CO₂ UNDERGROUND STORAGE AND WELLBORE INTEGRITY

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Abstract: Capturing and storing carbon dioxide (CO_2) underground for thousands of years is one way to reduce atmospheric greenhouse gases, often associated with global warming. CO_2 injection candidates may be new wells, or old wells that are active, closed or abandoned. In all cases, it is critical to ensure that the long-term integrity of the storage wells is kept; in others words wellbore integrity is one of the key performance criteria in the geological storage of CO_2.

Underground gas storage operations and CO_2 sequestration in aquifers relay on both proper wellbore construction and sealing function of the cap rock. 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 cement will determine how effective it is in preventing leakage. The integrity of the cap rock is assured by an adequate fracture gradient and by sufficient cement around the casing across the cap rock and without a micro-annulus.

The paper describes geochemical alteration of hydrated Portland cement due to supercritical CO_2 injection and new cement with better CO_2 resistance.

1. Introduction

Carbon capture and storage (CCS) is becoming a critically important part of global warming mitigation efforts, and this trend is expected to continue, with more and more wells being drilled for this purpose. Large-scale underground storage of CO_2 has the potential to play a key role in reducing 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. To date, the technology as a whole has only been deployed at a few pilot sites around the world: Sleipner field in Norway, Weyburn field in Canada, In Salah field in Algeria (Gallo et al., 2002, Jimenez and Chalaturnyk, 2002). The source of carbon dioxide can be from a number of large static emitters such as coal gasification plants, cement factories, coal power stations, steel mills, refineries, hydrogen generators (hydrogen from natural gas) or associated carbon dioxide separated from natural gas (Fig. 1).

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 emissions needed to limit climate disruption.

The geologic sequestration is defined as the process of injecting CO_2 into deep (greater than ≈ 1 km) geologic formations for the explicit purpose of avoiding atmospheric emission of CO_2. There are a number of different types of CO_2 injection scheme (Ennis-King and Paterson, 2002; Gallo et al., 2002; Nezhad et al., 2006; Bellarby, 2009):

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- Injection of CO_2 into a producing reservoir either to promote oil production or to sequester the CO_2,
- Water-alternating CO_2 injection for production enhancement,
- Injection of CO_2 into a previously producing reservoir (especially a depleted gas reservoir),
- Sequestering CO_2 into a saline formation that is independent of any oil or gas development,
- Sequestering CO_2 into deep (often thin and therefore uneconomic) coal seams.

The majority of locations that are being considered for carbon dioxide (CO_2) injection and sequestration are typically found in areas that have a history of oil, natural gas, and/or coalbed methane production. This is due to value-added opportunities such as enhanced oil recovery (EOR), enhanced gas recovery (EGR), and enhanced coal bed methane (ECBM) recovery (Bellarby, 2009). There also exists a greater knowledge base for saline formations that lie either above or below oil and gas reservoirs due to well logging and exploration activities.
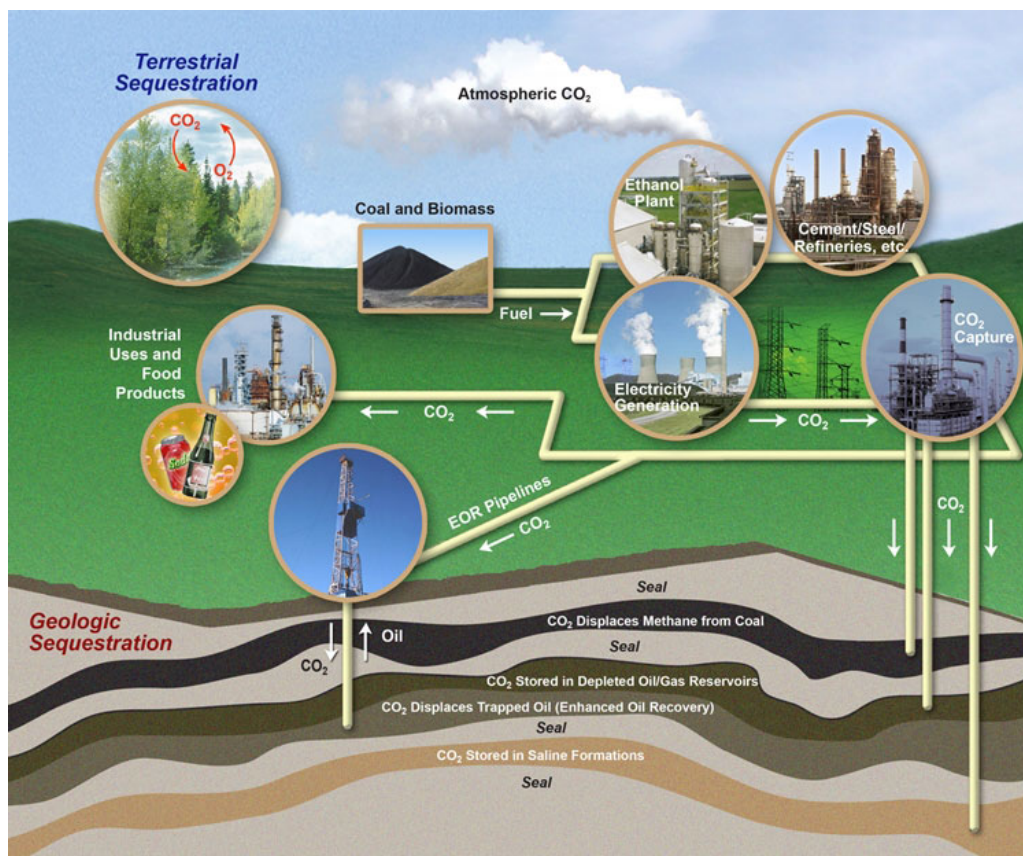

Fig. 1 *Sources and different types of CO_2 injection (www.netl.doe.gov).*

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).

2. CO_2 and its behaviour under reservoir conditions

Carbon dioxide is colourless and nearly odourless, but toxic. At concentrations of about 5 % by volume, CO_2 in air causes dizziness, confusion and breathing and hearing difficulties. Above around 8 %, CO_2 leads to a loss of consciousness after exposures of between 5 and 10 min (Bellarby, 2009). CO_2, being denser than air, will also follow terrain downhill. CO_2 has 30-40 % less density and 5-10 times less viscosity than formation brine under typical suburface conditions (Ennis-King and Paterson, 2002).

Under most reservoir conditions, CO_2 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 geologic storage, CO_2 is injected at sufficiently high pressures (>7,3 MPa) and temperatures (> 31 ºC) that

it becomes a *supercritical fluid* below 800 m (Onan, 1984). Supercritical fluids take up much less space as shown in figure 2 , 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 CO_2 at each depth compared to a volume of 100 at the surface. Supercritical CO_2 compresses further as the depth increases, increasing the amount that can be stored in the same volume of rock. High pressure at sufficient depths (i.e., greater than 800 meters) maintains the supercritical fluid state.
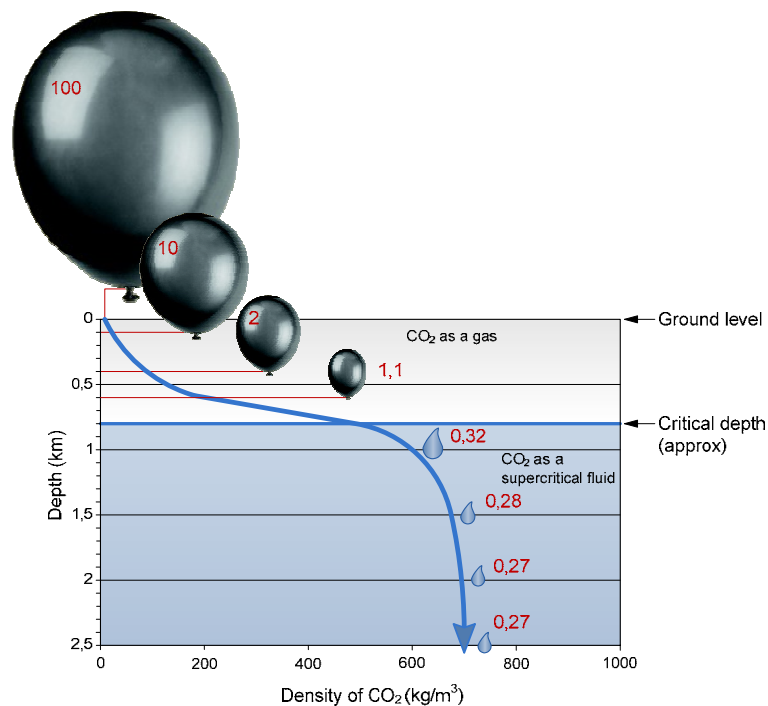

Fig. 2 *Change of density and volume of CO_2 with depth (Image Source: CO2CRC).*

Except at very high pressures, CO_2 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 CO_2 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 CO_2 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).

Once underground, a variety of mechanisms (structural/stratigraphic trapping, residual trapping, solubility trapping, and mineral trapping**)** keep the supercritical CO_2 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 CO_2 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 CO_2 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 CO_2 from underground storage sites. Well bores represent the most likely route for leakage of CO_2 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, Celia et al., 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 CO_2 injection and storage scenario. Long-term carbon sequestration conditions include contact with supercritical CO_2 and brine solutions at increased pressure and temperature and decreased pH (Kutchko et al., 2007).
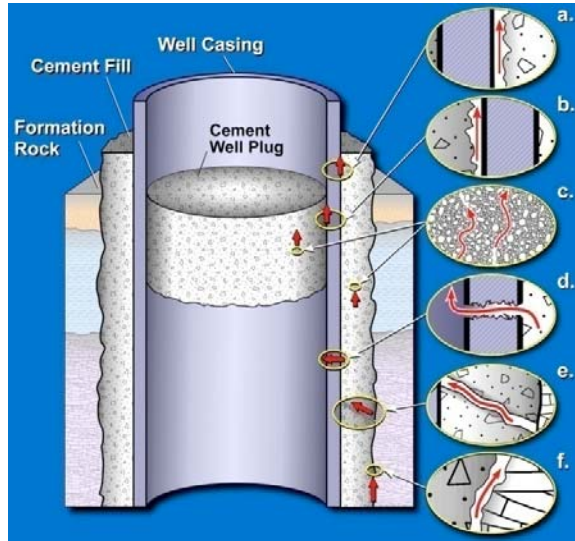

Fig. 3. *Possible leakage pathwys in an abondoned well.*

The greatest risk for escape of CO_2 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 CO_2 to escape into the atmosphere. Planning for geologic storage must take such wells into account. CO_2 escaping through water wells is much more unlikely since water wells are usually much shallower than the storage formation.

In injection wells, the precence of CO_2 may lead to corrosion on those parts coming in contact with CO_2 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, resistent to corrosion, and by inhibitor injection, if using carbon steel casing.

3. Degradation of Wellbore Cement Due to CO_2 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 CO_2-rich fluids and understand the chemical interactions between injected CO_2 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, K_2O, Na_2O, TiO_2, Mn_2O_3 and SO_3 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).

Tab. 1 *Mineralogical Composition of Portland Cement Clinker.*

Oxide Composition	Cement Notation	Common Name	Concentration (wt %)
$3CaO \cdot SiO_2$	C_3S	Alite	55-65
$2CaO \cdot SiO_2$	C_2S	Belite	15-25
$3CaO \cdot Al_2O_3$	C_3A	Aluminate	8-14
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	Ferrite phase	8-12

Portland cement is thermodynamically unstable in CO_2-rich environments and can degrade rapidly upon exposure to CO_2 in the presence of water (Onan, 2004). As CO_2-laden water diffuses into the cement matrix, the dissociated acid (H_2CO_3) reacts with the free calcium hydroxide and the calcium-silicate-hydrate gel. The reaction products are soluble and migrate out of the cement matrix. Eventually, the compressive strenght of the set cement decreases and the permeability and porosity increase, leading to loss of zonal isolation.
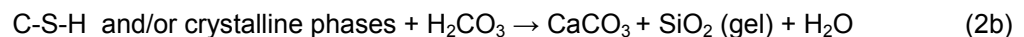
There are mainly three different chemical reactions involved in cement-CO_2 interaction: (1) formation of carbonic acid, (2) carbonation of calcium hydroxide and/or cement hydrates, and (3) dissolution of $CaCO_3$ which are shown below (Onan,1984; Bellarby, 2009; Santra et al.,2009):

1,   *Formation of Carbonic Acid.* CO_2 diffuses into the capillary pores of the cement which contain, to some extent, a water and dissolves in it to form carbonic acid as shown in Eq. 1:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad\qquad (1)$$

Forming of carbonic acid causes lowering in pH value, depending on temperature, partial pressure of CO_2, and other ions present in water, such as salt, etc.

2,   *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 (the reverse reaction to the manufacturing of cement). 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 and an amorphous silica (Eq. 2b):

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \qquad\qquad (2a)$$

$$\text{C-S-H and/or crystalline phases} + H_2CO_3 \rightarrow CaCO_3 + SiO_2 \text{ (gel)} + H_2O \qquad (2b)$$

The carbonation reactions cause densification, leading to increased hardness and reduced permeability thereby decreasing CO_2 diffusion and up to 6 % volume expansion, which can lead to development of micro to macro cracks in extreme cases. The rate at which cement degradation occurs depends primarily on temperature, but also on cement type, cement composition, water/cement ratio, moisture content, CO_2 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). Moderate degrees of carbonation can be beneficial to cement porosity, permeability, and strength; extensive carbonation can result in the loss of cement structural integrity (Carey et al, 2007).

3,   *Dissolution of $CaCO_3$.* It is a long-term phenomenon and happens only when the set cement is surrounded by liquid water containing dissolved CO_2 (Eq. 3):

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2 \qquad\qquad (3)$$

Effects of this reaction are increased porosity/permeability and loss of overall mechanical integrity, leading to inefficient or even potential loss of zonal isolation in extreme cases (Santra et al., 2009). In long-term scenario where the dissolution of $CaCO_3$ to $Ca(HCO_3)_2$ is unavoidable, portland cement with higher pozzolanic content wherein the total amount of $CaCO_3$ formed is much lower after carbonation will face less-severe effects of dissolution simply because there is less $CaCO_3$ to dissolve either by CO_2 or H_2CO_3 (Santra et al., 2009).

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 CO_2 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 CO_2 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 CO_2

environment exhibited greater reactivity under dynamic conditions as compared to static conditions, while increasing CO_2 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 CO_2. 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 ºC, 0,1 MPa; B: 22 ºC, 30,3 MPa; C: 50 ºC, 0,1 MPa; D: 50 ºC, 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 CO_2 at 50 ºC, 30,3 MPa in a high-pressure vessel. At this temperature and pressure, the CO_2 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 ºC) 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 ºC 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 ºC 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 CO_2 attack.

Carey et al. (2007) investigated the impact of CO_2 – cement interactions on cement performance by collecting wellbore samples from the world´s second oldest continuous CO_2-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 semples consisted of neat Portland cement exposed to CO_2 in the subsurface at 54 ºC and 18 MPa for 30 years. The recovered cement had air permeabilities in the tenth of a m^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 ºC 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 o the amount of pozzolanic supplement. After 90 days of CO_2 treatment (at 93,3 ºC and 13,79 MPa) carbonation slows down drastically because of the time dependant reduced porosity/permeability caused by the initial carbonation itself.

4. Conclusion

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 th 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 mechanical integrity and loss of zonal isolation.

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