




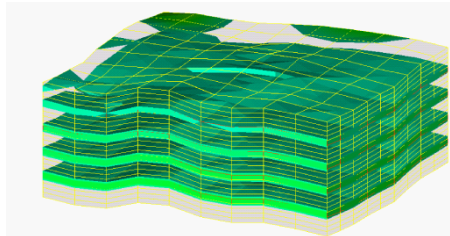
Interactions between CO₂, saline water and minerals

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The degree philosophiae doctor

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Preface

The thesis is produced as a part of the NFR project No. 151400/210 “Model studies of safe long term storage of CO₂ in aquifers”. The main aim of the project is to investigate the potential of long term disposal of CO₂ in deep saline aquifers and reservoirs using computational techniques. Such CO₂ injections represent complex and difficult processes, which push computational resources to its limits. The goal is to study some of the main mechanisms for CO₂ trapping in different types of reservoirs and to further develop the necessary computational tools for such tasks. The ongoing CO₂ injection into the Utsira Formation from the Sleipner West facility is a main focus with respect to the development and testing of the numerical tools. One central task for the project is to develop the Secondary Oil Migration (SOM) simulator to a full reactive transport simulator for CO₂ storage problems. This version of the SOM simulator has recently been renamed ATHENA.

The development of the ATHENA code requires inclusion of geochemical calculations such as equations covering interactions between minerals and formation waters. The geochemistry code ACCRETE is developed for this purpose and is the main goal for the present PhD study. The ACCRETE code is called as an external module for each Athena time step and updates the geochemistry according to directives given by the ATHENA code. ACCRETE can also be run as a stand-alone batch geochemistry solver. The present ACCRETE version simulates interactions between 16 mineral phases, 14 aqueous species, and CO₂ as a separate gaseous or supercritical phase.

In addition to work related to the numerical code, the thesis also comprises experimental work on reaction kinetics of the carbonate mineral dawsonite (NaAl(OH)₂CO₃). This mineral is believed to play a significant role during CO₂ storage. The thesis presents the first reported data on dawsonite reaction kinetics and is as such valuable for further experimental studies on dawsonite as well as numerical studies including the mineral.

The project combines personal and resources from Departments of Physics and Technology and Department of Mathematics at the University of Bergen. The thesis consists of five papers which of three papers are accepted or submitted to international journals, and two papers are conference proceeding, one submitted and one published.

Acknowledgements

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During three years as a PhD student I have had the chance to work in an interdisciplinary environment with physicists and mathematicians at the University of Bergen. My background as a geochemist has provided both me and my colleagues with plentiful of challenges both with respect to communication and common work tasks. I have learned a great deal from working in an interdisciplinary environment.

I would first like to thank Bjørn Kvamme for introducing me to the Department of Physics and Technology, to my work tasks as a geochemist in the project, and to advice me through my PhD. I highly appreciate both formal and informal dialogs with Bjorn.

I would also like to thank Per Aagaard at Department of Geosciences at the University of Oslo for advices regarding geological and geochemical issues, for introducing me to laboratory work and staff at Université Paul Sabatier/CNRS-UMR in Toulouse, and for the great hospitality he has showed me both in Toulouse and during short visits to Oslo. Dialogs with Per have been of great value for understanding the water-rock interactions we are modeling in the project. I highly appreciate the freedom Bjorn and Per have given me to follow up ideas that has emerged during the project.

During the second year of my PhD I got the opportunity to do laboratory work at Université Paul Sabatier/CNRS-UMR in Toulouse. I was introduced to Eric Oelkers, Jacques Schott, and several other highly skilled geochemists and technicians at their laboratories. I highly appreciate the hospitality they all showed me, all help they provided during my laboratory work, and for interesting and constructive discussions.

I highly appreciate the daily coffee breaks and discussions with my brother Bjarte and other friends at Department of Earth Science, and with other friends and colleagues at the University of Bergen.

Finally I would like to thank the administrative and technical staff at Department of Physics and Technology for always showing a positive attitude and for all the help they have given during my work.

Helge Hellevang

Bergen, April 2006.

List of papers

The thesis is based on the following papers:

Paper A:

Hellevang, H., Aagaard, P., Oelkers, E.H., and Kvamme, B., 2005. Can dawsonite permanently trap CO₂? *Environmental Science and Technology*, **39**, 8281-8287.

Paper B:

Hellevang, H., Kvamme, B., and Aagaard, P., 2004. Long term interactions between minerals and reactive fluids - Stability of dawsonite. *In Proceedings of the Third Annual Conference on Carbon Capture and Sequestration DOE/NETL, Alexandria, VA, May 3-6, 1-7*

Paper C:

Hellevang, H., and Kvamme, B. CO₂-water-rock interactions - ACCRETE simulations of geological storage of CO₂. Submitted to *Applied Geochemistry*.

Paper D:

Hellevang, H., Kumar, S., Fladmark, G., and Kvamme, B. CO₂ storage in the Utsira Formation – ATHENA 3D reactive transport simulations. Submitted to *Basin Research*.

Paper E:

Hellevang, H., and Kvamme, B. 2006. ACCRETE – Geochemistry solver for CO₂-water-rock interactions. Paper submitted to *GHGT8*, Trondheim, June 19-22, 2006.

Paper F:

Khatti, S.K., Hellevang, H., Fladmark, G.E., and Kvamme, B. 2006. Deposition of Green House Gases by Compositional Simulator: Long Term Reactive Transport of CO₂ in the Sand of Utsira. Submitted to *Transport in Porous Media*.

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PART II

Paper A: Can dawsonite permanently trap CO₂?

Paper B: Long term interactions between minerals and reactive fluids - Stability of dawsonite.

Paper C: CO₂-water-rock interactions - ACCRETE simulations of geological storage of CO₂.

Paper D: CO₂ storage in the Utsira Formation – ATHENA 3D reactive transport simulations.

Paper E: ACCRETE – Geochemistry solver for CO₂-water-rock interactions.

Paper F: Deposition of Green House Gases by Compositional Simulator: Long Term Reactive Transport of CO₂ in the Sand of Utsira.

Appendix A: Reactions and equations

i – x

Appendix B: Interface and IO

xi – xvi

Nomenclature

Constants and variables:

T	Temperature (K)
P	Pressure (bar)
ϕ	Fugacity coefficient ($1/P$)
a	Activity
f	Fugacity
y	Fraction gas in a gas mixture
$a, b, v, \zeta, \Omega_a, \Omega_b, \omega$	<i>SRK EOS</i> parameters
Z	Compressibility factor
α, β, A, B	Truesdell-Jones parameter
\bar{V}	Molar volume
ΔG_f	Gibbs free energy of formation
ΔG_R	Gibbs free energy of a reaction
ΔH_R	Enthalpy
ΔS_R	Entropy
ΔC_P	Constant pressure heat capacity
n	Moles
M	Molar mass
m	Mass (g)
C	Molar concentration (n/dm^3)
μ	Chemical potential
γ	Activity coefficient for ionic species.
x_{CO_2}	Molefraction CO_2 (n/n)
v	Reaction stoichiometric coefficient for ions
E_a	Apparent activation energy used for mineral kinetics
H_{CO_2}	Henry's law coefficient
K	Equilibrium constants for reactions
k	Kinetic constant (n/m^2s)
r	Rate (n/s)
R	Gas constant ($8.3145kJ/nK$)
S	Reactive surface area
s	Specific BET surface area
SI	Solubility index $\log(q/K)$
q	Ion activity product
Ω	q/K
ρ	Density CO_2 or aqueous phase

Part I

Chapter 1

Introduction

Increasing atmospheric concentrations of greenhouse gases may potentially lead to global climate changes. The 2002 global fossil-fuel CO₂ emission was estimated to approximately 7 Gt (Giga tons) of carbon with a 2% increase from 2001 (Marland et al., 2005). This increase is proportional to a global increase in demand for fossil fuel. Different strategies have been suggested of how to reduce CO₂ emissions. Ocean storage, replacement of methane by CO₂ in hydrate reservoirs, and storage of CO₂ into geological formations (coal seams, depleted oil reservoirs, producing oil reservoirs, saline aquifers, etc.), are some examples that are currently being investigated as feasible options for reducing emissions. This chapter gives a short introduction into different storage approaches, and a short introduction to the Sleipner injection site that is currently injecting CO₂ into the Utsira Formation. Both physical and chemical data from this site is used as a part of this study. Finally, the structure and contents of the thesis is presented.

CO₂ storage approaches

Ocean storage

The global ocean system has a large potential in retaining large amounts of CO₂, and can be considered as a natural buffer for changes in the atmospheric gas contents. A great deal of work, both experimentally (e.g., Ozaki et al., 1995; Aya et al., 2004) and theoretically (e.g., Ametistova et al., 2002; Kvamme, 2003; Chen et al., 2004), has been done in recent years. Ocean storage can grossly be divided into four different categories: (1) direct ocean storage at mid-level depths where $\rho_{CO_2} < \rho_{H_2O}$ (e.g., Aya et al., 2004); (2) direct ocean storage at depths larger than approximately 3500 meters where $\rho_{CO_2} \geq \rho_{H_2O}$ (e.g., Ozaki et al., 1995); (3) ocean storage into the seabed sediments (e.g., Koide et al., 1997); and (4) waste-stream storage of CO₂ by on-land reactions with carbonates to produce bicarbonate solutions that is dispersed into oceans or lakes (e.g., Rau and Caldeira, 1999). Of these four methods deep sea sequestration and injection into seabed sediments seems most promising as this could lead to retention of CO₂ for thousands of years. Transport of the CO₂ to great depths (>3.500 meters) is however challenging both technologically and economically. One issue that is seen by some as a limitation is possible unwanted impacts on the oceans biosphere. For example, dissolution of CO₂ into the ocean lowers the pH and the effect this has on the biosphere is largely unknown. Haugan et al., (1995) simulated sequestration of liquid CO₂ droplets at 1000 meters depth, the formation of a rising CO₂-affected plume, and concluded that zones with highly time variable pH and very low pH values could possibly form.

Hydrate reservoirs

Recent estimates indicate that the gas hydrates constitutes the largest accumulations of natural gas on Earth (Collet, 1994). CO₂ hydrate is thermodynamically significantly more stable than methane hydrate, and exploitation of methane hydrates through replacement with CO₂ is therefore considered as an interesting option of storage of CO₂ (Kvamme et al., 2004). This is still a novel concept, but both experimental work using magnetic resonance imaging (Kvamme et al., 2004; Graue et al., 2003) and theoretical work on hydrate growth (e.g., Kvamme, 2002) is at present on an advanced stage. One difficulty that may be encountered during hydrate exploitation is *in situ* separation of produced methane from injected CO₂. Effective dispersion of injected CO₂ in the reservoir to the methane hydrate interface may also be challenging.

Storage in geological formations

Capture of CO₂ from large anthropogenic point sources and capture in geological formations proximal to the source has received increasing attention as a safe and long-term storage option. The safety of the injected CO₂ on a short timescale is related to buoyancy driven flow of the immiscible part of the injected CO₂ and the trapping capabilities of the formation. On a longer timescale most CO₂ dissolves into the formation water, reacts with the formation minerals, and precipitate as carbonate minerals. This latter trapping mechanism is regarded as long-term or permanent storage. The present study focuses on this slow conversion from gaseous- or supercritical CO₂ to stable carbon minerals. A comprehensive introduction to geological

storage is given by Bouchard and Delaytermoz (2004). Storage reservoirs comprise for example deep unminable coal seams, saline aquifers, and abandoned oil and gas reservoirs. Geological storage can in addition be used in combination with enhanced oil or gas exploitation. Worldwide numerous sites can be regarded as potential storage sites, and the total CO₂ storage potential is vast.

CO₂ injection into the Utsira Formation

The first industrial scale CO₂ injection started in 1996 at the Sleipner injection site in the North Sea. Approximately 1 Mt is annually injected from the site (Korbøl and Kaddour, 1995). The CO₂ is injected at around 1000 meters into the Utsira Formation beneath a domal structure. The formation consists mainly of fine sands and silts interrupted by thin clay horizons (Zweigel et al., 2004). The sandy part of the formation, termed as the Utsira Sand, corresponds to the sandy part of the Utsira Formation. The sands extend for more than 400 km from north to south, reaching up to approximately 100 km in an east-west direction, and cover a total area of more than 26.000 km² (e.g., Gregersen et al., 1997; Torp and Gale, 2004; Chadwick et al., 2004). The total storage potential for the Utsira Sand is enormous and has been estimated to 6.6x10⁸ m³.

The immiscible CO₂, with its lower density than the formation water, is visible on seismic images. Injected CO₂ in the Utsira Sand is monitored by comparing seismic data sampled prior to injection with post-injection data (Arts et al., 2004). The data presented are valuable both with respect to assessing leakage potentials as well as providing information that is used

in relation to development and testing of numerical tools.

Structure and contents of the thesis

The topic of this thesis is to gain a better understanding of interactions between injected CO₂, aqueous solutions and formation mineralogies. The main focus is concerned with the potential role mineral reactions play in safe long term storage of CO₂. The work is divided into an experimental part concentrated on the potential of dawsonite (NaAl(OH)₂CO₃) as a permanent storage host of CO₂, and the development of a new geochemical code ACCRETE that is coupled with the ATHENA multiphase flow simulator.

The thesis is composed of two parts: (I) the first part introducing CO₂ storage, geochemical interactions and related work; and (II) the second part that consists of the papers. Part I is composed as follows: Chapter 2 gives a short introduction to geochemical reactions considered important during CO₂ storage, including a thermodynamic framework. Chapter 3 presents objectives of numerical work related to CO₂-water-rock interactions including a discussion of factors that influence the outcome of numerical simulations. Chapter 4 presents the main results from paper A to E. Chapter 5 give some details about further research that we propose based on the present work and related work in the project. Several new activities have emerged from research on CO₂-water-rock interaction during the project. Several of the proposed activities are already initiated. Papers A to F are then listed in Part II of the thesis after the citation list. The thesis presents the first data on the reaction kinetics of dawsonite at different pH (Paper A), and

comprehensive numerical simulations, both batch- and large scale 3D reactive transport, that illustrate the role different carbonates have for safe storage of CO₂ in geological formations (Papers C to F). The role of dawsonite in CO₂ storage settings is treated throughout the study (Papers A to E)

After the main part of the thesis (Part I and II), two appendices are included: Appendix A lists reactions that are included in the ACCRETE code, and corresponding equations that are solved; whereas Appendix B explains shortly how to use the ACCRETE geochemistry code in stand-alone simulations or coupled with the ATHENA code.

Chapter 2

CO₂-water-rock interactions

Geochemical reactions involved during CO₂ storage comprise interactions between CO₂, formation waters, and minerals. This chapter presents the thermodynamic framework and defines some key parameters that are needed to describe such interactions. The second part of the chapter presents some of the reactions that are expected to occur during CO₂ storage.

Thermodynamic framework

Standard states

The standard state adopted in this study is that of unit activity for pure minerals and H₂O at any temperature and pressure. For aqueous species other than H₂O, the standard state is unit activity of the species in a hypothetical 1 molal (mol/Kg) solution referenced to infinite dilution at any temperature and pressure. For gases, the standard state is for unit fugacity of a hypothetical ideal gas at 1 bar pressure. The superscript θ is used in the following chapters to denote standard state.

Fugacity

Fugacity f can be defined as the pressure value needed at a given temperature to make the properties of a non-ideal gas satisfy the equation for an ideal gas, i.e.,

$$f_i = \phi_i P y_i, \quad (1)$$

where ϕ and y are the fugacity coefficient and fraction of gas i respectively, and P is total pressure. A more rigorous thermodynamic definition of fugacity can be expressed by the difference in chemical potential at two different pressures:

$$\mu_2 - \mu_1 = RT \ln \left(\frac{f_2}{f_1} \right), \quad (2)$$

which can be expressed by change in molar volume as:

$$RT \ln \left(\frac{f_2}{f_1} \right) = \int_{P_1}^{P_2} \bar{V} dP. \quad (3)$$

Adding and subtracting the quantity RT/P in the integrand gives:

$$\begin{aligned} RT \ln \left(\frac{f_2}{f_1} \right) &= \int_{P_1}^{P_2} \left[\frac{RT}{P} + \left(\bar{V} - \frac{RT}{P} \right) \right] dP \quad (4) \\ &= RT \ln \left(\frac{P_1}{P_2} \right) + \int_{P_1}^{P_2} \left(\bar{V} - \frac{RT}{P} \right) dP \end{aligned}$$

Since the ratio f_1/P_1 becomes unity when P_1 approaches zero, rearranging equation (4) leads to:

$$\begin{aligned} \ln \left(\frac{f}{P} \right) &= \int_{P=0}^{P=P} \left(\frac{\bar{V}}{RT} - \frac{1}{P} \right) dP \quad (5) \\ &= \int_{P=0}^{P=P} \frac{1}{P} (Z - 1) dP \end{aligned}$$

where $Z = PV/RT$ is the compressibility factor for the gas. Z can be estimated using an equation of state (EOS) that is appropriate for the gas in question. In this work the Soave-Redlich-Kwong EOS (Soave, 1972) has been chosen to estimate CO₂ fugacity.

Soave-Redlich-Kwong equation of state

The cubic Soave-Redlich-Kwong (SRK) equation of state can be expressed as:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}, \quad (6)$$

where SRK parameters a and b are given by:

$$a(T) = \Omega_a \frac{R^2 T_c^2}{P_c} \zeta(T), \quad (7)$$

and

$$b = \Omega_b \frac{RT_c}{P_c}, \quad (8)$$

respectively, where T_c and P_c denotes critical temperature and pressure respectively, and $\zeta(T)$ is calculated by:

$$\zeta(T) = 0.48 + 1.574\omega - 0.176\omega^2. \quad (9)$$

The Ω_a and Ω_b are dimensionless constants with values of 0.42747 and 0.08664 respectively.

Activity

In much the same manner as the partial pressure of a gas has to be corrected for non-ideality by a fugacity coefficient, concentrations of ionic species need a correction term if the species occupy non-ideal solutions, i.e. solution that deviates significantly from infinite dilution. A non-ideal concentration is referred to as activity, and the correction term is an activity coefficient. The thermodynamic definition of activity can be expressed as:

$$\begin{aligned} \mu_i &= \mu_i^\theta + RT \ln \mathbf{a}_i \\ &= \mu_i^\theta + RT \left\{ \ln \left(\frac{m_i}{m_i^\theta} \right) + \ln \gamma_i \right\}, \end{aligned} \quad (10)$$

, where \mathbf{a}_i is activity, m_i is molar concentration (mol/l), and γ_i is the activity coefficient for ion i respectively.

Different models, many of which are extensions of the Debye-Hückel theory, account for electrostatic interactions between charged ions. The Truesdell-Jones activity model (Truesdell and Jones, 1974) is extended to take account for ion-specific interactions and is regarded as reliable for up to 2N NaCl dominated solutions. Equation (6) shows the Truesdell-Jones model for charged ionic species i :

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + \alpha_i B \sqrt{I}} + \beta_i I, \quad (11)$$

where z , α , and β are charge and ion specific parameters respectively, and A and B are Debye-Hückel parameters. In this work the Truesdell-Jones model is used for charged species, whereas non-charged species like H₂O, SiO_{2, aq}, and CO_{2, aq} are assumed to have unit activity.

Equilibrium constants

Standard state equilibrium constants for CO₂-water-rock interactions are calculated from the Gibbs free energy of the reactions according to:

$$K_r^\theta = e^{-\frac{\Delta G_R^\theta}{RT}}, \quad (12)$$

where the free energy is calculated from standard free energy of formation of the components that constitute the reactions:

$$\Delta G_R^\theta = \sum_{p=1}^{N_p} \Delta G_p^\theta \nu_p - \sum_{r=1}^{N_r} \Delta G_r^\theta \nu_r, \quad (13)$$

where subscripts p and r denotes product and reactant respectively, and ν is the stoichiometric coefficient of the products

and reactants. At higher temperatures than standard state conditions the equilibrium constants can be estimated from the partial differentiate of the Gibbs free energy with respect to temperature at constant pressure:

$$\left(\frac{\partial \ln K_R}{\partial T}\right)_P = -\frac{1}{R} \left\{ \frac{\partial}{\partial T} \left(\frac{\Delta H_R^\theta(T) - T\Delta S^\theta(T)}{T} \right) \right\}_P, \quad (14)$$

where ΔH , ΔS , and ΔC_p are enthalpy, entropy, and heat capacity of the reactions respectively. Integrating this expression gives equation (15):

$$K = K^\theta \cdot \exp \left\{ - \int_{T^\theta}^T \frac{\Delta H_r^\theta(T^\theta, P^\theta) + \int_{T^\theta}^T \Delta C_{p,r}(\tau, P^\theta) d\tau}{R} d\left(\frac{1}{T}\right) \right\} \quad (15)$$

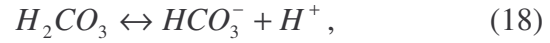
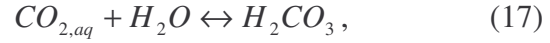
CO₂ dissociation and speciation

The amount of CO₂ that dissolves into an aqueous phase is determined by the salinity of the aqueous solution as well as temperature and pressure. The bubble point mole fraction of CO₂ can be estimated according to:

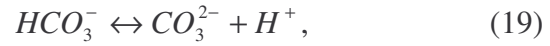
$$x_{CO_2}^b = \frac{Py\phi}{H_{CO_2}} \cdot \exp \left\{ \frac{\bar{V}_{CO_2}}{RT} (1-P) \right\}, \quad (16)$$

where ϕ , and H_{CO_2} are fugacity coefficient and Henrys law coefficient for CO₂ respectively, P is total pressure, and y is the fraction of CO₂ in a gas mixture. The Henrys law coefficient is strongly a function of salinity and temperature and is corrected for pressure by a pointing

correction term, whereas the fugacity coefficient is a function of temperature and pressure. The dissolved CO₂ reacts with water in the aqueous solution and forms carbonic acid, bicarbonate, and carbonate ions according to:

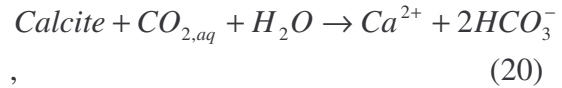


and



The sum of mole fractions of these species is at maximum at the bubble point when the sum equals the bubble point mole fraction. Release of H⁺ ions caused by CO₂ dissolution (see Eq. 17-19) acidifies the aqueous solution during CO₂ injection. The pH drop is proportional to the amount that dissolves, but is also a function of the pH-buffering capacity of the water-rock system. For example will the presence of fast dissolving carbonates like calcite buffer a pH drop.

The calcite dissolution reaction can be expressed by:



where the *pH* buffering effect of the reaction is given by the balanced addition of positive and negative charges to the solution by Ca^{2+} and HCO_3^- respectively. While Ca^{2+} is non-reactive in the solution, HCO_3^- is reduced by reactions with other species in the carbonate system (see Hellevang & Kvamme, 2006, for details). This leads to a net increase in positive charges in the solution. Using the criteria of electroneutrality we may express the concentration of H⁺ in terms of all the

other ion concentrations in the solution. Expression (21) shows pH defined by the sum of molar concentrations of all N dissolved ions excluding H^+ :

$$pH = -\log_{10} \left\{ -\gamma_{H^+} \sum_i^N m_i z_i \delta_i \right\},$$

$\delta_i = 0$ for $i = H^+$
and $\delta_i = 1$ for other ions i , (21)

where z is the charge, m is molar concentration and γ is the activity coefficient of H^+ . From this expression we see that a net increase in positive charge induced by calcite dissolution results in higher pH.

Mineral reactions

As CO₂ is injected and dissociates into the aqueous phase, pH drops and primary minerals that comprise the reservoir destabilize and start to dissolve. Eventually, new carbonate and silicate phases start to precipitate. Thus, the minerals that need to be considered as important during CO₂ storage are both the primary phases present before injection, and new secondary phases that are likely to form. Most mineral reactions that are considered with respect to CO₂ storage fall into two groups: silicate- and carbonate reactions. These two groups are presented shortly in the following sections.

Silicate reactions

Silicate reactions that need to be considered with respect to CO₂ storage are those commonly encountered in target reservoirs as well as possible secondary phases that may be important in

controlling the activities of ionic species in the aqueous solution. The importance of silicates may be evaluated according to: (1) their cation content; (2) their dissolution kinetics; and (3) their abundance. The cation content is instrumental in contributing constituents for the carbonate reactions. The divalent cations Mg²⁺ and Fe²⁺ are commonly found in phyllosilicates like glauconite, phlogopite, annite, and clinocllore, whereas minerals in the plagioclase solid solution series (albite to anorthite) contribute with Ca²⁺ ions. The dissolution kinetics of the silicates controls how fast the cations can be contributed to the solution at subsaturation. This varies from relatively fast reactions at the anorthite end of the plagioclase solid solution (e.g., approximately 2×10^{-10} n/m²s for labradorite; Carroll and Knauss, 2005) to slow phyllosilicate dissolution ($1-4 \times 10^{-13}$ n/m²s; e.g., Nagy, 1995). The abundance of silicate varies strongly from reservoir to reservoir. Some reservoirs are almost pure quartz sands with limited potential to store significant amounts of CO₂ as solid carbonates, whereas other reservoirs contains a substantial fraction of minerals that can contribute significantly to CO₂ storage.

Carbonate reactions

Solid carbonates are regarded as permanent storage hosts for injected CO₂. The nature of the precipitates is, with a perspective of hundred to thousands of years, strongly related to the initial reservoir mineralogy, whereas the water chemistry is crucial on a shorter timescale (a few years). If injection occurs in carboniferous silicate reservoirs or in carbonate reservoir, carbonate will initially dissolve to equilibrium and release CO₂ to

the aqueous solution. In this case it will take considerable time before the amount of CO₂ stored in solid carbonates is higher than what was initially present. If, on the other hand, the injection occurs in a pure siliclastic reservoir with no carbonate initially present, the CO₂ that is stored permanently is directly proportional to the amount of carbonate that form. Some of the carbonates that are likely to form are the divalent metal carbonates Calcite (CaCO₃), magnesite (MgCO₃), and siderite (FeCO₃), and the sodium aluminium carbonate dawsonite (NaAl(OH)₂CO₃).

Precipitation of the divalent metal carbonates requires that their constituent metal ions in addition to dissolved carbonate are present in the solution. Divalent metal ions commonly show low concentrations in saline aqueous solutions, or are already equilibrated with carbonates present in the reservoir. Thus, aqueous solutions by themselves are not likely to contribute significantly to long term storage of CO₂. Dissolution of silicate minerals like labradorite, glauconite or daphnite (see previous section for details) on the other hand can provide large amount of divalent metals. For example could dissolution of 1 mole of daphnite result in precipitation of 5 moles of siderite. Most silicate reactions are however slow, and timeframes of hundreds to thousands of years are commonly required to achieve carbonate precipitation in significant amounts.

Dawsonite precipitation is bound by the abundance of sodium, aluminium, and dissolved CO₂ in solution. Sodium is commonly highly concentrated in formation waters (>0.5N), whereas aluminium show low concentrations in most formation waters. As in the case with divalent metal carbonates, aluminium has to be provided from silicate dissolution. Since the concentration of aluminium is

very limited at close to neutral solutions, it has been suggested that dawsonite may only form during CO₂ injection at a narrow pH range at high sodium concentrations and at high CO₂ fugacities. Formation of dawsonite is supported by numerical simulations of CO₂ storage using different mineralogies, aqueous solutions, and at different temperatures and pressures (e.g., Johnson et al., 2001, 2004; White et al., 2003; Xu et al., 2004; Knauss et al., 2005). Also activity-fugacity diagrams such as Fig. 1 suggests that dawsonite show relative stability compared to the silicates at elevated CO₂ fugacities and at high sodium concentrations. Fig. 1 shows the dawsonite stability field relative to kaolinite and albite. Two different likely fluid composition paths are traced: (1) a dashed line that corresponds to the composition of seawater equilibrated with varying fugacities of CO₂; and (2) a fluid composition path shown as solid line that corresponds to the composition of seawater equilibrated simultaneously with varying fugacities of CO₂ and calcite. In the former case, dawsonite is not stable at any temperatures and CO₂ fugacities, whereas the pH-buffering effect of the calcite reaction in the latter case stabilize dawsonite even at fairly low CO₂ fugacities.

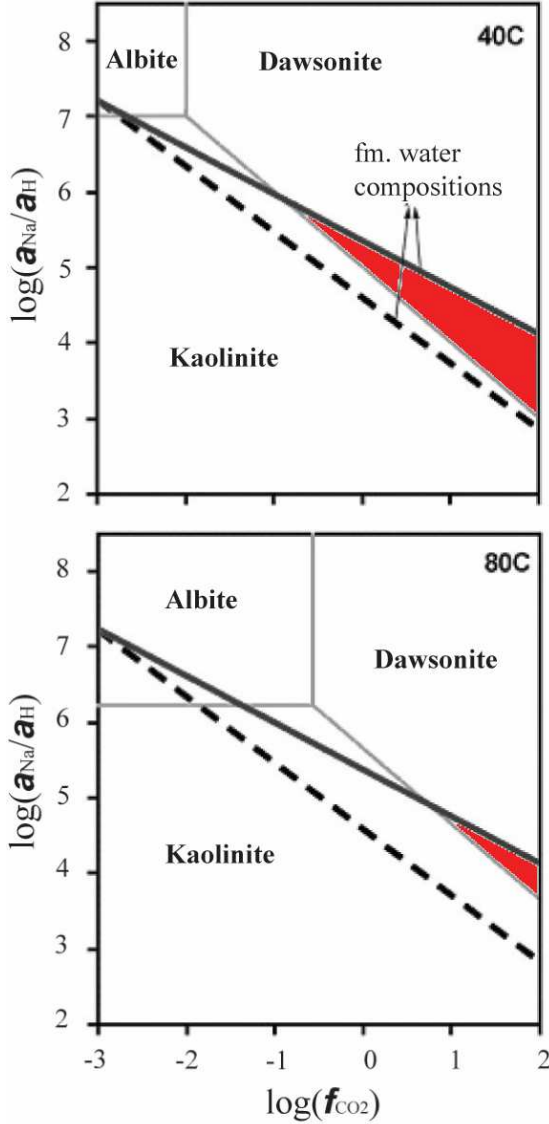


Fig. 1. Log fugacity-activity diagram depicting mineral stability fields in the system Na₂O-Al₂O₃-SiO₂-CO₂-H₂O at 40 and 80°C. The dashed and solid lines represent different formation water compositions. The colored field suggests the dawsonite stability region given a particular formation water composition (Modified from Hellevang et al., 2005).

Kinetics of mineral reactions

Mineral kinetics may be expressed by a general rate law according to Lasaga (1995, 1998):

$$r = k_{298} \cdot S \cdot e^{-\frac{E_a}{RT}} \cdot g(I) f(\Delta G_r) \cdot \prod_i a_i^{n_i}, \quad (22)$$

where k_{298} is the far-from-equilibrium rate constant valid at 298 K, S is the reactive surface area of the mineral, E_a is the apparent activation energy of the reaction, functions g and f provides rate dependence on ionic strength and distance from equilibrium respectively, and n provides inhibiting or catalyzing effects of ions i . Rate constants and temperature dependences are published for a large number of dissolution reactions. However, data is still lacking for minerals, some of which are considered as major participants in geological storage of CO₂ (e.g., some clay minerals). Thus, numerical simulations usually have to adopt known data from some reactions and use the same kinetic parameters for compositional or structural similar minerals. The reactive surface area of minerals is usually estimated either geometrically or by using B.E.T. (Brunauer et al., 1938) data. The former assumes that the total surface area can be approximated by a simple geometry, e.g. spherical, and an average mineral size (radius), and that the reactive surface area is a given fraction of the total surface. The B.E.T. method provides information about the adsorption of some inert gas molecule like N₂ on the surface. It is important to remember that reported experimental rate constants are surface normalized, and that the same convention should be used when calculating reactive surface areas for simulations as was used in the experimental work. According to the transition state theory (TST) the function f can be generalized to (Aagaard and Helgeson, 1982):

$$f(\Delta G_R) = 1 - \exp\left(\frac{\Delta\mu_R}{\sigma RT}\right), \quad (23)$$

where σ is the ratio of the rate of destruction of precursor complexes relative to the overall dissolution rate, and $\Delta\mu$ denotes the difference in chemical potential between equilibrium and the solution chemistry.

Numerical codes usually employ expressions that represent simplifications and variations of expression (20). For example is the reaction kinetics usually unaffected by ionic strength (e.g., Xu et al., 2004; Johnson et al. 2001; Gaus et al., 2003), and pH dependence is either not reported (e.g., Johnson et al., 2001; 2004), or simplified (e.g., Gaus et al., 2003). Simulations in this study use a general expression for all minerals derived from equation (20) without pH dependence and ionic strength dependences:

$$r = k_{298} \cdot \exp\left\{\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{298}\right)\right\} S \cdot (\Omega - 1), \quad (24)$$

where Ω is the solubility index expressed by:

$$\Omega = \frac{q}{K}, \quad (25)$$

where q is the ion activity product and K is the equilibrium constant for the reaction respectively.

Observed mineral reactions from natural occurring CO₂ reservoirs

Naturally occurring CO₂ deposits can be regarded as large-scale natural laboratories and they provide excellent

opportunities to study long-term CO₂-water-rock interactions. Such natural deposits occur worldwide in a wide range of different sediments and rock types. Examples of such deposits are the Springerville-St. Johns CO₂ field in USA, the Ladbroke Grove and Katnook gas fields in Australia, as well as several natural analogues in Europe (Stevens et al., 2001; Pearce et al., 2004). Since pure quartz sandstones and carbonate reservoirs show low potential of solid carbonate storage relative to sands with abundant aluminosilicates (e.g., Baines and Worden, 2004), the following examples of natural CO₂ storage is concerned with the latter types of reservoirs.

The Springerville-St. Johns CO₂ field is one of several similar reservoirs developed in domed Mesozoic and Paleozoic sedimentary rocks of the Colorado Plateau and Southern Rocky Mountain region of the western U.S. (Moore et al., 2003). Detailed petrographic analyzes were done for well 22-1X from depths between 462 to 472 meters, that represented the only interval that showed clear evidence for interactions with CO₂ charged fluids (Moore et al., 2003). The major reactions observed in the interval were dissolution of authigenic cements, dissolution of detrial feldspar grains, and formation of dawsonite and kaolinite. Textural evidence suggests that early dolomite and hematite was followed by anhydrite and calcite cements. Dawsonite and kaolinite is interpreted to be the latest phases, with kaolinite inferred to be the youngest of the two. While dawsonite is limited to the interval between 462 and 472 meters, Kaolinite is a common mineral in core samples from all wells and generally comprises from 2 to 7 weight% of the rock.

The Ladbroke Grove and Katnook gas fields are located within the Penola

Through of western Otway Basin (Watson et al., 2004). Recent volcanic activity (<1 Ma) lead to CO₂ migration into the Pretty Hill Formation, with CO₂ levels that range from 26 to 57 mol% in the Ladbroke Grove Field. The same formation in the Katnook Field less than 1 km away is charged with pure methane (Watson et al., 2004). The recent influx of CO₂ together with the difference in CO₂ levels makes these fields excellent as a natural laboratory for studying CO₂-water-rock interactions. The major reactant minerals interpreted to be in the formations prior to the CO₂ influx are feldspars, volcanic rock fragments, chlorite, and calcite. The feldspars are predominantly altered to sodium plagioclase, whereas the chlorite resulted from chloritization of volcanic rock fragments. Both these alterations are interpreted to be prior to the influx of CO₂. Calcite occurs as a cementing phase in concretions up to 5 cm in size. The minerals in the Pretty Hill Formation in the Ladbroke Grove Gas field show extensive evidence of interactions with CO₂. The main mineral products are secondary quartz, kaolinite, and ferroan carbonates. The chlorite in Katnook is almost totally replaced by kaolinite. Calcite cements as found in Katnook is only present below the gas-water contact in the Ladbroke field. Textural evidence suggests that secondary ferroan and magnesian carbonates like ankerite has grown as replacement of pre-CO₂ mineral phases. One important observation is that the porosity in Ladbroke only shows a slight increase because caused by the mineral reactions, whereas the permeability shows a significant increase, caused by dissolution of carbonate cements opening pore throats. Permeability of Ladbroke and Katnook are around 52 and 28 mD respectively (Watson et al., 2004).

Experimental work relevant to CO₂-water-rock interactions

Experimental work with aim to increase the understanding of CO₂-water-rock interactions can grossly be divided into two groups: (1) Large- or small scale experiments on 'real' material; and (2) experimental work on parts of the 'real' system.

The first type of experiments comprises both field scale in-situ CO₂ experiments (e.g., Hovorka, 2004; Worden and Smith, 2004), as well as laboratory scale batch or flow-through experiments (e.g., Pearce et al., 2000). In both cases short term effects, like fast dissolution of existing carbonates, can be observed on the geochemistry of the waters. The experiments are however too short to assess the long-term effects of water-rock interactions.

The second type of experiments study interactions between simplified mineralogies and aqueous solutions. This kind of experimental work typically produce data like thermodynamic stability and reaction kinetics of individual minerals (e.g., Busenberg and Plummer, 1986; Pokrovsky and Schott, 1999; Gautelier et al., 1999; Cubillas et al., 2004). These data are useful in numerical analyze of long-term interactions. Present day databases that contain data on thermodynamic stability and mineral reaction kinetics are, with respect to reactions that are assumed to play significant roles during CO₂ storage, far from complete. This may strongly affect the outcome of numerical analyzes.

Chapter 3

Numerical work related to CO₂ storage

Numerical analyses can be used to assess the fate of injected CO₂ both on short- and long timescales and can be used complementary to experimental work. The results of simulations are limited by the accuracy of input such as thermodynamic and kinetics data of individual mineral reactions. The numerical simulations are thus not only complementary, but also strongly reliant to experimental work. This chapter gives a short introduction to the objectives of running numerical simulations and examples of information we can gain. It also lists some of the factors that may influence the outcome of numerical simulations.

Objectives of numerical simulations

Information available from experimental work is more or less limited by the timeframe of experiments and by necessary simplifications done on experimental systems. Upscaling in time and in complexity by combining individual experiments is far from trivial. The main objective of numerical studies is to do such upscaling.

Numerical studies related to CO₂ storage can be divided into estimations of the short-term fate of injected CO₂, with timescales of a few years up to tens of years, or simulations to assess the long-term stability of CO₂ for thousands of years. The objective of simulations that cover a few years is usually to understand the flow of immiscible CO₂, trapping beneath low-permeable structural features, and possible leakage to the surface. Examples of recent works related to flow and leakage of CO₂ are Nordbotten et al. (2004; 2005a, b), whereas Johnson et al. (2001; 2004) shows short-term 2D reactive transport simulations to assess information on solubility of CO₂, immiscible flow, pH changes, and mineral reactions. Expansion of the timeframe of interest to hundreds or thousands of years is usually done when the main objective is to understand the reactivity of slow mineral reactions and possible trapping of CO₂ by solid carbonate precipitation. Examples of such simulations are White et al., (2003), Xu et al., (2004), and Knauss et al. (2005) as well as long-term batch and reactive transport simulations done in the present study.

What information can we gain from numerical studies?

Since the Utsira Sand in the North Sea hosts the first industrial scale CO₂ injection, the site and its operation have achieved massive attention. On a short timescale the main concern for a CO₂ injection site is possible migration pathways for injected CO₂ and risk for leakage to the surface.

The SACS project was initiated to model and verify the distribution of immiscible CO₂ in the reservoir on a short time-scale and to develop prediction methods for the future destiny of the CO₂ plume. To model CO₂ migration two different 3D flow simulators, Eclipse 100 and Simed II, were used. Comprehensive simulations using these numerical tools demonstrate that simulations can successfully model CO₂ migration given proper physical parameters for CO₂ and the aqueous solution (see SACS Best Practice Manual).

The above Eclipse 100 and Simed II simulations were done without including interactions between the solid reservoir matrix and also partially without considering CO₂ dissociation into the aqueous phase. Extensive reactive transport simulations of CO₂ migration in the Utsira reservoir have however been published (e.g., Johnson et al., 2001; 2004) and presented as a part of this study (Hellevang et al., 2006).

Simulations of interactions between CO₂ and varying host formations during long timespans predict the formation of various carbonates as the primary mineralogy is dissolved. The nature of the carbonate precipitates is mainly related to the initial mineralogy. Numerical studies suggest that carbonates like dawsonite (NaAl-carbonate), calcite (Ca-carbonate), magnesite (Mg-carbonate), and siderite

(Fe-carbonate) are promising candidates to bind CO₂ for thousands of years (e.g., Xu et al., 2004). The mineral reactions, although predicted to have a limited magnitude, may prove important on the long-term safety of host formations, as they may for example change porosity-permeability relations.

Can we trust the outcome of numerical simulations?

The previous section sketched some of the information we can gain from numerical simulations of CO₂ storage. The outcome of numerical simulations is strongly related to input information like mineralogy, water chemistry, physical parameters like temperature and pressure, as well as different numerical issues. As all input information carries some degree of uncertainty and with the possibility of numerical errors, it is natural to ask if we can trust the outcome of numerical simulations. The best way of answering this is to compare numerical simulations with natural analogues. With respect to CO₂ storage, several natural analogues exist (see Stevens et al., 2001; Pearce et al., 2004), some of which are well described and can be used for qualitative comparisons with respect to the nature and magnitude of geochemical reactions. This kind of comparison is attempted as a part of this study and simulations shows qualitative similarities with observed reactions in natural analogues (Hellevang and Kvamme, 2006). Such comparisons provide information about the nature of reactions, but fail in assessing the magnitude and natural reactions rates of the complex natural systems. Some degree of quantitative information is still accessible from natural CO₂ accumulations where the same initial

material has been allowed a different reaction history from locality to locality. One such example is the Ladbroke Grove and Katnook gas fields that are located within the Penola Through of western Otway Basin in Australia (Watson et al., 2004). In this formation, CO₂ charged water has reacted with the Ladbroke Grove gas field, whereas the Katnook gas field is charged with pure methane. The reactivity of the CO₂ charged aqueous solution is clearly visible from mineralogical differences in the two gas fields.

Defining simple well-defined benchmark problems are essential to identify errors in simulations that results from different numerical issues. To build confidence in numerical simulations of problems related to CO₂ storage, LBNL coordinated an intercomparison study of different numerical simulation codes on well-defined benchmark problems (Pruess et al., 2002; 2004). The study included simulations by ten groups from six countries using a large range of different simulation tools. The conclusion of the study was that the simulators were capable of modelling complex phenomena accompanying geological storage of CO₂ in a quantitatively similar manner (Pruess et al., 2004).

Factors influencing the outcome of numerical simulations

Even though studies show that numerical simulations can qualitatively reproduce natural reactions and that comparisons between different numerical codes show promising results, a close look at factors influencing the outcome of numerical simulations are valuable. Some of the factors that may strongly affect the

outcome of numerical simulations are presented here in the following section.

Thermodynamic data

The common practice is to choose the mineral assemblage that is in closest agreement with what is known for the target rock or sediment. This mineral assemblage is picked from comprehensive databases that contain the thermodynamic information needed for the simulations. Several comprehensive databases that contain hundreds of minerals are currently available. Codes like PHREEQC (Parkhurst and Appelo, 1999) and EQ3/6 (Wolery, 1992a, b; Wolery and Daveler, 1992) contains several databases, some of which are derived from the same sources (e.g., the thermo.com.X database files from LLNL). These databases consist of thermodynamic data that are compiled from various sources and modified if necessary to make up thermodynamic consistent databases. The data is commonly listed together with analytic expressions for the temperature dependence of the data and corresponding temperature limits.

Simulations show that dissolution of phyllosilicates play a major role in storage of CO₂ as solid carbonates. These silicates commonly show structural similarities, but are geochemically mixtures of various end-member compositions. Thermodynamic data are unfortunately only available for most end-member phyllosilicates, whereas the solid-solutions lack in the databases. Glauconite is one such mineral. The mineral typically occur in marine sediments such as the Utsira Sand, and could prove important for the long-term storage potential of reservoir sands. Glauconite is an illite-type of clay mineral with considerable replacement of

aluminum by iron and magnesium. Calcium and sodium as well as potassium occur as interlayer cations. Glauconites occur with a considerable variety of chemical compositions, and the thermodynamic stability varies from reservoir to reservoir. Since accurate chemical compositions of glauconites commonly lack in reservoir sands like the Utsira Sand, it is tempting to replace glauconite in simulations with other phyllosilicate like annite having similar chemical composition and known thermodynamic stability. This induces however an error that is primarily a function of the difference in thermodynamic stability of the minerals as well as differences in reaction kinetics.

If detailed compositional data is lacking for a mineral, one option is to use a synthetic composition and estimate thermodynamic data. One example of this is presented in simulations by Xu et al. (2004) that noted that using annite as a proxy for glauconite could lead to a significant error. Xu et al. (2004) instead used a thermodynamic value that was estimated for some average synthetic glauconite composition. One additional option is to use analytical expressions for mixtures that are based on the end-member experimental thermodynamic values in addition to one or more intermediate values. This would be of great practical use in simulations.

To summarize this section, choosing the right mineral assemblage for a reservoir reactive transport simulation is far from trivial. Researchers are commonly forced to use proxies instead of minerals with unknown chemical composition and lack of thermodynamic and kinetic data. Further experimental work on thermodynamic stability of phyllosilicates may be of great value for

improving numerical simulations of geological storage of CO₂.

Mineral reaction kinetics

The outcome of numerical simulations is more or less dependent on the accuracy of thermodynamic data as mentioned in the previous sections. In addition to this, simulations involving mineral reactions that are constrained by kinetics are also dependent on accurate kinetic expressions and kinetic data. The degree of uncertainty on measured mineral dissolution rates may sometimes be difficult to assess. One potential contribution to uncertainty is possible changing mineral surface area during experiments. The surface area used to compute rates is usually that measured prior to experiments on crushed powder. This surface area could change due to preferential dissolution of fine particles and/or precipitation of other secondary products on the mineral surfaces. Incongruent dissolution also results in a different ratio between element concentrations in the aqueous solution than original present in the dissolving mineral. Further errors occur from the various analytical procedures involved during the experiments. Even though there are several sources of errors involved during experimental work, the cumulative error is generally not considered dramatic, and rate variations with pH, chemical compositions, and temperature are usually easily recognized.

Another issue related to reaction rate calculations is the apparent discrepancy between laboratory rates and natural weathering rates that are commonly orders of magnitude slower than the former (e.g., Schnoor, 1990; Velbel, 1993; Blum, 2004; White, 2005). Discrepancies are suggested to stem from higher reactivity in crushed experimental material compared to the natural material, from upscaling of simple

systems to the highly complex geochemistry in natural systems, or from possible inhibiting effects on the reaction rates of ions in natural aqueous solutions. One issue related to the upscaling in complexity is the natural systems tendency to proceed towards a lowest free energy along the most effective reaction progress. Reactions that are coupled through common ions will affect each others reaction kinetics, and this effect can be evaluated through simulations of coupled reactions using a free energy minimization routine. This is beyond the scope of this work and is suggested as further research in Chapter 5.

Possible numerical errors

This section will focus on one specific numerical error that is highly relevant for treating coupled aluminosilicate reactions in numerical studies of CO₂ mineral storage. Aluminosilicate reactions are strongly influential in the amount of CO₂ that is transferred to carbonate minerals. The reaction kinetics and thermodynamic stabilities of these reactions are coupled through the presence of common ions of aluminium and silica and various cations in the formation water. Because of low solubility of aqueous aluminum at pH encountered during CO₂ storage, this element is highly influential in the stability of the aluminosilicates. The coupling of the reactions with respect to thermodynamic stability can be seen from the ion activity product q of the aluminosilicate reactions:

$$q = \alpha \cdot a_{Al^{3+}}^{\eta}, \quad (18)$$

where $a_{Al^{3+}}$ denotes activity of aluminum, α is a coefficient containing the

contribution from other ionic components to the ion activity product, and η is the stoichiometric number of Al³⁺ in the reactions. The saturation state of a mineral can be expressed by the solubility index as:

$$SI = \log\left(\frac{q}{K_{eq}}\right), \quad (19)$$

where K_{eq} is the equilibrium constant for the reaction. $SI < 0$ results in mineral dissolution, whereas $SI > 0$ leads to precipitation. If the integrated aluminosilicate reactions at a given time t results in a net consumption of Al³⁺, its concentration decreases according to some given rate law. This possibly results in a shift in saturation states (SI) for one or more aluminosilicates and a shift in reaction direction at time $t+1$. The reverse shift in saturation state may happen after the next integration. If, during a net consumption of aluminum, the integration produces a change in aluminum that is close to the actual Al³⁺ value, its concentration will fluctuate and the aluminosilicate reactions will jump back and forth. This results in a conservative estimate of the mineral reactions, i.e. less overall mineral reactivity than optimal runs, but is not believed to change the qualitative nature of the results significantly. Fluctuations are avoided by integrating over small timesteps. This results however in a larger number of iterations and longer simulation runtimes which may be problematic when studying large system over long time-spans.

Chapter 4

Summary of Papers

This study has been divided into the development of a numerical code to solve long-term CO₂-water-rock interactions, and experimental work on dawsonite reaction kinetics that was lacking in the databases prior to the study. The thesis consists of six papers of which one has been published as a journal paper (Paper A), one has been published in a conference proceeding (Paper B), three have been submitted to journal papers (Papers C, D, and F), and one is currently submitted as a conference paper (Paper E). The papers can be divided into two categories: (1) Experimental work and theoretical considerations on the stability of dawsonite (Papers A and B); and (2) work related to the development and use of the ACCRETE code to simulate CO₂-water-rock interactions (Papers C to F).

Dawsonite stability (Papers A and B)

Dawsonite ($\text{NaAl}(\text{OH})_2\text{CO}_3$) is one of the minerals that has been suggested could play a significant role during CO_2 storage (see Chapter 2). The reaction kinetics at the initiation of this project was however completely unknown. The lack of kinetic data together with the apparent discrepancy between large-scale formation of dawsonite in numerical simulations and few observations of massive dawsonite precipitation in CO_2 rich reservoirs resulted in the first study on dissolution kinetics of dawsonite.



Fig. 2. Natural dawsonite from Monticolo, Terlano, Alto Adige in Italy. The dawsonite is the fibrous white mineral filling up vugs and fractures in the hand specimen.

Dissolution experiments were done on natural dawsonite that were obtained from Monticolo, Terlano, Alto Adige in Italy. This dawsonite occurs as white fibrous or massive material in vugs and fractures in hand specimens (Fig. 2). Its fibrous habit and color contrast relative to the surrounding mineral phases facilitated dawsonite extraction from the host rock. All dawsonite dissolution rate experiments reported in the present

study were performed in 250 ml Polyethylene batch reactors covered with a fitted Teflon® cover. This cover had several holes allowing continuous contact between the reactive fluid and atmospheric CO_2 . The batch reactors were placed in a constant temperature (80°C) shaker bath to ensure fluid mixing and to avoid dawsonite powder grinding. Four to five ml of reactive solution was sampled regularly using syringes equipped with $0.45\mu\text{m}$ micro pore filters. Aqueous sodium and aluminum analyses were performed using a Perkin Elmer 5100 atomic absorption spectrophotometer. The pH at 80°C of each experiment was calculated from fluid composition measured at 25°C .

Results suggest that dawsonite dissolution rates are independent of pH at 1.58×10^{-9} moles/(m^2s) to within analytic uncertainty over the range $3.5 < \text{pH} < 8.6$. The pH independence of dawsonite dissolution is consistent with corresponding observations made on other carbonate minerals. For example, calcite, dolomite and magnesite dissolution rates at 25°C are found to be pH independent from $\sim 4.5 < \text{pH} < 11$ (Plummer and Wigley, 1976; Sjöberg, 1976; Busenberg and Plummer, 1986; Chou et al., 1989; Pokrovsky and Schott, 1999, 2001; Cubillas et al, 2004). The dissolution rate of dawsonite is somewhere between fast dissolving carbonates like calcite and dolomite and slow dissolving aluminosilicates (Paper A).

The kinetics of dawsonite relative to other mineral reactions is probably the key to understand the apparent discrepancy between large-scale

formation of dawsonite in numerical simulations and few observations of massive dawsonite precipitation in natural CO₂ rich formations. The amount that precipitates per time unit is a function of the precipitation rate of dawsonite relative to other phases in the system that contains a common limiting component. This common limiting component for dawsonite, aluminosilicates, gibbsite, and kaolinite is aqueous aluminum.

The experimental work on dissolution kinetics of dawsonite in Paper A shows that dawsonite is faster than rates for aluminosilicates. The concentration of aluminum is however determined by the sum of release and uptake from all competing phases in the system. If the rate of dawsonite precipitation is slower than the sum of precipitation from other aluminum consuming phases, the amount that precipitate out may be limited (Paper B).

Finally, the dissolution rate was used to calculate lifetime of a dawsonite grain as the CO₂ fugacity drops below the stability limit of dawsonite. The dissolution rate was assumed to vary as a function of chemical affinity. The calculation suggests that dawsonite will persist for only short time periods following a drop of CO₂ pressure from the dawsonite stability field. For example, a 1 mm dawsonite grain is estimated to persist less than one year in a solution having a typical formation water CO₂ fugacity of 1 (Paper A).

Development of a numerical code to solve CO₂-water-rock interactions (Papers C to F)

To better understand long-term CO₂-water-rock interactions, i.e. reactions that last for hundreds to thousands of years, numerical codes that integrate results from various geochemical experiments have to be used. In the present study we have developed ACCRETE which is a new research geochemistry solver for long-term CO₂ storage. The present section gives a brief overview of how the geochemistry is solved, and provides key results obtained in Papers C to F.

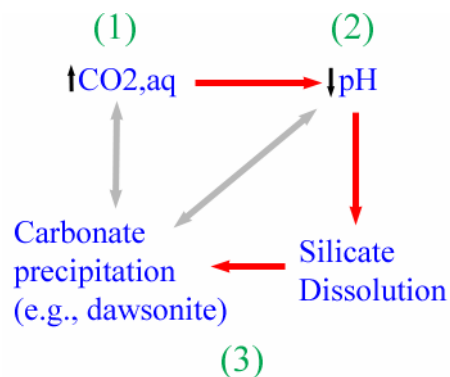


Fig. 3. The reaction path from increased aqueous concentration of CO₂ to the precipitation of solid carbonates like dawsonite. Gray arrows illustrates that the stability of the solid carbonates are strongly related to the aqueous concentration of CO₂ and pH. Numbers indicate, very simplified, the sequence of solvers in an ACCRETE run.

The reaction path from increased aqueous CO₂ following CO₂ injection to a lowering of pH, dissolution of primary silicates and precipitation of solid carbonates is illustrated in Fig. 3. Also illustrated is a simplified picture of the sequence of calculations in an ACCRETE run.

The first calculation is the solubility of CO₂ in the formation water as a

function of T , P , and salinity. This is solved according to equation (16) using the SRK EOS to calculate the compressibility factor. The next calculation is the speciation of the aqueous phase. This is solved when the solution is charge balanced and the carbonate speciation in expressions (17) to (19) (Chapter 2) is satisfied, constrained by the bubblepoint mole fraction of dissolved CO_2 . The last step in an ACCRETE run is to solve the mineral reactions. These are constrained by kinetics expressed in equation (24) (Chapter 2) that varies several orders of magnitude between individual reactions. The aqueous solution is updated after each predefined time step in the mineral solver.

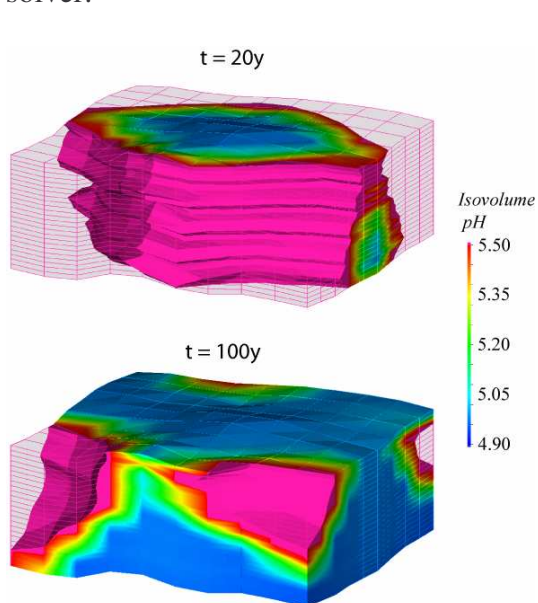


Fig. 4. Isovolumes that shows the pH at 20 (end of injection) and 100 years limited between 4.9 and 5.5 (Modified from Paper D).

The ACCRETE geochemistry code can be used as a stand-alone batch simulator as in Paper C and E or coupled with an external flow code to produce reactive transport simulations (Paper D, E and F). All four papers simulate injection into the Utsira Formation at

Sleipner. Paper C presents in addition a batch simulation of glauconitic sand at higher T and P than Utsira. Paper D and F reports data from the same numerical simulation focused on a geological (Paper D) and mathematical (Paper F) point of view respectively.

Simulations of the Utsira injection site show that pH decrease rapidly to around 4.9 as CO_2 dissolves into the aqueous phase to full saturation (Fig. 4). This pH is calculated in equilibrium with calcite which is considered to be at instant equilibrium with the solution. The pH drop leads to dissolution of primary minerals present and precipitation of secondary carbonates.

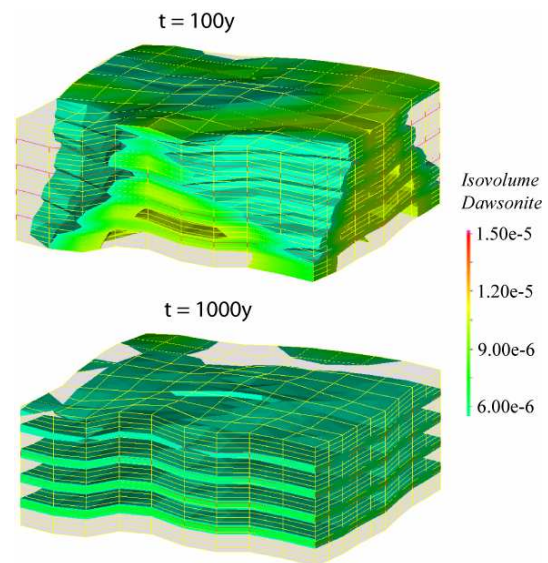


Fig. 5. Volume fraction dawsonite formed at 100 and 1000 years (Modified from Paper D).

Magnesite and siderite is by far the dominant reaction products resulting from phyllosilicate dissolution. Dawsonite was expected to form in the Utsira Sand at high CO_2 saturations (Papers A and B). In the present simulations we used the kinetic constant for dawsonite found from experimental work in Paper A. Both batch- and reactive transport simulations in the

present study suggest that dawsonite only form a minor precipitate during long-term interactions with the CO₂-charged waters. This can be explained by competition for aqueous Al³⁺ between dawsonite and other Al-bearing phases that precipitate during the simulations (Papers A to E). As the aqueous CO₂ saturation eventually drops, early formed dawsonite starts to dissolve (Fig. 5.; Paper D). This is in accordance with the destabilization of dawsonite caused by reduced CO₂ fugacity (Paper A).

Chapter 5

Further research

The thesis is focused on work that provides a better understanding of long-term CO₂-water-rock interactions. The work comprises experimental work on the reactivity of dawsonite as well as comprehensive batch- and reactive transport simulations. Results from the experimental and numerical work have resulted in new insight but also new questions. This chapter presents suggestions of further research to answer some of these questions.

Change in the relation between porosity and permeability?

Simulations suggest that porosity changes caused by mineral reactions are minor (Hellevang and Kvamme, 2006). The simulations can however not predict if the microscopic mobility of mineral phases at the pore scale changes the relation between porosity and permeability at core scale.

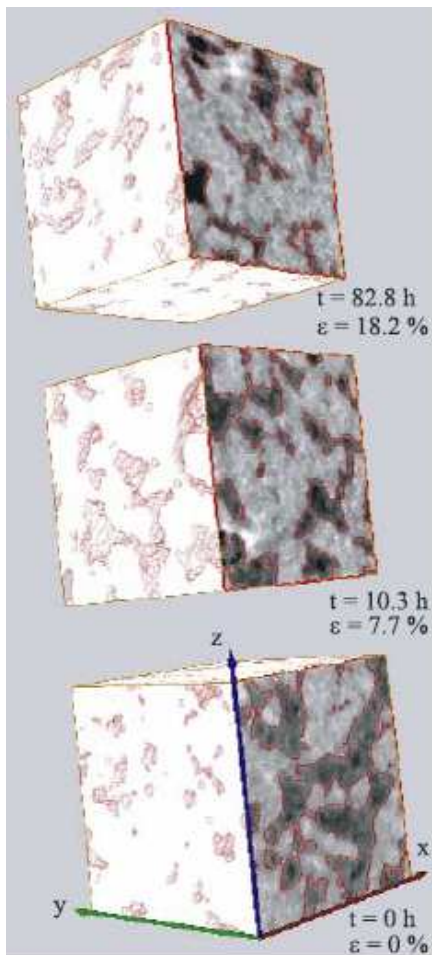


Fig. 6. 100x100x100 pixel subvolume (4.91 mm resolution, 491^3 mm^3) extracted from sample B at initial stage (bottom), after 10.3 hours (middle) and after 82.8 hours (top). These data, showing the reduction in porosity with deformation (ε), are used for permeability calculations (salt in light grey, pores in dark,

grain-pore interface in red) From Renard et al., 2004.

We suggest experiments on sandstone plugs to see if mobilization of the fast reactive carbonates caused by CO_2 -water-rock interactions can change the porosity-permeability relation of the plug. Permeability should be measured during the experiments and the porous network should be mapped at pore-scale between experiments. Mapping of the porous network can be done at high spatial resolution by synchrotron x-ray microtomography (e.g. Renard et al., 2004; Noiriél et al., 2004). Fig. 6. shows microtomography snapshots from an experiment to assess the temporal evolution of porosity and permeability for a halite specimen (Renard et al., 2004).

During the second part of 2004 we did preliminary work to prepare for the experiments. We have prepared sample holders to measure permeability for sandstone plugs with a diameter of approximately 1 cm, and had a visit to the European Synchrotron Radiation Facility (ESRF) assisted by Dominique Bernard at ICMCB-CNRS, Bordeaux, France. The small size of the plugs is to ensure high-resolution of the pore mapping (pixel size of $4.91 \mu\text{m}$) at ESRF.

Dawsonite reactivity

Experiments on natural dawsonite at 80°C show that BET surface area normalized dissolution rates are nearly independent of pH over the range $3.5 < \text{pH} < 8.6$. The average rate at this temperature is found to be $1.58 \times 10^{-9} \text{ n}/(\text{m}^2 \cdot \text{s})$ (Hellevang et al., 2005). More work is however needed to fully understand the importance of dawsonite as a storage host for CO_2 .

The first important step is to do experimental work on the temperature dependence of the reactions rate. At present reaction rates at temperatures other than 80°C is calculated by assuming similar temperature dependence as other carbonates. This may however prove to be a poor assumption. The next step would be to do experimental work on the reaction rate as a function of aqueous concentrations of sodium, aluminum, CO₂, and ionic strength.

The preliminary studies on dawsonite kinetics were done using batch reactors instead of the traditional mixed flow reactor because of little natural material available (Hellevang et al., 2005). Further studies should use synthetic instead of natural dawsonite to be able to use the mixed flow setup. Receipts exists on how to produce synthetic dawsonite with different crystallinity, homogeneity etc. (e.g., Zhang et al., 2004). It is however hard to make material that approach the quality and purity of the natural material. We propose a new method for dawsonite synthesis where an aluminum saturated solution is mixed with a NaHCO₃ solution and the mixture is subsequently evaporated. Dawsonite is at supersaturation during the evaporation process and precipitates on natural seed grains. We have done preliminary tests of this method and the results look promising.

Funding for further studies on the dawsonite stability has been granted by the Norwegian Research Council through the project #165697/I30. The project is a collaboration between University of Bergen, Per Aagaard at University of Oslo, and Eric Oelkers at Laboratoire de Géochimie, Université Paul Sabatier/CNRS-UMR.

Modifications of the ACCRETE code

At present the ACCRETE code uses expression (24) at page 13 to solve the reaction rate of mineral reactions. This expression results in precipitation even at infinitesimal positive values of the solubility index. Rigorously the kinetic rate should approach infinitely small values at equilibrium. Similar to any other phase transition the precipitation from liquid solution will have benefits related to the free energy change, but also penalties related to the corresponding work exposed on the surroundings during the precipitation. The critical size of the solid precipitation particle represents the size after which an individual particle would grow continuously. This critical size depends on temperature, pressure and initial concentration. A corresponding nucleation time will be the time needed for a system to reach this critical size. The dynamic progress towards precipitation depends on mass transport, dynamics of the phase transition (as governed by the free energy difference) and heat transport dynamics. There are several levels of refinements for treating these phase transitions theoretically. The simplest approach is the classical nucleation theory and of the more advanced approaches we find the Phase Field Theory (PFT). The latter concept has successfully been applied to predictions of nucleation kinetics as well as the kinetics of further crystal growth in many-particle systems. It has also been successfully applied to imitate dynamically experimental observations of crystal morphology (Gránásy et al., 2003; 2004).

It is also observed in natural systems that minerals like for instance magnesite may occur at supersaturations for very

long time scales without visible precipitation. One extension of the theoretical modelling would be to use the PFT approach to model the solid phase nucleation rate, as well as corresponding growth rates, for different driving forces in a similar fashion to has been done for methane and carbon dioxide hydrates growing from solution (Svandal et al., 2005; Kvamme et al., 2005a). Corresponding model parameters related to the interface properties can be estimated using Molecular Dynamics simulations (Kvamme et al., 2005b; Kvamme and Kuznetsova, 2005).

Another issue related to reaction rate calculations is the apparent discrepancy between laboratory rates and natural weathering rates that are commonly orders of magnitude slower than the former (e.g., Schnoor, 1990; Velbel, 1993; Blum, 2004; White, 2005). We suggest that differences may occur as a consequence of the natural systems tendency to proceed towards a lowest free energy along the most effective reaction progress. In natural systems several reactions compete for common reaction components (ions) and this competition may decrease reactions rates to accommodate an efficient reduction of the free energy of the whole system. The idea is to introduce a scaling parameter ξ in the kinetic expression for each mineral reactant, and to solve the reaction progress by minimizing the free energy of the whole system as a function of the progress vector ξ . A value of 1 implies that the reaction progress as if it were independent while any value below 1 implies that other competing reaction may surpass the reaction rate. The theoretical rationality of the approach is of course that different reactions compete in the exchange of components and ions between the liquid solution and the different precipitating or dissolving solids. Since

the total system has to progress along paths of minimum free energy the different scaling parameters can be estimated by the minimizing free energy of the system for every time step in the progress of the system. Theoretical simulation using PFT can also provide some insight into the relative competition between different reactions. Following this the reaction progress of each individual reaction i will be calculated from:

$$n_i = k_{298} \cdot e^{-\frac{E_a}{RT}} \cdot S \cdot (10^{SI} - 1) \cdot \tau \cdot \xi_i, \quad (26)$$

where τ is the reaction time.

Fluid/mineral interface properties

The chemical potential of all components in the fluid mixture at the surface of a solid mineral determines the interfacial tension, the interfacial free energy and the interface composition. The interface composition of the different ions and components in the aqueous solution may vary significantly from the bulk fluid composition and may thus have significant impact on the reaction rates. Advanced theories for reaction kinetics like for instance the reaction version of the phase field theory (Kvamme et al., 2005a) require the interfacial free energy as input parameter. The interfacial tension between solids and fluids determines the wetting properties. These properties are difficult to measure but can be obtained for corresponding model systems through molecular simulation.

As a spin off from this project a simulation study has been initiated and preliminary results are very promising (Kvamme et al., 2005b, Kvamme and Kuznetsova, 2005).

Effect of geochemical reactions on geomechanical properties.

Another spin off from this project is the establishment of a new project related to modeling of the effect of geochemical reaction on the geomechanical properties of the reservoir. This is a collaboration between Kvammes group at UoB and Lawrence Berkley National Laboratory. The aim of the project is to implement a geomechanical module into ATHENA, as well as into the TOUGHREACT simulator developed by Lawrence Berkley National Laboratory, and to use these tools to examine the effects of mineral dissolution as well a mineral precipitation on the local strength of the reservoir relative to local pressure gradient. While the Utsira formation has average content of rapidly dissolving carbonates of around 3 per cent this number is significantly higher for other relevant reservoirs, and increased porosity/mechanical strength can be a critical issue for these reservoirs.

Department of Energy (DOE) in USA is already in place and the chances for corresponding funding from the Norwegian Research Council are promising.

Shale reactions and potential breakup of clay sealing

Another spin off project from this project is the establishment of a collaboration between Los Alamos National Laboratory specifically dedicated to experimental and theoretical work on reactions between shale minerals and CO₂. The motivation for this is that the CO₂ plume that is captured beneath the sealing clay layers may eventually replace the water in the clay in the long run as well as dissolve the original clay minerals. As a result the sealing clay layer may break up and lead to leakage of CO₂. Partial funding from

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