

CO₂–brine–caprock interaction: Reactivity experiments on Eau Claire shale and a review of relevant literature

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ABSTRACT

Long term containment of stored CO₂ in deep geological reservoirs will depend on the performance of the caprock to prevent the buoyant CO₂ from escaping to shallow drinking water aquifers or the ground surface. Here we report new laboratory experiments on CO₂–brine–caprock interactions and a review of the relevant literature.

The Eau Claire Formation is the caprock overlying the Mount Simon sandstone formation, one of the target geological CO₂ storage reservoirs in the Midwest USA region. Batch experiments of Eau Claire shale dissolution in brine were conducted at 200 °C and 300 bars to test the extent of fluid–rock reactions. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis indicate minor dissolution of K-feldspar and anhydrite, and precipitation of pore-filling and pore-bridging illite and/or smectite, and siderite in the vicinity of pyrite.

We also reviewed relevant reactivity experiments, modeling work, and field observations in the literature in an attempt to help define the framework for future studies on the geochemical systems of the caprock overlain on geological CO₂ storage formations. Reactivity of the caprock is generally shown to be low and limited to the vicinity of the CO₂–caprock interface, and is related to the original caprock mineralogical and petrophysical properties. Stable isotope studies indicate that CO₂ exists in both free phase and dissolved phase within the caprock. Carbonate and feldspar dissolution is reported in most studies, along with clay and secondary carbonate precipitation. Currently, research is mainly focused on the micro-fracture scale geochemistry of the shaly caprock. More attention is required on the potential pore scale reactions that may become significant given the long time scale associated with geological carbon storage.

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1. Introduction

Injection of CO₂ into confined geological formations represents one of the most promising options for the long-term CO₂ storage and climate mitigation (Bachu et al., 2007). In a CO₂ storage system, the basal caprock will be likely in contact with CO₂ saturated brine and supercritical CO₂. Caprock is generally defined as a low to very low permeability (nD ~ μD level) formation above the CO₂ storage formation through which no CO₂ migration should occur (Fleury et al., 2010). Depending on the permeability of the caprock, a large amount of free phase CO₂ and dissolved CO₂ may migrate through the caprock under buoyancy force or pressure build-up (Birkholzer et al., 2008; Chabora and Benson, 2009). Therefore, the long-term containment of injected CO₂ in the deep reservoir will be crucially dependent on the performance of the

caprock in face of the chemical reactions with CO₂ charged brine. It is expected that supercritical CO₂ will dissolve into the native brine in the target reservoirs. The CO₂ charged brine then becomes acidic and will react with the solid matrix, which would bring uncertainty to large-scale CO₂ storage applications. Most of the studies on CO₂–water–rock interaction have focused on the host reservoirs (primarily sandstone or carbonate reservoirs) that store the CO₂ (Rochelle et al., 2004; Czernichowski-Lauriol et al., 2006; Izgec et al., 2008). Geochemical reactions of the caprock associated with the CO₂ sequestration have been much less studied. However, understanding CO₂–brine–caprock interactions is critical to the site selection, risk assessment, and the ultimate public acceptance of CO₂ storage programs.

The purpose of this study is to evaluate CO₂–brine–caprock interactions and develop a framework, within which, geochemical reactions in shale caprock due to CO₂ injection can be evaluated. Hydrothermal experiments were conducted with Eau Claire shale samples at 200 °C with 300 bars of CO₂ for 60 days. The relatively high temperature of 200 °C was selected in order to maximize the

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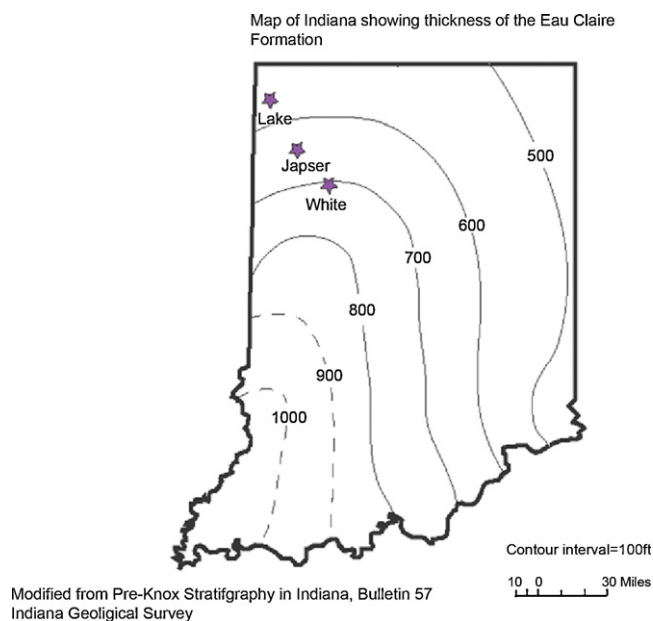


Fig. 1. Map of Indiana showing thickness of the Eau Claire Formation, after Yawar and Schieber (2008).

rates of silicate reactions within the time frame of the experiments. A pressure of 300 bars was chosen for consistency with and accessibility for sequestration scenarios. SEM and XRD studies were performed to characterize the reaction products. A relevant literature review has been conducted on the available research on CO₂-brine-caprock reactivity experiments, modeling works, and field observations.

2. Geological settings

The Cambrian Eau Claire Formation is named for the exposure of shaly sandstone near Eau Claire, Wisconsin (Walcott, 1914). The Eau Claire Formation underlies all of Indiana and is only found in the subsurface (Becker et al., 1978; Yawar and Schieber, 2008). However, the formation has been poorly defined in Indiana. A recent study based on data from cores and gamma ray logs has summarized the formation as a heterolithic, shallow marine succession, dominated by interbedded shale and siltstones (Yawar and Schieber, 2008). Variations in thickness of the Eau Claire Formation are illustrated in Fig. 1, an isopach map that shows the thickness of Eau Claire Formation in Indiana.

Exploration wells for water and hydrocarbon suggest that the formation is thicker in the southwest Indiana, thinning to the northwest (Fig. 2). The formation thickness ranges from approximately 122 m (400 feet) in northeastern Indiana to more than 305 m (1000 feet) in southwestern Indiana (Becker et al., 1978; Yawar and Schieber, 2008).

2.1. Lithology

Earlier studies by Becker et al. (1978) and Gutstadt (1958) described the characteristic lithologies of the Eau Claire Formation consisting of the following rock types: (1) feldspathic siltstone that is dolomitic and has varying amounts of glauconite; (2) sandstone that is very fine grained to fine grained and usually well sorted and contains some glauconite and feldspar; (3) shale that is maroon to very dark gray and micaceous; (4) dolomite that is silty and slightly glauconitic; and (5) limestone that is mottled brown and white and very oolitic. The formation in northern Indiana is predominantly sandstone, while siltstone, shale, dolomite, and limestone

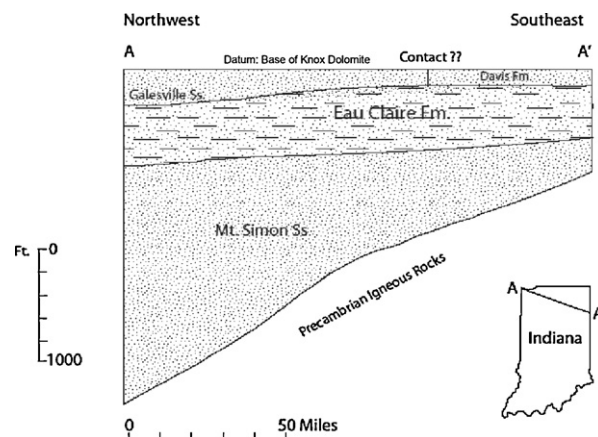


Fig. 2. The cross-section map showing the distribution of Eau Claire Formation from northwest to southeast Indiana, after Yawar and Schieber (2008).

are more prominent in the southern and eastern parts. A threefold subdivision of the Eau Claire in eastern Indiana has been reported by Bieberman and Esarey (1946) consisting of an upper member of glauconitic dolomite and gray-green and red shale, a middle member of pink glauconitic dolomite and no significant amount of shale, and a lower member of glauconitic sandstone and a few beds of shale. A similar sequence was observed in a deep test well in Johnson County, south-central Indiana (Gutstadt, 1958) as well as in the recent study of the northwest Indiana (Yawar and Schieber, 2008). Well data from Johnson County also indicated fragments of an oolitic limestone in the middle part of the Eau Claire Formation similar to that reported by Workman and Bell (1948). This limestone probably represents the east edge of the oolitic limestone found in Illinois.

A very important mineral constituent of the Eau Claire Formation is feldspar, which plays a significant role in the CO₂-water-rock interactions associated with the CO₂ injection. Becker et al. (1978) reported X-ray data from six tests in northern Indiana by R.K. Leineinger, indicating an average of 20% feldspar in the Eau Claire Formation with a few instances as high as 30–35%. They also reported thin section studies by C.J. Vitaliano suggesting that two types of feldspar are present: (1) predominantly potash feldspar (microcline mainly) and (2) minor quantities of albite. Much of the feldspar was reported to have well-defined authigenic overgrowths, and some quartz grains also have overgrowths.

Another characteristic constituent of the Eau Claire Formation in Indiana is glauconite. It generally occurs in the form of nodules and groups of nodules and is bright green. Rare fossil fragments, chiefly *Lingula* sp., are found in cuttings from the Eau Claire Formation (Gutstadt, 1958).

2.2. Contacts

The Eau Claire Formation overlies Mount Simon Sandstone conformably. Lithologic criteria are generally adopted in identifying the upper boundary of the Mount Simon sandstone in Indiana. The sand in the Eau Claire is cemented with dolomite, in contrast with the poorly consolidated or silica-cemented Mount Simon below. In addition, the sand in the Eau Claire is much finer than the underlying Mount Simon. The sand grains in the Eau Claire approach the silt-size range and are generally angular and clear, compared to the rounded and frosted grains in the Mount Simon (Gutstadt, 1958). Radioactivity logs, e.g., Gamma ray and neutron logs are also used in defining the contact between the Eau Claire and the subjacent Mount Simon (Becker et al., 1978; Yawar and Schieber, 2008).

The Eau Claire has higher shale content than the Mount Simon and therefore, shows an increase in gamma radiation.

The upper boundaries of Eau Claire Formation are differently defined in north and south Indiana (Fig. 2). The base of Galesville Sandstone is selected as the top of the Eau Claire in northwestern Indiana. Where the Davis Formation is present, the top of the Eau Claire is more difficult to identify, generally being distinguished where siltstone and shale predominate over carbonates. In southern Indiana, the top of the Eau Claire is chosen at the top of the thick oolitic limestones (Gutstadt, 1958; Becker et al., 1978).

2.3. Role in carbon sequestration projects in Midwest USA

One of the major concerns of the underground CO₂ sequestration is the CO₂ leakage from the host reservoir. After CO₂ is injected into the reservoir, buoyancy acts on CO₂ at all times, pushing it upwards, and, if a pathway is available, CO₂ will flow along this pathway (Bachu, 2008). Literature has reported this potential of gas leakage through caprock (Krooss et al., 1992; Hildenbrand et al., 2002). Therefore, extensive confining units (such as shale, or anhydrite beds) that are capable of safely sealing the storage formation are crucial to ensure that CO₂ does not escape into overlying, shallow rock units, especially drinking water aquifers, and ultimately to the ground surface.

The Eau Claire Formation overlies most of the Mount Simon sandstone, which is one of the deepest sedimentary saline formations in the Midwest region and is recognized as a potential host reservoir targeted for carbon sequestration due to its favorable depth, thickness, permeability, and the presence of caprocks with low permeability (Griffith et al., 2011). The Mount Simon formation underlies most of the Illinois Basin, which includes most of Illinois, western Indiana, and western Kentucky. The area has annual emissions exceeding 255 million metric tons of CO₂, primarily from 64 coal-fired electric generation facilities (Finley, 2007). Experimental study of the Eau Claire shale under the influence of CO₂ injection is scarce, and there is a great need to assess Mount Simon as one of the most potential CO₂ storage reservoirs in the Midwest region.

3. Experimental

The sample shale chips were obtained from the core samples of the basal Eau Claire Formation at depths of 1542 m to 1550 m from the Food Machinery Corp. – WD#-1 well located in Vermillion County, west central Indiana. The chips were handpicked, ground with an agate mortar and pestle, and subsequently dry sieved to retain the fraction between 0.355 and 2 mm in size. The sample was first ultrasonically cleaned using analytical grade ethanol to remove submicron-to-micron particles that adhered to the surface of large grains. This was performed six times on each aliquot for about 10 min per treatment. The cleaned shale grains were finally rinsed with deionized water and then freeze-dried.

Batch experiments of shale dissolution in synthetic brine were conducted in a 180 ml gold cell placed in a steel-alloy autoclave at National Energy Technology Laboratory (NETL). The chemical composition of the synthetic brine (Table 1) was modeled based on the fluid chemistry of the Mount Simon brine collected from the Vermillion County well (Keller, 1983). The synthetic brine was prepared using reagent grade salts. The tests started with 3.7 g of the prepared shale in the presence of 130 ml synthetic brine. Tests continued for 29 days under 300 bar system pressure at 200 °C to approach steady state with respect to major element concentration followed by 23 days under 300 bar CO₂ at 200 °C. After the 23 days of reaction, the sample was cooled down from 200 °C to 56 °C (to mimic the Eau Claire shale reservoir condition) during a period

Table 1

Chemical composition of the synthetic brine used as a starting solution in the experiments, after Keller (1983).

Property	Concentration, mg/L
Al	–
Ca	22,177
Fe	138
K	1382
Mg	2841
Na	49,004
Si	–
Sr	721
Cl	124,451
Br	523
SO ₄ ²⁻	–

of 28 h and then maintained at 56 °C and 300 bar CO₂ pressure for additional seven days before it was recovered for analysis.

Experimental run products were retrieved when the experiment was terminated after 60 days. Large (possibly remnant of shale) and small (possibly secondary minerals) particles after reaction were collected separately and were named as “shale products” and “precipitates”, respectively.

A variety of microscopic and analytical techniques were used to characterize solid reactants and experimental run products. Powder X-ray diffraction (XRD) analysis of samples before and after hydrothermal experiments were carried out using a Bruker D8 Advance diffractometer, equipped with a Cu anode at 20 kV and 5 mA, and with a SOLEX energy-dispersive detector. The scan parameters used were 2–70° 2θ, with a step size of 0.02° 2θ.

Scanning Electron Microscopy (SEM) was conducted with a Quanta 400 Field Emission Gun (FEG). The Energy Dispersive X-ray Spectrometer (EDS) system has an EDAX thin window and CDU LEAP detector. The low energy X-ray detection with FEG provided high spatial resolution for microanalysis down to ~0.1 μm² under optimum conditions.

4. Results and discussion

4.1. Observed mineral reactions

XRD results of the “reactants” before the experiments show the major minerals are quartz, orthoclase, illite, and a small amount of chlorite. SEM photomicrographs and XRD analyses revealed minor corrosion of feldspar and anhydrite surface, with precipitation of secondary minerals (Figs. 3–6). These secondary minerals include the pore-filling and pore-bridging clay minerals (illite and/or smectite) and siderite in the vicinity of pyrite (Figs. 7 and 8). Aggregates (with the size of 2–20 μm) of secondary minerals were observed often along the curved surfaces of the corroded feldspar, bridging the pores among the grains (Fig. 5A–C). These secondary minerals showed thin, flaky to crenulated morphology that is typical of clay minerals. EDS and XRD patterns indicated these secondary clay minerals to be illite/smectite. Though not identified in the SEM images directly, the presence of clinocllore is confirmed by XRD results (Fig. 3C and D). This clay mineral is most likely an original component of the shale sample, as Fig. 3C showed evidence of its pre-existence in the “reactant”. Formation of the secondary clay minerals was also observed on the quartz surface, but in lower abundance (Fig. 4A).

Existence of well-crystallized anhydrite grains was confirmed by both SEM and XRD analyses (Fig. 6). Dissolution features were visible on some of the surfaces of the elongated laths of anhydrite including dissolution pits (Fig. 6C) and dissolution steps (Fig. 6D). However, anhydrite dissolution may be due to the back reaction during the cooling stage, because anhydrite solubility increases when temperature decreases (Kuntze, 2008).

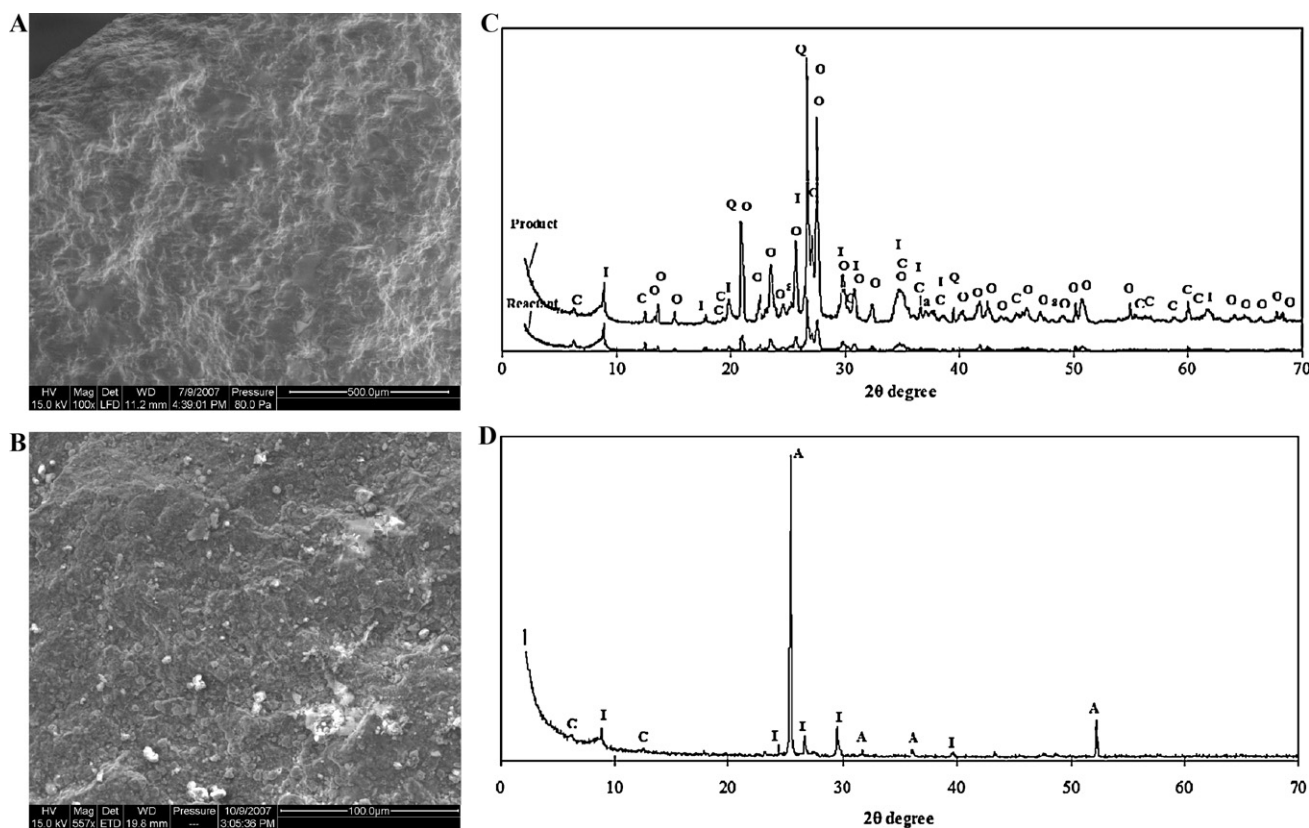


Fig. 3. Comparison of SEM images of the Eau Claire shale chips before (A) and after (B) the 60-day batch dissolution experiments. (C) X-ray diffraction pattern of “reactant” and “products” of Basal Eau Claire shale. Both reactant and product composed mainly of Q – quartz (46-1045), O – orthoclase (ICDD: 31-0966), I – illite (ICDD: 26-0911), and small amount of C – clinocllore (ICDD: 24-0506). Peaks of a-Anatase (ICDD: 21-1272) were identified in “products” (D) X-ray diffraction pattern of “precipitates” of basal Eau Claire shale. The “precipitates” are composed mainly of A – anhydrite (ICDD: 37-1496), I – illite (ICDD: 26-0911), and small amount of C – clinocllore (ICDD: 24-0506) were also possible. Note that both “products” in (C) and “precipitates” in (D) are products from experiments. NETL collected them separately.

The observations in this study only provided qualitative information on the potential geochemical reactions in the caprock associated with CO₂ injection. Quantitative results are very sensitive to the selected rock and fluid properties and the experimental conditions, i.e., 200 °C and 300 bars. The 200 °C temperature in this study is on the high end of temperature typically encountered in reservoirs relevant to underground CO₂ storage which is approximately 50–200 °C (Hitchon et al., 1999; Benson and Myer, 2000; Oldenburg et al., 2001; Bachu, 2003; NETL, 2010a,b). It was selected for this study to accelerate the rates of reactions with silicate minerals, which provide the cations for CO₂ mineral trapping in carbonate phases. High temperature also promotes CO₂ dissolution rates which triggers other geochemical reactions (Portier and Rochelle, 2005). Therefore, the experimental results may represent a relatively high reactivity case of potential geochemical reactions in the caprock associated with CO₂ injection. A pressure of 300 bars was chosen for consistency with and accessibility for sequestration scenarios.

5. Literature review on the CO₂–brine–caprock system

5.1. General considerations

A good understanding of the caprock performance is a prerequisite to ensure the effectiveness and safety of any geological storage projects. Valuable lessons could be learned from industrial practices of the underground nuclear and chemical waste storage. However, CO₂ storage also differs from those waste disposal projects in several aspects: (1) CO₂ exposes a relatively lower level of threat to the environment when compared to nuclear and

chemical waste, but the injection volume is typically much larger. Therefore, much larger volume of caprock may be involved; (2) CO₂ is buoyant and tends to migrate upward into the caprock; (3) despite of the low permeability, the caprock may have a relatively high porosity; (4) CO₂ is soluble and the dissolved CO₂ is chemically reactive. There are various processes that may take place in the CO₂–brine–caprock system before it evolves towards a new equilibrium state including flow and transport, geochemical reaction, geomechanical changes, etc. Our ability to predict the caprock performance relies on our understanding of the complex interplay between those processes.

The processes start with CO₂ entry into the caprock. Depending on the state of CO₂, there are generally three pathways: capillary breakthrough as supercritical CO₂, molecular diffusion as either supercritical CO₂ or dissolved CO₂, and as dissolved constituent in the brine that migrates through the caprocks.

Physically, under buoyancy force and the injection pressure, supercritical CO₂ may percolate into the originally water-wet caprock once the CO₂ capillary entry pressure is exceeded (note that CO₂ invasion as solute in the brine is relatively easier as it does not have to overcome this barrier). This CO₂ breakthrough behavior is crucial to the CO₂ entry at least in the early stages. Even though the reactivity between dry supercritical CO₂ and the caprock is generally low (Czernichowski-Lauriol et al., 1996), the shaly caprock typically contains organic matter which could sorb the CO₂ but could also be potentially extracted by the supercritical CO₂, causing alteration of pore structure (Okamoto et al., 2005; Busch et al., 2008).

Chemically, stable isotope studies of naturally occurring CO₂ reservoirs suggest that dissolution in formation brine is the major

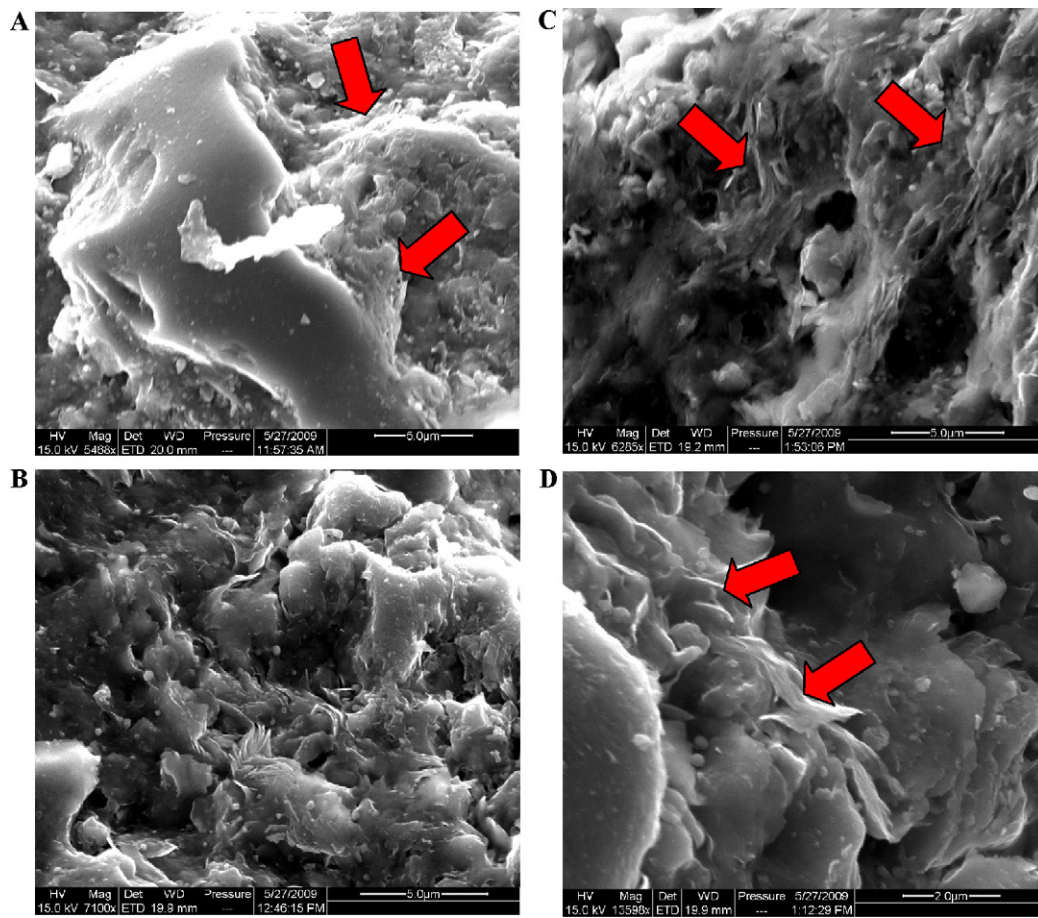


Fig. 4. SEM secondary electron images of Eau Claire shale dissolution effects following reaction after 60 days. (A) Secondary illite mats (pointed by the red arrows) trimming the quartz grain (on the left); (B) Aggregates of secondary crenulated to flaky clay minerals on the quartz surface, filling the pore spaces among grains; (C and D) Secondary flake-like clay minerals (pointed by the red arrows) coat on the corroded authigenic K-feldspar surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

sink for CO₂ in the long term, causing acidification of the native brine to pH of about 3–5 (Gilfillan et al., 2009; Liu et al., 2011). Although caprock typically has a low permeability of less than one millidarcy, the porosity can be relatively high (e.g. 30%) (Ortoleva, 1994; Fleury et al., 2010; Armitage et al., 2011). The acidified brine may invade into the pore space and trigger interactions with the minerals. Due to their fast reaction kinetics, the most immediate attack may occur on the carbonate minerals. In the long run, the acidified brine, even after carbonate buffering, may trigger reactions with the alumino-silicate minerals (feldspars and clays) present in the caprock. Such reactions may occur on the order of tens, hundreds, or thousands of years due to the slow rates of reactions with alumino-silicate minerals, but may contribute significantly to the porosity/permeability alteration of the caprock considering their large percentages in the caprock mineralogy. Those potential geochemical reactions may lead to various pathways for CO₂ leakage through the caprock. Therefore, it is crucial to understanding the direction, rate, and magnitude of the potential reactions both in terms of their impact to the integrity of the caprock, and in terms of the long-term effectiveness of CO₂ containment.

Shukla et al. (2010) conducted a comprehensive overview of CO₂ injection on caprock integrity focused mainly on geophysical aspects. They extensively reviewed and discussed the stability of the caprock during and after injection of CO₂, impact of pre-existing fractures and probabilities of fault reopening on seal integrity, and perturbation of the stress field in the reservoir due to the combination of injection pressure and upward pressure (due to buoyant

forces). In another comprehensive review on caprocks, Griffith et al. (2011) presented detailed structural, petrophysical, and chemical characteristics of caprocks across the U.S. considered for pilot and large-scale demonstration of Carbon Capture and Storage (CCS). In their review, they described several common features among the caprocks – particularly in three major geological basins. These common features included the frequent mineral occurrence of calcite, quartz, dolomite, illite, feldspar (potassium or sodium), glauconite, and kaolinite along with structural features containing fractures, faults, and salt structures. In their inventory of caprock mineralogy they note that feldspar and glauconite minerals, which can be constitutive to the Eau Claire in Indiana, are also common among other caprocks used for CCS. However, the geochemical influences were less emphasized in their study. In this study, we focused our review on the geochemical aspects of the injected CO₂ on caprock integrity, in attempt to supplement to the reviews of Shukla et al. (2010) and Griffith et al. (2011).

5.2. Observations from laboratory experiments

On the flow part, CO₂ percolation and diffusion tests through caprock, and on the geochemical part, caprock dissolution experiments in supercritical CO₂/CO₂-charged brine using batch reactors and triaxial cells, have been reported in previous studies (Kaszuba et al., 2005; Aplin et al., 2006; Busch et al., 2008; Soldal, 2008; Angeli et al., 2009; Credoz et al., 2009; Kohler et al., 2009; Wollenweber and Alles, 2009; Wollenweber et al., 2010; Alemu et al., 2011; Berthe et al., 2011; Navarre-Sitchler et al., 2011). Though less

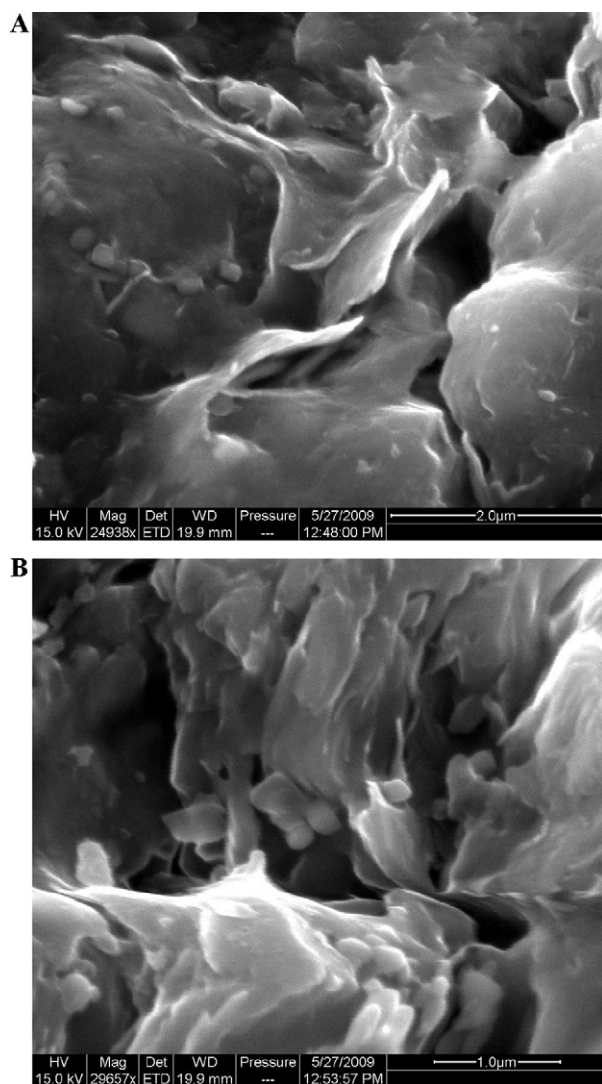


Fig. 5. (A, B) Zoom-in SEM secondary electron images of the aggregates of thin, flaky secondary clay minerals.

well constrained compared to research on host rocks, geochemical behavior of the original carbonate and feldspar dissolution has been commonly reported in previous experimental work, with secondary carbonate and clay mineral precipitation in the longer term. A reduction of the caprock capillary sealing efficiency and an increase in the effective CO_2 diffusion coefficient has been observed in the post-experiment samples. On the petrophysical side, tendency of re-activation of micro cracks in the caprock is suggested to be higher post CO_2 treatment due to pore pressure build-up. All the investigation of geochemical and petrophysical properties of the caprock before and after the repetitive CO_2 treatment indicated an increasing potential of CO_2 propagation into/across the caprock in the long term, but the magnitude is limited.

Supercritical CO_2 breakthrough experiments were reported by Angeli et al. (2009) and Soldal (2008) both on samples from the Upper Jurassic Draupne Formation, the third caprock above a potential off-shore CO_2 storage formation in the North Sea. These studies were not covered in either Shukla et al. (2010) or Griffith et al. (2011)'s reviews. Angeli et al. (2009) conducted supercritical CO_2 breakthrough experiments through a shale core with a focus on the micro-structural properties of the rock. The experiments were conducted at 35 °C and 75 bars. A pressure gradient was applied in order to obtain a breakthrough of CO_2 through the core.

Measurements of axial and radial strain together with acoustic velocities in the axial direction were taken at various stages during CO_2 flooding. The results suggested that CO_2 percolation potential is higher where there is higher pore pressure build-up, probably due to the higher chances of crack re-activation in the shale. CO_2 capillary breakthrough experiments were performed by Soldal (2008) on the powdered Draupne claystone samples with pH ranging from 2 to 10. An apparent breakthrough of the supercritical CO_2 was obtained at pressure of ~35 bars, by gradually applying an increasing pressure gradient across the sample. The time spans of these two studies are relatively short. For example, Angeli et al. (2009)'s study lasted 58 days at 35 °C. In this case, geochemical reaction is relatively insignificant. Under storage condition, the caprock is expected to be in contact with fluid (supercritical CO_2 and brine) for a long time (e.g., 1000 years) under high pressure induced by injection and addition of the mass. Geochemical reactions and combination of geochemical and geophysical interactions (e.g., pressure solution, Merino et al., 1983) may play important roles in this situation. Higher temperature and/or longer reaction time are desired in future CO_2 breakthrough experimental designs.

Alemu et al. (2011) reported shale dissolution experiments in expose to supercritical CO_2 and brine mixture at 80–250 °C and 110 bars and compared to control experiments without excess CO_2 . The shale samples in this laboratory study were collected from different layers of the Adventalen group overlying a proposed underground CO_2 storage site in Svalbard, near Longyearbyen, Norway. Crushed samples were exposed to CO_2 -brine mixtures for one to five weeks in batch reactions and analyzed using XRD and SEM both pre- and post-experiments. Observed geochemical reactions included original mineral dissolution, clay mineral transformation and secondary mineral formation. The experiments showed that the CO_2 increased the reactivity of the shale samples significantly as the CO_2 invasion reduced the pH. For all conditions, the bulk reactions released silica and the concentrations reached quartz saturation or higher after a few weeks. At 250 °C, calcite dissolved and re-precipitated, whereas ankerite dissolved. A large portion of the chlorite and illite initially present in the sample dissolved formed swelling clay (smectite). There were no traces of the formation of other carbonates than calcite after five weeks. Parallel controlled experiments were conducted in an effort to establish the type of reactions that took place and the extent of CO_2 contribution in the total reaction. Several practices in this study should be followed in the future study: (1) bubbling with N_2 (or co-inject N_2 with CO_2) during the reaction to mimic O_2 -depleted natural storage conditions. Reactions in oxidation environment may have different mechanisms to those in reduced environment. For example, Fe^{3+} may precipitate at $\text{pH} > 4$ but Fe^{+2} does not (Stumm and Morgan, 1996); (2) conduct a series of experiments at different temperatures (80–250 °C in their study). In order to accelerate the slow silicate reactions, using elevated temperatures is a common practice. However, one needs to ensure that higher temperature than reservoir condition does not change the reaction mechanism (e.g., inducing a different sets of dissolution/precipitation reactions and secondary minerals). One way to make sure is to conduct companion experiments at different temperatures with all others conditions to be the same. Sets of experiments can be designed in the future as longer reaction time for lower temperatures and shorter reaction time for higher temperatures to directly compare the results; (3) couple geochemical modeling with the experiments to interpret the results.

Creodoz et al. (2009) conducted batch reactor experiments on the reactivity of two caprock samples: Chinle Shale, widely occurring in the western USA, and Comblanchien Formation, from the Paris basin, France. Two sets of samples were exposed to supercritical CO_2 and brine, and brine and dissolved CO_2 , respectively. The purpose was to simulate conditions both at close to the wellbore

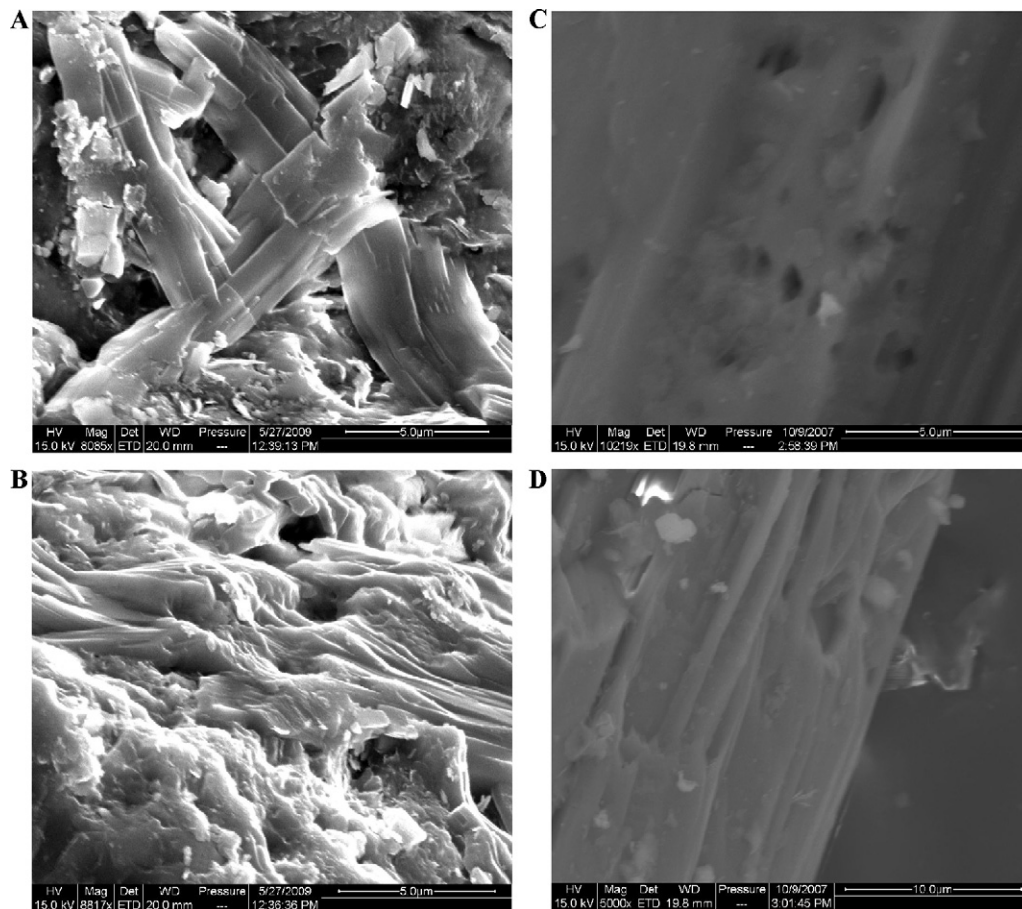


Fig. 6. SEM secondary electron images of anhydrite (A, B); (C) dissolution pitches on the anhydrite surface; (D) dissolution steps.

and further away from the wellbore. The experimental temperature was 80–150 °C and pressure was 1–150 bars. Duration was up to one year. XRD and SEM examinations of the samples showed carbonate dissolution and at 150 °C the precipitation of a more complex mixed carbonate (Fe, Ca, Mg), and partial dissolution of kaolinite, and precipitation of smectite in the long-term (365 days). They also monitored the solution chemistry. The dissolution of carbonate minerals buffered the initial ambient pH at 6.3 to 7–8 at the end of the experiments. Primary cation concentrations (Ca^{2+} , K^+ and Mg^{2+}) increased by approximately 50%, which is expected to promote secondary clay precipitation. [Credoz et al. \(2009\)](#) recognized the importance of carbonate cements in caprock to the long term safety of geological storage: the dissolution of carbonate minerals can create preferential pathways for CO_2 migration through caprock, but the buffering capacity of carbonates and mineral trapping favor long-term storage safety. The significance of clay evolution and clay mineral reactivity was also emphasized in their study. However, a connection between solution chemistry and mineralogy evolution has not been established; the interpretations on the two sides were isolated.

[Kohler et al. \(2009\)](#) also conducted batch experiments to test the reactivity of the Saint Martin de Bossenay (SMB, Paris basin, France) caprock. They used an elevated temperature of 150 °C, which is higher than the local reservoir temperature of 70 °C. The experimental pressure was 100 bars and experimental duration was 30–60 days. Examination of the samples post-experiments shows illitization of smectite, precipitation of kaolinite, and dissolution of anhydrite before reprecipitation. [Kohler et al. \(2009\)](#) focused on the evolution of clay minerals during the reaction. Characterization of clay minerals is a challenge due to their chemical and

mineralogical complexity. Kohler and co-workers put their emphasis on high quality mineralogical characterizations using XRD, microprobe, and TEM. The interpretations on clay evolution are thorough and convincing. They recognized that many of the mineralogical changes due to the temperature shift are associated with dehydration (e.g., gypsum–anhydrite and clay minerals). However, one thing that was insufficiently discussed in this study is the connection between secondary mineralization and mineral evolution to the porosity/permeability change. For example, dolomitization will typically increase the permeability with increasing porosity due to the volume change; however the associated anhydrite precipitation, if sulfate ion is present in the pore water, will potentially have negative impact on porosity/permeability ([Kupecz et al., 1998](#)).

Batch experiments were also conducted by [Kaszuba et al. \(2005\)](#). They used a “mixed aquifer and aquitard” charge with a synthetic arkose (as aquifer) and a chip from the Silurian shale (as aquitard). This setup has the merit of regarding aquifer and aquitard as one system. CO_2 –brine–rock interactions in aquifer may change the geochemistry of pore water in contact with the caprock. However, the reservoir rock and caprock set they used do not belong to the same reservoir. The shale is composed of clay minerals (illite and mica comprising 65 vol.% of the shale), quartz (27%), feldspar (5%), chlorite (2%), and trace framboidal pyrite. The experiments were conducted at 200 °C and 200 bars. The samples were first reacted with 5.5 molal NaCl brine for 32 days and then CO_2 was injected and reaction continued for another 45 days. The minerals were examined and solution chemistry evolution was monitored. Their observation of euhedral siderite and other mineral alterations indicate that shale is reactive (at the experimental temperature and

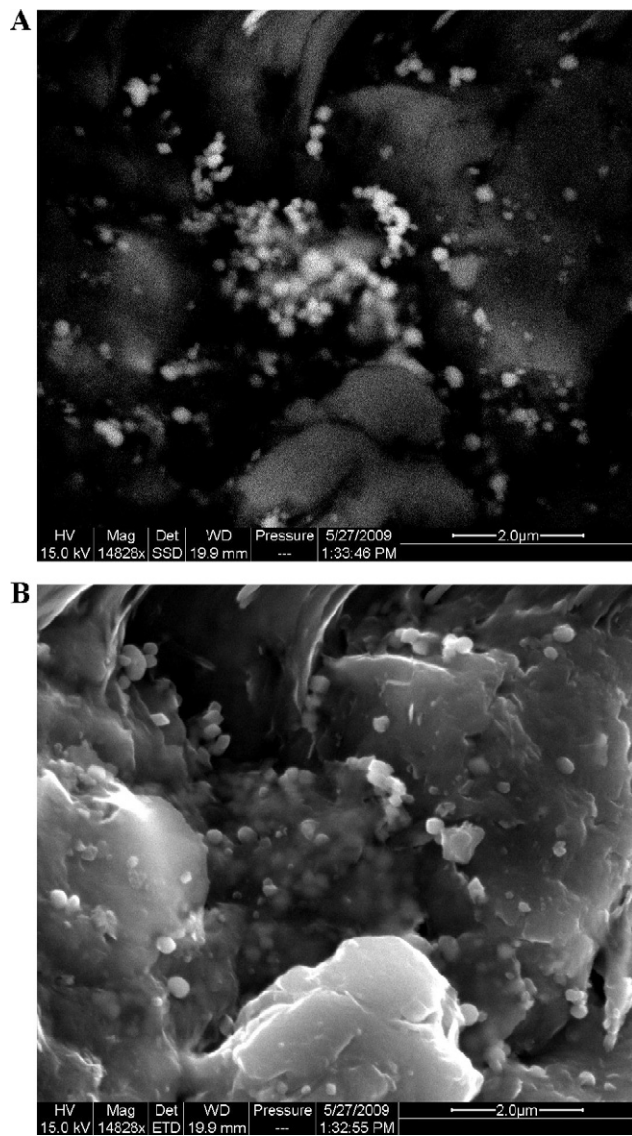


Fig. 7. Back-scattered (A) and SEM (B) images of an aggregate of secondary siderite minerals.

pressure). An initial pH decrease was reported following the CO₂ injection. pH was later restored, which is suspected to be associated with dissolved CO₂ transformation into mineral phase. However, clay mineralogy and clay evolution have not been emphasized in this study although the shale they used contains ~65 vol.% of clay minerals.

In addition to batch experiments discussed above, [Wollenweber and Alles \(2009\)](#) and [Wollenweber et al. \(2010\)](#) conducted reactivity, CO₂ permeability and diffusion experiments on shale plug (28.5 or 38 mm diameter and 10–20 mm by length) in a triaxial cell. The shale plug was first saturated with water by high pressure, and then CO₂ was allowed to flow through. The repetitive pre- and post-measurements of maximum effective gas permeability showed an increase by a factor 3–8. They also noticed a decrease of capillary entry pressure by 33–46% of the initial values, and an increase in the effective CO₂ diffusion coefficient about 50%. They attributed the changes to alteration of minerals and pore structures. However, how representative of the “selected” uniform and homogenous sample is an important question. In reality, the existence of faults and fractures may largely affect the physical properties of the caprock. In addition, longer reaction time is

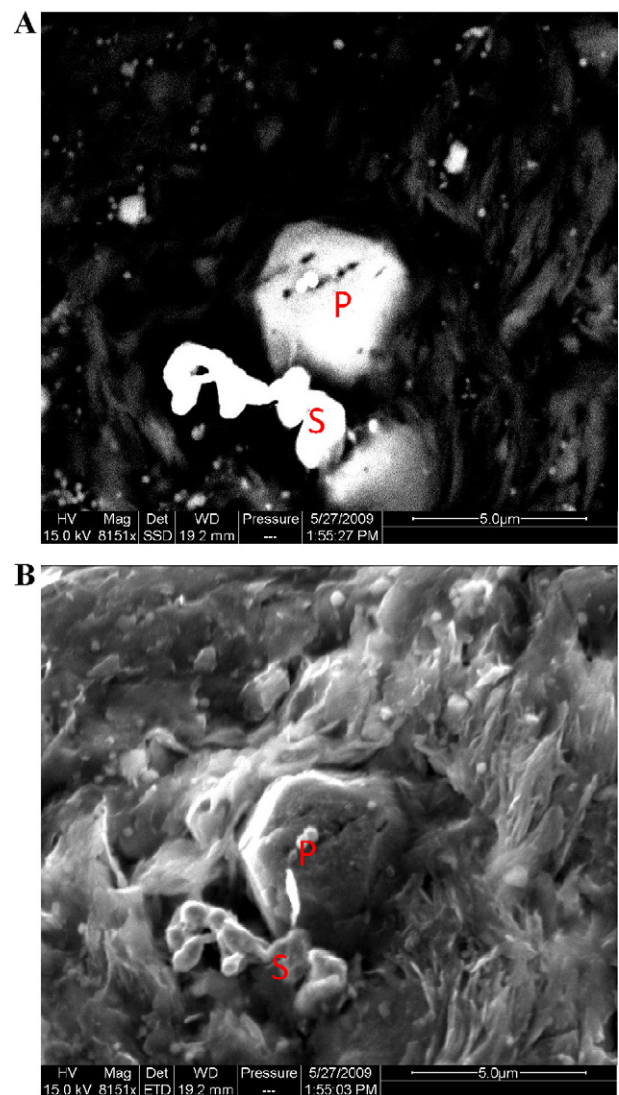


Fig. 8. Back-scattered (A) and SEM (B) images of authigenic pyrite grains with adjacent secondary siderite.

necessary in the future to study the long term sealing efficiency of caprock to the combined chemical–physical effects.

Experiments were also conducted on diffusion of CO₂ into samples. Shale typically has small pores, with 10–450 nm in diameter ([Aplin et al., 2006](#)). The batch experiments and plug flow experiments probably observed the reactions of CO₂ impregnated brine with microfracture surfaces in the samples, but not in the nano pores or more precisely, both the advective flow along fractures and nano pores, with the former being dominant. The diffusion experiments, on the other hand, measure the possible reactivity from CO₂ or CO₂ impregnated brine into the inter-connected nano pores. Both [Wollenweber and Alles \(2009\)](#) and [Busch et al. \(2008\)](#) observed an increase of approximately 55% in the effective diffusion coefficients of CO₂, compared to initial values, after successive CO₂ diffusion experiments. The changes in diffusivity were attributed to mineral alteration and the attendant changes of pore structures during the CO₂ experiments.

[Berthe et al. \(2011\)](#) conducted through-diffusion experiments on three argillite type caprocks with and without CO₂-enriched fluids using modified through-diffusion cells in which the suction is generated by the osmosis process ([Savoie et al., 2010](#)). ³⁶Cl, HTO, Br⁻ and D₂O were used as tracers. Chemical evolution was monitored for about 400 d. Results indicated a degradation of

the containment properties of the samples with the interaction of CO₂-enriched fluids. Initial petrophysical properties of the rocks and carbonate content were identified as main factors. The approach applied in this study is suitable to study the diffusion of charged and uncharged species through clayey rock although the temperature and pressure have not achieved the range of reservoir conditions.

Navarre-Sitchler et al. (2011) employed stacked scanning electron microscopy (SEM) images, 3D pore reconstructions and small angle neutron scattering (SANS) technologies to study porosity and pore structure change of mudstones resulting from CO₂-brine-rock interactions, which provide quantitative information on pore networks at length scales inaccessible by other techniques such as X-ray computed tomography. Two of the caprock samples were reacted with CO₂ and brine at 160 °C and 150 bars for ~50 days to evaluate pore network changes in a reactive environment. A marked increase in pores at length scales ranging from 10s of nm to over 1 μm was detected on the field-emission SEM images with new precipitates grown into the pore space observed in some cases. Some dissolution features (e.g., pitting and etching) were observed on mineral grain faces. The application of these new technologies may potentially resolve one challenge of pore scale coupled reaction and flow modeling: describing the dynamic complex 3D pore structures of real rocks in a reactive environment.

5.3. Insights from modeling work

The safety functions of the caprock include not only opposition to the upward migration of the buoyant CO₂ from the reservoir (usually in the initial hundreds of years), but also effective response to the intrusion of the induced acidic brine. Studies have shown that the acidic plume due to CO₂ dissolution into the brine could persist for thousands of years after the complete dissolution of the CO₂ (Liu et al., 2011). Therefore, even though the injection activity spans tens to hundreds of years, assessments of the post-closure risk in the much longer time scale are needed. The studies of modeling works on caprock integrity are still relatively scarce, and recently some insights on CO₂-brine-caprock interactions have been gained (Johnson et al., 2004, 2005; Gaus et al., 2005; Xu et al., 2005; Gherardi et al., 2007; Credoz et al., 2009; Bildstein et al., 2010).

Gherardi et al. (2007) performed both batch, 1-D, and 2-D reactive transport simulations in the caprock of a depleted gas reservoir for CO₂ sequestration, using the TOUGHREACT code (Xu et al., 2004). The caprock is composed of highly reactive, carbonate-rich shale. Their modeling work investigated in detail the alteration induced by CO₂-brine-rock interactions of both sealed and fractured caprock. The results demonstrated a “self-enhancing” process (porosity reduction) if the caprock was homogenous. However, sealing effectiveness was compromised when physical discontinuities occur (for instance, fractures). The dominant geochemical reaction driving the two different results (porosity reduction vs. enhancement) was inferred to be calcite dissolution/precipitation. When a free CO₂-dominated phase migrates into the caprock through pre-existing fractures, or through zones with high initial porosity acting as preferential flow paths for reservoir fluids, self-enhancing alteration were predicted. In contrast, when fluid-rock interactions occur under fully liquid-saturated conditions and a diffusion-controlled regime, further sealing of the storage reservoir was observed. The advantages of their model are: (1) multiphase fluid flow, (2) aqueous diffusion, (3) fracture-matrix interactions, (4) different reservoir gas saturation for near injection well and peripheral zones, respectively, (5) non-isotropic and heterogeneous spatial distribution of permeability, (6) sensitivity analysis, and (7) preliminary accounting for capillary pressure. This study may be representative for the current level of the modeling on caprock integrity studies. As the authors pointed out that further improvements are required in (1) more realistic hydraulic

conditions for the transport of gas and liquid phases between reservoir and caprock, (2) considering wettability behavior of CO₂-brine mixtures, and relative permeability and capillary entry pressure effects, (3) chemical heterogeneity of reservoir and caprock, (4) species-dependent variations in the aqueous phase diffusion coefficients (e.g., H⁺) (Oelkers and Helgeson, 1988). Besides these, more improvements are required in the future such as (1) Pitzer's ion-interaction activity coefficient model instead of ion association model to account for high salinity of pore water, (2) thermodynamic and kinetic data, especially kinetic data, and (3) more realistic porosity-permeability relationship. The authors indicated that calcite is the predominant mineral controlling the porosity/permeability, especially in the early stage. However, permeability reduction due to the same mass of calcite and clay mineral precipitation can be significantly different, especially when clay swelling occurs (Chilingar et al., 1989). In addition, one of the most critical issues in current modeling is the lack of field and experimental data to test against. Future work on the matching of real data and calibration of the model is required to validate the reliability of models.

Gaus et al. (2005) performed batch- and reaction-diffusion simulations of the impact of CO₂ on the clayey caprock at North Sea Sleipner injection site. They found that the effective diffusion coefficients are likely to be so low that diffusion of CO₂ will only affect a few meters of caprock after thousands of years. Moreover, as CO₂ diffuses into the cap-rock, silica as well as other constituents is released from the CO₂-caprock interactions leading to precipitation of chalcedony, kaolinite and calcite, which may further reduce the diffusion into the caprock.

Creoz et al. (2009) performed simplified reactive transport modeling to compare with their experimental efforts on two caprock samples under CO₂ storage conditions (see above). The Crunch code (Steeffel, 2001) was used for the simulation, and the duration is the same as that of the experiments, 30–365 days. The carbonate minerals were shown to be the most reactive minerals, with partial or total dissolution (depending on experimental conditions). However, the buffering capacity provided by the carbonate dissolution, and the potential mineral trapping and the geochemical/geomechanical properties of secondary clay minerals, favors the long-term integrity of the caprock. Nevertheless, not much details are provided for both model setup and modeling results. The authors did not provide the comparison of their experimental results with modeling results. No sensitivity analysis was performed either.

Bildstein et al. (2010) conducted a series of numerical simulations of caprock responses to CO₂ injection using various reactive transport modeling codes. Caprock initial composition was partially based on Charmotte/Saint Martin-deBossey, Paris Basin, with 50% initial weight of calcite. Both 1D and 2D single phase flow scenario in saturated porous media with or without fracture, and 1D multi-phase flow in unsaturated media without fracture, were modeled. Significant porosity changes were observed in the models for a period of 10,000 years, which were expected due to the high reactivity of the carbonate-rich caprock with the acidic CO₂-rich fluid. However, the reactions were shown to be limited to the first decimeters to meters into the caprock from the CO₂-caprock interface in 10,000 years and no leakage was reported. Their preliminary results on rock heterogeneity suggested similar results as indicated in the experimental works (Angeli et al., 2009), that re-activation of small cracks or fractures (especially those originally filled with calcite) could generate preferential pathways for CO₂ propagation in the caprock.

Most of the previous research focused on the risk due to increased geochemical reactivity, and suggested the migration of CO₂-impregnated brine into the caprock to be deleterious to the environmental performance of geological carbon sequestration

project. However, another uncertainty due to pressure build-up has been neglected when considering caprock integrity. Recent studies have indicated that the caprock failure due to pressure build-up could cause a profound concern, in respect to the confinement of CO₂, and to the adjacent groundwater resources (Birkholzer et al., 2009; Leetaru et al., 2009; Mathias et al., 2009; Ehlig-Economides and Economides, 2010). Modeling work by Benson and Chabora (2009) proposed that some brine migration through the seal could probably be advantageous by reducing the risk of leakage, due to released pressure buildup. While physics-based simulations look into the caprock degradation by flow mechanisms and geochemical reactions, several preliminary analytical modeling has also shown the potential risk related to geomechanical variation in the caprock due to pressure changes and/or geochemical processes (Chiaromonte, 2009; McPherson, 2009). Pham et al. (2011) modeled pressure changes associated with CO₂ injection into the Tubåen Formation in the Norwegian Barents Sea. The Tubåen formation has overall a fairly low permeability with smaller units with higher permeability. The formation is compartmentalized by steep faults. The simulations suggest a rapid pressure increase that after few years of operation reaches the estimated fracture pressure of the reservoir caprock. The modeled rapid pressure increases fits well with measured down-hole pressure data from the injection well (Eiken et al., 2011).

5.4. Field observation

Due to the short history of engineered CO₂ injection and storage sites, direct field observation is scarce. However, CO₂ occurs naturally in geologic reservoirs in numerous volcanic, geothermal, and sedimentary basin settings worldwide (IPCC, 2007; Lewicki et al., 2007). A few studies have been reported on such natural analogues, but they are primarily focused on the reactions in the host formation (Worden and Burley, 2003; Baines and Worden, 2004; Moore et al., 2005; Gilfillan et al., 2008, 2009).

An interesting piece of information has been collected by studying the stable isotopes of carbon from carbonate minerals in a mudrock seal overlying a natural CO₂ reservoir in the North Sea Miller oil field (Lu et al., 2009). Mudrock samples were taken immediately adjacent to the reservoir top from two drilling boreholes approximately 30 km apart. Both oxygen and carbon isotopes were measured from whole-rock samples with increasing sampling spacing further up from the reservoir–mudrock interface at ~20 cm. A strong linear upward-decreasing trend of δ¹³C is observed within 12 m vertically above the interface (infiltration rate as $\sim 9.8 \times 10^{-7} \text{ g cm}^{-2} \text{ yr}^{-1}$), which is interpreted as evidence of dissolution of the original carbonates followed by “regrowth incorporating signatures of infiltrated CO₂”. After careful examination of various plausible mechanisms of how the CO₂ influx changed the isotope ratios in the disrupted zone (12 m), they concluded that the observed isotope ratio was generated by mixing of three carbon sources: dissolution of original carbonates, CO₂ infiltration, and thermal decarboxylation of organic matter. Based on their mixing model and well log data, they also suggested the presence of free-phase CO₂ in the basal caprock, instead of dissolved CO₂ only. Evidence from SEM analysis also showed that some carbonates formed in secondary pores, suggesting late growth periods. The significance of this work lies in that the Kimmeridge Clay Formation mudrock is a widespread seal in the North Sea and the validation of the seal is proved by the long record of the natural CO₂ reservoir.

Gilfillan et al. (2008, 2009) have studied the source, migration, and fate of the naturally occurring CO₂ in gas fields using noble gas and stable carbon isotope tracers. Noble gas and δ¹³C(CO₂) isotope data were collected from nine natural CO₂-bearing gas reservoirs in North America, China, and Europe, with both siliciclastic and carbonate lithologies. Variation in the CO₂/³He ratio was used to

represent CO₂ loss from the reservoir as ³He is inert and highly insoluble with no significant income source in the studied formations. Coherent changes in CO₂/³He and δ¹³C(CO₂) were calculated considering sinks as CO₂ dissolution into the formation water at various pH values and CO₂ precipitation as carbonate minerals. The results suggested that dissolution in formation brine at pH of 5–5.8 is the primary sink for CO₂ among all nine reservoirs. Even though the studied system is the CO₂ reservoir, the results on the CO₂ fate may serve as a constraint to the CO₂ pathway into the caprock and help to prioritize research focus in the CO₂–brine–caprock system to geochemical aspects in the longer time frame.

5.5. Special issues

5.5.1. Challenges of studying caprock reactivity

- (1) Coupling of geomechanical with geochemical impact on caprock integrity, i.e., time dependent influences of geochemical reaction and induced geomechanical changes in rock property on the integrity of caprock is a challenge. Currently, experimental and modeling work only focused on one side. Considering that the timeframe for secure storage of CO₂ is in the order of 1000 years or longer, new equipment/designs need to be invented to study the above challenges mentioned above experimentally. In addition, a suitable theoretical and computational framework for modeling these behaviors is required.
- (2) The wide disparity in length scales ranging from pore to basin scale is a challenge to study injected CO₂–brine–caprock interaction. Experiments of geochemical and geomechanical impacts on caprock are mainly at small scale. At larger scales, natural material heterogeneity strongly affects flow behavior, chemical thermodynamics and kinetics, and quality of the caprock. This heterogeneity is site-dependent and scale-dependent. Different sites may have different lithology (shale, mudstone, and claystone) and mineralogy (Haszeldine et al., 2005; Lu et al., 2009). The behavior of a clay-rich shale can be highly different from a carbonate-rich shale (Alemu et al., 2011). At low resolution, the mineralogy of a specific reservoir can be viewed as homogenous and only major fracture and faults should be considered. However, at higher resolution, the mineralogy can be significantly different at different locations even in the same reservoir. Micro fractures and faults should be considered in this case and they are also highly location dependent. To make situation more complicated, the pH and dissolved carbon in the pore water can be significantly different at different distance to the injection well and it is time dependent. The pore water may be reactive to the caprock in the vicinity of the injection well and/or at the beginning of the storage program, but less reactive far away from the well and/or at the late stage of the storage program. Thus, site specific studies should be conducted at each injection activity. Sampling should be carefully designed to be representative, depend on the scale (resolution) of interest. Pore waters with supercritical CO₂ in contact with caprock should be carefully modeled to match the location of the representative rock sample at the time scale of interest. Heterogeneity of caprock also poses difficulties in geochemical modeling. The understanding of complex interplay of numerous dissolution/precipitation reactions involved is still poor. The overall chemical interaction will either inhibit or facilitate the rates of the individual reactions (Lasaga, 1998). One might isolate the reactions one by one and gradually increase the complexity to unravel the interplays.

5.5.2. Discussion on caprock porosity and permeability

Porosity/permeability change is of primary interest in the studies of CO₂–brine–caprock reactions as it is closely related to the

caprock integrity and safety (Gaus, 2010). Heath et al. (2011) have studied the pore networks in typical mudstones and their impacts to the sealing capacity. Core samples were collected from continental and marine mudstones, all of which have been proposed as caprock for geological CO₂ storage. Representative samples from each core were analyzed first by FIB-SEM (dual-beam focused ion beam-scanning electron microscopy) and then with MIP (mercury intrusion porosimetry). The sealing performance of the tested mudstone was indicated to be closely related to the pore network properties that are controlled by the depositional environment, burial history, and diagenesis. The dominant pore type identified among the samples was an elongate, silt- and/or sheet-like pore with sharp to curved tips. These pores showed small pore throat connections that contributed to high breakthrough pressures leading to high sealing capacity.

CO₂-brine-caprock reaction would lead to modification of the pore geometry and effective permeability. Variation of caprock porosity has been observed both in the relevant experimental and simulation studies (see detailed reviews above). The dissolution of original silicates, primarily feldspar as in our study, is likely to increase porosity and provide the cations for secondary mineral precipitation. Several studies have reported that the proportion of K-feldspar in Gulf Coast shales decreases significantly with increasing temperature (Weaver and Wampler, 1970; Hower et al., 1976; Boles and Franks, 1979). Their studies also showed that the decrease in K-feldspar abundance corresponded with the illite formation. Data from Hower et al. (1976) suggested that Al³⁺ and K⁺ required for illite formation were supplied by the breakdown of detrital K-feldspar. However, less is known of the impact of these geochemical reactions on reservoir permeability, which is a known hurdle in several other relevant areas (e.g. the storage of nuclear waste, aquifer storage and recovery, geothermal applications) as well (Gaus, 2010). Studies by Neasham (1977) demonstrated that secondary clay texture could severely reduce permeability, but not affect porosity. The precipitation of secondary clay minerals as observed in this study could bridge the pores between grains, creating permeability barriers to fluid flow or reduction in the effective permeability. Other studies have proved that minute amounts of diagenetic clay, including illite, smectite as well as other mixed-layered clay, can drastically reduce reservoir permeability, because of the high surface area and fibrous pore-bridging morphology of illite/smectite (McHardy et al., 1982; Pallatt et al., 1984; deWaal et al., 1988; Ehrenberg and Nadeau, 1989; Nadeau, 1998; Rochelle et al., 2004). Experimental study by Nadeau (1998) reported a brine permeability reduction of up to 98% from the growth of no more than approximately 5 wt% smectite. The formation of secondary clay minerals is also indicated to physically sorb the CO₂ with capacity as high as natural coals (Busch et al., 2008).

Most previous geochemical studies on the CO₂-brine-caprock reactions focused on the inorganic rock domains. However, it is worth to note that typical caprock such as shale and mudstone usually contains a noticeable amount of organic matter. This is particularly of concern in the scenario of CO₂ storage in depleted oil/gas fields for enhanced oil/gas recovery (EOR/EGR). Supercritical CO₂ is capable of extracting organic matter from the caprock and may cause minor alteration to porosity and permeability of the caprock (Rutqvist and Tsang, 2002; Okamoto et al., 2005). Kharaka et al. (2006) reported a significant increase of dissolved organic carbon (DOC) values in the brine samples from the Frio Sandstone Formation (Texas, USA) collected 20 days after the CO₂ injection. Approximately 1600 tons of CO₂ were injected to test the potential for enhanced oil recovery (EOR) and CO₂ storage in this depleted oil field. They believe that the high DOC values are most likely to represent organic matter mobilized by the injected CO₂.

5.5.3. Discussion on dry-out

At the interface between the CO₂ plume and unconsolidated caprocks such as the shallow clay overlying the Utsira Sand at Sleipner (North Sea), accumulations of water-undersaturated CO₂ may have significant effects on the transport properties into the caprock. At the interface, water will tend to evaporate into the CO₂ phase until the chemical potential for H₂O is the same in both the CO₂ and aqueous phases. First, residual water and pore water in the caprock may evaporate into the CO₂ phase. Then, if the CO₂ is still undersaturated, H₂O accessible from clay minerals may be released into the CO₂. This may lead to a drying-out effect of the interface clay, with tensional stress and infiltration of CO₂ into cracks. Pore space may also be reduced if salts form from the evaporated residual water. Several factors control the extent of such drying out of the caprock. First, as the initially dry CO₂ is transported through the reservoir sand from the injector, water will evaporate into the CO₂ and the water saturation will increase (Gaus et al., 2008); second, when the CO₂ phase reaches the caprock in a stagnant plume, significant fractions of residual water within the plume will be available (Suekane et al., 2005; Farcas and Woods, 2008); and third, capillary suction forces of water in the caprock may not be strong enough to hold the water from the caprock even for a strongly water-undersaturated CO₂ plume. As we are not aware of any reports that verify the drying-out phenomena from natural reservoirs or from laboratory experiments, we leave this as an open question for further discussions.

5.5.4. Discussion on pore water chemistry of clayrock

In a sense, the batch and plug flow experiments, as well as most of the reactive transport modeling in CCS caprock studies as reviewed above, are measuring or modeling reactivity of micro-fracture surfaces. In a time frame of thousands of years and a thick sequence of shale caprock with pressure build-up from CO₂ injection, reactions beneath the micro-fracture surfaces and within the pore space may become more significant. Therefore, knowledge on the pore water composition becomes crucial for evaluating the potential reactions and risks associated with the caprock for CO₂ storage.

It is known that the geochemical system of the clay-rich rocks may be dominated by different reactions on the micro-fracture scale and the pore scale (Mazurek et al., 2003). Mineral dissolution and precipitation may be the primary reactions on the micro-fracture scale. However, the geochemical system is less known and more complicated on the pore scale. Clayrocks have been chosen by many countries for long-term storage of radioactive waste primarily due to its favorable pore water geochemical environment (Gaucher et al., 2006, 2009). Some significant characteristics of the pore water composition in clay-rocks are identified from studies similar to clay-rich caprock for nuclear storage purposes. First, the pore water composition is greatly influenced by ion-exchange reactions, which are poorly defined and selectivity constants are not intrinsic thermodynamic properties that can be universally applied. Second, the large clay contents also mean large surface areas where surface adsorption is significant. This has shown to greatly delay the migration of heavy metals and radionuclides (Bradbury and Baeyens, 2005). At the same time, the small pore sizes in shale mostly from 10 to 50 nm (Aplin et al., 2006) mean the electric double layer are over-lapping (Sherwood, 1993). Third, diffusion is the principal transport mechanism in clay-rocks and diffusion rates are very slow. Consequently, the spreading of those non-sorbing matters (ions, gas, etc.) may also be very slow. Fourth, different diffusion behaviors of cations, anions and neutral species in a constant electrolyte background and cation sorption via surface complexation should be considered. Fifth, the pH values of the pore water in clay-rocks tend to be circum-neutral and the pore water is slightly reducing.

The available information on pore water composition in clay–rocks from research in the radioactive waste disposal indicates that the chemical environment on the pore scale tends to be more stable than the micro-fracture scale. However, these two systems, the clay–rocks used for nuclear waste disposal and the shale caprock overlying the CO₂ storage formations, are not completely identical in terms of mineralogical, petrophysical and hydrological properties. For instance, the CCS caprock usually contain a significant share (~20% as in Eau Claire shale) of feldspar. On the contrary, feldspar is absent in some of the studied sites for nuclear storage (e.g., Callovo-Oxfordian formation of the eastern Paris Basin). Direct studies on the pore water chemistry in the CCS caprock are still in need to further elucidate this problem.

6. Concluding remarks

Information on caprock reactivity is limited compared with those on the reservoir rocks. The results of our batch experiments on the Eau Claire shale, a caprock widely appearing in the Midwestern of USA, together with a review of literature on caprock reactivity experiments, modeling work, and field observations worldwide show the following:

- (1) Under CO₂ invasion, shale caprock is geochemically reactive, at temperatures near the high end of the range for geological sequestration (150–200 °C), but unlikely near the low end of the range (e.g., 50–80 °C). Experimentally observed chemical reactions include dissolution and precipitation of carbonates, dissolution of feldspars, and precipitation of clay minerals. Given a pH near 3 for CO₂ saturated brines and a temperature of 50–150 °C, and a timeframe of thousands of years, mineralogical alterations in the caprock will occur. However, well-designed experiments with reasonable temperature and pressure are needed to verify these chemical reactions unambiguously. Additional experimental data must be obtained to verify the conclusion of increased permeability and diffusion coefficients, as well as reduced capillary entry pressure of the caprock due to CO₂ treatment, as suggested in previous works (Aplin et al., 2006; Soldal, 2008; Angeli et al., 2009; Credoz et al., 2009; Kohler et al., 2009; Wollenweber and Alles, 2009; Wollenweber et al., 2010; Alemu et al., 2011). Properties like nano-Darcy level permeability, effective diffusion coefficients, and CO₂ capillary entry pressure in the caprock are difficult to measure precisely and the reproducibility in the laboratory experiments is low (Cui et al., 2009). A factor of 3–8 can easily be within measurement uncertainties (Letham, 2011). Intuitively, both precipitation of carbonates and clays or mobilization of clay particles would reduce permeability.
- (2) Reported experiments are fraught with a number of challenges: (a) it is difficult to identify small quantities of reactants with X-ray diffraction. Observations of reactions with SEM encounter the problems whether features were already present in the geological past and or those resulting from the experiments. Detailed mineralogical analysis is essential for these experiments. (b) Rates of heterogeneous reactions are an exponential function of temperature, and different mineral species, particularly clay, would precipitate at more moderate temperatures of 70–80 °C. Temperature and pressure conditions relevant to underground CO₂ storage vary widely, approximately 50–200 °C and 20–1000 bars (Hurter and Pollack, 1996; Carter et al., 1998; Hitchon et al., 1999; Bachu, 2000; Benson and Myer, 2000; Oldenburg et al., 2001). It is imperative to conduct companion experiments at more moderate temperatures (e.g., 70–80 °C) for longer duration. (c) Reactivity in mixed gas systems needs to be measured; H₂S and SO₂ are typical

impurities in the flue gas for subsurface disposal from coal gasification and combustion. Xu et al. (2007) and Xiao et al. (2009) reported different reservoir responses to co-injection of CO₂ with H₂S and SO₂, primarily due to the more acidic plume. How the shale caprock would response to the induced acidic plume is crucial to the sealing integrity in the co-injection scenario. (d) Previous studies have mostly focused on inorganic matters, i.e., CO₂, brine, and the minerals. However, typical shaly caprock contains a noticeable amount of organic matter but its impact has been largely overlooked. Organic matter and clay minerals could adsorb CO₂ gas, but may also be extracted by the supercritical CO₂ causing alteration to porosity and permeability of the caprock (Okamoto et al., 2005).

- (3) Geochemical modeling that is based on thermodynamics and kinetics must be employed to extrapolate short term laboratory experiment results of days to months, to thousands of years for performance assessment. The first step is probably to model those batch experiments that provided both mineralogical analysis and solution chemistry. Most experiments reported in the literature do not have sufficient details to provide a complete basis for geochemical modeling. Well-designed new batch and flow through experiments are needed.
- (4) Ultimately, laboratory experimental data need to feed to reactive transport modeling of CO₂ migration into shale caprock for performance assessment. However, reactive transport model is faced with some particular challenges. One major difficulty is the large uncertainties in the alumino-silicate mineral reactivity calculation due to our limited knowledge in their kinetic rates (Oelkers, 2001; Zhu, 2005, 2009; Zhu et al., 2006; Marini, 2007). Significant discrepancies between experimental and modeled solubility still exists, and further efforts are in need to either upscale measured laboratory rates, or to derive semi-quantitative kinetic rates from natural analogue studies.
- (5) Recent hydrological modeling of pressure build-up and caprock permeability indicates that, moderate brine migration through the caprock can be beneficial in terms of relief of pressure build-up in the reservoir and geomechanical stresses to the sealing caprock (Zhou et al., 2008; Benson and Chabora, 2009; Zhou and Birkholzer, 2011). However, the geochemical consequences of the brine migration through caprock have not been explored.

Though the flow velocity of upward percolating CO₂ is slow, large pore volumes of CO₂ and CO₂-impregnated brine could migrate through shale caprock in terms of pore volumes. Most of the previous studies on water chemistry of CCS caprock are measuring or modeling reactivity of micro-fracture surfaces. In a time frame of thousands of years and a thick sequence of shale caprock with pressure build-up, reactions beneath the micro-fracture surfaces and within the pore space may become crucial. Previous studies suggested that geochemical system of the clay-rich rocks may be dominated by different reactions on the micro-fracture scale and the pore scale. Though researches on pore water chemistry of clayrocks, particularly those for nuclear waste storage, suggested the chemical environment on the pore scale may be more stable (Bradbury and Baeyens, 2005; Gaucher et al., 2006, 2009), direct studies on the pore water composition in CCS caprock are in need to fully elucidate this problem.

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