Wellbore integrity and CO₂-brine flow along the casing-cement microannulus

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Abstract

Wellbore integrity is one of the key performance criteria in the geological storage of CO₂. This is significant in any proposed storage site but may be critical to the suitability of depleted oil and gas reservoirs that may have 10’s to 1000’s of abandoned wells. Much previous work has focused on Portland cement which is the primary material used to seal (create zonal isolation) wellbore systems. This work has emphasized the reactivity of Portland cement to form calcium carbonate. However, an increasing number of field studies [(e.g., 1], experimental studies [e.g., 2], and theoretical considerations indicate that the most significant leakage mechanism is likely to be flow of CO₂ along the casing-cement microannulus, cement-cement fractures, or the cement-caprock interface. The magnitude of flows along these interfaces is a complex function of the pressure gradient, geomechanical properties that support the interface and dissolution/precipitation reactions that lead to widening or closure of the interface.

In this study, we investigate the casing-cement microannulus through core-flood experiments. The experiments were conducted on a 5-cm diameter sample of cement that was cured with an embedded rectangular length of steel casing. Prior to the experiment, the casing was loosened creating a poorly bonded interface. However, we discovered that under confining pressure this interface was non-transmissive, suggesting that in the wellbore environment an open casing-cement microannulus requires a relatively low differential between pore and confining pressure. For the experiments, we created an artificially transmissive interface by scoring grooves in the steel casing (0.2-0.8 mm in depth).

The core-flood experiments were conducted at 40 ºC, 14 MPa pore pressure, and 28 MPa confining pressure for a period of 400 hours. During the experiment, 6.2 L of a 50:50 mixture of supercritical CO₂ and a 30,000 ppm NaCl-rich brine flowed through 10-cm of limestone before flowing through the 6-cm length cement-casing composite. Approximately 41,000 pore-volumes of fluid moved through the casing-cement grooves. Scanning electron microscopy revealed that the CO₂-brine mixture impacted both the casing and the cement. The Portland cement was carbonated to depths of 50-150 μm by a diffusion-dominated process. There was no evidence of mass loss or erosion of the Portland cement. By contrast, the steel casing reacted to form abundant precipitates of iron carbonate that lined the channels and in one case almost completely filled a channel. These results are compared to field studies to constrain the magnitude of possible CO₂ migration in real wellbore systems.
1. Introduction

Wellbore integrity is important to ensuring the long-term geological sequestration of CO$_2$ [3]. This is particularly true for depleted oil and gas reservoirs which may have 10’s to 1000’s of abandoned wells. However, it also concerns wells above the storage reservoir that could provide a path to the surface for CO$_2$ that escapes the primary reservoir. Wellbore integrity issues are usually divided into two types: improper completion and abandonment of the wells; and the long-term stability of wellbore materials in a CO$_2$-rich environment. Our study focuses on the latter condition, where the concern is for the steel casing and Portland cement used in typical well completions. In laboratory studies, CO$_2$ has been observed to accelerate the corrosion of steel both at the anode (dissolution of iron) and cathode (production of H$_2$) [4] according to the reaction:

$$\text{Fe} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{FeCO}_3 + \text{H}_2$$ (1)

CO$_2$ is also reactive with Portland cement transforming calcium hydroxide (portlandite) and calcium-silicate hydrate to calcite and mixtures of calcite and silica [5]:

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$ (2)

$$\text{Ca}_x\text{SiO}_{2x+x} + x\text{H}_2\text{O} + x\text{CO}_2 \rightarrow x\text{CaCO}_3 + \text{SiO}_2(\text{amorphous}) + x\text{H}_2\text{O}$$ (3)

While these reactions have the potential to be deleterious, the impact of CO$_2$ on wellbore integrity is a function of the detailed fluid dynamics and reaction kinetics in the wellbore environment. For example, reaction of steel with dissolved CO$_2$ can lead to scale formation (FeCO$_3$) and the passivating of the steel surface, protecting against further corrosion [4]. Similarly, the properties of Portland cement can improve with carbonation (e.g., strength increases and permeability decreases) [5].

Two recent field studies of wellbore materials suggest that wellbore materials can survive some period of exposure to CO$_2$. Carey et al. [1] studied a well with 35 year history as a CO$_2$ injector and producer in an enhanced oil recovery field in west Texas. They found evidence for CO$_2$ in carbonate deposits along the cement-casing interface and in carbonation of the cement at the cement-formation interface. However, they noted that the permeability of the carbonated cement was not significantly different from uncarbonated cement and that the cement otherwise appeared to provide a hydrologic barrier to fluid flow along the wellbore annulus. Crow et al. [6] studied a 30-year old well from a natural CO$_2$ reservoir. The pattern of carbonation they observed was different from the west Texas site but they also concluded that the hydrologic properties of the cement did not appear to be significantly deteriorated by interaction with CO$_2$. In both studies, the authors concluded that CO$_2$ had migrated along interfaces, either the casing-cement or the cement-caprock, and that the primary vulnerability of wellbore systems was the interfaces rather than complete material degradation. In both of these field sites, the steel casing in contact with the cement showed little to no evidence of corrosion.

If these conclusions drawn from field observations are correct, then the behavior of the cement-casing and cement-caprock interfaces is critical to the long-term performance of wellbores. In particular, if these interfaces exist, how do they evolve with exposure to CO$_2$ and brine? Are they dominated by dissolution and continually widening or do the solid products indicated in Equations 1-3 deposit in the interfaces and eventually seal the interface against further fluid flow? This behavior is almost certainly a function of the relative fluid flux as determined by the width of the defect and the hydraulic gradient and the relative chemical reaction rates for dissolution and precipitation.

In this study, we investigate these questions with core-flood experiments in which we flow CO$_2$-brine mixtures along a synthetic cement-casing interface under typical CO$_2$ storage conditions. Our intent is to map out the dynamic behavior of the interfaces. We found that under our experimental conditions, the steel was more reactive than the cement and that evidence of partial filling of the interface by iron carbonates was observed. Furthermore, the reactivity of the steel suggests that logging tools characterizing casing corrosion can be a sensitive probe of CO$_2$-brine flow along the cement-casing interface.
2. Methods

The core-flood experiments were conducted at 40 °C, 14 MPa pore-pressure, and 28 MPa confining pressure. The experimental system consisted of a 10-cm length of limestone followed by a synthetic wellbore system constructed of Portland cement with an embedded rectangular prism of standard grade steel casing (Figure 1). A 50:50 mixture of supercritical CO₂ and brine was flowed through the composite limestone/cement-system. The brine contained 25,000 ppm NaCl, 4,000 ppm CaCl₂, 1,000 ppm MgCl₂, and 200 ppm MnCl₂. The brine composition was designed such that the fluid encountering the cement was approximately at equilibrium with calcite. (The limestone-equilibrated fluid was calculated to be strongly out of equilibrium with both cement and the casing.) The very low permeability of Portland cement ensured that measurable fluid flow would occur only along cement-steel interface.

Our initial design simply embedded the steel in the cement and created an interface by knocking the steel free before the cement completely set. However, we found that the confining pressure in combination with the system mechanical properties completely sealed this interface. In order to create flow, we carved seven grooves in the steel (0.2-0.8 mm in depth) and in the cement (0.1 mm in depth; Figure 1). During the experiments, a CO₂-brine flow rate of 10-20 ml/hour was maintained through the limestone and along the cement-casing interface for 394 hours. The volume of fluids was approximately 6.2 L, which when scaled to the volume of the grooves (~0.15 cm³) is equivalent to 41,000 pore volumes.

The produced fluids were analyzed with inductively coupled plasma atomic emission spectrometry. The cement-casing composite was cross-sectioned and characterized with scanning electron microscopy. Numerical modeling of the experiments was done with the reactive transport code, FLOTRAN, which includes an equation of state for CO₂ and solubility of CO₂ dependent on ionic strength of the aqueous solution [7].

3. Results

The permeability of the composite limestone-cement-casing system increased during the experiment from ~0.52 Darcy to ~0.67 D (Figure 2). We attribute this change to the limestone because we estimate the permeability of the cement-casing composite at about 10 D based on a Poiseuille’s Law approximation for capillary flow. The jump in permeability following blow-down of the core (de-pressurization to one atm.) is attributed to movement of fine-grained materials.

All of the channels in the steel casing were characterized by some degree of corrosion and formation of a deposit at the interface of the casing with the fluid. In most cases, this deposit was relatively thin (~20-50 μm; Figure 3), however, in one channel the deposit nearly fills the space (Figure 4). In the latter case, SEM analysis shows arced
cracks in the deposit that we assume are artifacts of sample preparation and desiccation of the sample. Energy dispersive analysis of the deposits indicates they are iron carbonate (FeCO$_3$) corrosion products. Detailed examination of the deposits showed interesting variations in material density and relative iron concentration (Figure 5). We interpret this to indicate that the corrosion products are poorly crystalline and of variable stoichiometry.

We do not have precise measurements of the pre-experiment geometry of the channels. It is thus difficult to quantify changes in channel geometry due to the corrosion reaction. However, we note that the dimensions of the channels do not appear significantly larger than initial estimates. Of the seven channels, one is almost entirely filled another is partially filled and the remainder show thin corrosion deposits. We believe that these differences may reflect different fluxes with low flux channels characterized by deposition of iron carbonate and high flux channels characterized by formation of a thin passivating iron carbonate layer.

The Portland cement contact with the casing was not markedly affected by the CO$_2$ flux. There is no significant erosion of the cement or deposition of calcium carbonate reaction products within the interface. A detailed examination of cement texture shows that CO$_2$ did penetrate into the cement, resulting in carbonated cement to depths of 20-150 μm (Figure 3-Figure 4). This is shown in the figures by a slight change in gray-scale color and by a change in the abundance of the un-hydrated (bright) cement grains. The depth of CO$_2$ penetration is quite variable, but is greatest adjacent to the channels. Fractures that occur in the cement are attributed to sample preparation. For example, the fracture that extends away from the channel in Figure 3 does not have carbonation associated with it and was likely not active during the experiment.

CO$_2$-reactions at regions other than the channels are limited. The grooves scratched into the cement are not evident in the sections examined and were probably too small or were filled by deformation of the cement or chemical migration of portlandite. Some corners of the casing prism showed evidence for CO$_2$ migration in carbonation of cement and limited corrosion of the steel. Most other regions of the cement-casing interface had thin deposits of corrosion.

Fluid produced during the experiments was fairly constant in composition and reflected a rather limited chemistry. The pH ranged from 7.8 to 7.6 and other than Mn (which was removed from the fluid) was not strongly modified by chemical reactions.

4. Discussion

The experiment design was with a high-flux of CO$_2$-brine mixture and the expectation was that the system would be dominated by dissolution of cement and/or steel. The experimental evidence was contrary to this as instead of
extensive dissolution, we observed deposition of corrosion products and no indication of mass loss from the cement. In the following, we address these results in more detail.

4.1. Corrosion of Steel

The corrosion of steel in a casing-cement system is an electrochemical process in which both chemical reactions and flow of electrical current are involved. Due to the high alkalinity of the cement with a standard pH range of 12.5 to 13.5 [8], initially, a stable passivation layer protects the steel from corrosion. However, the ingress of carbon dioxide can reduce the pH to a value below 9 by reactions with cement hydration products such as Ca(OH)₂. The drop in pH will destroy the protective films resulting in corrosion of the steel in casing-cement system. In addition penetration of the cement by chloride ions can also result in damage to the passivation layer and increased susceptibility to corrosion. Based on the chemical reactions, the combined corrosion and carbonation mechanisms for the casing-cement system are shown in Figure 6.

The dominant corrosion product of steel in the presence of CO₂ is FeCO₃. FeCO₃ can be transported away from the steel resulting in mass loss of the steel, and it can also precipitate on the steel surface to form scales if it is supersaturated. A high supersaturation of FeCO₃ is necessary to form a protective film, and the film growth rate depends on the precipitation rate which is a function of the operation temperature and pH [9]. Considering the solubility of FeCO₃ decreases with increasing pH, the precipitation rate will be increased if the pH increases [4]. At room temperature, the precipitation rate is very small even at very high supersaturation, but at high temperature (>60 °C), the precipitation can proceed rapidly [4].

No significant mass loss of the steel was found under the present experimental conditions, but scales were found on the steel surface in all the channels. The scales were mainly composed of semi-crystalline FeCO₃, so it is reasonable to conclude that the scale is formed due to the precipitation of FeCO₃ from the solution. However, it is difficult to interpret why the precipitation process proceeds rapidly at such low temperature (40 °C) in contrast to previous experimental data [4]. The presence of high chloride concentration may be a factor that accelerates the corrosion and subsequent precipitation process. We cannot identify whether the scales provide protection from further corrosion based on the present experimental data.

Some iron-rich spots were also found in the cement phase. This is also because the deposition of FeCO₃ from the solution. The corrosion product of the steel is transported to cement surface by diffusion or turbulent mixing. The pH at the cement is much higher than the pH in bulk solution. Considering that the solubility of FeCO₃ decreases with increasing pH, the dissolved FeCO₃ should be supersaturated, leading to deposition in the cement.

4.2. Carbonation of Cement

The CO₂ attack on cement was limited to a mineralogical and textural alteration of the cement at depths ranging from 50 to 250 μm over the 394 hour experiment. The alteration pattern is consistent with diffusion of CO₂ from the fluid in the channel into the cement with the degree of penetration varying as a function of cement properties and supply of CO₂. Assuming a 1-D diffusion reaction, the depth of penetration is proportional to the characteristic diffusion time scale given by $\sqrt{4 D t}$ yielding effective diffusion coefficients ranging from $10^{-12}$ to $10^{-10}$ cm²/sec. The larger depth of penetration is about a factor of 3 smaller than observed in static diffusion studies of Kutchko et al. [10].

4.3. Fluid Chemistry
The produced fluid is a Ca-Na-Cl brine similar in composition to the initial brine (Figure 7). During the experiment, the Ca and Mg content rises slightly from the starting composition; HCO₃ rises abruptly from near zero and then continues to increase slightly during the experiment; Mn is scavenged completely by the limestone; pH rises abruptly and then drifts slightly downward (0.1 units); and iron rises from zero and behaves erratically with several high values early in the experiment before a steady rise ensues. The sampled fluids are calculated to be saturated or slightly supersaturated with respect to both calcite and siderite at laboratory conditions. (Siderite equilibrium is subject to assumptions concerning the oxidation state of the fluid; for these calculations we assume that fluids were dominated by Fe²⁺.) However, under experimental conditions (40 °C, 14 MPa CO₂), the solutions are calculated to be significantly undersaturated with respect to both calcite and siderite. We assume that the solutions precipitated these phases as they existed the core and before sampling.

5. Conclusions

A high flux of CO₂-brine at the casing-cement interface produced significant steel corrosion and deposition of FeCO₃ during a two week experiment under in situ sequestration conditions. The cement reactions were limited to slow diffusion of CO₂ into the matrix without significant erosion of cement by the CO₂-brine mixture. Despite the high flux, some of the grooved channels in the casing were partially filled with FeCO₃ corrosion products, suggesting that in this case flow could eventually be limited by a self-sealing carbonate deposition.

There are two field sites where wellbore integrity has been extensively studies [1,6]. In both environments, casing corrosion after 30 years of exposure was minimal to non-existent. The experimental evidence suggests that locations experiencing a significant flux of CO₂-brine along the casing-cement interface would produce significant corrosion of the casing. The absence of such corrosion at the field sites suggests that the flux of CO₂ producing carbonated wellbore cement at the field sites is relatively small or perhaps relatively dry. Furthermore, the sensitivity of casing to corrosion suggests that casing corrosion may be a useful indicator of behind-casing fluid flow. Relatively simple logging studies that show the presence of significant external casing corrosion may be a useful indicator of long-term flow along the casing-cement interface.

6. Acknowledgements

We wish to thank U.S. Department of Energy-NETL Contract #04FE04 and the CO₂ Capture Project for supporting this research.

7. References

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