

A review on cement degradation under CO₂-rich environment of sequestration projects

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Abstract

Global warming arising from the release of greenhouse gasses into the atmosphere is one of the biggest issues attracting a lot of attention in recent years. Carbon Capture and Sequestration (CCS) is one of the strategies used to capture CO₂ from different emission sites and inject it into suitable geological formations. It is, however, absolutely critical for CO₂ to remain confined and not allowed to leak into vital subsurface resources. One of the conventional problems faced in sequestration projects is the degradation of Portland cement due to its exposure to supercritical CO₂ under reservoir pressure and temperature. This paper gives a review on the laboratory work carried out in the recent years to understand the kinetic potential of CO₂-Cement reaction, and changes in the mechanical and transport properties of cement when it is in a CO₂ rich environment. The results presented in different studies were not similar due to variety of approaches used in developing different types of cements. However, almost all of these studies indicated carbonation of the cement as a self-healing process whereas degradation of the cement starts with the bi-carbonation of CaCO₃. It seems that adding a suitable quantity of Pozzolanic material could be useful in enhancing the resistance of cement against CO₂, although more studies are still required to confirm this conclusion.

1. Introduction

The concept of Carbon Capture and Sequestration (CCS) was first introduced in 1977 when it was found that carbon dioxide (CO₂) emitted from the coal power plant could be captured and injected into suitable geological formations (Marchetti, 1977). The main objective of CCS is to reduce the amount of greenhouse gases in the environment and to store CO₂ in the subsurface environment for thousands of years. In this practice, disposal of CO₂ in the geological formations is done by injecting the CO₂ in a dry supercritical state (i.e., scCO₂ corresponding to a state where pressure and temperature is greater than 7.38 MPa and 31°C respectively) into

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depleted reservoirs, coal beds or saline aquifers and cementing the injecting intervals (Bai et al., 2015; Barlet-Gouedard, et al., 2008).

The success of using CCS depends mainly on three fundamental parameters, known as, capacity, Injectivity, and confinement. Capacity of depleted reservoirs is generally defined as the amount of CO₂ which can be stored before fracturing the caprock. It depends to numerous parameters including total organic carbon, thickness, effective porosity, permeability, CO₂ absorption isotherm and apparent gas saturation of reservoirs selected for storage purposes (Godec et al., 2013). However, there are limitations such as technical, economical, regulatory and physical issues, which restrain a full utilization of storage capacity to its maximum theoretical limit (Bachu et al., 2007). Injectivity of storage reservoirs, on the other hand, is defined to ensure that CO₂ can be injected at a desired rate. This rate can be improved by changing completion techniques, but often reservoir itself has a limit at which CO₂ can be injected into it (Raza et al., 2015). The confinement is the last and probably the most important parameter playing a significant role in success of storage practice. It is crucial to be evaluated at early stages since leakage of CO₂ contaminates fresh water resources and may have an adverse effect on vegetation, the environment, animals and people, when it reaches the surface (Zhang and Bachu, 2010). This leakage comes not only from the cracks/fractures of the cap rock but can also occur through the micro annulus flaws created due to geochemical alteration\degradation of cement exposed to scCO₂. The most common types of cement used for cementing wells are Class G and H cements, both composed mainly of Portland cement. When scCO₂ is injected into these wells, it gets dissolved in formation water producing CO₂-saturated formation water (carbonic acid). This acid is a major cause of cement degradation as well as the creation of cracks and escape pathways (Bachu and Bennion, 2008; Carey, 2013). As a result of this degradation, scCO₂ is transported through the cement pore spaces and rate of reaction is controlled by diffusion rate of the reactants. It is therefore important to understand the chemical composition, hydration and kinetic reaction of the cement, and components susceptible to CO₂ attacks. It is also imperative to discuss the possible effects of carbonation/bicarbonation on mechanical and transfer properties of the cement to ensure the long-term integrity of CO₂ to the storage site.

Therefore, the aim of this paper is to provide a comprehensive review on different aspects of cement degradation and discuss on certain materials which can be used to enhance cement resistance in a CO₂ rich environment.

2. Portland Cement Degradation

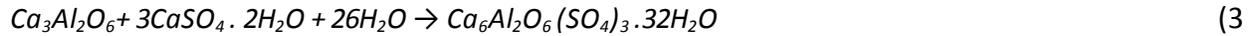
2.1. Hydration

Generally, Portland cement mainly comprises of Tricalcium silicate (C₃S), Dicalcium silicate (C₂S), Tricalcium Aluminate (C₃A) and Tetracalcium Aluminoferrite (C₃AF) which give specific functionality to the cement as presented in Table 1 (Nelson, 1990; Rabia, 2001). When water is

mixed with the cement, hydration takes place during which C_3S and C_2S are converted into C-S-H gel and portlandite ($Ca(OH)_2$), as expressed below (MacLaren and White, 2003):



Hydration of C_3AF is similar to that of the C_3A and forms ettringite when it reacts with gypsum.



Upon the hydration, cement is mainly composed of quasi-amorphous C-S-H and crystalline Portlandite (Nelson, 1990).

Table 1: Main constituents of Portland cement and their functionality (Adams and Charrier, 1985)

Compound	Cement Chemist Notation	Purpose
<i>Tricalcium Silicate</i> $(CaO)_3 \cdot SiO_2$	C_3S	Enhances the strength and develops early strength
<i>Dicalcium Silicate</i> $(CaO)_2 \cdot SiO_2$	C_2S	Hydrates slowly, Strength generated over extended period of time
<i>Tricalcium Aluminate</i> $(CaO)_3 \cdot Al_2O_3$	C_3A	Promotes rapid hydration, affects thickening time and initial setting of the cement, makes the cement susceptible to sulfate attack
<i>Tetracalcium Aluminoferrite</i> $(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$	C_3AF	Responsible for slow hydration

2.2. Carbonation and bi-carbonation

CO_2 attack on the cement is initiated with the carbonation of portlandite. As time passes and portlandite is consumed, calcium silicate hydrate (C-S-H phases) is decomposed into $CaCO_3$ and silica gel, resulting in a considerable reduction of the cement's strength. While it was shown in some publications that decomposition of C-S-H is concurrent with that of the portlandite, it is certain that carbonation leads to bi-carbonation, which in turn leads to the degradation of cement. This degradation can be expressed by the following chemical reactions (Kutchko, et al., 2007):

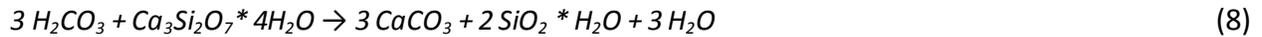




As a result of this degradation, Calcite (CaCO₃) is formed and carbonated water diffuses toward the cement sheath. This is known as carbonation in which a self-healing process takes place, porosity and permeability decreases, and mechanical properties of the cement increase (Nygaard, 2010). As diffusion of the corrosive fluid continues, abundance of HCO³⁻ leads to the formation of calcium bicarbonate, which is soluble in water and can be leached out of the cement matrix. This step is known as bi-carbonation and expressed using the following reaction:



At the end of bi-carbonation, complete degradation of the cement will be observed where C-S-H is reacted with H₂CO₃ to form CaCO₃ together with amorphous silica gel, as addressed below:



The degradation here is characterized by increasing of porosity and permeability, and reduction in the mechanical strength of the cement. The reason behind the increase of permeability and porosity is linked to the fact that molar volume of C-S-H is more than CaCO₃ produced during degradation (Nygaard, 2010). On the other hand, the release of amorphous silica gel from cement matrix is the reason why the mechanical strength of the cement decreases (Kutchko, et al., 2007).

3. Cement Degradation Analysis

3.1. Experimental Conditions

Many laboratory experiments have been carried out to understand the behaviour of the cement in a CO₂ rich environment. These experiments are usually carried out in a HPHT vessel in order to simulate reservoir conditions. The pressure vessel comprises of two parts, the bottom half contains a brine solution so that scCO₂ can dissolve in the solution to give brine saturated CO₂. On the other hand, the upper half contains scCO₂, known as wet scCO₂ (Barlet-Gouedard, et al., 2008). This vessel is able to simulate any reservoir conditions by maintaining the pressure and temperature in specific ranges. Figure 1 shows an example of a pressure vessel conventionally used for cement resistance analysis.

Using this apparatus, effect of curing period, additives, water to cement ratio and water salinity on the carbonation of the cement is usually examined. The time period of the experiment is typically from one month to one year during which the samples are monitored constantly to evaluate the depth of the carbonation front. Tests are carried out in both dynamic (i.e., certain flow rate of brine/water is maintained in the pressure vessel) and static (brine/water remains in the static state having no flow rate) conditions, although it is recommended to run the test under static conditions to have more representative results (Kutchko, et al., 2007). It should be

noticed that dynamic condition accelerates the rate of carbonation in the cement sample. Table 2 gives details of experimental conditions carried out in the past under laboratory conditions.

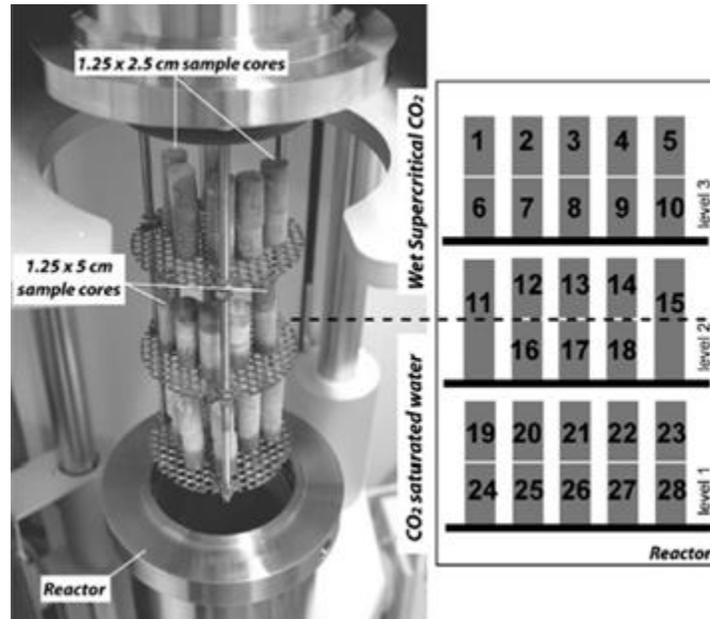


Figure 1: Pressure vessel used by Barlet-Gouedard, et al., (2008)

3.2. Neat Cement

Onan, (1984) initially delineated the carbonation of the cement in the presence of scCO_2 environments at laboratory scale. He concluded that the presence of Pozzolanic material in the cement makes it more resistible to corrosive environments. However, due to the low density of Pozzolan cement, it is beneficial to use it in the formations with low fracture pressure. He also found out that cement samples exposed to low temperatures and high pressure of scCO_2 , showed greater degrees of carbonation in dynamic conditions compared to static ones. Later Spyche and Pruess, (2005) and Huet et al., (2011) reported that the solubility of CO_2 and the rate of carbonation front is dependent on the pressure, temperature and salinity of the water. Duguid et al., (2004) carried out an experiment under dynamic conditions where CO_2 was injected into the flow through reactor by bubbling it through 0.5M of NaCl brine solution. Samples used were the neat cement (Class H) and the time period of the test was 1–7 days. They found that porosity of the neat cement can be increased to as much as 10 to 45% in CO_2 rich environment. It was also discovered that the rate of reaction in the sample containing bentonite was higher compared to neat cement. They concluded that the sealing properties of cement can be compromised even with a short-term exposure to carbonated brine. Duguid et al., (2005) carried out a series of experiments under dynamic conditions. They observed five coloured layers in the cement exposed to a carbonated brine solution. Although experiment was carried out at two different temperatures of 50°C and 20°C and pH of 2.4 and 3.7, the highest rate of reaction for the neat sample was observed at 50°C and pH of 2.4.

[Barlet-Gouedard et al., \(2006, 2007\)](#) stated that flow in reservoir conditions for a storage project consists of a static, not dynamic condition. They then performed a series of experiments under a static condition where temperature and pressure of the vessel was kept at 90°C and 28MPa for up to 6 months. The pressure vessel was half filled with water while supercritical CO₂ was at the top. After 6 months of exposure, spalling of the cement samples was recorded. A rapid increase in density was observed within 4 days of exposure but it stabilized afterwards. After 6 weeks of exposure, a large drop in the compressive strength was observed for the samples located in the CO₂ saturated water. The permeability remained below 8mD even after the exposure. The porosity, however, decreased initially but showed an increase in samples located at the top or bottom of the vessel. In fact, porosity decreases when CaCO₃ is formed during the carbonation of the cement but increases when CaCO₃ is converted into Ca(HCO₃)₂ and leached out of the cement. This leaching was, however, faster in CO₂ saturated water than scCO₂.

Effect of the curing condition on the cement resistance was examined by [Kutchko et al., \(2007\)](#), where Class H samples were exposed to a CO₂ rich environment for over 28 days in a 1% bath of NaCl. They observed that after 9 days of exposure, the depth of carbonation for all of the samples was less than 1mm while the lowest carbonation depth was in the sample cured under 50°C and 30MPa due to slightly higher degree of hydration. [Kutchko et al., \(2008\)](#) did further experiments to find out the difference in the carbonation depth between the sample located in CO₂ saturated brine and those present in scCO₂ section. At the end of the experiment, it was found that among the samples exposed to scCO₂, only a single front was observed while CO₂ saturated brine samples had complex carbonation fronts.

[Duguid et al., \(2009\)](#) carried out an experiment to evaluate the effect of formations on the degradation of the cement. Three leaching solutions with different pH (i.e., 3, 4 and 5) were prepared by adding NaOH or HCl. The test was carried out for the time period of more than one year. They concluded that in diffusion controlled systems, degradation of 25mm of neat sample in the sandstone sequestration environment takes around 30,000 to 70,000 of years, because sandstone acts as a barrier between cement and CO₂. However, these experiments were run under atmospheric pressure and may not be representative of a real reservoir condition

A suite of analytical techniques was used by [Pratt et al., \(2009\)](#) to characterize the cement samples exposed to wet scCO₂ at a temperature and pressure of 50°C and 10MPa, respectively. After 12 weeks of exposure, the carbonation depth of the sample was found to be 200µm.

[Condor and Asghari, \(2009\)](#) were examined two classes of cements, namely A and G, in wet scCO₂ and CO₂ saturated brine at a temperature and pressure of 55°C and 15MPa, respectively, for a period of 3 months. They reported that increase in the permeability of the samples is much faster when environmental temperature is high. The hydraulic and shear bonds were severely affected, and it was concluded that channels created between the cement plug and casing might have been a possible path for the CO₂ migration.

[Barlet-Gouedard et al., \(2009\)](#) indicated that formation fluid consists mainly of brine and it must be used rather than fresh water for simulating the reservoir condition. They ran similar experiments pervasively conducted by [Barlet-Gouedard et al., \(2006, 2007\)](#) on the cement and used a 0.4M NaCl brine solution instead of fresh water. A dramatic fall in the propagation\alteration rate was observed after two days of exposure to CO₂ saturated brine as compared to CO₂ saturated in fresh water. This trend was also observed in the study of [Verba et al., \(2010\)](#) where this phenomenon was indicated to be due to lower solubility of the CO₂ in saline water as compared to fresh water.

[Duguid and Scherer, \(2010\)](#) simulated condition of a limestone and sandstone sequestration formations. In that test, CO₂ was bubbled in the flow reactor through Ca-Na-Ca solution and was then passed through CaCO₃ (calcite) column. The pH of the effluent was maintained at pH 5 and experiments took 28 days to be done. It was found that the sample exposed to the limestone environment was not degraded because the solution was in equilibrium with the calcium carbonate. This was while the sample used for the sandstone environment was degraded extensively due to absence of such equilibrium. As a result, authors concluded that degradation of the cement in the sandstone sequestration environment is more severe than limestone or dolomite formations. Similar results were obtained by [Duguid et al., \(2011\)](#), where attempts were made to compare the effect of pH and temperature on the cement in the sandstone and limestone formations.

[Connell et al., \(2015\)](#) carried out a series of core flooding tests to evaluate the resistance of cement against scCO₂. They reported that leaching of CaCO₃ could only take place when there is a continuous flow of water under-saturated with calcium and carbonate. This sort of situation prevails in sandstone reservoirs.

Table 2: Experimental setup and finding of different authors

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
Duguid et al., (2004)	<ul style="list-style-type: none"> Two samples used: (1) Class H cement + DI water (2) Class H cement + 6% Bentonite + DI water Size (Dia *H) = 7.3-7.7mm*140-260mm 	<ul style="list-style-type: none"> Water to solid ratio: (1) 0.38 (2) 0.70 	<ul style="list-style-type: none"> Cured in 0.5M NaCl Room Temperature 28 Days 	<ul style="list-style-type: none"> CO₂ saturated brine with different pH i.e. 3.7 and 2.4 Exposure Time = 1.3 to 7.2 days Temperature = 23°C and 50° Condition = Dynamic 	<ul style="list-style-type: none"> Rate of reaction for sample containing 6% bentonite (By Weight of Solid) was higher than that of the neat cement Cement containing bentonite shows the degradation of 0.75 to 1.2mm within 7.2 days of exposure
Duguid et al., (2005)	<ul style="list-style-type: none"> One sample used: (1) Class H cement Size (Dia *H) = 7.5mm*200mm 	<ul style="list-style-type: none"> Water to solid ratio: (1) 0.38 	<ul style="list-style-type: none"> Cured in 0.5M NaCl Temperature = 20 and 50°C 12 months 	<ul style="list-style-type: none"> CO₂ saturated brine with different pH i.e. 3.7 and 2.4 Exposure Time = 31 days Temperature = 23°C and 50°C Condition = Dynamic 	<ul style="list-style-type: none"> Highest rate of reaction was observed at 50°C and pH of 2.4 which was about 0.07 to 0.24 mm/day Lower the pH, the greater the rate of carbonation will be
Barlet-Gouedard et al., (2006,2007)	<ul style="list-style-type: none"> Portland Cement + conventional additives Size (Dia *H) = 12.7mm*25.4mm and 25.4mm*50.8mm 	N/A	<ul style="list-style-type: none"> Cured for 72 Hours Temperature 90°C Pressure 20.68 MPa 	<ul style="list-style-type: none"> Wet scCO₂ CO₂ saturated water Exposure Time = Days (0.5, 2, 4, 7, 21, 42) & Months (3 and 6) Temperature = 90°C Pressure = 40 MPa Condition = Static 	<ul style="list-style-type: none"> The alteration rate was diffusion controlled and calculated by $L = 0.26 * t^{1/2}$ where L is in mm and t is in hour) Cement is more vulnerable to CO₂ saturated water than scCO₂

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
Kutchko et al., (2007)	<ul style="list-style-type: none"> • Class H cement • Size (Dia *H) = 12mm*130mm 	<ul style="list-style-type: none"> • Water to cement ratio (1) 0.38 	<ul style="list-style-type: none"> • Cured in 1% of NaCl • Under different temperature and pressure: <ol style="list-style-type: none"> (1) 22°C and 0.1 MPa (2) 22°C and 30.3 MPa (3) 50°C and 0.1 MPa (4) 50°C and 30.3 MPa • 28 Days 	<ul style="list-style-type: none"> • Wet scCO₂ • CO₂ saturated brine • Exposure Time = 9 days • Temperature = 50°C • Pressure = 30.3 MPa • Condition = Static 	<ul style="list-style-type: none"> • After 9 days of exposure, depth of carbonation for all samples was less than 1mm. -Lowest carbonation depth was observed in the sample cured under 50°C and 30.3 MPa
Kutchko et al., (2008)	<ul style="list-style-type: none"> • Class H cement • Size (Dia *H) = 12mm*130mm 	<ul style="list-style-type: none"> • Water to cement ratio (1) 0.38 	<ul style="list-style-type: none"> • Cured in 1% of NaCl • Temperature = 50°C • Pressure = 30.3 MPa • 28 Days 	<ul style="list-style-type: none"> • Wet scCO₂ • CO₂ saturated brine • Exposure Time = up to 12 months • Temperature = 50°C • Pressure = 30.3 MPa • Condition = Static 	<ul style="list-style-type: none"> • For the samples presented in the scCO₂, reaction was diffusion controlled and the depth of carbonation was given as $L = 0.016 * t^{1/2}$ (where L is in mm and t is in days) • Carbonation propagation was complex for the sample exposed to CO₂ saturated brine, and an empirical formula was developed to estimate the depth of carbonation i.e., $L = 0.09 \ln(t) + 0.17$
Barlet-Gouedard et al., (2009)	<ul style="list-style-type: none"> • Portland Cement + conventional additive • Size (Dia *H) = 12.7mm*25.4mm and 25.4mm*50.8mm 	N/A	<ul style="list-style-type: none"> • Cured for 72 Hours • Temperature = 90°C • Pressure = 20.68 MPa 	<ul style="list-style-type: none"> • Wet scCO₂ • CO₂ saturated brine • Exposure Time = 2 days • Temperature = 90°C • Pressure = 20.68 MPa • Condition = Static 	<ul style="list-style-type: none"> • Propagation\alteration rate decreases in CO₂ saturated brine compared to CO₂ saturated in fresh water (i.e., 200µm against 2mm)

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
Condor and Asghari, (2009)	<ul style="list-style-type: none"> Two samples use: (1) Class A Cement (2) Class G cement 	According to API standard	N/A	<ul style="list-style-type: none"> Wet scCO₂ CO₂ saturated brine Exposure time = 3 months Temperature = 55°C Pressure = 15 MPa Condition = Static 	<ul style="list-style-type: none"> Permeability of the cement reduces initially and then increases Compressive strength increases and then decreases
Pratt et al., (2009)	<ul style="list-style-type: none"> Portland cement Size (Dia*H) = 7.5mm*200mm 	N/A	<ul style="list-style-type: none"> Cured for 1 month at 100% RH and at room temperature 	<ul style="list-style-type: none"> Wet scCO₂ Exposure Time = 84 days Temperature = 50°C Pressure = 10 MPa Condition = Static 	<ul style="list-style-type: none"> Carbonation depth of the sample was around 200µm and different zones of reactions were reported
Santra et al., (2009)	<ul style="list-style-type: none"> Cement with varying quantity of silica fumes and fly Size (Dia*H) = 25.4mm*63.5mm 	<ul style="list-style-type: none"> Varying quantity of silica fume and fly ash For fly ash samples, w/s were (0.45 and 0.46) For silica fume, w/s ratio varied from 0.45 to 0.58, depending upon the quantity of silica fume added 	<ul style="list-style-type: none"> Cured in water Pressure = 14 MPa Temperature = 93°C 15 Days 	<ul style="list-style-type: none"> CO₂ saturated water Exposure time = 15 and 90 days Temperature = 93°C Pressure = 14 MPa Condition = Static 	<ul style="list-style-type: none"> Increasing the amount of silica fume (Ca/Si ratio of 0.47) did not improve the cement resistance. Neat sample had a penetration depth of 7mm, while that of others was up to 10mm. Partial carbonation of Pozzolanic cement did not lead to any loss of mechanical integrity

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
<p>Brandl et al., (2010)</p>	<ul style="list-style-type: none"> • Two sample used: (1) Class G cement + Silica Flour + (Chemically inert) Pozzolan (2) Class G cement + 35% BWOCSilica Flour • Size (Dia*H) = 25.4mm*50.8mm 	<ul style="list-style-type: none"> • Water to solid ratio (1) 0.55 (2) 0.72 	<ul style="list-style-type: none"> • Cured for 4 days • Temperature = 149°C • Pressure = 20.68 MPa 	<ul style="list-style-type: none"> • CO₂ saturated water • Exposure Time = 1, 3 and 6 months • Temperature = 149°C • Pressure = 20.68 MPa • Condition = Static 	<ul style="list-style-type: none"> • Permeability of samples was less than 0.01mD and compressive strength was greater than 5,000 Psi after the test • Sample No. 1 gave better results in terms of mechanical strength and durability
<p>Duguid and Scherer, (2010)</p>	<ul style="list-style-type: none"> • Two samples used: (1) Class H cement + DI water (2) Class H cement + 6% Bentonite + DI water • Size (Dia*H) = 7.5mm*200mm 	<ul style="list-style-type: none"> • Water to solid ratio (1) 0.38 (2) 0.70 	<ul style="list-style-type: none"> • Cured in 0.5M NaCl • Temperature = 20 or 50°C • 12 months 	<ul style="list-style-type: none"> • CO₂ saturated brine with different pH i.e. 3.7, 2.4 and 5 • Temperature = 50°C • Exposure Time: 26 Days • Condition: Dynamic 	<ul style="list-style-type: none"> • No carbonation was reported in the sample placed in the pH 5 solution

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
Garnier et al., (2010)	<ul style="list-style-type: none"> Two samples used: (1) Neat class G cement (2) Class G + Silica Flour • Size(Dia*H) = 20mm*40mm 	<ul style="list-style-type: none"> Silica flour added 40% BWOC 	<p>Cured at different condition:</p> <ul style="list-style-type: none"> First sample: Pressure = Atmospheric Temperature = 90°C 28 Days Second Sample: For first 10 days: Pressure = 20.7 MPa Temperature = 140°C For rest 18 days: Pressure = Atmospheric Temperature = 90°C 	<ul style="list-style-type: none"> For both samples: CO₂ saturated water Pressure = 8 MPa Condition = static First Sample: Exposure time = 7, 36, 65 and 90 days Temperature = 90°C Second Sample: Exposure time = 4, 12, 21, 31, 55, 88 days Temperature = 140°C 	<ul style="list-style-type: none"> Rate of alteration was 4mm after 65 days of exposure for sample No. 1 (Diffusion controlled event) Progress of carbonation front was 0.2 mm/day for the sample No.2 (reaction controlled event)
Duguid et al., (2011)	<ul style="list-style-type: none"> Two sample used: (1 and 2) Class H cement casted in hole of 25mm Dia of sandstone and limestone cylinder 55mm in height 	<ul style="list-style-type: none"> Water to cement ratio (1 and 2) 0.38 	<ul style="list-style-type: none"> Cured in 0.5M NaCl Temperature = 20 or 50°C 7 months 	<ul style="list-style-type: none"> CO₂ saturated brine with different pH i.e. from 3 to 7 Temperature = 50°C Exposure Time: 1, 2, 3, 6 and 12 months Condition: Dynamic 	<ul style="list-style-type: none"> Sample exposed to sandstone environment had a visual degradation of 0.577mm after 6 months No degradation was recorded for the sample placed in the limestone environment
Barlet-Gouedard et al., (2012)	<p>Two sample prepared:</p> <ul style="list-style-type: none"> Portland cement + Silica + Metakaolin + Hollow Micro sphere Slag cement + Micro Silica + Coarse particle + Hollow Micro sphere 	<ul style="list-style-type: none"> Blend Composition: Cement 100% + Silica 35% + Metakaolin 48.58% + Hollow microspher 32.90% + Fresh Water Blend composition: Slag Cement 100% + Micro Silica 28.76 + Coarse particle 180.81/72.32% + Hollow sphere 9.96/33.86% 	<ul style="list-style-type: none"> Cured for 3 days at 90°C 	<ul style="list-style-type: none"> Wet scCO₂ CO₂ saturated water Exposure Time = 31 days Temperature = 90°C Pressure = 28 MPa Condition = Static 	<ul style="list-style-type: none"> Both of cement compositions had good performances under CO₂ rich environment Compressive strength of the second composition varies from 19-40 MPa initially to 23.9–31.2 MPa after the test

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
<p>Letsi et al., (2013)</p>	<ul style="list-style-type: none"> • Four samples prepared: (1) Inorganic material + Cement (2) Slag cement + Fly Ash (3) Organic latex partide + Cement (4) Neat Class G cement <ul style="list-style-type: none"> • Size (Dia*H) = 30mm*50mm 	<ul style="list-style-type: none"> • Water to solid ratio: (1) 0.25 (2) 0.37 (3) 0.33 (4) 0.43 • Quantity added of additives can be seen from Letsi et al. (2013) 	<ul style="list-style-type: none"> • Cured in synthetic reservoir fluid • Pressure 40 MPa • Temperature 90°C <ul style="list-style-type: none"> • 28 Days 	<ul style="list-style-type: none"> • Wet scCO₂ • CO₂ saturated synthetic reservoir fluid • Exposure Time = 1 and 6 months <ul style="list-style-type: none"> • Temperature = 90°C • Pressure = 40 MPa • Condition = Static 	<ul style="list-style-type: none"> • Crystallization of CaCO₃ is the reason behinds the degradation of the cement. • Sample No. 2 gave the best result in terms of durability. -Change in permeability was almost negligible for the sample No. 2 in the gaseous phase while it could be slightly increased from 0.0001to 0.0016mD in the liquid phase
<p>Zhang et al., (2014)</p>	<ul style="list-style-type: none"> • Two samples were prepared with different quantity of Fly Ash: (1 and 2) Class H Cement + Fly ash (F) • Size (Dia*H) = 12mm*60mm 	<ul style="list-style-type: none"> • Ratio by volume of poz to cement: (1) 35:65, w/s (0.51) (2) 65:35, w/s (0.56) 	<ul style="list-style-type: none"> • Cured in 1% NaCl • Pressure = 15 MPa • Temperature = 50°C <ul style="list-style-type: none"> • Days 28 	<ul style="list-style-type: none"> • Wet scCO₂ and H₂S • CO₂ and H₂S saturated in 1% NaCl • Exposure time = 2.5 and 28 days <ul style="list-style-type: none"> • Temperature = 50°C • Pressure = 15 MPa • Condition = Static 	<ul style="list-style-type: none"> • Cement with lesser quantity of the Pozzolanic material performed better • Class G cement + silica fumes performed better than class H cement + fly ash

Authors	Preparation of the sample	Ratios of Pozzolan/water	Curing Condition	Experimental setup	Finding
Zhang and Talman (2014)	<ul style="list-style-type: none"> • Three samples used: (1) Neat Class G cement (2) Class G cement + Fly Ash + 2 %Bentonite (3) Class C cement + Fly Ash + 2% Bentonite + 1% Sodium Metasilicate (lightweight cement) 	<ul style="list-style-type: none"> • Poz mix ratio, cement to ash: (2) 59:41 (3) 59:41 • Water to solid ratio: (1) 0.44 (2) 0.554 (3) 1.130 	<ul style="list-style-type: none"> • Cured in 0.5M NaCl • Temperature = 53°C • Pressure = 10 MPa • 25 Days 	<ul style="list-style-type: none"> • CO₂ saturated brine • Exposure Time = 3, 7, 14, 28 and 84 days • Temperature = 53°C • Pressure = 10 MPa • Condition = Static 	<ul style="list-style-type: none"> • Pozzolanic mix sample was fully carbonated after 28 days but durability of the cement was remained unchanged • Lightweight cement totally lost its durability and fully carbonated within 7 days while its permeability increased from 0.16 to 1.1mD after 84 days of carbonation
Alex et al., (2015)	<ul style="list-style-type: none"> • Two samples prepared: (1) Neat cement (Class G cement + Pozzolan) (2) Cement Blend 	<ul style="list-style-type: none"> • Neat Cement (Class G cement 100% + 10% Pozzolan BWOc) • Reduced Portland (Cement Blend 100%) 	N/A	<ul style="list-style-type: none"> • Wet scCO₂ • CO₂ saturated DI water • Exposure Time = 12 months • Temperature = 74°C • Pressure = 14 MPa • Condition = Static 	<ul style="list-style-type: none"> • Fresh water must be used for the cement mixture rather than salt water • Certain quantity of Portland cement should be replaced by blast furnace slag or pozzolan

3.3. Developed approaches

There have been many discussions in recent years on how cement resistance can be improved against corrosive scCO_2 . The following strategies have therefore been recommended so far:

- i. Addition of pozzolanic material will reduce the permeability and the quantity of the portlandite (Brandl et al., 2010; Santra et al., 2009; Ilesanmi et al., 2013; Meyer, 2009; Bai et al., 2015). Pozzolanic material is mainly composed of SiO_2 (and Al_2O_3), which reacts with portlandite to give secondary C-S-H. It further reduces the water content in the cement and decreases Ca/Si ratio causing longer chain of C-S-H (high silicate polymerization), which increases the strength of the cement. As permeability of the cement decreases, the ingress of CO_2 is hindered and carbonation will be avoided.
- ii. Decreasing water to cement ratio (Barlet-Gouedard et al., 2012). As the water to cement ratio decreases, un-hydrated cement clinker increases causing the permeability of the cement to reduce and density to increase. This density increase, however, may result in raising the possibilities of fractures in heavy weight cement.
- iii. Using Non-Portland cements (Benge, 2005). Non-Portland cement is not generally recommended though because of its unavailability and cost (Benge, 2009).
- iv. Using of special additives like Epoxy resins to chemically coat the cement, although it is reported that cement with epoxy resin is degraded remarkably when tested at 90°C and 28MPa for 31 days (Barlet-Gouedard et al., 2012).

Among the afore-mentioned approaches, the effect of Pozzolanic material on cement resistance has gained lots of attentions. For instance, Santra et al., (2009) did an experiment where different quantities of silica fumes and fly ash were mixed with the cement. The test was carried out at 93°C and 14 MPa for a time period of 15 to 90 days in CO_2 saturated water. The result showed that, although the rate of penetration of CO_2 was higher in cement with pozzolanic materials, the carbonation of $\text{Ca}(\text{OH})_2$ or C-S-H was less than neat cement due to the absence of $\text{Ca}(\text{OH})_2$ in the samples. It was concluded that the more pozzolanic material, the greater the cement ability grew to survive in a CO_2 rich environment. It should be noticed, however, that when a high silica fume (44.4 and 50% By Weight of Cement (BWOC)) is used, it is very difficult to mix the cement paste due to air retention in the samples.

Brandl et al., (2010) carried out an experiment to compare two types of pozzolanic cement. In the first sample, a conventional method was used for the production of pozzolanic cement, i.e. Class G cement + 35% BWOC silica flour, while a second sample consisted of Class G cement + silica flour + pozzolan. They were subjected to a degradation test in the HPHT vessel at a temperature of 149°C and a pressure of 20.68MPa over a period of six months. At the end of the test, it was found that the pozzolanic sample, after 6 month of reaction, had not yet gone through full carbonation, but the conventional sample was completely carbonated and leached

of CaCO_3 . Moreover, severe flaking was observed with the conventional sample when placed in the water bath for testing the water permeability. Young's modulus and Poisson's ratio had decreased in both samples while an increase in the tensile strength was observed. They concluded that an optimum amount of pozzolanic material enhances the resistance to CO_2 exposure while, in contrast, an excessive amount of pozzolanic material may have a negative impact ([Ilesanmi et al., 2013](#)).

To gather information about the reaction kinetics and phenomenological changes in the cement, [Garnier et al., \(2010\)](#) reported an experiment with two sets of samples. One was neat Class G cement tested at a temperature of 90°C and a pressure of 8 MPa for a period of 90 days whilst the second sample was composited of Class G cement containing silica flour (35% BWOC). The second sample was exposed to a pressure of 8MPa at a temperature of 140°C for 88 days. The test was carried out under static conditions and it was found that the rate of alteration for the second sample was remarkably less than that of the neat sample. It should be noted that faster rates of carbonation in the samples are mainly due to presence of fresh water.

[Barlet-Gouedard et al., \(2012\)](#) developed a specific type of cement, which could resist against the CO_2 attack. They made two compositions consisting of:

1. Portland cement + Silica + Metakaolin + Hallow Micro sphere
2. Slag cement + Micro Silica + Coarse particle + Hallow Micro sphere

The first and second compositions were used for the preparation of low and high density cement respectively. They reported that above compositions provided a good resistance against CO_2 corrosive environment. In conjunction with this study, [Daou et al., \(2014a,b\)](#) added swelling elastomers in the above compositions, which could be expanded in the presence of CO_2 . A precautionary note was given in selecting the elastomer, as excessive swelling may cause stress and lead to cracks in the cement.

It was also recommended to use latex as one of the procurement methods for resisting CO_2 attack ([Bai et al., 2015](#); [Shahval et al., 2014](#); [Benge, 2005](#)). According to recent studies, adding latex in the cement structure improves the bonding strength, controls the filtration loss and allows good strength in the hardened cement paste. To enhance the knowledge of latex composite cement, [Letsi et al., \(2013\)](#) reported an experiment on different types of cements. They prepared samples consisting of 1) inorganic material + cement, 2) slag cement + fly Ash, 3) organic latex particle + cement and 4) neat class G cement. These samples were placed in an autoclave/pressure vessel while the temperature and pressure of injected scCO_2 were kept at 90°C and 40MPa respectively, for the duration of 6 months. After one month of exposure, sample No.1 was completely carbonated while the rest of the samples showed different carbonation depths. However, after 6 months of exposure, the first three samples were fully carbonated. The compressive strength of the samples was above the threshold limit i.e. 5MPa, and the least permeability was observed in sample No. 2 as summarized in Table 3. They

concluded that the degradation of the cement is due to the crystallization of CaCO_3 , which results in the creation of cracks in the cement matrix. Keeping this analogy in mind, the best result was obtained by sample No. 2 due to the low quantity of CaCO_3 and pozzolanic reaction of Fly Ash with portlandite.

Table 3: Permeability changes in different sample tested by [Letsi et al. \(2013\)](#)

Sample No.	Permeability (mD) of the cement sample				
	Before experiment	CO ₂ saturated liquid phase		scCO ₂ gas phase	
		1 Month	6 Months	1 Month	6 Months
1	<0.0001	0.0083	<0.0001	0.0025	0.089
2	<0.0001	<0.0001	0.0002	<0.0001	0.0016
3	<0.0001	0.0125	0.288	0.109	0.0061
4	<0.0001	<0.0001	0.554	0.307	1.54

[Zhang and Talman, \(2014\)](#) carried out a series of experiments on three different cement samples consisting of neat class G cement, pozzolanic cement (fly ash with 2% of bentonite) and light weight sample (fly ash with 1% of sodium metasilicate). Water to bulk ratio of the first two cement samples was 0.554, while it was 1.130 for the lightweight cement. Experiment was performed at the temperature and pressure of 53°C and 10MPa in the presence of 0.5M NaCl solution for the time period of 84 days. At the end, complete carbonation was observed for the pozzolanic mix cement and light weight cement within the time duration of 28 and 7 days respectively. However, the pozzolanic mix sample did not lose its durability and permeability throughout the test. This was while lightweight cement totally lost its durability and permeability after 84 days of reaction. Hence, it was postulated that perhaps cement containing pozzolanic material might be a good choice for a CO₂ rich environment. This was due to the fact that although rate of carbonation was high in this cement, its physical properties remained unchanged ([Strazisara et al., 2009](#)). [Brandl et al., \(2010\)](#) have therefore suggested that if an optimised quantity of pozzolanic material is used, a remarkable improvement in the resistance of the cement against CO₂ exposure could be achieved.

Having this recommendation in mind, [Zhang et al., \(2014\)](#) evaluated the effect of pozzolanic material quantity on the cement resistance. Two Class H cement samples with fly ash were tested consisting of 35:65 and 65:35 ratios of Pozzolan to cement. Samples were exposed to scCO₂, at temperature and pressure of 50°C and 15MPa for a period of 28 days. It was found that the pozzolanic cement resistance is less than what was mentioned by [Jacquemet et al., \(2008\)](#) who used Class G cement with silica fume in a corrosive environment. They also concluded that sample with lower amount of Pozzolan gives a better performance than the one having high pozzolan to cement ratio. [Zhang et al., \(2014\)](#) reached a very same conclusion and indicated that lower Pozzolan to cement ratio reveals better performance against CO₂ and H₂S

rich environment. However, there is not any straightforward way to determine the optimum amount of this ratio.

Alex et al., (2015) compared the performance of 100% Portland cement (Class G) to a 100% Cement blend exposed to scCO₂. The experiment was held in a scCO₂ environment for a period of 12 months. After exposure, it was recommended that fresh water would be a better choice than brine for mixing cement. It was also concluded that a certain amount of cement should be replaced either by blast furnace slag or pozzolanic material in order to perform well in a CO₂ rich environment.

As it was shown in this section, conclusions made for the effect of additives in the cement to resist degradation in a CO₂ rich environment are not the same and it is really hard to clearly recommend any of these additives as a final solution. Thus, it would be great to see the performance of these additives in the field, where cement is exposed to in-situ conditions. Crow et al., (2009, 2010) did studies on side wall cores obtained from a 30 years old reservoir with 96% CO₂. The reservoir was located in a sandstone environment at a depth of 1390m, with a prevailing temperature of 58°C and 10MPa. Pozzolanic cement was used in the well, comprising of 50:50 cement to fly ash with 3% of bentonite. It was found that although the permeability and porosity of the cement samples collected near the reservoir region had gone through alteration due to the reaction with CO₂, the properties of the cement remained unchanged and provided a hydraulic barrier to stop CO₂ penetration. It was also indicated that no calcium carbonate was formed near the cement casing surface and the casing was in a good condition. Thus, it can be concluded that, like in laboratory experiments, adding pozzolanic material will increase the resistance of the cement to scCO₂ even in the field scale.

4. Conclusion

From what it was mentioned throughout the paper, it was concluded that the carbonation of the cement is a self-healing process and reduces the porosity and increases the compressive strength of the cement. However, due to the continuous diffusion of HCO₃⁻ in the cement, bi-carbonation of CaCO₃ causes cement degradation. The degradation here is characterized by increasing of porosity and permeability, and reduction in the mechanical strength of the cement. The reason behind the increase of permeability and porosity is linked to the fact that molar volume of C-S-H is more than CaCO₃ produced during degradation.

According to the laboratory studies, parameters controlling the rate of carbonation in Portland cement can be divided into two categories of controllable and uncontrollable (See table 4). Uncontrollable parameters consist of in-situ conditions prevailing in the reservoir while controllable parameters include those enhancing the cement resistance to CO₂ attack.

Table 4: Parameters controlling the rate of carbonation of the Portland cement

Controllable	Uncontrollable
Water to cement ratio	Temperature
Use of Pozzolanic material	Partial pressure of CO ₂
Decrease in porosity	Water to rock ratio
Decrease in permeability	Salinity of the formation water
Provide tortious for CO ₂ diffusion	Static or dynamic condition

Pozzolanic material is one of the contradictory parameters which may have a positive or negative impact on the cement resistance. As it was mentioned, Pozzolanic material enhances the resistance against attack of an acidic fluid since it decreases or totally eliminates portlandite. However, a too large quantity of the Pozzolanic material has been indicated to have a negative impact on the cement resistance. Thus, if Pozzolanic material is used in the right/optimal amount, the efficiency of cement in a CO₂ rich environment can be improved. The result obtained from the field also suggested that pozzolanic cement could maintain its durability even after 30 years of exposure to a CO₂ rich environment. Thus this study recommends agricultural waste based pozzolanic material including Palm Oil Fuel Ash (POFA) and Rice Husk Ash (RHA) to be used in cement composition for CO₂ rich environment. These materials are very well-known to civil engineers but very new to petroleum industry. They have successfully passed through the tests against corrosive environment in civil industry and might be a good option for highlight acidic environment such as storage sites.

It is also recommended to consider static and saline water conditions for more accurate modelling of reservoir condition when cement is tested for degradation.

Nomenclature

BWOC	By Weight of Cement
CCS	Carbon Capture and Sequestration
DI	De-ionized
Dia	Diameter
H	Height
HPHT	High Pressure High Temperature
M	Molar
N/A	Not Available
POFA	Palm Oil Fuel Ash
RH	Relative Humidity
RHA	Rice Husk Ash
scCO ₂	Super critical CO ₂
SCM's	Supplementary Cementing Materials
w/s	water to solid

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