

GHGT-11

Mineralogical alterations during laboratory-scale carbon sequestration experiments for the Illinois Basin

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Abstract

During geological sequestration of carbon dioxide, the injected CO₂ will react with formation fluids and rocks in the injection zone and overlying cap rocks. The resulting acidification of the fluids may result in the dissolution of solid phases and the formation of new solid phases which can cause changes in rock composition and overall fabric. We are conducting laboratory-scale geochemical and mineralogical studies on reservoir and cap rock samples in the Illinois Basin that complement the on-going Illinois Basin - Decatur Project (IBDP), a large-scale one million tonne demonstration of geologic sequestration in the Mt Simon Sandstone, Illinois USA. Mt. Simon Sandstone, Eau Claire Shale, and Knox Supergroup samples from the IBDP injection and deep monitoring wells and locations with rocks analogous to those at the IBDP site have been selected for simulated reactions using synthetic brine and CO₂ in modified Parr pressure reactors at pressure and temperature conditions that correspond to ambient reservoir conditions (9.87 to 20.7 MPa and 38 to 50 °C) and for varying amounts of time (1 to 9 months). Using petrographic techniques and XRD analysis, samples have been analyzed before and after reactor experiments to define the mineralogical and textural baseline and report observed changes. Brine composition has also been analyzed for geochemical changes. The React[®] and Differential Evolution geochemical modeling programs are being used to simulate changes in mineral mass and brine chemistry. Post-reaction analyses of rock and brine samples from the Mt. Simon Sandstone show evidence of dissolution of diagenetic clays, increased porosity, and possible illitization of clay minerals. Three, six, and nine month post-reaction Eau Claire Shale rock and brine sample analyses indicate some degree of brine-rock-CO₂ reaction by showing weathered illite, mixed clay, feldspar, biotite, and pyrite crystals. Post-reaction Potosi Dolomite rock and brine samples show evidence of dissolution of dolomite. Overall, petrographic and geochemical observations from these experiments suggest that the Mt. Simon Sandstone reservoir and Eau Claire cap rock system serve as good CO₂ sequestration site. The competency of the Knox Supergroup as a CO₂ sequestration target is still under investigation.

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Keywords: Geologic sequestration; Illinois Basin; experimental; geochemistry; mineralogy; petrology; geochemical modeling

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1. Introduction

Emerging geologic CO₂ sequestration technology offers a promising solution to the reduction of carbon emissions from anthropogenic activities. The International Panel on Climate Change assessed this concept [16] as a potential technique for mitigation of greenhouse gases and geologic CO₂ sequestration is presently the focus of many of studies throughout the world e.g., [17][18][19]. Several pilot projects are now underway, some of the most promising results coming from projects that focus on injecting CO₂ into deep saline reservoirs. Illinois currently produces approximately 265.6 tonnes CO₂ annually from a variety of fixed sources. The sequestration capacity of the Illinois Basin is in the range of 12 to 161 billion tonnes in deep saline reservoirs that meet the geological requirements needed for long-term storage, making it an excellent target for sequestration [20].

The Illinois Basin – Decatur Project (IBDP) is a large-scale one million tonne demonstration of geologic sequestration in the Mt Simon Sandstone currently injecting CO₂ from an Archer-Daniels-Midland Company (ADM) ethanol plant in Decatur, Illinois. Regularly occurring geophysical surveys provide information on the plume size and position and a verification well drilled approximately 400 meters from the injection well allows access to the reservoir for brine and gas sampling. Understanding the geochemical interactions of the plume is necessary for determining the type of sequestration taking place (solubility, mineral, hydrodynamic trapping) and cap rock integrity. Numerous geochemical modeling studies of sandstone formations have been conducted e.g., [1][2][3][4][5][6][7] and the observation common to each of these studies was that the chemical reactivity of the sandstone was highly dependent on the concentration of feldspar and clay minerals, which are generally more chemically reactive than the quartz-rich sandstone. The observations made by studies of carbonate rocks and reservoirs e.g., [2][8][9][10][11][12] include evidence of the dissolution of dolomite, an increase of Ca and Mg in reacted brines, and that carbonates that contain Fe, Mg, and Ca have less CO₂ mineral trapping potential than that of siliciclastic reservoirs. Additionally, several studies looked specifically at the Knox Supergroup and its discrete vuggy zones of increased porosity and permeability [13][14][15] for site selection of waste injection in Illinois and Kentucky [13][14].

During geological sequestration, the injected supercritical CO₂ will react with formation fluids, reservoir, and cap rocks. The resulting acidification of the fluids may result in the dissolution or formation of solid phases which can cause changes in mineral composition and rock fabric. The purpose of this study is to evaluate supercritical CO₂-brine-rock interactions by conducting laboratory-scale batch experiments on rocks from the Mt. Simon Sandstone reservoir, Eau Claire Shale cap rock, and Knox Supergroup reservoir while simulating pressure and temperature conditions present at the IBDP site.

2. Methodology

2.1 Sample selection

When possible, we obtained samples from wells at the IBDP site for this study. We selected five Mt. Simon Sandstone samples from the CCS - #1 well core that exhibit different textures at depths of 6409.3 ft. (1953.6 m), 6414.7 ft. (1955.2 m), 6423.75 ft. (1958 m), 6757.6 ft. (2059.7 m), and 6776.6 ft. (2065.5 m). We chose four Eau Claire Shale samples from the CCS - #1 well core with slightly different

textures and compositions at depths of 5485.2 ft. (1671.9 m), 5488.2 ft. (1672.8 m), 5491.4 ft. (1673.8 m) and 5500.3 ft. (1676.5 m). Initially, Knox Supergroup samples from the IBDP site were not available and much of the initial experimental work within this unit focused on two Potosi Dolomite samples (MO-1-9A and MO-1-9B) collected from outcrop locations in the western portion of the Illinois Basin, in and around Potosi, Washington County, Missouri. The Potosi Dolomite is of particular interest to this study because of the extensive network of vugs that occur across the Illinois Basin (from the IBDP site to Potosi, Missouri). More recently, several experiments were completed on Potosi Dolomite from IBDP Verification #1 well core and the results are currently being analyzed.

2.2 Experimental procedure

Each rock sample was split into a several smaller, roughly homogenous units of approximately 20 grams for pre- and post-reaction experiment analyses. One portion of each sample was placed into a modified stainless steel Parr pressure vessel fitted with a Teflon[®] liner to minimize interaction between the brine-rock-CO₂ experiments and the stainless steel pressure vessel wall. Each vessel was filled with 200 mL of synthetic brine to make an approximately 1:10 solid to liquid ratio. Unique synthetic brines were formulated for each unit (Mt. Simon Sandstone, Eau Claire Shale, and Knox Supergroup) containing Na, Ca, K, Mg, Li, Sr, Cl, B, and SO₄ based measured and historical Illinois Basin data [21]. After assembly, each vessel was filled with research grade CO₂, brought to near reservoir pressure conditions using a displacement pump and placed in an air bath at reservoir temperature (Table 1). The pressure conditions within the experimental vessels typically stabilized within 24 to 48 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/or 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 fluids were immediately monitored for temperature, pH, and Eh for 10 minutes while maintaining the experimental temperature. We then filtered the fluid through a 0.45 µm MCE membrane and preserved it for chemical analyses. The rock sample was dried and reserved for petrographic and mineralogical analyses.

Table 1: Experimental conditions for the Mt. Simon Sandstone, Eau Claire Shale, and Knox Supergroup-Potosi Dolomite experiments.

Unit	Pressure (MPa)	Temperature (°C)	Experimental duration
Mt.Simon Sandstone	20.7	50	6 month
Eau Claire Shale	16.8	42	3, 6, and 9 month
Knox Supergroup - Potosi Dolomite	9.87	38	3 month

2.3 Analytical techniques

A variety of different 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 Illinois State Geological Survey (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). Additional high resolution mineralogical and textural characterization of shale samples using QEMSCAN and iDiscover image analysis software was performed by Advanced Reservoir Quality Services, SGS Canada, Inc. Semi-quantitative mineralogical analyses were performed at the ISGS X-Ray diffraction (XRD) Lab using random bulk-pack and orientated clay mineral slides analyzed with a Scintag[®] XDS2000. Step-scanned data was collected from

2° to 34° 2 θ for clay mineral analysis and 2° to 60° 2 θ for bulk mineral analysis with a fixed time of 5 seconds per 0.05°2 θ 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 the inductively coupled plasma-atomic emission spectrometry and ion chromatography facilities at the Illinois State Water Survey (ISWS) and the ISGS using the most current U.S. EPA methods [22] [23].

2.4 Geochemical modeling

To match the results of the Mt. Simon and Eau Claire experiments, the starting brine and mineral composition was input into a batch model run with React [24]. The model had a fixed CO₂ fugacity set according to the pressure and temperature of the experiment [25]. The program Differential Evolution [26] then iteratively adjusted the kinetic constraints of the silicate minerals to find the best fit to the changes in brine chemistry and mineralogy. The kinetic constraints for carbonates, pyrite, and amorphous silica were constants set high enough that the minerals were essentially at equilibrium throughout the simulation.

For Knox experiments, the method of modeling results differed because the minerals in the batch reactors reached equilibrium before the end of the experiment. We input final composition into a model where CO₂ fugacity increased to experimental conditions and then varied to pH to find the conditions where the carbonate minerals were at equilibrium. The model used Pitzer equations and database [27] to calculate the carbonate equilibrium state and the extended b-dot equations and database [28] for silicate minerals.

3. Results

3.1 Mt. Simon Sandstone experiments

The Lower Mt. Simon Sandstone samples chosen for this study are Cambrian fluvial-braided river and fluvial-eolian-playa/interdune sandstones. The fluvial braided river material is characterized by coarse-grained, cross bedded sands and conglomerates with relatively large pore throats and good interconnectivity. The fluvial-eolian-playa/interdune material is characterized by medium- to fine-grained, cross bedded, planar and ripple laminated, mottled sandstones [29]. Pore space is abundant; however the samples had relatively poor connectivity due to the large amount of clay minerals in pore throats. Samples from both depositional environments are mostly arkosic; containing clay lined quartz grains, feldspar, and matrix clay minerals. Porosity is predominantly framework with some secondary porosity resulting from potassium feldspar dissolution. Diagenetic minerals such as mixed-layered illite, chlorite, and authigenic quartz occlude pore space and commonly clog pore throats [29][30].

After exposure to the acidified brine for 6 months, the samples had very little physical change in macroscopic scale other than subtle color change in the coarser-grained material. We observed decreased amounts of clay surrounding quartz grains in petrographic samples (Fig. 1, (A) and (B) and Fig. 2) [29][30]. XRD analyses indicated little change in bulk mineral composition in the post-reaction samples. Although inconclusive due to limitations of quantification (it is difficult to identify small volumes of clay minerals in the quartz dominated sandstone with XRD), from bulk clay mineral XRD traces it appeared that illite k-alpha peaks were more intense in pre-reaction samples and expandable clay peaks were less intense in post-reaction samples; qualitative SEM-EDX observations appear support illitization (Fig. 2). Studies involving the Taiyuan Formation of the northeast Ordos Basin observed a similar illitization process involving the replacement of kaolinite [31]. The chemical compositions of the post-reaction brines indicate no significant change in chemistry.

3.2 Eau Claire Shale experiments

The Eau Claire Shale samples selected were from the IBDP CCS - #1 well core and are Cambrian shallow marine (upper shore face to offshore below storm wave base) mudstones characterized

by interstratified, planar laminated and wavy bedded siltstone, very fine-grained sandstone that are commonly bioturbated. Compositionally, these samples contain predominantly potassium feldspar, Fe-illite and illite-smectite clays; some of the shales are interbedded with glauconitic siltstone [29].

The 3, 6, and 9 month post-reaction sample all had an increased friability and significant color change (from dark grey to rust red color) on surfaces exposed to the acidified brine and in macroscopic scale. Due to the opaque nature of shale in transmitted light, analyses performed using polarizing light microscopy were limited to observations of grain size sedimentary structure. Three month samples analyzed by SEM-EDS had weathered illite and mixed clay, potassium feldspar, biotite, and pyrite crystals. The 6 and 9 month experimental samples both had continued weathering and degradation and areas where feldspar, biotite, and pyrite crystals preferentially dissolved from the clay matrix. Bulk and clay mineral XRD traces of pre- and post-reaction 3, 6 and 9 month experiments detect little change in composition. It should be noted that 6 month pre- and –post-reaction results had a significant change in bulk percentage of illite and chlorite, and, the intensity of the chlorite and illite peaks diminish as the experimental duration increases (Fig. 3). There was an increase in the 3 and 6 month post-reaction brines of Ca, Mg, Si, and K and a decrease in S in the 6 month experiments relative to the 3 month experiments. Nine month fluid analyses have not been completed.

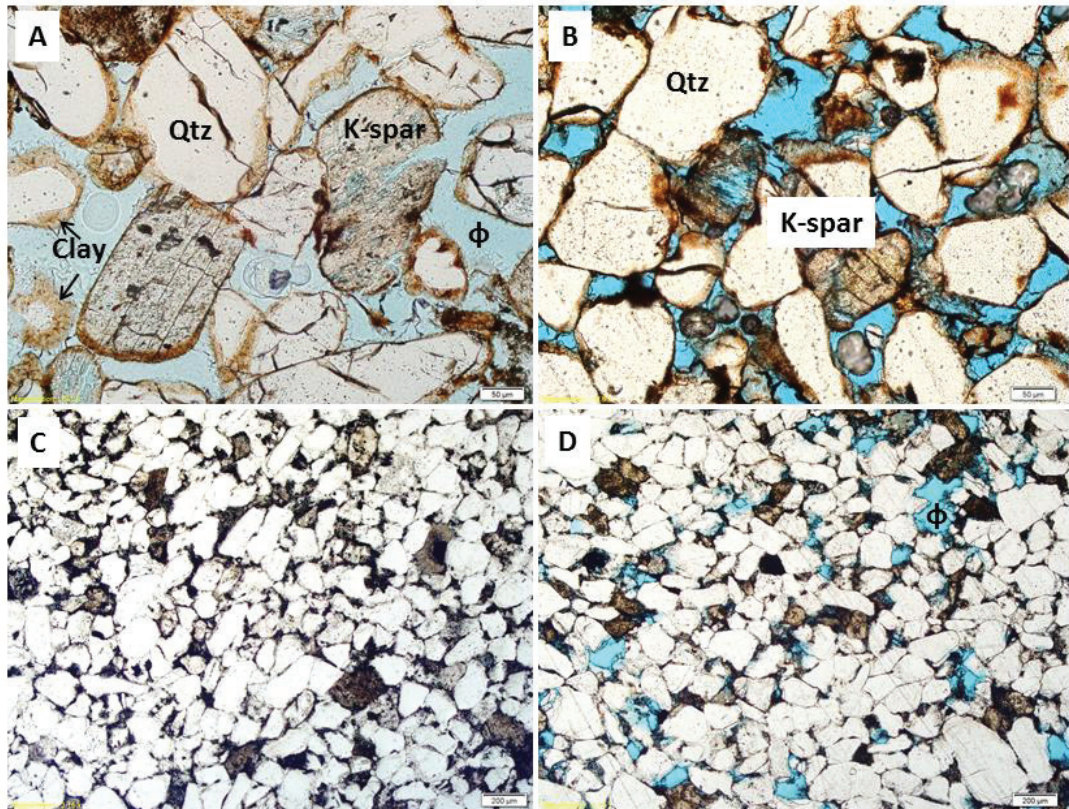


Figure 1: Pre (A, C) and post-reaction (C,D) photomicrographs of Mt. Simon Sandstone. Note the decrease in thickness of clay lining around quartz crystals from image A to B. Image D shows an average porosity increase of 6.4% from image C due to clay loosening and dissolution/alteration (porosity analysis performed using Olympus Stream Image Analysis Software phase analysis). Images A and B are from sample depth 6757.6 ft. (2059.7 m) and images C and D are from sample depth 6414.7 ft. (1955.2 m). Qtz = quartz; K-spar = potassium feldspar; ϕ = porosity. Modified from [30].

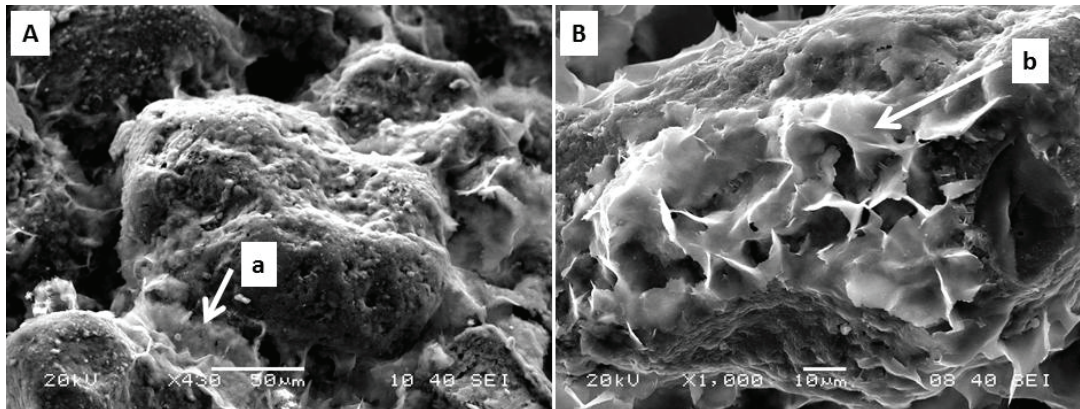


Figure 2: SEM images of pre- (A) and post-reaction (B) Mt. Simon Sandstone sample 6757.6 ft. (2059.7 m). Each image shows a clay coated quartz grain. Arrow (a) shows massive clay filling pore space between two quartz grains in the pre-reaction sample. Arrow (b) shows illite filling the pore space and the massive clay now non-existent or present in trace amounts in the post-reaction sample.

3.3 Knox Supergroup-Potosi Dolomite experiments

The Potosi Dolomite samples selected for this study are from the basal-most formation within the Knox Supergroup and include Cambrian and Ordovician-age strata dominantly comprised of dolomite with relatively thinner sandstone formations. The environment of deposition is mostly sub-tidal environment and consists of highly dolomitized mudstones and wackestones with the occasional digitate stromatolite bed. Collapse breccias are common with sucrosic dolomite matrixes. Fractures occur with apparent dolomite alteration occurring along fractures which commonly intersect mm- to cm-scale vugs. The vugs are lined with multiple generations of dolomite, chalcedony, and mega-quartz cements. Chalcedony and mega-quartz cements are most prominent in larger solution enhanced vugs, as where the smaller vugs are lined only with dolomite. The potential reservoir rocks in the Potosi include sucrosic dolomite matrixes in collapse breccias, vuggy intervals in digitate stromatolite beds and near fractured sections in the formations, and cavernous zones that are mostly planar subhedral dolomites with very low matrix porosity and contain mm- to cm-scale vugs [13].

In post-reaction samples there was no noticeable change along edges and vugs exposed to CO₂-brine water solution under polarized-light and cathodoluminescent light microscopy. However, under high magnification ($\leq 10 \mu\text{m}$) SEM, we observed evidence of dissolution along the edges of dolomite crystals in some areas of both MO-1-9A and MO-1-9B; the pristine dolomite rhombohedra of the unreacted samples appeared pitted and jagged along crystal faces of the post-reaction samples (Fig. 4). In post-reaction bulk mineral XRD analyses of sample MO-1-9A there was an increase from about 80% dolomite in the pre-reaction sample to 90% dolomite post-reaction sample. Post-reaction chemical analyses of the brine had an increase beyond background levels of Ca, Mg, and Si.

4. Discussion

The increased porosity observed in the post-reaction Mt. Simon Sandstone experiments was likely a result of loosening (evidenced by clay residue in unfiltered post-reaction brine) and dissolution of lined quartz and matrix clays (Fig 1, (C) and (D)). Although geochemical modeling suggested that illite formation was unlikely, results from XRD and SEM-EDX analyses (Fig. 2) indicate that some type of illitization of the clay minerals occurred; similar results have been reported by [32], and references therein. Long term modeling predicts precipitation of potassium feldspar; however this has yet to be observed. Chemical analyses of the 6 month Mt. Simon Sandstone experimental brine has not revealed any evidence of other significant CO₂-brine-rock interaction. We are currently performing several single-

phase (microcline) experiments due to the predicted reactivity of potassium feldspar. Additionally, longer term experiments (1 year +) are being proposed.

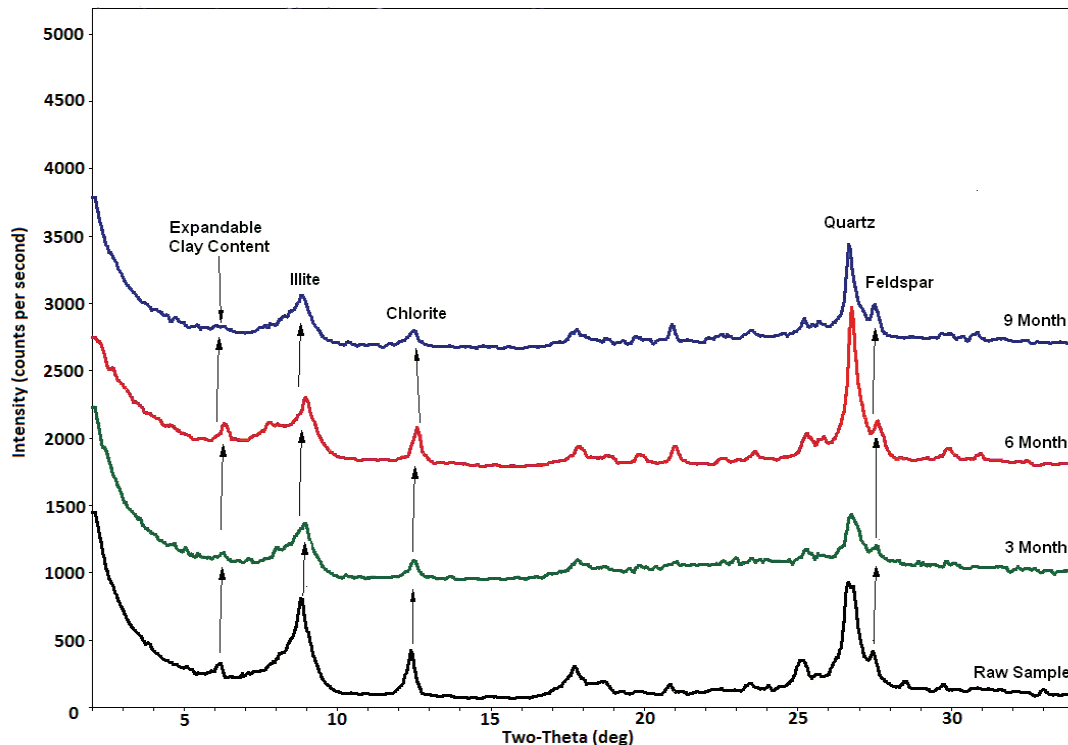


Figure 3: Overlay of multiple XRD traces for ethylene-glycol treated, orientated clay minerals of samples exposed to varied periods of time in reaction vessels from the Eau Claire Shale sample at a depth of 5488.2 ft. (1672.8 m). Peak ratios of illite and chlorite do not change dramatically with increased time in reaction vessels. Semi-quantitative analysis of the clay minerals shows the samples to have about 85% illite and 8% chlorite. What is noticeable is the shape of the k-alpha peaks for the minerals present. They become broader and less pronounced with more time in the reaction vessels. This could be from weathering effects (seen in SEM) impacting the crystal structure and the subsequent x-ray reflections from these samples.

The color change and increased friability, along with mineral weathering and degradation observed in SEM-EDS and XRD analyses of the post-reaction Eau Claire Shale indicate some degree of brine-rock-supercritical CO₂ interaction under reservoir conditions, and evidence of this is seen in qualitative SEM-EDS analysis. As noted above, the intensity of the chlorite and illite peaks diminished as the experimental duration increased (Fig. 3). This is likely a result of the crystals becoming increasingly weathered over time (as seen in the qualitative SEM-EDS observations) causing the quality of the XRD reflections to diminish. Also noted above, the 6 month pre- and –post-reaction results of sample 5488.2 ft. (1671.9 m), had a significant change in percentage of illite and chlorite when compared to those of the pre-reaction 3 and 9 month experiments. We believe that this is most likely the result of sample heterogeneity and is a result that can be dismissed. Post-reaction chemical analyses of the brines support dissolution, as the values for Ca, Mg, Si, and K were greater in the 6 month experiments relative to the 3 month experiments. There was a decrease in S seen in the 6 month experiments relative to the 3 month experiments, which may suggest the precipitation of an S-rich phase, however this is not observed in the XRD results which may indicate that was a result of sample heterogeneity and/or that S was present in an amorphous state. Results from the Eau Claire Shale experiments support some degree of chemical reactivity when exposed to the acidified brine at reservoir conditions; however, it was difficult to quantify

the magnitude of this reactivity, the rate at which it was occurring and its effect on porosity and permeability. Further studies and geochemical modeling should yield more quantifiable results.

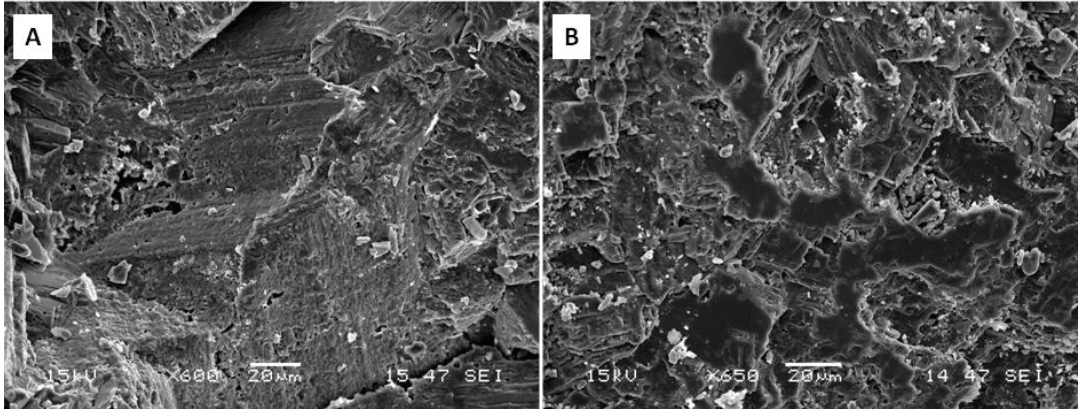


Figure 4: SEM images of pre- (A) and post-reaction (B) Potosi Dolomite sample MO-1-9A. (A) Pre-reaction sample shows dolomite crystals that are slightly pitted in areas but mostly clean of defects and (B) shows extremely etched dolomite crystals and dissolution features.

Pitting and degradation of dolomite crystals observed in SEM-EDS analyses and the increase beyond background levels of Ca, Mg, and Si in brine support dissolution of dolomite in post-reaction Potosi Dolomite samples. Similar brine chemistry results have been reported by others [8]. 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 analytical uncertainty which is very difficult to account for. For example, the 10% increase in bulk dolomite may have been an artifact of sample heterogeneity and not a true experimental result. The effects of various types of vugs on the dissolution of the potential reservoir or the formation of new solid phases are currently under study.

Table 2 contains the optimized kinetic constraints for the Mt. Simon and Eau Claire experiments. In the Eau Claire models, K-feldspar and non-illite clays dissolved and precipitated as Illite. The quartz fraction remained inert throughout and the final observed silicic concentration was roughly at equilibrium with amorphous silica for both models. Overall, the kinetic rates from the Mt. Simon experiments are slightly faster than the Eau Claire, which is logical considering the Mt. Simon experiments ran at a higher temperature. The inertness of quartz in an acidic environment explains the very low kinetic constraints obtained for the mineral in both sets of experiments. The precision of the kinetic rate for quartz was limited by the difficulty in measuring the small amount of change in quartz mass over the experiments. The models calculated that illite should precipitate in the Eau Claire experiments and dissolve in the Mt. Simon experiments while the reverse was true for k-feldspar. The discrepancy of the rates for these two minerals between sets of experiments was therefore probably the difference between precipitation and dissolution.

Table 2. Kinetic constraints on mineral dissolution and precipitation normalized to $1 \text{ cm}^2/\text{g}$ for the Mt. Simon Sandstone and Eau Claire Shale.

	Eau Claire Shale mole/m ² /s	Mt. Simon Sandstone mole/m ² /s
Smectite	9.76E-07	9.55E-07
Illite	1.28E-08	9.31E-07
Kaolinite	1.56E-07	8.03E-07
Chlorite	7.51E-07	5.81E-07
Quartz	3.31E-14	3.80E-12
K-feldspar	8.31E-07	8.04E-08

According to the speciation calculations we made for the Knox experiments, the brine was at equilibrium with amorphous silica. Assuming equilibrium with dolomite and calcite, the pH inside the reactors during the experiments were approximately 4.7 (Fig. 5). The measured pH values, once the reactors were open, were slightly higher than the calculated values. The experiments on Knox 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 Knox do not need kinetic constraints to create an accurate picture of reservoir processes. The small discrepancy between measured and calculated pH values was probably due to degassing after the reactors depressurized.

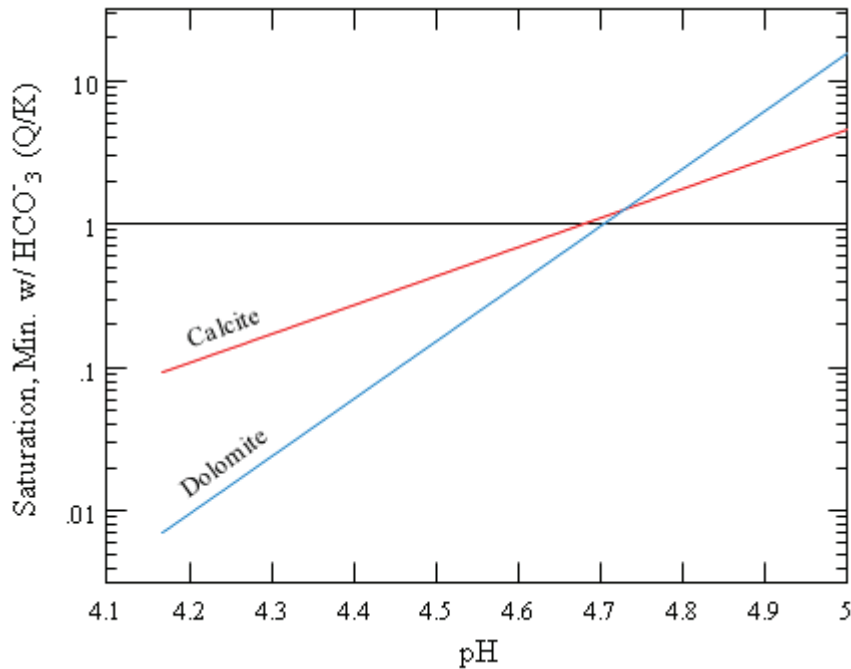


Figure 5. Saturation state of calcite and dolomite as a function of pH in the Knox experiments.

5. Preliminary conclusions

- Petrographic and geochemical observations suggest that the low level of chemical reactivity of the Mt. Simon Sandstone and increased porosity enhanced by clay-mineral dissolution may increase its capacity to accept CO₂.
- Eau Claire Shale experiments support some degree of chemical reactivity when exposed to supercritical CO₂ at reservoir conditions; however, it is difficult to quantify the magnitude of this reactivity, the rate at which it is occurring and its effect on porosity, permeability, and overall competency of the Eau Claire shale to serve as a cap rock.
- Petrographic and geochemical analyses appear to support dissolution of dolomite within the Potosi Dolomite when exposed to supercritical CO₂. The effects of various types of vugs in the Potosi Dolomite on the dissolution of the potential reservoir or the formation of new solid phases are unclear and currently under study.

Acknowledgements

We thank Hannes Leetaru, Rob Finley, Riley Hoss, Ashley Howell and Brittany Schnepel of the Illinois State Geological Survey. This research is funded by the United States EPA-Science to Achieve Results (STAR) Program Grant # 488220 and by the U.S. Department of Energy through the National Energy Technology Laboratory (NETL) and by a cost share agreement with the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development through the Illinois Clean Coal Institute.

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