{trap}) \). An update is made to obtain the current \( \theta_i \) for the elements (see Paper IV for details), used in calculations of phase saturation and conductance.

The phase saturation after drainage in individual elements is dependent on the shape of the cross section. Elements with a circular cross section contain only one phase, i.e. this shape allows no corner flow. However, a capillary duct with an angular cross-section contains two fluid phases after drainage. A throat with an equilateral triangular cross section is almost completely filled with non-wetting phase; however, some wetting phase is still left in the corners of the cross section. The saturation of a phase in a two-phase containing element, where the non-wetting phase is not trapped, is \( P_c \) dependent. The cross section area of wetting phase \( (A_w) \) is given by eq. 37 (Øren et al., 1998), with \( \theta = \theta_r \) during drainage, and \( \theta = \theta_h \) or \( \theta_a \) during imbibition.

\[
A_w = \left( \frac{\sigma}{P_c} \right)^2 \sum_{i=1}^{3} \left( \frac{\cos \theta \cos(\theta + \beta_i)}{\sin \beta_i} - \frac{\pi}{2} + \theta + \beta_i \right)
\] (37)
In a throat the wetting phase saturation \( S_w^{\text{element}} \) is given by eq. 38, where \( A \) is the cross sectional area of the throat.

\[
S_w^{\text{element}} = \frac{A_w}{A}
\]  

For cubic bodies the wetting phase saturation after drainage is determined by an equation from Joekar-Niasar et al. (2010). Details concerning this are given in Paper IV.

In an element containing trapped non-wetting phase the contact angle has a value corresponding to \( \theta_{\text{trap}} \), and the volume of the trapped non-wetting phase remains at the volume it had when trapping occurred.

To determine the phase saturation of the network; first the wetting phase saturation and volume of each element is multiplied, resulting in the wetting phase volume of each element. The wetting phase saturation of the network \( S_w \) is equal to the sum of all these volumes divided by the total volume of all elements. The non-wetting phase saturation of the network \( S_{nw} \) is \( 1 - S_w \).

The absolute permeability \( k \) and relative permeability \( k_r \) can be determined by the PNM. These are functions of e.g. the effective conductance. The effective conductance \( (g_{ij}) \) for phase i, between two body centers (I and J), is set to the harmonic mean of the conductance of the involved elements. The hydraulic conductance \( (g) \) for one- and two-phase conditions in an element is calculated as suggested by Patzek and Silin (2001) and Patzek and Kristensen (2001), respectively. Details concerning this elaborate procedure are given in Paper IV. In elements with corners, occurrence of corner flow is considered by the PNM.

The \( k \) is calculated for a subpart of the network, i.e. not including bodies at the in- and outflow boundaries. \( k \) is determined for a static fluid configuration and with a pressure difference introduced between the boundaries. By assuming that mass (/volume) is conserved, using an equation relating flow rate to the difference in pressure between two adjacent nodes and boundary conditions, a linear system of equations is derived by the PNM. The ITPACK 2C (Hageman and Young, 1981; Kincaid et al., 1982) solvers are used by the PNM; Jacobi-preconditioned conjugate gradients (JCG), SSOR-preconditioned conjugate gradients (SSORCG), Successive overrelaxation (SOR), Jacobi semi-iteration (JSI) and SSOR semi-iteration (SSORSI). In Paper IV the 'symmetric successive overrelaxation'-preconditioned conjugate gradient (SSORCG) solver was used. The system of equations is solved for the pressure field in the network. From this the flow in individual throats and the total flow \( (Q_{tot}) \) can be determined. The latter is the sum of the flow rates across the boundary. \( k \) is calculated using the expression in eq. 39. \( \Delta x \), \( \Delta y \) and \( \Delta z \) are the length of the subpart network in the three dimensions. The flow occurs in the x-direction.
\[ k = Q_{\text{tot}} \cdot \mu_w \cdot \Delta x / (\Delta y \cdot \Delta z \cdot \Delta P) \]  

(39)

For \( k_{rw} \) and \( k_{rnw} \) (eq. 40) each phase is considered separately, with \( k_{ri} = 0 \) if a continuous path of phase \( i \) is not present across the network.

\[ k_{ri} = Q_{\text{tot},i} \cdot \mu_i \cdot \Delta x / (k \cdot \Delta y \cdot \Delta z \cdot \Delta P) \]  

(40)

The next step in the PNM workflow is the analysis step. In this step the trapped clusters of CO\(_2\) in the network are identified and several measures are made. For each ganglion the following is determined;

- the number of throats and bodies occupied by the ganglion
- the volume of the ganglion
- the elongatedness
- the \( P_c \) at which trapping occurred

Additionally the \( S_{gr} \) is calculated.

The last step in the PNM workflow is the output step. The output file contains information not only on the input data used but also information concerning e.g. the frequency of coordination numbers in the network, mean coordination number, network volume, effective porosity, tortuosity, result of the trapped cluster analysis, \( k \) and a summary of the displacement events that have occurred. Additional output from the PNM includes:

- the spatial distribution of phase saturations in the network elements at each \( P_c \) level (optional)
- the \( S_w \) and \( S_{nw} \) of the network at each \( P_c \) level
- the drainage \( P_c-S_w \) curve
- the drainage \( k_{rw}-S_w \) and \( k_{rnw}-S_w \) curves
- the imbibition \( P_c-S_w \) curve
- the imbibition \( k_{rw}-S_w \) and \( k_{rnw}-S_w \) curves
- a detailed list over all displacement events occurring during drainage and imbibition

The PNM code employs a few subroutines which are originally developed by other programmers and modified slightly to be compatible with the PNM code. These are except the already mentioned ITPACK 2C code (Hageman and Young, 1981; Kincaid et al., 1982), the functions GASDEV and RAN1 for producing normal deviates and uniform random deviates, respectively (these are used when sampling from different statistical distributions) (Press et al., 1989), subroutines providing Heapsort (SORT, SORT2) (Press et al., 1989) and a subroutine for determining all possible combinations of M values from a set of N entities (CMBN) (Grimes, 1971). Optionally, a reworked version of a simulated annealing subroutine from GSLIB can be used to reduce the throat radii variance for throats connected to the same body by
switching the position of the throats in the network and/or to incorporate spatial correlation between the radii of the bodies.

The source files used to compile the PNM includes pnm.f, itpack2c.f (solvers) and optionally gslib.f (a reworked GSLIB subroutine for simulated annealing). Once compiled, the executable file (pnm.exe) can be run together with the input file (pnm_input). When the program runs several files containing output is created; pnm_con (containing information regarding the throats such as bodies connected to the throat, direction, radius, length, volume and shape), pnm_matrix (containing information regarding the bodies such as coordinates, radius, volume and shape), matrix_output (main output file), pnm_imb_events (containing information regarding displacement and trapping events during imbibition), and files containing simulated $P_c-S_w$, $k_r-S_w$ and spatial phase distribution information. Figure 9 illustrates the modeling procedure when using the PNM.
**Figure 9.** Pore-network modeling from input to output.
4. Results and discussion

4.1 Analysis of alternative field-test-designs for determining residual CO$_2$ trapping (PI)

As residual trapping has been identified as a potentially greatly important and secure mechanism to hold CO$_2$ in the subsurface, development of field-test sequences that can aid the estimate of residual CO$_2$ trapping is valuable. In Paper I focus is on analyzing and comparing alternative experimental field test sequences for characterization of in-situ residual CO$_2$ saturation ($S_{gr}$). These alternative push-pull-test-designs were potential candidates to be carried out as part of the injection tests at the Heletz site. A new approach for establishing residual gas conditions in-situ; using withdrawal and an indicator-tracer was studied. Additionally, the effect on the parameter estimation of including data sets of pressure measurements from an observation well at a distance of 40 m from the injection well was explored. The analysis included (i) numerical simulations to retrieve synthetic responses for the alternative test sequences, (ii) a sensitivity analysis to investigate the relative importance of the measurement data sets, and (iii) parameter estimation (inverse modeling) on synthetic test response data, from which the estimation uncertainties were used to compare the relative ability of the test sequences to determine the $S_{gr}$.

In the study the TOUGH2/iTOUGH2 (Finsterle, 2007; Pruess et al., 1999) simulator with the EOS7C (Oldenburg et al., 2004) module was employed, see section 3.1 for details concerning these. A conceptual model representing the Heletz site, by a 2D radially symmetric homogeneous 10.6 m thick sandstone layer$^{10}$ with a radius of 500 m, was used. The outer boundary was of no-flow type, with a volume such that the model’s volume agreed with the estimated volume of the site’s sandstone layers. No data concerning site-specific characteristic functions existed when the study was carried out. Instead the non-hysteretic Brooks-Corey Burdine (Brooks and Corey, 1964; Burdine, 1953) characteristic functions with parameters adopted from literature (Dana and Skoczylas, 2002a; 2002b) and adjusted by Leverett scaling (Leverett, 1941), were used. Further details concerning parameter values and assumptions can be found in Paper I.

---

$^{10}$ The combined thickness of the three sandstone layers planned as target layers for injection, at that point in time.
With the test sequence for characterizing $S_{gr}$ suggested by Zhang et al. (2011) as a base; three alternative single-well CO$_2$ push-pull test sequences (Figure 10-12) were set up, simulated and evaluated. The test sequence uses a combination of thermal, hydraulic and partitioning tracer test stages to retrieve pressure (P), temperature (T) and dissolved gas tracer concentration (C) measurement responses from which $S_{gr}$ can be inferred through an inverse modeling approach. The test takes advantage of dependencies between these responses and the in-situ phase saturation conditions. The tests are repeated at different in-situ gas saturation conditions; before CO$_2$ injection (reference test), after CO$_2$ injection and at residual gas saturation. The sampling intervals for data sets collected during respective test sequence are shown in Figure 10-12. An O means that the data set was retrieved from the passive observation well, otherwise it was retrieved from the injection well. In the simulated scenarios 100 tons of CO$_2$ was injected. All test sequences employ dissolved gas tracers, which are co-injected with water during a part of the hydraulic test stages. The dissolved gas tracers were Krypton (Kr) and Xenon (Xe). These are partitioning tracers and their partitioning between the phases results in a difference in breakthrough curve (BTC) when a tracer test is performed at conditions of complete water saturation compared to at residual gas saturation. Test sequences 2 and 3 uses an additional type of tracer, referred to as an indicator tracer. It is assumed to be non-reactive, remain in the aqueous phase, not precipitate and be possible to continuously measure. When withdrawal is employed to create the residual gas zone, the indicator tracer should function as an indication of when residual gas saturation conditions has established in situ. Here a tracer given bromide (Br$^-$) like properties was used.

![Figure 10. Test sequence 1, with the collection periods of the P, T and C data sets displayed. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2014).](image-url)
gas saturation condition is created in-situ by injecting CO₂, and then injecting CO₂-saturated water. The latter injection should drive the mobile gas phase further into the target layer, leaving behind immobilized gas phase, at residual saturation, without causing dissolution.

**Figure 11.** Test sequence 2 (when $S_{gr} = 0.2$), with the collection periods of the P, T and C data sets displayed. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2014).

Test sequence 2 employs a new approach for creating residual gas saturation conditions. The stage of establishing the residual gas saturation zone comprises; co-injecting an indicator tracer with water (1h pulse), followed by the CO₂ injection, after which formation fluid is withdrawn while indicator-tracer concentration in the aqueous phase is measured. Numerical simulations indicate that the establishment of residual gas conditions in situ (and therefore also the point in time when the withdrawal should cease), coincides with the online-measured indicator-tracer concentration approaching zero.

**Figure 12.** Test sequence 3 (when $S_{gr} = 0.2$), with the collection periods of the P, T and C data sets displayed. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2014).
Test sequence 3, compared to the two former, does not employ thermal tests (i.e. heating stages) or any injections of CO₂-saturated water. So, less instrumentation is needed and the bother of preparing CO₂-saturated water is avoided with this test sequence. It uses the same procedure as test sequence 2 to establish the residual gas saturation conditions. Specific for test sequence 3 is data set TX; temperature measurements collected during the CO₂ injection, soaking, withdrawal and second soaking stages. In contrast to other temperature data sets this one is not a response of a thermal test. Due to the use of water injection (instead of CO₂-saturated water) during the last hydraulic test some dissolution of residual gas occurs, and the last stage of test sequence 3 is therefore executed at semi-residual gas conditions (partly residual-gas saturation and partly fully water-saturated conditions).

Test responses for the simulated scenarios: The simulated responses for each test sequence, when assuming a $S_{gr}$ of 0.1, 0.2 and 0.3, are shown in Figure 13-15. For test sequences 2 and 3 the time for establishing the residual gas saturation zone was dependent on the $S_{gr}$ value, giving rise to a small displacement in time of the test stages, and corresponding responses, relative to each other. The simulator allows one tracer, so each tracer BTC originates from one simulation run. Figure 13a and 14a show that the increase in temperature due to the thermal test at residual gas saturation conditions depended on the assumed $S_{gr}$ value. Test sequence 3 (Figure 15a), which lacks thermal test stages, still had a temperature response during the CO₂ injection stage which was $S_{gr}$ dependent. Figure 13b, 14b and 15b show that the pressure response in the injection well, during injection and withdrawal stages, depended on the assumed $S_{gr}$ value. Such a dependence was, however, not discernible for the pressure response in the observation well. Figure 13c and 14c display the dissolved gas tracer BTCs for test sequence 1 and 2, respectively. A higher BTC peak value was observed during the first tracer test (at water saturated conditions) than during the second tracer test (at residual gas saturation conditions). For the latter case the shape and peak magnitude of the BTCs depended on the $S_{gr}$ value and the dissolved gas tracer in use. This is because the dissolved gas tracers, at residual gas saturation conditions, partitions between the gaseous and aqueous phases. Part of the dissolved gas tracer transfers to the immobile gaseous phase, leading to a retardation of the tracer manifested by a lower peak concentration and a more elongated tail (higher apparent dispersion) of the BTC. This effect is enhanced as $S_{gr}$ increases. The difference in Kr and Xe BTCs, is due to the difference in the tracer's inverse Henry's constant. Kr, compared to Xe, has a higher preference to transfer to the gaseous phase. However, for test sequence 3 the dissolved gas tracer BTCs (Figure 15c) were dissimilar to those of the other two test sequences. A higher relative concentration was observed in the BTC responses resulting from the tracer
Figure 13. The simulated response of test sequence 1. a) Temperature in the injection well bottom, b) pressure in the injection and observation well bottom, and c) tracer BTC for different values of $S_{gr}$. A miniature schematic of the test stages is included for clarity. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2014).
Figure 14. The simulated response of test sequence 2. a) Temperature in the injection well bottom, b) pressure in the injection and observation well bottom, and c) tracer BTC for different values of $S_{gr}$. A miniature schematic of the test stages (for $S_{gr}=0.2$) is included for clarity. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2014).
Figure 15. The simulated response of test sequence 3. a) Temperature in the injection well bottom, b) pressure in the injection and observation well bottom, and c) tracer BTC for different values of $S_{gr}$. A miniature schematic of the test stages (for $S_{gr}=0.2$) is included for clarity. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2014).
test performed at semi-residual gas saturation conditions, than that performed at water-saturated conditions. Also the BTC responses were similar, independent of whether Kr or Xe was used. This was due to co-injection of the dissolved gas tracer with water (instead of CO₂-saturated water) during the last tracer/hydraulic test stage, which resulted in semi-residual conditions. The tracers partitioned into residual gas phase and as chasing water dissolved part of the residual gas saturation zone they were retransferred into the aqueous phase (resulting in enrichment). This interplay continues throughout the injection. At the start of withdrawal the spatial distribution of the tracers in situ was smaller than that of the reference tracer test. This produced the slim appearances and higher relative concentration peak values of the BTC. Concerning the indicator tracer used in test sequences 2 and 3, the BTCs exhibited peak values of ca 2.5. This means that during a period of the withdrawal, a higher tracer concentration was recovered, than was originally injected. This is due to the enrichment of indicator tracer that occurs when water from the aqueous phase, in which the indicator tracer remains, transfers to the gas phase during the CO₂ injection.

Test sequences 1 and 2 produced a residual gas saturation zone out to ~8 m from the injection well. Due to pure-water injection during the last hydraulic test stage in test sequence 3, the residual gas saturation conditions deteriorated as CO₂ phase was dissolved close to the well. At the end of the last water injection the residual gas saturation conditions remained from ~3 m out to 8 m from the well, with water-saturated conditions existing between the well and the residual gas zone.

**Sensitivity analysis:** The sensitivity of the data sets (i.e. the sum of scaled sensitivity coefficients for all calibration points in a data set, see section 3.1 and eq. 26, here based on calibration points with two hour intervals) to 10 parameters; residual gas saturation (S_{gr}), residual liquid saturation (S_{lr}), permeability (k), porosity (ϕ), Brooks-Corey parameter lambda (λ), Brooks-Corey parameter entry pressure (P_d), dry heat conductivity (λ_{dry}), wet heat conductivity (λ_{wet}), pore compressibility (c_ϕ) and inverse Henry’s constant for the dissolved gas tracer (H^{-1}) was investigated. Further details concerning assumptions can be found in Paper I. The results are shown in Figure 16. A high sensitivity shows that the data set contains information concerning that parameter. For S_{gr}, the pressure data sets from the injection well (P4, P2, P3A and P3 B) and the dissolved gas tracer concentration data set from the second tracer test (C2) showed the highest sensitivity. Several data sets of pressure in the observation well showed high sensitivity to various parameters. In case of multiple parameter estimation in the future, these data sets can potentially provide useful information on these parameters and thereby reduce the uncertainty in the estimates. However, the sensitivity of these data sets in regard to S_{gr} is of the same order as that of the temperature data sets.
Figure 16. Sensitivity of different data sets to the parameters (hydraulic and mechanical properties of the rock and a property of the tracer) for test sequence; a) 1, b) 2 and c) 3, respectively. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2014).
The responses at the calibration points, provided by a test sequence, must exhibit high enough sensitivity to changes in the parameter to be estimated; otherwise, the parameter estimation will not work. The sensitivity of temperature, pressure and dissolved gas tracer concentration with regard to the 10 parameters above with time was determined for all sequences. Figure 17 displays some of the scaled sensitivity coefficients \( \left( \frac{\partial z_i}{\partial p_j} \right) \cdot \left( \frac{\sigma_{p_j}}{\sigma_{z_i}} \right) \) with time, providing a measure of the value of different measurement types at specific points in time. This aided the choice of appropriate data points to include in the parameter estimation. More precisely, Figure 17 displays the scaled sensitivity coefficients of temperature, pressure and dissolved gas tracer concentration with regard to \( S_{gr} \), with time. A scaled sensitivity coefficient deviating from zero indicates sensitivity, with a high absolute value corresponding to high sensitivity. Figure 17a shows that even if no thermal test was carried out for test sequence 3, the temperature response was sensitive with regard to \( S_{gr} \) during the time interval corresponding to TX. Further, the analysis showed that the scaled sensitivity coefficients of the dissolved gas tracer concentration exhibited sensitivity with regard to \( S_{gr} \) during the last withdrawal step (except at the time corresponding to the arrival of the peak of the BTC) (Figure 17b). Among these, that of test sequence 3 exhibited the highest sensitivity and an oscillating appearance. This was due to the use of water during the last hydraulic test which dissolved gas phase near the well. The distance from the well to where the maximum mass fraction of dissolved gas tracer in the aqueous phase was found at the end of the water injection depended on the \( S_{gr} \) value. The largest distance corresponded to the lowest \( S_{gr} \) value, etc. At the onset of the following withdrawal stage, water-saturated conditions prevailed between the injection well and the location of the maximum tracer concentration. The prior gas saturation condition thereby determined the travel time of the tracer to the well during withdrawal, giving rise to the additional sensitivity peak (oscillating appearance), which coincides with the tracer arrival. It is the difference in gas saturation conditions which the tracer is subjected to, as it migrates away from and back to the well, which creates this peak for test sequence 3. The \( S_{gr} \)-dependent arrival time and narrower BTC produced a higher sensitivity of C2 with regard to \( S_{gr} \) for test sequence 3, compared to test sequences 1 and 2, although only semi-residual gas saturation conditions were achieved. Figure 17c-17e display the scaled sensitivity coefficients of pressure with regard to \( S_{gr} \) for respective test sequence. Sensitivity was exhibited during injection and withdrawal stages, with the response of test sequence 3 exhibiting a lower sensitivity compared to those of test sequences 1 and 2. This was due to the dissolution of residual CO2 close to the well when water, instead of CO2-saturated water, was injected during the last tracer test stage of test sequence 3. However, a residual gas saturation zone remained at a distance from the well, giving rise to the lower sensitivity in the pressure response with regard to \( S_{gr} \).
Figure 17. Some selected results concerning scaled sensitivity coefficients. a) The scaled sensitivity coefficients of the temperature ($T_i$) response with regard to $S_{gr}$ for test sequence 3, b) the scaled sensitivity coefficient of the Xe concentration ($C_i$) response with regard to $S_{gr}$ during the last withdrawal step shown for each test sequence, and the scaled sensitivity coefficients of the pressure ($P_i$) response with regard to $S_{gr}$ during test sequence; c) 1, d) 2 and e) 3, respectively. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2014).

Parameter estimation: The relative ability of the alternative test sequences, with different data sets, to determine $S_{gr}$ (when $S_{gr}=0.2$) was compared by means of parameter estimation (Table 3). The uncertainties in the $S_{gr}$ estimates were used for the comparison. All parameters except $S_{gr}$ were assumed to be known (i.e. no interdependencies between other parameter uncertainties were included). High sensitive calibration points were selected from the data sets to use in the parameter estimations. The parameter estimations were carried out using simulated synthetic field data; temperature, pressure and dissolved gas tracer concentration responses, with added random noise following the expected measurement errors. The least squares objective function and the Levenberg-Marquardt minimization method were employed (see section 3.1 and eq. 18). Table 3 displays the best-estimate values of $S_{gr}$ and the estimation uncertainty ($\pm$ standard deviation) for the alternative test sequences and the data sets included. Observe that it is the uncertainty in the $S_{gr}$ estimates, under the assumptions and conditions of the study, which are compared relative each other; the aim is not to quantify the absolute estimation uncertainty. The uncertainty would be larger if uncertainty associated with e.g. the geological heterogeneity and/or correlated parameters also were accounted for.
Table 3. Results from parameter estimation (when the true $S_{gr}=0.2$) for the different test sequences and the data sets included. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2014).

<table>
<thead>
<tr>
<th>Test sequence</th>
<th>Data sets</th>
<th>Best-estimate $S_{gr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>T1, T2, T3, P1, P2, P3 A, P4, C1, C2</td>
<td>0.2001 ± 0.5x10^{-3}</td>
</tr>
<tr>
<td>1 + passive obs. well</td>
<td>T1, T2, T3, P1, P2, P3 A, P4, C1, C2, PO1, PO2, PO3 A, PO4</td>
<td>0.2000 ± 0.4x10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>T1, T2, T3, P1, P2, P3 B, P4, C1, C2</td>
<td>0.2003 ± 0.5x10^{-3}</td>
</tr>
<tr>
<td>2 + passive obs. well</td>
<td>T1, T2, T3, P1, P2, P3 B, P4, C1, C2, PO1, PO2, PO3 B, PO4</td>
<td>0.2002 ± 0.4x10^{-3}</td>
</tr>
<tr>
<td>3 without data set TX</td>
<td>P1, P2, P3 B, P4, C1, C2</td>
<td>0.2001 ± 0.18x10^{-2}</td>
</tr>
<tr>
<td>3 with data set TX</td>
<td>TX, P1, P2, P3 B, P4, C1, C2</td>
<td>0.2004 ± 0.15x10^{-2}</td>
</tr>
<tr>
<td>3 without data set TX + passive obs. well</td>
<td>P1, P2, P3 B, P4, C1, C2, PO1, PO2, PO3 B, PO4</td>
<td>0.2003 ± 0.12x10^{-2}</td>
</tr>
<tr>
<td>3 with data set TX + passive obs. well</td>
<td>TX, P1, P2, P3 B, P4, C1, C2, PO1, PO2, PO3 B, PO4</td>
<td>0.2001 ± 0.14x10^{-2}</td>
</tr>
</tbody>
</table>

Test sequence 1 and 2 produced $S_{gr}$ estimates with uncertainties of the same order of magnitude, while test sequence 3 resulted in a ca 3-4 times larger estimation uncertainty compared to these. Further analysis showed that this higher uncertainty can be attributed to the lack of thermal test stages. Including pressure measurements from the passive observation well in the parameter estimation resulted in a decreased estimation uncertainty. The use of data set TX in the parameter estimation resulted in an increased or decreased estimation uncertainty depending on the case. The parameter estimation results suggest that the indicator-tracer approach for establishing residual gas saturation conditions would not increase the estimation uncertainty of $S_{gr}$, compared to the approach with injection of CO$_2$-saturated water. Another advantage of this approach is that less CO$_2$-saturated water is required than for the original test sequence.

In future research concerning the Heletz injection test, it would be of interest to perform multiple parameter estimation, as correlations between parameters (which are not necessary the same for all test sequences) may affect the estimation uncertainty. Further it is vital to physically study, through laboratory or field tests, the capability of the indicator-tracer approach to establish the residual gas saturation zone, verifying that the findings from the numerical simulations are reproducible.
4.2 Distribution of injected CO₂ in a stratified saline reservoir (PII)

Motivated by the preparation of injection experiments at the Heletz test site, Paper II focuses on studying the distribution of CO₂ in a stratified saline reservoir with a well screened over two high-permeable layers. This was done by means of coupled wellbore-reservoir flow simulations. The partitioning may influence the use of a formation as storage space. The study included (i) identifying formation and wellbore properties governing the distribution of CO₂ between high-permeable layers, (ii) a comparison of the distribution of CO₂ and water between the layers and the dependence on geometric and operational parameters and (iii) an estimation of the likely distribution of injected CO₂ at the Heletz test site (of interest for future field tests). The study also provided insight into the effect of neglecting the wellbore-reservoir flow coupling in numerical simulations of CO₂ injection.

Numerical modeling was carried out with T2Well/ECO2N (Pan et al., 2011) coupled to iTOUGH2 (Finsterle, 2007) through the PEST protocol (Doherty, 2008; Finsterle, 2011), see section 3.1 for details concerning these. Two different conceptual models were used; a Heletz-specific and a generic one, here referred to as the hypothetical model.

Figure 18 shows the conceptual model of the Heletz site. It had two high-permeable sandstone layers, referred to as H1 and H2 (2 and 9 m thick, respectively), over which the wellbore was perforated. The layers were separated and overlaid by impermeable layers, referred to as H3 and H4. The outer boundary was of no-flow type, but given a volume such that the estimated total layer volume of the site was accurately modeled.

The hypothetical model had two high-permeable layers, referred to as L1 and L2 (each 20 m thick), over which the wellbore was perforated. The layers were separated by a low-permeable layer, referred to as L3 (with a thickness of 1, 10 or 20 m). The model is displayed in Paper II. The outer boundary was open (Dirichlet boundary condition).

The same characteristic functions, as in Paper I was used here. Further details concerning parameters and assumptions can be found in Paper II.

The scenario simulated was injection of CO₂ at the wellhead. The total amounts of injected CO₂ were 1000 tons and 100 tons for the hypothetical and the Heletz-specific conceptual model, respectively. These amounts are of the magnitude used for characterization tests (prior to large-scale injection).

A code development was made specifically to enable the study:

- Automatic Leverett scaling of the Brooks-Corey gas entry pressure, depending on permeability and porosity, to use at the start of each simulation during the Morris sensitivity analysis.
Identification of parameters effecting the distribution: Parameters governing the distribution of CO$_2$ between the two high-permeable layers during injection were identified, by means of global sensitivity analysis using the Morris One-At-A-Time method (Morris, 1991), see section 3.1 for further details. The sensitivity of the CO$_2$ mass in the top layer at the end of injection, to 17 parameters was determined. These parameters were permeability ($k$), porosity ($\phi$), pore compressibility ($c_\phi$) and residual saturations ($S_{tr}$ and $S_{gr}$) of the different layers, the pipe wall roughness ($\varepsilon$) and injection temperature ($T_{inj}$). Further details can be found in Paper II. The calculated elementary effect (EE) for each parameter is displayed in Figure 19, when using the hypothetical model with the 10 m thick in-between layer and an injection rate of 5 kg/s. Here, a large mean EE reveals that the parameter has a high influence on the output. The parameter with the highest influence on the CO$_2$ distribution was the $k$ of the top layer ($k_1$). Other influential parameters were the $S_{gr}$ of the top layer ($S_{gr1}$), the $k$ of the bottom layer ($k_2$), the $S_{tr}$ of the top layer ($S_{tr1}$), the $S_{tr}$ of the bottom layer ($S_{tr2}$), the $S_{gr}$ of the bottom layer ($S_{gr2}$) and the $T_{inj}$. The properties of the top layer compared to those of the bottom layer, exhibited a relative higher influence on the partitioning of
Parameters with low influence on the partitioning included the $\phi$ for all layers ($\phi_{1-3}$), $c_{\phi}$ for all layers ($c_{\phi_{1-3}}$), in-between layer properties ($k_3$, $S_{tr3}$, $S_{gr3}$) and $\varepsilon$. A large variance of the EE reveals the presence of non-linearity or correlated parameters. This was seen for e.g. $S_{gr1}$, $S_{tr1}$, $k_1$ and $k_2$.

Here, the permeability values of the layers were varied independently. Carrying out the sensitivity analysis with $k_1$ and $k_2$ constrained to be identical showed that the influence (mean EE value) of $k$ on the distribution of CO$_2$ between the layers, was reduced by a factor of 4. Such a reduced influence was also found in sensitivity analysis of $S_{gr}$ when $S_{gr1}$ and $S_{gr2}$ was identical. This implies that the partitioning of CO$_2$ is most sensitive to the permeability ratio and residual saturation ratio of the layers.

**Comparison of water and CO$_2$ distribution and the dependence on geometric and operational parameters:** The hypothetical conceptual model was used to study the distribution of CO$_2$ and water between the layers during injection, and the influence of geometric and operational parameters. These parameters were the in-between layer thickness, perforation lengths and injection rate.

Figure 20 displays the partitioning of CO$_2$ and water between the layers for different in-between layer thicknesses. Cases with in-between layer thicknesses of 1, 10 or 20 m were run, in combination with several permeability ratios of the high-permeable layers, i.e. $k_1/k_2$ from 0.1 to 10, and different permeability values of the L3 layer. The partitioning is quantified by...
the logarithm mass ratio \( \log_{10}(M_1/M_2) \) of fluid that has partitioned to the top layer compared to the bottom layer. There was a one-to-one relationship between the logarithm mass ratio of water and the logarithm permeability ratio. The partitioning of water during injection was not dependent on the in-between layer thickness. For the injection of CO\(_2\), a larger part of the fluid partitioned to the top layer, than for the injection of water. This effect increased with increased in-between layer thickness. The CO\(_2\) partitioning depended on the permeability ratio as well as the actual permeability values of the layers. For the simulated scenarios the part of CO\(_2\) ending up in the top layer was at most 2-4.8 times higher than the corresponding part of water. The permeability of the in-between layer had negligible or at most minor effect on the partitioning.

The difference in water and CO\(_2\) distribution was attributed to that the latter experiencing buoyancy and the difference in pressure gradient experienced along the top and bottom layers in the case of a gas-filled well (i.e. for CO\(_2\) the pressure gradient along the top layer was somewhat larger than along the bottom layer).

The results highlight the importance of including the wellbore-reservoir flow coupling when simulating CO\(_2\) injection into a layered formation. Ignoring the coupling by using a boundary condition such as an injection rate of CO\(_2\) to each layer proportional to the layer transmissivity\(^\text{11}\) to water, corresponds to a partitioning equal to that of water. Therefore, the deviation of the CO\(_2\) partitioning from that of water in Figure 20, quantifies the inaccuracy when ignoring the wellbore-reservoir flow coupling for the different cases.

Further, the perforation lengths had a considerably effect on the simulated partitioning of CO\(_2\) and water between the layers during injection. The perforation length for each high-permeable layer ranged from 1/4\(^{th}\) of the thickness to the full thickness of the layer. Different combinations of perforation lengths for the two layers and three different permeability values were considered in the simulations. More details concerning results are given in Paper II. While the partitioning between the top and bottom layer of injected water depended on the perforation lengths of the layers, the partitioning of CO\(_2\) depended not only of the perforation lengths, but also on the permeability value of the layers (assumed equal). The results showed that more CO\(_2\) partitioned to the top layer compared to the bottom layer for some cases even when the perforation length of the top one was shorter compared to the bottom one. The effect was increased for higher permeability values.

\(^{11}\) Transmissivity is the product of the hydraulic conductivity, \( K \) \( ( = kpg/\mu) \), and the layer thickness, \( b \) (Freeze and Cherry, 1979). For water injection (single-phase system) the expected part of fluid partitioning to the top layer is equal to the relative transmissivity of the layer i.e. \( K_1*b_1/(K_1*b_1+ K_2*b_2) \), which is \( \approx k_1 * b_1/(k_1 * b_1 + k_2 * b_2) \). Here, 1 and 2 represents the top and bottom layer properties, respectively.
Figure 20. The logarithmized mass ratio (fluid mass in the top layer to fluid mass in the bottom layer) at the end of fluid injection as a function of the logarithmized layer permeability ratio, for an in-between layer thickness of a) 1 m, b) 10 m and c) 20 m. Reprinted with permission from John Wiley and Sons, originally published in Rasmussen et al. (2015a).

The results also showed that the injection rate can be used to slightly affect the partitioning of CO$_2$ between the two layers. Injection rates from 1 to 7
kg/s were considered. The fraction of CO₂ mass in the top layer at the end of injection, \( \frac{M_1}{M_1 + M_2} \), increased from 0.51 to 0.59 as the simulated injection rate was reduced from 7 to 1 kg/s. The density of the gas phase at the entrance to the top and bottom layer decreased (from ca 650 to 560 kg/m³) as the injection rate decreased (from 7 to 1 kg/s), making it more buoyant.

**Estimating the likely distribution of CO₂ at the Heletz site:** The distribution of CO₂ between two high-permeable layers during injection at the Heletz test site was simulated. Further, the potential to operationally affect this was investigated. The Heletz-specific conceptual model and Monte Carlo analysis were used (see section 3.1 for details). This approach yields an estimate of the uncertainty of the output (in this case the part of the injected CO₂ ending up in the top layer) using the probability distributions of the input parameters. Three input parameters were considered for each high-permeable layer; \( k \), \( S_{gr} \), and \( S_{tr} \). These were expected to be highly influential as indicated by the prior Morris sensitivity analysis. The parameter distribution for the permeability of each layer were based on analysis of field data for each layer\(^ {12} \), and the range of the residual saturations were based on a span seen in literature. For more details see Paper II.

Cases with different injection rates (0.6 to 1.2 kg/s), and perforation lengths for H1:H2 (2:9 or 2:7 m:m) were simulated. Some results of the analysis are shown in Figure 21. Figure 21a displays the probability \( F(x) \) for the part of CO₂ ending up in the top layer (H1) to be less or equal to \( x \). There is a 50% probability that \( \leq 23\% \) of the CO₂ partitions to H1, and a 60% probability that the part is \( \leq 32\% \), and so on. The relative small part is due to the considerably thinner layer thickness of H1, compared to H2.

In the case of the Heletz site, a change in injection rate from 1.2 to 0.6 kg/s resulted in a changed partitioning of CO₂ mass to the top layer (H1), see Figure 21b. Generally such a change resulted in an increase of the CO₂ mass partitioning to H1 with a few %, and for some cases with several tens of %.

Modifying the perforation length ratio of the layers (by reducing the screen of the bottom layer (H2) by two meters) from 2:9 m to 2:7 m, increased the mass of CO₂ partitioning to H1, see Figure 21c. The max increase was 7%.

It was concluded that the potential to operationally modify the distribution of CO₂ at the Heletz site was rather limited. The considerable difference in thickness of the layers strongly influenced the partitioning.

\(^{12}\) The \( k \) distributions were based on field logs of \( \phi \) from each layer collected over a larger area, 314 respectively 1326 data values, converted to \( k \) using a site-specific empirical \( \phi-k \) relationship (GII, 2010; Niemi et al., 2016). For one of the high-permeable layers, 41 \( k \) measurements on core samples were added to the data set (Niemi et al., 2016). These distributions were truncated and let to represent the possible \( k \) distribution for respective layer.
Figure 21. Result of the Monte Carlo analysis a) an empirical cumulative distribution function, where \( x \) is the part of \( \text{CO}_2 \) in the top layer (H1). The distribution of the change in \( \text{CO}_2 \) mass in H1 b) when the injection rate was reduced from 1.2 to 0.6 kg/s and c) when the bottom-layer perforation length was reduced by two meters. Reprinted with permission from John Wiley and Sons, originally published in Rasmusson et al. (2015a).
4.3 The effect of trapping model, geological heterogeneity and injection strategies on estimates of CO₂ trapping (PIII)

Residual and solubility trapping are two key processes for trapping during geological CO₂ storage. Motivated by the preparation of injection experiments at the Heletz test site, numerical modeling was carried out providing a systematic analysis concerning factors that may affect such trapping. The study included (i) an analysis of the capillary number conditions during the simulated scenarios (to evaluate whether dependence of this on residual trapping needed to be included in the simulator), (ii) a comparison of how different trapping models effect the simulated trapping, (iii) an analysis of how different injection strategies effect the trapping, and (iv) an analysis of how geological heterogeneity effects the trapping. A trapping model (also referred to as an IR curve) is a relationship relating the initial gas saturation \( S_{g1} \), i.e. the gas saturation at the end of drainage, to the residual gas saturation \( S_{gr} \) after imbibition. The simulator used was TOUGH2/iTOUGH2 (Finsterle, 2007; Pruess et al., 1999) with the ECO2N module (Pruess, 2005), GSLIB (Deutsch and Journel, 1998; Finsterle and Kowalsky, 2007) and hysteretic characteristic functions (Doughty, 2008), see section 3.1 for details. These have a capillary pressure function after van Genuchten (1980), and a relative permeability function after Parker and Lenhard (1987), Lenhard and Parker (1987) and van Genuchten (1980). Parameter values for these functions were found by manual fitting to Heletz-specific data provided by Benson et al. (2014); \( k_r \) for the CO₂ and water phase during drainage and imbibition from core-flooding experiments, and \( P_c \) during drainage from Mercury Intrusion Porosimetry (converted to scCO₂/water). The latter was adjusted using Leverett scaling. See Paper III for further details concerning parameter values and assumptions. Heterogeneous realizations were created using the Sequential Gaussian Simulation method (see section 3.1). The description of the geological heterogeneity was based on the work of Olofsson (2011), who used e.g. porosity data derived from resistivity logs from the site to determine a semi-variogram model.

In the study, the Heletz injection test site was depicted by the conceptual model displayed in Figure 22. Injection took place in the center of the model, along the thickness of two high-permeability sandstone layers (2 and 9 m thick) separated by an impermeable layer of shale (3 m thick).

Several code developments were made to enable the study:

- A user-defined observation, of the apparent \( N_c \), was added to the iTOUGH2 code. This made it possible to estimate the capillary number in a grid element during the simulation. See Paper III for further details.
- Additions were made in the hysteresis subroutine of TOUGH2 in the...
Figure 22. The 2D radially symmetric model used in the study. Here displayed with a) a cutthrough along the radius, b) a close-up of the inner 50 meters of the grid and c) one of the heterogeneous $k$-field realizations used. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2016).
form of four new trapping model options \((S_{gi}-S_{gr})\) relationships, see Table 4. The trapping models were the ones presented by Aissaoui, Jerauld, Spiteri et al. and the simplified version of Land.

- An addition was made in the TOUGH2 code, so that for each grid block the local porosity was correlated with the local absolute permeability, following a Heletz-specific empirical relationship\(^{13}\), i.e. providing simultaneously heterogeneous and correlated \(k\) and \(\varphi\)-fields.

- A development was made by including a version of Leverett scaling (Leverett, 1941) of capillary pressure which in addition to the standard one\(^{14}\) in the code also considers deviations of the porosity from that of the reference \((P_c = P_{c,ref} \cdot \sqrt{k_{ref} \cdot \varphi / k \cdot q_{ref}})\). This was employed for simulations featuring heterogeneity. Locally varying capillary entry pressures affect the spreading and migration pathways of the CO\(_2\) plume.

The standard trapping model in the TOUGH2 hysteretic code is the modified Land’s trapping model\(^{15}\); an altered version of the Land trapping model (Land, 1968). The modified Land model has the two input parameters, \(S_{gr_{max}}\) and \(S_{tr}\). Here, these were 0.2 and 0.61, respectively.

**Table 4. Added trapping models.**

<table>
<thead>
<tr>
<th>Name</th>
<th>Relationship</th>
<th>Parameter values used in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aissaoui(^{a,b})</td>
<td>(S_{gr} = \frac{S_{gr_{max}} \cdot S_{gi}}{S_{go}} ) if (S_{gi} &lt; S_{go}) (S_{gr} = S_{gr_{max}} ) if (S_{gi} \geq S_{go})</td>
<td>(S_{gr_{max}}=0.2) (S_{go}=0.6)</td>
</tr>
<tr>
<td>Jerauld(^{c})</td>
<td>(S_{gr} = \frac{S_{gi}}{1 + \left(\frac{1}{S_{gr_{max}}} - 1\right) \cdot S_{gi}^{\frac{1}{S_{gr_{max}}}}})</td>
<td>(S_{gr_{max}}=0.2)</td>
</tr>
<tr>
<td>Spiteri et al.(^{d})</td>
<td>(S_{gr} = \alpha \cdot S_{gi} - \beta \cdot S_{gi}^2)</td>
<td>(\alpha=0.676) (\beta=0.306)</td>
</tr>
<tr>
<td>Simplified Land</td>
<td>(S_{gr} = \frac{S_{gi}}{1 + CS_{gi}})</td>
<td>(C=2.2)</td>
</tr>
</tbody>
</table>

\(^{a}\)Suzanne et al. (2003) citing Aissaoui (1983). \(^{b}\)\(S_{go}\) is equal to \(1-S_{wir}\) if \(\varphi<0.10\) and is a value in the range \([0.60, 0.70]\) if \(\varphi>0.13\), with \(S_{wir}\) being the maximum residual water saturation.

\(^{c}\)Jerauld (1997). \(^{d}\)Spiteri et al. (2005). \(^{e}\)Same value as that fitted from the characteristic curves.

\(^{f}\)Estimated by Hingerl et al. (2016), who fitted the relationship to Heletz data, i.e. \(S_{gi}-S_{gr}\) data pairs measured using X-ray CT scanning. Note that the trapping model implicitly assumes a slightly different \(S_{gr_{max}}\) than the others.

\(^{13}\)\(k=0.006exp(0.5*\varphi)\) with \(k\) expressed in mD and \(\varphi\) in \% (GII, 2010).

\(^{14}\)\(P_c = P_{c,ref} \cdot \sqrt{k_{ref} / k} \) where \(1 - S_{t}^3\) is equal to \(S_{gr}\).
The schedules of the alternative injection strategies in the study are displayed in Table 5. 'Conventional injection' means that the CO₂ is injected and no further intervention is made. The proposed injection strategies for enhanced trapping add to the CO₂ injection, co-injection of fluid or chase-fluid stages, or partition the CO₂ injection into multiple smaller injections. For information concerning earlier studies on injection strategies see Paper III. 500 tons of CO₂ was injected, i.e. an amount suitable for a small-scale field test. The run time (injection and observation period) was 30 days.

Table 5. Alternative injection strategies. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2016).

<table>
<thead>
<tr>
<th>Strategy</th>
<th>Description</th>
<th>Duration of stages [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: 'Conventional injection'</td>
<td>-CO₂ injection (500 tons, 1 kg/s)</td>
<td>~5.8</td>
</tr>
<tr>
<td>2: 'Chased injection'</td>
<td>-CO₂ injection (500 tons, 1 kg/s)</td>
<td>~5.8</td>
</tr>
<tr>
<td></td>
<td>-Chase water injection (125 tons, 0.8 kg/s)</td>
<td>~1.8</td>
</tr>
<tr>
<td>3: 'Co-injection'</td>
<td>-Co-injection of CO₂ with a small portion of water</td>
<td>~5.8</td>
</tr>
<tr>
<td></td>
<td>(500 tons, 1 kg/s and 85 tons, 0.17 kg/s, respectively)</td>
<td></td>
</tr>
<tr>
<td>4: 'Mixed co-injection and chased injection'</td>
<td>-Co-injection of CO₂ with a small portion of water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(500 tons, 1 kg/s and 85 tons, 0.17 kg/s, respectively)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-Chase water injection (125 tons, 0.8 kg/s)</td>
<td>~1.8</td>
</tr>
<tr>
<td>5: 'Cyclic injection'</td>
<td>-CO₂ injection (250 tons, 1 kg/s)</td>
<td>~2.9</td>
</tr>
<tr>
<td></td>
<td>-Break (0.9 days)</td>
<td>~0.9</td>
</tr>
<tr>
<td>6: 'Small WAG injection'</td>
<td>-CO₂ injection (250 tons, 1 kg/s)</td>
<td>~2.9</td>
</tr>
<tr>
<td></td>
<td>-Water injection (62.5 tons, 0.8 kg/s)</td>
<td>~0.9</td>
</tr>
<tr>
<td></td>
<td>-CO₂ injection (250 tons, 1 kg/s)</td>
<td>~2.9</td>
</tr>
<tr>
<td></td>
<td>-Water injection (62.5 tons, 0.8 kg/s)</td>
<td>~0.9</td>
</tr>
</tbody>
</table>

*aCorresponds to 0.10 volumetric flow of water during co-injection.

In the study, trapping was quantified using indexes from Nghiem et al. (2009). The residual gas trapping index, RTI(t), is the ratio of the residual CO₂ mass to the total mass of CO₂ injected, at time t. The solubility trapping index, STI(t), is the ratio of the dissolved CO₂ mass to the total mass of CO₂ injected, at time t. The trapping efficiency index, TEI(t), is the sum of the two former indexes. Trapping indexes at day 30 for the simulated cases can be found in Table 6. Under the prevailing conditions and time scale, residual trapping was the dominant trapping mechanism, while solubility trapping played a secondary role.
Table 6. Summary of trapping indexes at the end of the observation period, when simulating different injection strategies and using different trapping models; modified Land (A) - TOUGH2 standard, Aissaoui (B), Jerauld (C), Spiteri et al. (D) or simplified Land (E). The parentheses contain the median followed by the [min max] values of the trapping indexes for the heterogeneous realizations. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2016).

<table>
<thead>
<tr>
<th>Injection strategy</th>
<th>RTI</th>
<th>STI</th>
<th>TEI</th>
</tr>
</thead>
<tbody>
<tr>
<td>'Conventional injection'</td>
<td>A: 0.52 (0.46 [0.36 0.54])</td>
<td>A: 0.23 (0.23 [0.22 0.27])</td>
<td>A: 0.75 (0.70 [0.59 0.81])</td>
</tr>
<tr>
<td></td>
<td>B: 0.26</td>
<td>B: 0.26</td>
<td>B: 0.52</td>
</tr>
<tr>
<td></td>
<td>C: 0.47</td>
<td>C: 0.24</td>
<td>C: 0.71</td>
</tr>
<tr>
<td></td>
<td>D: 0.51</td>
<td>D: 0.24</td>
<td>D: 0.75</td>
</tr>
<tr>
<td></td>
<td>E: 0.54</td>
<td>E: 0.23</td>
<td>E: 0.78</td>
</tr>
<tr>
<td>'Chased injection'</td>
<td>A: 0.59 (0.53 [0.45 0.60])</td>
<td>A: 0.25 (0.26 [0.24 0.29])</td>
<td>A: 0.84 (0.78 [0.69 0.88])</td>
</tr>
<tr>
<td></td>
<td>B: 0.29</td>
<td>B: 0.27</td>
<td>B: 0.57</td>
</tr>
<tr>
<td></td>
<td>C: 0.54</td>
<td>C: 0.26</td>
<td>C: 0.80</td>
</tr>
<tr>
<td></td>
<td>D: 0.58</td>
<td>D: 0.25</td>
<td>D: 0.83</td>
</tr>
<tr>
<td></td>
<td>E: 0.61</td>
<td>E: 0.25</td>
<td>E: 0.86</td>
</tr>
<tr>
<td>'Co-injection'</td>
<td>A: 0.54 (0.48 [0.40 0.54])</td>
<td>A: 0.25 (0.25 [0.23 0.29])</td>
<td>A: 0.79 (0.74 [0.63 0.81])</td>
</tr>
<tr>
<td></td>
<td>B: 0.27</td>
<td>B: 0.27</td>
<td>B: 0.54</td>
</tr>
<tr>
<td></td>
<td>C: 0.50</td>
<td>C: 0.25</td>
<td>C: 0.75</td>
</tr>
<tr>
<td></td>
<td>D: 0.52</td>
<td>D: 0.25</td>
<td>D: 0.78</td>
</tr>
<tr>
<td></td>
<td>E: 0.57</td>
<td>E: 0.25</td>
<td>E: 0.81</td>
</tr>
<tr>
<td>'Mixed co-injection and chased injection'</td>
<td>A: 0.59 (0.54 [0.47 0.59])</td>
<td>A: 0.27 (0.27 [0.25 0.30])</td>
<td>A: 0.86 (0.81 [0.72 0.89])</td>
</tr>
<tr>
<td></td>
<td>B: 0.29</td>
<td>B: 0.29</td>
<td>B: 0.57</td>
</tr>
<tr>
<td></td>
<td>C: 0.55</td>
<td>C: 0.27</td>
<td>C: 0.82</td>
</tr>
<tr>
<td></td>
<td>D: 0.56</td>
<td>D: 0.27</td>
<td>D: 0.83</td>
</tr>
<tr>
<td></td>
<td>E: 0.61</td>
<td>E: 0.26</td>
<td>E: 0.88</td>
</tr>
<tr>
<td>'Cyclic injection'</td>
<td>A: 0.51 (0.46 [0.37 0.51])</td>
<td>A: 0.23 (0.23 [0.22 0.27])</td>
<td>A: 0.74 (0.69 [0.60 0.77])</td>
</tr>
<tr>
<td></td>
<td>B: 0.26</td>
<td>B: 0.25</td>
<td>B: 0.51</td>
</tr>
<tr>
<td></td>
<td>C: 0.46</td>
<td>C: 0.23</td>
<td>C: 0.69</td>
</tr>
<tr>
<td></td>
<td>D: 0.50</td>
<td>D: 0.23</td>
<td>D: 0.74</td>
</tr>
<tr>
<td></td>
<td>E: 0.53</td>
<td>E: 0.23</td>
<td>E: 0.76</td>
</tr>
<tr>
<td>'Small WAG injection'</td>
<td>A: 0.56 (0.52 [0.44 0.58])</td>
<td>A: 0.25 (0.25 [0.23 0.28])</td>
<td>A: 0.81 (0.77 [0.68 0.86])</td>
</tr>
<tr>
<td></td>
<td>B: 0.27</td>
<td>B: 0.27</td>
<td>B: 0.54</td>
</tr>
<tr>
<td></td>
<td>C: 0.52</td>
<td>C: 0.25</td>
<td>C: 0.77</td>
</tr>
<tr>
<td></td>
<td>D: 0.55</td>
<td>D: 0.25</td>
<td>D: 0.80</td>
</tr>
<tr>
<td></td>
<td>E: 0.59</td>
<td>E: 0.24</td>
<td>E: 0.83</td>
</tr>
</tbody>
</table>

**Analysis of capillary number:** The analysis of the capillary numbers showed that under the simulated conditions, no dependence of $N_c$ on $S_{gr}$ was needed to be included in the trapping model. See **Paper II** for further details. Although this is the case in the current study, other rock properties or injection rates may make such dependence significant, and needed to be accounted for.

**The effect of trapping model on trapping:** The magnitude of the simulated trapping was affected by the choice of trapping model (Figure 23 and Table 6).
The simulated trapping results were more similar when employing four of the trapping models, while the result of the Aissaoui trapping model deviated from these. The difference in RTI was 0.28 between the results for the simplified Land model and the Aissaoui model at the end of the observation period. The difference is caused by the difference in shape of the IR curves.
for low $S_{gi}$ values. The highest solubility trapping index was produced by the Aissaoui trapping model.

The evidently considerably impact the choice of trapping model may have on the outcome of the simulation results urges the use of an appropriate trapping model, i.e. selecting an as correct as possible description of the process for the specific site. A comparison study by Suzanne et al. (2003) examining a large number of experimental $S_{gr}$-$S_{gi}$ relationships of gas trapping in sandstone concludes that the Aissaoui trapping model is in best agreement with experimental data. However, for a specific case the trapping model is best selected on individual basis. Here, the constants for the Spiteri and simplified Land models were fitted from direct $S_{gr}$-$S_{g}$ measurements on core samples from the actual site, and therefore likely to be an appropriate choice. Potentially the two trapping models producing the most extreme results in this study could be used in parallel in predictive modeling studies, thereby giving an indication of the uncertainty the choice of trapping model brings into the estimated residual trapping.

The effect of injection strategy on trapping: Table 6 shows results concerning trapping when using different injection strategies\textsuperscript{16}. The most enhancement of trapping compared to the 'conventional injection' (TEI of 0.75) was given by the 'mixed co-injection and chased injection' (TEI of 0.86) and the 'chased injection' (TEI of 0.84).

All the strategies but the 'cyclic injection' (TEI of 0.74) had enhanced the trapping at the end of observation. Enhancement was primarily achieved through increased residual trapping. Figure 24 shows that 'cyclic injection' and 'small WAG injection' compared to 'conventional injection', can enhance the short-time residual trapping considerably.

The greatest enhancement in RTI was given by the 'mixed co-injection and chased injection' and the 'chased injection' strategies (with RTIs of 0.59), compared to the 'conventional injection' (RTI of 0.52).

The greatest enhancement in STI was given by the 'mixed co-injection and chased injection' strategy (STI of 0.27), providing a small increased solubility trapping compared to 'conventional injection' (STI of 0.23).

When chase-water injections were used ('chased injection', 'mixed co-injection and chased injection' and 'small WAG injection'), no residually trapped CO$_2$ remained near the well at day 30, as a result of dissolution.

\textsuperscript{16} In this section results when employing the modified Land trapping model are featured (similar trends were however seen independent of the choice of trapping model).
Figure 24. The a) RTI, b) STI and c) TEI, when simulating different injection strategies in a homogenous formation. Reprinted with permission from Elsevier, originally published in Rasmusson et al. (2016).

The effect of geological heterogeneity on trapping: When studying the influence of geological heterogeneity on solubility and residual trapping, simulations were carried for 31 different $k/\phi$-field realizations\textsuperscript{17}, for each injection strategy. Results are shown in Table 6.

\textsuperscript{17} For these simulations the modified Land trapping model (standard) was used.
Most simulations featuring heterogeneous realizations exhibited less trapping than the homogeneous case, at the end of observation. The median TEI was 0.05 lower for the heterogeneous cases compared to the TEI for the homogeneous case when a 'conventional injection' was employed. This behavior was similar for all strategies. The behavior of TEI was primarily explained by the evolution of RTI. For most of the observation time, RTI exhibited a lower median RTI for the heterogeneous cases compared to the RTI for the homogeneous case. However, STI for the homogeneous and heterogeneous cases exhibited only a slight difference.

Analysis of the simulation results showed a strong correlation between the value of TEI and the n.o. elements with residual gas, and a slightly weaker correlation between the value of TEI and the n.o. elements with gas phase. Further, the magnitude of TEI was correlated with the location and spread of the mass center of the gas phase (plume) in the vertical direction. A higher TEI corresponded to a mass center located lower in the vertical direction and a larger vertical spread. A gas-phase mass center situated deeper in the storage layers at the end of injection, offers the potential of more mobile gas phase available for buoyant migration over a longer vertical distance. This leads to more imbibition taking place during the observation period. A significant correlation was also identified between the magnitude of TEI and the change in location in the vertical direction of the gas-phase mass center (from the injection stop to the end of observation). A higher TEI was associated with a longer displacement.

The plume of the gas phase had a more distinct radial character in a homogeneous $k/\phi$-field, compared to heterogeneous fields. Heterogeneity caused channeling and preferential flow paths. In this study, geological heterogeneity, in comparison to the homogeneous case, usually caused a shortened vertical displacement of the gas-phase mass center (from that the injection stopped to the end of the observation period), i.e. heterogeneity hampered the gas plume’s buoyant migration. This in turn resulted in less imbibition and thereby less residual CO$_2$ trapping.

For the simulated scenarios in the study, the choice of trapping model resulted in a maximum difference of 0.31 in TEI (comparing the Aissaoui trapping model with the simplified Land trapping model when simulating the 'mixed co-injection and chased injection' strategy, Table 6). The choice of injection strategy changed the TEI by a maximum of 0.12 (comparing the 'mixed co-injection and chased injection' and the 'cyclic injection' strategy, Table 6) and the geological heterogeneity resulted in a maximum difference of 0.22 in TEI (comparing the lowest and highest TEI for the 'conventional injection', Table 6). This shows the significance of using an appropriate trapping model and geological heterogeneity model when simulating CO$_2$ sequestration projects.
4.4 Residual trapping of CO₂ at the pore-scale (PIV)

To investigate residual trapping at the pore-scale during geological storage, a quasi-static\textsuperscript{18} pore-network model (PNM) was developed by the author of this thesis. The code is part of the results of the graduate studies and is presented in section 3.2. The PNM can simulate drainage (CO₂ intrusion) followed by imbibition (water flooding).

The study included (i) a sensitivity analysis of residual trapping to some key parameters to verify the PNM’s ability to capture the trapping behavior in agreement with earlier studies, (ii) a calibration of a network to Heletz sandstone data, and (iii) an estimation of the initial-residual gas saturation curve (IR curve) for CO₂ in a network representation of Heletz sandstone. Such a curve may be used in macroscopic simulations.

Prior to the sensitivity study, a study of the effect of lattice size on the simulation result ($S_{gr}$, absolute permeability and effective porosity) showed that a lattice size of $20^3$ would be sufficient for the result not to be affected by the lattice size, itself.

Figure 25 shows result from the sensitivity analysis involving network realizations of a generic sandstone (based on 26 realizations of lattice size $20^3$). The mean coordination number ($\bar{z}$), aspect ratio ($R_{asp}$) and advancing contact angle ($\theta_a$) were all shown to influence the predicted $S_{gr}$. The parameter ranges considered were 3.5-4.5, 1.5-2.5 and 0°-40°, respectively.

An increased $\bar{z}$ resulted in a lower $S_{gr}$, as piston-type displacement in throats and cooperative pore body filling were favored, while the occurrence of snap-off events in throats was hampered (Table 7). Therefore a higher $\bar{z}$ leads to more non-wetting phase leaving the system during imbibition. A high $\bar{z}$ offers a higher number of potential escape paths for the non-wetting phase (here CO₂) during imbibition.

An increased $R_{asp}$ resulted in a higher $S_{gr}$, as snap-off events in throats were favoured and piston-type displacement was hampered (Table 7). Snap-off in throats divides the CO₂, thereby producing immobile clusters. The number of residual clusters were higher for higher values of the $R_{asp}$ (Table 7).

An increased $\theta_a$ resulted in a lower $S_{gr}$, as piston-type displacement in throats and cooperative pore body filling were promoted and snap-off in throats was impeded. This led to improved displacement of CO₂ from the network and less clusters formed (Table 7).

The residual-trapping behavior of the PNM, with regard to the key parameters, was consistent with findings from laboratory and pore network modeling studies on two-phase flow.

\textsuperscript{18} Quasi-static simulations are valid for conditions where the flow is governed by capillary forces.
Figure 25. Result from drainage-imbibition simulations, showing the effect of a) $\bar{z}$, b) $R_{asp}$ and c) $\theta_a$ on the magnitude of simulated $S_{gr}$ (26 realizations were run).
Table 7. Percentage occurrences of displacement and trapping events in the simulations included in the sensitivity analysis (average based on 26 networks). Also shown are the number of residual CO₂ clusters at the end of imbibition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Piston-type disp. in throats [%]</th>
<th>Piston-type disp. in bodies [%]</th>
<th>Snap-off in throats [%]</th>
<th>Snap-off in bodies [%]</th>
<th>Cooperative pore body filling [%]</th>
<th>Clusters [no]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{z}$</td>
<td>3.5</td>
<td>28</td>
<td>23</td>
<td>44</td>
<td>0.08</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>31</td>
<td>22</td>
<td>41</td>
<td>0.06</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>35</td>
<td>21</td>
<td>36</td>
<td>0.05</td>
<td>8</td>
</tr>
<tr>
<td>$R_{asp}$</td>
<td>1.5</td>
<td>35</td>
<td>26</td>
<td>33</td>
<td>0.1</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>31</td>
<td>22</td>
<td>41</td>
<td>0.06</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>30</td>
<td>19</td>
<td>44</td>
<td>0.04</td>
<td>7</td>
</tr>
<tr>
<td>$\theta_d$</td>
<td>0</td>
<td>31</td>
<td>22</td>
<td>41</td>
<td>0.06</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>33</td>
<td>25</td>
<td>36</td>
<td>0.008</td>
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<td>28</td>
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<td></td>
<td>40</td>
<td>49</td>
<td>25</td>
<td>14</td>
<td>0</td>
<td>13</td>
</tr>
</tbody>
</table>

The PNM was manually calibrated to experimental data from core samples of Heletz sandstone. This was done to find a network representation that had properties and exhibited a flow-behavior (absolute permeability, porosity, tortuosity, drainage $P_c-S_w$ and drainage $k_T-S_w$ curves) similar to that of the real rock. The calibration comprised of adjusting PNM-input parameters such as the mean coordination number, body center distances, parameters for the throat size distribution, etc. to obtain a reasonable match between PNM-output and experimental data.

Drainage-imbibition scenarios were simulated with the calibrated network (Figure 26). Different turning point saturations were used to obtain many $S_{gl}-S_{gr}$ pairs (Figure 27). From these pairs, IR curves for CO₂ in Heletz sandstone were estimated (eq. 41 and 42) by fitting of 5th degree polynomials. Additionally, Figure 27 display the experimental $S_{gl}-S_{gr}$ pairs and the two trapping models which Hingerl et al. (2016) fitted parameters for using the direct measurements. Hingerl et al. used a X-ray CT scanning procedure to make these measurements.
Figure 26. Network representing Heletz sandstone. It consists of 7615 connected pores and 13807 throats, and has a volume of 4.1 mm$^3$.

\[
S_{gr} = -7.1895 \times S_{gi}^5 + 14.455 \times S_{gi}^4 - 10.739 \times S_{gi}^3 + 3.7112 \times S_{gi}^2 + 0.24129 \times S_{gi} + 0.0034776 \quad (\text{for } \theta_a=0^\circ) \quad (41)
\]

\[
S_{gr} = -8.8183 \times S_{gi}^5 + 16.908 \times S_{gi}^4 - 11.63 \times S_{gi}^3 + 3.4727 \times S_{gi}^2 + 0.19157 \times S_{gi} + 0.0043037 \quad (\text{for } \theta_a=40^\circ) \quad (42)
\]

In Figure 27 the red vertical lines subdivide the $S_{gi}$ space into three parts. Direct measurements of $S_{gi}$-$S_{gr}$ pairs have only been made for the middle interval. In this middle interval the results of the PNM simulations when assuming an $\theta_a=40^\circ$, agreed well with the experimental data. However, results from the PNM simulations when assuming an $\theta_a=0^\circ$, estimated a higher trapping.

Outside the middle interval direct measurement data are lacking, and the fitted IR curves can be seen as an extrapolation. For low $S_{gi}$ values the PNM simulation resulted in a slightly lower estimated trapping than the fitted IR curves indicated. For high $S_{gi}$ values the discrepancy between the PNM simulation results and the IR curves fitted by Hingerl et al. (2016) was quite substantial. Discrepancies between the PNM-simulation results and direct measurements may arise from failure of the model to capture the geological
heterogeneity of the rock e.g. aspects of connectivity, or making incorrect assumptions regarding the advancing contact angle.

Further the PNM simulation estimated the residual water saturation to be 0.05 for the network representing Heletz sandstone. The corresponding residual CO$_2$ saturation was estimated to be 0.58 or 0.29 (for an $\theta_a$ of 0° and 40°, respectively). The cluster size distribution was shown to be bimodal, likely arising from the bimodal radii size distribution of the throats.

When the advancing contact angle was 0°, the most commonly occurring pore-scale mechanism in the simulations was snap-off. However, if the advancing contact angle was higher, piston-type displacement in throats and bodies was instead the most commonly occurring pore-scale mechanism. A higher advancing contact angle hampers the snap-off mechanism, leading to more CO$_2$ escaping the system and fewer residual clusters appearing.

A correct IR curve is crucial for large scale simulations, as it affects estimations of trapping. The PNM was used to estimate $S_{gi}$-$S_{gr}$ pairs, complementing data or substituting for data where no direct measurements were available, or were difficult to measure. The results thereby gave valuable benefits in understanding residual saturation and trapping efficiency.
insight into the IR curve. The findings of this study improve the understanding of residual CO$_2$ trapping in Heletz sandstone at the pore scale and the simulation results complement measured data.
Geological storage of carbon dioxide (geological CO$_2$ sequestration) in deep saline aquifers is one way of mitigating the release of this exhaust greenhouse gas to the atmosphere. Understanding of the processes taking place during geological CO$_2$ sequestration, development of methods that can characterize such processes and development of models that can capture this behavior is essential for the planning of future CO$_2$ storage projects and predicting their outcomes. In this thesis attention is given to numerical modeling of geohydrological processes, in particular residual trapping, occurring during CO$_2$ injection tests at the Heletz site. The work features both field-scale and pore-scale studies of this trapping mechanism. Capillary trapping not only provides opportunity of containment of phases, it also affects the ease with which fluid phases can migrate in porous media.

As residual trapping has been identified as a potentially greatly important and secure mechanism to hold stored CO$_2$ in the subsurface, development of field-test sequences that can aid the estimation of in-situ residual trapping is valuable. Providing such an estimate of the residual gas saturation ($S_{gr}$) can lead to improved assessment of the storage potential at a site. In Paper I alternative push-pull test sequences, intermediate-scale characterization tests, for estimating the in-situ residual CO$_2$ saturation were analyzed and compared for their ability to quantify $S_{gr}$. A new approach for establishing residual gas saturation conditions in-situ by using withdrawal and an indicator-tracer was studied. Additionally, the effect (on the parameter estimation) of including data sets of pressure measurements from a closely located observation well was explored. Results from numerical modeling, including sensitivity analysis and parameter estimation, indicate that under the assumptions of the study, the use of a novel indicator-tracer approach to establish the residual gas saturation zone may be a viable alternative to the use of CO$_2$-saturated water injection. This leads to $S_{gr}$ estimates with an uncertainty of the same magnitude, but using less CO$_2$-saturated water than the original test sequence. Excluding thermal test stages was seen to increase the estimation uncertainty. Including data sets of pressure from a nearby observation well in the parameter estimation reduced the estimation uncertainty. The result of Paper I aided decisions concerning the test design to employ for the field experiment at the Heletz site, within the EU FP7 MUSTANG and TRUST projects.
Paper II concerns injection of CO\textsubscript{2} into a multi-layered formation with a wellbore perforated over multiple high-permeable layers. For CO\textsubscript{2} injection into such a system, the proportion of CO\textsubscript{2} partitioning to individual layers may influence the storage in the formation, e.g. the plume footprint (affecting issues such as storage security and monitoring). In Paper II, the distribution of CO\textsubscript{2} during injection into a layered formation was studied by means of numerical modeling with a coupled wellbore-reservoir flow simulator. Results showed that the CO\textsubscript{2} partitioning was dependent on parameters such as the permeability of the layers and the ratio of these, residual saturations, in-between layer thickness, perforation lengths and the injection rate. The two latter, operational parameters, can be used to modify to some degree the distribution of CO\textsubscript{2} between the layers. However, for the case of the Heletz site the analysis results indicated that the potential to operationally modify the CO\textsubscript{2} distribution between the layers was limited. Compared to water, a larger part of the CO\textsubscript{2} distribute to the top layer, due to density differences and a difference in pressure gradient along the layers. The results indicate the importance of including the coupling of wellbore-reservoir flow in numerical simulations of CO\textsubscript{2} injection. If instead a boundary condition such as an inflow rate to each layer proportional to the layer's transmissivity to water is used, a considerable underestimation of the part of CO\textsubscript{2} partitioning to the top layer may occur.

The use of a simulator with properly described trapping mechanisms and accounting for properties pertinent to these mechanisms is essential for credible predictions concerning storage operations. This can be used to estimate the fraction of stored CO\textsubscript{2} trapped by different mechanism and to develop operational methods (such as special injection designs) to maximize the total trapping in a formation. In Paper III residual trapping and solubility trapping occurring during a small-scale field injection were studied using numerical modeling. The influence of the assumed IR curve\textsuperscript{19} (trapping model), the geological heterogeneity and the injection strategy on the estimated trapping was studied. Conclusion drawn from the result of Paper III include that residual trapping can be expected to be the dominant trapping mechanism under the conditions and time scale of the study. The addition of chase-fluid stages to a conventional CO\textsubscript{2} injection can provide enhanced trapping. A maximal enhancement of 0.11 TEI (the ratio of mass of the residually and solubility trapped CO\textsubscript{2} to the total mass of injected CO\textsubscript{2}), was found for the simulated scenarios at the end of observation. Primarily, the enhancement arises from increased residual trapping; however, the solubility trapping is also promoted by such a procedure. Further, the result indicates that geological heterogeneity generally decreases trapping, due to retardation of the buoyant migration of the gas plume, causing less imbibition and thereby less residual trapping to occur. The choice of employed IR curve had a signifi-

\textsuperscript{19} Relationship between the initial gas saturation and the residual gas saturation.
cant effect on the magnitude of the predicted residual trapping; the simplified Land trapping model giving the highest residual trapping, and the Aissaoui trapping model the lowest. However, most of the IR curves in the study yielded similar trapping results. The paper highlights the importance of employing an appropriate trapping model and description of geological heterogeneity for a site when carrying out simulations of CO₂ sequestration, as different assumptions may result in substantial discrepancies in estimated trapping. When a less appropriate trapping model is employed this may result in under- or overestimation of the CO₂ trapping, giving a false impression of the quantity of CO₂ that can be securely stored.

Residual trapping is a result of pore-scale displacement and trapping mechanisms. In Paper IV a closer investigation was carried out concerning these pore-scale events. A pore-network model (PNM) was developed and used for simulating drainage-imbibition scenarios, i.e. CO₂ intrusion followed by water flooding. In the paper a sensitivity analysis of the effect of three pore-scale features (mean coordination number, aspect ratio and advancing contact angle) on the predicted residual CO₂ saturation in generic sandstone was made. The results showed that the PNM was able to capture the influence of these parameters on $S_{gr}$ in agreement with earlier studies on two-phase flow systems. Further a network representation of Heletz sandstone was generated and used to simulate scenarios providing $S_{gi}$-$S_{gr}$ (initial gas saturation – residual gas saturation) pairs. These were used to estimate an IR curve (trapping curve) for the entire physical $S_{gi}$ range, also where experimental data was lacking. The advancing contact angle had a significant effect on the prediction results. The occurrence of different pore-scale displacement and trapping mechanisms was also determined. The retrieved IR curve can be used in larger-scale simulations and the PNM can be used to further analyze the effect of different conditions on the residual trapping.

To summarize, this thesis has covered numerical modeling and analysis of hydrogeological processes, with focus on residual trapping, occurring during geological CO₂ storage in deep saline aquifers. The subject was approached both through pore-scale and field-scale modeling. Results of the work included analysis of different field test sequences for characterization of trapping, analysis of aspects of how to model such processes and development of a simulator for pore-scale trapping simulations to be used in future studies.
6. Acknowledgements

I would like to thank my supervisor Auli Niemi and co-supervisor Fritjof Fagerlund, Yvonne Tsang and Chin-Fu Tsang for advices and commenting of manuscripts, which have been of great value to my work. Further I would like to thank the co-authors of the papers in this thesis for their contributions, the anonymous reviewers of the published papers whose constructive comments have improved the papers and colleagues at the Department of Earth Sciences and Geocentrum for these years.

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7. Sammanfattning på svenska

Geologisk lagring av koldioxid (CO$_2$) i djupt belägna saltvattenakvifärer är en metod för att motverka utsläpp av växthusgas till atmosfären. Kunskap om de geohydrologiska processer som sker vid geologisk koldioxidlagring, utveckling av metoder för att karakterisera dessa processer, samt utveckling av modeller som kan beskriva dessa är av stor betydelse för planering av framtida koldioxidlagringsprojekt och vid estimering av vad som kommer att ske med den lagrade koldioxiden. Denna avhandling behandlar numerisk modellering av geohydrologiska processer, med fokus på kapillär fastläggning\textsuperscript{20} (residual trapping), under injekteringsexperiment vid Heletz. Arbetet omfattar studier av denna mekanism både på fält- och por-skalan. Förutom att kapillär fastläggning möjliggör lagring, påverkar den även flödet av fluider i det porösa mediet.

Kapillär fastläggning har identifierats som en betydande och säker mekanism för lagring av CO$_2$ i berggrunden. Utveckling av fälttest för estimering av kapillärt bunden CO$_2$-mättnad ($S_{gr}$) in-situ är därför värdefull. Sådana test kan ge en uppskattning av lagringspotentialen på en plats. I Paper I analyseras och jämförs alternativa karakteriseringstestsekvenser (så kallad push-pull tests) med avseende på deras förmåga att kvantifiera $S_{gr}$ in-situ. Ett nytt tillvägagångssätt för att skapa en zon av kapillärt bunden CO$_2$ genom utpumpning och användning av ett indikatorspårämne undersökt. Dessutom studerades effekten (på parameterestimeringen) av att inkludera data i form av tryckmätningar från en närliggande observationsbrunn. Resultat från den numeriska modelleringen, bestående av känslighetsanalys och parameterestimering, indikerar att för de antaganden gjorda i studien, kan det nya tillvägagångssättet att upprätta en sådan zon vara ett alternativ till tillvägagångssättet där CO$_2$-mättat vatten injekteras. Den nya metoden estimerar $S_{gr}$ med en osäkerhet av samma storlek som den gamla, men använder en mindre mängd CO$_2$-mättat vatten än originaltestsekvensen. Att utesluta termiska tester i testsekvensen ökade osäkerheten i estimeringen. Att inkludera data gällande tryck från en närliggande observationsbrunn i parameterestimeringen minskade osäkerheten i uppskattningen. Resultat från Paper I ligger till grund för beslut kring testdesignen för ett CO$_2$-injekteringsexperiment i fält som utfördes vid Heletz, inom EU FP7-projekteten MUSTANG och TRUST.

\textsuperscript{20} Då koldioxid blir kapillärt bunden.
**Paper II** behandlar injektering av CO$_2$ i stratifierade formationer (dvs. sådana bestående av multila lager) med en brunn perforerad över flera högpermeabla lager. Vid injektering av CO$_2$ i ett sådant system, kan andelen av CO$_2$ som fördelas till individuella lager påverka lagringen i formationen, t.ex. plymens bredd (vilket påverkar frågor så som lagringssäkerhet och övervakningsmöjligheter). I **Paper II** användes numerisk modellering med en kopplad brunn-reservoar-flödessimulator för att undersöka fördelningen av CO$_2$ under injektering i en stratifierad formation. Resultat visade att fördelningen av CO$_2$ berodde på parametrar så som lagrens permeabilitet och kvoten av dessa, mättmarden av kapillärt bundna faser, det mellanliggande lagrets tjocklek, perforeringens längd samt injekteringstidspannet. De två sistnämnda, operationella parametrarna, kan användas för att till viss grad modifiera fördelningen av CO$_2$ mellan lagren. Dock visade analyserna på en begränsad möjlighet att operationellt styra fördelningen av CO$_2$ mellan lagren vid Heletz. Jämfört med vatten, hamnar en större andel av CO$_2$ i övre lagret, på grund av densitetsskillnadseffekter och en skillnad i tryckgradient längs med lagren. Resultaten visar på vikten av att inkludera kopplade flöden mellan brunn och reservoar i numeriska simuleringar av CO$_2$-injektering. Om ett gränsvillkor så som en inflödesstabilitet till varje lager proportionell till lagrets transmissivitet med avseende på vatten används skulle detta kunna leda till en betydande underskattning av den andel av CO$_2$ som hamnar i det övre lagret.

För trovärdiga simuleringar av ett lagringsprojekt behövs en simulator med korrekt beskrivna lagringsmekanismer och som tar hänsyn till faktorer av vikt för dessa. En sådan kan användas för att estimeran den andel av den lagrade koldioxiden som fastläggs av olika mekanismer och för att utveckla operationella metoder (injekteringsdesign) för att maximera fastläggningen i en formation. I **Paper III** undersöktes, genom numerisk modellering, kapillär fastläggning och lagring genom lösning i formationsvatten (solubility trapping) i samband med en småskalig fältinjektering. Påverkan av den antagna IR-kurvan$^{21}$ (trapping model), geologisk heterogeniteten och injektionsstrategin på den estimerade fastläggningen studerades. Slutsatser dragna från resultatet i **Paper III** inkluderar att kapillär fastläggning kan förväntas vara den dominerande fastläggningsmekanismen vid de förhållanden och den tidsskala som förelåg i studien. Användning av vatteninjektering efter koldioxidinjektionen (så kallad ”chase-fluid”) kan bidra till ökad fastläggning. Simuleringsresultatet visade på en maximalökning på 0,11 TEI (kvoten av massan CO$_2$ som är kapillärt bundet samt löst i formationsvattnet till den totala massan injekterad CO$_2$) vid slutet av observationsperioden. Ökningen berodde huvudsakligen på ökad kapillär fastläggning, men även lösningslagring i formationsvattnet förbättrades av en sådan strategi. Resultaten indikerar också att geologisk heterogenitet generellt minskar fastlägg-

$^{21}$ Relation mellan initial gas mättnad och kapillärt bunden gas mättnad.
ning, då den förflyttning av gasplymen som orsakas av densitetsskillnader mellan faserna retarderas, vilket leder till att mindre imbibition och därmed att mindre kapillär fastläggning sker. Valet av IR-kurva som användes i simulatorn hade en signifikant effekt på den beräknade kvantiteten av kapillärt bundet CO$_2$; förenklad Land IR-kurva (simplified Land) resulterade i den högsta kvantiteten, och Aissaoui IR-kurva i den lägsta kvantiteten. De flesta av de testade IR-kurvorna i studien producerade dock liknande resultat för fastläggning. Studien framhåller vikten av att vid modellering använda en lämplig IR-kurva samt beskrivning av den geologiska heterogeniteten för en plats då man simulerar koldioxidlagring, eftersom olika antaganden kan resultera i betydande avvikelse i beräknad fastläggning. Om en mindre lämplig IR-kurva används vid beräkningarna kan detta leda till under- eller överskattning av den fastlagda mängden CO$_2$ och resultera i ett felaktigt intryck av den mängd CO$_2$ som kan lagras säkert.

Kapillär fastläggning är ett resultat av undanträngnings- och fångstmekanismer på porskalan. I **Paper IV** genomfördes en närmare analys av dessa småskaliga processer. En pornätverksmodell (PNM) utvecklades och användes för simulerande av dränering-fyllnings-scenario, dvs. inträngning av CO$_2$ följt av återinträngning av vatten. I studien genomfördes en känslighetsanalys för påverkan av tre viktiga parametrar (det genomsnittliga koordinat-ten, radie-förhållandet mellan porhals och porkropp samt den avancerande kontaktvinkeln) på beräknad $S_{gr}$ i en artificiell sandsten. Resultatet visade att PNM:et fångar dessa parametrars påverkan på $S_{gr}$ i enlighet med tidigare studier av tvåfassystem. Vidare genererades ett pornätverk som efterliknade sandsten från Heletz. Detta användes för att simulera scenariot som resulterade i en avancerande kontaktvinkeln på $S_{gi}$ (initial gas mättanad) och $S_{gr}$ (kapillärt bunden gas mättanad) data, som i sin tur användes för att estimerar en IR-kurva som täckte hela den fysiska räckvidden på $S_{gi}$-värden, även där experimentellt data saknades. Den avancerande kontaktvinkeln hade en påtaglig effekt på simuleringens resultatet. Förekomsten av olika typer av undanträngnings- och fångstmekanismer bestämmer också. Den funna IR kurvan kan komma till användning i mer storskaliga simuleringar och PNM:et kan användas för ytterligare analyser av olika aspekters och förutsättningars effekt på kapillär fastläggning.

Denna avhandling omfattade numerisk modellering och analys av hydroteologiska processer, med fokus på kapillär fastläggning, som sker vid geologisk lagring av CO$_2$ i djupt belägna saltvattenakvifer. Ämnet behandlades både på por- och fältskalan. Resultatet av arbetet inkluderade analyser av olika testsekvenser för karaktärisering av fastläggning i fält, analyser av aspekter som rör modellering av sådana processer samt utveckling av en simulator för modellering av fastläggning på porskalen för framtida studier.
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