Salinity-enhanced Release of Trace Metals from Sandstone and Variations in Mineral Compositions after Water-rock Interactions in the Presence of Supercritical CO₂

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ABSTRACT

This research is aimed toward an understanding of the effects of the chemical characteristics and mineral compositions of sandstone and formation water based on saline water-rock-supercritical CO₂ interaction simulation experiments. These experiments were conducted to assess whether toxic trace elements could be dissolved and released in formation water from sandstone in a CO₂ storage layer after CO₂ geological sequestration, thus affecting groundwater quality. The experimental results reveal that the concentrations of Cd and Pb in the water under examination exceeded the national primary drinking standard as a result of saline/fresh water-rock-supercritical CO₂ interactions after 40 d of sandstone immersion in saline/fresh water and 20 d of interaction. In addition, the Mn concentration in the saline/fresh water exceeded the national secondary drinking standard after 40 d of sandstone immersion and 20–80 d of interaction. However, Cd, Pb, and Mn were released to a greater extent (in terms of concentration, 2-fold for Cd, 7-fold for Pb, and 1.7-fold for Mn) in the presence of salinity, revealing that salinity may enhance the dissolution of Cd, Pb, and Mn after 20 d of saline water-rock-scCO₂ interaction. After a long period of supercritical CO₂-sandstone interaction, the trace metals previously mobilized can be immobilized again by an increase in alkalinity due to aragonite dissolution.

Keywords: Carbon dioxide geological sequestration; Water-rock-supercritical CO₂ interactions; Dissolution of trace elements; Salinity; Sandstone.

INTRODUCTION

Global warming caused by increased CO₂ emissions into the atmosphere is an international concern. To reduce CO₂ emissions, carbon dioxide sequestration in the deep subsurface environment has been tested worldwide at the pilot scale, e.g., Frio in U.S.A. (Hovorka *et al.*, 2006; Kharaka *et al.*, 2009), Weyburn in Canada (Moberg *et al.*, 2003; Carroll *et al.*, 2011a), Ketzin in Germany (Frster *et al.*, 2006; Würdemann *et al.*, 2010), Sleipner at North Sea (Chadwick *et al.*, 2004), Snøhvit at Norwegian Sea (Estublier and Lackner, 2009), Salah in Algeria (Carroll *et al.*, 2011b), CarbFix site in Iceland (Matter *et al.*, 2016). In a Sleipner-sized reservoir in the North Sea, Fe, Cu, Zn, and Na were mobilized after 14 Mt of CO₂ were stored, leading to the

precipitation of carbonate minerals in the shallower and more distal regions of the aquifer (Rempel *et al.*, 2011). Laboratory studies have indicated that the rate of carbonate mineral formation is much higher in host rocks that are rich in magnesium- and calcium-bearing minerals (Matter and Kelemen, 2009). Over 95% of the CO₂ injected into the CarbFix site in Iceland was mineralized to carbonate minerals in less than 2 years (Matter *et al.*, 2016). This precluded the risk of leakage and thus significantly reduced any monitoring program required for the storage site. For permanent CO₂ sequestration, CO₂ is chemically sequestered in carbonates by carbonation of minerals (Huijgen and Comans, 2003; Chang *et al.*, 2012; Pan *et al.*, 2015). In Taiwan, several potential sites for geological sequestration of CO₂ have been selected. The Talu Sandstone Reservoir at a depth of 3270–3271.6 m in a depleted gas oil well (Y-6) in Miaoli, central Taiwan, is one of the potential formations. In this study, a high-pressure autoclave was used to experimentally simulate the degree of trace elements released from Talu sandstone under field conditions of 30 Mpa and 120°C after coming in contact with CO₂. The concentrations

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of trace elements released into the formation water that exceed the maximum contaminant level (MCL) can provide information suggesting unacceptable levels of contamination.

Kharaka *et al.* (2010)'s laboratory results at the Zero Emission Research and Technology field site, Bozeman, Montana, U.S.A., demonstrated that the concentrations of Ca, Mg, Fe, Mn, and trace elements in both formation water and groundwater were increased during and following CO₂ injection. Trautz *et al.* (2012) displayed experimental field results indicating that several trace constituents, including As and Pb, remained below their respective background levels, whereas other constituents (Ba, Ca, Cr, Sr, Mg, Mn, and Fe) exhibited an initial increase in concentration followed by concentrations slightly greater than those of the background levels. Salinity has been shown to enhance the dissolution of minerals (e.g., phlogopite) and to affect the morphology of secondary minerals (Shao *et al.*, 2011). Nanoscale secondary mineral particles have been shown to form much faster in low salinity solutions than in high salinity solutions (Shao *et al.*, 2011). Considerable amounts of trace elements can be released from sandstone and shale as compared to rocks such as carbonate, basalt, etc. at various pressures and temperatures (Karamalidis *et al.*, 2012). Brine-rock-CO₂ interaction experiments conducted for 43 d under high pressure (34.4 MPa) and high temperature (120°C) on sandstone collected from the lower Tuscaloosa Formation, Mississippi, U.S.A., at a depth of 3193 m revealed high release of Pb and Cr exceeding the MCLs by an order of magnitude (Karamalidis *et al.*, 2012; Lu *et al.*, 2012). However, in most of these studies, only liquid samples were collected to confirm trace elements released into water, despite the fact that CO₂ injection into the subsurface environment can clearly induce alterations in rock minerals and changes in the chemical and mineral structure of the rock mass (Rathnaweera *et al.*, 2016).

Several studies (Kaszuba *et al.*, 2005; Bertier *et al.*, 2006; Lin *et al.*, 2008; Carroll *et al.*, 2011b; Rempel *et al.*, 2011; Jean *et al.*, 2015; Jean *et al.*, 2016; Rathnaweera *et al.*, 2016) have been conducted to experimentally evaluate the interactions in water-rock-supercritical CO₂ mineral systems under geologic CO₂ sequestration conditions. After injection of CO₂, CO₂ will dissolve into the local formation water and generate a variety of geochemical reactions (Rochelle *et al.*, 2004). The variations in mineral composition after saline-rock-CO₂ interactions have been less studied. In addition, trace elements in water may be adsorbed on sandstone, thereby resulting in changes in the concentrations of the trace elements in the sandstone after rock-water-supercritical CO₂ (scCO₂) interactions under high temperature and high pressure conditions. It is still unclear what exact concentrations of trace elements can be released from sandstone and adsorbed on sandstone after rock-water-scCO₂ interactions. In this study, we designed a unique experiment to react sandstone fragments (without grinding) with saline water and supercritical CO₂ for 20, 40, 60, and 80 d in a time series, from which the reacted water and sandstone fragment samples were collected for measurements of dissolved trace elements and mineral composition. This unique experimental approach is different

from that of our previous study (Jean *et al.*, 2015), in which the reaction times among saline water-rock-CO₂ interactions were set to be constant at 20 d. The aim of this research was to understand (1) the extent to which trace elements are released from sandstone and the effect on the quality of drinking water as well as (2) the effect of supercritical carbon dioxide (scCO₂) on the chemical characteristics and mineral composition of sandstone after the rock-water-scCO₂ interactions. This information can provide the basis for site selection in terms of in-situ environmental conditions to secure the safe geological sequestration of CO₂.

EXPERIMENTAL PROCEDURE

Saline Water-Rock-CO₂ Interactions Experiment

In order to understand the extent to which salinity promotes the release of trace elements from sandstone under conditions of high pressure (30 MPa) and elevated temperature (120°C) in the presence of supercritical CO₂, an anoxic high pressure autoclave was used in this study to conduct the experiment. The experimental setup is described in our previous papers (Jean *et al.*, 2015; Jean *et al.*, 2016). During the course of the experiment, 6 g of sandstone fragment samples (without grinding) immersed in 60 mL of a 26.3‰ NaCl solution (100% purity, Merck) as synthetic saline water was placed in a high-pressure autoclave (filled with 12 L deionized water to maintain the desired pressure) followed by injection of liquid CO₂ fluid into the autoclave to observe the interactions among the saline water-rock-CO₂. The temperature and pressure were set to simulate the field conditions corresponding to the injection depth.

Sampling and Analysis

During the course of the water-rock interaction experiments for the release of trace elements and variations in mineral composition, eight glass beakers were prepared. In each beaker, 6 g of sandstone fragments (without grinding), collected at the depth of 3270–3271.6 m at the Y-6 gas oil well in the Miaoli area of northern Taiwan (details are shown in Supplemental Information, Fig. S1), were immersed simultaneously in 60 mL of a 26.3‰ NaCl solution (100% purity, Merck) as synthetic saline water (formation water) or in deionized water (fresh water). Beakers 1, 2, 3, and 4 were immersed for 10, 20, 30, and 40 d, respectively, whereas Beakers 5, 6, 7, and 8 were immersed for 40 d before CO₂ was injected into the system. After immersion, Beakers 5, 6, 7, and 8 were separately placed into the high-pressure autoclave to obtain the water-rock-CO₂ reactions at 20, 40, 60, and 80 d, respectively, under 30 MPa of pressure and a temperature of 120°C in the presence of scCO₂. The reacted solution and sandstone fragments after the water-rock reaction were sampled. The solution was analyzed for trace elements (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Cd, Ba, and Pb) and major cations (Na, K, Ca, and Mg) using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500ce, U.S.A.). Each 1 g of the sandstone fragment samples taken from these eight beakers and the original sandstone before immersion was separately mixed with 10 mL of 0.1 N HNO₃ (Panreac,

Spain), in which the mixture was placed for 24 h without shaking and then filtered with 0.22 μm of a mixed cellulose ester membrane filter. The extracted solution was then analyzed for trace elements (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Cd, Ba, and Pb) adsorbed on the sandstone using ICP-MS (Agilent 7500ce, U.S.A.).

Mineralogy Analysis of Rocks

For the powder X-ray diffraction analyses, bulk sandstone specimens were ground into a powder (< 375 mesh), from which 0.5 g was sampled and uniformly placed on the sample holder. The measurements were performed on a Dandong Fangyuan DX-2700 X-ray diffractometer (Liaoning, China) with a Sol-X solid state detector and CuK α 1 ($\lambda = 1.5406$ Å) radiation set at 35 kV and 30 mA. The samples were scanned from 5–80° 2 θ with a scanning step of 0.04° per step. Scanning electron microscopy (SEM) (Hitachi S4100, Tokyo, Japan) was used to observe the microstructures of the sandstones. Energy dispersive spectroscopy (EDS) was used to compare the composition of the sandstone samples before and after reacting with supercritical CO₂.

RESULTS AND DISCUSSION

Chemical Constituents and Mineral Composition of the Sandstone

The concentration percentages of trace elements extracted from sandstone using 10 mL 0.1 N HNO₃ over those digested from sandstone after microwave digestion are listed in Table 1, where it can be seen that Mn is the largest extracted fraction (26.2%), and Ba is the smallest extracted fraction (0.25%) (Table 1). The mineral composition of the sandstone as analyzed by XRD was mainly quartz, microcline, albite, illite-montmorillonite, clinochlore, muscovite, etc.

Effect of Salinity on the Major Cations in Aqueous Solution after the Interactions of Saline Water-Rock-Supercritical CO₂

By comparison (Fig. 1), greater Na⁺, K⁺, Ca²⁺, and Mg²⁺ concentrations were released in the presence of the saline water (26.3% NaCl solution) as compared to in the absence of the saline water after 20–80 d of saline water-

rock-scCO₂ interaction, which reflected a nearly 100% increase in the concentrations of Na⁺, a 41.5–78.6% increase in K⁺, a 62.6–83.8% increase in Ca²⁺, and a 0.621–94.8% increase in Mg²⁺. These results suggest that salinity can promote the release of major cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) in water after saline water-rock-scCO₂ interactions. Intriguingly, more Mg²⁺ was released in the water in the absence of the saline water than in the presence of the saline water before the interactions. Ion-exchange reactions between interlayer K in mica and Na⁺ in the solution were promoted at higher salinities (Zhang *et al.*, 2016), leading to higher concentrations of K released into the solutions after more than 40–60 d of interaction.

Sandstone fragments were separately immersed in a 26.3% NaCl solution and deionized water as a function of 20 d- reaction time, continuously immersed for 40 d, and placed in the high pressure autoclave for 80 d of the interactions. Na concentrations in the saline water (a 26.3% NaCl solution) and fresh water (deionized water) were reduced by 3.1-fold and 2.3-fold, respectively (Fig. 1(a)). This suggests that the Na ions in the water tended to be adsorbed on the sandstone at the beginning of the interactions, whereas Na⁺ ions in the sandstone tended to be released into water as the reaction time was increased to 40–80 d. By comparison, Na⁺ concentrations were much higher in the saline water than in the fresh water (Fig. 1(a)), indicating that salinity can promote the release of Na⁺ from sandstone into water; K⁺ and Ca²⁺ had similar trends of distribution to those of Na⁺ (Figs. 1(b) and 1(c)). However, lower Mg²⁺ concentrations were released in the water in the presence of saline water as compared to the presence of fresh water before the interactions. Furthermore, salinity did not cause more Na⁺ to be released from the sandstone into the water before the interactions but did cause Na⁺ release after the interactions (Fig. 1(d)). These results suggest that the ion-exchange reactions between trace metals (Cd, Pb, and Mn) adsorbed onto the sandstone and major cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) may occur rapidly after supercritical CO₂ injections, resulting in the precipitation of Na, K, Ca, and Mg and thus a rapid decrease in the concentrations of these cations at 20 d of interaction.

Major cations were released from minerals into the formation water after the sandstone reacted with scCO₂, resulting in potential changes in the chemical characteristics

Table 1. The trace element percentage in concentration between the fraction extracted from sandstone and in total concentration digested from sandstone.

Element	Total concentration in whole rock (mg kg ⁻¹) (a)	Concentration (mg kg ⁻¹) of extracted fractions from whole rock (b)	Percentage (%) (b/a) $\times$ 100
Fe	8252.8	1028.0	12.5
Ba	423.6	1.08	0.25
Mn	34.83	9.14	26.2
Zn	24.48	1.72	7.0
Pb	15.56	0.40	2.6
Cr	11.19	2.14	19.1
As	6.95	1.30	18.7
Cu	2.29	0.30	13.1
Cd	0.63	0.01	1.59

Fig. 1. Total concentrations (mg L^{-1} solution) of dissolved major cations desorbed from sandstone for (a) Na, (b) K, (c) Ca, and (d) Mg while reacting with synthetic saline water with or without CO_2 as a function of reaction time (days). Time represents the time CO_2 was injected into the reaction system.

of the formation water. However, the temperature, pressure, reaction time, and original constituents of sandstone can affect the patterns of formation of secondary minerals. The major reaction processes are as shown below:

The reaction of scCO_2 and water can result in the formation of carbonic acid, or hydrogen and bicarbonate, which can cause the dissolution of carbonates and feldspar (Gaus, 2010). The dissolution rate decreased with increases in the reaction time in the feldspar-water- scCO_2 interaction experiment, indicating the dissolution of a large quantity of major cations in a short time (Chang, 2011). The increase in the concentrations of K, Na, Ca, and Mg after interaction for 40–60 d may be attributed to the dissolution of microcline, albite, and carbonate minerals. Our experimental results show that most of the Na, K, Ca, and Mg ions were released into the water and were positively correlated in the beginning of the interactions, but the concentrations of major cations in the water gradually decreased as a result of their saturation in the water and subsequent precipitation as

the reaction time increased. Although salinity enhancement of the release of Na, K, Ca, and Mg ions during the reaction reached an equilibrium, the concentrations began to decline due to the precipitation that occurred after 20 d of reaction and increased up to 60 d and then decreased at 80 d.

Effect of Supercritical CO_2 on the Dissolution of Trace Elements from Sandstone in Saline Formation Water

Cd ($63.4 \mu\text{g L}^{-1}$) and Pb ($627 \mu\text{g L}^{-1}$) (Fig. 2) were released into saline water after 20 d of saline water-rock- scCO_2 interaction, which exceeded the maximum contaminant levels (MCL) of Cd ($5 \mu\text{g L}^{-1}$) and Pb ($15 \mu\text{g L}^{-1}$). The concentrations of Mn in the water after 10, 20, 30, and 40 d of sandstone immersion and 40 d and 80 d of reaction time were 225.5, 200.8, 393.6, 75.6, 85.91, and $112.5 \mu\text{g L}^{-1}$, respectively, which also exceeded the MCL ($50 \mu\text{g L}^{-1}$) (Fig. 2). However, the concentrations of As, Cr, Cu, Ba, Fe, and Zn (Fig. 2) were lower than those of the MCLs ($10 \mu\text{g L}^{-1}$ for As, $100 \mu\text{g L}^{-1}$ for Cr, $1300 \mu\text{g L}^{-1}$ for Cu, $2000 \mu\text{g L}^{-1}$ for Ba, $300 \mu\text{g L}^{-1}$ for Fe, and $5000 \mu\text{g L}^{-1}$ for Zn). In comparison to fresh water (deionized water), Cd ($32.24 \mu\text{g L}^{-1}$), Pb ($85.34 \mu\text{g L}^{-1}$), and Mn ($50.03 \mu\text{g L}^{-1}$) were released into fresh water after 20 d of fresh water-rock- scCO_2 interaction. The concentrations of Cd, Pb, and

Fig. 2. Total concentrations (mg L^{-1} solution) of dissolved trace elements desorbed from sandstone while reacting with synthetic saline water with or without CO_2 as a function of reaction time (days). Time represents the time CO_2 was injected into the reaction system.

Mn were greater (2-fold for Cd, 7-fold for Pb, and 1.7-fold for Mn) in the presence of salinity than they were in the absence of salinity (Table 2), which indicates that salinity may promote the dissolution of Cd, Pb, and Mn after 20 d of saline water-rock-sc CO_2 interaction. Similar to the distribution trend of dissolved trace elements released from sandstone when reacted with or without CO_2 -saturated natural brine as a function of reaction time in the work by Karamalidis *et al.* (2012) and Lu *et al.* (2012), the trace element dissolution experiments in this research revealed that Cd was insignificantly released from sandstone into the saline formation water ($< 0.14 \mu\text{g L}^{-1}$) (Fig. 2) in the absence of sc CO_2 , but it was obviously released into the water ($63.4 \mu\text{g L}^{-1}$) after 20 d of saline water-rock-sc CO_2 interaction and then insignificantly released into the water ($< 0.14 \mu\text{g L}^{-1}$) after 40, 60, and 80 d of reactions. Similarly, Pb was insignificantly released into the water ($< 1.25 \mu\text{g L}^{-1}$) (Fig. 2) in the absence of sc CO_2 but was released significantly into the water ($626.8 \mu\text{g L}^{-1}$) after 20 d of reaction and then insignificantly released into the water ($< 3.32 \mu\text{g L}^{-1}$) after 40, 60, and 80 d of reactions. Mn was released more from the sandstone into the water ($200.8\text{--}392.6 \mu\text{g L}^{-1}$) (Fig. 2) in the absence of sc CO_2 than it was in the presence of sc CO_2 after 20, 40, 60, and 80 d of reactions with released concentrations of 85.9, 48.1, 29.2, and $112.5 \mu\text{g L}^{-1}$, respectively. These results are consistent with a similar

distribution trend in the work by Karamalidis *et al.* (2012) and Lu *et al.* (2012) under similar experimental conditions of high pressure (30 MPa) and elevated temperature (120°C) in the presence of sc CO_2 in this research in contrast to experimental conditions of 34.4 MPa and 120°C in their studies.

The correlation analysis revealed that the salinity in the saline formation water was not significantly correlated with V, Cr, Mn, Co, Ni, Cu, Zn, Sr, and Ba, but was significantly correlated with Fe ($r = 0.734^*$, $p < 0.05$, $n = 9$) and closely correlated with Cd ($r = 0.987^{**}$, $p < 0.01$, $n = 9$) and Pb ($r = 0.978^{**}$, $p < 0.01$, $n = 9$). Iron sulfides could be the source of As in an aquifer (Zheng *et al.*, 2009). Cd and Pb in the saline formation water after the saline water-rock-sc CO_2 interactions were closely correlated ($r = 1.0^{**}$, $p < 0.01$, $n = 4$) and exceeded the national primary drinking standards.

Salinity promoted Cd, Pb, and Mn mobilization, and the concentrations of Cd, Pb, and Mn in the water rapidly declined below the detection limit as the interaction time was extended to a period longer than 40 d. However, the concentrations of As, Cr, Cu, Ba, Fe, and Zn in the water were all lower than their respective national primary and secondary drinking standards for the studied periods. Sandstone contains clay minerals such as illite-montmorillonite, clinochlore, and muscovite, which will adsorb both heavy and trace metals. CO_2 that could be

Table 2. Total concentrations of dissolved trace elements desorbed from sandstone while reacting with or without synthetic saline water (26.3‰ NaCl solution) in the presence or absence of scCO₂.

	Cd (μg L ⁻¹ solution)		Pb (μg L ⁻¹ solution)		Mn (μg L ⁻¹ solution)	
	With saline water	Without saline water	With saline water	Without saline water	With saline water	Without saline water
Immerse for 10 d	0.14 ± 0.13	0.41 ± 0.10	1.25 ± 0.09	0.29 ± 0.04	226 ± 4.84	202 ± 6.05
Immerse for 20 d	ND	0.30 ± 0.16	0.19 ± 0.04	0.83 ± 0.08	201 ± 4.08	284 ± 4.67
Immerse for 30 d	0.14 ± 0.02	0.32 ± 0.12	0.12 ± 0.05	1.89 ± 0.12	393 ± 28.20	18.2 ± 1.07
Immerse for 40 d	ND	0.28 ± 0.18	0.97 ± 0.02	1.49 ± 0.04	75.6 ± 1.87	92.1 ± 1.89
Immerse for 40 d and react with scCO ₂ for 20 d	63.4 ± 1.13	32.2 ± 1.23	627 ± 14.62	85.3 ± 0.85	85.9 ± 2.23	50.0 ± 1.03
Immerse for 40 d and react with scCO ₂ for 40 d	0.13 ± 0.13	0.23 ± 0.11	3.32 ± 0.22	0.68 ± 0.03	48.1 ± 0.79	8.18 ± 0.18
Immerse for 40 d and react with scCO ₂ for 60 d	0.10 ± 0.08	0.09 ± 0.05	0.24 ± 0.09	1.05 ± 0.10	29.9 ± 1.64	3.28 ± 0.44
Immerse for 40 d and react with scCO ₂ for 80 d	ND	ND	0.09 ± 0.06	2.24 ± 0.05	113 ± 3.81	67.7 ± 2.02

ND: nondetectable.

dissolved remains in formation water as CO₂ (aq) and subsequently hydrates to form either carbonic acid or bicarbonate, resulting in a rapid decrease in pH. The rapid release of trace metals (Cd, Pb, and Mn) after reaction with supercritical CO₂ can be attributed to pH-driven desorption from the mineral surfaces (Kampman *et al.*, 2014). As the reaction was prolonged to more than 20 d, the calcium concentration in the solution reflecting the alkalinity increased rapidly, as shown in Fig. 1. CO₂ acidification has been shown to depend on the degree of alkalinity, which can buffer pH changes by limiting carbonic acid dissociation (Horner *et al.*, 2015). Frye *et al.* (2012) investigated the aragonite effect on cadmium desorption during CO₂ leakage and observed that the existence of aragonite can mitigate the effect of pH reduction and result in zero desorption. Therefore, Cd, Pb, and Mn elements may be subsequently removed from solution as the pH rises or by re-adsorption by clay minerals and iron oxides. These observations suggest that a supercritical CO₂-sandstone interaction for a long period of time will immobilize trace metals previously mobilized by supercritical CO₂ (Frye *et al.*, 2012). By comparison, in terms of the pH of sandstone dissolved in NaCl solution and that of deionized water (fresh water) (Fig. 3), the pH values are lower in the presence of salinity than in the absence of salinity before CO₂ injection. However, the pH values increase more significantly in the presence of salinity after CO₂ injection, suggesting an increase in water alkalinity due to aragonite dissolution from sandstone after the supercritical CO₂-sandstone interaction.

Effect of Supercritical CO₂ on the Mineral Composition of Reacted Sandstone

The mineral composition of the reacted sandstone after 20–80 d of rock-water-scCO₂ interaction as identified using XRD was mainly quartz, microcline, albite, illite-montmorillonite, clinochlore, muscovite, aragonite, etc. (< 5% of the mineral content was not detected) without the

Fig. 3. pH variations with a function of reaction time (days) while sandstone reacted with or without synthetic saline water in the presence or absence of CO₂. Time represents the time CO₂ was injected into the reaction system.

formation of any new mineral phase (Fig. 4). The XRD results showed that no significant XRD differences in the mineral composition of the samples were found in the presence or absence of the NaCl solution. Aragonite was observed for the reacted sandstone after scCO₂ interaction. Fig. 5 shows the SEM microstructures of the sandstone before the supercritical CO₂ reaction. Tables 3 and 4 show the EDS results for the points shown in Fig. 5. It can be seen that the mineral phases of the sandstone before the supercritical CO₂ reaction based on the SEM/EDS are coarse clear-surface quartz grains (C in Fig. 5(a) and A and B in Fig. 5(b)), flaky silicate minerals (A, B, and D in Fig. 5(a) and D in Fig. 5(b)), and nanosized iron sulfide (C in Fig. 5(b)). Fig. 6 and Table 5 show the SEM microstructure

and EDS results for the sandstone immersion in a 26.3% NaCl solution for 40 d followed by the reaction with supercritical CO₂ for 80 d. Note that no clear-surface quartz grains were found, but sodium chloride (C in Fig. 6) and secondary silicate mineral (A, B, and D in Fig. 6) seemed to have formed over the quartz surface. A significant CO₂ drying-out effect and NaCl crystal precipitate in the system was observed (Kaszuba *et al.*, 2005; Rathnaweera *et al.*, 2016), which indicated that silica concentrations and dissolution rates are enhanced with pH increases after mixed fluid reactions between scCO₂ and NaCl brine. Fig. 7 and Table 6 show the SEM microstructure and EDS results for the sandstone immersion in distilled water (fresh water) for 40 d followed by reaction with supercritical CO₂ for

Fig. 4. XRD patterns of the sandstone after 20–80 d of interaction with saline water-rock-scCO₂ (Y-6: Y6 sandstone; N-1: immersed for 10 d; N-2: immersed for 20 d; N-3: immersed for 30 d; N-4: immersed for 40 d; N-5: immersed for 40 d and reacted with scCO₂ for 20 d; N-6: immersed for 40 d and reacted with scCO₂ for 40 d; N-7: immersed for 40 d and reacted with scCO₂ for 60 d; and N-8: immersed for 40 d and reacted with scCO₂ for 80 d).

Fig. 5. SEM/EDS results for the surface of the sandstone before the reaction.

Table 3. EDS results for points A–D in Fig. 5(a).

Atom%	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe
A	17.67	2.88	1.76	6.82	41.90	0.93	0.16	0.76	0.09	27.05
B	56.09	0.5	6.89	11.98	13.35	0.08	0.09	0.26	0	10.76
C	43.87	0.12	0.47	2.08	52.54	0.1	0.18	0.19	0	0.45
D	48.89	0.34	4.39	9.3	28.5	0.36	0	0.19	0.2	7.83

Table 4. EDS results for points A–D in Fig. 5(b)

Atom%	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe
A	39.74	0.48	0	0.47	58.68	0.29	0.17	0	0.11	0.06
B	39.49	0	0.03	0.94	58.83	0	0.11	0.12	0	0.48
C	26.79	0	0	0.13	17.58	36.27	0.18	0.04	0.1	18.9
D	52.34	0	2.48	6.46	36.66	0.39	0	0.4	0.05	1.22

Fig. 6. SEM/EDS results for the sandstone immersion in a 26.3% NaCl solution for 40 d followed by reaction with supercritical CO₂ for 80 d.**Table 5.** EDS results for points A–D in Fig. 6

Atom%	O	Na	Mg	Al	Si	S	Cl	K	Ca	Fe
A	49.96	0.75	1.15	4.61	40.74	0.23	0.08	0.53	0.29	1.64
B	54.72	1.60	0.15	6.64	30.18	0	0.58	5.74	0.06	0.33
C	37.9	19.78	0.04	3.90	14.41	0.23	20.37	3.09	0.04	0.23
D	55.99	0.36	0.16	3.73	33.66	0	0.7	4.99	0.07	0.36

Fig. 7. SEM/EDS results for the sandstone immersion in distilled water (fresh water) for 40 d followed by reaction with supercritical CO₂ for 40 d.

40 d. Quartz grain (B in Fig. 7) and iron oxides (A, C, and D in Fig. 7) were found over the quartz grain surface. Lu *et al.* (2014) also reported that secondary iron oxyhydroxides derived from the oxidation of iron sulfides will precipitate on mineral surfaces. It is well known that clay and iron oxides are the important adsorbents for heavy metal elements (Lee *et al.*, 2011; Shi *et al.*, 2013; Noerpel *et al.*, 2016). The secondary silicate minerals and iron oxides formed by the interaction of supercritical CO₂ and sandstone for long periods can adsorb and immobilize trace metals such as Cd, Pb, and Mn (Frye *et al.*, 2012).

CONCLUSION

While the major cations and trace elements in a CO₂ storage layer can be dissolved and released into formation water as a result of water-rock- supercritical CO₂ interaction, salinity can enhance the dissolution of major cations and trace elements after CO₂ is injected into a CO₂ storage layer containing saline water. Greater amounts of Cd, Pb, and Mn can be released (in concentrations that are 2-fold, 7-fold, and 1.7-fold higher, respectively) in the presence of salinity vs. in its absence, suggesting that salinity can enhance the dissolution of these elements after saline water-rock-scCO₂ interaction. If the released toxic trace elements are not adsorbed by secondary silicate minerals or iron oxides, they may migrate upward and thus contaminate shallow aquifers, resulting in a health risk to residents. To secure safe drinking water, the released trace elements from a CO₂ storage layer should be contained by an impermeable clay-rich caprock that prevents upward migration. Trace metals (Cd, Pb, and Mn) adsorbed onto the mineral surfaces of rocks may be rapidly released after reacting with supercritical CO₂ due to low pH-driven desorption. After a long period of supercritical CO₂-sandstone interaction, the trace metals previously mobilized can be immobilized again by an increase in alkalinity due to aragonite dissolution.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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