GEOCHEMICAL INVESTIGATIONS OF CO_2-BRINE-ROCK INTERACTIONS OF THE KNOX GROUP IN THE ILLINOIS BASIN

Topical Report

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An Evaluation of the Carbon Sequestration Potential of the Cambro-Ordovician
Strata of the Illinois and Michigan Basins

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ABSTRACT

Increased output of greenhouse gases, particularly carbon dioxide (CO_2), into the atmosphere from anthropogenic sources is of great concern. A potential technology to reduce CO_2 emissions is geologic carbon sequestration. This technology is currently being evaluated in the United States and throughout the world. The geology of the Illinois Basin exhibits outstanding potential as a carbon sequestration target, as demonstrated by the ongoing Illinois Basin – Decatur Project that is using the Mt. Simon Sandstone reservoir and Eau Claire Shale seal system to store and contain 1 million tonnes of CO_2. The Knox Group-Maquoketa Shale reservoir and seal system, located stratigraphically above the Mt. Simon Sandstone-Eau Claire Shale reservoir and seal system, has little economic value as a resource for fossil fuels or as a potable water source, making it ideal as a potential carbon sequestration target. In order for a reservoir-seal system to be effective, it must be able to contain the injected CO_2 without the potential for the release of harmful contaminants liberated by the reaction between CO_2-formation fluids and reservoir and seal rocks.

This study examines portions of the Knox Group (Potosi Dolomite, Gunter Sandstone, New Richmond Sandstone) and St. Peter Sandstone, and Maquoketa Shale from various locations around the Illinois Basin. A total of 14 rock and fluid samples were exposed to simulated sequestration conditions (9101–9860 kPa [1320–1430 psi] and 32°–42°C [90°–108°F]) for varying amounts of time (6 hours to 4 months). Knox Group reservoir rocks exhibited dissolution of dolomite in the presence of CO_2 as indicated by petrographic examination, X-ray diffraction analysis, and fluid chemistry analysis. These reactions equilibrated rapidly, and geochemical modeling confirmed that these reactions reached equilibrium within the time frames of the experiments. Pre-reaction sample mineralogy and post-reaction fluid geochemistry from this study suggests only limited potential for the release of United States Environmental Protection Agency regulated inorganic contaminants into potable water sources.

Short-term core flood experiments further verify that the carbonate reactions occurring in Knox Group reservoir samples reach equilibrium rapidly. The core flood experiments also lend insight to pressure changes that may occur during CO_2 injection. The Maquoketa Shale experiments reveal that this rock is initially chemically reactive when in contact with CO_2 and brine. However, due to the conservative nature of silicate and clay reaction kinetics and the rapid equilibration of carbonate reactions that occur in the shale, these reactions would not present a significant risk to the competency of the shale as an effective seal rock.

EXECUTIVE SUMMARY

Interest in carbon capture and storage of carbon dioxide (CO_2) within deep saline reservoirs has steadily increased throughout the United States with the recent developments in shale gas and with the country's efforts to mitigate the release of anthropogenic CO_2. Portions of the Knox Group (Potosi Dolomite, Gunter Sandstone, and New Richmond Sandstone), St. Peter Sandstone, and Maquoketa Shale have been assessed for carbon sequestration potential as part of a regional study of the Illinois and Michigan Basins.

A total of 12 laboratory experiments were completed to identify the reaction mechanisms, kinetics, and solid-phase products that are likely to occur in the Knox Dolomite and the Maquoketa Shale when exposed to supercritical CO_2. Samples were obtained from the Illinois Basin – Decatur Project (IBDP), outcrops and cores from within the Illinois Basin, and laboratory produced synthetic and reservoir brines. Nine high-pressure, high-temperature batch reactor experiments were conducted using Potosi Dolomite (southwest Missouri outcrop), Gunter and New Richmond Sandstone (Morgan Co, IL), and Maquoketa Shale (IBDP site). Additionally, five core flood experiments were conducted using Potosi Dolomite (IBDP site), Gunter (Blan well, Hancock Co., KY) and St. Peter (Marion Co., IL) Sandstones, using either laboratory produced synthetic brine or deionized water (DI).

A variety of analytical techniques were used to characterize the physical, geochemical, and mineralogical changes between the pre- and post-reaction products from the batch reactor and core flood experiments. These included standard petrography, scanning electron microcopy (SEM), X-ray diffraction, ion chromatography, and inductively coupled plasma analyses. Results were used to compare pre- and post-reaction petrographic and geochemical conditions, as well as kinetic and equilibrium predictions from numerical geochemical modeling.

Results from the Knox Group reservoir experiments show the dissolution of dolomite, the dominant mineral present throughout the Knox Group, while in the presence of supercritical CO_2 and brine as expected. SEM analysis of the Potosi Dolomite batch reactor experiments revealed pitting and degradation of dolomite crystals that appeared pristine and unaltered in pre-reaction samples. Post-reaction brines from the Potosi Dolomite, Gunter and New Richmond Sandstone experiments all contained elevated concentrations of calcium, magnesium, strontium, and barium greater than in the non-reacted brines. These elevated concentrations indicate that carbonate minerals such as dolomite dissolved during the experiments. There is no evidence for the formation of measureable amount of new solid-phase products during the duration (1 to 4 months) of the batch reactor studies using the Knox Group reservoir rock; however, very small amounts of solid phase material produced during the experiments were observed, but could not be identified or quantified by the techniques used in this study.

Post-reaction brine chemistry results for all experiments were compared to United States Environmental Protection Agency (USEPA) drinking water standards for the regulated analytes As, Ba, Be, Cd, Cr, Cu, Pb, Se, and Tl (where applicable, F and NO_3 were compared as well) to provide context for the results of this project. However, in some cases the results of the analytes As, Be, Cd, Pb, Se and Tl were inconclusive because analytical MDLs were up to 150 times greater than the USEPA minimum contaminant levels (MCLs). The results of the Potosi Dolomite, New Richmond and Gunter Sandstone, and Maquoketa Shale batch experiments indicated that the concentrations of the analytes of concern were generally less than the USEPA minimum MCLs. Core flood experiments performed on the suggest the potential release of the

USEPA regulated analytes Ba, Cu and Cd in the Potosi Dolomite and As, Ba, Cd, and Se in the St. Peter Sandstone.

Speciation calculations based on the post-reaction brine composition during the Potosi Dolomite experiment indicate that the system reached equilibrium before the end of the 4 month experimental duration. As a result, five short-term (approximately 6 hour) core flood experiments were performed. Interpretation of post-reaction brine chemistry and equilibrium modeling of these short-term experiments indicate that the systems still reacted quickly enough to reach equilibrium with respect to carbonates. Geochemical modeling and optimization estimated reaction rate parameters for some potential reactions that could occur in the Knox Group. The observed and modeled rapid reactions suggest that larger scale models simulating CO_2 sequestration reactive transport for the Knox Group do not need kinetic constraints for carbonates to create an accurate understanding of reservoir processes.

The Maquoketa Shale (primary seal) batch reactor experiments indicated that feldspars, clays, carbonates and sulfide minerals dissolved as suggested by elevated concentrations of aluminum, barium, calcium, potassium, magnesium, sulfur, silicon, and strontium in the post-reaction brines. Using rate parameters derived from pre-reaction mineralogy and post-reaction fluid geochemistry, a model estimating the expected mineral reactions after 10 years indicates that alteration of k-feldspar to kaolinite and quartz dominate the changes in silicate mineralogy. These alterations contribute little to changes in porosity and therefore would not be expected to have a significant impact on seal integrity. Carbonate minerals were 48.2% of the initial volume in samples used in the experiments, and the modeled dissolution of these minerals could at most lead to a 2.2% decrease in mineral volume. However, in an actual sequestration scenario, the lower water-to-mineral ratio would limit the carbonate dissolution further.

In summary, project results indicate that the Knox Group-CO_2-brine system could be initially chemically reactive in a CO_2 sequestration scenario. The effect of this reactivity would likely reach equilibrium shortly after injection of CO_2 into the reservoir had stopped. According to IBDP site geophysical logs, the Maquoketa Shale is approximately 61 m (200 ft) thick in the central Illinois Basin, and a secondary (New Albany Shale) seal is 40 m (130 ft) thick. Thus, even if significant mineral dissolution occurred in the caprock, it would be highly unlikely that caprock integrity would be in jeopardy given the rapid equilibration of the Knox-CO_2-brine system.

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INTRODUCTION AND BACKGROUND

Considerable interest in deep reservoir injection, storage, and waste disposal has steadily increased throughout the United States with the recent shale gas boom and with the country's efforts to curb the release of man-made greenhouse gas through efforts such as carbon capture and storage (CCS). The Illinois Basin Cambrian-age Knox Group reservoirs have little economic interest with respect to oil and gas, but may have great potential as a storage reservoir for carbon dioxide (CO_2). This study examines laboratory simulated geochemical interactions between reservoir and seal rock, fluid, and CO_2 of the Knox Group rocks from various locations within the Illinois Basin. This report provides an understanding of the potential interactions of the Knox Group-Maquoketa Shale seal system and its efficacy as a CO_2 sequestration target.

Portions of the Knox Group (Potosi Dolomite, Gunter Sandstone, Shakopee Dolomite, New Richmond Sandstone, and Maquoketa Shale) are being assessed for CO_2 sequestration potential as part of a regional study of the Illinois and Michigan Basins. The Illinois State Geological Survey (ISGS) is involved in a related project, the Illinois Basin – Decatur Project (IBDP) (Finley et al. 2013; Finley et al., 2011), a large-scale carbon capture and storage project in Decatur, Illinois, USA, which allowed access to well core and fluid sampling for our study.

A series of experiments using samples obtained from the IBDP site (rock and brine), other rock samples from within the Illinois Basin (outcrop and core), and laboratory produced synthetic and reservoir brines were developed to identify the reaction mechanisms, kinetics, and solid-phase products that are likely to occur in the Knox Dolomite and the Maquoketa Shale when exposed to supercritical CO_2. A total of 12 high-pressure, high-temperature batch reactor experiments were conducted using Potosi Dolomite (southwest Missouri outcrop), Gunter and New Richmond Sandstone (Morgan Co, IL), and Maquoketa Shale (IBDP site). In addition to batch experiments five core flood experiments were conducted using Potosi Dolomite (IBDP site), Gunter (Kentucky Blan well, Hancock Co.) and St. Peter (Marion Co., IL) Sandstones. The core flood experiments used either laboratory produced synthetic brine or deionized water (DI).

PROCEDURES

Sample Selection

To obtain a good representation of possible geochemical scenarios, chosen samples exhibited a range of Illinois Basin locations, textures, and composition. Outcrop and core samples of the Knox units, including Potosi Dolomite, Gunter Sandstone, New Richmond Sandstone, St. Peter Sandstone, and Maquoketa Shale, were collected by ISGS staff from the Potosi, Washington Co., Missouri area; IBDP Verification well core no. 1 (VW1); IBDP Verification well core no. 2 (VW2); Morgan County, IL C-13678 well core; IBDP Geophysical Monitoring well core no. 2 (GM2); and Marion County, IL C-4831 well core. Additionally, one core segment (Gunter Sandstone) from the Hancock County, KY, Blan well was received from project partners at the Kentucky State Geological Survey (KGS). Outcrop samples were plugged using a 6.4 cm (2.5 in.) bit to produce plugs approximately 8 to 10 cm (3 to 4 in.) in length. For core samples, intervals that show obvious facies changes (color, grain size, bed forms, etc.) were also plugged using the 6.4 cm (2.5 in.) diameter bit. Plugs were drilled parallel to bedding for both core and outcrop samples. Each plug was then cut into three roughly 20 g sections. One section was used for pre-experimental analysis, another for the reaction vessel experiments, and the other(s) were reserved to allow for multiple experiments to be performed, if needed.

Brine Selection

Existing Knox Group brine compositional data is very limited within the Illinois Basin, and when available only provides concentration data for a few analytes. A search of historical Illinois Basin brine literature yielded concentration data for the analytes Ca, Cl, Mg, and Na for the Shakopee Dolomite formation waters (Meents, 1952). This brine composition was chosen for the reaction vessel experiments because it is the only data available for the Knox Group waters collected from a depth comparable to where the majority of the samples used for the experiments were collected. The synthetic Shakopee brine was reproduced in the laboratory by dissolving the reagent grade salts NaCl, $CaCl_2 \cdot 2H_2O$, and $MgCl_2 \cdot 6H_2O$ into DI at standard laboratory conditions (1 atm at 25°C; Table 1). Later in the project, one brine from IBDP Zone 11, the Ironton-Galesville Sandstone (Knox Group) collected at a depth of 1500 m (4920 ft), became available and was used for a second set of experiments and contained B, Ba, Br, Ca, Cl, Fe, K, Li, Mg, Mn, Ni, Pb, S, Se, Si, Tl, and Zn (Table 1).

Batch Reactor Experiments

A total of nine batch reactor experiments were conducted using well core and outcrop samples collected from the Potosi Dolomite, Gunter and New Richmond Sandstones, and the Maquoketa Shale (Table 2). Three different fluids were used in these experiments: the synthetic Shakopee brine, the Ironton-Galesville reservoir brine, and DI water. To evaluate changes in only mineral dissolution in the reactor experiments, DI was chosen for some of the experiments to assure that post-reaction changes in fluid chemistry could be attributed to mineral dissolution rather than changes occurring as a result of constituents in the brine interacting with CO_2 .

The batch reactors selected for the project are Parr Series 4605 500 ml capacity non-stirred high pressure vessels with a maximum working pressure of 34475 kPa (5000 psi) and temperature of 350°C (662°F). Several preliminary experiments were performed in order to develop the final experimental design and assess the method for effectiveness in maintaining formation conditions. Several modifications were made to the reactors in order to meet the specific needs of the experiment. The first modification was the addition of a second valve to act as an outlet to prevent contamination of the inlet between experiments. A ball valve was chosen to allow for slow degassing of CO_2 at the completion of the experiment; degassing the vessels too quickly produced dry ice and clogged the outlet valve. The second modification to the vessels was the addition of quick-connect adaptors on the inlet valves for safer vessel charging at the high pressures required for the experiments. These modifications were made by ISGS staff using Parr specifications. The third modification was the addition of Teflon liners to the inside of the pressure vessels to prevent reaction between the stainless steel material of the vessels and the highly corrosive brine.

Table 1. Measured compositions of synthetic Shakopee brine and Ironton-Galesville formation brine. MDL = method detection limit. Concentrations are in mg/L.

Analyte	MDL	Synthetic Shakopee	Ironton-Galesville
Br	0.11	<0.11	191
Cl	0.04	1876	38643
F	0.03	<0.03	<0.03
NO_3-N	0.07	<0.07	<0.07
SO_4	0.13	<0.13	1246
Al	0.37	<0.37	<0.37
As	1.1	<1.1	<1.1
B	0.23	<0.23	8.0
Ba	0.0085	<0.0085	0.2465
Be	0.0055	<0.0055	<0.0055
Ca	0.29	119	5081
Cd	0.12	<0.12	0.02
Co	0.13	<0.13	<0.13
Cr	0.058	<0.058	0.018
Cu	0.20	<0.2	<0.2
Fe	0.24	<0.24	27.2
K	0.16	<0.16	472
Li	1.1	<1.1	8.5
Mg	0.27	57.0	935
Mn	0.015	<0.015	1.719
Mo	0.22	<0.22	<0.22
Na	0.26	974	15818
Ni	0.43	<0.43	<0.43
P	0.73	<0.73	<0.73
Pb	0.41	<0.41	<0.41
S	2.2	<2.2	427
Sb	1.5	<0.59	<0.59
Se	1.3	<1.3	<1.3
Si	1.7	<0.66	9.2
Sn	0.86	<0.86	<0.86
Sr	0.0037	<0.0037	124.9665
Ti	0.0056	<0.0056	<0.0056
Tl	0.43	<0.43	<0.43
V	0.47	<0.47	<0.47
Zn	0.097	<0.097	<0.097

An approximately 20 g portion of sample was placed into the pressure vessel. Each vessel was filled with 200 ml of synthetic or reservoir brine to make an approximately 1:10 solid-to-liquid ratio. This ratio was used to allow for enough fluid to be available to produce detectable levels of mineral dissolution and precipitation, provide a system that would not equilibrate too rapidly, and provide sufficient liquid sample to measure pH, alkalinity, and dissolved constituent concentrations. After assembly, each vessel was filled with CO_2, brought to near-reservoir pressure conditions using a displacement pump and placed in an air bath at reservoir temperature (Table 2). These conditions were based on downhole temperature and pressure measurements at the IBDP injection well (CCS1). The pressure conditions within the experimental vessels typically stabilized within 12 to 24 hours while they were brought up to experimental temperature. Once stabilization occurred, the vessels were left to react for the prescribed experimental duration and were regularly monitored for leaks and other malfunctions. Upon completion of the experiments, pressure vessels were slowly degassed at the experimental temperature to prevent formation of dry ice. When degassing was complete, vessels were opened and a subsample of the brine was immediately measured for pH and redox (Eh) for 10 minutes while maintaining the experimental temperature. Although not representative of experimental conditions because they were measured after degassing, the pH values serve as a rough reference point. The brine was then filtered through a 0.45-µm methylcellulose ester (MCE) membrane and preserved according to EPA-600/4-79-020. The rock sample was dried at room temperature in a glass laboratory desiccator until the samples mass stabilized, indicating that all moisture measurable to approximately 0.0001 g had dissipated. Some rock samples were stored temporarily (typically for less than 1 week) within the desiccator until preparation for petrographic and mineralogical analyses.

Table 2. Summary of batch reactor experiments using reservoir rock and synthetic and reservoir brines.

Experiment Name	Sample IDs	Duration	Pressure (PSI)	Temperature (C°)
DOE-K-2 (Synthetic Shakopee Brine)	MO-1-9 (Potosi Dolomite)	4 month	1430	43
	C-13687-2485.2' (Gunter Sandstone)	4 month	1430	43
	C-13678-2533.9' (New Richmond Sandstone)	1 month	1430	43
	Control	4 month	1430	43
DOE-K-3 (Ironton-Galesville Reservoir Brine)	IBDP-VW1-4522.3'(Potosi Dolomite)	1 month	1430	43
	IBDP-VW1-4533.5' (Potosi Dolomite)	1 month	1430	43
	IBDP-VW1-4536.5'(Potosi Dolomite)	1 month	1430	43
	Control	1 month	1430	43
DI H_2O	IBDP-GM2-2518.2' (Maquoketa Shale)	24 hour	1320	32
	IBDP-GM2-2518.3' (Maquoketa Shale)	38 hour	1320	32
	IBDP-GM2-2518.4' (Maquoketa Shale)	43 hour	1320	32
	Control	43 hour	1320	32

Core Flood Experiments

In addition to batch experiments, five core flood experiments were conducted using samples from the Potosi Dolomite, Gunter and St. Peter Sandstones. These samples were chosen for these experiments because the batch reactor tests showed the minerals reacted quickly and would be suitable for core flood testing. While these tests are for shorter times than the batch reactor experiments, they provided the opportunity for collection of multiple fluid samples throughout the experiment to look at changes in concentration with time.

For each of the core flood experiments, the core holder and cylinders containing the fluid (either DI water or synthetic brine; Table 3) and CO_2 were in an airbath at reservoir temperature for at least 24 hours before the experiment began. Three centimeter (1-inch) diameter core plugs with a length of approximately 3.18 cm (1.25 in.) were placed into a Hassler-type core holder and a confining pressure of approximately 20685 kPa (3000 psi) was applied. A vacuum removed the air from the core holder and inlet and outlet tubing. After evacuation, the core was flooded with water and a reference pressure was applied to the back pressure regulator, followed by injection of more water until flow was apparent at the outlet. A data logger recorded pressures measured by silicon on sapphire pressure transmitters that have an accuracy of ±0.25% full scale (FS) on either end of the core throughout each experiment. A 41370 kPa (6000 psi) FS pressure transmitter was used at the core inlet and a 20685 kPa (3000 psi) FS transmitter was used on the outlet side. Isco 500D syringe pumps controlled the rate of water and CO_2 flow from piston cylinders during the experiments by injecting mineral oil into one end of the cylinder and forcing a piston to move in the cylinder, thereby displacing either water or CO_2 on the other side of the piston into the core.

The Potosi samples were chosen from depths (Table 3) where the Potosi Dolomite was vuggy and sucrosic in texture, so the samples would have sufficient permeability for fluid flow without an exceedingly high pressure differential (<3448 kPa [500 psi]). For the first two experiments on Potosi Dolomite samples, the synthetic Shakopee brine was injected at a rate of 1 ml/min for 60 minutes followed by 60 minutes of CO_2 injection at 1 ml/min. After the CO_2 injection, brine was injected for 3 more hours at a rate of 1 ml/min for the first experiment and 0.5 ml/min for the second experiment. Samples of effluent were collected every 60 ml and preserved for cation analysis. In the third Potosi Dolomite experiment, the core was flooded with DI water followed by the injection of 1.0 ml/min DI water for 30 minutes and then 1.0 ml/min of DI water and 0.163 ml/min of CO_2 for 2 hours. This ratio of CO_2 to DI water was chosen to put the water at its saturation point for CO_2 at this temperature and pressure condition, and DI water was chosen as the liquid to maximize rock dissolution. A fraction collector with tubes rotating every 5 minutes collected the effluent. The effluent from each set of four sequential tubes were combined and preserved with ultra-pure nitric acid for cation analysis.

The experiments on St. Peter and Gunter Sandstones followed a procedure similar to the third Potosi Dolomite experiment. The plugs were initially flooded with DI and then had 1.0 ml/min DI water injected through them for 30 minutes. For these experiments, DI water was chosen to maximize rock dissolution and reduce analytical interferences caused by the high ionic strength of the synthetic brine when measuring small changes in analyte concentrations. After the initial flood with DI water, there was a second 3 hour injection period using 1.0 ml/min of DI water and 0.102 ml/min of CO_2—the ratio needed for complete CO_2 saturation of the water. A fraction collector rotating tubes every 8 minutes collected the effluent. Sequential samples were combined to create 32 ml samples that were preserved for cation analysis.

Table 3. Summary of core flood experiments using reservoir rock and synthetic and reservoir brines.

Experiment Name Sample IDs	(Depths in feet)	Confining Pressure (PSI)	Temperature (C°)	Fluid
FT-1:Potosi Dolomite IBDP VW2	4524.7’	3000	38	Synthetic Shakopee Brine
FT-2:Potosi Dolomite IBDP VW2	4524.4’	3000	38	Synthetic Shakopee Brine
FT-3:Potosi Dolomite IBDP VW2	4550.1’	3000	40	DI
FT-4:Gunter Sandstone Kentucky Blan Well	5107’	3500	32	DI
FT-5:St. Peter Sandstone C-4831-Marion Co., IL	5250.3’	3800	32	DI

Analytical Techniques

A variety of analytical techniques were utilized to determine physical, geochemical, and mineralogical changes for pre- and post-reaction rock and brine samples. Quantitative and qualitative petrographic analyses of rock samples were performed using a Zeiss Axiophot trinocular polarizing microscope equipped with an Olympus DP72 camera at the ISGS Petrography Lab. Images were captured and analyzed using Olympus Stream Image Analysis Software. High-magnification and semi-quantitative morphological and mineralogical analyses were performed at the University of Illinois Fredrick Seitz Materials Research Lab (MRL) using a 30 KV JEOL JSM-6060LV scanning electron microscope coupled with an Oxford Instruments ISIS energy-dispersive X-ray spectroscopy microanalysis system (SEM-EDX). Semi-quantitative mineralogical analyses were performed at the ISGS X-Ray Diffraction (XRD) Lab using random bulk powder mounts and orientated clay mineral slides with a Scintag® XDS2000 Diffractometer. Step-scanned data were collected from 2° to 34° 2θ for clay mineral analysis and 2° to 60° 2θ for bulk mineral analysis with a fixed time of 5 seconds per 0.05° 2θ for each sample. All resulting traces were analyzed using the semi-quantitative data reduction software from Materials Data Inc. (MDI) known as Jade+®.

Pre- and post-reaction brine samples were analyzed for inorganic anions, metals and trace elements utilizing inductively coupled plasma-atomic emission spectrometry (ICP) and ion chromatography (IC). All ICP and some IC analyses were performed at the Illinois State Water Survey (ISWS) using U.S. EPA methods 300 and 200.7. All remaining IC analysis was performed at the ISGS using U.S. EPA method 200.7. MDLs are established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit using calculations and techniques defined in EPA methods 300 and 200.7. Sample pH was measured according to EPA Method 9040C using a Thermo Scientific Orion Ross Sure-Flow pH electrode. Oxidation-Reduction potential was measured and calculated using a Thermo Scientific Orion Ross Sure-Flow Combination Redox/ORP electrode according to APHA (2005). Alkalinity was measured using the Thermo Scientific Orion Ross Sure-Flow pH electrode according to APHA Titration Method 2320 (2005).

Establishment of QA/QC Measures

Control samples consisting of only brine and CO_2 in the vessels were subjected to the same experimental conditions as the brine-rock-CO_2 experimental simulations to determine any potential interactions of the brine to the Parr reaction vessels and changes in brine constituent concentrations due to CO_2 rock interactions. Changes measured in constituent concentrations between the initial brine before exposure to the reaction vessel, CO_2 and experimental temperature and pressure and the control brine were used to compare concentrations in post-reaction fluids. For data analysis purposes, corrections were made to the post-reaction results so that changes in concentration could be clearly identified against possible effects that may be caused by the experimental process. This correction was done by subtracting the analyte concentration measured in the control brine from the analyte concentration measured in the initial and post-reaction brines. In situations where the concentration of an analyte in the control sample was greater than the initial brine concentration, the concentration of the initial brine was used for the correction. Corrected post-reaction brine data were compared to the corrected initial brine data, and elemental concentrations that increased or decreased outside of a prescribed statistical range were determined to be statistically significant. The error range used in this study was plus or minus one standard deviation of concentrations determined by triplicate measurements of the brine of the Ironton-Galesville reservoir brine (Table 4). This correction was performed to batch reaction experiments containing synthetic and reservoir brines, but not with experiments using DI because changes in analyte concentrations were easily identified against DI (near or below MDL) concentrations.

Geochemical Modeling

Batch Reactor Experiments

Geochemical modeling enabled the identification of minerals in the rock samples that might be reacting with the brine and CO_2 in the batch reactors and provided a preliminary estimate of the kinetics of those reactions. Final brine composition was input into a React model (Bethke, 1996) where CO_2 fugacity increased to experimental conditions and the pH was varied to find the conditions where the carbonate minerals were at equilibrium. The model used the Pitzer equations and database (Plummer et al., 1988) to calculate the carbonate equilibrium state and the extended b-dot equations and database (Wolery, 1992) for silicate mineral calculations.

For the three Maquoketa sample batch reactions, one model was created using the average mineralogy from the three samples. The modeling software simulated the reaction of the average mineralogy with DI water and CO_2. The model held the CO_2 at a constant fugacity, which was calculated based on the temperature and pressure used in the experiments (Duan et al., 1996). The equation (Lasaga, 1984)

$$R = \mathrm{s} \times k \times (1 - \tfrac{\mathrm{Q}}{\mathrm{K}})[\mathrm{H}^{+}]^{\mathrm{n}} \qquad \text{Eq.1}$$

governed the reaction rate of each mineral with the water in the model, where s is the mineral surface area, k is the rate parameter, Q is the reaction quotient, K is the equilibrium constant, $[H^+]$ is the activity of hydrogen, and n is a reaction dependent power. The three post-reaction water analyses were treated as a time series from one experiment and optimization software UCODE (Poeter et al., 2005) iteratively altered the parameter k in Eq. 1 to match the water chemistry data.

Table 4. Triplicate analyses of Ironton-Galesville reservoir brine used to establish a ± 1 standard deviation range of variability used in evaluating batch reactor brine data. MDL = method detection limit. Concentrations are in mg/L.

Analyte	MDL	Ironton-Galesville Brine-1	Ironton-Galesville Brine-2	Ironton-Galesville Brine-3	1STDEV
Br	0.11	197	202	203	3
Cl	0.04	40002	39092	38963	566
F	0.03	<MDL	<MDL	<MDL	NA
NO_3	0.07	<MDL	<MDL	<MDL	NA
SO_4	0.13	1236	1288	1319	42
Al	0.37	<MDL	<MDL	<MDL	NA
As	1.1	<MDL	<MDL	<MDL	NA
B	0.23	8.1	8.1	8.3	0.1
Ba	0.0085	0.2321	0.2466	0.2466	0.0084
Be	0.0055	<MDL	<MDL	<MDL	NA
Ca	0.29	4988	5089	5200	105
Cd	0.12	<MDL	<MDL	<MDL	NA
Co	0.13	<MDL	<MDL	<MDL	NA
Cr	0.058	<MDL	<MDL	<MDL	NA
Cu	0.20	<MDL	<MDL	<MDL	NA
Fe	0.24	30.3	30.1	29.8	0.3
K	0.16	434	478	440	23
Li	1.1	8.9	9.1	8.9	0.1
Mg	0.27	956	934	953	12
Mn	0.015	1.7	1.7	1.7	0
Mo	0.22	<MDL	<MDL	<MDL	NA
Na	0.26	15819	15816	15791	15
Ni	0.43	<MDL	<MDL	<MDL	NA
P	0.73	<MDL	<MDL	<MDL	NA
Pb	0.41	<MDL	<MDL	<MDL	NA
S	2.2	443	445	445	1
Sb	1.5	<MDL	<MDL	<MDL	NA
Se	1.3	<MDL	<MDL	<MDL	NA
Si	1.7	9.2	9.1	9.1	0.1
Sn	0.86	<MDL	<MDL	<MDL	NA
Sr	0.0037	121	121	121	0
Ti	0.0056	<MDL	<MDL	<MDL	NA
Tl	0.43	<MDL	<MDL	<MDL	NA
V	0.47	<MDL	<MDL	<MDL	NA
Zn	0.097	0.183	0.192	0.183	0.005

Core Flood Experiments

Geochemical modeling to evaluate the kinetics of reactions taking place in the core flood experiments was limited. No quantitative mineralogic analysis was performed on these samples and therefore the kinetics of mineral dissolution or precipitation could not be determined. We input the water chemistry of the column effluent into a React model and increased the CO_2 concentrations until the model reached the water-CO_2 injection ratio we used in the experiments. These models used the extended b-dot equations and database (Wolery, 1992). The saturation indices of select minerals, mainly SiO_2 polymorphs, for expected reactions were identified to determine if the fluids reached equilibrium with respect to these phases.

RESULTS AND DISCUSSION

Batch Reactor Experiments

Pre-reaction Petrography and XRD analysis

Potosi Dolomite

The Potosi Dolomite outcrop sample chosen for the batch reactor experiments is a dolomite with very low matrix porosity and little to no intercrystalline matrix containing an extensive network of quartz lined vugs (Figure 1). Semi-quantitative bulk mineral analyses by XRD confirm that the composition of sample MO-1-9 is dominated by dolomite (79%), with lesser amounts of quartz (11%), siderite (3%), and pyrite/marcasite (6%). The clay-sized fraction of minerals in MO-1-9 makes up a very small percentage, 1% by volume (Table 5).

Gunter Sandstone

The Morgan Co., IL, Gunter Sandstone sample used in the batch reactor experiments is a micrite with interlaminated fine- to medium-grain quartz sand with a micrite matrix (Figure 2). Quartz grains are fine to medium grain and sub-rounded to well-rounded and the sample shows no porosity. Semi-quantitative bulk mineral analyses by XRD of the Gunter Sandstone confirm sandstone (75% quartz and 4% feldspar) with a micrite matrix (18% dolomite). The clay-sized fraction of minerals makes up 1 % by volume (Table 5).

New Richmond Sandstone

The New Richmond Sandstone sample selected for the batch experiments is a very fine- to medium-grained, poorly to moderately sorted quartz arenite (Figure 3). The quartz grains are well-consolidated with little pore space (<2% porosity, as measured by phase analysis). The small pore throats are typically well cemented by clay minerals and authigenic quartz overgrowths. A semi-quantitative bulk mineral analysis of the New Richmond Sandstone sample by XRD (Table 5) confirms that the composition of the sample is dominated by quartz (63%). Lesser amounts of dolomite (30%) suggest the presence of carbonate cement and small volumes of feldspar (4%) appear to be present, possibly as lithic fragments. The clay-sized fractions of minerals account for 1% of the total bulk volume.

Figure 1. Photomicrograph of Potosi Dolomite sample MO-1-9, a planar subhedral dolomite with very low matrix porosity and little to no intercrystalline matrix. Vugs are lined with chalcedony and quartz druze.

Figure 2. Photomicrograph of Morgan Co., IL, Gunter Sandstone sample C-13687-2485.2’, a micrite (fine gray matrix) with interbedded quartz (larger colorless grains) laminations.

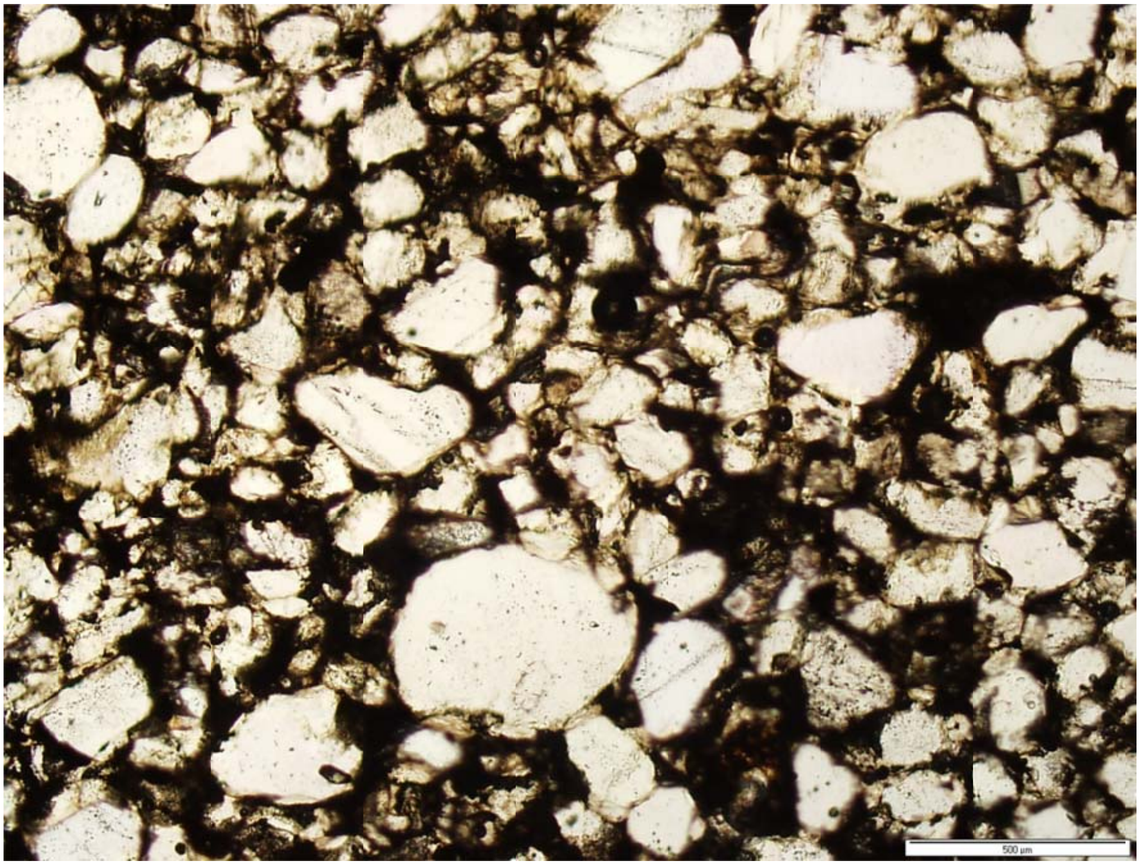

Figure 3. Photomicrograph of Morgan Co., IL, New Richmond Sandstone sample C-13687-2533.9’, an arenite containing quartz (colorless grains) cemented by clay minerals (dark matrix).

IBDP VW1 Potosi Dolomite samples used in the Ironton-Galesville reservoir brine experiments contained tightly interlocking dolomite crystals. There appears to be two types of vugs in these samples: one quartz lined and one dolomite lined. Semi-quantitative bulk mineral analyses by XRD confirm that these samples are dominated by dolomite (71–88%) and quartz (8–26%), with minor percentages of calcite and siderite. Clay minerals account for 1% or less of the bulk mineral composition (Table 6).

Table 5. Summary of the pre- and post-reaction semi-quantitative mineral compositions of samples used in the synthetic Shakopee brine experiments. Bulk mineral data was obtained from random powder mounts while clay mineral data was obtained from orientated clay slides.

Sample	**MO-1-9** **Potosi Dolomite**		**C-13678-2433.9’** **New Richmond Sandstone**		**C-13678-2485.2’** **Gunter Sandstone**	
Bulk Mineralogy						
	Pre	**Post**	**Pre**	**Post**	**Pre**	**Post**
%Clays	1	1	1	0	1	NA*
%Quartz	11	29	63	77	75	NA
%K-spar	0	1	3	3	1	NA
%Plag	0	1	1	1	3	NA
%Calcite	0	1	1	0	1	NA
%Dolomite	79	66	30	18	18	NA
%Siderite	3	1	1	1	0	NA
%Pyr/Mar	6	0	0	1	1	NA
Clay Mineralogy from Orientated Clay Slide (% relative to each other)						
%Illite-smectite	35	42	35	41	38	NA
%Illite	50	45	45	41	51	NA
%Kaolinte	3	4	2	8	1	NA
%Chlorite	8	8	18	10	11	NA

*NA: Not applicable. There was not enough Gunter Sandstone remaining after the experiment to run XRD analysis.

Table 6. Summary of the pre- and post-reaction semi-quantitative mineral compositions of samples used in the Ironton-Galesville reservoir brine experiments. Bulk mineral data was obtained from random powder mounts while clay mineral data was obtained from orientated clay slides.

Sample	**VW1-4522.3’** **Potosi Dolomite**		**VW1-4533.5’** **Potosi Dolomite**		**VW1-4536.5’** **Potosi Dolomite**	
Bulk Mineralogy						
	Pre	**Post**	**Pre**	**Post**	**Pre**	**Post**
%Clays	1	0	0	1	0	1
%Quartz	8	3	26	71	8	7
%K-spar	0	0	0	2	1	1
%Plag	0	0	0	1	0	0
%Calcite	1	1	1	1	0	2
%Dolomite	87	93	71	24	88	87
%Siderite	2	1	1	1	1	2
%Pyr/Mar	1	0	0	0	0	1
Clay Mineralogy from Orientated Clay Slide (% relative to each other)						
%Illite-smectite	53	42	58	55	51	40
%Illite	34	34	28	38	38	40
%Kaolinte	6	6	5	3	5	2
%Chlorite	7	17	10	5	5	18

Maquoketa Shale

The Maquoketa Shale samples selected for the batch reactor kinetic experiments are well-consolidated, carbonate-rich shales (Figure 4). Carbonates include abundant silt- to very fine-sized crystals of dolomite and calcite cemented in a clay matrix and make up almost 50% of the sample. Semi-quantitative bulk XRD analysis confirms a high percentage of carbonate minerals (33–45% dolomite and lesser amounts of calcite and siderite) and also detected a large quantity of quartz (25–33%). The samples contain less than 12% clay minerals in addition to minor amounts of feldspars (4–6%; Table 7). No post-reaction XRD was run on the Maquoketa Shale because of equipment problems and time constraints.

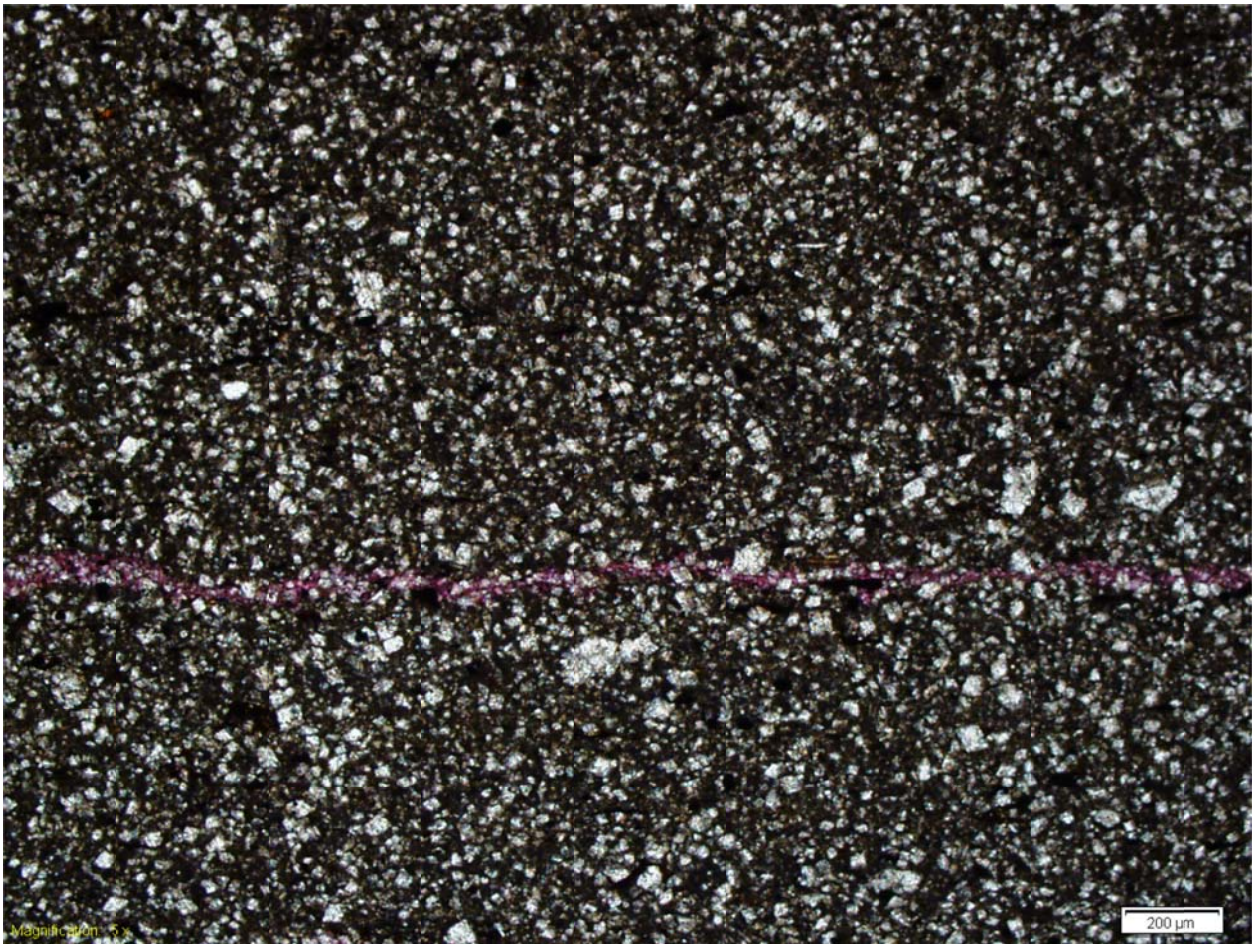

Figure 4. Photomicrograph of Maquoketa Shale sample number IBDP GM2-4522.3’, a well consolidated shale containing quartz (colorless and grey grains), carbonates (colorless, gray, and pastel grains) and clay minerals (dark matrix). The thin horizontal pink line represents mounting epoxy filling a laminar parting most likely produced by sample preparation process.

Table 7. Summary of the pre- and post-reaction semi-quantitative mineral compositions of samples used in the Maquoketa Shale kinetic experiments. Bulk mineral data was obtained from random powder mounts.

Sample	**GM2-2815.2'** **Maquoketa Shale**	**GM2-2815.3'** **Maquoketa Shale**	**GM2-2851.4'** **Maquoketa Shale**
Bulk Mineralogy			
%Clays	12	8	7
%Quartz	33	26	25
%K-spar	6	5	4
%Plag	3	3	3
%Calcite	1	1	1
%Dolomite	33	45	45
%Siderite	8	6	6
%Pyr/Mar	4	7	10

Post-reaction Petrography and XRD Analysis

Carbonate minerals are a highly reactive component in CO_2 sequestration scenarios of the Knox Group mineral assemblage and it would be expected that petrographic evidence of reaction would be clearly evident, as seen in other studies (Bateman et al., 2011). Post-reaction Potosi Dolomite samples from both the synthetic Shakopee brine and Iron-Galesville reservoir brine experiments exhibit no noticeable change along edges and vugs exposed to CO_2-brine solution under polarized-light and cathodoluminescent light microscopy, most likely due to the small reaction volumes. However, scanning electron microscopy (SEM) revealed evidence of dissolution along the edges of dolomite crystals in some areas; the pristine dolomite rhombohedra of the pre-reaction samples appeared pitted and jagged along crystal faces in the post-reaction samples (Figure 5).

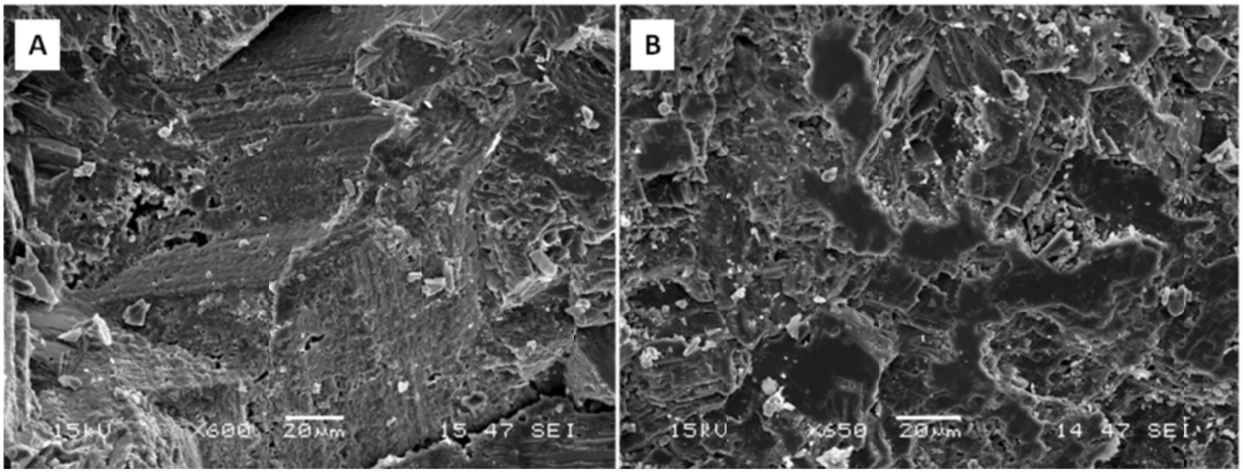

Figure 5. SEM images of pre- (A) and post-reaction (B) Potosi Dolomite sample MO-1-9. (A) Pre-reaction sample shows dolomite crystals that are slightly pitted in areas but mostly clean of defects and (B) shows extremely etched dolomite crystals and dissolution features.

Post-reaction Potosi Dolomite samples indicate an increase in bulk dolomite and decrease in bulk quartz composition by XRD. This is observed in the both the synthetic Shakopee brine and Ironton-Galesville reservoir brine experiments, with the exception of sample VW1-4533.5' which contains an anomalously high percentage of quartz, most likely due to sample heterogeneity caused by quartz-lined vugs. It must be noted that the random nature of the size, frequency, and composition of vug linings in the Potosi Dolomite add a significant amount of uncertainty in collecting a representative sample of the Potosi Dolomite and in comparing pre- and post-reaction mineralogy. For example, the 7% increase in bulk dolomite in the post-reaction sample MO-1-9 may have be an artifact of sample heterogeneity and not a true experimental result.

There was no detectable petrographic difference between the pre- and post-reaction Gunter and New Richmond Sandstone samples. Post-reaction XRD analysis of the New Richmond Sandstone sample indicates a decrease in bulk dolomite composition (from 30% to 18%) and an increase in quartz content (from 63% to 77%). Unfortunately, the size of the remaining post-batch reactor experiment Gunter sample did not contain enough mass for XRD analysis so post-reaction petrographic analysis was not possible.

Post-reaction Brine Analysis

Synthetic Shakopee Brine Experiments

Brine pH, Eh, and alkalinity for the synthetic Shakopee brine experiments were immediately measured after opening of the pressure vessels. The pH and Eh were measured for a 10 minute period and the starting and ending values during this period are shown in Table 8. Brine pH for the two Potosi Dolomite fluid samples was acidic (pH 5.9 and 6). In all experiments, pH increased after the vessels were opened, as expected, indicating the degassing of CO_2 alkalinity measurements reflect a combination of the supercritical CO_2 dissolution into the brine and the dissolution of carbonate minerals. As expected, the alkalinity is almost two times greater for brine reacted with the dolomite sample (MO-1-9) compared to the sandstone samples (Gunter and New Richmond), which likely reflects the greater carbonate mineral content of the dolomite.

Table 8. Synthetic Shakopee post-reaction brine pH, Eh, and alkalinity data.

Sample No.	Starting pH	Ending pH	Starting Eh (mV)	Ending Eh (mV)	Alkalinity (mg/L $CaCO_3$)
MO-1-9 (Potosi Dolomite)	6.0	6.4	529	458	1880
C-13678-2485.2' (Gunter Sandstone)	5.9	6.2	541	491	1032
C-13678-2533.9' (New Richmond Sandstone)	6.0	6.6	513	447	823
Control	6.3	6.5	411	376	49

Post-reaction brine chemistry of the synthetic Shakopee brine experiments (Table 9 and Figure 6) indicate a statistically significant (as defined by QA/QC measures) increase in the concentration of Ba, Ca, Mg, Mn, Na, Si, and Sr for all samples; the post-reaction concentration of Na is only about 1.1 times that of the initial concentration, and the concentration of Ba increases approximately 208 times (New Richmond Sandstone) that of the control concentration. The reason for the increase in Ba is unknown. Potassium and Zn concentrations increased in the Potosi Dolomite and New Richmond Sandstone experiments, while S increased in both sandstone experiments. Strontium and Ba commonly substitute for Ca and Mg in carbonate rocks because of their similar ionic radius and valence (Jacobson and Usdowski, 1976; Shen and Boyle, 1988) such that dissolution of dolomite could result in the concurrent increase of these constituents in solution. The presence of these analytes in the post-reaction solutions support the petrographic analysis that suggest dissolution of dolomite occurred in these experiments. Also, Ca concentrations increased the most in the Potosi Dolomite post-reaction brine because of the large amount of carbonate minerals in this sample compared to the sandstone samples and the rapid reaction of these minerals to the CO_2-brine fluid. Unexpectedly, Mn and Na concentrations increased in the control brine. Possible explanations for this observation are reaction of the CO_2 and brine with the reaction vessel and the evaporation of the brine into the CO_2. Batemen et al. (2011) also observed elevated Mn concentrations in post-reaction fluids from large-scale column experiments involving CO_2 and attributed these concentrations to interactions between CO_2 and brine and the experimental equipment. The increase in K and S concentrations is likely the result of the dissolution of clay and sulfide minerals, respectively, that were observed in the XRD mineralogical analysis. The increased concentration of Si in post-reaction brine may result from the dissolution of silicate minerals (quartz and clay) found in the rock matrix and as linings in pores. However, petrographic analysis of the post-reaction core samples was unable to observe detectable changes in the rock matrix.

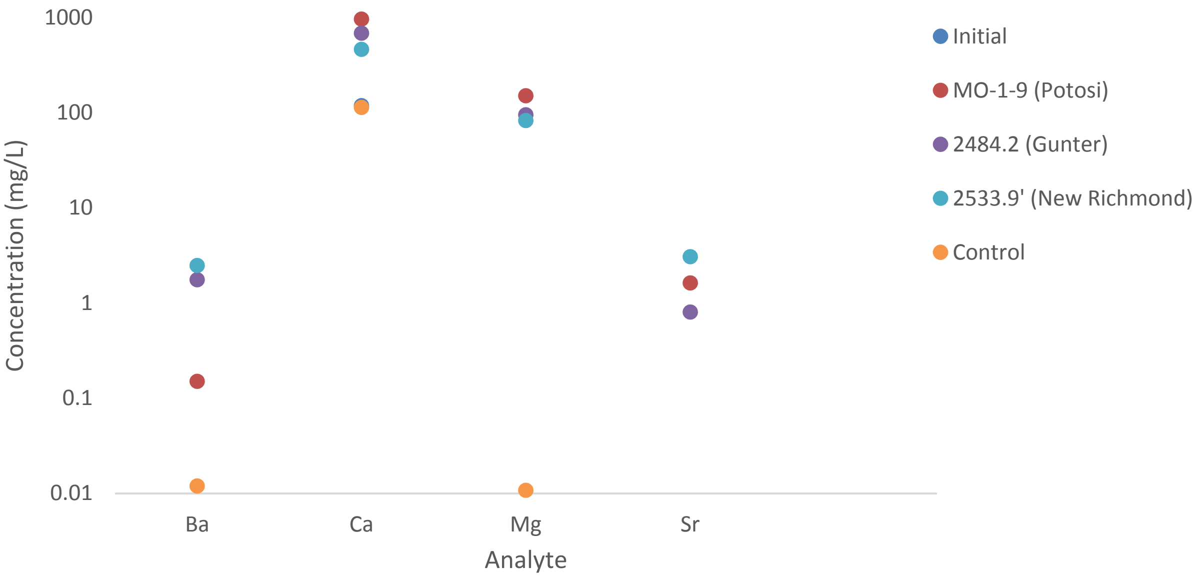

Figure 6. Concentration of select constituents in pre- and post-reaction brine for the synthetic Shakopee brine experiments. Data points for the initial composition are obscured by other data.

Table 9. Post-reaction brine chemistry analyses using the synthetic Shakopee brine and Potosi Dolomite and Gunter and New Richmond Sandstones. MDL = method detection limit. Concentrations are in mg/L. Bold italic values indicate results that are statistically significant, as defined by QA/QC procedures. Shaded cells represent the values used to perform corrections.

							Corrected Concentrations		
Analyte	**MDL**	**Initial**	**MO-1-9** **Potosi Dolomite**	**2485.2′** **Gunter Sandstone**	**2533.9′** **New Richmond Sandstone**	**Control**	**MO-1-9**	**2485.2′**	**2533.9′**
Br	0.11	<0.11	2.7	<0.11	0.86	<0.11	2.7	<0.11	0.86
Cl	0.04	1876	2053	1989	2204	1719	177	113	328
F	0.03	<0.03	0.76	2.9	<0.03	<0.03	0.76	2.9	<0.03
NO_3-N	0.07	<0.07	0.63	4.6	0.40	0.40	0.23	4.2	0
SO_4	0.13	<0.13	6.0	25.2	7.8	<0.13	6.0	25.2	7.8
Al	0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37
As	1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1
B	0.23	<0.23	<0.23	<0.23	0.380	0.905	<0.23	<0.23	***0.380***
Ba	0.0085	<0.0085	0.1498	1.8	2.5	0.0119	***0.1379***	1.8	2.5
Be	0.0055	<0.0055	<0.0055	<0.0055	<0.0055	<0.00055	<0.0055	<0.0055	<0.0055
Ca	0.29	119	962	684	463	113	***849***	***571***	***350***
Cd	0.12	<0.12	0.029	<0.12	<0.12	<0.12	0.029	<0.12	<0.12
Co	0.13	<0.13	0.063	0.042	0.121	<0.13	0.063	0.042	0.121
Cr	0.058	<0.058	<0.058	<0.058	0.0910	<0.058	<0.058	<0.058	0.0910
Cu	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Fe	0.24	<0.24	0.43	0.30	0.98	<0.24	0.43	0.30	0.98
K	0.16	<0.16	38.8	11.8	90.7	<0.16	38.8	11.8	90.7
Li	1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1
Mg	0.27	57.0	151	94.9	82.6	57.0	***94***	***37.9***	***25.6***
Mn	0.015	<0.015	0.947	0.574	0.560	0.111	***0.836***	***0.463***	***0.449***
Mo	0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22
Na	0.26	974	1038	1038	1091	1151	***64***	***64***	***117***
Ni	0.43	<0.43	7.2	1.8	0.84	<0.43	7.2	1.8	0.84
P	0.73	<0.73	<0.73	<0.73	<0.73	<0.73	<0.73	<0.73	<0.73
Pb	0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41
S	2.2	<2.2	<2.2	4.7	3.9	<2.2	<2.2	4.7	3.9
Sb	0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59
Se	1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3
Si	0.66	<0.66	61.1	41.0	20.3	<0.66	61.1	41.0	20.3
Sn	0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86
Sr	0.0037	<0.0037	1.6	0.8009	3.1	0.0187	1.6	***0.7822***	3.1
Ti	0.0056	<0.0056	<0.0056	<0.0056	<0.0056	<0.0056	<0.0056	<0.0056	<0.0056
Tl	0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43
V	0.47	<0.47	<0.47	<0.47	<0.47	<0.47	<0.47	<0.47	<0.47
Zn	0.097	<0.097	1.5	<0.097	0.098	<0.097	1.5	<0.097	0.098

The concentrations of constituents that have United States Environmental Protection Agency (USEPA) drinking water standards (As, Ba, Be, Cd, Cr, Cu, F, Pb, NO_3, Se, and Tl) were compared to uncorrected post-reaction concentrations for the synthetic Shakopee brine, Potosi Dolomite, and Gunter and New Richmond Sandstone experiments (Table 10). Concentrations of the regulated analytes were less than the MDL for some matrices, and for the concentrations of the analytes that did increase (Ba, Cd, Cr, F, and NO_3), all but Ba in the New Richmond Sandstone sample fluid were below the USEPA MCL or water standards, suggesting the potential for mobilization. However, the results for analytes that have MDLs greater than that of the USEPA MCLs (As, Be, Cd, Pb, Se, and Tl) are inconclusive because of the analytical method used.

Table 10. Comparison of USEPA minimum contaminant level (MCL) to uncorrected post-reaction brine chemistry analyses using the synthetic Shakopee brine, Potosi Dolomite, and Gunter and New Richmond Sandstones. Shaded cells represent analytes that have MDLs greater than EPA MCLs. Concentrations are in mg/L.

Analyte	**USEPA MCL**	**MO-1-9** **Potosi Dolomite**	**2485.2'** **Gunter Sandstone**	**2533.9'** **New Richmond Sandstone**
As	0.010	<1.1	<1.1	<1.1
Ba	2	0.1498	1.8	***2.5***
Be	0.004	<0.0055	<0.0055	<0.0055
Cd	0.005	0.029	<0.12	<0.12
Cr	0.1	<0.058	<0.058	0.0910
Cu	1.3	<0.2	<0.2	<0.2
F	4.0	0.76	2.9	<0.03
Pb	0.015	<0.41	<0.41	<0.41
NO_3	10	0.63	4.6	0.40
Se	0.05	<1.3	<1.3	<1.3
Tl	0.002	<0.43	<0.43	<0.43

Ironton-Galesville Reservoir Brine Experiments

Brine pH, Eh, and alkalinity of the Ironton-Galesville reservoir brine experiments using the Potosi Dolomite were immediately measured after opening of the pressure vessels. The pH and Eh were measured for a 10 minute period and the starting and ending values during this period are shown in Table 11. Starting pH was acidic and ranged from 5.0 to 5.7 and increased by approximately 0.5 on average after 10 minutes of CO_2 degassing. The pH of these solutions was lower than those from synthetic Shakopee brine with the Potosi Dolomite, which was unexpected considering that the buffering capacity of the Ironton-Galesville brine should be greater (higher calcium concentration than synthetic Shakopee brine, 5080 mg/L and 118 mg/L, respectively). Alkalinity measurements reflect a combination of the supercritical CO_2 degassing and the dissolution of carbonate minerals.

Table 11. Ironton-Galesville reservoir post-reaction brine pH, Eh, and alkalinity data.

Sample No.	Starting pH	Ending pH	Starting Eh (mV)	Ending Eh (mV)	Alkalinity (mg/L $CaCO_3$)
VW1-4522.3’ (Potosi Dolomite)	5.7	6.0	475	211	835
VW1-4533.5’ (Potosi Dolomite)	5.0	5.5	495	188	806
VW1-4536.5’ (Potosi Dolomite)	5.1	5.6	495	177	806
Control	4.1	4.5	601	587	88

Post-reaction brine chemistry of the Ironton-Galesville reservoir brine experiments (Table 12 and Figure 7) indicate a statistically significant (as defined by QA/QC measures) increase when compared to the initial and control brine concentrations for Br, B, Ba, Ca, Mg, Mn, Na, Sr, and Zn for all dolomite samples, depending on the analyte and initial concentrations. Concentrations increased by less than 0.5 mg/L to as much as 1140 mg/L depending on the analyte and initial concentrations resulting in increases between 1.4% (Na) to 26% (B) of either the initial or control concentration. Potassium concentrations increased in post-reaction brines using the Potosi Dolomite collected at depths of 1378.4 and 1381.8 m (4522.3 and 4533.5 ft). In addition, Li concentrations increased for samples collected at depths of 1381.8 and 1382.7 m (4533.5 and 4536.5 ft), and S increased in brine using the dolomite collected from a depth of 1378.4 m (4522.3 ft). However, decreases in concentrations of these same analytes were observed in the post-reaction brines for K (Dolomite collected at 1382.7 m [4536.5 ft]), Li (Dolomite collected at 1378.4 m [4522.3 ft]), and S (Dolomite collected at 1381.8 and 1382.7 m [4533.5 and 4536.5 ft]). The increased concentrations of Ba, Ca, Mg, and Sr strongly suggest dissolution of dolomite, which is supported by SEM observations of dolomite crystal degradation and pitting. Increased concentrations of Br, B, Na, and Zn may be the result of evaporation of the brine into the CO_2, thereby concentrating those constituents in the remaining brine and also interactions between the CO_2-brine and experimental equipment. The increase in K and S/SO_4 concentrations are likely the result of dissolution of clay and sulfide minerals. Because Li commonly occurs in dolomite (Chen, 1999) and forms ion pairs with sulfate as $LiSO_4^-$, the increased SO_4 concentrations may have shifted Li equilibrium allowing more Li into solution (Lyons and Welch, 1997). Decreased concentration of these analytes could be the result of the formation of new minerals or complexation with newly formed surfaces caused by dolomite dissolution; however, because of the difficulty in quantification of small volumes of mineral material using XRD (Liu et al., 2012), it is not possible to detect mineral formation in these experiments.

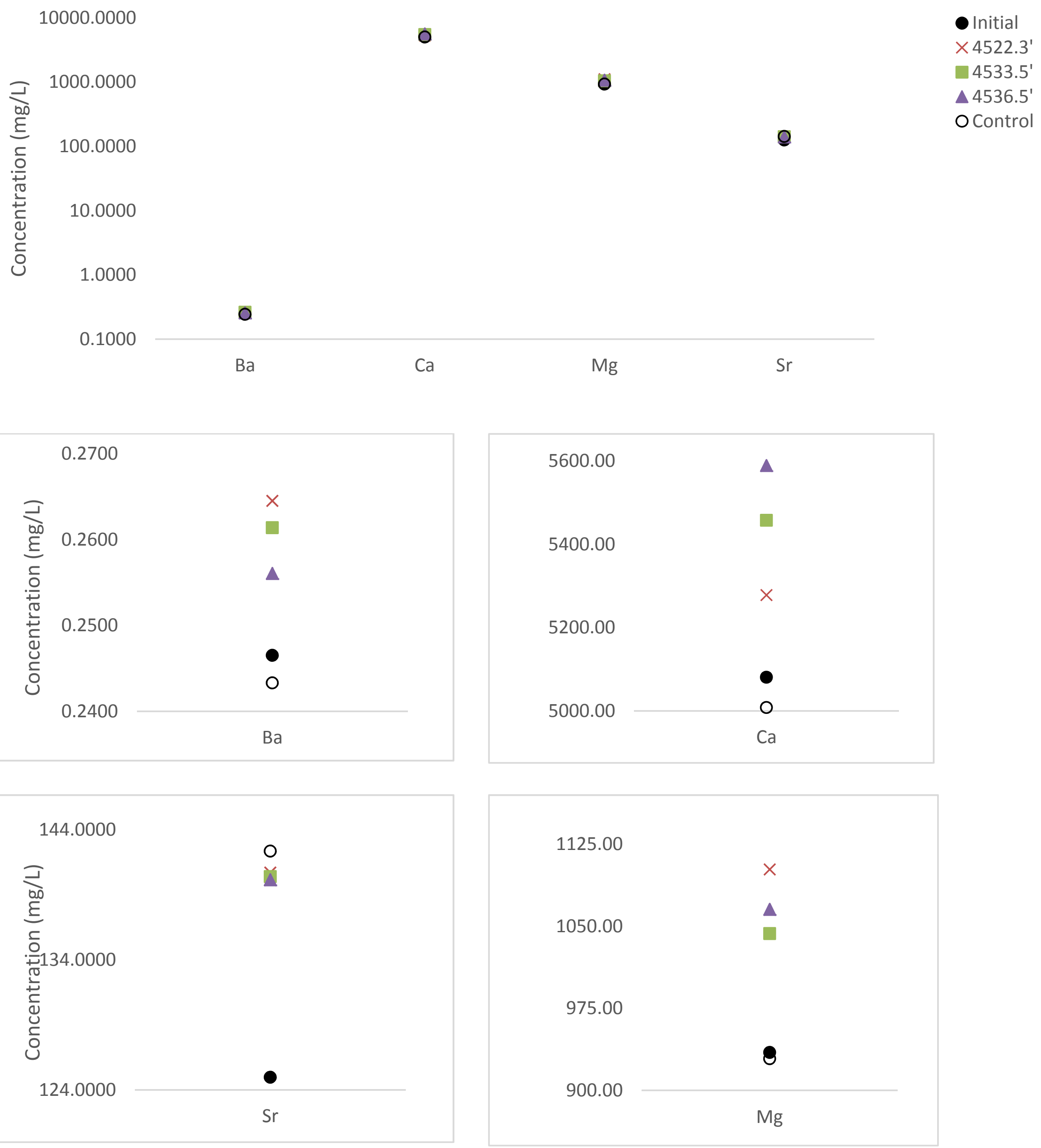

Figure 7. Concentration of select constituents in pre- and post-reaction brine for the Potosi Dolomite samples from Ironton-Galesville experiments; plots were expanded for individual analytes below. Concentrations are in mg/L.

Table 12. Post-reaction brine chemistry analyses using the Ironton-Galesville brine and Potosi Dolomite. MDL = method detection limit. Concentrations are in mg/L. Bold italic values indicate results that are statistically significant, as defined by QA/QC procedures. Shaded cells represent the values used to perform corrections.

							Corrected Concentrations		
Analyte	MDL	Initial	VW1-4522.3’ Potosi Dolomite	VW1-4533.5’ Potosi Dolomite	VW1-4536.5’ Potosi Dolomite	Control	VW1-4522.3’ Potosi Dolomite	VW1-4533.5’ Potosi Dolomite	VW1-4536.5’ Potosi Dolomite
Br	0.11	191	197	203	233	214	***6***	***12***	***42***
Cl	0.04	38643	36391	36452	36382	36790	-399	-338	-408
F	0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
NO_3	0.07	<0.07	4.4	<0.07	5.6	<0.07	4.4	<0.07	5.6
SO_4	0.13	1246	1226	1223	1242	1215	11	8	27
Al	0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37	<0.37
As	1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1
B	0.23	8.0	10.0	10.0	10.0	8.0	***2.0***	***2.0***	***2.0***
Ba	0.0085	0.2465	0.2645	0.2614	0.2561	0.2433	***0.0032***	***0.0181***	***0.0128***
Be	0.0055	<0.0055	<0.0055	<0.0055	<0.0055	<0.0055	<0.0055	<0.0055	<0.0055
Ca	0.29	5081	5278	5458	5589	5008	***270***	***450***	***581***
Cd	0.12	0.02	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
Co	0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Cr	0.058	0.018	<0.058	<0.058	0.012	0.018	<0.058	<0.058	-0.01
Cu	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Fe	0.24	27.2	1.2	0.74	0.05	0.63	***0.6***	***0.11***	***-0.58***
K	0.16	472	507	480	471	481	***35***	***8***	***-1***
Li	1.1	8.5	6.6	9.2	9.3	9.6	***-1.9***	***0.7***	***0.8***
Mg	0.27	935	1102	1043	1065	929	***167***	***108***	***130***
Mn	0.015	1.7	2.1	2.0	2.0	2.2	***0.4***	***0.3***	***0.3***
Mo	0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22	<0.22
Na	0.26	15818	16040	16958	16754	16914	***222***	***1140***	***936***
Ni	0.43	<0.43	<0.43	<0.43	<0.43	1.83	<0.43	<0.43	<0.43
P	0.73	<0.73	1.2	<0.73	<0.73	<0.73	1.15	<0.73	<0.73
Pb	0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41	<0.41
S	2.2	427	446	385	379	391	***55***	***-6***	***-12***
Sb	0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59	<0.59
Se	1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3
Si	0.66	9.2	8.7	13.0	12.7	13.3	-0.50	***3.80***	***3.50***
Sn	0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86	<0.86
Sr	0.0037	125	141	140	140	142	***16***	***15***	***15***
Ti	0.0056	<0.0056	<0.0056	<0.0056	<0.0056	<0.0056	<0.0056	<0.0056	<0.0056
Tl	0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43	<0.43
V	0.47	<0.47	<0.47	<0.47	<0.47	<0.47	<0.47	<0.47	<0.47
Zn	0.097	<0.097	0.170	0.156	0.117	0.120	0.170	0.156	0.117

The concentrations of constituents that have USEPA drinking water standards were compared to uncorrected post-reaction concentrations for the Ironton-Galesville Potosi Dolomite experiments (Table 13). Concentrations of the regulated analytes were less than the MDL for some matrices, and for the concentrations of the analytes that did increase (Ba, Cr, and NO_3), all were below the USEPA MCLs. However, results for the analytes that have MDLs greater than that of the EPA MCLs (As, Be, Cd, Pb, Se, and Tl) are inconclusive because of the analytical method used.

Table 13. Comparison of USEPA regulated analyte minimum contaminant levels (MCL) to uncorrected post-reaction brine chemistry analyses from the Ironton-Galesville brine and Potosi Dolomite experiments. Shaded cells represent analytes that have MDLs greater than EPA MCLs. Concentrations are in mg/L.

Analyte	USEPA MCL	VW1-4522.3' Potosi Dolomite	VW1-4533.5' Potosi Dolomite	VW1-4536.5' Potosi Dolomite
As	0.010	<1.1	<1.1	<1.1
Ba	2	0.2645	0.2614	0.2561
Be	0.004	<0.0055	<0.0055	<0.0055
Cd	0.005	<0.12	<0.12	<0.12
Cr	0.1	<0.058	<0.058	0.012
Cu	1.3	<0.2	<0.2	<0.2
F	4.0	<0.03	<0.03	<0.03
Pb	0.015	<0.41	<0.41	<0.41
NO_3	10	4.4	<0.07	5.6
Se	0.05	<1.3	<1.3	<1.3
Tl	0.002	<0.43	<0.43	<0.43

Maquoketa Shale Kinetic Experiments

Brine pH, Eh, and alkalinity for the Maquoketa Shale kinetic experiments were immediately measured after opening of the pressure vessels. The pH and Eh were measured for a 10 minute period and the starting and ending values during this period are shown in Table 14. The brine was acidic with pH values of 5.8 for all Maquoketa Shale samples. Brine pH increased during the measurement period by 0.5 to 0.6 pH units. The Eh values decreased as much as 47 mV during the measurement period, which may have resulted from the shifts in pH as hydrogen concentrations partially control some redox reactions. Brine alkalinity concentrations remained fairly consistent between 872 and 897 mg/L as $CaCO_3$ and did not appear to be related to the length of the experiment (Table 14). Alkalinity is likely controlled by both carbonate minerals present in the samples and the dissolution of supercritical CO_2 into the brine.

Table 14. Maquoketa Shale kinetic experiments post-reaction brine pH, Eh, and alkalinity data.

Sample No.	Starting pH	Ending pH	Starting Eh (mV)	Ending Eh (mV)	Alkalinity (mg/L $CaCO_3$)
MAQ-2815.2'	5.8	6.3	431	400	897
MAQ-2815.3'	5.8	6.4	444	397	872
MAQ-2815.4'	5.8	6.3	422	401	897
Control	4.1	4.4	529	474	37

The post-reaction chemistry data for the Maquoketa Shale kinetic experiments indicates several very small changes in constituent concentration over the duration of the experiment that suggest a low level of chemical reactivity between the rock, CO_2, and fluid, particularly among the carbonate and clay minerals (Table 15 and Figure 8). Magnesium and Sr concentrations increase in concentration above a background of 0 mg/L in the initial sample; however, the concentrations in the remaining samples are small and inconsistent across the experiment duration. Magnesium concentration rises from <MDL in the initial sample to 49.9 mg/L in the 24 hour sample, 50.8 mg/L in the 38 hour sample, and remains relatively constant at 50.7 mg/L in the 48 hour sample. Strontium concentration increases from <MDL in the initial sample to 0.765 mg/L in the 24 hour sample, decreases to 0.575 mg/L in the 38 hour sample, and increases again to 0.758 mg/L in the 43 hour sample. Barium and Ca concentrations actually decrease over the experimental duration; however, these decreases are relatively small. Barium concentration increases from <MDL in the initial sample to 0.0135 mg/L in the 24 hour sample, decreases to 0.0083 mg/L in the 38 hour sample, and increases again to 0.0122 mg/L in the 43 hour sample. Calcium concentration increases from <MDL in the initial sample to 117 mg/L in the 24 hour sample, decreases to 114 mg/L in the 38 hour sample, and remains essentially constant at 113 mg/L in the 48 hour sample. These changes in Ca, Mg, Ba, and Sr suggest a small level of reactivity among the carbonate minerals in the Maquoketa Shale as a result of rock-CO_2-fluid interactions.

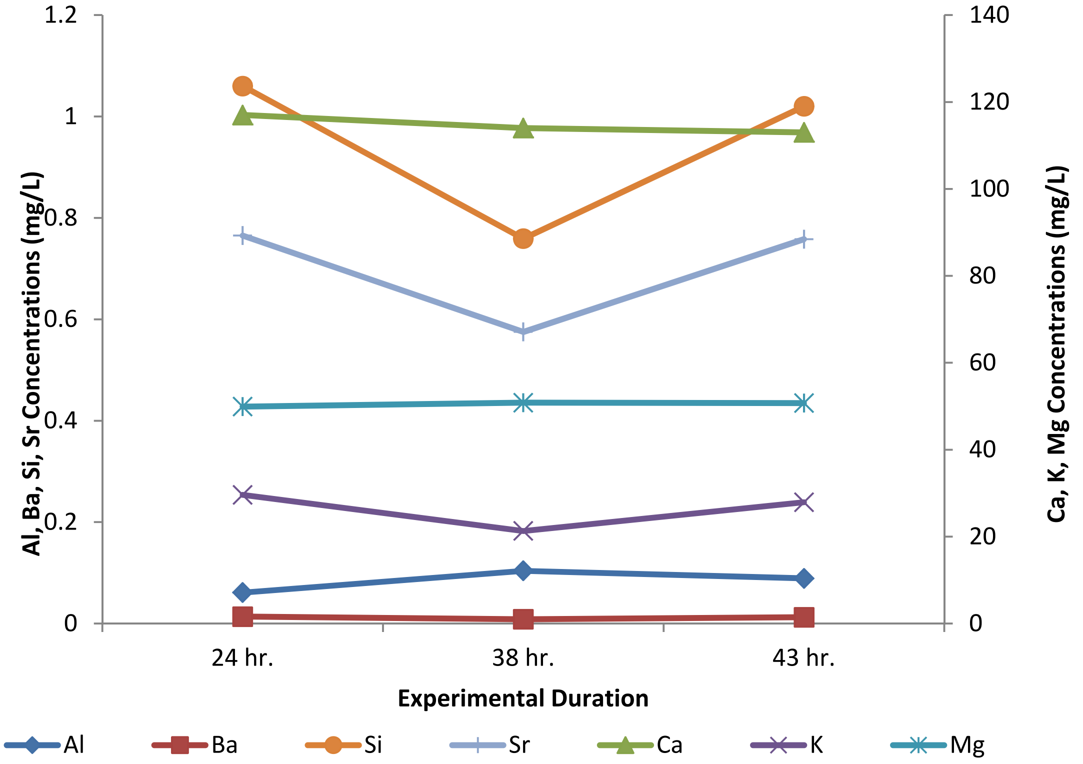

Figure 8. Variation in concentration of selected analytes throughout the duration of the Maquoketa Shale kinetic experiments.

Similar trends are observed in Al, K, and Si concentrations. The Al concentration increases from <MDL in the initial sample, rises to 0.061 mg/L in the 24 hour sample, rises to

0.104 mg/L in the 38 hour sample, and decreases in concentration again to 0.089 mg/L in the 43 hour sample. Potassium concentration increases from <MDL in the initial sample to 29.6 mg/L in the 24 hour sample, falls to 21.3 mg/L in the 38 hour sample, and increases to 27.9 mg/L in the 43 hour sample. Finally, Si concentration increases from <MDL in the initial sample to 1.06 mg/L in the 24 hour sample, decreases to 0.575 mg/L in the 38 hour sample, and increases again to 1.02 mg/L in the 43 hour sample. These changes in Al, K, and Si concentrations suggest small-level reactivity among the feldspar and clay minerals in the Maquoketa Shale as a result of rock-CO_2-fluid interactions. Post-reaction mineralogical analysis by XRD was not performed on these samples, making it difficult to confirm these reactions. The reasons for the inconsistency in increases and decreases of analyte concentrations throughout the duration of the experiment are not clear; however, observations regarding the longer term effect of these results are discussed in the Maquoketa shale modeling discussion below.

The concentrations of the measured constituents that have USEPA drinking water standards were compared to post-reaction concentrations for the Maquoketa Shale kinetics experiments (Table 16). Concentrations of the regulated analytes Ba, Cr and Cu were elevated beyond the control sample, but less than the USEPA MCL, and indicate no significant release of these regulated chemicals. However, the results for analytes that have MDLs greater than that of the EPA MCLs (As, Be, Cd, Pb, Se, and Tl) are inconclusive because of the analytical method used.

Table 15. Post-reaction fluid analysis from Maquoketa Shale kinetic experiments. MDL= method detection limit. Concentrations are in mg/L.

Analyte	MDL	Initial (DI)	MAQ-2815.2’ Maquoketa Shale–24 hour	MAQ-2815.3’ Maquoketa Shale–38 hour	MAQ-2815.4’ Maquoketa Shale 43–hour	Control
Al	0.037	<0.037	0.061	0.104	0.089	<0.037
As	0.11	<0.11	<0.11	<0.11	<0.11	<0.11
B	0.023	<0.023	0.358	0.300	0.370	<0.023
Ba	0.00085	<0.00085	0.0135	0.0083	0.0122	<0.00085
Be	0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055
Ca	0.29	<0.29	117	114	113	0.12
Cd	0.012	<0.012	<0.012	<0.012	<0.012	<0.012
Co	0.013	<0.013	0.039	0.055	0.051	<0.013
Cr	0.0058	<0.0058	<0.0058	<0.0058	<0.0058	<0.0058
Cu	0.0016	<0.0016	0.0047	0.0059	0.0056	<0.0016
Fe	0.024	<0.024	5.2	3.3	4.3	<0.024
K	0.016	<0.016	29.6	21.3	27.9	0.032
Li	0.011	<0.011	<0.11	<0.11	<0.11	<0.11
Mg	0.027	<0.027	49.9	50.8	50.7	<0.027
Mn	0.0015	<0.0015	0.746	0.735	0.774	0.0031
Mo	0.022	<0.022	<0.022	<0.022	<0.022	<0.022
Na	0.026	<0.026	114	98.5	127	0.089
Ni	0.043	<0.043	0.098	0.166	1.6	0.275
P	0.073	<0.073	<0.073	<0.073	<0.073	<0.073
Pb	0.041	<0.041	<0.041	<0.041	<0.041	<0.041
S	0.22	<0.22	13.2	19.4	18.5	<0.22
Sb	0.059	<0.059	<0.059	<0.059	<0.059	<0.059
Se	0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Si	0.066	<0.066	1.1	0.759	1.0	<0.066
Sn	0.086	<0.086	<0.086	<0.086	<0.086	<0.086
Sr	0.00037	<0.00037	0.765	0.575	0.758	<0.00037
Ti	0.00056	<0.00056	<0.00056	<0.00056	<0.00056	<0.00056
Tl	0.017	<0.017	<0.017	<0.017	<0.017	<0.017
V	0.047	<0.047	<0.047	<0.047	<0.047	<0.047
Zn	0.0097	<0.0097	0.0215	0.0242	0.0256	<0.0097

Geochemical Modeling

Potosi Dolomite Equilibrium Modeling

According to the speciation calculations we made for the Potosi Dolomite experiments, the final brine was at equilibrium with amorphous silica. The estimated pH inside the batch reactors during the experiments was approximately 4.7, assuming equilibrium with dolomite and calcite (Figure 9). The assumption of dolomite equilibrium is supported by the measured brine pH values that ranged between 5.0 and 6.0, when the reactors were opened. The higher calculated pH values are likely the result of CO_2 degassing from the brine while the pH measurement was taken. The experiments on Potosi Dolomite samples confirmed that the system reached equilibrium over a short time span. The fast reaction rate means that larger scale models of reactive transport for the Potosi do not need kinetic constraints to create an accurate picture of reservoir processes.

Table 16. Comparison of USEPA regulated analyte minimum contaminant levels (MCL) to uncorrected post-reaction brine chemistry analyses from the Maquoketa Shale kinetic experiments. Shaded cells represent analytes that have MDLs greater than EPA MCLs. Concentrations are in mg/L.

Analyte	USEPA MCL	GM2-2815.2' Maquoketa Shale–24 hour	GM2-2815.3' Maquoketa Shale–38 hour	GM2-2815.4' Maquoketa Shale 43–hour
As	0.010	<0.11	<0.11	<0.11
Ba	2	0.0135	0.0083	0.0122
Be	0.004	<0.00055	<0.00055	<0.00055
Cd	0.005	<0.012	<0.012	<0.012
Cr	0.1	<0.0058	<0.0058	<0.0058
Cu	1.3	0.0047	0.0059	0.0056
Pb	0.015	<0.041	<0.041	<0.041
Se	0.05	<0.13	<0.13	<0.13
Tl	0.002	<0.017	<0.017	<0.017

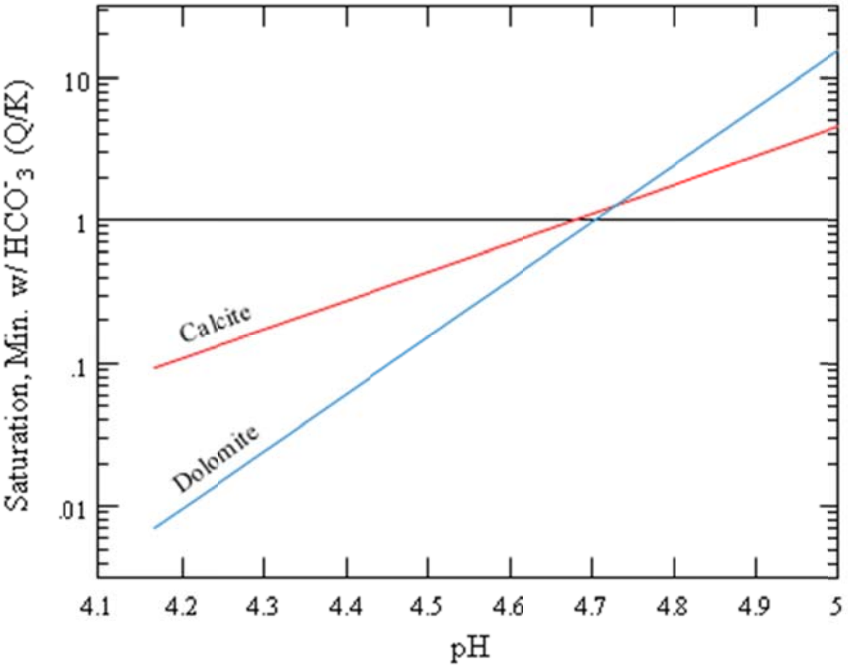

Figure 9. Saturation state of calcite and dolomite (minerals in the system containing HCO$_3^-$) as a function of pH in the Knox experiments. If Q/K = 1, then the system is at equilibrium; if Q/K > 1, then the system is saturated; and if Q/K < 1, then the system is undersaturated with respect to calcite and dolomite.

Maquoketa Shale Kinetic Modeling

Data from the Maquoketa Shale batch reactor kinetic experiments were used as input into the geochemical modeling effort to optimize for the kinetic parameters in Eq. 1 and listed in Table 17. The most reactive minerals were the carbonates (Figure 10) as expected in an acidic solution. As a group, the carbonates had the fastest kinetic parameters (Table 17) and showed the greatest amount of dissolution. In the model, this dissolution led to increases in Ca and Mg (Figure 11) through calcite and dolomite dissolution. The measured kinetic parameters may be underestimations considering the almost constant Ca and Mg concentrations in the post-experimental chemistry, which would suggest mineral equilibrium. While there was some siderite dissolution, the extent of this may have been hindered by the dissolution of the Fe-bearing minerals pyrite and daphnite (Figures 12 and 13, respectively) which could have saturated the solution with iron (Figure 14).

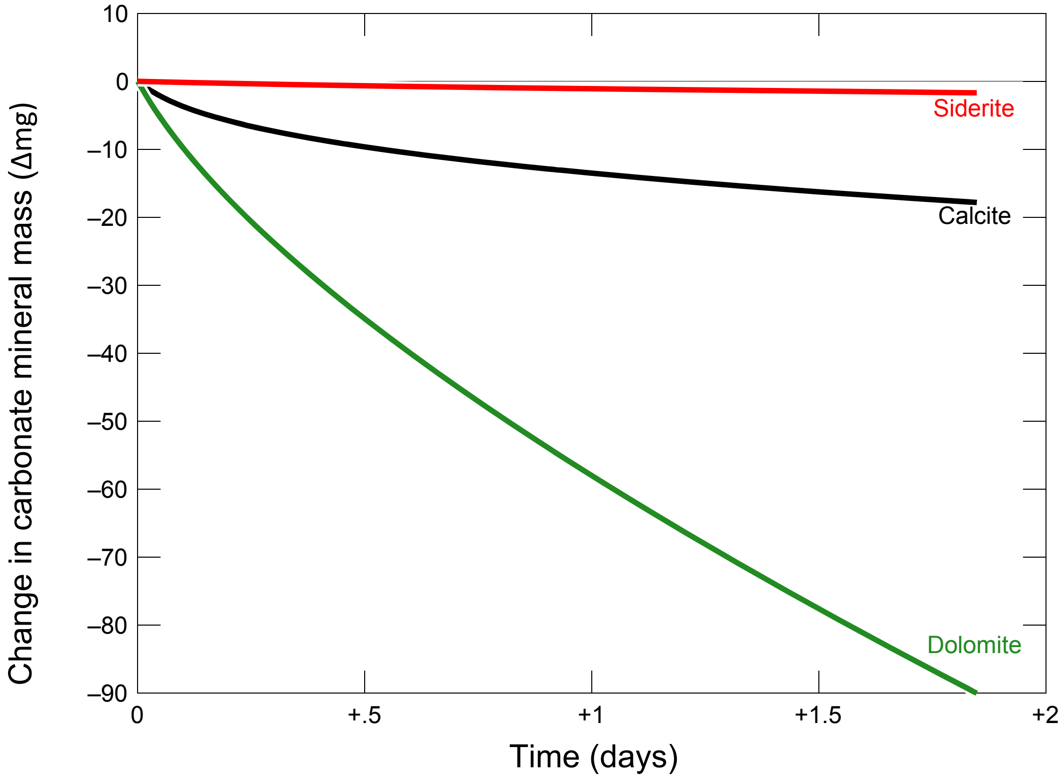

Figure 10. Modeled change in carbonate mineral mass over the experiment for Maquoketa Shale kinetic experiments.

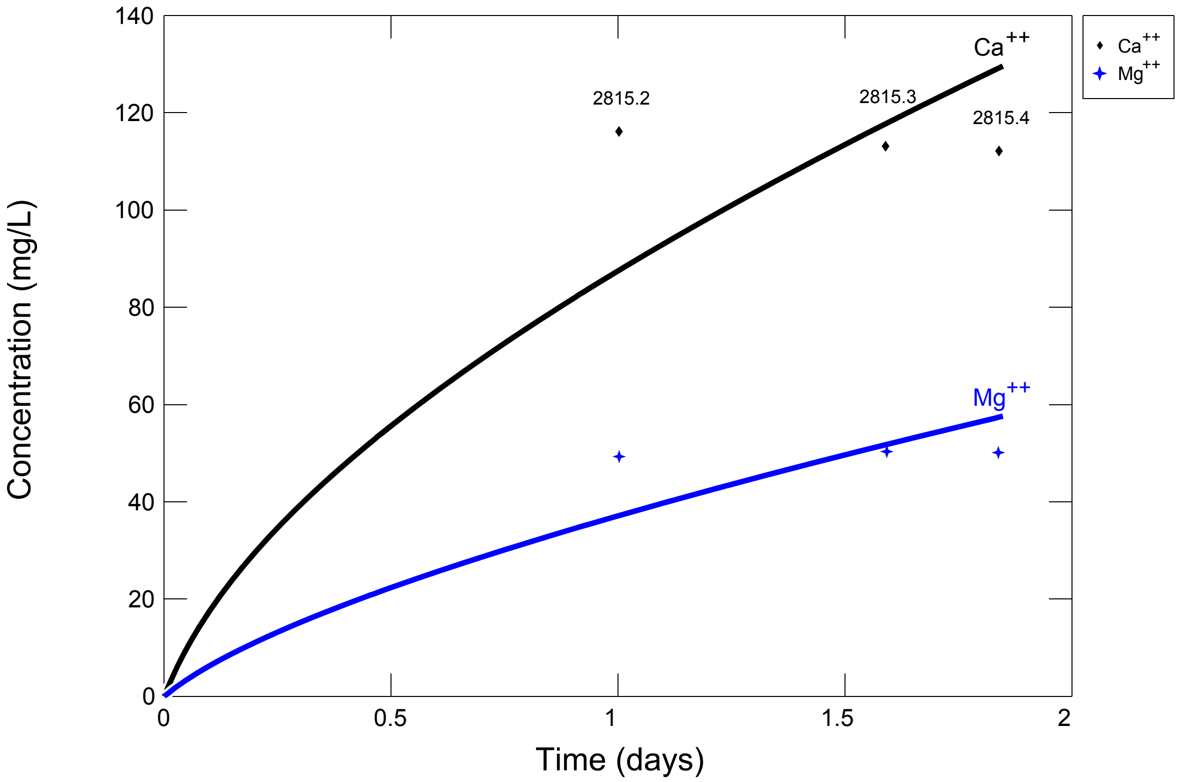

Figure 11. The modeled change in Ca and Mg concentrations in the Maquoketa Shale kinetic experiments plotted with the observed changes in water chemistry.

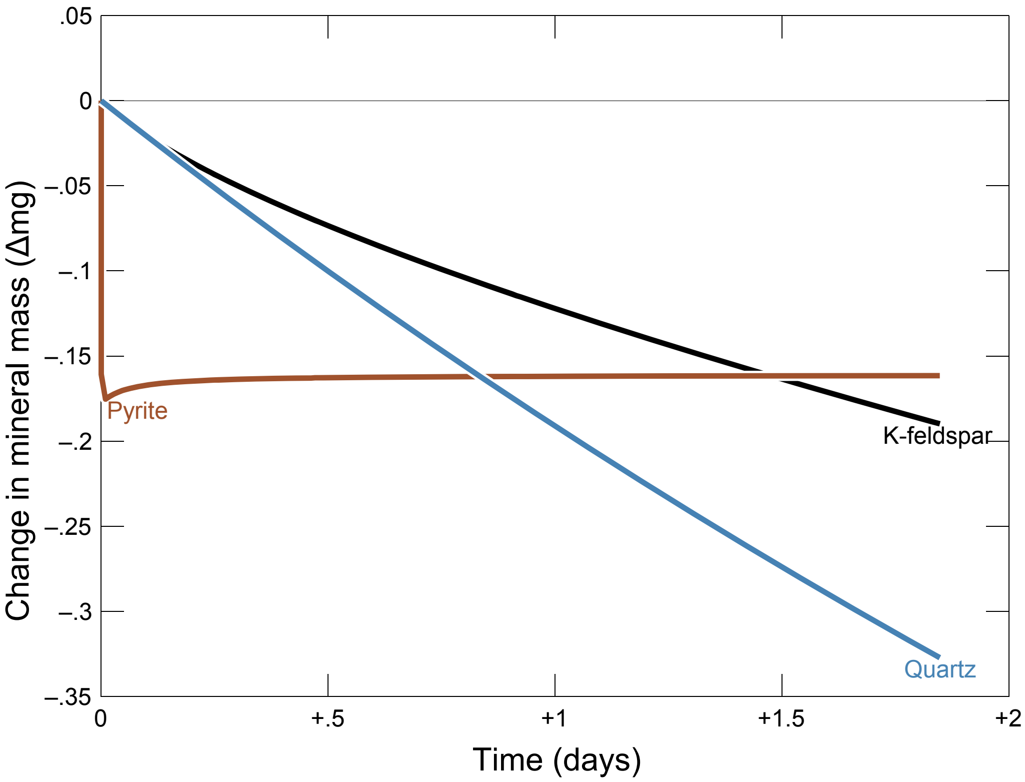

Figure 12. The modeled change in mass for quartz, k-feldspar, and pyrite during the Maquoketa Shale kinetic experiments.

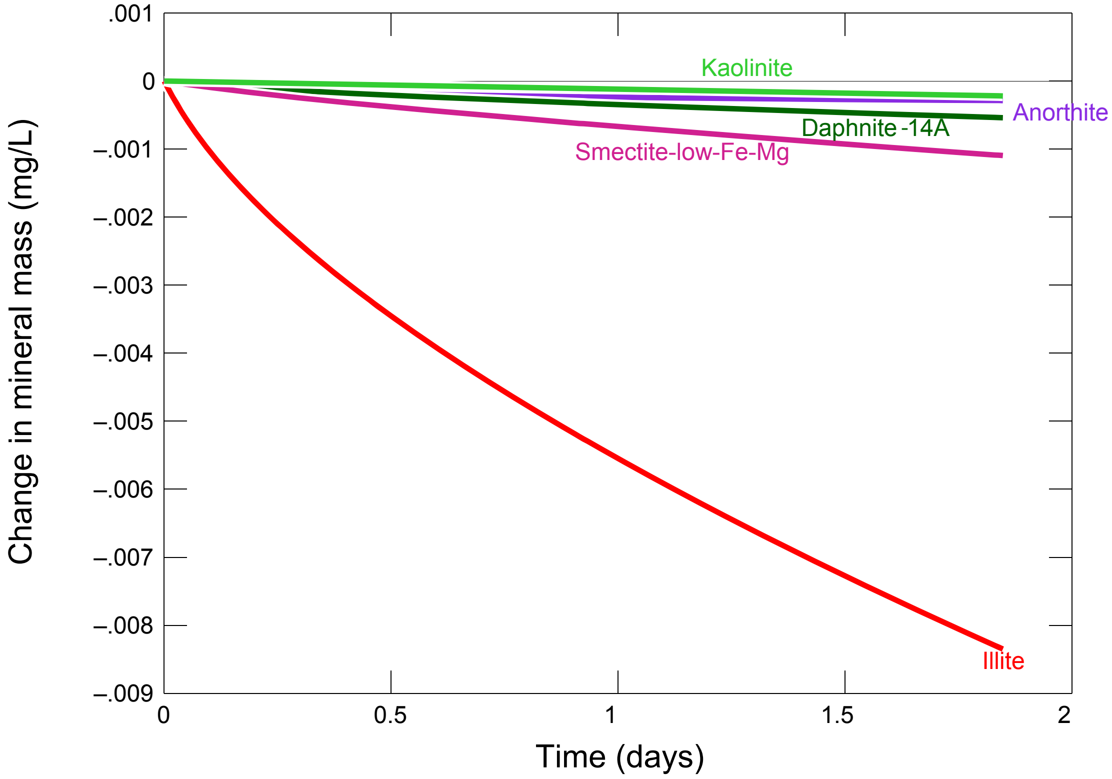

Figure 13. The modeled change in mineral mass for kaolinite, anorthite, daphnite, low Fe-Mg smectite, and illite during the Maquoketa Shale kinetic experiments.

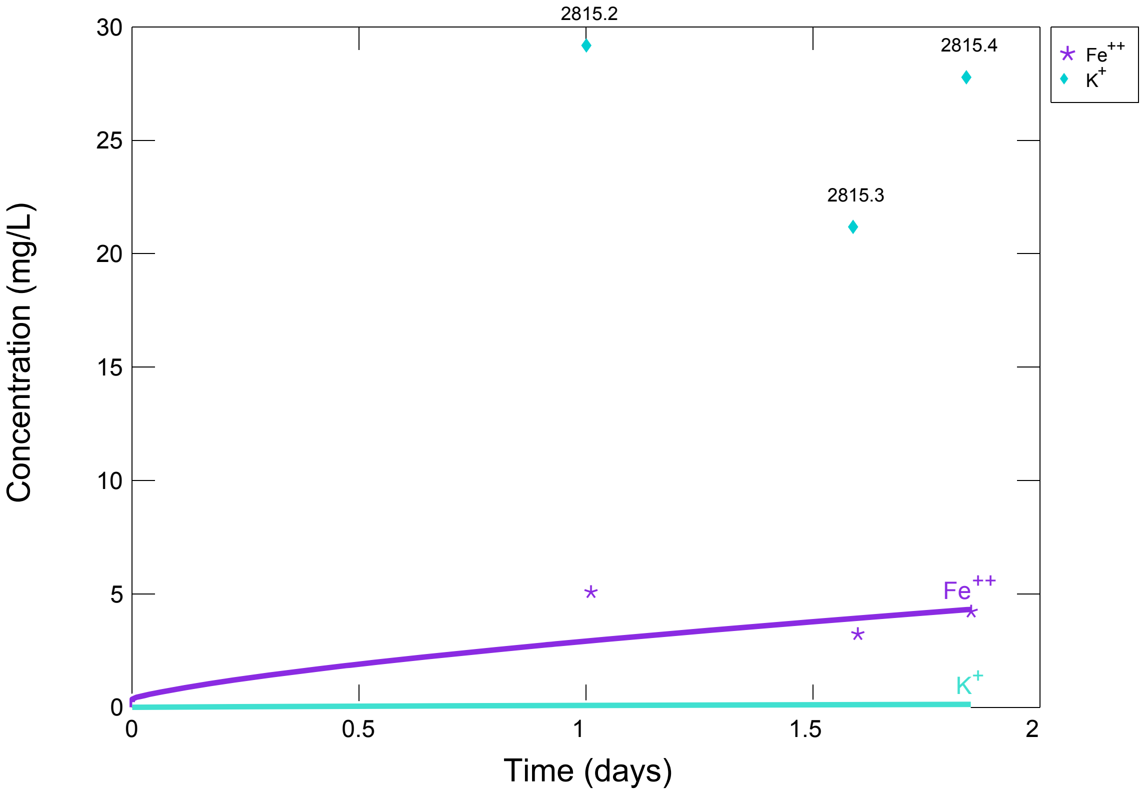

Figure 14. The modeled change concentration of Fe^{2+} and K during the Maquoketa Shale kinetic experiments.

The dissolution of quartz and k-feldspar dominated the modeled changes in silicate mineralogy (Figure 12). In the model, 0.2 and 0.33 mg of k-feldspar and quartz, respectively, dissolve during the 43-hour duration of the experiment. This modeled dissolution of these minerals increased the Al and Si concentrations in the reaction fluid to approximately 0.1 and 2.2 mg/L (Figure 15). In contrast, other silicate minerals such as illite, smectite, and kaolinite were predicted by the model to have very limited dissolution. The modeled dissolution of the mineral was less than 0.01 mg (Figure 13). This is an order of magnitude less of mass dissolved than for quartz and feldspar. The model calculated this limited dissolution because Al and Si concentrations in the fluid were very near or at saturation because of quartz and feldspar dissolution, which inhibited other silicates from dissolving. However, it is difficult to definitively state what reactions dominated the interactions within the reaction vessels. The dissolution of illite and/or another clay mineral could create similar increases in Al and Si. The difficulty of quantifying small changes in mineralogy in the post-reaction samples (Lui et al., 2012) means the optimization was not constrained adequately to find a unique solution.

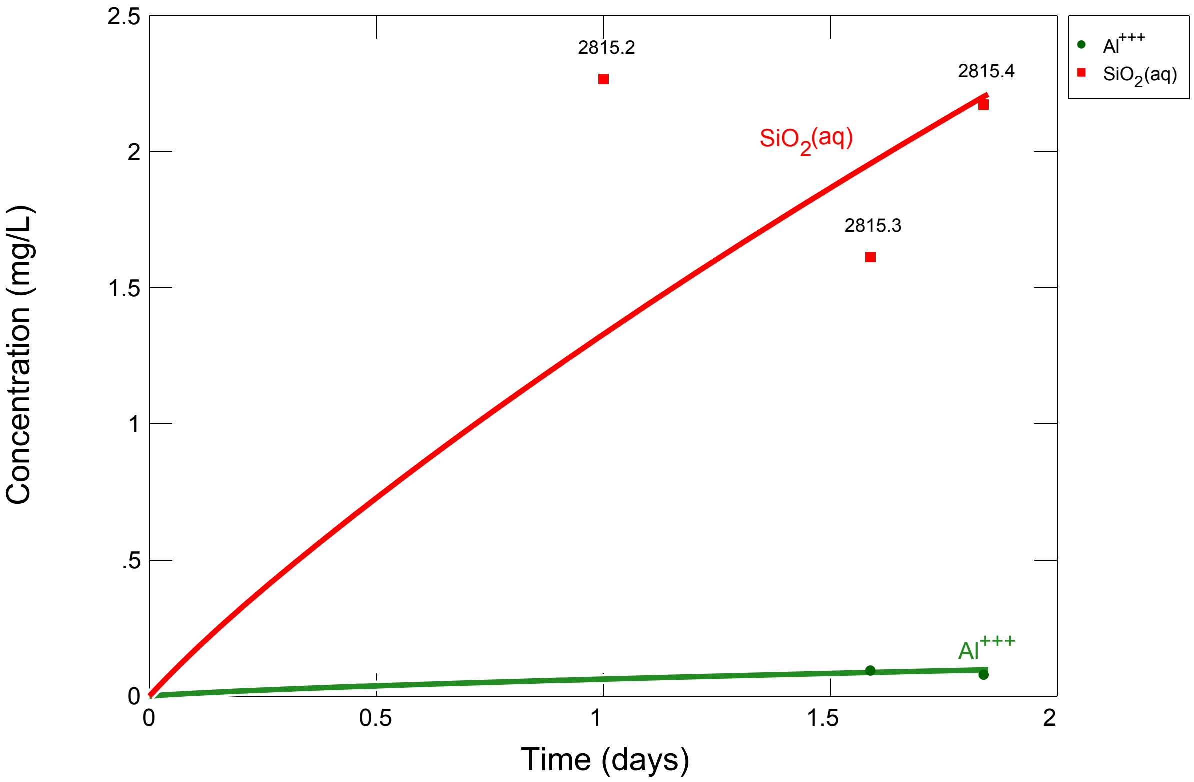

Figure 15. The modeled change in Si and Al concentrations plotted against the measured concentration in post-reaction fluids from the Maquoketa Shale kinetic experiments.

In the model, k-feldspar and clay dissolution (Figures 12 and 13, respectively) increase K concentrations in the reaction fluid by less than 0.1 mg/L (Figure 14). However, K concentrations measured in the reaction solution were greater than 20 mg/L. Thus, model-predicted and -measured concentrations were significantly different. A review of drilling logs indicated the use of a KCl drilling mud during the collection of the Maquoketa Shale cores. The drilling mud may have contaminated the samples and could account for the disparate modeled and measured K concentrations. If mineral dissolution alone were to account for the K concentrations measured in the reaction fluid, then feldspar and clay dissolutions would have to be orders of magnitude faster with the concurrent precipitation of a quartz polymorph and possibly kaolinite to remove excess Al and Si from solution.

Using the derived rate parameters, the model can be extended to 10 years in order to make an estimate of the expected mineral reactions CO_2-rich waters would cause with the Maquoketa Shale. Based on this modeling, the alteration of k-feldspar to kaolinite and quartz dominate the changes in silicate mineralogy. In reality, it is unlikely that quartz would form over this time scale. Amorphous silica or a quartz polymorph would precipitate and then slowly change into the more stable quartz form. Al and Si both have low solubility; therefore, any dissolution of a silicate mineral must have a corresponding precipitation or alteration reaction that maintains these elements in the solid phase. Because the silicate dissolution is soon followed by precipitation, these reactions contribute little to changes in porosity and would likely not have a significant impact on the Maquoketa Shale's performance as a seal for CO_2 migration. However, carbonate minerals compose up to 52% of the initial volume used in the experiment and the modeled dissolution of these minerals has a 2.2% decrease in mineral volume that could affect the porosity of the shale. Because of the fast kinetics, the largest factor influencing changes in porosity of any carbonate rich seal will most likely be the amount of acidified water coming into contact with the unit. Once the carbonate reacts, the brine will quickly reach equilibrium and further dissolution can only take place once the water has flowed or diffused away. The areas of most reactivity would therefore be not directly above a stagnant plume where diffusion is the primary mode of transport, but along the edges of the plume where acidified water adjacent to the seal can flow by convection and advection at higher rates.

Table 17. Optimized reaction rate parameters and constants from Eq. 1 for minerals in the Maquoketa Shale kinetic experiments.

Mineral	Reaction rate parameter (mol/cm^2)	Surface area (cm^2/g)	n
Quartz	5.29×10^{-14}	100	0.0
K-feldspar	4.62×10^{-12}	100	0.5
Anorthite	2.56×10^{-11}	100	1.411
Illite	9.26×10^{-15}	1000	0.6
Smectite	3.68×10^{-14}	1000	0.34
Kaolinite	5.37×10^{-13}	1000	0.0
Chlorite	1.15×10^{-15}	1000	0.5
Calcite	4.88×10^{-07}	100	1.0
Dolomite	2.88×10^{-10}	100	0.5
Siderite	3.40×10^{-11}	100	0.5
Pyrite	equilibrium		

Core Flood Experiments

Pre-reaction Petrography

To successfully complete core flood experiments, rock samples were selected that had sufficient porosity to allow the fluids to move through core segments. The Potosi Dolomite samples (FT-1 through FT-3) selected from the IBDP VW2 well core for the core flood experiments are dolomites containing quartz-lined vugs and have a sucrosic texture; however, porosity has not been measured for these samples (Figure 16). The Kentucky Blan well Gunter Sandstone sample (FT-4) is a fine- to coarse-grained quartz arenite that is moderately consolidated with minor compaction and cementation and has approximately 20% porosity based on phase analysis (Figure 17). The Marion Co., IL, St. Peter Sandstone sample selected is a fine- to medium-grained, moderately sorted quartz arenite containing trace amounts of clay throughout. Based on phase analysis, porosity is approximately 10 to 15%. It is common for pore space to be isolated as a result of quartz cementing pore throats (Figure 18).

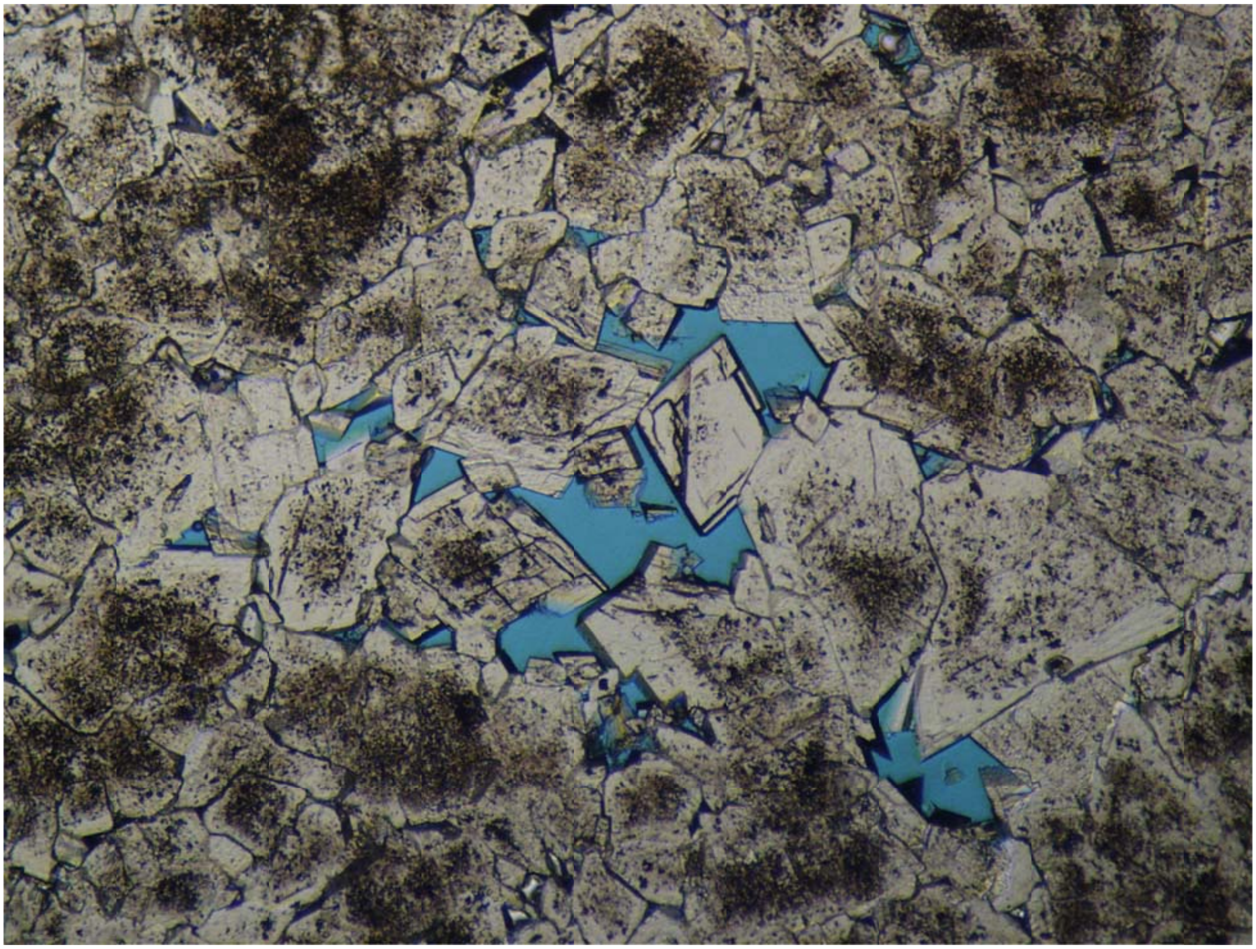

Figure 16. Photomicrograph of pre-reaction Potosi Dolomite sample IBDP VW2-4522.3’ used in the core flood experiments showing sucrosic texture and porosity.

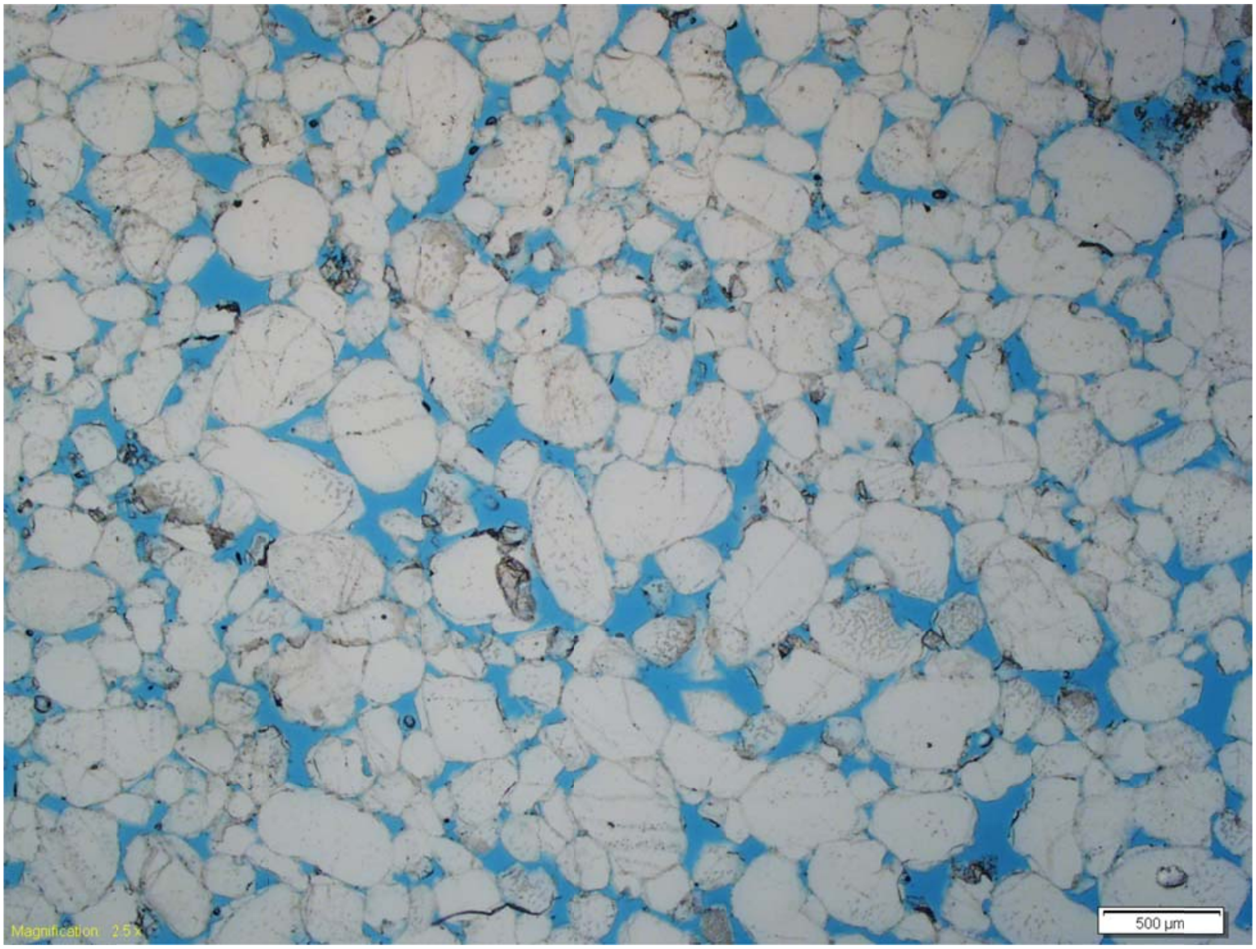

Figure 17. Photomicrograph of pre-reaction Gunter Sandstone sample 5107' from the Kentucky Blan well used in the core flood experiments, a quartz (colorless grains) arenite with 20% porosity.

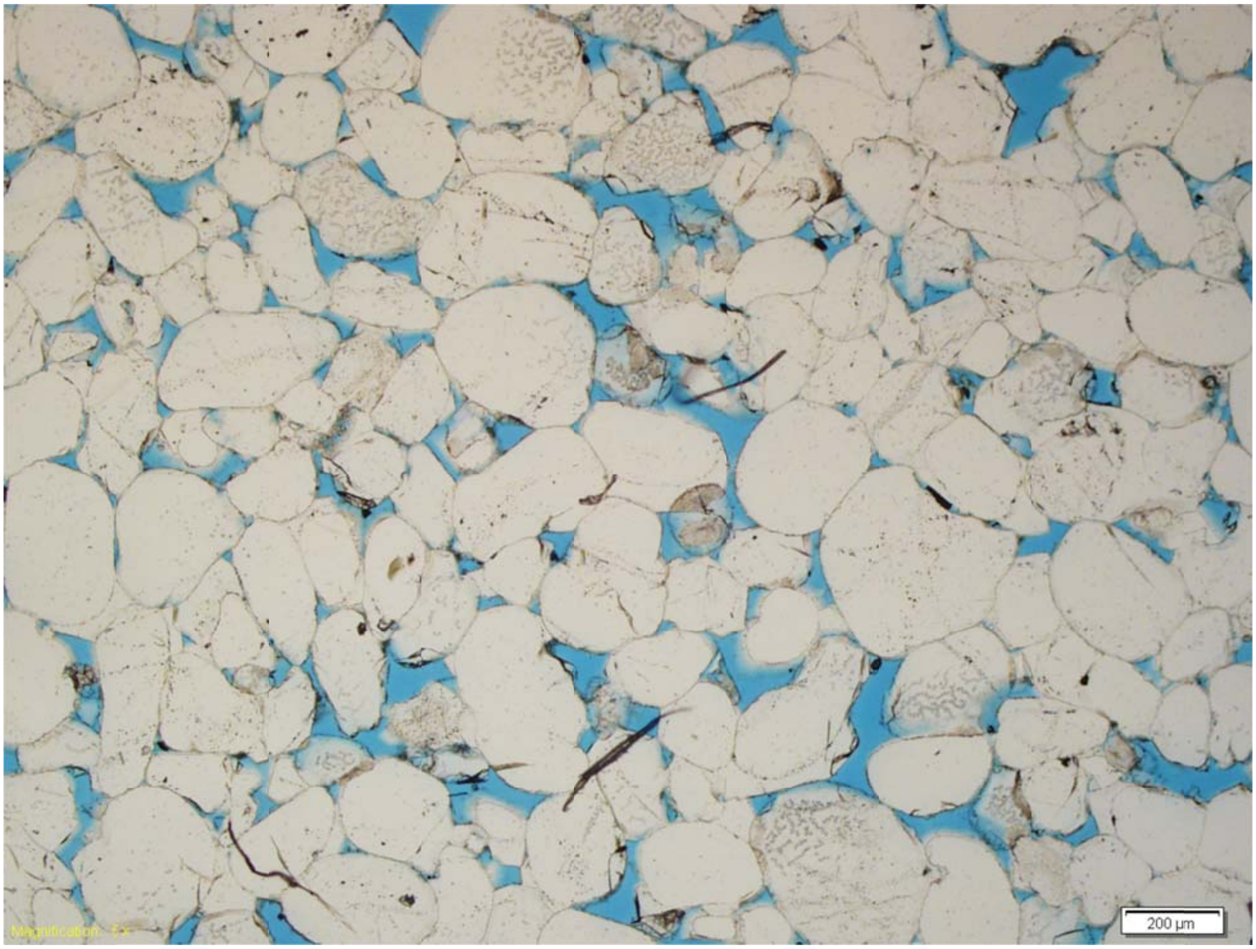

Figure 18. Photomicrograph of pre-reaction St. Peter Sandstone sample C-4831-5250.2’, Marion Co., IL, used in the core flood experiments, a quartz (colorless grains) arenite with 10–15% porosity.

Post-reaction Petrography

The post-reaction Potosi Dolomite flow-through experiment rock samples (FT-1 through FT-3) showed no discernable physical and mineralogical alterations, such as dissolution of dolomite crystals, which would be expected based upon the results of the batch experiments and past studies (Bateman et al., 2011). The Kentucky Blan Well Gunter Sandstone (FT-4) showed minor etching of dolomite crystals. The post-reaction St. Peter Sandstone (FT-5) samples contained an unidentified residuum observed within the pore space. Although there is a minimal amount of clay present in the pre-reaction samples, it is possible that the flooding fluids may have reacted with the clay to form this material (Figure 19).

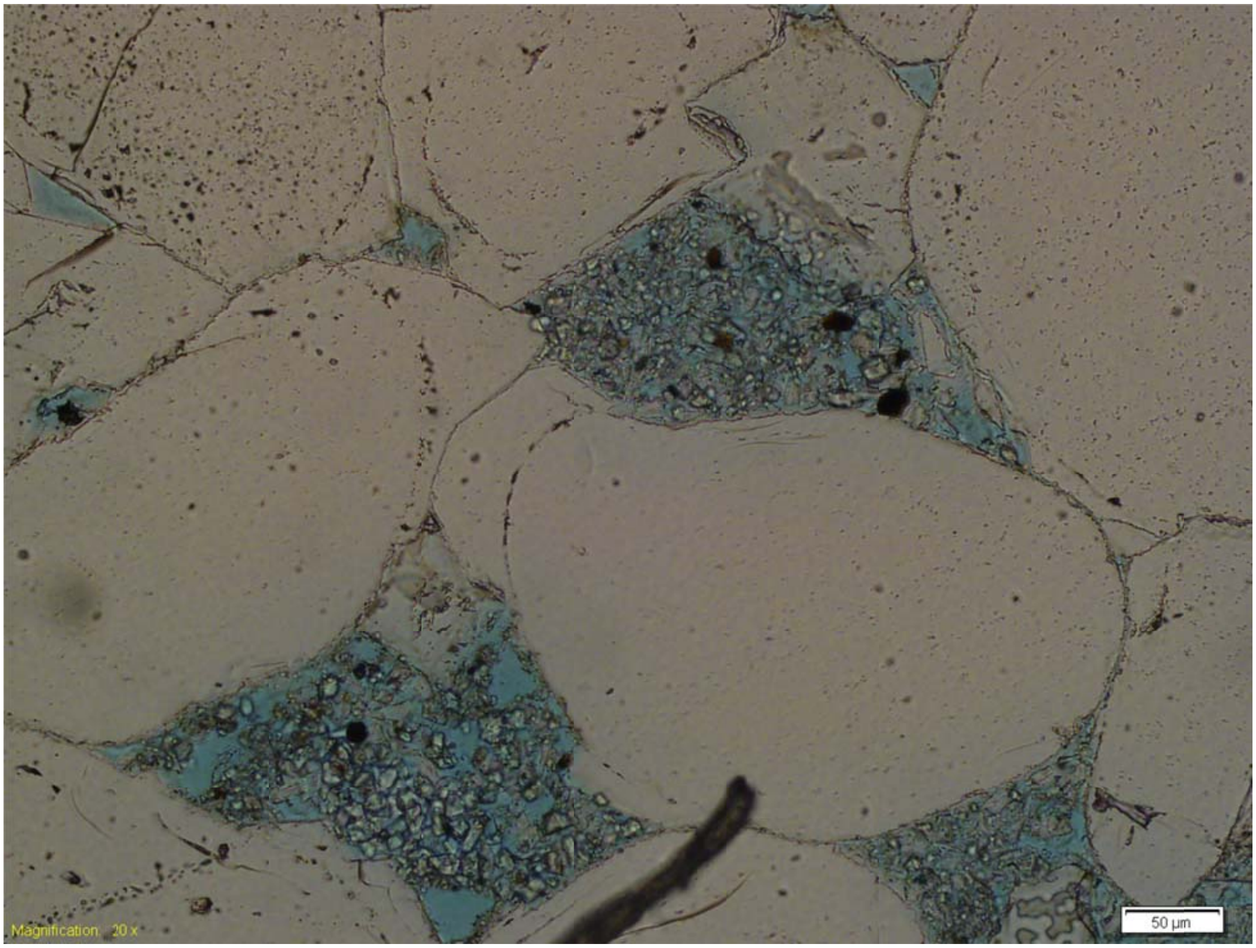

Figure 19. Photomicrograph of post-reaction St. Peter Sandstone sample C-4831-5250.2’, Marion Co., IL, used in the core flood experiments, showing unidentified residuum material between quartz (large colorless grains).

Post-reaction Brine Analysis and Geochemical Modeling

Potosi Dolomite (Experiments FT-1 through FT-3)

The water chemistry of the brine before flowing through the core (FT1-control) and the effluent brine collected after migration through the core, but before the introduction of CO_2 (FT1-Initial), had no significant differences (Table 18), except for a slight increase in Ca (Table 18). However, after the introduction of CO_2, the Ca concentration in the effluent was reduced by approximately 50% after 2 hours of flow (Sample FT1-2 and FT1-3; Table 18), and a further reduction of 20% (FT1-3) compared to the inlet concentration was measured in samples collected during the final hour of flow. The time period when Ca concentrations decreased the second time also corresponds to a period when an approximately 552 kPa (80 psi) rise in the core inlet pressure occurred. Calcite most likely precipitated during this period and potentially influenced the effective permeability of the core. The dissolution of clay minerals can account for the increases in Si, Al, and K after the introduction of CO_2. Petrographic analysis of the Potosi Dolomite suggested no observable alterations in minerals, which may be the result of the mineralogic changes being small and spread evenly throughout the core sample. Cobalt, Cr, Mo, Mn, Ni, and Zn were detected in some of the column effluent and are likely due to the acidic effluent interacting with the stainless steel tubing and pressurized containers of the experimental equipment. However, the specific composition of the equipment used is unknown.

Table 18. Post-reaction brine cation chemistry from the core flood experiment FT-1 (Synthetic Shakopee brine and Potosi Dolomite sample VW1-4524.7’). MDL = method detection limit. Concentrations are in mg/L.

Analyte	MDL	FT1- Initial (hour 1) Interval 1 Pre-CO_2	FT1-1 (hour 3) Interval 2 Post-CO_2	FT1-2 (hour 4) Interval 3 Post-CO_2	FT1-3 (hour 5) Interval 4 Post-CO_2	FT1-Control
Al	0.037	<0.037	<0.037	<0.037	<0.037	<0.037
As	0.11	<0.11	0.25	0.23	<0.11	<0.11
B	0.023	961	970	973	957	982
Ba	0.00085	0.562	0.445	0.472	0.182	0.00552
Be	0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055
Ca	0.29	106	57.8	54.5	19.3	97.1
Cd	0.012	<0.012	<0.012	<0.012	<0.012	<0.012
Co	0.013	<0.013	0.066	<0.013	<0.013	<0.013
Cr	0.0058	<0.0058	0.0108	<0.0058	<0.0058	<0.0058
Cu	0.0016	0.110	1.4	0.575	<0.0016	<0.0016
Fe	0.024	<0.024	0.038	0.033	<0.024	<0.024
K	0.016	18.6	8.1	7.5	7.8	0.149
Li	0.011	0.18	0.17	0.17	0.19	0.17
Mg	0.027	51.0	49.7	49.5	48.2	51.0
Mn	0.0015	0.0247	0.0518	0.0145	<0.0015	<0.0015
Mo	0.022	0.199	1.8	0.473	0.247	<0.022
Na	0.026	1352	1310	1324	1316	1299
Ni	0.043	0.080	3.4	0.525	0.126	<0.043
P	0.073	0.094	0.144	<0.073	0.078	<0.073
Pb	0.041	<0.041	<0.041	<0.041	<0.041	<0.041
S	0.22	2.0	2.1	1.6	1.1	<0.22
Sb	0.059	<0.059	<0.059	<0.059	<0.059	<0.059
Se	0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Si	0.066	1.3	1.2	0.965	0.958	0.827
Sn	0.086	<0.086	0.387	0.303	<0.086	<0.086
Sr	0.00037	0.446	0.393	0.338	0.196	0.108
Ti	0.00056	<0.00056	<0.00056	<0.00056	<0.00056	<0.00056
Tl	0.017	<0.017	<0.017	<0.017	<0.017	<0.017
V	0.047	<0.047	<0.047	<0.047	<0.047	<0.047
Zn	0.0097	0.0168	0.25	0.0818	<0.0097	<0.0097

The concentrations of constituents that have USEPA drinking water standards were compared to each post-reaction core flood interval concentration for experiment FT1 using Potosi Dolomite and synthetic Shakopee brine (Table 19). For some analytes (As, Be, Pb, Se, and Tl), the MDL of the analytical method used to determine the concentrations in the post-reaction brines was greater than the USEPA MCL; therefore, results are inconclusive. The concentration of As increases from the analytical MDL of 0.11 mg/L (pre-CO_2 injection) to 0.25 mg/L upon injection of CO_2 and then decreases slightly to 0.23 mg/L after injection ceases during the second sampling interval, well above the MCL of 0.010 mg/L. Additionally, the concentration of Cu increases from the initial value of 0.110 mg/L pre-CO_2 injection to 1.4 mg/L upon CO_2 after injection, above the MCL of 1.3 mg/L. However, when averaged over the duration of the experiment, the Cu concentration is below the MCL at a value of 0.70 mg/L, suggesting no significant release of the contaminant over the entire sampling interval. The concentrations of As in both interval 2 and 4 are very near the analytical MDL and only occur in two Potosi Dolomite analyses; therefore, further verification by reproducible results is recommended.

Table 19. Comparison of USEPA regulated analyte minimum contaminant levels (MCL) to post-reaction brine chemistry analyses from core flood experiment FT-1 (Synthetic Shakopee brine and Potosi Dolomite sample VW1-4524.7'). Bold italic numbers indicate values above the EPA MCL. Shaded cells represent analytes that have MDLs greater than EPA MCLs. Concentrations are in mg/L.

Analyte	USEPA MCL	FT1- Initial (hour 1) Interval 1 Pre-CO_2	FT1-1 (hour 3) Interval 2 Post-CO_2	FT1-2 (hour 4) Interval 3 Post-CO_2	FT1-3 (hour 5) Interval 4 Post-CO_2
As	0.010	<0.11	***0.25***	***0.23***	<0.11
Ba	2	0.562	0.445	0.472	0.182
Be	0.004	<0.00055	<0.00055	<0.00055	<0.00055
Cd	0.005	<0.012	<0.012	<0.012	<0.012
Cr	0.1	<0.0058	0.0108	<0.0058	<0.0058
Cu	1.3	0.110	***1.4***	0.575	<0.0016
Pb	0.015	<0.041	<0.041	<0.041	<0.041
Se	0.05	<0.13	<0.13	<0.13	<0.13
Tl	0.002	<0.017	<0.017	<0.017	<0.017

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The effluent chemistry data collected during the core flood experiment for the Potosi Dolomite sample FT2-2 (Table 20) was input into the geochemical model to evaluate saturation states of various mineral phases. Based on the modeling results, all effluent samples were undersaturated with respect to quartz and amorphous silica. The increase in Si from an initial concentration of 1.36 mg/L in the initial brine to 2.31 mg/L in the core effluent is likely the result of dissolution of the quartz that lined the dolomite sample vugs. Similar to the effluent Ca concentrations using dolomite sample FT1, Ca concentrations also decrease (effluent sample FT2-3) after the period of CO_2 injection in sample FT2, probably as a result of calcite precipitation. However, in this experiment the Ca concentrations never decreased to less than 50% of the initial inlet brine concentration, unlike the FT-1 experiment, and never had the associated increase in inlet pressure. Chromium, Mn, Ni, and Zn were detected in some of the column effluent and are likely due to the acidic effluent interacting with the stainless steel tubing and pressurized containers of the experimental equipment, however the specific composition of the equipment is unknown.

Table 20. Post-reaction brine cation chemistry from core flood experiment FT-2 (Synthetic Shakopee brine and Potosi Dolomite sample VW1-4524.4'). Concentrations are in mg/L.

Analyte	MDL	FT2-Control	FT2-Initial (hours 0-1) Interval 1 Pre-CO_2	FT2-2 (hours 1.5-3.5) Interval 2 Post-CO_2	FT2-3 (hours 3.5-5.5) Interval 3 Post-CO_2	FT2-4 (hours 5.5-7.5) Interval 4 Post-CO_2
Al	0.037	<0.037	0.059	0.038	0.056	0.060
As	0.11	<0.11	<0.11	<0.11	<0.11	<0.11
B	0.023	967	977	975	957	966
Ba	0.00085	0.00545	0.0643	0.146	0.0674	0.0965
Be	0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055
Ca	0.29	89.6	82.1	88.5	45.6	60.2
Cd	0.012	<0.012	<0.012	0.016	<0.012	<0.012
Co	0.013	<0.013	<0.013	<0.013	<0.013	<0.013
Cr	0.0058	<0.0058	0.0076	0.0094	<0.0058	0.0063
Cu	0.0016	<0.0016	0.0220	0.852	0.0999	0.0446
Fe	0.024	<0.024	<0.024	<0.024	0.034	<0.024
K	0.016	0.107	9.5	2.9	1.0	0.761
Li	0.011	0.17	0.18	0.17	0.16	0.16
Mg	0.027	50.3	48.0	48.1	50.5	49.4
Mn	0.0015	<0.0015	0.0045	0.101	0.0026	<0.0015
Mo	0.022	<0.022	0.153	2.6	0.335	0.182
Na	0.026	1322	1343	1297	1266	1266
Ni	0.043	<0.043	0.122	4.8	0.220	0.090
P	0.073	0.085	0.100	0.078	0.083	<0.073
Pb	0.041	<0.041	<0.041	<0.041	<0.041	<0.041
S	0.22	<0.22	1.9	1.4	0.56	0.44
Sb	0.059	<0.059	<0.059	<0.059	<0.059	<0.059
Se	0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Si	0.066	1.4	2.1	2.3	1.6	1.5
Sn	0.086	<0.086	<0.086	0.103	<0.086	<0.086
Sr	0.00037	0.123	0.250	0.196	0.0870	0.0969
Ti	0.00056	<0.00056	<0.00056	<0.00056	<0.00056	<0.00056
Tl	0.017	<0.017	<0.017	<0.017	<0.017	<0.017
V	0.047	<0.047	<0.047	<0.047	<0.047	<0.047
Zn	0.0097	<0.0097	0.0233	1.4	0.0294	0.0181

The concentrations of the constituents that have USEPA drinking water standards were compared with each post-reaction core flood interval concentration for experiment FT2 using Potosi Dolomite and synthetic Shakopee brine (Table 21). For some results, the MDL of As, Be, Cd, Pb, Se, and Tl was greater than the USEPA MCL because of the analysis method used, and thus results for these are inconclusive. The concentration of Cd increases from less than the analytical MDL of <0.012 mg/L during interval 1 (pre-CO_2) to 0.16 mg/L during the second interval (post-CO_2 injection), above the MCL of 0.005 mg/L. Although it is above the MCL, the increase in the concentration of Cd only occurs in one sample and is just over the analytical MDL of 0.012 mg/L; therefore, these results should be confirmed by further experimentation and analysis to be considered conclusive.

Table 21. Comparison of USEPA regulated analyte minimum contaminant levels (MCL) to post-reaction brine chemistry analyses from core flood experiment FT-2 (Synthetic Shakopee brine and Potosi Dolomite sample VW1-4524.4'). Bold italic numbers indicate values above the EPA MCL.Shaded cells represent analytes that have MDLs greater than EPA MCLs. Concentrations are in mg/L.

Analyte	**USEPA MCL**	**FT2- Initial (hours 0-1) Interval 1 Pre-CO_2)**	**FT2-2 (hours 1.5-3.5) Interval 2 Post-CO_2 injection**	**FT2-3 (hours 3.5-5.5) Interval 3**	**FT2-4 (hours 5.5-7.5) Interval 4**
As	0.010	<0.11	<0.11	<0.11	<0.11
Ba	2	0.0643	0.146	0.0674	0.0965
Be	0.004	<0.00055	<0.00055	<0.00055	<0.00055
Cd	0.005	<0.012	***0.016***	<0.012	<0.012
Cr	0.1	0.0076	0.0094	<0.0058	0.0063
Cu	1.3	0.0220	0.852	0.0999	0.0446
Pb	0.015	<0.041	<0.041	<0.041	<0.041
Se	0.05	<0.13	<0.13	<0.13	<0.13
Tl	0.002	<0.017	<0.017	<0.017	<0.017

A final core flood experiment (FT-3) was performed using the Potosi Dolomite and DI water as the eluent rather than the synthetic Shakopee brine. DI water was chosen as the eluent to investigate the dissolution of the carbonates in a Potosi Dolomite sample and how the dissolution process evolved during changing eluent conditions and experiment duration. Calcium and Mg concentrations increased from detection limits in the initial DI water to as much as 341 mg/L and 58 mg/L, respectively, in the core effluent. These increased concentrations are likely due to carbonate dissolution, which is supported by geochemical modeling results that indicated all core effluent samples were significantly undersaturated (log Q/K about –3 and –5 for calcite and dolomite, respectively) with respect to dolomite and calcite (Figure 20). The ratio of Ca/Mg decreases over time (Table 22), indicating the dissolution is changing from faster reacting calcite to the slower reacting dolomite. Based on mass balance calculations on the effluent samples (not all effluent was analyzed), at least 160 mg of the core dissolved during the entire experimental duration. As with other core flood experiments, Co, Cr, Mn, Ni, and Zn were detected in some of the column effluent and are likely due to the acidic effluent interacting with the stainless steel tubing and pressurized containers of the experimental equipment, how the specific composition of the equipment is unknown.

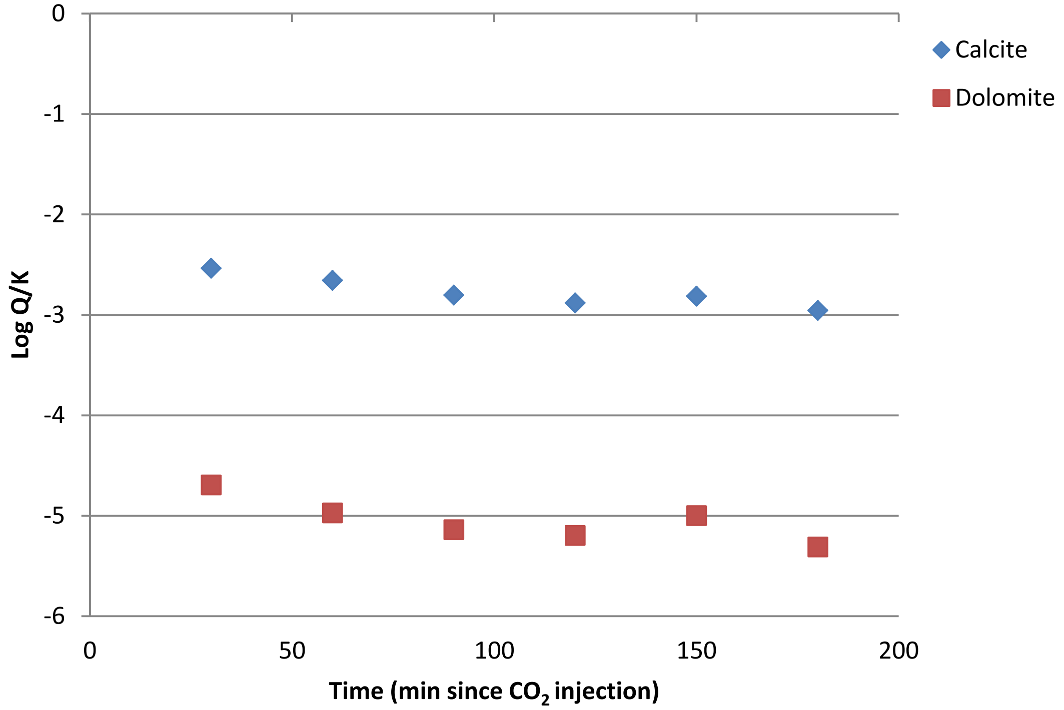

Figure 20. Mineral saturation of fluid throughout the duration of core flood experiment FT-3 (Potosi Dolomite sample VW2-4550.1’). Log Q/K > 1 indicates that the system is saturated with respect to calcite and dolomite; log Q/K < 1 indicates that the system is undersaturated with respect to calcite and dolomite.

Table 22. Post-reaction fluid cation chemistry from the core flood experiment FT-3 (DI and Potosi Dolomite sample VW1-4550.1'). MDL = method detection limit. Concentrations are in mg/L.

Analyte	MDL	Initial (DI)	FT3-1 0-30 min Interval 1 Pre-CO_2	FT3-2 31-51 min Interval 2 Simultaneous CO_2-DI	FT3-3 52-72 min Interval 3 Simultaneous CO_2-DI	FT3-4 73-93 min Interval 4 Simultaneous CO_2-DI	FT3-5 94-114 min Interval 5 Simultaneous CO_2-DI	FT3-6 115-135 min Interval 6 Simultaneous CO_2-DI	FT3-7 136-156 min Interval 7 Simultaneous CO_2-DI
Al	0.037	<0.037	1.7	0.133	0.202	0.206	0.208	0.246	0.185
As	0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
B	0.023	<0.023	4.1	2.1	0.578	0.357	0.292	1.2	0.277
Ba	0.00085	<0.00085	0.0145	0.121	0.126	0.0889	0.0789	0.0763	0.0765
Be	0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055
Ca	0.29	<0.29	6.4	262	341	321	275	229	259
Cd	0.012	<0.012	<0.012	0.045	0.037	0.032	0.029	0.040	0.031
Co	0.013	<0.013	<0.013	0.056	0.042	0.029	0.023	0.020	0.020
Cr	0.0058	<0.0058	<0.0058	0.0587	0.0589	0.0552	0.0505	0.0517	0.0412
Cu	0.0016	<0.0016	0.0229	0.0644	0.0881	0.0660	0.0679	0.186	0.0762
Fe	0.024	<0.024	0.178	0.287	0.641	1.1	1.7	3.0	2.3
K	0.016	<0.016	11.3	8.2	2.6	1.4	1.1	2.4	0.814
Li	0.011	<0.011	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
Mg	0.027	<0.027	2.7	36.3	43.0	54.1	58.8	58.6	59.8
Mn	0.0015	<0.0015	0.155	0.623	0.927	0.970	0.921	0.780	0.846
Mo	0.022	<0.022	1.6	9.7	6.5	6.0	5.5	5.3	4.9
Na	0.026	<0.026	174	40.3	9.6	3.7	2.8	40.4	2.2
Ni	0.043	<0.043	1.0	29.9	24.2	17.5	15.6	14.5	13.7
P	0.073	<0.073	0.485	<0.073	<0.073	<0.073	<0.073	<0.073	<0.073
Pb	0.041	<0.041	<0.041	<0.041	<0.041	<0.041	<0.041	<0.041	<0.041
S	0.22	<0.22	15.1	3.6	1.5	1.1	0.93	3.9	0.83
Sb	0.059	<0.059	<0.059	<0.059	<0.059	<0.059	<0.059	<0.059	<0.059
Se	0.13	<0.13	<0.13	<0.13	<0.13	0.20	<0.13	<0.13	0.21
Si	0.066	<0.066	15.2	2.3	0.857	0.563	0.505	2.1	0.500
Sn	0.086	<0.086	<0.086	<0.086	<0.086	<0.086	<0.086	<0.086	<0.086
Sr	0.00037	<0.00037	0.142	1.0	0.493	0.311	0.264	0.288	0.234
Ti	0.00056	<0.00056	0.0338	<0.00056	<0.00056	<0.00056	<0.00056	0.00108	<0.00056
Tl	0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017
V	0.047	<0.047	<0.047	<0.047	<0.047	<0.047	<0.047	<0.047	<0.047
Zn	0.0097	<0.0097	0.0484	5.9	2.9	2.1	1.7	1.6	1.5

The concentrations of constituents that have USEPA drinking water standards were compared with each post-reaction core flood interval concentration for experiment FT3 using Potosi Dolomite and DI (Table 23). In some cases, the MDL of the analytical method used to determine the concentrations in the post-reaction brines were greater than the minimum MCL. The concentration of Se increases above the USEPA MCL of 0.05 to 0.20 and 0.21 mg/L in sample intervals 4 and 7, respectively. The reason for the sporadic nature of these unclear, however, because the MDL of the analytical method used is greater than the MCL; the possibility of Se release during Potosi Dolomite-CO_2-DI cannot be eliminated. The concentration of Cd increases from less than the analytical MDL of <0.012 mg/L in the first interval to 0.045 mg/L during the second sampling interval. The Cd concentration remains above the MCL of

0.005 mg/L throughout the remaining duration of the experiment. This strongly suggests a potential for Cd mobility in concentrations above that of the USEPA MCL of 0.005 mg/L during Potosi Dolomite-CO_2-DI interactions.

Table 23. Comparison of USEPA regulated analyte minimum contaminant levels (MCL) to post-reaction fluid chemistry analyses from core flood experiment FT-3 (DI and Potosi Dolomite sample VW1-4550.1'). Bold italic numbers indicate values about the EPA MCL.Shaded cells represent analytes that have MDLs greater than EPA MCLs. Concentrations are in mg/L.

Analyte	USEPA MCL	FT3-1 0-30 min Interval 1 Pre-CO_2	FT3-2 31-51 min Interval 2 Simultaneous CO_2-DI	FT3-3 52-72 min Interval 3 Simultaneous CO_2-DI	FT3-4 73-93 min Interval 4 Simultaneous CO_2-DI	FT3-5 94-114 min Interval 5 Simultaneous CO_2-DI	FT3-6 115-135 min Interval 6 Simultaneous CO_2-DI	FT3-7 136-156 min Interval 7 Simultaneous CO_2-DI
As	0.010	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
Ba	2	0.0145	0.121	0.126	0.0889	0.0789	0.0763	0.0765
Be	0.004	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055
Cd	0.005	<0.012	***0.045***	***0.037***	***0.032***	***0.029***	***0.040***	***0.031***
Cr	0.1	<0.0058	0.0587	0.0589	0.0552	0.0505	0.0517	0.0412
Cu	1.3	0.0229	0.0644	0.0881	0.0660	0.0679	0.186	0.0762
Pb	0.015	<0.041	<0.041	<0.041	<0.041	<0.041	<0.041	<0.041
Se	0.05	<0.13	<0.13	<0.13	***0.20***	<0.13	<0.13	***0.21***
Tl	0.002	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017

Gunter Sandstone (Experiment FT-4)

Another core flood experiment was performed using the Gunter Sandstone core and DI water as the eluent. Potassium and Na concentrations in the core effluent increased from the initial concentration of the MDL to 82.8 and 12.6 mg/L, respectively, during the initial flushing of the core. These effluent analyte concentrations then decreased to less than 1 mg/L with additional flushing of the sandstone core. A review of drilling logs indicated that a drilling mud containing KCl was used when this sandstone core was collected. Likely, drilling mud and formation fluids occluded the core's pores during the initial flooding of the core. Cobalt, Cr, Mn, Ni, and Zn were detected in some of the column effluent and are likely due to the acidic effluent interacting with the stainless steel tubing and pressurized containers of the experimental equipment.

Calcium and Mg concentrations significantly increased in column effluent from 7.2 to 58.3 mg/L and 3.5 to 24.5 mg/L, respectively, as CO_2 was added to the DI water and passed through the core (Table 24; sample FT4-2). Dolomite and calcite dissolution likely resulted in the increased Ca and Mg effluent concentrations. Petrographic analysis indicated some etching of dolomite crystals that support the expectation of dolomite dissolution. The increase in Al and Si concentrations in the effluent are likely the result of amorphous silica, k-feldspar, and clay mineral dissolution. Petrographic analysis of the Gunter Sandstone indicates that it is a quartz arenite suggesting the presence of clay minerals in the sandstone matrix. Based on the geochemical modeling of the effluent chemistry, these phases remained undersaturated throughout the experiment. In these same models, some clays, such as kaolinite, remained oversaturated during the experiment, while saturation indices for illite and some smectite minerals varied from oversaturated to undersaturated during the course of the experiment. These undersaturated clay minerals could also have contributed to increased Al and Si concentrations in the effluent (Figure 21).

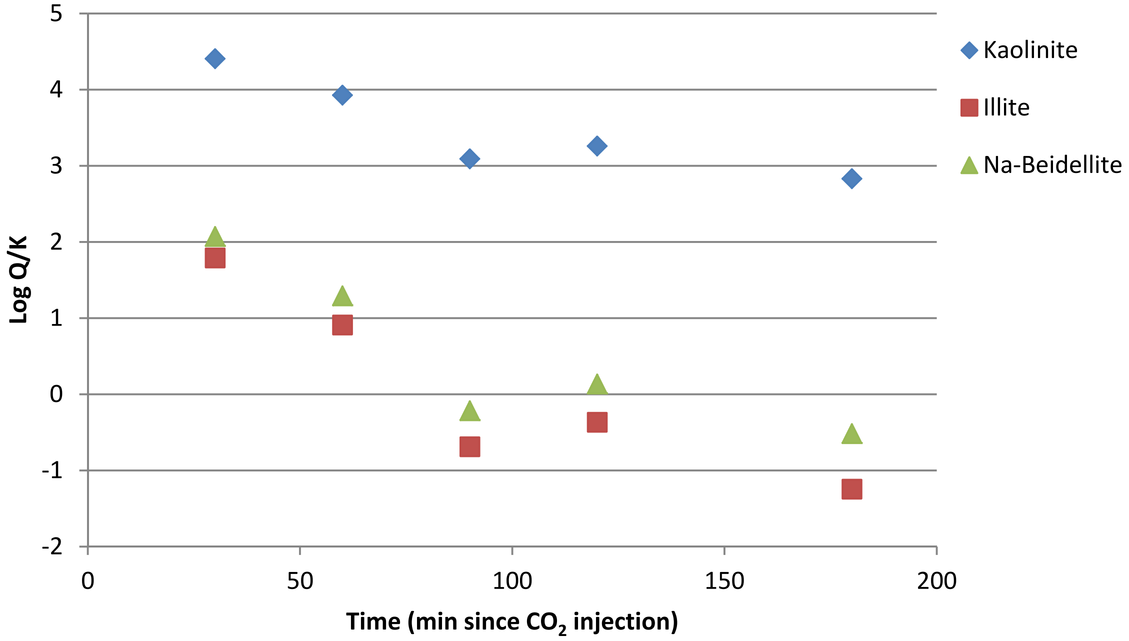

Figure 21. Mineral saturation of fluid throughout the duration of core flood experiment FT-4 (Gunter Sandstone sample Kentucky Blan well 5107’). Log Q/K > 1 indicates that the system is saturated with respect to kaolinite, illite, and Na-Beidellite; log Q/K < 1 indicates that the system is undersaturated with respect to kaolinite, illite, and Na-Beidellite.

Table 24. Post-reaction fluid cation chemistry from the core flood experiment FT-4 (DI and Gunter Sandstone sample, Kentucky Blan well 5107’). MDL = method detection limit. Concentrations are in mg/L.

Analyte	MDL	Control (DI)	FT4-1 (Initial) Pre-CO_2 Minutes 0-30 Interval 1 Pre CO_2	FT4-2 Minutes 30-62 30-62 Interval 2 Simultaneous CO_2-DI	FT4-3 Minutes 63-94 Interval 3 Simultaneous CO_2-DI	FT4-4 Minutes 95-126 Interval 4 Simultaneous CO_2-DI	FT4-5 Minutes 127-158 Interval 5 Simultaneous CO_2-DI	FT4-7 Minutes 191-210 Interval 6 Simultaneous CO_2-DI
Al	0.037	<0.037	0.501	0.603	0.505	0.318	0.277	0.196
As	0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
B	0.023	<0.023	0.756	0.214	0.225	0.137	0.115	0.077
Ba	0.00085	<0.00085	0.184	0.981	1.1	1.1	1.1	1.0
Be	0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055
Ca	0.29	<0.29	7.2	58.3	69.1	69.9	69.7	73.2
Cd	0.012	<0.012	<0.012	<0.012	0.016	0.015	<0.012	<0.012
Co	0.013	<0.013	<0.013	0.027	0.026	0.017	0.019	0.014
Cr	0.0058	<0.0058	<0.0058	0.0417	0.0594	0.0390	0.0538	0.0360
Cu	0.0016	<0.0016	0.173	0.331	0.336	0.235	0.221	0.176
Fe	0.024	<0.024	0.714	1.2	1.5	1.3	1.4	1.2
K	0.016	<0.016	82.8	1.7	0.972	0.515	0.415	0.191
Li	0.011	<0.011	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
Mg	0.027	<0.027	3.5	24.5	36.2	36.0	38.8	41.3
Mn	0.0015	<0.0015	0.0679	0.182	0.243	0.218	0.217	0.208
Mo	0.022	<0.022	1.6	6.3	8.5	5.2	5.5	3.8
Na	0.026	<0.026	12.6	1.6	1.8	0.667	0.503	0.419
Ni	0.043	<0.043	1.8	19.9	21.8	14.1	16.1	12.2
P	0.073	<0.073	<0.073	<0.073	<0.073	<0.073	<0.073	<0.073
Pb	0.041	<0.041	<0.041	<0.041	<0.041	<0.041	<0.041	<0.041
S	0.22	<0.22	7.5	1.3	1.2	0.90	0.73	0.80
Sb	0.059	<0.059	<0.059	<0.059	<0.059	<0.059	<0.059	<0.059
Se	0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Si	0.066	<0.066	2.1	1.3	0.852	0.473	0.659	0.559
Sn	0.086	<0.086	<0.086	<0.086	<0.086	<0.086	<0.086	<0.086
Sr	0.00037	<0.00037	0.0746	0.0941	0.0989	0.0840	0.0798	0.0784
Ti	0.00056	<0.00056	0.00831	<0.00056	<0.00056	<0.00056	<0.00056	<0.00056
Tl	0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017
V	0.047	<0.047	<0.047	<0.047	<0.047	<0.047	<0.047	<0.047
Zn	0.0097	<0.0097	0.332	2.4	3.4	1.9	1.5	0.938

The concentrations of analytes that have USEPA drinking water standards were compared to the post-reaction core flood sample interval concentration for experiment FT4 using Gunter Sandstone and DI (Table 25). The concentration of Ba for all samples, Cr in all but interval 1, and Cu in all samples is elevated above that of the control sample, yet below that of the USEPA MCLs, and indicate no significant release of these regulated chemicals. The concentration of Cd increases above the USEPA MCL of 0.005 to 0.016 and 0.015 mg/L in sample intervals 3 and 4, respectively. The results for analytes that have MDLs greater than that of the EPA MCLs (As, Be, Cd [sample intervals 1, 2, 5, and 6], Pb, Se, and Tl) are inconclusive because of the analytical method used. The elevated Cd concentration in intervals 3 and 4 are only slightly greater than the analytical MDL of 0.012 mg/L and only occur in two samples, and thus should be confirmed with further experimentation and analysis to be considered conclusive.

Table 25. Comparison of USEPA regulated analyte minimum contaminant levels (MCL) to post-reaction fluid chemistry analyses from core flood experiment FT-4 (DI and Gunter Sandstone sample, Kentucky Blan well 5107'). Bold italic numbers indicate values above the EPA MCL. Shaded cells represent analytes that have MDLs greater than EPA MCLs. MDL = method detection limit. Concentrations are in mg/L.

Analyte	**USEPA MCL**	**FT4-1 (Initial) Minutes 0-30 Interval 1 Pre-CO_2**	**FT4-2 Minutes 30-62 Interval 2 Simultaneous CO_2-DI**	**FT4-3 Minutes 63-94 Interval 3 Simultaneous CO_2-DI**	**FT4-4 Minutes 95-126 Interval 4 Simultaneous CO_2-DI**	**FT4-5 Minutes 127-158 Interval 5 Simultaneous CO_2-DI**	**FT4-7 Minutes 191-210 Interval 6 Simultaneous CO_2-DI**
As	0.010	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
Ba	2	0.184	0.981	1.08	1.13	1.11	1.04
Be	0.004	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055
Cd	0.005	<0.012	<0.012	***0.016***	***0.015***	<0.012	<0.012
Cr	0.1	<0.0058	0.0417	0.0594	0.0390	0.0538	0.0360
Cu	1.3	0.173	0.331	0.336	0.235	0.221	0.176
Pb	0.015	<0.041	<0.041	<0.041	<0.041	<0.041	<0.041
Se	0.05	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13
Tl	0.002	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017

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St. Peter Sandstone (Experiment FT-5)

The Si, Al, K, Fe, S, and Na concentrations all follow similar trends once CO_2 is injected along with the DI water into the core. The core effluent concentrations decreased between the second and third samples and increased in the final sample. In the geochemical models, the core effluent solutions approached equilibrium with respect to chalcedony (a SiO_2 phase) toward the end of the experiment that may explain the decrease in effluent Si (Figure 22).

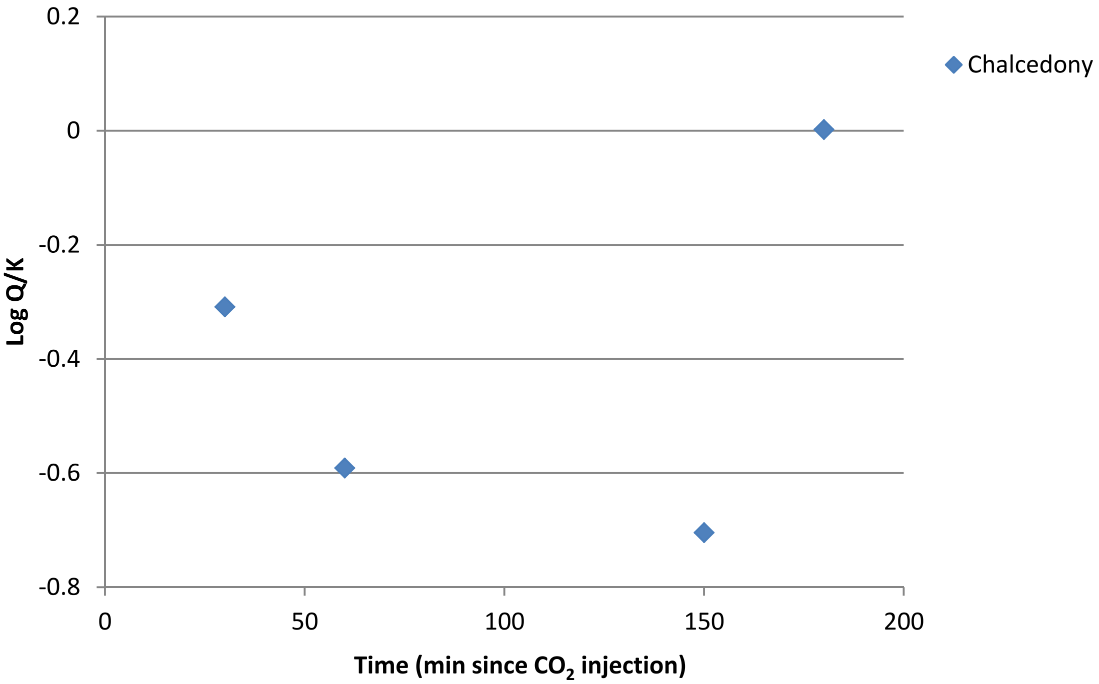

Figure 22. Mineral saturation of fluid throughout the duration of core flood experiment FT-5 (St. Peter Sandstone sample C-4831-5250.2'). Log Q/K > 1 indicates that the system is saturated with respect to Chalcedony; log Q/K < 1 indicates that the system is undersaturated with respect to Chalcedony.

For the final core flood experiment, St. Peter sandstone was flooded with DI water. Sodium and Zn concentrations during the initial flooding of the core with water increased from method detection limits to 136 and 3.2 mg/L, respectively (sample FT5-1; Table 26). Likely, formation fluid occluded in the core when it was collected during this initial flushing period. Aluminum, K, and Si concentrations in the core effluent increased from method detection limits in the initial DI water to maximum concentrations of 0.45, 0.944, and 3.02 mg/L, respectively, in the core effluent. Petrographic analysis of the post-reaction core indicated residuum in the core pores that likely were the result of reactions with the limited amount of clay in the core. These clay reactions, such as dissolution of feldspar, may account for the increased Al, K and Si concentrations in the core effluent. Sodium, Ca, and Mg concentrations increased dramatically during the initial flushing of the core (sample FT5-1; Table 26) from below detection limits to 136, 469, and 29.8 mg/, respectively. These concentrations decreased throughout the experiment as additional fluids passed through the sandstone core. This initial increase is somewhat unexpected but may be due to initial flushing of the formation fluid that was occluded in the core at the time of collection. The Ca, Mg, and Sr could be from either carbonate dissolution or the remnants of the original brine (Table 26). Both Fe and S concentrations increased during the initial flushing of the core from detection limits to 1.37 and 13.8 mg/L, respectively, and decreased during the experiment. This initial increase may be the result of pyrite/marcasite dissolution as the initial DI water was at equilibrium with the atmosphere and likely contained oxygen. Krapac (1987) reported that, in a compressed air energy storage project, oxygen from air injected into St. Peter sandstone was depleted within weeks because of marcasite oxidation present in the sandstone.

The Si, Al, K, Fe, S, and Na concentrations all follow similar trends once CO_2 is injected along with the DI water into the core. The core effluent concentrations decreased between the second and third samples and increased in the final sample. In the geochemical models, the core effluent solutions approached equilibrium with respect to chalcedony (a SiO_2 phase) toward the end of the experiment that may explain the decrease in effluent Si (Figure 22).

Table 26. Post-reaction fluid cation chemistry from the core flood experiment FT-5 (DI and St. Peter Sandstone sample C-4831-5250.2'). MDL = method detection limit. Concentrations are in mg/L.

Analyte	MDL	Control (DI)	FT5-1 (Initial) Minutes 0-30 Interval 1 Pre-CO_2	FT5-2 Minutes 31-63 Interval 2 Simultaneous CO_2-DI	FT5-3 Minutes 64-96 Interval 3 Simultaneous CO_2-DI	FT5-4 Minutes 96-120 Interval 4 Simultaneous CO_2-DI
Al	0.037	<0.037	0.452	0.245	0.162	0.725
As	0.11	<0.11	<0.11	<0.11	<0.11	<0.11
B	0.023	<0.023	1.1	0.123	0.090	0.328
Ba	0.00085	<0.00085	4.4	2.6	1.9	2.1
Be	0.00055	<0.00055	<0.00055	<0.00055	<0.00055	<0.00055
Ca	0.29	<0.29	469	154	57.0	59.4
Cd	0.012	<0.012	0.058	0.015	<0.012	0.018
Co	0.013	<0.013	0.071	0.020	0.016	0.029
Cr	0.0058	<0.0058	0.282	0.0968	0.0781	0.125
Cu	0.0016	<0.0016	0.944	0.370	0.267	0.730
Fe	0.024	<0.024	1.4	1.3	1.1	1.5
K	0.016	<0.016	12.8	0.647	0.296	1.9
Li	0.011	<0.011	<0.11	<0.11	<0.11	<0.11
Mg	0.027	<0.027	29.8	25.2	17.2	19.0
Mn	0.0015	<0.0015	0.508	0.161	0.0867	0.133
Mo	0.022	<0.022	9.4	3.5	3.7	6.3
Na	0.026	<0.026	136	2.12	0.802	9.9
Ni	0.043	<0.043	27.9	9.8	10.0	18.4
P	0.073	<0.073	0.119	<0.073	<0.073	0.113
Pb	0.041	<0.041	<0.041	<0.041	<0.041	<0.041
S	0.22	<0.22	13.8	2.6	2.2	4.7
Sb	0.059	<0.059	<0.059	<0.059	<0.059	<0.059
Se	0.13	<0.13	0.22	<0.13	<0.13	<0.13
Si	0.066	<0.066	3.0	1.7	1.3	6.7
Sn	0.086	<0.086	0.105	<0.086	<0.086	<0.086
Sr	0.00037	<0.00037	5.0	1.2	0.545	0.608
Ti	0.00056	<0.00056	0.00726	0.00081	<0.00056	0.0217
Tl	0.017	<0.017	<0.017	<0.017	<0.017	<0.017
V	0.047	<0.047	<0.047	<0.047	<0.047	<0.047
Zn	0.0097	<0.0097	3.2	1.4	1.2	3.0

Of all of the experiments performed for this project, the interactions that occurred between the St. Peter Sandstone, CO_2, and DI during core flood experiment FT5 indicated the highest risk for inorganic contaminant mobility. The concentrations of analytes that have USEPA drinking water standards were compared with each post-reaction core flood sample interval concentration for experiment FT5 (Table 27). The As concentration was above the USEPA MCL of 0.010 mg/L immediately upon injection of CO_2 within the first interval. Once CO_2 injection was stopped, the concentration began to drop and continued through the third interval. However, the concentration jumped to 0.725 mg/L in the final interval; the reason for this is unclear. A similar trend is observed with Ba, Cd, and Cr; concentrations above the MCL upon CO_2 injection with a drop in the second and third intervals (some below the MCL), and increased concentrations again within the final interval. Finally, the concentration of Se immediately increased above the MCL of 0.05 mg/L at 0.22 mg/L upon DI injection, but dropped below the MDL at the onset of simultaneous CO_2-DI injection, yet possibly greater than the MCL. These results suggest the potential for contamination by As, Ba, Cd, Cr (possibly a result of equipment interaction) and Se in concentrations above USEPA MCL during St. Peter-CO_2-DI interactions.

Table 27. Comparison of USEPA regulated analyte minimum contaminant levels (MCL) to post-reaction fluid chemistry analyses from core flood experiment FT-4 (DI and St. Peter Sandstone sample C-4831-5250.2'). Bold italic numbers indicate values above the EPA MCL. Shaded cells represent analytes that have MDLs greater than EPA MCLs. Concentrations are in mg/L.

Analyte	**USEPA MCL**	**FT5-1 (Initial) Minutes 0-30 Interval 1 Pre-CO_2**	**FT5-2 Minutes 31-63 Interval 2 Simultaneous CO_2-DI**	**FT5-3 Minutes 64-96 Interval 3 Simultaneous CO_2-DI**	**FT5-4 Minutes 96-120 Interval 4 Simultaneous CO_2-DI**
As	0.010	***0.452***	***0.245***	***0.162***	***0.725***
Ba	2	***4.4***	***2.6***	1.9	***2.1***
Be	0.004	<0.00055	<0.00055	<0.00055	<0.00055
Cd	0.005	***0.058***	***0.015***	<0.012	***0.018***
Cr	0.1	***0.282***	0.0968	0.0781	***0.125***
Cu	1.3	0.944	0.370	0.267	0.730
Pb	0.015	<0.041	<0.041	<0.041	<0.041
Se	0.05	***0.22***	<0.13	<0.13	<0.13
Tl	0.002	<0.017	<0.017	<0.017	<0.017

Pressure Curve Interpretation

Potosi Dolomite (Experiments FT-1 through FT-3)

Core inlet and pressures were measured during the core flood experiments. During the first 60 minutes of the FT-1 experiment, when the synthetic Shakopee brine was being injected into the dolomite core (Figure 23), pressures quickly reached a steady state condition with an approximately 414 kPa (60 psi) pressure differential between the core inlet and outlet. The switch to injection of only CO_2 after brine injection (60 min. mark; Figure 23) caused the inlet pressure to increase by about 2069 (300 psi) as the CO_2 forced the brine out of the core pore space. The inlet pressure decreased as CO_2 injection continued as the pores went from 100% water saturation down to residual water saturation. The outlet pressure did not change significantly during this period and remained at about 9998 kPa (1450 psi). The inlet pressure increased again at the 120 min. mark as the inlet flow switched back to brine. The brine quickly forced CO_2 from the pores; however, the inlet pressure did not recover to the original steady state pressure, likely because of irreducible CO_2 saturation. The subsequent increase in inlet pressure may be due to the calcite precipitation that is evident from the change in effluent chemistry.

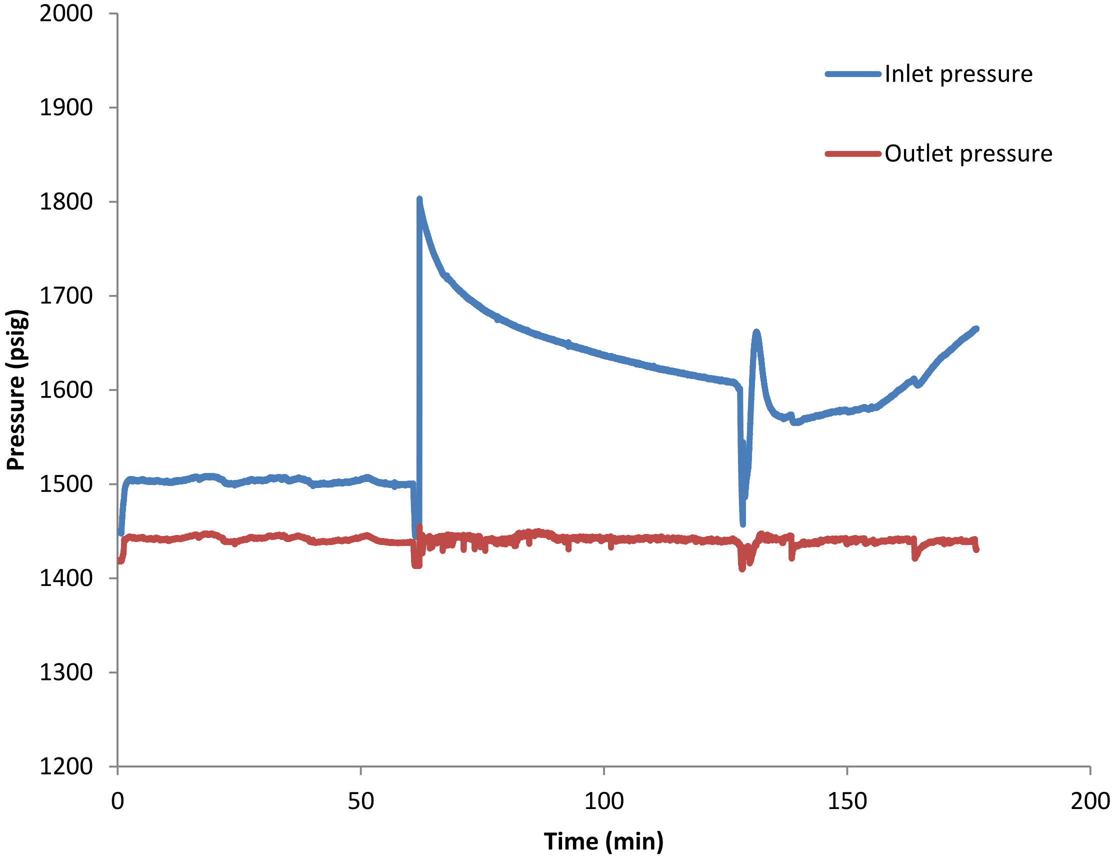

Figure 23. Inlet and outlet pressure during core flood experiment FT-1 (Potosi Dolomite sample VW1-4524.7’). During the first 60 minutes, brine was injected at a rate of 1 ml/min; during the second 60 minutes, CO_2 was injected at a rate of 1 ml/min; and at the 120 minute mark, the brine was injected at a rate of 1 ml/min.

The pressure during the initial period of brine injection in the FT-2 (Figure 24) sample experiment continued to slowly increase during the initial 60 minutes of brine injection and did not quite reach steady state as was observed in experiment FT-1. A 896 kPa(130 psi) pressure differential between the inlet and outlet was measured at the end of 60 minutes of injection. The inlet pressure spiked, as in the previous experiment (FT-1), at the 60 minute mark when the core eluent was switched from brine to $CO_{2.}$ Inlet pressure decreased as CO_2 continued to be injected into the core as was observed in experiment FT-1 while outlet pressure remained relatively constant. After 60 minutes of CO_2 injection, brine was injected but at a lower flow rate than during experiment FT-1 (1 vs. 0.5 ml/min). When the input fluid switched back to brine, the pressure spiked to a lesser extent then the first experiment and remained steady. The flow rate during the second brine injection period was half that of the initial period (0.5 ml/min), resulting in a smaller pressure differential (100 vs. 150 psi [690 vs. 1034 kPa]) between the inlet and outlet during this period. The pressure differential remained relatively steady through the final phase of the experiment, supporting the core effluent chemistry that suggested no significant carbonate dissolution or precipitation.

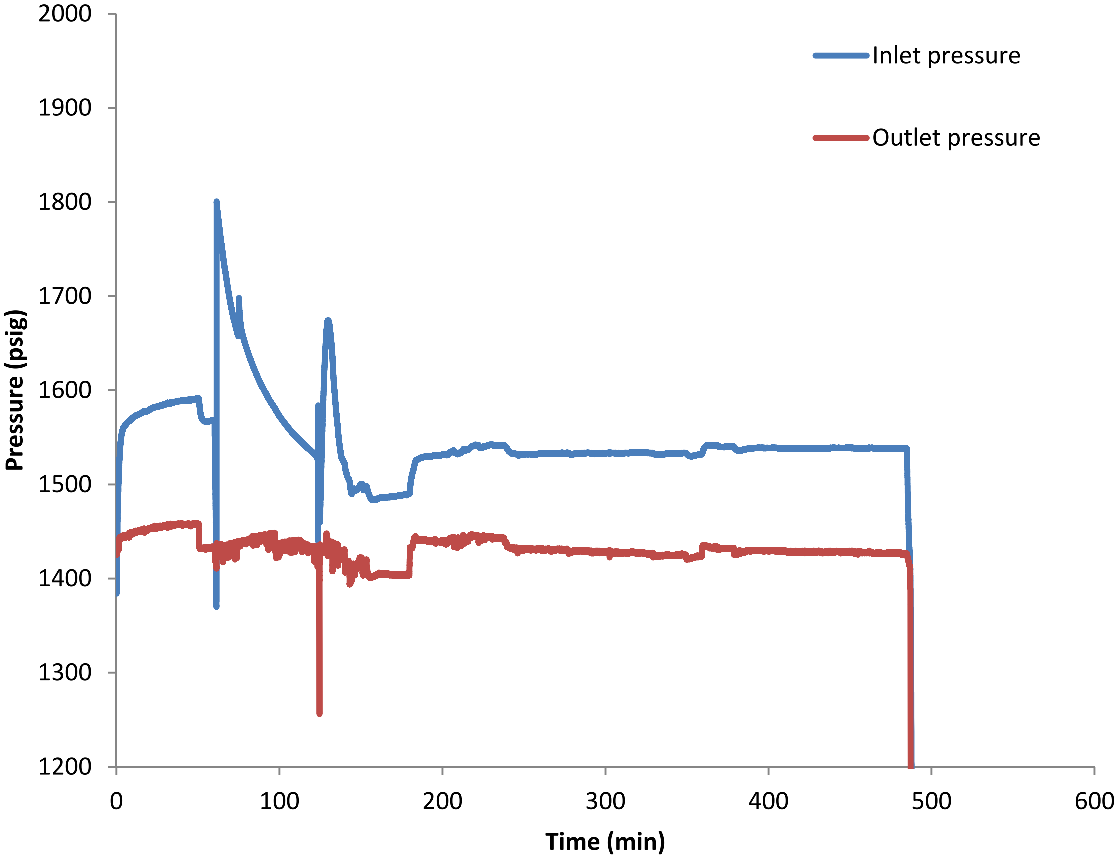

Figure 24. Inlet and outlet pressure during core flood experiment FT-2 (Potosi Dolomite sample VW1-4524.4'). During the first 60 minutes, brine was injected at a rate of 1 ml/min; during the second 60 minutes, CO_2 was injected at a rate of 1 ml/min; and at the 120 minute mark, the brine was injected at a rate of 0.5 ml/min.

Unlike the other core flood experiments using Potosi Dolomite, experiment FT-3 (Figure 25) only had two periods in which fluids injected into the core were compositionally different. During the first 30 minutes DI water was injected and then for the remainder of the experiment DI water and CO_2 were injected. During the initial injection period, the inlet pressure increases about 345 kPa (50 psi) and then decreases to slightly greater than initial pressure conditions. This change in pressure is probably due to the conflicting effects of increasing pressure to establish flow from an unsaturated to saturated condition and mineral dissolution. In the second flow period, the inlet pressure rapidly rises to 1034 kPa (150 psi) and continues to rise during most of the experimental period to almost 12411 kPa (1800 psi). The increasing inlet pressure is likely due to the onset of steady two-phase flow. The subsequent increase in inlet pressure is probably due to either CO_2 coming out of solution and accumulating in the pore space or the clogging of the pore network with mineral particulates that were seen in the effluent.

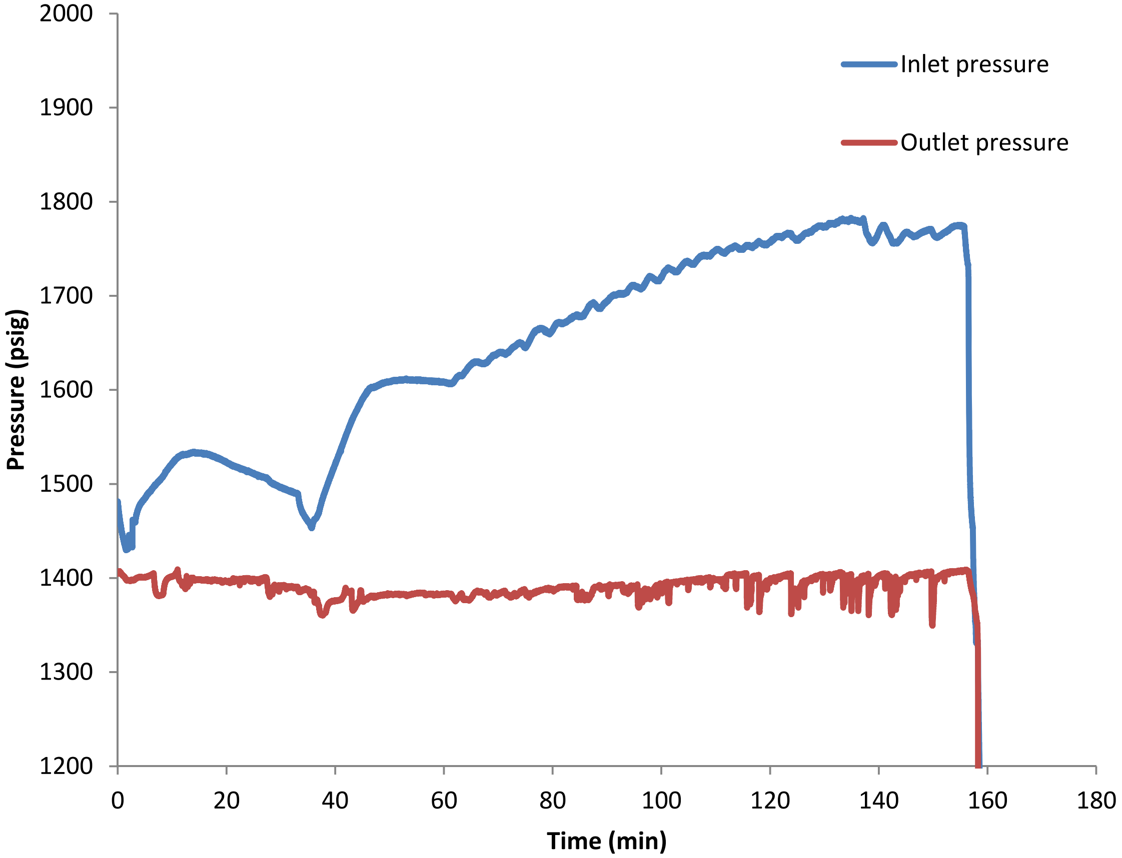

Figure 25. Inlet and outlet pressure during core flood experiment FT-3 (Potosi Dolomite sample VW1-4550.1'). During the first 30 minutes, DI water was injected at a rate of 1 ml/min, and at the 30 minute mark, the DI water and CO_2 were injected at a rate of 1 ml/min and 0.163 ml/min respectively.

<u>Gunter and St. Peter Sandstones (Experiments FT-4 and FT-5)</u>

In both of these experiments, the pressure differential between the inlet and outlet was relatively constant at around 241–276 kPa (35–40 psi) while flow was at steady state. Based on these consistent pressure differentials, the permeability of the cores did not appear to significantly vary during the experiments. However, mechanical difficulties with the back pressure regulator led to unintended variations in the experimental pressures (Figure 26).

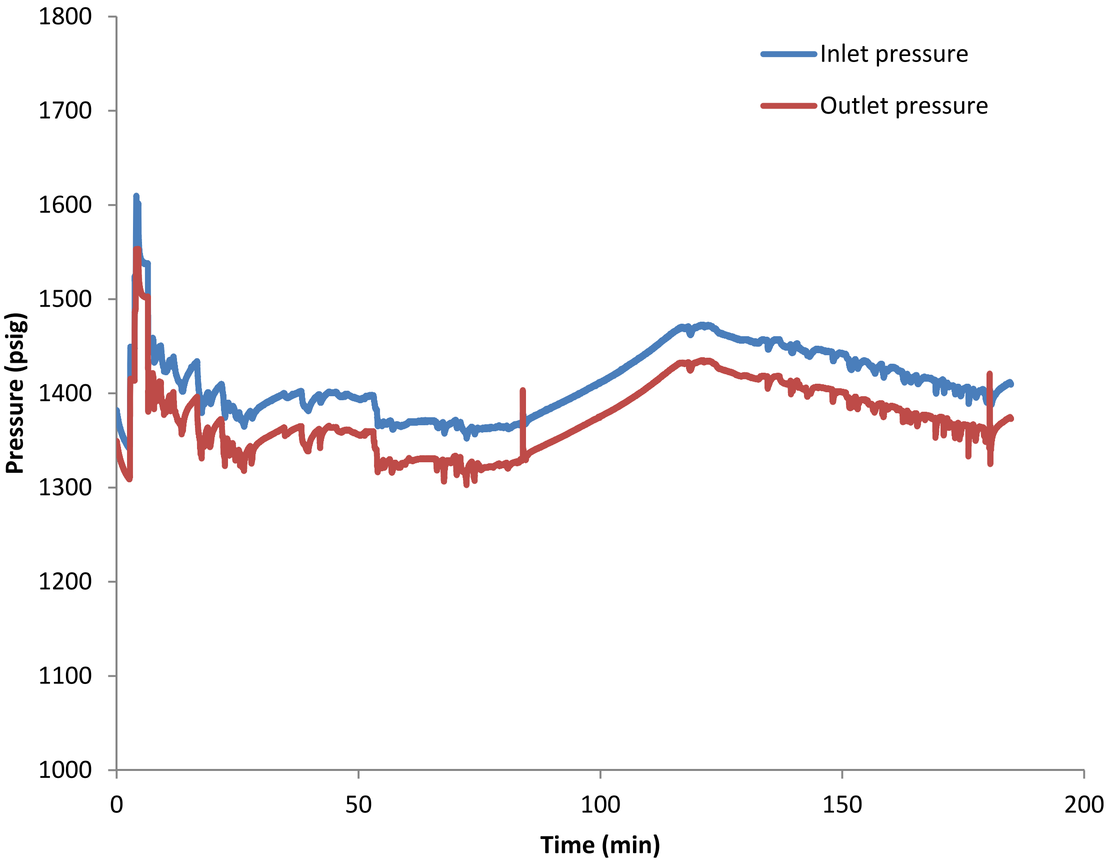

Figure 26. An example of the large pressure variations during a flow through experiment while maintaining a steady pressure differential. Inlet and outlet pressure during core flood experiment FT-4 (Gunter Sandstone sample Kentucky Blan well 5107'). During the first 30 minutes, DI water was injected at a rate of 1 ml/min, and at the 30 minute mark, the DI water and CO_2 were injected at a rate of 1 ml/min and 0.163 ml/min, respectively.

CONCLUSIONS

A total of fourteen laboratory experiments using samples of Knox Group (Potosi Dolomite and Gunter and New Richmond Sandstones), St. Peter Sandstone, and Maquoketa Shale were obtained from various locations throughout Illinois Basin to assess their efficacy and safety as a potential CO_2 sequestration target. This was achieved using laboratory produced synthetic and reservoir brines and CO_2 to simulate actual reservoir conditions to identify the reaction mechanisms, kinetics, and solid-phase products that are likely to occur in each rock unit studied in this project.

- **Potosi Dolomite** samples were subjected to both batch reactor and core flood experiments to simulate rock-CO_2-fluid interactions. Evidence supporting the dissolution of dolomite was observed as etching and pitting of dolomite crystals in petrographic and SEM analysis, decreases in bulk volume of dolomite ranging from 12 to 47% in post-reaction rock samples by XRD, and increases in concentrations of Ca, Mg, Ba, and Sr in post-reaction brine chemistry. Computer modeling suggests that the system reached equilibrium quickly, most likely within 6 hours as observed in the post-CO_2 injection interval fluid chemistry during the core flood experiments. Post-reaction core flood fluid suggests the potential release of Ba, Cu, and Cd as they were observed in concentrations above the USEPA MCL. Arsenic was detected in levels slightly above the analytical MDL and in only two out of 15 flow-through samples run on the Potosi Dolomite. Moreover, it was not detected in any of the Potosi Dolomite batch experiments, and therefore further verification (reproducibility) is suggested for conclusive results. Pressure differential observations made during core flood experiments suggest that, during sequestration activities, an initial spike in injection pressure may occur immediately upon injection as CO_2 forces the brine out of pore space, and then a decrease as CO_2 injection continues, possibly as a result of dolomite dissolution. When CO_2 injection ceases, another pressure spike may occur, possibly because of carbonate precipitation, the onset of two-phase flow, or a combination of the two.

- The **Gunter Sandstone** was subjected to both batch reactor and core flood experiments. Minor etching of dolomite crystal faces and edges was observed in petrographic analysis, along with increases beyond background concentrations of Ca, Mg, Ba, and Sr in post-reaction fluid analysis. Both batch reactor and core flood experiments support dolomite dissolution during Gunter Sandstone-CO_2-fluid interactions. Cadmium was detected in levels above the USEPA MCL, yet only slightly above the analytical MDL in only two analyses in the core flood experiment and not in the batch experiments; therefore, further verification (reproducibility) is suggested for conclusive results. Pressure differential observations were inconclusive because of mechanical difficulties.

- A single batch reactor experiment on the **New Richmond Sandstone** revealed no remarkable change in post-reaction petrography. However, a 12% decrease in bulk dolomite was observed via XRD analysis along with increases in post-reaction fluid concentrations of Ca, Mg, Ba, and Sr beyond background concentrations, both of which strongly suggest the dissolution of dolomite. Additionally, an increase in the concentration of Ba beyond that of the USEPA MCL suggests the potential for mobilization of that constituent as a result of CO_2 sequestration activity.

- A single core flood experiment on the **St. Peter Sandstone** revealed petrographic evidence of some level of reactivity of the clay minerals present, as evidenced by residuum present in the pore spaces in the post-reaction sample. Evidence of this clay reactivity is also observed as increases in the concentration Al, K, and Si in the core flood effluent. Of all of the units studied, the St. Peter Sandstone appears to have the highest potential for the release of USEPA regulated inorganic contaminants. Evidence is seen for the release of As, Ba, Cd, Cr (possible component of experimental equipment), and Se through various stages of the core flood experiments, including the final interval, which suggests that the effects of CO_2 injection may continue on the well after CO_2 injection has ceased. Pressure differential observations were inconclusive because of mechanical difficulties.

- One short-term (43 hour) kinetic experiment was performed on the **Maquoketa Shale.** Computational modeling suggests that mineralogical alterations within the Maquoketa Shale are conservative in nature (dissolution of silicate minerals must have a corresponding precipitation or alteration reaction that keeps these elements in the solid phase), and are therefore unlikely to have a major impact on seal integrity over a 10-year period. Further work is needed to better constrain long-term kinetic rates and validate these results. A comparison of the post-reaction fluid chemistry to USEPA inorganic containment regulations suggests no potential release of the regulated analytes Ba, Cr, and Cu. Results for the regulated analytes As, Be, Cd, Pb, Se and Tl are inconclusive because analytical MDLs are greater than that of the USEPA MCLs. However, the duration of the experiment was very short and should be validated by longer tests.

In summary, the analysis of post-CO_2 reaction rock and brine samples strongly indicate an initially reactive system, as evidenced by the dissolution of dolomite (the dominant mineral present throughout the Knox Group) within the reservoir rocks examined in this study under simulated sequestration scenarios. Mineral speciation calculations using chemistry data of the post-reaction fluid from the batch reactor experiments indicated that the systems reached equilibrium before the end of the 4 month experimental duration, indicating that the effect of this reactivity would likely reach equilibrium shortly after injection of CO_2 into the reservoir ceased. Based on that information, five short-term (approximately 6 hour) core flood experiments were performed. Interpretation of post-reaction brine chemistry and equilibrium modeling of these short-term experiments indicated that they also reached equilibrium.

To provide a context for comparison, the concentrations of those constituents that have USEPA drinking water standards (As, Ba, Be, Cd, Cr, Cu, F, Pb, NO_3, Se, and Tl) were compared to uncorrected (worst case scenario) post-reaction concentrations for both the batch reactor and core flood experiments. Batch reactor experiments indicate that the concentrations of USEPA regulated analytes in brines that had been in contact with CO_2 and Potosi Dolomite and Gunter and New Richmond Sandstone samples for up to 4 months were generally not greater than EPA drinking water regulations for those present in concentrations with analytical MDLs lower than the USEPA MCLs (Ba, Cr, Cu, F, and NO_3). However, results of the analytes As, Be, Cd, Se and Tl are inconclusive because analytical MDLs were up to 150 times greater than the USEPA MCLs. Core flood experiments suggested the potential release of several USEPA regulated analytes (Cu and Cd in Potosi Dolomite, Ba in the New Richmond Sandstone, and As, Ba, and Cd in the St. Peter Sandstone).

According to IBDP site geophysical logs, the Maquoketa Shale is approximately 61 m (200 ft) thick in the central Illinois Basin, and a secondary (New Albany Shale) seal is 40 m (130 ft) thick. Thus, even if significant mineral dissolution occurred in the caprock, it would be highly unlikely that caprock integrity would be in jeopardy given the rapid equilibration of the Knox-CO_2-brine system.

Additionally, waters from the formations in this study are not currently used as drinking water resources because of TDS concentrations greater than acceptable levels (10,000 mg/L). Migration of these waters into formations containing potable waters would likely result in dilution with the less mineralized potable water. Results from the batch and core flood experiments that indicate that constituent leaching from these formations is relatively small with concentrations less than MDLs or MCLs and that a dilution of these reaction brines of 150 (based on MDLs) would likely result in all constituents being at acceptable levels.

Interpretation of the limited pressure curve data from the Potosi Dolomite core flood experiments suggests that displacement of brine by CO_2 in the core pores, mineral dissolution and/or precipitation, and changes in fluid and pore CO_2 saturation may impact pressure regimes during sequestration activities.

Results from this study and work that continues at the ISGS will aid in the development of improved methods for similar studies and provide needed data for computational modeling relevant to the Illinois Basin and elsewhere. Data from this study and further modeling efforts will provide information about the ability for deep saline reservoirs and shale seal rocks to safely store injected CO_2 while minimizing the likelihood of contamination.

REFERENCES

American Public Health Association (APHA), American Water Works Association, and Water Environment Federation, 2005, Standard Methods for the Examination of Water and Waste Water, 21st ed.: American Public Health Association, Washington, DC.

Bateman, K., C. Rochelle, A. Lacinska, and D. Wagner, 2011, CO_2-porewater-rock reactions – Large-scale column experiment (Big Rig II): Energy Procedia, v. 4, p. 4,937–4,944.

Bethke, C.M, 1996, Geochemical Reaction Modeling: New York, Oxford University Press.

Chen, C., 1999, Lithium: Element and geochemistry, *in* C.P. Marshall, and R.W. Fairbridge, eds., Encyclopedia of geochemistry: Kluwer Academic Publishers, p. 369–370.

Duan, Z., N. Moller, and J.H. Weare, 1996, A general equation of state for supercritical fluid mixtures and molecular dynamics simulation of mixture PVTX properties: Geochemica Cosmochimica Acta, v. 60, p. 1,209–1,216.

Finley, R.J., S.M. Frailey, H.E. Leetaru, S. Ozgur, M.L. Coueslan, S. Marsteller, 2013, Early Operational Experience at a one-million tonne CCS demonstration project, Decatur, Illinois, USA: Energy Procedia, v. 37, p. 6,149–6,155.

Finley, R.J., S.E. Greenberg, S.M. Frailey, I.G. Krapac, H.E. Leetaru, and S. Marsteller, 2011, The path to a successful one-million tonne demonstration of geological sequestration: characterization, cooperation, and collaboration: Energy Procedia, v. 4, p. 4,770–4,776.

Jacobson, R.L., and H.E. Usdowski, 1976, Partioning of strontium between calcite, dolomite, and liquids: an experimental study under higher temperature diagenetic conditions, and a model for the predication of mineral pairs for geothermometry. Contributions to Mineralogy and Petrology 59, p. 171–185.

Krapac, I.G., 1987, Assessment of oxygen depletion by inorganic constituents at the Pittsfield, Illinois Compressed Air Energy Storage Site: University of Illinois, M.S. thesis, 176 p.

Lasaga, A., 1984, Chemical kinetics of water-rock interactions: Journal of Geophysical Research, B 89 B6, p. 4,009–4,025.

Lui, F., P. Lu, C. Griffith, S.W. Hedges, Y. Soong, H. Hellevang, and X. Chen, 2012, CO_2-brine-caprock interaction: reactivity experiments on Eau Clare shale and a review of relevant literature. International Journal of Greenhouse Gas Control 7, p. 153–167.

Lyons, W.B., and K.A. Welch, 1997, Lithium in waters of a polar desert. Geochimica et Cosmochimica Acta 61, p. 4,309–4,319.

Meents, W.F., A.H. Bell, O.W. Rees, and W.G. Tilbury, 1952, Illinois oilfield brines: their occurrence and chemical composition. Illinois Petroleum 66, 37 p.

Plummer, L.N., D.L. Parkhurst, G.W. Fleming, and S.A. Dunkle, 1988, A computer program incorporation Pitzer's equations to calculations of geochemical reactions in brines: U.S. Geological Survey, Water-Resources Investigations Report 88, p. 4,153.

Poeter, E.P., M.C. Hill, E.R. Banta, S. Mehl, and S. Christensen, 2005, UCODE_2005 and Six Other Computer Codes for Universal Sensitivity Analysis, Calibration, and Uncertainty Evaluation: U.S. Geological Survey, Techniques and Methods 6-A11.

Shen, G.T., and E.A. Boyle, 1988, Determination of lead, cadmium, and other trace metals in annually banded corals. *Chemical Geology* 67, 47–62.

Wolery, T.J., 1992, EQ3/EQ6, a software package for geochemical modeling of aqueous systems, package overview and installation guide (version 7.0): Lawrence Livermore National Laboratory, Report UCRL-MA-110662.