

Invited review

Geochemistry in geologic CO₂ utilization and storage: A brief review

Liwei Zhang^{1,2}*, Yan Wang¹, Xiuxiu Miao^{1,2}, Manguang Gan^{1,2}, Xiaochun Li^{1,2}

¹State Key Laboratory of Geomechanics and Geotechnical Engineering, Institute of Rock and Soil Mechanics, Chinese Academy of Sciences, Wuhan 430071, P. R. China

²University of Chinese Academy of Sciences, Beijing 100049, P. R. China

(Received August 5, 2019; revised August 12, 2019; accepted August 12, 2019; available online August 19, 2019)

Citation:

Zhang, L., Wang, Y., Miao, X., Gan, M., Li, X. Geochemistry in geologic CO₂ utilization and storage: A brief review. *Advances in Geo-Energy Research*, 2019, 3(3): 304-313, doi: 10.26804/ager.2019.03.08.

Corresponding author:

*E-mail: zlw_85@foxmail.com

Keywords:

Geologic CO₂ storage
CO₂-rock reaction
mineral
wellbore cement
permeability

Abstract:

In this brief review, a comprehensive collection of previous studies about geochemistry in geologic CO₂ utilization and storage is presented and discussed to demonstrate the importance of CO₂-rock and CO₂-wellbore cement interactions in geologic CO₂ utilization and storage scenarios. For CO₂-rock interaction, CO₂ injection reduces the pH of brine in CO₂ storage reservoir, which triggers dissolution of silicate and oxide minerals in the reservoir. Dissolution of silicate and oxide minerals causes concentration increase of cations and anions, which induces secondary precipitation of silica, silicates and carbonates. For CO₂-cement interaction, the interaction between CO₂ and wellbore cement results in formation of a unique sandwich structure in cement (i.e., one carbonate precipitation zone in the middle and two dissolution zones on two sides). For both CO₂-rock and CO₂-cement interactions, pH plays a key role in the extent of mineral dissolution and precipitation, and the extent is dependent on pH buffering capacity of the CO₂ storage reservoir. The potential of CO₂-induced contaminant mobilization in deep CO₂ storage reservoir and shallow aquifer is also discussed, and the chance for CO₂ injection and CO₂ leakage to cause severe shallow aquifer contamination is low.

1. Subsurface CO₂ utilization and storage: An effective technology to mitigate climate change

Industrialization since the 18th century has increased the atmospheric carbon dioxide (CO₂) concentration from 280 parts per million (ppm) before industrial revolution to 400 ppm in 2014. Major CO₂ emitting sources include large fossil fuel power plants, cement and steel plants, biomass energy facilities, synthetic fuel plants, fossil fuel-based hydrogen production plants, etc. Anthropogenic CO₂ emissions contribute to a globally averaged land and ocean surface temperature increase of 0.85 °C over the period 1880 to 2012 (Pachaur et al., 2014). This temperature increase has caused a significant impact on the earth's eco-system and the commonwealth of human beings.

Geologic CO₂ utilization and storage (GCUS) is regarded as one of the best options with existing technologies to significantly reduce CO₂ emissions into the atmosphere (Bachu and Adams, 2003). GCUS requires storage of captured CO₂ from CO₂ emitting sources in the subsurface for hundreds and even thousands of years. This storage can be a stand-alone CO₂

storage (e.g., CO₂ storage in deep saline aquifers), or the CO₂ storage can be accompanied by production of natural resources like oil, natural gas, coalbed methane and geothermal energy, which is regarded as geologic CO₂ utilization. A demonstration of GCUS technology is shown in Fig. 1.

Candidate formations for CO₂ injection in GCUS operations include oil and natural gas reservoirs, shale gas reservoirs, deep saline aquifers and unminable coalbeds. Compared with other CO₂ injection formations, deep saline aquifers have the highest CO₂ storage capacity. In China, the estimated CO₂ storage capacity of deep saline aquifers is 1573 gigatonnes CO₂ (Wei et al., 2013, with 50% confidence with 50% by the U.S. Department of Energy method), which equals to ~130 years of total CO₂ emissions in China. In North America, a conservative estimation of total CO₂ storage capacity of deep saline aquifers is 2379 gigatonnes of CO₂, which equals to ~600 years of total CO₂ emissions in North America (U.S. DOE, 2015). Despite the adoption of alternative energy sources and energy efficient systems to reduce the rate of CO₂ emissions, the cumulative amount of CO₂ in the atmosphere needs to be reduced to limit the detrimental impacts of climate



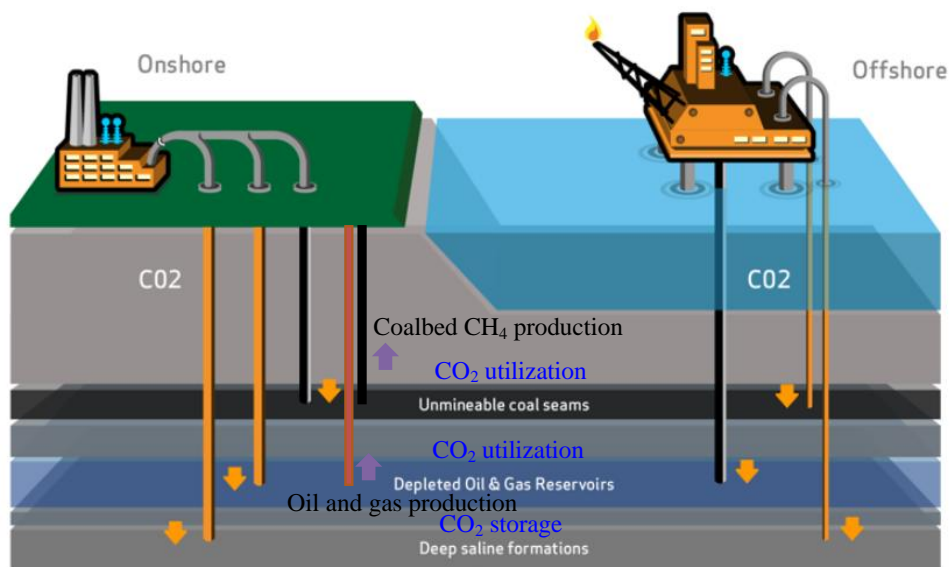


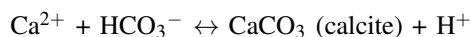
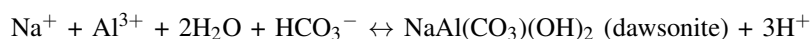
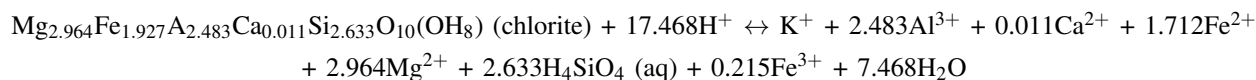
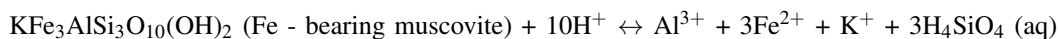
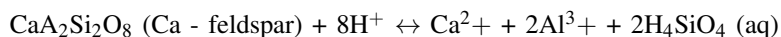
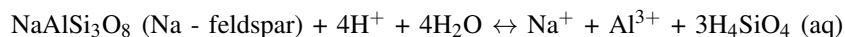
Fig. 1. Demonstration of GCUS technology (modified from worldcoal.org, 2019).

change (Pachaur et al., 2014). Therefore, regardless of the deployment of clean and efficient energy solutions, GCUS technologies need to be globally implemented (AiChE, 2019).

2. Geochemistry in geologic CO₂ utilization and storage

Geochemistry plays a very important role in geologic CO₂ utilization and storage. Mineral trapping is an important mechanism that determines the long-term fate of injected CO₂. In the short term, mineral dissolution and precipitation in flow channels of reservoir rocks may change permeability of the reservoir rocks and thus influence the migration behaviour of injected CO₂.

A key factor that controls geochemical reactions at GCUS conditions is pH. After CO₂ is injected into deep saline aquifers, CO₂ gets dissolved into, and reduces the pH of brine, which triggers dissolution of silicate and oxide minerals (Allen et al., 2005; Luquot and Gouze, 2009; Farquhar et al., 2013; Bacon et al., 2014; Luhmann et al., 2014; Gislason et al., 2014; Yang et al., 2015a, 2015b). Dissolution of silicate and oxide minerals concentration increase of ions such as Ca²⁺, Mg²⁺, Na⁺, SiO₄⁴⁻, Fe²⁺ etc. in solution, which induces secondary precipitation of silica, silicates and carbonates (Xu et al., 2005; Zhang et al., 2015a; Miller et al., 2016; Li et al., 2016). Some representative mineral dissolution and precipitation reactions are specified below:



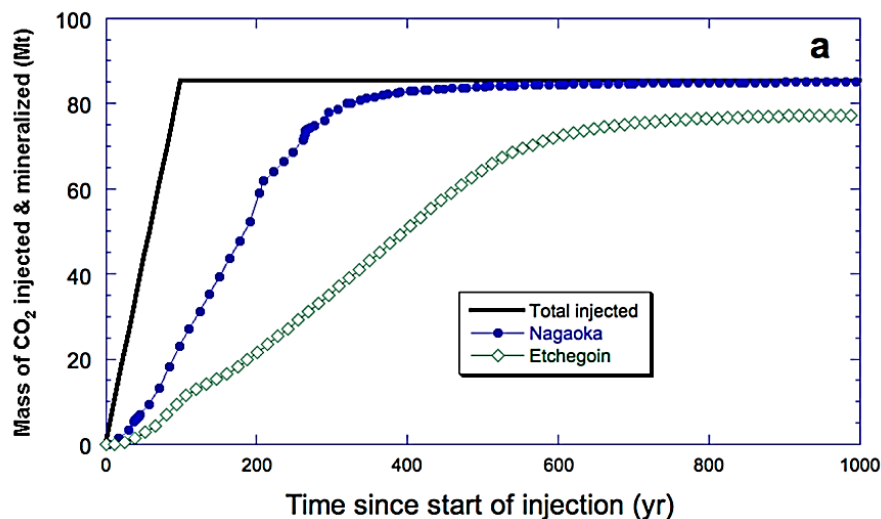


Fig. 2. Simulated values for the amount of injected supercritical CO₂, and the amounts that are converted to minerals over a 1000-year time span after the start of injection for two scenarios: Etchegoin CO₂ storage reservoir rock and the Nagaoka CO₂ storage reservoir rock (Zhang and DePaolo, 2017).

Mineral trapping is considered to be the most secure form of CO₂ storage, but it is slow to develop because it depends on the release of cations like Ca²⁺, Fe²⁺ and Mg²⁺ by dissolution of rock minerals (Zhang and DePaolo, 2017). Zhang et al. (2015a) calculated the amount of mineralized CO₂ by mineral trapping mechanism using a numerical simulator, with the Etchegoin CO₂ storage reservoir rock and the Nagaoka CO₂ storage reservoir rock as two cases. They found that for the Etchegoin case, mineralization of CO₂ reached a maximum of 90% injected CO₂, and the time needed for 60% mineralization was 400 – 500 years. For the Nagaoka example, mineralization of CO₂ reached ~99% within 200 – 300 years (Fig. 2.). Also, aforementioned mineral dissolution and precipitation processes can modify pore networks to increase or decrease porosity and permeability of both CO₂ storage formation and caprock (Gao et al., 2017). Zhang et al. (2015b) developed a numerical model with the use of reactive transport code CrunchFlow to estimate permeability and mineral composition changes of a sandstone core representing Mount Simon CO₂ storage formation, IL, USA under typical CO₂ storage environment. The model predicted a permeability decrease from 1.60 mD to 1.02 mD for the core after 180 days of exposure to CO₂-saturated brine. Secondary CO₂ (am) and kaolinite precipitation was the primary reason that caused permeability decrease. The numerical simulation result was verified by Soong et al. (2016), which conducted CO₂-saturated brine exposure experiment for the same type of sandstone core and the same exposure conditions as in Zhang et al. (2015b), and they measured a 50% permeability reduction for the sandstone core after 180 days of exposure to CO₂-saturated brine.

Key factors that determine the extent of mineral dissolution and secondary mineral precipitation are rock type, distribution of reactive mineral phases and diffusive mass transport conditions (Adeoye et al., 2017; Wang et al., 2019). In the following section, impact of rock type on CO₂-brine-rock interactions in GCUS conditions is discussed in detail.

3. CO₂-brine-rock interactions in GCUS conditions: Impact of rock type

Based on mineral compositions and reactivity of minerals contained in the rock, the rocks of CO₂ storage reservoir can be divided into three types (from simple to complicated mineral compositions): limestone, sandstone and basalt. Rock type has an impact on CO₂-brine-rock interactions. For limestone, the presence of minerals such as CaCO₃ and CaMg(CO₃)₂ in limestone has strong pH-buffering capacity, therefore, the pH reduction of pore water induced by CO₂ injection is very limited for limestone, thus reducing the extent of CO₂-limestone interaction. Lagneau et al. (2005) conducted a numerical simulation of CO₂ injection into Dogger carbonate reservoir in the Paris Basin, and they observed pH buffering due to the presence of calcium carbonate in Dogger carbonate reservoir. The pH at the interface between the injected supercritical CO₂ and brine was maintained at about 4.8, at which the impact of CO₂-brine-rock interaction on pore structure of the reservoir was limited. After the injection of CO₂, the amount of calcium carbonate dissolved in the reservoir accounted for only 5% of the total amount of calcium carbonate in the reservoir. Luquot and Gouze (2009) conducted an experiment of reactive CO₂-saturated brine flowing through a limestone core under CO₂ geological storage conditions (T = 100°C and pore pressure = 12 MPa). They found that CO₂-limestone reaction caused a small decrease in rock porosity and permeability, and this decrease was mainly due to the precipitation of CaCO₃ and MgCO₃. Liu et al. (2013) exposed a rock core taken from Ordovician reef limestone in Bachu area of Tarim Basin to CO₂-saturated brine under a temperature of 40 to 120°C and a CO₂ partial pressure of 8 to 20 MPa, so as to observe macro and micro-structure changes of the rock core before and after the exposure experiment. The results show that CO₂-induced dissolution occurred at the surface of the core in contact with bulk brine, causing a significant porosity increase

at the surface of the core. However, porosity increase did not occur in the interior of the core, and the net porosity increase of the entire core was very small. Meng et al. (2013) carried out a series of experimental studies under different temperature and pressure conditions ($T = 85^{\circ}\text{C}$, $P_{\text{CO}_2} = 5.0$ MPa; $T = 135^{\circ}\text{C}$, $P_{\text{CO}_2} = 5.7$ MPa; $T = 185^{\circ}\text{C}$, $P_{\text{CO}_2} = 8.8$ MPa) to investigate calcite– CO_2 saturated brine interaction. They found that CO_2 -induced dissolution of calcite was the highest at $T = 135^{\circ}\text{C}$, followed by $T = 185^{\circ}\text{C}$ and $T = 85^{\circ}\text{C}$. Characteristic cavities formed as a result of calcite dissolution were observed in all scenarios, but the dissolution only occurred at the exterior of calcite samples, and the integrity of all calcite samples remained. Lebedev et al. (2017) used an in-situ micro-CT scanner to image a heterogeneous limestone core before and after flooding with CO_2 -saturated brine at representative reservoir conditions. Though a partial dissolution of carbonate rock matrix and an increase in absolute and effective porosity and permeability were observed after flooding with CO_2 -saturated brine, the dissolution was confined to the original flow channels and inlet points.

For sandstone, if quartz content in sandstone is high, and contents of reactive minerals (e.g., feldspars, chlorite, hematite, etc.) are low, the CO_2 -brine-sandstone interaction is expected to be limited. However, if the sandstone contains large amounts of reactive minerals, the CO_2 -brine-sandstone interaction will become obvious. Early studies on geochemical reactions between CO_2 and sandstone are mostly numerical simulation studies. Xu and Pruess (2004) used geochemical models to study the chemical reaction between sandstone aquifer and CO_2 , and found that the reaction between sandstone and CO_2 will lead to the precipitation of secondary carbonate minerals such as dawsonite, calcite, muscovite, siderite, magnesite, etc., resulting in a decrease in porosity and permeability of the CO_2 injection formation. Gunter et al. (1997) carried out a batch-soak CO_2 exposure study using powdered sandstone in the presence of CO_2 saturated brine at 105°C and 9 MPa. SEM and XRD analysis did not show evidence of significant reaction between CO_2 and sandstone, despite this particular sandstone consisted of reactive minerals like anorthite, albite and kaolinite. This was basically because the alkalinity of the brine solution buffered the pH when CO_2 was mixed with brine. Moore et al. (2005) studied the water- CO_2 -rock interaction between a mixture of albite, dolomite, orthoclase, quartz and anorthite (mimicking typical sandstone compositions) and natural aquifer water (obtained from the Springerville-St. Johns CO_2 field). They observed precipitation of kaolinite when the CO_2 concentration was 0.03 mol/kg, and precipitation of dawsonite when the CO_2 concentration was 0.07 mol/kg. Moore et al. added CO_2 until the concentration of CO_2 reached 1 mol/kg, and reduction of pH caused the formation of alunite and some of the precipitated kaolinite at 0.03 mol/kg was dissolved. This study exhibits the significant effect of CO_2 concentration and aquifer pH on mineral dissolution and precipitation. Lagneau et al. (2005) conducted a numerical simulation to study geochemical interaction between injected CO_2 and sandstone at Bunter CO_2 storage formation, North Sea, and the simulation results predicted precipitation of CaCO_3 , which caused a 20% porosity

reduction of the sandstone.

Zerai et al. (2006) simulated geochemical interaction between injected CO_2 and Rose Run sandstone CO_2 storage formation in Ohio, USA, and they observed precipitation of dawsonite, FeCO_3 , SiO_2 and muscovite, as well as dissolution of Na-feldspar, K-feldspar and kaolinite. The aforementioned mineral precipitation and dissolution caused a net porosity reduction of 0.1% ~ 0.2%. Yu et al. (2012) conducted a CO_2 -saturated brine flow-through experiment under a temperature of 100°C and a pore pressure of 24 MPa for a sandstone core, and the geochemical reactions that occurred during the flow-through process were investigated. They found that the carbonate minerals in the sandstone core partially dissolved after the flow-through experiment, and a small amount of kaolinite and amorphous silicate minerals were produced. Kaolinite and amorphous silicate minerals were transported to pore throats, clogging flow channels and reducing the permeability of the sandstone core. Li et al. (2013) carried out a water-rock- CO_2 reaction experiment at a temperature of 100°C and a pressure of 10 MPa for 10 days using a core retrieved from a tertiary sandstone reservoir of Guantao formation in Beitang sag of the Middle of Huanghua Depression. It was found that feldspar and calcite in the core dissolved after water-rock- CO_2 reaction, while the reaction led to an increase in the content of clay minerals such as montmorillonite and illite. Those mineral dissolution and precipitation reactions did not have a significant impact on the pore structure of the sandstone core.

For basalt, since basalt contains large amounts of reactive minerals like feldspars, pyroxene and olivine, basalt is generally more reactive to CO_2 , compared with sandstone and limestone. As a result, injection of CO_2 into a basalt-rich reservoir may cause significant reservoir alteration. Verba et al. (2014) carried out experiments on the reaction of basalt-cement composite samples with brine solution saturated by CO_2 for 84 days. The SEM analysis shows that after 84 days of reaction, CO_2 was able to penetrate from different directions into the interior of the basalt, causing a significant change in basalt (Fig. 3). If CO_2 was mixed with impurity gases (e.g. SO_2 , O_2 , etc.), the mixture gas caused more structure alteration of basalt than the case with only CO_2 , and some sulfur-bearing minerals might precipitate. Schaeff et al. (2014) found that after 98 days of reaction with distilled water containing CO_2 (with 1 wt% SO_2 and 1 wt% O_2 as impurities), there were many corrosion marks on the surface of basalt. Also, a large amount of CaSO_4 precipitation was observed. The precipitated CaSO_4 particles served as nuclei for the deposition of other secondary minerals such as $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, $\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, $\text{Fe}(\text{OH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$, etc. The processes of corrosion and precipitation of secondary minerals make the surface of basalt rough and uneven, and the reacted areas are easier to peel off from the surface than before the reaction, reducing the mechanical strength of basalt.

In general, the reactivity of reservoir rock with injected CO_2 (from low to high) can be ordered as: sandstone (low feldspar and chlorite content) < limestone < sandstone (high feldspar and chlorite content) < basalt. For sandstone, the

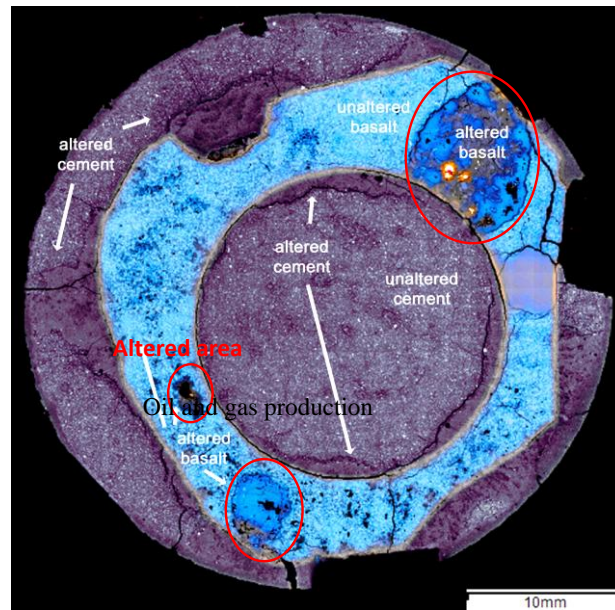


Fig. 3. A SEM-BSE montage image of the Grande Ronde basalt-Portland cement interface after exposure to CO₂ saturated brine (Verba et al., 2014). Alteration areas of basalt can be clearly seen.

availability of feldspar and chlorite in sandstone determines the rate of sandstone-CO₂ interaction and the amount of CO₂ uptake by mineral trapping, due to the high reactivity of feldspar and chlorite through a number of complex reactions under in-situ conditions. For limestone, the carbonate minerals in limestone are less reactive than feldspar and chlorite in sandstone. Preferential dissolution of carbonate minerals along flow channels is possible, but the dissolution is not expected to significantly alter the matrix structure of limestone. The CO₂ mineral trapping capacity is generally low in limestone, due to an unfavorable environment for carbonate mineral precipitation in limestone. For basalt, the content of reactive minerals (e.g., feldspars, pyroxene, olivine, etc.) is higher than that in sandstone and limestone, which enables basalt to have a higher mineral trapping capacity than sandstone and limestone.

In summary, basalt is the most reactive type of reservoir rock and is expected to have the highest mineral trapping potential, but significant reaction between basalt and CO₂ may cause mechanical strength loss of basalt, which needs to be carefully evaluated before CO₂ injection. For sandstone and carbonated rock, though some core-scale laboratory tests and numerical simulations predict notable changes in porosity and permeability after exposure to CO₂ saturated brine, no reservoir-scale numerical simulations have shown notable changes in porosity and permeability. Instead, all reservoir-scale numerical simulations predict very small changes in porosity and permeability for sandstone and carbonated rock after exposure to CO₂ saturated brine.

4. CO₂-brine-wellbore cement interactions

The majority of locations that are being considered for GCUS operations are in areas that have a history of fossil

resource exploitation, in which candidate formations are typically penetrated by a large number of wells from previous fossil resource exploration and production (Zhang et al., 2015c). The penetrating wells connect deep CO₂ storage formations with shallow aquifers and land surface above the CO₂ storage formations, and thus the sealing integrity of injected CO₂ may be compromised by the presence of active or abandoned wells, if the cement job of those wells is poorly done. CO₂-brine-wellbore cement interactions may cause debonding at cement-caprock and cement-casing interfaces, which causes CO₂ leakage at cement-caprock and cement-casing interfaces, resulting in loss of sealing integrity. Therefore, it is necessary to study the chemical interactions between CO₂ and wellbore cement under GCUS conditions.

Previous studies have been done to investigate CO₂-brine-wellbore cement interactions under GCUS conditions. Kutchko et al. (2008) conducted CO₂ exposure experiments to study the degradation of hardened cement paste under geologic CO₂ storage conditions (T = 50°C and P = 30.3 MPa). They observed formation of a degradation zone near cement surface, and the expansion of this degradation zone was extremely slow (the zone became 1.00 ± 0.07 mm thick after 30 years of exposure to CO₂-saturated brine, based on extrapolation of the hydrated cement alteration rate obtained in the experiments). Brunet et al. (2016) developed a process-based reactive transport model that explicitly simulates CO₂ saturated flow and multi-component reactive transport in fractured cement, and they used the model to investigate the impact of flow residence time (defined as the ratio of fracture volume over flow rate) on fracture aperture of cement. They found that a long residence time led to slow replenishment of CO₂ saturated water, calcite precipitation in fracture, and self-sealing of fracture. The opposite (fracture opening) occurred when the residence time

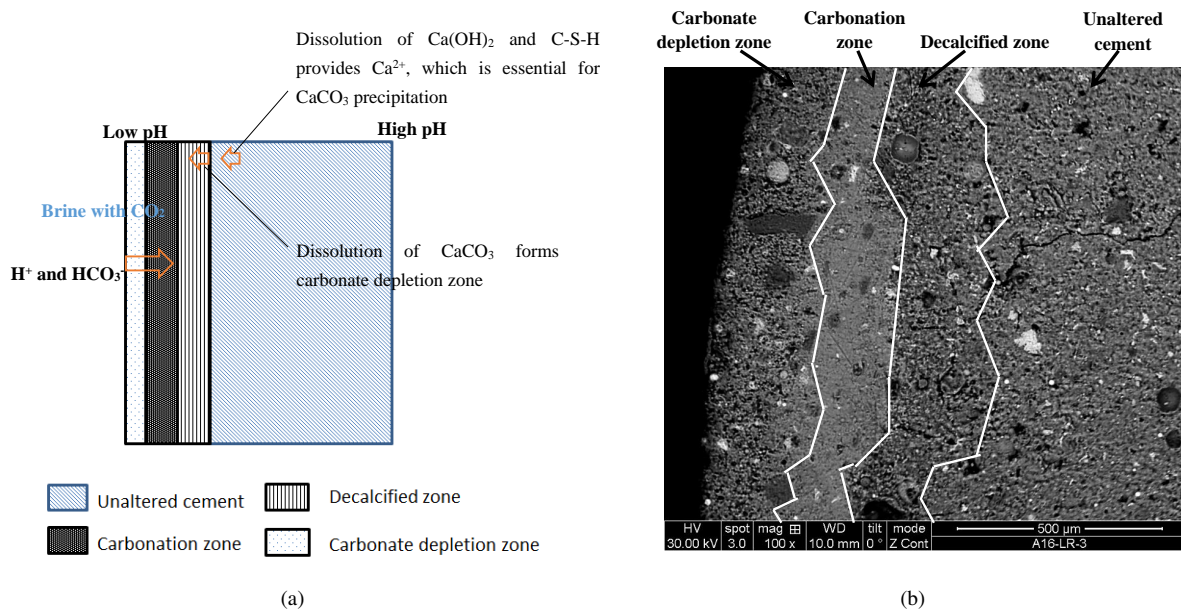


Fig. 4. (a) Schematic of the four distinctive zones as a result of CO₂-cement interaction; (b) Appearances of the four zones in an SEM-BSE image (Zhang et al., 2015c).

was short. Zhang et al. (2013) prepared pozzolan-amended wellbore cement samples and the cement samples were exposed to a mixture of CO₂ and H₂S under geologic CO₂ storage conditions (T = 50°C and P = 15.1 MPa). They found that pozzolan content governed the rate of interaction between pozzolan-amended cement and CO₂ + H₂S. The samples with higher pozzolan content (65 vol% pozzolan) had a higher reaction rate with CO₂ and H₂S than that with lower pozzolan content (35 vol% pozzolan). Jacquemet et al. (2012) conducted 15 and 60 days duration batch experiments in which wellbore cement samples were immersed in brine saturated by a mixture of CO₂ and H₂S under a pressure of 50 MPa and a temperature of 120°C. They observed fast formation of a non-porous calcite coating at surface of cement samples due to CO₂-cement interaction, which resulted in global porosity decrease of the cement. Gherardi et al. (2012) conducted a set of numerical simulations to predict mineral alteration at wellbore cement-caprock interface of an idealized abandoned well at the top of the Dogger aquifer in Paris Basin, France. They observed early replacement of portlandite and other dissolving primary cement minerals with calcite, which leads to a significant decrease in cement porosity, down to 15%. Overall, after 1000 years simulation time, cement porosity was lower than in the initial state.

Aforementioned previous studies have revealed the mechanism of CO₂-brine-cement interaction. The mechanism can be divided into four stages:

Stage 1: Dissolution of CO₂ in brine, which causes drop of brine pH;

Stage 2: Dissolution of cement hydration products like amorphous calcium silicate hydrate (C-S-H) and portlandite, which contributes to formation of a decalcified zone, as specified in Fig. 4.;

Stage 3: Cations like Ca and Mg released from dissolution

of cement hydration products react with dissolved CO₂ to form carbonate precipitates (carbonation zone in Fig. 4.);

Stage 4: The outer region of the carbonation zone, where precipitated CaCO₃ is exposed to low-pH brine, begins to dissolve, which forms a porous carbonate depletion zone.

A schematic of the four aforementioned zones as a result of CO₂-cement interaction and an SEM-BSE image showing the four zones is provided in Fig. 4.

This unique CO₂-induced cement alteration pattern of a precipitation zone sandwiched by two dissolution zones is commonly seen in laboratory experiments, in which the cement reacts with bulk brine with dissolved CO₂. Some researchers have pointed out that the laboratory-simulated exposure environment is generally more severe compared with real reservoir conditions. as shown by Gherardi et al. (2012), the CO₂-cement interaction at cement-caprock interface, where the pH is buffered by minerals in caprock, may not cause formation of a carbonate depletion zone, and the absence of the carbonate depletion zone significantly reduces the risk of CO₂ leakage at cement-caprock interface.

5. Impact of geochemical reactions on mechanical strength of sandstone and cement

After reacting with CO₂, the mechanical strength of the sandstone may be weakened due to dissolution of cementing agents in the sandstone (De Silva et al., 2015). This phenomenon was examined by Marbler et al. (2013) by performing uni-axial and tri-axial tests on sandstone samples after exposure to CO₂. They found that the strength and elastic deformation behaviour of all the sandstone samples were significantly reduced upon exposure to CO₂. The observed strength reduction is mainly due to the weakening of the bonds between the detritus minerals and the cementitious phase in

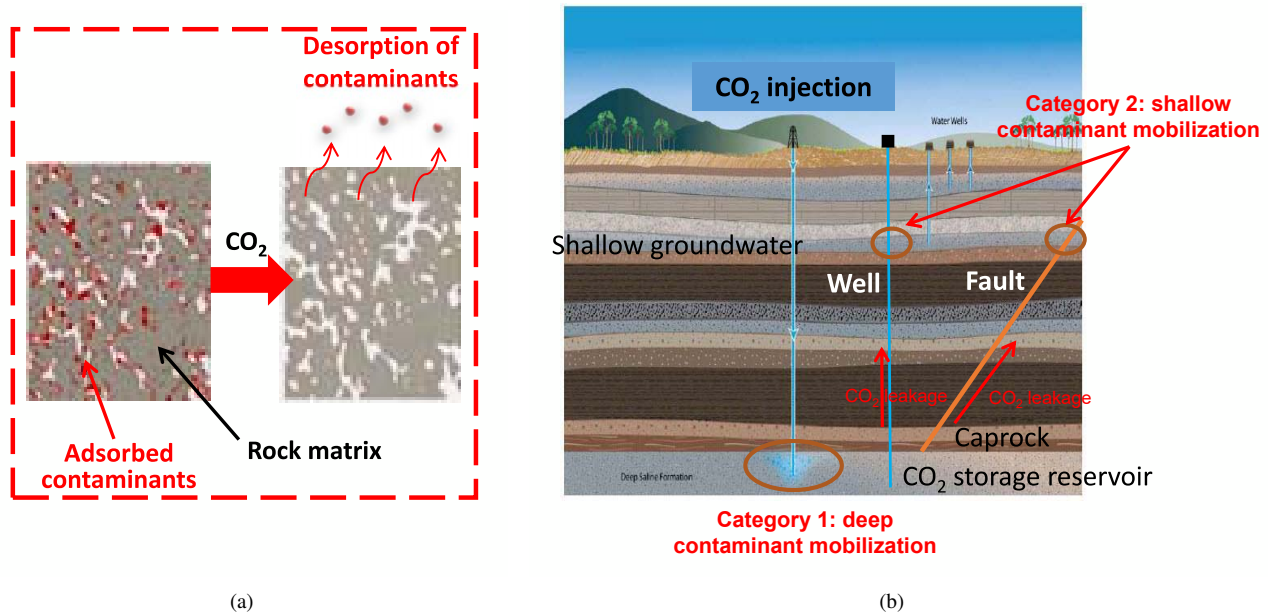


Fig. 5. (a) Demonstration of CO₂-induced contaminant mobilization and (b) two categories of contaminant mobilization.

sandstone, and the formation of minerals with low mechanical strength such as kaolinite. Also, depletion of hard minerals like feldspar causes debonding between grains and loss of mechanical strength. In Marbler et al.'s experiments, alteration in mineral structure due to reaction with CO₂ changed the internal friction angle, cohesion and uni-axial strength by up to 24%, 30% and 67%, respectively.

Field and laboratory evidences, and modeling results of CO₂-cement interaction (e.g. Barlet-Gouédard et al., 2007; Carey and Lichtner, 2007; Duguid, 2008; Rimmel et al., 2008; Fabbri et al., 2009; Wigand et al., 2009) show that, whereas moderate carbonation can be beneficial to cement strength, the formation of cracks is usually related to extensive carbonation. For example, Barlet-Gouédard et al. (2007) reported a strength loss of up to 65% for heavily carbonated Portland cement samples exposed to CO₂-saturated water for 6 weeks, and an occurrence of cracks in the carbonation layer during compressive strength measurements. Fabbri et al. (2009) observed a significant degradation of mechanical strength of carbonated cement under wet supercritical CO₂ conditions at 90°C, and a formation of micro-cracks in the carbonated layer of cement was also observed. Although the deposition of CaCO₃ in cement pores may locally decrease the porosity, massive carbonation occurring within cement does not only contribute to sealing of the cement, but also cause late mechanical degradation of cement (Gherardi et al., 2012). The mechanism of crack formation due to carbonation still remains unclear, and only some studies observed formation of cracks as a result of extensive carbonation. Therefore, more studies in this area are necessary in the future.

6. CO₂-induced contaminant mobilization

CO₂-induced contaminant mobilization is one concern as-

sociated with GCUS, because injection of CO₂ causes drop of pH and increase of HCO₃⁻ and CO₃²⁻ concentrations, which may lead to dissolution of contaminant-bearing minerals and de-sorption of contaminants (Harvey et al., 2012). CO₂-induced contaminant mobilization can be classified into two categories: deep contaminant mobilization and shallow contaminant mobilization. Deep contaminant mobilization is the release of contaminant at CO₂ storage reservoir or caprock above the CO₂ storage reservoir, and shallow contaminant mobilization is the release of contaminant in shallow groundwater due to leakage of injected CO₂ to shallow groundwater. A demonstration of contaminant mobilization as a result of CO₂ injection can be found in Fig. 5.

Some researchers have looked into contaminant mobilization in deep CO₂ storage reservoirs, and representative contaminants include organic compounds, arsenic (As) and uranium (U). Zheng et al. (2013) found that injection of CO₂ may mobilize organic compounds such as benzene in depleted oil reservoirs, and the released organic compounds can be entrained to shallow aquifer by leaking CO₂ if a CO₂ leakage pathway is present. Zhang et al. (2017) investigated the causes and the extent of arsenic mobilization in deep CO₂ storage reservoir, and the potential of shallow aquifer contamination by arsenic migration from deep CO₂ storage reservoir to shallow aquifer. Zhang et al. (2019) developed a TOUGHREACT model to investigate the dissolution potential of a U-bearing mineral (i.e., UO₂) in a hypothetical deep CO₂ storage reservoir. They found that HCO₃⁻ concentration increased as a result of CO₂ injection, which led to uranium-HCO₃⁻ complexation and subsequent release of uranium. However, the region with increased uranium concentration was restrained in deep subsurface and notable migration of uranium to shallow aquifer caused by CO₂ injection did not occur.

A number of works discussed mobilization of contaminants

in near-surface environments due to CO₂ migration from deep geologic CO₂ storage formations to shallow aquifers. Bacon et al. (2014) simulated CO₂ and brine leakage into an unconfined, oxidizing carbonate shallow aquifer, and they found that shallow aquifer pH and TDS were influenced by CO₂ leakage, while trace metal concentrations were mostly influenced by brine concentrations entering the shallow aquifer. Yang et al. (2011) found that given a 3-day incubation period with high-pressure CO₂ (25°C and 25 bars) in a humid environment, concentrations of chromium, lead, copper, arsenic and uranium in pore water contained in an agricultural soil sample increased by up to 500%. Trautz et al. (2012) conducted a field study with the controlled release of CO₂ to groundwater to investigate potential impacts. They found that dissolution of CO₂ in the groundwater resulted in a sustained and easily detected decrease of ~ 3 pH units. However, several trace constituents, including As and Pb, remained below their respective detection limits. Agnelli et al. (2018) reported an intrusion of natural CO₂ fluxes from the Earth's mantle into shallow aquifers in Campo de Calatrava region (Spain), resulting in significant changes in physical and chemical properties of shallow aquifers. Wei et al. (2015) conducted a pilot-scale experiment of CO₂ storage with impurity (containing N₂ and O₂) in the upper Yaojia Formation (China), and field monitoring results suggested that co-injection of oxygen enhanced dissolution of certain minerals in the aquifer formation and provided soluble ions such as uranium and SO₄²⁻. In summary, the chance for CO₂ injection and CO₂ leakage to cause severe shallow aquifer contamination is low, and the contamination can be monitored and remediated.

7. Summary

Geochemistry plays a very important role in geologic CO₂ utilization and storage. The primary reasons to cause geochemical reactions between CO₂ and reservoir rock/caprock in deep subsurface are drop of pH and formation of bicarbonate and carbonate ions due to CO₂ dissolution. Drop of pH induces dissolution of silicate and oxide minerals in the reservoir, leading to concentration increase of Ca²⁺, Mg²⁺, Na⁺, SiO₄⁴⁻, Fe²⁺, etc. Ca²⁺, Mg²⁺ and Fe²⁺ are able to react with bicarbonate and carbonate ions to form carbonates, as well as to react with SiO₄⁴⁻ to form silicate precipitates. Formation of amorphous silica (SiO₂, am) is also common in GCUS scenarios. For CO₂-wellbore cement interaction, the interaction results in formation of a unique sandwich structure in cement (i.e., one carbonate precipitation zone in the middle and two dissolution zones on two sides). For both CO₂-rock and CO₂-cement interactions, pH plays a key role to determine the extent of mineral dissolution and precipitation, and the extent is dependent on pH buffering capacity of the CO₂ storage reservoir. The potential of CO₂-induced contaminant mobilization in deep CO₂ storage reservoir and shallow aquifer is discussed, and the chance for CO₂ injection and CO₂ leakage to cause notable shallow aquifer contamination is low.

Acknowledgments

The authors would like to acknowledge funding support from Thousand Talent Program for Outstanding Young Scientists (Grant No. Y731101B01), the National Science Foundation of China (Grant No. 41807275), the National Science Foundation for Post-doctoral Scientists of China (Grant No. 2018M632948), and CAS-ITRI collaborative research funding (CAS-ITRI2019011).

Open Access This article is distributed under the terms and conditions of the Creative Commons Attribution (CC BY-NC-ND) license, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

References

- Adeoye, J.T., Menefee, A.H., Xiong, W., et al. Effect of transport limitations and fluid properties on reaction products in fractures of unaltered and serpentinized basalt exposed to high PCO₂ fluids. *Int. J. Greenh. Gas Con.* 2017, 63: 310-320.
- Agnelli, M., Grandia, F., Soler, D., et al. Metal release in shallow aquifers impacted by deep CO₂ fluxes. *Energ. Procedia* 2018, 146: 38-46.
- AiChE. What is CCUS? Available at: <https://www.aiche.org/ccusnetwork/what-ccus>, 2019.
- Allen, D.E., Strazisar, B.R., Soong, Y., et al. Modeling carbon dioxide sequestration in saline aquifer: Significance of elevated pressures and salinities. *Fuel Process. Technol.* 2005, 86(14-15): 1569-1580.
- Bachu, S., Adams, J.J. Sequestration of CO₂ in geological media in response to climate change: Capacity of deep saline aquifers to sequester CO₂ in solution. *Energ. Convers. Manage.* 2003, 44: 3151-3175.
- Bacon, D.H., Dai, Z., Zheng, L. Geochemical impacts of carbon dioxide, brine, trace metal and organic leakage into an unconfined, oxidizing limestone aquifer. *Energ. Procedia* 2014, 63: 4684-4707.
- Barlet-Gouédard, V., Rimmelé, G., Goffé, B., et al. Well technologies for CO₂ geological storage: CO₂-resistant cement. *Oil Gas Sci. Technol.* 2007, 62(3): 325-334.
- Brunet, J.P.L., Li, L., Karpyn, Z. T., et al. Fracture opening or self-sealing: Critical residence time as a unifying parameter for cement-CO₂-brine interactions. *Int. J. Greenh. Gas Con.* 2016, 47: 25-37.
- Carey, J.W., Lichtner, P.C. Calcium silicate hydrate (CSH) solid solution model applied to cement degradation using the continuum reactive transport model FLOTRAN, in *Transport properties and concrete quality: Materials Science of Concrete*, edited by Mobasher, B. and Skalny, J., American Ceramic Society; John Wiley & Sons, Inc., pp. 73-106, 2007
- De Silva, G.P.D., Ranjith, P.G., Perera, M.S.A. Geochemical aspects of CO₂ sequestration in deep saline aquifers: A review. *Fuel* 2015, 155: 128-143.
- Duguid, A. The effect of carbonic acid on well cements as identified through lab and field studies. Paper SPE 119504 Presented at the SPE Eastern Regional/AAPG Eastern Section Joint Meeting, Pittsburgh, Pennsylvania,

- USA, 11-15 October, 2008.
- Fabbri, A., Corvisier, J., Schnubel, A., et al. Effect of carbonation on the hydro-mechanical properties of Portland cements. *Cement Concrete Res.* 2009, 39(12): 1156-1163.
- Farquhar, S.M., Dawson, G.K.W., Esterle, J.S., et al. Mineralogical characterisation of a potential reservoir system for CO₂ sequestration in the Surat Basin. *Aust. J. Earth Sci.* 2013, 60 (1): 91-110.
- Gao, J., Xing, H., Tian, Z., et al. Reactive transport in porous media for CO₂ sequestration: Pore scale modeling using the lattice Boltzmann method. *Comput. Geosci.* 2017, 98: 9-20.
- Gherardi, F., Audigane, P., Gaucher, E. C. Predicting long-term geochemical alteration of wellbore cement in a generic geological CO₂ confinement site: Tackling a difficult reactive transport modeling challenge. *J. Hydrol.* 2012, 420: 340-359.
- Gislason, S.R., Broecker, W.S., Gunnlaugsson, E., et al. Rapid solubility and mineral storage of CO₂ in basalt. *Energ. Procedia* 2014, 63: 4561-4574.
- Gunter, W.D., Wiwchar, B., Perkins, E.H. Aquifer disposal of CO₂-rich greenhouse gases: Extension of the time scale of experiment for CO₂-sequestering reactions by geochemical modelling. *Miner. Petrol.* 1997, 59(1-2): 121-140.
- Harvey, O.R., Qafoku, N., Cantrell, K.J., et al. Geochemical implications of CO₂ leakage associated with geologic storage: A review. U.S. Department of Energy Report Series, 2012.
- Jacquemet, N., Pironon, J., Lagneau, V., et al. Armouring of well cement in H₂S-CO₂ saturated brine by calcite coating-Experiments and numerical modelling. *Appl. Geochem.* 2012, 27(3): 782-795.
- Kutchko, B.G., Strazisar, B.R., Lowry, G.V., et al. Rate of CO₂ uptake on hydrated class H well cement under geologic sequestration conditions. *Environ. Sci. Technol.* 2008, 42(16): 6237-6242.
- Lagneau, V., Pipart, A., Catalette, H., et al. Reactive transport modelling of CO₂ sequestration in deep saline aquifers. *Oil Gas Sci. Technol.* 2005, 60(2): 231-247.
- Liu, K., Sun, Y., Yu, Q. Characteristics of dissolution of CO₂ geological storage applied to the ordovician reef limestone in bachu area of Tarim Basin. *J. Earth Sci. Environ.* 2013, 35(3): 106-112.
- Li, Y., Pang, Z., Yang, F. CO₂-EATER model on guantao formation of beitaogang sag. *Sci. Technol. Rev.* 2013, 31(27): 15-20.
- Li, Y., Pang, Z., Yang, F., et al. Geochemical responses of a saline aquifer to CO₂ injection: Experimental study on Guantao formation of Bohai Bay Basin, East China. *Greenh. Gas Sci. Technol.* 2016, 6(1): 125-137.
- Luhmann, A.J., Kong, X.Z., Tutolo, B.M., et al. Experimental dissolution of dolomite by CO₂-charged brine at 100°C and 150 bar: Evolution of porosity, permeability, and reactive surface area. *Chem. Geol.* 2014, 380: 145-160.
- Luquot, L., Gouze, P. Experimental determination of porosity and permeability changes induced by injection of CO₂ into carbonate rocks. *Chem. Geol.* 2009, 265 (1-2): 148-159.
- Marbler, H., Erickson, K.P., Schmidt, M., et al. Geomechanical and geochemical effects on sandstones caused by the reaction with supercritical CO₂: An experimental approach to in situ conditions in deep geological reservoirs. *Environ. Earth Sci.* 2013, 69(6): 1981-1998.
- Meng, F., Li, C., Liu, L., et al. Experiment of CO₂-saline water-calcite interactions. *Geol. Sci. Technol. Info.* 2013, 32(3): 171-176.
- Miller, Q.R., Wang, X., Kaszuba, J.P., et al. Experimental study of porosity changes in shale caprocks exposed to carbon dioxide-saturated brine II: Insights from aqueous geochemistry. *Environ. Eng. Sci.* 2016, 33 (10): 736-744.
- Moore, J., Adams, M., Allis, R., et al. 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, USA. *Chem. Geol.* 2005, 217(3-4): 365-385.
- Pachauri, R.K., Allen, M.R., Barros, V.R., et al. Climate change 2014: Synthesis report. Contribution of Working Groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change. Geneva, Switzerland: IPCC, 2014.
- Rimmelé, G., Barlet-Gouédard, V., Porcherié, O., et al. Heterogeneous porosity distribution in Portland cement exposed to CO₂-rich fluids. *Cement Concrete Res.* 2008, 38(8-9): 1038-1048.
- Schaefer, H.T., Horner, J.A., Owen, A.T., et al. Mineralization of basalts in the CO₂-H₂O-SO₂-O₂ system. *Environ. Sci. Technol.* 2014, 48(9): 5298-5305.
- Soong, Y., Howard, B.H., Dilmore, R.M., et al. CO₂/brine/rock interactions in Lower Tuscaloosa formation. *Greenh. Gas Sci. Technol.* 2016, 6(6): 824-837.
- Trautz, R.C., Pugh, J.D., Varadharajan, C., et al. Effect of dissolved CO₂ on a shallow groundwater system: A controlled release field experiment. *Environ. Sci. Technol.* 2012, 47(1): 298-305.
- U.S. DOE. Carbon Storage Atlas - Fifth Edition (Atlas V). Available at: <https://edx.netl.doe.gov/dataset/netl-carbon-storage-atlas-fifth-edition>.
- Verba, C., O'Connor, W., Rush, G., et al. Geochemical alteration of simulated wellbores of CO₂ injection sites within the Illinois and Pasco Basins. *Int. J. Greenh. Gas Con.* 2014, 23: 119-134.
- Wang, Y., Zhang, L., Soong, Y., et al. From core-scale experiment to reservoir-scale modeling: A scale-up approach to investigate reaction-induced permeability evolution of CO₂ storage reservoir and caprock at a U.S. CO₂ storage site. *Comp. Geosci.* 2019, 125: 55-68.
- Wei, N., Li, X., Wang, Y., et al. Geochemical impact of aquifer storage for impure CO₂ containing O₂ and N₂: Tongliao field experiment. *Appl. Energ.* 2015, 145: 198-210.
- Wigand, M., Kaszuba, J.P., Carey, J.W., et al. Geochemical effects of CO₂ sequestration on fractured wellbore cement at the cement/caprock interface. *Chem. Geol.* 2009, 205(1-2): 122-133.

- Worldcoal.org. Carbon-Capture Use and Storage. Available at: https://www.worldcoal.org/sites/default/files/Storage_0.png, 2019.
- Xu, T., Apps, J. A., Pruess, K., et al. Numerical simulation of CO₂ disposal by mineral trapping in deep aquifers. *Appl. Geochem.* 2004, 19(6): 917-936.
- Xu, T., Apps, J.A., Pruess, K. Mineral sequestration of carbon dioxide in a sandstoneshale system. *Chem. Geol.* 2005, 217(3): 295-318.
- Yang, C., Hovorka, S.D., Trevino, R.H., et al. Integrated framework for assessing impacts of CO₂ leakage on groundwater quality and monitoring-network efficiency: Case study at a CO₂ enhanced oil recovery site. *Environ. Sci. Technol.* 2015a, 49(14): 8887-8898.
- Yang, C., Trevino, R.H., Hovorka, S.D., et al. Semi-analytical approach to reactive transport of CO₂ leakage into aquifers at carbon sequestration sites. *Greenh. Gas Sci. Technol.* 2015b, 5(6): 786-801.
- Yang, W., Maroto-valer, M., Steven, M.D. Environmental consequences of potential leaks of CO₂ in soil. *Energ. Procedia* 2011, 4: 3224-3230.
- Yu, Z., Yang, S., Liu, L., et al. An experimental study on water-rock interaction during water flooding in formations saturated with CO₂. *Acta Petrolei Sinica* 2012, 33(6): 1032-1042.
- Zerai, B., Saylor, B.Z., Matisoff, G. Computer simulation of CO₂ trapped through mineral precipitation in the Rose Run Sandstone, Ohio. *Appl. Geochem.* 2006, 21(2): 223-240.
- Zhang, L., Dzombak, D.A., Kutcho B.G., Wellbore cement integrity under geologic carbon sequestration conditions. United States of America: Elsevier, 2015c.
- Zhang, L., Dzombak, D.A., Nakles, D.V., et al. Characterization of pozzolan-amended wellbore cement exposed to CO₂ and H₂S gas mixtures under geologic carbon storage conditions. *Int. J. Greenh. Gas Con.* 2013, 19: 358-368.
- Zhang, L., Miao, X., Wang, Y., et al. Numerical simulation of subsurface uranium (U) leaching and migration under geologic carbon storage conditions. In: Zhan L., Chen Y., Bouazza A. (eds) *Proceedings of the 8th International Congress on Environmental Geotechnics Volume 3. ICEG 2018. Environmental Science and Engineering*. Springer, Singapore, 2019b.
- Zhang, L., Parthasarathy, H., Karamalidis, A. Investigation on arsenopyrite dissolution and As (III) migration under geologic carbon storage conditions: A numerical simulation approach. *Greenh. Gas Sci. Technol.* 2017, 7(3): 460-473.
- Zhang, L., Soong, Y., Dilmore, R., et al. Numerical simulation of porosity and permeability evolution of Mount Simon sandstone under geological carbon sequestration conditions. *Chem. Geol.*, 2015b, 403: 1-12.
- Zheng, L., Spycher, N., Birkholzer, J., et al. On modeling the potential impacts of CO₂ sequestration on shallow groundwater: Transport of organics and co-injected H₂S by supercritical CO₂ to shallow aquifers. *Int. J. Greenh. Gas Con.* 2013, 14: 113-127.
- Zhang, S., DePaolo, D.J. Rates of CO₂ mineralization in geological carbon storage. *Accounts Chem. Res.* 2017, 50(9): 2075-2084.
- Zhang, S., DePaolo, D.J., Voltolini, M., et al. CO₂ mineralization in volcanogenic sandstones: Geochemical characterization of the Etchegoin formation, San Joaquin Basin. *Greenh. Gas Sci. Technol.* 2015a, 5: 622-644.