Effect of Carbon Dioxide on Oilwell Cement

by

Erica Goldie Joshua

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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TRONOH, PERAK

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

ERICA GOLDIE JOSHUA

ABSTRACT

The most effective way to store carbon dioxide (CO_2) for long term safe and low cost CO_2 sequestration is by storing it underground. However, this application will requires long term wellbore integrity. A leaking wellbore annulus can be a pathway for CO_2 migration into unplanned zones (other formations, adjacent reservoir zones and other areas) leading to economic loss, reduction of CO_2 storage efficiency and potential compromise of the field for storage.

This CO_2 leakage through annulus may occurs much more rapidly than geologic leakage through the formation rock. The possibility of such leaks raises considerable concern about the long term wellbore isolation and the durability of hydrated cement that is used to isolate the annulus across the producing or injection intervals in CO_2-related wells. With the lack of industry standard practices dealing with wellbore isolation for the time scale of geological storage, a methodology to mitigate the associated risks is required. This requirement led to the need and development of a laboratory qualification of resistant cements and the long term modelling of cement-sheath integrity.

This project presents the result of a study on the degradation of cement paste due to exposure to CO_2 under the condition of 100 °F and 1500 psi. The objective is to determine the effect of carbonation on cement structure. Carbonation can affects the microstructures of the cement which will affect the mechanical and physical properties of the cement and causes cement corrosion. Several parameters are analyzed in order to see the effect of CO_2 attack on cement structures. The cements are exposed in two different fluids which are the wet supercritical CO_2 and CO_2-saturated brine.

The cement samples are prepared according to the API specification for Portland cement and the properties of the cement are examined to ensure it met with the API regulations for oilwell cement. The cement samples are then undergoing the curing process for 8 hours. The hardened cubic samples result from the curing process is then exposed to the CO_2 in the autoclave at various conditions of CO_2 and at different times of exposure.

After the exposure period, the samples are then analyzed to examine the mechanical and chemical properties after the CO_2 attack.

The discussions based on the results obtained are made. The finding shows that the cement samples that had been exposed to CO_2 loss their compressive strength and also their structural integrity. The sample analysis using the Scanning Electron Microscopic reveals the formation of calcium carbonate ($CaCO_3$) and amorphous silica gel that lacks structural integrity and contributes to the decrease in mechanical and physical properties of the cement.

Some recommendations are also provided in order to develop a more resistant-corrosion cement towards CO_2.

ACKNOWLEDGEMENT

First and foremost, I would like to praise God Almighty for His guidance and blessing that He had given to me in completing this project. Without His guidance and blessing, I might not been able to complete this project on time. Thank God for the strengths that He had given to me to overcome all the weaknesses and difficulties that I am facing throughout the period.

I would like to express my deepest gratitude to my supervisor, Dr. Sonny Irawan for his tireless support and guidance. Dr. Sonny has been a valuable supervisor throughout my time in doing this project and his encouragements throughout the year will not be forgotten.

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I would also like to thank the lab technicians for their assistances in this project; Mr. Amirul Qhalis for his assistance in drilling lab and Mr. Irwan Othman for his tremendous help in the analysis of my samples. Also, I would like to express my greatest appreciation to the management of Universiti Teknologi Mara (UTM) for granted me permission to use the facility that only available in their lab.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

The construction of carbon dioxide (CO_2) injection wells starts with drilling followed by the well completion before starting CO_2 injection operations. In the framework of well completion, the cementation phase guarantees well isolation from the reservoir to the surface and isolation between geological formations.

A crucial technical problem in CO_2 sequestration is that the chemical resistant of the cement to CO_2 exposure over time. Conventional materials used for well isolation for oil and gas production are Portland based cement systems. The systems present the advantage of being low cost and efficient for conventional well construction.

Efforts have focused on enhancing the properties of Portland cement for CO_2 injection wells by reducing the permeability of the cement, lowering the concentration of materials in the system that react with CO_2 or replacing the conventional Portland cement with specialty materials.

One of the major factors that cause structure deterioration of the cement is carbonation. Carbonation is the reaction of hydration products dissolved in the pore water with the CO_2 in the air which reduces the pH of cement pure solution from 12.6 to less than 9.

The effect of carbonation has become significance in the development of cement technology. This is because of the usage of thinner structures and the more exact utilization of the real properties of cement.

Carbonation will change the microstructure of the cement paste and affects the strength and creep in which will cause cement corrosion and deformation properties of the cement.

1.2 Problem Statement

Carbonation affects the microstructures of the cement which will affect both porosity and compressive strength of the cement and will cause corrosion to the cement. In cement chemistry, major attention has been made to weathering processes of Portland cement (Carrasco, Rius and Miravitlles, 2008). Due to the action of CO_2 on the mineralogical compounds of Portland cement, transformation of portlandite into calcium carbonate occurs. This will causes the modification of the microstructure and the mechanical and durability properties.

After prolonged exposure to CO_2 under supercritical conditions, the hydration products formed in the hydration of common Portland cement undergo decomposition into calcium carbonate and siliceous residue.

The effect of CO_2 on cement has been considered to be the same as any other acid attack (with available moisture) that is, it should attack the alkaline constituents in the set cement. Based on present investigation (Onan, 1984), it was revealed that the calcium silicate hydrate phases resulting from the normal hydration of Portland well cementing compositions will undergo a type of pseudomorphosis into any three calcium carbonate phase that are calcite, aragonite and vaterite and an amorphous silica similar to common silica gel when exposed to a CO_2-rich environment.

1.3 Objectives

The objective of this project is to determine the effect of carbonic acid (carbonation) on the cement structures. The effect of carbonation can be examined by analyzing the following parameters:

1. the alteration front of the cement samples
2. the depth of carbonation
3. the changes in the structure and chemistry of the samples
4. the microstructure development
5. the compressive strength of the cement samples
6. weight changes before and after carbonation

1.4 Scope of Works

The cement samples are prepared according to the API specification for Portland cement. Then, the cement slurries are mixed with constant speed mixer. The samples later will undergo the curing process for 8 hours at different pressures and temperature. After the curing process, the samples will be exposed to CO_2 in two exposure conditions. One is in the CO_2-saturated brine and the other is in the wet supercritical CO_2. The durations of the exposure are 24, 72 and 120 hours. Then, after the exposure period, the carbonated samples are analyzed to examine the effect of CO_2 attack on the cement structure.

CHAPTER 2

LITERATURE REVIEW

1.1 Carbonation

A well known phenomenon is associated with cement-based materials is the environmental CO_2 attack, generally referred to as carbonation. Carbonation is the result of the interaction of atmospheric CO_2 gas with the initially alkaline cement material. The absorbed CO_2 dissolves in the pore water of the cement paste to form a weak carbonic acid. This acid dissociates into the carbonate and hydrogen ions and reacts with hydroxide compounds in the pore water to form less soluble carbonated. This is because the solubility of calcium carbonate in the pore solution is low and it tends to precipitate out of the solution within the pore structure, leading to physical as well as chemical changes to cementitious waste form. CO_2 will also cause a decrease in the pH of the system, which in turn alters the solubility of the waste toxic species either decreasing or increasing it. Additionally, carbonation may cause certain toxic species to go into solid solution in the calcium carbonate which may limit the release of the species.

2.2 Cement as Primary Seal

Portland cement has been used as the primary sealant in oil, gas and water wells and has shown to provide effective annular seals in these wells throughout the world. The concern regarding the CO_2 injection wells are the carbonation reactions that resulted from the reaction of CO_2 in the form of carbonic acid with Portland cement.

Cement is known to be thermodynamically unstable in CO_2 rich environments. It tends to degrade rapidly once exposed to such acid gases by reacting with calcium hydroxide formed from hydrated calcium silicate phases (Bruckdorfer, 1986).

As carbonates are dissolved in low pH environment, the cement carbonation process will not become a self plugging effect in the cement sheath. Recent analysis on one cement sample collected in CO_2 Enhanced Oil Recovery (EOR) well, the cement sample demonstrates that at least in one location, the Portland cement has retained its structural integrity after 30 years in near CO_2 reservoir environment (Carey et al., 2006).

Long term isolation and integrity of CO_2 injection wells clearly must be improved in order to ensure the long term environmental safety. In the processes involving the injection of CO_2 for EOR, a number of failures have been reported due to the poor cement properties. Failure of the cement, in the injection interval and above it, may create preferential channels for carbon dioxide to migrate back to the surface.

Optimization of advanced systems allowing long term well isolation is critical to allow safe and efficient underground storage for CO_2 and thus keep the greenhouse effect gas out of the atmosphere for long duration.

2.3 Cement Carbonation theory

The literature (Bruckdorfer, 1986) documented the corrosion of cement structures by the leeching action of the carbon dioxide laden waters. Carbon dioxide laden water can reduce the hydrated cement to a soft, amorphous, silica gel.

The basic chemistry describing the process is as follows:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (2.1)$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \qquad (2.2)$$

$$\text{Ca-Si-H} + H + H_2CO_3 \rightarrow CaCO_3 + \text{amorphous } SiO_2 \qquad (2.3)$$

In step (2.1), approximately 1% of the dissolved carbon dioxide (CO_2) reacts with water (H_2O) to form carbonic acid. As the carbon dioxide laden water diffuses into the cement matrix, the dissolved acid is free to react with the calcium hydroxide ($Ca(OH_2)$) which makes up 20% of the cement composition and the hydrated calcium silicates (step (2.2) and step (2.3) respectively). If the reaction would stop after the initial carbonation of the calcium hydroxide, the cementitious calcium carbonate ($CaCO_3$) formed would cause the increase in compressive strength.

Although a strength increase is observed, as more carbon dioxide laden water invades the matrix, several new equilibria are established.

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca(HCO_3)_2 \qquad (2.4)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3 + H_2O \qquad (2.5)$$

In the presence of excess CO_2 in step (2.4), the calcium carbonate is converted to water soluble calcium bicarbonate. As more carbon dioxide laden water enters the matrix, the equilibrium is moved to the right. The end result is more water soluble calcium bicarbonate which can diffuse out of the matrix. As the calcium bicarbonate forms, another equilibrium reaction is established (step (2.5)). The dissolved calcium bicarbonate reacts with more calcium hydroxide to form calcium carbonate and fresh water.

The importance of step (2.5) is that the fresh water formed in the cement matrix is now available to dissolve more calcium bicarbonate. Providing there is a continuing supply of carbon dioxide laden water, the reactions will continue to leach cementitious material from the matrix. As the process continues, an increase in permeability and porosity occurs. This will result in the lacks of structural integrity in amorphous silica gel. This equates to a loss of casing corrosion protection and zonal isolation.

2.4 Characteristics of Reaction

The carbonation mechanism in the study is of a vigorous nature in Portland cement (Onan, 1984). It is not confined to the conversion of calcium hydroxide alone, but also includes the removal of calcium ions (Ca^{2+}) from the calcium silicate hydrate (Ca-Si-H) process.

$Ca_3Si + x\ H_2O \rightarrow Ca\text{-}Si\text{-}H^a + y\ Ca(OH)_2$ (2.6)

$\beta\text{-}Ca_2Si + x\ H_2O \rightarrow Ca\text{-}Si\text{-}H_a + y\ Ca(OH)_2$ (2.7)

$Ca(OH)_2 + 2H^+ + CO_3{}^{2-} \rightarrow CaCO_3 + 2H_2O$ (2.8)

$Ca_x\text{-}Si\text{-}H_y + (x\text{-}x')\ CO_2 \rightarrow Ca_{x'}\text{-}Si\text{-}H_{y'} + (x\text{-}x')\ CaCO_3 + (y\text{-}y')\ H_2O$ (2.9)

A calcium silicate hydrate has an approximate composition of $Ca_5Si_6H_5$. The latter reaction results in the production of a highly polymerized silica gel. This is characterized by the arrangement of the silica tetrahedral into tridimensional array. In the previous work, Onan (1984) stated that by utilizing infrared spectroscopy, it indicates that this reaction is preferential to the $Ca(OH)_2$-CO_2 reaction. It is not clear whether this phenomenon is due to the kinetics or whether the controlling factor is the chemical thermodynamics.

In the immediate carbonation of freshly prepared Portland cement, this reaction is also tends to dampen the compressive strength development due to the lowered calcium to silica ratio. The lowered calcium content causes significant gelation as a result in the shift from an electropositive dispersion to one that is neutral or slightly negative. Beyond this point, thinning occurs and at extremely high levels of carbonation, the silicate hydrations are accelerating according to the following reaction.

$Ca_n\text{-}Si + (n\text{-}x)\ CO_2 + y\ H_2O \rightarrow Ca_x\text{-}Si\text{-}H_y + (n\text{-}x)\ CaCO_3$ (2.10)

The aggresivity of CO_2 on Portland cement is depending on several factors. Apart from the properties of the CO_2 medium such as partial pressure, temperature and relative humidity, the composition and properties of the cementing composition are also taken into consideration.

2.5 Cement in Contact with CO_2-saturated brine and supercritical CO_2

The sequestration of CO_2 in deep (>1000 m) geologic formations requires a through evaluation of potential leakage through any wellbores which penetrate them (Kutchko et al. (2008)). It has been proposed that leakage rates less than 1% of stored CO_2 per 100 years are necessary for geologic sequestration to be viable.

There are two exposure conditions that are likely for wellbore cement in a CO_2 storage reservoir. Once CO_2 is injected, some will remain as a separate free phase (hydrodynamic trapping), while some will dissolve in the brine (solubility trapping). Hydrodynamic trapping occurs because the density of CO2 is less than that of the brine even at the depth of $\geq$ 800 m where CO_2 is a supercritical fluid. Buoyancy causes the CO_2 to rise and spread laterally beneath the reservoir caprock, leading to cement/supercritical CO_2 contact. When supercritical CO_2 contacts with formation water, it eventually dissolves to form CO_2-saturated brine with pH of less than 4. The dissolves CO_2 leads to cement/carbonated brine contact.

2.6 Alteration Process

The alteration process for Portland cement during CO_2 attack is a very effective process (Barlet-Gouédard V., Rimmelé G., Goffé B. and Porcherie O., 2007). A sharp alteration front is already clearly observed at the rim of the samples after half-day of CO_2 attack. The thickness of this alteration front increases with time. After a long exposure, the carbonated samples exhibit a strong degradation as attested by cracking occurrences and high deterioration is observed in both CO_2 fluids and spalling effect is observed on the sample core. Figure 2.1 shows the samples before exposure and after exposure (in this case, the exposure period is 6 months).

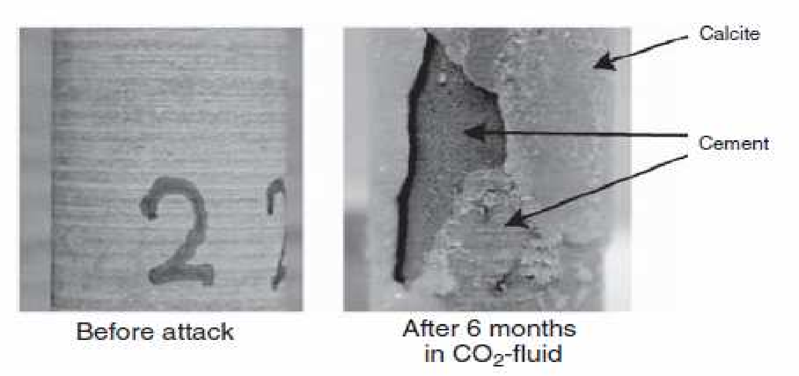

Figure 2.1: Samples before and after exposure

Porlandite ($Ca(OH)_2$) and calcium silicate hydrates (Ca-Si-H) of set cement are progressively consumed to produce calcium carbonates (aragonite, vaterite and/or calcite), silica amorphous gel and water. Figure 2.2 below shows the different zones in the attacked Portland cement. From the rim towards the core of the sample, the cement sample consists of carbonated zone, a carbonation front, a dissolution front and a non-carbonated zone.

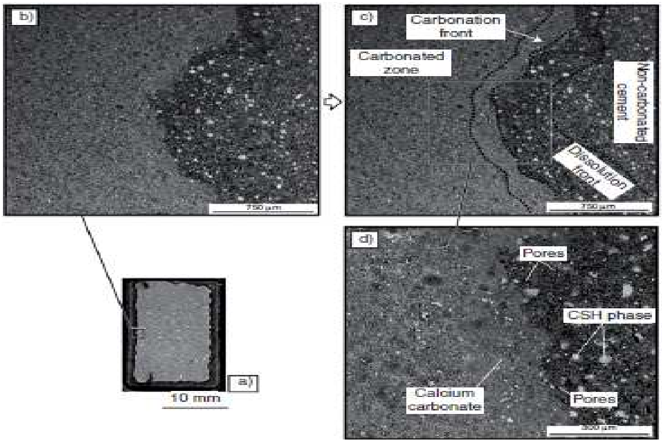

Figure 2.2: Different zone in attacked Portland cement

The carbonated zone contains calcium carbonate, silica gel and calcium-depleted calcium silicate phases. Then, the carbonation front is a thin front about 50-100 µm large of very low porosity and mainly made of calcium carbonates. It contrasts with the dissolution front that is a zone of high porosity where calcium silicate phases progressively dissolve. The uncarbonated zone is the internal part of the cement. It is noteworthy that the dissolution front and the carbonation are chemical reaction fronts.

The dissolution front is the zone in which Portland cement phases react with CO_2 to form calcium carbonates forwards in the carbonation front. At longer exposure duration, this geometry of reaction fronts is translated towards the central part of the samples and relicts of these fronts are commonly observed backwards in the carbonated zones. This complex series of "paleofronts" as shown in Figure 2.3 marks several physical discontinuities in the sample and participate to the weakening of Portland cement in terms of mechanical properties.

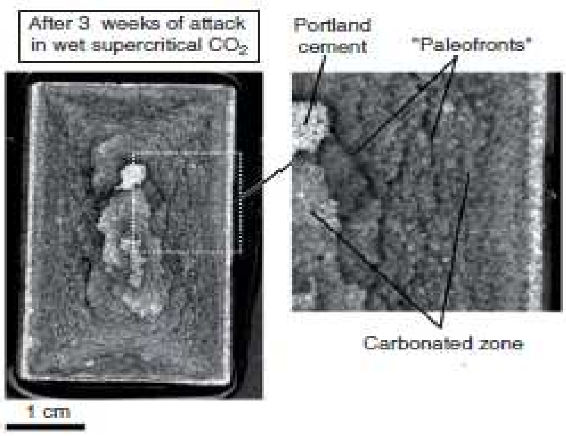

Figure 2.3: Several discontinuities in the sample

2.7 Cement Compressive Strength

The compressive strength of Portland cement samples tested at several durations of CO_2 exposure, under similar pressure and temperature conditions is shown in Figure 2.4 (Barlet-Gouédard V., Rimmelé G., Goffé B. and Porcherie O., 2007). From the figure, 30% of strength loss is measured after about 6 weeks of exposure.

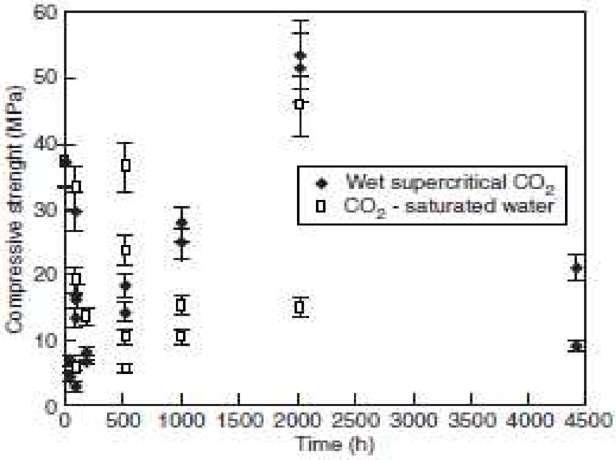

Figure 2.4: Compressive strength of Portland cement at different time of exposure

In CO_2-saturated water fluid, the compressive strength loses about 65%, However, the compressive strength measurements are very dispersed in both fluids. It may come from the heterogeneity of the samples due to the carbonation process. During the compressive strength measurements, the carbonation layer cracks. These results cannot be used as absolute compressive strength values but they indicate clearly the weakness of the carbonate layer or the interface at the front.

After a longer time of CO_2 exposure, the compressive strength of Portland cement is not measureable for the samples located in the CO_2-saturated water phase due to their high decrease of their mechanical properties.

2.8 SEM Analysis

SEM analysis reveals that during the course of carbonation a pseudomorphosis of the microstructure occurs converting a majority of calcium silicate hydrates (Ca-Si-H) crystals into vaterite, aragonite and eventually into stable calcite and SiO gel (Onan, 1984).

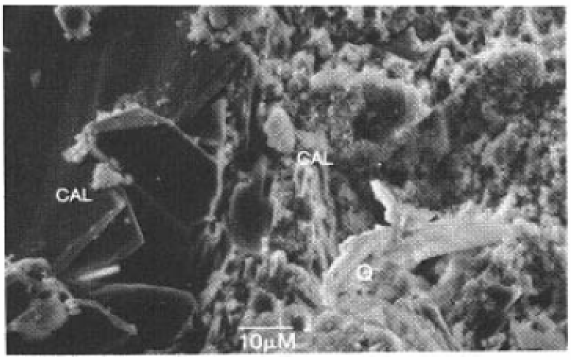

Figure 2.5: Microstructure of Portland cement

However, in comparison to the morphology of the uncarbonated samples, there appears to be no substantial change in the "binding framework" in the crystals. The latter appear to be plate-shaped and interlined (Figure 2.6) while the calcite crystallites appear poorly developed and intimately dispersed in the microstructure (Figure 2.7).

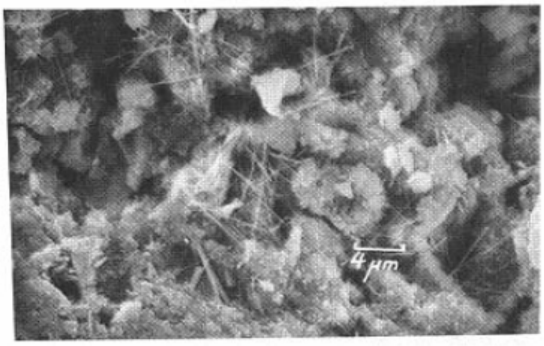

Figure 2.6: Microstructure of uncarbonated sample

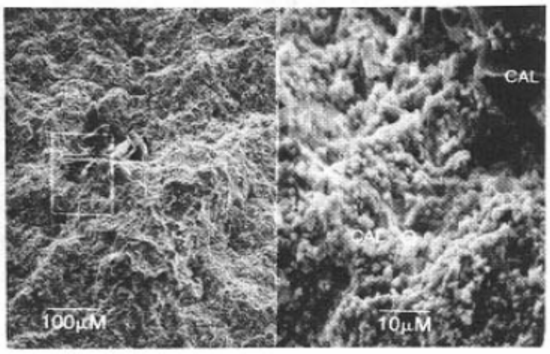

Figure 2.7: Microstructure of carbonated sample revealing growth of calcite crytallites

CHAPTER 3

METHODOLOGY

3.1 Sample Preparation

Class G oilwell cement (Lafarge cement) is used to prepare the cement slurry sample. The preparation of the cement slurry is shown in the following flow chart. The cement is mixed according to API Recommended Practice 10B (refer Appendix A).

349.0 gram of water and 792.0 gram of cement are weight using the weighing scale.

⇩

The mixture is mixed using Model 7000 Constant Speed Mixer

⇩

The mixer is turn on and the water is pour into the mixer.

⇩

Then, the cement is pour slowly into the mixer and allows it to mix with water.

Figure 3.1: Model 7000 Constant Speed Mixer

3.2 Curing Process

Cement samples are cast by slowly pouring the degassed slurry down the cubical mould containing eight cubic samples.

⇩

Launching the curing chamber.

⇩

Samples are cured for 8 hours.

⇩

The samples are cured under 1500 psi and temperature of 100°F.

⇩

After 8 hours of curing period, the samples are demoulded and being washed to remove grease on the surface.

⇩

The samples are examined. Only the perfect cubes are selected for testing.

⇩

The cubes undergo the coring process so that the samples will be in cylindrical shape.

⇩

The cubes are weighed and the dimensions are measured.

Figure 3.2: Curing chamber

3.3 Exposure Test

The experimental set up in the cement autoclave is used to get the overview of the behavior of cements with supercritical CO_2. The set up simultaneously obtained data for the two exposure situations: CO_2-saturated brine and wet supercritical CO_2 so that the exposure to both situations could be studied. Flow chart below shows the process flow for the CO_2 exposure to the cement.

The samples are placed in the autoclave in two crowns,

- the bottom crown submerged in brine (1% NaCl) solution
- the top crown in wet supercritical CO_2.

⇩

The Autoclave is pressurized with CO_2 at 1500 psi and 100°F.

⇩

The exposure test is done at different durations (24 hrs, 72 hrs and 120 hrs).

⇩

After the exposure durations, pressure is released slowly over a period of one hour to prevent sample damage in order to remove each of the samples.

The samples are removed from the vessel and weighted.

Mechanical strength, chemical and microscopic composition are analyzed.

Figure 3.3: Autoclave

3.4 Sample Analysis

The samples are tested mechanically and chemically after the CO_2 exposure to determine the changes in the cement structure, compressive strength and other indirect measurements. The non-CO_2 exposure samples are also being tested after the curing period to compare the cement structures.

3.4.1 Scanning Electron Microscopy (SEM)

Cubic samples are cut into slices with approximately 3.5 mm thick to prepare a thin section in axial plane.

The depth of the altered zone within each samples are measured. The results are plotted against the exposure time.

⇩

The changes in the structure and the chemistry of the cement are analyzed.

⇩

Microstructural development, alteration front and the depth of carbonation are examined using the SEM.

3.4.2 Compressive Strength

Compressive strengths of the carbonated samples are determined using the OFITE Automated Compressive Strength Tester.

⇩

The force is applied to the carbonated samples at constant rate until the samples fail.

⇩

The maximum loading where the samples fail is the cement’s compressive strength.

The compressive strength of each sample is measured before and after the CO_2 attack without any additional treatment. The results obtained are then being compared.

3.4.3 Other Indirect Measurement

The weight of the samples before and after exposure and the thickness of the alteration front are measured.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Scanning Electron Microscopic (SEM) Analysis

The analysis using Scanning Electron Microscopic (SEM) is done on the samples which have been exposed to CO_2. SEM analysis reveals that during the carbonation, a pseudomorphosis of the microstructure occurs converting a majority of calcium silicate hydrates crystals into calcium carbonate (calcite) and amorphous silica gel. As the comparison, the non-carbonated sample is also analyzed.

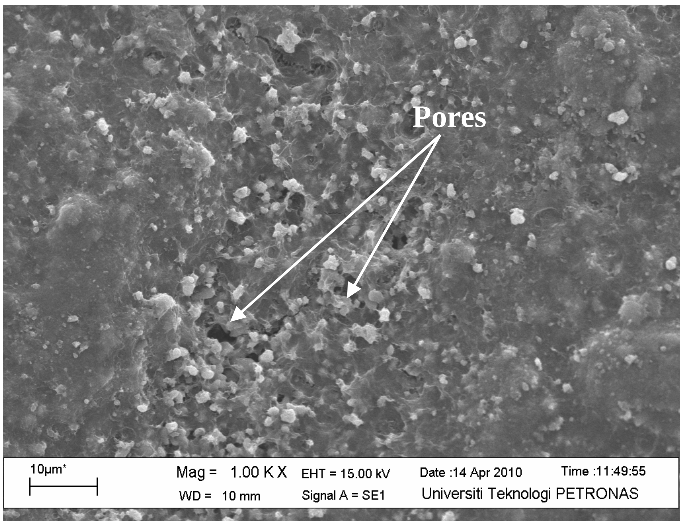

Figure 4.1: Non-carbonated sample at 1000x magnifying

Based on Figure 4.1, the microstructure of non-carbonated sample shows that there is no substantial change in the “binding framework” in the crystals. On the other hand, after being exposed to CO_2, the microstructures of the cements reveal the growth of calcium carbonate (calcite) and amorphous silica gel in the structure as shown in Figure 4.2 until Figure 4.7 below.

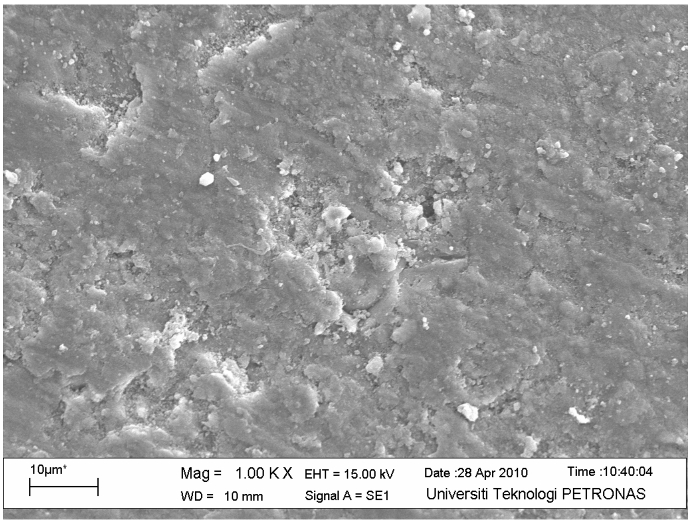

Figure 4.2: Sample in wet supercritical CO_2 after 24 hours of exposure

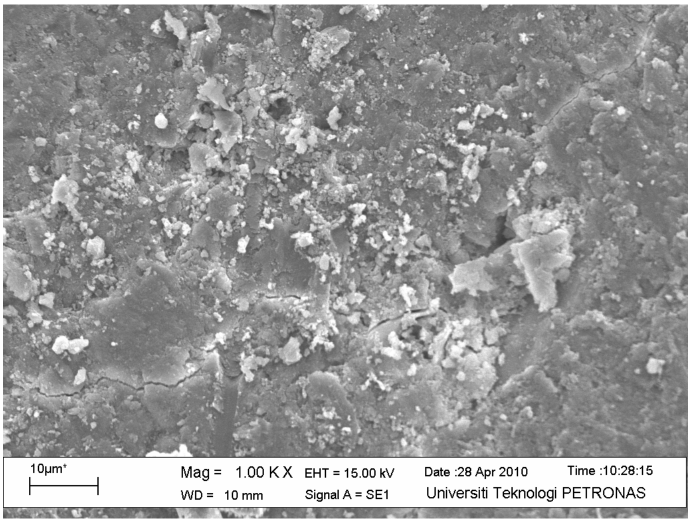

Figure 4.3: Sample in wet supercritical CO_2 after 72 hours of exposure

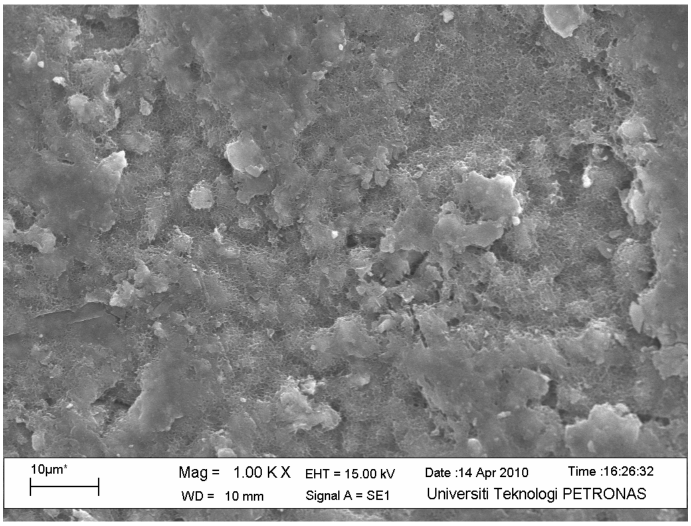

Figure 4.4: Sample in wet supercritical CO_2 after 120 hours of exposure

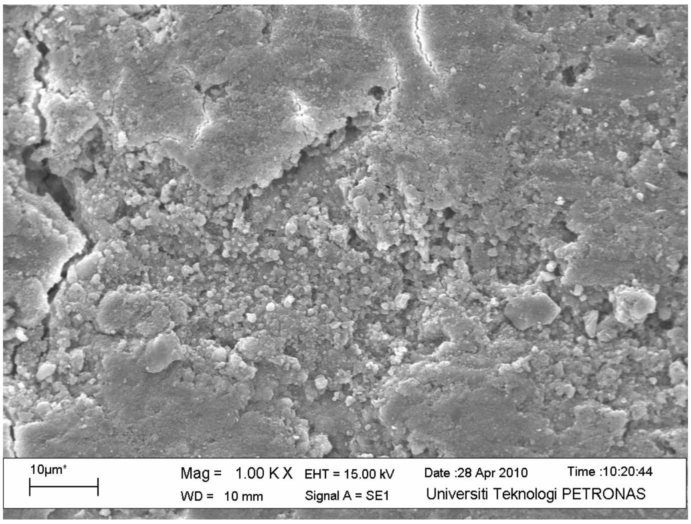

Figure 4.5: Sample in brine after 24 hours of exposure

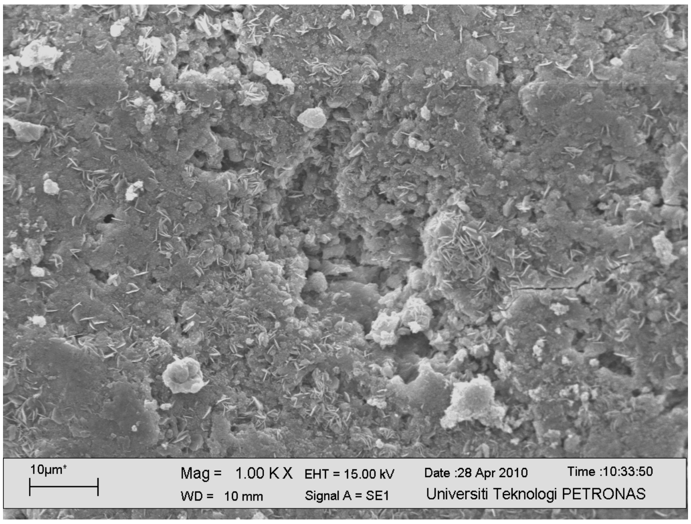

Figure 4.6: Sample in brine after 72 hours of exposure

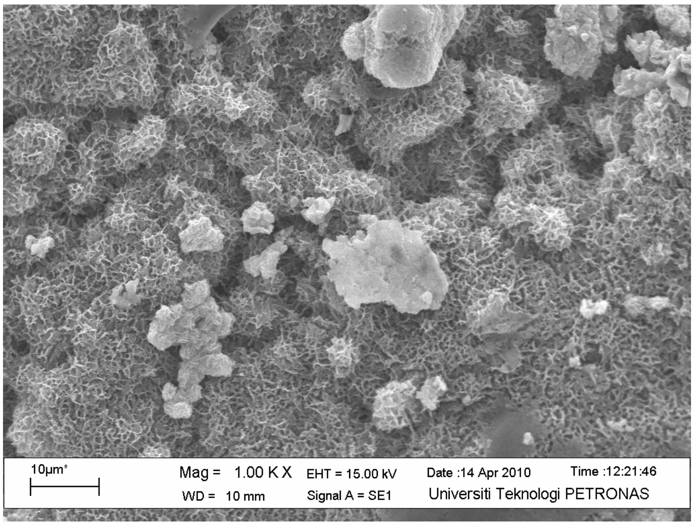

Figure 4.7: Sample in brine after 120 hours of exposure

After CO_2 exposure, the growth of calcium carbonate and amorphous silica gel can be seen in the structure of each of the cement sample. The calcium carbonate and amorphous silica gel formation occur rapidly in sample in brine compare to sample in wet supercritical CO_2 (Figure 4.4 and Figure 4.7) after 120 hours of exposure. Also, the formation of a complex series of “paleofronts” can be observed for the sample submerged in brine.

The formation of calcium carbonate and amorphous silica gel in cement resulted from the following reactions;

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (4.1)$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \qquad (4.2)$$

$$Ca\text{-}Si\text{-}H + H + H_2CO_3 \rightarrow CaCO_3 + \text{amorphous } SiO_2 \qquad (4.3)$$

The carbon dioxide will react with water in cement to form carbonic acid (4.1). The dissolved acid is then free to react with calcium hydroxide (4.2) and calcium silicate hydrates (4.3) to form calcium carbonate and amorphous silica. If these reactions would stop after the initial carbonation of calcium hydroxide, the calcium carbonate formed will cause an increase in cement compressive strength.

As more carbon dioxide invades the cement matrix, several new equilibra established.

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca(HCO_3)_2 \qquad (4.4)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3 + H_2O \qquad (4.5)$$

In step 4.4, in the presence of excess CO_2, calcium carbonate will be converted to calcium bicarbonate. As the calcium bicarbonate formed, another equilibrium reaction occurs (4.5). The dissolved calcium bicarbonate will reacts with calcium hydroxide to produce more calcium carbonate and water.

4.2 Alteration Process

Alteration process of the cement reveals a sharp alteration front during the CO_2 attack. The SEM analysis allows distinguishing the different zones in the attacked cement. There are four zones that can be observed from the rim towards the core of the cement sample. After the carbonation, the cement samples consist of a carbonated zone, a carbonation front, a dissolution front and a non-carbonated zone.

The carbonated zone contains calcium carbonate (calcite), silica gel and calcium-depleted calcium silicate phases. The carbonation front is mainly made of calcium carbonates and of very low porosity. Meanwhile, the dissolution front is a zone of high porosity where calcium silicate phases progressively dissolve. The non-carbonated zone is the internal part of the cement that has not been attack by CO_2.

The reaction process of the carbonation starts with the dissolution of $Ca(OH)_2$ in the dissolution front zone (4.6) followed by subsequent precipitation of $CaCO_3$ in carbonation front zone (4.7). The reactions of the process are shown below.

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \tag{4.6}$$

$$Ca^{2+} + HCO^{3-} + OH^- \rightarrow CaCO_3 + H_2O \tag{4.7}$$

The formation of $CaCO_3$ decreases cement permeability and increases the cement compressive strength. The next step initiated with the dissolution of $CaCO_3$ resulting in leaching of calcium ions from the cement matrix. Without $CaCO_3$, the cement paste are no longer has the ability to buffer the pH so the remaining calcium silicate hydrates (C-S-H) is converted to amorphous silica gel.

$$H^+ + CaCO_3 \rightarrow Ca^{2+} + HCO^{3-} \tag{4.8}$$

$$2H^+ + \text{C-S-H} \rightarrow Ca^{2+} + H_2O + \text{amorphous } SiO_2 \tag{4.9}$$

The resulting cement paste of amorphous SiO_2 has a significant increase in porosity and lacks of structural integrity.

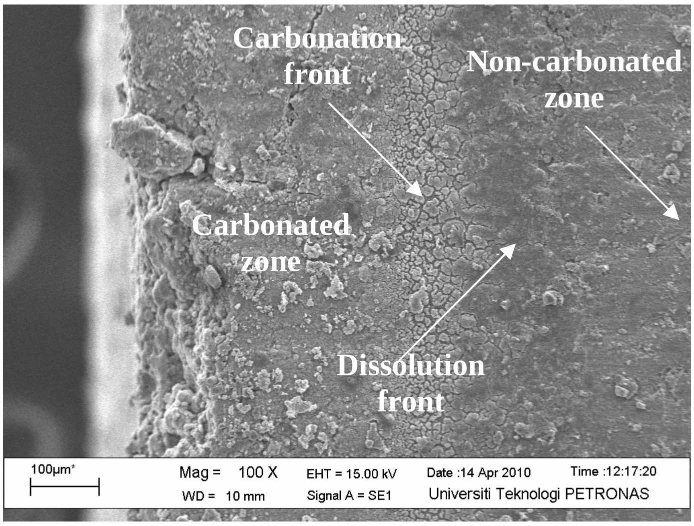

Figure 4.8: Different zones in sample submerged in brine after 120 hours of exposure

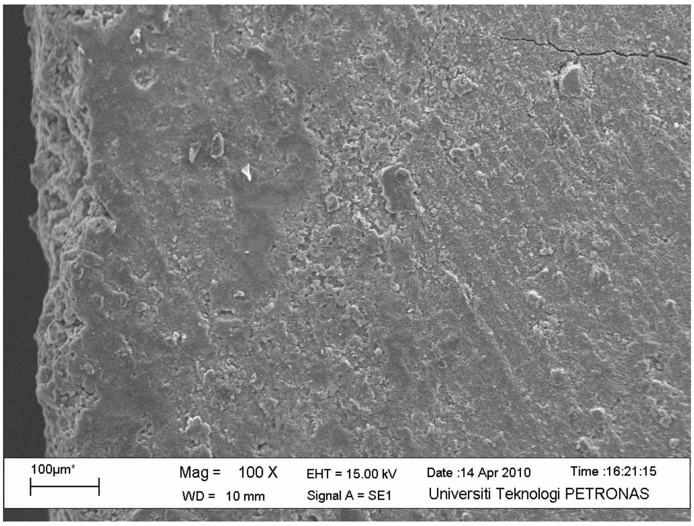

Figure 4.9: Different zones not observed in sample in wet supercritical CO_2 after 120 hours of exposure

These different zones were not observed in sample submerged in wet supercritical CO_2 and it indicates different mode of carbonation attack in both fluids. The cement in wet supercritical CO_2 had a single reaction front and $CaCO_3$ was distributed throughout the reacted portion rather than isolated in a well defined band. Some supercritical CO_2-exposed samples contained large porous intrusions that deviated significantly from typical uniform pattern of the reaction. The intrusions were only seen in some of the samples and appeared to be random and spatially isolated. There were likely artifacts from condensed droplets of surface moisture on the outer surface of the cement sample and were not included in the measurements to determine the thickness alteration front.

Table 4.1 below shows the alteration thickness of the cement samples after CO_2 exposure measured using the optical microscope.

Table 4.1: Thickness of alteration after exposure

Duration (hr)	**Alteration Thickness (mm)**	
	Brine	**Wet Supercritical CO_2**
24	0.815	0.740
72	0.900	0.810
120	1.060	0.845

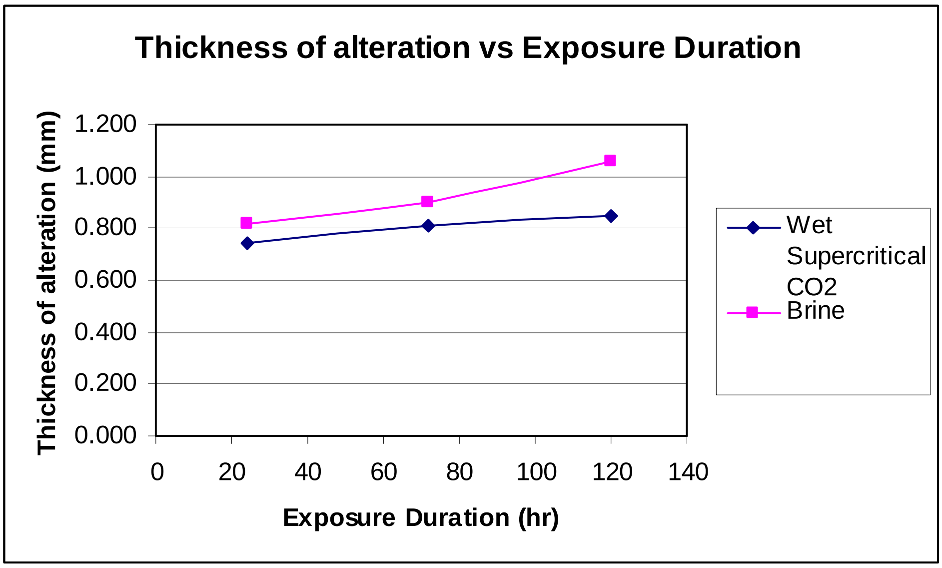

Figure 4.10: Thickness of alteration vs. Exposure Duration

From Table 4.1 and Figure 4.10, it is observed that the thickness of alteration front increases with time and is greater in samples submerged in brine than in wet supercritical CO_2 at each of exposure duration. This observation clearly indicates that the alteration process is more efficient in the brine fluid compare to wet supercritical CO_2 fluid.

4.3 Compressive Strength

Compressive strengths of the cement samples cured under the condition of 1500 psi and 100 °F before and after CO_2 exposure are measured. The compressive strength of the samples before the CO_2 attack is shown in Table 4.2.

Table 4.2: Compressive strength of samples before the CO_2 exposure

Sample	Compressive Strength (MPa)
01	18.34
02	14.30
03	12.30

The average compressive strength for the cement samples before exposure is;

$$\text{Average} = (18.34 + 14.30 + 12.30)/3$$
$$= 14.98 \text{ MPa}$$

After the CO_2 exposure, the compressive strengths for the cement samples are shown in the following table.

Table 4.3: Compressive strength after CO_2 exposure

Exposure Duration (hrs)	Compressive Strength (MPa)	
	Wet supercritical CO_2	Brine
24	79.40	66.50
72	85.20	69.10
120	71.20	63.60

From Table 4.2 and Table 4.3, we can see that the average compressive strength of the cement before CO_2 exposure is lower than the compressive strength of the cement after CO_2 exposure. This can be explained from the reactions occur during carbonation as previously shown in step 4.1 until step 4.3.

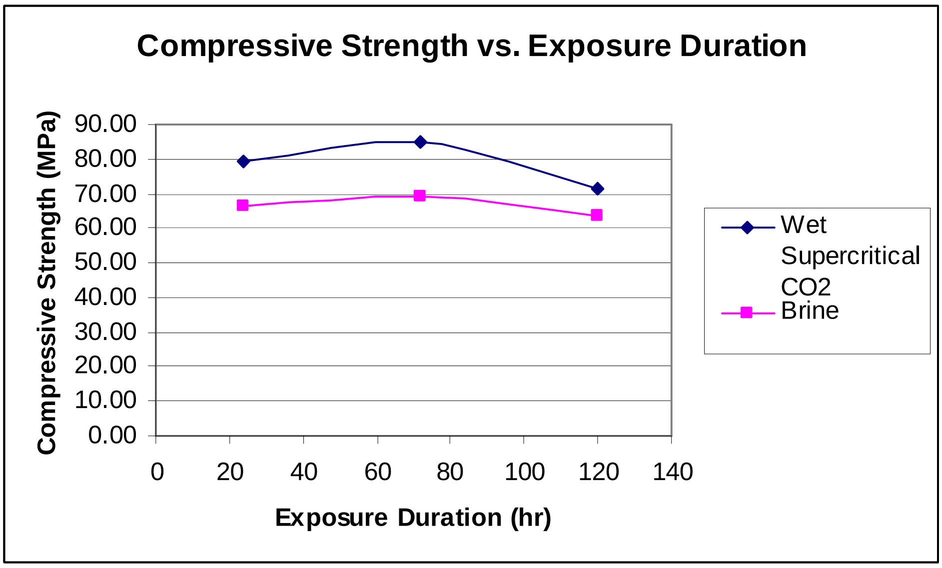

Figure 4.11: Compressive Strength vs. Exposure Duration

Figure 4.11 is obtained when the compressive strengths of the cement samples are being plotted against the CO_2 exposure durations. From the graph, we can see that the compressive strength of the cement increases initially but then after a longer exposure time, the compressive strength decreases. Also, we can see that the compressive strength of the cements in wet supercritical CO_2 is higher compare to the cements submerged in brine. The lower compressive strength of the sample in brine is likely due to the formation of the “paleofronts” in the structure which marks several discontinuities in the sample and participate to weakening the cement in terms of mechanical properties.

The increase in compressive strength from 24 hours to 72 hours duration resulted from the initial carbonation of calcium hydroxide in which the cementitious calcium carbonate formed would cause the increase in compressive strength.

After 120 hours of exposure, the compressive strength decreases. This is because of the continuous supply of CO_2 will let the reactions to continue leaching the cementitious material from the cement matrix. This will increase the permeability and porosity which contribute to the lack of structural integrity and decreases in cement mechanical properties.

In wet supercritical CO_2, the compressive strength loss after 120 hours of exposure is 10.33%. For cement samples submerged in brine, the compressive strength loss is about 4.36% after the same exposure durations. Although the cements in wet supercritical CO_2 show higher percentage of compressive strength loss, their compressive strengths are higher than the cements in brine. Thus, we can say that the mechanical properties of cements in wet supercritical CO_2 are much tougher compare to brine due to the slow penetration of carbonation.

4.4 Weight Changes

The weights of the cement samples measured before and after the CO_2 exposure are shown in the table 4.4.

Table 4.4: Weights of the cements before and after the exposure

Sample	**Brine**	**Wet Supercritical CO2**	**Weight (g)**		**Percentage of weight increase (%)**
			Before Exposure	**After Exposure**	
1	√		108.90	109.60	0.64
2		√	105.90	109.00	2.93
3	√		109.50	111.80	2.10
4	√		101.90	105.10	3.14
5		√	102.00	106.90	4.80
6		√	102.60	106.00	3.31

As we can observe from the table, the weights of each sample increases after the exposure. The increase in weights are likely due to the reaction of calcium bicarbonate $Ca(HCO_3)_2$ with calcium hydroxide ($Ca(OH)_2$) to form more calcium carbonate ($CaCO_3$) and fresh water.

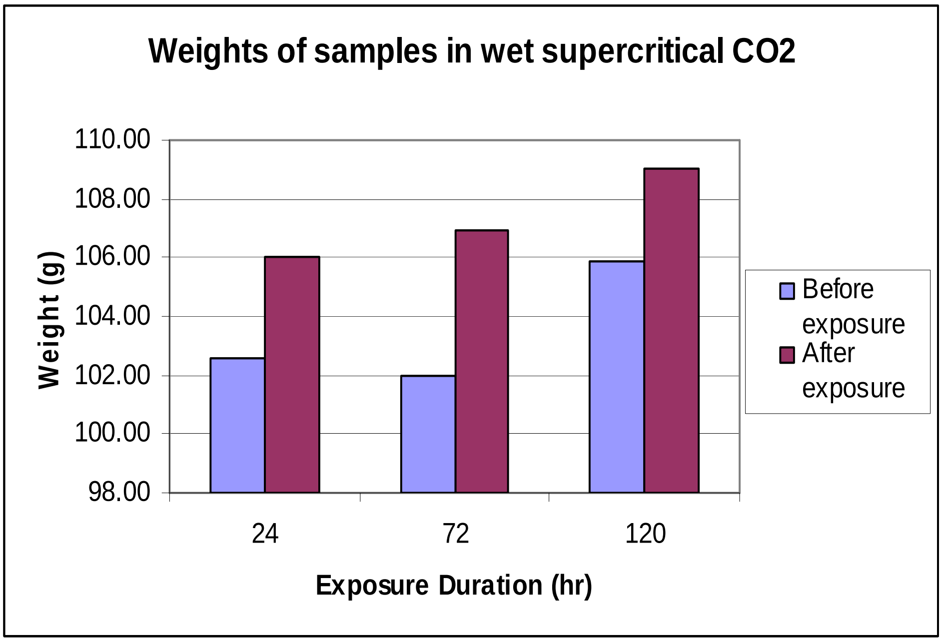

Figure 4.12: Weights for samples in wet supercritical CO_2 before and after exposure

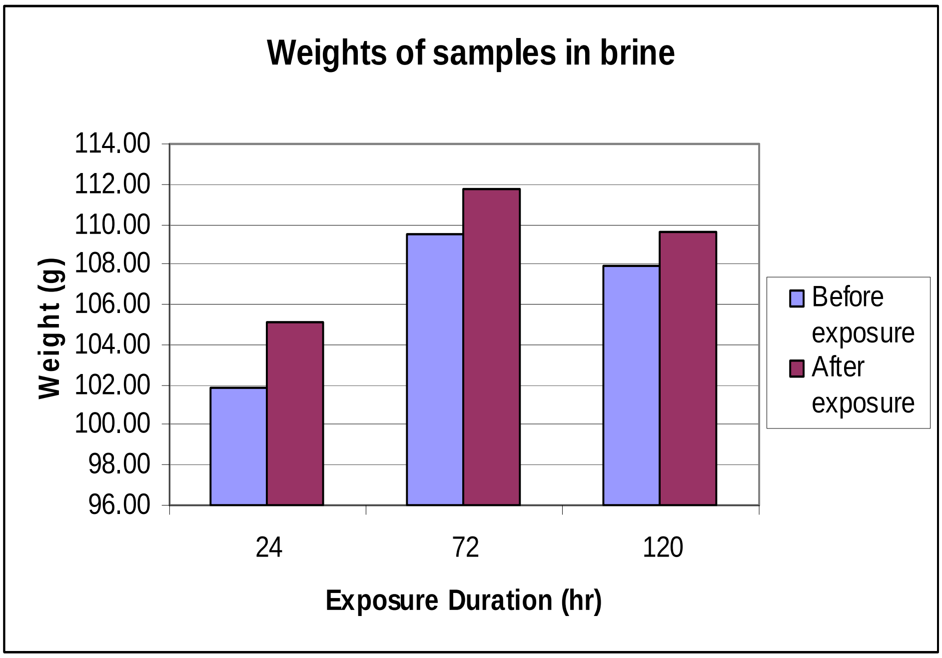

Figure 4.13: Weights for samples in brine before and after exposure

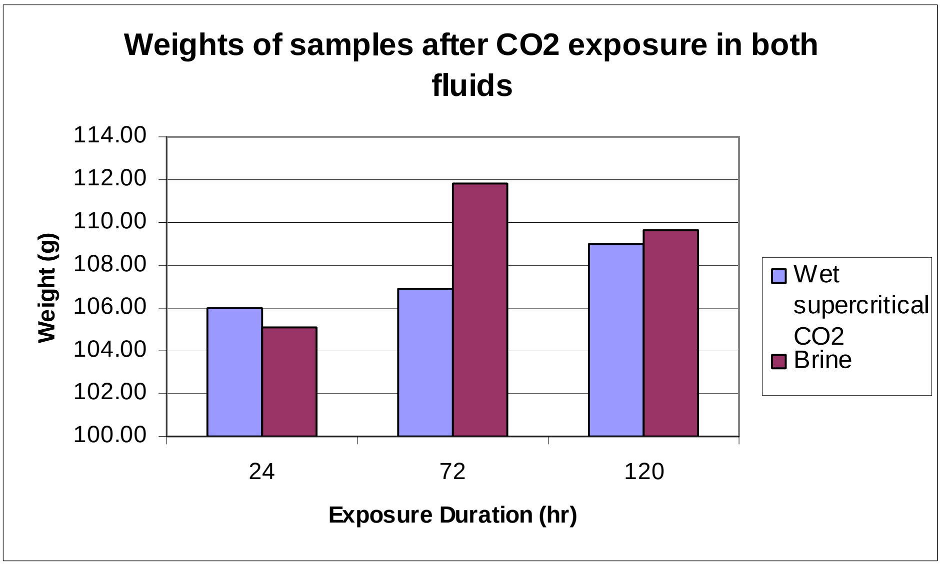

Figure 4.14: Weights for samples in both fluids after the exposure

From Table 4.4, Figure 4.12, Figure 4.13 and Figure 4.14, we can conclude that the weights of the cement samples increase in both fluids after 120 hours of CO_2 exposure. After a longer time of exposure, the weight of the sample in wet supercritical CO_2 increases for about 3.36% and 0.70% for the sample located in brine.

4.5 Comparison between Samples in Both Fluids

The obvious differences observed between the samples submerged in brine and wet supercritical CO_2 are the outer surface of the samples. The outer surface of the sample submerged in brine is orange in color and had a smooth texture (Figure 4.15). On the other hand, sample in wet supercritical CO_2 appears in light gray color and had a rough texture (Figure 4.16). Based on SEM analysis (Figure 4.8 and Figure 4.9), the cement sample in brine revealed the four different zones and the distinct zones are clearly observed. However, these zones were not observed in sample in wet supercritical CO_2. This is due to the single reaction front and the different mode of attack. The rough texture of sample in wet supercritical CO_2 resulted from the deposition of $CaCO_3$.

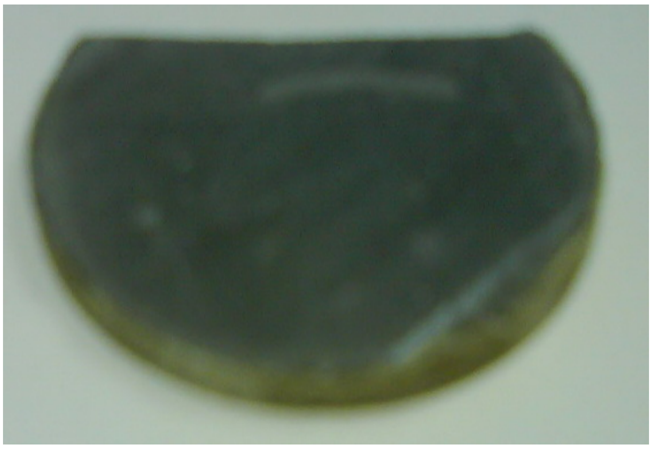

Figure 4.15: Sample submerged in brine

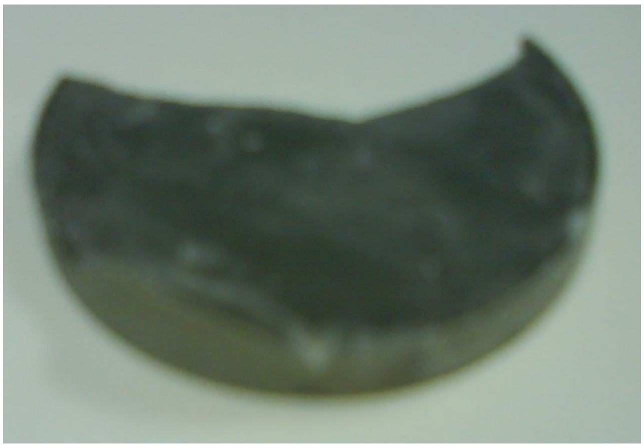

Figure 4.16: Sample submerged in wet supercritical CO_2

By definition, ordinary carbonation is the dissolution of CO_2 in the cement pore solution of the cement paste, the production of CO_3^{2-} ions and the subsequent reaction with Ca^{2+} in order to produce $CaCO_3$ with the pore structure of the cement paste. The process observed in samples submerged in brine is typically of acid attack and not the ordinary carbonation. This is due to the rate of acid-base carbonation reactions which is much faster than the diffusion of ionic species in the cement matrix. Thus, the cement degradation observed for cement sample submerged in brine is best described as an acid attack by carbonic acid.

The cement in wet supercritical CO_2 produced a slow penetration which yields carbonated paste that did not develop individual distinct alteration zones (Figure 4.9). This is likely due to a lack of water to diffuse ions out of the cement matrix. The lacks of a dense carbonate barrier allows the reaction to be controlled by the rate of diffusion of CO_2 into the cement matrix. Thus, the cement in wet supercritical CO_2 showed a more limited penetration and in all cases, the degradation of cement in wet supercritical CO_2 is not as deep as the sample submerged in brine.

CHAPTER 5

CONCLUSION

From the results obtained and based on the discussion that has been made, it can be concluded that, the cement is not resistant enough to carbon dioxide attack. This can be seen in the decrease of the cement compressive strengths which show that the structural integrity and mechanical properties of the cement has been affected by carbonation. Under microscopic analysis, the growth of calcium carbonate and amorphous silica gel in the cement structure were revealed. The formation of calcium carbonate and amorphous silica gel contribute to the increase in porosity and lacks structural integrity.

Carbonation causes the degradation of cement structures as observed in terms of their compressive strengths, the weight changes after carbonation and the thickness of alteration front. Carbonation contributed to the lack of mechanical and physical properties of the cement.

CHAPTER 6

RECOMMENDATION

Although CO_2 corrosion in Portland cement is difficult to stop, cementing formulations are now available which resist the leaching action of carbonic acid. In order to provide a long term seal integrity for the full life cycle of the wellbore, proper design of the cement system for the current and future wellbore conditions is crucial.

There are several available technologies that have been shown to be effective in providing long term seal integrity in oilwells. These technologies can provide long term seal integrity for the full life cycle of the wellbore if they are used in combination with each other and supplemented with advanced simulation work.

The following section will discuss on the alternative ways or methods that can be applied in order to improve the Portland based cement resistant to corrosion based on the previous researches that have been done.

6.1 Modifying Portland Based Cement Systems

Portland cement system can be modified in number of ways in order to slow or prevent the reaction with CO_2. The main methods of system modification are by reducing the permeability of the cement matrix, reducing the concentration of reactive species by dilution with carefully chosen non-reactive materials or chemically protecting the species through some sort of coating. These methods have been used with success in number of applications in oil and gas wells.

One of the most effective means of reducing the reactivity of the cement with CO_2 is by reducing the permeability of the cement matrix. This method is one of the easiest to obtain. The most common method use to reduce the permeability of cement is by simply change the cement to water ratio which will increase the proportion of the cement. While the increase in viscosity can be countered by the use of dispersants, changing this ratio will also increase the density of the cement. However, the disadvantage of this approach is that not all wellbores can withstand the higher hydrostatic pressures brought on by the high density cement slurry.

The permeability of cement can be reduced by adding specialty materials to the slurry that fill the pore spaces in the cement. The “tri-modal” or three particle approach has led to the development of high performance cement systems. These systems can cover an entire range of slurry densities in which will make them applicable to a wide range of wellbore conditions.

The addition of the specifically sized particles will not only reduce the permeability of the cement but also the function to dilute the concentration of reactive species. Thus, this technique offers benefits beyond simple permeability reduction. Latex has been used successfully in these systems to aid in fluid loss control which provide permeability reduction through pore space plugging.

Protecting the reactive species through addition of other additives in also an additional method used in modifying Portland cement based system. The development of a Portland based system that completely resistant to CO_2 attack has been reported by Barlet-Gouedard et al. (2007).

6.2 Non-Portland Cements

Another approach that can be done to assure the long term seal quality in the annulus is to replace Portland based cement with non-Portland system. Limestone, the principal raw material in Portland cement clinker is geologically abundant and forms the basis for binder in the Portland cement. The raw materials used to make non-Portland cements are less abundant and less widely dispersed and makes them more difficult to obtain. Some of the examples of non-Portland cements include calcium sulfoaluminate-based cements, geopolymeric cements (alkali aluminosilicates), magnesium oxide cements and hydrocarbon-based cements.

The systems are commercially available while less abundant and selected ones have been applied in injection wells for decades. One of the most resistant systems is calcium aluminates cement that does not react with CO_2. This specialty cement has been used in many applications in oil and gas wells and specifically in one of the highest rate acid gas injection wells in United States.

Additional steps in planning and execution phases are not required in using specialty cements. These materials are not compatible with non-Portland cement and operations must be planned to eliminate the potential for any cross contamination. In conventional cementing, additives do not react the same way as they react with Portland cement with these systems thus they require additional testing prior to their use. The effective density range for these slurries is narrower than with Portland cement which limiting their application in some fields. The non-Portland based cement also has limited availability and will not be available in some areas.

6.3 Swelling Technologies

Swelling technologies is use to identify materials that, when placed in the well, have the ability to react to changing the wellbore conditions and more importantly the intrusion of specific wellbore fluids or gases. The interactions with the wellbore fluids will cause an expansion of the materials in which resulting in tighter annular seal.

These materials do not change the cement itself but will enhance the seal in the wellbore if there is an intrusion of particular fluids or gases.

6.3.1 Self Healing and Specialty Cements

Failure of a cement casing can occur for a number of reasons. The common reasons for casing failure related to cracking of the cement from some stress change in the wellbore, followed by de-bonding of the cement casing either from the formation of the casing is indicates by the stress modeling and field experience. These changes can be caused by the rapid increase in temperature or pressure, either due to completion or stimulation operations or simply long term production of the well.

The cracks or the de-bonded areas of the cement casing can open up the paths for gases or fluids to flow in the annulus. Self healing cements involve the use of specific additives that are designed to interact with these gases or fluids to eliminate the flow. The technique is similar to that found in swelling packers though specifically adapted to work within a cement system. The self healing cements will react to a failure of the cement casing through their interaction with the flowing material in the well.

Other specialty cement systems are also designed to prevent the failure from initial placement of the cement. One of the techniques incorporates flexible materials in the cement to enhance the ability to withstand changes in the pressure environment while other technique incorporates in reducing the cement Young’s Modulus. The materials used in these applications can be solid, flexible additives or foamed cement technologies.

Many recommendations are now being made that include the self healing cements that contain both flexible and expanding agents. Further investigation of the long term mechanical properties of these various systems and their effectiveness in changing stress environments will be required.

6.3.2 Swell Packers

A swellable packer element that is placed on the outside of the cement casing is one of the recently developed technologies. This swellable packer element acts as a passive seal element and designed to swell in the presence of various materials. The packers are designed to swell the presence of hydrocarbon, water or both in oil and gas applications. These elements do not act as the initial seal in wellbore but in the event of any failure of the cement casing or movement of gases or fluids, they will respond by swelling and will isolate the flow thus preventing the migration along the wellbore.

Some applications of swelling packer technologies have completely eliminated the cement as the sealing in the well. The well has been drilled with a hydrocarbon based fluid and the packer element has been designed to swell in hydrocarbon. After running the casing to the total depth (TD), the well is left idle for a period of time to allow the element to swell and affect an annular seal. These elements are designed to withstand up to 5000 psi differential pressure across the element and have shown to be an effective method in providing a seal.

Eliminating completely the cement from the annulus would not be recommended in CO_2 injection wells. Incorporating the swelling packer with proper cementing could provide additional security for long term seal integrity.

REFERENCES

Jack M. Chi, Ran Huang and C.C. Yang. 2002, “Effects of Carbonation on Mechanical Properties and Durability of Concrete Using Accelerated Testing Method”, *Journal of Marine Science and Technology*, Vol. 10, No.1, pp. 14-20.

Ginneken L.V et al, 2004, “Effect of liquid and supercritical carbon dioxide treatments on the leaching performance of a cement-stabilised waste form”, *Journal of Supercritical Fluids 30 175-188.*

Bruckdorfer R.A, Dowell Schlumberger. 1986, “Carbon Dioxide Corrosion in Oilwell Cements”, *SPE 15167 Billings*, MT, May 19-21.

Onan D.D, Haliburton Services. 1984, “Effects of Supercritical Carbon Dioxide on Well Cements”, *SPE 12593*, Society of Petroleum Engineers of AIME.

Barlet-Gouédard V., Rimmelé G., Goffé B. and Porcherie O. 2007, “Well Technologies for CO_2 Geological Storage: CO2-Resistant Cement”, *Oil & Gas Science and Technology – Rev. IFP*, Vol. 62, No.3, pp. 325-334.

Carey, J.W., Wigand, M., Chipera, S. et al. (2006), “Analysis and performance of oil well cement with 30 years of CO_2 exposure from the SACROC unit, West Texas, USA”, *8th International conference on Greenhouse Gas Control Technologies*, Trondheim, Norway, June 19-22.

Van Gerven,T., Van Baelen, D., Dutré, V. and Vandecasteele, C. (2004a), “Influence of Carbonation and Carbonation Methods on Leaching of Metals from Mortars”, *Cement Concrete Res.*, 34, 149-156.

Benge Glen (2009), “Improving Wellbore Seal Integrity in CO_2 Injection Wells”, *Energy Procedia I* (2009) 3523 – 3529.

Kutchko, B.G. et al. (2008), “Rate of CO2 attack on Hydrated Class H Well Cement under Geologic Sequestration Conditions”, *Environ. Sci. Technol*. (2008), 42, 6237-6242.

APPENDICES

Appendix A: API Recommended Practice 10B for Class G Oilwell Cement

Class G Oilwell Cement

Conforms to API Specifications for Materials and Testing for Well Cementing API Spec. 10A

Chemical Requirements	**API Class G Requirements**	**Typical Lehigh Inland Performance**
MgO max %	6.0	3.6
SO_3 max %	3.0	2.5
Loss on Ign. max %	3.0	1.2
Insoluble Res. max %	0.75	0.16
C_3S max %	48 - 58	53.0
C_3A max %	8.0	2.8
Total Alkali as Na20%	0.75	0.6
Physical Requirements	**API Class G Requirements**	**Typical Lehigh Inland Performance**
Water % by wt. of cement	44.0	44.0
Soundness % max	0.8	0.09
Free water max ml	5.8	3.9
Min compr. str. MPa (8 hours) at temp. 38C, Atm. pressure at temp. 60C, Atm. pressure	2.1 10.3	3.5 15.0
Max consistency	30.0	10.0
Thickening Time (schedule 5) minimum (minutes)	90 - 120	110

The table above compares the properties of Lehigh Inland's Class G Oilwell Cement with the requirements of API Spec. 10A.

**Based on 250 ml volume, percentage equivalent of 3.5 ml is 1.4%*

Uses

Class G Oilwell Cement is intended for use as a basic well cement for surface 2,440 m (8000 ft.) depth as manufactured or can be used with accelerators and retarders to cover a wide range of well depths and temperatures.

Lehigh Inland's Class G Oilwell Cement is available in bulk or in 40 kg bags.

Specifications

Due to rigid manufacturing standards, Lehigh Inland's Oilwell Cement has increased uniformity of physical and chemical properties. Class G Oilwell Cement offers dependable performance over extreme ranges of well conditions and better compatibility with additives.

For further information on Class G Oilwell Cement, please contact your nearest Lehigh Inland Cement representative.

Important Note

Because of the chemical properties of all types of cement, it is important to be aware of the following: ***Freshly mixed cement, mortar, concrete or grout may cause skin injury. Avoid contact with skin where possible. In the event of contact, wash exposed skin areas promptly with water. If any cement or cement mixtures come into contact with the eyes, rinse immediately and repeatedly with water and get prompt medical attention.***

Appendix B: Gantt chart for 2 Semesters Final Year Project

GANTT CHART FOR THE 1ST SEMESTER OF 2 SEMESTERS FINAL YEAR PROJECT

Table B.1: Gantt Chart for 1st semester

DETAIL / WEEKS	1	2	3	4	5	6	7	8	9		10	11	12	13	14
Selection of Project Topic	🟦	🟦								**MID SEMESTER BREAK**					
Submission of Form 01 (Title Proposal)			🟦												
Preliminary Research Work • Literature review • Identifying tools or equipment required • Methodology			🟦	🟦											
Submission of Preliminary Report				🟪											
Seminar 1 (optional)					🟦	🟦	🟦								
Project Work • Methodology Analysis • Availability of equipments required					🟦	🟦	🟦								
Submission of Progress Report • Literature review • Project description and progress • Data gathering								🟦	🟦						
Seminar 2 (compulsory)									🟪		🟦	🟦	🟦		
Project Work Continues • Project research continue • Data gathering												🟦	🟦	🟦	
Submission of Interim Report Final Draft														🟪	
Oral Presentation															🟪

GANTT CHART FOR THE 2ND SEMESTER OF 2 SEMESTERS FINAL YEAR PROJECT

Table B.2: Gantt Chart for 2nd semester

DETAIL / WEEKS	1	2	3	4	5	6	7		8	9	10	11	12	13	14
Project Work Continue • Sample preparation • Data gathering and analysis • Equipment research	🟦	🟦	🟦	🟦	🟦	🟦	🟦	**MID SEMESTER BREAK**							
Submission of Progress Report 1					🟪										
Project Work Continue • CO_2 Exposure • Alteration Measurements • Findings • Data gathering and analysis									🟦	🟦	🟦	🟦	🟦	🟦	🟦
Submission of Progress Report 2												🟪			
Project Work Continue • Sample Analysis • Results and findings • Data analysis and discussion									🟦	🟦	🟦	🟦	🟦	🟦	🟦
Poster Exhibition												🟪			
Submission of Dissertation (soft bound)															🟪
Oral Presentation									31st May 2010 – 11th June 2010						
Submission of Project Dissertation (hard bound)									18th June 2010						

🟦 Process
🟪 Suggested Milestone