GHGT-10

Wellbore Integrity in Carbon Sequestration Environments: 1. Experimental Study of Cement – Sandstone/Shale – Brine – CO₂

Susan Carroll, Walt McNab, Sharon Torres, Mike Singleton, and Pihong Zhao

Lawrence Livermore National Laboratory, Livermore CA 94550, USA

Abstract

It is important to determine the geochemical reactions between common cements used in wellbore construction, formation mineralogy, and supercritical CO₂ stored in deep saline reservoirs, because abandoned and completed wells provide a pathway for release of the stored CO₂ back to overlying aquifers and to the atmosphere. Although it is known that alkaline cements readily react with acidic CO₂-rich waters, the influence of the formation and cement mineralogy on the bonding of the wellbore cement to the caprock at pressure and temperature conditions associated with saline CO₂ storage reservoirs is uncertain.

We reacted end member components of the heterolithic sandstone and shale unit that forms the upper section of the carbon storage reservoir at the Krechba Field, In Salah, Algeria with supercritical CO₂ and class G cement in a representative brine at 95°C and 10 MPa in gold bag autoclaves to identify geochemical reactions that occur in the wellbore environment. The experimental system allows reaction progress of complex geochemical environments to be tracked by sampling the aqueous phase periodically over the two-month long experiments.

Analysis of the solution chemistry over time and the solid products show that the wellbore environment is dominated by reactions between cement, carbonate, and clay minerals when exposed to CO₂-rich fluid. Reaction of the hydrated cement with synthetic brine equilibrated with supercritical CO₂ rapidly forms amorphous silica, calcite, and aragonite. Similar reaction products were observed when cement reacted with sandstone and CO₂ (reservoir). However in the vicinity of the shale (caprock) cement minerals altered to calcium carbonate minerals and smectite (clay).

© 2011 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: CO₂, Cement Carbontion, Geochemistry, Wellbore Integrity

doi:10.1016/j.egypro.2011.02.496
1. Introduction

Ensuring that large-scale CO₂ storage is safe and effective requires predicting the long-term integrity of storage sites as well as demonstrating the comprehensive consideration of potential site-specific risks. Wellbores are a potential high-risk pathway for leakage of CO₂ from the storage reservoir to overlying drinking water aquifers and back into the atmosphere, because the alkaline cement is highly reactive with the CO₂-rich brines. A large data gap for risk assessment for the long-term storage of industrial CO₂ is the permeability evolution in the wellbore environment. Field, experimental and modeling studies suggest that carbonation of hydrated cements results in a lower porosity and has the potential to heal fractures within the cement [1-6]. Carey [3] and Wigand [5] found three reaction zones perpendicular to fracture flow when cured cement was reacted with supercritical CO₂, CO₂-rich brine, and shale mineral assemblage. The dense silica and fully carbonated layers closest to the shale showed reduced porosity relative to the hydrated cement, while the partially carbonated zone at the diffusion front indicated an increase in porosity. Calcite precipitation on the fracture surface both expands the fracture thickness and at discrete points seals the fracture. Carey [3] noted that differences observed in the extent of cement carbonation in other studies [1-2] was likely to depend on reaction temperature and pressure as well as transport regimes within the wellbore environment.

The focus of this work was to determine the key geochemical reactions between common cements used in wellbore construction, formation mineralogy, and supercritical CO₂ stored in deep saline reservoirs. We reacted the end member components of the heterolithic sandstone and shale unit that forms the upper section of the carbon storage reservoir at the Krechba Field, In Salah, Algeria with supercritical CO₂ and class G cement in representative brine at 95°C and 10 MPa in gold bag autoclaves. This experimental system allows reaction progress of complex geochemical environments to be tracked by sampling the aqueous phase periodically over the two-month long experiments. The results are used to constrain a reactive transport modeling study of wellbore integrity at the Krechba Field [7].

2. Methods

Sandstone and shale rock fragments (C10.2 and C10.3) from the upper section of the carbon storage reservoir at the Krechba Field, In Salah, Algeria were used in the experiments (see Armitage [8] for detailed mineralogical description). The shale end member, sample 14, consisted of 44% illite, 30% chlorite, 20% quartz, 4% kaolinite, 2% feldspar and trace amounts of pyrite by weight. The sandstone end member, sample 7, consisted of 88% quartz, 6% chlorite, 4% kaolinite and 2% siderite by weight. The powdered class G oil well cement used in the experiments was provided by Mountain Cement Company and consisted of 56% Ca₃SiO₅, 39% Ca₂SiO₄, 5% Ca₃AlO₄.₅, + 0.5% Na₂O and K₂O by weight as determined by standard ASTM C 150. In some experiments bentonite was added to the cement (bentonite to cement ratio = 1:39 by weight) to reflect mixtures identified in well logs from the Krechba site. Curing of the cement was done in the reaction vessels at experimental conditions.

The experiments were conducted in a synthetic brine using reagent grade salts (1.8 molal NaCl, 0.55 molal CalCl₂, and 0.1 molal MgCl₂ ) to capture the major ion chemistry measured at the site. High purity liquid CO₂ was pressurized at temperature to generate supercritical CO₂ for the experiments.

Static Dickson-type Au reactors housed in water-filled pressure vessels were used to react combinations of cement, sandstone, shale, synthetic brine and supercritical CO₂. We monitored reaction kinetics and the approach to equilibrium by sampling the solution as a function time. All metals measured in solution were from the solid reactants, because the supercritical CO₂ and
the brine contacted only gold or passivated-titanium. About 200 g of brine and equal weights of
the class G cement (with bentonite additive) and the sandstone or the shale end members were
reacted at 95˚C and 10 MPa. About 10 g sandstone or shale rock fragments were used in the
experiments due to limited availability. After one month of reaction, excess supercritical CO₂
(about 20 g) was injected into the gold bag and reacted for an additional month. Several brine
samples were taken and analyzed for solution chemistry over the duration of the experiment. At
the end of the experiment, the reaction vessel was cooled to room temperature, excess CO₂ was
removed, and solid reactants were rinsed with distilled and deionized water several times to
remove brine. The solids were dried at 60˚C prior to XRD and ESEM/EDS analysis. Samples
for dissolved Al, Ca, Fe, Mg, and Si analyses were filtered, and diluted with distilled and
deionized water, acidified with high purity nitric acid. Samples for total dissolved inorganic
carbon were injected directly into 1 N NaOH solution to trap the CO₂, filtered to remove any
carbonate solids that precipitated, and analyzed for dissolved inorganic carbon, calcium, and
magnesium. The total dissolved carbon in the experiment was equal to the measured inorganic
carbon in the filtered sample plus the amount of carbon trapped as carbonate minerals in the
NaOH extract. The amount of carbon trap as inorganic carbon in the NaOH extraction was
calculated as the difference between the total dissolved Ca and Mg measured in the bulk sample
and in the filtered NaOH extraction.

Major and trace metals in the samples and the stock solution were analyzed using ICP-
MS. Samples were prepared volumetrically with a 20:1 dilution using an internal standard
solution in 2% nitric acid. A fully quantitative analysis using a linear calibration curve based on
known standards was performed. The internal standard was corrected for instrument drift and
suppression from the sodium chloride matrix. Silica was run in collision cell technology mode
to avoid polyatomic interferences. Detection levels were established from duplicate blanks and
serial dilution preparations. Matrix spike samples were analyzed for quality control.

Total inorganic carbon concentrations were determined using an automated OI Analytical
Aurora 1030W Carbon Analyzer and model 1088 rotary autosampler. The Aurora 1030W used a
syringe pump to transfer samples and reagents to a temperature-controlled reaction chamber.
Samples were reacted with 5% phosphoric acid to evolve CO₂ gas, which was purged by a
stream of N₂ gas and quantified using a NDIR detector.

The pH was estimated at temperature from the measured solution composition assuming
portlandite and calcite solubility prior to and after injection of supercritical CO₂. This was a
reasonable approach, because calcite and portlandite were identified as major products when the
class G cement was reacted with and without supercritical CO₂, respectively. We used the
PHREEQC 2.15.0 geochemical speciation code [9] and the LLNL database augmented by
cemdata (http://www.empa.ch/cemdata) in a format consistent with the LLNL database used in
PHREEQC. The B-dot ion-interaction model was used to approximate the non-ideal behavior of
solutions at elevated ionic strength and temperature.
3. Results and Discussion

Pre-existing, injection and monitoring wells are potential leakage pathways for CO$_2$ from the saline storage reservoir to overlying drinking water sources and the atmosphere. The integrity of the wells is largely dependent on the seal between cement and the geologic formation. Here we discuss the carbonation of the cement and identify reaction products that may alter the bond between the carbonated cement and the geologic formation. The cement/sandstone and cement/shale experiments are meant to represent the wellbore environment near the storage reservoir and the caprock respectively (although the materials themselves are from the heterolithic sandstone and shale unit that forms the upper section of the carbon storage reservoir at the Krechba Field, In Salah).

Cement was rapidly altered to aragonite, calcite, and amorphous silica by the CO$_2$-rich brines. Figure 1 shows the change in solution composition for the reaction of cement, brine, and supercritical CO$_2$ at 95˚C and 10 MPa as solution pH (95˚C), total dissolved CO$_2$, Ca, Mg, Si, Fe, and Al. Cement hydration produced an alkaline solution with pH = 9.7, elevated Ca and depleted Mg controlled by solubility of portlandite and amorphous or poorly crystalline calcium/magnesium silica hydrates (CSH/MSH) phases. Depletion of Mg from the brines suggests that Mg forms a silica hydrate phase referred to here as MSH. Low concentrations of Si reflect the low solubility of CSH/MSH phases. The low Fe and Al may reflect the solubility of monoaluminosulfate for Al and an iron hydroxide for Fe or their substitution in the CSH phases. The alkaline cement mineral assemblage underwent rapid carbonation when supercritical CO$_2$
was injected into the brine. Dissolved CO$_2$ concentrations increased by several orders of magnitude to values near 0.8 molal. There was a marked increase in brine acidity with pH (95°C) = 4.2. Dissolved Ca concentrations decreased as the cement phases were altered to calcium carbonate minerals, dissolved Mg concentrations increased to their initial brine concentration as the MSH dissolved, dissolved Si also increased to a constant value bracketed by chalcedony and quartz solubility, and dissolved Fe and Al were quite low.

One would expect that the reaction products between the cement and the formation mineralogy to be the same because the cement provides a very large and reactive supply of calcium and silica to form carbonate and amorphous silica precipitates, compared to the much slower dissolution of quartz, chlorite, and illite in the sandstone and shale rock fragments. However, we observe different reaction products and solution chemistry when CO$_2$-rich brines react with cement and sandstone or cement and shale. The primary mineralogical differences between the shale and the sandstone prior to reaction, is that the shale contains a significant amount of illite clay and the sandstone does not. Below we describe the experimental results for these two experiments. The sandstone and shale were also reacted with supercritical CO$_2$ without cement and are described and modelled in McNab [5].

Comparison of the solution chemistry profiles from the cement and cement/sandstone experiments suggest that cement carbonation will drive reaction chemistry in the wellbore environment where the cement contacts sandstone geology. In this environment carbonate and
Figure 3 Carbonation of Class G cement and shale plotted as solution composition versus reaction time.

amorphous silica are the dominant reaction products (Fig. 1, 2). In both experiments cement hydration produced alkaline solutions with elevated Ca and depleted Mg controlled by solubility of portlandite and amorphous or poorly crystalline CSH/MSH phases. Any Fe, Al, or Si from higher chlorite dissolution rates expected at alkaline pH have been consumed by the precipitation of cement phases. The cement mineral assemblage underwent rapid carbonation when supercritical CO2 was injected into the brine. Dissolved CO2 concentrations increased by several orders of magnitude to values between 1 and 0.8 molal and brine acidity increased to pH (95°C) = 4.2. Dissolved Ca decreased as the cement phases dissolved and calcium carbonate minerals precipitated from solution, dissolved Mg increased to their initial brine concentration just below magnesite solubility, dissolved Si also increased to a constant value bracketed by chalcedony and quartz solubility, and dissolved Al concentrations were quite low. Despite the dominance for the cement carbonation reactions, some chlorite in the sandstone dissolved in the CO2-rich brine. Upon injection of the CO2, the dissolved Fe increased by 3 orders of magnitude to a peak concentration, and then decreased over time decreased to a constant concentration. It is likely that Fe from chlorite dissolution is taken up in the abundant carbonate phases. Qualitative EDS analysis show some Fe in rhombahedral shaped calcium carbonate alteration products (Fig 4).

Comparison of the solution profiles and the secondary precipitates from all three experiments suggest that carbonate and smectite are the dominant reaction products in the cement/shale system instead of carbonate and amorphous silica as identified in the cement and
Figure 4. Secondary precipitates from the reaction of cement/sandstone/CO2-rich brine (top) and the reaction of cement/shale/CO2-rich brine (bottom).

cement/sandstone experiments (Fig 1-4). All three experiments produce an alkaline solution with elevated Ca and depleted Mg controlled by solubility of portlandite and amorphous or poorly crystalline CSH and MSH phases during cement hydration. Although the solution chemistry provided no indication of reaction of the shale by the alkaline pH waters during cement hydration, dissolution features preserved in layered silicates were likely to have formed during this phase of the experiment because clay mineral dissolution is much higher at alkaline pH and no such features were observed when the shale was reacted with CO2 without cement (data not shown). Reaction of supercritical CO2, brine, shale and cement yield Mg, Si, and Fe profiles that are different from their respective profiles from the cement and cement/sandstone experiments. About half of the Mg in the initial brine redissolved in the solution compared to near 100% redissolution for the experiments with cement and cement/sandstone. Dissolved Si
increased to quartz saturation in the cement/shale experiment, a level below that observed for experiments with cement and cement/sandstone. Fe concentrations in the final samples of the cement/shale and the cement/sandstone experiments suggest that Fe dissolved from chlorite was taken up as Fe-Ca carbonate. Aluminum also shows a peak in concentration compared with the other experiments. Dissolved Ca reflected carbonation of the cement to aragonite and calcite. ESEM images show that sheet silicates are highly reactive when the shale reacts with the cement and CO$_2$-rich brines (Fig. 4). Extensive dissolution grooves formed along the edges of the sheet silicates and fibrous precipitates formed on the planar surfaces of the sheet silicates, in addition to calcium carbonate precipitation from cement carbonation. No amorphous silica was observed. The difference between the Mg and Si dissolution features and fibrous precipitates on the sheet silicates, and the lack of amorphous silica precipitates suggest that secondary smectite precipitation and calcium carbonate are key reaction products at the caprock-cement interface.

4. Conclusions

Our research shows that alkaline cements are highly reactive in the presence of CO$_2$-rich brines and are quickly transformed to carbonate minerals and amorphous silica. These reactions can be easily modeled as the transformation of portlandite, and Ca- and Mg-silicates to aragonite or calcite and amorphous silica, in agreement with other studies [1-6]. A new result from this study is that distinct geochemical reactions occur between assemblages of CO$_2$/brine/cement/sandstone and assemblages CO$_2$/brine/cement/shale. The alteration of cement minerals and the dissolution of chlorite lining the sandstone pores yielded calcium carbonate minerals with some Fe and amorphous silica. In the caprock environment, the alteration of cement minerals, illite and chlorite dissolution yielded calcium carbonate minerals and smectite clays.

Differences between the sandstone and shale experiments with cement and CO$_2$ raise questions about geochemical models of wellbore integrity for carbon sequestration reservoirs. Development of a geochemical model requires consistency across the geochemical landscape. Carbonation of the cement provides a large reservoir of dissolved Si in the wellbore environment. The precipitation of amorphous silica when cement reacts with sandstone and CO$_2$ is at odds with the precipitation of smectite when cement reacts with shale and CO$_2$. One possible explanation is that the abundance of illite and chlorite in shale provides surface sites that lead to heterogenous nucleation and growth of smectite on the layered silicates. The lack of these surface sites in the sandstone, with much less chlorite and no illite, results in the homogenous nucleation and growth of amorphous silica.

Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore national Laboratory under contract DE-AC52-07NA27344. We acknowledge funding from the Joint Industry Project (a consortium of BP, Statoil and Sonatrach) and the U.S. Department of Energy to investigate the importance of geochemical alteration at the In Salah CO$_2$ storage project.

References

1. Kutchko, BG, Strazissar, BR., Dzombak DA, Lowry GV, Thaulow, N. Degradation of well cement by CO$_2$ under geologic sequestration conditions. Environmental Science and Technology 2007; 41: 4787-4792.
2. Barlet-Gouedard et al, 2006;
3. Carey JW, Wigand M, Chipera SJ, WoldeGabriel G, Pawar R, Lichtner PC, Wehner SC, Raines MA, Guthrie
GD. Analysis and performance of oil well cement with 30 years of CO2 exposure from the SACROC Unit, West Texas, USA. International Journal of Greenhouse Gas Control 2007; 1:75-85.

4. Duguid A. An estimate of the time to degrade the cement sheath in a well exposed to carbonated brine. Energy Procedia 2009; 3181-3188.

5. Wigand, M, Kazuba, JP, Carey JW, Hollis WK. Geochemical effects of CO2 sequestration on fractured wellbore cement at the cement caprock interface. Chemical Geology 2009; 265:122-133.

6. Huet BM, Prevost JH, Scherer GW. Quantitative reactive transport modeling of Portland cement in CO2-saturated water, Internation Journal of Greenhouse Gas Control 2010; doi:10.1016/j.ijggc.2009.11.003.

7. McNab WW, Carroll SA. Wellbore integrity at the Krechba carbon storage site, In Salah, Algeria: 2. Reactive transport modeling of geochemical interactions near the cement-formation interface. Int. Conference on Greenhouse Gas Technologies, 2010 (GHGT); www.sciencedirect.com

8. Armitage PJ, Worden RH, Faulkner DR, Aplin AC, Butcher AR, Iliffe J. Diagenetic and sedimentary controls on porosity in Lower Carboniferous fine-grained lithologies, Krechba field, Algeria: A petrological study of a caprock to a carbon capture site. Marine and Petroleum Geology 2010 (in press).

9. Parkhurst DL, Appelo CAJ. User’s Guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Water-Resources Investigations Report 99-4259, 1999, 312p.