

Review

Role and impact of CO₂–rock interactions during CO₂ storage in sedimentary rocks

Irina Gaus*

Nagra, Hardstrasse 73, 5430 Wettingen, Switzerland

ARTICLE INFO

Article history:

Received 17 April 2009

Received in revised form 27 August 2009

Accepted 24 September 2009

Available online 1 November 2009

Keywords:

CO₂–rock interactions

Coupled modelling

Natural analogues

Experiments

CO₂ geological storage

ABSTRACT

Before implementing CO₂ storage on a large scale its viability regarding injectivity, containment and long-term safety for both humans and environment is crucial. Assessing CO₂–rock interactions is an important part of that as these potentially affect physical properties through highly coupled processes. Increased understanding of the physical impact of injected CO₂ during recent years including buoyancy driven two-phase flow and convective mixing elucidated potential CO₂ pathways and indicated where and when CO₂–rock interactions are potentially occurring. Several areas of interactions can be defined: (1) interactions during the injection phase and in the near well environment, (2) long-term reservoir and cap rock interactions, (3) CO₂–rock interactions along leakage pathways (well, cap rock and fault), (4) CO₂–rock interactions causing potable aquifer contamination as a consequence of leakage, (5) water–rock interactions caused by aquifer contamination through the CO₂ induced displacement of brines and finally engineered CO₂–rock interactions (6). The driving processes of CO₂–rock interactions are discussed as well as their potential impact in terms of changing physical parameters. This includes dissolution of CO₂ in brines, acid induced reactions, reactions due to brine concentration, clay desiccation, pure CO₂–rock interactions and reactions induced by other gases than CO₂. Based on each interaction environment the main aspects that are possibly affecting the safety and/or feasibility of the CO₂ storage scheme are reviewed and identified. Then the methodologies for assessing CO₂–rock interactions are discussed. High priority research topics include the impact of other gaseous compounds in the CO₂ stream on rock and cement materials, the reactivity of dry CO₂ in the absence of water, how CO₂ induced precipitation reactions affect the pore space evolution and thus the physical properties and the need for the development of coupled flow, geochemical and geomechanical models.

© 2009 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	74
2. Where do CO ₂ –rock interactions occur in CO ₂ storage?	74
2.1. Injection phase—near well environment	74
2.2. Long-term reservoir and cap rock interactions	75
2.3. CO ₂ –rock interactions along leakage pathways (well, cap rock and fault).	75
2.4. Consequences of leakages—potable aquifer contamination	76
2.5. Brine displacement leading to aquifer contamination	76
2.6. Engineered CO ₂ –rock interactions	76
3. Drivers of CO ₂ –rock interactions and impact on porosity and permeability.	77
3.1. Dissolution of CO ₂ in brines.	77
3.2. Chemical interactions inducing porosity–permeability changes and mineral trapping.	77
3.2.1. Reactions induced by dissolved CO ₂ and acid induced reactions	77
3.2.2. Dissolution and precipitation kinetics	78
3.2.3. Chemical interactions as a consequence of evaporation leading to porosity reduction	79
3.2.4. Linking geochemical reactions with porosity and permeability changes	80
3.3. Chemical reactions leading up to potable water contamination	80
3.4. Clay shrinking through CO ₂ drying	81
3.5. Pure SC-CO ₂ –rock interactions.	81
3.6. Presence and impact of other components than CO ₂	81

* Tel.: +41 56 4371 334; fax: +41 56 4371 317.

E-mail address: irina.gaus@nagra.ch.

4.	How can CO ₂ –rock interactions be assessed?	81
4.1.	Laboratory experiments	82
4.1.1.	“Total impact” experiments	82
4.1.2.	Specific experiments	82
4.2.	Natural analogues	82
4.3.	Demonstration, field experiments and monitoring	83
4.4.	Geochemical and coupled modelling	83
5.	Outlook and future challenges	85
5.1.	Based on the interaction environment	85
5.2.	Based on the assessment method	85
	Acknowledgements	86
	References	86

1. Introduction

CO₂ capture and storage (CCS) is considered as one of the options for reducing atmospheric emissions of CO₂ from human activities (IPCC, 2005). Geological formations having most potential for CO₂ storage are deep saline aquifers, and depleted or active oil reservoirs. Before implementing the technology on a large scale, the confirmation of its viability regarding injectivity, containment and long-term safety for both humans and environment is crucial. CO₂–water–rock interactions play an important role in assessing this viability as at the moment of injection the brine rock environment shifts from a rock-dominated reaction system (reactivity driven by the mineralogy of the present rocks) to a fluid-dominated system, controlled by acid-generating reactions due to the dissolution of CO₂ and mixed-fluid equilibria (Kaszuba and Janeky, *in press*). This affects physical properties through highly coupled processes, first in the vicinity of the injection well, but with time also at larger distances in the geological sequence.

Because of the known corrosive character of CO₂, the assessment of CO₂–rock interactions has been a research topic since CO₂ storage emerged (Czernichowski-Lauriol *et al.*, 1996a; Gunter *et al.*, 1997). Initially focus was on long-term impact of host rock through simple batch experiments and long-term geochemical modelling. Gradually models have become more complex, including 3D grids representing geology and more detailed processes, while experimental work is focussing on specific CO₂–rock interactions, occasionally at a very detailed level. Furthermore, increased understanding of the physical impact of injected CO₂ including buoyancy driven two-phase flow and gravitational instabilities potentially inducing convective mixing elucidated CO₂ pathways (Lindeberg and Bergmo, 2003; Lindeberg *et al.*, 2000; Pruess and García, 2002; Pruess *et al.*, 2004) both of supercritical and dissolved CO₂ and indicated where and when CO₂–rock interactions are likely to occur.

With the substantial increase in understanding of the CO₂ storage process it became clear however, that CO₂–rock interactions intervene in more areas than initially anticipated whereby certain areas have received little attention so far. It is the objective of this position paper in first instance to identify where CO₂–rock interactions play a role and are potentially affecting safety and viability of the CO₂ storage scheme. This includes both interactions which have been subject of many papers as well as interactions that have hardly been investigated (first section). In a second section, the driving processes of CO₂–rock interactions are discussed as well as their potential impact in terms of changing physical parameters. In a third section, methods to investigate the processes and assess their potential impact are highlighted. Finally, main challenges and future research topics for assessing the viability and safety of the CO₂ scheme are discussed.

The focus of this paper is on CO₂–rock interactions only and their impact on porosity and permeability of various rocks encountered in the geological sequence and specific CO₂ storage

environments. The focus is not on discussing the displacement of CO₂ and pure physical behaviour (e.g. impact on wettability) of injected CO₂. However, this paper assumes that the reader is familiar with current understanding of CO₂ displacement in reservoir and cap rock, as well as most likely leakage pathways and various trapping mechanisms. Furthermore, familiarity with geochemical principles including thermodynamic equilibria, the concept of activities and role of chemical kinetics will enhance its understanding.

2. Where do CO₂–rock interactions occur in CO₂ storage?

During the lifetime of a CO₂ storage scheme various groups of CO₂–rock interactions can be distinguished. Once injection has started, supercritical CO₂ (SC-CO₂) will dissolve and interactions will occur between the injected CO₂ and well materials. If CO₂ is injected as a liquid, either in the well or in the well environment it will become supercritical. In the direct well environment dry supercritical CO₂ will prevail which might still be at a different temperature than the reservoir. Gradually CO₂ temperature will adjust to the reservoir temperature and temperature driven CO₂–rock interactions will disappear. Longer-term interactions between host rock and cap rock are the subsequent group of interactions assuming that CO₂ remains contained in the target host rock. Leakage scenarios need to be investigated for each site. Depending on the specific circumstances, CO₂–rock interactions might occur whereby the coupling between the interaction and the flow regime is of crucial importance. If CO₂ has escaped along these leakage pathways it might enter potable aquifers and cause unwanted indirect impacts on the quality of the water which might be used for human consumption. Also because of the induced pressure built-up during many years of injection, displacement of brine in adjacent layers might occur, again with potential deleterious effects on potable aquifers. A last type of interactions are these that are enhanced or induced through engineering practices with the objective to immobilise CO₂ faster, prohibit CO₂ induced reactions or maximise dissolution (and then chemical reactions) for enhancing storage capacity. Fig. 1 illustrates groups of interactions as listed above and discussed individually in the following paragraphs.

2.1. Injection phase—near well environment

The injection phase is generally assumed to be of the order of 25 years, but could be longer. It is perceived as the phase where risk of leakage and unwanted effects is highest (IPCC, 2005; Scherer *et al.*, 2004) especially in terms of pressure built-up. The main concern in terms of CO₂–rock interactions relates in this stage to a potential decrease in permeability around the well that might affect injection rates and/or required injection pressures and generate overpressures in the target reservoir. The water–rock interactions in the injection phase are multiple and can be divided in interactions:

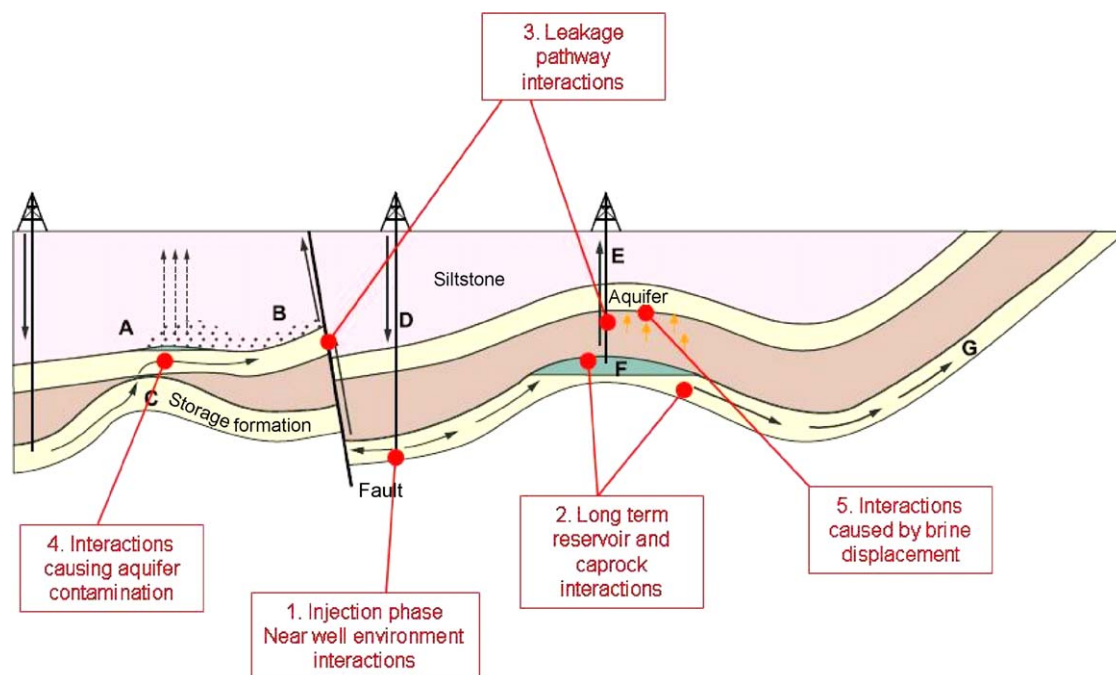


Fig. 1. Conceptual diagram of a CO₂ injection scheme and identified clusters of CO₂–rock interactions (modified from IPCC, 2005).

- Between injected CO₂ and cement of the well completion.
- Between injected CO₂, cement and host rock.
- Through brine concentration as a consequence of water dissolving in injected dry CO₂.

The injection phase is characterised by large transfers of mass through the pore space under high pressures and potentially large temperature gradients. Indeed, CO₂ is injected at a relative low temperature (e.g. around 20 °C) while reservoir temperature can be significantly different (e.g. Utsira sands in the Sleipner case are at approximately 37 °C, but other reservoirs, such as K12b (at 128 °C), are at significantly higher temperatures). Large temperature gradients can be at the base of CO₂–rock interactions, but also of pure water–rock interactions. In terms of geochemical interactions, fast occurring reactions are of concern in this stage. These reactions include carbonate minerals, as well as sulphate and evaporite minerals as their reaction kinetics is fast and equilibrium is reached almost instantaneously. The dominant phase in the near well environment will be SC-CO₂ after a short while as modelled in André et al. (2007) and this will determine the impact of reactions. Concentration of brine through dissolution of water in dry injected CO₂ can generate precipitation reactions of mainly salts on top of pure CO₂ induced reactions.

CO₂–rock interactions during the injection phase can be investigated through field experiments and observation of pressure changes and through modelling studies. Although reduction and/or loss of injectivity would be perceived as a major problem, also in terms of financial viability of the project, little has been published on the topic. Indirect evidence of CO₂–rock interactions in the near well environment during industrial operations can be occasional injectivity difficulties encountered during enhanced oil recovery (EOR) operations. However, real causes of these injectivity changes are poorly explained and vaguely attributed to multiphase flow, CO₂/oil interactions and/or CO₂/mineral interactions (Cailly et al., 2005). Revisiting literature on injection issues during EOR projects (an onset is given in Czernichowski-Lauriol et al., 1996a) might clarify the importance of these interactions and conditions that ultimately result in reduced injectivity.

2.2. Long-term reservoir and cap rock interactions

Long-term reservoir interactions between injected CO₂ and rock refer to interactions that occur between dissolved CO₂ and brine in the reservoir. The buoyant behaviour of supercritical CO₂ is described accurately (Lindeberg and Bergmo, 2003; Lindeberg et al., 2000; Pruess and García, 2002; Pruess et al., 2004) and dissolution of injected CO₂ is anticipated to occur within a couple of thousands of years after injection (Lindeberg and Bergmo, 2003) depending on geology and heterogeneity of the reservoir and the defined dissolution rate. Both dissolved CO₂ in brine and acidification of the brine will generate chemical interactions with the minerals of the reservoir rock. The importance of studying long-term reservoir interactions is predicting the capacity of the reservoir to permanently trap CO₂ in a mineral phase as part of naturally occurring geochemical interactions (known as mineral trapping). In the case of cap rock the interest is to assess induced porosity–permeability changes, especially in its lower part. These geochemical interactions, affecting mainly (but not only) aluminosilicate minerals that are characterised by very slow reaction rates, which require in certain cases thousands of years to reach equilibrium, have been studied extensively using coupled flow-geochemical numerical codes. Key publications describing host rock interactions are Audigane et al. (2007), Xu et al. (2003, 2005) and White et al. (2005). Although these studies are important in predicting long-term behaviour and assessing mineral trapping capacity and thus contribute to the assessment of long-term leakage risk, they typically suffer from poor knowledge regarding key parameters on the impact of geochemical reactions since no model calibration is possible on these long-term time scales (see further).

2.3. CO₂–rock interactions along leakage pathways (well, cap rock and fault)

Potential leakage of CO₂ from the target reservoir can, when described in its most simplified way, occur along three pathways (Kreft et al., 2007):

- Leakage along the wellbore of an injection well or an abandoned well.
- Leakage across a fault (pre-existing or not).
- Leakage through the cap rock when the pressure exceeds the capillary entry pressure for SC-CO₂.

Although it is likely that CO₂–rock interactions will occur in case of leakage, it seems extremely unlikely that CO₂–rock interactions are capable of triggering leakage paths. Creating a leakage path by CO₂–rock interactions only requires quantitatively significant dissolution reactions at particular sites which cannot be generated in the absence of a flow regime. This is an important statement, as no experimental or modelling evidence currently suggests that CO₂–rock interactions can generate a non pre-existing leakage pathway when occurring in isolation.

However, once a leakage pathway is in place, CO₂–rock interactions have potential to either enhance leakage through dissolution (and shrinkage of clay minerals) or inhibit it through precipitation reactions of fast reacting minerals. For this to have a significant impact, it is assumed that advective flow of either SC-CO₂, CO₂ saturated brine, or both occurs, either along the well bore, in the fracture or in the cap rock. In this case, the minerals in contact with CO₂ determine interactions and the impact needs to be assessed case by case. For example, in case of fracture flow, while interaction with evaporite minerals (e.g. salts filling a fracture) is unlikely from a geochemical point of view, a carbonate mineral filling in a fracture containing a CO₂ flow path will quickly dissolve with potential widening of the existing flow path.

In case of leakage along the well bore, potential interactions are discussed extensively in Scherer et al. (2004). Other models, taking into account well geometry in more detail, either provide analytical solutions describing well leakage (Nordbotten et al., 2004), in which geochemistry is not included, or bulk the assumed geochemical impact in a permeability relationship (Viswanathan et al., 2008).

The third leakage pathway, a leaking cap rock, is a very unlikely scenario and would require that the estimation of the permeability of the cap rock and its capillary entry pressure has been incorrect or that important heterogeneities have been overseen from the beginning, indicating that the site characterisation was insufficient.

2.4. Consequences of leakages—potable aquifer contamination

Especially in case of onshore storage, CO₂ storage reservoirs are likely to be overlain by potable aquifers located at shallow depth. Leakage of CO₂ into potable aquifers could potentially induce geochemical reactions affecting water quality. In deeper saline (non potable) aquifers the chemical composition of the brine is not of major interest and assessment of CO₂–rock interactions ultimately focuses on porosity and/or permeability changes or on mineral trapping capacity. CO₂ induced changes of the composition of the brine are not a concern in this case as the changes are relatively minor compared with the high salinity of the brine and the brine will never be exploited for drinking water purposes. However, similar reactions occurring in dilute potable water can modify significantly its potable character. Indeed, in shallow aquifers, changes in the formation of water are the main concern, which implies that the amount of CO₂ that is required to have an impact is much smaller than in previous groups of interactions where substantial amounts of minerals and CO₂ need to react.

Dissolution of leaking CO₂ into water of potable aquifers could potentially acidify the water, while acidification is well known to trigger metal mobilisation. Furthermore, CO₂-rich fluids play a well known role in the mobilisation and transport of trace metals and

bitumens (see Czernichowski-Lauriol et al., 1996a). Although aquifer contamination is often cited as a risk regarding onshore CO₂ storage (Bouc et al., 2007), the actual chance of this happening has not been evaluated in detail so far. Modelling studies exist (Wang and Jaffe, 2004), some predicting a large impact, although these necessarily are based on fairly crude geochemical assumptions.

The natural occurrence of CO₂ pressurised water sources that are used for human consumption, such as those in the French carbogaseous province (Pearce, 2003; Czernichowski-Lauriol et al., 2002) is a clear proof that interaction of CO₂ charged waters not necessarily leads to inferior water qualities as a consequence of CO₂–rock interactions.

This is an area where experimental work could elucidate the plausibility and extent to which aquifer contamination could occur. Initial work is currently being done (Smyth et al., 2009; Birkholzer et al., 2008).

2.5. Brine displacement leading to aquifer contamination

Although not directly a CO₂–rock interaction, geochemical consequences of brine displacement into aquifers are also discussed here as this topic is generally not included in studies that assess brine displacement. Generally, these studies analyse the consequences of imposed pressures in the reservoir and the surrounding aquifers and aquitards. Although no direct leakage of CO₂ is occurring in this case, overpressures, especially during the injection phase but also thereafter can induce large pressure gradients and (re)activate natural pressure and groundwater flow regimes whereby water types of inferior quality (e.g. highly mineralised water normally immobilised in clays) can be pushed into potable aquifers. The mixing, diffusion and water–rock interactions will determine the ultimate impact on water quality in terms of potability and violation of environmental regulations. Strong contrasts in mineralisation between highly concentrated brines and fresh aquifer water require only a contamination of a few percentages in order to induce a permanent quality degradation of freshwater.

Assessing the risk of brine displacement in case of high pressure built-ups during storage has been investigated to a limited extent recently (e.g. Nicot et al., 2009; Le Gallo, 2009) and requires reservoir model development that includes the overburden and the lateral extension of the storage reservoir and adjacent layers in order to model pressure propagation in an accurate way. These larger models should be capable of reproducing regional pressure regimes at several depths in different geological units and should therefore be populated with the required data over a large scale, which are difficult to obtain. Only in case significant changes in natural flow regimes are demonstrated using these models, then the issue of brine contamination should be addressed from a water–rock interaction point of view.

Note that, the mixing of brines with potable water of fresh aquifers is not a CO₂ storage specific topic and has been investigated in detail in the context of salt water intrusion studies where coastal waters are entering fresh aquifers and induce density driven flow regimes thereby creating complex mixing zones and geochemical interactions.

2.6. Engineered CO₂–rock interactions

In order to enhance immobilisation of CO₂ one could consider measures to enhance CO₂ rock trapping reactions on one hand and/or inhibit reactions that might decrease injectivity on the other hand. A couple of studies have been published describing injection of dissolved CO₂ (Burton and Bryant, 2007), imposing a flow regime in the reservoir (Leonenko and Keith, 2008) to enhance dissolution,

or introducing bacteria to enhance reaction rates (Mitchell et al., 2008). These applications are still at the academic level and no general conclusions can be drawn from them.

3. Drivers of CO₂–rock interactions and impact on porosity and permeability

Brine containing reservoirs that are candidates for CO₂ storage will be rock-dominated from a geochemical point of view prior to CO₂ injection. These rock-dominated brine aquifers become fluid-dominated systems in which acid-dominated and related reactions are controlled by mixed-fluid (CO₂–H₂O) equilibria. This perturbation of ongoing reactions will profoundly change the manner in which the geochemistry of the system evolves (Kaszuba and Janecky, in press).

The impact of these reactions is determined by a number of site specific conditions such as the prevailing pressure and temperature conditions, the mineralogy of the host rock (or cement) and the composition of the brine. This site specific nature of CO₂–rock interactions prohibits the description of detailed reaction patterns that are valid for a wide range of host and cap rocks. Because of this, a geochemical baseline characterisation of each future storage site should be performed before starting injection. As described in Chadwick et al. (2007) ideally such a baseline programme should consist of the analysis of the cap rock and host rock mineralogy, the composition of the host rock and cap rock pore water, prevailing pressure and temperatures in the CO₂ storage environment including natural and induced gradients. In case of CO₂–cement interactions, since cement is an engineered product with a known composition, reaction pathways are more universal and thus applicable to many CO₂ storage sites.

This section focuses on pure CO₂–rock interactions in an aqueous environment as currently the overwhelming percentage of research is based on these assumptions. However, the option of injecting CO₂ containing other components than CO₂ is considered for several reasons and injection of other gases is anticipated to have an important impact in terms of rock interactions. As this topic is only emerging it is discussed in a separate paragraph. Equally, geochemical interactions are assumed to occur in an aqueous environment. In the context of CO₂ storage two other non-aqueous types of interactions are possible: chemical interactions between water dissolved in SC-CO₂ and rock and pure SC-CO₂–rock interactions in complete absence of water. As research with respect to these is also preliminary these are discussed separately.

3.1. Dissolution of CO₂ in brines

In one assumes that interactions occur in an aqueous context, in order for injected CO₂ to be able to react with rock materials in an aqueous environment it needs to dissolve in the brine first. The maximum concentration of CO₂ under the prevailing pressure, temperature and brine salinities thus determines the reactivity of the system. As shown in Kervévan et al. (2005) an accurate estimation of the solubility needs to include corrections regarding the activity for dissolved species and density calculations involving Pitzer's formalism as well as the impact of pressure and temperature on thermodynamic equilibrium constants. The impact of pressure and temperature on CO₂ solubility in case of pure water and a 200 g/l brine as derived from the Duan and Sun (2003) model is given in Fig. 2 and illustrates that the solubility in the brine is significantly lower than in pure water. The mixing of a concentrated brine with a CO₂ saturated less saline brine can therefore lead to partly exsolution of dissolved CO₂, creating a separate phase. This is also the case if temperature increases or pressure decreases as both effects reduce CO₂ solubility.

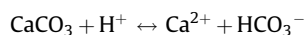
3.2. Chemical interactions inducing porosity–permeability changes and mineral trapping

3.2.1. Reactions induced by dissolved CO₂ and acid induced reactions

The main trigger of geochemical reactions is dissolution of CO₂ in water forming the acid H₂CO₃ which dissociates in the brine:

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$$

This will cause an imminent drop in pH of the brine and cause an acid attack on the minerals of the cement and/or the host rock. Interactions with carbonate minerals, generally present to some extent in sedimentary rocks, will rapidly buffer the pH and render the brine less acid:



Under certain conditions this can induce secondary reactions such as precipitation of gypsum. These reactions, involving carbonate and sulphate minerals are characterised by fast reaction kinetics and can reach equilibrium within a couple of hours at ambient temperatures. As a consequence these reactions are the most important reactions occurring during the injection phase having an impact on the direct well environment.

The acidity of the brine, even after pH buffering due to carbonate dissolution, will however still be sufficient to attack

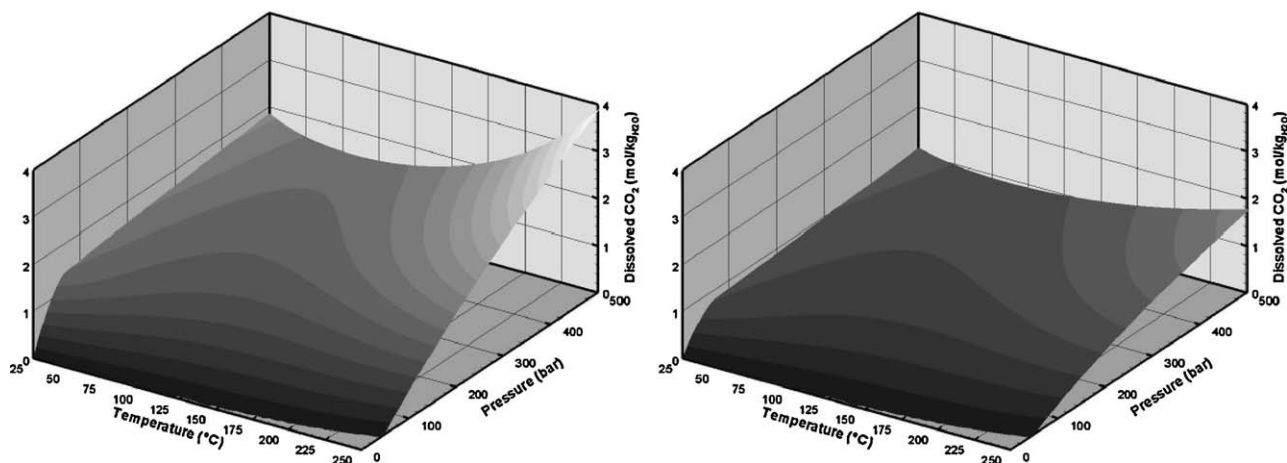
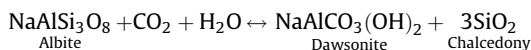


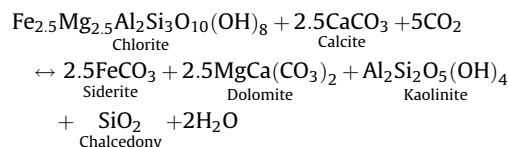
Fig. 2. Concentration of dissolved CO₂ (in mol/kg water) as a function of temperature and pressure in pure water (left) and in a 200 g/l brine (right) as derived from the Duan and Sun (2003) model (Gaus et al., 2008).

alumino-silicate minerals (clays and feldspars) that are present to a large extent in sedimentary rocks. These reactions are at low temperatures (30–50 °C) slow and take up to the order of several thousands of years as modelled in multiple papers (Audigane et al., 2007; White et al., 2001, 2005) based on known kinetic rates. For the permanent trapping of CO₂, alumino-silicate minerals that can function as cation donors will be able to precipitate secondary carbonates according to the following example reactions:

- (a) An example of feldspar alteration is alteration of albite resulting in permanent trapping of CO₂ as the sodium silicate mineral dawsonite:



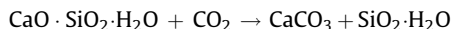
- (b) As an example for alteration of clay minerals, chlorite is capable of trapping CO₂ permanently under the form of siderite and dolomite whereby iron and magnesium are the donor cations:



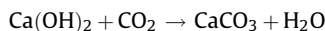
The permanent trapping capacity of many rock compositions is calculated and modelled covering a wide range of mineralogies (see previous references but also Johnson et al., 2001, 2004) but is subject to large uncertainties at various levels as discussed in following paragraphs.

As both feldspars and clay minerals are present in both typical reservoirs and clayey and shaly cap rocks (but not in evaporite cap rocks) long-term alumino-silicate interactions are similar in both environments. However, in case of permeable host rock where advective flow is dominant, impact of long-term reactions and mineral trapping capacity is important. In case of an intact cap rock, CO₂ transported in the cap rock will only occur through very slow diffusion, which limits interactions as only small amounts of CO₂ are capable of entering the cap rock. In this case, where mineral trapping is quantitatively insignificant, impact on porosity and permeability are of major interest. Gaus et al. (2005) describe coupled modelling in the case of the Sleipner cap rock indicating that the geochemical impacts and consequent porosity changes induced through cap rock diffusion of CO₂ are minor and limited to the host rock/cap rock interface. These results are confirmed for other types of cap rocks as described in Chadwick et al. (2007).

Alteration of cement through CO₂ is a known process (Rochelle et al., 2004). The carbonation reaction is described as the main process of hydrated cement minerals alteration consisting of the carbonation of calcium silicate hydrate (CSH), in its simplest manner it can be described as:



And the carbonation of portlandite:



Although it is clear that cement is degraded by exposure to CO₂ under storage conditions, Kutchko et al. (2007) state that the degradation processes are slow. Work on 30 years old CO₂ altered cement is cited in Carey et al. (2007). Long-term experiments are needed and currently ongoing to study the kinetics under the relevant conditions.

3.2.2. Dissolution and precipitation kinetics

Although a chemical reaction might be thermodynamically favourable, the impact of the reaction will ultimately depend on the rate at which the reaction occurs. A key issue when evaluating

the trapping capacity or the impact on permeability during CO₂ storage is therefore assessing the rate at which the reactions occur. While for certain minerals the dissolution and precipitation kinetics is reasonably well known (at least for CO₂ storage applications) since the kinetic rates are high and can be measured directly in the laboratory (e.g. most carbonates, certain sulphates) this is generally not the case for alumino-silicate minerals which are dissolving very slowly at reservoir temperatures (Palandri and Kharaka, 2004). To assess the impact of these reactions indirect techniques must be used:

- Observations from natural analogues.
- Determination of individual reaction rates in the laboratory on the short-term and integration in geochemical models for the prediction of the impact on the long term.

As will be discussed later, the information derived from natural CO₂ analogues is of rather qualitative nature. Therefore numerical modelling including reactions kinetic laws is currently the main method to assess the impact of alumino-silicate reactions on the long term.

Many kinetic laws are described in the literature (Plummer et al., 1978; Pokrovsky et al., 2005; Lasaga et al., 1994) and are applied in many domains in geosciences. For CO₂ applications generally the rate law as described in Lasaga et al. (1994) is applied in a simplified manner:

$$\text{rate}_m = A_m k(T)_m (a_{\text{H}^+})^n \left[1 - \frac{Q_m}{K_m} \right] \quad (1)$$

where m is the mineral index, rate is the dissolution/precipitation rate (positive values indicate dissolution and negative values precipitation), A is the reactive surface per kg water, $k(T)$ is the temperature dependent rate constant, a_{H^+} is the proton activity, n is the order of the reaction ($0 < n < 1$), K is the equilibrium constant for the mineral water reaction written for the dissolution of 1 mol of mineral and Q is the corresponding ion activity product.

The major uncertainty in this law is the product of the reactive surface area and the kinetic rate ($A_m k(T)_m$) as both parameters are difficult to quantify.

The determination of kinetic constants is subject to many complexities and experimental data should be available over a wide range of pressures and temperatures both far from and close to equilibrium. Furthermore, potential catalysers or inhibitors should be identified, constants should be measured for varying mineral compositions in solid solutions series as well as for minerals that are not perfectly crystalline etc. Most of these data do not exist until now and kinetic data compilations show large variations in kinetic rates as a consequence of different experimental setups, experimental conditions and selected mineralogies as shown in Palandri and Kharaka (2004). For slow reacting minerals these differences can easily span several orders of magnitude. When comparing laboratory derived kinetic rates with kinetic rates derived in the field, then the results suggest that reactions are taking place much faster in the case of laboratory data. For example, in situ derived silicate reactions rates have been found to be far slower than laboratory studies at comparable temperatures and pH values with differences of up to 2–5 orders of magnitude (e.g. Zhu, 2006). The formation of mineral coatings is sometimes suggested to play a role in this discrepancy (Cubillas et al., 2005).

The definition of the reactive surface area and representing it by the geometric or the BET surface area introduces further uncertainty (Aagaard and Helgeson, 1982; Gautier et al., 2001). Interaction with the minerals is generally expected to occur only at selective sites at the surface and the difference between total surface area and reactive surface area can be between 1 and 3 orders of magnitude (White and Peterson, 1990). For example,

Gautier et al. (2001) suggest that the increase in reactive surface area during dissolution consists primarily of unreactive etch pitch walls. The definition of the precipitating surface is, compared to that of the dissolving surface, even more complex as it is generally assumed that precipitation does not occur everywhere in the pore space but takes place at specific places initially. The initial precipitation surface is small and precipitation occurs slowly around nuclei. Steefel and Van Capellen (1990) describe the role of nucleation, precursors and Ostwald ripening. Savage et al. (in press) are probably the first to implement these concepts in coupled codes and demonstrate this in the domain of nuclear waste storage.

Consequently, even in the case where all modelling parameters are known and processes are correctly implemented in the long-term coupled model, the product of the reaction rate and the reactive surface areas alone introduces uncertainties up to several orders of magnitude on the mineral trapping capacity and potential porosity changes on the long term.

The difficulties of capturing the uncertainties in the long-term modelling and assessing the trapping capacity are illustrated based on the Sleipner example where several research groups modelled the long-term trapping in the Utsira formation. Even in this low reactive formation, where mineral trapping is not assumed to play a major role, model outcomes differ significantly due to the uncertainties in the underlying data and the different assumptions and parameter choices that are made by the modellers as a consequence of that. This is illustrated in Table 1 where the major conclusions of the various modelling studies and their underlying assumptions are compared. However, also because the impact of mineral trapping is minor in the case of the Utsira Sands, the models do not lead to contradictory results when considering the impact of the assumptions made. For example, the reason why no CO₂ trapping in the study of Frangeul et al. (2004) was modelled is that no aluminosilicate minerals were included. These minerals are the potential cation donors for the precipitating carbonates which trap the CO₂.

3.2.3. Chemical interactions as a consequence of evaporation leading to porosity reduction

A second type of chemical reactions is linked to brine concentration and occurs in the direct vicinity of the well. As CO₂ is injected in dry state, once in contact with the reservoir brine, H₂O is able to dissolve in the dense CO₂. In case of high fluxes, as are occurring in the well vicinity, substantial amounts of H₂O can transfer to the CO₂ phase thereby concentrating the species in the brine. This brine concentration subsequently induces precipitation

reactions of kinetically fast reactions such as carbonates, sulphates and evaporites. The sequence of minerals precipitating depends on the initial brine composition and can be modelled using Pitzer (1991, 1973) based geochemical models. An example of a mineral precipitation sequence based on a brine composition similar to Triassic seawater is described in Pauwels et al. (2007) indicating the mineral sequence consists of the following precipitation stages: gypsum–halite–epsomite–sylvite–carnallite–bischofite.

Experimental evidence indicating chloride increase in the brine as a consequence of brine concentration at high pressure and temperature conditions is cited in Kaszuba et al. (2003). The authors conclude that the impact of brine concentration can be twofold:

- Increased density of the brine leading up to gravitational instability and vertical components of flow.
- Fluid rock interactions at high ionic strengths differing in a significant way from reactions in the bulk system.

This phenomenon around the well including the “drying out” phase is modelled in one dimension in André et al. (2007) using the example of a carbonate aquifer. The “drying out” phase is here defined as the phase where the pore space is completely filled with CO₂ and the remaining water consists of residual water which no longer can be displaced. High dry SC-CO₂ fluxes remove the water from the brine thereby increasing the concentration of the diluted species. Modelled ionic strengths increase from values typical for brines up to values above 30 and mainly carbonates, but also chalcedony are supersaturated suggesting the potential for precipitation reactions. However, at these high ionic strengths, classic coupled geochemical codes do no longer describe geochemical reactions correctly.

Carpita et al. (2006) model modifications in the porosity and permeability, due to evaporation effects in medium saline brines in two dimensions, but taking into account halite precipitation only. Although their model is only to a limited extent capable of representing the geochemical interactions, a significant result is that the potential of halite precipitation affecting the permeability is essentially depending on the brine mobility. Only in case the brine is sufficiently mobile, the precipitation front is recharged by the brine flowing to the wellbore, due to the strong capillary pressure gradient driven by evaporation. In this case it is modelled that precipitation can significantly reduce permeability depending on the injection rate.

Little experimental evidence whereby precipitation is observed exists. Muller et al. (2009) performing experiments on Berea sandstone indicate halite precipitation after flushing a NaCl

Table 1

Overview of published coupled models that refer to the Utsira saline aquifer storage case at the Sleipner site, their main characteristics and finding (Gaus et al., 2008).

Reference	Geometry	Geochemistry	Simulation time	Major conclusions
Gaus et al. (2005)	1D aqueous-phase modelling assuming diffusion in the cap rock only	Complete cap rock mineralogy using transition state theory reaction kinetics	3000 years	Porosity change in cap rock negligible, overall only slight decrease in porosity modelled possible, except at the reservoir/cap rock interface
Johnson et al. (2001, 2004)	2D two-phase flow model including reservoir, cap rock, with inter aquifer clay layers	Complete cap rock and host rock mineralogy using transition state theory reaction kinetics	20 years	Intra-aquifer shales enhance the volumetric extent of plume–aquifer interaction, 85% remains as SC-CO ₂ , 15% dissolves and <1% precipitates in the near field environment. Important reduction in microfracture porosity in the cap rock calculated
Frangeul et al. (2004)	3D homogeneous two-phase flow reservoir model	Carbonate host rock mineralogy only. Not clear if kinetics is included	6000 years	After 6000 years 55% of the CO ₂ in dissolved form, 42% in ionic form, no CO ₂ precipitated
Thibeau et al. (2007)	3D homogeneous two-phase flow reservoir model, on a coarse grid	Complete host rock mineralogy using transition state theory kinetics	18,000 years	Depending on the initial mineralogy, between 40% and 100% of the CO ₂ is trapped in minerals after 10,000 years
Audigane et al. (2007)	2D radial two-phase flow reservoir model with inter aquifer clay layers	Complete host rock (sand and shale) mineralogy using transition state theory kinetics	10,000 years	95% of CO ₂ dissolved in the brine, 5% taken up by minerals after 10,000 years

saturated core with dry SC-CO₂. Subsequent modelling suggests that this can potentially reduce injectivity of CO₂ on saline aquifers but also that simple reservoir engineering measures, such as a brief (hours) preflush with fresh water, could mitigate adverse effects.

Further research is needed to assess if this brine concentration is relevant to the point where it affects porosity and permeability in a significant way in real CO₂ storage schemes. The Frio formation experiment clearly demonstrated that CO₂ saturations up to 100% were reached in high permeability parts close to the injection well indicating that drying of residual water occurred (Hovorka et al., 2006).

Mass balance calculations taking into account the amount of residual brines, the porosity and permeability and total amount of species that can precipitate might be able to provide a first assessment.

There is a clear need to couple Pitzer based geochemical models to two-phase flow models. Although code development is ongoing (Zhang et al., 2006), this has not been applied to this aspect of CO₂ storage. However, also these codes will remain restricted to certain geochemical interactions only in the distant future as experimental data for aluminium based minerals are currently lacking, preventing the extension of the Pitzer based approach to this type of minerals. How precipitation reactions affect porosity and permeability in this well environment is of crucial importance when assessing this phenomenon and is addressed in the next paragraph.

3.2.4. Linking geochemical reactions with porosity and permeability changes

Permeability changes as a consequence of dissolution and precipitation processes form the major feedback of CO₂–water–rock interactions to the physical behaviour of the CO₂ storage scheme. However, this relationship is also the Achilles' heel of assessing the impact of water–CO₂–rock interactions at the same time. It is well known that drastic permeability reductions can result from the growth of minute amounts of secondary minerals as this might change the geometry of the hydraulic capillaries. It is exactly this phenomenon that one tries to assess in, for example, coupled models. In coupled geochemical–flow models (TOUGH-REACT (Pruess, 2004), PHREEQC (Parkhurst and Appelo, 1999)) however, the impact of dissolving and precipitating minerals is calculated based on the molar volume of the individual minerals and the porosity of the rock. Minerals that are dissolving free up space according to the dissolved mass, while precipitating minerals take up open space. The balance between both allows calculating the porosity change.

In a next step, based on a pre-defined porosity–permeability relationship, which is independent from the rock type, the permeability changes are calculated. This permeability change subsequently impacts the flow. However, it is well known that there is no “universal” permeability–porosity relationship valid in all porous media and that the evolution of permeability and porosity in rocks depends on how the precipitation and dissolution reactions affect the pore space. This is the topic of many diagenesis studies and cannot be discussed here. In practice, the permeability change is calculated based on the porosity change using a porosity–permeability relationship, often based on the Kozeny–Carman equation (Carman, 1956). In rare occasions more advanced porosity–permeability relationships are used, for example, based on the fractal “pigeon hole” model which represent the porosity–permeability relation in sandstones more accurately as discussed in Pape et al. (1999). Also precipitation can be described based on the Verma and Pruess porosity–permeability model describing the porous medium as a composition of channels whose axis is parallel to the fluid flow as in TOUGH2 (Pruess, 2004).

The link between geochemical reactions and the impact on permeability is a known difficulty in several related areas (e.g. aquifer storage and recovery, the storage of nuclear waste, geothermal applications) and will not be resolved in the distant future. However, the fact that it is of crucial importance for assessing the impact of CO₂ induced reactions requires that it receives further attention. Especially, pore scale modelling of CO₂ induced reactions and experimental work characterizing changes in the pore space geometry under conditions relevant to CO₂ storage seem promising in improving the understanding of the impact.

3.3. Chemical reactions leading up to potable water contamination

In contrast to the chemical reactions discussed in the previous paragraphs which take place in concentrated brines and which induce large transfers of mass between the aqueous and the solid phase, geochemical reactions affecting drinking water quality occur in very dilute waters where minor mineral dissolution might affect the water quality in such a way that environmental laws are violated. This is especially the case for trace metals where standards of water quality for human consumption are extremely low as set by the World Health Organisation (e.g. Arsenic: 50 µg/l, Lead: 50 µg/l).

As reported in Smyth et al. (2009), preliminary results from a series of laboratory experiments and field experiments suggest that effects on parameters that can be measured easily include increased alkalinity, elevated dissolved inorganic carbon (DIC) and elevation of cation concentrations. Reactions causing these effects are similar to the acid attack reactions described in Section 3.2.1. Dissolution of CO₂ generates bicarbonates and protons leading to acid attack of the aquifer minerals. For aquifers to contain water of potable quality, carbonate minerals are most likely to be present to some extent, leading to a buffering of pH in case CO₂ leaks into the aquifer. The buffering of the CO₂ contaminated water reduces the risk of further substantial degradation of the water quality.

Unless massive leakage occurs, locally consuming all carbonates that are present, and no further carbonate buffering takes place, pH values are unlikely to drop sufficiently to dissolve minerals containing heavy metals, as confirmed in the modelling work conducted by Wang and Jaffe (2004) using lead as an example. The authors point out the need to assess the areal extent of the CO₂ release as well as the need to understand the key kinetic processes regarding the dissolution of CO₂ and the dissolution of trace metal containing mineral phases.

Trace metal dissolution in aquifers due to acidification is a known phenomenon and has been observed in the field and modelled in other contexts such as acidification through acid rain leading to medium pH waters (e.g. Kjoller et al., 2004). Also on the topic of trace metal dissolution due to acid mine drainage, potentially leading to very low pH environments, a large amount of literature exists.

Although the risk that leakage of CO₂ in aquifers deteriorates the water quality is assumed to be limited based on the limited experimental and modelling evidence and reinforced by the good quality of many bottled waters containing CO₂ naturally, systematic research especially assuming leakage on a large scale is needed. This should include the existing literature on kinetics and mechanisms relevant in these aquifer conditions. The demonstration through experimental work, field observations and modelling that CO₂ leakage is unlikely to affect drinking water quality, would mean a strong argument in terms of obtaining a licence where injection of CO₂ is planned to take place in reservoirs overlain by potable aquifers, which is the case for most onshore injection sites.

3.4. Clay shrinking through CO₂ drying

Since the injected CO₂ is likely to be dry in order to avoid corrosion in the infrastructure, as a consequence, water can dissolve in dry CO₂ up to the maximum solubility limits as indicated in King et al. (1992). Clays or clay/sand mixtures contain a large amount of water when saturated. Once the water content drops below a certain limit, as a consequence of water dissolution in dry CO₂, shrinkage and cracking, affecting the physical properties, might theoretically occur. Similar phenomena, induced by air drying are known from other geoscience areas. For example, shrinkage and cracking of clay is a known phenomenon in soils (e.g. Osinubi and Nwaiwu, 2008 and references therein) and is also investigated in a context of engineered barriers containing bentonite (Tay et al., 2001).

It is suggested that, once SC-CO₂ reaches the cap rock as a consequence of buoyancy, water might be extracted from the cap rock clays at the contact between dry CO₂ and cap rock. This “drying out” of the cap rock clays might induce shrinkage and an increase in permeability, affecting in turn the cap rock properties and the function of the cap rock as a barrier as a consequence (Rochelle et al., 2004). Since the solubility of H₂O in CO₂ is small (0.2%, w/w) a large amount of dry CO₂ must be able to contact the clay minerals to dissolve the necessary amount of water into the CO₂. This renewal process, whereby fresh dry CO₂ is constantly extracting water from the clay surfaces, is more likely to be met in an advective environment than in a pure diffusive environment. In case a cap rock is functioning properly as a barrier, which implies that diffusion in the cap rock is the only mass transport mechanism of CO₂, the amount of H₂O that could potentially dissolve in SC-CO₂ is very small making clay desiccation rather unlikely. Initial estimations to quantify this phenomenon could be performed using mass balance calculations.

However, where advective flow of dry CO₂ is dominant, the process could become potentially relevant. One could imagine that in the case of leakage along a fault in the cap rock or along a well crosscutting the cap rock, a constant flux of dry CO₂ might be in place which continues to exist for a certain time so that the potential for clay dehydration and desiccation increases.

It is currently unclear if this process is relevant in the context of CO₂ storage. Crucial for assessing its relevance is to identify if in a highly pressurised initially fully water saturated environment, typical for a CO₂ storage site, the water saturation in the clays, locally or over a larger area, can become sufficiently low. Indeed, it might be that at a certain level of decreased saturation, unsaturated clay, through suction, will “attract” water from the fully saturated surrounding areas.

In the context of CO₂ storage, so far, no substantial research has taken place to explore the relevance of this phenomenon thereby forming a knowledge gap that could be addressed through laboratory work and revisiting literature on the mechanisms of clay dehydration and desiccation.

3.5. Pure SC-CO₂–rock interactions

Aqueous-phase mediated chemical reactions with dissolved CO₂ have so far been the only reactive process triggering chemical interactions with the rock and/or well materials in research conducted. However, two other types of chemical reactions can theoretically be considered: reactions occurring between dry SC-CO₂ and rock/well materials and interactions between water saturated SC-CO₂ and rock/well materials.

Regnault et al. (2005) and Jacquemet (2006) demonstrate experimentally that significant carbonation of cement can occur in the complete absence of brine. Jacquemet et al. (2007) performing experiments with a dry H₂S-CO₂ supercritical phase on crushed cement conclude that carbonation of well cement sheath would be

completed in zones along the wellbore where liquid water is suspected to be negligible or absent. Furthermore, they observe that the impact of a pure H₂S-CO₂ phase is more important than those of a brine with dissolved CO₂ and H₂S.

Regarding chemical interactions between SC-CO₂ saturated with H₂O and rock and well material minerals only initial work has been conducted. McGrail et al. (2009) report based on both experiments and molecular dynamic simulations, that molecular water solvated in liquid and supercritical CO₂ is quite reactive towards both iron and silicate mineral surfaces under conditions that approximate those anticipated for CO₂ storage systems.

These initial papers on pure CO₂–rock interactions are of high importance and the result needs to be confirmed in additional experimental work as this could have a significant impact on all aspects of CO₂–rock and well material interactions, while so far the general assumption is that the SC-CO₂ phase is chemically inert.

In both cases traditional geochemical modelling as it is currently implemented in common codes cannot be applied to model these types of interactions as all models rely on aqueous chemistry.

3.6. Presence and impact of other components than CO₂

The injection of CO₂ containing other chemical components (e.g. as a result of the separation process) can be considered for economical reasons. It is estimated, for example, that as a result of the oxycombustion process, next to CO₂ the gas will contain low quantities of H₂O, Ar, O₂, SO₂, NO and N₂ (Anheden, personal communication). The presence of these components will affect the behaviour of the gas stream in terms of miscibility, migration and geochemical interactions and could influence the minimal storage depth at which the mixture is in the supercritical state.

Assessing the gas rock interactions of CO₂ containing other components essentially consists of two aspects. First, the thermo-physical properties of the gas mixtures have to be modelled using existing equations of state (EOS) which have to be adjusted based on experimental data. Apart from the CO₂–H₂O, CO₂–N₂, CH₄–CO₂ and N₂–CO₂–CH₄ mixtures, currently data are very scarce. Then the reactivities of the gas mixtures with the host rock and well materials have to be assessed through experiments and modelling. Based on individual solubilities of the other gasses and their chemical characteristics, SO₂ has the potential to cause strong interactions as indicated in publications that focus on the impurities in the CO₂ stream (Jacquemet et al., 2009). Knauss et al. (2005) describe the impact of a gas mixture of CO₂ and H₂S and of CO₂ with traces of SO₂ using 1D modelling. Another example is Gunter et al. (2000) performing batch modelling of interactions of acid wastes containing CO₂, H₂SO₄ and H₂S. Palandri and Kharaka (2005) modelled the trapping of CO₂ through iron reduction using sulphur bearing waste gas.

If co-injection of other components than CO₂ is seen as a realistic option, then research available today to assess gas–rock interactions is clearly insufficient. In that case additional experimental work supported by model development is needed to assess the physical and geochemical impact of the additional gasses and the resulting gas mixtures.

4. How can CO₂–rock interactions be assessed?

There are four techniques to assess CO₂–rock interactions. The first is through laboratory experiments providing experimental data and direct observations on a timescale similar to the length of the experiment, so at best a couple of years. CO₂–rock interactions can also be studied using natural CO₂ analogues. The timescale of interest is here the geological timescale, going beyond the anticipated impact period of a CO₂ storage scheme. Direct observations are possible, but these are the result of many factors

and changing boundary conditions and therefore difficult to interpret uniquely. Assessing CO₂–rock interactions during field and demonstration tests lead to observations stretching over several years at the scale of the CO₂ storage scheme. However, generally no direct observations on the host rock are possible and water samples need to deliver the bulk of the information on CO₂–rock interactions. Finally, modelling can be used to interpret the experiments, model the natural analogues and the field and demonstration sites. Modelling requires a large data support and detailed parameter and process knowledge to be able to make accurate predictions, but can cover the timescale of a CO₂ storage scheme.

All four techniques have to be combined as also highlighted in the recommended best practice for assessing the geochemical effects of CO₂ storage (Chadwick et al., 2007; Czernichowski-Lauriol et al., 2006).

4.1. Laboratory experiments

In this paragraph two types of experiments are distinguished. With the “total impact” experiments a host rock, cap rock or cement is brought in contact with CO₂ saturated brine or with brine and dense CO₂ at specific temperature and pressure conditions. The evolution of the species in the brine is monitored and dissolving and precipitating phases are identified, for example, through SEM (microprobe). These experiments are based on real rock compositions and realistic brine compositions. In “specific experiments” the focus is generally on one or more aspects of the CO₂–rock interaction. These experiments focus on the determination of dissolution rates, dissolution or precipitation mechanisms of specific minerals, or thermodynamic characteristics of minerals that potentially participate in CO₂–rock interactions. These experiments do not necessarily have to be conducted in a CO₂ storage specific context.

4.1.1. “Total impact” experiments

Initial experiments have been published by Gunter et al. (1997, 2000), Czernichowski-Lauriol et al. (1996b) and are also cited in Rochelle et al. (2004). These experiments have shown changes in the brine chemistry, however no changes in the primary minerals or no new secondary minerals have been observed although the temperature was at 105 °C and pressures at 90 bar. A large scale column experiment with CO₂ saturated synthetic brine at 70 °C and 100 bar and a synthetic mineral composition reacting over 7.5 months also showed changes in the fluid chemistry in accordance with the observed carbonate dissolution. On top of that, changes in the silica concentration were measured while no staining of silica minerals was observed (Bateman et al., 2005). Bunter sandstone dynamic testing in a triaxial pressure cell at 60 °C and 150 bar (Wigand et al., 2008) showed the dissolution of dolomite and the alteration of aluminosilicates such as K-feldspar and albite in a later stage. The precipitation of montmorillonite was observed by SEM. Although this is not a comprehensive list of experiments (other examples are in Grigg et al., 2003; Bertier et al., 2004), the overall outcome of the “Total impact” experiments is that changes in the fluid composition as well as carbonate dissolution can be observed but major aluminosilicate interactions either trapping the CO₂ or causing large changes in porosity or permeability are more difficult to observe. This is not surprising as individual kinetic rates for aluminosilicates indicate that reactions take place only at a slow pace and these types of experiments are limited in time compared to the timescale at which these reactions need to be evaluated in a CO₂ storage context. Exceptions are Wollenweber et al. (2009) measuring sealing efficiencies and mineral alteration in 10 mm long limestone samples and observing fast anorthite dissolution between 21 °C and 45 °C, whereby the impact of the sample size might explain certain results. Also experiments on

powdered samples (Busch et al., 2009) indicate important aluminosilicate reactivity. Generally, only at elevated temperatures increased reactivity can be observed as described in Kaszuba et al. (2005) describing batch experiments at 200 °C and 200 bar indicating precipitation of siderite and magnesite and also analcime next to significantly increased silica concentrations.

The interpretation of the experimental results using geochemical models clearly showed that not all species concentrations can be matched and that not all processes occurring in the experiments are captured in the models (e.g. Bateman et al., 2005; Wigand et al., 2008). Extrapolation of modelling results obtained for certain rock compositions to other rock compositions is therefore difficult. One should therefore strive to support geochemical modelling with as much constraints on the boundary and initial conditions as possible defined by experimental work on in situ material and using conditions as close as possible to the in situ conditions. This is a necessity in order to obtain relevant information for each CO₂ storage site.

A series of experiments have been conducted to assess the impact of CO₂ or acid brine on cement and the cement degradation process. Key papers are Scherer et al. (2004) stressing that in case a large flux is in place the attack can be rapid, and Kutchko et al. (2007) and Jacquemet et al. (Jacquemet et al., 2005, 2007). Recent highly relevant experiments focus on pure CO₂–rock/cement interactions (McGrail et al., 2009) and the modelling of the brine evaporation process based on core flooding with dry SC-CO₂ (Muller et al., 2009).

4.1.2. Specific experiments

With specific experiments, the purpose of the experiment is not the assessment of the impact of brine and CO₂ on a certain rock type, but rather the characterisation of mineral phases and their thermodynamic and kinetic properties. The outcome of these experiments then feeds either into the conceptualisation of the geochemical models or in their parameterisation.

It is not the purpose of this paper to be comprehensive on these experiments determining kinetic rates as many are carried out in wider geosciences contexts and not specific to CO₂ storage. A comprehensive list of all references describing experimental work on the determination of kinetic rates is given in Palandri and Kharaka (2004). It is remarkable however that, although the kinetic constants are determined under a wide variety of conditions, they are implemented in the coupled codes for CO₂ storage without considering the impact of this. Verification of rate constants for certain key minerals under specific CO₂ storage conditions (relevant pressure and temperatures, brines, high CO₂ pressures, etc.) would allow to reduce the uncertainty. The role of microbiological catalysts for the CO₂–rock interactions forms a recent research topic and first results are discussed in Dupraz et al. (2008) and Mitchell et al. (2008).

Specific experiments have also proven to be useful for the characterisation of secondary minerals such as dawsonite, a rare mineral that has been linked to natural CO₂ reservoirs, and that is responsible for the trapping of significant amounts of CO₂ based on geochemical models (Gaus et al., 2005; Audigane et al., 2007; Xu et al., 2005). Thermodynamic data have been confirmed (Bénézech et al., 2007) and also recently dissolution and precipitation rates have been established (Declercq et al., 2008) whereby measured dissolution rates by Hellevang et al. (2005) suggest that dawsonite will provide a permanent mineral storage host only in systems that maintain high CO₂ pressures, and might dissolve once high CO₂ pressures dissipate.

4.2. Natural analogues

Although not always straightforward to interpret due to their complex geological histories, studying natural systems that have

been in contact with CO₂ for geological timescales provide valuable opportunities to study CO₂–rock interactions on the appropriate timescales (10³–10⁵ years).

Several large scale initiatives have been undertaken studying natural analogues such as the NASCENT project in Europe, the NACS effort in the US and as part of the GEODISC programme in Australia. As part of natural analogue studies, CO₂–rock interactions have been addressed regarding cap rocks, wells, reservoirs and fractures and contributed to the assessment of the potential long-term impact of CO₂.

One of the first striking observations was the presence of large amounts of dawsonite, the sodium aluminium silicate with a potential to trap CO₂ permanently, in a couple of natural analogues such as the Bowen–Gunnedah–Sydney basin in Australia (Baker et al., 1995), beneath the Colorado Plateau and Southern Rocky Mountains (Moore et al., 2005) and in Yemen (Worden, 2006). This observation was used as an argument to include the mineral as a secondary mineral in many long-term geochemical models. However, dawsonite has not been observed in other natural analogues where sodium rich brines have been in contact with sedimentary rock and CO₂ for millions of years, and where apart from feldspar dissolution little impact of the CO₂ on the reservoir chemistry has been observed (Gaus et al., 2004). Chemical equilibrium also seems not to be reached in some natural CO₂ fields in the North Sea analogues where 5–20% of the rock still consists of calcite and feldspar and dawsonite is absent, even when subjected to very long (geological) contact times (Haszeldine et al., 2005). This suggests that chemical equilibrium might not be the natural state of the injected CO₂ during the whole duration of the storage period and that kinetic reaction rates might be far lower in reality than the ones observed in the laboratory and implemented in the long-term geochemical models.

Similar observations are made in the context of mineral weathering and aquifer water qualities which showed experimentally that the weathering rate in CO₂-rich waters decreases exponentially with duration of weathering for certain rock forming minerals. Recent work by Assayag et al. (2009), based on measurements on natural fluids from a natural analogue at green River, Utah, suggests that feldspar dissolution rates are 3–5 orders of magnitude slower than those estimated in the laboratory.

Some evidence from natural analogues also illustrates cap rock interactions. Watson et al. (2004) describe the enhancement of the cap rock function from a natural CO₂ accumulation in the Otway basin (Australia) attributed to the late stage siderite cement precipitation near fracture edges and in the pore space which contains mineralogically trapped CO₂ as shown based on isotopic evidence. The formation of minerals on fracture planes of natural CO₂ leakage paths, and carbonates and anhydrite in fractures and cracks has been documented in May (2005) and Fischer et al. (2006) respectively.

This shows that studying natural analogues has led to accurate information on the mineralogical and petrographical conditions as well as on the nature of the CO₂ trapped in these analogues. In certain cases plausible reaction pathways have been identified and it has been confirmed that relevant amounts of CO₂ can be trapped in mineral phases as predicted in the geochemical models. However, the geological complexity of the sites, with tectonic activities, variations in temperature and pressure conditions, the displacement, leakage and recharge history of the CO₂ and changing groundwater flow regimes in general do not allow for a sufficient reconstruction of the evolution of the CO₂ in the host rock. As a consequence, boundary conditions to constrain the geochemical models allowing calibrating the kinetic aspects of the identified reactions pathways cannot be formulated apart from one or two rare cases.

Natural analogues have thus so far not been capable to aid significantly the calibration of numerical models regarding the kinetic aspects of the long-term water–rock interactions in the subsurface behaviour of the injected CO₂.

It is striking that a similar observation is made in the area of the storage of nuclear waste where many studies on natural analogues were performed, quantitative observations regarding reactions paths and reaction products were made, but estimation of reactions rates proved extremely difficult.

4.3. Demonstration, field experiments and monitoring

Several demonstration sites have gone in operation (e.g. Sleipner, In Salah, Weyburn) during the last years with Sleipner being the first in the late nineties. Also field experiments such as the Frio formation experiment provided valuable information on the site scale. Although direct access to the host rock is not possible in this type of experiments, and at best host rock brine can be sampled to assess water quality changes as a consequence of CO₂–rock interactions, important observations can be made in most cases. Demonstration sites and field experiment currently cover the time span of up to 10 years and CO₂–rock interactions occurring within this period are consequently those characterised by fast reaction kinetics. Only experiments with significant data on CO₂–rock interactions are listed here.

The Frio brine pilot was a closely monitored, small volume (1600 tonnes), short duration experiment injecting CO₂ into high permeability brine bearing sandstone at a depth of 1500 m (Hovorka et al., 2006). Monitoring of the brine occurred in both the injection well and the observation well. Following breakthrough after 52 h, samples showed sharp drops in pH to values of (6.5–5.7), pronounced increases in alkalinity and iron and significant shifts in the isotopic compositions of H₂O, dissolved inorganic carbon and CH₄ which have been attributed to carbonate dissolution and dissolution of oxyhydroxides have been observed (Kharaka et al., 2006).

The Weyburn Oil Field, Saskatchewan is the site of a large (5000 tonnes/day of CO₂) CO₂-EOR injection project by EnCana Corporation. Pre- and post-injection samples from around 45 wells were taken and chemically analysed to determine changes in fluid chemistry. After 6 months of CO₂ injection spatial mapping and contour plots showing decreasing calculated pH values, increases in bicarbonates and changes in $\delta^{13}\text{C}$ and $\delta^{13}\text{C-HCO}_3^-$ values indicate that carbonate dissolution is taking place (Emberley et al., 2005). Isotope and mass balance calculations indicate that, after 40 months of injection, approximately 80% of the HCO₃[−] in the reservoir brines sampled from four example wells formed from dissolved injected CO₂ (Raistrick et al., 2006).

The Nagaoka CO₂ injection site in a sandstone at 48 °C (Japan) is another example (Mito et al., 2008) where 1 year after stopping the injection and sampling in observation wells, chemical analysis of the post-injection samples indicate a high bicarbonate concentration and increased Ca, Mg, Fe, Mn and Si concentrations.

These examples from the field clearly indicate an almost instantaneous impact of the injected CO₂ on the host rock as predicted by the models and the laboratory experiments and thus provides a confirmation of the impact of CO₂–rock interactions. However, the length of these experiments does not allow identifying aluminosilicate reactions in the field with sufficient certainty up to now.

4.4. Geochemical and coupled modelling

Modelling has proven to be a valuable tool when assessing CO₂–rock interactions. During the latest years, driven by the interest in coupled processes caused by CO₂ injection, considerable effort

went into both the inclusion of additional processes in the models and the improvement of the calculation efficiency allowing for calculations on larger grids taking into account more complex chemistries relevant to CO₂ storage. Examples are the development of additional CO₂ specific modules (such as CO₂-EOS for TOUGHREACT) and the development of new codes such as COORES (Le Gallo et al., 2006, 2009) and GEM-GHG (Nghiem et al., 2004) that are capable of modelling the geochemical interactions caused by the CO₂ injection on a large scale thereby fully taking into account multiple phase flow and density effects as well as detailed geochemistry. Other significant efforts are currently ongoing in the domain of incorporating geomechanics (Rudqvist et al., 2006; Le Gallo et al., 2006) and assessing chemical interactions in highly concentrated brines with large ionic strengths (based on the Pitzer based approach), going beyond the currently often applied ion activity models (Azaroual et al., 2004; Zhang et al., 2005, 2006).

A distinction can be made between pure geochemical modelling not taking into account of transport processes and coupled modelling, which can be coupled flow and chemistry modelling (also including the effect of temperature), but also the geomechanical interactions can be included (THMC modelling: thermal hydraulic mechanical chemistry coupled modelling). A review on coupled flow and transport modelling is given in Gaus et al. (2008). In this paper four main types of modelling applications are distinguished: long-term integrity applications (1), near well applications and impacts on injectivity (2), well integrity (3) and calibration and validation of experiments (4) each having its own spatial and time scale of interest. For each application an overview of the existing literature and the state of the art is given. This will not be repeated here and the reader is referred to the paper.

For each of the modelling applications as listed above, key issues for improvement have been identified.

For long-term integrity applications one of the major uncertainties is the impact of the alumino-silicate reactivities especially with respect to their kinetic rates and the extent to which they are impacting the host rock (as influenced by the reactive surface areas, mineral availabilities and precipitation mechanisms). The predictive value of these models could be improved significantly if more effort would be made to determine kinetics rates that are applicable to the timescale of the models either by upscaling measured laboratory rates or by further attempting to derive semi-quantitative kinetic rates from the analysis of natural analogues or other systems.

Regarding injectivity modelling, the complex phenomena occurring around the injection well in terms of brine concentration leading to very high ionic strengths and inducing precipitation reactions, interactions with violent flow regimes around the injection well with large pressures differentials, potential flushing

of preferential flow paths and potential geomechanical impacts form the main challenges. In this stage it is not possible to prioritise the dominant processes that affect the well environment in the short and the long term. Model applications are still in the early stage and are only partly capturing the phenomena described above. The relative importance of the dominant processes that should be included in the models could further be explored using adequate laboratory experiments.

For geochemical well integrity modelling the difficulties for defining the correct conceptual models are twofold.

Firstly, the characterisation of reactions between low pH brine and cement requires further investigation, especially with respect to altered cements. Many papers focus on high pH-water-cement interactions due to the importance of the topic in the context of the disposal of nuclear waste. There it became clear that the inclusion of CSH gels and solid solutions as well as the selection of the secondary minerals plays a crucial role (Lothenbach and Winnefeld, 2006; Savage et al., 2007) in correctly representing the interactions.

Secondly, it remains unclear in this stage which combined CO₂ transport mechanism is capable of causing a significant impact in terms of geochemical interactions as many paths along various interfaces are suggested (see Fig. 3). Current detailed geochemical modelling efforts are restricted to simple 1-dimensional interface models (Jacquemet et al., 2007; Carey and Lichtner, 2007; Carey et al., 2007).

Recurring uncertainties in all modelling applications aiming at assessing the impact of geochemical interactions on porosity and the permeability is the fact that the relationship between precipitation and porosity and permeability remains extremely difficult to quantify. The implementation of this relationship in the numerical codes has not been revised in the context of CO₂ storage. Improving the characterisation of how CO₂ induced precipitation and dissolution reactions influences the permeability in diffusion dominant systems in low permeability rocks as well as advection dominant systems in host rocks remains an important challenge. Upscaling results from pore scale modelling could address (part of) this issue.

The coupling of geomechanical codes with coupled flow-transport codes remains a further challenge, although much needed to assess the interplay between the two phenomena. This does not only require code development, but also the development of the datasets to feed into these codes and the correct treatment of uncertainties since both geomechanical and geochemical processes are defined by highly uncertain parameters.

In the context of risk assessment modelling, certain modelling approaches simplify geochemical interactions by including only the anticipated result of the geochemical impact in the models, namely the corresponding porosity and permeability changes.

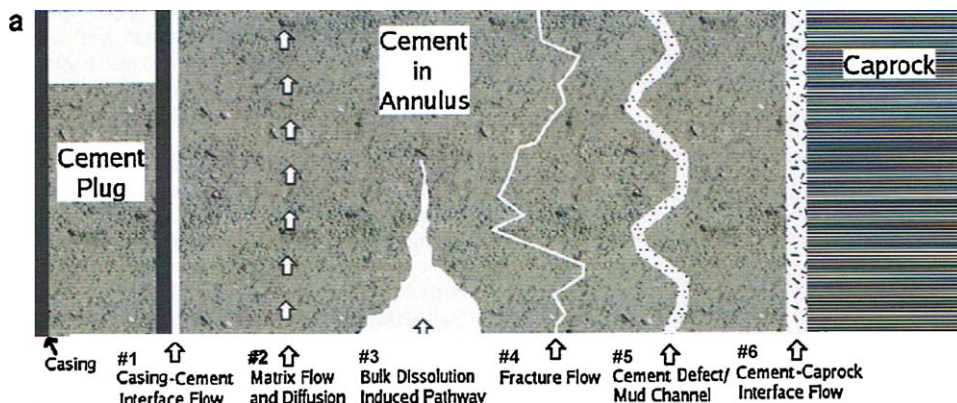


Fig. 3. Schematic of wellbore leakage processes (Viswanathan et al., 2008).

Examples are described for the CO₂-PENS modelling approach (Viswanathan et al., 2008), but are also indirectly included in the approach described by Kreft et al. (2007). Although for certain scenarios it has been shown that geochemical reactions are not influencing risk in a significant way (e.g. geochemical cap rock interactions in diffusion dominated systems), many of the issues listed above illustrate the need for more detailed research to verify that the geochemical reactions and their coupled impact on flow and geomechanics are not capable of dominating the system at a certain point in time and space and thus determining the risk. Therefore detailed models need to be developed and supported by laboratory experiments.

5. Outlook and future challenges

5.1. Based on the interaction environment

Research on the *near well environment* addresses not only safety but also feasibility of the CO₂ storage system in terms of injectivity. In this context following topics can be identified:

- The potential of pure SC-CO₂ or H₂O dissolved in SC-CO₂ causing interactions with cement or host rock should be investigated more deeply as only a few recent publications on this topic exist and during the injection stage the near well environment will be dominated by SC-CO₂.
- Water–cement interactions, their kinetics and their impact on cement degradation at specific CO₂ storage conditions should be further addressed.
- The results of brine evaporation and precipitation as a consequence of H₂O dissolution in SC-CO₂ that should be investigated through modelling and experimental work. Coupled flow-geochemistry models need to be adapted to be able to model highly saline brine interactions.
- The complex flow regime in the near well, including temperature and density effects, and potential existence of heterogeneities and preferential flow paths should be studied in order to identify where geochemical interactions are likely to occur and where permeability is likely to be affected.
- The literature on CO₂-EOR should be revisited in the light of injectivity issues due to CO₂ injection.
- The impact of potential temperature differences between injected CO₂ and reservoir on geochemical interactions should be addressed.

With respect to the long-term host rock interactions and cap rock interactions, one can identify the following:

- The uncertainty in the kinetics of long-term reactions should be reduced in order to allow the mineral trapping capacity versus time to be assessed more reliably. To achieve that, the product of the reactive surface area and the rate constant in the rate laws should be defined more accurately and included in coupled models. This can be obtained by deriving kinetic rate constants from natural analogues or equivalent natural systems, determining laboratory rates under conditions applicable to CO₂ storage and upscaling results, reassessing reactive surface areas and using novel approaches to define the precipitation surfaces. All long-term models should include a correct treatment of uncertainty due to kinetics.
- Long-term reaction paths should be investigated further, especially with respect to the existence of intermediate mineral phases.
- The relationship between precipitation and impact on porosity and permeability should be revisited in a CO₂ storage specific context, both for diffusion dominated systems in low permeability cap rocks as in advection dominated systems in the host rock.

Regarding *leakage pathways*, so far there is no evidence that geochemical interactions are capable of causing leakage when occurring in isolation. However, in case leakage exists, CO₂–rock interactions might enhance or inhibit leakage. Especially leakage pathways that are characterised by a large flux of SC-CO₂ or acidified brine are most prone to extensive geochemical reactions as large mass transfers can generate a significant impact.

- In the case of leakage along a wellbore especially interactions along interfaces (steel/cement, cement/host rock, cement/cap rock) need to be investigated under CO₂ relevant conditions for both pure SC-CO₂ and acidified brine in experiments and through modelling. To make progress beyond current interface modelling, the geometry of the well and the pressure regime needs to be taking into account in modelling applications. Reaction sequences in pure materials, but also at the interfaces should be further refined (inclusion of solid solutions, CSH gels, etc.)
- In case of leakage along faults, little is published on geochemical interactions. The specific mineralogy of rock and fracture fillings, as well as the fault geometry needs to be taken into account. As this is necessarily site specific, generic assessments are difficult.
- It is in a leakage context that the possibility of desiccation of clay minerals through H₂O dissolution in dry SC-CO₂, potentially inducing shrinking of clays and thus affecting permeability, seems most likely. However, research needs to be conducted if this phenomenon could occur at all in a CO₂ storage context. In the light of this existing literature on clay shrinking and desiccation should be revisited.
- As leakage is typically part of risk assessment models, it should be watched closely that the impact of geochemistry is integrated correctly in overall risk assessment models and not neglected or downplayed because of its inherent complexity.

With respect to *aquifer contamination through acidification* by dissolved CO₂, one should realise that mass transfer of geochemical reactions is orders of magnitude smaller than in reservoir interactions at great depth. More refined geochemical processes are needed (ion exchange, surface complexation and redox reactions) to explain relatively small changes in water chemistry (e.g. heavy metal concentrations) that might affect the quality. In this context the following should be investigated:

- Only few experimental studies and relatively simple modelling studies are published, results should be refined and confirmed as aquifer contamination is perceived as a dangerous consequence of leakage.
- It should be established at which scale leakage of CO₂ into aquifers should occur to have a relevant impact. Therefore classic regional hydrogeological models could aid.
- Many natural CO₂ waters exist and are bottled as drinking water; these cases should be investigated in detail to establish the processes that impact the water composition.

In case of *brine displacement* and subsequent aquifer contamination, in first instance, it should be investigated using large scale regional flow models, taking into account the geological sequence from the reservoir up to the level of the potable aquifers, if induced pressure differentials are capable of displacing brines into shallower aquifers. If this is the case, modelling and revisiting existing saline/fresh water mixing literature are strategies to investigate the impact.

5.2. Based on the assessment method

Regarding *laboratory experiments*, one can identify the following issues:

- Characterising the impact of pure SC-CO₂ on rock and cement materials is of high priority in order to confirm few recent existing results and to further identify reaction pathways.
- The impact of other gaseous compounds in the CO₂ stream on rock and cement materials is another high priority that has hardly been addressed.
- As shown by many earlier experiments reacting whole rocks with CO₂ saturated brine, the derived results are always rock specific and individual reactions difficult to identify. Although these experiments are needed, the value in terms of extrapolation of results to other rock types is little. This is different for cement based studies, which are based on engineered reproducible mineral compositions. In the latter case a consistent database can be developed applicable to different cases.
- Continuous effort should be invested in determining adequate kinetic rates under CO₂ storage relevant conditions, characterising reactive surface areas and precipitation mechanisms and development of methods on how to upscale laboratory results.
- The thermodynamic properties of relevant mineral phases that precipitate as a result of CO₂–rock or CO₂–cement interactions should receive further attention.
- Impact of CO₂ induced precipitation reactions on pore space evolution and how to upscale this would aid improving the link between CO₂–rock interactions and permeability.
- The chance of occurrence of clay desiccation under CO₂ storage relevant conditions needs to be evaluated.

Natural analogues and demonstration sites—natural analogues have a well established place in research on CO₂ storage, but information seems so far to be mainly of qualitative nature.

- Natural analogues should be assessed to what extent they can bring quantitative information that can potentially be integrated in long-term coupled models.
- Natural analogues could further be of use to refine reaction pathways, especially with an eye on defining intermediate mineral phases.
- Geochemical analogues spanning the lifetime of a CO₂ storage scheme should be identified, in order to upscale kinetic rates from the laboratory.
- As during field and demonstration experiments no direct observation of the host rock is possible, it would be useful to produce a review to establish the maximum amount of information on flow and geochemical interactions that can be derived from water sampling using isotopic and non-isotopic tracers. This should include methods for water sampling and analysis at high *P–T* conditions.

Regarding *modelling*, following key areas for further development are identified.

- The relationship between flow, geochemical interactions and geomechanical impacts is a key topic that would require investment in model development and validation. This would contribute significantly to the assessment of the near well environment in first instance but also to long-term integrity.
- The possibility of co-injecting other gaseous compounds seems attractive from an economical point of view. However, including other gaseous compounds will require an important research effort with respect to development of adequate equations of state (EOS) and solubility models.
- The relationship between dissolution–precipitation reactions and impact on porosity and permeability is a weak point in all of the coupled codes. Pore scale modelling applied to CO₂ storage, describing geochemical impacts at the pore scale and refining the relationship between geochemical reactivity and

porosity and permeability for key host and cap rock types are required.

- Completing the Pitzer databases and including Pitzer based ion association models in coupled codes would allow significant progress in reliable modelling of geochemical interactions in highly saline brines, in the reservoir but especially around the injection well.

As a concluding remark it needs to be mentioned that some of the research topics indicated above are far from CO₂ storage specific and have been in the focus of geosciences for over decades. Especially regarding reaction kinetics, precipitation surfaces, impact of precipitation on permeability, upscaling of laboratory results in space and time, progress has been made, but a major breakthrough reducing uncertainty orders of magnitude might not be on the agenda for the next couple of years either. For other topics, which are relatively new, such as impact of pure SC-CO₂ on rocks but also development of coupled codes including both geochemistry and geomechanics, Pitzer based coupled models, impact of evaporation around the injection wells and impact of CO₂ on potable aquifers, progress is anticipated to be more rapid.

Acknowledgements

This study has been performed under contract from StatoilHydro, Research Centre Trondheim, Norway. The author would like to thank S. Vomvoris (Nagra) for his comments which greatly improved this paper.

References

- Aagaard, P., Helgeson, H.C., 1982. Thermodynamic and kinetic constraints on the reaction rates among minerals and aqueous solutions. I. Theoretical considerations. *American Journal of Science* 282, 237–285.
- André, L., Audigane, P., Azaroual, M., Menjoz, A., 2007. Numerical modelling of fluid-rock chemical interactions at the supercritical CO₂–liquid interface during supercritical CO₂ injection into a carbonate reservoir, the Dogger aquifer (Paris Basin, France). *Energy Conversion and Management* 48, 1782–1797.
- Assayag, N., Bickle, M., Kampman, N., Becker, J., 2009. Carbon isotopic constraints on CO₂ degassing in cold-water Geysers, Green River, Utah. *Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9)*, November 16–20, 2008, Washington, DC, USA, *Energy Procedia* 1 (1), 2361–2366.
- Audigane, P., Gaus, I., Czernichowski-Lauriol, I., Pruess, K., Xu, T., 2007. Two dimensional reactive transport modelling of CO₂ injection in a saline aquifer at the Sleipner site, North Sea. *American Journal of Science* 307, 974–1008.
- Azaroual, M., Kervévan, C., Durand, M.V., Durst, P., 2004. SCALE2000: a reaction-transport software dedicated to thermo-kinetic prediction and quantification of scales. *Applicability to desalination problems*. *Desalination* 156, 409–419.
- Baker, J.C., Bai, G.P., Hamilton, P.J., Golding, S.D., Keene, J.B., 1995. Continental-scale magmatic carbon dioxide seepage recorded by dawsonite in the Bowen-Gunnedah-Sydney Basin System, eastern Australia. *Journal of Sedimentary Petrology* A65, 22–530.
- Bateman, K., Turner, G., Pearce, J.M., Noy, D.J., Birchall, D., Rochelle, C.A., 2005. Large-scale column experiment: study of CO₂, porewater, rock reactions and model test case. *Oil and Gas Science and Technology—Rev. IFP* 60 (1), 161–175.
- Bénézeith, P., Palmer, D.A., Anovitz, L.M., Horita, J., 2007. Dawsonite synthesis and re-evaluation of its thermodynamic properties from solubility measurements: implications for mineral trapping of CO₂. *Geochimica et Cosmochimica Acta* 71 (18), 4438–4455.
- Bertier, P., Swennen, R., Laenen, B., Lagrou, D., Dreesen, R., 2004. Experimental identification of CO₂–water–rock interactions caused by sequestration of CO₂ in Westphalian and Buntsandstein sandstones of the Campine Basin (NE-Belgium). *Journal of Geochemical Exploration* 89, 10–14.
- Birkholzer, J.T., Zhou, Q., Tsang, C.F., 2008. Large-scale impact of CO₂ storage in deep saline aquifers: a sensitivity study on pressure response in stratified systems. *International Journal of Greenhouse Gas Control* 3 (2), 181–194.
- Bouc, O., Quisel, N., Le Gouevic, J., 2007. Risk and safety evaluation for CO₂ geological storage. *GEOTECHNOLOGIEN Science Report No. 9*. In: 1st French–German Symposium on Geological Storage of CO₂, June 21–22, 2007, Geoforschungszentrum Potsdam.
- Burton, M., Bryant, S., 2007. Eliminating buoyant migration of sequestered CO₂ through surface dissolution: implementation costs and technical challenges, SPE 110650. In: *Proceedings of the 2007 SPE Annual Technical Conference and Exhibition*, November 11–14, 2007, Anaheim, CA, USA.
- Busch, A., Alles, S., Krooss, B.M., Stanjek, H., Dewhurst, D., 2009. Effects of physical sorption and chemical reactions of CO₂ in shaly caprocks. *Proceedings of the 9th*

- International Conference on Greenhouse Gas Control Technologies (GHGT-9), November 16–20, 2008, Washington, DC, USA, *Energy Procedia* 1 (1), 3229–3235.
- Caillly, B., Le Thiez, P., Egermann, P., Audibert, A., Vidal-Gilbert, S., Longaygue, X., 2005. Geological storage of CO₂: a state of the art of injection processes and technologies. *Oil and Gas Science and Technology* 60, 517–525.
- Carey, J.W., Lichtner, P.C., 2007. Calcium silicate hydrate (C–S–H) solid solution model applied to cement degradation using the continuum reactive transport model FLOTRAN. In: Mobasher, B., Skalny, J. (Eds.), *Transport Properties and Concrete Quality. Materials Science of Concrete, Special Volume*. American Ceramic Society/John Wiley & Sons, Inc., pp. 73–106.
- Carey, J.W., Wigand, M., Chipera, S.J., Wolde, G.G., Pawar, R., Lichtner, P.C., Wehner, S.C., Raines, M.A., Guthrie, G.D., 2007. Analysis and performance of oil well cement with 30 years of CO₂ exposure from the SACROC Unit, West Texas, USA. *International Journal of Greenhouse Gas Control* 1, 75–85.
- Carman, P.C., 1956. *Flow of Gases Through Porous Media*. Academic, San Diego, CA, 182 pp.
- Carpi, M., Gioris, T., Battistelli, A., 2006. Modeling CO₂ injection with halite precipitation using an extended Verma & Pruess porosity–permeability model. In: *Proceedings of TOUGH Symposium 2006*, May 15–17, 2006, Lawrence Berkeley National Laboratory, Berkeley, California.
- Chadwick, A., Arts, R., Bernstone, C., May, F., Thibeau, S., Zweigel, P., 2007. Best Practice for the Storage of CO₂ in Saline Aquifers—Observations and Guidelines from the SACS and CO₂STORE Projects. *British Geological Survey, Nottingham*, p. 267.
- Cubillas, P., Kohler, S., Prieto, M., Causserand, C., Oelkers, E.H., 2005. How do mineral coatings affect dissolution rates? An experimental study of coupled CaCO₃ dissolution–CdCO₃ precipitation. *Geochimica et Cosmochimica Acta* 69, 5459–5476.
- Czernichowski-Lauriol, I., Sanjuan, B., Rochelle, C., Bateman, K., Pearce, J.M., Blackwell, P., 1996a. Analysis of the geochemical aspects of the underground disposal of CO₂. In: Apps, J.A., Tsang, C.F. (Eds.), *Deep Injection Disposal of Hazardous and Industrial Waste: Scientific and Engineering Aspects*. Academic Press, pp. 565–585.
- Czernichowski-Lauriol, I., Sanjuan, B., Rochelle, C., Bateman, K., Pearce, J.M., Blackwell, P., 1996b. Inorganic geochemistry. In: Holloway, S. (Ed.), Chapter 7 in *The Underground Disposal of Carbon Dioxide*, Final Report of the Joule II Project Number CT92-0031, British Geological Survey, Keyworth, Nottingham, UK, pp. 183–276.
- Czernichowski-Lauriol, I., Pauwels, H., Vigouroux, P., Le Nindre, Y.M., 2002. The French carbogaseous province: an illustration of natural processes of CO₂ generation, migration, accumulation and leakage. In: *Proceedings of the GHGT-6 International Conference on Greenhouse Gas Control Technologies*, vol. 1, October 1–4, 2002, Kyoto, Japan, pp. 411–416.
- Czernichowski-Lauriol, I., Rochelle, C.A., Gaus, I., Azaroual, M., Pearce, J., Durst, P., 2006. Geochemical interactions between CO₂, pore-waters and reservoir rocks: lessons learned from laboratory experiments, field studies and computer simulations. In: *Advances in the Geological Storage of Carbon Dioxide. NATO Science Series IV*, pp. 157–174.
- Declercq, J., Oelkers, E.H., Aagaard, P., 2008. Experimental determination of the dawsonite dissolution/precipitation rates and their application to CO₂ sequestration. *Geophysical Research Abstracts* 10 EGU2008-A-08482.
- Duan, Z., Sun, R., 2003. An improved model for calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chemical Geology* 193, 253–327.
- Dupraz, S., Parmentier, M., Menez, B., Guyot, F., 2008. Experimental study of biomineralisation processes relevant to CO₂ geological sequestration. *Geochimica et Cosmochimica Acta* 72, A233.
- Emberley, S., Hutcheon, I., Shevalier, M., Durocher, K., Mayer, B., Gunter, W., Perkins, E., 2005. Monitoring of fluid–rock interaction and CO₂ storage through produced fluid sampling at the Weyburn CO₂-injection enhanced oil recovery site, Saskatchewan, Canada. *Applied Geochemistry* 20, 1131–1157.
- Fischer, M., Botz, R., Schmidt, M., Rockenbach, K., Garbe-Schönberg, D., Glodny, J., Gerling, P., Littke, R., 2006. Origins of CO₂ in Permian carbonate reservoir rocks (Zechstein, Ca₂) of the NW-German Basin (Lower Saxony). *Chemical Geology* 227, 184–213.
- Frangoul, J., Nghiem, L., Emmanuel, C., Thibeau, S., 2004. Sleipner/Utsira CO₂ geological storage: full field flow and geochemical coupling to assess the long-term fate of the CO₂. In: *Proceedings AAPG Annual Conference*, 18–21 April, 2004, Dallas, Texas, Paper AAPG 86278.
- Gaus, I., Audigane, P., André, L., Lions, J., Jacquemet, N., Durst, P., Czernichowski-Lauriol, I., Azaroual, M., 2008. Geochemical modelling and solute transport modelling for CO₂ storage, what to expect from it? *International Journal of Greenhouse Gas Control* 2, 605–625.
- Gaus, I., Azaroual, M., Czernichowski-Lauriol, I., 2005. Reactive transport modelling of the impact of CO₂ injection on the clayey cap rock at Sleipner (North Sea). *Chemical Geology* 217, 319–337.
- Gaus, I., Le Guern, C., Pearce, J., Pauwels, H., Shepherd, T., Hatzianannis, G., Metaxas, A., 2004. Comparison of long-term geochemical interactions at two natural CO₂-analogues. Montmiral (Southeast basin, France) and Messokampos (Florina basin, Greece) case studies. In: Rubin, E.S., Keith, D.W., Gilboy, C.F. (Eds.), *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies*, vol. 1, Peer-Reviewed Papers and Plenary Presentations: Cheltenham, UK, IEA Greenhouse Gas Program, pp. 561–569.
- Gautier, J.-M., Oelkers, E.H., Schott, J., 2001. Are quartz dissolution rates proportional to B.E.T. surface areas? *Geochimica et Cosmochimica Acta* 65, 1059–1070.
- Grigg, R.B., McPherson, B.J., Svec, R.K., 2003. Laboratory and model tests at reservoir conditions for CO₂–brine–carbonate rock systems interactions. In: *Proceedings of the Second Annual Carbon Sequestration Conference*, May 5–8, 2003, Alexandria, VA.
- Gunter, W.D., Perkins, E.H., Hutcheon, I., 2000. Aquifer disposal of acid gases: modelling of water–rock reactions for trapping of acid wastes. *Applied Geochemistry* 15, 1085–1095.
- Gunter, W.D., Wiwchar, B., Perkins, E.H., 1997. Aquifer disposal of CO₂-rich greenhouse gases: extension of the time scale of experiment for CO₂-sequestering reactions by geochemical modelling. *Mineralogy and Petrology* 59, 121–140.
- Haszeldine, R.S., Quinn, O., England, G., Wilkinson, M., Shipton, Z.K., Evans, J.P., Heath, J., Crossey, L., Ballentine, C.J., Graham, C.M., 2005. Natural geochemical analogues for carbon dioxide storage and sequestration in deep geological porous reservoirs. *Oil and Gas Science and Technology* 60, 33–49.
- Hellevang, H., Aagaard, P., Oelkers, E., Kvamme, B., 2005. Can dawsonite permanently trap CO₂? *Environmental Science & Technology* 39, 8281–8287.
- Hovorka, S.D., Benson, S.M., Doughty, C., Freifeld, B.M., Sakurai, S., Daley, T.M., Kharaka, Y.K., Holtz, M.H., Trautz, R.C., Seay Nance, H., Myer, L.R., Knauss, K.G., 2006. Measuring permanence of CO₂ storage in saline formations: the Frio experiment. *Environmental Geosciences* 13 (2), 105–121.
- IPCC, 2005. IPCC special report on carbon dioxide capture and storage. In: Metz, B., Davidson, O., de Coninck, H.C., Loos, M., Meyer, L.A. (Eds.), *Prepared by Working Group III of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK/New York, NY, USA, 442 pp.
- Jacquemet, N., Pironon, J., Caroli, E., 2005. A new experimental procedure for simulation of H₂S + CO₂ geological storage. Application to well cement aging. *Oil and Gas Science and Technology* 60 (2005), 193–206.
- Jacquemet, N., 2006. Durabilité des matériaux de puits pétroliers dans le cadre d'une sequestration géologique de dioxyde de carbone et d'hydrogène sulfuré (Well materials durability in case of carbon dioxide and hydrogen sulphide geological sequestration), PhD, Université Henri Poincaré, Nancy, France. Available at <http://tel.archives-ouvertes.fr/tel-00084391/en/>.
- Jacquemet, N., Pironon, J., Saint-Marc, J., 2007. Mineralogical changes of a well cement in various H₂S–CO₂ (–brine) fluids at high pressure and temperature. *Environmental Science & Technology* 42, 282–288.
- Jacquemet, N., Le Gallo, Y., Estublier, A., Lachet, V., von Dalwigk, I., Yanc, J., Azaroual, M., Audigane, P., 2009. CO₂ streams containing associated components—a review of the thermodynamic and geochemical properties and assessment of some reactive transport codes. *Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9)*, November 16–20, 2008, Washington, DC, USA, *Energy Procedia* 1 (1), 3739–3746.
- Johnson, J.W., Nitao, J.J., Knauss, K.G., 2004. Reactive transport modeling of CO₂ storage in saline aquifers to elucidate fundamental processes, trapping mechanisms, and sequestration partitioning. In: Baines, S.J., Worden, R.H. (Eds.), *Geologic Storage of Carbon Dioxide*. Geological Society, London, Special Publication 233, pp. 107–128.
- Johnson, J.W., Nitao, J.J., Steefel, C., Knauss, K.G., 2001. Reactive transport modelling of geological CO₂ sequestration in saline aquifers: the influence of intra-aquifer shales and the relative effectiveness of structural, solubility, and mineral trapping during prograde and retrograde sequestration. In: *First Annual Conference on Carbon Sequestration*, May 14–17, 2001, Washington.
- Kaszuba, J.P., Janecky, D.R., in press. Geochemical impacts of sequestering carbon dioxide in brine formations. In: Sundquist, E., McPherson, B. (Eds.), *The Technology of Carbon Sequestration*, AGU Monograph.
- Kaszuba, J.P., Janecky, D.R., Snow, M.G., 2005. Experimental evaluation of mixed fluid reactions between supercritical carbon dioxide and NaCl brine: relevance to the integrity of a geologic carbon repository. *Chemical Geology* 217, 277–293.
- Kaszuba, J.P., Janecky, D.R., Snow, M.G., 2003. Carbon dioxide reaction processes in a model brine aquifer at 200 °C and 200 bars: implications for geologic sequestration of carbon. *Applied Geochemistry* 18, 1065–1080.
- Kervévan, C., Azaroual, M., Durst, P., 2005. Improvement of the calculation accuracy of acid gas solubility in deep reservoir brines: application to the geological storage of CO₂. *Oil and Gas Science and Technology* 60, 357–379.
- Kharaka, Y.K., Cole, D.R., Hovorka, S.D., Gunter, W.D., Knauss, K.G., Freifeld, B.M., 2006. Gas–water–rock interactions in Frio Formation following CO₂ injection: implications for the storage of greenhouse gases in sedimentary basins. *Geology* 34, 577–580.
- King, M.B., Mubarak, A., Kim, J.D., Bott, T.R., 1992. The mutual solubilities of water with supercritical and liquid carbon dioxide. *Journal of Supercritical Fluids* 5, 296–302.
- Kjoller, K., Postma, D., Larsen, F., 2004. Groundwater acidification and the mobilization of trace metals in a sandy aquifer. *Environmental Science & Technology* 38, 2829–2835.
- Knauss, K., Johnson, J.W., Steefel, C.I., 2005. Evaluation of the impact of CO₂, co-contaminant gas, aqueous fluid and reservoir–rock interactions on the geologic sequestration of CO₂. *Chemical Geology* 217, 339–350.
- Kreft, E., Bernstone, C., Meyer, R., May, F., Arts, R., Obdam, A., Svensson, R., Eriksson, S., Durst, P., Gaus, I., van der Meer, B., Geel, C., 2007. The Schweinfurt structure, a potential site for industrial scale CO₂ storage and a test case for safety assessment in Germany. *International Journal of Greenhouse Gas Control* 1, 69–74.

- Kutchko, B., Strazisar, B.R., Dzombak, D.A., Lowry, G.V., Thaulow, N., 2007. Degradation of well cement by CO₂ under geologic sequestration conditions. *Environmental Science & Technology* 41, 4787–4792.
- Lasaga, A.C., Soler, J.M., Ganor, J., Burch, T.E., Nagy, K.L., 1994. Chemical weathering rate laws and global geochemical cycles. *Geochimica et Cosmochimica Acta* 58, 2361–2386.
- Le Gallo, Y., 2009. Post-closure migration for CO₂ geological storage and regional pressure inferences. Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), November 16–20, 2008, Washington, DC, USA, Energy Procedia 1 (1), 3259–3266.
- Le Gallo, Y., Trenty, L., Michel, A., Vidal-Gilbert, S., Parra, T., Jeannin, L., 2006. Long-term flow simulations of CO₂ storage in saline aquifer. In: Proceedings of the GHGT8 Conference, June 18–22, 2006, Trondheim, Norway.
- Leonenko, Y., Keith, D.W., 2008. Reservoir engineering to accelerate the dissolution of CO₂ stored in aquifers. *Environmental Science & Technology* 42, 2742–2747.
- Lindeberg, E., Bergmo, P., 2003. The long-term fate of CO₂ injected into an aquifer. In: Gale, J., Kaya, Y. (Eds.), *Proceeding of the 6th International Greenhouse Gas Control Technologies*, vol. 1, Elsevier Science Ltd., Kyoto, pp. 489–494.
- Lindeberg, E., Zweigel, P., Bergmo, P., Ghaderi, A., Lothe, A., 2000. Prediction of CO₂ dispersal pattern improved by geology and reservoir simulation and verified by time lapse seismic. In: Proceedings of the 5th International Conference on Greenhouse Gas Control Technologies, August, 2000, Cairns, Australia.
- Lothenbach, B., Winnefeld, F., 2006. Thermodynamic modelling of the hydration of Portland cement. *Cement and Concrete Research* 36, 209–226.
- May, F., 2005. Alteration of wall rocks by CO₂-rich water ascending in fault zones: natural analogues for reactions induced by CO₂ migrating along faults in siliclastic reservoir and caprocks. *Oil and Gas Science and Technology* 60, 19–32.
- McGrail, B.P., Schaeff, H.T., Glezakou, V.A., Dang, L.X., Owen, A.T., 2009. Water reactivity in the liquid and supercritical CO₂ phase: has half of the story been neglected? Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), November 16–20, 2008, Washington, DC, USA, Energy Procedia 1 (1), 3415–3419.
- Mitchell, A.C., Phillips, A.J., Kaszuba, J.P., Hollis, W.K., Cunningham, A.L.B., Gerlach, R., 2008. Microbially enhanced carbonate mineralisation and the geological containment of CO₂. *Geochimica et Cosmochimica Acta* 72, A636.
- Mito, S., Xue, Z., Ohsumi, T., 2008. Case study of the geochemical reactions at the Nagaoka CO₂ injection site, Japan. *International Journal of Greenhouse Gas Control* 2, 309–318.
- Moore, J., Adams, M., Allis, R., Lutz, S., Rauzi, S., 2005. Mineralogical and geochemical consequences of the long-term presence of CO₂ in natural reservoirs: an example from the Springerville-St. Johns field, Arizona and New Mexico, U.S.A. *Chemical Geology* 217, 183–186.
- Muller, N., Qi, R., Mackie, E., Pruess, K., Blunt, M., 2009. CO₂ injection impairment due to halite precipitation. Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), November 16–20, 2008, Washington, DC, USA, Energy Procedia 1 (1), 3507–3514.
- Nghiem, L., Sammon, P., Grabenstetter, J., Ohkuma, H., 2004. Modelling CO₂ storage in aquifers with a fully-coupled geochemical EOS compositional simulator. In: Paper SPE 89474 for the SPE/DOE 14th Symposium on Improved Oil Recovery, April 17–21, 2004, Tulsa, Oklahoma.
- Nicot, J.-P., Hovorka, S.D., Choi, J.W., 2009. Investigation of water displacement following large CO₂ sequestration operations. Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), November 16–20, 2008, Washington, DC, USA, Energy Procedia 1 (1), 4411–4418.
- Nordbotten, J., Celia, M.A., Bachu, S., 2004. Analytical solutions for leakage rates through abandoned wells. *Water Resources Research* 40, WK04204.
- Osinubi, K., Nwaiwu, C.M.O., 2008. Desiccation-induced shrinkage in compacted lateritic soils. *Geotechnical and Geological Engineering* 26, 603–611.
- Palandri, J.L., Kharaka, Y.K., 2005. Ferric iron-bearing sediments as a mineral trap for CO₂ sequestration: iron reduction using sulfur-bearing waste gas. *Chemical Geology* 217, 351–364.
- Palandri, J., Kharaka, Y.K., 2004. A compilation of rate parameters of water–mineral interaction kinetics for application to geochemical modelling. US Geological Survey Open File Report 2004-1068, 64 pp.
- Pape, H., Clausen, C., Iffland, J., 1999. Permeability prediction based on fractal pore-space geometry. *Geophysics* 64 (5), 1447–1460.
- Parkhurst, D.L., Appelo, C.A.J., 1999. User's Guide to PHREEQC (version 2)—A Computer Program for speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Water-Resources Investigations, Report 99-4259, 312 pp.
- Pauwels, H., Gaus, I., Le Nindre, Y.M., Pearce, J., Czernichowski-Lauriol, I., 2007. Chemistry of fluids from a natural analogue for a geological CO₂ storage site (Montmiral, France): lessons for CO₂–water–rock interaction assessment and monitoring. *Applied Geochemistry* 22, 2817–2833.
- Pearce, J.M. (Ed.), 2003. Natural analogues for the storage of CO₂ in the geological environment: report on field characterization including soil gas surveys, characterisation of offshore shallow gas seeps, hydrogeochemistry and diagenetic studies. British Geological Survey External Report CR/03/147.
- Pitzer, K.S., 1973. Thermodynamics of electrolytes. 1. Theoretical basis and general equations. *Journal of Physical Chemistry* 77, 268–277.
- Pitzer, K.S., 1991. Ion interaction approach: theory and data correlation. In: Pitzer, K.S. (Ed.), *Activity Coefficients in Electrolyte Solutions*. 2nd ed. CRC Press, pp. 75–155.
- Plummer, L.N., Parkhurst, D.L., Wigley, T.M.L., 1978. The kinetics of calcite dissolution in CO₂–water systems at 5–60 °C and 0.0–1.0 atm CO₂. *American Journal of Science* 278, 176–216.
- Pokrovsky, O.S., Golubev, S.V., Schott, J., 2005. Dissolution kinetics of calcite, dolomite and magnesite at 25 °C and 0 to 50 atm pCO₂. *Chemical Geology* 217, 239–255.
- Pruess, K., 2004. The TOUGH codes—a family of simulation tools for multiphase flow and transport processes in permeable media: Vadose Zone Journal, Special section, Research advances in vadose zone hydrology through simulations with the TOUGH codes, vol. 3, pp. 738–746.
- Pruess, K., García, J., Kovscek, T., Oldenburg, C., Rutqvist, J., Steefel, C., Xu, T., 2004. Code intercomparison builds confidence in numerical simulation models for geologic disposal of CO₂. *Energy* 29, 1431–1444.
- Pruess, K., García, J., 2002. Multiphase flow dynamics during CO₂ disposal into saline aquifers. *Environmental Geology* 42, 282–295.
- Raistrick, M., Shevalier, M., Mayer, B., Durocher, K., Rene Perez, R., Hutcheon, I., Perkins, E., Gunter, B., 2006. Using carbon isotope ratios and chemical data to trace the fate of injected CO₂ in a hydrocarbon reservoir at the IEA Weyburn Greenhouse Gas Monitoring and Storage Project, Saskatchewan, Canada. In: Proceedings of GHGT8, 8th International Conference on Greenhouse Gas Technologies, June 19–22, 2006, Trondheim, Norway.
- Regnault, O., Lagneau, V., Catalette, H., Schneider, H., 2005. Etude expérimentale de la réactivité du CO₂ supercritique vis-à-vis de phases minérales pures. Implications pour la séquestration géologique de CO₂. *Comptes Rendus Geosciences* 337, 1331–1339.
- Rochelle, C.A., Czernichowski-Lauriol, I., Milodowski, A.E., 2004. The impact of chemical reactions in CO₂ storage in geological formations: a brief review. In: Baines, S.J., Worden, R.H. (Eds.), *Geological Storage of Carbon Dioxide*, Geological Society, London, pp. 87–106, Special Publication 233.
- Rudqvist, J., Birkholzer, J., Tsang, C.-F., 2006. Modelling hydrological and geochemical processes related to CO₂ injection in a faulted multilayer system. In: Proceedings of the GHGT8 Conference, June 18–22, 2006, Trondheim, Norway.
- Savage, D., Walker, C., Arthur, R., Rochelle, C., Oda, C., Takase, H., 2007. Alteration of bentonite by hyperalkaline fluids: a review of secondary minerals. *Physics and Chemistry of the Earth* 32, 287–297.
- Savage, D., Watson, C., Benbow, S., Wilson, J., in press. Modelling iron-bentonite interactions. *Applied Clay Science*.
- Scherer, G.W., Celia, M.A., Prevost, J.H., Bachu, S., Bruant, R., Duguid, A., Fuller, R., Gasda, S.E., Radonjic, M., Vicjit-Vadkan, W., 2004. Leakage of CO₂ through abandoned wells: role of corrosion of cement. In: Benson, S.M. (Ed.), *The CO₂ Capture and Storage Project (CCP) for Carbon Dioxide Storage in Deep Geologic Formations for Climate Change Mitigation*, vol. 2. Elsevier, London, pp. 827–848.
- Smyth, R.C., Hovorka, S.D., Lu, J., Romanak, K.D., Partin, J.W., Wong, C., 2009. Assessing risk to fresh water resources from long-term CO₂ injection—laboratory and field studies. Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), November 16–20, 2008, Washington, DC, USA, Energy Procedia 1 (1), 1957–1964.
- Steefel, C.I., Van Capellen, P., 1990. A new kinetic approach to modeling water–rock interaction: the role of nucleation, precursors, and Oswald ripening. *Geochimica et Cosmochimica Acta* 54 (10), 2657–2677.
- Tay, Y.Y., Stewart, D.I., Cousens, T.W., 2001. Shrinkage and desiccation cracking in bentonite–sand landfill liners. *Engineering Geology* 60, 263–274.
- Thibeau, S., Nghiem, L.X., Okhuma, H., 2007. A modelling study of the role of selected minerals in enhancing CO₂ mineralisation during CO₂ aquifer storage. In: 2007 Annual Technical Conference and Exhibition, November 11–14, 2007, Anaheim, California, USA, Paper SPE109739.
- Viswanathan, H., Pawar, R.J., Staufer, P.H., Kaszuba, J.P., Carey, J.W., Olsen, S.C., Keating, G.N., Kevetski, D., Guthrie, G.D., 2008. Development of a hybrid process and system model for the assessment of wellbore leakage at a geologic CO₂ sequestration site. *Environmental Science & Technology* 42, 7280–7286.
- Wang, S., Jaffe, P.R., 2004. Dissolution of a mineral phase in potable aquifers due to CO₂ releases from deep formations: effect of dissolution kinetics. *Energy Conversion and Management* 45 (18–19), 2833–2848.
- Watson, M.N., Zwingmann, N., Lemon, N.M., 2004. The Ladbroke Grove-Katnook carbon dioxide natural laboratory: a recent CO₂ accumulation in a lithic sandstone reservoir. *Energy* 29, 1457–1466.
- White, S.P., Allis, R.G., Moore, J., Chidsey, T., Morgan, C., Gwynn, W., Adams, M., 2005. Simulation of reactive transport of injected CO₂ on the Colorado Plateau, Utah, USA. *Chemical Geology* 217, 387–405.
- White, A.F., Peterson, M.L., 1990. Role of reactive surface area characterisation in geochemical models. In: Basset, R.D., Melchior, R.L. (Eds.), *Chemical Modeling of Aqueous Systems II*, vol. 416. American Chemical Society, Advances in Chemistry Series 213, pp. 461–475.
- White, S.P., Weir, G., Kissling, W., 2001. Numerical simulation of CO₂ sequestration in natural CO₂ reservoirs on the Colorado Plateau. In: Proceedings of the 1st National Conference on Carbon Sequestration, May 2001, Washington, DC.
- Wigand, M., Carey, J.W., Schütt, H., Spangenberg, E., Erzinger, J., 2008. Geochemical effects of CO₂ sequestration in sandstones under simulated in situ conditions of deep saline aquifers. *Applied Geochemistry* 23, 2735–2745.
- Wollenweber, J., Alles, S., Kronimus, A., Busch, A., Stanjek, H., Krooss, B.M., 2009. Cap rock and overburden processes in geological storage: an experimental study on sealing efficiency and mineral alterations. Proceedings of the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), November 16–20, 2008, Washington, DC, USA, Energy Procedia 1 (1), 3469–3476.
- Worden, R.H., 2006. Dawsonite cement in the Triassic Lam Formation, Shabwa Basin, Yemen: a natural analogue for a potential mineral product of subsurface CO₂ storage for greenhouse gas reduction. *Marine and Petroleum Geology* 23, 61–77.

- Xu, T., Apps, J., Pruess, K., 2003. Reactive geochemical transport simulation to study mineral trapping for CO₂ disposal in deep arenaceous formations. *Journal of Geophysical Research* 108 (B2), 2071, doi:[10.1029/2002JB001979](https://doi.org/10.1029/2002JB001979).
- Xu, T., Apps, J., Pruess, K., 2005. Mineral sequestration of a sandstone-shale system. *Chemical Geology* 217, 295–318.
- Zhang, G., Spycher, N., Sonnenthal, E., Steefel, C., 2006. Implementation of a Pitzer activity model into TOUGHREACT for modelling concentrated solutions. In: Proceedings, TOUGH Symposium 2006, May 15–17, Lawrence Berkeley National Laboratory, Berkeley, California (Report LBNL-60016).
- Zhang, G., Zheng, Z., Wan, J., 2005. Modeling reactive geochemical transport of concentrated aqueous solutions. *Water Resources Research* 41, W02018, doi:[10.1029/2004WR003097](https://doi.org/10.1029/2004WR003097).
- Zhu, C., 2006. In situ silicate reaction rates in sandy aquifers. *Geochimica et Cosmochimica Acta* 70 (18), A753.