

**Three-Dimensional Imaging and
Numerical Modelling of Convective Dissolution
in Complex Porous Media**

Anna-Maria Elisabeth Eckel

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Department of Chemical Engineering
The Imperial College of Science, Technology and Medicine
London, UK

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and the Diploma of Imperial College London

Declaration of Originality

I certify that the work included in this thesis is entirely my own and is performed under the supervision of Dr Ronny Pini at the Department of Chemical Engineering, Imperial College London. All else is appropriately referenced. Some of the work has been published or submitted for publication and the relevant references can be found at the start of each chapter.

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Abstract

Convective mixing is a process that greatly enhances the transport of mass between two miscible fluids and plays an important role in many engineered and natural processes. In the context of subsurface CO₂ storage, density-driven convection of CO₂-rich brines promotes the dissolution of the CO₂-rich supercritical gas phase, thereby contributing to the storage capacity of the host reservoir. The process is triggered by the occurrence of a gravitational instability induced by the dissolution process, which further develops into perpendicular elongated finger-like patterns that sink in deeper parts of the reservoir. This thesis presents modelling and experimental approaches to study these convective structures and to evaluate their impact on the CO₂ storage process.

By presenting a systematic quantitative assessment of the mixing process, this work fills a knowledge gap in previous work on the subject. To this end, a two-dimensional CFD model is used to investigate the density-driven convection over a range of Rayleigh numbers that is relevant to CO₂ storage applications. The macroscopic evolution of the convective process is quantified by employing fundamental measures of mixing that use the local spatial structure of the solute concentration field. These are implemented to obtain scaling relationships that may be used for the appraisal of potential CO₂ sequestration sites.

This thesis also addresses the limitations of previous experimental work that has largely focused on two-dimensional domains. An approach is presented that applies X-ray Computed Tomography to generate three-dimensional imagery of the mixing process in both unconsolidated and consolidated porous media. The analysis of this rich dataset reveals that the individual plume structures are strongly affected by the characteristic microscopic morphology of the porous space, with an impact observed on the macroscopic spreading process. By providing direct observations of the mixing process in natural porous media, these results represent a useful benchmark for future numerical and experimental studies.

Publications

A.-M. Eckel, R. Liyanage, T. Kurotori and R. Pini “Spatial Moment Analysis of Convective Mixing in Three-Dimensional Porous Media Using X-ray CT Images” *Industrial & Engineering Chemistry Research*, 2023, *62* (1), 762-774

A.-M. Eckel and R. Pini “Spreading and mixing during solutal convection in uniform porous media with application to geologic CO₂ storage” *Physics of Fluids*, 2021, *33*, 066604

A.-M. Eckel, R. Liyanage, T. Kurotori and R. Pini “Three-Dimensional Imaging of Dissolution-Driven Convection in Simple Porous Media Using X-ray CT Scanning” *Proceedings of the 15th Greenhouse Gas Control Technologies Conference*, 2021, 15-18 March

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Conference and Selected Seminar Presentations

Conference/Seminar	Location	Participation
<u>2019:</u>		
GRS on Carbon Capture, Utilization and Storage	Les Diablerets (Switzerland)	poster
Chemical Engineering PhD Symposium (Imperial College London)	London (UK)	poster “Best poster prize (public vote)” & “Best poster prize (1. year PhD students)”
COMSOL conference	Cambridge (UK)	poster “Best poster award”
AGU Fall Meeting 2019	San Francisco (US)	poster
<u>2020:</u>		
InterPore 2020	online	oral presentation
AGU Fall Meeting 2020	online	oral presentation
Porous Media Tea Time Talks	online	oral presentation
<u>2021:</u>		
GHGT-15	online	oral presentation
InterPore 2021	online	oral presentation
AGU Fall Meeting 2021	New Orleans (US)	oral presentation
<u>2022:</u>		
GRS and GRC on Carbon Capture, Utilization and Storage	Ventura (US)	oral presentation
InterPore 2022	Abu Dhabi (UAE)	oral presentation
Chemical Engineering PhD Symposium (Imperial College)	London (UK)	oral presentation “Best presentation prize (academic panel)” & “Best presentation prize (public vote)”
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List of Abbreviations

CCS Carbon Capture and Storage

CH₄ Methane

CI Confidence interval

CO₂ Carbon dioxide

CT Computed Tomography

GCS Geological Carbon Storage

GHG Greenhouse gas

HRPF heterogeneity High-Randomess Pattern-Free heterogeneity

KI Potassium iodide

KMnO₄ Potassium permanganate

NMSE Normalised mean square error

MEG Methanol and ethylene-glycol

MRI Magnetic resonance imaging

PET Positron Emission Tomography

PPG Propylene glycol

REV Representative Elementary Volume

Nomenclature

List of symbols used in this thesis together with the units in which they are expressed.

$\alpha_L, \alpha_{L,t}$	longitudinal dispersivity, longitudinal dispersivity in unidirectional advective process [cm]
Δ_{CT}	repeatability on a voxel-by-voxel level of CT measurements [HU]
ϵ_g	relative gradient error [1/mm]
γ_{nw}	surface tension [mN/m]
λ_c	critical wavelength [m]
$\mathcal{L}$	characteristic or diffusive length scale [m]
$\mathcal{U}$	characteristic diffusive velocity scale $\mathcal{U} = \phi D / \mathcal{L}$ [m/s]
μ	viscosity [Pa s] or linear attenuation coefficient [1/cm]
μ_k	k^{th} raw moment
ϕ, ϕ_t, ϕ_p	(intergranular) porosity, total porosity, intragranular porosity
$\rho, \rho_0, \rho_w, \Delta\rho$	(mixture) density, reservoir or pure fluid density, water density, density difference [kg/m ³]
σ	spreading length [m] or standard deviation
σ_H	strength of heterogeneity of packing
τ, τ_{on}	dimensionless time (or tortuosity), dimensionless onset time
Θ	pore-space heterogeneity factor
θ_{nw}	contact angle
ξ	shape parameter in Berryman equation
A, A_p	area, void space [m ²]
a, b	coefficients of natural logarithmic function in Chapter 6 and prefactor and the exponent of a power law in Chapter 7 and 8
$c, c_y, c_{\max}$	molar concentration, transverse-averaged concentration, maximum and constant concentration at top boundary [mol/m ³]

CN	coordination number
CT	CT number [HU]
D	effective diffusion coefficient [m^2/s], $D = D_{\text{m}}/\tau$ with tortuosity and molecular diffusion coefficient D_{m}
$d_{\text{p}}, d_{\text{p},50}, d_{\text{p},\text{l}}, d_{\text{p},\text{u}}$	particle diameter, median, lower and upper particle diameter [μm]
D_{L}	longitudinal dispersion coefficient [cm^2/min]
E, E_{max}	dilution index, maximum dilution index [m^3]
F	dissolution flux [$\text{mol}/\text{m}^2/\text{s}$]
H	height [m]
I	intensity of segregation
J	dimensionless dissolution flux
K	Kozeny constant
k	permeability [m^2]
K_{c}	contrast factor for X-ray imaging
L	iso-contour line or length [m]
L_{c}	characteristic length [mm]
L_{s}	system depth in modelling study $L_{\text{s}} = 1 \text{ m}$
$M, M_{90}, M_{\text{norm}}$	(total) amount of solute, amount of solute when second moment $\sigma = 0.9\sigma_{\text{max}}$, normalised amount of solute [mol]
m_2	2 nd central moment
M_{KI}	molar mass of KI [g/mol]
n, α	prefactor and exponent of a power law in Chapter 6
$p, p_{\text{c}}, p_{\text{f}}$	pressure (or normalised concentration), capillary pressure, correction factor for pressure in permeability measurements [Pa]
Pe	Péclet number
Q	flow rate [m^3/s]
R^2	coefficient of determination
r_{p}	pore throat radius [m]
Ra, Ra_{c}	Rayleigh number, critical Rayleigh number
S	area of the pore-solid interface [m^2]
$S_{\text{w}}, S_{\text{nw}}$	saturation wetting phase, saturation non-wetting phase
Sh	Sherwood number
t, t_{av}	time, advective time scale [s]

$t_B = H/u_B$	buoyancy time [s]
u, u_y	superficial velocity, displacement of vertical centre of mass velocity [cm/min]
$u_B = k\Delta\rho g/\mu$	buoyancy velocity [cm/min]
V	volume [m ³]
v	interstitial velocity [cm/min]
W	width [m]
w	mass fraction
$w, w_{\max}$	mass fraction, maximum mass fraction
Y_{com}	position of centre of mass [m]
$\mathbf{g}, g$	gravitational acceleration vector, gravitational acceleration in y-direction [$g = 9.81 \text{ m/s}^2$]
$\mathbf{u} = [u_x, u_y, u_z]$	velocity vector in 3D experimental study
$\mathbf{u} = [u_x, u_y]$	velocity vector in 2D modelling study
$\mathbf{x} = [x, y, z]$	coordinate vector in 3D experimental study
$\mathbf{x} = [x, y]$	coordinate vector in 2D modelling study

Chapter 1

Introduction

Natural density-driven convection results from a fluid-fluid interaction where an interfacial instability is triggered by an unstable density stratification in the fluids (Elder, 1967; Horton and Rogers, 1945; Lapwood, 1948; Voss and Souza, 1987). The instability produces column-like plumes resulting in counter-current flow and a vigorous chaotic vertical mixing, known as convective mixing (Kämpf, 2010). Convective mixing plays a significant role in many natural processes and can be provoked by either dissolution or thermal gradients. Examples include the convection in the atmosphere (convective cloud elements, Hartmann et al. 2001), in the oceans (mixing of surface waters to great depths, Marshall and Schott 1999) and in the shallow subsurface such as in salt deserts, where convection induces characteristic polygonal salt patterns visible on the surface (Lasser et al., 2019, 2023). It can also be exploited for engineering applications, as in the design of buildings (natural ventilation, Hunt and Linden 1999) or in metal-production processes (natural-convection flow in melting process, Brent et al. 1988). Natural convection is also relevant in chemical and petroleum engineering, where convective mixing affects the flow in deviated wells or tilted tubes (Séon et al., 2005) or promotes the effect of heat transfer in heat exchangers of nuclear reactors (Xue et al., 2010). Convective mixing in porous media has recently received particular attention. It is highly relevant in the porous rock formations of coastal aquifers where density-driven circulation of seawater with freshwater promotes seawater intrusion. The global problem of seawater intrusion is expected to be exacerbated by climate change (Werner et al., 2013). Moreover, density-driven natural convection in porous structures is extremely important in the context of Carbon Capture and Storage (CCS). CCS is currently one of the best available technologies to reduce anthropogenic greenhouse gas emissions to the atmosphere by storing carbon dioxide (CO_2) in the subsurface, for instance in deep saline aquifers (Haszeldine, 2009; Metz et al., 2005; Orr, 2009; Ringrose et al., 2021). Convection currents across several scales

result in the convective mixing of CO₂ with reservoir brines which is expected to positively impact the solubility trapping and therefore subsurface storage (Kneafsey and Pruess, 2011; Lindeberg and Wessel-Berg, 1997; Yang and Gu, 2006; Zhang et al., 2011). The phenomenon of convective dissolution during the solubility trapping of CCS is the focus of this thesis.

The complex solute field arising from density-driven convection is a synergy of solute spreading and mixing. The former refers to the stretching and deformation of the solute plume, owing to spatial fluctuations of the fluid velocity. On the contrary, mixing (or dilution) is associated with a diffusive process and thus refers to the process that increases the volume occupied by the plume. Previous studies largely focus on the quantification of the accelerated CO₂ dissolution rate (or flux) in reservoir fluids. While the dissolution rate represents an important measure that allows us to derive useful empirical relations, the impact of the convective mixing process on the time- and length-scale of the CO₂ transport within the reservoir remains largely uncertain. This requires an analysis of the spatio-temporal evolution of the convective mixing process by means of the fundamental measures of spreading and mixing that are directly inferred from the local spatial structure of the concentration field in the medium. Further, the process needs to be evaluated by considering different scaling measures (*e.g.*, Rayleigh number) to enable the upscaling of observations done at the laboratory scale.

Despite extensive research on CO₂ sequestration in deep saline aquifers, most of the work on convective dissolution has considered two-dimensional and idealised homogeneous systems, such as Hele-Shaw cells or packs of spherical beads, while applying analogous fluid pairs with properties different from those of the subsurface CO₂/brine system. However, convective mixing is expected to be controlled by spatial variations of key petrophysical properties of the reservoir rock, such as porosity and permeability. These structures can yield highly heterogeneous fluid velocity fields and generate complex concentration distributions of the solute (Emami-Meybodi et al., 2015). This requires an analysis of the mixing process in more complex (and realistic) situations, including those characterised by structural heterogeneity. To the author's best knowledge, there is to date no experimental study that observes convective dissolution in natural consolidated materials (*i.e.*, rock samples). This experimental data is crucial to provide direct evidence of density-driven convection in the subsurface and to make reliable estimates of its potential in accelerating the CO₂ transport behaviour.

1.1 Research Objectives

There are still major questions to be answered about the convective mixing process in porous media and on its application to CCS. The overall research objectives of this work, designed to address these

issues, can be summarised as follows:

- To develop a numerical simulation environment for the study of convective mixing induced by density-driven dissolution in a uniform porous media over a wide range of Rayleigh numbers (*i.e.*, strength of convection).
- To identify and apply fundamental measures that can quantify the shape of the resulting solute structures and their evolution.
- To capture and investigate the evolution of the convective mixing process experimentally in three-dimensional porous media while using uniform as well as heterogeneous systems (*i.e.*, rocks).
- To extract from both numerical and experimental studies scaling relationships that include measures of mixing, porous media properties and global transport parameters, which can be used for upscaling.

To accomplish these objectives and to fill the research gaps, this work uses a combination of experimental, numerical and analytical methods. A two-dimensional model of a homogeneous porous medium was considered and the workflow for interpreting and analysing the simulation results was created. A novel experimental approach to investigate the evolution of the convective mixing process in three-dimensional porous media using X-ray Computed Tomography (CT) was developed that allows the observation of the mixing structures in consolidated and unconsolidated porous structures. A key advantage of the method is the possibility to monitor and compare the temporal evolution of individual plume structures between, for instance, the different rock types. Besides uniform bead packs, consolidated rock samples are considered for which observations have thus far been lacking.

1.2 Thesis Outline

The thesis begins with Chapter 2 that covers the essential background on natural convection. A general review of the existing literature is presented, including numerical and experimental techniques to characterise convective mixing in porous media. The main research gaps are identified.

Chapter 3 covers the principles of the numerical and computational techniques applied in this thesis. First, the theoretical formulation of the two-dimensional model applied in Chapter 6 is described. It is followed by a description of the metrics and methods used for the characterisation of the dissolution process. This includes various measures of mixing and spreading, and a derivation of the 0th–2nd

spatial moments of mass applied on the modelling and experimental results presented in subsequent chapters. The last section addresses the one-dimensional advective-dispersive transport model that is used to upscale the experimental results.

A key element of novelty in this thesis is the experimental approach that allows for sustaining a constant concentration boundary condition in a 3D porous medium. There are two classes of porous materials examined in this work: homogeneous synthetic bead packs and heterogeneous natural rocks (Bentheimer and Boise sandstone, Mount Gambier and Ketton limestone). The porous materials are characterised in Chapter 4 by determining structural and transport properties such as porosity and permeability. Additionally, a full characterisation of the spatial heterogeneities of the rock pore space is presented, including the characteristic length of the pore space or the Representative Elementary Volume.

This is followed by the description of the free convection experiments and imaging techniques in Chapter 5. To this end, the properties of the surrogate fluids, the developed experimental set-up, together with the required equipment, and the procedure are outlined. The imaging methods using X-ray Computed Tomography that are employed in this study are illustrated, including image reconstruction and data processing.

The results of the numerical simulation work are presented in Chapter 6. A two-dimensional uniform formulation is applied, and the Rayleigh number is varied between $Ra = 100 - 10\,000$. The dissolution process is analysed by macroscopic measures of mixing, including isocontour lines, the intensity of segregation, the spreading length, the dilution index, and the dissolution flux. Results of the latter are validated against data from a benchmark study.

In Chapter 7, results of the novel experimental approach using 3D porous media (homogeneous packs of glass beads) are presented. The evolution of the convective mixing process and the concentration structures that arise upon dissolution are investigated in a range of Rayleigh numbers ($Ra = 3\,000 - 55\,000$). The temporal evolution of the spatial moments of the concentration distribution, including the cumulative dissolved mass, the location of the centre of mass, and the standard deviation of the concentration field, are computed. A simplified representation of the mixing process by analogy with the 1D advection-dispersion model is proposed, enabling the estimation of the bulk advective velocity and the effective longitudinal dispersion coefficient.

A second major aspect of novelty of this thesis is the observation and analysis of density-driven convection in consolidated natural material (*i.e.*, rocks). A combination of three-dimensional visual and quantitative analysis is provided in Chapter 8 to improve the understanding towards the impact of

structured geological media on convective dissolution. To this end, the temporal evolution of individual plume structures between the rock types is monitored and compared. Further, the spatial moments of mass, the dispersion coefficients and the dilution index are computed and correlated with characteristics of the advective transport and pore-space heterogeneity measures.

In Chapter 9, the main achievements of this PhD thesis are summarised and suggestions for future work are presented.

Chapter 2

Background and Literature Review

This chapter covers the general principles density-driven convection together with a review of the relevant literature. Further concepts and theories that are not presented in this chapter are explained in the remaining chapters of the thesis where they are most relevant. In the following sections, the fundamentals of density-driven natural convection are outlined which are closely associated with the work performed in this thesis:

- Modelling of solutal convection in the CO₂-brine system in homogeneous porous media.
- Experimental study on convective dissolution in three-dimensional porous media.
- Experimental study on convective dissolution in three-dimensional consolidated natural rocks.

Section 2.1 focuses on convective mixing and its relevance during geological CO₂ storage in saline aquifers. The fundamental properties of unstable density-driven convection are introduced in Section 2.2. Concepts used in the experimental and modelling studies on convective mixing together with a summary of the research progress are covered in Section 2.3. The realisation of heterogeneous porous structures in recent literature is presented in Section 2.4.

Some of the material presented in this chapter has been published in Eckel and Pini (2021) and Eckel et al. (2023).

2.1 CO₂ Geological Storage and Primary Trapping Mechanisms

The increase in the concentration of greenhouse gases (GHG) concentrations in the atmosphere such as carbon dioxide (CO₂) or methane (CH₄) is most likely the main cause of global warming (IPCC, 2022). The growth of the average temperature of the Earth's climate system is associated with harmful

effects on ecosystems, biodiversity, and human society. Therefore, climate change might be the most challenging environmental problem the world will be facing in the future (Shahbazi and Rezaei Nasab, 2016). Most GHGs originate from the use of fossil fuels (*e.g.*, oil, gas, coal) in chemical plants, factories, or vehicles while CO₂ is considered to be the primary anthropogenic greenhouse gas. It contributes about three-quarters of the total GHG emissions when weighted according to the warming potential of other GHGs (Ritchie et al., 2020). In line with the Paris Agreement, it is necessary to limit the temperature increase this century well below 2 °C compared to pre-industrial levels to avoid the worst impacts of climate change (UNFCCC, 2015). However, this is not conceivable by relying only on increasing energy efficiency and reducing the use of resources (*e.g.*, by increasing the contribution from renewable resources). Most significantly, it requires large-scale application of negative emissions technologies, *i.e.*, technologies that lead to the net removal of GHGs from the atmosphere (Smith et al., 2016). Many techniques have been proposed to reduce CO₂ emissions and to prevent the release of large quantities of CO₂. Carbon Capture and Storage (CCS) is seen as one of the most promising options (English and English, 2022; Holloway, 2005; IPCC, 2022). CCS is the process of capturing CO₂ at the point of emission from major sources (*e.g.*, existing fossil fuel-burning power plants), the transport via pipelines and the injection of the CO₂ in supercritical state in underground geological formations (Nazari Moghaddam et al., 2012). The considerable advantage of this method is the vast capacity of raw material for binding the CO₂, in particular saline aquifers, oil and gas reservoirs or un-minable coal seams. Saline formations are generally unused but are available in many parts around the globe and injection points are easily accessible to existing large CO₂ point sources (Li et al., 2011; Orr, 2009). Thus, deep saline aquifers provide the highest potential capacity of CO₂ storage in contrast to the other storage facilities (Javaheri et al., 2009; Mojtaba et al., 2014).

Once in the target storage formation, the CO₂ displaces the resident fluid (brine) from the pore space (Ott et al., 2015). CO₂ is less dense than brine and the displacement is largely controlled by gravity until the CO₂ reaches an impermeable caprock at the top of the formation (see schematic in Figure 2.1). This prevents buoyant CO₂ to escape and enables the CO₂ to spread laterally, known as *structural trapping* (Benson et al., 2012; Garcia, 2001; Krevor et al., 2015). At the trailing edge of the CO₂ plume, brine imbibes back into the rock driven by capillary action, leaving behind a so-called residual CO₂ phase in the form of disconnected immobile bubbles (Gershenzon et al., 2015). This process is called *capillary* or *residual trapping* and leads to the creation of a two-phase capillary transition zone between the CO₂ plume and the free water level in the aquifer, which is explained more in detail in Section 2.2. The CO₂ slowly dissolves into the surrounding brine through molecular diffusion. Because brine density increases approximately linearly with CO₂ concentration, natural convection is

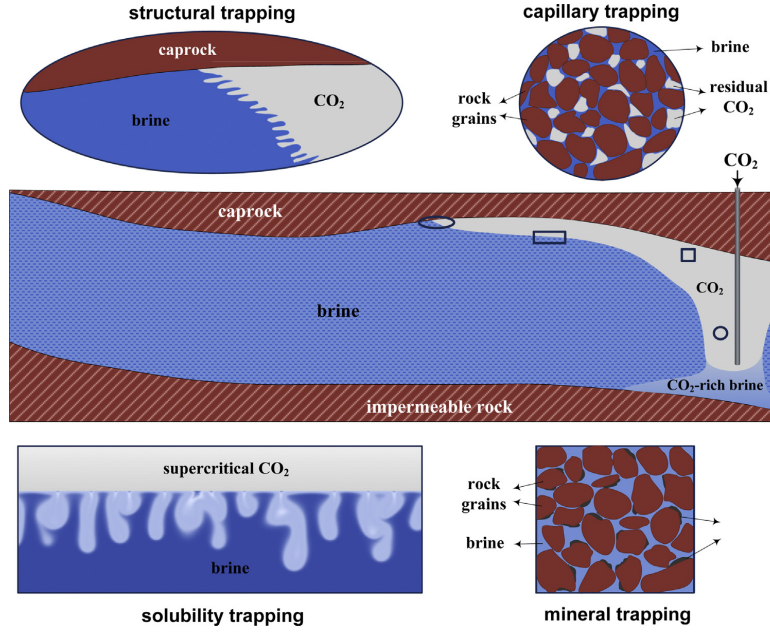


Figure 2.1: Illustration of fluid dynamics and primary trapping mechanisms associated with carbon sequestration in saline aquifers (slightly modified, taken from Emami-Meybodi et al. 2015).

induced, whereby the CO_2 -concentrated plumes move downward accompanied by an upward movement of fresh fluid (Ennis-King and Paterson, 2005). Eventually, convection currents across several scales result in the convective mixing of CO_2 -rich brine (Kneafsey and Pruess, 2011; Lindeberg and Wessel-Berg, 1997), which is expected to enhance the CO_2 dissolution flux into the resident fluid and to accelerate the rate of CO_2 dissolution compared diffusion alone (Yang and Gu, 2006; Zhang et al., 2011). Therefore, *solubility trapping*, in general, and convective mixing, in particular, reduces the risk that CO_2 trapped beneath the caprock seal leaks from the reservoir due to fractures in the caprock. Once dissolved, the CO_2 can react chemically with minerals in the formation rock to form ionic species and precipitates. This mechanism is the most permanent form of geological storage and is referred to as *mineral trapping* (Cherezov, 2017; Shahbazi and Rezaei Nasab, 2016).

2.2 Fundamentals of Unstable Density-Driven Convection

As described in Section 2.1, structural trapping is the mechanism by which supercritical CO_2 rises towards the top of the reservoir formation due to buoyancy effects and spreads along a low-permeability caprock seal. Accordingly, the CO_2 plume resides between the caprock and a region of single-phase water (density supercritical CO_2 : $\rho \approx 780 \text{ kg/m}^3$, density brine: $\rho \approx 1030 \text{ kg/m}^3$, Elenius et al. 2012, 2014; Morgado and Esteves 2014). Due to natural imbibition at the interface between the CO_2 phase and the water phase, a transition zone is created, depicted in the schematic in Figure 2.2. In the so-

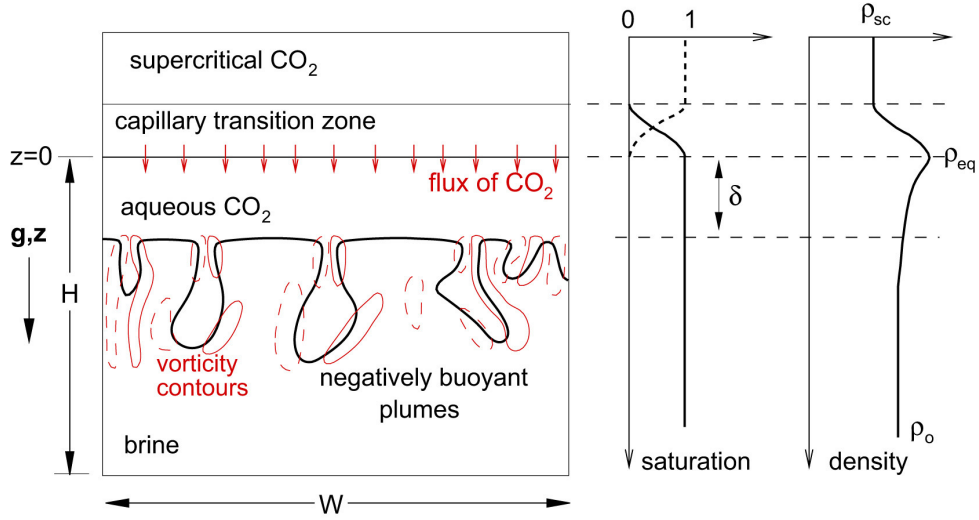


Figure 2.2: Schematic of the physical layout employed in and taken from Riaz and Cinar (2014) to model the solubility trapping process. Supercritical CO_2 with lower density lies on top of brine with higher density, both are separated by the capillary transition zone in which dissolution of CO_2 in brine occurs. The average density increases towards $z = 0$ and then reduces to the brine density as $z \rightarrow H$.

called “capillary transition zone” both phases coexist and the zone thickness depends on the specific capillary pressure function and the respective densities of the two fluids.

Initially, as diffusion takes place, the dissolved CO_2 spreads beneath the capillary transition zone forming a diffusive boundary layer of aqueous CO_2 . In Figure 2.2 the average fluid density is presented which increases across the capillary transition zone from the density of pure supercritical CO_2 to the maximum equilibrium density of the aqueous CO_2 -brine solution. On the contrary, the solution density in the diffusive boundary layer decreases gradually until it is equal to the one of pure brine (Emami-Meybodi et al., 2015; Riaz and Cinar, 2014). This density stratification is gravitationally very unstable and can experience a Rayleigh-Taylor instability: Small disturbances, such as thermal fluctuations, create instabilities which cause the lighter fluid to rise and the heavier fluid to sink (Emami-Meybodi et al., 2015; Zhao et al., 2002). The instability of the interface grows exponentially over time along with its wavelength and amplitude and leads to the formation of small fingers which are extending vertically downwards (schematic contours of fingers in Figure 2.2). Adjacent fingers can coalesce to form larger fingers inducing the process of density-driven natural convection (Nakanishi et al., 2016).

Fluid flowing through a porous media experiences the effect of porous medium resistance. This can be described by Darcy’s law, that is, in fact, the porous analogue of the Navier-Stokes equation and describes the proportionality between flow rate and the pressure gradient in the direction of flow

(Nield and Bejan, 2006). It is expressed as:

$$\mathbf{u} = -\frac{k}{\mu}\nabla p \quad (2.1)$$

where $\mathbf{u}$ is the Darcy velocity, k the permeability (as a scalar), μ the fluid viscosity and Δp the fluid pressure drop over a given distance. With application to groundwater hydrology, a modified version of Darcy's law is commonly applied in order to take into account the effect of Earth's gravity. The pressure is expressed as a gravity-modified pressure $\hat{p} = p + \rho \mathbf{g}h$ where h is the height of a point within a porous medium, ρ the fluid density and $\mathbf{g}$ the vector of acceleration of gravity (Bear, 1988; Loodts et al., 2015):

$$\mathbf{u} = -\frac{k}{\mu}\nabla \hat{p} = -\frac{k}{\mu}\nabla(p + \rho \mathbf{g}h). \quad (2.2)$$

2.2.1 Rayleigh Number Estimation

To determine the occurrence of solutal convection in a given system (or in the context of CCS in a given aquifer), commonly used is the Rayleigh number, Ra . It is expressing the balance of density-driven and diffusive mass transport (Lindeberg and Wessel-Berg, 1997):

$$Ra = \frac{k\Delta\rho_{\max}gH}{\mu\phi D} > Ra_c \quad (2.3)$$

where g is the acceleration due to gravity, $\Delta\rho_{\max}$ is the maximum density difference between saturated and unsaturated brine, H is the thickness of the aquifer, ϕ is the average porosity and D is the effective diffusion coefficient of CO_2 in brine (combination of the bulk diffusion coefficient D_m and tortuosity effects, Eq. 4.11). As indicated by the right-hand side of Eq. 2.3, convective instability occurs when Ra exceeds a critical value. For a homogeneous and two-dimensional porous medium, it has been shown that $Ra_c = 4\pi^2 \approx 40$ (Katto and Masuoka, 1967), whereas the Rayleigh number needs to be $Ra \geq 55$ to observe an enhancement in the mass transfer through convection (Szulczewski et al., 2013). For large values of Ra (≥ 2000), the dissolution process undergoes a constant flux regime, after an initial period of flux growth which is discussed more in detail in Section 2.2.2. It was demonstrated that in such cases the dissolution flux represents an important measure to evaluate the convective process and to derive useful empirical relations for upscaling purposes (Emami-Meybodi et al., 2015; Hidalgo et al., 2012; Pau et al., 2010).

2.2.2 Dissolution Flux and Dissolution Regimes

The dissolution flux is a measure of the dissolution process quantifying the rate of change of the total dissolved CO_2 in brine and is therefore related to the time scale over which free-phase CO_2 has a chance to leak out (Mojtaba et al., 2014). Commonly, the dissolution flux, $F(t)$, is expressed as moles of solute that dissolve into the ambient fluid per unit time and unit area of an open interface. It is defined in two-dimensional form as:

$$F(t) = \frac{1}{W} \frac{d}{dt} \int_{A_p} c(\mathbf{x}, t) dA_p \quad (2.4)$$

where $A_p = A \phi$ and W are the void space and width of the domain, respectively, t is the time and $c(\mathbf{x}, t)$ is the solute concentration. The three-dimensional formulation for a cubic geometry (with dimensions $W \times W \times H$) is:

$$F(t) = \frac{1}{W^2} \frac{d}{dt} \int_{V_p} c(\mathbf{x}, t) dV_p. \quad (2.5)$$

with $V_p = V \phi$ as the volumetric void space. We follow the approach described in Slim (2014) and Emami-Meybodi et al. (2015) to scale the dissolution flux by $\mathcal{U} c_{\max}$, where $\mathcal{U} = \phi D / \mathcal{L}$ is a characteristic diffusive velocity scale and $c_{\max}$ the maximum solute concentration. Using $\mathcal{L} = H$ as the characteristic length scale yields:

$$J(\tau) = \frac{H}{D \phi c_{\max}} F(t) \quad (2.6)$$

with the dimensionless time:

$$\tau = Dt / H^2. \quad (2.7)$$

Further scaling of $J(\tau)$ by Ra removes any dependence of the dissolution flux on diffusivity:

$$\hat{J}(\hat{\tau}) = \frac{\mu}{k \Delta \rho_{\max} g c_{\max}} F(t) \quad (2.8)$$

with the dimensionless time:

$$\hat{\tau} = Ra^2 \tau. \quad (2.9)$$

According to Slim (2014), five main regimes describing the different stages of solutal convection in a porous medium can be distinguished by means of the dissolution flux. Figure 2.3 shows the dimensionless dissolution flux $J(\hat{\tau})$ which is independent of the Rayleigh number through the normalisation (Emami-Meybodi et al., 2015; Wen and Hesse, 2018). The first regime (*diffusive regime*) is domi-

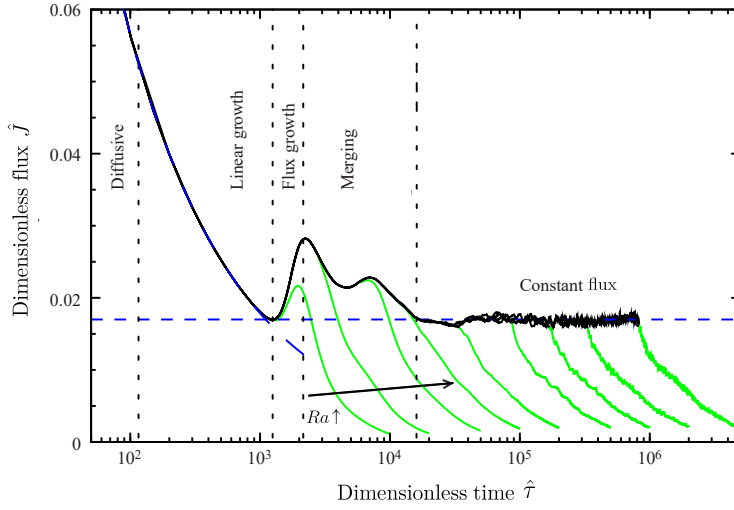


Figure 2.3: The dimensionless dissolution flux versus dimensionless time for different Rayleigh numbers (from left to right, $Ra = 100, 200, 500, 1000, 2000, 5000, 10^4, 2 \times 10^4, 5 \times 10^4$; taken from the numerical study of Slim (2014) and slightly modified). The black curve becoming green indicates the transition to the shutdown regime for each Rayleigh number.

nated by diffusion alone. The dissolution flux reproduces the purely diffusive transport and decays proportionally to the dimensionless time $\hat{\tau}^{-1/2}$. Eventually, the onset of convection occurs when the perturbations at the upper boundary intensify in a *linear-growth regime* owing to sufficient accumulation of denser fluid. For the time of onset, diverse estimations can be found in the literature (*e.g.*, Ennis-King et al. 2005; Slim and Ramakrishnan 2010, further discussed in Chapter 6). In the linear-growth regime, the flux still follows $\hat{\tau}^{-1/2}$ but the convective fingers grow and accelerate downwards, whereas a lateral spread is almost not existent. This results in a drag of more dense brine from the interface, a deviation from $\hat{\tau}^{-1/2}$ and subsequently, in a growth of the dissolution flux until it reaches a local maximum (*i.e.*, the *flux growth regime*). Merging occurs as soon as the fingers are long enough to interact with neighbouring fingers, generating a complex pattern followed by a reduction of the dissolution rate. These regimes can be observed for a broad spectrum of Rayleigh numbers. For low Ra , the system progressively saturates as the fingers travel downwards, the dissolution rate reduces further and the whole process comes to a standstill because the density gradient at the interface reduces to zero (*shutdown regime*, Amooie et al. 2018). For high Ra , while the fingers travel down into the domain, a period of constant dissolution flux is present (*constant flux regime*) between the onset of convection and the shutdown regime in which the flux oscillates about a constant value and is independent of Ra (Ching et al., 2017; Green and Ennis-King, 2014).

Estimates of Ra for 45 saline aquifers worldwide indicate that solutal convection is in fact possible ($Ra \geq Ra_c$ for the majority of aquifers in Figure 2.4), albeit Ra is often well below 1 000 or even of

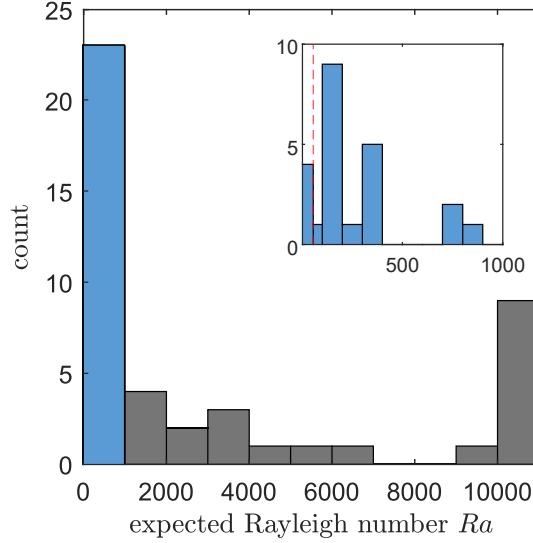


Figure 2.4: Histogram of 45 aquifers worldwide according to their expected Rayleigh number. Data gathered from Nazari Moghaddam et al. (2015) (10 reservoirs in the Alberta Basin, Canada), Hosa et al. (2011) (6 in the United States, one each in Japan, Germany, Algeria, Norway, Australia), Lindeberg and Wessel-Berg (1997) (4 in the North Sea) and Szulczewski et al. (2012) (20 in the United States). The Rayleigh numbers used for the plot are calculated according to the data provided in the references. In some cases, parameters such as the diffusion coefficient, the fluid viscosity or the change in density were estimated. The red dashed line in the inset indicates the critical Rayleigh number Ra_c . The properties of the aquifers used are listed in Appendix A in Table A.1.

the same order of magnitude as Ra_c (see inset of Figure 2.4). The analysis of these aquifers based solely on the dissolution flux becomes more difficult because the dissolution process does not reach a stabilised state. In these cases, other measures may prove to be more suited to the analysis of the convective process, particularly those that quantify mixing directly from the CO_2 distribution pattern in the porous medium.

2.3 Gravitational Instability Models of Two- and Three-Dimensional Natural Convection

The Rayleigh-Taylor and the Rayleigh-Bénard model are commonly used, simplified models of the natural convection process in a porous medium with the objective to investigate the convective mixing process. A Rayleigh-Taylor convection implies an instability at the interface between a heavier fluid on top of a lighter fluid and corresponds to a closed two-phase problem. Boundaries which are unaffected by the fluid flow are assumed to be infinitely far from this interface. The Rayleigh-Taylor system involves a moving interface between the fluids and is usually used to describe miscible systems. The Rayleigh-Bénard model refers to an open single-phase system with a constant (equilibrium)

concentration at a sharp and rigid top boundary of the system. This is a common assumption in numerical studies as the CO₂-brine system is only slightly miscible and the CO₂ dissolution rate is small compared to the available volume of resident fluid. Further, it is assumed that density stratification damps out possible flow disturbances in the capillary transition zone (Riaz and Cinar, 2014; Wang et al., 2016). We note that a continuous and ongoing injection of supercritical CO₂ into an reservoir could impact the vertical location and movement of the interface. However, in that specific case lateral spreading of the supercritical CO₂ plume needs to be considered and estimated in relation to the reservoir dimensions and slope which determines the height and migration of the interface. Since the time-scale of the dissolution process is in the majority of sequestration cases expected to be much larger than the time-scale of injection, this scenario is not further considered and discussed in this work.

The classification of the density-driven convective systems in Rayleigh-Taylor and Rayleigh-Bénard model, as well as the application of either miscible or immiscible fluids and monotonic or non-monotonic density profiles, leads to four different typical systems (a, b, c, d; Figure 2.5). The notation of Hewitt et al. (2013) is used in this section. Each system is described by an equation of state $\rho^*(C^*)$, a vertical concentration profile $C^*(z^*)$ and a vertical density profile $\rho^*(z^*)$. While systems a–c are dissolution- (and therefore also gravity-) driven concepts, system d is purely gravity-driven. Examples of numerical and experimental studies with an emphasis on recent work are discussed in the following section and classified into the physical system used (a–d). Further, their realisation and implementation in numerical simulations or experimental systems are discussed together with their limitations.

2.3.1 Realizations of the Rayleigh-Taylor Model

Most experimental studies simplify the fluid system of CO₂ and brine by applying a closed system with the unstable boundary layer as a receding interface between two stratified (mostly fully miscible) fluids (Rayleigh-Taylor model, system b–d). Analogue fluid pairs at ambient conditions are applied to avoid difficulties when working under reservoir conditions. Neufeld et al. (2010), Liyanage et al. (2019), Liyanage et al. (2020) and Wang et al. (2017) use methanol and ethylene-glycol (MEG) and water (or brine) in their experiments. Water and propylene glycol (PPG) is used by, *e.g.*, Backhaus et al. (2011) and Tsai et al. (2013). Both fluid pairs are fully miscible and follow a non-monotonic behaviour of fluid density with concentration (system c). This results in fundamental differences in the evolution of the buoyancy-driven instability and dynamics of convective mixing compared to the partially miscible CO₂-water system with a linear density behaviour. So, it is suggested that fluids with non-monotonic

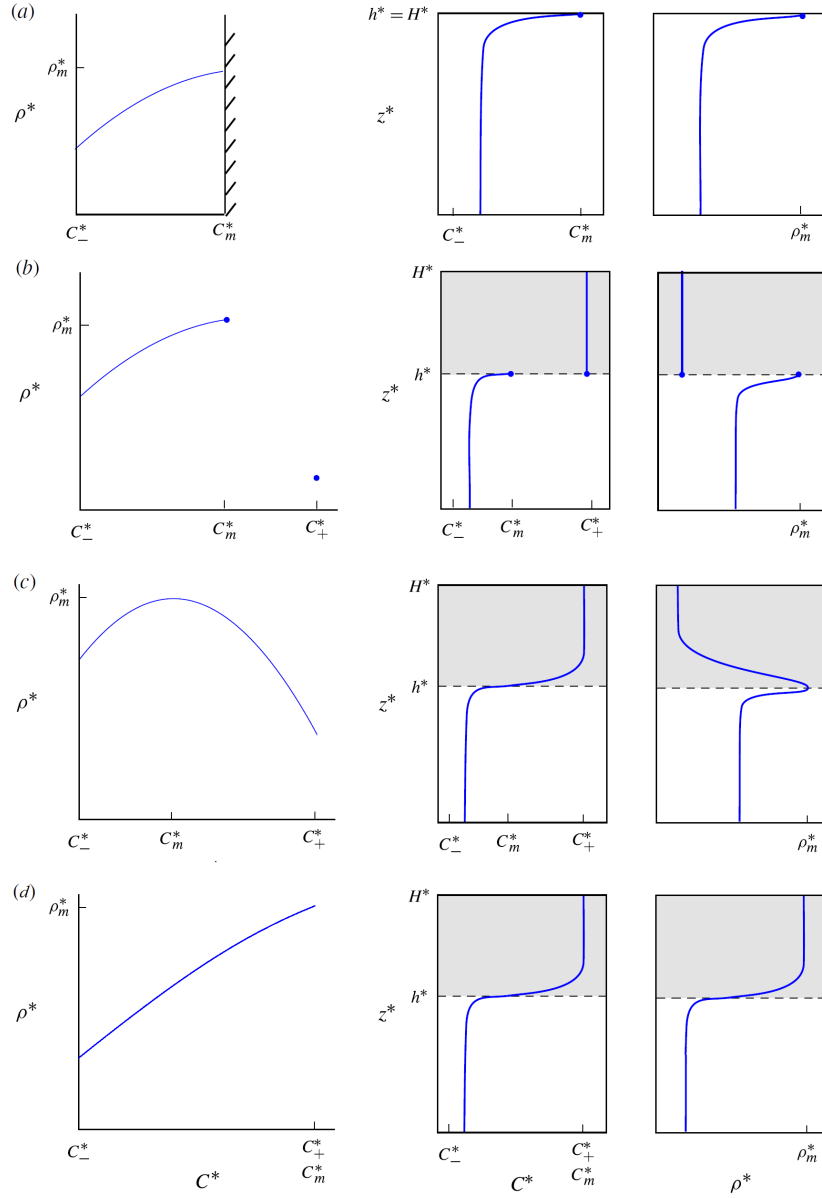


Figure 2.5: Schematic diagrams showing typical equations of state $\rho^*(C^*)$, vertical concentration profile $C^*(z^*)$ and vertical density profile $\rho^*(z^*)$. In each case the maximum density ρ_m^* is attained at concentration C_m^* . The interfacial height is at $z^* = h^*$ and the domain has a constant depth H^* . Diagrams a–c are taken from Hewitt et al. (2013) and diagram d was additionally drawn by the author of this thesis.

- (a) ‘Fixed-interface’ system (Rayleigh-Bénard) with stationary upper boundary at $z^* = h^* = H^*$ and constant concentration C_m^*
- (b) ‘Immiscible’ Rayleigh-Taylor system, fluid with concentration C_+^* overlies fluid with initial concentration C_-^* , the upper fluid is partially soluble in the lower fluid
- (c) ‘Miscible’ Rayleigh-Taylor system, the two fluids are fully soluble and the density of the upper pure fluid is lower than of lower pure fluid $\rho^*(C_+^*) < \rho^*(C_-^*)$ (non-monotonic density profile), the interfacial height $z^* = h^*$ is given by the isopycnal of the maximum density ρ_m^*
- (d) ‘Miscible’ Rayleigh-Taylor system, the two fluids are fully soluble, and the density of the upper pure fluid is higher than of lower pure fluid $\rho^*(C_+^*) > \rho^*(C_-^*)$, the interfacial height $z^* = h^*$ is given by the sharp interface between the fluids at $t = 0$

density profiles cannot accurately represent, for instance, the onset of convection, or scaling relations of the convective flux (Hidalgo et al., 2012; Jafari Raad et al., 2016; Jafari Raad and Hassanzadeh, 2015; Liyanage et al., 2019). To solve this issue, some researchers have implemented methodologies with partially miscible fluids with linear (or approximately linear) density profiles (system b). Nazari Moghaddam et al. (2012), Mojtaba et al. (2014), Nazari Moghaddam et al. (2015), Newell et al. (2018) and Shi et al. (2018) use the two-phase system CO₂-water or CO₂-brine. Some of these studies take place in three-dimensional pressure, temperature and volume cells filled with unconsolidated porous media. Whilst a quantitative dissolution analysis in blind cells is possible, they do not allow direct visualisation of the development of density fingers. Conversely, experimental investigations with two-dimensional Hele-Shaw cells enable visual analysis of convection and the characterisation of the plume dynamics, such as plume width and the vertical convective velocity (Ecke and Backhaus, 2016; Slim et al., 2013). A Hele-Shaw cell consists of two parallel flat plates separated by a narrow gap in which two miscible fluids are overlaid on each other (system c or d), with or without a porous medium. One advantage of Hele-Shaw experiments is their easy accessibility in laboratories. Conventional cameras can be used to study the convective instability and to visualise the two-dimensional finger formation along with the dynamics of CO₂ solute-driven convection (Emami-Meybodi et al., 2015). Many studies have been performed using Hele-Shaw cells to imitate the convective behaviour of CO₂-dissolved in brine such as the work of Wooding (1959) or Fernandez et al. (2002) who carried out experiments in two-dimensional Hele-Shaw cells with two miscible fluids of different densities (system d). They monitored the growth of fingers at the interface and extracted detailed information on finger growth and wavelength. A detailed review of recent Hele-Shaw experiments with and without porous media can be found in the review study of Emami-Meybodi et al. (2015). The results of Hele-Shaw experiments provide tangible evidence of the enhancement of mixing through the gravity-driven flow which is quantified by different mixing quantities (Kneafsey and Pruess, 2010). However, the results do not represent the complex truly three-dimension behaviour of the flow. The assumption that mixing in the orthogonal direction is not relevant is unrealistic in natural convection and the additional degrees of freedom may add significant complexity to the fingering phenomenon and the mixing dynamics, influencing the onset of convection or the magnitude of the convective flux (Emami-Meybodi et al., 2015; Pau et al., 2010). To bridge this gap, a few papers have employed X-ray Computed Tomography (X-ray CT) technology (Liyanage et al., 2019, 2020; Nakanishi et al., 2016) or Magnetic Resonance Image (MRI) technology (Teng et al., 2017; Wang et al., 2021a,b, 2020) to non-destructively observe three-dimensional density-driven convective mixing in opaque porous media. These three-dimensional studies provide important insights into the evolution of buoyancy instability and the spatial and

temporal distribution of the solute structures.

Some numerical studies are available that apply the Rayleigh-Taylor instability: Two-dimensional homogeneous porous media under consideration of a non-monotonically varying density curve (system c) is studied, for instance, by Pramanik and Mishra (2017) and Neufeld et al. (2010). Lindeberg and Bergmo (2002) showed with numerical simulations that the interface between CO₂-rich brine and pure brine remains flat and is rather unaffected by the growth of the underlying fingers (presumably system b). Their results indicate that a local equilibrium between CO₂-rich brine and pure brine is justified and the simplification of a sharp and rigid interface to study gravitational instability is legitimate supporting the assumptions of a Rayleigh-Bénard cell.

2.3.2 Realizations of the Rayleigh-Bénard Model

Modelling efforts exist on linear and non-linear stability analysis (*e.g.*, Ennis-King et al. 2005; Hassanzadeh et al. 2006; Rapaka et al. 2008; Riaz et al. 2006; Slim and Ramakrishnan 2010) to study the convective instabilities but primarily on non-linear simulations applying the Rayleigh-Bénard model. A constant concentration at the sharp and rigid interface (system a, $z^* = h^* = H^*$ in Figure 2.5) can be considered because the CO₂ phase on top of the reservoir is assumed to be thermodynamically in equilibrium with the water phase (Ghesmat et al., 2011). The majority of studies are two-dimensional and a selection with noteworthy results is presented in the following.

Ghesmat et al. (2011) examined the effect of anisotropic dispersion on convective mixing in the context of CO₂ sequestration by applying full nonlinear two-dimensional numerical simulations. They found that the dispersion strength highly affects the finger pattern. The effect of dispersion, specifically the onset of convection, was studied numerically by Hidalgo and Carrera (2009). They demonstrated that by accounting for dispersion, the onset time reduces by up to two orders of magnitude. Pau et al. (2010) showed with high-resolution simulations that the value of the CO₂ flux is proportional to the mean permeability of the porous medium and independent of porosity and effective diffusivity. This evidences that the constant flux regime is a predominately convection-dominated flow regime. The speed of convective fingers in a porous medium and the effect of different parameters, such as permeability or porosity, on the finger speed was analysed in the numerical study of Xie et al. (2011). Hidalgo et al. (2012) showed that the mean scalar dissipation rates and the dimensionless constant flux are independent of the Rayleigh number (in the range of high Rayleigh numbers $Ra = 5\,000 - 30\,000$). Slim (2014) characterised by means of Rayleigh-Bénard simulations the temporal regimes of solutal convection numerically and showed that the (dimensionless) constant flux takes a value of $\hat{J} = 0.017$. Hassanzadeh et al. (2007) reports that for $Ra < 600$ the dissolution flux

(expressed by the dimensionless Sherwood number Sh) follows a scaling relationship proportional to $Ra^{1/2}$ (definition of Sh in Section 3.2.1). A characterisation of the shutdown of convection is presented by Hewitt et al. (2013) as well as the decay of the convective flux over time during the shutdown. Other noteworthy studies using two-dimensional simulations and the Rayleigh-Bénard configuration are Hassanzadeh et al. (2005), Riaz et al. (2006), Farajzadeh et al. (2007), Pruess and Zhang, Elenius and Johannsen (2012), Li et al. (2020), Tsinober et al. (2022) and Erfani et al. (2022). Due to the high computational effort, only a few three-dimensional numerical studies are available, such as the work of Pau et al. (2010) who compared numerical studies in two and three dimensions. Fu et al. (2013) investigate the pattern-formation of convective mixing by means of high-resolution three-dimensional simulations. Not dissolution-, but temperature-driven Rayleigh-Bénard convection was investigated by three-dimensional numerical simulations in Pirozzoli et al. (2021) and de Paoli et al. (2022).

As discussed in Section 2.3.1, experimental studies predominantly apply the Rayleigh-Taylor model as the realisation of a stationary upper boundary with constant concentration poses an experimental challenge. However, the assumption of a sharp and rigid interface is valid in the context of CO_2 geological sequestration (Elenius and Gasda, 2013; Riaz and Cinar, 2014). This is in contrast to the majority of numerical studies applying the Rayleigh-Bénard model, making it difficult to compare key metrics, such as the dissolution flux of the experimental to the numerical results. Solely the experimental study of Slim et al. (2013) applies a fixed interface with constant concentration that allows for visual investigation of the dissolution pattern. A two-dimensional Hele-Shaw cell is applied and potassium permanganate (KMnO_4) in water is used as an analogy for CO_2 in brine. To the author's best knowledge, there is not a combination of quantitative and three-dimensional visual analysis of convective mixing behaviour in porous media that uses fluid pairs that can represent the CO_2 -brine system, justifying the need for such experimental analysis.

2.4 Density-Driven Convection in Heterogeneous Porous Media

The majority of work on solutal convection focuses on homogeneous porous materials where its strength directly depends on the magnitude of the permeability. CO_2 dissolution in heterogeneous porous systems has been far less studied despite the predominance of heterogeneities in geological storage sites (Kong and Saar, 2013). Real geological reservoirs are heterogeneous at all length scales and it is evident that spatial variations in any porous property (*e.g.*, permeability, porosity) can alter the efficiency and the characteristics of the convective mixing process (Emami-Meybodi et al., 2015; Jensen and Lake, 1988).

The two-dimensional modelling studies of Ennis-King et al. (2005), Xu et al. (2006), Rapaka et al. (2008), Hong and Kim (2008), Cheng et al. (2012), Li et al. (2019a), Li et al. (2019b), and Li et al. (2020) discuss the effect of permeability anisotropy in the porous medium. An increase in vertical permeability results in a delay of the onset of the convective process and a decrease of the dissolution rate. Li and Benson (2015) performed simulations to study the influence of small-scale heterogeneities on large-scale CO₂ migration during geological storage. Nield and Simmons (2007) distinguish between moderate and high heterogeneity of the permeability and suggest a stability criterion for strongly heterogeneous structures. Green et al. (2009) investigates multiple heterogeneous porous media with randomly distributed impermeable flow barriers aiming to represent thin horizontal shales. The results show a shorter onset time of convection compared to a homogeneous medium. Farajzadeh et al. (2011) studied the CO₂ dissolution for various permeability field realisations and report a dissolution flux that is higher for heterogeneous compared to homogenous porous media. Similar studies have been performed by Kong and Saar (2013) and Ranganathan et al. (2012), analysing the CO₂ concentration patterns and profiles and the CO₂ mass flux. Kim et al. (2019) quantifies the effect of fractures on density-driven convection. They found that fractures generate positive feedback on the CO₂ circulation by serving as a preferential pathway for both up- and downward migration of fluid.

Due to high computational requirements, three-dimensional work on convective mixing in heterogeneous porous media is scarce. Some work focuses on natural convection caused by temperature gradients, such as Yang et al. (2021) who studied the effect of vertical and horizontal heterogeneity on entropy generation. To the author's best knowledge solely Green and Ennis-King (2014) studied real three-dimensional solutal convection in heterogeneous material by introducing randomly distributed elliptical flow barriers in the otherwise homogeneous model.

A common approach in experimental studies is to use packed beds consisting of glass beads (*e.g.*, Liyanage et al. 2019, 2020; Nazari Moghaddam et al. 2012; Teng et al. 2017), plastic beads (*e.g.*, Lister 1990; Shattuck et al. 1995) or melamine resin particles (*e.g.*, Nakanishi et al. 2016; Wang et al. 2016) as porous media. The majority of those beds is packed homogeneously and only a few studies investigate the effect of porous media heterogeneities on convective dissolution and its flow pattern. Amarasinghe et al. (2021) visualised CO₂ convective mixing in heterogeneous packed glass beads (horizontal or vertical layers) using CO₂ and water at reservoir conditions in a two-dimensional Hele-Shaw cell. They studied transport velocity deviation due to the heterogeneity and the effects of the different permeability zones. Aggelopoulos and Tsakiroglou (2012) studied in a pressure column the effect of micro-heterogeneity in sand packs on the CO₂ dissolution rate. The micro-heterogeneity was realised by a broad sand grain size distribution that creates spatial variations

of permeability. They reported that the rate accelerates with the extent of the micro-heterogeneity. Wang et al. (2021a) used magnetic resonance imaging (MRI) technology to investigate the three-dimensional natural convection in mixed packs of glass beads with different particle sizes. Wang et al. (2021b) quantified the effect of permeability heterogeneity on density-driven convection in several kinds of heterogeneous packed glass beads representing various geological structures. Although a strong impact of the heterogeneous structures of natural rocks on the dissolution behaviour is expected, to the author's best knowledge, there is to date no experimental study in the literature that observes convective dissolution in heterogeneous natural and consolidated materials. Therefore, the role of heterogeneity on the growth and decay of instability fingers and the rate of dissolution is of practical importance and requires more investigation (Hassanzadeh et al., 2005).

Chapter 3

Numerical and Computational Methodology

This chapter covers the principles of the numerical and computational techniques applied in Chapter 6, 7 and 8. At first, the two-dimensional model is presented that is applied in Chapter 6 to quantify systematically the mixing dynamics during density-driven solutal convection in homogeneous porous media. This is followed by the description of the fundamentals of important dissolution measures and of the spatial moments of mass used to evaluate the convective process. The last section addresses the one-dimensional advective-dispersive transport model that is compared to the experimental results in Chapter 7.

Some of the material presented in this chapter has been published in Eckel and Pini (2021) and Eckel et al. (2023).

3.1 Theoretical Formulation of the Two-Dimensional Model

In Chapter 6, we study numerically the transport process within a (field-scale) porous medium below a migrating CO₂ plume in a saline aquifer. Therefore, we consider the situation depicted in Figure 3.1, with properties summarised in Table 3.1. The two-dimensional porous medium has uniform porosity ϕ , and permeability k , and is initially saturated with the ambient fluid. The diffusive length scale $\mathcal{L}$ is a measure of the thickness of the boundary layer at the time of instability. To ensure that the onset of convection is independent of the vertical extent of the reservoir, we choose $H = 400$ m, so that $H/\mathcal{L} \gg 1$ for all Ra . Its width, W , was varied between 300 m and 800 m to account for the dependency of the critical wavelength λ_c on Ra (Ennis-King et al., 2005; Hassanzadeh et al., 2007;

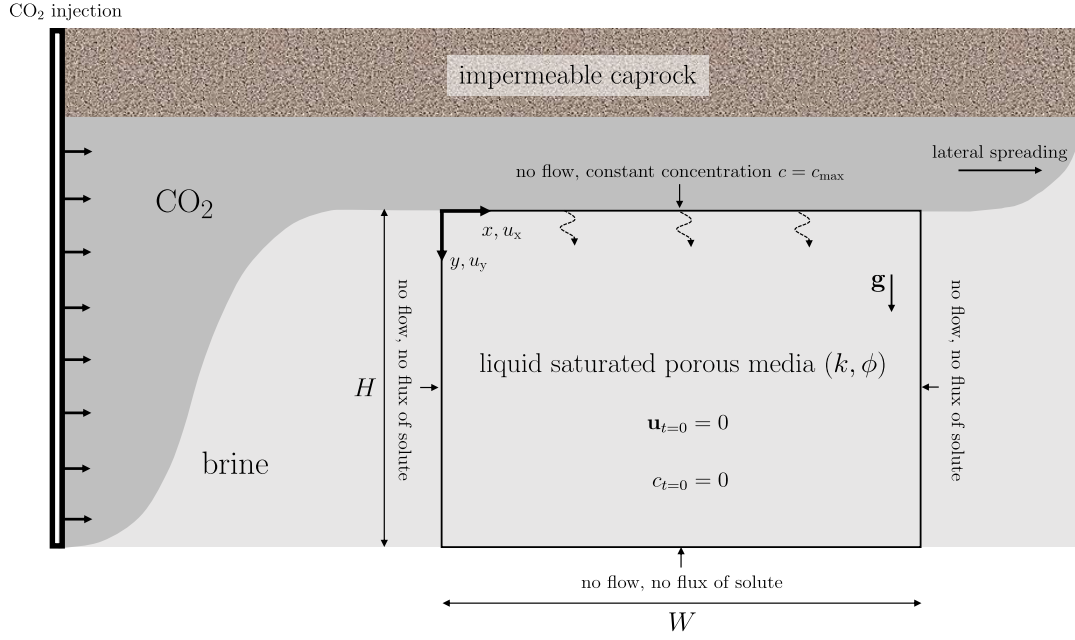


Figure 3.1: Simplified schematic of a saline aquifer with CO₂ injection. Numerical simulations of transport are carried out in a two-dimensional domain below the CO₂/brine interface of height H and width W . Initial and boundary conditions are indicated in the figure. Sketch not drawn to scale.

Slim and Ramakrishnan, 2010) and to ensure that W is larger than λ_c (Andres and Cardoso, 2012; Xu et al., 2006). To vary Ra , the permeability was adapted for each simulation (five cases, see Table 3.1). As done in previous studies, *e.g.* Riaz et al. (2006) or Hassanzadeh et al. (2007), we apply an open and stationary upper boundary of constant dissolved CO₂ concentration, $c_{\max}$ (reservoir conditions: temperature 320 K, pressure 100 bar, 2×10^5 ppm salinity) assuming that CO₂ and brine are in local equilibrium within the capillary transition zone (Rayleigh-Bénard configuration, see Section 2.2 and 2.3). At first, a diffusive boundary layer of CO₂-rich fluid builds up and convection ensues when

Table 3.1: Parameters for the numerical simulation study. Values of permeability, k , and domain width, W , are changing with Ra , while all other parameters are kept constant. In this table, the characteristic length scale is the diffusive length scale $\mathcal{L} = \phi D \mu / (k \Delta \rho_{\max} g)$. The critical wavelength is calculated according to Xu et al. (2006) with $\lambda_c = 96.23 \phi D \mu / (k \Delta \rho_{\max} g)$.

Parameters		Cases				
		Ra [-]	k [m ²]	W [m]	$\mathcal{L}$ [m]	λ_c [m]
H [m]	400	100	9.17×10^{-16}	800	4.00	385.0
$\Delta \rho_{\max}$ [kg m ⁻³]	10	250	2.29×10^{-15}	700	1.60	154.0
ϕ [-]	0.18	1 000	9.17×10^{-15}	600	0.40	38.5
D [m ² s ⁻¹]	2×10^{-9}	2 500	2.29×10^{-14}	440	0.16	15.4
μ [Pa s]	10^{-3}	10 000	9.17×10^{-14}	300	0.04	3.9
$c_{\max}$ [mole m ⁻³]	1 033					

perturbations at the upper boundary intensify owing to a sufficient accumulation of denser fluid. We further assume here that the low relative permeability to brine in the capillary transition zone prevents the brine to flow upwards outside of the domain.

3.1.1 Governing Equations

The phenomenon of single-phase density-driven convection is described by partial differential equations presented here in dimensional form (quantities defined in the nomenclature section). Mass conservation is expressed by Eq. 3.1, whereby the fluid velocity vector, $\mathbf{u}$, is computed using Darcy’s law (Eq. 3.2). Eq. 3.3 is the advection-diffusion equation that describes solute transport in the domain in terms of the dissolved concentration, $c(\mathbf{x}, t)$:

$$\phi \frac{\partial}{\partial t} \rho + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (3.1)$$

$$\mathbf{u} = -\frac{k}{\mu} (\nabla p + \rho \mathbf{g}) \quad (3.2)$$

$$\phi \frac{\partial}{\partial t} c + \nabla \cdot (-\phi D \nabla c + \mathbf{u} c) = 0 \quad (3.3)$$

$$\rho = (\rho_{\max} - \rho_0) \frac{c}{c_{\max}} + \rho_0 = \Delta \rho_{\max} \frac{c}{c_{\max}} + \rho_0. \quad (3.4)$$

CO₂ is only partially miscible in brine with a low saturation concentration (Li et al., 2004; Zhao et al., 2015). Densities of aqueous solutions of CO₂ obtained from various experimental studies are collected and presented in Figure 3.2. The density is normalised with $\rho^* = \frac{\rho - \rho_0}{m}$ and $m = \frac{\rho_{\max} - \rho_0}{c_{\max} - c_0}$ where ρ_0 and c_0 are the density and the concentration of pure brine. The subscript “max” denotes the saturated condition. A comparison of all data sets with the identity line in Figure 3.2 reveals that the mixture density follows a linear relationship with the CO₂ concentration for a broad range of temperatures, pressures and salinities. Therefore, a linear relationship between the mixture density, $\rho(\mathbf{x}, t)$, and the dissolved CO₂ concentration is assumed (Eq. 3.4). Hidalgo et al. (2012) shows numerically a weak effect of the viscosity contrast between a heavy (μ_1) and a light fluid (μ_2 , $0.1 < \mu_1/\mu_2 < 7.4$) on the density-driven convection process (*i.e.*, on the scalar dissipation rate). However, a viscosity ratio between the heavier saturated brine and the lighter pure brine no larger than 1.3 is to expect under reservoir conditions (Bando et al., 2004; McBride-Wright et al., 2015). Accordingly, the viscosity, μ , is assumed to be constant and independent of the CO₂ concentration. We note that the commonly adopted Boussinesq simplification (*e.g.*, Hassanzadeh et al. 2007, Riaz et al. 2006), that states that density variations do not impact the flow field except for creating buoyancy forces, is not fully implemented and density gradients are therefore fully accounted for in the continuity equation to ensure the conservation

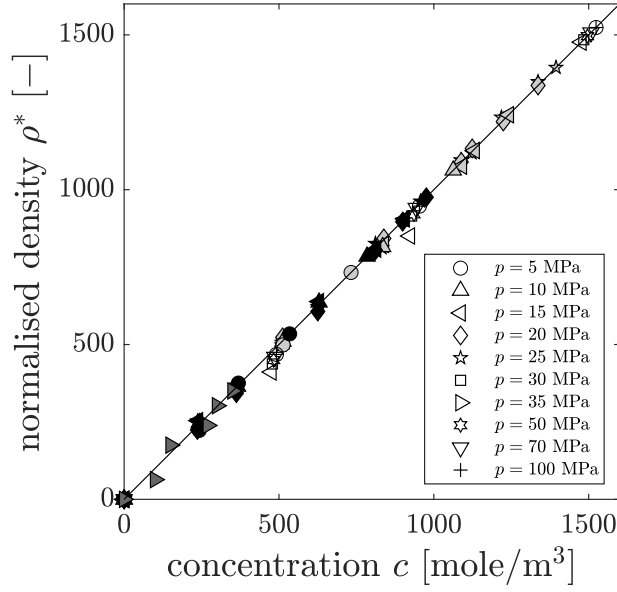


Figure 3.2: Normalised density ρ^* as a function of the molar CO_2 concentration c , data from the literature includes experimental measurements using the binary system CO_2 and H_2O (light grey filled symbols: Li et al. (2004), temperature $T = 59^\circ\text{C}$; white filled symbols: McBride-Wright et al. (2015), $T = 23^\circ\text{C}$; dark grey filled symbols: Ohsumi et al. (1992), $T = 3^\circ\text{C}$) and the binary system brine and CO_2 (black filled symbols: Li et al. (2004), $T = 59^\circ\text{C}$). Data available in molar fractions were converted to molar concentration c . The data points fit linearly with a coefficient of determination of $R^2 > 0.99$.

of mass (Eq. 3.1). However, the change of the pressure head due to density variations is negligible compared to the absolute density and density variations are only included in the buoyancy term in Eq. 3.2. Further basic assumptions associated with Eqs. 3.1–3.4 and the fluid flow and the solute transport are:

- Darcy’s law is applicable, *i.e.* the flow is in the laminar regime.
- The fluid is incompressible in response to a pressure change and non-reactive.
- Natural background flow is neglected.
- Molecular diffusion is expressed by Fick’s laws of diffusion.
- At the top boundary is the equilibrium saturation concentration of CO_2 applied (single-phase problem).
- Velocity-induced dispersion effects are neglected.
- Molecular and ionic interactions between solute particles are neglected.

3.1.2 Initial and Boundary Conditions

The governing equations are closed with appropriate initial and boundary conditions, as depicted in Figure 3.1. At the time $t = 0$ the bulk consists of pure brine and the fluid is motionless:

$$c = 0, \quad \mathbf{u} = 0. \quad (3.5)$$

A no-flow boundary condition is imposed at each boundary:

$$-\mathbf{n} \cdot (\rho \mathbf{u}) = 0 \quad (3.6)$$

with $\mathbf{n}$ being the normal vector (perpendicular) to the boundary. A no-flux boundary condition is also applied to lateral and bottom boundaries:

$$-\mathbf{n} \cdot (-\phi D \nabla c + \mathbf{u} c) = 0. \quad (3.7)$$

At the top boundary ($y = 0$), a constant concentration is defined ($c = c_{\max}$), meaning that solute enters the domain by diffusion.

3.1.3 Numerical Scheme and Solution Procedure

The numerical simulations were performed using the finite element method in COMSOL Multiphysics (version 5.3a). To this end, two physics interfaces have been used concomitantly, namely “Porous Media and Subsurface Flow” (from the “Fluid Flow” interface) and “Transport of Diluted Species in Porous Media” (from the “Chemical Species Transport” interface). The numerical method of the time-dependent solver is the implicit BDF solver that uses backward differentiation formulas with a variable order of accuracy between 2 and 1. Similar to previous studies (Andres and Cardoso, 2012; Hassanzadeh et al., 2007), we exploited the propagation of numerical noise to seed a density instability in the diffusive boundary layer. A grid with triangular mesh elements was used in this study, with a grid element size that increases gradually along the y-direction towards the centre of the domain. The grid spacing at the top boundary is chosen to be much smaller than the critical wavelength λ_c for all Ra (see Table 3.1 and Table 3.2). To ensure that the solution is largely independent of the chosen mesh resolution, a mesh independence study was carried out by employing the Grid Convergence Index (GCI). The GCI approach is commonly used in computational fluid dynamics and applies the concept of the Richardson extrapolation. For the detailed equations used for the calculation, please refer to Kwaśniewski (2013) or Celik et al. (2008). Based on the results obtained from three meshes of varying

grid resolutions (“fine, mesh 1”, “medium, mesh 2”, “coarse, mesh 3”, shown in Table 3.2), the GCI value is considered as a relative error bound. It provides information about how far the solution of the finer mesh is from the asymptotic value, *i.e.* how a further refinement would change the results (Kwaśniewski, 2013). The grid sensitivity study is based on the dissolution flux results of $Ra = 10\,000$. The flux of the first maximum, the second maximum and the average constant flux are chosen for comparison. The GCI values of the meshes 1 and 2 (GCI_{21}) and 2 and 3 (GCI_{23}) are presented in Table 3.2. The refinement from mesh 3 to mesh 2 improved the results (the most the flux of the second maximum by $GCI_{32} \approx 5\%$). Further refinement is not required since no significant change is achieved between mesh 2 and mesh 1 ($GCI_{21} < 2\%$). Consequently, mesh 2 is seen as adequate and sufficiently fine and implemented in the current work for all simulations. The element size at the top boundary is 0.1 m. That corresponds to a dimensionless grid spacing at the top of $x/\mathcal{L} = 2.5$ for $Ra = 10\,000$ which is smaller than the one of the benchmark study (Slim (2014) used $x/\mathcal{L} \approx 12$).

The simulations are solved with an adaptive time-stepping scheme and the time step is not fixed by the user but controlled by the physics. The simulations were conducted between 30 min and 24 h (depending on the Rayleigh number) and stopped when the dissolution flux dropped sufficiently low in the shutdown regime. The machine used was a Microsoft Windows Server with Intel[®] Xeon[®] processors (28 cores and 56 local processors). Additionally, the dissolution flux results were validated against results from the literature (see Section 6.3).

Table 3.2: Properties of the three grids applied in the sensitivity study, resulting GCI_{21} and GCI_{32} values based on the dissolution flux values (a safety factor of 1.25 is used in the evaluation of the grid convergence).

	Fine, mesh 1	Medium, mesh 2 (used for study)	Coarse, mesh 3	GCI_{21}	GCI_{32}
Number of Mesh Elements	334 444	145 561	64 359		
Triangular Element Size					
– Top Boundary	0.05 m	0.10 m	0.21 m		
– Bottom Boundary	1.95 m	3.90 m	8.11 m		
Flux $\hat{J}$ of 1. Maximum	2.65×10^{-2}	2.68×10^{-2}	2.76×10^{-2}	0.83 %	2.19 %
Flux $\hat{J}$ of 2. Maximum	2.18×10^{-2}	2.23×10^{-2}	2.36×10^{-2}	1.67 %	4.45 %
Average Constant Flux $\bar{\hat{J}}$	1.78×10^{-2}	1.79×10^{-2}	1.72×10^{-2}	0.15 %	0.95 %

3.2 Metrics and Methods to Characterise Solute Dissolution

Solutal convection is a complex process that is founded on the synergy between the mechanisms of spreading and mixing. As originally described in Kitaniidis (1994), the former refers to the stretching

and deformation of the solute plume, owing to spatial fluctuations of the fluid velocity. On the contrary, mixing (or dilution) is associated with a diffusive process and thus refers to the process that increases the volume occupied by the solute plume (*i.e.*, the mixing volume). While spreading and mixing are strongly coupled, they also act over distinct time scales, giving rise to complex distributions of solute concentration in the medium (Le Borgne et al., 2010). It follows that solutal convection should be better evaluated in relation to the local spatial structure of the concentration field and its evolution (Dentz et al., 2011; Kapoor and Kitanidis, 1998; Le Borgne et al., 2015). To this end, we define in the following the concepts of the spreading length and the mixing volume, expressed in form of the dilution index, in addition to other fundamental measures of mixing applied in the modelling study in Chapter 6 together with the concept of the spatial moment analysis applied in Chapter 7 and 8. Other measures that are commonly used in the literature to quantify the solute distribution and that are not used in this study are, for example, the mixing degree and the scalar dissipation rate. The former is developed and used to quantify the quality of mixing of particles. An increase in the mixing degree relates to a more uniform mixing (Yamamoto et al., 2016) and is giving similar information as the (inverse) intensity of segregation. Hidalgo et al. (2012) showed that in the context of dissolution-driven convection in porous media, any dependence of the dissolution flux on the Rayleigh number also translates to a dependence on the scalar dissipation rate on Ra and has therefore not been additionally calculated.

3.2.1 Dissolution Flux and Sherwood Number

Studies that use the dissolution flux (see Section 2.2.2) to quantify the degree of mixing during solutal convection often present the data in dimensionless form by using the Sherwood number, Sh (*e.g.*, Ecke and Backhaus 2016; Neufeld et al. 2010; Wang et al. 2016). Different definitions to calculate the Sherwood number exist in the literature (Emami-Meybodi et al., 2015). One version of Sh represents the ratio of the convective mass transfer to the rate of diffusive mass transport that both depend on the (dimensionless) time $\tau = Dt/H^2$:

$$Sh = \frac{J(\tau)}{J_{\text{diff}}(\tau)}. \quad (3.8)$$

The second definition involves the normalisation of a characteristic mass flux (F_c) by the diffusive mass flux over the sample height (F_m) with (Mojtaba et al., 2014; Neufeld et al., 2010; Teng et al., 2020):

$$Sh(\tau) = \frac{F_c}{F_m} = \frac{F_c}{\phi c_{\text{max}} D_m / H}. \quad (3.9)$$

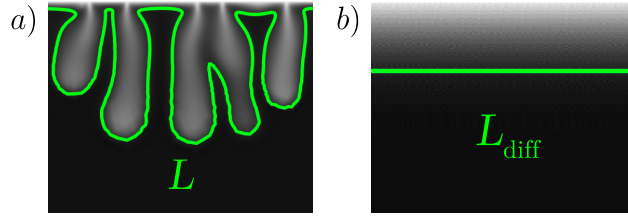


Figure 3.3: Qualitative comparison of the concentration iso-contour line L ($c/c_{\max} = 0.1$, green colour) computed for a mixing process driven by a) solutal convection ($Ra > Ra_c$) and b) pure diffusion ($Ra < Ra_c$). The images are sections near the top boundary from the simulation results of a) $Ra = 10\,000$ and b) a simulation without gravity term in Darcy's law.

This version is comparable with the non-dimensional dissolution flux in Eq. 2.6 but applying a characteristic value of the flux F_c , such as the average dissolution flux or the maximum dissolution flux.

3.2.2 Iso-Contour Line

The extent of interfacial area that is generated during the mixing of two fluids can be used to quantify the degree of mixing (Spencer and Wiley, 1951). As shown qualitatively in Figure 3.3 for the case of two-dimensional solutal convection, we have chosen to define the mixing interface as the iso-contour line of the concentration $c/c_{\max} = 0.1$ (Figure 3.3a). The length of this iso-contour line, L , is computed as a function of time and compared to its counterpart for pure diffusion, $L_{\text{diff}} = W$ (Figure 3.3b). In the literature this measure is also known as the (fluid-fluid) interface length (Jiménez-Martínez et al., 2020). It can be computed at various concentrations or saturations, depending on the system and the geometry of the mixing zone.

3.2.3 Intensity of Segregation

Originally proposed by Danckwerts (1952), the intensity of segregation, I , uses the spatial variation of the concentration to quantify mixing and is nowadays widely used in the analysis of industrial processes (Schwartz, 1963). We adopt here the formulation given by Le Borgne et al. (2015):

$$I(t) = \frac{\langle c(\mathbf{x}, t)^2 \rangle - \langle c(\mathbf{x}, t) \rangle^2}{\langle c(\mathbf{x}, t) \rangle (c_{\max} - \langle c(\mathbf{x}, t) \rangle)} \quad (3.10)$$

where the angled brackets denote the average in space. Therefore, $I \in [0, 1]$, with 0 and 1 referring to a state characterised by complete mixing and segregation, respectively. We note that the numerator in Eq. 3.10 represents the concentration variance and has been previously used by others to quantify the macroscopic evolution of convective mixing (Amooie et al., 2018; Soltanian et al., 2017).

3.2.4 Spreading Length

The spreading length, σ , is used to quantify the spatial extent of the solute plume by computing the average length of the concentration field in the mean direction of flow (Amooie et al., 2018). We adopt here a formulation similar to the one by Jiménez-Martínez et al. (2017):

$$\sigma^2(t) = \frac{W L_s}{M_{\text{tot}}(t)} \int_0^H (y - Y_{\text{com}}(t))^2 c_y(y, t) dy \quad (3.11)$$

where L_s is the system depth (in the two-dimensional case it is $L_s = 1$ m to be consistent with units), $M_{\text{tot}}(t)$ represents the total amount of solute, y is the vertical coordinate, $Y_{\text{com}}(t)$ is the vertical position of the centre of mass (see Eq. 3.19) and $c_y(y, t)$ is the transverse-averaged concentration at each vertical position y . We note that $\sigma^2 \rightarrow H^2/12$ as the time approaches infinity and the system reaches uniform concentration, (*i.e.*, $c(\mathbf{x}, t) = \langle c(\mathbf{x}, t) \rangle$ and $Y_{\text{com}} = H/2$).

3.2.5 Dilution Index

The degree of mixing is quantified through the dilution index, which is an entropy-based measure introduced by Kitanidis (1994), with the two-dimensional formulation:

$$E(t) = \exp \left[- \int_A p(\mathbf{x}, t) \ln p(\mathbf{x}, t) dA \right] \quad (3.12)$$

$$p(\mathbf{x}, t) = \frac{c(\mathbf{x}, t)}{\int_A c(\mathbf{x}, t) dA} \quad (3.13)$$

and the three-dimensional formulation:

$$E(t) = \exp \left[- \int_V p(\mathbf{x}, t) \ln p(\mathbf{x}, t) dV \right] \approx \exp \left[- \sum_1^{N_V} p(\mathbf{x}, t) \ln p(\mathbf{x}, t) \Delta V \right] \quad (3.14)$$

$$p(\mathbf{x}, t) = \frac{c(\mathbf{x}, t)}{\int_V c(\mathbf{x}, t) dV} \approx \frac{c(\mathbf{x}, t)}{\sum_1^{N_V} c(\mathbf{x}, t) \Delta V}. \quad (3.15)$$

The normalised concentration is represented by $p(\mathbf{x}, t)$. $E \in [0, E_{\text{max}}]$ and $E_{\text{max}} = HWL$ is the theoretically maximum value of E with H as the height, W as the width and L as the length of the volume of interest. If applied to the three-dimensional experimental results, the numerical approximations of the integration operation (terms on the right side of Eq. 3.14 and 3.15) are used due to the discrete nature of the data set. We note that the dilution index differs from the intensity of segregation because it accounts for the expansion of the solute plume (in addition to quantifying the degree of concentration homogeneity as in I).

3.3 Spatial Moment Analysis

A systematic study of the longitudinal spreading of the solute during natural convection in porous media is crucial for the understanding of the evolution of buoyancy instability and the spatial and temporal distribution of the solute, hence allowing to estimate the long-term behaviour of the dissolved CO₂ in an aquifer. Spatial moment analysis has been proven to be a useful measure to describe and analyse the longitudinal spreading of the plumes by, for instance, Trevisan et al. (2017) and Ren et al. (2022). From solute concentration distributions (*e.g.*, in form of two- or three-dimensional images), the temporal evolution of the spatial moments of the concentration distribution, including the total mass (0th moment), the centre of mass (1st moment) and the standard deviation (2nd moment) along the main direction of flow are extracted (Silva Lomba and Fraga Alves, 2020). To this end, we use the one-dimensional transverse-averaged concentration function $c_y(y, t)$. The k^{th} raw moment of $c_y(y, t)$ is defined as:

$$\mu_k = \int_0^H y^k c_y dy \quad (3.16)$$

where the limits of the integration represent the location of the interface ($y = 0$) and the bottom of the domain ($y = H$). The 0th raw moment is thus computed as:

$$\mu_0 = \int_0^H c_y dy \approx \sum_{n=1}^{N_H} c_{y,n} \Delta y \quad (3.17)$$

where the numerical approximation of the integral reflects the discrete nature of the experimental data set. Here, the domain is discretised into N_H slices of thickness Δy where $c_{y,n}$ is c_y computed at $y = n \cdot \Delta y$. The total mass of the solute in the imaged domain is thus obtained as $M = \mu_0 A_p$, where $A_p = A\phi$ is the void cross-section. Applying the time derivative of the 0th moment leads to the calculation of the dissolution flux:

$$F(t) = \phi \frac{d\mu_0}{dt}. \quad (3.18)$$

The 1st raw moment in continuous and discrete form is defined as:

$$\mu_1 = \int_0^H y c_y dy \approx \sum_{n=1}^{N_H} n c_{y,n} \Delta y^2 \quad (3.19)$$

which can be applied to compute the location of the centre of mass in the longitudinal direction, $Y_{\text{com}} = \mu_1/\mu_0$. The 2nd order moment is computed about the centre of mass:

$$m_2 = \int_0^H (y - Y_{\text{com}})^2 c_y dy \approx \sum_{n=1}^{N_H} (n\Delta y - Y_{\text{com}})^2 c_{y,n} \Delta y \quad (3.20)$$

which represents the spread of the distribution and is used to calculate the standard deviation of the solute concentration distribution:

$$\sigma = \sqrt{m_2/\mu_0}. \quad (3.21)$$

and is equivalent to the definition of the spreading length in Eq.3.11.

3.4 Solute Transport Model and Longitudinal Dispersion

A classical way to describe solute transport in a uniform porous medium is the advection-dispersion equation (ADE) and is applied in Chapter 7. The equation is based on an analogy of mechanical dispersion to Fick's laws of diffusion. Using the results of the moments, we propose a simplified representation of the mixing process in uniform bead packs by analogy with the one-dimensional advection-dispersion model. For a one-dimensional system and in the absence of chemical reactions, the ADE reads (Neuman and Tartakovsky, 2009):

$$\phi \frac{\partial c_y}{\partial t} = -u_y \frac{\partial c_y}{\partial y} + \phi D_L \frac{\partial^2 c_y}{\partial y^2} \quad (3.22)$$

where c_y is the transverse-averaged solute concentration, u_y is the average superficial fluid velocity in the main direction of flow (here y -direction, $u_y = v_y \phi$) and D_L is the longitudinal dispersion coefficient D_L . The assumptions associated with the use of the ADE are (Berkowitz et al., 2006):

- The porous medium is homogeneous.
- The porous medium is fully saturated.
- Darcy's law applies.
- Mechanical dispersion can be described by Fick's second law of diffusion.
- The transport velocity is equivalent to the fluid velocity.
- The spatial variation of the fluid velocity inside the representative elementary volume is neglected.

The longitudinal dispersion coefficient includes contributions of both molecular diffusion and advection (Berkowitz et al., 2006):

$$D_L = D + v_y \alpha_L \quad (3.23)$$

where D is the effective diffusion coefficient and α_L is the longitudinal dispersivity. For uniform bead packs, the latter increases with effective bead size and is thus considered a characteristic property of the porous medium:

$$\alpha_L = c_p \sigma_H d_p \quad (3.24)$$

where $c_p = 0.5$ based on the mixing-cell theory (Aris and Amundson, 1957; Carberry, 1958; Prausnitz, 1958). The parameter $\sigma_H \geq 1$ describes the strength of heterogeneity of the packing, where $\sigma_H = 1$ represents the most uniform system (Perkins and Johnston, 1963; Sahimi et al., 1986).

The ADE model is solved in MATLAB with the (`ode15s` solver) by defining initial and boundary conditions. In our experiments, the sample does not contain any solute initially, hence:

$$c_y(y, t = 0) = 0 \quad (0 \leq y \leq H). \quad (3.25)$$

The boundary conditions at $y = 0$ (inlet) and $y = H$ (outlet) follow the classic expressions by Danckwerts (Kurotori et al., 2019), namely:

$$c_y(y = 0, t) = c_0 + \frac{\phi D_L}{u_y} \frac{\partial c_y}{\partial y} \Big|_{y=0} \quad (t > 0) \quad (3.26)$$

$$\frac{\partial c_y}{\partial y} \Big|_{y=H} = 0 \quad (t > 0) \quad (3.27)$$

where c_0 is the feed concentration. We note that important differences exist between the boundary conditions in the ADE model and in the dissolution experiments presented in Chapter 7. These differences and the comparison are further discussed in Section 7.4.1 in Chapter 7.

Two important elements connect the ADE to the analysis of moments. First, the average transport velocity is related to the motion of the centre of mass (Aris and Amundson, 1957; Natarajan and Kumar, 2018):

$$u_y = \frac{dY_{\text{com}}}{dt} \approx \frac{\Delta Y_{\text{com}}}{\Delta t}. \quad (3.28)$$

Second, the longitudinal dispersion coefficient is related to the temporal evolution of the 2nd spatial central moment:

$$D_L(t) = \frac{1}{2} \frac{d\sigma^2}{dt} \approx \frac{1}{2} \frac{\Delta \sigma^2}{\Delta t} \quad (3.29)$$

whereby the definition of the 2nd central moment, spreading length, in Eq. 3.21 is applied. The numerical approximation of the derivatives in Eq. 3.28 and 3.29 reflects the discrete nature of the experimental CT data set.

Chapter 4

Materials and Characterisation

This chapter covers the two classes of porous materials, homogeneous synthetic bead packs and natural rocks, deployed in the dissolution experiments to study convective mixing. The first section gives an overview of the porous materials used. This is followed by a detailed characterisation of various physical features by experimental or image processing analysis.

Some of the material presented in this chapter has been published in Eckel et al. (2023).

4.1 Overview of Materials

The samples used in the dissolution experiments of this thesis are shown in Figure 4.1 together with cross-sections of micro Computed Tomography (micro CT) scans taken of dry sub-samples. The tomographic high-resolution images (g–j) have been acquired by Edward Bailey (experimental officer in the Department of Earth Science & Engineering) using a Thermo Fisher Heliscan micro CT scanner at a resolution of $3.9\text{ }\mu\text{m}$.

Three homogeneous packed samples were generated with monodispersed soda glass ballotini with average diameters of $250\text{ }\mu\text{m}$, $100\text{ }\mu\text{m}$ (SiLibeads, supplied by VWR, UK) and $55\text{ }\mu\text{m}$ (Oberflächentechnik Seelmann e.K., Germany), respectively. The beads form a uniform random packing of the size $15\text{ cm}\times 13\text{ cm}\times 15\text{ cm}$ in an acrylic plastic cube (details on the procedure are given in Section 5.2). The natural rocks used in this thesis are Bentheimer sandstone, Boise sandstone, Mount Gambier limestone and Ketton limestone. Bentheimer sandstone is a well-sorted sedimentary rock taken from the lower Cretaceous basins (Germany). It mainly consists of quartz and is considered to be ideal for reservoir studies due to its homogeneous block-scale nature (Peksa et al., 2015) and therefore similarity between individual samples. Boise sandstone is rich in clay and taken from the Upper Miocene

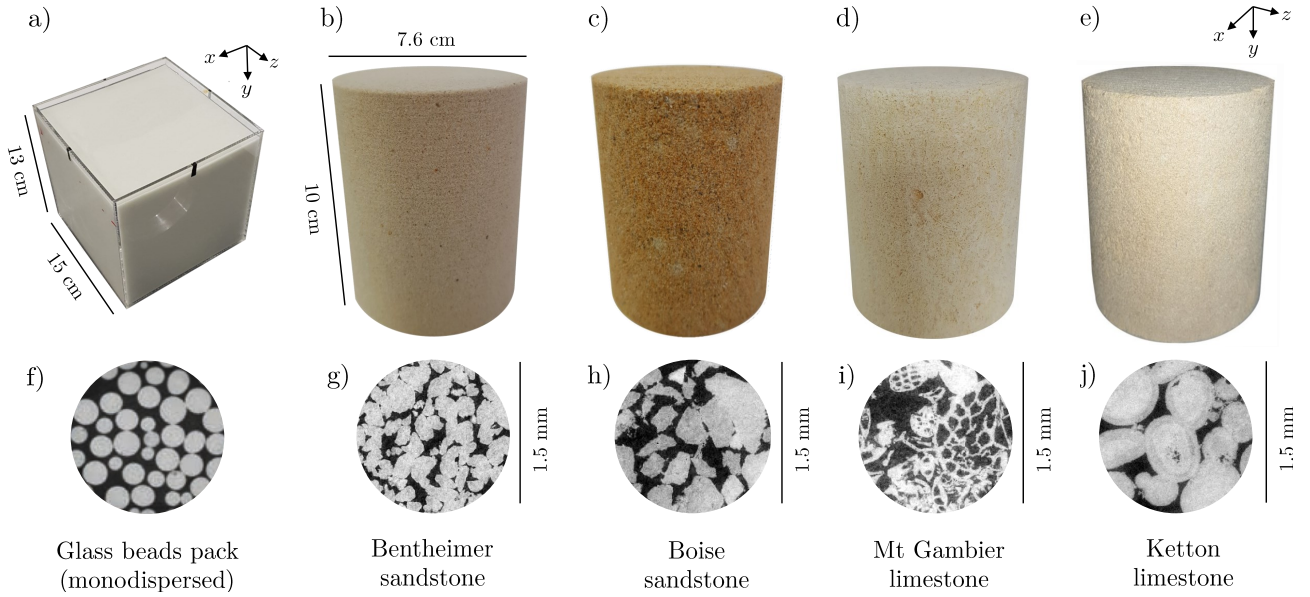


Figure 4.1: Samples used for the dissolution experiments. The upper panel of images shows pictures taken with a conventional camera of a) the water-saturated bead pack and b)–e) of the rock samples A. The lower panel of images shows cross sections taken from the micro CT images of f) a pack of glass beads (image only for qualitative presentation and taken from existing data set taken from Kurotori et al. 2019) and g)–j) of rock samples D.

Idaho Formation (USA) with fairly uniform characteristics but a higher permeability. Mount Gambier limestone (in the following referred to as Mt Gambier) from South Australia (Australia) is a highly porous, fossiliferous limestone. It has a macro- and microscopic heterogeneity caused by fossil shells and bryozoa (Chen et al., 2020). Ketton limestone has bimodally distributed pore sizes caused by cemented bead-pack-like grains with an intragranular microporous structure (Andrew et al., 2013). Cylindrical rock samples of Bentheimer, Boise and Mt Gambier are supplied from Kocurek Industries INC (Caldwell, TX, USA) and samples of Ketton from Ketton Stone Masonry & Fixing (Ketton Stamford, Lincolnshire, UK).

Different sample sizes of the rocks are used in the characterisation and the dissolution experiments. For a clear distinction, the samples are listed in Figure 4.2 and designated capital letters A–E. The two cube subsamples E at two arbitrarily chosen locations are digitally cropped out of the micro CT images of the cylindrical sample D for further analysis. Hence, the characteristics calculated in this section are an average over the two subsamples. Solely for Mt Gambier, three cubes were used to reduce the uncertainty of the extracted properties.

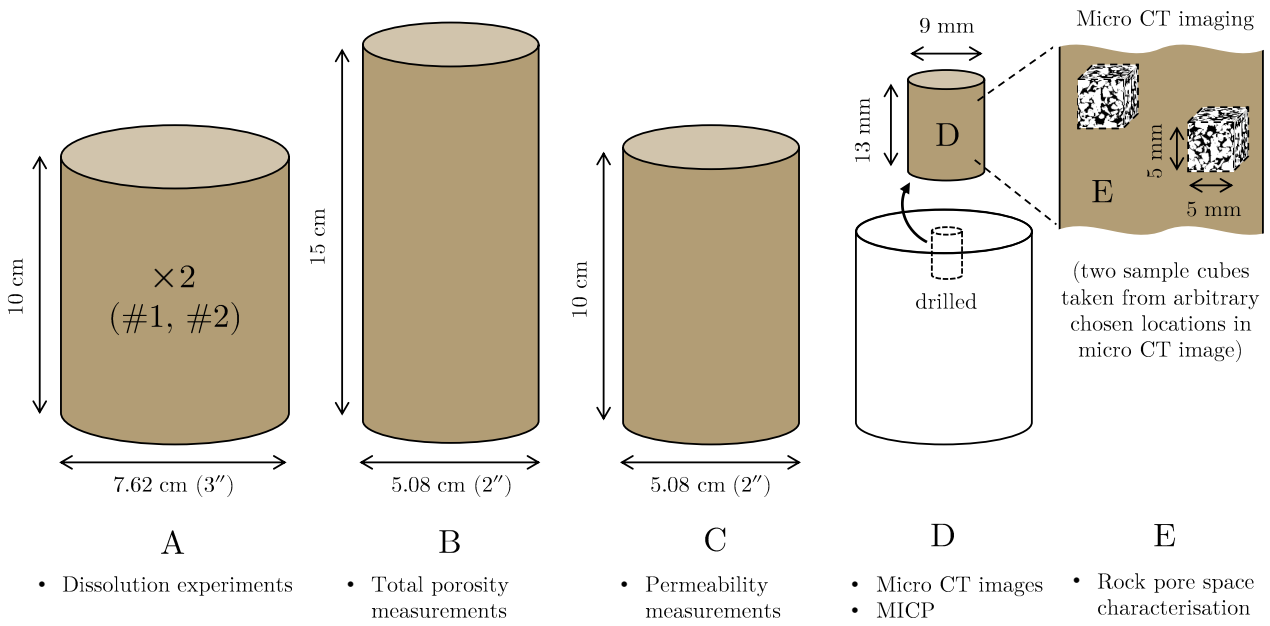


Figure 4.2: Schematic representation of rocks with dimensions, quantities and indication of primary use in this study. Each one cylindrical rock samples B and C and each two samples A (#1 and #2) were ordered from the manufacturer in indented sizes. Samples D were drilled from a larger core using a Scheppach Top Pillar DP16SL bench drill (1 cm diameter drill bit). Cubes E (two for each rock type, three for Mt Gambier) were cropped out of the micro CT images taken of sample D at arbitrarily chosen locations.

4.2 Spatial Scales of Heterogeneities

Mono-dispersed glass beads are used for the packed beds and the packing can therefore be considered uniform and homogenous. In contrast, natural geological materials always show heterogeneities and it is crucial to characterise those to support the understanding of how the pore space impacts the solute dissolution behaviour in the experiments. Figure 4.3 applies the concept of the Representative Elementary Volume (REV) that allows to quantitatively characterise heterogeneity on various length scales. It shows how a system parameter (*e.g.*, porosity) changes with the volume size it is calculated for until it reaches the size of the REV ($= V_{\min}$). The parameter of interest in the subsample volume becomes independent of the size of the volume (Corbett et al., 1999) and therefore yields a value representative of the whole domain. In the bottom images of Figure 4.3, the various scales of heterogeneities are illustrated. Rock heterogeneity in geological formation exists at pore-scale (μm -scale, bottom image to the left), grain-scale (mm-scale, bottom image in the middle), core-scale (0.1 to 10 cm, bottom image to the right), and field-scale (>10 cm, not included in the schematic, Kuo and Benson 2015; Li and Benson 2015). While in the schematic example, the microscopic inhomogeneity

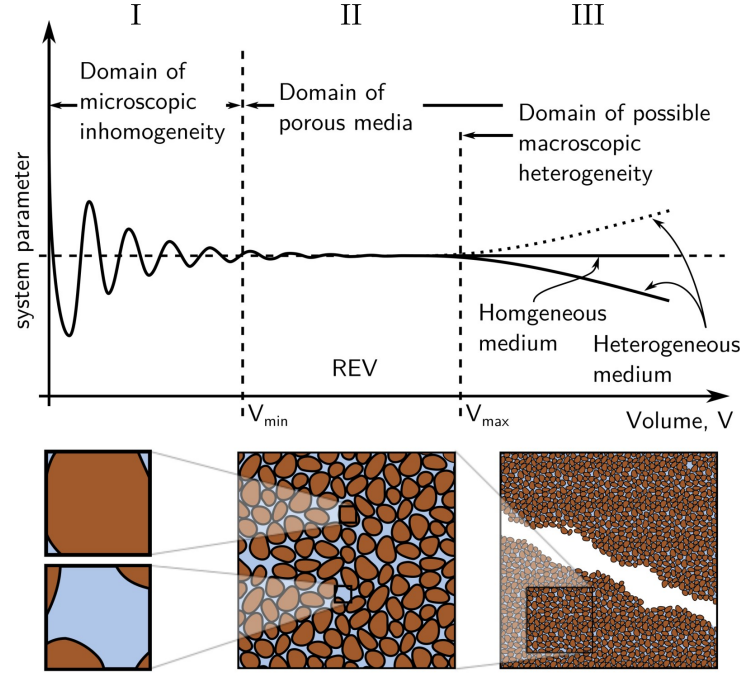


Figure 4.3: Concept of Representative Elementary Volume (REV) after Bear (1988), taken from Böttcher (2014) (slightly modified). The REV is the smallest volume over which a measurement can be made and be representative of the whole domain. REV is theoretically achieved at scales intermediate between the erratic fluctuations of region I and the macroscopic heterogeneity of region III.

is high, since the system parameter strongly fluctuates, it reaches a plateau in the subsequent range (grain-scale). In other words, this particular rock appears homogeneous from a grain-scale while heterogeneities are present at the millimetre scale. In the literature, it is referred to such heterogeneities as High-Randomness Pattern-Free (HRPF) heterogeneities (Li and Benson, 2015), characterised by a high degree of randomness and short correlation length (more details in Section 4.7). If larger volumes are considered, macroscopic heterogeneities, in form of fractures or channels, can be made visible by an in- or decrease of the system parameter. Homogeneity on a core-scale reflects as a flat curve.

In the following sections, various methods and measurements are used to extract porous media properties and measures of heterogeneity that allow a *in-situ* characterisation of the porous materials applied in this thesis. A flow chart of the material characterisation techniques used, including the spatial scales they apply to, is given in Figure 4.4. Although the focus of this chapter is on the characterisation of the rocks, most metrics are determined for both types of materials (bead packs and rocks).

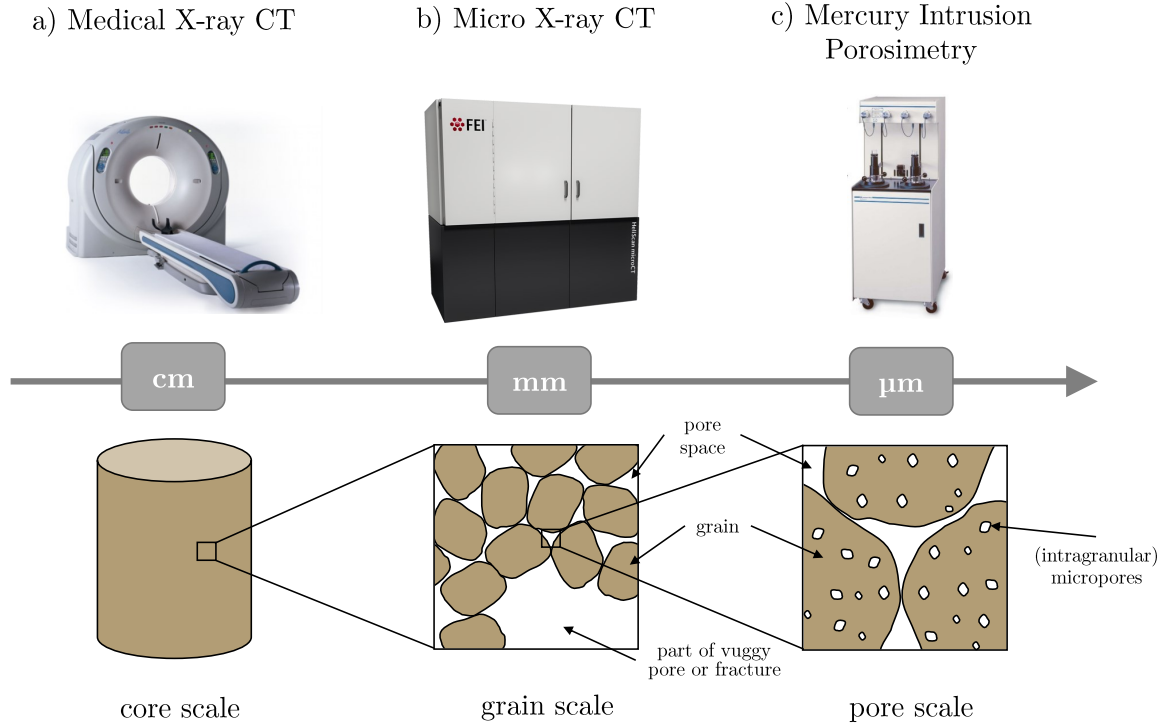


Figure 4.4: Flow chart of the material characterisation techniques considered in this chapter together with illustrations of the scales they apply to (here in a grain structured rock). Images of the instruments are taken from the websites a) Medsystems (2023), b) CEITEC (2023) and c) Environmental XPRT (2023).

4.3 Total Porosity

We define the total porosity ϕ_t of a porous material according to:

$$\phi_t = \phi + (1 - \phi)\phi_p \quad (4.1)$$

with ϕ_p as the intra- and ϕ as the intergranular porosity. Since the glass ballotini are made of dense soda-lime glass, no intragranular porosity exists ($\phi_p = 0$) and the total porosity is equivalent to the intergranular porosity ($\phi_t = \phi$). Therefore, we solely refer to “porosity” (ϕ) in the context of the bead packs and estimate it by applying the weight change of samples before and after water saturation, using the following equation:

$$\phi = \frac{M_w / \rho_w}{V} \quad (4.2)$$

where M_w is the weighted mass of water filling the pore space, ρ_w the density of water and V the size of the sample (in water-saturated condition). The values of the porosities together with the particle diameters are listed in Table 4.1.

Table 4.1: Properties of the water-saturated glass bead packs: ϕ is the porosity, k is the permeability $d_{p,50}$, $d_{p,l}$ and $d_{p,u}$ are the median, lower and upper particle diameters.

$d_{p,50}$ [μm]	$d_{p,l}$ [μm]	$d_{p,u}$ [μm]	ϕ [–]	k [m^2]	Δk [m^2]
250	200	300	0.32	2.5×10^{-11}	3.3×10^{-12}
100	88	112	0.33	4.4×10^{-12}	3.6×10^{-13}
55	40	70	0.34	1.5×10^{-12}	2.8×10^{-13}

To obtain the total porosity ϕ_t of the rocks (core samples B), we applied the X-ray saturation technique (Pini and Madonna, 2016). Two end-caps are secured on each face of the sample and secured with a shrink tube (51 mm sleeve diameter, purchased from TE Connectivity) by carefully applying heat all around. After placing them on the medical CT scanner bed, the rocks were first scanned in air-saturated condition. The images were reconstructed at a spatial resolution of 0.5 mm in the z-direction and roughly 0.1–0.2 mm in the x- and y-direction (in-plane resolution). This value changes slightly between the different samples used. The sample is then flushed with gaseous CO_2 for several minutes and afterwards saturated with water (7–8 pore volumes). The samples are again scanned in the same position, this time in water-saturated condition. The following equation is applied for the calculation of the total (connected) porosity on voxel-basis (Kurotori et al., 2019; Pini and Madonna, 2016):

$$\phi_{t,i} = \frac{CT_{\text{wet},i} - CT_{\text{dry},i}}{CT_w - CT_{\text{air}}}. \quad (4.3)$$

$CT_w = 40 \text{ HU}$ and $CT_{\text{air}} = -976 \text{ HU}$ are the CT numbers (in Hounsfield units, background on the CT number see Section 5.3) of pure water and air. $CT_{\text{dry},i}$ and $CT_{\text{wet},i}$ are the CT numbers of a voxel when i the rock is saturated with either air or water. The theoretical background on CT imaging and CT numbers is given in Section 5.3.1. The obtained CT-images have been resampled with a coarsening scheme of 30×30 (initial voxel dimensions: $(0.1 \times 0.1 \times 0.5) \text{ mm}^3$ to $(3 \times 3 \times 0.5) \text{ mm}^3$) which reduces the uncertainty on the voxel scale significantly (Pini and Madonna, 2016). The total porosity is the sample-average of the voxel porosities ($\phi_t = \sum \phi_{t,i}/N$, with N being the number of voxels) and the values are listed in Table 4.2. The highest total porosity is reported for Mt Gambier ($\phi_t = 0.51$). Bentheimer, Ketton and Boise, in ascending order, have total porosity values between 20–30 %. The porosity values predicted using Eq. 4.3 are affected by an uncertainty ($\sigma_{\phi_{t,n=2}}$). This uncertainty is calculated from the “CT noise” $\sigma_{\Delta CT_{n=2}}$ by subtracting $n = 2$ coarsened images of the dry rock (details on the calculation see Appendix B). We calculate the uncertainty with (Pini et al., 2012):

$$\sigma_{\phi_{t,n=2}} \approx \frac{\sigma_{\Delta CT_{n=2}}}{1000}. \quad (4.4)$$

Table 4.2: Porosity and permeability values of the rock samples. The total porosity ϕ_t is measured with the saturation technique (medical X-ray CT scanner). In brackets is the uncertainty of the total porosity $\sigma_{\phi_{t,n=2}}$ (30×30 voxel coarsened). The intergranular porosity ϕ is derived from the binarised micro CT images and the intragranular porosity ϕ_p is calculated according to Eq. 4.1. The uncertainty of the intergranular porosity σ_ϕ is the standard deviation between the intergranular porosity values of the two cubes. Except for Ketton limestone, the intragranular porosity is close to zero and considering the uncertainty it results to $\phi_p = 0 - 0.01$ for Bentheimer, Boise and Mt Gambier. The uncertainty of the Ketton intergranular porosity is calculated by applying Eq. 4.1 and classic rules of error propagation. The permeability values k are obtained during steady-state brine injection and uncertainty values are in brackets.

Rock sample	ϕ_t ($\sigma_{\phi_{t,n=2}}$) [-]	ϕ (σ_ϕ) [-]	ϕ_p (σ_{ϕ_p}) [-]	k (Δk) [D]
Bentheimer	0.21 (0.01)	0.22 (< 0.01)	0 – 0.01	1.42 (0.01)
Boise	0.28 (0.01)	0.26 (< 0.01)	0 – 0.01	4.48 (0.01)
Mt Gambier	0.51 (0.01)	0.51 (< 0.01)	0 – 0.01	12.99 (0.07)
Ketton	0.22 (< 0.01)	0.12 (0.01)	0.11 (0.02)	3.47 (0.01)

and the values, given in brackets in Table 4.2, are all around $\sigma_{\phi_{t,n=2}} = 1\%$. The value in the denominator results from the combination of dry and wet images, *i.e.*, the difference of the CT numbers of the two pure reference fluids, water ($CT_w - CT_{air} \approx 1000$ HU). More details on the derivation of Eq. 4.4 can be found in Pini et al. (2012). The distribution of voxel porosity values for each sample is shown in Figure 4.5. Mt Gambier has the broadest porosity distribution and highest absolute standard deviation with 4 %. Boise and Ketton follow with 3 % and the lowest deviation, and therefore the most homogeneous rock in terms of the porosity distribution is Bentheimer (1 %).

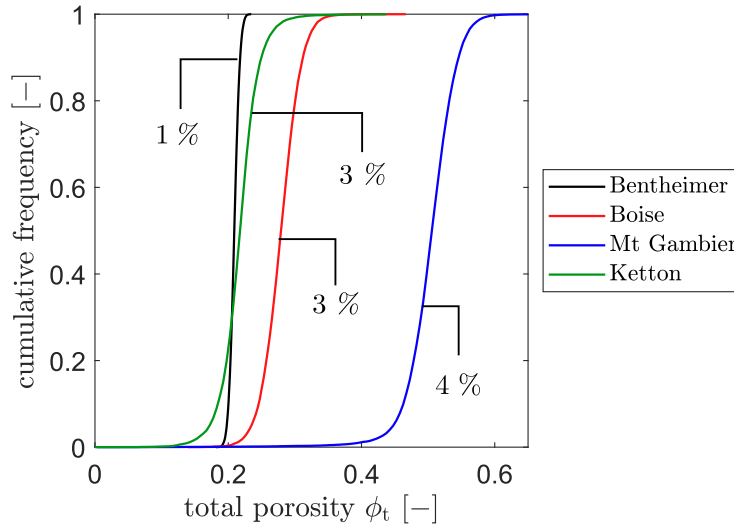


Figure 4.5: Total porosity values on voxel scale as a cumulative frequency histogram together with indicated absolute standard deviation over all porosity values $\phi_{t,i}$ (coarsened).

4.4 Inter- and Intragranular Porosity

As mentioned in Section 4.3, no intragranular porosity is to expect in the glass bead packs and this section addresses solely the estimation of the inter- and intragranular porosity of the natural rocks. All four rock types are well documented in the literature and based on these studies we expect only Ketton Limestone to have a significant number of intragranular pores (in form of micropores, see schematic in Figure 4.4 and estimation in Section 4.11). Although the micro CT resolution is very high, pores smaller than the voxel size ($< 3.9 \mu\text{m}$) or other small features cannot be resolved. Thus, we interpret the porosity values extracted from the micro CT as the intergranular porosity ϕ . First, the micro CT images are binarised using an interactive thresholding operation in the image analysis software AVIZO-9 (ThermoFisher Scientific). The threshold for each rock type is chosen based on the minimum between the high- and the low-intensity peak in the image histogram and validated by qualitatively comparing cross-sectional greyscale images with the computed binary images. The determined threshold for each rock is given in Appendix C (Table C.1). Exemplary cross-sections of the cube samples are shown in Figure 4.6. The intergranular porosity is calculated by taking the ratio of the number of voxels labelled to be part of the pore space N_{pore} divided by the total number of

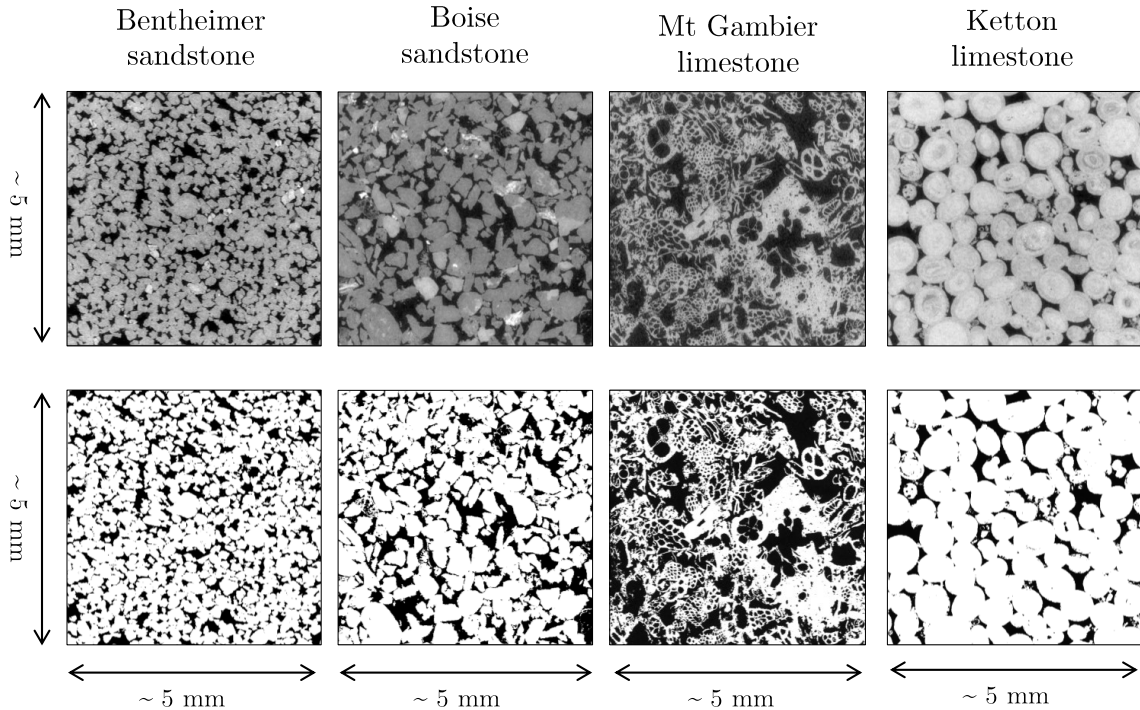


Figure 4.6: Top images: cross-sections taken from the micro CT images (samples E), bottom images: binarised version of the same sections (black is pore space, white is rock material).

voxels N_{total} (Table 4.2):

$$\phi = \frac{N_{\text{pore}}}{N_{\text{total}}}. \quad (4.5)$$

Accordingly, the intragranular porosity of Ketton is calculated with Eq. 4.1 to yield $\phi_p = 11\%$ which agrees very well with the value from the literature ($\phi_p = 11\%$, Shah et al. 2013). The uncertainty (in units of porosity) is calculated to $\sigma_{\phi_p} = 0.02$ using classic rules of error propagation (Table 4.2). The total porosity and intergranular porosity are very similar for Bentheimer, Boise and Mt Gambier, implying that the vast majority of pores are larger than the image resolution (of the micro CT scans) and are connected and therefore accessible to flow. The intragranular porosity of Bentheimer, Boise and Mt Gambier is negligibly small and lies in the range of uncertainty of $\phi_p = 0 - 0.01$.

4.5 Permeability

The average single-phase permeability k of the three beads packs was estimated with the Kozeny-Carman equation model which is one of the most commonly used models for spherical glass beads particles (Kimura, 2018):

$$k = \frac{\phi^3}{36K(1 - \phi)^2} d_{p,50} \quad (4.6)$$

that applies the (total) porosity ϕ , the mean grain diameter $d_{p,50}$ and the Kozeny constant K which is approximately 5 for spherical grains. A normal distribution of the bead sizes between the upper and lower bead size specifications was assumed. The standard deviation of the curve and a one-sigma tolerance was used to estimate the uncertainty values of the permeability Δk . The results are given in Table 4.1.

The measurements of the permeability of the rock samples are discussed in the following and were performed by Andrea Rovelli, PhD student in the research group. The absolute permeability k of each rock sample is determined during steady-state brine injection by measuring the flow rate Q and the mean pressure drop Δp at various flow rates. The permeability can be extracted according to Darcy's law (McPhee et al., 2015):

$$\frac{Q\mu L}{A} = k\Delta p. \quad (4.7)$$

The measurements were performed at ambient pressure and temperature conditions. The experimental apparatus consists of a custom-built aluminium core holder containing rock samples C. The sample was wrapped in a shrink tube to prevent fluid loss. A constant confining annular pressure between the jacketed sample was maintained with a high-pressure syringe pump (Teledyne ISCO, Model 1000D) and tap water as the confining fluid. A differential pressure transducer (Keller UK, model PRD-33X)

is connected to the inlet and outlet faces of the sample. A back pressure of roughly 8 bar was employed on the outer face of the sample. The system was purged with gaseous CO_2 and then saturated with brine (3.7% NaCl brine). Various flow rates were applied and the associated pressure drop along the core was measured. The pressure drop is corrected with a correction factor which is equal to the measured pressure drop when the flow is turned off. The measured pressure drop Δp^* is assumed to be equal to the true pressure drop Δp plus the correction factor Δp_f :

$$\Delta p^* = \Delta p + \Delta p_f. \quad (4.8)$$

In Figure 4.7, the flow rate as $Q\mu L/A$ is plotted against the corrected (true) pressure drop Δp . The permeability and its uncertainty are estimated using weighted linear regression. The permeability of Bentheimer sandstone is $k = 1.44 \text{ D}$ and therefore in the expected range that is reported in the literature ($k = 1.7 \pm 0.1 \text{ D}$ taken from Kurotori (2019) and $k = 1.04 - 2.27 \pm 0.1 \text{ D}$ taken from Peksa et al. (2015), both measured with flow experiments). All remaining permeability values are

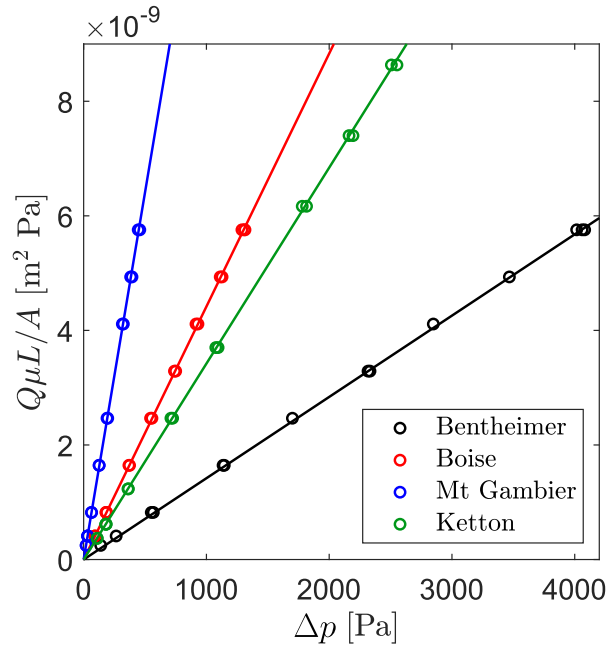


Figure 4.7: Flow rate $Q\mu L/A$ versus pressure drops Δp across the core samples during multi-rate water injection tests. Once the pressure drop is stabilised, pressure values are reported over an average of at least 5 minutes. The symbols correspond to the experimental data and the solid lines are the weighted linear regression to the experimental measurements. Darcy’s equation (Eq. 4.7) is used to estimate the permeability k of the samples. The viscosity of the brine takes a value of $1 \times 10^{-3} \text{ Pa}\cdot\text{s}$. The absolute permeability values are given in Table 4.2. Samples C were used for Bentheimer, Boise and Mt Gambier. For Ketton a longer sample (B) was used but the results are independent of sample length.

Table 4.3: Characteristic properties of the rocks with uncertainty in brackets. For all rocks, the average and uncertainty were calculated using two cube samples E, solely for Mt Gambier three samples were used to reduce the uncertainty (uncertainty is the standard deviation of all values computed). Pore-space heterogeneity factor Φ is calculated with Eq. 4.14 and no uncertainty value is available as only one MICP measurement was taken for each rock.

Rock sample	Bentheimer	Boise	Mt Gambier	Ketton
characteristic length L_c [μm]	260.1 (2.2)	248.7 (16.0)	149.5 (7.6)	534.4 (54.2)
REV edge length $L_{\min}$ [mm]	1.62 (0.11)	1.59 (0.08)	1.73 (0.20)	2.49 (0.11)
tortuosity τ [-]	3.85 (0.19)	3.22 (0.54)	3.47 (0.34)	3.66 (0.83)
coordination number CN [-]	3.86 (0.04)	4.33 (0.01)	6.64 (0.17)	4.09 (0.07)
heterogeneity factor Φ [-]	0.20	0.65	0.62	1.95

reported in Table 4.2. The largest permeability is extracted for Mt Gambier, taking a value that is one magnitude larger than the permeability of Bentheimer. Boise and Ketton lie in a similar range and their permeability is around 2-3 times the value of Bentheimer.

4.6 Characteristic Length

To calculate the Péclet number (definition see Section 8.3.6), a characteristic length L_c of the control volume of the porous media is needed. A common approach is to use the diameter of rock grains or synthetic beads ($d_{p,50}$). However, in some cases, it is difficult to identify individual grains unambiguously. Additionally, the fossiliferous Mt Gambier limestone does not show a grain structure. Hence, we follow the approach described in Bijeljic et al. (2011, 2013) to calculate a physical representative grain size L_c based on a cubic packing of regular spheres. They calculate the characteristic length with $L_c = \pi V/S$ with V as the volume of the porous medium (solid and pore space) and S as the area of the pore-solid interface. An image processing routine was developed in the MATLAB environment and the relevant steps are illustrated in Figure 4.8 by means of one sandstone (Bentheimer) and one carbonate (Mt Gambier). Details on the routine are given in the figure caption. After importing the binary images of the cube samples E into the software (images on the left), in the first step, the unconnected pixels are cleaned by a morphological operation (images in the middle). The perimeter of the rock solid-phase is determined (images on the right panel) and the sum of the perimeter voxels is assumed to be the pore-solid interface ($S = \sum N_{\text{peri}} l_{\text{vox}}$, with N_{peri} as the number of perimeter voxels and l_{vox} as the voxel side length). The values of the characteristic length L_c are shown in Table 4.3 together with uncertainty values. As expected, the largest characteristic length is determined for Ketton (534 μm) due to the largest grains that are even visible to the naked eye. It is followed by Bentheimer sandstone (260 μm). Ketton and Bentheimer are characterised in detail in the literature

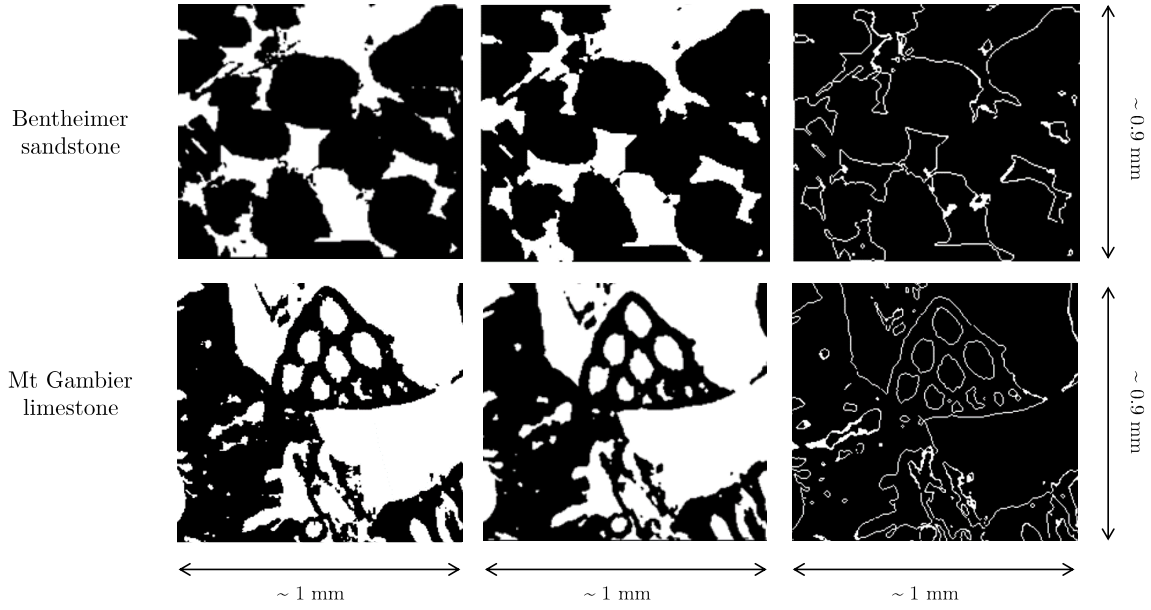


Figure 4.8: Steps of the MATLAB routine to extract the pore-solid interface for the calculation of the characteristic length. The routine is shown exemplarily for one sandstone (Bentheimer) and one carbonate (Mt Gambier). The two images on the left show a section of the binarised micro CT image (solid black, air white), the images in the middle are cleared with morphological operations that only retain voxels if more than half of the voxels in the neighbourhood of the target voxel are set to 1. The images to the right show the detected perimeter (white) around the solid phase (black). A voxel is part of the perimeter if it is non-zero and connected to at least one zero-valued pixel and voxels are connected if their faces touch.

and average grain sizes of $541\text{ }\mu\text{m}$ and $257\text{ }\mu\text{m}$ are reported in Kurotori (2019) that are very close to our results. We report a slightly smaller value for Boise ($248\text{ }\mu\text{m}$) than for Bentheimer sandstone albeit the grains of Boise appear visually larger (Figure 4.6). This could be caused by grains in Boise that are less spherical in shape in addition to its broader grain and pore size distribution (see Section 4.3 and 4.11). The lowest characteristic length is determined for Mt Gambier with around $150\text{ }\mu\text{m}$ due to the different shapes and sizes of the fossil and bryozoae fragments and its complex porous structure that creates a lot of pore-solid interfaces. For a rough comparison, the visible average grain size is estimated by measuring the length and width of 10 random grains in the 2D cross sections of Figure 4.6. The average grain sizes estimate to $\sim 200\text{ }\mu\text{m}$ (Bentheimer), $\sim 300\text{ }\mu\text{m}$ (Boise) and $\sim 500\text{ }\mu\text{m}$ (Ketton) which broadly corresponds to the values calculated with the characteristic length method. It was not practicable to perform this comparison for Mt Gambier due to the strongly varying structures and structure sizes.

4.7 Representative Elementary Volume

To characterise the rocks heterogeneities on the millimetre scale (HRPF heterogeneities), we apply the concept of the Representative Elementary Volume (REV) on the binary images of the cube samples E which is presented in Section 4.2. As a parameter of interest, we use the intergranular porosity ϕ because it is an additive property and therefore suitable for upscaling by a simple averaging scheme. A classical REV estimation has been applied using point-centred cube subsamples. The edge length of the subsample volume is calculated to $L = \sqrt[3]{V}$. Starting from a single voxel in the middle of the cube, the cube dimensions were increased symmetrically by ΔL on each end of the previous edge length using:

$$L_i = 2\Delta L + L_{i-1} \quad (4.9)$$

with i as the window increment number (Costanza-Robinson et al., 2011). This is done in all spatial directions (x, y, z) . A schematic representation of the method is shown in Figure 4.9. We choose ΔL to be five times the voxel length. A smaller number did not improve the accuracy substantially. The (intergranular) porosity ϕ is shown as a function for the cube length L in Figure 4.10a. We

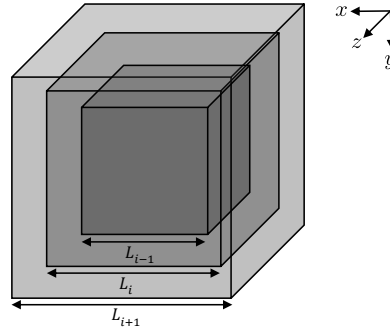


Figure 4.9: Schematic of the point-centred cube REV analysis. L_i is the side length of the point-centred cube at the window increment number i .

determine the REV ($= V_{\min}$) using the criterion for the porosity after Li et al. (2009) reported in Costanza-Robinson et al. (2011). It uses the relative gradient error ϵ_g calculated with:

$$\epsilon_g = \frac{1}{\Delta L} \left| \frac{\phi_{i+1} - \phi_{i-1}}{\phi_{i+1} + \phi_{i-1}} \right| \quad (4.10)$$

and is shown plotted in Figure 4.10b. The REV is reached when ϵ_g remains below 0.2 mm^{-1} (Costanza-Robinson et al., 2011). For each rock sample E one REV value is computed (shown as symbols in Figure 4.10a and b). The average REV edge length for each rock type is calculated to be the mean of

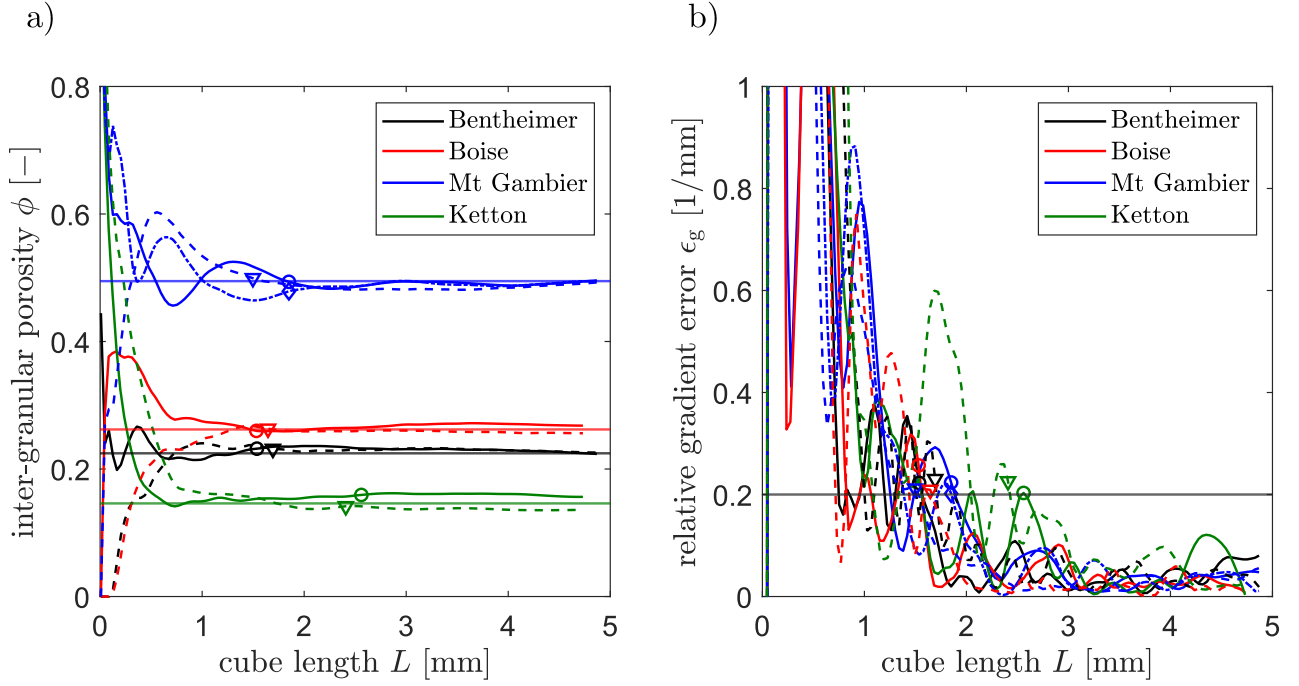


Figure 4.10: Variability (a) and relative error gradient (b) of the average intergranular porosity of the point-centred cube sample with side length L for 125 realisations. The data is colour-coded to represent different rock types (Bentheimer in black, Boise in red, Mt Gambier in blue and Ketton in green). The colour-coded solid and dashed lines represent the results using the different samples E (one additional for Mt Gambier as a dash-dotted line). The symbols mark the determined REV where ϵ_g falls below 0.2 according to the criterion (grey solid line).

the REV edge lengths in the samples E and is reported in Table 4.3. The rocks with grainy structure follow the predicted trend that the REV is linked to the average grain diameter of the porous medium (Costanza-Robinson et al., 2011): Ketton, with roughly double-sized grains compared to Boise and Bentheimer, has a 50 % larger REV value (≈ 2.5 mm). Bentheimer and Boise show a very similar value around 1.6 mm. Mt Gambier is strongly heterogeneous on a microscopic level due to a complex diagenesis which reflects in a high distribution of, for instance, the total porosity values on a voxel basis. Despite its pore-scale heterogeneity, the random arrangement of the fossil shells and bryozoae (Chen et al., 2020) of low characteristic length (see Section 4.6) yield a REV only slightly higher than the sandstones (1.73 mm). Therefore, Mt Gambier can be seen as fairly homogeneous on a scale larger than $\gtrsim 1$ cm.

4.8 Tortuosity

The effect of the reduction in diffusive transport caused by the complex geometry of the pores and pore network is captured in the tortuosity factor τ . The effective diffusion coefficient is defined as:

$$D = \frac{D_m}{\tau} \quad (4.11)$$

using the intergranular porosity ϕ and the molecular diffusion coefficient D_m . The latter is estimated according to the popularly used Berryman equation (Berryman, 1980, 1981; Kimura, 2018):

$$\tau = 1 + \xi \left(\frac{1}{\phi} - 1 \right) \quad (4.12)$$

which is a function of the porosity ϕ and includes the parameter ξ that depends on the shape of the particles (in this case spherical, $\xi = 0.5$). The tortuosity value changes slightly with the bead size, resulting in $\tau = 1.97$ for $55 \mu\text{m}$, $\tau = 2.02$ for $100 \mu\text{m}$ and $\tau = 2.06$ for $250 \mu\text{m}$. More information on the equation can be found in Kimura (2018).

We are applying *TauFactor* (Cooper, 2016; Cooper et al., 2016), an open-source MATLAB application, that used finite difference-type discretisation to solve Fick's law of diffusion to approximate the tortuosity factor of the rock samples. The tortuosity is obtained from diffusion simulations by comparing the steady-state diffusive flow through a pore network to the flow through a non-porous control volume of the same size, diffusivity and flow (Cooper, 2016). For the computation, we use again the binarised 3D micro CT images (cubes E). The tortuosity factor reported in Table 4.3 is the average of 6 values (2 representative cubes, 3 directions each) and 9 values for Mt Gambier (3 representative cubes, 3 directions each). The average values of the rocks are similar and between $3 < \tau < 4$. Since the standard deviation values are relatively high, an ordering of the rocks according to their tortuosity would be too ambitious. However, an approximate value of the tortuosity is sufficient as it is mainly needed to estimate the effective diffusion coefficient for the calculation of the Rayleigh number.

4.9 Core-Scale Heterogeneity and Representativeness of Ketton Limestone Samples

Vuggy pores are quite common in carbonate rocks, usually present as fractures or channels, leached particles and large irregular cavities (Li et al., 2017). In this study, their pore space is included in the intergranular porosity, but vuggy pores are significantly larger than the majority of the intergranular

pores. We evaluate whether vuggy pores exist in the rock core matrix and qualitatively characterise the samples according to their core-scale heterogeneity. The rock samples A are applied since they are used for the dissolution experiments and have the largest sample size. The samples are scanned (horizontally) in dry condition. The voxel size of the reconstructed images is $(0.18 \times 0.18 \times 0.5) \text{ mm}^3$. Figure 4.11 shows the vuggy pore and channel topology in panels a)–d) for each rock samples (#1, #2) created in the open-source visualisation application ParaView. Vuggy pores and channels are made visible through contouring, while the solid rock material and air are made transparent (for details and procedure see figure caption). Bentheimer sandstone (a) shows only a few vuggy pores scattered in the sample. Those vugs are up to, approximately, 3 mm in size and the rock can be described as fairly (core-scale) homogeneous. Boise sandstone (b) encloses more pores of that size but they are very distributed. With this technique, no fractures or channels can be found in any of the sandstones with the naked eye. Figure 4.11c shows the topology of Mt Gambier limestone. The fossiliferous structure of Mt Gambier creates a pore network that is made of large interconnected pores resulting in an image appearing much darker compared to the other rocks due to the substantial amount of air-rock interfaces contouring the pores. Even though the porosity distribution and the pore size distribution are wider in Mt Gambier (see Section 4.3 and 4.11), the rock appears fairly homogeneous to the naked eye on a core-scale. Comparing the two samples of Bentheimer, Boise and Mt Gambier (left and right image of each rock type), reveals a fairly similar topology. This could not be ascertained for the Ketton limestone samples (Figure 4.11d). We identify locally concentrated clusters of vuggy pores and, solely in the right sample, channels (of natural origin) that span over the whole sample dimensions in the axial direction of the core. It has been demonstrated in the literature that sub-core scale heterogeneity significantly affects solute migration and, for instance, structured heterogeneity favours dissolution in fast flow channels, as opposed to uniform dissolution throughout the entire volume (Al-Khulaifi et al., 2017). It is expected that the anisotropy, caused by the presence of vugs and channels, creates local permeability values that are significantly higher than the average permeability extracted in Section 4.5 (Sadeghnejad and Gostick, 2020). Therefore, results obtained in the dissolution experiments for Ketton limestone are affected by the individual vug topology and are not reproducible on that length scale. Hence, we cannot use the results for quantitative analysis but included the data in some sections (*e.g.*, Section 8.3.1) as it allows valuable insights on the solute transport and convective mixing behaviour under the presence of large scale heterogeneities. The procedure was not performed with the bead packs as the wet-packed samples were shaken carefully to ensure a dense packing and no large heterogeneities or void spaces are to expect.

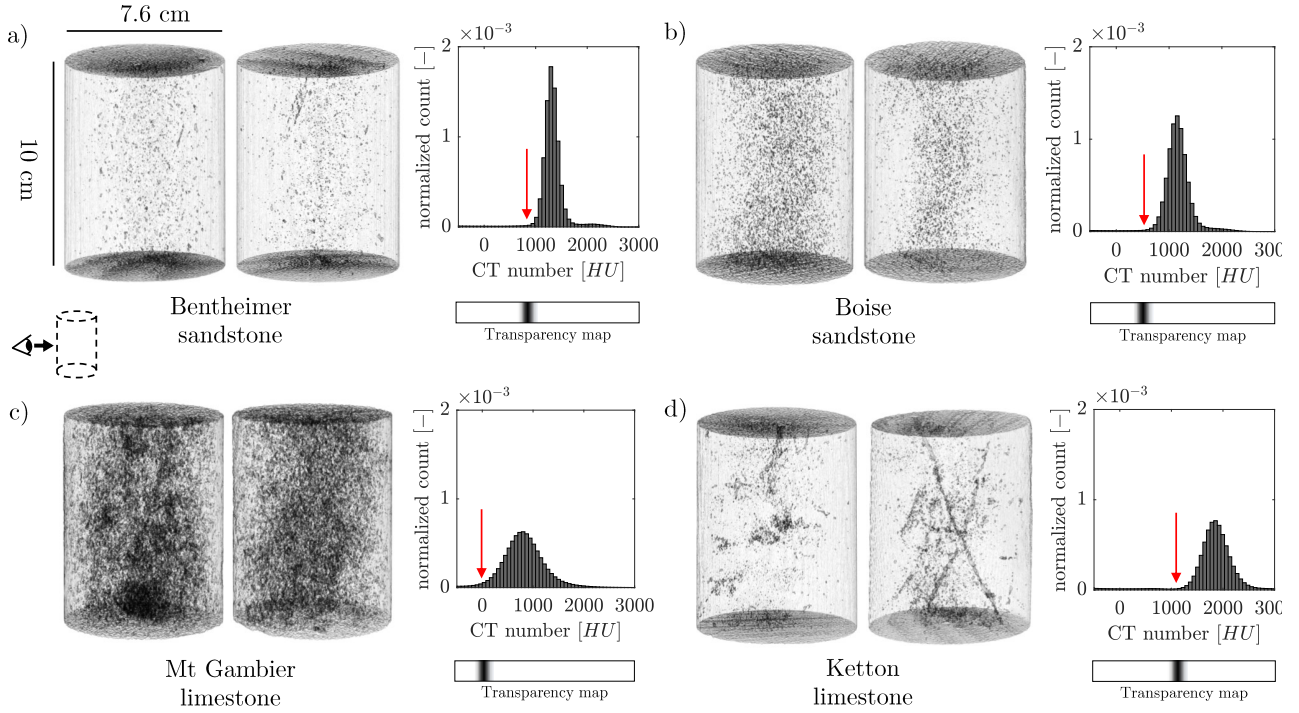


Figure 4.11: Volume rendering visualisation of the rock samples A created in the open source visualisation application ParaView. The images include the two samples used for the dissolution experiments (#1 on the left and #2 on the right side of each panel). The core-scale heterogeneities are made visible by solely showing the contours of the vuggy pores and channels. The red arrow in each CT value histogram marks the first bin with an increased value compared to the plateau at low CT numbers to the left side. Only the CT numbers with this selected bin value are opaque, therefore we are only showing voxels that are part of the rock-air interface. All other values, including the air and rock material, are made transparent. The width of the bins is chosen to be approximately the uncertainty in the individual CT number on a voxel basis acquired by subtracting two scans of the dry rocks (here without a coarsening scheme, $\sigma_{CT\Delta n=2} \approx 70$).

4.10 Coordination Number

The coordination number CN is defined as the number of pore throats associated to a pore body in the pore network (Raoof and Hassanizadeh, 2010). We used OpenPNM which is an open-source framework for performing a wide range of pore network simulations of porous materials (Gostick et al., 2016). OpenPNM is written in the Python environment using the libraries *NumPy* and *SciPy* for most mathematical operations. After generating the pore-networks for each binarised 3D image (cube images E), we apply the function `num_neighbors`. It returns the number of neighbouring pores for each given input pore. By averaging those values over the total number of pores, the coordination number in 3D (CN) is calculated (Table 4.3). The lowest coordination number is determined for Bentheimer sandstone ($CN = 3.86$) and Ketton limestone ($CN = 4.09$) followed by Boise sandstone

($CN = 4.33$). All three rocks are cemented during the formation process: Bentheimer and Boise are quartz-cemented and Ketton is spar-cemented. The highest coordination number is determined for Mt Gambier limestone ($CN = 6.64$), resulting from its complex porous structures with many open pores, high porosity and high connectivity. We additionally determine the coordination number of a glass bead pack (dry condition). Since it is not expected that the coordination number changes much with the size of the glass beads (Jiang et al., 2017), we use an existing data set of micro CT images of a pack of glass beads with bead diameter ($d_p = 0.4 - 0.6$ mm) imaged as part of the work of Kurotori et al. (2019). The coordination number extracted takes a value of $CN = 3.75$ which is similar to the value extracted for Bentheimer sandstone.

4.11 Characteristic Properties Extracted Using Mercury Intrusion

To collect information on the throat and pore size distribution of the rock samples, MICP (Mercury Injection Capillary Pressure) measurements were conducted. Measurements were performed on natural rock samples and not on bead pack samples as the size distribution of the pores and pore throats in a bead pack is expected to be unimodal and the distribution to be very narrow (Minagawa et al., 2009).

The small rock plug samples (D) of Boise and Mt Gambier were used for the measurements that were performed by MCA Services (Cambridgeshire, UK) with a Micromeritics AutoPore V 9620. Existing measurements on the Bentheimer and Ketton samples are used in this work that were performed by the Analytical Services at the Department of Chemical Engineering (Imperial College London) using a Micromeritics Autopore IV 9500 as part of the work of Kurotori et al. (2019). All measurements were carried out at room temperature at around 23 °C. By applying the Washburn’s equation to an assumed cylindrical pore geometry (here the pore throat):

$$r_p = \frac{2\gamma_{nw} \cos(\theta_{nw})}{p_c} \quad (4.13)$$

we calculate the equivalent pore throat radius r_p (Cai and Hu, 2019; Pini et al., 2012). The subscripts “n” and “w” are referring to the non-wetting (mercury) and wetting (mercury vapour) phase while $\gamma_{nw} = 485$ mN/m and $\theta_{nw} = 140^\circ$ are the surface tension and the contact angle for mercury/air and p_c is the capillary pressure (Kaufmann, 2009). The cumulative volume-weighted pore-throat size distribution is shown in Figure 4.12 where the saturation of the wetting phase is plotted as a function of the pore throat radius. The saturation of the wetting phase is $S_w(p_c) = 1 - S_{nw}(p_c)$ while $S_{nw}(p_c)$ is the cumulative pore volume of the non-wetting phase normalised by the total intruded volume. We define a way to quantify pore-scale heterogeneity of the rock samples according to the span of pore

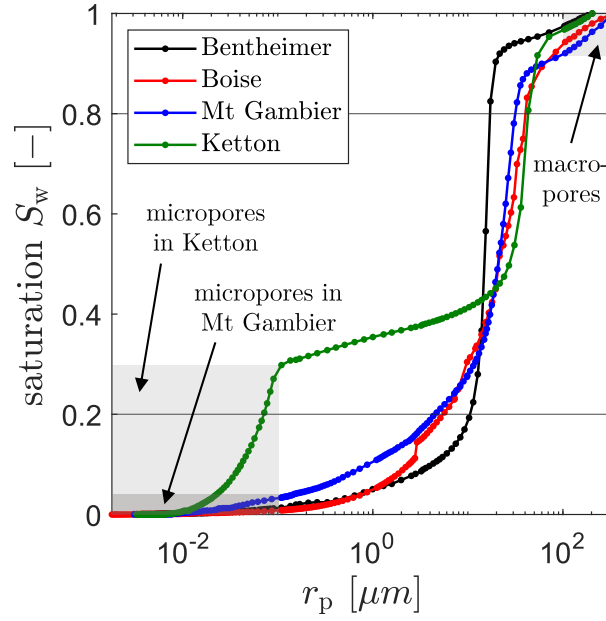


Figure 4.12: Cumulative volume-weighted pore-throat size distribution as obtained by MICP measurements on small sample plugs. The saturation values were obtained by normalising the cumulative intrusion by the total intrusion volume (Bentheimer: 0.114 mL/g, Boise: 0.339 mL/g, Mt Gambier: 0.188 mL/g, Ketton: 0.121 mL/g). Very large throat sizes ($>100 \mu\text{m}$) are likely induced by unexpected fractures made during sample preparation. The horizontal lines refer to 20 % and 80 % of saturation. The shaded areas in the lower left corner highlight the fraction of micropores in Ketton limestone (30 %, light grey) and Mt Gambier (4 %, darker grey). The shaded area in the upper right corner highlights the fraction of the pore space filled by macropores ($r_p > 100 \mu\text{m}$).

throat radii that makes up the majority (60 % percent) of the pore volume. We specify the pore-space heterogeneity factor as:

$$\Theta = \frac{\log(r_{p,80}) - \log(r_{p,20})}{\log(r_{p,50})} \quad (4.14)$$

with $r_{p,80}$, $r_{p,20}$ and $r_{p,50}$ as the pore throat radius at 20 %, 50 % and 80 % saturation S_w . The result values are given in Table 4.3. Bentheimer has the narrowest unimodal pore throat distribution, with the majority falling in the range between $10 \mu\text{m}$ and $17 \mu\text{m}$ and a heterogeneity factor of $\Theta = 0.20$. It is followed by Mt Gambier with a range between $5 \mu\text{m}$ and $33 \mu\text{m}$ ($\Theta = 0.62$) and Boise between $6 \mu\text{m}$ and $43 \mu\text{m}$ ($\Theta = 0.65$). Ketton exhibits a distinct bimodal distribution and demonstrates the broadest distribution range with 60 % falling between $0.07 \mu\text{m}$ and $43 \mu\text{m}$ ($\Theta = 1.95$). We interpret pores with a pore throat radius smaller than $0.1 \mu\text{m}$ to be micropores and pores with a pore throat radius larger than $100 \mu\text{m}$ to be considered macropores or fractures. Around 30 % of the total pore space in Ketton and 4 % in Mt Gambier accounts for micropores (see grey shaded regions in left corner of Figure 4.12). Comparing this with the values of the porosities in Table 4.2 and Eq. 4.5 shows that the majority of

the intragranular porosity of Ketton consists of micropores while the 4 % microporosity of Mt Gambier falls within the uncertainty of the intragranular porosity.

The MICP data is converted to a differential intrusion curve assuming cylindrical pores using:

$$f(r_p) = \frac{dS_w(p_c)}{dr_p}. \quad (4.15)$$

We weight the distribution by the radius, *i.e.* $r_p f(r_p)$, so that the incremental area under the curve is proportional to the fractional volume of the pores associated with that r_p (Kurotori et al., 2019). Figure 4.13 shows the pore-throat distribution curves and more details on the distribution and the plot are given in the figure caption. Bentheimer sandstone has a single distinct peak between $r_p = 10 \mu\text{m}$ and $r_p = 20 \mu\text{m}$. Boise has the largest peak around $30 \mu\text{m}$ but several smaller ones between $6 \mu\text{m}$ and $30 \mu\text{m}$. The carbonate rock Mt Gambier shows small peaks in the microporous size region (caused by bryozoae formations) but the fraction of pore volume increases gradually towards larger sizes and peaks at around $30 \mu\text{m}$. The bimodal distribution of Ketton peaks at around $0.08 \mu\text{m}$ and $40 \mu\text{m}$. Due to uniformly sized grains, the fraction of pore throat sizes in between remains low. It additionally indicates the high volumetric amount of microporous space. We identify a larger amount

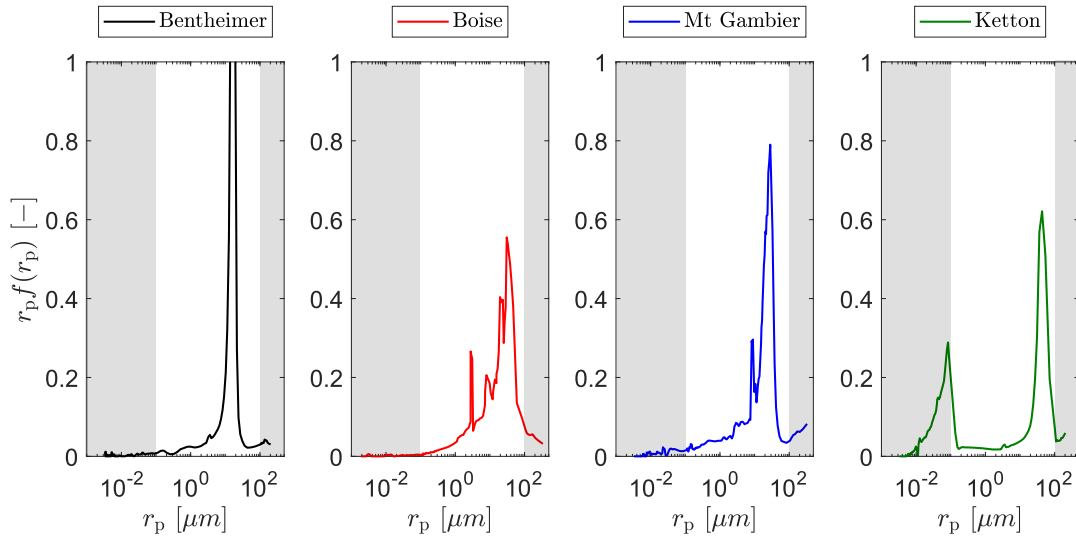


Figure 4.13: The pore-throat radius distribution curves derived using Eq. 4.15. The data is smoothed with a moving average function with a span of 3 points. The shaded areas towards smaller throat radius ($\leq 0.1 \mu\text{m}$) are classified as micropores and towards larger radius ($\geq 100 \mu\text{m}$) as macropores. The peaks around $r_p = 3 \mu\text{m}$ in the Boise data and $r_p = 10 \mu\text{m}$ in the Mt Gambier data are caused due to changing of the low- to the high-pressure chamber on the instrument and should be ignored.

of macropores ($r_p \geq 100 \mu\text{m}$) in the Mt Gambier sample (around 10 %) compared to the other rock samples. Those macropore heterogeneities are likely to be caused by fossil shells in the rock host. However, the MICP measurements are representative of a sample with a volume of roughly 1 cm^3 and therefore less suitable to quantify the macropore space. Additionally, the fraction of pore throats of size $r_p \geq 100 \mu\text{m}$ can be influenced by fractures caused during the sample preparation.

Chapter 5

Free Convection Experiments and Imaging

The focus of this chapter is on the implementation of the dissolution experiments using glass beads and natural rocks. First, background on and characteristic properties of the surrogate fluids is given. This is followed by the description of the set-up, equipment and procedures of the experiments. The chapter is concluded with details on the imaging method, image reconstruction and data processing.

Some of the material presented in this chapter has been published in Eckel et al. (2023).

5.1 Properties of Surrogate Fluid Pair

Potassium iodide (KI) and water were used in the experiments to mimic a solution saturated with dissolved CO₂. By applying a surrogate fluid pair with monotonic density behaviour, we address important limitations of past experimental studies that restrict the transfer of results to the CO₂-brine system. The following properties of the surrogate fluid pair, aqueous KI solution and water, are noted:

- The densities of both, the aqueous solution of KI and the CO₂-water system, increase monotonically and approximately linearly with the solute mass fraction w as shown in Figure 5.1. Even though the KI-water system deviates to some extent from a perfectly linear behaviour and the CO₂-water pair (see relative change with mass fraction in Figure 5.2), the deviations are substantially larger for the other analogue fluid pairs used in previous 3D studies on convective mixing in the context of CO₂-sequestration (MEG-brine, MEG-NaCl(aq), water-PPG).

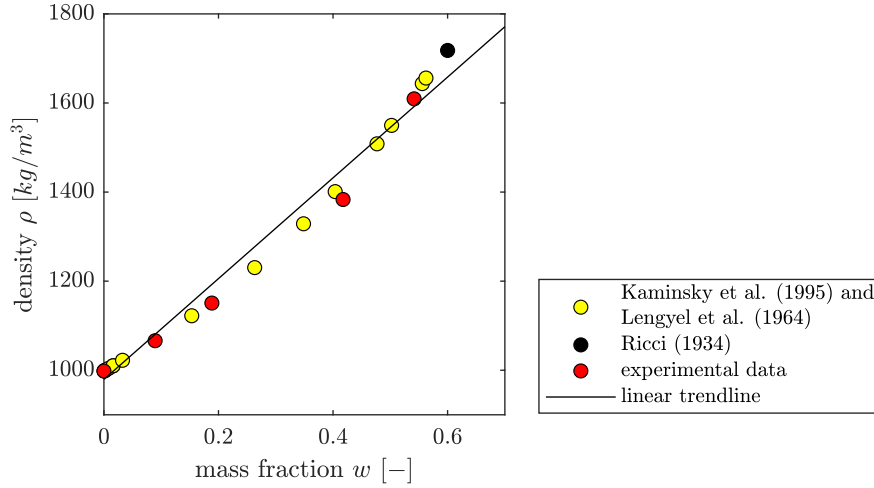


Figure 5.1: Density of aqueous KI-solution as function of KI mass fraction w . Yellow symbols are taken from literature data (Kaminsky, 1957; Lengyel et al., 1964) and the single black symbol is the literature value taken as maximum saturation value (Ricci, 1934). Red symbols are from our own measurements with oscillating U-tube density meter (model: Anton Paar, DMA 48) at 20 °C and 1 atm. The solid line is the linear scaling (coefficient of determination $R^2 = 0.99$ valid for $w = [0, 0.6]$).

- The maximum density of the solution at maximum solubility ($w_{\max} = 0.6$) is $\rho_{\max} = 1\,718\,\text{kg}/\text{m}^3$ (298.15 K, Ricci 1934). The density difference between $\rho_{\max}$ and the density of pure water ($w = 0$, $\rho_w = 997\,\text{kg}/\text{m}^3$ at 298.15 K) is large enough to drive convection in the fluid underneath the interface even for media with moderate and low permeability (such as natural rocks). Investigating the natural convection of CO_2 and brine or water till the shutdown regime in realistic porous material is expected to lead to an experimental time of days to weeks. The use of the proposed fluid pair allows for reducing the time to minutes while working in laboratory conditions without high pressure.
- The density difference in the experiments is approximately two magnitudes larger than the one expected during a geological CO_2 trapping ($\Delta\rho_{\max} \approx 100\Delta\rho_{\text{geo}}$ with $\rho_{\text{geo}} \approx 5\,\text{kg}/\text{m}^3$, Ohsumi et al. 1992). The scalability of the dimensionless Rayleigh number allows comparing our results to other experiments or geological systems with similar Ra (Backhaus et al., 2011; Neufeld et al., 2010; Newell et al., 2018). In a homogeneous case, the results obtained can be related to a reservoir with a height of $H_{\text{geo}} \approx 100H \approx 10\,\text{m}$. In heterogeneous porous systems, the scale and the impact of the heterogeneities need to be considered.
- The X-ray mass attenuation coefficient of the saturated solution is roughly four times higher than the one of pure water, leading to a strong difference in X-ray absorption and high contrast in the CT-images (Seltzer, 1987). More background on the X-ray mass attenuation is

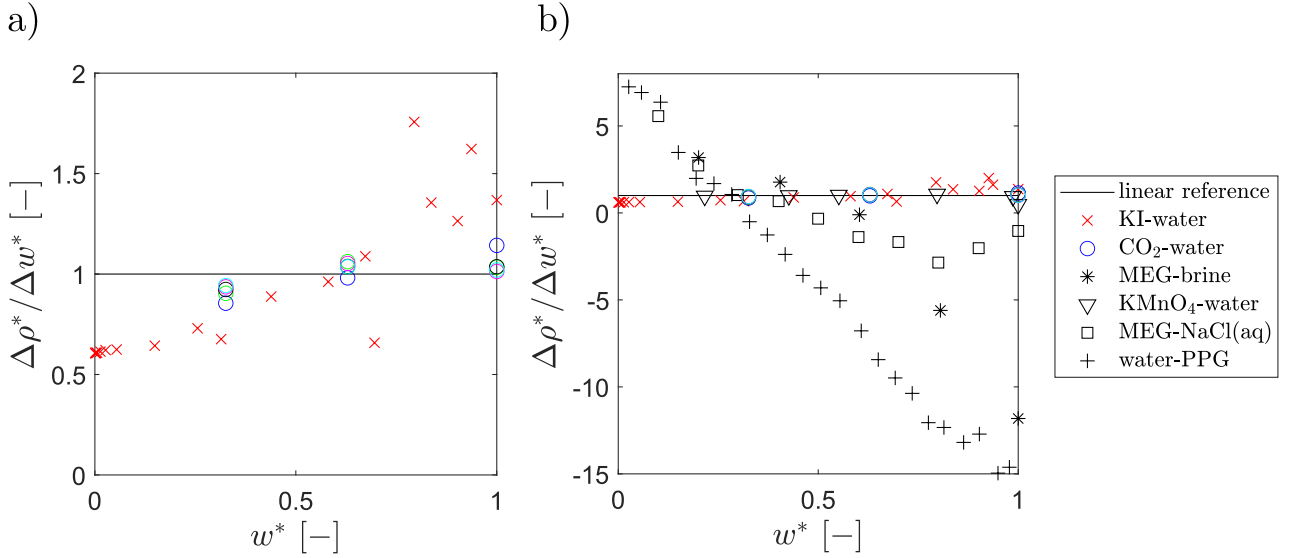


Figure 5.2: Relative change of fluid density with mass fraction, $\Delta\rho^*/\Delta w^*$. Both density and mass fraction are normalised to facilitate comparison between different fluid pairs. The normalised mass fraction is calculated with $w^* = (w - w_0)/(w_{\max} - w_0)$ with $w_0 = 0$ and $w_{\max}$ as the mass fraction at maximum solubility. The normalised density is calculated with $\rho^* = (\rho - \rho_0)/(\rho_{\max} - \rho_0)$ with ρ_0 as the density at $w_0 = 0$ and $\rho_{\max}$ as the maximum density.

a) Includes data of the fluid model KI-water (red cross, see references in the caption of Figure 5.1) and CO₂-water (circles, one colour represents one pressure at which the measurement was taken McBride-Wright et al. 2015).

b) Additionally includes non-linear fluid models used in 2D and 3D experiments: MEG57-brine (black asterisk, Liyanage et al. 2019), KMnO₄-water (black triangle, Trimble 1922), MEG-NaCl(aq) (black square, Wang et al. 2017), water-PPG (black cross, Jafari Raad and Hassanzadeh 2015). The black solid line is the reference line for linear behaviour.

presented in Section 5.3.

- We use the commercial database DETHERM (accessed via the *Physical Sciences Data-Science Service*) to acquire the volumetric change of the KI solution. For instance, an aqueous solution that changes the molar concentration from $c = 0 \text{ mol/m}^3$ to $c = 250 \text{ mol/m}^3$ increases the volume by $1.165 \times 10^{-5} \text{ m}^3$ and we conclude that the neglect of a volumetric expansion due to the dissolution of KI in the water is valid.

5.2 Dissolution Experiments (Method and Equipment)

Inspired by the Hele-Shaw experiments in Slim et al. (2013), we developed an experimental method that allows maintaining a constant concentration at the top boundary of the porous medium for the entire duration of the experiment (Rayleigh-Bénard model, system a in Figure 2.5 in Section 2.3). We

extend the approach here to three-dimensional porous media and use X-ray CT technology to visualise the temporal and spatial evolution of the convective process. In the following, the experimental method developed for this purpose is described, first for the application of bead packs (Section 5.2.1) followed by the application of rocks (Section 5.2.2).

5.2.1 Sample Preparation (Bead Packs)

A schematic representation of the experimental set-up used to image natural convection in the bead packs is shown in Figure 5.3. The cubic sample holder, containing the water-saturated uniform random packing, is open to the top to allow the exchange of mass at the interface (Figure 5.3 a). A picture of the filled cube placed on the CT scanner bed is shown in Figure 5.4a. Three samples were generated with the mono-dispersed soda glass ballotini (in this thesis referred to as 'glass beads', details in Chapter 4). The sample holder is an acrylic cube with a side length of $15\text{ cm} \times 15\text{ cm} \times 15\text{ cm}$ (Figure 5.3a). Prior to the start of each experiment, the cube was wet-packed with tap water up to a height of 13 cm with the glass beads to yield a water-saturated uniform packing. The wet-packed sample was shaken carefully to ensure a random dense packing and to get rid of larger void spaces that might be created during the packing process (Figure 5.4a). A thin square-shaped melamine resin foam (dimensions $0.5\text{ cm} \times 13\text{ cm} \times 13\text{ cm}$, Basotect[®], supplied by BASF SE, Germany) was used as the source of solute. Before the foam was placed on the packing surface (equivalent to the start of the experiment), it was saturated with a saturated aqueous solution of KI, followed by the sieving of powdered KI to form a 2 mm-thick layer on its surface.

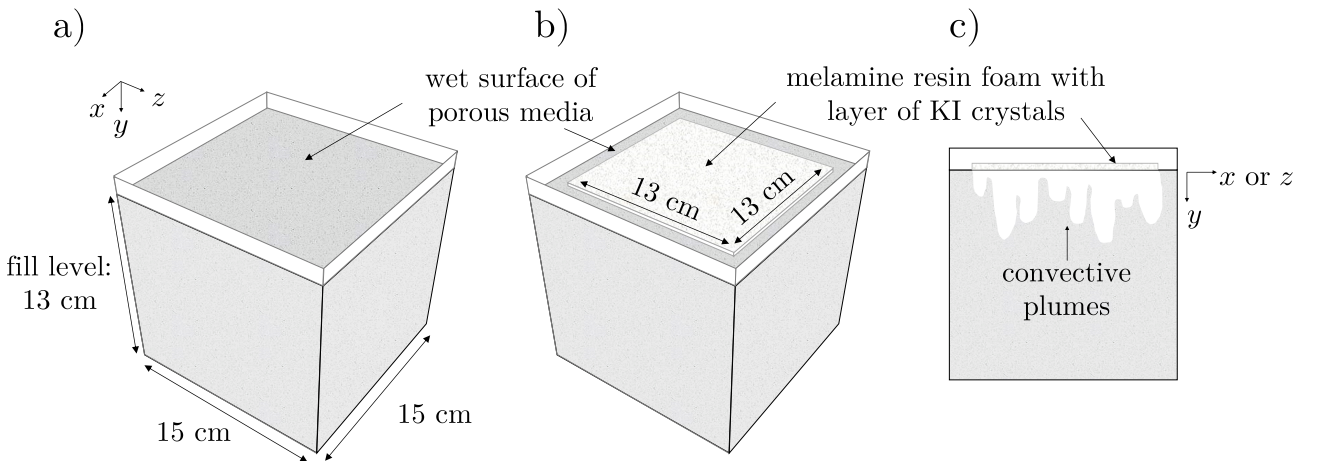


Figure 5.3: Sample holder used for the X-ray CT imaging experiments consisting of an acrylic plastic cube filled with water-saturated glass beads. a) Before start of experiment, b) with melamine resin foam saturated with aqueous KI-saturated solution ($t = 0$), c) during experiment ($t > 0$), frontal view.

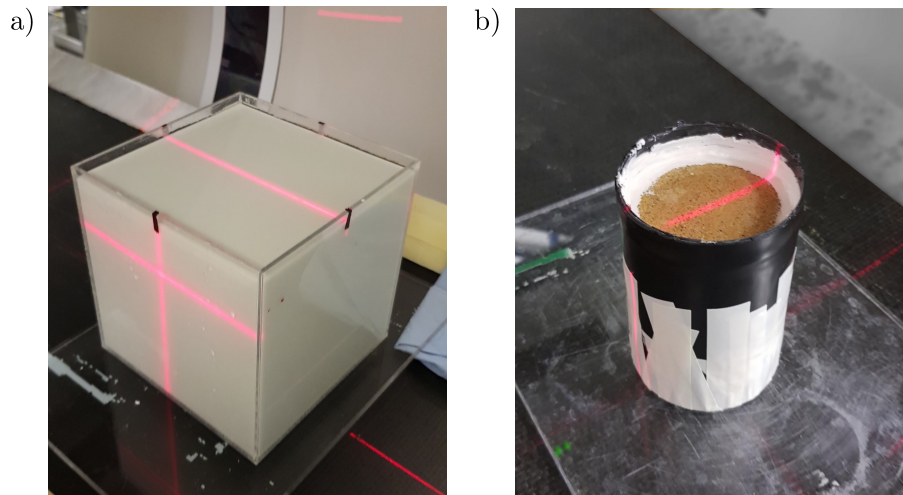


Figure 5.4: a) Picture of the cube filled with glass beads placed and aligned on the CT scanner bed. b) Picture of the water-saturated rock sample wrapped by shrink-tube (black). Sealing film is closing the bottom face, fixated with (white) waterproof tape. The white grab adhesive is visible around the perimeter of the top face of the sample.

5.2.2 Sample Preparation (Consolidated Rocks)

The experimental procedure developed for the bead packs in Section 5.2.1 can equally be applied to natural and consolidated porous media but the sample preparation required additional steps which are outlined in the following.

Two end-caps (with nitrile O-rings) are placed at the ends of sample (A). An adhesive-lined heat shrink tube (polyolefin, 85 mm sleeve diameter, TE Connectivity, Switzerland) is slid over the sample and the end-caps. The sleeves are heated evenly to melt the adhesive and to create a tight seal between the tube and the rock surface. The system is flushed first with gaseous CO_2 (purity < 99%, BOC Ltd., UK) to displace the air and therefore improve solubility. This is followed by flushing the sample with 7–8 pore volumes of tap water through the system using a high-pressure syringe pump (Teledyne ISCO, Model 500D). After removing the end caps, the shrink tube is cut right at one end of the sample and 1 cm from the other end. The shrink tube prevents the water from draining out and the excess of 1 cm hinders that highly concentrated KI-water spills along the sides of the sample during the experiment. Two layers of sealing film (Parafilm M, 4×4”) are used to close the bottom end of the sample and fixated with waterproof tape (see Figure 5.4b). To ensure complete saturation, the sample is submerged in water for 24 h. While keeping it submerged, waterproof grab adhesive (Heavy-Duty Grab Adhesive, Gorilla Glue, USA) is applied with a small spatula around the perimeter of the sample. This roughly 4 mm wide layer creates a seal between the shrink tube material and rock sample to prevent the KI-rich solution from immediately channelising near the boundary where flow

permeability is slightly higher. To cure the adhesive, the prepared sample was submerged for an additional 2–3 h in water. Separately, a thin round-shaped melamine resin foam (radius 6.5 cm, 0.5 cm thickness) is saturated with KI-solution and a layer of KI salt of roughly 2 mm is spread on top. A schematic representation of the prepared sample at the start of the experiment is shown in Figure 5.5.

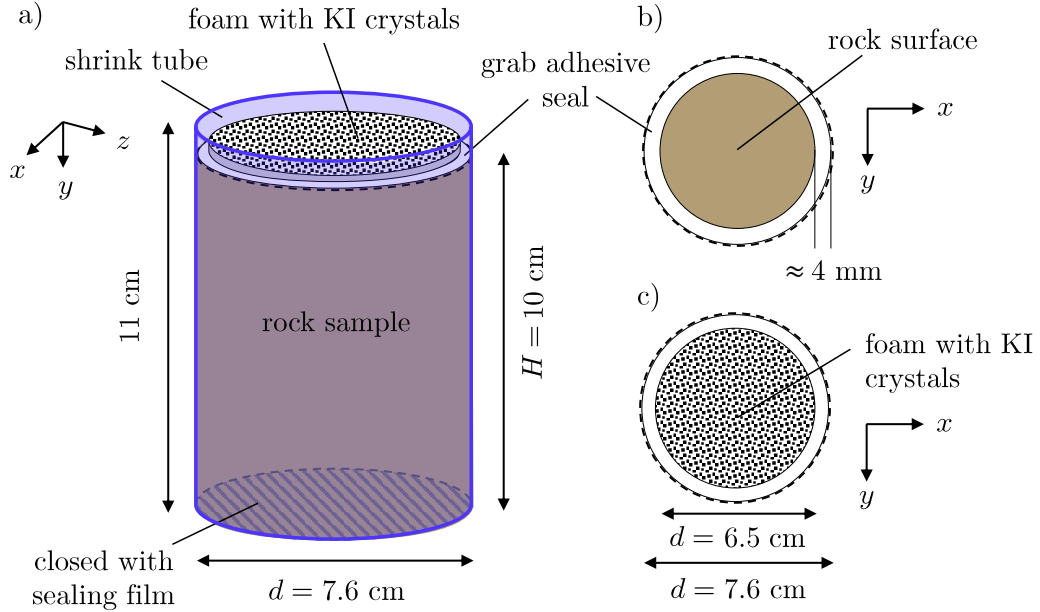


Figure 5.5: Drawing of the prepared rock sample (samples A) used for the convective dissolution experiments. The pore space is initially saturated with water. a) View from the side. The lower end of the sample is closed with sealing film and waterproof tape and the sides with the shrink tube. b) View from the top before the start of the experiment. c) View from the top during the experiment.

5.2.3 Experimental Procedure

The experiments were conducted at ambient conditions. To initiate the experiment, the foam is carefully placed on top of the bead pack (Figure 5.3b) or the rock sample (Figure 5.5). The KI-saturated aqueous solution immediately starts to mix with the water present in the pore space near the top boundary, creating a fluid mixture that is denser than the pure water and causing a gravitationally unstable stratification. This instability leads to the formation of dense dissolution plumes (early convective regime) and, eventually, initiates natural density-driven convection (see schematic for bead pack in Figure 5.3c). Since the crystalline KI is very fine-grained, it readily dissolves in fresh water, yielding a solution at maximum solubility at the interface for the duration of the experiment. To preserve saturation concentration in the foam throughout the experiment, more crystalline KI is

supplied by sieving it on top carefully and quickly between a set of scans. A multislice CT scan system was used to acquire tomograms of the entire sample holder during the experiment (details see Section 5.3). For image acquisition, the peak potential of the X-ray tube was set to 120 kVp and the tube current was set to 200 mA. Scans were taken at regular intervals, spanning from a few seconds (during the early convective regime) to a few minutes (during the shutdown regime). The scanning time is only a few seconds and therefore it is assumed that the solute plumes do not move while the scan is taken. The experiment ends once the solute plumes accumulate at the bottom of the sample, *i.e.* initiating the shutdown regime. The CT instrument applies a three-dimensional quantum de-noising filter to reconstruct images at a spatial resolution of 1 mm in the z-direction and roughly 0.4 mm (bead packs) and 0.2 mm (rocks) in the x- and y-direction (in-plane resolution, this value changes slightly between each experiment). Each experiment was repeated to assess the variability of the results. The experiment with glass beads of one size of size 250 μm and 55 μm was performed twice and three times for 100 μm bead. The rock experiments were repeated twice for each rock type while using two independent rock samples A (#1 and #2, overall 8 experiments with 8 rocks).

5.2.4 Rayleigh Number Estimation

We estimate the Rayleigh number, Ra , by applying Eq. 2.3. The maximum density difference between saturated and unsaturated KI solution is $\Delta\rho_{\text{max}} = 721 \text{ kg}\times\text{m}^{-3}$ (details see Figure 5.1), the viscosity of pure water at ambient conditions is $\mu = 1.002 \text{ mPa}\times\text{s}$ (Korson et al., 1969) and the acceleration due to gravity is $g = 9.81 \text{ m}\times\text{s}^{-2}$. D is the effective diffusion coefficient in the porous medium ($D = D_{\text{m}}/\tau$) and determined using the molecular bulk diffusion coefficient $D_{\text{m}} = 2.61 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ (McCall and Douglass, 1965) and the tortuosity τ . Further, it applies the values obtained for the permeability k , the (intergranular) porosity ϕ and the sample height which is $H = 13 \text{ cm}$ for the bead pack (Figure 5.3) and $H = 10 \text{ cm}$ (Figure 5.5) for the rocks. The calculated Rayleigh numbers are given in Table 5.1. At their initial condition, the three glass beads systems used in this study yield $Ra \approx 3\,000$, $Ra \approx 10\,000$,

Table 5.1: Rayleigh number values Ra of the bead packs and the rock samples together with their uncertainty values ΔRa . The uncertainty of the Rayleigh number is calculated using the classic rules of error propagation (Eq. B.1 in Appendix B) while using the respective uncertainty values of k for the bead packs and k , ϕ and τ for the rocks. The contributions of the other variables in Eq. 2.3 are relatively small and neglected.

	bead packs			rock samples			
	250 μm	100 μm	55 μm	Bentheimer	Boise	Mt Gambier	Ketton
Ra [–]	55 066	9 430	3 052	6 569	14 669	24 323	27 630
ΔRa [–]	7 744	812	645	438	2 523	2 433	6 660

$Ra \approx 55\,000$, which we refer to as low, medium and high Ra . In terms of the rock samples, the values range from $Ra = 6\,500 - 28\,000$ with the highest value being calculated for Ketton and the lowest for Bentheimer. The uncertainty values estimated for the Rayleigh number values are also presented in Table 5.1.

5.3 X-Ray CT Imaging Methods

X-ray-CT imaging techniques have been applied as part of this thesis and the working principles are outlined in the following together with the image analysis performed on the acquired data.

5.3.1 Fundamental Principles of Computed Tomography

Originally developed for application in healthcare, X-ray Computed Tomography finds increasing use in the field of non-destructive imaging and testing of a wide range of materials, *e.g.*, rock, bone, ceramic, metal and soft tissue (Desrues et al., 2006). In simple terms, Computed Tomography involves radiation passing through an object which is attenuated and measured by a detector (Figure 5.6). By using mathematical image processing on the projections, two-dimensional slices are generated and stacked together to produce a three-dimensional reconstruction of the object (Seeram, 2016).

For the time-resolved experiments (Chapter 7 and 8) and sub-core scale sample characterisation, a medical grade X-ray CT scanner in helical mode is used (Toshiba Aquilion TSX-101A, referred to as “medical CT scanner” in this thesis). The helical scan method is sketched in Figure 5.6a. The X-ray beams and X-ray detectors move in a circular pattern around the sample (or patient as in the illustration) which is moved through the scanner gantry. This positively affects the examination times, which are shortened in comparison to the sequential (*stop-and-shoot*) scanning method. The scanner is equipped with a multislice CT scan system, meaning that there are multiple, parallel rows of detectors encompassing the fan beam. The benefit of multislice scanning is the reduced thickness of the slices while keeping the tube heating lower than in single slice scanners (Goldman, 2008). Different to medical CT scanners have micro CT scanners much longer acquisition times and the image data sizes are much larger allowing to resolve details as small as a few microns in size, even when imaging objects are made of high-density materials (Desrues et al., 2006). In this study, high-resolution images of the rock samples are acquired with a Thermo Fisher Heliscan micro CT.

With both instruments (medical and micro CT), the data collected by the detectors is sent to the computer for processing. During image reconstruction, relative values of the linear attenuation coefficient μ are computed for each pixel. The linear attenuation coefficient quantifies the amount

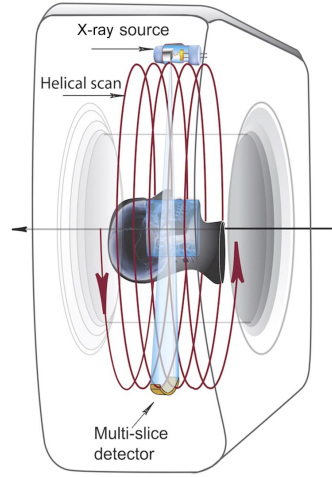


Figure 5.6: Principal components of a multislice medical CT scanner in helical mode (image taken from Koivisto et al. 2017). An X-ray tube generates radiation that is collimated (collimator not shown here), passes through the object (here a patient) and is measured by the detector.

of attenuation of the beam and is a function of both, the local electron density (bulk density) and the effective atomic number (Mees, 2003; Seeram, 2016). When imaging is performed with a micro CT, the images have been reconstructed using the built-in algorithm of the instrument that produces greyscale images. A particular phase (*i.e.*, material) takes a unique greyscale value and is proportional to its attenuation coefficient (Kumar and Foster, 2021). The attenuation readings of the medical CT are converted into a digital image characterised by CT numbers. The CT number (CT) is a computed value calculated with linear transformation (He et al., 2015; Seeram, 2016):

$$CT = \frac{\mu_{\text{material}} - \mu_{\text{w}}}{\mu_{\text{w}}} K_c \quad (5.1)$$

and using the linear attenuation coefficient of the material in a pixel μ_{material} , the linear attenuation coefficient of water μ_{w} and a contrast factor K_c . Using a contrast factor of $K = 1000$ results in CT numbers expressed in Hounsfield units (HU). By definition, vacuum takes a value of -1000 HU and water of 0 HU which provides two energy independent calibration points (Brent et al., 1988; Seeram, 2016). The reconstructed numerical image in CT numbers can be displayed in greyscale and stored for later analysis (Seeram, 2016).

5.3.2 Image Conversion (Free Convection Experiment Data)

Image analysis of the data acquired with the medical CT scanner during the dissolution experiments using bead packs and rocks was carried out using in-house MATLAB routines. Since in the experiments KI is used as a solute and tap water as a solvent, in the following the conversion of the numerical CT

images in HU units into solute mass fraction values and solute molar concentration is described. The conversion is necessary for the computation of fundamental measures of spreading and mixing that use the local values of the solute mass fraction or solute concentration field (Section 3.2 in Chapter 3). CT values at each voxel location i are converted to solute mass fraction w_i using the following equation (Liyanage et al., 2019):

$$w_i(t) = 0.6 \frac{CT_i(t) - CT_i^0}{\phi_t(CT_{\text{sat}} - CT_w)} \quad (5.2)$$

where $CT_i(t)$ is the CT number in Hounsfield units of voxel i at time t , CT_i^0 is the corresponding value at $t = 0$ and ϕ_t the total porosity. $CT_{\text{sat}} = 9\,505$ HU and $CT_w = 40$ HU are the constant CT numbers of the KI-saturated solution and pure (tap) water, respectively. The prefactor 0.6 originates from the maximum solubility of KI in water ($w_{\text{max}} = 0.6$). This equation approximates the CT value in a voxel i as the linear combination of the CT values of its constituents (*i.e.*, glass beads or rock material and solution) in their volumetric proportion (Ketcham and Carlson, 2001; Liyanage et al., 2019; Wellington and Vinegar, 1987). Eq. 5.2 further applies the assumption that the CT number changes linearly with the mass fraction of KI of the aqueous solution. This is demonstrated in Figure 5.7 where a linear trendline describes the relationship between CT number and KI mass fraction obtained from calibration scans. Mass fraction values are converted into molar concentration

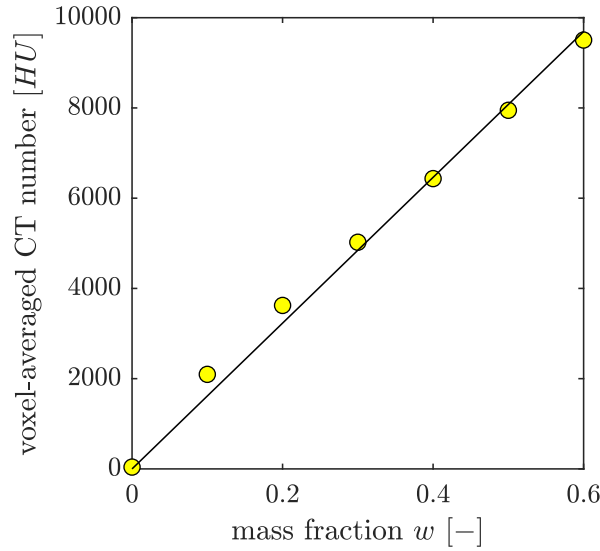


Figure 5.7: Voxel-averaged CT number plotted against the KI-mass fraction. Data from calibration experiments with aqueous KI-solutions without glass beads, the black trendline is linear and follows $CT = 1\,6145\,w$ with $R^2 > 0.99$.

values c_i using the following formula:

$$c_i(t) = w_i(t) \frac{\rho(t)}{M_{KI}} = w_i(t) \frac{\frac{w_i(t)}{w_{\max}} \rho_{\max} + (1 - \frac{w_i(t)}{w_{\max}}) \rho_w}{M_{KI}} \quad (5.3)$$

where $M_{KI} = 166 \text{ g mol}^{-1}$ is the molar mass of the solute, ρ is the mixture density, $\rho_{\max}$ is the mixture density and ρ_w is the density of pure water.

Chapter 6

Modelling of Two-Dimensional Solutal Convection

This chapter discusses the modelling results acquired to investigate the spreading and mixing during solutal convection in uniform porous media with application to geologic CO₂ storage. The two-dimensional finite element model, presented in Chapter 3 in Section 3.1, has been deployed for this purpose. Results are successfully validated against data from a benchmark study (Section 6.3). The macroscopic evolution of the convective process is characterised by employing fundamental macroscopic measures of mixing and spreading (Section 6.4). We derive and discuss scaling relationships in Section 7.4 and apply them in a practical example to two existing reservoirs.

The material presented in this chapter has been published in Eckel and Pini (2021).

6.1 Introduction

The analysis of solute dissolution in the context of Geological Carbon Storage (GCS) has convincingly shown that the process is subject to a sequence of temporal regimes, the appearance of which depends on Ra (Slim, 2014; Szulczewski et al., 2013). As indicated by Eq. 2.3 in Section 2.2.1, convective instability occurs when Ra exceeds a critical value ($Ra_c \approx 40$). For large values of Ra (≥ 2000), the dissolution process is characterised by a constant flux regime following the initial period of flux growth (see Section 2.2.2). Solutal convection is expected for the majority of saline aquifers ($Ra \geq Ra_c$), although Ra takes often a value well below 1000 or even of the same order of magnitude as Ra_c . As in this Rayleigh number range the process does not reach a stabilised state, relying solely on the dissolution flux becomes more challenging. Other measures may prove to be more suitable for

the analysis of convective dissolution, particularly those that quantify solute spreading and mixing directly from the CO_2 distribution pattern in the porous medium.

As anticipated in Section 3.2, a rigorous analysis of the mass transfer process in the two-dimensional domain requires a distinction between the concepts of spreading and mixing (Kitanidis, 1994). While the former enhances concentration contrasts, the latter tends to homogenise (*i.e.*, “dilute”) the concentration field (Le Borgne et al., 2010). During solutal convection, these two mechanisms are necessarily coupled, because the advective process that drives spreading can only exist *if* mixing (and therefore dissolution) occurs. This is in contrast with a situation, where *e.g.* advection is driven by an external pressure gradient. Hence, the evaluation of solutal convection, in general, and the independent quantification of spreading and mixing, in particular, should better be achieved in relation to the local spatial structure of the concentration field and its evolution (Dentz et al., 2011; Kapoor and Kitanidis, 1998; Le Borgne et al., 2015). In the context of GCS, initial efforts in this direction are found (Amooie et al., 2018; Hidalgo et al., 2012; Soltanian et al., 2017), where measures such as the scalar dissipation rate, dispersion width and global variance have been considered. These initial studies indicate that these measures of spreading and mixing provide a useful means to characterise solutal convection as well as a rigorous framework to identify scaling relations for Ra .

In this study, we analyse numerically the fundamental behaviour of solutal convection in the CO_2 -brine system in the more relevant situation of unsteady flux ($Ra = 100 - 10\,000$). We use the two-dimensional model formulated in Section 3.1 that applies a boundary condition with constant concentration. Even though the dissolution dynamics in a porous medium are inherently three-dimensional (Fu et al., 2013; Pirozzoli et al., 2021), the studies of Pau et al. (2010) and Meng and Jiang (2014) show that changes in integral measures, *i.e.*, the onset time and the constant dissolution flux, are modest when comparing three- and two-dimensional simulations ($Ra \approx 9\,000$ and $Ra = 2\,155$, respectively). Therefore, this study addresses the problem by considering two-dimensional simulations to achieve a very high spatial resolution, while keeping computational costs at a reasonable level. A uniform and isotropic porous medium is chosen, to exclude the effects of heterogeneity or anisotropy on the results of the flow and mixing dynamics and to provide a benchmark for future studies. The study extends previous analyses reported in the literature that discuss the dissolution flux in detail but lack a systematic evaluation of the macroscopic mixing behaviour. We aim to build on the findings in the literature to carry out a systematic investigation where metrics are evaluated and compared in the context of GCS. We shed light on the natural interplay between the two processes of mixing and spreading by examining the emerging dissolution behaviour that includes the iso-contour lines, the intensity of segregation, the spreading length, and the dilution index. We analyse the temporal

evolution of these measures and derive scaling relationships against Ra .

6.2 Numerical Evaluation of Mixing Measures

All metrics discussed in this chapter are introduced in Section 3.2. Except for the spreading length, the measures were calculated numerically in the post-processing tool of the software (COMSOL Multiphysics). The 2D contour data for the iso-contour lines (Section 3.2.2) was evaluated and summarised using line integration. In the implementation of the dilution index (Section 3.2.5), concentrations of zero or with slightly negative values are replaced with a very small number ($c = 1 \times 10^{-10} \text{ mol m}^{-3}$) to avoid undefined contributions to Eq. 3.12. To compute the spreading length (Section 3.2.4), the concentration values were first mapped on a structured mesh with quadrilateral elements and exported from COMSOL Multiphysics into the MATLAB environment. Additional to the convective results, data for all metrics obtained from the numerical solution of a purely diffusive one-dimensional problem in a homogeneous porous system is included in the analysis.

6.3 Dissolution Flux and Validation

We present first our results in terms of the dissolution flux as a means of validation against previous studies. To this end, we consider the work by Slim (2014), who reports a comprehensive set of numerical simulations for $Ra = 100 - 50\,000$. The difference between our (finite elements) and their numerical scheme (spectral method) provides further support to the comparison. In Figure 6.1, the dimensionless dissolution flux, $\hat{J}$, is plotted as a function of the dimensionless time, $\hat{\tau}$, for simulations conducted at $Ra = 100, 250, 1\,000, 2\,500, 10\,000$. The curves obtained in this study reproduce by and large those reported in the benchmark study (Figure 9 in Slim 2014). Each simulation undergoes an initial “incubation” period, where the dissolution process is dominated by molecular diffusion across the interface. Irrespective of Ra , the dissolution flux closely follows the pure diffusion case (dashed line, details on the diffusive model provided in Section 6.2) and decays proportionally to $\hat{\tau}^{-0.5}$. We define the onset time of convection as the point when $\hat{J}$ reaches a minimum and starts to grow. Our estimates of the onset time of convection appear at later times than the single value reported in Slim (2014, vertical solid line), where random concentrations were used to initially perturb the domain. Although the onset time of convection shows sensitivity towards the origin and structure of perturbations and can vary by one order of magnitude (Emami-Meybodi et al., 2015), the long-term behaviour of the solute mixing is largely unaffected by discrepancies in the onset time (Pau et al., 2010). As convection ensues, the flux starts growing significantly. Except for the simulation carried

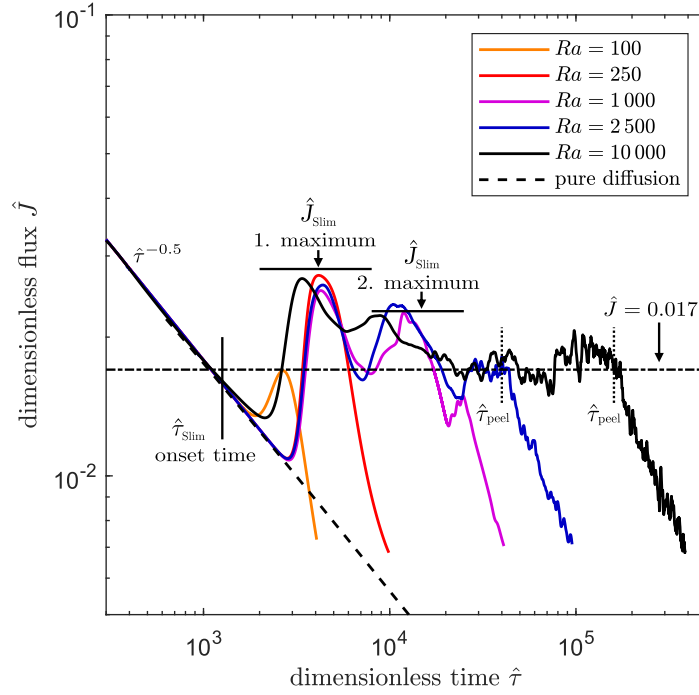


Figure 6.1: Dimensionless dissolution flux $\hat{J}$ as a function of the dimensionless time $\hat{\tau}$. Elements of comparison against the results by Slim (2014) are shown by the horizontal and vertical lines, including the onset time ($\hat{\tau}_{\text{Slim}}$, vertical solid line), the flux of the first and second maximum ($\hat{J}_{\text{Slim}}$, horizontal solid lines), the value of the constant flux regime ($\hat{J} = 0.017$, horizontal dash-dotted line), end of the constant flux regime ($\hat{\tau}_{\text{peel}} = 16Ra$, vertical dotted lines).

out at $Ra = 100$, all curves outline a similar pattern, characterised by two distinct maxima located around $\hat{\tau} = 4 \times 10^3$ and $\hat{\tau} = 1 \times 10^4$, respectively. The values of the flux at these locations compare well with those obtained in Slim (2014) and are denoted by the solid horizontal lines in Figure 6.1 (average relative difference of 7% and 2% for the first and second maximum, respectively). While for $Ra < 1000$ the system comes to a standstill after the first or second maximum, a period of constant flux is observed for $Ra \geq 2500$, in which the flux oscillates around a constant value ($\hat{J} = 0.018$ for $Ra = 10000$ and $\hat{J} = 0.017$ for $Ra = 2500$). These values agree well with $\hat{J} = 0.017$ reported in Slim (2014, horizontal dot-dashed line) and with the observation that for high Ra the constant dissolution flux should be independent of Ra (Hidalgo et al., 2012). According to Slim (2014), the start of the shutdown period (the “peel-off time”) is expected to be $\hat{\tau}_{\text{peel}} = 16Ra$ (vertical dotted lines), which agrees well with our observations on the time when the flux starts to reduce significantly.

6.4 Results of Solute Dissolution and of Key Metrics

Figure 6.2 and 6.3 show snapshots of the concentration field for all realisations simulated at four distinct times. As an example of general validity, we focus on the simulation conducted at $Ra = 10\,000$ (Figure 6.2, left side). We observe the pattern reported in previous studies, where the system evolves from the formation of many small fingers (panel b, with approx. 60 fingers of 5 m width each) to a situation dominated by fewer separated fingers (approximately 6) that extend over the whole length of the domain (panel d). The reason for this behaviour lies in the merging with neighbouring fingers owing to transverse mixing. To better understand the characteristic stretching of individual fingers, we look at the characteristic fluid velocity field that is generated around an individual lobe, as represented in Figure 6.4. We follow the path lines of 24 massless particles released in the flow field (panel a) at distinct initial distances from the top boundary. The red-coloured particles, initially located right underneath the diffusive boundary, are pulled in by the flow in the neck of the solute plume. They are accelerated to higher velocities towards the core of the plume (panel b), eventually reaching its

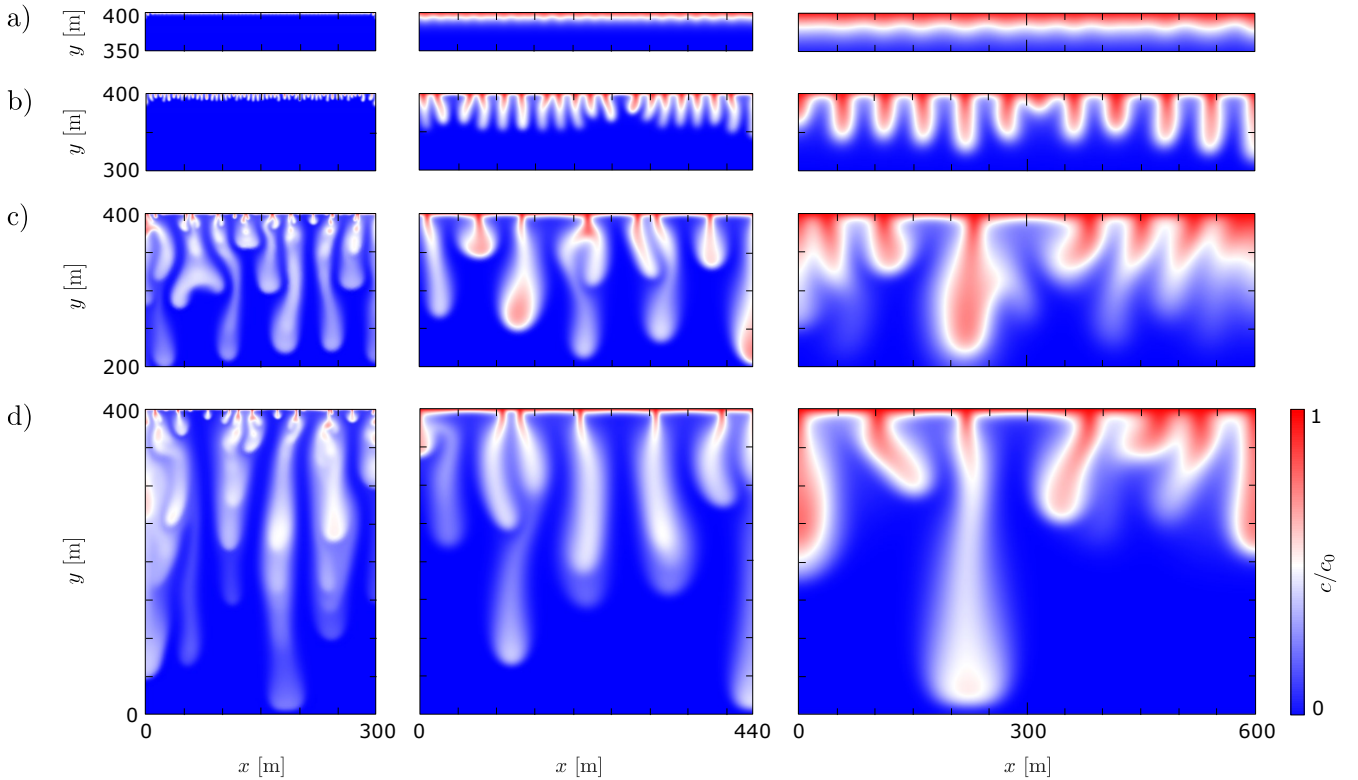


Figure 6.2: Snapshots of the concentration distribution during solutal convection a) time when the flux is at minimum, b) time when the flux is at maximum, c) first finger reaches $y = 0.5 H$, d) first finger reaches $y = H$; Left: $Ra = 10\,000$, a) $\hat{\tau} = 1.97 \times 10^3$, b) 3.82×10^3 , c) 4.56×10^4 , d) 8.87×10^4 ; Centre: $Ra = 2\,500$, a) $\hat{\tau} = 2.59 \times 10^3$, b) 4.93×10^3 , c) 1.16×10^4 , d) 1.66×10^4 ; Right: $Ra = 1\,000$, a) $\hat{\tau} = 2.73 \times 10^3$, b) 3.92×10^3 , c) 7.99×10^3 , d) 1.00×10^4

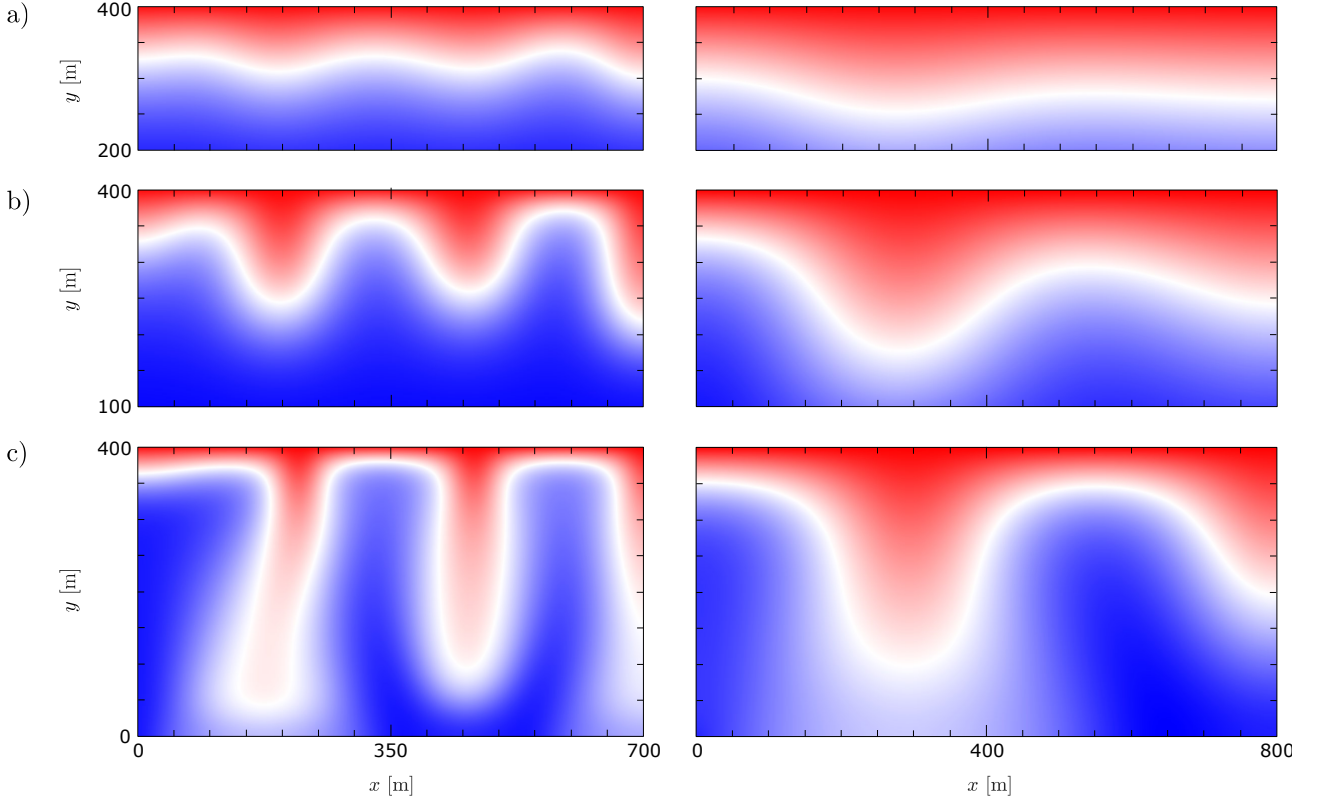


Figure 6.3: Snapshots of concentration distribution of $Ra = 250$ (left): a) time when the flux is at minimum ($\hat{\tau} = 2.80 \times 10^3$), b) first finger reaches $y = 0.5 H$ ($\hat{\tau} = 3.32 \times 10^3$), c) time when the flux is at maximum ($\hat{\tau} = 4.38 \times 10^3$) and of $Ra = 100$ (right): a) first finger reaches $y = 0.5 H$ ($\hat{\tau} = 1.67 \times 10^3$), b) time when the flux is at minimum ($\hat{\tau} = 2.14 \times 10^3$), c) time when the flux is at maximum ($\hat{\tau} = 2.96 \times 10^3$). The colour scheme is the same as in Figure 6.2.

head (panels c, d). The black particles outline a similar pattern, albeit following the outer edge of the solute plume. On the contrary, particles that are initially located below the solute plume (yellow and green) are swept around (panel b) and carried away from the solute-free fluid that experiences negative buoyancy (panels c, d). The macroscopic result of this complex dynamic behaviour is that the lobe-shaped finger first elongates vertically (panels b, c) and subsequently stretches (panel d). This advective process generates a solute plume of non-uniform concentration, whereby its neck and tip feature higher solute concentration than its base. The plume is also surrounded by a low-concentration shell that is stripped away but continuously rebuilt through molecular diffusion. The latter is unable to suppress concentration contrasts between fingers and solute-free fluid over the time scale of advection. This leads to a situation where the elongation-stretching behaviour of the plumes promoted by the differences in fluid density might slow down with time but is not completely held up.

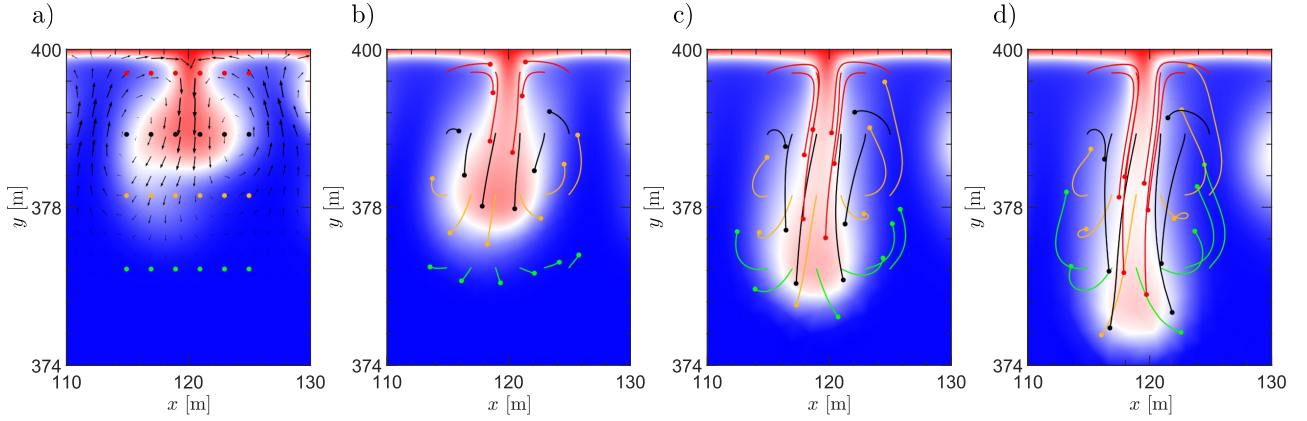


Figure 6.4: Snapshots of the concentration distribution during solutal convection at $Ra = 10\,000$ with focus on a single solute plume near the top boundary layer at $\hat{\tau} = 5.95 \times 10^3$, 6.70×10^3 , 7.37×10^3 , 8.55×10^3 , respectively (times are between onset time and time of maximum flux). In panel a the black arrows indicate Darcy’s velocity field, whereas the trajectories of 24 massless particles are followed in panels b–d (particles are colour-coded to represent the increasing distance from the upper boundary, as shown in panel a). The colour scheme is the same as in Figure 6.2.

6.4.1 Iso-Contour Line and Intensity of Segregation

The characteristic growth of the lobe-shaped structures during convective mixing is quantified in Figure 6.5a in terms of the evolution of the iso-contour line at each Ra . In the plot, the length of the iso-contour line, L , is normalised by its value during pure diffusion, L_{diff} (corresponding to the width of the domain, W). As expected and irrespective of Ra , $L/L_{\text{diff}} = 1$ before the convective process ensues (time indicated by the colour-coded vertical dotted lines). Soon after that and for $Ra > 100$, the iso-contour lines grow markedly at a rate $L/L_{\text{diff}} \propto \tau^{1.5}$. Notably, in each case the growth is interrupted temporarily at $L/L_{\text{diff}} \approx 2$, corresponding to the point where the dissolution flux reduces after the first maximum, as observed in Figure 6.1. This “stagnation” is representative of the lateral spreading and the resulting merging of neighbouring fingers, as opposed to significant longitudinal movement. The fact that similar values of L/L_{diff} are reached, further implies that at high Ra the fingers have traversed a shorter distance compared to those at lower values of Ra . As the dissolution flux increases towards the second maximum (see Figure 6.1), the iso-contour lines resume their growth as a result of the stretching of the larger fingers, following again the power law behaviour $L/L_{\text{diff}} \propto \tau^{1.5}$. In this regime, small fingers that originate at the top of the domain play only a subordinate role towards the growth of L/L_{diff} , because they are quickly swept into existing larger ones (Slim, 2014). A second slowdown in the growth of L/L_{diff} is observed by the time the system reaches the constant flux regime ($Ra = 2\,500$ and $Ra = 10\,000$, time indicated by the filled arrows, colour-coded). L/L_{diff} continues to grow, albeit in a fluctuating manner, as a result of plumes that decelerate, but regain speed when new

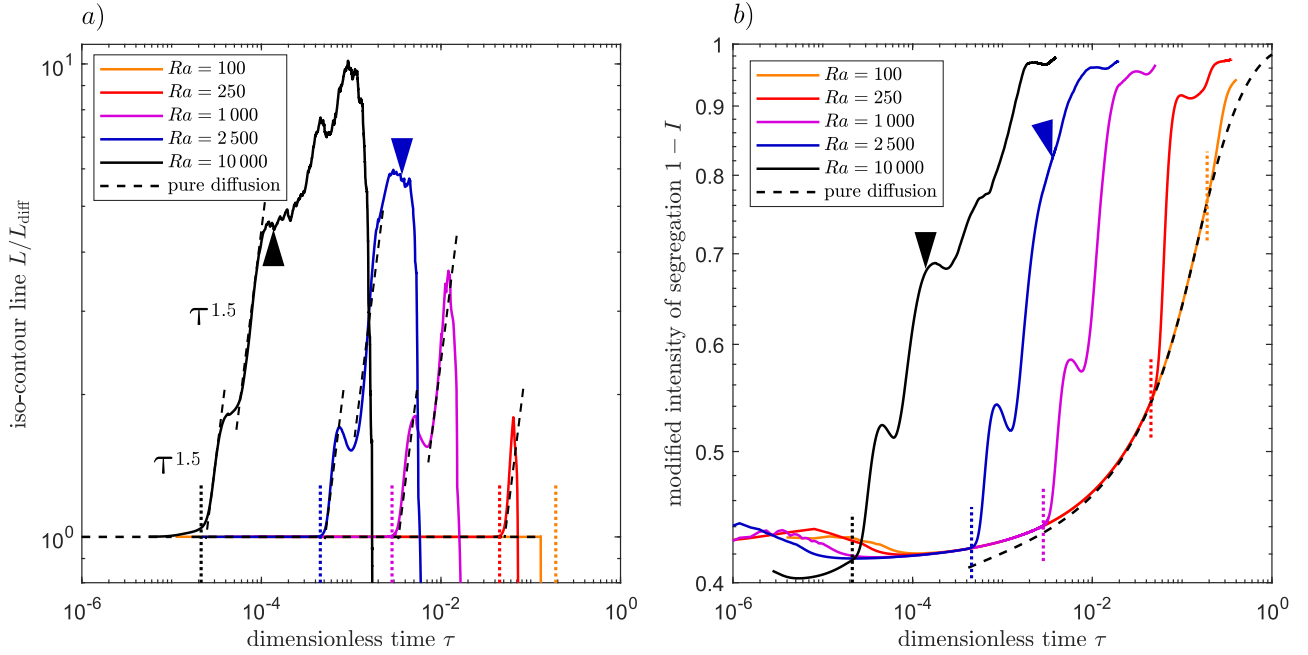


Figure 6.5: (a) Iso-contour line L/L_{diff} and (b) modified intensity of segregation $1 - I$ as a function of the dimensionless time τ . The time for the onset of convection is marked by the vertical dotted lines and the start of the constant flux regime for $Ra = 2500$ and $Ra = 10000$ by the filled arrows (all colour-coded). Since the initial concentration distribution is not strongly bimodal, the modified intensity of segregation starts with approximately $1 - I = 0.4 - 0.45$ and stays in that range during the diffusive regime while $L/L_{\text{diff}} = 1$.

plumes merge into them (Slim, 2014). Once the large plumes hit the bottom boundary of the domain, the system saturates with solute and the iso-contour lines reduce to zero. We note that for $Ra = 100$, $L/L_{\text{diff}} \approx 1$ over the whole duration of the simulation, despite plume-like structures are formed (see also Figure 6.3). However, these are much larger and billow through the domain, in contrast to the structures observed at high values of Ra , which are narrower and well-defined (see also Figure 6.2). A key difference is that at $Ra = 100$ the plumes are formed at very late times when the domain already starts to fully saturate with the solute.

We show in Figure 6.5b the evolution of the intensity of segregation, plotted here as $1 - I$ to facilitate the comparison against L/L_{diff} . The similarity between the two plots is striking and the growth of $1 - I$ closely follows the behaviour described above. We note that the humps (after the first local dissolution flux maxima, $Ra = 1000, 2500, 10000$) in the two sets of curves precisely match. These humps mark the start of the vigorous merging of the fingers with neighbouring fingers. The resulting drop in the iso-contour lines is an indication that this merging reduces temporarily the effectiveness of diffusive mass transport in the transverse direction. Additionally, high-concentrated solute continues to enter from the top boundary (see Figure 6.2), which increases the overall segregation (and reduces

$1 - I$). Upon generation of new small plumes at the top boundary, the overall solute segregation sinks and the increases in $1 - I$ resume. Further, both mixing measures indicate a reduced growth in the constant flux regime, as compared to the early times. This demonstrates that the intensity of segregation is very sensitive to the mixing patterns that form during convection and to their temporal evolution. This unique sensitivity is also reflected in the behaviour at $Ra = 100$, where we do now observe a slight, yet measurable deviation from the diffusion case (black dashed curve), confirming a slight degree of convective overturn in the domain (see also Figure 6.3). During the shutdown regime, we observe a reduction in $1 - I$ when the iso-contour suddenly drops due to a pooling of the solute in the lower part of the system. However, it continues to grow towards unity, reflecting the slow approach to uniform concentration.

6.4.2 Spreading Length and Dilution Index

The temporal evolution of the spreading length, σ , and of the dilution index, E , are plotted as a function of the dimensionless time, τ , in Figure 6.6a and b, respectively. The spreading length is normalised by the domain height, H , and the dilution index by the domain “volume”, $E_{\max} = HWL_s$. The length of the “third-dimension” is set to $L_s = 1$ m to ensure conformity of the units. Again, results are shown for simulations carried out for $Ra = 100 - 10\,000$.

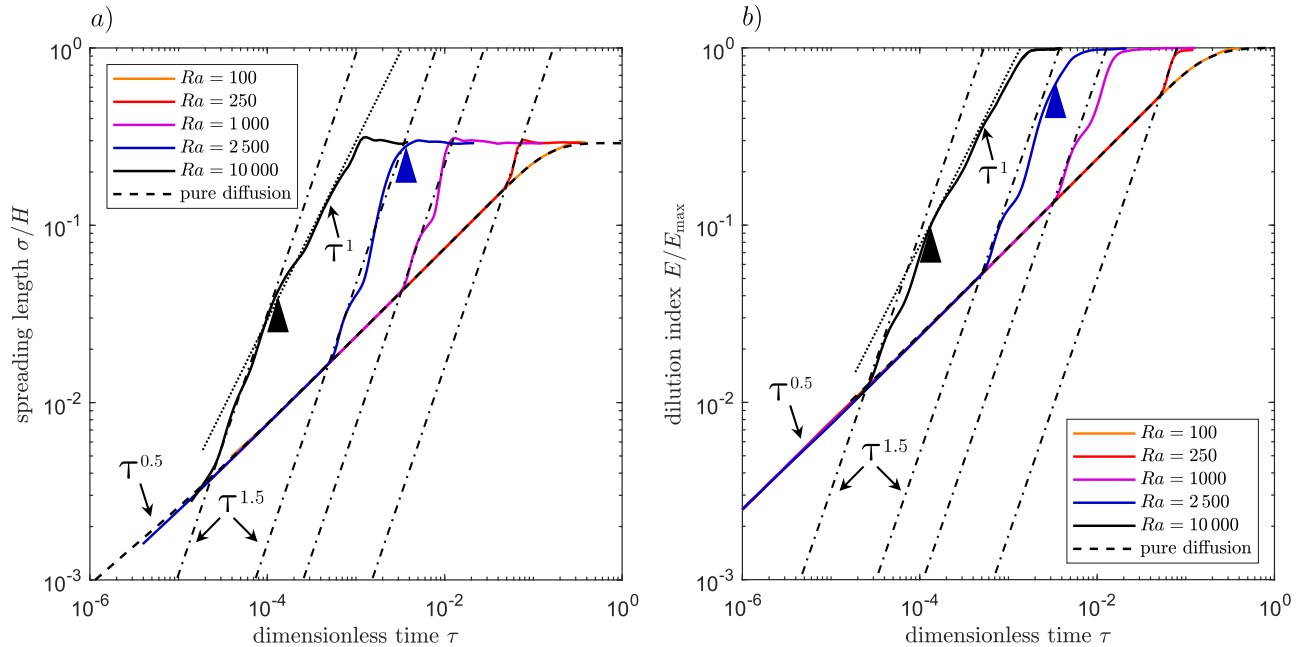


Figure 6.6: (a) Spreading length σ normalised by the height H and (b) dilution index E normalised by the domain’s “volume” $E_{\max} = WHL_s$ and plotted as function of the dimensionless time τ . The start of the constant flux regime for $Ra = 2500$ and $Ra = 10000$ is marked by the filled arrows (colour-coded).

The two plots are remarkably similar, whereby the temporal evolution of σ/H (or $E/E_{\max}$) for $Ra \geq 250$ can be described by a power law ($\propto \tau^\alpha$) with the order of scaling changing in the sequence: $\alpha = 0.5$, $\alpha \geq 1$ and $\alpha = 0$. For $Ra = 100$, the behaviour of both mixing measures retraces the curve associated with pure diffusion (dashed line, $\alpha = 0.5$ followed by a smooth transition to $\alpha = 0$). Irrespective of Ra , σ/H reaches a final value of $0.3 \approx 1/\sqrt{12}$ (in agreement with the theoretical limits discussed in Section 3.2.4) as soon as the first finger hits the bottom boundary. On the contrary, the dilution of the solute in the system continues and $E/E_{\max}$ converges slowly towards a value of unity.

Anomalous diffusion (Oliveira et al., 2019) is referred to as a transport process with a root mean square displacement, $\sqrt{\langle x^2 \rangle}$, that deviates from the power law scaling $\sqrt{\langle x^2 \rangle} \propto t^{0.5}$. By analogy, we can interpret the two initial growth regimes outlined by the spreading length in Figure 6.6a as diffusive ($\tau^{0.5}$) and super-diffusive ($\tau^{1.5}$). There is a clear transition from one regime to the other, indicating that the spreading length is very well suited to identify the time when convective mixing prevails over diffusion. For $Ra = 10\,000$, an additional transition to ballistic transport ($\alpha = 1$) is observed, which coincides with the onset of the constant flux regime (start time indicated by the filled arrow in the plot), where merging dominates over longitudinal migration. It is worth pointing out that the exact same regimes (diffusive, super-diffusive and, for $Ra = 10\,000$, ballistic) appear at the same times in the curves computed for the dilution index in Figure 6.6b. This demonstrates that spreading and mixing during solutal convection are uniquely bound and their evolution is dictated by the longitudinal finger-induced stretching to a very similar rate. In other words, for solutal convection in a uniform domain, these two mixing measures provide equivalent, rather than complementary information to the analysis of mass transfer.

6.5 Discussion

Potential CO₂ storage reservoirs are characterised by a number of dimensional and petrophysical parameters, which are lumped into the Rayleigh number for dimensional analysis. Previous studies have shown that the latter is a useful parameter to develop correlations in terms of achievable dissolution rates for a given CO₂ trap. However, as anticipated in Section 2.2, traps with low Ra ($< 1\,000$) are very likely and caution should be used when using Ra -scaling relationships that assume the attainment of a constant dissolution flux regime. We have shown in Section 6.4 that measures other than the dissolution flux can be used to characterise the temporal evolution of the dissolution process. In particular, the spreading length and the dilution index both show a well-behaved pattern, demonstrating a clear transition from diffusive (*i.e.*, a “worst-case scenario”) to super-diffusive mass

transfer, where convection significantly accelerates the mixing process. A practical result is that this transition can be unequivocally identified from the graphical representation of $E(\tau)/E_{\max}$ (or $\sigma(\tau)/H$) by the intersection of the two scaling regimes – see Figure 6.6. We plot in Figure 6.7 the onset time of the super-diffusive regime obtained by this approach as a function of Ra alongside estimates of the onset time of convection extracted from the evolution of the dissolution flux (see Section 6.3). The three data sets consistently indicate that $\tau_{\text{on}} = n Ra^{-2}$ (n is a constant). The prefactor varies from $n \approx 2000$ (calculated based on the minimum dissolution flux and in agreement with previous studies, Hassanzadeh et al. 2007; Meybodi and Hassanzadeh 2013; Pau et al. 2010) to $n \approx 3200$ when $E(\tau)/E_{\max}$ or $\sigma(\tau)/H$ is used. We conclude that for $Ra \geq 250$ the transition from diffusive to super-diffusive mixing behaviour happens after the dissolution flux starts to grow. In practical terms, for a trap with $Ra = 1\,000$ (and the reservoir properties given in Table 3.1), the onset time of convection is expected at approximately 5000 years while the onset time of the super-diffusive regime of $E(\tau)/E_{\max}$ (or $\sigma(\tau)/H$) appears after approximately 8000 years. We proceed in the following with the derivation of Ra -scaling relations for the dissolution flux and the dilution index obtained from the numerical simulations and apply them to a practical example.

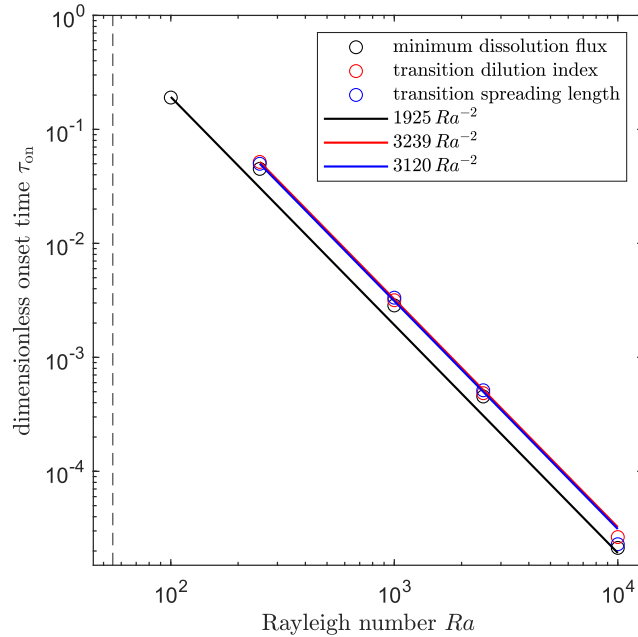


Figure 6.7: Dimensionless onset time of convection, τ_{on} , as a function of Ra , defined as the time at which J departs from the diffusive curve and reaches its minimum (black coded) and as the time $E(\tau)/E_{\max}$ (or $\sigma(\tau)/H$) transitions from the diffusive to the super-diffusive scaling in Figure 6.6 (red and blue coded). The solid lines are power law functions fitted to the three data sets (all $R^2 \geq 0.99$) and apply for the investigated Rayleigh numbers range between $Ra = 100 - 10\,000$ (black) and $Ra = 250 - 10\,000$ (red, blue). The dashed vertical line marks the Rayleigh number $Ra = 55$ below which convective enhancement in the mass transfer is not to expect.

6.5.1 Sherwood Number Scaling

Studies often employ the Sherwood number, Sh , that applies the dissolution flux in the dimensionless form to quantify the degree of mixing during solutal convection. In this section, we use the definition of the Sherwood number in Eq. 3.8 (Section 3.2.1) which represents the Sherwood number as the ratio of convective flux to the diffusive flux across the interface. With this definition, Sh is time-dependent (see Figure 6.8) and the identification of a correlation with Ra is not straightforward. We use here the maximum value of the Sherwood number, $Sh_{\max}$, of each data set and plot it in Figure 6.9 as a function of Ra . The simulation data outline two distinct correlations (solid and dashed lines in the plot). For $Ra \geq 2500$, a power law scaling ($Sh = nRa^\alpha$) is obtained with coefficients $n = 0.023$ and $\alpha = 0.69$ and a coefficient of determination, $R^2 = 0.97$. In the literature, a power law scaling for the Sherwood number at high Ra is reported, albeit the order of scaling, α , varies among the studies. In particular, some authors report a linear scaling ($\alpha = 1$, including simulations, *e.g.*, Slim 2014 and Hidalgo et al. 2012, and experiments, *e.g.*, Liyanage et al. 2019), while others observe sub-linear scaling ($\alpha < 1$, including simulations, *e.g.*, Farajzadeh et al. 2013 and Neufeld et al. 2010, and experiments, *e.g.*, Backhaus et al. 2011 and Tsai et al. 2013). Previous studies have convincingly shown that the use of fluid pairs with non-monotonic density-concentration curves leads to nonlinear scaling of the

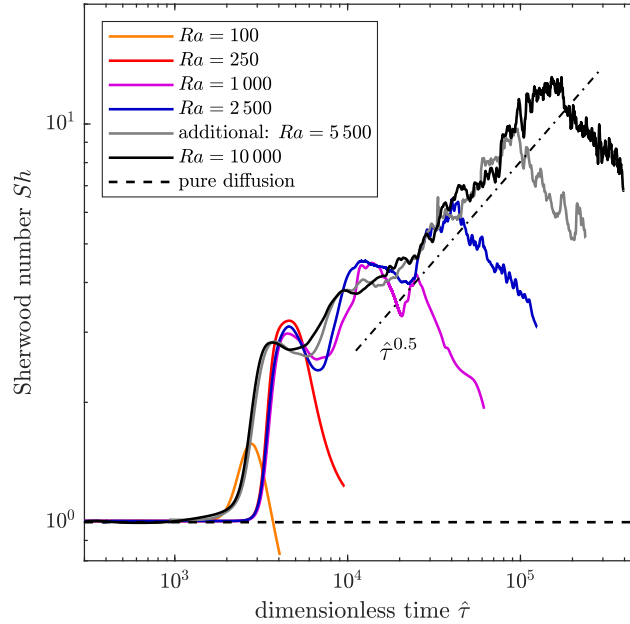


Figure 6.8: Sherwood number, $Sh = J/J_{\text{diff}}$, plotted as a function of the dimensionless time, $\hat{\tau}$, for simulations carried out at different Ra . An additional simulation was performed at $Ra = 5500$. It can be seen that for $\hat{\tau} > 10^4$ and prior to the start of the shutdown regime, all simulation data outline a power law scaling, $Sh \propto \hat{\tau}^{0.5}$, confirming that J reaches a constant value.

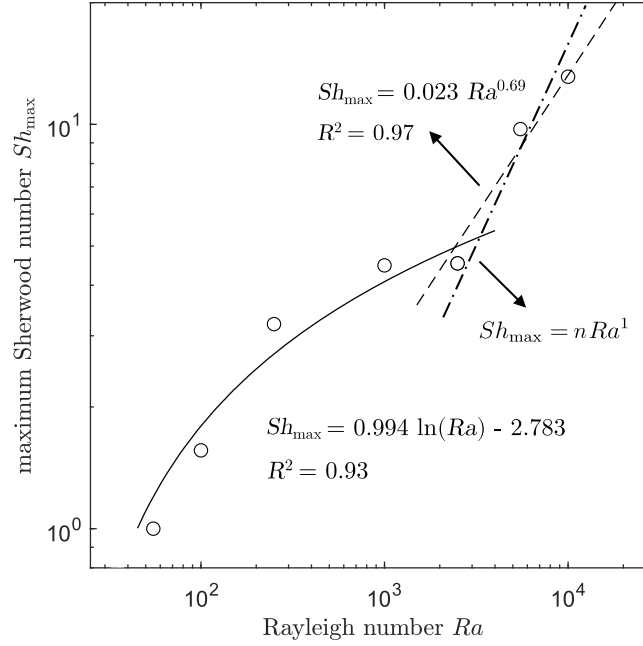


Figure 6.9: $Sh_{\max}$ as function of Ra , with the addition of $Ra_c = 55$ at $Sh_{\max} = 1$. An additional simulation was performed at $Ra = 5\,500$ to support the derivation of a Sherwood number scaling in that range. The solid line is a natural logarithmic function fitted to data obtained at $Ra \leq 2\,500$, while the dashed and the dashed-dotted lines are power law functions that describe the data obtained at $Ra \geq 2\,500$.

dissolution flux with Ra (Hidalgo et al., 2012; Jafari Raad et al., 2016). We agree with this conclusion, but add that the use of different approaches to determine the flux (and, thus a representative value of Sh) may also be at the origin of this apparent discrepancy in the order of scaling. Nevertheless, our simulations cover only a narrow range of “high” Ra and do not necessarily rule out the appearance of the linear scaling, $Sh \propto Ra$, as indicated in Figure 6.9 by forcing a linear fit to the data (dashed-dotted line),

Our main focus is on the results obtained at $Ra \leq 2\,500$, since the majority of saline aquifers worldwide are found in this range (see Section 2.2.2) and no scaling has previously been reported in the context of GCS, to the best of the author’s knowledge. We show here that the data fit a natural logarithmic function of the form $Sh = a \ln x + b$ with $a = 0.994$ and $b = -2.783$ ($R^2 = 0.93$). The observed values are thus substantially larger than those that would be predicted by extrapolating the power law behaviour discussed above to low Ra . It has been shown in the literature that a Rayleigh-Bénard convection, as the one in this study, is analogous to a thermal convection phenomenon in a porous medium which is rapidly heated from the top (Diersch and Kolditz, 2002; Elder, 1967, 1968; Riaz et al., 2006). The observation of the logarithmic behaviour outlined by our simulations at $Ra \leq 2\,500$ followed by a power law scaling can also be recognised in results reported for the convective

mixing process driven by thermal effects in the equivalent Ra regime and quantified in terms of the Nusselt number, Nu (Hewitt et al., 2014; Otero et al., 2004). The quantitative agreement between our values and those reported in these studies supports the indication that the heat and mass transfer analogy is fulfilled.

6.5.2 Scaling of Mixing Measures

In the following, we derive Ra -scaling relations for the dilution index presented in Section 6.4.2. To this end, we consider the situation of close-to-complete mixing ($E = 0.9 E_{\max}$) and compute the ratio of the times needed to reach this state through diffusive and convective mixing, $\tau_{\text{diff}}/\tau_{\text{conv}}$. The obtained result is shown in Figure 6.10.

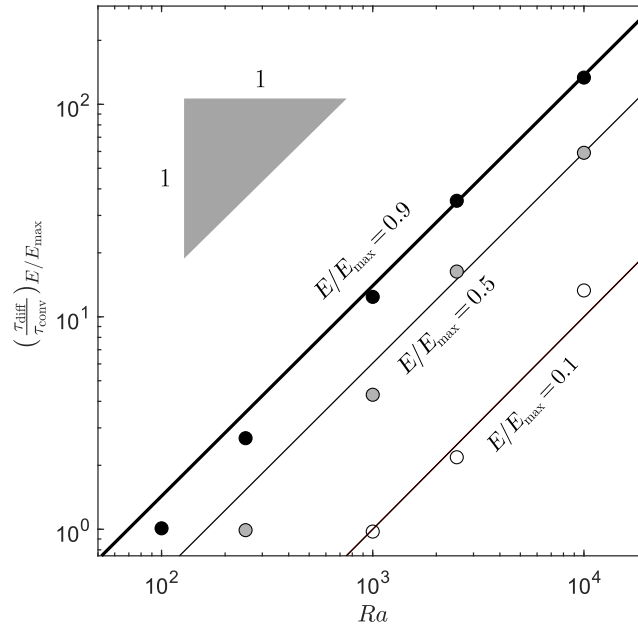


Figure 6.10: Ra -scaling of the dilution index. Symbols refer to the ratio of the times needed to reach a given state of mixing ($E = x E_{\max}$ with $x = 0.9, 0.5, 0.1$) through diffusion and convection, $\tau_{\text{diff}}/\tau_{\text{conv}}$. The solid lines are power law functions fitted to the data (equations given in the manuscript text).

The data is best fitted with a power law with the order of scaling near one ($R^2 \geq 0.99$), implying that the time needed to achieve nearly complete mixing reduces proportionally to the increase of Ra . In particular, the following relation is found:

$$\left. \frac{\tau_{\text{diff}}}{\tau_{\text{conv}}} \right|_{E=0.9E_{\max}} = 0.015 Ra^{0.99}. \quad (6.1)$$

Two additional cases are considered in Figure 6.10, namely $E = 0.5E_{\max}$ and $E = 0.1E_{\max}$:

$$\left. \frac{\tau_{\text{diff}}}{\tau_{\text{conv}}} \right|_{E=0.5E_{\max}} = 0.006Ra^{0.99} \quad (6.2a)$$

$$\left. \frac{\tau_{\text{diff}}}{\tau_{\text{conv}}} \right|_{E=0.1E_{\max}} = 0.001Ra^{1.00}. \quad (6.2b)$$

Again, a linear scaling with Ra is found, indicating that the analysis of the mixing time based on the dilution index resembles the one of a purely diffusive Fickian system. A greater diffusion coefficient leads to a faster expansion of the mixing zone and the mixing time scales proportionally with the process-dependent variable (*i.e.*, the diffusion coefficient). Here, the same concept applies when considering $\tau_{\text{diff}}/\tau_{\text{conv}}$ vs. Ra . Remarkably, while diffusion appears macroscopically as well-behaved, with the concentration at each point changing monotonically with time, the pattern of convective mixing is largely chaotic and subject to various time-dependent regimes. Nevertheless, the same process can be parameterised in terms of useful macroscopic variables, such as the dilution index and the Rayleigh number, which can thus be used for up-scaling purposes.

Difficulties arise in the evaluation of the lifetime of sequestration projects that are injecting or planning to inject CO_2 in reservoirs. Only limited techniques are available for the assessment of the long-term potential of solubility trapping (Szulczewski et al., 2013). The present results are based on a two-dimensional model and many assumptions. However, the application of the derived scaling laws can provide estimates of the onset time of convection and the time scale for achieving substantial mixing in the aquifer – parameters that can guide the selection of suitable sites for GCS (Hassanzadeh et al., 2007). As a practical example, we apply the derived scaling laws to two existing reservoirs and assume homogeneous porous formations. We choose one site with a low Rayleigh number ($Ra = 364$) from the Alberta Basin in Canada (Bachu et al., 2005) and a site with a higher Rayleigh number ($Ra = 6\,223$) from the Black Warrior River aquifer in the USA (Szulczewski et al., 2012). Relevant parameters and references are given in Table 6.1 and the caption. Since for both $Ra > 55$, it is expected that convection will eventually overcome diffusion and govern the dissolution process. Based on the

Table 6.1: Parameters for two potential storage sites (Bachu et al., 2005; Nazari Moghaddam et al., 2015; Szulczewski et al., 2012). The Rayleigh number of the Black Warrior River site was calculated with the diffusion coefficient that was estimated with Cadogan et al. (2015).

Parameters	Alberta Basin site	Black Warrior River site
H [m]	10	200
D [$\text{m}^2 \text{s}^{-1}$]	5×10^{-9}	2×10^{-9}
Ra [–]	364	6 223

scaling reported in this study, it is estimated that the transition from a diffusion- to a convection-dominated mass transfer process will take place after ~ 9 years and ~ 30 years for the Alberta Basin and the Black Warrior River aquifer, respectively. Results also show that the dissolution flux will never be larger than $\sim 3 - 10$ times the flux observed in a scenario where mass transfer is due to diffusion only. The distribution of CO_2 in the aquifer is accelerated to a higher extent for the Black Warrior reservoir due to a higher Rayleigh number, with the CO_2 -rich plume occupying approximately 50 % of the available aquifer volume after 800 years, as compared to the 30 000 years needed for the purely diffusive scenario. For the reservoir in the Alberta Basin, these numbers are much lower (due to the low aquifer height) and are estimated to be 14 and 30 years, respectively. In other words, a normalised dilution index of $E/E_{\text{max}} = 0.5$ is reached in $\sim 1/40$ (Black Warrior aquifer) and half of the time (Alberta Basin) needed if only diffusion would contribute to the mass transfer. Further, results demonstrate that after ~ 20 years for the Alberta Basin and $\sim 1\,500$ years for the Black Warrior River reservoir, CO_2 has dissolved in 90 % of the pores ($E/E_{\text{max}} = 0.9$). This additionally exemplifies the need, especially for reservoirs with large net aquifer thickness and slow convection, for safe and leak-free storage of CO_2 in the underground.

6.6 Conclusion

Numerical simulations are performed to quantify systematically the mixing dynamics during density-driven solutal convection in homogeneous porous media with application to CO_2 storage. A two-dimensional formulation is applied, and the Rayleigh number is varied between $Ra = 100$ and $Ra = 10\,000$. We examine the dissolution process by analysing macroscopic measures of mixing, including iso-contour lines, the intensity of segregation, the spreading length, the dilution index and the dissolution flux. Results of the latter are successfully validated against data from a benchmark study (Slim, 2014).

We show that the generation of lobe-shaped fingers drives the mixing process: their elongation and stretching produce a largely non-uniform distribution of solute within the dissolved plume, which in turns intensifies horizontal diffusive mass transfer. The intensity of segregation is very sensitive to this mixing pattern since its temporal evolution closely resembles the one of the iso-contour line. The temporal behaviour of the spreading length can be described by a power law scaling ($\propto t^\alpha$). The acceleration of the mixing process unveils a clear transition of the power law exponent from diffusive ($\alpha = 0.5$) to super-diffusive mixing ($\alpha \geq 1$). This transition time scales $\propto Ra^{-2}$. We find the same scaling exponents in the temporal evolution of the dilution index and infer that the spreading length

and the dilution index of solutal convection are analogous when evaluated for a uniform domain. The Sherwood number is used to compare convective to diffusive mass transport and reveals a distinct scaling behaviour for low ($Ra \leq 2500$) and high ($Ra > 2500$) Rayleigh numbers. The former regime follows a logarithmic function that resembles the behaviour observed in the classical thermal convection problem for the corresponding regime in terms of the Nusselt number. We derive scaling relationships for the dilution index as a function of Ra and observe that the time needed to achieve nearly complete mixing reduces proportionally to the increase of Ra . We apply the scalings to two representative geologic traps to obtain guideline figures for the dissolution times over the lifetime of a GCS project.

The novel mixing relationships and Ra -scalings support studies on geochemical reactions between dissolved CO_2 and rock minerals in GCS applications. We could show that we need, additionally to the dimensionless Rayleigh number, diagnostics such as the ones used and derived in this study as indicators for the importance of convective mixing in the various time-scales of a sequestration operation process. Significant for the operator time-scale (1-50 years) is the time when the mass transfer process transitions from diffusive to convective dominated together with an estimate of the mass flux expressed in the Sherwood number. For the long-term and site closure time-scales (20-100 years), the attained mixing volume is of strong relevance which can be estimated with, for instance, Eq. 6.1 and 6.2.

Knowledge of the spreading of CO_2 , going beyond spatially averaged concentrations, is needed to understand the coupling of the geochemical reactions and convective mixing and to accurately predict reaction rates (Li et al., 2007). Further, the spreading of dissolved CO_2 and the relevant dissolution time-scales will be affected by the presence of highly heterogeneous domains (Green et al., 2009; Green and Ennis-King, 2018; Li et al., 2019b). Studies investigating the dissolution process in systems characterised by distinct degrees of heterogeneity and anisotropy will benefit from the comparison with results obtained for the homogeneous and isotropic porous medium investigated in the present work.

Chapter 7

Convective Dissolution in Unconsolidated Bead Packs

In this chapter, results of the novel experimental approach to investigate the evolution of the convective mixing process in 3D porous media using X-ray Computed Tomography are presented. The experiments are performed with homogeneous packs of glass beads. Key elements of the results include the evaluation of the three-dimensional dissolution pattern, the analysis of the temporal evolution of the spatial moments (details in Section 3.3) and the interpretation of the experimental observations with a simplified mathematical representation of the convective dissolution process (details in Section 3.4).

The material presented in this chapter has been published in Eckel et al. (2023).

7.1 Introduction

Various experimental and modelling studies presented in the literature have addressed fundamental aspects of density-driven convection, which evolves through the concomitant action of diffusion, advection and hydrodynamic dispersion. The ratio of density-driven and diffusive mass transport (*i.e.*, the Rayleigh number) is commonly used as the basis for the derivation of scaling relationships that predict the occurrence of solutal convection and quantify its strength. Despite it being a fundamental component of convective mixing in porous media, the role of hydrodynamic dispersion is only rarely discussed in experimental studies (Chevalier et al., 2015; Dejam and Hassanzadeh, 2022; Jiménez-Martínez et al., 2015; Liang et al., 2018; Ren et al., 2022). Dispersion is associated with the discrete and irregular connectivity of the pore network of a porous medium. Spatial variations in the porosity and permeability of the medium yield highly heterogeneous fluid velocity fields and generate complex

concentration distributions of the solute. Dispersion can act along the main flow direction (longitudinal dispersion) or perpendicular to it (transverse dispersion), thereby affecting the structure of the downwelling fingers (Liyanage et al., 2020; Nakanishi et al., 2016; Wang et al., 2017). Dispersion has been shown to also reduce the onset time of convection (Hidalgo and Carrera, 2009) and to contribute to the dissolution process in the presence of a background advective flow (Michel-Meyer et al., 2020; Tsinober et al., 2022).

Density-driven convection can enhance the transport of mass, heat, and energy in contrast to the slow diffusive process alone. As mentioned in the preceding chapters, this aspect bears implications for the dissolution of supercritical CO₂ and its long-term storage. However, the characterisation of density-driven convection in porous media remains challenging and requires the development and application of advanced laboratory protocols to unravel the evolving concentration field in the medium. Experimental approaches to studying accelerated dissolution by density-driven convection suffer from numerous limitations, which have complicated their interpretation and comparison with numerical studies. Several studies use analogue fluid pairs that are fully miscible and produce a non-monotonic behaviour of fluid density with concentration (Backhaus et al. 2011; Liyanage et al. 2019, 2020; Neufeld et al. 2010; Tsai et al. 2013; Wang et al. 2017, see Section 2.3.1). It has been shown that these systems cannot be used to identify scaling relationships that apply to the partially miscible CO₂-water system with a linear density behaviour (Hidalgo et al., 2012; Jafari Raad et al., 2016; Jafari Raad and Hassanzadeh, 2015; Liyanage et al., 2019). Some experimental studies with the CO₂-water or CO₂-brine have been reported (Mojtaba et al., 2014; Nazari Moghaddam et al., 2015, 2012; Newell et al., 2018), but they use blind cells and do not allow for the direct visualisation of the mixing process. Experimental studies with transparent Hele-Shaw cells have convincingly demonstrated the importance of measuring the evolving concentration field (Ecke and Backhaus, 2016; Slim et al., 2013) but constrain the mixing process to two dimensions. As mentioned in Section 2.3.1, to bridge this gap, recent efforts have employed X-ray CT technology (Liyanage et al., 2019, 2020; Nakanishi et al., 2016) or MRI technology (Teng et al., 2017; Wang et al., 2021a,b, 2020) to observe three-dimensional density-driven convective mixing in opaque porous media. However, a feature that is also common to most of these studies is the application of a closed boundary, meaning that the unstable boundary layer is a receding interface between the two stratified fluids (*i.e.*, Rayleigh-Taylor Model). This is in contrast to the majority of numerical studies, where a constant concentration boundary is applied (*i.e.*, Rayleigh-Bénard Model), making it difficult to compare key metrics, such as the dissolution flux. The assumption of a sharp and rigid interface is valid when the stable stratification of density damps out flow disturbances and CO₂ and brine are in thermodynamic equilibrium across

the interface (Elenius and Gasda, 2013; Riaz and Cinar, 2014). The different models are discussed more in detail in Section 2.3.

In this chapter, we present an experimental approach to study the convective mixing process in three-dimensional unconsolidated and uniform porous media. By applying a surrogate fluid pair with monotonic density behaviour, we address important limitations of past experimental studies that restrict the transfer of results to the CO₂-brine system. Upon application of X-ray CT technology, we produce three-dimensional imagery of the solute concentration field at a spatial resolution of a few millimetres. This information is used to carry out an analysis of the spatial moments of the solute concentration distribution throughout various stages of the experiments. Spatial moment analysis has been proven to be a useful measure to describe and analyse the longitudinal spreading of the plumes by, for instance, Trevisan et al. (2017) and Ren et al. (2022). Based on our experimental findings, we propose a simplified representation of the mixing process by analogy with the one-dimensional advection-dispersion model (presented in Section 3.4).

7.2 Methodology

We use the experimental routine described in Section 5.2 that allows maintaining a constant concentration at the top boundary of the three-dimensional porous medium for the entire duration of the experiment by using a solid, powdered salt (KI). Unconsolidated uniform glass bead packs with three different bead sizes (55 μm , 100 μm , 250 μm) are used as porous media (see Chapter 4). The downwelling KI-rich plumes are imaged, reconstructed and analysed in three dimensions using the medical CT scanner and the tools described in Section 5.3.

Image analysis is performed according to Section 5.3.2. The image noise encountered in this study is likely to be caused by a combination of photon starvation (Mori et al., 2013) and quantum mottle (*i.e.*, random imaging noise). The uncertainty of the CT number caused by quantum mottle of a given voxel (of size 0.4 mm $\times$ 0.4 mm $\times$ 1 mm) was estimated using two scans of the saturated porous media taken prior to the start of the experiment to yield $\sigma_{\Delta_{\text{CT}}} = 17 \text{ HU}$. Upon application of statistical rules of error propagation on Eq. 5.2, the uncertainty of the computed mass fraction of solute is estimated to be between $\sigma_{w_i=0} = 0.01$ (pure water) and $\sigma_{w_i=0.6} = 0.02$ (maximum saturation). Accordingly, the uncertainty in the computed concentration of solute (Eq. 5.3) is estimated to be $\sigma_{c_i} = 28 \text{ mol/m}^3$ (pure water) and $\sigma_{c_i} = 663 \text{ mol/m}^3$ (saturated solution, $c_{\text{max}} = 6198 \text{ mol/m}^3$). The procedures for the uncertainty estimations are described in Appendix B.

7.3 Results on Convective Dissolution in Unconsolidated Bead Packs

7.3.1 Three-Dimensional Dissolution Patterns

Figure 7.1 shows still frames of the mixing process between the aqueous KI solution and water represented as three-dimensional reconstructions of the sample cell for the three bead packs. The images are made using the open-source application ParaView. The 3D images are cropped at the foam-beads interface and around the lateral walls of the cube. The times of the still frames have been selected to

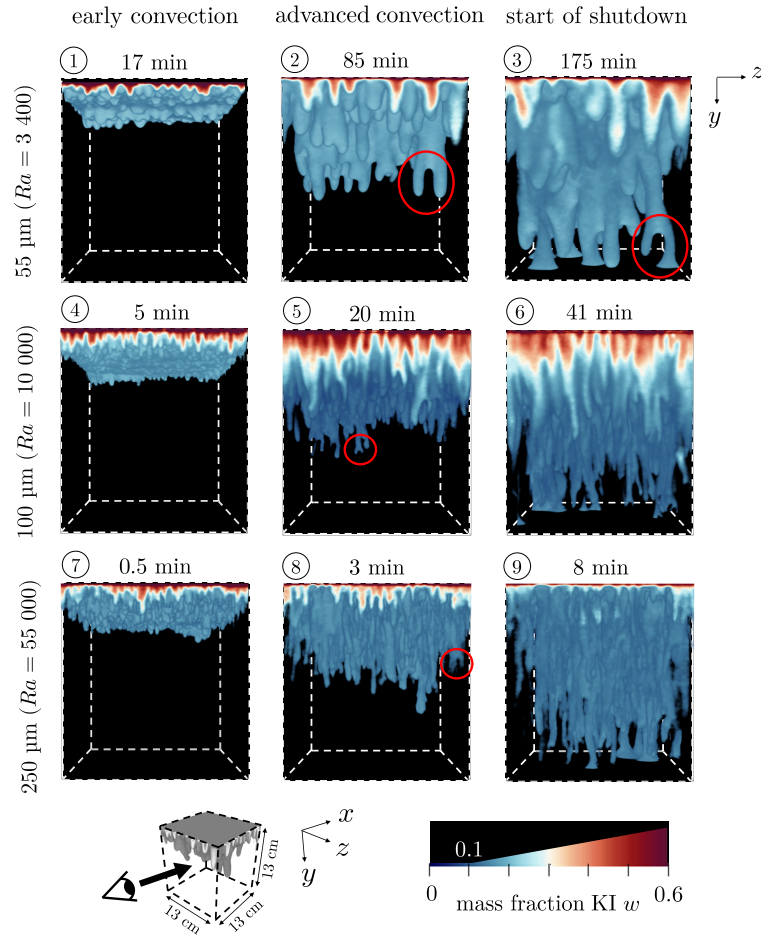


Figure 7.1: Three-dimensional reconstructions of the finger development during the density-driven convective process. Images are cropped at the interface between the foam and the bead pack and approximately 1 cm from the lateral walls of the cube. The spatial resolution is 0.4 mm in x- and y-direction and 1 mm in the z-direction. The voxels are shown in terms of solute (KI) mass fractions, w_i , and the pure water ($w_i < 0.1$) is made transparent. Three stages in the dissolution process are selected that are represented for each bead size experiment: 1), 4) and 7) during the early convection regime, when the fingers have just formed near the interface, 2) 5) and 8) during the advanced convection regime, when the fingers have gained in speed, merged and reached roughly half of the domain height, 3), 6) and 9) beginning of the shutdown when the fingers hit the end of the domain and start to pool at the lower boundary. The red circles highlight examples of tip-splitting.

represent the early convective regime, the advanced-convective regime and the start of the shutdown regime. The time of each stage varies between the three packs, in accordance with the change in Ra (Table 5.1). Specifically, for larger bead sizes we observe an earlier onset of convection and faster dissolution due to the higher permeability of the packing. In all three cases, the finger width increases slightly from the early convective regime to the advanced convective regime. The packing with 55 μm beads features downwelling plumes with the largest width (1 – 2 cm), while the width of the plumes is only a few millimetre for the packs with 100 μm and 250 μm . We note that the expected reduction in plume width with increasing bead size (Agartan et al., 2015) is counteracted by the increase in mechanical transverse dispersion with increasing Ra (Nakanishi et al., 2016), yielding similar plume widths for the packs with 100 μm and 250 μm . As a result of the higher permeability and stronger dispersion, the finger bodies in the 250 μm packing are only highly concentrated close to the interface and get dispersed when travelling downwards.

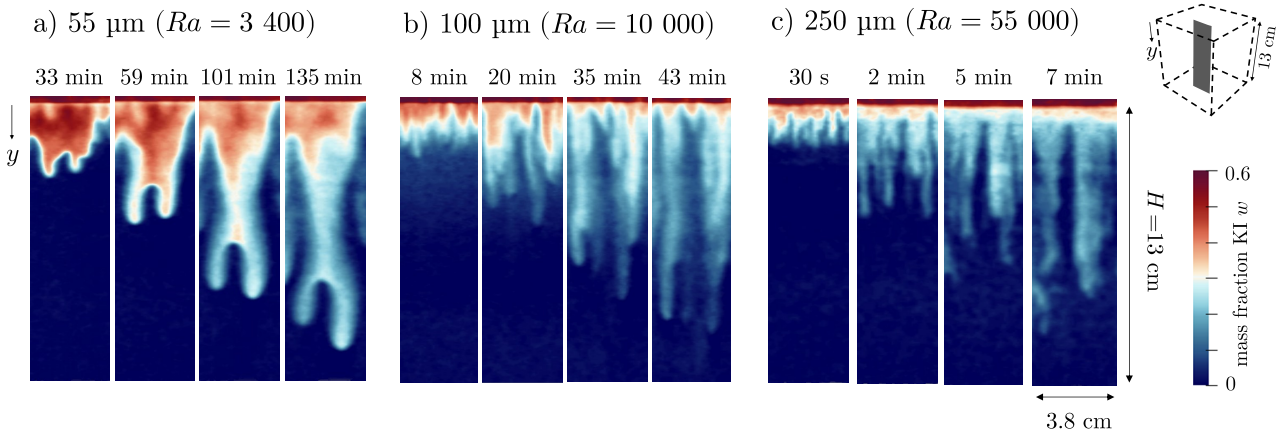


Figure 7.2: Evolution of discrete solute plumes for the three bead packs over the time of the experiment. The panels show two-dimensional sections taken from the middle of the 3D reconstructions. In comparison to Figure 7.1, the surrounding pure water is not made transparent.

The still frames a, b and c in Figure 7.2 highlight the distinct features of the finger pattern generated in the experiments with different bead sizes. Differences are also observed at the level of individual fingers, whereby the concentration in the finger bodies decreases with increasing Rayleigh number. Coalescence of fingers can be observed for all three packs while in the 250 μm packing vigorous merging makes it more difficult to distinguish individual fingers. However, merged fingers (or even individual fingers) can be separated again by, so-called, tip splitting. Tip splitting is the mechanism by which the tip of a finger splits into two or more fingers by the upwelling flow (Malhotra et al., 2015). Examples of tip splitting are seen in image 2, 3 or 5 in Figure 7.1 (red circles) and in Figure 7.2 a.

We compute the number of plumes over time inside a 10 cm $\times$ 10 cm horizontal plane located at

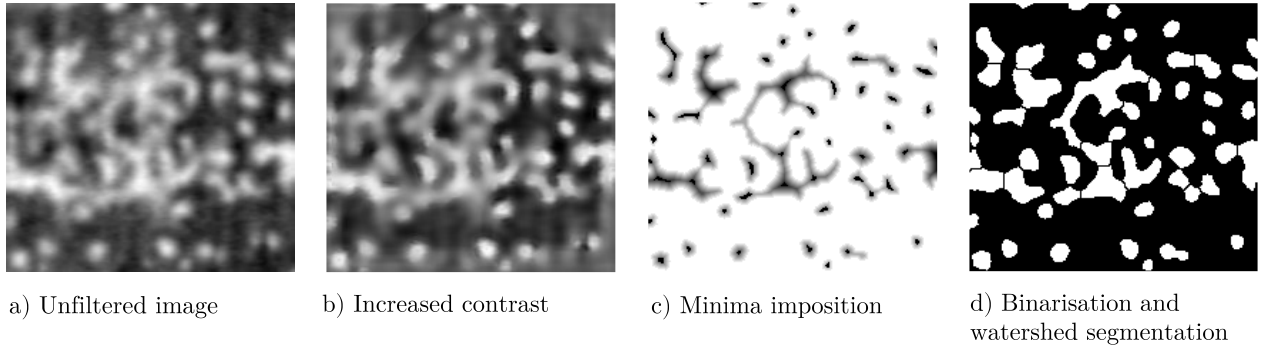


Figure 7.3: Relevant steps of the segmentation routine used to distinguish and count the number of single and fully merged fingers. Example shows cropped 2D horizontal plane taken from the centre of the geometry of a 100 μm glass beads experiment.

$y = H/2$ and compare it for the different packs in Figure 7.4. To this end, the images were segmented to identify and separate cross-sections of individual fingers from the surrounding water. Figure 7.3 shows relevant steps of the segmentation routine by means of an experiment with 100 μm bead packing that is applied in the MATLAB software. The segmentation routine includes an enhancement of the image contrast by using bottom-hat and top-hat filtering (Figure 7.3b). In the following step, the greyscale image is binarised by applying a threshold ($0.2 w_{\text{max}} = 0.12$) that has been chosen after the evaluation of several sample planes. A watershed segmentation is implemented (c and d) that segments contiguous regions of interest (*i.e.*, the single or fully merged fingers) into distinct objects. As shown in Figure 7.4, a similar evolution is observed for the three packs and for repeated experiments with each packing which is the first indication of good reproducibility of the experiments. Once the first plume has reached the reference plane, the number of fingers increases quickly, until it reaches a maximum. The latter increases with increasing bead size, namely ~ 15 fingers (55 μm) $< \sim 55$ fingers (100 μm) $< \sim 65$ fingers (250 μm). This is in accordance with the observation of the finger width in Figure 7.1 and 7.2 and the three-dimensional experimental study of Nakanishi et al. (2016). The maximum finger count is reached by the time the first plumes reach the bottom boundary of the cell, as indicated by the vertical shaded area in the plot (colour-coded). Beyond this point, the finger count in the horizontal plane reduces sharply.

7.3.2 Onset Time of Convection

We determine the onset time of convection, t_{on} , directly from the 3D images by identifying the time when individual fingers are formed out of the initial disturbance. The results of this analysis are plotted in Figure 7.5 in terms of the dimensionless onset time $\tau_{\text{on}} = Dt_{\text{on}}/H^2$ as a function of Ra . Vertical

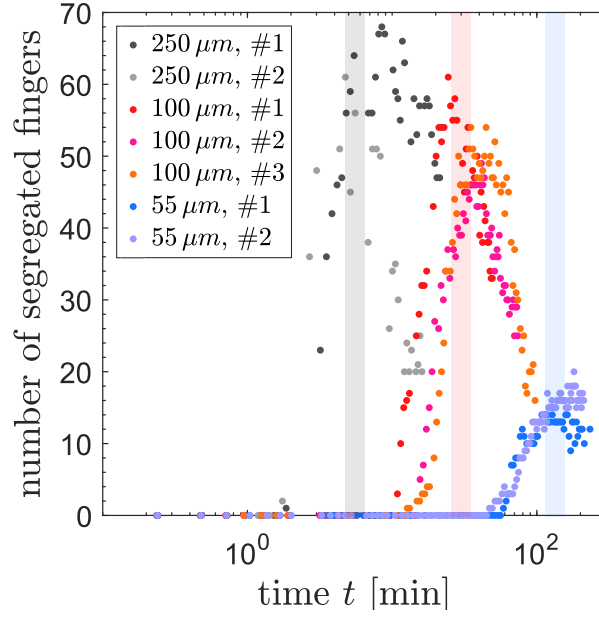


Figure 7.4: Number of segregated fingers over time in a $10\text{ cm} \times 10\text{ cm}$ horizontal slice located at $y = H/2$. The data points are colour-coded to represent different bead sizes ($55\text{ }\mu\text{m}$ in blue, $100\text{ }\mu\text{m}$ in red and $250\text{ }\mu\text{m}$ in grey). The data was slightly smoothed with a moving average function (2-point centred) to better identify the peaks of the curves. The vertical shaded areas represent the time period during which the first plumes reach the bottom boundary.

error bars reflect the discrete nature of the image acquisition approach and represent the time between two consecutive scans. The horizontal error bars quantify the effect of permeability uncertainty on the estimated value of Ra (see Table 5.1). We have fitted the power law function aRa^b to the data and obtained $a = 84.05 [-43.26, 211.36]$ and $b = -1.83 [-1.65, -2.02]$. We evaluate the goodness of fit based on the NMSE (normalised mean square error). Given an error value of $\text{NMSE} = 0.002$, we contend that the results agree reasonably well with the theoretical scaling $\tau_{\text{on}} \propto Ra^{-2}$ (Ennis-King et al., 2005). In fact, it has been shown numerically (Riaz et al., 2006) and experimentally (Liyanage et al., 2019; Nakanishi et al., 2016) that this is valid in two- and three-dimensional porous media. A reference line (in grey) with $\tau_{\text{on}} = 400Ra^{-2}$ is included in Figure 7.5. We note that the prefactor a is sensitive to the strength and type of perturbation that induces convection at the interface as well as the method used to determine the onset time (Emami-Meybodi et al., 2015). The effect of dispersion on the onset of convection was studied numerically by Hidalgo and Carrera (2009). They demonstrated that by accounting for dispersion, the onset time reduces significantly. Therefore, we expect that numerical studies, that do not consider dispersion effects, show higher onset times ($a \approx 1000 - 5000$) than predicted experimentally (see Table 2 in Emami-Meybodi et al. 2015).

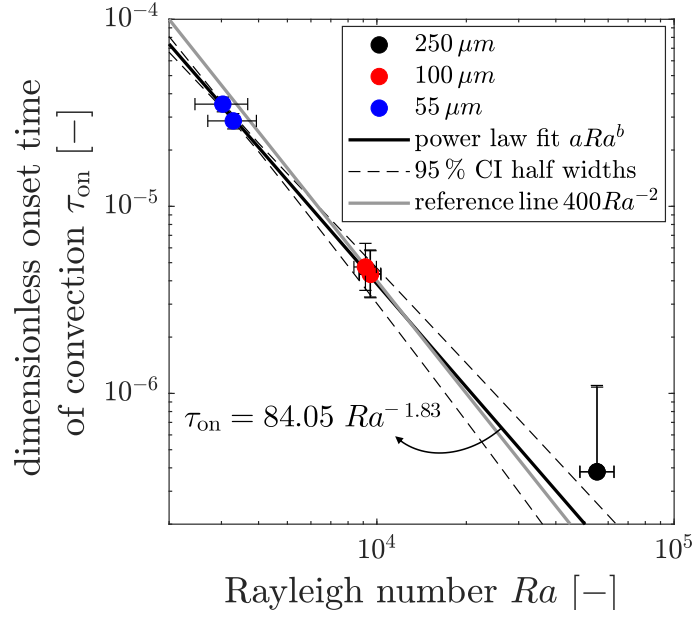


Figure 7.5: Dimensionless onset time of convection, τ_{on} , as a function of the Rayleigh number, Ra . For the experiment with 250 μm glass beads, the onset time was approximated to $\tau_{on} 5s$, because convection ensued prior to the first scan (taken after roughly 10 seconds). The vertical error bars represent the lag between the onset time and the time at which the scans were taken. No negative error bar is available for 250 μm as the chosen onset time is the time of the first scan. The solid black line is the power law scaling $\tau_{on} = 84.05 Ra^{-1.83}$ and the solid grey line is a reference line. The dashed lines are representing the 95 % confidence interval (CI) half-widths in distance to the model predictions. The values of the onset time, their uncertainties and details on the confidence intervals are reported in Appendix D in Table D.1.

7.3.3 Zeroth Moment (Total Mass)

For the spatial moment analysis in Section 7.3.3–7.3.5 and the dissolution flux in Section 7.3.6, all 3D images are cropped at the foam-beads interface and approximately 1 cm from the lateral walls of the cube. We note that at early times, the so-called photon starvation phenomenon (Mori et al., 2013) creates imaging artefacts in the region that extends from the foam-beads interface to approximately 2 cm into the bead pack. This phenomenon is caused by the strongly attenuating aqueous KI solution, yielding an apparent increase in the CT number and, accordingly, the solute concentration. Their impact on the computation of the global mixing measures will be further evaluated in the following sections.

Figure 7.6 shows the total mass of solute as a function of time computed from the X-ray scans for all experiments. For the plotting, the computed mass has been corrected by subtracting the initial scan ($M_{t=0}$, no dissolution) and by normalising the obtained value with the mass at near-

completed mixing:

$$M_{\text{norm}}(t) = \frac{M(t) - M_{t=0}}{M_{90} - M_{t=0}} \quad (7.1)$$

where M_{90} is computed at the time when the second central moment of the concentration field attains $\sigma = 0.9\sigma_{\text{max}}$ (see Section 7.3.5). As mentioned in Section 5.3.2, artefacts are occurring mainly in the first few centimetres below the foam-beads interface and are affecting the early time values of the total mass values. The subtraction in Eq. 7.1 reduces the impact of image artefacts on the total mass values. Even though slight differences between the experimental runs of the same bead size can be observed, which likely reflect variations in the quality of the packing, we note that the 0th moment shows qualitatively a high reproducibility between the experimental runs of the same bead size. There is a clear horizontal shift between experiments carried out with different bead sizes, reflecting the impact of permeability (and hence Ra) on the rate of mixing. The numerical solution of the corresponding one-dimensional purely diffusive scenario is included for comparison (see Section 6.2 in Chapter 6). While the latter follows the expected behaviour, *i.e.* $M_{\text{norm}} \propto t^{0.5}$, the experiments show a ballistic behaviour ($M_{\text{norm}} \propto t^1$), as indicated by the trend lines fitted to the data in the advanced convective regime (additional details in the caption of Figure 7.6). The NMSE values and the 95 % confidence

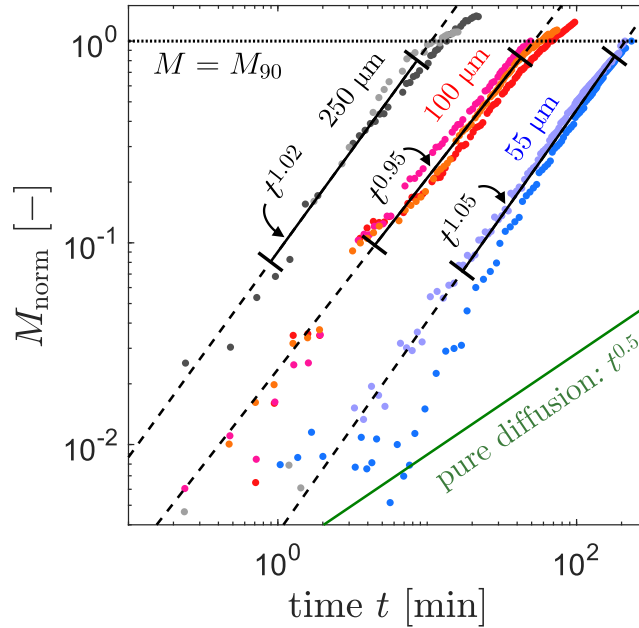


Figure 7.6: Normalised total mass M_{norm} plotted as function of time. The data is colour-coded (grey-, red- and blue-shaded symbols indicate a bead size of 250 μm , 100 μm and 55 μm , respectively). The dashed black lines are obtained upon fitting a power law function to the experimental data in the advanced convective regime (see Figure 7.9), which is indicated by the dashed turning to solid. The horizontal dotted line is the reference line for the (nearly complete) mixing state.

bounds of the three scalings are reported in Appendix D in Table D.2. A ballistic increase of the 0th moment in the advanced convective regime is evidence for a quasi-steady flux (see Figure 7.9) and gives an indication for a constant vertical fluid velocity of the downwelling plumes (see Chapter 6 and Ecke and Backhaus 2016).

7.3.4 First Moment (Centre of Mass)

Figure 7.7 shows the normalised vertical centre of mass, Y_{com}/H , plotted as a function of time. Because it represents the distance relative to the foam-beads interface, this measure provides a quantification for the effective displacement of the solute in y -direction. Again, we note a clear distinction between experiments carried out with the different bead sizes, with the largest bead size showing the fastest downward spreading. Each experiment features a similar pattern, whereby after an initial period where Y_{com}/H is largely constant, it increases following a power law behaviour up to approximately $Y_{\text{com}}/H = 0.5$. We note that the initial “incubation” period is affected by the image artefacts caused

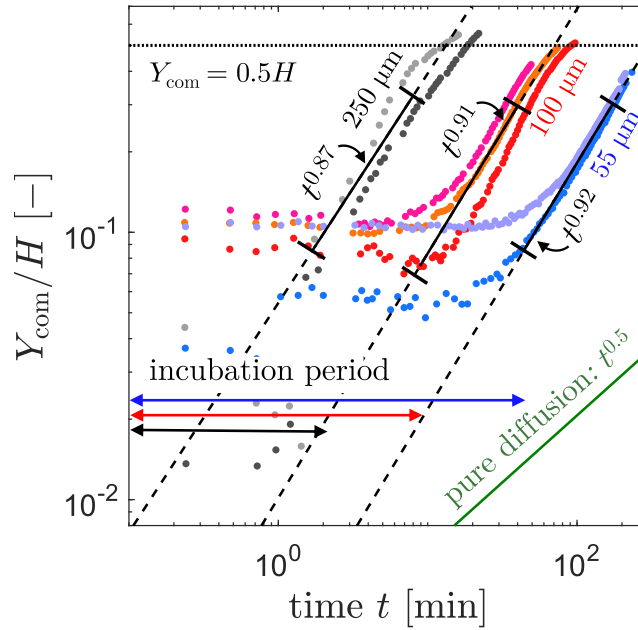


Figure 7.7: Vertical centre of mass normalised by the sample height plotted as a function of time. The data is colour-coded (grey-, red- and blue-shaded symbols indicate a bead size of 250 μm , 100 μm and 55 μm , respectively). The dashed black lines are obtained upon fitting a power law function to the experimental data in the advanced convective regime, which is indicated by the dashed line turning to solid. Due to the presence of the incubation period (time frame marked by the arrows), the scaling is obtained in the advanced convective regime between the points at which the curve is tangent to the straight line and the points that mark the start of pooling of solute at the bottom. The horizontal dotted line is the reference line that indicates the expected long-time stabilisation of the centre of mass at $Y_{\text{com}}/H = 0.5$.

by the strongly attenuating KI, as explained in the first paragraph of Section 7.3.3. This implies that a precise analysis of the initial growth of the dissolution plume cannot be carried out with this set of experiments. The data beyond this initial period indicate a power law scaling, $Y_{\text{com}}/H \propto t^{0.9}$ for each bead size, with a slight increase in the value of the exponent with decreasing bead size. This is further indicated by the solid trend lines shown in Figure 7.7. The NMSE values and the 95 % confidence bounds of the three scalings are reported in Appendix D in Table D.2.

7.3.5 Second Moment (Standard Deviation)

Figure 7.8 shows the normalised standard deviation of the solute concentration distribution around the mean in the vertical direction, σ/H , plotted as a function of time. This measure is also referred to as spreading length (see Section 3.2.4) and is expected to reach a constant value of $\sigma/H = \sqrt{1/12}$ upon attainment of a uniform concentration in the domain. Again, a clear distinction between experiments carried out with the different bead sizes is observed, with the largest bead size showing the fastest mixing. We note that the limit $\sigma/H = \sqrt{1/12}$ is not reached asymptotically from below (dotted line).

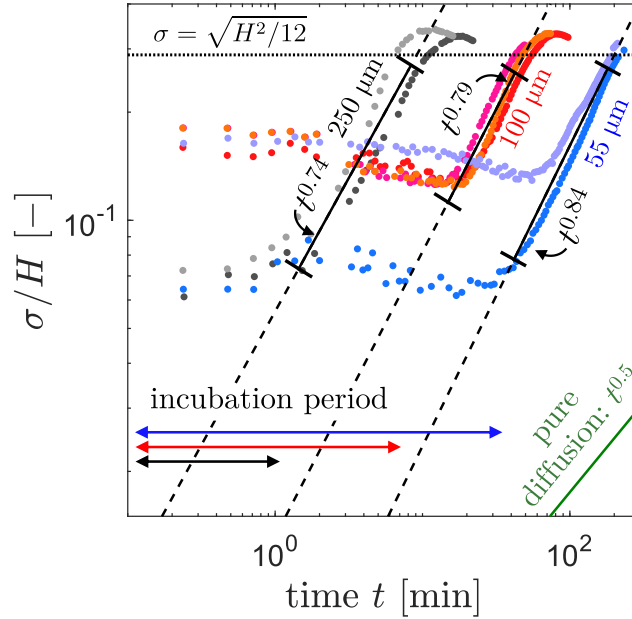


Figure 7.8: Standard deviation of the solute concentration distribution around the mean in the vertical direction normalised by the sample height plotted as a function of time. The data is colour-coded (grey-, red- and blue-shaded symbols indicate a bead size of 250 μm , 100 μm and 55 μm , respectively). The dashed black lines are obtained upon fitting a power law function to the experimental data in the advanced convective regime, which is indicated by the dashed turning to solid (for details see Figure 7.7). The horizontal dotted line is the reference line that indicates the expected long-time stabilisation of the standard deviation at $\sigma = \sqrt{H^2/12}$.

Rather, pooling at the bottom of the domain causes an overshoot of the experimental data, which will eventually converge to the expected long-time behaviour. After an initial period of unresolved behaviour (see previous section), the experimental data indicate a power law growth in the advanced convective regime, with an exponent that is smaller than one ($0.74 - 0.84$) and that increases with decreasing bead size. The NMSE values and the 95 % confidence bounds of the three scalings are reported in Appendix D in Table D.2. This is in contrast to the linear growth behaviour ($\sigma/H \propto t$) reported in previous numerical studies that do not include hydrodynamic dispersion in their applied models (see Chapter 6 and Amooie et al. 2018). The reduction in the exponent values in both the standard deviation and the centre of mass suggests that the effect of hydrodynamic dispersion on the longitudinal mixing needs to be further evaluated.

7.3.6 Convective Mass Flux

Figure 7.9 plots the dissolution flux as a function of time. After an initial phase, mainly governed by diffusive mass transport, fingers begin to form. As described in the first paragraph of Section 7.3.3 data extracted from images of this initial phase are impacted by image artefacts and the flux data in

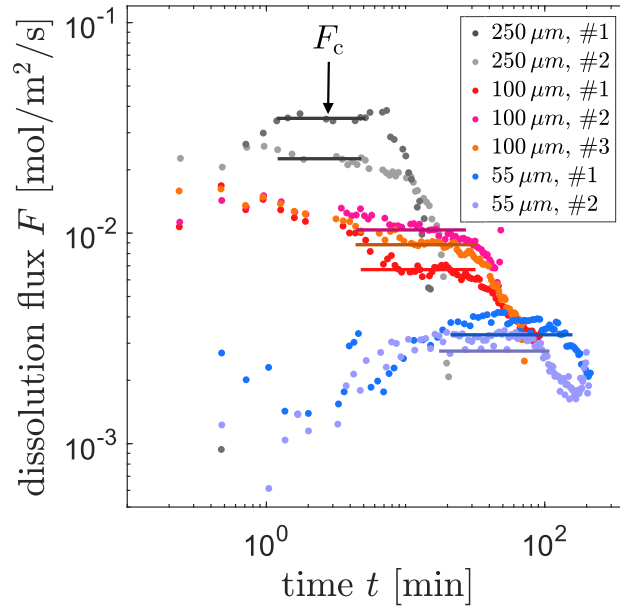


Figure 7.9: The dissolution flux $F(t)$ as function of time. The data is colour-coded (grey-, red- and blue-shaded symbols indicate a bead size of $250\ \mu\text{m}$, $100\ \mu\text{m}$ and $55\ \mu\text{m}$, respectively). Due to experimental noise (that is intensified by the time derivative in equation 3.18), the response data was smoothed with a moving average function (20-point centred). For each experiment, the period of constant dissolution flux is indicated by the colour-coded horizontal lines. These values and their uncertainties are reported in Appendix D in Table D.3.

that time period should be disregarded. Once the plumes have grown and the convective process is more advanced, a quasi-steady state is reached that is characterised by the attainment of a constant flux F_c (Amooie et al., 2018; Slim, 2014). To determine F_c we take the average of $F(t)$ from the time the flux stabilises until the fingers reach the bottom boundary. For each experiment, this time period is indicated by the horizontal solid lines in Figure 7.9. The values and the standard deviations are reported in Appendix D in Table D.3. The absolute values of F_c increase with increasing bead size. The relative standard deviation between the repeats of the same bead size is calculated to 13 % (55 μm), 20 % (100 μm) and 30 % (250 μm). The uncertainty increases due to a reduced number of data points available during the advanced convective regime with increasing bead size due to limitations in the scanning speed. Additionally, a higher Rayleigh number and therefore stronger convection and faster dissolution leads to a weaker reproducibility in the average constant flux.

A non-dimensional measure for the long-term convective mass flux is the Sherwood number, Sh . It is determined as the average mass flux normalised by the diffusive mass flux over the sample height H . We apply Eq. 3.9, using $\Delta c = c_{\text{max}}$ as the concentration difference between the liquids (pure and saturated water). In Figure 7.10 the computed values of the Sherwood number are plotted as a function of Ra for each experiment. A power law fit to the data further indicates that $Sh = aRa^b$,

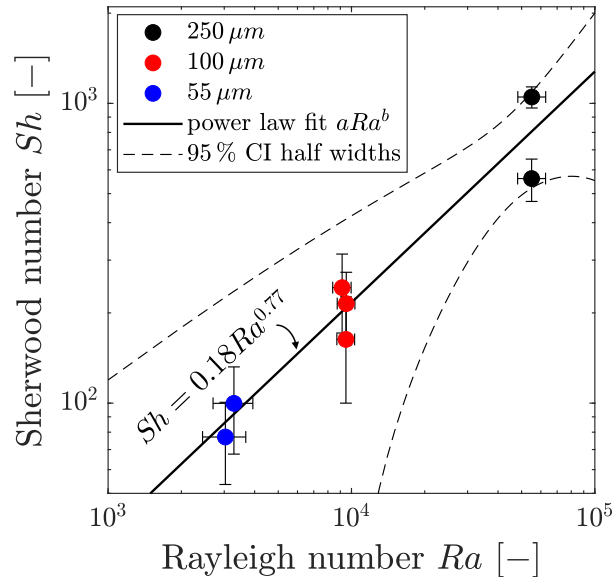


Figure 7.10: Sherwood number Sh as function of the Rayleigh number Ra . The results from the experiments are shown in colour-coded symbols. The error bars indicate three standard deviations σ from the mean, where σ is calculated based on the fluctuations around the mean dissolution flux shown in Figure 7.9. The solid black line is the power law scaling $Sh = 0.18Ra^{0.77}$ and the dashed lines are representing the 95 % CI half-widths in distance to the model predictions. The values of Sh , their uncertainties and details on the confidence intervals are reported in Appendix D in Table D.4.

with parameters $a = 0.18 [-0.94, 1.3]$ and $b = 0.77 [0.19, 1.35]$ (normalised mean square error NMSE = 0.167). All values lie inside the 95 % confidence half widths which are shown in dashed lines. The description of the precise Sh – Ra scaling (sub-linear vs. linear behaviour) is still a point of contention in the literature (Riaz and Cinar, 2014). With relevance to this work, we consider observations from three-dimensional experimental studies. In particular Teng et al. (2020), Wang et al. (2017) and Liyanage et al. (2019) indicate a power law exponent between 0.9 and 1.0, which is larger than the value reported here. However, their data were collected using fluid pairs that feature either a non-monotonic density profile (Liyanage et al., 2019; Wang et al., 2017) or a viscosity contrast (Teng et al., 2020) that might impact the scaling. Therefore, a comparison should be done with caution. In the experiments of Mojtaba et al. (2014), gaseous CO_2 and water are used as working fluids in a pressure cell. The CO_2 equilibrium concentration at the interface is constant over time and the density profile is linear, *i.e.* mimicking the conditions applied in our study. They report a power law scaling of $b = 0.79$ which matches closely our result. Despite this good match, the confidence intervals of the present work are still quite broad ($[0.19, 1.35]$) which most likely results from the uncertainties in the constant flux values discussed before and the low number of sample points. Therefore, the scaling acquired with these experiments is still too vague and more experiments are needed to provide a definitive answer to the $Sh - Ra$ scaling.

7.4 Discussion

7.4.1 Simplified Representation of the Convective Dissolution Process

We hypothesise that in the advanced regime, the density-driven convective process can be effectively described as a steady advective transport process, characterised by a constant advective transport velocity and a macroscopic dispersion coefficient (details see Section 3.4). In Figure 7.11a cross-section averaged concentration profiles are plotted as a function of the normalised distance in the domain, y/H , for the experiment with 100 μm beads. The analogous profiles obtained by solving the ADE are plotted in Figure 7.11b in terms of the normalised concentration, c/c_0 (simulation parameters are given in the figure caption) over the same time span. When the whole domain is considered in Figure 7.11, substantial differences are visible (especially near the boundaries) between experiments and ADE predictions, which are largely associated with the distinct boundary conditions and phenomenological nature of the transport process (see Section 3.4). The model uses a constant mean advective fluid velocity and boundaries that are open for flow, while in the experiments, the volume-averaged mean fluid velocity is balanced around 0 since the flow of the solute-rich downwelling plumes is opposed

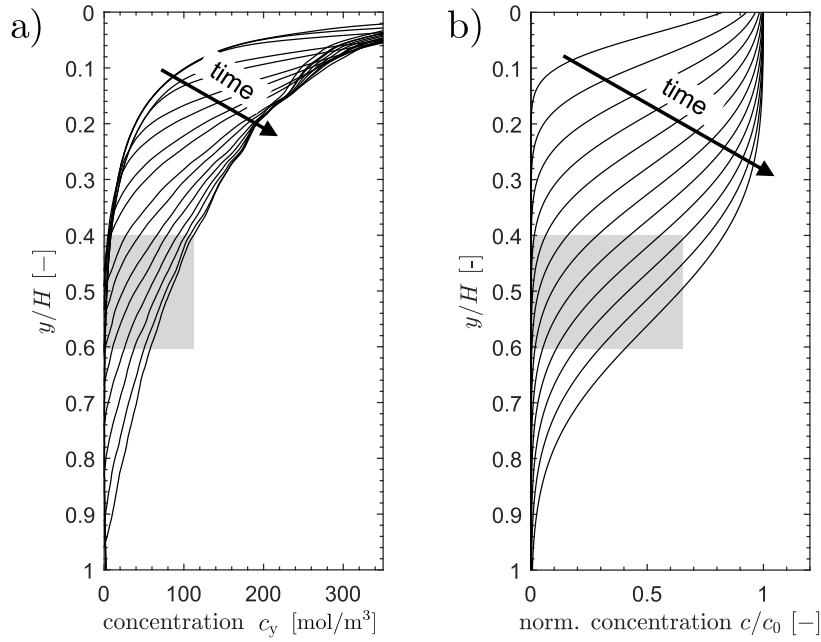


Figure 7.11: Cross-section averaged concentration profiles along the normalised length of the domain, y/H , at different times (as indicated by the arrow) over the same time span. a) Results from the experiments with 100 μm beads; grey-shaded area highlights section of $0.4 \leq y/H \leq 0.6$; b) ADE predictions shown as normalised concentration (model parameters: $\phi = 0.33$, $u_y = 7.20 \times 10^{-2} \text{ cm/min}$, $\alpha_L = 0.35 \text{ cm}$); grey-shaded area highlights section of $0.4 \leq y/H \leq 0.6$.

by the flow of the solute-lean upwelling plumes. However, in the central part of the domain (grey-shaded section of the domain $0.4 \leq y/H \leq 0.6$ in panels a and b), we observe a very similar spatial and temporal evolution of the concentration profiles in the experiments and the numerical results, indicating that it may be possible to relate the downward movement of the centre of solute mass to an effective constant transport velocity. This observation is supported by the results presented in Section 7.3.4 where the analysis of the temporal evolution of the 0th spatial moment yielded a power law exponent close to unity.

Figure 7.12a-c shows the comparison between the scalings of the spatial moments of mass predicted by the numerical solution of the ADE (solid lines) that uses values of the superficial velocity, u_y , and the dispersion coefficient, D_L , to match the profiles obtained experimentally. We observe that the ADE describes well the temporal evolution of the three spatial moments for each bead size in the advanced convective regime. This further implies that mixing (and thus dissolution) progresses at a constant rate, once the density-driven convective process has been established. While this observation was brought forward in earlier numerical studies (Gasda et al., 2011; Riaz et al., 2006), we provide here experimental confirmation of this important finding. In fact, the 0th moment follows a linear growth

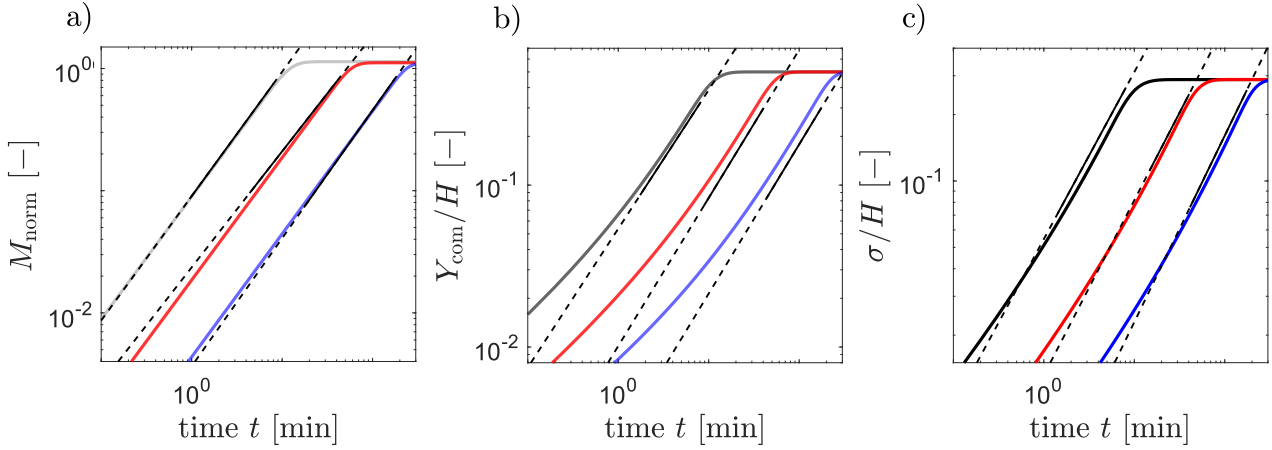


Figure 7.12: Comparison between the evolution of the scalings of the 0th, 1st and 2nd spatial moments of mass obtained from the experiments (black solid lines) and those predicted upon application of the ADE (solid coloured curves). The ADE uses a constant superficial velocity u_y and dispersion coefficient D_L (values reported in Table 7.1). The data is colour-coded (grey-, red- and blue-shaded symbols indicate a bead size of 250 μm , 100 μm and 55 μm , respectively).

($\propto t^1$) for both the experiments and the numerical predictions. For the higher moments, a power law behaviour is observed ($\propto t^b$, with $b < 1$); as reported in Table 7.1, the ADE predicts values of the associated power law exponents that are similar to those observed experimentally. We note that with increasing dispersion coefficient, the scaling exponent reduces and deviates more strongly from ballistic behaviour ($\propto t^1$). A more detailed explanation of how the scaling can vary between dispersion- or advection-dominated flow in the ADE model can be found in Figure 7.13 where different strengths of the ratio of advection to dispersion are applied. A lower ratio is expressed by a higher dispersion coefficient resulting from a more heterogeneous fluid velocity field. The 0th moment gives a ballistic trend for all three cases, while the 1st and 2nd moment show diffusion-like behaviour (t^b , $b = 0.5$) when dispersion term is dominant and ballistic ($b = 1$) when advection term is dominant. A medium-high dispersion coefficient shows first diffusion-dominated behaviour and then converges towards an advection-dominated behaviour with a power law exponent in that regime of $b > 0.5$.

The values of the transport velocity and the dispersion coefficient used in the ADE are reported in Table 7.1. We note that the values of both parameters increase with bead size, in agreement with expectations based on the scaling with Ra and results reported in the literature (Emami Meybodi and Hassanzadeh, 2011). The dimensionless dispersion coefficient, D_L/D , takes a value of 50, 300 and 2120 for the experiments carried out with 55 μm , 100 μm and 250 μm , respectively. In Table 7.1 are also reported estimates of the same parameters (u_y and D_L) by applying Eq. 3.28 and 3.29 on the analysis of the experimental spatial moments. Time-averaged quantities of u_y and D_L are calculated

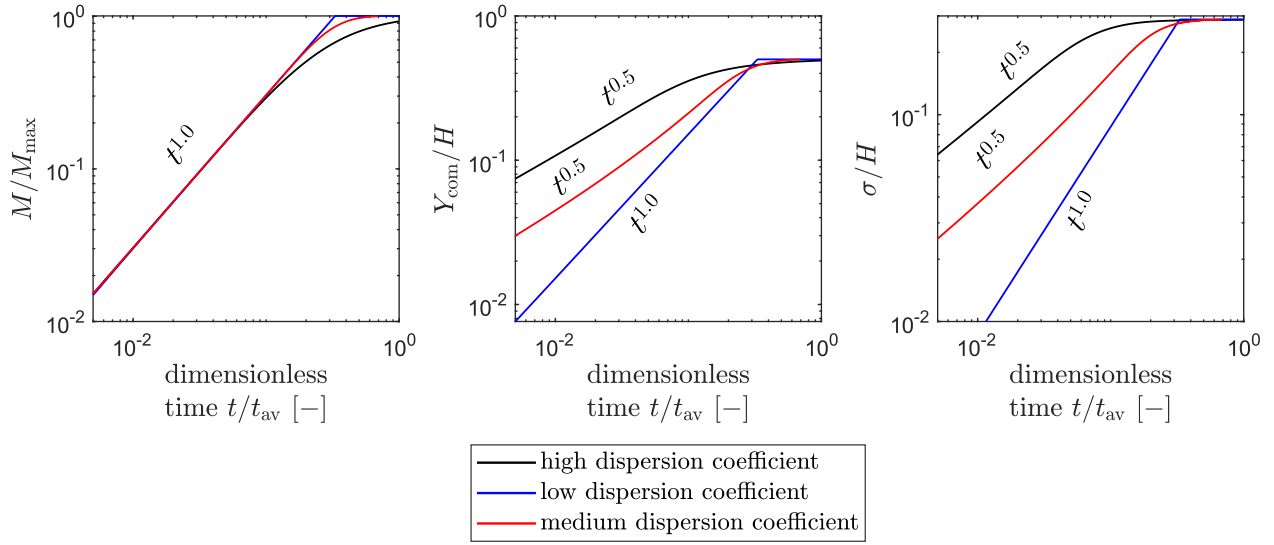


Figure 7.13: Qualitative comparison of the moments with different strength of the ratio of advection to dispersion by changing the dispersion coefficient in the ADE model (high, medium, low) and keeping the velocity constant. The time is made non-dimensional using the advective time scale $t_{av} = H/u_{av}$.

from the onset time of convection until the fingers reach the bottom boundary (start of shutdown regime). There is a very good agreement between the two sets of data (ADE analysis and spatial moments analysis) in both the trends indicated and their absolute values, supporting the proposed description of the complex three-dimensional convective transport process by the one-dimensional plume spreading in the direction of gravity. This conformity is additionally shown in Figure 7.14 where the transport velocity u_y , derived from the 1st spatial moment, is plotted together with the fitted constant ADE velocity values (solid lines). During the advanced convective time (before the shutdown starts, indicated by the shaded area), the velocity values of the experiments fluctuate around the ADE velocity values.

Values of the dispersivity α_L obtained upon applying Eq. 3.23 to results from both the ADE and spatial moments analyses are also reported in Table 7.1. The estimated dispersivities are 0.25–0.35 cm (55 μ m beads), 0.33–0.35 cm (100 μ m beads) and 0.21–0.50 cm (250 μ m beads). The values range around the same magnitude for all bead sizes. By means of comparison, we determine from Eq. 3.24 the theoretical dispersivity values $\alpha_{L,t}$ expected for a single tracer plume driven by advection and dispersion in a uniform bead pack with spherical particles. For random packs of spherical beads, σ_H is expected to decrease with increasing bead size. Based on Perkins and Johnston (1963) and the range of the bead size of our packs, we anticipate that for the experiments considered in this study, $3 \leq \sigma_H \leq 10$, yielding $1.5 d_p \leq \alpha_L \leq 5 d_p$. We note that the “effective” dispersivity associated with density-driven mixing is much larger than values associated with a unidirectional advection process

Table 7.1: Transport parameters associated with the simplified representation of the convective dissolution process in the experiments carried out with different bead sizes, d_p . $\alpha_{L,t}$ is a theoretical dispersivity for unidirectional advective transport in uniform bead packs and calculated using Eq. 3.24 with $\sigma_{H,\min} = 3$ and $\sigma_{H,\max} = 10$. u_y , D_L and α_L are the superficial transport velocity, the dispersion coefficient and the dispersivity, respectively, which have been obtained from the ADE and moment analysis of the three-dimensional experiments. $u_B = k\Delta\rho_{\max}g/\mu$ is the Darcy buoyancy velocity (see Section 7.4.2). The exponents of the power law fittings to the spatial moments of mass in the advanced convective regime are also listed. These are reported for both the experiments and ADE analysis and have been estimated by considering the exact same time period (indicated by the solid black lines in Figure 7.12). The normalised mean square error of all the scalings (experimental and ADE) are reported in Appendix D in Table D.2.

d_p [μm]		250	100	55
$\alpha_{L,t}$ [cm]	single tracer plume	0.04–0.13	0.02–0.05	0.01–0.03
u_y [cm/min]	ADE	3.30×10^{-1}	7.20×10^{-2}	1.80×10^{-2}
D_L [cm^2/min]		0.516	0.076	0.013
D_L/D [–]		2120	300	50
α_L [cm]		0.50	0.35	0.25
u_y [cm/min]	moment analysis	4.90×10^{-1}	6.39×10^{-2}	1.66×10^{-2}
D_L [cm^2/min]		0.317	0.065	0.017
D_L/D [–]		1303	251	64
α_L [cm]		0.21	0.33	0.35
u_B [cm/min]	buoyancy velocity	1.04×10^0	1.88×10^{-1}	6.40×10^{-2}
power law exponents (t^b):				
total mass M_{norm}	experimental	1.02	0.96	1.05
	ADE	1.00	1.00	1.00
centre of mass Y_{com}/H	experimental	0.86	0.91	0.92
	ADE	0.85	0.89	0.92
standard deviation σ/H	experimental	0.74	0.79	0.84
	ADE	0.75	0.80	0.84

(see Table 7.1). The ratio $\alpha_L/\alpha_{L,t}$ takes a value of approximately 5 (250 μm beads), 10 (100 μm beads) and 20 (55 μm beads) as a result of the characteristic finger pattern in density-driven convection. In other words, the length scale at which significant hydrodynamic dispersion takes place in the main direction of transport is highly extended (from mm to cm scale) when convective mixing plays a role, causing an increase in the plume dispersion length and enhanced blurring of concentration gradients. This effect appears to be stronger for smaller beads.

7.4.2 Transfer of Findings to a Practical Example

Limited techniques are available for predicting the spreading and mixing of CO_2 in brine and thus assessing the long-term potential of solubility trapping of potential reservoirs remains difficult (Szul-

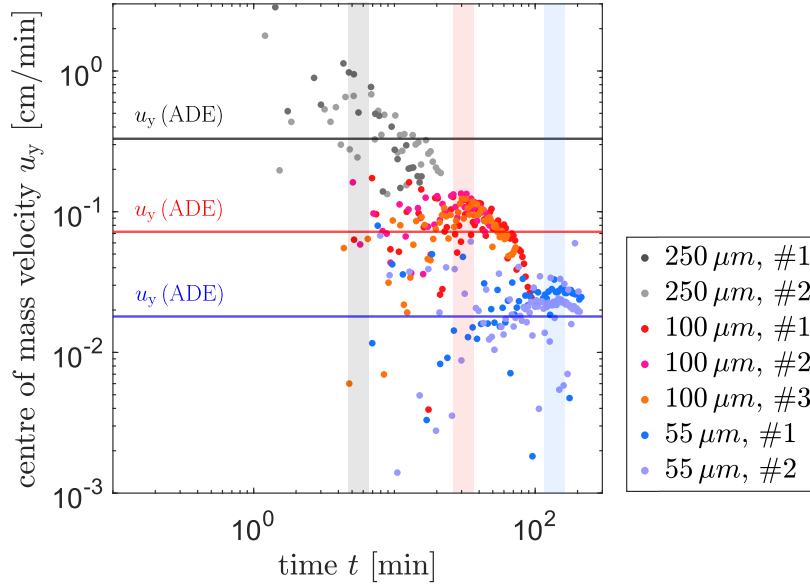


Figure 7.14: Comparison of transport velocity (calculated from centre of mass, $u_y = dY_{\text{com}}/dt$) and the fitted ADE velocity (solid lines). The data is colour-coded (grey-, red- and blue-shaded symbols indicate a bead size of $250\ \mu\text{m}$, $100\ \mu\text{m}$ and $55\ \mu\text{m}$, respectively). The vertical shaded areas represent the start of the shutdown regime and data after that time can be ignored.

czewski et al., 2013). As a practical example, we consider the Utsira Sand reservoir at Sleipner in the North Sea, the world's first commercial-scale CCS project (Falcon-Suarez et al., 2018). The reservoir has high permeability and consists of largely unconsolidated fine-grained sand with medium and occasional coarse grains (Chadwick et al., 2004). We assume a uniform grain-size distribution of fine spherical sand grains for this example calculation. We presume the dissolution of CO_2 sustains density-driven convection in the resident brine because the Rayleigh number is sufficiently large ($Ra = 6 \times 10^5$, details and parameter values can be found in Hewitt et al. 2013). In Figure 7.15, we have plotted values of the Darcy buoyancy velocity $u_B = k\Delta\rho_{\text{max}}g/\mu$ for the glass beads experiments as a function of the ADE velocity (see Table 7.1). We find a linear relationship between these two velocities, whereby the values of the Darcy buoyancy velocity are higher than the ADE velocity values. We use this relationship to extrapolate an advective velocity $u_y = 3.1 \times 10^{-3}\ \text{cm/min}$ for the Utsira sand reservoir using the Darcy buoyancy velocity $u_B = 8.8 \times 10^{-3}\ \text{cm/min}$. Based on the comparison described in Section 7.4.1, the ADE velocity reflects the displacement of the centre of mass. It allows us to roughly estimate that the centre of mass travels around 30 m deep in 2 years. This is in strong contrast to a purely diffusive transport where the time needed to reach the same dislocation of the centre of mass extends by four orders of magnitude.

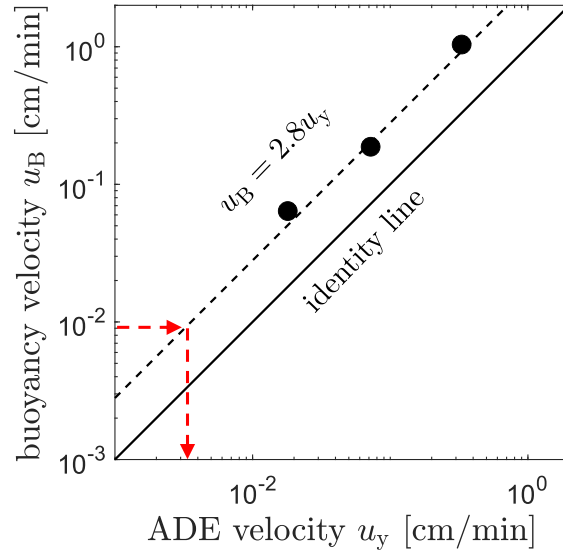


Figure 7.15: Darcy buoyancy velocity plotted versus the ADE velocity (filled dots). The dashed line is a linear trend line and the red arrows mark the Utsira sand case study velocities.

7.5 Concluding Remarks

We have presented in high spatial and high temporal resolution an experimental study of density-driven natural convection process in uniform and unconsolidated glass bead packs over a range of Rayleigh numbers. Potassium iodide and water were used as fluid pairs with the intent of monitoring the downwelling solute-rich plumes in three dimensions by X-ray Computed Tomography. The experimental set-up allows for maintaining a constant concentration boundary condition in a three-dimensional porous medium, which constitutes a useful comparison relative to current approaches presented in the literature. We determined three convective regimes in the finger growth process, namely the early convective regime, the advanced convective regime and the shutdown regime. Solute transport in direction of flow was systematically analysed by characterising the spatial moments of the concentration distribution in the advanced convective regime. The main points, from the discussion above, are as follows:

- The estimated onset times of convection closely follow the predicted trend of $\propto Ra^{-2}$.
- The Sherwood number was computed by using the constant flux in the advanced convective regime and a sublinear scaling of $Sh = 0.18Ra^{0.77}$ was found.
- The 0th moment follows a ballistic power law behaviour, independent of the bead size, while a slight reduction of the power law exponents of the 1st and 2nd moment with increasing bead size suggests an impact of hydrodynamic dispersion on the longitudinal mixing.

- Mean advective velocities and mean dispersion coefficients for each bead size were extracted by comparing the experimental results with a theoretical one-dimensional advective solute transport model.
- A comparison of the dispersivities with the values expected for a single plume driven by advection and dispersion shows an enhancement of the longitudinal plume dispersion length by one order of magnitude, suggesting that the presence of the finger pattern significantly impacts the longitudinal dissolution of solute.

Despite the chaotic nature of the convective flow and the interaction of several transport processes, we were able to derive scaling relationships to describe the (longitudinal) mixing dynamics in the advanced convective regime. Even though results are based on several comparisons and assumptions, the present study provides estimates of the enhanced dispersion caused by finger-like structures and, therefore, new insights into the fundamental understanding and predictive capabilities of CO₂ sequestration. In realistic geologic porous media, dispersion is enhanced through heterogeneities in microstructural parameters such as grain size, porosity or permeability. To understand the role of heterogeneities on the dissolution and distribution of the CO₂, three-dimensional dissolution experiments in consolidated rocks are needed.

Chapter 8

Convective Dissolution in Consolidated Natural Rocks

This chapter presents the results of the novel experimental approach to investigate the evolution of the convective mixing process in 3D porous media using X-ray Computed Tomography. The experiments are performed with various consolidated natural rock samples. First, the motivation to conduct experiments in geologic material is discussed. The result section commences with an evaluation of the three-dimensional dissolution patterns and their systematic analysis by applying the spatial moments of the vertical concentration distribution and the dilution index. This is followed by the estimation of transport parameters including the hydrodynamic dispersion coefficient, the transport velocity and the Péclet number.

8.1 Introduction

The study of solute transport processes associated with fluid flow and transport in geological and heterogeneous porous media (*e.g.*, rocks, sediments, soils) has become increasingly important for a wide range of environmental and industrial applications such as subsurface contaminant remediation (Kitanidis et al., 2012; Rolle et al., 2009), nuclear waste disposal (Corkhill et al., 2013; Medved' and Černý, 2019), enhanced oil recovery (Karadimitriou et al., 2017; Vishnudas and Chaudhuri, 2017) and geological CO₂ sequestration (Haszeldine, 2009; Metz et al., 2005; Orr, 2009; Ringrose et al., 2021) which is the main interest of this work. As discussed in Section 2.1, depleted oil and gas reservoirs or coal seams are suitable for CO₂ injection, but the largest storage potential is identified for saline aquifers in terms of storage capacity and their distribution around the globe (Bachu, 2003; Celia, 2017; Firoozabadi and Myint, 2010; Szulczewski et al., 2012). Saline aquifer formations are mainly

composed of permeable sedimentary rocks such as sandstone or carbonate rocks. As in all natural geological formations, heterogeneities at all length scales (pore-, grain-, core-, field-scale) are expected to affect key petrophysical properties such as the local porosity and permeability. The latter can vary by up to several orders of magnitudes between rock types (Jensen and Lake, 1988).

In the preceding chapters of this thesis and in the vast majority of theoretical and experimental work in the literature, idealised porous systems are applied to examine the enhanced CO₂ mass transport. It was observed that the strength of the convective mixing is directly proportional to the permeability. The few available studies on convective mixing in more realistic, heterogeneous structures (mainly theoretical, see Section 2.4) show that (permeability) heterogeneities can significantly influence the onset of convection, the dissolution rate, and the characteristic behaviour of convective mixing (Emami-Meybodi et al., 2015). Only very few experimental analyses available in the literature include porous media heterogeneities. Aggelopoulos and Tsakiroglou (2012) studied in a pressure column the effect of micro-heterogeneity in sand packs on the CO₂ dissolution rate. The micro-heterogeneity was realised by a broad sand grain size distribution that creates spatial variations of permeability. They reported that the dissolution rate accelerates with the extent of the micro-heterogeneity. Wang et al. (2021a) investigated the convective process in heterogeneous porous media while using synthetic structures made of packed glass beads. The mixing process in these more complex situations, characterised by structural heterogeneity, generates complex concentration distributions of the solute and local variations in pore-scale velocities resulting in mechanical dispersion (Emami-Meybodi et al., 2015). Despite it being a fundamental component of convective mixing, the role of hydrodynamic dispersion is only rarely discussed in experimental studies (Chevalier et al., 2015; Dejam and Hassanzadeh, 2022; Jiménez-Martínez et al., 2015; Liang et al., 2018; Ren et al., 2022).

Addressing important limitations of past experimental studies, we study the impact of heterogeneities in consolidated porous media (*i.e.*, natural rocks) on convective mixing. In this chapter, we present the results of an experimental study and the novel aspects of the experimental approach are briefly summarised in the following:

- To the author’s best knowledge, experimental evidence for three-dimensional convective dissolution in natural consolidated media is still lacking in the literature despite the importance of the fundamental understanding and predictive capabilities of geological CO₂ sequestration. To prove the occurrence and to understand the role of heterogeneities on the dissolution and solute distribution, experiments in heterogeneous natural materials (*i.e.*, in four different rock types) are performed. The rocks are selected to represent more homogeneous structures (two sandstones) and structures with heterogeneities (two carbonates).

- As mentioned in Section 2.3, only very few experimental studies apply three-dimensional imaging (*e.g.*, MRI) to enable to spatial and temporal monitoring of the fluid (or solute) distribution. In this study, direct observation of convective dissolution is achieved by taking three-dimensional images with high temporal and spatial resolution using X-ray CT scanning.
- An aqueous KI-solution is applied to create an approximately constant concentration that approximates the dissolution of CO₂ from the supercritical plume above the domain. KI is partially miscible in water and the densities of both, the aqueous solution of KI and the CO₂-water system, increase monotonically and approximately linearly with the solute mass fraction, therefore, representing the same dynamics of the partially miscible CO₂-water system.
- The effect of hydrodynamic dispersion on the longitudinal mixing and spreading is systemically analysed and compared between the different porous media applied.

We produce three-dimensional imagery of the solute concentration field in the rocks at a spatial resolution of a few millimetres. This key advantage allows us to monitor and compare the temporal evolution of individual plume structures between the different rock types. We compute the temporal evolution of the spatial moments of the solute concentration distribution and the dilution index throughout various stages of the experiments. We further estimate transport characteristics including the hydrodynamic dispersion coefficient, the transport velocity and the Péclet number. Based on our experimental findings, we propose a comparison of the mixing and spreading effectiveness between the rocks and homogeneous bead packs and discuss possible implications of heterogeneities and their length scales on the large-scale CO₂ storage. The findings will provide more representative information towards the concomitant action of diffusion, convection and hydrodynamic dispersion on convective mixing in the context of subsurface CO₂ storage.

8.2 Applied Methods and Noise Analysis

We use the experimental routine for sample preparation and experimental procedure described in Chapter 5. Namely, two sandstones and two carbonates are used as porous media (Section 4.2). The *in-situ* characterisation of their spatial properties at various spatial scales is given in Chapter 4. Downwelling solute-rich plumes are imaged, reconstructed and analysed in three dimensions using the medical CT scanner and the tools described in Section 5.3. The image noise observed in this study is likely to be caused by a combination of photon starvation (Mori et al., 2013) and quantum mottle (*i.e.*, random imaging noise). The uncertainty of the CT number caused by quantum mottle

was estimated using scans of the saturated rocks taken prior to the start of the experiment and calculated to $\sigma_{\Delta_{CT}} = 18$ HU (Bentheimer), $\sigma_{\Delta_{CT}} = 19$ HU (Boise), $\sigma_{\Delta_{CT}} = 16$ HU (Mt Gambier) and $\sigma_{\Delta_{CT}} = 16$ HU (Ketton). Using statistical methods of error propagation (Chapter 5), the uncertainty of the computed mass fraction of solute is estimated to be between $\sigma_{w_i=0} = 0.01$ (pure water) and $\sigma_{w_i=0.6} = 0.09$ (maximum saturation). Accordingly, the uncertainty in the computed concentration of solute (Eq. 5.3) is estimated to be $\sigma_{c_i} = 46$ mol/m³ (pure water) and $\sigma_{c_i} = 1\,421$ mol/m³ (saturated solution, $c_{\max} = 6\,198$ mol/m³). The presented uncertainty values are calculated for Bentheimer but the values of the other rocks are very similar or smaller. The procedures for the uncertainty estimations are described in Appendix B.

We note that at early times, the photon starvation phenomenon creates imaging artefacts in the region that extends from the foam-rock interface to approximately 1 cm into the sample yielding an apparent increase in the solute concentration. As already discussed in Chapter 7, a precise analysis of the initial growth of the dissolution plume cannot be carried out with this set of experiments and the dissolution in the early convective regime is evaluated qualitatively. The length of the high-artefact region is, relative to the sample height, higher in this study compared to the experiments with glass beads (bead pack volume approximately 6 times larger). Therefore, the impact of that region on quantities, such as the first spatial moment or the centre of mass, is stronger. To avoid including the highly impacted region and to additionally reduce potential wall effects in the computation of global quantities in Section 8.3 and Section 8.4, we use the bulk part of the sample volume for the analysis of global quantities. The 3D volume is cropped 13 mm from the foam-rock interface and roughly 15 mm from the outer boundary of the sample. Solely for the zeroth moment, cropping at the top is not necessary as the apparent increase in the solute concentration due to artefacts is cancelled by a subtraction operation (details see Section 7.3.3).

8.3 Results on Convective Dissolution in Natural Rocks

8.3.1 Three-Dimensional Dissolution Pattern

We use the open-source application ParaView to create 3D visualisations that provide qualitative insights into the morphology of the observed dissolution patterns. Snapshots at various times that are representative of the three main convective regimes (early convection, advanced convection, start of shutdown) are shown in Figure 8.1. Snapshots of horizontal layers at the same times are given in Figure 8.2 (close to the rock-foam interface and the mid-section of the sample). The images in the middle panel (advanced convection) in Figure 8.1 and Figure 8.2 show the dissolution pattern at the

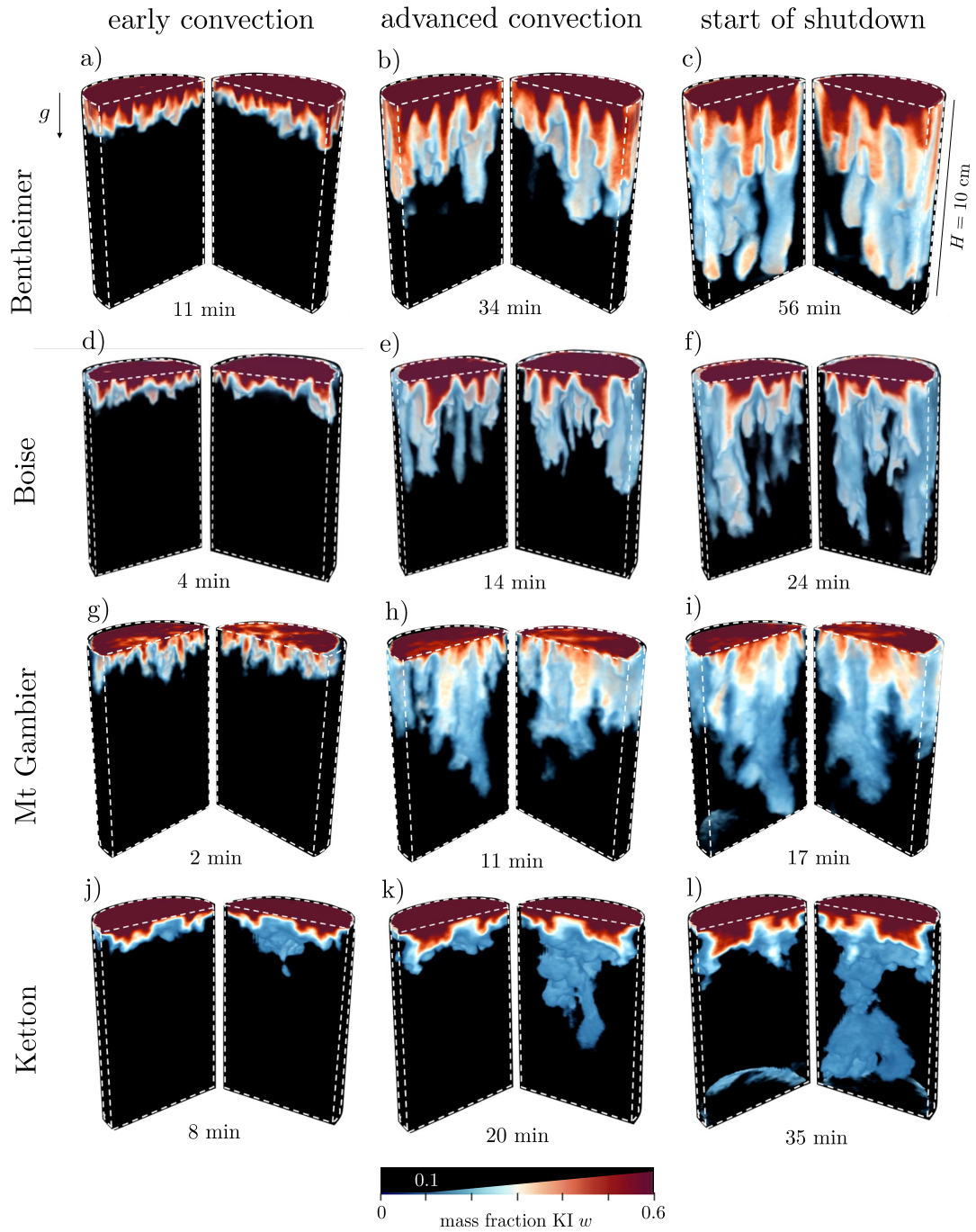


Figure 8.1: Snapshots of the dissolution process at times that represent the three main regimes (early convection, advanced convection, start of shutdown). The 3D reconstruction is cut vertically in two halves to allow the view inside. Pure and very low concentrated water ($w < 0.1$) is made transparent (background is black) and the intensity of the colour bar is gradually increasing between $0.1 < w < 0.6$. Voxels containing solution of mass fractions higher than $w = 0.6$, caused by the photo starvation phenomenon, are coloured with the same colour as $w = 0.6$.

time when the first plumes enter $Y = H/2$ while the panel on the right at the time when the first plumes reach $Y = H$ (start of shutdown). Additionally, the evolution of a discrete solute plume for each rock is given in Figure 8.3.

The plumes forming at the interface in Bentheimer sandstone are column-like shaped, with a round

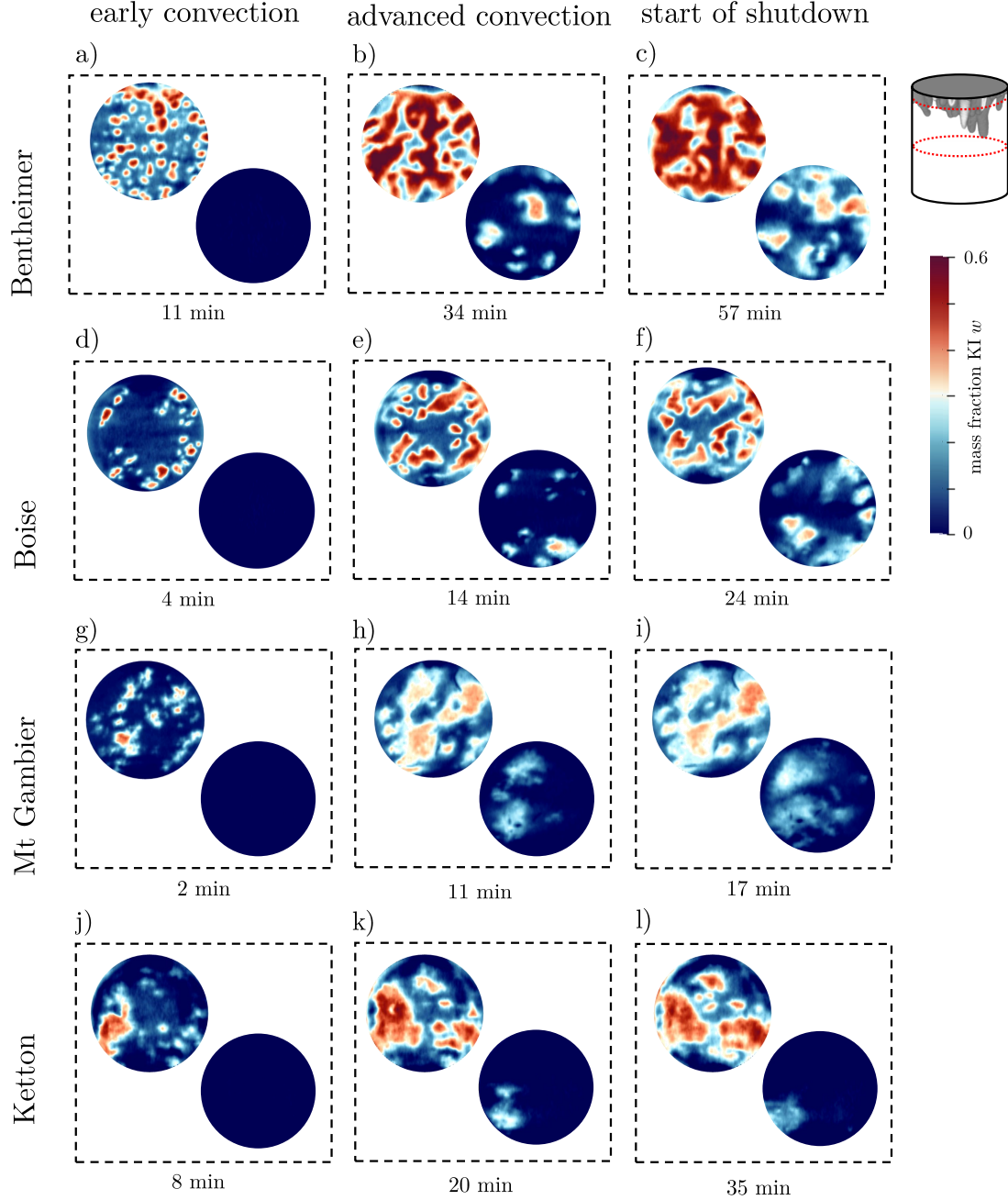


Figure 8.2: Snapshots of the dissolution process at times that represent the three main regimes (early convection, advanced convection, start of shutdown). Shown are 2D slices of the 3D reconstructions, 50 voxels ($Y \approx H - 14$ mm) from the rock-foam interface (top left in each panel) and 2D slices from the centre ($Y = H/2$). In comparison to Figure 8.1, the surrounding pure water is not made transparent.

cross-section and are evenly distributed among the cross-section of the sample (Figure 8.2, top left image in a). The individual fingers are highly concentrated with solute (Figure 8.3a) and clearly separated from the surrounding pure water by a sharp concentration gradient which appears like a “white contour” in the horizontal 2D images (Figure 8.2, top left image in a). As the plumes elongate downwards, the merging of (3 or more) fingers to form larger columnar plumes results in lateral growth. Figure 8.2b and c show the resulting complex maze-like pattern after merging, with only a few individual round plumes left ($Y = H/2$, bottom right images) which is in contrast to the high number of small fingers entering the plane near the interface (top left image in a). The plume diameter increased to complex structures but the inside of the elongated plumes (plume body and plume tip) is still at a high mass fraction (around $0.4 < w < 0.5$) and the contours relatively sharp despite the distance travelled by the plumes (Figure 8.2b and c and Figure 8.3a). At the start of the shutdown (when the first plumes reach the bottom boundary), a connected network of highly concentrated fluid has been created, covering most of the sample cross-section (Figure 8.2 c).

Figure 8.1d–f show the evolution of the plume pattern in Boise sandstone. Small fingers emerge at the interface in the early convective regime, showing similarities to Bentheimer sandstone but with

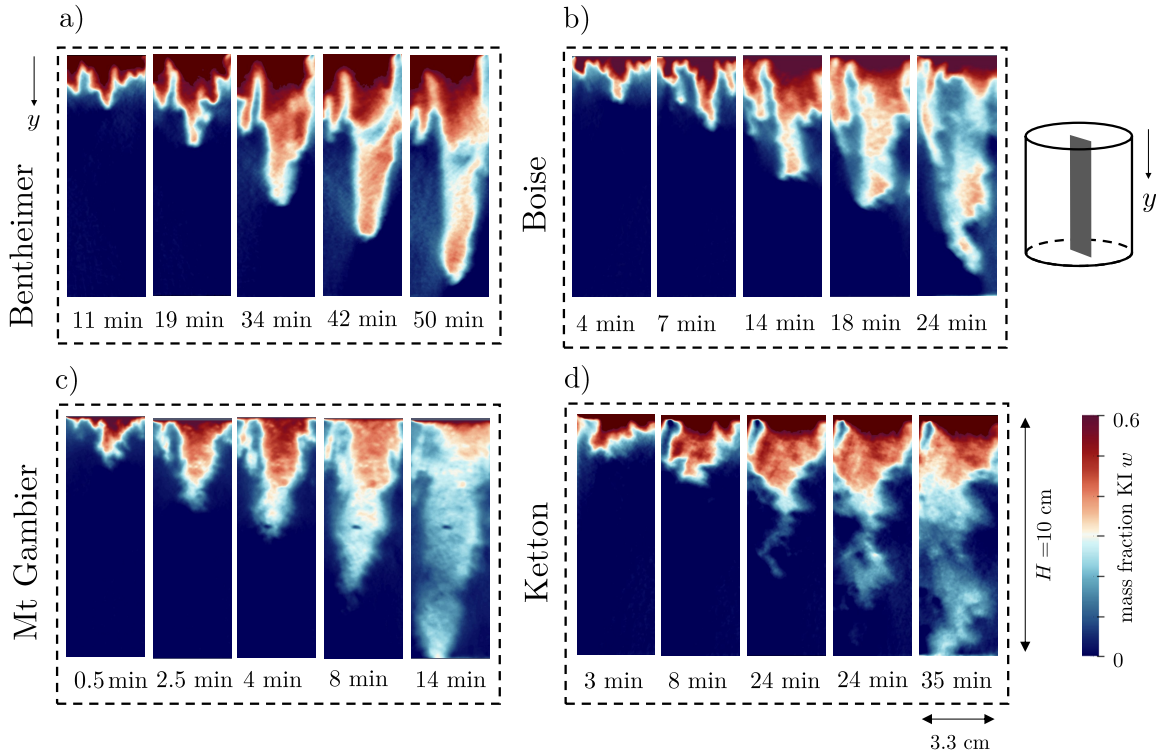


Figure 8.3: Evolution of discrete solute plumes over time. The panels show two-dimensional sections taken from the 3D reconstructions. In comparison to Figure 8.1, the surrounding pure water is not made transparent.

a reduced number of fingers. Merging is observed in the advanced convection regime in Figure 8.1e. Comparing Figure 8.2b (Bentheimer) and e (Boise), we observe that the network developed in Boise is less connected as compared to Bentheimer sandstone. Similar to Bentheimer, even after some elongation the plume bodies remain rather highly concentrated (Figure 8.3b). Only in the last few centimetres from the bottom boundary do the plumes reduce in concentration.

The morphology of the dissolution pattern in Mt Gambier is in strong contrast to the sandstones. The dissolution structures forming out of the initial instability appear frayed out without a clear contour (Figure 8.1g–i, Figure 8.2g–i). Instead of a columnar-plume pattern, the solute travels in two to three large clouds. Merging is evidenced at the early convective regime but lateral expansion is strongly influenced by the cloud branching off and diluting of concentration gradients. Figure 8.3c gives evidence of the reduction of the mass fraction inside the cloud, in contrast to the highly concentrated sandstone plumes (Figure 8.3a and b). Further, it is not possible to make out contours and to distinguish individual plume bodies at the start of shutdown (Figure 8.2i).

Figure 8.1j–l shows the evolution of the plume pattern in Ketton carbonate. While the majority of the plumes that emerge out of the gravitational instability at the interface slowly elongate (image j), one single plume quickly migrates downwards, spreads out laterally and eventually reaches the bottom of the sample (image k–l). This specific plume, being very dispersed and low in concentration (see bottom right image in Figure 8.2k and l), resembles the cloudy plumes observed in Mt Gambier. The porous structure of Ketton limestone is composed of round and uniformly sized grains and one would expect a similar pattern morphology as in the sandstones. However, Section 4.9 describes the core-scale heterogeneities that are apparent in the Ketton samples and span over the whole sample width and height. We expect that a single plume, formed near the interface, reaches and extends into a macroscopic heterogeneity (*e.g.*, a fracture or channel). Due to the local permeability, which is (much) higher than the mean permeability of the surrounding host rock, the solute quickly travels along this preferred path. The remaining plumes grow way slower into more homogeneous parts of the rock sample. This behaviour has also been reported in Kim (2014). They found in a numerical study that fractures serve as conduits for both CO₂-rich plume and CO₂-free water during density-driven convection. Figure 8.1l shows how the cloud reaches the sample bottom and how accumulation at the bottom starts while the remaining plume did not extend further than a few centimetres inside the rock material. By comparing the cross-sections (Figure 8.2j–l), we note that the mass fraction inside the plumes of Ketton limestone is high but immediately reduces as the cloud migrates downwards reaching a similar mass fraction as in Mt Gambier. We conclude that the plumes appear compact and high in concentration in homogeneous parts of the rocks. In contrast, the solute-rich fluid bypasses

through the most permeable path (*i.e.*, macroscopic heterogeneities), implying that the dissolution pattern is individual for each sample (of that length scale) used in this study.

8.3.2 Spatial Moments of Mass and Time Normalisation

Although the images presented in Section 8.3.1 provide qualitative insights into the morphology and structure of the dissolution patterns, other methods are needed to provide more quantitative details on the solute transport arising from the dissolution. Following the approach presented in the preceding chapter, a spatial moment analysis is applied to estimate the distribution of solute in the main direction of flow (y -direction) by using average statistical properties of solute distribution at each horizontal location. Time scalings of the moments in the convective regime are performed in the same way as in Chapter 7. The time period starts when the 2nd spatial moment starts to increase which is approximately the time when solute enters the bulk volume. It ends with the time when the 2nd moment attains $\sigma = 0.9\sigma_{\max}$ which is approximately the time when the solute reaches the bottom of the sample. Since the two Ketton samples (A) used for the dissolution experiments have very different macroscopic heterogeneity maps (see Section 4.9), a comparison of the spatial moments or other global measures between the two experimental repetitions is too ambitious. However, we included the results in some of the graphs as they give interesting insights but are not further discussed in detail.

The spatial moments are plotted versus the absolute time and versus the normalised time by dividing it by the buoyancy time t_B . We calculate t_B using the buoyancy velocity scale $u_B = \Delta\rho_{\max}gk/\mu$ (Emami-Meybodi et al., 2015; Hewitt et al., 2014):

$$t_B = \frac{H}{u_B} = \frac{H\mu}{k\Delta\rho_{\max}g} \quad (8.1)$$

where H is the height of the rock sample in the main direction of transport. The approach to use t_B in the normalisation is to evaluate the time scale in relation to its “limit” which is determined by the maximal buoyancy force. The latter is related to a sinking fluid parcel which is defined by maximum and constant properties ($\Delta\rho_{\max}$, μ), in a porous system with size H and permeability k . Within Eq. 8.1, transport is controlled solely by convection and other mechanisms, such as dispersion or diffusion, are not included. We test the normalisation using the results of the first moment of the homogeneous and uniform glass bead packs. Figure 8.4 shows the normalised first moment versus the normalised time. The curves are very close together but show a slight horizontal shift between the trendlines. This could be a result of a small discrepancy between the calculated (see Section 4.5) and the real permeability values of the bead packs, *e.g.* arising from packing inconsistencies.

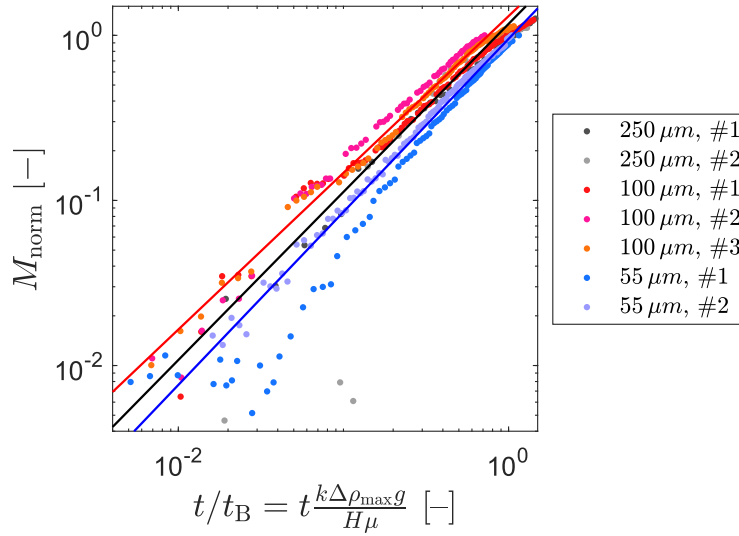


Figure 8.4: Normalised total mass M_{norm} of the bead packs experiments plotted as a function of the normalised time t/t_B . The solid lines are obtained upon fitting a power law function to the experimental data in the convective regime (as performed in Section 7.3).

8.3.3 Zeroth Moment (Total Mass)

The 0th moment of mass is shown in Figure 8.5. The computed mass has been corrected to $M_{\text{norm}}(t)$ by subtracting the initial scan (no dissolution) and by normalising the obtained value with the mass at near-completed mixing using Eq. 7.1. In Figure 8.5a $M_{\text{norm}}(t)$ is plotted versus the absolute time. The data of the 0th moment shows qualitatively a high reproducibility between the experimental runs of the same rock type. We note that the curves shift from left (smaller times) to right (larger times) following the sorting of the rock according to their permeability values (Ketton limestone ignored). Also included in the graph is the data fit of a glass bead experiment (55 μm bead size, dash-dotted line in Figure 8.5). The Rayleigh number of this bead packing is estimated to $Ra = 3052$ and the increase in dissolved mass is, as expected due to the low Rayleigh number, much slower (curve located to the right of the rocks in the plots). We fit power law trend lines ($M_{\text{norm}} = at^b$) to the data and the power law exponents b are reported in Table 8.1 and the coefficients a and the 95 % confidence intervals in Appendix E in Table E.1. The data of the sandstones and the glass bead pack show a ballistic ($b \approx 1$) power law behaviour. On the contrary, the 0th moment of Mt Gambier shows a reduced exponent of $b = 0.81$ (with 95 % confidence intervals $[0.78, 0.84]$). M_{norm} is shown against the normalised time t/t_B in Figure 8.5b. The curves of the sandstones are shifted a bit horizontally while the one of Mt Gambier and of the 55 μm bead pack are located much more to the right. Those horizontal shifts are larger than the ones observed between the normalised bead pack data in Figure 8.4 and most likely

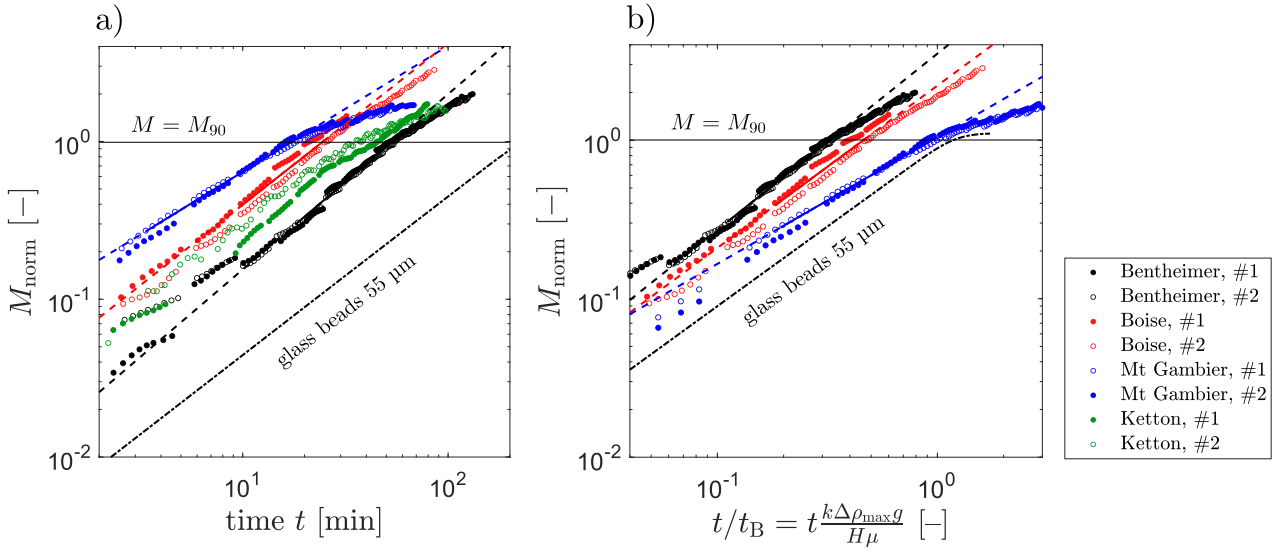


Figure 8.5: Normalised total mass M_{norm} plotted as function of time t (a) and normalised time t/t_B (b). The solid lines are obtained upon fitting a power law function to the experimental data in the convective regime, after and before this time the line turns dashed. No trendline is obtained for Ketton limestone and the moment results have been omitted in (b) due to a lack of confidence in the data. The trendline obtained from the experiments with glass beads (55 μm bead size) is additionally included as a dash-dotted line. The horizontal solid reference line indicates the (nearly complete) mixing state $M = M_{90}$.

arise from the value of the density difference in the calculation of the buoyancy time t_B which is taken to be the maximum ($\Delta\rho_{\text{max}} = 721 \text{ kg/m}^3$). Strictly speaking, this is only valid for fluid with maximum loading ($w = 0.6$) surrounded by pure fluid ($w = 0$) and only applies to dense fluid packs such as dense dissolution plumes. If the plumes rapidly lose concentration as they travel through the sample (and thus density), it ultimately leads to a reduced buoyancy force with distance and time. As discussed in Section 8.3.1, the fluid inside the plumes of Bentheimer is, even after some travel distance, still high in concentration. Also, the pattern in Boise shows high concentrations but slightly less than in Bentheimer. On the contrary, the plumes in Mt Gambier (and also in the bead packs, see Figure 7.2) quickly dilute which leads to an overestimation of the buoyancy velocity, an underestimation of t_B

Table 8.1: Exponents b of the power law fittings ($M_{\text{norm}} = at^b$) determined in the advanced convective regime for the moments of mass (the 95 % confidence bounds for the fitted exponents are given in Appendix E in Table E.1).

	Bentheimer	Boise	Mt Gambier	Glass beads (55 μm)
Zeroth moment	1.11	1.02	0.81	1.05
First moment	0.86	1.03	0.63	0.92
Second moment	1.34	1.21	0.89	0.84

and to the horizontal shift in Figure 8.4. We aim to estimate an “effective” density difference by forcing the trendlines to overlay the one located leftmost which is the porous media with the most concentrated pattern (Bentheimer sandstone). Shifting the trendline of Boise and the 55 μm beads to match the trendline of Bentheimer results in a broad estimate of an “effective” density difference of around 540 kg/m^3 (refers to $1.3 t_B$) and 230 kg/m^3 (refers to $3.1 t_B$) respectively. The approach is only applicable on curves of very similar behaviour (here a ballistic behaviour of beads and sandstones) while Mt Gambier carbonate shows a sub-linear power law exponent of the first moment. An attempt to match the results with the sandstones would be erroneous but it is the first indication that the longitudinal mass transport in Mt Gambier is successively slowed down. This is discussed further in the following sections.

8.3.4 First Moment (Centre of Mass)

Figure 8.6a shows the normalised vertical centre of mass, Y_{com}/H , plotted as a function of time, providing a quantification for the effective displacement of the solute in y -direction. For the computation, the 3D data is cropped as explained in Section 8.2. The data of the repeated experiments

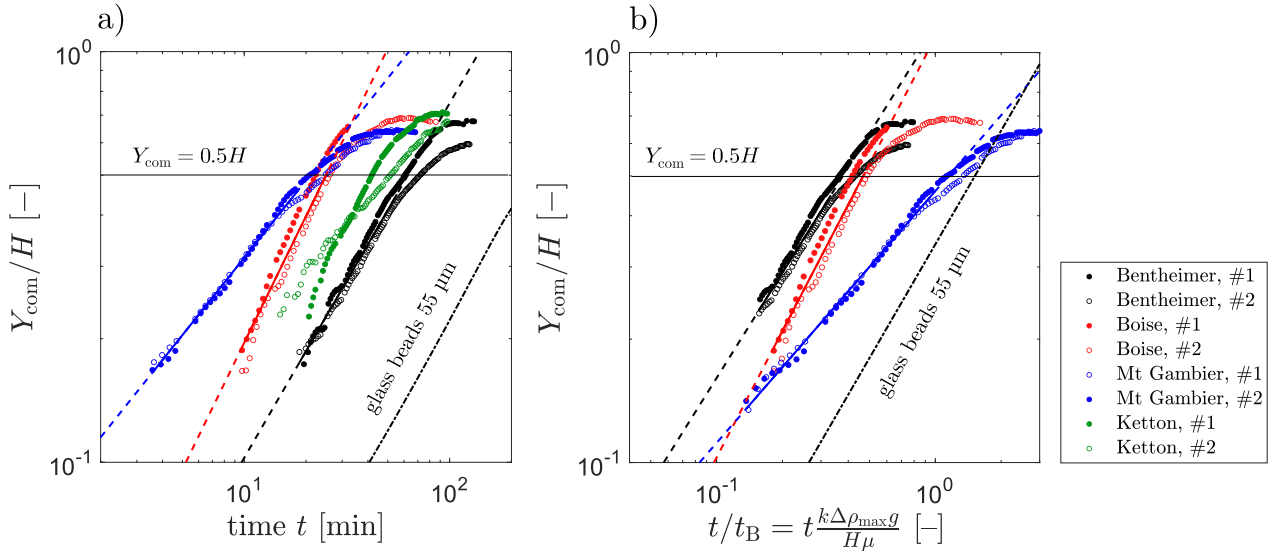


Figure 8.6: Vertical centre of mass normalised by the sample height H plotted as a function of time t (a) and the normalised time t/t_B (b). The centre of mass is calculated along the vertical direction between $y = 1.4 \text{ cm}$ below the interface and the bottom boundary $y = H$ to reduce the impact on the results. The solid lines (colour-coded) are obtained upon fitting a power law function to the experimental data in the advanced convective regime, after and before this time the line turns dashed. No trendline is obtained for Ketton limestone and the moment results have been omitted in (b) due to a lack of confidence in the data. The trendline obtained from the experiments with glass beads (55 μm bead size) is additionally included as a dash-dotted line. The horizontal line is the reference line that indicates the expected long-time stabilisation of the centre of mass at $Y_{\text{com}}/H = 0.5$.

of Bentheimer, Boise and Mt Gambier are in very good agreement in the convective regime. In the shutdown regime, it is expected to reach a constant value of $Y_{\text{com}}/H = 0.5$ upon attainment of a uniform concentration in the domain. We note that the limit is not reached asymptotically from below (horizontal black line). Rather, pooling at the bottom of the domain causes an overshoot of the experimental data. Again, the horizontal shift of the curves sorts from left to right according to the decreasing absolute permeability of the rocks. Power law fittings are obtained in the convective regime and a clear distinction in the scaling coefficients is observed. While a power law exponent is determined for Bentheimer sandstone ($b = 0.86 [0.82, 0.90]$) that fits in the range of the glass beads experiments ($b = 0.87 - 0.92$, see Section 7.3.4), the exponent found for Mt Gambier is significantly lower ($b = 0.63 [0.61, 0.64]$). A smaller exponent means a slower downward movement of the centre of mass, which in turn is related to the decrease in fluid density with travel distance and thus a decrease in the speed of the descending plumes, as discussed in the previous sections. In contrast to that is the trend determined for Boise sandstone. We expected a similar exponent to Bentheimer due to a similar regular porous structure. However, we determine a (slightly) higher scaling than ballistic ($b = 1.03 [0.93, 1.12]$). We hypothesise that unlike in Mt Gambier where the overall high permeability together with the stronger HRPF heterogeneities (see Section 4.7) intensifies a dilution of the plume in all directions, in Boise (local) variations in permeability due to core-scale heterogeneities might cause focusing of the solute flow which could result in an enhanced longitudinal displacement of the solute. We support this hypothesis by comparing it to the results of Ketton in Figure 8.6a. Despite the long channels apparent in the axial direction of the core, the scaling of at least one of the samples shows ballistic to super-linear behaviour ($b \geq 1$). However, we are aware that no significant core-scale heterogeneities are visible in the visualisations of Boise in Section 4.9 and the samples are characterised as fairly homogeneous on a grain-scale. A more systematic method to quantify core-scale heterogeneities in the rocks might be needed.

Figure 8.6b plots the normalised vertical centre of mass, Y_{com}/H , as a function of the normalised time t/t_B . The horizontal ordering follows the same as in Figure 8.5b. It implies that the centre of solute mass advances slower in Mt Gambier than in the sandstones relative to their mean permeabilities. This further indicates a distinct mass transport behaviour in Mt Gambier that is discussed further in the following sections.

8.3.5 Second Moment (Standard Deviation)

Figure 8.7 shows the normalised standard deviation of the solute concentration distribution around the mean in the vertical direction, σ/H , plotted as a function of time t (a) and normalised time

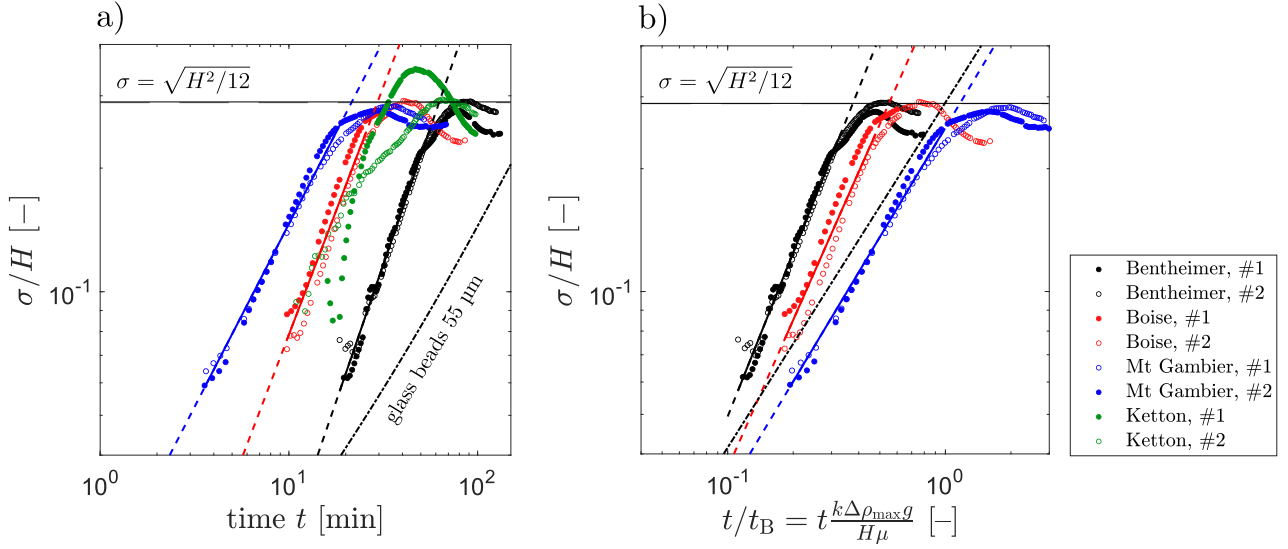


Figure 8.7: Standard deviation of the solute concentration distribution around the mean in the vertical direction normalised by the sample height plotted as a function of time t (a) and the normalised time t/t_B (b). The standard deviation is calculated along the vertical direction between $y = 1.4\text{ cm}$ below the interface and the bottom boundary $y = H$ to reduce the impact on the results. The solid lines (colour-coded) are obtained upon fitting a power law function to the experimental data in the convective regime, after and before this time the line turns dashed. No trendline is obtained for Ketton limestone and the moment results have been omitted in (b) due to a lack of confidence in the data. The trendline obtained from the experiments with glass beads (55 μm bead size) is additionally included as a dash-dotted line. The horizontal line is the reference line that indicates the expected long-time stabilisation of the centre of mass at $\sigma = \sqrt{H^2/12}$.

t/t_B (b). This measure is also referred to as spreading length and is expected to reach a constant value of $\sigma/H = \sqrt{1/12}$ upon attainment of a uniform concentration in the domain (horizontal solid line). Again, the experimental data shows good reproducibility and indicates a power law behaviour in the advanced convective regime and all fitting exponents are $b > 0.5$.

The sandstones show unexpectedly high exponents (around $b = 1.2 - 1.3$, Table 8.1). This is in contrast to the much lower exponents of the experiments with glass beads ($b = 0.74 - 0.84$, dependent on the glass bead size). Both systems, the bead packs and the sandstones, can be considered fairly uniform in their grain-scale structure. For instance, the coordination number of the bead packs and the sandstones is similar (see Section 4.10) and they are characterised by a small porosity distribution (see Section 4.3). However, one major structural difference is apparent: While glass bead packs are unconsolidated, sandstones are consolidated due to cementation. Mass transport, and specifically diffusion, is more restricted in consolidated media than in unconsolidated media (Bijeljic et al., 2004). Additionally, Bentheimer and Boise both have lower (inter-granular) porosities ($\phi \approx 0.22 - 0.26$) compared to the glass beads ($\phi \approx 0.34$), implying less volume is available for dissolution and mixing.

We suggest that the cementation and the low porosity values lead to an effect that we describe here as ‘plume-concentrating’. We hypothesise that plume-concentrating results from a displacement of dense plumes in consolidated and cemented media that does show limited plume expansion in transverse direction but an effective longitudinal spreading (compare Figure 7.2 and Figure 8.3). In contrast to this, Mt Gambier shows a damped scaling of the 2nd moment ($b = 0.89$). The concept of un- or consolidated porous media cannot be directly related to the fossiliferous limestone and additionally Gambier is characterised by a much higher porosity together with a high coordination number. This leads to stronger mixing and dispersion in the transverse direction in comparison to the sandstones and bead pack. Moreover, Mt Gambier has stronger HRPF heterogeneities and is characterised by a slightly higher REV value and a relatively large MICP pore size distribution. We suggest that a (microscopic) heterogeneous porous structure, in addition to strong convection, intensifies dispersion at the macroscopic scale since the flow field between the downward flowing dense fingers and the upward flowing pure fluid increases in its complexity and its non-uniformity (*e.g.*, Charlaix and Gayvallet 1991; Sahimi 2011).

8.3.6 Péclet Number and Averaged Dispersion Coefficient

We follow the procedure described in Section 3.4 for the bead pack experiments to estimate the effective longitudinal dispersion coefficient as half the time rate of change of the 2nd moment (Eq. 3.29). To calculate an average dispersion coefficient, $D_L(t)$ is averaged over the advanced convective regime (the same time period is used as for the determination of the scalings in Sections 8.3.3–8.3.5). It is normalised with the molecular diffusion coefficient D_m and reported in Table 8.2. The highest normalised dispersion coefficients are determined for Mt Gambier and Boise followed by Bentheimer. We want to exemplify that two different porous media (*e.g.*, Bentheimer and Boise) can be characterised by similar longitudinal spreading dynamics but different longitudinal dispersion coefficients. The former and its efficiency is quantified from the exponent of the scaling of the 2nd moment and describes how the standard deviation of the solute distribution changes with time. Since we are not looking at the prefactor a and solely at the power law exponent b , we consider it to be decoupled from the permeability values or the Rayleigh number. The latter is the average time derivative of the 2nd moment and characterises how fast the spreading with respect to time changes in the advanced convective regime and depends therefore (additionally) on the absolute transport properties of the porous media (*e.g.*, porosity, permeability).

We estimate the longitudinal Péclet number, which represents the ratio between the time needed for the solute to traverse a characteristic length L_c by advection (or convection) t_{adv} compared to the

Table 8.2: Péclet number Pe , averaged transport velocity u_y , normalised averaged dispersion coefficient D_L/D_m and the inhomogeneity factor σ_H . The latter is extracted from the fitting of the data to the empirical correlation presented in Eq. 8.3. The uncertainty values are given in brackets. The uncertainty is calculated as the standard deviation around the mean for u_y and D_L/D_m and for Pe by applying classic rules of error propagation.

		Pe	u_y [cm/min]	D_L/D_m	σ_H	NMSE
Bentheimer	#1	7.11 (1.45)	0.09 (0.02)	44.48 (0.96)	13.28	4.39
	#2	5.22 (0.72)	0.07 (0.01)	40.40 (0.77)		
	fit					
Boise	#1	14.27 (3.15)	0.25 (0.05)	110.91 (5.04)	15.59	0.01
	#2	11.56 (2.06)	0.20 (0.03)	92.02 (2.81)		
	fit					
Mt Gambier	#1	3.75 (0.88)	0.20 (0.05)	105.81 (7.15)	62.17	0.46
	#2	4.08 (1.05)	0.22 (0.06)	137.59 (7.59)		
	fit					

time needed by diffusion t_{diff} (Keable et al., 2022; Plumb and Whitaker, 1990; Quintard and Whitaker, 1994; Seymour and Callaghan, 1997; Singh et al., 2018):

$$Pe = \frac{t_{\text{adv}}}{t_{\text{diff}}} = \frac{\frac{v}{L_c}}{\frac{D_m}{L_c^2}} = \frac{vL_c}{D_m} = \frac{uL_c}{\phi D_m}. \quad (8.2)$$

The average vertical fluid velocities (super- and interstitial respectively) are u and v and the molecular diffusion coefficient is D_m . The length scale for advection is the characteristic length (see Section 4.6). We use the average transport velocity in direction of flow u_y that is related to the displacement of the centre of mass (Eq. 3.28). The results are reported in Table 8.2. The Péclet numbers are all of the magnitude $\mathcal{O}(Pe) = 10$ and therefore below the purely *advective-dominated regime* ($Pe > 300$) and in the so-called *power law regime* ($5 < Pe < 300$, Perkins and Johnston 1963).

8.4 Discussion

8.4.1 Longitudinal Dispersion

A common way to describe longitudinal dispersion as a function of the Péclet number is (Bijeljic et al., 2004; Sahimi, 2011; Sahimi et al., 1986):

$$\frac{D_L}{D_m} = \frac{1}{\mathcal{F}\phi} + c_p \sigma_H Pe^m. \quad (8.3)$$

High Péclet number regimes such as *mechanical dispersion* ($300 < Pe < 10^5$) or *hold-up dispersion* ($Pe \gg 10^5$) are not relevant for the present study (and the terms are neglected in Eq. 8.3, more information can be found in Sahimi 2011). For small Péclet numbers ($Pe < 0.3$, *diffusion regime*), convection is slow and molecular diffusion controls the mixing almost completely. This regime is controlled by the first term on the right side of Eq. 8.3, where $\mathcal{F}$ is the formation factor and ϕ is the porosity. The second term accounts for (mechanical) dispersion ($5 < Pe < 300$, *power law regime*) with $c_p = 0.5$ (see Section 3.4), σ_H and m as constants (see also Section 3.4). In this regime, convection dominates dispersion, but the effect of molecular diffusion should still not be neglected. It has been demonstrated with experimental literature data on longitudinal solute dispersion, that the power law exponent m is between $1 \lesssim m \lesssim 1.2$ (Sahimi, 2011). However, we follow the approach as in Kurotori et al. (2019) and set m to unity ($m = 1$, Scheidegger parameterisation) as it is often done in solute transport applications (Sahimi, 2011). The coefficient σ_H is the (longitudinal) inhomogeneity factor, describing the strength of heterogeneity in the longitudinal direction and depending on the pore space. The inhomogeneity factor takes $\sigma_H = 1$ for a perfectly homogeneous system (Section 3.3) but increases with increasing bead diameter (see Section 7.4) and with increasing polydispersity. In the context of consolidated porous media, the inhomogeneity factor should be seen as a characteristic of the type of rock (Kwok et al., 1995). Figure 8.8 shows the normalised dispersion coefficient D_L/D_m plotted against the Péclet number. The results of the bead packs are shown as grey-filled symbols and are located above the range of the literature data for pulsed systems (unfilled symbols). In other words, they show higher dispersion ratios for similar Péclet numbers. This is in agreement with the results in Section 7.4.1 in Chapter 7, determining that the convective mixing process is enhancing the longitudinal spreading compared to a unidirectional advection process. The rock results are close together and also located above the data for uniform flow. Since transport in this study is based on free convection, it is not possible to take measurements at different average transport velocities with the same porous medium. However, we still use the two available points and fit the correlation in Eq. 8.3 to extract an approximate value of the inhomogeneity factors σ_H for each rock type (Figure 8.8). The formation factor $\mathcal{F}$ depends on the conductivity of the porous media (*i.e.*, rock type) and we use values taken from the literature for the sandstones ($\mathcal{F} = 5.5$) and the carbonates ($\mathcal{F} = 4.4$, Mohammadmoradi et al. 2016). The correlation values of σ_H of the rocks are reported in Table 8.2 together with the NMSE values for an error estimate. We derive a high inhomogeneity factor for Mt Gambier limestone ($\sigma_H \approx 60$). It is followed by the sandstones, Boise and Bentheimer, with very similar inhomogeneity factors of $\sigma_H \approx 15$. The inhomogeneity factor from the literature determined from single tracer plumes driven by unidirectional advection are much smaller: For instance, for Bentheimer a value of $\sigma_H \approx 4$

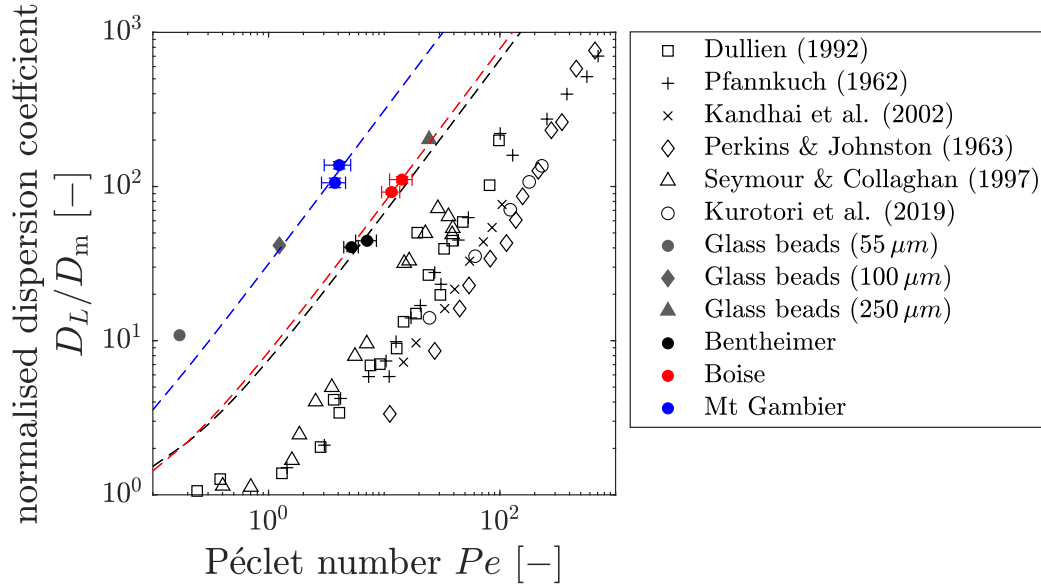


Figure 8.8: Comparison of the experimental results for the normalised longitudinal dispersion coefficient D_L/D_m versus the Péclet number Pe calculated with Eq. 8.2. The limits of D_L/D_m of the rocks represent a one-sigma confidence interval around the mean and the limits of Pe the uncertainty given in Table 8.2. The dashed lines (colour-coded) are the fitted empirical correlation (Eq. 8.3) with the correlation factors σ_H and m . The latter is assumed to be unity and the fitted values of σ_H are listed in Table 8.2. Shown are also the experimental data on unconsolidated bead packs as grey-filled symbols (bead particle diameter 55 μm , 100 μm , 250 μm). In addition, a comparison to experimental measurements from the literature of the longitudinal dispersion coefficients in pulsed systems (unconsolidated bead packs) is included (Dullien, 1992; Kandhai et al., 2002; Kurotori et al., 2019; Pfannkuch, 1962; Seymour and Callaghan, 1997) as unfilled symbols.

is found in Kurotori (2019), which is 3–4 times smaller than the one determined for free convection in this work. As the bead packs differ in the bead diameter, the correlation is not applied to the combined data. However, applying Eq. 8.3 to each data point (each bead size) allows to estimate the range of the inhomogeneity factor which is up to one order of magnitude higher than the ones expected for uniform advective transport in uniform bead packs ($\sigma_H = 3 - 10$, Section 7.4.1 in Chapter 7). This is in agreement with the findings in Chapter 7 in Section 8.4 where it is shown that the “effective” dispersivity associated with density-driven mixing is, due to the presence of the finger pattern and the counter-current flow structures, much larger than values associated with a unidirectional advection process of a single-solute plume.

We note that in Figure 8.8 only longitudinal dispersion is considered and no transverse dispersion is included. However, transverse dispersion seems to be more relevant in more heterogeneous structures, such as Mt Gambier limestone, compared to homogeneous structures. This is discussed further in

the following section where the longitudinal spreading and three-dimensional mixing efficiencies are compared. Additionally, the correlation in Eq. 8.3 concentrates on one inhomogeneity metric only that might not be able to represent the complex differences in the heterogeneities and their length scales that impact the plume dispersion length and concentration gradients. For a convective process where dispersion results from the up- and downwelling of solute plumes, a more complex correlation that combines longitudinal and transverse dispersion together with more experiential data points is needed.

8.4.2 Comparison of Longitudinal Spreading and Mixing

In the preceding sections, we determined the dispersion coefficients within the applied porous media. However, we need to keep in mind that stronger dispersion does not necessarily mean more efficient spreading, in the long term, as concentration gradients (that drive convection) are diminished. Since, as discussed in Chapter 7, the transport of solute in a porous media is a coupled process of spreading and mixing we aim in this section to compare and evaluate the spreading and mixing efficiency in bead packs and rocks. Therefore, we make use of the time scaling relationships of the representative measures for longitudinal spreading and three-dimensional mixing.

A measure that accounts for the mixing (and thus the expansion of the solute plume in all three dimensions and its change in concentration) is the dilution index $E(t)$, an entropy-based measure introduced in Section 3.2.5. Figure 8.9 shows the with $E_{\max} = V$ normalised dilution index of the rocks (a) and of the glass bead packs (b) as a function of time. The normalised dilution index increases in both graphs with time ($E/E_{\max} = at^{b_E}$) in the advanced convective regime and converges towards $E/E_{\max} = 1$ in the shutdown regime. The exponents of the power law scaling (b_E) are reported in Table 8.3 and we define an efficient dilution (over the time of the advanced convective regime) by a high power law exponent. Respectively, we use the exponents of the scalings of the second moment of mass (b_σ) from Section 8.3.5 (also reported in Table 8.3) to evaluate the efficiency of the spreading of the solute plumes in the longitudinal direction. The error of all power law scaling parameters (rocks, beads) are given in Appendix E in Table E.1 and Table E.2.

By means of the numerical simulations in this thesis, we found the same scaling exponents in the temporal evolution of the dilution index and the spreading length and concluded that both measures are analogous and equally efficient for solutal convection in a uniform and homogeneous two-dimensional porous media (Section 6.4.2 in Chapter 6). To test this for 3D convection in porous materials, the power law exponents of the spreading length b_σ and of the dilution index b_E are compared. Table 8.3 shows that the mixing efficiency in the beads is lower than the spreading efficiency

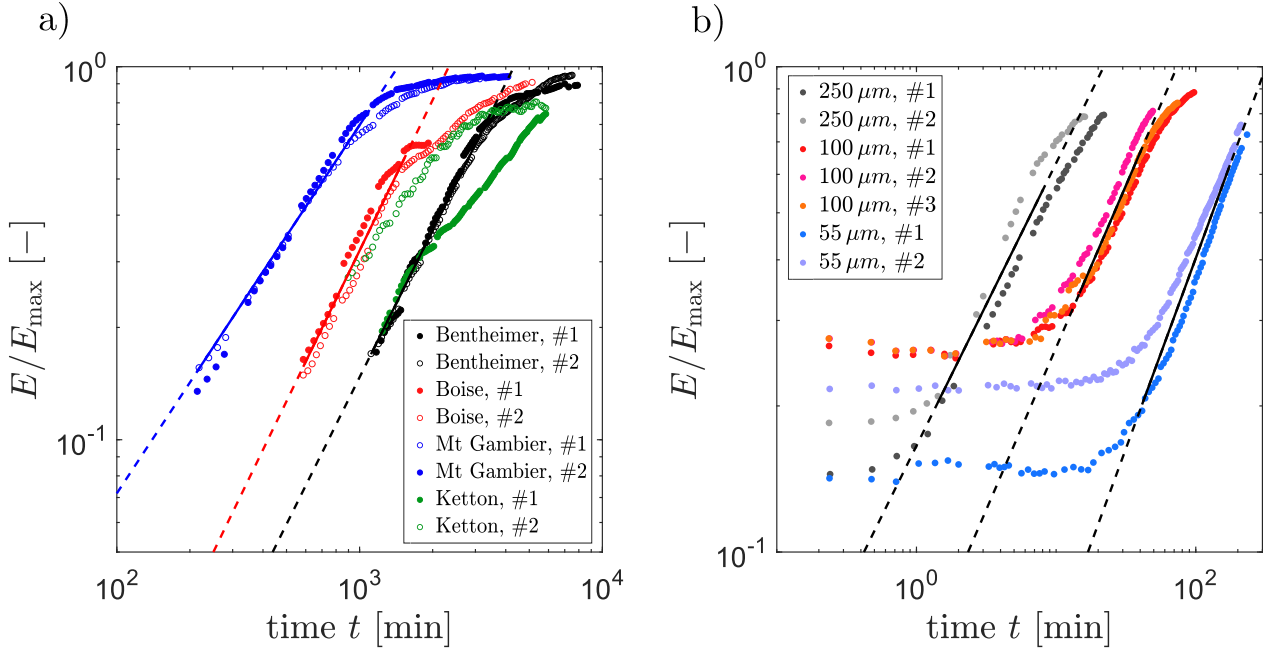


Figure 8.9: Dilution index is normalised with the maximum dilution index as function of time t of the rocks (a) and the glass bead packs (b). The solid lines (colour-coded) are obtained upon fitting a power law function to the experimental data in the convective regime, after and before this time the line turns dashed. No trendline is obtained for Ketton limestone. Details on the glass bead experiments are in Chapter 7.

($b_E < b_\sigma$) while it is the opposite for the rocks ($b_E > b_\sigma$). Therefore, spreading and mixing dynamics are no longer in conformity and (three-dimensional) dilution is more efficient in rocks than in uniform and homogeneous bead packs. Solely for the most homogeneous and ordered Bentheimer sandstone two very similar exponents are reported. A reason for the stronger dilution efficiency in the rocks could be the strengthening of the transverse spreading by the apparent heterogeneities of the pore space. We visually support the differences in longitudinal and transverse plume expansion qualitatively in Figure 8.10 showing cross-sections of early and advanced plumes in a bead pack (100 μm)

Table 8.3: Power law scaling exponents of the advanced convection regime of the 2nd spatial moment (standard deviation, b_σ) and the normalised dilution index (b_E) for the rocks and bead packs.

Porous media	b_σ (2 nd moment)	b_E (dilution index)
Bentheimer	1.34	1.31
Boise	1.21	1.34
Mount Gambier	0.99	1.08
Glass beads 55 μm	0.84	0.78
100 μm	0.79	0.67
250 μm	0.74	0.58

and in Mt Gambier. We note that the Rayleigh number of the bead pack is lower than that of the

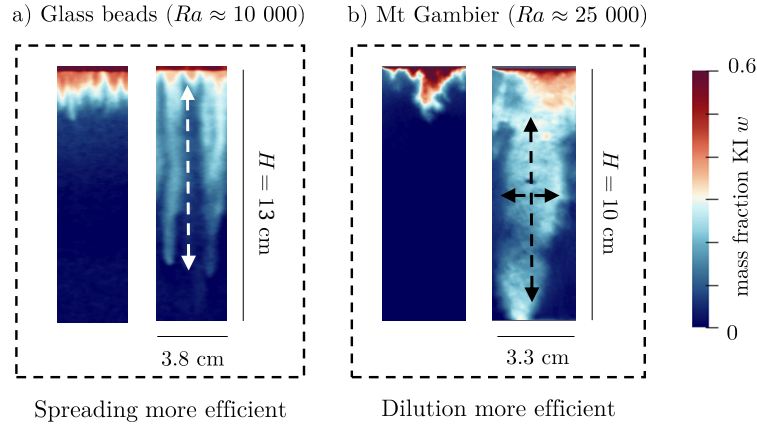


Figure 8.10: Qualitative comparison of the spreading and mixing dynamics by means of the plume evolution in (a) the glass bead pack of 100 μm , (b) the carbonate rock Mt Gambier. The images to the left of (a) and (b) are taken from an early stage of the convective dissolution and the image to the right at the time the shutdown starts. The plume in Mt Gambier (b) is strongly expanding laterally (dilation more efficient, demonstrated by black arrows) while in the bead pack (a) the plumes are more elongated in the direction of flow (spreading more efficiently, demonstrated by white arrow).

Mt Gambier rock. For a homogeneous packing, a larger Rayleigh number would result in a decrease of the wavelength and therefore a thinning of the plume width (Jiang et al., 2019; Teng et al., 2017, 2020). But the opposite effect is observed and a much stronger transverse expansion of the plumes is observed in the morphology of Mt Gambier compared to the plumes in the bead pack despite a lower Ra . This visually supports the statement that in a heterogeneous porous media, three-dimensional expansion (and also dilation) is stronger than longitudinal spreading. To confirm this, future studies should include a detailed analysis of the transverse spreading and dispersion of solute in bead packs and rocks.

8.4.3 Correlation of Porous Media Properties with Mixing Efficiency

As discussed, the dissolution behaviour and solute distribution are clearly influenced by the porous media structure. We suggest comparing the dissolution behaviour to the heterogeneity and pore space characteristics presented in Chapter 4. Figure 8.11 correlates values of the normalised dilution index with porous media properties (rock samples as black symbols and bead packs as red symbols). The dilution index is extracted at the time when the 2nd moment has reached half of its maximum value (unfilled symbols) and the start time of the shutdown regime (filled symbols). In some of the graphs in Figure 8.11, correlations with the dilution index are recognised. For instance, the dilution index tends to be larger if the total porosity is high (graph a). This trend is in agreement with the

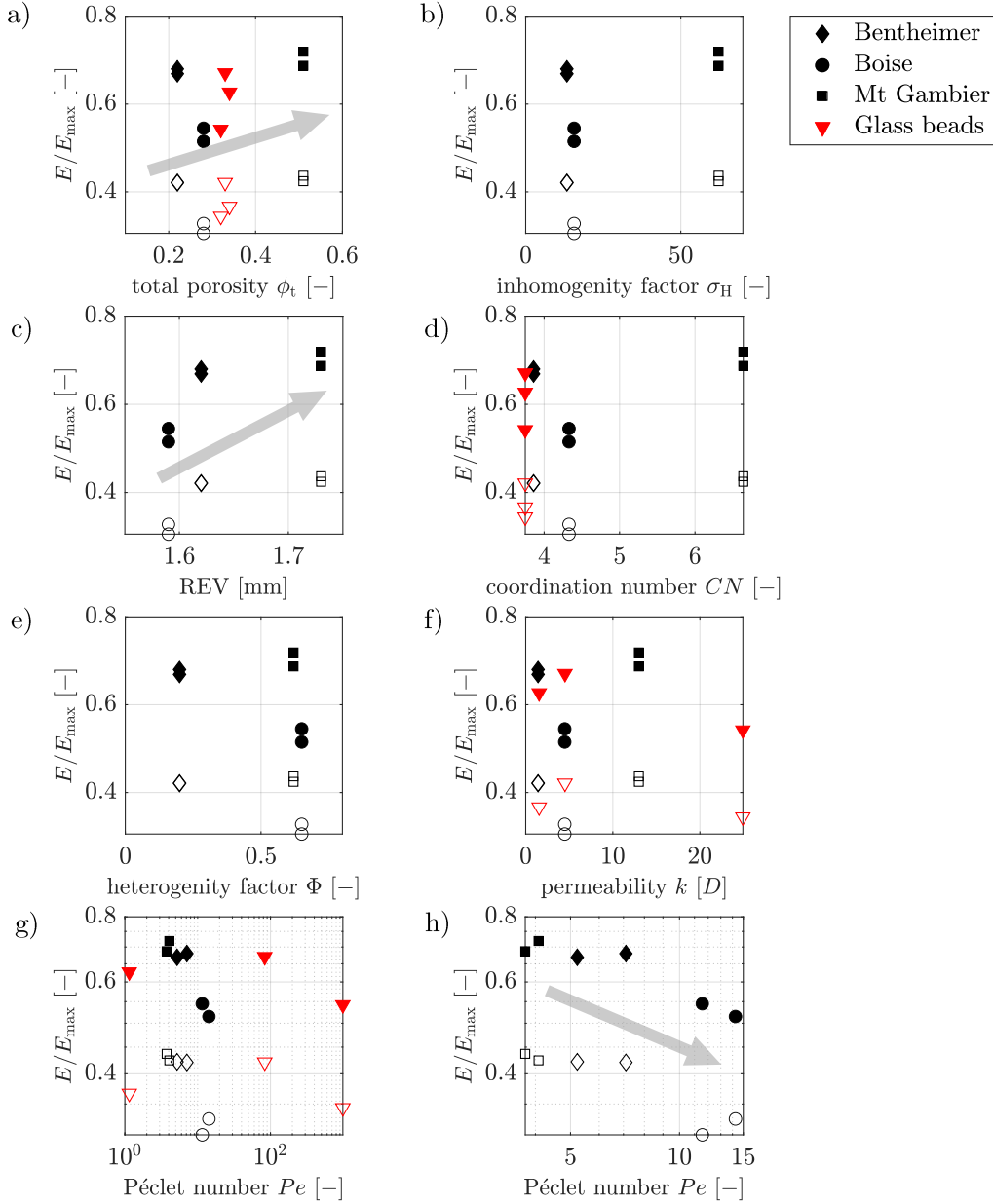


Figure 8.11: Normalised dilution index $E/E_{\max}$ versus various porous media properties or heterogeneity measures. The black symbols represent the rock data and the red symbols the glass bead pack data. Unfilled symbols mark the dilution index at the time when the 2nd moment has reached half of its maximum value ($\sigma = 0.5\sqrt{H^2/12}$) and filled symbols at the start of the shutdown regime ($\sigma = 0.9\sqrt{H^2/12}$). No inhomogeneity factor (σ_H), REV value and heterogeneity factor Φ are available for the glass beads and are therefore not included in the respective graphs. The Péclet number is plotted in logarithmic scaling in graphs g and h.

observation that a high porosity favours mixing (see Section 8.3.1). Similar is observed in graph c and a larger REV tends to correspond to a higher dilution index. The permeability and the Péclet number is plotted in logarithmic scale in graph f and g, respectively. No clear trend is visible in either

of the graphs but a decreasing trend is indicated with the Péclet number if only the rock values are considered (graph h). Although some trends are indicated in Figure 8.11, no relationship is found, for instance, with the coordination number (graph d). Other graphs might even show contradictory trends, such as the inhomogeneity factor (graph b, slight upwards trend) or the heterogeneity factor extracted from the MICP measurements (graph e, slight downwards trend). Convective dissolution is a complex interaction of various pore space properties, creating velocity and concentration distributions of different spatial scales simultaneously. Therefore, it is a challenging task to find correlations to isolated pore space characteristics. Additionally, an insufficient number of data points is available for a clear indication of a correlation and more experiments with different types of rock and degrees of heterogeneities should be applied to support or disprove the described trends.

8.4.4 Implications to CO₂ Storage

The present study aims to support the selection of suitable sites for large-scale CO₂ storage in saline aquifers. We found that high porous rocks with (small-scale) HRPF heterogeneities show efficient mixing in all three spatial directions but convection slows down over the travel distance due to a reduction in the plume solute density. On the other hand, homogeneous rocks keep a strong downward convection but show a less efficient spreading in the transverse direction. Therefore, we suggest that highly porous and heterogeneous rocks (such as Mt Gambier) are more favourable in saline aquifers with a shorter reservoir height because fast and efficient mixing within the large available pore space is expected. Aquifers with a deep confining bed, a homogeneous host rock of low- or medium-high porosity (such as the sandstones Bentheimer and Boise) could provide the advantage that plumes stay more compact and the reduced lateral spreading leads to greater amounts of CO₂ that is transported into large depths. The experiments with Ketton limestone showed that the effects of anisotropy due to macroscopic heterogeneities could play a significant role since it alters the dissolution pattern and dissolution behaviour. On the one hand, the available pore space is exploited very little since preferred pathways are created. On the other hand, large-scale heterogeneities can be favourable if the solute is accelerated quickly deep in the reservoir.

Even though the results of this study are obtained for the experimental scale (cm scale), they are crucial to develop and to validate mathematical models to upscale schemes for enhanced dissolution towards the whole reservoir scale. Results provided in this study can assist to create fine-scale (heterogeneous) processes to be included in coarse simulation models.

8.5 Concluding Remarks

In this chapter, we present in high spatial and high temporal resolution an experimental study of density-driven natural convection process in three-dimensional geologic materials while maintaining a constant concentration boundary condition. Four different natural rock types are considered for the experiments: two sandstones (Bentheimer, Boise) and two carbonates (Mt Gambier, Ketton). We characterised the rock samples in terms of structural heterogeneity over various spatial length-scales (pore-, grain-, and core-scale) while applying computational techniques on 3D images acquired with a medical or micro CT, and data of Mercury Intrusion Measurements (Chapter 4). Bentheimer and Boise are considered homogeneous on all scales investigated, with Boise showing a slightly higher heterogeneity on the grain-scale. Mt Gambier is locally very heterogeneous but characterised as fairly homogeneous on the core-scale. Ketton limestone has a regular intragranular microporous structure and contains a considerable amount of fractures and vuggy pore space which creates strong dissimilarities between the samples.

Potassium iodide and water were used as fluid pairs in the experiments with the intent of monitoring the downwelling solute-rich plumes in three dimensions by X-ray CT. We monitor the temporal evolution of individual plume structures and indicate three convective regimes in all rocks (early and advanced convective, shutdown regime) but stark differences in the pattern of advanced dissolution: Boise and Bentheimer create, in the vertical direction, elongated dense plumes while Mt Gambier establishes cloud-like plumes that branch off and dilute laterally and vertically. In Ketton, the solute-rich fluid bypasses through most permeable paths (*i.e.*, core-scale heterogeneities) making the results non-representative.

Solute spreading and mixing are systematically analysed in the advanced-convective regime by applying the spatial moments of the vertical concentration distribution and the dilution index. We estimate transport characteristics including the hydrodynamic dispersion coefficient, the transport velocity and the Péclet number. A comparison with the findings obtained with bead packs (55 μm glass ballotini, Chapter 7) was included. The results suggest that solute dissolution from gravity instabilities in rocks is strongly impacted by the inherent micro- and macro-structural features of the pore space and their length scales and does not solely depend on the magnitude of the permeability or the Rayleigh number. The main points are as follows:

- Using the maximum density difference $\Delta\rho_{\text{max}}$ to describe the strength of gravity between up- and downwelling fluid (*e.g.*, for time normalisation) is strictly speaking only valid if the dissolution plumes are compact and dense (Bentheimer, Boise). In contrast, for diluted plumes (Mt Gambier,

bead pack) an “effective” density difference ($\Delta\rho_{\text{eff}} < \Delta\rho_{\text{max}}$) seems more applicable.

- The zeroth moment of the sandstones and the bead pack follows a ballistic behaviour, while Mt Gambier indicates a sub-linear (t^b , $b < 1$) power law behaviour.
- The strongest dynamics (highest power law exponent) of the first spatial moment are determined for Boise sandstone. The enhanced longitudinal displacement of the solute most likely results from a vertical focusing of the solute flow due to heterogeneities that go beyond the characterised HRPF heterogeneities. We suggest advancing the evaluation of the core-scale heterogeneity by a more systematic and quantitative characterisation of the core-scale heterogeneities.
- The second moment of mass shows super-linear longitudinal spreading dynamics in Bentheimer and Boise resulting from ‘plume-concentrating’ which seems to occur in consolidated porous media with rather low porosity.
- The heterogeneous pore space and high permeability of Mt Gambier lead to a strongly non-uniform flow field and intensified transverse dispersion thereby reducing the effectiveness of the longitudinal spreading and resulting in a sub-linear scaling of the zeroth, first and second moment of mass. This leads to fundamentally distinct mass transport mechanisms of Mt Gambier and the sandstones which also reflects in the comparison of the dilution dynamics.
- The mean longitudinal dispersion coefficients are compared to the Péclet number and inhomogeneity factors are extracted using an empirical correlation derived for unidirectional advection. All values are higher than the literature values on pulse systems in uniform bead packs due to the longitudinal spreading that is enhanced by the counter-current flow structures.
- We find that dilution is more efficient in (heterogeneous) rocks due to the three-dimensional expansion of the plume volume as in the uniform and homogeneous bead packs. The effect of plume expansion is the strongest in Mt Gambier as the solute dilutes vertically and laterally.
- As a result, in addition to the increase in the longitudinal dispersion coefficient with increasing transport velocity (as shown by the uniform bead pack experiments in Chapter 7), apparent heterogeneities in the porous media impact the solute distribution by making (transverse) dispersion more pronounced as in a homogeneous case. This means that strong heterogeneities and a high average transport velocity could lead to a flow that is dispersion-dominated instead of advection-dominated.

- An attempt to correlate mixing efficiency with individual porous structural properties proves to be challenging as convective dissolution is a complex interaction of various properties, creating velocity and concentration distributions of various spatial scales.
- We discuss the possible implications of the findings to the large-scale CO₂ storage. We conclude that heterogeneities could impact the spreading and mixing in saline aquifers differently, depending on their length scale.

The results obtained in this study provide a major step towards a better understanding of the development of convective instabilities in different types of natural geological porous media. The gained knowledge on the behaviour and location of the solute plume and the controlling transport mechanisms at a given time is crucial for estimates of storage capacity and security and needs to be implemented in, for instance, large-scale simulations of heterogeneous reservoirs. Future studies should focus on other forms of (large-scale) rock heterogeneities and anisotropies such as vertically layered or sloping formations. In addition to the longitudinal dispersion studied in this work, transverse dispersion should be investigated and estimated to answer remaining questions on the interaction and effect of the consolidated rock structure on the solute distribution and establish their role in long-term geological CO₂ trapping.

Chapter 9

Conclusions and Future Work

Dissolution trapping is one of the primary mechanisms of carbon dioxide (CO_2) storage in deep saline aquifers. The process relies on convective dissolution and is thus expected to positively impact the subsurface storage by accelerating the dissolution rate of CO_2 into reservoir brines. The determination of the realised rates of CO_2 dissolution requires an understanding of the mixing process that takes place following the emplacement of CO_2 into the formation. Additionally, a more elaborated prediction of the spatio-temporal CO_2 distribution and knowledge of its length- and time-scales are crucial for evaluating potential storage sites. In this thesis, we applied experimental methods and numerical modelling to contribute to the understanding of convective dissolution in porous media, with a focus on subsurface rock formations to support safe and reliable sequestration. The outcomes of this work highlight the importance to understand the interaction of gravitational instabilities with the rock-specific porous space and the impact on the flow and the solute (longitudinal) spreading and mixing. The results and findings are valuable input to models that consider field-scale plume migration to advance the predictive ability, scale-up and validation. Although the focus of this thesis is on Carbon Capture and Storage (CCS), the findings help to improve the fundamental understanding of density-driven convection in general and convective mixing in particular. Additionally, results may assist as a benchmark for future studies in a range of engineered and natural applications, such as underground waste disposal or groundwater contamination.

This summary chapter is divided into four sections: Three sections summarise the outcomes of this thesis with a focus on the main findings of Chapters 6–8. Recommended areas for an extension of this thesis are discussed in the last section.

9.1 Research Outcomes and Conclusions

In Chapter 6, numerical simulations are performed to quantify systematically the mixing dynamics during density-driven solutal convection in homogeneous porous media with application to CO₂ storage. A two-dimensional formulation is applied, and the Rayleigh number is varied between $Ra = 100$ and $Ra = 10\,000$. We show that the generation of lobe-shaped fingers drives the mixing process: their elongation and stretching produce a largely nonuniform distribution of solute within the dissolved plume, which in turns intensifies horizontal diffusive mass transfer. The macroscopic evolution of the convective process is characterised by means of fundamental macroscopic measures of mixing that use the local spatial structure of the solute concentration field including isocontour lines, the intensity of segregation, the spreading length, the dilution index, and the dissolution flux. Results of the latter are successfully validated against data from a benchmark study. We show that the intensity of segregation closely mimics the evolution of the *in-situ* convective pattern arising from the stretching and merging of downwelling plumes. The spreading length and the dilution index both confirm that the mixing process accelerates over time (t) with a power law scaling ($\propto t^\alpha$) that transitions from diffusive ($\alpha = 0.5$) to super-diffusive mixing ($\alpha \geq 1$) irrespective of Ra . This transition time scales $\tau_{\text{on}} \propto Ra^2$ and is used as a measure of the onset time of convection. The dilution index indicates that the time needed to reach close-to-complete mixing reduces linearly with Ra . On the contrary, the non-dimensional mass flux, expressed in terms of the Sherwood number, Sh , reveals a natural logarithmic scaling for $Ra \leq 2\,500$. As a practical example, we apply the derived scaling laws to two existing reservoirs, namely the Alberta Basin and the Black Warrior River aquifer. We estimate that the same mixing state is achieved 40 times faster in the Black Warrior aquifer and two times faster in the Alberta Basin by the contribution of convective dissolution as compared to a purely diffusive scenario.

Owing to the difficulty of reproducing the time-dependent convective process in porous media, experiments reported in the literature have largely focused on 2D systems (*e.g.*, Hele-Shaw cells) and have used analogue fluid pairs with properties that differ from the subsurface CO₂/brine system. In this thesis, we present a novel experimental approach to investigate the evolution of the convective mixing process non-invasively in opaque porous media by using X-ray Computed Tomography. The 3D imaging of the dissolution process adds a valuable and novel key element to the experimental approach: the possibility of monitoring the downwelling solute-rich plumes in three dimensions. This enables the quantification of the pattern formation and the plume evolution in a three-dimensional porous medium. The experimental set-up used water and saturated aqueous solution of potassium iodide as

surrogate fluid pairs. Due to the density function of potassium iodide solution, which increases monotonically and approximately linearly with the solute mass fraction, it proves to be suitable to mimic a solution saturated with dissolved CO_2 . It further allows the maintenance of a constant concentration boundary condition and constitutes a useful comparison relative to current approaches presented in the literature. The strongly attenuating potassium iodide facilitates high contrast in the CT images but, on the other hand, limits a precise analysis of the initial growth of the dissolution plume. The density difference of the proposed fluids is approximately two magnitudes larger than the one expected during a geological CO_2 trapping which allows reducing the experimental time from days or weeks down to minutes while working in laboratory conditions without high pressure. The scalability of dimensionless numbers allows comparing our results to other experiments or geological systems.

We explore density-driven natural convection process in uniform and unconsolidated glass bead packings over a range of Rayleigh numbers ($Ra = 3\,000 - 55\,000$) and observe directly the mixing structures that arise upon dissolution. We determined three convective regimes in the finger growth process, namely, the early convective regime, the advanced convective regime and the shutdown regime. The temporal evolution of the spatial moments in the direction of flow of the concentration distribution is systematically computed from the images, including the cumulative dissolved mass, the location of the centre of mass, and the standard deviation of the concentration field. The zeroth moment follows a ballistic power law behaviour, independent of the bead size, while a reduction of the power law exponents of the first and second moment with increasing bead size (and increasing transport velocity) suggests an impact of hydrodynamic dispersion on the longitudinal mixing. The Sherwood number was computed by using the constant flux in the advanced convective regime and a sublinear scaling of $Sh = 0.18Ra^{0.77}$ was found. We propose a simplified representation of the mixing process by analogy with the 1D advection-dispersion model. Bulk advective velocities and effective longitudinal dispersion coefficients for each bead size were extracted by comparing the experimental with the theoretical model results. These estimates suggest that the presence of the finger pattern and the counter-current flow structure enhance the longitudinal spreading of the solute by roughly one order of magnitude compared to the unidirectional dispersion of a single-solute plume.

Experimental evidence for three-dimensional convective dissolution in natural consolidated media is still lacking in the literature despite the importance of proving its occurrence within geological CO_2 traps. The imaging and the analysis of 3D density-driven convection in rocks with the described experimental method is the major novelty of this thesis. We have considered different types of consolidated rock samples (two sandstones, two carbonates) for the dissolution experiments. The rock samples are

characterised in terms of structural heterogeneity over various spatial length scales (pore-, grain-, and core-scale) while applying computational techniques on 3D images acquired with a medical or micro CT scanner as well as data of Mercury Intrusion Measurements and core-flooding measurements. Bentheimer and Boise are considered relatively homogeneous sandstone rocks. Mt Gambier limestone is heterogeneous on the small scale ($< \text{mm}$) but characterised as fairly homogeneous if regarded from the core-scale. We monitor the temporal evolution of individual plume structures between the different rock types and indicate strong differences in the pattern of (advanced) dissolution: Boise and Bentheimer create in vertical direction elongated dense plumes while Mt Gambier establishes cloud-like plumes that branch off and dilute laterally and vertically. We compute the temporal evolution of the zeroth, the first and second spatial moment of mass of the vertical concentration distribution and the dilution index and estimate transport characteristics including the hydrodynamic dispersion coefficient, the transport velocity and the Péclet number. The results suggest that solute dissolution from gravity instabilities in rocks is strongly impacted by the inherent micro- and macro-structural features and their length scales compared to the uniform numerical simulations or the uniform bead packs where dissolution depends directly on the magnitude of the permeability or the Rayleigh number. Boise shows a more effective longitudinal solute displacement which most likely results from a vertical focusing of the solute flow due to heterogeneities larger than the characterised small-scale heterogeneities. Super-linear longitudinal spreading dynamics are determined in Bentheimer and Boise resulting from 'plume-concentrating' due to limited solute spreading in lateral direction which seems to occur in consolidated porous media with rather low porosity. The strongly non-uniform flow field in the highly-porous Mt Gambier samples leads to intensified transverse dispersion and increased effectiveness of the three-dimensional mixing compared to more homogeneous porous media such as uniform bead packs. Finally, we investigate the possible implications of heterogeneities and their length scales on the large-scale CO_2 storage. We conclude that heterogeneities could impact the spreading and mixing in saline aquifers differently, depending on their length-scale.

9.2 Future Work

The following sections highlight some recommended areas for further research.

9.2.1 Extended Analysis on Mechanical Dispersion

Spreading, in general, and mechanical dispersion, in particular, have been discussed in the longitudinal direction in this thesis and the findings of this work give reason to expect that spatial heterogeneities in the pore space intensify the transverse dispersive behaviour. The dispersivities, in longitudinal and transverse directions, should be further investigated on homogeneous and heterogeneous porous media to complement the understanding of the contribution of dispersive solute transport. Transverse dispersion in heterogeneous rocks has been studied experimentally by Boon et al. (2017, 2016) by applying core flood test with uniform solute injection. An evaluation of the transverse dispersion coefficient in natural convective systems is not straightforward and difficulties arise due to the finger pattern that leads to a maze-like solute concentration in radial core slices (see Figure 8.2). This strongly differs to the radially uniform solute distribution known from core flood tests. Only very few experimental studies address its estimation in natural convection such as the study of Wang et al. (2020). They calculate the transverse dispersion coefficient by applying the approach of mass conservation of individual fingers. We suggest developing a more systematic and efficient approach that does not involve the manual extraction of individual plumes as this is not practical with a morphology pattern such as the one in Mt Gambier. Further, having an understanding of the magnitude of transverse dispersion and its coefficients would allow the testing of existing empirical correlations that were derived for unidirectional flow experiments (see for longitudinal dispersion in Section 7.4.1 in Chapter 7). We further suggest combining transverse and longitudinal dispersion coefficients since mixing and spreading in all spatial dimensions play a role during convective dissolution, mainly when heterogeneities are present.

Velocity-induced dispersion effects are not additionally modelled in the numerical study in Chapter 6, because we aimed to focus on the transport by convection and diffusion solely. In further steps, the model can be successively extended to study the impact of mechanical dispersion effects on vertical and horizontal mass transfer. In the past, transverse dispersion has been investigated numerically by Hassanzadeh et al. (2009), Emami-Meybodi (2017) and Tsinober et al. (2022). They determined the impact of (transverse) dispersion on, for instance, the onset of convection. Additional modelled dispersion will allow for a systematic comparison of the spreading and mixing behaviour between the existing results of this thesis and future results.

9.2.2 Dissolution During Shutdown Regime

So far, dissolution in the shutdown regime was not included in the discussion of this work. However, we observed an interesting phenomenon that could be of interest regarding the long-term storage of CO_2 in saline aquifers: After the start of the shutdown regime, the dense CO_2 -rich moves laterally along the bottom of the formation, pools and form an accumulation of higher concentrated fluid. On the one hand, this could fasten the dissolution rate of CO_2 at the interface, on the other hand, the storage capacity is not efficiently exploited for the mixing of the solute with the reservoir fluid. Some numerical effort to study the shutdown regime has been taken by Hewitt et al. (2013) and de Paoli et al. (2017) but evaluations based on experiments are very limited. An experimental set-up similar to the one shown in this work could be used to study the solute build-up at the bottom and its impact on the solute dissolution in the whole domain during the shutdown regime.

9.2.3 Three-Dimensional Numerical Studies

Two-dimensional simulations are performed as part of this thesis with the aim to build on existing findings and to expand the knowledge on solute spreading and mixing in porous media. However, the results of the three-dimensional simulations are expected to provide more representative information towards the investigation of convective mixing under realistic subsurface conditions. The present model can be extended to three spatial dimensions. By maintaining the same mesh resolution as in the 2D simulation of this work, the number of elements in a 3D simulation increases to around 100 million. First test runs with a 3D model have shown that the working cluster (56 CPUs) used for this study is impractical for such large simulations as the calculations are very resource expensive. One should explore options to perform the simulations on facilities such as the Research Computing Service of Imperial College London which offers a High-End Computing cluster and up to 15 000 CPU can be allocated to one job.

9.2.4 Combination of Numerical and Experimental Studies in Heterogeneous Porous Media

A larger number of three-dimensional numerical and experimental studies are needed to gain a deeper understanding of the impact of spatial heterogeneities on convective dissolution. In particular, the impact of large-scale heterogeneities and anisotropies, such as the channels or vuggy clusters found in Ketton limestone, on the distribution of the CO_2 resulting in the channelling of flow is crucial for the prediction of the convective mixing behaviour. This also requires a systematic characterisation

of the core-scale heterogeneities as the approach presented in this thesis has its limitations. Further, rocks such as Ketton limestone are additionally characterised by a large amount of microporosity. So far we did not expect that the microporous space significantly contributes to the flow (the scale of convection is much larger than the time scale of diffusion), but especially in carbonates some regions can be connected only by micropores and the contribution to the permeability and the flow should be investigated (Blunt, 2017; Karlsons et al., 2022).

Numerical studies on heterogeneous porous media are, to date, rare and more modelling studies are needed applying porous matrices that represent different types and strengths of heterogeneities characteristic of geological rock material. Out of the various possibilities, one option could be to include small-scale porosity variations with different representative correlation lengths (REV) to the porous matrix. To study the impact of macro-heterogeneities, one could introduce fractures in different spatial directions to the porous matrix.

9.2.5 Advancement of Existing Experimental Set-Up

One of the limitations of the presented experimental approach is the locally strong imaging artefacts when the KI concentration is close to the maximum solubility. We suggest trying different potassium salts such as potassium bromide (KBr), potassium nitrate (KNO_3) and potassium hydrogen carbonate (KHCO_3) due to their 2-3 times lower mass attenuation coefficients at the relevant energy level. However, the aqueous solutions of these salts are characterised by a lower maximum density difference than KI-water which affects the experimental time and the contrast in the images.

Future experimental studies may also be carried out using CO_2 (either gaseous or supercritical) and brine instead of surrogate fluids. However, this presents difficulties when studying convective dissipation under actual storage conditions. Much longer experimental times need to be expected and, if imaged with an X-ray CT scanner, a dopant might be needed to enhance the X-ray attenuation to clearly distinguish the CO_2 saturation from the resident fluid.

Future studies might also explore the possibility to apply Positron Emission Tomography (PET) to image and therefore visualise the fluid pathways inside the porous samples (Pini et al., 2016). PET imaging produces quantitative four-dimensional images of a radioactive tracer that is transported through the porous media (Zahasky and Benson, 2018). One of the benefits of PET imaging is the higher sensitivity to measure small changes in solute concentration compared to CT scanners. However, one of the limitations is the reduced spatial resolution. A combined application of both imaging technologies (PET and CT) has been proven to be an effective approach to gaining multidimensional images with high resolution (Pini et al., 2016; Zahasky and Benson, 2018).

9.2.6 Dissolution Experiments with Geochemical Reactions

Geochemical reactions can have a significant impact on the long-term storage of CO_2 where the formations have suitable mineralogy. Dissolution of CO_2 in brine creates an acidic solution which increases the solubility of many minerals composed of the host rock matrix which is ultimately leading to mineral dissolution. Further, the dissolved CO_2 will dissociate into ionic species and react with minerals in the geological formation and form precipitates (*i.e.*, undergo mineral trapping). Ennis-King and Paterson (2007) investigated numerically the coupling of geochemical reactions and convective dissolution and concluded that a strong coupling between the reaction behaviour and the convective mixing could be expected when fast-acting reactions are involved. Fast-acting reactions include rock dissolution reactions which cause an alteration of the porosity and permeability field (Gharbi et al., 2013). It is, therefore, necessary to regard the interaction between density-driven convection and geochemical reactions and to evaluate to what extent the distribution of CO_2 is affected (Cherezov, 2017; Ennis-King and Paterson, 2007). Some efforts have been made in numerical simulations investigating the effects of reactions and rock dissolution on the convective mixing process (Andres and Cardoso, 2011, 2012; Fu et al., 2015; Ghesmat et al., 2011; Hidalgo et al., 2015; Islam et al., 2016) but only very few studies regard the effect of geochemical reactions experimentally. To the knowledge of the author, the only experimental study on convection enhancement due to geochemical reactions is reported in Cherezov (2017).

Challenges towards a conceivable experimental set-up are, for instance, the large time scales of the reactions or the realisation of rock dissolution and alteration of porosity. This could be circumvented by using alternative fluids that precipitate on the rock matrix. One approach could be to continue using KI as a solute but to saturate the rock with a mixture of water and lead(III)nitrate. Mixing aqueous solutions of KI with lead(III)nitrate results in a formation of a solid salt (lead(II)iodide, Nývlt and Žáček 1994; Olmsted and Williams 1997) that would most likely precipitate on the rock surfaces. The difference in attenuation between the KI solution and lead(III)nitrate solution should be sufficient to monitor the change in KI concentration. However, the immediate and complete precipitation in the pore space in the top region near the interface could be a limiting factor with the result that the KI solution does not reach into the lower part of the rock. Further, one needs to study the change in density caused by the precipitation and its impact on the growth of the convective instabilities.

Appendix A

Details of Reservoir Sites

Table A.1: Details of the reservoir sites used in the histogram in Figure 4.5 of the main manuscript. The diffusion coefficient ($2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), the fluid viscosity and the change in density were estimated by the author's of this study (marked with an asterisk). The Rayleigh numbers taken from Lindeberg and Wessel-Berg (1997) are recalculated to exclude the temperature gradient. The table continues on the following page.

Reference	Name of reservoir	H [m]	ϕ [-]	k [m ²]	$\Delta\rho$ [kg/m ³]	μ [Pa s]	Ra [-]
Szulczewski et al. (2012)	Mt Simon Sandstone a	400	0.2	9.87×10^{-14}	6	0.8	726
	Mt Simon Sandstone b	200	0.2	9.87×10^{-14}	8	1	387
	Mt Simon Sandstone c	100	0.2	9.87×10^{-14}	7	1	169
	Black Warrior a	1000	0.2	9.87×10^{-14}	8	0.8	2420
	Black Warrior b	300	0.2	3.95×10^{-13}	10	0.7	4149
	Black Warrior c	200	0.2	8.88×10^{-13}	10	0.7	6224
	Black Warrior d	2000	0.2	5.92×10^{-14}	9	0.7	3734
	Frio a	2000	0.2	3.95×10^{-13}	8	0.8	19363
	Frio b	900	0.2	3.95×10^{-13}	8	0.6	11618
	Frio c	700	0.2	3.95×10^{-13}	8	0.6	9036
	Madison Limestone a	600	0.08	5.92×10^{-14}	5	0.4	2723
	Madison Limestone b	500	0.08	5.92×10^{-14}	11	0.6	3328
	Navajo-Nugget a	200	0.2	9.87×10^{-14}	9	0.4	1089
	Navajo-Nugget b	200	0.2	9.87×10^{-14}	10	0.4	1210
	Morrison	200	0.2	6.91×10^{-14}	10	0.4	847
	Lower Potomac	400	0.2	2.96×10^{-12}	10	0.7	41492
	Fox Hills	200	0.2	9.97×10^{-14}	11	0.7	761
	Paluxy Sandstone	15	0.2	2.96×10^{-13}	7	0.5	152
	St. Peter	40	0.06	4.93×10^{-14}	8	1	129
	Cedar Keys and Lawson Dolomites	400	0.2	9.87×10^{-15}	8	0.7	111

Reference	Name of reservoir	H [m]	ϕ [-]	k [m ²]	$\Delta\rho$ [kg/m ³]	μ [Pa s]	Ra [-]
Lindeberg and Wessel-Berg (1997)	North Sea reservoir 1	-	-	-	-	-	29
	North Sea reservoir 2	-	-	-	-	-	21
	North Sea reservoir 3	-	-	-	-	-	14
	North Sea reservoir 4	-	-	-	-	-	4
Nazari Moghaddam et al. (2015)	Alberta Basin	15	0.06	2.96×10^{-14}	4.7	0.6	142
	Alberta Basin	10	0.18	1.84×10^{-13}	3.6	0.66	139
	Alberta Basin	8	0.1	9.87×10^{-14}	4.3	0.65	141
	Alberta Basin	81	0.04	8.88×10^{-15}	4.3	0.67	318
	Alberta Basin	60	0.09	1.35×10^{-13}	4.1	0.36	1359
	Alberta Basin	10	0.06	7.40×10^{-14}	3.4	0.39	146
	Alberta Basin	10	0.08	1.13×10^{-13}	6.1	0.48	364
	Alberta Basin	40	0.22	6.61×10^{-14}	6	0.82	351
	Alberta Basin	4	0.1	3.41×10^{-13}	5.3	0.6	329
	Alberta Basin	40	0.05	2.66×10^{-14}	1.9	0.63	127
Hosa et al. (2011)	MRCSP R.E. Burger	20	0.032	7.90×10^{-17}	10*	1*	2
	WESTCARB Cholla	200	0.15	1.48×10^{-17}	10*	1*	1
	WESTCARB Rosetta	200	0.35	9.87×10^{-13}	10*	1*	27661
	SECARB Escatawpa	64	0.21	1.16×10^{-12}	10*	1*	17408
	Nagaoka	60	0.225	5.92×10^{-15}	10*	1*	77
	MRCSP Gaylord	21	0.125	2.21×10^{-14}	10*	1*	182
	Ketzin	80	0.23	7.40×10^{-13}	10*	1*	12628
	SECARB Cranfield	60	0.2	9.87×10^{-13}	10*	1*	14522
	In Salah	29	0.17	4.93×10^{-15}	10*	1*	41
	Snøhvit	60	0.13	4.44×10^{-13}	10*	1*	10054
	Gorgon	500	0.2	2.47×10^{-14}	10*	1*	3025

Appendix B

Uncertainty Propagation

The uncertainty of a function $f(x_1, x_2, \dots, x_n, \dots, x_p)$ can be propagated using the variances of its independent variables σ_{x_n} (Rouaud, 2017):

$$\sigma_f^2 = \sum_{n=1}^p \left(\frac{\partial f}{\partial x_n} \right)^2 \sigma_{x_n}^2 \quad (\text{B.1})$$

Porosity Uncertainty (Glass Bead Packs)

The average porosity ϕ was estimated by the weight change of samples before and after water saturation, using equation 4.2. In this case, the variables are the values of the experimental measurements and have uncertainties due to measurement limitations, such as the instrument precision. We apply Eq. B.1 and use the absolute estimated errors as the variables uncertainties. The uncertainty of the porosity σ_ϕ is propagated as following:

$$\sigma_\phi^2 = \left(\frac{1}{V\rho_w} \sigma_M \right)^2 + \left(\frac{M}{\rho_w V^2} \sigma_V \right)^2 + \left(\frac{M}{\rho_w^2 V} \sigma_{\rho_w} \right)^2 \quad (\text{B.2})$$

while $\sigma_{M_w} = 0.01$ g is the estimated error of the weighted water, $\sigma_V = 5$ ml the precision limit of the volume measurement and $\sigma_{\rho_w} = 0.001$ g/ml the estimated error of the density value. The values have been evaluated using available information such as the resolution of the scale. The uncertainty of the porosity is rounded up to $\sigma_\phi = 0.01$ (assumed to be the same for all glass bead sizes).

Uncertainty of KI Mass Fraction and KI Molar Concentration

The following procedure estimates the uncertainty of the CT values caused by quantum mottle. We assume that the uncertainty in the CT number does not change with bead size. We use independent

raw scans taken of the saturated porous media taken prior to the start of the experiment at identical conditions. The 3D scans are cropped as described in the main publication. We follow the procedure (here shown for the glass bead pack 100 μm) described in Pini et al. (2012) to assess the X-ray CT scanner precision. The repeatability on a voxel-by-voxel level of the CT measurements can be calculated by subtracting two images, here written for total number of $n = 4$ scans:

$$\Delta_{\text{CT}} = \frac{1}{2} \left(\sum_{i=1}^2 CT^i - \sum_{j=3}^4 CT^j \right) \quad (\text{B.3})$$

or $n = 2$ scans:

$$\Delta_{\text{CT}} = (CT^1 - CT^2) \quad (\text{B.4})$$

where Δ_{CT} is the difference in Hounsfield units. The subscript has been omitted from the CT number for the sake of simpler notation. The data of Δ_{CT} is normal distributed, characterised by (for the bead packs) a mean centred at zero ($\mu_{\Delta_{\text{CT}}} = 0.09 \text{ HU}$) and a standard deviation of $\sigma_{\Delta_{\text{CT}}} = 17.60 \text{ HU}$. Eq. B.1 is applied to the expression of the mass fraction on the voxel-level, as done below:

$$w_i = 0.6 \frac{CT_i - CT_i^0}{\phi(CT_{\text{sat}} - CT_w)} = 0.6 \frac{a - b}{c(\text{const})} \quad (\text{B.5})$$

$$\begin{aligned} \sigma_{w_i}^2 &= \frac{0.6^2}{\text{const}^2} \left[\sigma_a^2 \left(\frac{1}{c} \right)^2 + \sigma_b^2 \left(\frac{-1}{c} \right)^2 + \sigma_c^2 \left(\frac{b-a}{c^2} \right)^2 \right] \\ &= \frac{0.6^2}{\text{const}^2} \left[\frac{2\sigma_{\Delta_{\text{CT}}}^2}{c^2} + \sigma_\phi^2 \left(\frac{b-a}{c^2} \right)^2 \right] \\ &= \frac{0.6}{(CT_{\text{sat}} - CT_w)^2} \left[\frac{2\sigma_{\Delta_{\text{CT}}}^2}{\phi^2} + \sigma_\phi^2 \left(\frac{CT_i - CT_i^0}{\phi^2} \right)^2 \right]. \end{aligned} \quad (\text{B.6})$$

using the values of $\sigma_{\Delta_{\text{CT}}} = 17.60 \text{ HU}$, $\sigma_\phi = 0.01$, $CT_{\text{sat}} = 9505 \text{ HU}$, $CT_w = 40 \text{ HU}$ and $\phi = 0.33$, we calculate the uncertainty of the mass fraction. The applied CT numbers of water-saturated glass beads (1300.5 HU) and KI-saturated glass beads (7229 HU) were estimated using sample scans by averaging the CT values over the sample size. Eq. B.6 takes values between $\sigma_{w_i} = 0.01$ (pure water $w_i = 0$, $CT_i = CT_i^0 = 1300.5 \text{ HU}$) and $\sigma_{w_i} = 0.02$ (maximum saturated $w_i = 0.6$, $CT_i = 7229.6 \text{ HU}$) depending on the mass fraction KI in voxel i .

A similar approach is taken to calculate the uncertainty of the molar concentration by applying Eq. B.1 on the equation of the molar concentration c_i (neglecting the uncertainty on the molar mass value):

$$c_i = w_i \frac{\rho}{M_{\text{KI}}} = w_i \frac{\frac{w_i}{w_{\text{max}}} \rho_{\text{max}} + (1 - \frac{w_i}{w_{\text{max}}}) \rho_w}{M_{\text{KI}}} = \frac{a}{M_{\text{KI}}} \left(\frac{a}{w_{\text{max}}} b + (1 - \frac{a}{w_{\text{max}}}) c \right) \quad (\text{B.7})$$

resulting in:

$$\sigma_{c_i}^2 = \left(\frac{2a(b-c)}{M_{KI}w_{\max}} + \frac{c}{M_{KI}} \right)^2 \sigma_a^2 + \left(\frac{a^2}{M_{KI}w_{\max}} \right)^2 \sigma_b^2 + \left(\frac{a}{M_{KI}} - \frac{a^2}{M_{KI}w_{\max}} \right)^2 \sigma_c^2 \quad (\text{B.8})$$

yielding:

$$\sigma_{c_i}^2 = \frac{1}{M_{KI}^2} \left(\left(\frac{2w_i(\rho_{\max} - \rho_w)}{w_{\max}} + \rho_w \right)^2 \sigma_{w_i}^2 + \left(\frac{w_i^2}{w_{\max}} \right)^2 \sigma_{\rho_{\max}}^2 + \left(w_i - \frac{w_i^2}{w_{\max}} \right)^2 \sigma_{\rho_w}^2 \right). \quad (\text{B.9})$$

Using $M_{KI} = 166 \text{ g/mol}$ as the molar mass, $\sigma_{\rho_w} = \sigma_{\rho_{\max}} = 0.001 \text{ g/ml}$ as the estimated uncertainty of the density values, the uncertainty of the molar concentration takes values between $\sigma_{c_i} = 28 \text{ mol/m}^3$ (pure water $w_i = 0$) and $\sigma_{c_i} = 663$ (maximum saturated $w_i = 0.6$). The absolute values of the molar mass range from $c_{\min} = 0 \text{ mol/m}^3$ to $c_{\max} = 6\,198 \text{ mol/m}^3$.

Appendix C

Details Rock Characterisation

Table C.1: Threshold of the binarisation of the micro CT images applied in AVIZO-9. The values are valid for the files in tiff-format where 0 represents the minimum intensity, and 65 535 represents the maximum intensity.

Rock sample	threshold
Bentheimer	12 900
Boise	13 100
Mt Gambier	16 670
Ketton	15 000

Appendix D

Chapter 7: Result and Error Values

Table D.1: Dimensionless onset time of convection, τ_{on} , including the positive and negative error limits in brackets (no negative error limits available for 250 μm). The confidence bounds for the fitted coefficients of the power law scaling $\tau_{\text{on}} = aRa^b$ are $a = 84.05 [-43.26, 211.36]$, $b = -1.83 [-2.02, -1.65]$. The normalised mean squared error of the scaling is $\text{NMSE} = 0.0015$.

$d_p [\mu\text{m}]$		250	100	55
$\tau_{\text{on}}/10^{-7} [-]$	exp. run 1	3.8 (+7.2)	47.4 (-11.9, +16.0)	286.3 (-27.0, +27.0)
	exp. run 1	3.8 (+7.0)	43.3 (-10.8, +14.6)	351.9 (-31.7, +31.7)
	exp. run 1		43.7 (-10.9, +14.8)	

Table D.2: Exponents of the power law fittings determined in the advanced convective regime for the moments of mass including the 95 % confidence bounds for the fitted exponents together with the normalised mean square error NMSE values.

$d_p [\mu\text{m}]$		250	100	55
$Ra [-]$		55 000	10 000	3 400
total mass M_{norm}	exp.	1.02 (0.84, 1.12)	0.95 (0.89, 1.00)	1.05 (1.01, 1.09)
	NMSE	0.08	0.06	0.02
	ADE	1.00 (± 0)	1.00 (± 0)	1.00 (± 0)
	NMSE	1.65×10^{-5}	7.31×10^{-6}	5.00×10^{-6}
centre of mass Y_{com}/H	exp.	0.86 (0.54, 1.18)	0.91 (0.80, 1.03)	0.92 (0.89, 0.96)
	NMSE	0.31	0.22	0.02
	ADE	0.85 (0.84, 0.85)	0.89 (± 0)	0.92 (± 0)
	NMSE	1.77×10^{-4}	1.46×10^{-4}	1.82×10^{-5}
standard deviation σ/H	exp.	0.74 (0.53, 0.96)	0.79 (0.71, 0.88)	0.84 (0.76, 0.97)
	NMSE	0.23	0.16	0.10
	ADE	0.75 (± 0)	0.80 (± 0)	0.84 (± 0)
	NMSE	1.99×10^{-4}	1.04×10^{-4}	1.47×10^{-4}

Table D.3: Constant flux values and in brackets the respective relative standard deviation around its mean

d_p [μm]		250	100	55
$F_c/10^{-3}$ [$\text{mol}/\text{m}^2/\text{s}$]	exp. run 1	22.6 (4.4 %)	10.4 (8.8 %)	3.3 (11.1 %)
	exp. run 2	35.1 (3.1 %)	8.8 (8.8 %)	2.8 (10.3 %)
	exp. run 3		6.7 (10.9 %)	

Table D.4: Sherwood number values including the positive and negative error limits in brackets. The confidence bounds for the fitted coefficients of the power law scaling $\tau_{\text{on}} = aRa^b$ are $a = 0.18[-0.94, 1.30]$, $b = 0.77[0.19, 1.35]$. The normalised mean squared error of the scaling is $\text{NMSE} = 0.1668$

d_p [μm]		250	100	55
Sh [–]	exp. run 1	561.30 (± 90.51)	242.82 (± 71.46)	99.83 (± 32.24)
	exp. run 2	1050.09 (± 85.03)	214.78 (± 58.44)	77.09 (± 23.56)
	exp. run 3		163.12 (± 63.13)	

Appendix E

Chapter 8: Result and Error Values

Table E.1: Exponents of the power law fittings (at^b) determined in the advanced convective regime for the moments of mass and the dilution index including the 95 % confidence bounds for the fitted exponents.

	Bentheimer	Boise	Mt Gambier
Total mass M_{norm}			
Coefficient a	0.01 (0.01, 0.01)	0.03 (0.02, 0.05)	0.10 (0.09, 0.10)
Coefficient b	1.11 (1.08, 1.15)	1.02 (0.89, 1.16)	0.81 (0.78, 0.84)
Centre of mass Y_{com}/H			
Coefficient a	0.01 (0.01, 0.02)	0.02 (0.01, 0.02)	0.07 (0.07, 0.08)
Coefficient b	0.86 (0.82, 0.90)	1.03 (0.93, 1.12)	0.63 (0.61, 0.64)
Standard deviation σ/H			
Coefficient a	0.01 (0.01, 0.01)	0.01 (0.01, 0.01)	0.02 (0.02, 0.03)
Coefficient b	1.34 (1.30, 1.38)	1.21 (1.10, 1.32)	0.89 (0.85, 0.93)
Dilution index E/E_{max}			
Coefficient $a / 10^{-5}$	1.78 (1.13, 3.42)	2.18 (0.16, 4.20)	42.35 (34.68, 50.02)
Coefficient b	1.31 (1.26, 1.35)	1.39 (1.26, 1.52)	1.08 (1.05, 1.11)

Table E.2: Exponents of the power law fittings (at^b) of the dilution index E/E_{max} determined in the advanced convective regime for the the dilution index including the 95 % confidence bounds for the fitted exponents.

d_p [μm]	250	100	55
coefficient $a / 10^{-2}$	16.55 (12.5, 20.6)	5.67 (4.39, 6.94)	1.09 (0.72, 1.46)
coefficient b	0.58 (0.44, 0.73)	0.67 (0.60, 0.73)	0.78 (0.71, 0.86)

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