The Impact of Reactive Surface Area on Brine-Rock-Carbon Dioxide Reactions in CO₂ Sequestration

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Abstract

Injection of carbon dioxide into saline aquifers is one the most promising methods for mitigating the increase in atmospheric CO₂ concentrations. Reactions of CO₂ with brine and formation rocks are important in determining the ultimate fate of CO₂. Rates of reactions of the different relevant minerals are dependent on rate constants and mineral surface area. It is important to quantify the effect of surface area on reaction rates when different types of rock samples are employed in experiments. Batch experiments with different forms of the Berea sandstone were set up and performed at high pressure (2,000 psi) and reservoir temperature (60 °C) for two-week under reservoir CO₂ sequestration conditions. Experiments were performed with markedly different samples (cores, rock chips, and powdered) with progressively increased surface areas. Experiments with the different forms of sandstones showed similar trends in major minerals dissolution with increase in cation concentrations of iron, magnesium, and calcium in

the effluent brine. Under realistic aquifer pressure and temperature conditions, iron chemistry plays an important role in the dissolution reactions in the Berea sandstone. Reactivities increased leading to larger cationic concentrations in brine (as determined using ICP-MS) as the surface areas increased. Morphology of the reacted volume was viewed using QEMSCAN and Micro-CT for core plug samples. These experiments helped quantify the effect of surface area (higher surface area leading to more dissolution) and revealed that reactions appear to be limited more to the surface in Berea sandstone. It was shown that the factor used to obtain geometric surface area from a core decreased when samples with higher surface areas were used. This indicated that some internal surface area became available for fragmented (fractured), and powdered samples. Mineral dissolution caused the growth and expansion of pores in Berea sandstone and surface area measurements (BET) showed that the new porosity generated was characterized by a smaller pore size distribution in comparison to the unreacted one.

Keywords: Carbon dioxide Sequestration, BET surface area, Reactive surface area

1. Introduction

Fossil fuels are still dominating the total world energy consumption because of low cost, high energy density and abundant supply. Use of fossil fuels results in large amounts of emissions of CO₂ into the atmosphere. Certain industrial processes such as cement making and land use change also emit CO₂ [1-3]. It is important to address the growing anthropogenic emissions by considering geologic sequestration [4, 5]. Geological storage of CO₂ has grown and could help to make deep cuts to atmospheric CO₂ emissions. However, for the potential to be realized, geological storage must be the technically safe, environmentally sustainable, and

capable of being broadly applied. CO₂ dissolves in saline aquifer to form carbonic acid which reacts with host rocks causing dissolution and precipitation. This reactive environment causes changes in porosities and permeabilities in the rock-brine interface near a wellbore [6]. The rock phases become soluble and release cations that buffer the water's acidity. Field-scale studies of wellbore exposed to CO₂-rich fluids for years show significant reaction [7-9].

Peysson et al. (2014), Oh et al. (2013), Bacci et al. (2011), and McMillan et al. (2008) reported experimental studies on dissolution of host rocks in a CO₂ sequestration setting [10-13]. Modeling studies have predicted that dissolution/precipitation will occur when supercritical CO₂ is injected into a brine-saturated saline aquifer (Kim et al. (2012), Alkan et al. (2010), André et al. (2007)[14-16]). Development of process simulation models requires a good understanding of the dissolution and precipitation processes. Zhu et al. (2006), Beig and Lüttge (2006), and Lasaga and Lüttge (2001) proposed a number of mineral dissolution mechanisms [17-19]. Lüttge (2006) also described that rapidly dissolving mineral layers are dominated by dissolution at point defects on crystal edges and corners [20]. Most geochemical modelers such as Hellmann et al. (2010) and Arvidson and Lüttge (2010) use a general equation based on the transition state theory to incorporate rate-controlling mechanisms into an overall rate law [21, 22]. The rate law shows a dependence on the reactive surface area, catalyzing or inhibiting aqueous species and the Gibbs free energy of reaction. Despite the importance of understanding pore-scale petrophysical and mineralogical changes with different surface area, much remains poorly understood.

Before understanding the long-term fluid and rock interaction in geological reservoirs affected by different surface area, the short-term fluid and rock interaction processes at the pore-scale should be understood. A number of studies have been designed and conducted based on the

CO₂-brine-rock interaction in a high-pressure and temperature batch system. Fu et al. (2009)[23] studied alkali feldspar dissolution in a high-pressure and temperature batch system without CO₂. Carroll et al. (2013)[24] identified iron clay mineral reactions under CO₂ storage conditions in sandstone formations. However, Carroll et al. (2013) did not measure petrophysical changes. Dawson et al. (2015)[25] investigated the geochemical changes at geological CO₂ storage conditions, but reactive surface area was not measured. There are few studies of statistical descriptions of rock properties such as porosity, mineral composition, reactive surface area at the pore scale [26-28]. In this study, comprehensive reactive surface area measurements from Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN), X-ray Microtomography (Micro-CT), and Surface Area Analysis (BET), are undertaken along with descriptions of iron clay minerals for Berea sandstone.

In order to measure pore-scale petrophysical and mineralogical changes for samples with different surface areas, experimental studies of the CO₂-brine-rock interaction in a high-pressure, high-temperature batch system were designed and conducted. Three different forms of rock samples were used examining the impact of changing surface area. The samples were reacted with 2 wt. % NaCl brine and CO₂ at pressures around 2,000 psi and temperatures of 60 °C. The measurements were used to assess how the overall reaction rate (which is a combined manifestation of reaction rate and surface area) was impacted by surface areas of the different types of samples used.

2. Methods

2.1. Reactive batch system

Batch experiments were organized in four similarly constructed batch reactors. The

reactor system is shown in Figure 1. Brine (2 wt.% NaCl) was charged into the reactor in which the rock samples were placed. CO₂ was injected into the system, first at the pressure available through the cylinder (~740 psi); the reactor was pressurized with CO₂ to 2000 psi and the temperature was equilibrated at 60 °C. CO₂ is supercritical under these conditions. For all of the sample types (core plug, fractured rock, and powder), results obtained at different times were experiments conducted individually and separately. (Separate batch experiments were conducted with end times of: 4 h, 8h, 12 h, 24 h, 48 h, 96h, 168h, 240h, and 336 h; h=hours). After each experiment, the reactors were removed from the oven and cooled to room temperature. Liquid effluent and solid samples were collected. Powder samples were carefully cleaned with DI water before drying. The amount of dilution caused by this rinsing was accounted for when the liquid samples were analyzed by ICP-MS.

2.2. Characterization techniques used

2.2.1. Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN)

Quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) was used for the analysis of pre- and post- experiment core plugs. The analysis was conducted on a QEMSCAN 4300, which is built on a Zeiss Evo 50 SEM platform with four light element BrukerX flash energy dispersive X-ray detectors. Energy dispersive X-ray spectral analysis (EDX) involves the interpretation of secondary X-ray spectra to determine elemental composition, and ultimately mineralogy. The measurements were collected in field-scan mode, and X-ray data were collected every 4 µm on the polished thin sections. The QEMSCAN was operated using an accelerating voltage of 20 kV and a specimen current of approximately 5 nA.

2.2.2. Micro-Computed Tomography (Micro-CT)

Application of the computed tomography at the micro scale (micro tomography) allows for the examination of porosity evolution [29-31]. In order to measure changes in pore structure, a Micro-CT (XCT-400) was used. XCT-400 instrument allows 3D reconstruction from one-thousand 2D radiographs of the X-ray attenuation properties of various materials forming the object [32]. The optical system used in the experiment provides an optical resolution of 1.85 microns. Each data set is $1014 \times 1024 \times 1012$ voxels. The reconstruction provided 3D images of the X-ray absorption by the different materials in the sample.

2.2.3. X-ray Diffraction (XRD)

XRD was performed on each sample using a Bruker D8 Advanced X-ray diffractometer. The instrument is equipped with a lynx eye detector which collects data over 2.6 mm, rather than at a single point, greatly increasing X-ray counts collected and decreasing acquisition time; a rotating sample stage, which increases the mineral grain orientations encountered by the incident electron beam. Phase quantification using the Rietveld method was performed using TOPAS software, developed by Bruker AXS. The Rietveld method fits the peak intensities calculated from a model of the crystalline structure to the observed X-ray powder pattern by a least squares refinement. This is done by varying the parameters of the crystal structures to minimize the difference between the observed and calculated powder patterns. Because the whole powder pattern is taken into consideration, problems of peak overlap are minimized and accurate quantitative analyses can be obtained. The following operating parameters were used when analyzing the bulk samples: Cu-K- α radiation at 40 kV and 40 mA, 0.02° 2θ step size, and 0.6 seconds per step, for bulk samples. Bulk samples were examined from 4 to $65^\circ 2\theta$.

2.2.4. Surface Area Analysis (BET)

The BET surface area and porous structure of the various forms of core samples were determined by the single point BET/Nitrogen (N₂) method based on the quantity of gas that adsorbs as a single layer of molecules on the rock surface at a temperature of -196 °C using a Micrometric Tristar II instrument. Approximately 0.6 g of each sample was loaded into a glass sample tube. Immediately preceding surface area analysis, the samples were degassed at a minimum temperature of 100 °C for at least 4 hours on the degassing station. A mixture of 30 % N₂ / 70 % Helium (He) was used as a gas supply and analyses were carried out at atmospheric pressure and at liquid N₂ temperature.

2.2.5. Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

The determination of iron, calcium, magnesium, and potassium was performed using a quadrupole inductively coupled plasma mass spectrometer (Agilent, 7500ce) with a double-pass spray chamber; PTFE 100 µl/min nebulizer, platinum cones and sapphire injector within a quartz shielded torch [33]. An external calibration curve containing iron, calcium, magnesium, and potassium was prepared from 1000 mg/l single elemental standard solutions in HNO₃ (Inorganic Ventures). Indium at a concentration of 20 ppb was added to calibration curve, samples and blanks as internal standard. Samples were diluted 1:200 and run in the ICP-MS using 4 ml He/min in the collision cell.

2.3. Berea sandstone sample

Before conducting the batch experiments, it was necessary to measure the composition of the Berea sandstone. The Berea sandstone (Product ID, A-101) was obtained from Kocurek Industries INC. Hard Rock Division (Caldwell, Texas). The Berea sandstone was ground using a wire-saw to make powder samples. To determine these properties, XRD and ICP-MS were

utilized. XRD was used to detect all relevant constituents found in the unreacted sample. For XRD analysis, the samples were mixed with deionized water (DI H₂O) and further ground in a micronizing mill until fine enough to pass through a 325 mesh screen. The solution was then applied to a glass slide using a pipette. Once the sample had dried, an XRD pattern was obtained. Prior to ICP-MS analysis, unreacted core samples were digested using hydrofluoric acids (HF) for ICP-MS. Typically 100 mg of solid are treated with 5 ml concentration of HNO₃ and 5 ml concentration of HF. The samples are dried, and the process repeated a couple of times. As expected, the sandstone is primarily quartz, but contains iron, calcium, magnesium, and potassium. Mineral composition (XRD) and elemental measurements (ICP-MS) are tabulated in Table 1.

Figure 2 shows the three types of samples used in the batch experiments. First, smaller cores were taken out of the 1-inch Berea cores. Multiple core plugs (0.5 in. in length and 0.275 in. in diameter) were extracted. For the second type of sample, ‘fractured rock (D₅₀ = 0.103 in.)’ made by simply fragmenting the core was prepared. Size distribution of the fractured sample is shown in Figure 2(b). This was obtained by sampling 1000 pieces and measuring the dimensions manually. Powdered samples prepared by crushing to cores to 325 mesh were the third type. The particle size distribution of this sample measured using Sympatec HELOS analyzer is shown in Figure 2(c). Using fractured and powder samples (D₅₀ = 3.677×10^{-4} in.) enhanced reactivity and increased reaction rates [34].

2.4. Kinetic modeling approach

2.4.1. General form of rate expression

In order to interpret the mineral dissolution and precipitation kinetics, many scientists and researchers have developed expressions that describe the dependence of mineral dissolution on rate constant and surface area. A general form of rate expression is shown in equation (1).

$$r = kA \left[1 - \left(\frac{Q}{K} \right)^\theta \right]^\eta \quad (1)$$

where r is the reaction rate, k is the rate constant which is temperature dependent, A is the specific reactive surface area, K is the equilibrium constant for the mineral-water reaction, and Q is the reaction quotient. Parameters θ and η are typically determined by experiments.

All mineral and solution equilibria were computed using the geochemistry thermodynamic program - EQ3/6 v8.0a. For example, illite solubility is expressed by the reaction,

In EQ3/6 v8.0a, the reactants and products account for mass balances of all derived dependent species and solution complexes that may form under the defined conditions. Therefore, equation (2) simply provides a means of evaluating the distance from equilibrium from pure ordered illite:

$$Q = a_{\text{Mg}^{2+}}^{0.25} a_{\text{K}^+}^{0.6} a_{\text{Al}^{3+}}^{2.3} a_{\text{SiO}_2}^{3.5} a_{\text{H}_2\text{O}}^5 a_{\text{H}^+}^{-8} \quad (3)$$

Activity coefficients are computed using EQ3/6's "B-dot" function. In the case of minerals, data0.cmp contains thermodynamic reference mineral data.

2.4.2. Estimated reactive surface area

Surface areas available for the reaction affect overall reaction rates of dissolution. By using samples of differing surface areas, it is possible to quantify this effect. L. Li et al. (2007) [35] explained differences caused by having different surface areas by performing modeling. The mineralogical composition used in that work was generally similar to the Berea sandstone in this study. It was established that heterogeneity in the distribution of reactive surface area in the pore space could give rise to large deviations in effective reaction rates. In this work, surface area measurements on all of the samples used are available and the distributions are based on results from specific analytical instruments such as QEMSCAN and BET surface analyzer.

Mineral distributions in Berea sandstone were measured by QEMSCAN which were then converted to surface area values. An accurate conversion depends on a characterization of correlations between the geometric area of a mineral and the observations with BET adsorption specific to those minerals which were unavailable for this work. Lai et al. (2015)[27] provided a first order estimate of what this conversion might look like based on surface area measurements of various mineral groups reported in the literature.

$$A_{BET} = \beta A_{geom} \quad (4)$$

where the average roughness factor, β , relates BET surface area, A_{BET} , to QEMSCAN derived geometric surface area for Berea sandstone, A_{geom} . The calculation for the roughness factor was reported in P. Lai et al. (2015). This roughness factor can be thought to be made up of contributions from the surfaces of specific minerals,

$$\beta = f_{qtz}\beta_{qtz} + f_{clay}\beta_{clay} + f_{fsp}\beta_{fsp} + f_{other}\beta_{other} \quad (5)$$

where f_i is the fraction of the geometric surface area made up of mineral group i , $\sum_i f_i = 1$ and β_i are roughness factors following the same relationship as shown in equation (4).

3. Results and Discussion

After a two-week period of experiments, the core samples were taken out of the batch reactors, and were analyzed using various methods, such as QEMSCAN for mineralogical changes on the core samples, Micro-CT for porosity and permeability, X-ray diffraction analyses (XRD) for mineralogy, and BET for surface area and porosity. Post-experiment fluid samples were taken and analyzed using ICP-MS for the relevant cation concentrations.

3.1. Petrophysical Changes for Core Plug Samples: QEMSCAN and Micro-CT

QEMSCAN was used to obtain better understanding of petrophysical and mineralogical changes in the batch experiments with core plug sample but not for fracture and powder samples. The QEMSCAN images of different unreacted and reacted core plugs are presented in Figure 3. The QEMSCAN analysis confirmed that quartz, illite, Alkali feldspar, kaolinite, and plagioclase were the dominant minerals in the Berea sandstone, with minor amounts of chlorite, silicate, smectite, ankerite, muscovite, micrite and other lower amounts of various minerals.

Figure 3 (a) shows the surface image and the mineralogical composition of the unreacted Berea sandstone core plug. Quartz is the main mineral with a composition around 77.83 % by area. Illite is the second most dominant at 5.74 % by area. Figure 3 (b) shows the image and mineralogical composition of the reacted Berea sandstone core plug after the two-week batch experiment. The two most dominant mineral compositions are compared. Quartz concentration increased to 84.50 % by area, and illite concentration decreased to 3.84 % by area relatively. The

reactive minerals like illite dissolved during the batch experiment causing unreactive mineral concentration such as quartz to increase. Also, the background surface area increased meaning the porosity increased.

The QEMSCAN images also show the pore surface area (background area) of the samples. This surface area is represented as the background in the images. Due to the 2D nature of the images, the pore surface area is approximated as the area of the blank regions of the sample image. These surface area approximations can be compared with the surface area results from the BET analysis. The QEMSCAN results with the core plugs showed that dissolution on the surface was dominant for the Berea sandstone.

Analysis via Micro-CT was performed on the unreacted and reacted core plug sample. The Micro-CT machine was capable of supplying the necessary amount of energy to penetrate core plugs with a 1.85 micron resolution. The pre- and post-experiment core plug scans were taken at the same location to compare petrophysical changes. Figure 4 shows the Micro-CT images of (a) solid portion, (b) cross section, and (c) void portion of the unreacted and reacted Berea sandstone core plugs. By converting to a negative image and showing the void portion of each core plug, the reactivity of each core sample is more readily determined. Notice the definite porosity change at the circled sections indicating mineral dissolution within the core. In the cross section 2D images, there are spots marked by A, B, and C that indicate specific spots on the surface. These markers do not have any purpose other than to indicate the same spots on the unreacted and reacted surface images. The cross sectional 2D images show recognizable porosity changes in the circled area. It is difficult to see mineral dissolution in the 3D solid images. On the other hand, the 3D negative image shows more clearly the dissolution of minerals within the

Berea sandstone core plug, but it is impossible to determine which minerals are dissolved. Based on the previous experiments the dissolved mineral is thought to be ankerite and siderite or reactive clay minerals such as illite, chlorite, and smectite [36].

3.2. Surface Area Measurement Analysis

In the post-experiment core plug sample images using QEMSCAN, background area change is prominent at the boundaries of the samples exposed to the fluids. Also, visible porosity changes in Micro-CT results reveal some minor changes in the fluid-rock interface area over the two-week period. There is some evidence that CO₂-related reactions are present to some extent in all studied samples. The surface area increase is related to changes in pore volume and pore size. These changes are explained by a decrease in mineral mass/concentration and an increase in the pore volume as porosity increases. High quality observations of the Micro-CT images show that pore size increases with reaction time in the Berea sandstone core plug sample (Figure 4) [37]. BET surface area measurements help quantitate these observations.

Pre and post surface area measurements for the three types of samples are shown in Table 2. In general, BET surface area values for both unreacted and reacted samples were low. Differences between measurements for unreacted samples (0.83 m²/g to 1.10 m²/g) and reacted samples (1.02 m²/g to 1.48 m²/g) were small. On a percentage basis, surface areas increased by 23.21 % for core plugs, 29.90 % for fractured samples and 35.47 % for powdered samples. It was seen that the concomitant increase in volume was associated with decrease in the pore size. The reaction occurs on the core surface, where it generates new pores. The implications are that the generation of new pores is more dominant than the expansion of existing pores, thus resulting in a lower average pore size and a greater surface area.

If the reactions were to be continued for more than the two-week period, it is speculated that the pore size would increase and the surface area would decrease. This would be the result of new pores being generated and connecting to each other, as well as increased dissolution of the rock. To sum up, the reactions occur primarily on the surface of the minerals, and then secondary pores - new small pores - are generated by the reactions.

3.3 Mineralogical Changes by Different Reactive Surface Area: XRD

XRD was used to detect mineralogical changes found in the different unreacted and reacted surface area (form) samples. Even though the form of the rock was changed (core plug, fractured, powder) there was no significant change of minor minerals in the XRD results. This is because the XRD analysis is more of a bulk measurement, and does not accurately detect the small changes that accompany the difference in sample form. Therefore, in order to compare quantitative differences, one method is to measure the unreacted dominant mineral intensity before and after the reaction. In the mineralogical composition of sandstone core samples (See Table 1), quartz is the dominant mineral. The quartz intensity in each sandstone core was determined before and after the reaction, and the quartz intensity in each sandstone form was determined before and after the experiment. The unreacted core is made up of around 86 % quartz. This value was compared with the value found for each of the various Berea sandstone forms. Figure 5 shows the quartz intensities for unreacted, reacted core plug, reacted fractured core, and reacted powder. The quartz intensities of the reacted core plug, fractured core, and powder are around 88 %, 90 %, and 92 %, respectively. The increased reaction extent in powdered samples is clearly observed.

Comparison of the QEMSCAN and XRD data shows broad agreement between the two

techniques because of differences in sampling location (i.e. the analyses are collected on adjacent rock surfaces but are still not exactly the same piece of material). In both QEMSCAN and XRD analysis, the mineralogical percentages are based on relative amounts of each mineral in the sample. This makes comparing absolute mineralogical amounts between samples and analytical methods difficult. In addition, the QEMSCAN percentages are based on a surface area, whereas, XRD represents volumetric mass fractions, and the analytical techniques are different.

3.4. Mineralogy Changes by Reaction Time and Different Reactive Surface Area: ICP-MS

Analysis of the effluents from the experiments are shown in Figure 6. Constituents, reactions and parameters are shown in Table 3. The proportions of surface areas assigned to different minerals were obtained using the QEMSCAN mineral proportions. Certain minerals dissolved and concentrations of associated cations increased in the effluents. Four major element cations are plotted in Figure 6 along with the simulation results; (a) iron, (b) magnesium, (c) calcium, and (d) potassium. The scattered data points are the experimental ICP-MS data, and the solid line represents the simulation data. The simulation data points were obtained by calculating the dissolution using equations (1)-(5). The concentrations have not leveled off indicating that the dissolution may not be complete. This is likely due to the slowness of these reactions [38]. Rates of dissolution of iron minerals appear to be different for the first 48 hours and after 48 hours by observing the slopes of the iron concentration-time curves in Figure 6 (a). This is believed to be caused by the rapid and complete dissolution of ankerite, as explained by Kweon (2015). Additionally, in the case of iron, siderite dissolution also contributes to the initially steep iron concentration profile. Chlorite and smectite which also contain iron dissolve at lower rates. The dissolution rates of iron minerals are affected by reactive surface area. The slope of the

magnesium cation concentration (Figure 6 (b)) is relatively low since ankerite is the main contributor initially. The calcium concentration profile (Figure 6 (c)) differs slightly compared to that of iron and magnesium. During 48 hours, the profile identifies similar trends due to ankerite dissolution. The extended time of rapid dissolution is caused by simultaneous dissolution of highly reactive calcium containing minerals such as smectite, ankerite, and micrite. As is well known, calcite is a very active mineral for dissolution. The potassium concentration profile (Figure 6 (d)) shows a completely different pattern. Unlike the aforementioned cations, smectite affects potassium concentration in the beginning rather than ankerite. After 48 hours, other potassium source minerals such as illite, alkali feldspar, and muscovite participate in the reactions.

Effluent samples were collected on completion of the experiments with powdered and fragmented (fractured) samples. This data is shown in Table 4. Sodium was used as a standard cation to check the accuracy of ICP-MS analysis because the 2 wt. % NaCl brine was used for all of the experiments. In the blank test, the concentrations of minerals such as magnesium, aluminum, and iron were slightly above the ICP-MS detection limit. This suggests possible evidence for limited 316 stainless steel reactor corrosion.

As shown in Table 4, concentrations of all of the cations increased. The BET surface areas of the different samples shown in Table 2 indicate that the fractured samples have higher surface area than the core plugs and the powdered samples have the highest surface area. The relevant concentrations at the end of the two-week experimental period of all relevant cations increased as the sample surface areas increased. In addition to the Fe, Mg, Ca and K plots shown earlier, there is a large concentration difference in aluminum concentration when compared with

silica, especially in powder samples. Ankerite, micrite, and siderite do not have an aluminum source, but most of the other minerals listed in Table 3 have aluminum. Alkali feldspar and plagioclase have the highest mineral surface area contributing most to the cationic effluents observed. Silicon concentration changes are observed, but not to the same degree as other minerals. There are many possible sources of silicon such as quartz, illite, alkali feldspar, plagioclase, chlorite and smectite. Quartz is a dominant mineral in the Berea sandstone (Figure 3) but is relatively unreactive with the CO₂ and brine solution. Therefore, illite and alkali feldspar are the primary source of silicon in the effluent because of their higher volume fraction and surface area compared with other minerals.

Potassium, calcium, and iron each show similar increases in concentration with increasing surface area. The main reactive minerals containing potassium in the Berea sandstone are illite, alkali feldspar, smectite, and muscovite. Plagioclase, smectite, and ankerite are the main calcium-containing minerals found in the Berea sandstone. Illite and alkali feldspar have a relatively high volume fraction and surface area when compared to smectite and muscovite; therefore, illite and alkali feldspar have the greatest effect on the concentration of potassium. Plagioclase, smectite, and ankerite contribute to increasing calcium concentrations due to the high volume fractions and surface areas. Sandstone effluent samples show large concentrations of iron, indicating dissolution of iron containing minerals. Based on the previous core flooding experimental and simulation results, these Fe cations in solution are mainly attributed to dissolutions of chlorite, smectite, ankerite and siderite [38]. Carroll et al. (2013) touched on dissolution reactions with iron-containing clay minerals in sandstone under CO₂ storage conditions. It can be seen that not only clay minerals such as chlorite and smectite, but also carbonate minerals such as ankerite and siderite, influence iron concentrations.

The total mineralogical changes in the batch experiments are lower than those found in the core flooding experiments and simulation results (Kweon (2015)). In the core flooding experiments, reactive fluid was continuously injected. However, in the batch experiments the rock samples were contained in the unchanged fluid over the two-week period. The different fluid conditions caused different dissolved element concentrations. In the non-flowing environment of the batch system, reactivity of mineral dissolution is affected by reactive surface area changes. However, measuring the true reactive surface area presents significant challenges. Therefore, the reactive surface area is regarded as being the geometric surface area in this study. In order to calculate the geometric surface area, the roughness factor (β) was applied. By means of the roughness factor (β), correlations between the geometric area of a mineral and the BET surface area of that mineral, were generated.

In Figure 7, four major cations in the effluent concentrations are compared with the simulation results; (a) iron, (b) magnesium, (c) calcium, and (d) potassium. The scattered data points without lines are the batch experimental ICP-MS data, and the solid and dotted lines are the simulation data by using different reactive surface areas. Effluent concentrations were measured for the batch experiments with core plugs at several different times. Roughness factor was calculated using equation (4) on the basis of BET and QEMSCAN measurement. The measured A_{BET} and A_{geom} for the core plug sample were used to calculate an average roughness factor of 37.4 for the Berea sandstone. Experimental A_{geom} values were not available for the fractured and powder samples, and the same roughness factor (37.4) was used for those sample types in the simulations. A two-week experiment was carried out for the powder and fractured samples and the data points are shown in Figure 7. These experimental data points are above the simulation results (solid line) using the roughness factor of 37.4. The difference between the

simulation results and these experimental data points for the powder and fractured samples is caused by the assumption of using the average roughness factor in equation (4) that was calculated using the core plug sample. In order to find roughness factor for fracture and powder samples, geometric surface area was modified based on BET surface area and experimental data points. As shown in Table 5, the calculated roughness factors for fracture and powder samples are 33.6 and 31.3, respectively. The dotted lines are plotted by means of the calculated roughness factor value in Figure 7. Mineral dissolution trends and the data points of effluent cation concentration were well matched when calculated roughness factors were used.

4. Conclusions

Batch experiments with different forms of the Berea sandstone were performed under geological CO₂ sequestration conditions. In order to determine petrophysical changes, QEMSCAN, Micro-CT and BET instruments were used. Especially, the QEMSCAN and Micro-CT results with the core plugs showed that dissolution on the surface was dominant in the batch system. The 3D negative images of Micro-CT displayed removed particles and increased porosity. Surface area changes in the samples were measured by BET instruments. Surface areas from 23.21 % to 35.47 % depending on the type of sample employed. Patterns of cation concentration changes were measured over time using ICP-MS. The level of dissolution of iron-bearing minerals in sandstone in the two-week experimental period was unexpected. The effect of surface area on reactivity was quantified. Using QEMSCAN and BET measurements, it was assessed that the geometric surface area available for reactions, and used in reactive models is 36.7 times lower than the BET surface area. Applying the same factor to other types of samples with higher surface areas (fractured rock, powdered samples) did not match experimental results,

and lower factors had to be used. This showed that some internal surface area became available for reactions when these types of samples were used in the experiments. The roughness factor for fracture and powder samples were calculated and the values are 33.6 and 31.3, respectively. It was also determined that pores smaller than the original were created as a result of the dissolution.

5. Acknowledgements

This work was funded by a grant from the U.S. Department of Energy (DOE Award Number: DE-FE009773).

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Table 5. The calculated roughness factors for core plug, fracture, and powder samples

Table 1

Composition (Based on XRD)	Kaolinite	2.51 %
	Oligoclase	1.52 %
	Clinochlore	1.08 %
	Illite	4.58 %
	Sanidine	4.20 %
	Quartz	86 %
Elements (Based on ICP-MS)	Mg (mg/kg)	1034
	K (mg/kg)	1047
	Ca (mg/kg)	1703
	Fe (mg/kg)	4655

Table 2

	Average surface area (m ² /g)			Average pore volume (cm ³ /g)						Average pore size (Å)					
				BJH Adsorption			BJH Desorption			BJH Adsorption			BJH Desorption		
	Before	After	Variation	Before	After	Variation	Before	After	Variation	Before	After	Variation	Before	After	Variation
Core plug	0.8269	1.0188	23.21%	0.00311	0.00345	11.01%	0.00665	0.01039	56.20%	205.146	178.477	-13.00%	284.877	193.789	-31.97%
Fracture	0.8926	1.1595	29.90%	0.00346	0.00404	16.55%	0.00541	0.01079	99.33%	202.368	157.662	-22.09%	424.687	183.089	-56.89%
Powder	1.0953	1.4838	35.47%	0.00454	0.00639	40.67%	0.01355	0.00990	-26.92%	188.044	206.468	9.80%	453.838	275.288	-39.34%

Table 3.

	K ₂₅	Ea (kJ/mol)	Area (cm ² /g)			Log K	Ref.
			Core plug	Fracture	Powder		
Illite	1.00E-13	22	2.854	3.081	3.781	5.5551	Arvidson and Luttge(2010)[21]
Alkali feldspar	1.78E-10	51.7	27.201	29.363	36.031	-0.9610	Arvidson and Luttge(2010)[21]
Plagioclase	1.00E-12	30	13.775	14.869	18.246	2.6839	Baccar, et al. (1993)[39]
Chlorite	1.00E-9.91	25.1	0.413	0.446	0.547	55.7725	Smith, et al. (2013)[40]
Smectite	8.08E-14	28	0.343	0.370	0.455	13.4522	Elliott and Matisoff(1996)[41]
Ankerite	1.26E-09	62.76	1.193	1.288	1.581	1.3314	Arvidson and Luttge(2010)[21]
Muscovite	1.00E-13	22	0.104	0.113	0.138	8.8387	Arvidson and Luttge(2010)[21]
Micrite	1.50E-06	41.9	0.845	0.913	1.120	1.3330	Arvidson and Luttge(2010)[21]
Siderite	1.00E-09	62.8	0.497	0.537	0.659	-0.8309	Arvidson and Luttge(2010)[21]

Table 4.

	Na (mg/kg)	Mg (mg/kg)	Al (mg/kg)	Si (mg/kg)	K (mg/kg)	Ca (mg/kg)	Fe (mg/kg)
LoD	2	0.004	0.06	0.06	7	13	0.05
Blank	7024	0.68	0.64	0.22	<7	<13	1.92
Core plug	7108	60.2	27.2	3.8	72	154	126
Fracture	7103	109	64.9	8.4	140	204	192.1
Powder	6904	167.2	98.5	17.2	211	384	271.44

Table 5

	A_{BET} (cm ² /g)	β	A_{geom} (cm ² /g)	β_{m}^*	A_{geom} (cm ² /g)
Core plug	8269	37.4	221.09	37.4	221.09
Fracture	8926	37.4	238.66	33.6	265.81
Powder	10953	37.4	292.86	31.3	350.11

* β_{m} : modified β value based on the dissolved mineral concentration using TOUGHREACT

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

(a)

(b)

Figure 7