Diagenetic Influence on Fracture Conductivity in Tight Shale and CO₂ Sequestration

Abiola Olabodea*, Mileva Radonjic

Louisiana State University, 2117/2131 Patrick F. Taylor Hall, Baton Rouge 70803, USA

Abstract

Most sedimentary rock formations (tight or highly porous) have geochemical characteristics that can lead to significant reactive ion exchange processes in aqueous media in the presence of carbon dioxide. While geomechanical properties such as rock stiffness, poisson’s ratio and fracture geometry largely govern fluid flow characteristics in deep fractured formations, the effect of mineralization can lead to flow impedance in the presence of favorable geochemical and thermodynamic conditions. Shale caprock which seals more than two-thirds of oil and gas reservoirs have natural fractures that are unevenly distributed in the geosystem. Experimental works which employed the use of analytical techniques such ICP-OES, XRD, SEM/EDS and BET techniques in investigating diagenetic and micro-structural property of crushed shale caprock/CO₂-brine system concluded that net precipitation reaction processes can affect the distribution of petrophysical nanopores in the seal rock. XRD analyses indicated the presence of quartz, feldspar and bulk clays (muscovite, chlorite, kaolinite with the quantitative mineralogy estimates varying significantly with respect to quartz-bulk clay ratio in the six samples that were analyzed. Quartz and feldspar are reactive at low pH with the tendency to impact seal integrity. The presence of quartz in shale gives a reasonably high mechanical strength whereas clays make shale easily deformable with a potential to creep. The results showed that geochemical precipitates can be formed such that fluid flow through open micro and macro fractures may be constrained. Peclet-Damköhler reactive flow dimensionless number confirmed diffusion as the governing transport mechanism in aqueous CO₂-caprock interaction. Simulation results reported by various researchers suggested that influx-induced mineral dissolution/precipitation reactions within shale caprocks can continuously close micro-fracture networks, while pressure and effective-stress transformation first rapidly expand then progressively constrict them. The presence of traces of carbonate streaks which are soluble in low acidic pH environment is undesirable in caprocks. This experimental research investigated the impact of in-situ geochemical precipitation on conductivity of open micro-fractures under geomechanical stress conditions. Fracture conductivity in core samples of shale caprock with known mineralogical composition from different formations where CO₂ injection is on-going are quantitatively evaluated under axial and radial stress using pulse-decay liquid permeametry/core flooding systems. This system incorporates

* Corresponding author. Tel.: +1-225-921-8309; fax: +1-888-965-9518.
E-mail address: aolabo2@lsu.edu
high temperature and pressure conditions. The shale caprock cores were obtained during the drilling of vertical and short-radii injection wells in Alabama and South Louisiana as part of reservoir characterization for CO₂ sequestration/enhanced oil recovery projects. Nano-indentation of multiple representative samples was applied to determine geomechanical properties evolution which can be correlated with the geochemistry of the shale caprock. This information will be useful as input data for simulation of subsurface CO₂ plume in contact with overlying shale caprock. Modeling of the diffusion controlled fluid flow and induced fracture diagenetic alterations in the shale caprocks are performed using CMG-GEM numerical simulators with imposed axial and radial geomechanical stress. The possibility of rock-fluid geochemical interactions constricting natural fracture conductivity in long term subsurface CO₂ sequestration can lead to significant improvement in shale caprock seal integrity and mitigate injection induced perturbation.

© 2013 The Authors. Published by Elsevier Ltd.
Selection and peer-review under responsibility of GHGT.

Keywords: fracture diagenesis; conductivity loss; aqueous carbon dioxide; shale geochemistry; natural fractures.

1. Introduction

In naturally fractured geologic formations, conductivity of fractures are important in fluid extraction and injection. The role of mineralization in the loss of fracture conductivity due to aqueous precipitation of insoluble substances has been discussed by several researchers. It is generally thought that aside geomechanical properties of sedimentary rocks, the geochemical properties of rocks and reservoir fluids can favorably or unfavorably lead to the constriction of fractures in the subsurface given the right temperature, pressure and chemical composition [1]. This type of constrict is desired in CO₂ sequestration and containment. Different formation evaluation scales can be considered when describing tight shaly rocks (caprock): from the pore or grain scale in petrophysics and geochemistry, to regional scale in geology and geomechanics. For clayey caprocks, the amount and type of clay is critical in characterizing its petrophysics unlike tight carbonate formation where dolomitization is the key feature. [2]. When injecting CO₂, mechanical constraints are generated in both the storage and caprock formations, and the bottom of the caprock can be affected by geochemical reactions. Several studies have shown that in large scale carbon sequestration, the CO₂ migrates a few meters during one thousand years, and that the porosity mostly decreases by precipitation, and increases very locally at the base of the caprock by dissolution [3]. Naturally occurring fractures in shaly caprocks under CO₂ sequestration and subsurface fluid extraction make significant contribution to flow and any natural or artificial geologic process that can impact them should be adequately researched [4].

Diagenesis is the process of physical and chemical changes in sediment, after deposition that converts it to consolidated rock. Classical diagenesis is considered to be a slow process occurring over centuries, but in fact, the reactions occur fairly rapidly, requiring fractions of years at reservoir conditions. The centuries of time normally associated with diagenesis is the time required to bury sediment deep enough to reach the pressure and temperature conditions conducive to diagenetic change [5]. Common minerals, dissolved in or precipitated from an aqueous phase can be grouped into those that are relatively reactive or inert in that their dissolution or precipitation rates are fast or slow, respectively, relative to the flow rate of the aqueous phase. Multiple investigators have outlined the consequences of variations in reaction rates relative to flow rate of the fluid in which the minerals are reacting. These minerals can be further grouped according to simple and complex stoichiometry [1, 6]. Those minerals with complex stoichiometry are much less likely to reach the solubility equilibrium than those with simple stoichiometry. Since calcite is a reactive mineral and has simple stoichiometry, it is considered as an example of water-rock reaction problem whenever it is present in substantial amounts [6]. Physical, chemical, and organic processes begin acting on carbonate sediments after their deposition, leaving an influence on the mineral composition and structure. Diagenesis typically changes porosity, permeability and capillary pressure characteristics [4, 7].

Shale caprock constitutes more than 60% of effective seals for geologic hydrocarbon bearing formations and are therefore of considerable interest in underground CO₂ storage into depleted oil and gas formations [4]. Experimental studies of wettability, contact angle and interfacial tension on shale using CO₂-rich fluid have not been widely
reported. Porosity, permeability, fractures and other petrophysical properties of the seal rock are of importance in seal integrity analysis and can be experimentally determined. Organic-rich shale is considered to have limited potential as membrane seals in CO$_2$ containment [8]. Shale rocks are predominantly composed of clay. They might also have other silica and carbonate based minerals that contribute to their geomechanical strength [9].

Different mechanisms for CO$_2$ migration are possible, from small to large scales: (i) molecular diffusion of dissolved CO$_2$ in the pore water from the reservoir zone into the caprock formation, (ii) CO$_2$ diphasic flow after capillary breakthrough, (iii) CO$_2$ flow through existing open fractures. The following mechanisms can accelerate or slow down the migration: (i) chemical alteration of the mineralogical assemblage of the caprock formation under the influence of acid water, (ii) re-opening of pre-existing fractures or micro-cracks induced by overpressure of the reservoir below, (iii) a combination of the above (chemical alteration of the mineral filling the fractures). Several simulation results have predicted that influx-triggered mineral dissolution/precipitation reactions within typical shale cap rocks can continuously reduce microfracture apertures, while pressure and effective-stress evolution first rapidly increase then slowly constrict them [10]. The extent of geochemical alteration is considered to be nearly independent of the injection rate while that of geomechanical deformation is thought to be more pronounced during engineered storage [5]. There have been suggestions that ultimate restoration of pre-influx hydrodynamic seal integrity—in both EOR-EGR/storage and natural accumulation settings—hinges on ultimate geochemical counterbalancing of the resultant geomechanical effect. The geochemical reactivity of caprock formations should be evaluated gradually, essentially in two steps: classical batch experiments on crushed or small pieces of rock samples to evaluate reaction paths and possibly the reaction kinetics, and flow tests on plugs to evaluate, among other important quantities, the porosity variations [11].

Fractures are nearly ubiquitous in rocks that have experienced even slight deformation and most of these are mineral filled [10]. Their presence indicates that: (1) dilation of the rock took place for fractures to be both open and provide pathways for fluid flow and (2) fluid was present and perhaps moving during and after the deformation event, and it carried sufficient mass of fracture constituents in solution to precipitate in the observed fracture void space [12]. Pressure solution and compaction mechanism as a result of enormous formation stress is a driver for the diagenetic loss of fracture conductivity and adjoining formation permeability.

2. Experimental Methodology

Crushed samples of shale rocks from the Pottsville Formation in the Black Warrior Basin of Alabama, USA were flooded with CO$_2$-brine at gradually increased pressure in steps of 0.67MPa/hour up to a maximum of 6.7MPa. This gradual pressure increase was to prevent localized fracturing of the samples particularly during the first 10 hours of the start of the experiment. Three samples of similar mineralogy but different percentage composition, obtained from cored CO$_2$ injection monitoring wells in the Pottsville Formation, were tightly packed manually into flow cells A and B. Figure 1 shows the experimental setup theory and the schematics of the fluid-rock interaction taking place. The X-ray Diffraction (XRD) mineralogical analysis indicated the presence of (bulk) clay, quartz and feldspar and their relative percentages are shown in Table 1.

| Samples | Bulk Clay | Quartz | Feldspar | Ratio (C:Q;%F) |
|---------|-----------|--------|----------|---------------|
| A       | 75.21     | 23.19  | 1.6      | 3:1;1.6%      |
| B       | 65.02     | 32.58  | 2.4      | 2:1;2.4%      |
The crushed samples are 3mm to 5mm in diameter. Each cell held an average of 265g of shale samples and was subjected to a flow rate of 0.2cm³/min at a regulated back pressure of 6.70MPa and 25°C temperature throughout the three months of the experiment. The 6.70MPa pressure value was accurately determined as the capillary entry pressure of the shale caprock using High Pressure Mercury Intrusion (HPMI) analysis carried out at Core Laboratories, Houston TX. HPMI analysis also quantified the initial nanopores distribution responsible for the relatively high value of the estimated capillary entry pressure. Five nanodarcy (5nD) was determined as the effective permeability of the shale caprock. The CO₂-brine fluid used during the experiment was prepared by bubbling CO₂ into a brine solution (0.35mol/liter NaCl + 0.005mol/liter KCl) at 0.17MPa for 2hrs in a stainless steel storage tank. This yielded CO₂-brine pH of 3.7 on the average. The limitation of using one back pressure regulator during the experiment implied that mixed effluent from the singular outlet of the three cells was analyzed for cationic content. The flooding experiment was continued for three months with only two interruptions during which the 1st and 2nd months samples were collected for analysis. Samples of shale rock were analyzed each month using XRD, SEM, EDS. The results obtained were used to determine the extent of the impact of reactive CO₂-brine on the shale caprock integrity.
3. Results and Discussion

3.1 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

The surface imaging of the shale caprocks and the effluent’s precipitate using SEM revealed the nature of the microscopic pores and the possible growth of new secondary features. This was combined with the average spot and areal EDS analysis (location shown by the red dotted points and lines) of the imaged surfaces. Figure 2a represents the control specimen for sample A and it showed that there are fewer flow paths in the CO₂-brine flooded sample (figure 3a) after 3 months. However, figures (4a and 5a) which are the control samples and CO₂-brine flooded samples for specimen B revealed surface morphological alterations with visible secondary precipitates that are responsible for flow path constriction. These SEM images for the two samples also showed that pore spaces in the shale caprock are of the sub-micron level. The EDS analysis was performed on the original shale caprock samples, the CO₂-brine contacted samples (figures 2b and 4b) and the effluent precipitates. The results showed the presence of Iron (Fe), Sodium (Na), Potassium (K), Silicon (Si), Carbon (C), Oxygen (O), Chromium (Cr), Manganese (Mn), Calcium (Ca), Magnesium (Mg) and Aluminum (Al). They are present in rock minerals capable of exchanging ions with carbonic acid. The relative ratio of the metals confirms that Calcium-based minerals (like anhydrite and carbonates) are susceptible to carbonic acid attack. The elemental concentration of Ca in samples A and B were low as shown in Figures 3b and 5b which were the surface elemental profile of the CO₂-brine flooded samples. This is in addition to alkali metals (e.g Na and K) that form compounds which are generally soluble in acidic or alkaline fluids. This implies that compounds of Na, K, Ca, Mg, Al and Mn which were identified in the shale caprock samples would be reactively soluble (with slow kinetics) in aqueous CO₂ with the possibility of re-precipitation to form new minerals. The ratio of the elements identified at the surface of the samples over the 3 months of CO₂-brine flooding showed mixed variations which could be partially attributed to mineral dissolution/precipitation and sample heterogeneity. The insert represents the ratio of clay to quartz and the percentage of feldspar in each sample.

Fig. 2a (left). 5μm resolution SEM image of control sample for specimen A showing mineral grains sizes of platelet structure and sub-micron pores at the site around EDS multi-spot analysis. Figure 2b (right). Average EDS plot of surface mineralogy of control sample for specimen A showing the relative elemental composition of multiple spots on the corresponding SEM image.
Fig. 3a (left). 5μm resolution SEM image for specimen A showing mineral grains sizes of platelet structure and sub-micron pores at the site around EDS multi-spot analysis after 3 months of CO2-brine flooding. Figure 3b (right). Average EDS plot of surface mineralogy for specimen A showing the relative elemental composition of multiple spots on the corresponding SEM image after 3 months of CO2-brine flooding.

Fig. 4a (left). 5μm resolution SEM image of control sample for specimen B showing mineral grains sizes of platelet structure and sub-micron pores at the site around EDS multi-spot analysis. Figure 4b (right). Average EDS plot of surface mineralogy of control sample for specimen B showing the relative elemental composition of multiple spots on the corresponding SEM image.
Fig. 5a (left). 5μm resolution SEM image for specimen B showing mineral grains sizes of platelet structure and sub-micron pores at the site around EDS multi-spot analysis after 3 months of CO₂-brine flooding. Figure 5b (right). Average EDS plot of surface mineralogy for specimen B showing the relative elemental composition of multiple spots on the corresponding SEM image after 3 months of CO₂-brine flooding.

Fig. 6a (left). 1μm resolution SEM image of the effluent precipitate with no crystalline micro-structure visible. The surface appears amorphous. Figure 6b (right). Average EDS plot of surface elemental mineralogy of effluent precipitate showing high Fe, O and Si concentration after 3 months of CO₂-brine flooding.

Figure 6a shows the SEM image of the amorphous precipitate with no crystalline particle visible at the 1μm resolution. Figure 6b shows the elements that are preponderance in the effluents precipitate that XRD (figure 7)
analysis indicated as amorphous in characteristics. Fe and Si are the two prominent mineral forming elements which confirm the presence of Quartz (SiO$_2$) and most-likely amorphous Iron Oxide that resulted from the oxidation of leached Fe$^{2+}$ to Fe$^{3+}$ giving the brown-like coloration of the effluent after exposure to the atmosphere over time.

3.2 X-Ray Diffraction Spectrometry Analysis of Precipitates

However, bulk XRD analysis showed mineralogical heterogeneity in the rock which consists of complex alkali and alkaline earth metal compounds that are relatively reactive under mildly acidic conditions such as in CO$_2$-brine mixture. The common feature of the XRD analysis performed on the two sample sets was a finer peak response for the major minerals. This indicated that the amorphous contents of the rock which masked crystallinity response of the minerals in the rock have been largely removed by the continuous injection of CO$_2$-brine fluid. Diagenetic quartz of reduced crystallinity was identifiable with distinct peak.

In the bulk analysis of the crushed samples, most significant changes were in the ratio of feldspar to muscovite and chlorite with an increased presence of the later clay mineral in sample A as the experiment progressed. There was a decrease in the muscovite content for sample B at the end of the third month of CO$_2$-brine flooding with a corresponding increase in chlorite while feldspar appeared unchanged. This changes are responsible for precipitate formation in the effluent over time.

XRD analysis of precipitates (figure 7) that were formed from the effluent collected showed an amorphous material with some quartz content. The quantitative percent changes in the shaly rock samples for bulk XRD analysis are presented in tables 2 and 3.
Table 2. Percentage (%) change in the mineralogical composition of Sample A after months of CO₂-flooding.

|         | Muscovite | Chlorite | K-Feldspar | Quartz | Albite | Kaolinite |
|---------|-----------|----------|------------|--------|--------|-----------|
| 1st month | -1.45     | -2.20    | -0.33      | 1.67   | 1.38   | 2.92      |
| 2nd month | -1.45     | -1.71    | -1.33      | 1.67   | 2.41   | 2.5       |
| 3rd month | 1.23      | -1.22    | -1.33      | 1.75   | 3.10   | 3.33      |

Table 3. Percentage (%) change in the mineralogical composition of Sample B after months of CO₂-flooding.

|         | Muscovite | Chlorite | K-Feldspar | Quartz | Albite | Kaolinite |
|---------|-----------|----------|------------|--------|--------|-----------|
| 1st month | -2.8      | -1.88    | -0.37      | 1.31   | -3.68  | -0.28     |
| 2nd month | -0.6      | -0.94    | -1.48      | 1.39   | -2.11  | -1.39     |
| 3rd month | -0.8      | -0.94    | -0.74      | 1.64   | -2.89  | 1.11      |

3.3 Electron Micro-Probe Analysis

Electron Probe Microanalysis (EMPA) of shale fragment exposed to CO₂ brine over a 3-month period. Area covered was 25μm by 50μm. EPMA is traditionally used for detailed geochemical analysis when subtle differences in composition of minerals are present. The samples used were uncoated polished thin sections. Back Scattered Electron Microscopy (BSE) images clearly shows presence of two micro-fractures that are not completely connected. Elemental maps (figures 8a and 8b) point out that the fracture is depleted in Si, Ca, S and some Al. The fracture contains Na, Mg, K. These types of analysis can be fully qualitative and provide insights into geochemical and geomechanical coupling effect in rock – fluid interactions. The effect of mineral crystallization within the fracture walls can lead to closure of undesired fractures in caprocks over CO₂ sequestration sites.

Fig. 8a. BSE micrograph for crushed shale showing fracture geochemistry with corresponding elemental maps of Si, K and Al, (left to right) for a sample flooded with CO₂ brine for 3 months.
Fig. 8b. BSE micrograph for crushed shale showing fracture geochemistry with corresponding elemental maps of Mg, Ca, S and Na, (left to right) for a sample flooded with CO₂ brine for 3 months.

3.4 Micro-fracture Filling in Homogeneous Model

Particulate size of precipitates from SEM and XRD analysis is approximately 0.01μm. Using the assumption of uniformity of precipitates and micro-fracture dimensions (~25 μm for a single fracture aperture) such as shown in

![Micro-fractures (25 μm ID)](image)

Fig. 9. The cross section of the composite core made of kaolinite, cement and microtubing designed to mimic natural fractures. It shows 8 single fractures in a 3in by 1in core.
figure 9, an aggregate of 2500 particles is required to completely occlude the uniform cross section of a single fracture. Volumetrically, $3.74 \times 10^{13}$ particulate precipitates are required to completely fill the entire single fracture length. This implies that a cracked reservoir wide precipitation process can fill limited number of homogeneous fractures. Carbon sequestration conditions under high temperature and pressure conditions can provide the representative net precipitation-dissolution rate to accomplish defective natural fracture filling over the long term.

4. Conclusion

The formation of precipitates resulting from CO$_2$-brine contact with shaly rocks has been investigated. The mineralogical composition of these precipitates show that continued aggregation over time can fill up existing or induced fractures in shale rocks that cap target reservoirs in CO$_2$ sequestration projects. The XRD analysis reveal their amorphous nature suggesting the preponderance of non-crystalline oxides of silicon, iron and magnesium. The presence of alkaline earth metals in trace amounts in both reservoir and seal rocks could provide the necessary substrate for natural and induced fracture healing as desired in CO$_2$ sequestration and containment.

Acknowledgements

Funding for this research work was generously provided by the Craft & Hawkins Department of Petroleum Engineering, Louisiana State University and the GDL Foundation, Austin TX.

References

[1] Kampman, N., Bickle, M.J, Maskell, A., Chapman, H.J, Evans, J.P., Purser, G., Zhou, Z., Schaller, M.F., Gattacceca, J.C., and Bertier, P. Drilling and sampling a natural CO$_2$ reservoir: Implications for fluid flow and CO$_2$-fluid–rock reactions during CO$_2$ migration through the overburden. Chemical Geology, 2014. 369(1): p. 51–82.
[2] Edlmann, K., Haszeldine, S. and McDermott, C. Experimental investigation into the sealing capability of naturally fractured shale caprocks to supercritical carbon dioxide flow. Environmental Earth Sciences, 2013. 70(7): p. 3393-3409.
[3] Noh, M.H. and Lake, L.W. Geochemical modeling of fracture filling. in SPE/DOE Improved Oil Recovery Symposium 2002. Society of Petroleum Engineers.
[4] Olabode, A. and Radonjic, M. Experimental Investigations of Caprock Integrity in CO$_2$ Sequestration. Energy Procedia, 2013. 37(1): p. 5014-5025.
[5] Javadpour, F. CO$_2$ injection in geological formations: determining macroscale coefficients from pore scale processes. Transport in porous media, 2009. 79(1): p. 87-105.
[6] Kang, Q., Zhang, D. and Chen, S. Simulation of dissolution and precipitation in porous media. Journal of Geophysical Research, 2003: Solid Earth (1978–2012). 108(B10).
[7] Olabode, A. and Radonjic, M. Shale Caprock/Acidic Brine Interaction in Underground CO$_2$ Storage. Journal of Energy Resources Technology, 2014. 136(4); pp. 6. doi:10.1115/1.4027567.
[8] Bobko, C.P. Assessing the mechanical microstructure of shale by nanoindentation: The link between mineral composition and mechanical properties. MIT, 2008. http://hdl.handle.net/1721.1/47731.
[9] Katsube, T.J. and Williamson, M.A. Effects of diagenesis on shale nano-pore structure and implications for sealing capacity. Clay Minerals, 1994. 29(4): p. 451-472.
[10] Smith, J., Durucan, S., Korr, A., and Shi, J-q., 2011. Carbon dioxide storage risk assessment: Analysis of caprock fracture network connectivity. International Journal of Greenhouse Gas Control, 2011. 5(2): p. 226-240.
[11] Weaver, J.D. and Rickman, R.D. Productivity Impact from Geochemical Degradation of Hydraulic Fractures. in SPE Deep Gas Conference and Exhibition, 2010. Society of Petroleum Engineers.
[12] Weaver, J.D., Parker, M., Van Batenburg. D., and Nguyen, P. Fracture-Related Diagenesis May Impact Conductivity. SPE Journal, 2007, 12(03): p. 272-281.