THE INFLUENCE OF CO$_2$ ON WELL CEMENT

UTJECAJ CO$_2$ NA CEMENTNI KAMEN

NEDILJKA GAURINA-MEDIMUREC

University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, 10 000 Zagreb, Croatia

Key words: Portland cement, injection well, CO$_2$ injection, set cement permeability

Abstract
Carbon capture and storage is one way to reduce emissions of greenhouse gases in the atmosphere. Underground gas storage operations and CO$_2$ sequestration in aquifers relay on both the proper wellbore construction and sealing properties of the cap rock. CO$_2$ injection candidates may be new wells or old wells. In both cases, the long-term wellbore integrity (up to 1 000 years) is one of the key performance criteria in the geological storage of CO$_2$. The potential leakage paths are the migration CO$_2$ along the wellbore due to poor cementation and flow through the cap rock. The permeability and integrity of the set cement will determine how effective it is in preventing the leakage. The integrity of the cap rock is assured by an adequate fracture gradient and by sufficient set cement around the casing across the cap rock and without a microannulus. CO$_2$ storage in underground formations has revived the research of long term influence of the injected CO$_2$ on Portland cements and methods for improving the long term efficiency of the wellbore sealant. Some researchers predicted that set cement will fail when exposed to CO$_2$ leading to potential leakage to the atmosphere or into underground formations that may contain potable water. Other researchers show set cement samples from 30 to 50 year-old wells (CO$_2$ EOR projects) that have maintained sealing integrity and prevented CO$_2$ leakage, in spite of some degree of carbonation. One of reasons for the discrepancy between certain research lab tests and actual field performance measurements is the absence of standard protocol for CO$_2$ resistance-testing devices, conditions, or procedures.
This paper presents potential flow paths along the wellbore, CO$_2$ behaviour under reservoir conditions, and geochemical alteration of hydrated Portland cement due to supercritical CO$_2$ injection.

Introduction

According to the International Energy Agency (IEA), by 2050, 5 billion tons of CO$_2$ per year could be avoided through CO$_2$ capture and storage, representing a 16% contribution to the reduction of global greenhouse gas emissions. Typical underground storage reservoirs would lie at depths of 1 km or more and contain tens or even hundreds of millions of tonnes of CO$_2$. In the last 10 years, most of the technologies developed through the last 44 years of CO$_2$ EOR experience have been successfully applied in GS (geologic sequestration) for CCS (carbon capture and storage) in saline aquifers (Sweatman et al., 2009). To date, the technology as a whole has only been deployed so far at a few pilot sites.
around the world such as the Sleipner field in Norway, Weyburn field in Canada, In Salah field in Algeria (Gallo et al., 2002, Jimenez and Chalaturnyk, 2002). The majority of locations that are being considered for carbon dioxide (CO₂) injection and sequestration are typically found in the areas that have a history of oil, natural gas, and/or coalbed methane production (Ennis-King and Paterson, 2002; Gallo et al., 2002; Nezhad et al., 2006; Bellarby, 2009). Due to well logging and exploration activities in these regions, there is also a greater knowledge base for saline formations that lie either above or below oil and gas reservoirs. As a result of human activity, these formations are typically punctured by a significant number of wells from both exploration and production. No matter how impermeable an overlying caprock is, the sealing integrity may be compromised by the presence of wells. Diffusion through the cap rock is normally less of a concern than fracturing or fault-related leakage (Jimenez and Chalaturnyk, 2002).

**CO₂ behaviour under reservoir conditions**

Under most reservoir conditions, CO₂ does not behave like a gas, but more like a low-viscosity liquid. This will affect the injection performance (in the tubing and near wellbore area). In geological storage, CO₂ is injected at sufficiently high pressures (>7.3 MPa) and temperatures (> 31 °C) that it becomes a supercritical fluid below 800 m (Onan, 1984). Supercritical fluids take up much less space as shown in Figure 1, and diffuse better than either gases or ordinary liquids through the tiny pore spaces in storage rocks (Price and Smith, 2008). The red numbers in this figure show the volume of CO₂ at each depth compared to a volume of 100 at the surface. Supercritical CO₂ compresses further as the depth increases, increasing the amount that can be stored in the same volume of rock. CO₂ has 30-40 % less density and 5-10 times less viscosity than formation brine under typical sub-surface conditions (Ennis-King and Paterson, 2002). High pressure at sufficient depths (i.e., greater than 800 meters) maintains the supercritical fluid state.

Except at very high pressures, CO₂ is lighter than most oils, but it is denser than hydrocarbon gases such as methane. It will therefore naturally migrate to the top of oil or water bearing structures due to buoyancy and spread laterally beneath the reservoir cap rock. This is important as this CO₂ will then potentially interact with wells and completions at the top of the reservoir. Over time, carbon dioxide will tend to gradually dissolve in formation water, and then slowly sink, being denser than unsaturated water by around 1% (Ennis-King and Paterson, 2002). In both of these processes CO₂ can come into contact with existing wells and change the physical and chemical properties of cements under deep-well conditions (e.g., elevated pressure, temperature, and salinity).

![Figure 1 Change of density and volume of CO₂ with depth (IEA, 2008) Slika 1. Promjena gustoće i volumena CO₂ s dubinom (IEA, 2008)](image-url)

The effect of pressure and temperature on carbon dioxide behaviour is showed in Figure 2 (Sweatman et al., 2009). The presence of CO₂-induced carbonic acid in the vicinity of injection well is dependent on many factors such as pressure, temperature, buffering mineral content, salinity, etc. The CO₂ plume front moving away from the injection well causes decreasing of injection pressure to values close to the original reservoir pressure and the reversible conversion of carbonic acid into CO₂ and water.

Below saturation line CO₂ exists as a gas and the CO₂-plume’s acidic conditions are weakened significantly posing little or no threat of casing and liner corrosion (Sweatman et al., 2009).

Once underground, a variety of mechanisms (structural/stratigraphic trapping, residual trapping, solubility trapping, and mineral trapping) keep the supercritical CO₂ securely stored. These trapping processes take place over many years at different rates from days to years to thousands of years, but in general, geologically stored CO₂ becomes more securely trapped with time. Best estimates of leakage rates by geologists are well below levels that would cause any significant increase in atmospheric CO₂ or risk to public safety. Studies of geologic storage test sites suggest leakage rates of less than 1 percent over thousands of years (Imbus et al., 2006).
Well integrity

Well integrity has been identified as the biggest risk contributing to leakage of CO₂ from underground storage sites. Well bores represent the most likely route for leakage of CO₂ from geologic carbon sequestration. Abandoned wells are typically sealed with cement plugs intended to block vertical migration of fluids. In addition, active wells are usually lined with steel casing, with cement filling the outer annulus in order to prevent leakage between the casing and formation rock.

Several potential leakage pathways can occur along cased holes and/or abandoned wells as illustrated in Figure 3 (Gasda et al., 2004 and 2005). These include leakage between the cement and the outside of the casing (Fig. 3a), between the cement and the inside of the casing (Fig. 3b), through the cement plug (Fig. 3c), through deterioration (corrosion) of the casing (Fig. 3d), deterioration of the cement in the annulus (cement fractures) (Fig. 3e), and leakage in the annular region between the formation and the cement (Fig. 3f).

The permeability and integrity of the cement in the annulus and in the wellbore will determine how effective the cement is in preventing fluid leakage. The cement must be able to maintain a low permeability over lengthy exposure to reservoir conditions in a CO₂ injection and storage scenario. Long-term carbon sequestration conditions include contact with supercritical CO₂ and brine solutions at increased pressure and temperature and decreased pH (Kutchko et al., 2007).

The greatest risk for escape of CO₂ may come from other wells, typically for oil and gas, which penetrate the storage formation. Such wells need to be properly sealed in order to ensure that they do not provide pathways for the CO₂ to escape into the atmosphere. Planning for geologic storage must take such wells into account. CO₂ escaping through water wells is much more unlikely since water wells are usually much shallower than the storage formation. In injection wells, the presence of CO₂ may lead to corrosion on those parts coming in contact with CO₂ which normally...
means the production tubing and part of the production casing below the packer. Corrosion may be limited by: the selection of high alloy chromium steels, resistant to corrosion, and by inhibitor injection, if using carbon steel casing.

Degradation of wellbore cement due to CO₂ injection

Portland cement systems are used conventionally for zonal isolation in oil or gas production wells. It is thus crucial to study how such cement behaves at depth in CO₂-rich fluids and understand the chemical interactions between injected CO₂ and existing cements that could potentially lead to leakage. The properties of Portland cement are determined by the mineralogical composition of the Portland cement clinker (Table 1) (Nelson and Guillot, 2006). The total content of minor compounds such as CaO (free lime), MgO, K₂O, Na₂O, TiO₂, Mn₂O₃ and SO₃ is normally under 5%. When Portland cement is mixed with water, its compounds form hydration products. The main products formed by the cement hydration process are calcium silicate hydrate gel – CSH and calcium hydroxide - Ca(OH)₂. CSH is a semi-amorphous gel-like material that comprises approximately 70 wt % of the hydrated cement and is the primary binding material. Ca(OH)₂ is crystalline and comprises roughly 15 – 20 wt % of the hydrated cement (Nelson and Guillot, 2006).

<table>
<thead>
<tr>
<th>Oxide Composition</th>
<th>Cement Notation</th>
<th>Common Name</th>
<th>Concentration (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3CaO·SiO₂</td>
<td>C₃S</td>
<td>Alite</td>
<td>55-65</td>
</tr>
<tr>
<td>2CaO·SiO₂</td>
<td>C₂S</td>
<td>Belite</td>
<td>15-25</td>
</tr>
<tr>
<td>3CaO·Al₂O₃</td>
<td>C₃A</td>
<td>Aluminate</td>
<td>8-14</td>
</tr>
<tr>
<td>4CaO·Al₂O₃·Fe₂O₅</td>
<td>C₄AF</td>
<td>Ferrite phase</td>
<td>8-12</td>
</tr>
</tbody>
</table>

Portland cement is thermodynamically unstable in CO₂-rich environments and can degrade rapidly upon exposure to CO₂ in the presence of water (Onan, 2004). As CO₂-laden water diffuses into the cement matrix, the dissociated acid (H₂CO₃) reacts with the free calcium hydroxide and the calcium-silicate-hydrate gel (Fig 4, Kutchko et al., 2007). The reaction products are soluble and migrate out of the cement matrix. Eventually, the compressive strength of the set cement decreases and the permeability and porosity increase, leading to loss of zonal isolation.

There are mainly three different chemical reactions: (1) formation of carbonic acid, (2) carbonation of calcium hydroxide and/or cement hydrates, and (3) dissolution of CaCO₃ which are shown below (Onan, 1984; Bellarby, 2009; Santra et al., 2009; Benge, 2009):

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \quad (1)
\]

\[
\text{Ca(OH)}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{2H}_2\text{O} \quad (2a)
\]

\[
\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \quad (2b)
\]

\[
\text{Ca}^{2+} + \text{HCO}_3^- \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}^+ \quad (2c)
\]

Formation of Carbonic Acid

Carbonic acid is formed when CO₂ is dissolved into the aqueous phase (Fig 4). Moreover, CO₂ diffuses into the capillary pores of the set cement which contain, to some extent, a water and dissolves in it to form carbonic acid as shown in Eq. 1:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \quad (1)
\]

Forming of carbonic acid causes lowering in pH value, depending on temperature, partial pressure of CO₂ and other ions present in water, such as salt, etc. As the carbonated water diffuses into the cement matrix, Ca(OH)₂ is dissolved (into Ca²⁺ and 2OH⁻) by the acidic solution increasing slightly the porosity and enhancing leaching of Ca²⁺ out of the cement matrix (Fig. 4, zone 1).

Carbonation of calcium hydroxide and/or cement hydrates

When carbonic acid comes in contact with hydrated cements, corrosion can occur. Conventional Portland cement will react with dissolved carbon dioxide and revert to calcium carbonate (Fig 4, zone 2). Carbonic acid reacts with calcium hydroxide (also named as hydrated lime or portlandite) in the cement causing carbonation of Ca(OH)₂ (Eq. 2a) and/or decomposition of calcium silicate hydrate gel, the main binding component in hydrated cement, into calcium carbonate.
CaCO₃ is less soluble than Ca(OH)₂ and result in the loss of cement structural integrity (Carey et al., 2007). In other words, moderate degrees of carbonation can be beneficial to cement porosity, permeability, and strength but extensive carbonation can drastically because of the time dependant reduced porosity/permeability caused by the initial carbonation itself (Santra et al., 2009). The rate at which cement degradation occurs depends primarily on temperature, but also on cement type, cement composition, water/cement ratio, moisture content, CO₂ partial pressure, and porosity/permeability (Kutchko et al., 2007; Santra et al., 2009). Carbonation is extremely fast in the early days but later slows down drastically because of the time dependant reduced porosity/permeability caused by the initial carbonation itself (Santra et al., 2009). Calcium carbonate by itself may not be a problem unless and until so much of it is formed that it could crack the cement sheath (Sweatman et al., 2009). In other words, moderate degrees of carbonation can be beneficial to cement porosity, permeability, and strength but extensive carbonation can result in the loss of cement structural integrity (Carey et al., 2007). CaCO₃ is less soluble than Ca(OH)₂ and begins to dissolve when Ca(OH)₂ has been depleted.

Dissolution of CaCO₃

It is a long-term phenomenon and happens only when the set cement is surrounded by liquid water containing dissolved CO₂ (Eq. 3):

\[
CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2
\]  (3)

The result of bicarbonation process is water-soluble calcium bicarbonate which can easily diffuse out of the cement matrix (Fig. 4, the front between zones 2 and 3). Effects of this reaction are increased porosity/permeability and loss of overall mechanical integrity, leading to increased hardness and reduced permeability otherwise decreasing CO₂ diffusion and up to 6% volume expansion, which can lead to development of micro to macro cracks in extreme cases. Calcite precipitation is a result of Ca²⁺ diffusion out of the cement coupled with inward diffusion of carbonated water (Kutchko et al., 2007). The rate at which cement degradation occurs depends on temperature, but also on cement type, cement composition, water/cement ratio, moisture content, CO₂ partial pressure, and porosity/permeability (Kutchko et al., 2007; Santra et al., 2009). Carbonation is extremely fast in the early days but later slows down drastically because of the time dependant reduced porosity/permeability caused by the initial carbonation itself (Santra et al., 2009). Calcium carbonate by itself may not be a problem unless and until so much of it is formed that it could crack the cement sheath (Sweatman et al., 2009). In other words, moderate degrees of carbonation can be beneficial to cement porosity, permeability, and strength but extensive carbonation can result in the loss of cement structural integrity (Carey et al., 2007). CaCO₃ is less soluble than Ca(OH)₂ and begins to dissolve when Ca(OH)₂ has been depleted.

Summary of some research results

For over three decades, mostly laboratory based studies have indicated that pure Portland-cement-based formulations could fail to maintain zonal isolation over a long period of time.

Onan (1984) studied effects of supercritical CO₂ on present cement, as well as influence of carbonation on the early stages of the cement hydration process. He concluded that after prolonged exposure to CO₂ under supercritical conditions, the hydration products formed in the hydration of portland cement undergo decomposition into calcium carbonate and a siliceous residue. Cement samples exposed to the lower extremes (temperature and pressure) of a supercritical CO₂ environment exhibited greater reactivity under dynamic conditions as compared to static conditions, while increasing CO₂ pressure increased the degree of reaction regardless of the carbonation conditions used.

The carbonation front is reported by Barlet-Gouedard et al. (2006 and 2009) to progress at 5–6 mm over 3 weeks under specific laboratory conditions, with the front slowing over time as diffusion through the carbonated cement reduces the feed of acidic water. Kutchko et al. (2007) conducted experiments to assess the durability of cements in wells penetrating candidate formations for geological sequestration of CO₂. Cement samples were prepared using Class H Portland cement and a water-to-cement ratio of 0,38. Cement was allowed to cure 28 days under different condition (A: 22 °C, 0,1 MPa; B: 22 °C, 30,3 MPa; C: 50 °C, 0,1 MPa; D: 50 °C, 30,3 MPa) in a 1% NaCl/brine solution in a high-pressure vessel to simulate well cement in contact with a deep saline aquifer. Portland cement cured under each condition was subsequently exposed to a brine solution saturated with CO₂ at 50 °C, 30,3 MPa in a high-pressure vessel. At this temperature and pressure, the CO₂ is supercritical. These experiments showed a significant variation in the initial degradation (9 days of exposure) based on the curing conditions. The high temperature (50 °C) and high pressure (30,3 MPa) curing environment increased the degree of hydration and caused a change in the microstructure and distribution of the Ca(OH)₂ phase within the cement. Cement cured at 50 °C and 30,3 MPa (representing sequestration conditions) proved to be more resistant to carbonic acid attack, exhibited a shallower depth of degradation (0,22 mm) than cement cured at 22 °C and 0,1 MPa (0,59 mm). This is likely due to smaller, more evenly distributed Ca(OH)₂ crystals that provide a uniform and effective barrier to CO₂ attack.

Carey et al. (2007) investigated the impact of CO₂ – cement interactions on cement performance by collecting wellbore samples from the world’s second oldest continuous CO₂-flooding operation (since 1972), the SACROC Unit, located in West Texas. The coring operation recovered samples of casing and cement. The casing was in excellent conditions and showed little evidence of corrosion. The SACROC samples consisted

\[
Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \quad (2a)
\]

\[
C-S-H \text{ and/or crystalline phases} + H_2CO_3 \rightarrow CaCO_3 + SiO_2 (gel) + H_2O \quad (2b)
\]
of neat Portland cement exposed to CO$_2$ in the subsurface at 54 °C and 18 MPa for 30 years. The recovered cement had air permeabilities in the tenth of a μm$^2$ range and thus retained its capacity to prevent significant flow of CO$_2$. There was evidence, however, for CO$_2$ migration along both the casing-cement and cement-shale interfaces. A 0.1 - 0.3 cm thick carbonate precipitate occurs adjacent to the casing. The CO$_2$ producing this deposit may have traveled up the casing wall or may have infiltrated through the casing threads or points of corrosion. The cement in contact with the shale (0.1 – 1 cm thick) was heavily carbonated. The CO$_2$ causing this reaction originated by migration along the cement-shale interface where the presence of filter cake may have provided a fluid pathway.

Santra et al. (2009) studied the role of pozzolanic substitution (silica fume and fly ash ) and concluded that, before CO$_2$ treatment, addition of either silica fume or fly ash, the amount of Ca(OH)$_2$ still present in cement either decreases or completely disappears. After 15 days of CO$_2$ treatment (at 93.3 °C and 13.79 MPa) the cement samples with increasing amount of pozzolanic substitutions (up to 50%) were less affected by the CO$_2$, and the depth of carbonation during a period of up to 15 days is directly proportional to the amount of pozzolanic supplement. After 90 days of CO$_2$ treatment (at 93.3 °C and 13.79 MPa) carbonation slows down drastically because of the time dependent reduced porosity/permeability caused by the initial carbonation itself.

Conclusion

In order to have the safe underground storage of carbon, the injection wells as well as any well penetrating through the cap rock have to maintain sufficient integrity over a long time period. The chemical interactions between injected CO$_2$ and existing set cements could potentially lead to leakage because of cement degradation. The integrity of the casing-cement and cement-formation interfaces appears to be the most important issue in the performance of wellbore systems in a CO$_2$ sequestration reservoir. Reducing the amount of Portland cement by incorporating pozzolanic materials, reducing porosity/permeability, and adding reactive supplementary materials to reduce the Ca(OH)$_2$, as well as changing the C-S-H composition to a more CO$_2$-resistive one could reduce detrimental effects of carbonation on the mechanical integrity and loss of zonal isolation. Certain mismatching between the research lab tests results and actual field measurements implies necessity of further investigation and standardisation of CO$_2$ resistance-testing devices, conditions and procedures.

References


Emmis-King, J. and Paterson, L. (2002): Engineering Aspects of Geological Sequestration of Carbon Dioxide, SPE 77809, SPE Asia Pacific Oil and Gas Conference and Exhibition, Melbourne, Australia, 8-10 October.


Accepted: 30.10.2010.
Received: 05.10.2010.
Water-Alternating-CO$_2$ Injection in the Secondary and Tertiary Recovery, SPE 103988 presented at First International Oil Conference and Exhibition, Mexico, 31 August-2 September.


