

Water Rock Interaction [WRI 14]

Trace metal mobilization in an experimental carbon sequestration scenario

Virginia Marcon^{a,*} and John Kaszuba^{a,b}

^aUniversity of Wyoming, Geology and Geophysics, Laramie, WY, 82070 USA

^bUniversity of Wyoming, School of Energy Resources, Laramie, WY, 82070 USA

Abstract

Mobilizing trace metals with injection of supercritical CO₂ into deep saline aquifers is a concern for geologic carbon sequestration. Hydrothermal experiments investigate the release of harmful metals from two zones of a sequestration injection reservoir: at the caprock-reservoir boundary and deeper within the reservoir, away from the caprock. In both systems, Cd, Cr, Cu, Pb, and Zn behave in a similar manner, increasing in concentration with injection, but subsequently decreasing in concentration over time. SEM images and geochemical models indicate initial dissolution of minerals and precipitation of Ca-Mg-Fe carbonates, metal sulfides (i.e. Fe, As, Ag, and Co sulfides), and anhydrite in both systems. The results suggest that Ba, Cu, and Zn will not be contaminants of concern, but Pb, Fe, and As may require careful attention.

© 2013 The Authors. Published by Elsevier B.V.

Selection and/or peer-review under responsibility of the Organizing and Scientific Committee of WRI 14 – 2013

Keywords: fluid-rock interactions; geologic carbon sequestration; supercritical carbon dioxide; trace metal.

1. Introduction

Carbon capture and storage (CCS) is being viewed as a viable means to reduce anthropogenic carbon dioxide (CO₂). Injection of CO₂ into deep geologic formations, such as saline aquifers, is one of the more accepted techniques proposed for long-term storage of CO₂. Injection of supercritical CO₂ (scCO₂) into a saline reservoir decreases pH 1 to 2 units [1, 2]. The decrease in pH can lead to mineral dissolution [3], which may release harmful metals such as arsenic (As), lead (Pb), and barium (Ba) from the reservoir and/or caprock. Small discontinuities in the caprock along faults, fractures, old petroleum wells, or horizontal migration inclusions could allow the reservoir brine and/or CO₂ to seep out of the saline aquifer and into an overlying potable aquifer impacting the shallower zones. In order for CCS to become viable, an understanding of how leakage may affect overlying potable aquifers is imperative. Hydrothermal experiments were performed to investigate the release of harmful metals into solution as a result of CO₂ injection into a saline reservoir.

* Corresponding author. Tel.: +1-832-671-5324; fax: +1-307-766-6679.

E-mail address: vmarcon@uwyo.edu.

2. Methods and Materials

2.1 Experimental and Analytical Methods

Table 1: Experimental conditions and parameters for hydrothermal experiments

Experiment	Brine-Reservoir Caprock Interface + scCO ₂ [†]	Brine-Deep Reservoir + scCO ₂ [†]
Initial pH	6.6 ± 0.1	6.7 ± 0.1
Temperature (°C)	160.4 ± 6.5	160.0 ± 0.4
Pressure (MPa), Pre-scCO ₂ Injection	24.6 ± 1.3	25.4 ± 0.4
Pressure (MPa), Post-scCO ₂ Injection	38.4 ± 5.4	37.8 ± 1.0
Initial Water:Rock Ratio	21.5	21.5
Mineral Proportions (Cc:Do:Py:Sh*)	31:31:2:0:36	47:47:5:0:0
Water-Rock Reaction Time (hours)	673	676
Water-Rock-scCO ₂ Reaction Time (hours)	1157	815
Surface Area of Unreacted Powders (m ² /g)	3.2914 ± 0.1910	0.5394 ± 0.0180
Surface Area of Reacted Powders (m ² /g)	1.5442 ± 0.0203	0.2106 ± 0.0116

*Gothic shale core samples from the Greater Aneth Field were used in experiments

[†]Parallel experiments without CO₂ were performed; results not shown here

The experimental methods used in this project are based on techniques developed in previous works [4, 5]. The experiments reacted rock and brine saturated with constituent minerals at 160°C and 25MPa, followed by injection of scCO₂. The temperature was selected to accelerate kinetics without changing in-situ water-rock reactions, an approach used in similar studies [6-8]. Table 1 outlines experimental conditions and parameters for both experiments.

2.2 Field Analogy

The experiments replicate the Desert Creek Limestone reservoir and Gothic Shale caprock in the Paradox Basin in southeastern Utah (Fig. 1). The Pennsylvanian Desert Creek Limestone, an evaporite carbon sequence, is the main producing zone within the Greater Aneth Field [9]. This formation is currently a combined enhanced oil recovery and sequestration pilot site for the Southwest Regional Partnership on Sequestration. The organic rich Gothic Shale is the sealing unit above the Desert Creek Limestone. The overlying shallow aquifer in the region is the Navajo Sandstone. Experiments emulate injection of scCO₂ at two different zones within a sequestration reservoir; near the top of the reservoir, where water-rock interactions encompass both reservoir and caprock, and deep within the reservoir, away from the shale caprock.

2.3 Geochemical Modelling

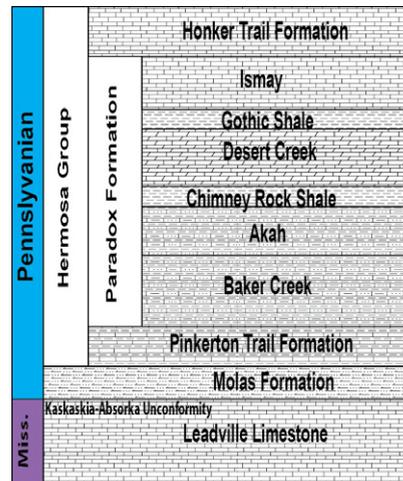


Fig. 1. Stratigraphic column of the producing zones in the Aneth Field within the Paradox Basin, Utah. This project focuses on the Desert Creek limestone and Gothic Shale caprock

Equilibrium modelling is done using Geochemist Work Bench (GWB) [10] to calculate the initial brine compositions and interpret the experimental results. The initial brine composition is calculated to be in equilibrium or as close as possible to the rocks so that there is little to no reaction between rocks and brine prior to scCO₂ injection.

3. Results and Discussion

In both experiments, major ion concentrations remain relatively constant with a few exceptions. In the experiment replicating the caprock-reservoir boundary, an increase in SiO₂ and Fe is seen with injection of scCO₂. As the experiment continues, the concentration of both dissolved species decreases. These data are consistent with SEM and modeling results that suggest initial dissolution of minerals followed by precipitation of clays, Fe-sulfides, and Fe-carbonates (Fig. 2). The experiment replicating injection deeper into the reservoir does not exhibit a large change in Fe. Sulfate concentrations increase after scCO₂ injection, and subsequently decrease over time. Aqueous chemistry, SEM and modeling results indicate initial dissolution followed by precipitation of anhydrite, pyrite, and various metal sulfides.

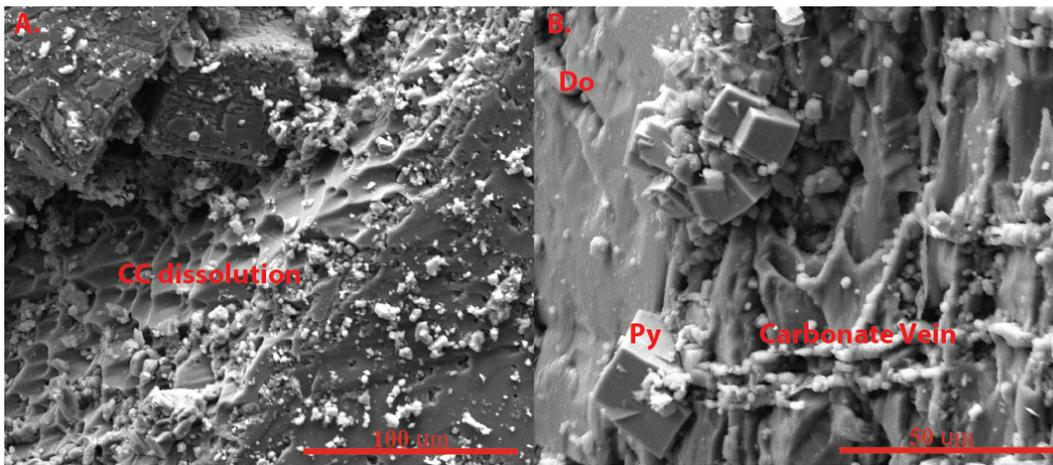


Fig. 2. SEM image of calcite (A) and dolomite (B) reacted in synthetic brine and CO₂. Figure 2A shows extreme dissolution of calcite when reacted with CO₂ – saturated brine allowing metals to be released from the calcite. Figure 2B shows CO₂ triggered secondary pyrite and carbonate precipitation on primary dolomite.

Ba, Cu, Pb, and Zn concentrations increase with injection in both experiments. Concentrations subsequently decrease to approximately steady state values 120-330 hours after injection of CO₂. In experiments that emulate the caprock-reservoir boundary, final Fe (700 ppb), an element of secondary concern for the US Environmental Protection Agency (EPA), and Pb (50 ppb) concentrations exceed EPA limits, whereas Ba (140 ppb), Cu (48 ppb), and Zn (~450-500 ppb) concentrations remain well below EPA limits. In experiments that simulate deeper reservoir conditions, away from the caprock boundary, final Fe (3500 ppb), Pb (17 ppb) and Ba (155 ppb) concentrations exceed values seen at the caprock-reservoir boundary; whereas Zn (50 ppb) is far less in the deeper reservoir than at the caprock-reservoir boundary. Arsenic values in both experiments exceed the EPA limit. Unfortunately, reliable determination of As concentrations in waters with high ionic strength such as used in this study ($I = 3.3$ m) is an analytical issue and currently under evaluation.

The experimental results suggest that if brines leak from a storage reservoir and mix with a potable aquifer, Ba, Cu, and Zn will not be contaminants of concern. Lead, Fe and As (still under consideration) initially exceed the EPA threshold and may require careful attention in a sequestration scenario. The

caprock plays an active role as a source of metals, although subsequent precipitation may remove metals from solution. However, experimentally observed trends of decreasing trace metal concentrations suggest that these metals could become less of a concern during the life of a carbon repository.

4. Conclusions

If CCS is going to be a practical option to mitigate anthropogenic CO₂, understanding and quantifying the potential impact to potable aquifers from leakage of formation brine and CO₂ during sequestration is essential. Hydrothermal experiments examine the release of potentially harmful metals in the saline injection reservoir at both the caprock-reservoir boundary, and deep within the injection reservoir. The results indicate that, in both systems, trace elements behave in a similar manner: increasing in concentration with the injection of scCO₂ but decreasing with time which suggests mobilization followed by precipitation of these elements. However, sorption cannot be excluded, possibly affecting trace elements such as Pb and As. Lead, Fe, and As exceed the EPA limits in these experiments, suggesting that these may be elements of concern. This work will be useful for any site being reviewed for future geologic carbon sequestration or current work with enhanced oil and/or gas recovery.

Acknowledgements

This project was supported by an EPA Start Grant R834387 to Kaszuba (UW) and to J. McCray, R. J. Maxwell, and A. Sitchler at the Colorado School of Mines, and a McMurry Fellowship in Energy Research in Geology and Geophysics scholarship to Marcon. John Kaszuba's work was also supported by the UW School of Energy Resources. We acknowledge The Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, particularly Fredrick G. Luiszer, for aqueous analyses. We thank Susan Swapp and Norbert Swoboda-Colberg for assistance with XRD and SEM analyses and Kellie Antrobus for performing BET measurements at the University of Wyoming.

References

- [1] Kaszuba JP, Janecky DR. Geochemical Impacts of Sequestering Carbon Dioxide in Brine Formations, in Sundquist, E., and McPherson, B., eds., *Carbon Sequestration and its Role in the Global Carbon Cycle: Washington, DC, American Geophysical Union*; 2009, p. 239-247.
- [2] Little MG, Jackson RB. Potential impacts of leakage from deep CO₂ geosequestration on overlying freshwater aquifers: *Environ Sci Tech* 2010; **44**: 9225-9232.
- [3] Bandstra JZ, Brantley SL. Data fitting techniques with applications to mineral dissolution kinetics, in Brantley SL, Kubicki JD, White AF, editors, *Kinetics of Water-Rock Interaction*. New York: Springer Science+Business Media ; 2008, p 211-257.
- [4] Seyfried W, Janecky D, Berndt M., Rocking autoclaves for hydrothermal experiments II: The flexible reaction-cell system. In Ulmer G, Barnes H. editors, *Hydrothermal Experimental Techniques*. New York: John Wiley & Sons; 1987, p. 216-239.
- [5] Kaszuba JP, Janecky DR, Snow MG. Experimental evaluation of mixed fluid reactions between supercritical carbon dioxide and NaCl brine: Relevance to the integrity of a geologic carbon repository: *Chem Geol* 2005; **217(3-4)**: 277-293.
- [6] Gunter WD, Wiwchar B, Perkins EH. Aquifer disposal of CO₂-rich greenhouse gases: extension of the time scale of experiment for CO₂-sequestering reactions by geochemical modelling: *Mineralogy and Petrology* 1997; **59**: 121-140.
- [7] Credoza A, Bildstein O, Jullien M, Raynal J, Pétronin JC, Lillo M, et al. Experimental and modeling study of geochemical reactivity between clayey caprocks and CO₂ in geological storage conditions: *Energy Procedia* 2009; **1(1)**: 3445-3452.
- [8] Alemu BL, Aagaard P, Munz IA, Skurtveit E. Caprock interaction with CO₂: A laboratory study of reactivity of shale with supercritical CO₂ and brine. *App Geochem* 2011; **26(12)**: 1975-1989.
- [9] McClure K, Morgan C, Thomas Chidsey J, Survey UG, Eby D. Heterogeneous shallow-shelf carbonate buildups in the paradox basin, Utah and Colorado: targets for increased oil production and reserves using horizontal drilling techniques. Utah Geological Survey; 2003.
- [10] Bethke CM. *Geochemical and Biogeochemical Reaction Modeling*. New York: Cambridge University Press; 2008.