Spring 2019

Investigating the use of class C flyash-based geopolymer cement as a potential alternative to Portland cement to seal CO_2 storage wells

Priyesh Parimal Jani

Recommended Citation

Jani, Priyesh Parimal, "Investigating the use of class C flyash-based geopolymer cement as a potential alternative to Portland cement to seal CO_2 storage wells" (2019). *Masters Theses*. 7886.
https://scholarsmine.mst.edu/masters_theses/7886

INVESTIGATING THE USE OF CLASS C FLYASH-BASED GEOPOLYMER CEMENT AS A POTENTIAL ALTERNATIVE TO PORTLAND CEMENT TO SEAL CO_2 STORAGE WELLS

By

PRIYESH PARIMAL JANI

A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN PETROLEUM ENGINEERING

2019

Approved by:

Dr. Abdulmohsin Imqam, Advisor
Dr. Shari Dunn Norman
Dr. Ralph Flori

PUBLICATION THESIS OPTION

This thesis consists of the following three submitted articles, formatted in the style utilized by Missouri University of Science and Technology:

Paper I: Pages 9-53 are intended for submission in international journal of greenhouse gas control.

Paper II: Pages 54-75 have been accepted in SPE conference in China; IPTC 19393 MS-2018.

Paper III: Pages 76-104 are intended for submission in international journal of greenhouse gas control.

ABSTRACT

Capturing emitted carbon dioxide from the source of emission and storing it underground is one effective way to reduce the amount of CO_2 in the atmosphere and is called carbon capture and storage (CCS). For the successful CCS project, it is necessary to ensure long term storage of injected CO_2 inside these selected reservoirs. Portland cement used to cast wells in these reservoirs degrade in CO_2 environment and can create migration path for leakage of CO_2. The aim of this study was to provide a comprehensive review about the problem, to propose a new geopolymer cement as an alternative to Portland cement, optimize geopolymer slurry for oil well cementing operations and compare the performance of both cement in CO_2 environment. The chemical alterations of cement and its effect on the mechanical properties of the cement was analyzed and discussed. Additives used till now with cement to obtain CO_2 resistant cement were discussed. Optimization of geopolymer cement slurry using different alkaline activator to flyash ratios, sodium silicate to sodium hydroxide ratios and sodium hydroxide concentrations was performed. The aim of this study was to obtain a formulation of class C flyash-based geopolymer slurry that can be used in oil well cementing purposes. The result concluded that optimized geopolymer slurry has higher strength, lower fluid loss, no free fluid and rheological properties same as Portland cement. Optimized geopolymer cement and Class H Portland cement were then exposed to CO_2 environment at two different phases of CO_2 for different duration. Variations in the density, strength, and surface of the cement cores were analyzed and compared. Class C flyash-based geopolymer performed better in CO_2 environment than Portland cement.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my parents and sister; without their constant support and encouragement, I would not be able to achieve this degree.

I would like to gratefully thank my advisor, Dr. Abdulmohsin Imqam, for approving me to join his research group, and for his encouragement, inspiration, and critical comments.

I would like to thank my defense committee members, Dr. Ralph Flori and Dr. Shari Dunn Norman, for their time and efforts in examining the thesis and for all their constructive feedback.

I would to acknowledge my research group members for their great help and valuable discussions.

I want to express my sincere gratitude to the members of the Center for Infrastructure Engineering Studies for their support.

TABLE OF CONTENTS

Page

SECTION

LIST OF FIGURES

SECTION Page

PAPER I

PAPER II

PAPER III

LIST OF TABLES

PAPER I Page

PAPER II

PAPER III

1. INTRODUCTION

1.1. STATEMENT AND SIGNIFICANCE OF THE PROBLEM

Emission of carbon dioxide from various energy generating processes is hazardous to environment and living organisms. Globe tries to cope up with the increasing demand of energy which is creating high amount of greenhouse gas CO_2 emissions. Technological inventions to overcome this problem is going on with high pace as concern over this issue is increasing. One of the solutions to address this issue is to capture the emitted CO_2 and inject it underground for storage purposes i.e. Carbon Capture and Storage (CCS). It is considered as the most effective way to reduce the amount of the greenhouse gas in the atmosphere.

Captured CO_2 was injected inside the three main geological reservoirs with sufficient capacity of long-term storage i.e. depleted oil and gas reservoirs, deep saline aquifers or Unmineable coal beds. The reservoirs selected for the storage purposes has be at depth greater than 800 meters for the CO_2 to be in its supercritical state. Storage of CO_2 is possible in a relatively small volume at supercritical state thus the depth needs to be more than 800 m. After the injection of CO_2 inside the reservoir, it is necessary to provide long term storage without any leakage for the success of CCS project. Leakage rate lower than 0.1% per year is required (Taylor et al. 1997) for the successful CCS project.

Understanding of the leakage pathways is necessary to ensure long term confinement of CO_2 inside the geological reservoirs. There are two types of pathways: 1) Natural pathways 2) Artificial pathways (Bachu and Bennion 2009). Natural pathways like faults, fractures and breaches or interruptions in confining strata is not controllable by humans. However, manmade pathways are controllable which consist mainly of active or abandoned oil and gas wells on these reservoirs of the exploration and production purposes. Oil and gas industry use Portland cement to cast these types of wells or for the well abandonment. Injected CO_2 gets dissolved inside the formation water to form carbonic acid which reacts with cement. Hardened Portland cement mainly contains $Ca(OH)_2$ and C-S-H which chemically reacts with the injected CO_2 and converts into $CaCO_3$ and after long exposure converts into calcium bicarbonate. These reactions alters the chemistry of Portland cement which can lead to mechanical alterations in the cement like strength degradation, creation of micro fractures. The alterations in the Portland cement can lead to leakage of carbon dioxide form the storage reservoir. Carbon dioxide can also leak through cement/formation interface, cement/casing interface or pre-existing micro fractures inside the cement matrix (Duguid et al. 2010, Garnier and Laudet 2012). However, this is not scope of our study. The scope of this study is to evaluate the chemical and mechanical alterations inside the cement matrix and the possible migration of CO_2 due to these alterations.

In-depth analysis was conducted to evaluate the performance of neat Portland cement, cement mixed with additives in CO_2 environment. Pozzolans are best known additives that had been used with the cement for well sealing purposes (API 1991). They are used in order to reduce the density of the cement slurry (Nelson et al. 1990) and also less quantity of cement needed thus low cost. Addition of pozzolan in the cement mix will help in reducing the density, permeability of set cement (Nelson and Guillot 2006), amount of cement needed, cost, and amount of $Ca(OH)_2$ (Kutchko et al. 2009, Brandl et al. 2010). Flyash proved to perform better with the cement in CO_2 environment. However, higher amount of flyash is not recommended when mixed with cement (Brandl et al. 2010; Zhang et al. 2014).

Flyash-based geopolymer cement is made up of alumino-silicate material and it does not contain $Ca(OH)_2$ and C-S-H. The probability of reacting with injected CO_2 is less. Thus, this cement was proposed to cast the wells drilled in these storage reservoirs. In this study, performance of this cement in CO_2 environment was analyzed and discussed.

In this research, first a thorough review was conducted to understand the risk of CO_2 leakage from the storage reservoirs through chemically altered cement, to list the additives that had been used to make CO_2 resistant cement. An alternative to Portland cement, Class C flyash-based geopolymer cement was proposed. An intensive laboratory work with all API tests was conducted on geopolymer cement to obtain a formulation of this cement for oil well cementing purposes. At last, both geopolymer cement and Portland cement was exposed to CO_2 environment at higher pressure and temperature conditions.

1.2. EXPECTED IMPACTS AND CONTRIBUTION

This research work provides an insight to problems associated with using Portland cement in CO_2 storage applications and advantages of using class C flyash-based geopolymer cement as an alternative.

The review of the previous experimental and field studies conducted in this research work provided information on performance of Portland cement and cement additives in CO_2 environment and associated risk of leakage. This work will impact the industry in the following manner:

- Nowadays, Carbon capture and storage is proved an effective way to reduce the amount of carbon dioxide in the atmosphere. For the success of this project it is necessary to provide long term storage of CO_2 underground.
- Experimental studies that had been conducted in the past to analyze the performance of neat cement in CO_2 environment were tabulated. It helped in understanding the chemical alterations of cement and induced mechanical changes due to the chemical alteration.
- Chemical reactions between injected CO_2 and Portland cement were discussed. These chemical reactions guided in analyzing the risk of CO_2 leakage from the storage reservoir.
- Histograms and graphs were made from the quantitative data extracted from these studies provides more clear understanding of degradation of cement.
- Experimental studies that used various kinds of additives to get CO_2 resistant cement were tabulated. It helped in understanding the performance of these additives in CO_2 environment. Histograms and graphs were made same as earlier to better understand the degradation process.
- The comprehensive review conducted here provided list of additives that can be used with cement in CO_2 storage reservoirs. The study of quantitative data also helped in knowing the most used pozzolan and its advantages.
- Lastly, class C flyash-based geopolymer cement was proposed to be used in wells drilled in CO_2 storage reservoirs. Brief introduction of geopolymer cement, chemistry of the cement and mixing procedures were provided.

An intensive laboratory work was conducted on proposed geopolymer cement to obtain formulation that can be used in oil well cementing operations. New formulation was obtained by analyzing API tests results conducted on slurries with different alkaline activator to flyash ratios, sodium silicate to sodium hydroxide ratios at three different sodium hydroxide concentrations. The following contributions were obtained:

- Formulation of class C flyash-based geopolymer that can work in oil and gas well environment was established from the results of API tests density, rheology and compressive strength.
- Aided in knowing the advantages of using the obtained new formulation of geopolymer cement in oil well cementing over neat Portland cement.

Finally, obtained formulation of geopolymer cement and class H Portland cement was exposed to CO_2 environment in a specially designed setup. The degradation of both of this cement was compared after exposure. Class C flyash-based geopolymer performed better than Portland cement. The following work will help industry in:

- Understanding the effect of CO_2 partial pressure, CO_2 physical state and exposure time on degradation of Portland cement and Geopolymer cement.
- Knowing the alteration in density, compressive strength of cement cores after CO_2 exposure. Also, analyzing the changes in surface of cement cores after CO_2 exposure.
- Analyzing the benefits of using geopolymer cement over Portland cement in CO_2 storage wells.

1.3. RESEARCH OBJECTIVES

The primary objective of this research study was to provide an alternative cement to cast oil and gas wells drilled in CO_2 storage applications. Carbon capture and storage is very effective way in reducing the impact of this greenhouse gas globally. Thorough review of previous experimental and field studies which used Portland cement and cement additives were conducted. An experimental study was conducted on proposed geopolymer cement to make it work as an oil well cement and to compare its performance in CO_2 environment with Portland cement. The objectives of this research were:

- Conducting a critical analysis of previous experimental and field studies conducted to analyze performance of neat cement and cement additives in CO_2 environment
- Introducing class C flyash-based geopolymer cement with the benefits of using it in CO_2 environment
- Performing an experimental study to obtain new formulation of Class C flyash-based geopolymer cement to utilize it in oil well cementing operations
- Analyzing the benefits of obtained formulation of geopolymer cement over Portland cement in oil well cementing
- Evaluating the performance of obtained formulation of geopolymer cement in CO_2 environment and their comparison with performance of Portland cement in CO_2 environment.
- Investigating the effect of increasing CO_2 partial pressure, changing CO_2 physical state on the degradation of cement.

This work initially provided a thorough review of previous experimental and field studies, proposed solutions and their performance and an alternative cement to be used. An intensive laboratory work was conducted to obtain formulation for geopolymer slurry that can be used to cast oil and gas wells. Finally, performance of this new formulation of geopolymer slurry in CO_2 environment was studied and compared with Portland cement.

1.4. RESEARCH SCOPE

This study was performed in three tasks (Figure 1.1): First was to conduct an intensive review to understand the chemical and mechanical alterations in CO_2 environment,

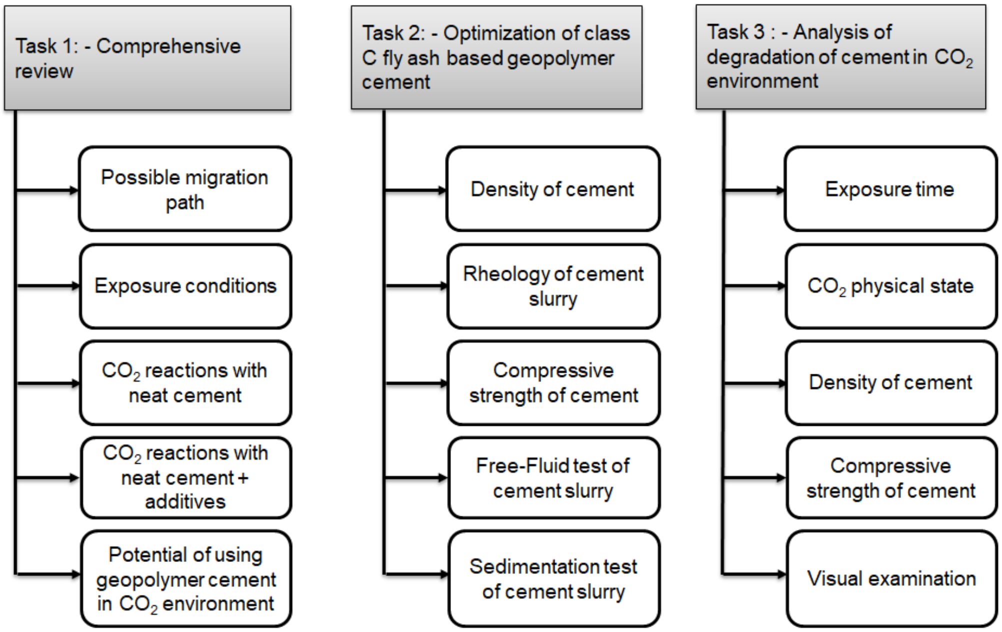


Figure 1.1. Scope of this study

get the information about the additives used and propose an alternative to this problem. Second was to obtain a formulation for class C flyash-based geopolymer cement for their usage in oil well cementing as an alternative to Portland cement. Third was to compare the performance of Portland cement and optimized geopolymer cement in CO_2 environment to validate our proposal in the first task.

PAPER

I. COMPREHENSIVE REVIEW OF CHEMICAL AND MECHANICAL DEGRADATION OF WELL CEMENT IN CO_2 ENVIRONMENT FOR CCS OPERATIONS

ABSTRACT

Carbon capture and storage operations reduce emission of carbon dioxide into the atmosphere which has a large impact on the environment. Long-term storage of carbon dioxide in a reservoir depends on the degradation of Portland cement used to cast these wells due to carbon dioxide. The objective of this research is to provide a comprehensive review of past investigations to help understand the cement's degradation, the provided solutions to this problem and discuss a potential alternative. Tables were made with information about the types of cement, the curing conditions and the exposure conditions (experimental conditions) used in different studies and their conclusions. Tables comprised of experimental studies conducted on neat Portland cement and cement mix (Portland cement + additives) were included. Field studies were also discussed. Possible migration paths of CO_2 and exposure conditions that are likely to happen inside the reservoir were discussed. Quantitative data was extracted from these investigations to understand the structural changes after the exposure. Histograms were made from the data acquired to determine the most used type of cement, exposure condition and additive. The data were constructed to explain different curing and exposure conditions. Data analysis shows that wide ranges of curing and exposure conditions made the comparison of structural changes impossible between the studies. However, the increase or decrease in porosity, strength, permeability and density of cement cores after CO_2 exposure, and alteration depths were

compared. Mostly, researchers used class H and class G well cement with CO_2 saturated brine/water at static conditions. Flyash is found to be best known pozzolan and can be reliably mixed with cement to provide long term integrity in CO_2 storage operations. However, studies suggest that higher amounts of this additive have a negative impact on the cement mix for this environment. Flyash-based geopolymer cement was suggested to be used in CO_2 storage operations due to its environmentally friendly nature and higher durability in CO_2 environment than Portland cement. The research provided a critical review about the past investigations, which became helpful in understanding the degradation process of Portland cement in a CO_2 environment and the behavior of additives. A new flyash-based geopolymer cement was proposed and discussed.

1. INTRODUCTION

Carbon dioxide (CO_2) emissions are increasing as the world tries to deal with the increasing demand for energy (Figure 1). Burning fossil fuels and electricity generation creates energy but emits CO_2. Globally, many projects are underway to reduce the emission of CO_2, as its increasing the amount in the atmosphere is affecting climate, animal and plant life and ultimately humans. Recently, carbon capture and storage projects overlook other solutions, as it is the best way to reduce the amount of CO_2 emissions in the atmosphere. The basic concept behind these projects is to inject the emitted CO_2 underground for the storage purposes.

Marchetti presented the idea of carbon capture and sequestration after realizing that emitted CO_2 from the coal combustion process can be injected inside geological formations in 1977. Geological reservoirs must meet three important conditions in order to qualify for CO_2 storage operations. The conditions are listed below (Bachu and Bennion 2009):

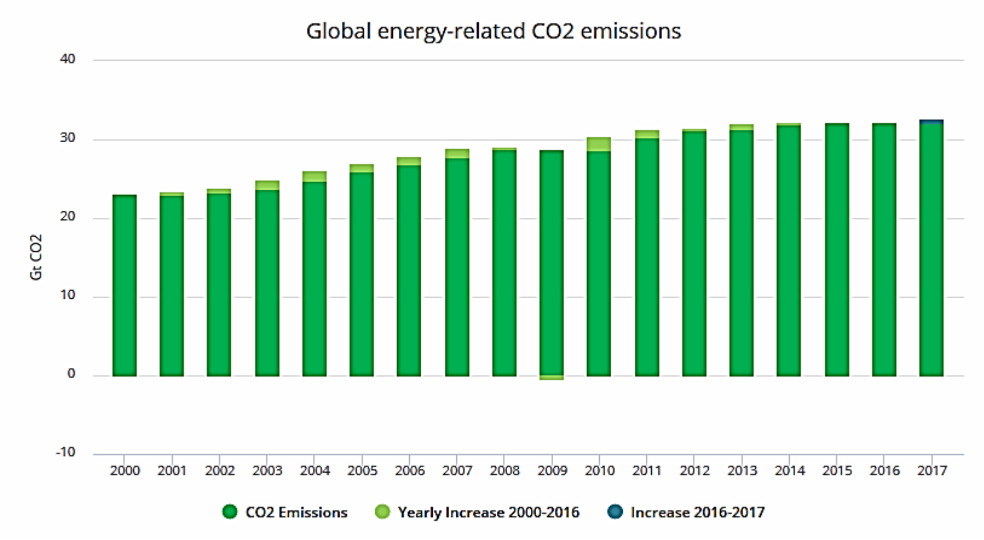


Figure 1. Yearly increase in energy-related CO_2 emissions (Global energy and CO_2 status report, 2017)

1. Capacity: Geological reservoirs must be large enough to accept the huge amount of CO_2 and keep it stored for a long period of time. This characteristic of the reservoir depends on thickness, porosity, permeability, total organic carbon, and apparent gas saturation (Godec et al. 2013, Abid and Gholami 2015).
2. Injectivity: This is defined as the ability of a reservoir to accept CO_2 at a desired injection rate. Sometimes a reservoir has a limit beyond which injection rate is not possible (Raza et al. 2015)
3. Confinement: This is the most important among all, as it is necessary to prevent the leakage of CO_2 from the reservoir for the successful CCS project. Leakage rates should be below 0.1% per year is necessary for a successful project (Taylor et al. 1997)

Also, these reservoirs need to be at a depth greater than 800 m. At this depth, carbon dioxide will be in supercritical state which will allow storage in a very small volume. High pressure and lowest possible temperature are perfect for storage, as CO_2 will be in its most dense state at these conditions (Barlet-Gouedard and Rimmele 2006).

Three types of reservoirs are mainly used for CO_2 storage:

- Depleted oil and gas reservoirs
- Deep saline aquifers
- Unmineable coal beds

These reservoirs will be deeply penetrated by several wells from the exploration and production projects. Thus, the most vulnerable site for the CO_2 leakage will be from active or abandoned wells. During the development of an oil or gas well after drilling, a casing will be placed inside the well, and which will be cemented with Portland cement to provide integrity. Cementing helps to prevent fluid migration from the annulus and to provide integrity to the well. However, the degradation of Portland cement when exposed to CO_2 is well known. This degradation can lead to leakage of CO_2 from the reservoir.

Injected carbon dioxide dissolves inside the formation fluids to form carbonic acid, which reacts with Portland cement and alters the chemistry of the cement. The chemical reactions involved will be discussed in detail later in the paper. Till now, numerous experimental and field investigations have been conducted to understand the performance of Portland cement in the CO_2 storage sites. The aim of these studies was to understand the chemical reactions behind the degradation, the reaction rate of these reactions, and the effects of these chemical reactions on the mechanical and transport properties of the cement.

This paper provides a critical review of the studies conducted in the field of CO_2 storage operations. It also discusses the approaches to obtain CO_2 resistant cement that has been proposed by the previous researchers. At last in this review, a class C flyash-based geopolymer cement was recommended as a potential alternative to Portland cement.

2. POSSIBLE CO_2 MIGRATION PATH

CO_2 from the geological reservoirs can leak through natural or artificial paths (Bachu and Bennion 2009).

Natural Pathways:

a. Active or reactive faults: a gap that creates an offset between the rocks is a fault, and it can be a path for the migration of gas from the reservoir
b. Open fractures: any type of separation between the rocks is a fracture. Open fractures can also provide pathways for the leakage of gas from the formation.
c. Gas from the reservoir can also leak through the present interruptions and breaches in confining strata

Artificial pathways (Oil and Gas wells):

Figure 2 shows the pathways of CO_2 migration through the wells from reservoir. CO_2 can migrate through the cement in the annulus or plug cement in the well, cement-formation interface, or cement and casing interface (Duguid et al. 2010**,** Garnier and Laudet

2012). It can also migrate through the pre-existing micro annulus between the cement and casing or between the cement and formation. Formation of micro-annuli can be due to cement's shrinkage, improper mud removal, or a faulty primary cementing job. CO_2 can leak through the preexisting or created micro fractures in the cement matrix due to degradation of cement in a CO_2 environment. In this paper, we will focus mainly on the created pathways inside the cement caused by degradation of cement matrix because of CO_2.

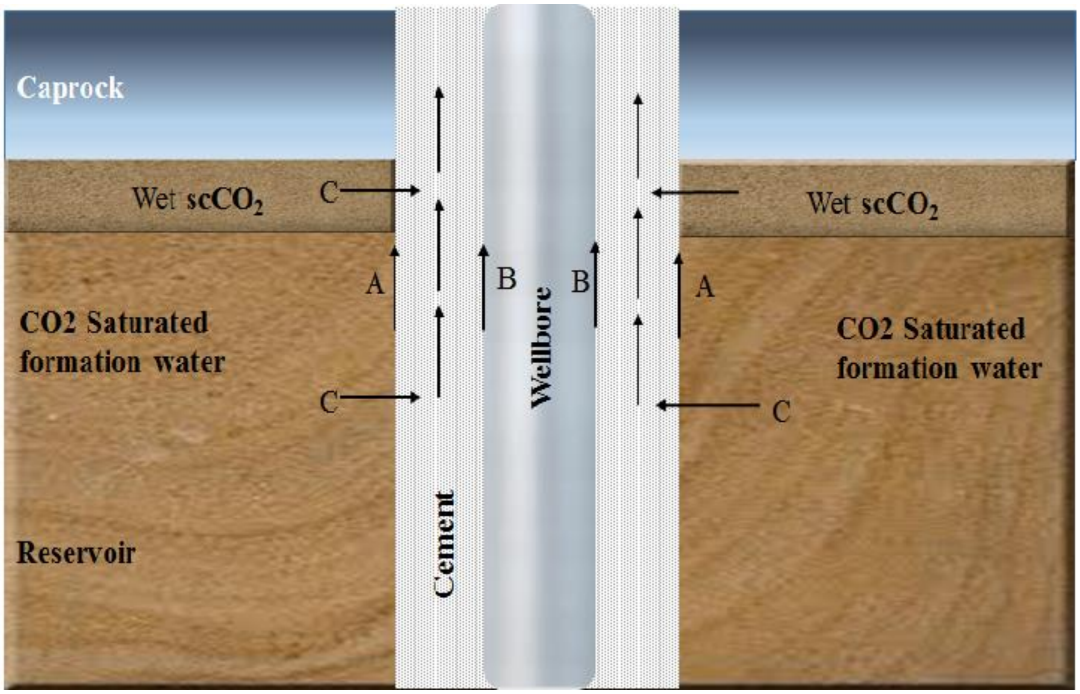


Figure 2. Hypothetical wellbore showing the probable path of CO_2 migration through degradation (A) Cement/Formation interface (B) Cement/Casing interface (C) Cement matrix/Cement micro-fractures

3. CO_2 EXPOSURE CONDITIONS

Two types of CO_2 exposure will likely to happen inside the wellbore, depending upon the nature and mobility of the fluids.

3.1. NATURE OF FLUIDS

When CO_2 is injected inside the CO_2 storage reservoir, cement will be exposed to two kinds of fluids (Kutchko et al. 2008): 1. Wet super critical CO_2 2. CO_2 saturated formation water. Carbon dioxide will be injected inside the geological reservoirs where the temperature and pressure will be very high. Thus, CO_2 will be in supercritical state (CO_2 reaches supercritical state above 1070 psi and 31^oC). Injected carbon dioxide will be trapped inside the geological reservoir by two types of trapping mechanisms, which creates two kinds of fluid exposure.

a) Hydrodynamic Trapping: Supercritical CO_2 will be in a free phase and will be lying laterally beneath the cap rock. This happens due to buoyancy and the lower density of the supercritical CO_2 compared to the brine causing the fluid to rise and spread beneath the caprock. This will lead to cement/wet super critical CO_2 contact. (Dry Carbonation)
b) Solubility Trapping: - Supercritical CO_2 dissolve into the formation water/brine. This will reduce the pH of brine because of the formation of carbonic acid. This will lead to cement/ CO_2 saturated formation water/brine contact. (Wet Carbonation)

3.2. MOBILITY OF FLUIDS

Exposure conditions also depends on whether the CO_2 is static or in motion (Barlet-Gouedard and Rimmele 2006). Thus, it can be divided further into two categories:

a) Static Condition: Normally, at the cement sheath/formation interface, wet $scCO_2$ or CO_2 saturated brine/water will be in a static condition. To simulate the actual downhole scenario, researchers use this condition for their experiments as it is the most realistic.

b) Dynamic Condition: This situation will likely occur around the perforations, where at the time of injection, CO_2 will be in motion and thus in a dynamic state.

To investigate the carbonation effect on cements, it is necessary to understand the degradation effect on cement by these both types of fluid wet $scCO_2$ and CO_2 saturated brine/formation water on cement at static or dynamic conditions.

4. PERFORMANCE OF NEAT PORTLAND CEMENT IN CO_2 ENVIRONMENT

Portland cement was patented by Joseph Aspdin in 1824. He called it as Portland cement because the color resembled the color of a stone quarried on the Isle of Portland off the British coast. There are many kinds of Portland cement, with differences in their chemical composition or the fineness of the powder. Class G and Class H Portland cement are most commonly used in the oil and gas field operations. They differ from each other only in fineness of the powder (Nelson et al. 1990). The typical components of Portland cement and their basic functions are as follows (Nelson, 1990; Rabia, 2001; Adams and Charrier, 1985; Abid and Gholani 2015):

(1) Dicalcium silicate (Ca_2SiO_4) – Generates strength after a long period of time, and slow hydration

(2) Tricalcium silicate (Ca_3SiO_5) – Provides early strength to the cement upon hydration and increases the strength

(3) Tricalcium Aluminate ($Ca_3Al_2O_6$) – Affects the thickening time and the early setting of cement and provides faster hydration. Its presence makes cement vulnerable to sulphate attack

(4) Tetracalcium Aluminoferrite ($Ca_4Al_2Fe_2O_{10}$) – Promotes slow hydration

When the cement is mixed with water, dicalcium silicate and tricalcium silicate convert to calcium silicate hydrate (C-S-H) gel and Portlandite ($Ca(OH)_2$) (Equation 1 and 2) (MacLaren and White, 2003).

$$2Ca_3SiO_5 + 6H_2O \rightarrow Ca_3Si_2O_7.3H_2O + 3Ca(OH)_2 \quad (1)$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow Ca_3Si_2O_7.\ 3H_2O + 3Ca(OH)_2 \quad (2)$$

Hydrated cement will have 70 wt% of C-S-H, a semi-amorphous gel, which is the main binding material in the cement and provides strength. It will also have 15-20 wt% $Ca(OH)_2$, which is crystalline in nature. Cement mainly composed of these two materials.

4.1. CARBONATION REACTIONS

4.1.1. Degradation of Cement by Wet $scCO_2$. The reaction of wet $scCO_2$ with the cement generally follows ordinary carbonation. CO_2 gets dissolved in Portland cement porewater to form CO_3^{2-} which combines with Ca^{2+} to form $CaCO_3$ within the pore structure of Portland cement (Taylor et al. 1997).

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)} \quad (3)$$

4.1.2. Degradation of Cement by CO_2 Saturated Water/Brine. The effect of CO_2 saturated water/brine on Portland cement is similar to a typical acidic attack on cement. Kutchko (2008) analyzed Class H Portland cement after exposure to CO_2 saturated brine using scanning electron microscope (SEM) equipped with back scattered electron imaging (BSE) and energy dispersive spectroscopy (EDS). This helped in understanding the chemical and textural changes in Portland cement after CO_2 exposure. Figure 3 shows the alteration zones observed in the cement by previous studies.

The chemical reactions (Santra et al. 2009) involved in the alteration of Portland cement, and different zones are explained below:

1) Formation of carbonic acid (Aqueous Solution):

Injected CO_2 is dissolved in the formation water to form carbonic acid (Equation 4). This will lower the pH of the solution to around 3, depending on the temperature and pressure inside the solution. Portland cement has a pH above 12.5 (Taylor et al. 1997, Neville et al. 2012, Rendell et al. 2002). This difference in pH will lead to the reaction of carbonic acid with Portland cement.

$$CO_{2\,(g)} + H_2O_{(l)} \rightarrow H_2CO_{3\,(aq)} \tag{4}$$

2) Carbonation of Portlandite (Zone 1 and 2):

This carbonated water will diffuse inside the cement matrix and dissolve Portlandite ($Ca(OH)_2$) to form calcium carbonate ($CaCO_3$) (Equation 5). Zone 1 and 2 in the Figure 3 are result of this reaction. Formation of $CaCO_3$ will lead to volume expansion and will decrease porosity/permeability, as the molar volume of $CaCO_3$ is 36.9 cubic centimeters, which is higher than 33.6 cubic centimeter volume of $Ca(OH)_2$ (Shen et al. 1989).

$$Ca(OH)_{2(s)} + H_2CO_{3\,(aq)} \rightarrow CaCO_{3(s)} + 2H_2O_{(l)} \tag{5}$$

Kutchko (2008) observed an increase in hardness in Zone 2 compared to other zones and unaltered cement. This is due to the precipitation of calcite ($CaCO_3$) deposits inside the available pores of the cement, thus creating a denser material. These phenomena were observed by many researchers in their experiments. This process is known as self-healing process, as it increases the mechanical properties and decreases the porosity/permeability (Nygaard 2010).

3) Dissolution of $CaCO_3$ (Bicarbonation):- (Zone 3)

Ca(OH)$_2$ is responsible for buffering the pH of the pore water above 10.5 (Kutchko et al. 2007). At this time, the dissolved CO_2 will be in the form of CO_3^{2-}, which will keep CaCO3 stable. When all the Ca(OH)$_2$ will be dissolved the cement will no longer have the ability to cradle the pH. This will reduce the pH of the pore water below 10.5 making $CaCO_3$ unstable. CO_3^{2-} concentration will decrease and HCO^{3-} will become the dominant carbonation species at this time (Thaulow et al. 2001). It will dissolve $CaCO_3$ to form water soluble calcium bicarbonate, which can diffuse out of the cement matrix (Equation 6) (Duguid et al. 2010, Kutchko et al. 2007). This reaction will increase the porosity/permeability and will decrease the strength (Santra et al. 2009).

$$CaCO_{3(s)} + H_2CO_{3\,(aq)} \rightarrow Ca(HCO_3)_2 \tag{6}$$

4) Carbonation of C-S-H and/or other crystalline phases:- (Zone 3)

Carbonic acid will dissolve C-S-H and/or other crystalline phases to form amorphous silica (Equation 7). This reaction will result in an increase in porosity/permeability because the molar volume of C-S-H is higher than CaCO3 produced (Nygaard 2010). Amorphous silica lacks in structure and is highly porous, thus causing a decrease in mechanical strength (Kutchko et al. 2007).

$$\text{C-S-H and/or crystalline phases} + H_2CO_{3\,(aq)} \rightarrow SiO_2\ (gel) + CaCO_{3(s)} + H_2O_{\,(l)} \tag{7}$$

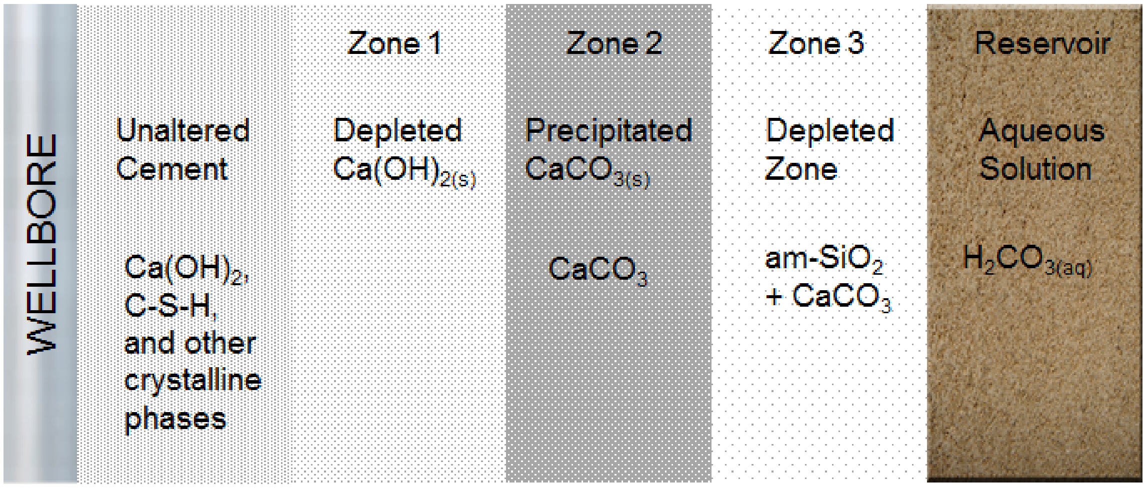


Figure 3. Alteration zones inside the cement cores after reactions with carbon dioxide as mentioned in Kutchko et al. 2008

4.2. EXPERIMENTAL STUDIES

Carbon capture and storage proved to be very effective in reducing the emissions of carbon dioxide into the atmosphere. The only vulnerable path for the leakage of CO_2 that mankind can control is through well cements. Degradation of Portland cement by carbon dioxide is a well-known process, and numerous studies have been carried out to better understand the mechanisms behind the degradation and to provide solutions for this problem. Table 1 provides a list of different experimental studies that have been carried out, the curing conditions used, the experimental conditions used, and the findings of these studies. The aim of these studies was to understand the mechanisms of degradation of neat Portland cement in the presence of carbon dioxide. Quantitative data was extracted from the research studies in order to better understand the alteration process (Table 2).

Hunt (1958) conducted an experiment to investigate the effect of dry CO_2 and moist CO_2 on the cement. The investigation concluded that carbonation in a humid environment is faster than in a dry environment. Thus, water is an important factor for the carbonation process. Duguid (2005) conducted an experiment in dynamic conditions using two different temperatures and two different pHs. The result indicated that a low pH and a high temperature results in higher degradation. Also, changing the temperature has more effect than changing the pH. Barlet-Gouedard and Rimmele (2006) found a very high alteration depth, high strength reduction and increase in density in their experiment. However, Kutchko (2007) found a very low alteration depth in an experiment conducted to see the effect of curing condition on the carbonation of cement. It was found that high temperature and high-pressure curing makes cement resistant to CO_2 environment. This experiment exposed the cement cores for only nine days.

Barlet-Gouedard and Rimmele (2006) suggested that carbonation of cement cores in presence of wet $scCO_2$ and CO_2 saturated water is a diffusion-controlled process. Kutchko (2008) found that reaction of wet $scCO_2$ with cement is diffusion-controlled process. However, reaction of cores with CO_2 saturated brine behaves like an acidic attack on the cement. Moroni and Santra (2009) observed that reduced amount of portlandite in cement mix leads to CO_2 resistant cement.

4.2.1. Experimental Data Analysis. The difference between the studies is because of the different curing condition and different exposure condition used in their experiment. Thus, the comparison between the studies is not possible. Histograms were made in order to understand which material and which exposure conditions were used the most in different studies (Figure 4). Figure 4a suggests that researchers mainly used Class H and Class G Portland cement in their studies, through some of them also used ordinary Portland cement. Figure 4b explains the exposure conditions used by different studies.

Table 1. Experimental studies on performance of neat cement in CO_2 environment

Authors	Year	Types of Cement	Water to Solids Ratio	Curing Condition	CO_2 Experimental Condition	Findings
Hunt et al.	1958	Four different type I cements	0.5	Cylinder Size: - • 0.5 in. cylinders • 24 hrs.	Atmospheric condition	• Water is an important limiting factor in rate of carbonation of cement
Duguid et al.	2005	Class H cement	0.38	Cylinder Size: - • 0.3 in. * 7.9 in. Cured in: - • 0.5 M NaCl • Temperature: 20 and 50°C Total 12 months	• Brine caturated with CO_2 • pH = 2.4; 3.7 • Temperature = 23 and 50°C Exposure time= 31 Days in dynamic condition	• Highest rate of reaction was observed at 50°C and pH of 2.4 which was about 0.07/0.24 mm/day • Lower the pH, the greater the rate of carbonation will be
Barlet-Gouedard and G. Rimmele	2006	• Class G Portland cement + fresh Water + an antifoam agent + a retarder + a dispersant • A new CO_2 resistant cement (Contains reduced amount of Portland cement)	0.44	Cylinder Size: - • 0.5 in * 1 in • 1 in * 2 in Cured in: - • water • 3000 psi pressure and 90°C temp. Total 72 hours	• Wet $scCO_2$ • CO_2 saturated water • 4061 psi pressure and 90°C temperature • Exposure time= Days (2,4) Week (1,3,6) and 3 months in static condition	• A new validated methodology has been established in order to simulate carbonation on Portland cement under downhole conditions. • The alteration front was slightly thicker in cased of wet $scCO_2$ than in CO_2 saturated with water • This model predicts an alteration front of 100 mm after 20 years of CO_2 attack. • A new proposed CO_2 resistant material remained comparably inert in both wet $scCO_2$ and CO_2 saturated water
Kutchko et al.	2007	Class H well cement	0.38	Cylinder Size: - • 0.5 in * 5 in Cured in: - • 1% NaCl/brine solution • Under different temp. and pressure: 1) 22° C, 14.5 psi 2) 22° C, 4400 psi 3) 50° C, 14.5 psi 4) 50° C, 4400 psi Total 28 Days	• Wet $scCO_2$ • CO_2 saturated water • 1% NaCl/Brine solution • 4400 psi pressure and 50° C temperature Exposure time= 9 Days in static condition	• Curing under higher temperature and pressure increased the cement's resistance to CO_2 attack due to more evenly distributed $Ca(OH)_2$ crystals in the cement matrix because of increase in the degree of hydration. • Depth of carbonation was smaller than 1 mm for all the samples after 9 days of exposure.

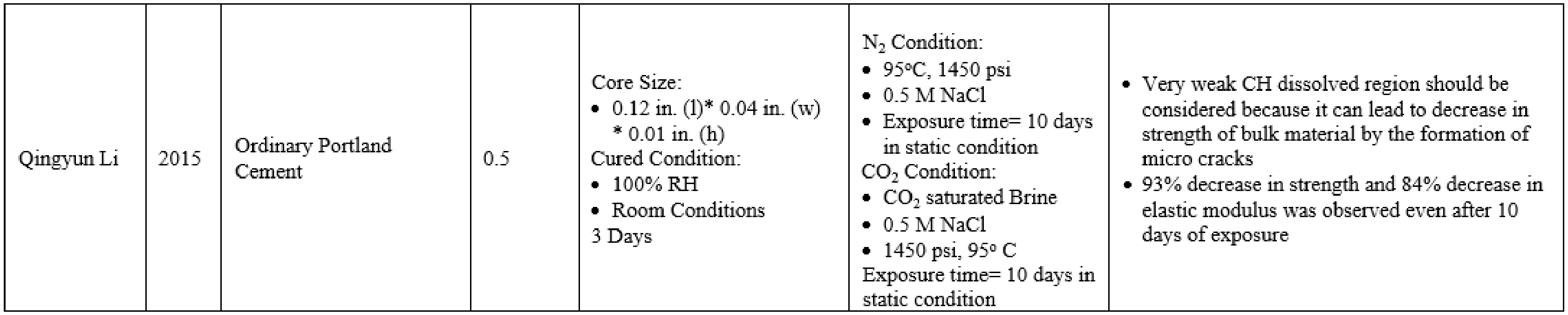
Table 1. Experimental studies on performance of neat cement in CO_2 environment (Cont.)

Kutchko et al.	2008	Class H well cement	0.38	Cylinder Size: - • 0.5 in. * 5 in. Cured in: - • 1% NaCl/brine solution Under 50° C, 4400 psi • Total 28 Days	• Wet $scCO_2$ • CO_2 saturated water • 1% NaCl/Brine solution • 4400 psi pressure and 50°C temperature Exposure time= up to 12 months in static condition	• Exposure of wet $scCO_2$ to Portland cement exhibited linear relationship between penetration depth and square root of time thus it was diffusion-controlled process. • For the CO_2-saturated brine exposure linear relationship was not observed between penetration depth and square root of time and alteration process was more complex than simple diffusion. CO_2-saturated Brine exposure was more like an acid attack than ordinary carbonation.
G. Rimmele and Barlet-Gouedard	2008	Class G well Cement + fresh water		Cylinder Size: - • 0.5 in. * 1 in. or 5.08 cm Cured in: - • cubic molds • 1% NaCl/brine solution • Under 90° C, 3002 psi Total 72 hours	• Wet $scCO_2$ • CO_2 saturated water • Water • 4061 psi pressure and 90° C temperature Exposure time= half day, two days, four days, one week, three weeks, six weeks, three months, six months in static condition	• Two different techniques (MIP and SEM image analysis) is used to determine the global porosity, pore entrance size and local porosity gradients of the affected Portland cement by wet $scCO_2$ and CO_2 saturated water • By analyzing both methods it is clear that Portland cement undergoes an initial sealing stage related to precipitation of CaCO3 that plugs the porosity and dissolution stage which will increase the porosity. • X-Ray diffraction analysis showed that alteration of cement by CO_2 is not restricted to the outer part of the core, but inner part of the cores also reacts rapidly in first days of exposure
Bachu and Bennion	2009	Class G well cement (Actual Field Batches from Sanjel cementing services of cement currently used in Alberta region)		Cement sample disk: - • 1.5 in. OD * 1.2 in. Length Cement-Casing Pair: - J55 casing rod with 1.5 in. OD casted in Class G cement (OD- 2.75 in.) * Total system length 3.76 in.	Cement Permeability tests using • 15000, 60000 and 80000 mg/l salinity of NaCl saline solution • Brine saturated with CO_2 at 2200 psi and 65°C temp. • Confining Pressure 4200 psi and 2200 psi pressure drop • Total 90 days Cement-Casing pair	• In this experiment, permeability of cement reduced initially and remained constant afterwards due to the protective layer formed by carbonation reaction. • A good quality cement-casing bond is necessary to prevent fluid/gas migration; however, presence of an annular gap or micro cracks leads to increase in effective permeability. • Good quality cement and/or proper bonding of cement/casing can provide a good barrier to upward flow of CO_2 and/or CO_2 saturated brine.

Table 1. Experimental studies on performance of neat cement in CO_2 environment (Cont.)

					effective permeability using 3500 psi overburden pressure and 2000 psi pore pressure, 60°C temp.	
Pratt et al.	2009	Portland cement	NA	Cylinder Size: - • 0.5 in.* 1 in. • 1 in. * 2 in. Cured in: - • 100 % RH • room temperature 1 month	• Wet $scCO_2$ • 1450 psi pressure and 50° C temperature Exposure time= 84 days in static condition	• Carbonation depth of the sample was around 200 micro meter and different zones of reactions were reported
Moroni and Santra	2009	• Class G cement • Cement Sample A		Cylinder Size: - • 1 in. * 2.5 in. length Cured in: - • Water • Under 93.3°C, 2000 psi Total 15 days	• Fully immersed in fresh water • 2000 psi pressure and 93.3° C temperature Exposure time= 15 days for one set and 90 days for another set	• Reduction of Portlandite in cement system A leads to better CO_2 resistant cement.
Yalcinkaya et al.	2010	Class H Well cement	0.38	Cylinder Size: - • 1 in. * 12 in. Cured in: - Tap water bath 1) 6 months for LP experiment 2) 120 days for HP experiment	Core flooding tests using • Brine saturated with CO_2 LP experiment: • 10 psi, Room Temp. • 600 psi net overburden pressure • Total 30 days HP experiment: • 1800 psi, Room temp. 600 psi net overburden pressure	• After LP experiment cement showed porosity reduction from 26% to 22% • No remarkable change observed after HP experiment due to shorter period of exposure
Tarco and Asghari	2010	• Class A Cement • Class G Cement	NA	Cylindrial Samples	• CO_2 saturated Brine • 55°C, 2200 psi Exposure time= 2, 4, 6, 8, 10 months in static condition	• Permeability of both types of cement decreased 30% due to CO_2 exposure after 10 months • Compressive strength of both types of cement increased initially and then decreased in 10 months duration • Shear and Hydraulic bond strength decreased drastically after the 2 months exposure

Table 1. Experimental studies on performance of neat cement in CO_2 environment (Cont.)



Qingyun Li	2015	Ordinary Portland Cement	0.5	Core Size: • 0.12 in. (l)* 0.04 in. (w) * 0.01 in. (h) Cured Condition: • 100% RH • Room Conditions 3 Days	N_2 Condition: • 95°C, 1450 psi • 0.5 M NaCl • Exposure time= 10 days in static condition CO_2 Condition: • CO_2 saturated Brine • 0.5 M NaCl • 1450 psi, 95° C Exposure time= 10 days in static condition	• Very weak CH dissolved region should be considered because it can lead to decrease in strength of bulk material by the formation of micro cracks • 93% decrease in strength and 84% decrease in elastic modulus was observed even after 10 days of exposure

Table 2. Quantitative experimental data from the mentioned studies in Table 1

Author/Year	Type of Cement	Alteration Depth (mm)	Initial Density (ppg)	Density (ppg)	Initial Porosity (%)	Porosity (%)	Initial permeability (mD)	Permeability (mD)	Strength Reduction (%)
Barlet-Gouedard and G.Rimmele/ 2006	Class G Cement + an antifoam agent + a retarder + a dispersant	8.5	16	18.5	32.5	15			65
		7	16	18	32.5	21			33
	CO_2 resistant cement	0	17	18.02	23	23			
		0	17	18.02	23	25			
Kutchko/2007	Class H cement	0.59							
		0.45							
		0.47							
		0.22							
Kutchko/2008	Class H Cement	0.3							
		0.65							
G. Rimmele and Barlet-Gouedard/2008	Class G Cement	7			33	27			
		7			33	30			
Bachu and Bennion/2009	Class G Cement (Actual Field Batches)						0.000232	0.00001	
							0.000116	0.00001	
Barlet-Gouedard et al./2009	Portland Cement	0.2			34	32			
		0.2			34	34			
									28(90)
	Cement system A							0	0%
Yalcinkaya/2010	Class H cement				26	22			
					21.26	21.64			
Tarco and Asghari/2010	Cement type 10						0.0627	0.04389	21.43
	Class G Cement						0.0453	0.02809	19.35
Qingyun/2015	OPC	1.22							93

Two types of fluids were used: brine and water. Degradation is more severe in water as CO_2 is more soluble in water than brine (Spycher and Pruess 2005). Barlet-Gouedard and Rimmele (2009) found that more degradation occurs in CO_2 saturated water than in CO_2 saturated brine. Static conditions are mainly used as they are the most realistic simulation of downhole conditions. Duguid et al. (2004; 2005) used dynamic conditions with two different pH's (2.4; 3.7) and temperatures (20 and 50^oC). Higher degradation was observed at a low pH and higher temperature. Also, an increase in temperature increased the rate of degradation more than a decrease in the pH.

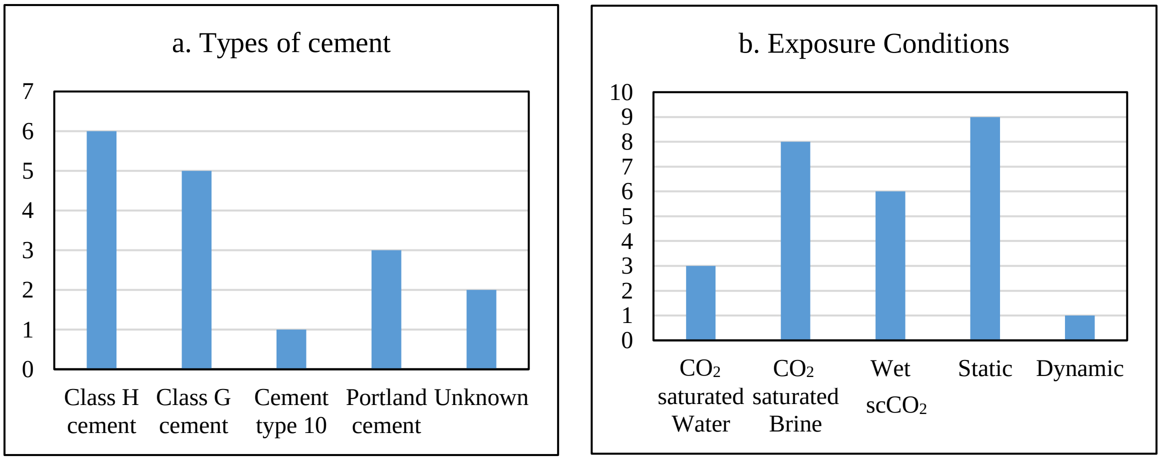


Figure 4. List of (a) different types of cements and (b) different exposure conditions used by the mentioned studies in Table 1

Figure 5a shows different curing pressures at different curing temperatures and different curing times at different curing temperatures. Most studies used CO_2 partial pressure higher than 1400 psi and a temperature higher than 50^oC as CO_2 behaves as supercritical fluid at this pressure and temperature which is mostly the case in the reservoir. Figure 5 indicates that studies used a wide range of curing temperatures, pressures and curing times. Also, a wide range of CO_2 partial pressures, temperatures and exposure times were used. Thus, it is not possible to compare the data acquired from these studies; however, it is possible to compare the changes happening in the structure of the cement after exposure (Figure 6 and Figure 7).

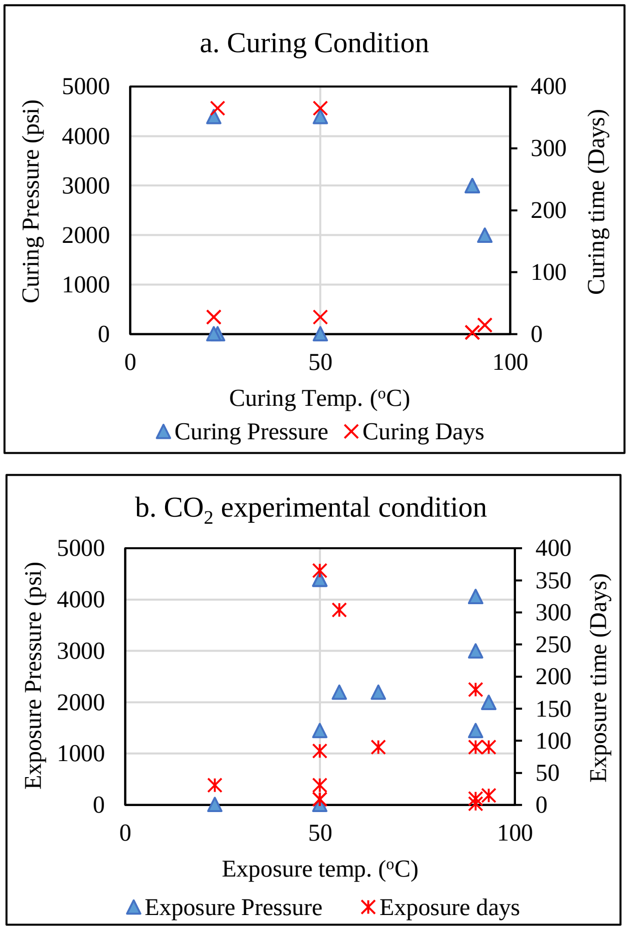


Figure 5. List of (a) different curing conditions and (b) different CO_2 exposure conditions used by the studies mentioned in Table 1

Figure 6a depicts the alteration depth to core diameter ratio observed by previous studies at different CO_2 exposure pressure and exposure temperature. Most studies observed a low alteration depth. Kutchko et al. (2007, 2008) observed a very low alteration depth compared to Barlet-Gouedard and Rimmele (2006, 2008) probably due to the higher experimental temperature and pressure used by the later study (Table 2). Also, Barlet-Gouedard and Rimmele used CO_2 saturated water instead of brine, which can explain the higher alteration depth. Figure 6b shows the change in the porosity of cores at different CO_2 exposure pressures and exposure temperatures after the exposure to CO_2. Porosity reduced mainly after the exposure, but there was no change observed in CO_2 resistant cement proposed by Barlet-Gouedard and Rimmele (2006). Reduction of porosity is a sign of precipitation of calcium carbonate in the pore spaces of the cement matrix and dissolution of $Ca(OH)_2$, as explained in equation 5.

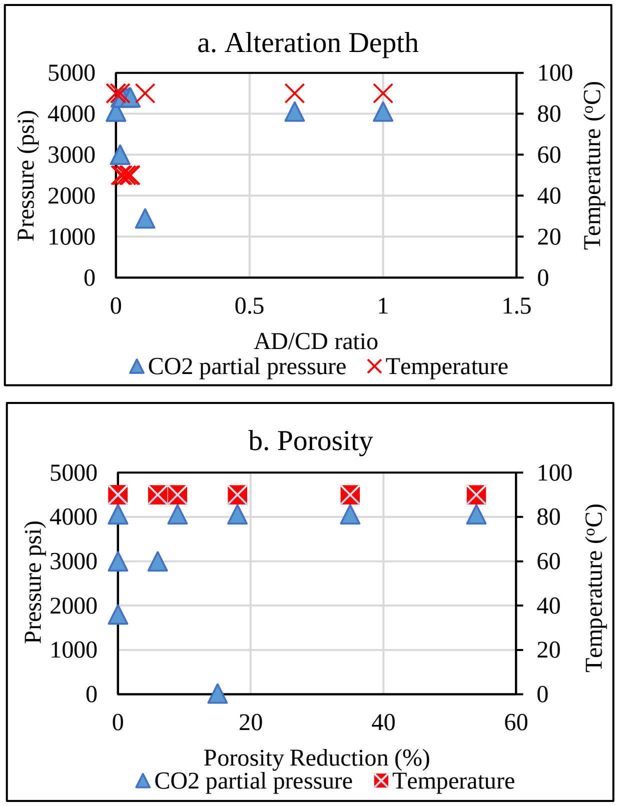


Figure 6. (a) Alteration depth/core diameter ratios (b) change in the porosity at different experimental pressure and temperature obtained from the data tabulated in Table 2

Permeability reduction was also observed by Bachu and Bennion (2009) and Tarco and Asghari (2010), which is also a sign of $CaCO_3$ precipitation (Table 2). Figure 7 explains that compressive strength of cement cores reduces after the CO_2 exposure. Qingyun (2015) observed a 93% reduction in strength in OPC after only 10 days of CO_2 exposure. For Class G well cement Barlet-Gouedard and Rimmele (2006) observed 65% strength reduction in wet $scCO_2$ and 33% reduction in CO_2 saturated water. Moroni and Santra (2009) proposed cement system A, which would increase in the strength rather than a decrease.

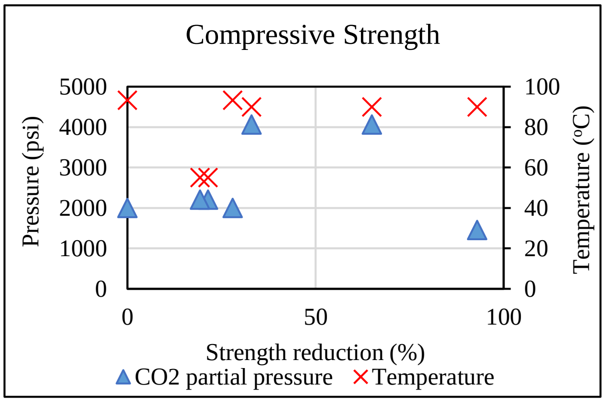


Figure 7. Reduction of neat cement's strength at different experimental pressures and temperatures obtained from the data tabulated in Table 2

4.3. FIELD STUDIES

Carey et al. (2007) studied a recovered core from the world's second-oldest CO_2 flooding operation, the SARCOC unit (an oil reservoir in Texas). This well was exposed to CO_2 for about 30 years. Portland cement without any additives was used beyond 534 m depth. Sidetracking technique is used to recover the core sample, which includes the casing, cement and shale rock. Different carbonation zones were observed when these cores were examined. However, the structural integrity of the cement was left intact to prevent CO_2 migration. However, the SACROC unit is a CO_2 flooding reservoir, not an actual storage reservoir. The investigation of these recovered cores concluded that proper completion of the wellbore with full coverage of cement inside the annulus can prevent migration of CO_2 from the reservoirs.

5. PERFORMANCE OF CEMENT ADDITIVES IN CO_2 ENVIRONMENT

After analyzing the performance of neat cement in CO_2 environment, researchers have tried to use some additives in order to make a CO_2-resistant cement. The main idea behind adding an additive is to reduce the amount of $Ca(OH)_2$ present in the neat cement, forming more C-S-H since C-S-H dissolves slower than Portlandite. This may result in a reduction in the precipitation of $CaCO_3$ and therefore reduced reactions with CO_2 (Duguid and scherer 2010). Pozzolans are the most common additives for the well sealing purposes (API 1991). They are used to reduce the density of the cement slurry (Nelson et al. 1990) and reduce the amount of cement needed thus reducing the cost. Some of the most common pozzolans are (1) Silica fume (2) metakaolin (3) Calcined clay (4) flyash. Addition of pozzolan to the cement mix will help reduce the density, permeability of set cement (Nelson and Guillot 2006), amount of cement needed, cost, and amount of $Ca(OH)_2$ (Kutchko et al. 2009, Brandl et al. 2010). Carbonation reactions with the cement mix will occur exactly as described in the previous section.

5.1. HYDRATION OF CEMENT MIX

Pozzolans mainly consist of SiO_2 and Al_2O_3 constituents. During the hydration of Portland cement mixes (cement + pozzolan), pozzolanic reactions will occur in which SiO_2 and Al_2O_3 will react with Portlandite ($Ca(OH)_2$) to form secondary C-S-H (Equation 8) (Brandl et al. 2010). This will further reduce the amount of Portlandite in the set cement and thus less Portlandite will be available for carbonation.

$$Ca(OH)_2 + \text{“}SiO_2\text{”} \ (\text{“}Al_2O_3\text{”}) \rightarrow \text{C-S-H (C-A-S-H) phases} \tag{8}$$

5.2. EXPERIMENTAL STUDIES

A list of studies that use additives in the cement mix to investigate the effect of carbonation is provided in Table 3. The table contains different curing conditions, exposure conditions, and types of cement and additives used along with the findings of these investigations. Quantitative data extracted from these studies has been tabulated in Table 4 to better understand the changes after the CO_2 exposure.

Onan (1984) used pozzolanic material in the cement and investigated the effect of wet $scCO_2$ on the mix. The analysis concluded that the presence of pozzolanic material makes cement mix CO_2 resistant. In 1999, Andac and Glasser used municipal waste flyash with Portland cement. Thus, the method of using pozzolanic material in the cement mix is four decades old. There have been many investigations in which pozzolanic material is used to reduce the amount of Portlandite as seen in the table 3. These materials have been found to make cement more resistive to CO_2 environment by making it more durable.

5.2.1. Experimental Data Analysis. The different exposure conditions used, and additives used by the studies mentioned in Table 3 were put into histograms to see the most commonly used exposure conditions and additive (Figure 8a and 8b). CO_2 saturated water and CO_2 saturated brine were used with the wet $scCO_2$ at static condition. Lesti (2013) used CO_2 saturated synthetic reservoir fluid to create a more realistic simulation of downhole conditions. Figure 8b shows the different additives that have been used to obtain CO_2 resistant cement. Bentonite is generally used to improve the slurry properties (Duguid et al. 2010)**.**

Flyash and Silica flour are the most common additives used for CO_2 storage purposes. These additives are easily available at a low cost. They are also the best known pozzolans in the world. These materials help to reduce the amount of Portland cement. This method has been used for many years (Onan 1984; Andac and Glasser 1999; Kutchko et al 2009). Santra (2009) observed that higher amounts of silica fume do not make cement CO_2 resistant. Thus, flyash is the best option to use in the cement mix for these purposes. Barlet-Gouedard (2012) patented two different mixes that work very well in CO_2 environment which is described in Table 3. Lesti (2013) used three different types of cement, as described in Table 3 and the best results were obtained by the cement mix containing flyash due to low quantity of $CaCO_3$ and pozzolanic reaction of flyash.

Figure 9 shows different curing conditions and CO_2 exposure conditions used in the studies mentioned in Table 3. Figure 9a represents different curing pressures and different curing times used at different curing temperatures. Again, a wide range of pressures and temperatures were used, which made comparison impossible between the studies; however, the changes in structure are compared below.

Table 3. Experimental studies on performance of cement + additives in CO_2 environment

Authors	Year	Types of Cement	Water to Solids Ratio	Curing Condition	CO_2 Experimental Condition	Findings
Shen et al.	1989	Class G Cement + 40 % Silica Flour • Field samples; 0.88 in. dia. Samples were drilled from the field samples • Research samples	N/A	• Research samples of cement cured under geothermal pressure 3000 psi and temperature 232°C	• Research samples: - 232°C and 1500 psi CO_2 Pressure	• CO_2 diffusion coefficient in the cement solid matrix was estimated to be 8.0 * 10-7 cm2/sec by a technique used in this paper • The degree of cement carbonation was found to be dependent on factors such as, temperature, CO_2 content in the fluid and cement additives. • The mechanism of carbonation can be affected by whether the CO_2 is in a moist gaseous state or is dissolved in water.
Duguid et al.	2004	• Class H cement + DI water • Class H cement + 6% bentonite + DI water	• 0.38 • 0.70	Cylinder Size: - • 0.29-0.3 in. dia • 5.5-10.2 in. length Cured in: - • 0.5 M NaCl at room temp. for one day • then at 23 and 50°C Total 28 days	• Brine saturated with CO_2 • pH = 2.4; 3.7 • Temperature = 23 and 50°C • Exposure time= 1.3-7.2 days in Dynamic condition	• Samples reacted at higher temperature (50 deg C) for both pH conditions showed more damage than at lower temperatures • Samples containing 6% bentonite reacted faster than the neat cement, 0.75-1.3 mm degradation was evident in this sample after 7.2 days
Kutchko et al.	2009	• 35:65 (by volume) Class F flyash and Class H well cement + 2% by volume bentonite • 65:35 (by volume) Class F flyash and Class H well cement + 2% by volume bentonite • Class H neat cement	• 0.51 • 0.56 • 0.38	Cylinder Size: - • 0.5 in. * 5 in. • 2 in. * 1.57 in. Cured in: - • 1% NaCl/brine solution • Under 50° C, 2175 psi • Total 28 days	• Wet $scCO_2$ • CO_2 saturated water • 1% NaCl/Brine solution • 2175 psi pressure and 50°C temperature • Exposure time for 35:65 blend= 5,7,9,14 and 31 days • Exposure time for 65:35 blend= 2,8,9 and 31 days	• Faster rate of penetration observed in 65:35 pozzolan blend than 35:65 blend. • 35:65 pozzolan blend followed fick's law of diffusion for both fluids whereas it became hard to determine the alteration rate for 65:35 blend due to faster rate of penetration. • No differences observed in Wet $scCO_2$ and CO_2 saturated water exposure to pozzolan blend as it was observed in Class H neat cement.

Table 3. Experimental studies on performance of cement + additives in CO_2 environment (Cont.)

Barlet-Gouedard et al.	2009	• Portland cement + conventional additive		Cylinder Size: - • 0.5 in. * 1 in. • 1 in. * 2 in. Cured in: - • 1% NaCl/brine solution • Under 90° C, 3000 psi • Total 72 Hours	• Wet $scCO_2$ • CO_2 saturated brine • Water • 3000 psi pressure and 90° C temperature • Exposure time= 2 days in static condition	• Propagation/alteration rate decreases in CO_2 saturated brine compared to CO_2 saturated in fresh water
Santra et al.	2009	• Cement • Cement + (16.7,28.6,37.5,44.4,50) % silica fume • Cement + (16.7,28.6,37.5,44.4,50) % Class F flyash	•0.45 •0.47 •0.48 •0.53 •0.56 •0.58 •0.46 •0.45;0.46 0.45;0.45	Cylinder Size: - • 1 in. * 2.5 in. length Cured in: - • Water • Under 93.3°C, 2000 psi • Total 15 days	• Fully immersed in fresh water • 2000 psi pressure and 93.3° C temperature • Exposure time= 15 days for one set and 90 days for another set	• TGA analysis confirmed that addition of pozzolan reduced the amount of $Ca(OH)_2$ present in the neat cement. • Cement samples with pozzolan were less affected by CO_2. • A simple dye test or visual inspection is not sufficient enough to determine the depth of carbonation. • Rate of carbonation depends on the Cement type, moisture content, CO_2 partial pressure, porosity/permeability and temperature.
Brandl et al.	2010	• Class G cement + silica flour + pozzolan • Class G cement + 35 wt% silica Flour	• 0.55 • 0.72	Cylinder Size: - • 1 in. * 2 in. Cured in: - • 0.5 M NaCl solution • 149°C, 3000 psi	• CO_2 saturated Water • 149°C, 3000 psi • Exposure time= 1,3 and 6 days in static condition	• Very less permeability and higher compressive strength observed after the exposure • Better durability and mechanical strength observed in Sample No. 1
Duguid and Scherer	2010	• Class H neat cement • Class H cement + 6 wt% bentonite	• 0.38 • 0.7	Cylinder Size: - • 0.3 in. * 7.9 in. Cured in: - • 0.5 M NaCl solution • 20°C or 50°C Total 12 months	• CO_2 saturated Brine • pH= 2.4, 3.7 for sandstone like conditions • pH= 5 for limestone like conditions • Exposure time= 31 days in dynamic condition	• Rate of degradation is more affected by the change of temperature than change in pH • Low pH and higher temperature lead to faster degradation. • Addition of bentonite leads to faster degradation due to increased porosity • No degradation was observed in limestone like conditions
Garnier et al.	2010	• Class G cement • Class G cement + 35 wt% silica flour	NA	Cylinder Size: - • 0.8 in. * 9.5 in. Cured in: - • Lime saturated water • Neat cement: - Atmospheric Pressure, 90°C for 28 days • Cement with silica flour: -Initial 10 days	• CO_2 saturated Water Neat cement: - • 90°C, 1160 psi • Exposure time= 7,36,65 and 90 days in static condition Cement with silica flour: - • 140°C, 1160 psi	• Higher temperature leads to faster degradation of Cement cores • Degradation process in the neat class G cement is diffusion controlled while addition of silica flour made it follow reaction kinetics

Table 3. Experimental studies on performance of cement + additives in CO_2 environment (Cont.)

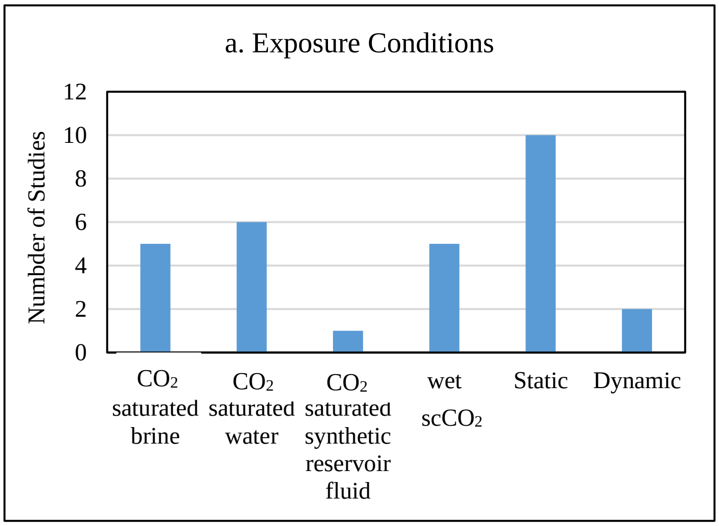
				3000 psi pressure, 140°C; Next 28 days with atmospheric pressure, 140°C	• Exposure time= 4,12,21.31,55 and 88 days in static condition	
Barlet-Gouedard et al.	2012	%by weight • Portland Cement 100% + Metakaolin 48.58% + Hollow microsphere 40.50% + Silica 35% • Slag Cement 100% + Micro Silica 28.76% + Coarse Particle 180.81/72.32% + Hollow Microsphere 9.96/33.86%	NA	• Cylinder size: - • 1 in. * 2 in. Curing in • 90°C for 3 days	• Wet $scCO_2$ • CO_2 saturated water • 4061 psi pressure and 90° C temperature • Exposure time= 31 days in static condition	• Two different mix for CO_2 resistant cement patented by Barlet-Gouedard performed very well against CO_2.
Garnier et al.	2012	• CO_2 resistant cement • Class G cement • Class G cement + 35 wt% silica flour	NA	1) 80°C for 24 Hrs 2) 90°C 3) 140°C	• CO_2 saturated Water 1) 90°C, 1160 psi • Exposure time= For a period of 3 months 2) 140°C, 1160 psi • Exposure time= For a period of 3 months	• Very less effect of CO_2 was observed on CO_2 resistant cement than Class G neat cement or Class G cement + 35 wt% silica flour
Lesti et al.	2013	• Inorganic material + cement • Slag cement + flyash • Organic latex particle + cement • Class G neat cement	• 0.25 • 0.37 • 0.33 • 0.43	Cylinder Size: - • 1.2 in. * 2 in. Cured in: - • Synthetic reservoir fluid • Under 90°C, 5800 psi • Total 28 days	• Wet $scCO_2$ • CO_2 saturated synthetic reservoir fluid • 5800 psi pressure and 90° C temperature • Exposure time= 1 and 6 months in static condition	• All the cement mix which we used here were not able to entirely prevent carbonation • $CaCO_3$ precipitation and crystallization which can create fractures inside cement matrix is the reason behind the cement degradation • Slag cement blended with fly ash gave best results compared to all others

Table 3. Experimental studies on performance of cement + additives in CO_2 environment (Cont.)

Zhang et al.	2014	• 35:65 (by volume) Class F flyash and Class H well cement • 65:35 (by volume) Class F flyash and Class H well cement	• 0.51 • 0.56	Cylinder Size: - • 0.5 in. * 2.36 in. Cured in: - • 1% NaCl • Under 50ºC, 2175 psi • Total 28 days	• Wet $scCO_2$ and H_2S • CO_2 and H_2S saturated in 1% NaCl • 2175 psi pressure and 50º C temperature • Exposure time= 2.5 and 28 days in static condition	• Protective layer of carbonate in the exterior of the cement: pozzolan blend will reduce the alteration of cement. • Cement blend will low amount of pozzolan resisted CO_2 attack better than blend with higher amount of pozzolan
Zhang and Talman et al.	2014	• Class G cement • 59:41 (by volume) Class G cement + Flyash + 2vb % bentonite • 59:41 (by volume) Class C cement + Flyash + 2% bentonite + 2% sodium metasilicate	• 0.44 • 0.55 • 1.13	Cured in: - • 0.5 M NaCl • Under 53ºC, 1450 psi • Total 25 days	• CO_2 saturated Brine • 53ºC, 1450 psi • Exposure time= 3,7,14,28 and 84 days in static condition	• Cement blend with pozzolan remained durable even after getting fully carbonated after 28 days • Increase in permeability was observed in light weight cement from 0.16 to 1.1 mD after 84 days of exposure
Alex et al.	2015	• Class G cement + 10 wt% pozzolan • Reduced portland (Cement blend)	NA	NA	• Wet $scCO_2$ • CO_2 saturated DI water • 2030 psi pressure and 74º C temperature • Exposure time= 12 months in static condition	• Adding blast furnace slag or pozzolan leads to CO_2 resistant cement by reducing portland cement content

Table 4. Quantitative experimental data from the mentioned studies in Table 3

Author/Year	Type of Cement	Alteration Depth (mm)	Initial Density (ppg)	Density (ppg)	Initial Porosity (%)	Porosity (%)	Initial k	Permeability(mD)	Strength Reduction (%)
kutchko/2009	Class H cement								
	35:65 (by volume) Class F flyash + Class H cement						0.0011	0.0135	
							0.0011	0.0263	
	65:35 (by volume) Class F flyash + Class H cement						0.0011	0.0208	
							0.0011	0.0208	
Santra/2009	Cement	4.4							
	Cement + 16.7% silica fume	5.2							
	Cement + 28.6% silica fume	6.4							
	Cement + 37.5% silica fume	10.1							
	Cement + 44.4% silica fume	12.4							
	Cement + 50% silica fume	12.4							
	Cement + 16.7% flyash (F)	7.6							
	Cement + 28.6% flyash (F)	8							
	Cement + 37.5% flyash (F)	9.2							
	Cement + 44.4% flyash (F)	10.4							
	Cement + 50% flyash (F)	11.2							
Brandl/2010	Class G Cement + silica Flour + pozzolan		15	16.1			0.00021	0.00442	0
	Class G cement + 35 wt% silica flour		15	16.5			0.00032	0.00375	0
Garnier/2010	Class G cement	4			30		0.0016	0	
	Class G Cement + 35 wt% silica flour	17.6			28				
Letsi/2013	Inorganic Material + cement	15			19	27	<0.0001	0.089	58
					19	34	<0.0001	<0.0001	70
	Slag Cement + flyash	10			22	22	<0.0001	0.0016	35.7
					22	22	<0.0001	0.0002	40
	Organic latex particle + cement	3				15	<0.0001	0.0061	
						15	<0.0001	0.288	
	Class G neat cement	0.5				14-20	<0.0001	1.54	
						14-20	<0.0001	0.554	
Zhang and Talman/2014	Class G cement		16.66	17	25.5				
	59:41 (by volume) Class G cement + Flyash + 2% bentonite		14.66	16.49	20.8	32	0.03	0.03	
	59:41 (by volume) Class C cement + Flyash + 2% bentonite + 2% sodium metasilicate (lightweight cement)		12.66	13.74	44		0.16	1.1	



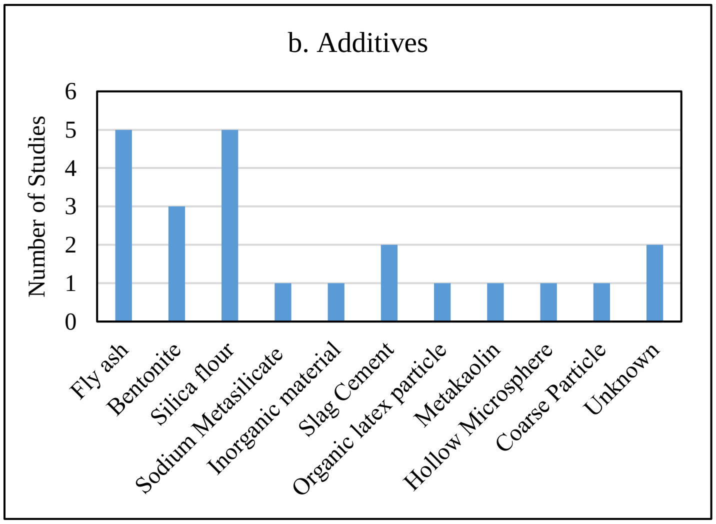


Figure 8. List of (a) different exposure conditions and (b) different additives used in the mentioned studies in Table 3

Figure 9b represents different CO_2 exposure pressures and exposure durations at CO_2 exposure temperatures. CO_2 partial pressures higher than 1100 psi and temperatures higher than 50^oC were used by most studies to create a supercritical CO_2 environment. Figure 10a shows the ratio of alteration depth to core diameter for different CO_2 experimental pressure and temperature conditions. Higher alteration depths were observed, but comparison was not possible due to the wide variety of pozzolans used in the studies.

Notably higher penetration depth was observed in the pozzolan amended cement mix, but this alteration of chemical properties did not result in a change in physical properties in the cement matrix (Santra et al. 2009; Kutchko et al. 2009).

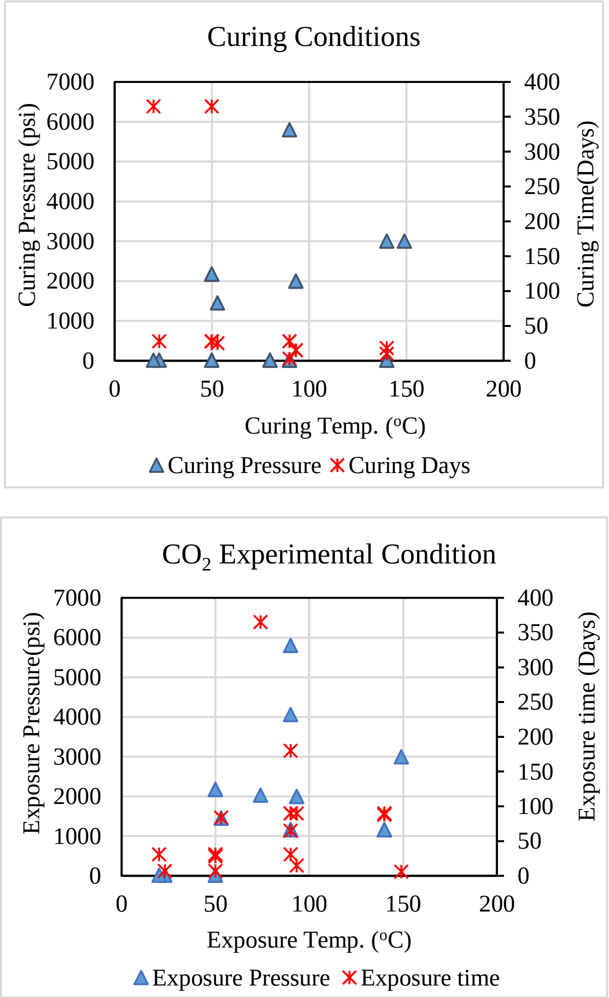
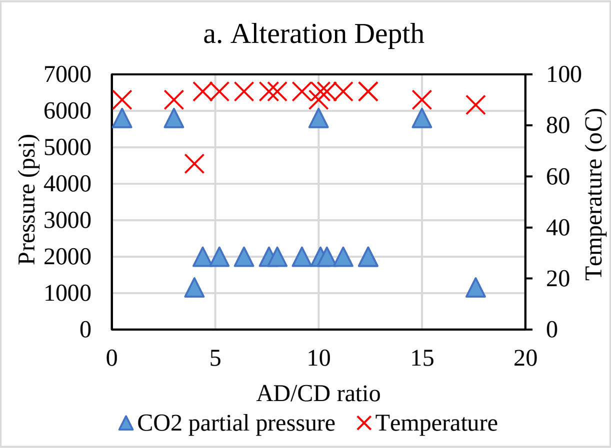


Figure 9. List of (a) different curing conditions and (b) CO_2 exposure conditions used in the mentioned studies in Table 3

Kutchko (2009) observed an increase in the permeability of this pozzolan amended system but the porosity was decreased. This was inconsistent as a decrease in porosity generally results in a decrease in permeability. Thus, researchers provided an explanation that this might be due to fractures created in the cores when they were removed from the pressurized system. Figure 10b shows the porosity changes after the CO_2 exposure at different CO_2 exposure temperatures and exposure times. An increase in porosity was observed by Lesti (2013) with the cement mix containing inorganic material, no change in porosity was observed with flyash.



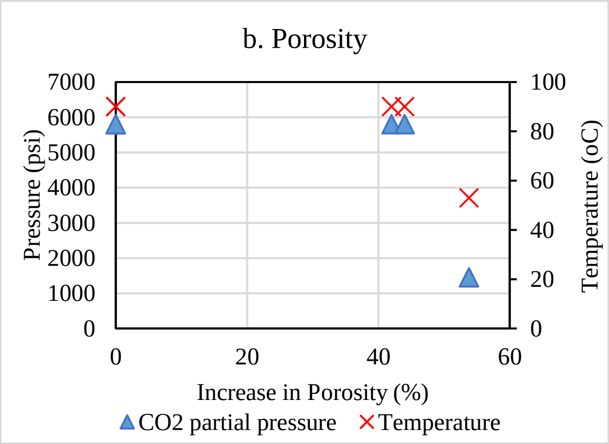


Figure 10. (a) Alteration depth/core diameter ratios (b) change in the porosity at different experimental pressures and temperatures obtained from the data tabulated in Table 4

The permeability changes observed in the cement mix are tabulated in Table 4. Permeability's were increased but was still below the accepted API range of 200 micro darcy for the well. Strength reduction was also observed, as shown in Figure 11. Higher strength reduction was observed with inorganic material + cement than in flyash mixed with slag cement by Lesti (2013).

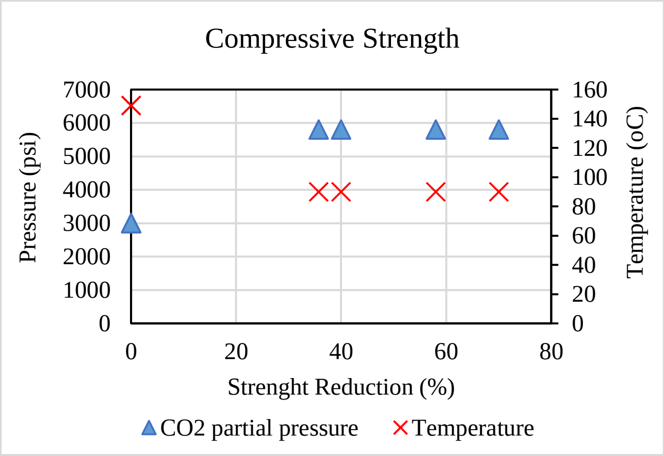


Figure 11. Reduction of cement mix's strength at different experimental pressures and temperatures obtained from the data tabulated in Table 4

From the data and findings of the investigations, addition of pozzolan to the cement mix will lead to CO_2 resistant cement. However, an appropriate quantity of pozzolan is recommended in the cement mix as higher amounts have a negative impact (Brandl et al. 2010; Zhang et al. 2014). Also, flyash is a more appropriate pozzolan for CO_2 storage operations than other pozzolans, due to its availability, low cost, and greater ability to increase the durability of cement in a CO_2 environment.

5.3. FIELD STUDIES

Crow et al. (2009, 2010) investigated a natural CO_2 producing well that was 30 years old. This well was different than Carey (2007), as it was exposed to CO_2 from the beginning. It was not an EOR well so it had large quantities of saturated CO_2. To cast this well, Class H Portland cement with 50% flyash and 3% bentonite was used. Investigations were carried out on obtained sidewall cores taken from the CO_2 reservoir to 70 m above the reservoir in the cap rock. An increase in permeability and porosity were observed in the near reservoir cores, but low permeability and porosity were observed in the cores near the cap rock. An even distribution of carbonate minerals was found in the cement, rather than different alteration zones. The cement/casing and cement/formation interface was intact. The increase in porosity/permeability did not reflect in a loss of hydraulic barrier as it was still very low. The researcher concluded that the cement mix containing flyash provided an effective barrier to CO_2 migration and could be a suitable option for long-term CO_2 storage.

6. POTENTIAL OF USING CLASS C FLYASH-BASED GEOPOLYMER CEMENT

As reviewed earlier, the addition of flyash to the cement mix reduces the amount of Portlandite and increases the durability of cement in a CO_2 environment. Thus, in this research a pure 100% flyash-based geopolymer cement is proposed as an alternative for the wells in CO_2 geological storage reservoirs. The reasoning behind this is that flyash-based geopolymer cement does not have Portlandite ($Ca(OH)_2$) in its structure, which can be helpful as CO_2 and carbonic acid do not react with this material. Thus, this can be an inert material without any reaction with the CO_2 and can be helpful in reducing CO_2 leakage.

An inorganic poly-condensation reaction of tetrahedral alumino-silicate units, with alkali metal ions balancing the charge associated with tetrahedral Al, produces framework structures called geopolymers. This poly-condensation reaction from which geopolymer cement results is called a geopolymerisation reaction. Synthesis of geopolymers occurs in two parts, one consisting of an alkaline solution (often soluble silicate) and the other solid alumino silicate materials. This binding system geopolymer generally hardens at room temperature or higher like ordinary Portland cement. There are many alumino silicate materials that can be used in the synthesis of geopolymer cement. In this research, we are proposing flyash as an alumino-silicate material to be used to make geopolymer cement.

6.1. LOW CO_2 EMISSION OF GEOPOLYMER CEMENT

Another advantage of flyash-based geopolymer cement is its environmentally friendly nature as manufacturing of this cement material does not emit any carbon dioxide. In contrast, Portland cement creates heavy pollution, its manufacture involves emission of high amounts of CO_2 (Equation 9)

$$5CaCO_3 + 2SiO_2 \rightarrow (3CaO, SiO_2)\ (2CaO, SiO_2) + 5CO_2 \qquad (9)$$

It is said that manufacturing 1 ton of Portland cement emits 0.95 tons of carbon dioxide (Concrete CO_2 fact sheet, 2008).

6.2. FLYASH

Flyash is the best known pozzolan in the world. It can be used with the Portland cement to improve compressive strength, durability in acidic environments, early strength Flyash is a by-product of burning pulverized coal in electric power generating plants and is basically considered a waste product. Utilizing it in making geopolymer cement solves the problem of disposing it. Properties of flyash depend on the nature of coal, coal rank, furnace design and furnace operation. Thus, there is wide variety of flyash available in the market. ASTM classifies flyash on the basis of chemical properties into two types: Class C and Class F. These differ in the amount of chemical components of flyash, as explained in Table 5. Similar chemical components are found in flyash and Portland cement, but differ in their amount. Thus, Class F flyash contains large amounts of Al_2O_3 and SiO_2, but less than 10% CaO, whereas Class C flyash has higher amounts of CaO.

Table 5. Chemical compositions of Flyash and Portland cement (%/weight)

Element	Class C flyash	Class F flyash	Class H Portland Cement
SiO_2	28.93	48.3	20.36
Al_2O_3	14.82	30.5	3.17
Fe_2O_3	6.4	12.1	6.19
CaO	39.8	2.8	65.72
MgO	4.86	1.2	1.32
Na_2O	1.1	0.2	2.26
K_2O	0.56	0.4	0.43
Other components	3.53	4.5	0.55

Chemical composition of Class C flyash and Portland cement (Ahdaya and Jani, 2018); Class F flyash (Nasvi et al. 2012)

6.3. ALKALI ACTIVATION OF FLYASH

Alkaline solution is a mixture of sodium or potassium hydroxide (NaOH or KOH) and sodium or potassium silicates (Na_2SiO_3 or K_2SiO_3). Flyash is activated by alkaline solution and converts into a geopolymer precursor (Figure 9), which behaves as cement as explained earlier.

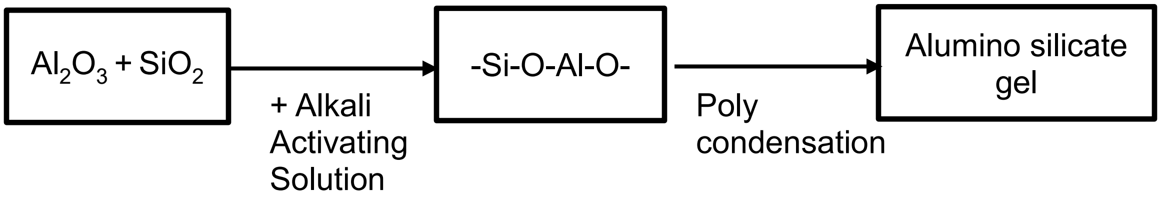


Figure 12. Alkali activation of flyash

6.4. MIXING OF FLYASH BASED GEOPOLYMER

Alkaline solution is prepared first by mixing sodium silicate and sodium hydroxide. Appropriate amounts of flyash are mixed with water at low speed. Prepared alkaline solution is added into the mixture and then mixed at low speed for some time, then at high speed to obtain geopolymer cement slurry.

6.5. PERFORMANCE OF GEOPOLYMER CEMENT IN CO_2 ENVIRONMENT

The results of our study conducted to evaluate the performance of Class C flyash based geopolymer cement in CO_2 environment (Jani et al. 2018) are tabulated below in Table 6.

Table 6. Performance of Portland cement and Geopolymer cement after 14 days of CO_2 exposure

Types of cement	Portland cement		Geopolymer cement	
CO_2 partial pressure	500 psi	1500 psi	500 psi	1500 psi
Temperature (°F)	110	110	110	110
pH of water	6.9	6.9	7.3	7.3
Density	Negligible change	Negligible change	Negligible change	Negligible change
Strength reduction (%)	27.7	41.5	0	12.06

The results suggest that the reduction in the strength of geopolymer is very little compared to Portland cement after 14 days of CO_2 exposure. Thus, this can explain the idea of using geopolymer cement in CO_2 storage purposes since it remains inert. Still, there are many more experiments to conduct on this new cement to totally replace Portland cement.

7. CONCLUSIONS

A critical review of past investigations was carried out to better understand the degradation process of cement in the presence of CO_2 environments. The main aim behind this was to understand the risk of CO_2 migration from the CO_2 storage reservoirs. Analysis of provided solutions to address CO_2 migration problem by previous studies were carried out. Class C flyash based geopolymer cement was introduced as a potential alternative to Portland cement for CO_2 storage reservoirs.

- Portland cement degrades in the presence of CO_2. This chemical alteration affects the mechanical properties of the cement like porosity, permeability, density and compressive strength.
- The degradation of Portland cement raised concerns due to possible risk of CO_2 leakage from the storage reservoir.
- Till now, Pozzolans are used as additives with Portland cement to obtain CO_2 resistant cement. These are durable in CO_2 environments. However, an optimum quantity of pozzolan is recommended.

- Based on our data analysis flyash and silica fume are the most used pozzolans. However, due to the availability of flyash and its easy mixing capacity, flyash is recommended.
- Cement mix containing flyash also degrades in a CO_2 environment because of the availability of Portland cement constituents which react with CO_2.
- A pure flyash-based geopolymer cement is proposed to use in CO_2 storage reservoirs as there is no $Ca(OH)_2$ or C-S-H present. Also, this cement is environmentally friendly.
- Results of our study performed to assess the performance of geopolymer cement in CO_2 environment suggest that geopolymer cement can be a potential alternative to Portland cement.

REFERENCES

Ahdaya, M., Jani, P., Imqam, A. et al., (2018). The Development of New Formulation of Geopolymer Cement for Wellbore Integrity Improvements. IPTC 19393 MS-2018

Andrew Duguid, George W. Scherer, Degradation of oil well cement due to exposure to carbonated brine, International Journal of Greenhouse Gas Control, Volume 4, Issue 3, 2010, Pages 546-560, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2009.11.001

A. Duguid, M. Radonjic, R. Bruant, G.W. Scherer, Degradation of well cements exposed to carbonated brine, Proceedings of the 4th annual conference on carbon capture and sequestration, May 2-5, 2005, Monitor and exchange publications and forum, Washington D.C.

A. Duguid; M. Radonjic; R. Bruant; T. Mandecki; G. Scherer; M. Celia (Princeton Univ., Princeton, NJ, United States); The effect of CO_2 sequestration on oil well cements; Dept. of Civil and Environmental Engineering; Proceedings of the 7. International conference on greenhouse gas control technologies.

Adams, N., Charrier, T., 1985. Drilling Engineering: a Complete Well Planning Approach. Penn Well Pub. Co.

American Petroleum Institute. Worldwide Cementing Practices; API: Dallas, TX, 1991.

Andac, M., Glasser, F.P., 1999. Long-term leaching mechanisms of Portland cement stabilized municipal solid waste flyash in carbonated water. Cement and Concrete Research 29, 179–186.

Alex, C., Campos, G., Deshpande, A., Chiney, A., Patil, S., & Ravi, K. (2015, May 4). An Experimental Study on Effects of Static CO_2 on Cement under High-Pressure/High-Temperature Conditions. Offshore Technology Conference. Doi: 10.4043/25659-MS

Barlet-Gouedard, V., Rimmele, G., Goffe, B., & Porcherie, O. (2006, January 1). Mitigation strategies for the risk of CO_2 migration through wellbores. Society of Petroleum Engineers. Doi: 10.2118/98924-MS

Barlet-Gouedard, V., Rimmele, G., Goffe, B., & Porcherie, O. (2006, January 1). Mitigation strategies for the risk of CO_2 migration through wellbores. Society of Petroleum Engineers. doi:10.2118/98924-MS.

Barlet-Gouédard, G. Rimmelé, O. Porcherie, N. Quisel, J. Desroches, A solution against well cement degradation under CO_2 geological storage environment, International Journal of Greenhouse Gas Control, Volume 3, Issue 2, 2009, Pages 206-216, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2008.07.005.

Brandl, A., Cutler, J., Seholm, A. J., Sansil, M., & Braun, G. (2010, January 1). Cementing Solutions for Corrosive Well Environments. Society of Petroleum Engineers. doi:10.2118/132228-MS.

Black, L, Breen, C. Yarwood, J., Garev, K., and Stemmermann, P. "Structural Features of C-S-H (I) and its Carbonation in Air–A Raman Spectroscopic Study–Part II: Carbonated Phases, Journal of the American Ceramic Society. 2007. 90:908–917.

Barlet-Gouedard, V., James, S., Drochon, B., Piot, B., Jean-Philippe, C., 2012. Cement composition for carbon dioxide supercritical environment. US Patent, US 8,091,642 B2.

Barbara G. Kutchko, Brian R. Strazisar, Nicolas Huerta, Gregory V. Lowry, David A. Dzombak, and Niels Thaulow, CO_2 Reaction with Hydrated Class H Well Cement under Geologic Sequestration Conditions: Effects of Flyash Admixtures. Environmental Science & Technology, 2009, 43 (10), 3947-3952, DOI: 10.1021/es803007e.

Barbara G. Kutchko, Brian R. Strazisar, David A. Dzombak, Gregory V. Lowry and, and Niels Thaulow, Degradation of Well Cement by CO_2 under Geologic Sequestration Conditions; Environmental Science & Technology, 2007, 41 (13), 4787-4792 DOI: 10.1021/es062828c.

Barbara G. Kutchko, Brian R. Strazisar, Gregory V. Lowry, David A. Dzombak, and Niels Thaulow, Rate of CO_2 Attack on Hydrated Class H Well Cement under Geologic Sequestration Conditions, Environmental Science & Technology 2008 42 (16), 6237-6242 DOI: 10.1021/es800049r.

Carey, J.W., Wigand, M., Chipera, S.J., WoldeGabriel, G., Pawar, R., Lichtner, P.C., Wehner, S.C., Raines, M.A., Guthrie Jr., G.D., 2007. Analysis and performance of oil well cement with 30 years of CO_2 exposure from the SACROC unit, west Texas, U.S.A. International Journal of Greenhouse Gas Control 1 (1), 75–85.

Crow, W., Williams, B., Carey, J.W., Celia, M., Gasda, S., 2009. Wellbore integrity analysis of a natural CO_2 producer. In: Proceedings of the 9th Annual Conference on Greenhouse Gas Control Technologies, Washington, DC, U.S.A., November 16–20, 2008, Energy Procedia, pp. 3561–3569.

Crow, W., Carey, J.W., Gasda, S., Williams, D.B., Celia, M., 2010. Wellbore integrity analysis of a natural CO_2 producer. International Journal of Greenhouse Gas Control 4 (2), 186–197.

Concrete CO_2 fact sheet, 2008, NRMCA Publication Number 2PCO2.

Charles M. Hunt, Vernon Dantzler, Lewis A. Tomes/ and Raymond L Blaine, Reaction of Portland cement with carbon dioxide; Journal of Research of the national bureau of standards, Vol. 60, No. 5, May 1958; Research paper 2858.

Godec, M., Koperna, G., Petrusak, R., Oudinot, A., 2013. Assessment of factors influencing CO_2 storage capacity and Injectivity in Eastsern U.S. Gas Shales. Energy Procedia 37, 6644e6655.

Gaëtan Rimmelé, Véronique Barlet-Gouédard, Olivier Porcherie, Bruno Goffé, Fabrice Brunet, Heterogeneous porosity distribution in Portland cement exposed to CO_2-rich fluids, Cement and Concrete Research, Volume 38, Issues 8–9, 2008, Pages 1038-1048, ISSN 0008-8846, https://doi.org/10.1016/j.cemconres.2008.03.022.

Garev, K. Stemmermann, P. Black, L. Breen, C. and Yarwood, J. Structural Features of C-S-H(I) and its Carbonation in air—A Raman Spectroscopic Study–Part I : Fresh Phases." Journal of the American Ceramic Society. 2007. Soc. 90:900–907.

Garnier, A., Laudet, J.-B., Neuville, N., Le Guen, Y., Fourmaintraux, D. M., Rafai, N., Shao, J. F. (2010, January 1). CO_2-Induced Changes in Oilwell Cements Under Downhole Conditions: First Experimental Results. Society of Petroleum Engineers. doi:10.2118/134473-MS.

Garnier, A., Laudet, J. B., Patil, S., Patil, R., Ravi, K., & Ferreira, L. (2012, January 1). Effect of Acid Gas on Cement Sheath Integrity: Experimental Findings. Society of Petroleum Engineers. doi:10.2118/160890-MS.

https://www.iea.org/publications/freepublications/publication/GECO2017.pdf

Khizar Abid, Raoof Gholami, Paul Choate, Brabha Hari Nagaratnam, A review on cement degradation under CO_2-rich environment of sequestration projects, Journal of Natural Gas Science and Engineering, Volume 27, Part 2, 2015, Pages 1149-1157, ISSN 1875-5100, https://doi.org/10.1016/j.jngse.2015.09.061

Liwei Zhang, David A. Dzombak, David V. Nakles, Steven B. Hawthorne, David J. Miller, Barbara Kutchko, Christina Lopano, Brian Strazisar, Effect of exposure environment on the interactions between acid gas (H_2S and CO_2) and pozzolan-amended wellbore cement under acid gas co-sequestration conditions, International Journal of Greenhouse Gas Control, Volume 27, 2014, Pages 309-318, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2014.06.030

MacLaren, D.C., White, M.A., 2003. Cement: its chemistry and properties. J. Chem. Edu. 80 (6), 623e635.

Moroni, N., Santra, A. K., Ravi, K., & Hunter, W. J. (2009, January 1). Holistic Design of Cement Systems to Survive CO_2 Environment. Society of Petroleum Engineers. doi:10.2118/124733-MS.

M. Lesti, C. Tiemeyer, J. Plank, CO_2 stability of Portland cement based well cementing systems for use on carbon capture & storage (CCS) wells, Cement and Concrete Research, Volume 45, 2013, Pages 45-54, ISSN 0008-8846, https://doi.org/10.1016/j.cemconres.2012.12.001.

Min Zhang, Stephen Talman, Experimental Study of Well Cement Carbonation under Geological Storage Conditions, Energy Procedia, Volume 63, 2014, Pages 5813-5821, ISSN 1876-6102, https://doi.org/10.1016/j.egypro.2014.11.614.

Min Zhang, Stefan Bachu, Review of integrity of existing wells in relation to CO_2 geological storage: What do we know? International Journal of Greenhouse Gas Control, Volume 5, Issue 4, 2011, Pages 826-840, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2010.11.006.

N. Spycher, K. Pruess, CO_2-H_2O mixtures in the geological sequestration of CO_2. II. Partitioning in chloride brines at 12–100 °C and up to 600 bar, Geochimica et Cosmochimica Acta 69 (13) (2005) 3309–3320.

Nasvi, Mohamed & P.G, Ranjith. (2012). Mechanical properties of geopolymer cement in brine: its suitability as well cement for geological sequestration of carbon dioxide (CO_2).

Nelson, E. B. Well Cementing; Schlumberger Educational Services: Sugar Land, TX, 1990.

Neville, A. M. Properties of Concrete; Fifth ed.; Prentice Hall: Upper Saddle River, NJ, 2012.

Nygaard, R., 2010. Well Design and Well Integrity (Energy and Environmental Systems Group).

Nelson, E.B., Guillot, D., Well cementing, 2nd Edition, Schlumberger, Sugar Land (2006), 3-5.

Onan, D. D. (1984, January 1). Effects of Supercritical Carbon Dioxide on Well Cements. Society of Petroleum Engineers. doi:10.2118/12593-MS.

Qingyun Li, Yun Mook Lim, Katharine M. Flores, Kelly Kranjc, and Young-Shin Jun, Chemical Reactions of Portland Cement with Aqueous CO_2 and Their Impacts on Cement's Mechanical Properties under Geologic CO_2 Sequestration Conditions. Environmental Science & Technology 2015 49 (10), 6335-6343 DOI: 10.1021/es5063488.

Raza, A., Rezaee, R., Gholami, R., Rasouli, V., Bing, C.H., Nagarajan, R., Hamid, M.A., 2015. Injectivity and quantification of capillary trapping for CO_2 storage: a review of influencing parameters. J. Nat. Gas Sci. Eng 2 (2015), 510e517.

Rabia, H., 2001. Well Engineering and Construction.

Rendell, F.; Jauberthie, R.; Grantham, M. Deteriorated Concrete: Inspection and Physicochemical Analysis; Thomas Telford: London, 2002.

Shen, J. C., & Pye, D. S. (1989, January 1). Effects of CO_2 Attack on Cement in High-Temperature Applications. Society of Petroleum Engineers. doi:10.2118/18618-MS.

Santra, A. K., Reddy, B. R., Liang, F., & Fitzgerald, R. (2009, January 1). Reaction of CO_2 with Portland cement at Downhole Conditions and the Role of Pozzolanic Supplements. Society of Petroleum Engineers. doi:10.2118/121103-MS.

Scherer, G.W., Kutchko, B., Thaulow, N., Duguid, A., Mook, B. Characterization of cement from a well at Teapot Dome oil field: implications for geological sequestration. International Journal of Greenhouse Gas Control, in press.

Thaulow, N.; Lee, R. J.; Wagner, K.; Sahu, S. Effect of calcium hydroxide on the form, extent, and significance of carbonation. In Calcium Hydroxide in Concrete; Skalny, J., Gebauer, J., Odler, I., Eds.; The American Ceramic Society: Westerville, OH, 2001; pp 191-201

Taylor, H. F. Cement Chemistry; Thomas Telford: London, 1997

Tarco, J. C., & Asghari, K. (2010, October 1). Experimental Study of Stability and Integrity of Cement in Wellbores Used for CO_2 Storage. Society of Petroleum Engineers. doi:10.2118/142004-PA.

Yalcinkaya, T., Radonjic, M., Hughes, R. G., Willson, C., & Ham, K. (2010, January 1). The Effect of CO_2-Saturated Brine on the Conductivity of Wellbore-Cement Fractures. Society of Petroleum Engineers. doi:10.2118/139713-MS.

II. NEW FORMULATION OF CLASS C FLYASH-BASED GEOPOLYMER CEMENT FOR OIL WELL CEMENTING OPERATIONS

ABSTRACT

Wellbore cementing is a major step in drilling operations, as cement provides wellbore integrity. Currently, Portland cement is mainly used in the oil industry. However, it has many drawbacks, including operational and environmental problems. Flyash based geopolymer cement has recently gained more attention due to its low cost and environmental friendliness. This research aims to obtain a new formulation of class C flyash-based geopolymer cement to be used as an oil well cement and as an alternative to Portland cement. Twenty-four different geopolymers were prepared and compared to decide which will be the optimum formulation to use. The alkaline activator to flyash ratios used include 0.2, 0.4, and 1, and the sodium hydroxide to sodium silicate ratios include 0.25, 0.5, 1, and 2 for three different sodium hydroxide concentrations, having 5, 10, and 15 molarity. The optimum formulation was chosen based on five different API recommended tests, including rheology, density, compressive strength, LPLT fluid loss and stability. The optimum formulation was then compared to Portland cement using all the tests mentioned. This research started with the development of the optimum geopolymer formulation. The results showed that increasing the alkaline activator to flyash ratio increased plastic viscosity and reduced the workability of the cement slurry. Increased concentration of sodium hydroxide slightly reduced the plastic viscosity of the geopolymer slurry. An increase in sodium hydroxide concentration resulted in an increase in the compressive strength of geopolymer cement. A significant reduction in fluid loss was observed by increasing sodium silicate to sodium hydroxide ratios. The formulation with sufficient compressive strength, density in the range of normal weight cement, good rheological behavior and lower fluid loss was selected as an optimized formulation. Optimized formulation has 60% higher compressive strength and fluid losses lower than Portland cement. Results from the stability tests showed that optimized geopolymer does not have any free fluid and sedimentation. These results indicate that Class C flyash-based geopolymer can be a replacement to Portland cement. This research formulated a novel geopolymer with enhanced properties and evaluated its performance compared to Portland cement. Based on the obtained results, this research aims to provide the oil and gas industry with a new environmentally friendly Class C flyash-based geopolymer cement as an alternative to ordinary Portland cement.

1. INTRODUCTION

Successful primary cementing is very important for oil and gas wells because it provides zonal isolation, prevents underground blowout, prevents fresh water contamination, and provides a barrier to the fluid flow to prevent leakage. Loss of zonal isolation can result in operational hazards, environmental pollution, and higher remedy costs (Alkhamis and Imqam 2018). Portland cement is being used mainly for oil and gas well cementing operations. There are many disadvantages in using this cement, such as radial cracks within the cement sheath, micro-annuli at the interfaces of the cement, channels through the cement matrix, and cement shrinkage (Bois et al. 2012). Recently, a new cost effective and environmentally friendly cement has come to light that has properties similar to Portland cement. It is called geopolymer cement. Geopolymer was first researched by Davidovitts, who began searching for a non-flammable, noncombustible construction material after a fire in France in 1970. Davidovis experimented with several types of cement mixes involving flyash for his research. Flyash is a by-product from burning pulverized coal in electric power generating plants. The fine powder resembles Portland cement, but is chemically different. Class F and Class C flyash are the two basic types of flyash available in the market. According to the American Society for Testing and Materials (ASTM), the differences between these two types is that Class C has a higher content (more than 20%) of calcium oxide (CaO) than Class F (less than 20%). A geopolymer binder will form by activation of flyash by alkaline activator, which after adding water will behave as cement. Class C flyash (higher calcium flyash) was used in this research. This type of cement has many advantages over Portland cement due to its cost effectiveness, sustainability, and operational benefits like higher compressive strength, lower fluid loss, and no chemical shrinkage. Manufacturing of Portland cement requires burning a huge amount of fuel and decomposing limestone, causing enormous amounts of carbon dioxide (CO_2) emissions (Kong and Sanjayan, 2008), whereas this geopolymer cement does not emit any kind of greenhouse gas. Portland cement consists of calcium hydroxide and calcium silicate, while geopolymer consists of an alumino-silicate gel (Salehi et al. 2016).

This new flyash based geopolymer cement has recently attracted the attention of many researchers because of its ability to replace Portland cement. Reasonable compressive strength geopolymers can be produced at different NaOH concentrations and different curing conditions (Bakkali et al. 2016). The compressive strength of geopolymer cement increases when higher concentrations of sodium hydroxide are used. An increase in the ratio of alkaline activator to flyash also increases the compressive strength of geopolymer cement (Al-Bakri et al, 2012). Nasvi (2012) used geopolymer and Class G Portland cement to compare mechanical behavior at different curing temperatures. An investigation of low calcium flyash (Class F) was conducted by Sugumran (2015) to study the effects of water ratios and sodium hydroxide ratios. Investigations have been conducted by Suppiah (2016) to examine the compressive strength of geopolymer cement by utilizing different sodium hydroxide concentrations and different ratios of silicate to hydroxide. Their results showed that as sodium hydroxide concentrations increase, compressive strength increases. Furthermore, another investigation of using low calcium flyash (ASTM class F) was performed by Salehi (2016), who made a comparison between geopolymer and Portland cement; it showed that the compressive strength of geopolymer improved greatly after seven days compared to Portland cement. Moreover, the results showed that geopolymer has a higher bond strength than Portland cement, similar to the results that were obtained by Liu in 2017. Besides bonding strength, Liu compared other properties, including compressive strength between geopolymers, geopolymer hybrids and Portland cement. In terms of viscosity and density, the viscosity of geopolymer is directly proportional to sodium hydroxide concentrations. The viscosity increases with increasing sodium hydroxide concentrations, and the density increases as the ratios of flyash to alkaline activator increase (Suppiah et al. 2016). Furthermore, Salehi (2016) studied the effects of different temperatures on the thickening time of the geopolymer cements. According to Uehar (2010), geopolymer has better acid resistance than Portland cement. Class C flyash-based geopolymer cement has higher compressive strength at higher pressures than Portland cement (Khalifeh et al. 2014). It was observed from the literature review that flyash-based geopolymer cement has higher compressive and shear strength, better durability in acidic environment. Thus, it can be a potential alternative to portland cement for oil-well cementing purposes. Investigations based on evaluating class C flyash-based geopolymer was very less and needs more attention.

This paper aims to investigate the performance of using Class C flyash based geopolymer cement for oil well cement applications. Different ratios of alkaline activator to flyash (AA/FA), sodium silicate to sodium hydroxide (SS/SH), and sodium hydroxide concentrations were used to choose the optimized design depending on the rheology, density, compressive strength, and fluid loss. Other tests were conducted to the optimized geopolymer to compare it with Portland cement.

2. EXPERIMENTAL DESCRIPTION

2.1. MATERIALS

2.1.1. Portland Cement. In this research, Class H Portland cement provided by Haliburton Company was used. After obtaining the cement, an X-ray fluorescence (XRF) test was run in order to determine cement's elemental composition. Results of this test are shown in Table 1.

2.1.2. Flyash. This material is basically a by-product from coal power plants and is generally considered a waste product. The two types of flyash are Class C and Class F. Classification of flyash is on the basis of the elemental composition, like lime, SiO_2 and Al_2O_3, as per ASTM. An XRF test was conducted on the flyash to determine the elemental composition. The results from this test was listed below in Table 2. The results from XRF scanning showed that the amount of lime (CaO) was higher than 20%, which according to ASTM, is Class C flyash.

Table 1. The elemental compositions of Class H cement

Element	Concentration (%)
SiO_2	20.36
Al_2O_3	3.17
Fe_2O_3	6.19
CaO	65.72
MgO	1.32
SO_3	2.26
K_2O	0.43
Other components	0.55

Table 2. The elemental compositions of Class C flyash

Element	Concentration (%)
SiO_2	28.93
Al_2O_3	14.82
Fe_2O_3	6.40
CaO	39.80
MgO	4.86
Na_2O	1.10
K_2O	0.56
Other components	2.63

2.1.3. Sodium Hydroxide. Sodium hydroxide ordered from a company was 96% pure. Different proportions of sodium hydroxide powder were mixed with distilled water in order to obtain 1-liter solutions of 5, 10 and 15 M NaOH.

2.1.4. Sodium Silicate. Sodium silicate was used in this study to prepare the alkaline solution for the activation of flyash. Sodium silicate provides another source of silicate and is also known as water glass.

2.2. CEMENT SLURRY PREPARATION

2.2.1. Portland Cement. Class H Portland cement slurry was prepared as per API procedure. Tap water was used in all experiments. Water/cement ratio was taken to be 0.38 following API specification 10A (API 2010). Dry cement was added to the water while being mixed at low speed for 15 seconds and was mixed for 35 seconds at high speed.

2.2.2. Class C Flyash-based Geopolymer Cement. Before mixing geopolymer cement slurry, an alkaline activator was prepared by mixing NaOH solution and Na_2SiO_3 as per the design. First, water and flyash were mixed in a blender for 10 seconds at low speed. Then, an alkaline activator was added to the mixture while mixing at low speed for 10 seconds. Then, mixing continued for 30 seconds at high speed. All geopolymer slurries have a water ratio of 33%. Different ratios of alkaline activator to flyash (AA/FA) (0.2 and 0.4), sodium silicate to sodium hydroxide (SS/SH) (0.25, 0.5, 1, and 2), and sodium hydroxide concentrations (5 M, 10 M, and 15 M) were investigated in this study in order to select the optimum design. The mix design used is described in Table 3. Along with the previous AA/FA ratios mentioned, an additional alkaline activator to flyash ratio 0.8 was used to investigate the impacts of increasing the ratio of alkaline activator to flyash. The mix design is described in Table 3.

Table 3. Geopolymer mix designs for different ratios of SS/SH and AA/FA

Flyash : - 600 gm	AA/FA	0.2		0.4		0.8	
	SS/SH ratio	SH Solution (gm)	SS Solution (gm)	SH Solution (gm)	SS Solution (gm)	SH Solution (gm)	SS Solution (gm)
	0.25	96	24	192	48		
	0.5	80	40	160	80		
	1	60	60	120	120	240	240
	2	40	80	80	160		

2.3. EXPERIMENTAL METHODOLOGY

This section is a description of the test procedures that were used to find the optimum design of geopolymer. Tests included density, rheology, compressive strength, and fluid loss. Stability tests, including free fluid tests and sedimentations tests, were performed to make a comparison between the optimized geopolymer and Portland cement. Twenty-four samples were prepared according to the mix design described in Table 3 for three different NaOH concentrations (5M, 10M, and 15M) and were used to measure rheology, density and fluid loss. Another twenty-four samples were prepared for compressive strength measurements.

2.3.1. Density and Rheology. Density was measured using a standard mud balance. An OFITE viscometer was used to obtain the rheological behavior of these samples. All rheology and density tests were performed at atmospheric pressure and room temperature.

2.3.2. LPLT Fluid Loss Test. To test the ability of geopolymer cement to retain water, fluid loss tests were conducted for all slurries. The fluid loss was measured by a low-pressure, low- temperature filtrate cell (LPLT) at 100 psi, and room temperature.

2.3.3. Compressive Strength Test. To determine and compare the compressive strength of different geopolymer cement samples, the slurries were poured into 2×2×2 in. molds. Then, the molds were placed in a water bath and cured at atmospheric pressure and room temperature for 24 hours. After 24 hours, the prepared cores were removed from the molds, and the compressive strength was measured using a hydraulic press testing machine.

2.3.4. Stability Test. Stability tests ensure that the cement maintains its desired properties. In this study, free fluid and sedimentation tests were performed to test the stability of the optimum design of geopolymer cement. In order to perform the free fluid test, 250 ml of geopolymer was left in a graduated cylinder for 2 hours. The sedimentation test was conducted by preparing a one to one sample of geopolymer and Portland cement, and then letting it set for 24 hours in a mold 7.9 in. in length and 1 in. in diameter in accordance to API RP 10B-2 2013. The sample was cut into six segments including top, bottom, and four segments in between, and the weight of every segment in air and water was taken by using the setup in Figure 1.

The density of every segment was calculated using the following equations:

$$\rho = \frac{Wt_a}{Volume} \tag{1}$$

$$V = \frac{Wt_a - Wt_w}{\rho_w} \tag{2}$$

Where ρ is the density in gm/cm^3, Wt_a is the weight in air in gm, Wt_w is the weight in water in gm, and ρ_w is the water density in gm/cm^3.

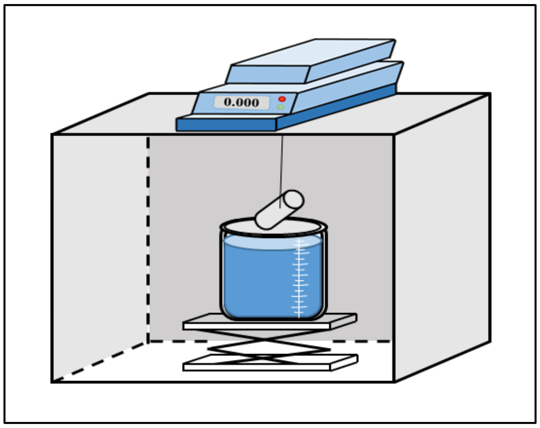


Figure 1. Mass measurement setup

3. RESULTS AND DISCUSSIONS

API tests for rheology, density, compressive strength, fluid loss, and stability were conducted on all geopolymer cement slurries. Additionally, three samples were prepared with different sodium hydroxide concentrations (5 M, 10 M, and 15 M) using the ratio of alkaline activator to flyash (AA/FA) = 0.8 and sodium silicate to sodium hydroxide ratio (SS/SH) = 1 to investigate the effect of increasing alkaline activator to flyash ratio (AA/FA) ratio. The result of this increase showed that geopolymer sets in an extremely rapid manner (less than 10 seconds).

3.1. DENSITY AND RHEOLOGY RESULTS

Geopolymer slurries had densities similar to regular Portland cement. Changing the SS/SH ratios did not show any effect on the density. Thus, the SS/SH ratio was kept constant to see how the density changed when the alkaline activator to flyash ratio was changed (from 0.2 to 0.4) for three different sodium hydroxide concentrations (5, 10, and 15M). Sodium hydroxide concentrations have no effect on the density of the cement slurry as shown in Figure 2. However, changing the alkaline activator to flyash ratio has a slight effect and is inversely proportional to the density. This also means that as the amount of flyash in the slurry increases, the density increases.

After rheological tests, a graph of shear stress versus shear strain was plotted as a reference for Portland cement slurry and geopolymer cement slurries with different SS/SH ratios, for the concentration of 10 M of sodium hydroxide and AA/FA = 0.2 and 0.4 (Figure 3). It showed that although the geopolymer has less viscosity than Portland cement, it has almost the same rheological behavior.

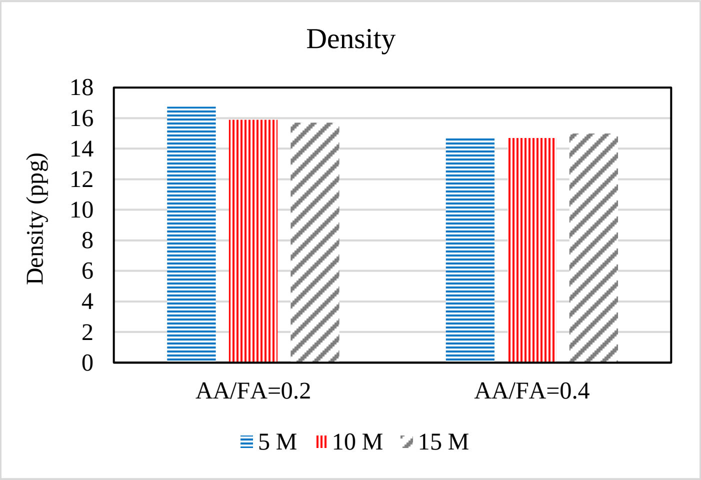
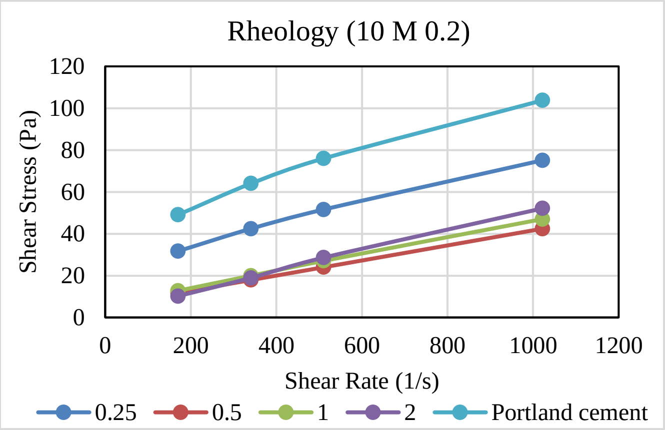


Figure 2. Density for different AA/FA ratios and different sodium hydroxide concentrations for SS/SH=1

An important factor in determining cement workability is the plastic viscosity. It was calculated by subtracting the shear stress value at 300 RPM from the shear stress value at 600 RPM (Equation 3).

$$PV=\Theta_{600} - \Theta_{300} \tag{3}$$



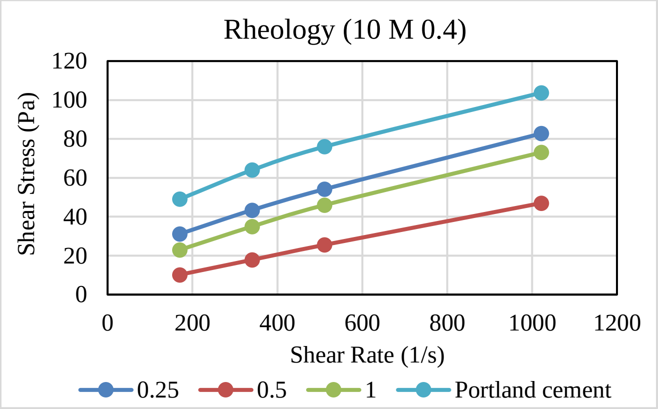


Figure 3. Shear stress vs. shear rate for different SS/SH ratios for the concentration of 10 M of sodium hydroxide and AA/FA = 0.2, 0.4, and Portland cement

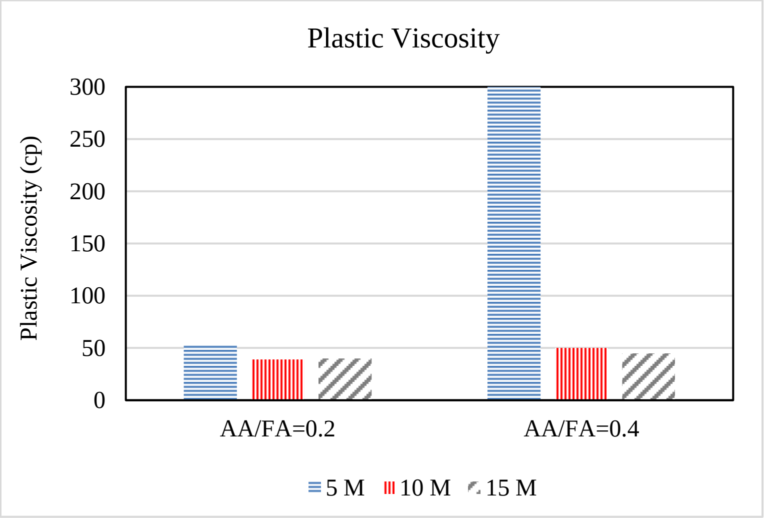


Figure 4. Plastic viscosity results for different AA/FA ratios with different sodium hydroxide concentrations at SS/SH=1

3.2. COMPRESSIVE STRENGTH RESULTS

The measured compressive strength of all the specimens were plotted on two graphs. Figure 5 shows the compressive strength of specimens with different alkaline activator to sodium silicate ratios of 5, 10, and 15 M NaOH for SS/SH=1. It was observed that by increasing the molarity of sodium hydroxide, the compressive strength increased. This trend was also found when AA/FA ratios were increased. The reason behind the increase in strength with the molarity is that when flyash comes in contact with higher molar NaOH, leaching of Si and Al increases, which results in higher strength (Rattanasak and Chindaprasirt. 2009). The higher compressive strength of geopolymer is due to the alumino-silicate gel, which is formed due to the geopolymerisation process (Abdullah et al., 2012). Increasing the AA/FA ratio also positively affected the strength, as a higher strength was observed for all molarities at AA/FA 0.4.

Then, strength results were obtained for four different SS/SH ratios at an AA/FA of 0.2 and 0.4 for 10 M sodium hydroxide (Figure 6). Specimens with 10 M NaOH had a higher strength than specimens with 5 M NaOH. Specimens with 15 M NaOH were very toxic and the rheological properties of these slurries were not acceptable for oil well cement slurries as per API. Thus, 10 M was chosen. For 0.2 AA/FA, strength was decreased when SS/SH was increased from 0.25 to 2, but the opposite trend was observed with 0.4 AA/FA.

3.3. FLUID LOSS TEST RESULTS

Loss of fluid from the cement slurry during the setting is a big concern as it can lead to some operational difficulties like change in properties of cement slurry or cracks

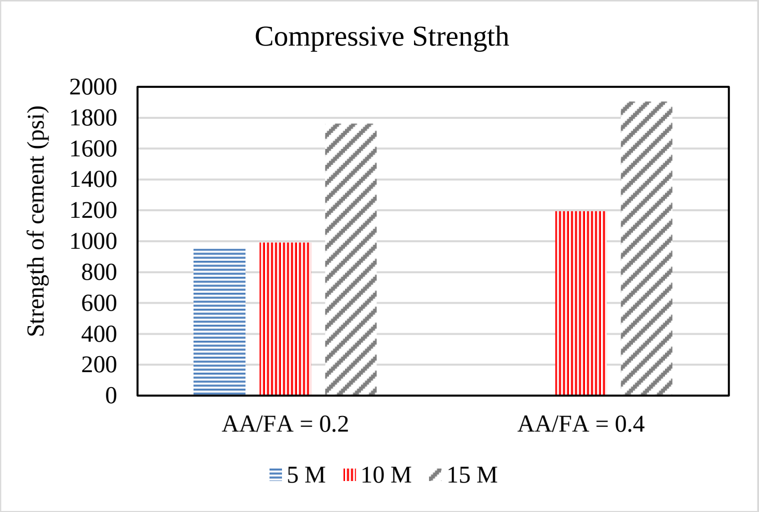


Figure 5. Compressive strength of different AA/FA ratios and different concentrations of sodium hydroxide with SS/SH = 1

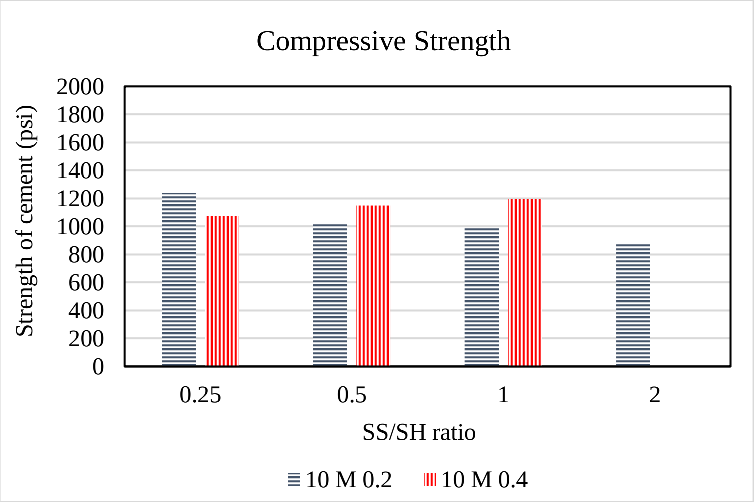


Figure 6. Compressive strength of different SS/SH ratios and different AA/FA ratios for 10 M NaOH

inside the cement formation. Many companies use fluid loss additives in order to control it. In this research, low-pressure, and low-temperature fluid loss tests were conducted on geopolymer slurries. However, cement slurries experience high-pressure, high-temperature conditions in actual field conditions. However, LPLT tests can also provide us with a basic idea about the cement slurries effectiveness under HPHT conditions. Results of fluid loss from different alkaline activator to flyash ratios for different sodium hydroxide concentrations at SS/SH = 1 were plotted (Figure 7).

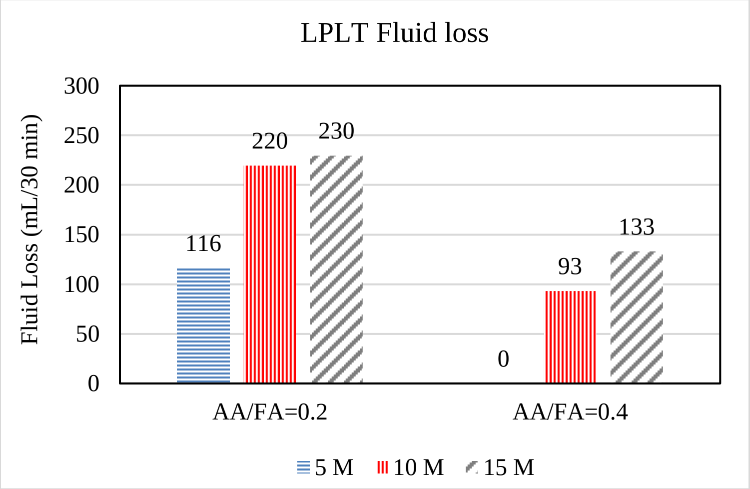


Figure 7. Fluid loss for different AA/FA ratios and different sodium hydroxide concentrations for SS/SH = 1

These results show that alkaline activator to flyash ratios have an inverse relationship with fluid loss values. As per API, a good cement should have less than 100 ml of fluid loss in 30 minutes. Only 93 ml of fluid loss in 30 minutes was shown by geopolymer slurry with an AA/FA ratio of 0.4, a NaOH concentration of 10 M and an SS/SH ratio of 1. The reason for the reduction of fluid loss is due to the huge availability of silicates (Si). These silicates react with aluminum (Al) and form alumino-silicate gels (Suppiah et al., 2016). This result indicates that this formulation of geopolymer slurry has a lower fluid loss value according to API, and it does not require any fluid loss additive. Also, this geopolymer slurry can retain its properties since it has a low fluid loss compared to Portland cement, which would reduce the probability of having channels inside the cement.

3.4. OPTIMIZED GEOPOLYMER SLURRY

Based on the results of density, rheology, compressive strength and fluid loss test, an optimized geopolymer slurry was selected (i.e an AA/FA ratio of 0.4, an NaOH concentration of 10 M, and a SS/SH ratio 1). Density and rheology were the same for almost all cement slurries. Compressive strength of this optimized slurry was 67% higher than Portland cement. Also, it had fluid loss less than 100 ml/30 min, which as per API was excellent because there is no need to add any fluid loss additives. This lower fluid loss reduced the probability of having channels within the cement sheath. Stability tests were performed on this optimum formulation, and then it was compared with the results of Portland cement. Also, the other test results were compared with Portland cement, which are described later.

3.5. STABILITY TEST RESULTS

Stability of the optimum design and Portland cement was tested and compared by performing free fluids and sedimentation tests. To determine the free fluid, the optimized geopolymer and Portland cement were left for two hours in a 250 ml graduated cylinder. The volume of free fluid was measured after 2 hours. After the two hours, 5.7 ml of free fluid was found in Portland cement, whereas there was no sign of free fluid in the optimized geopolymer slurry (Figure 8). The free fluid portion of Portland cement was 2.28%. This result indicates that geopolymer can hold water, which will reduce the potential of having channels during cementing operations.

Figure 8. Free fluid test

Table 4 shows the results of the sedimentation test. The difference in density for the optimized geopolymer sample was 0.008 gm/cc, which is very low compared to 0.028 gm/cc for Portland cement. This indicates that there are no particles settling in the optimized geopolymer.

Table 4. Sedimentation test results

	Downgrade (mm)	**$\Delta\rho\ (\frac{gm}{cm^3})$**
Optimized Geopolymer	1.95	0.008
Portland Cement	3.30	0.028

4. COMPARISON BETWEEN THE OPTIMIZED GEOPOLYMER AND PORTLAND CEMENT

Rheological results of optimized geopolymer slurry and Portland cement slurry were plotted for the comparison (Figure 9). The geopolymer showed similar behavior in rheology as Portland cement. Table 5 shows a comparison between optimized geopolymer cement and Portland cement in terms of the results obtained from API tests.

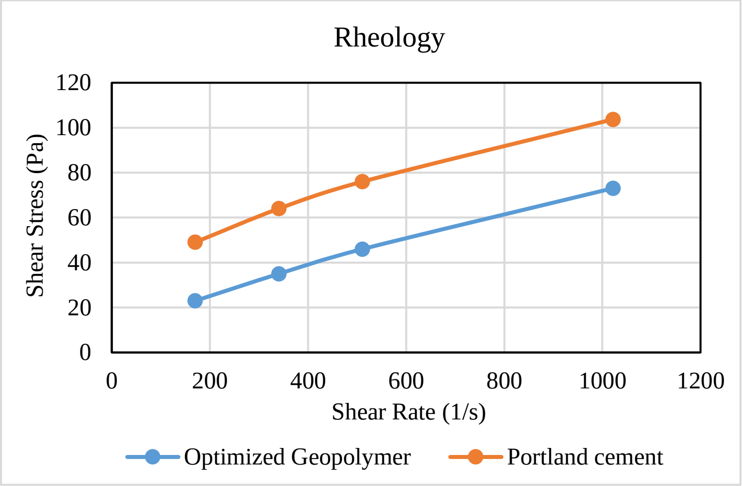


Figure 9. Comparison in rheological behavior of optimized geopolymer slurry and Portland cement slurry

Table 5. Comparison between Portland cement and optimized geopolymer cement

API tests	Optimized Geopolymer cement	Portland cement	API Recommendations
Density	14.7 ppg	17.2 ppg	14-17 ppg
PV	50 cp	46 cp	45-55
Strength	1195 psi	717 psi	>500 psi
LPLT fluid loss	93 mL/30 min	199 mL/30 min	<100 mL/30 min
Free fluid	0	5.7 mL	
Sedimentation	0.008 gm/cc	0.028 gm/cc	

The mentioned results in the table indicate that both cements have similar PV, although the density of geopolymer is slightly lower than Portland cement. Geopolymer has a 67% higher compressive strength than Portland cement. Thus, geopolymer can withstand harsher downhole conditions. The results also show that the optimized geopolymer has less fluid loss than Portland cement after 30 minutes, which is due to the alumino-silicate gels that formed as a result of the reaction between silicate (Si) and aluminum (Al). These results show that optimized geopolymer has the ability to retain its water which would reduce the probability of having channels inside the cement.

5. CONCLUSION

An optimum design containing an AA/FA ratio of 0.4, an NaOH concentration of 10 M, and a SS/SH ratio of 1 were obtained based on the results of the rheology, compressive strength, and fluid loss tests. This optimum design provides 67% higher compressive strength when compared to Portland cement. In addition, this system can retain its properties as it has a low fluid loss, which would reduce the probability of having channels within the cement sheath.

- Sodium hydroxide concentrations are inversely proportional to the plastic viscosity; as the sodium hydroxide concentration increases, plastic viscosity has a slight decrease.
- Sodium hydroxide concentrations positively affect the compressive strength for the AA/FA ratio 0.2, but one unusual trend was found in the AA/FA ratio of 0.4.

- An increase in sodium silicate to sodium hydroxide ratios results in a decrease in fluid loss, which is due to the alumino-silicate gels that formed due to the high availability of silicates.
- Stability tests indicate that there are no free fluids or particles settling for the optimized geopolymer.
- The optimized geopolymer has a 67% higher compressive strength than Portland cement.
- The optimized geopolymer has a lower fluid loss than Portland cement in 30 minutes.

NOMENCLATURE

kg/m^3 = Kilogram per meter cube.

psi = Pounds per square inch.

lb/gal = Pounds per gallon.

°C = Degree Celsius.

BWOC = By weight of cement.

V_{FF} = Volume of free fluids, ml.

V_i = Initial volume of cement, ml.

Φ = Free fluids content, vol%.

m = Mass of cement, gm, kg.

d_{rel} = Relative density, frac.

ρ = Gram per cubic centimeter, Pounds per gallon.

REFERENCES

Abdullah, Mohd Mustafa Al Bakri & Kamarudin, H & Binhussain, Mohammed & Razak, Rafiza & Yahya, Zarina. (2012). Effect of Na2SiO3/NaOH Ratios and NaOH Molarities on Compressive Strength of Flyash-Based Geopolymer. Aci Materials Journal. 109. 503-508.

Al-Bakari, A. M., Kareem, A., & Myint, S. (2012). Optimization of Alkaline Activator/Fly Ash Ratio on the Compressive Strength of Flyash-Based Geopolymer. Kanger: University Malaysia Perlis (UniMAP).

API RP 10B-2, Recommended Practice for Testing Well Cements, second edition. 2012. Washington, DC: API.

API Specification 10A/ISO 10426-1, Specification for Cements and Materials for Well Cementing, Twenty-third Edition.

ASTM C 618, Standard Specification for Coal Flyash and Raw or Calcined Natural Pozzolan for Use in Concrete, 100 Barr Harbour Dr. P.O. box C-700 West Conshohocken, Pennsylvania United States

Bakkali, H., Ammari, M., Frar, I., NaOH Alkali-Activated Class F Flyash: NaOH molarity, Curing Conditions and Mass Ratio Effect. J. Mater. Environ. Sci. 2016. Morocco. Vol.7 No.2 (397-401).

Bois, A.-P., Garnier, A., Galdiolo, G., & Laudet, J.-B. (2012, June 1). Use of a Mechanistic Model To Forecast Cement-Sheath Integrity. Society of Petroleum Engineers. doi:10.2118/139668-PA.

Davidovits, J. (1994, October). Properties of geopolymer cements. In First international conference on alkaline cements and concretes (Vol. 1, pp. 131-149). Kiev State Technical University, Ukraine: Scientific Research Institute on Binders and Materials.

Khalifeh, M., Saasen, A., Vralstad, T., & Hodne, H. (2014, April 2). Potential Utilization of Geopolymers in Plug and Abandonment Operations. Society of Petroleum Engineers. doi:10.2118/169231-MS.

Kong DLY, Sanjayan JG (2008). Damage behaviour of geopolymer composites exposed to elevated temperature. Cement and Concrete Composites, Volume 30, Issue 10: pg986–991.

Liu, X., Aughenbaugh, K., Lee, H., Nair, S., & Oort, E. van. (2017, April 3). Geopolymer - Synthetic Based Mud Hybrid Cements for Primary Cementing and Lost Circulation Control. Society of Petroleum Engineers. doi:10.2118/184558-MS.

Nasvi, M. C. M., Ranjith, P. G., & Sanjayan, J. (2012, January 1). Comparison of Mechanical Behaviors of Geopolymer And Class G Cement as Well Cement At Different Curing Temperatures For Geological Sequestration of Carbon Dioxide. American Rock Mechanics Association.

Rattanasak U., Chindaprasirt P., Miner. Eng., 22 (2009) 1073-1078.

Salehi, S., Ali, N., Khattak, M. J., & Rizvi, H. (2016, September 26). Geopolymer Composites as Efficient and Economical Plugging Materials in Peanuts Price Oil Market. Society of Petroleum Engineers. doi:10.2118/181426-MS.

Salehi, S., Khattak, M. J., Ali, N., & Rizvi, H. R. (2016, March 1). Development of Geopolymer-based Cement Slurries with Enhanced Thickening Time, Compressive and Shear Bond Strength and Durability. Society of Petroleum Engineers. doi:10.2118/178793-MS.

Sugumaran, M. (2015, October 20). Study on Effect of Low Calcium Flyash on Geopolymer Cement for Oil Well Cementing. Society of Petroleum Engineers. doi:10.2118/176454-MS.

Suppiah, R. R., Rahman, S. H. A., Irawan, S., & Shafiq, N. (2016, November 12). Development of New Formulation of Geopolymer Cement for Oil Well Cementing. International Petroleum Technology Conference. doi:10.2523/IPTC-18757-MS.

UEHARA, M. (2010, March 03). New Concrete with Low Environmental Load Using the Geopolymer Method. Retrieved from https://www.jstage.jst.go.jp/article/rtriqr/51/1/51_1_1/_article

III. ASSESSING THE PERFORMANCE OF CLASS C FLYASH-BASED GEOPOLYMER CEMENT IN CO_2 ENVIRONMENT AS A POTENTIAL ALTERNATIVE CEMENT

ABSTRACT

Long-term storage of carbon dioxide (CO_2) inside depleted reservoirs can help reduce the impact of greenhouse gas emissions. Portland cement has been shown to degrade significantly during long-term contact with CO_2. This research aims to provide a new environmentally friendly Class C flyash-based geopolymer cement as a potential alternative of Portland cement for CO_2 storage wells. This was achieved by comparing mechanical degradation of Portland cement and Class C flyash-based geopolymer cement in a CO_2 environment. A specially designed setup was made in order to create an in-situ high pressure, high temperature CO_2 environment. Seventy-two cores of Portland cement and Class C flyash-based geopolymer cement were cured at atmospheric pressure and 110 ºF for three days. For each experiment, three cores were placed inside the designed setup filled with water and then CO_2 was injected. Experiments were conducted at 500 and 1500 psi CO_2 injection pressures for 3, 7 and 14 days. After all the experiments, pH of water was measured, the cores were visually examined and then density and compressive strength were measured. This research examined the effect of both gaseous and supercritical CO_2 exposure duration, and CO_2 partial pressure on both types of cement at constant temperature. The CO_2 reacted with the water in the vessel and formed carbonic acid, which reduced the water pH to 6.8-6.9. Millimeter-sized crystals of $CaCO_3$ were observed on the surface of Portland cement cores after the CO_2 exposure. Surface of geopolymer cement cores was not changed much after the exposure. No significant change in density was

observed, however. For the 500-psi pressure, after three days of exposure there was no noticeable reduction in compressive strength for both types of cement. But, as the exposure time increased, Portland cement showed an increase in strength reduction percentage, which reached 20% reduction in compressive strength after 14 days of 500 psi CO_2 exposure. Interestingly, Class C flyash-based geopolymer cement showed no reduction in compressive strength when using 500 psi pressure. At 1500 psi pressure, when CO_2 was in supercritical state, Portland cement showed an even more significant strength reduction percentage, reaching 41.54% strength reduction after 14 days of exposure. Class C flyash-based geopolymer cement had a much smaller strength reduction of 12.06% after 14 days of exposure. This research compared the mechanical degradation of Portland cement and Class C flyash-based geopolymer cement in a high-pressure high-temperature CO_2 environment. This research aims to provide the oil and gas industry with a new environment-friendly Class C flyash-based geopolymer cement as a potential alternative to Portland cement for geological CO_2 storage wells.

1. INTRODUCTION

Long-term underground storage of carbon dioxide is an effective solution to provide safe and low-cost CO_2 sequestration (Gielen et al. 2003, and Sarmiento et al. 2002). Marchetti introduced the concept of carbon capture and storage in 1977. Three main types of storage medium are available to store carbon dioxide: 1. Depleted oil and gas reservoir, 2. Deep saline aquifer, and 3. Unmineable coal beds. It should be noted that these reservoirs need to be at depths higher than 800 m to store carbon dioxide in supercritical state as this allows storage in a relatively very small volume. Also, it is necessary to only allow less than 0.1%/year leakage rate to make sequestration processes successful. (White et al. 2003)

Leakage path can be natural through faults or open fractures, or it can be artificially made through cap rock or wells drilled in that formation (Bachu and Bennion 2009). Portland cement is used to cast wells in order to provide integrity to wells and to mitigate leakage from the production zones. Thus, primary cementing is very important to provide long-term zonal isolation and to prevent gas leakage. However, carbon dioxide can chemically react with Portland cement to form calcium carbonate and amorphous silica, which leads to formation of micro-cracks, reduction in strength, and ultimately loss of zonal isolation. This effect can be reduced by reducing surface area of cement that can be contacted by CO_2 by proper primary cementing job, reducing the materials inside the cement matrix that can chemically react with CO_2.

In this research, Class H Portland cement was used. It mainly consists of 30% dicalcium silicate (C2S), 50% tricalcium silicate (C3S), 5% tricalcium aluminate, and 12% tetra calcium aluminoferrite (Kutchko et al. 2008, Nelson 1999). Upon hydration the main product form is 70% C-S-H gel and 15-20% Portlandite ($Ca(OH)_2$) (Kutchko et al. 2008). The main binding material in the hydrated cement is C-S-H. Chemical reactions involved in Portland cement carbonation are extensively discussed in Task 1.

Carbonation of cement paste ultimately leads to an increase in the density as $CaCO_3$ gets deposited, a decrease in strength, and an increase in porosity/permeability that can pose the risk of gas migration from the cement matrix (discussed thoroughly in Task 1).

Previous studies observed this behavior of the cement and provided some solutions to make cement CO_2 resistant:

1. Reduce the amount of Portlandite ($Ca(OH)_2$), and change the structure of C-S-H.
2. Reduce water/cement ratio to reduce porosity/permeability of cement

Many researchers conducted the experiments by adding the pozzolanic material such as flyash or silica flour to the cement. Pozzolans are generally introduced to reduce the amount of Portlandite. Also, pozzolans mainly react with $Ca(OH)_2$ to form secondary C-S-H, thus reducing the Portlandite content. Class F flyash is the most common type of pozzolan used in the cement. Santra et al. (2009) did an experiment with five different cement mixes containing (16.7, 28.6, 37.5, 44.4, 50) % of flyash with Portland cement. The results found that due to the absence of $Ca(OH)_2$ the effect of carbon dioxide on cement was less instead of having higher rate of penetration. Kutchko et al. (2009) conducted an experiment with cement mix containing flyash and found out that although after total carbonation, this chemical alteration did not reflect in the mechanical alteration as was found with the Class H cement. Zhang and Talman (2014) conducted an experiment by using lightweight cement and normal weight cement. Lightweight cement was prepared by adding of 1% sodium metasilicate to the flyash: cement mix and normal weight cement was prepared by addition of 2% bentonite in the flyash: cement mix. The results showed that the normal weight cement experienced no reduction in durability or permeability. Zhang (2014) conducted the carbonation experiment with the same proportion of flyash: cement which was used by kutchko (2009) but with different experimental conditions. They found the cement mix containing flyash performed better in the CO_2 environment. Thus, flyash was found to increase performance of cement in CO_2 environment. Till now, no one has used 100% flyash based geopolymer cement and also, only class F flyash was used as an additive in the previously-mentioned studies.

In this research, 100% Class C flyash-based geopolymer cement was used and compared with the Portland cement. Class C flyash differs from class F in chemical composition and is mentioned below in the description of materials. Class C flyash provides early strength which can be beneficial in the CO_2 environment. Flyash is a byproduct of the coal combustion process and is basically a waste material. Flyash is mainly composed of alumina and silica, which when combined with alkaline solution undergoes a geopolymerisation process. This convert’s flyash into a binder, mainly an alumino-silicate gel, which when mixed with water behaves as a cement. Huge amounts of carbon dioxide are emitted in the manufacturing process of Portland cement. This is not the case for flyash-based geopolymer cement. Class C flyash-based geopolymer cement is environment friendly and cost effective. Previous studies performed experiments with flyash-based geopolymer cement and found that this cement has higher compressive and shear strength, better durability in acidic environment, lower chemical shrinkage than Portland cement (Sugumuran et al. 2015, Salehi et al. 2016). Thus, this cement was selected to provide as a potential alternative to Portland cement for CCS applications.

The durability of class C flyash-based geopolymer cement in CO_2 environments of this was measured by performing a carbonation experiment on this cement. Carbonation of both types of cement was indirectly measured by a change in the density, visual degradation, and change in the compressive strength. Carbonation experiments were carried out under static conditions as this was most realistic representation of downhole carbonation. Two pressure conditions of 500 and 1500 psi were used to see the effect of pressure. In these two conditions carbon dioxides behaved as a gas and as a supercritical. Thus, the effect on CO_2's physical state was observed. The tests were carried out for 3, 7, and 14 days to see the effect of exposure duration on the carbonation of cement.

2. EXPERIMENTAL DESCRIPTION

2.1. MATERIALS

2.1.1. Portland Cement. Class H Portland cement, obtained from Haliburton Company, was used in this study. X-ray fluorescence (XRF) was used to determine the elemental composition of Class H Portland cement. The results from this test are listed in Table 1.

Table 1. The elemental compositions of Class H cement

Element	Concentration (%)
SiO_2	20.36
Al_2O_3	3.17
Fe_2O_3	6.19
CaO	65.72
MgO	1.32
SO_3	2.26
K_2O	0.43
Other components	0.55

2.1.2. Flyash. A by-product of burning pulverized coal, flyash has two types: Class C and Class F. ASTM (American society for Testing and Materials) classifies these two types on the bases of lime (CaO) content. Class C flyash has lime content greater than 20%

while Class F has a lime content lower than 20%. XRF scanning on the obtained flyash helped in determining the elemental composition and type. The results from this test are listed below in Table 2.

Table 2. The elemental compositions of Class C flyash

Element	Concentration (%)
SiO_2	28.93
Al_2O_3	14.82
Fe_2O_3	6.40
CaO	39.80
MgO	4.86
Na_2O	1.10
K_2O	0.56
Other components	2.63

The results of XRF scanning showed that the amount of lime (CaO) was higher than 20%, which according to the ASTM, is Class C flyash.

2.1.3. Sodium Hydroxide. Obtained sodium hydroxide powder was 96 % pure. One liter of 400 gm of sodium 10 M sodium hydroxide solution was prepared by mixing 400 gm of sodium hydroxide pellets with distilled water. This 10 M solution was further mixed with sodium silicate to make an alkaline activator for geopolymer slurry preparation.

2.1.4. Sodium Silicate. Sodium silicate was used, which is also known as water glass. Sodium silicate is an important material in providing another source of silicate (other than flyash) to the mixture.

2.1.5. Carbon Dioxide. A CO_2 cylinder with a pressure of 1000 psi was used as a source of carbon dioxide.

2.2. CEMENT MIXING AND CURING

Class H Portland cement slurry was prepared as per API procedure. Water/cement ratio was taken to be 0.38, which follows API specification 10A (API 2010). Dry cement was added to the water while mixing at low speed for 15 seconds; mixing then continued for 35 seconds at high speed. The mix design for geopolymer cement was selected from our previous work. Optimum mix design (Table 3) for Class C flyash-based geopolymer cement for oil and gas well cementing applications was found in our previous study (Ahdaya and Jani, 2018). However, all the experiments in that study were at room temperature and atmospheric pressure. Before mixing geopolymer cement slurry, an alkaline activator was prepared by mixing 10M NaOH and Na_2SiO_3. First, water and flyash were mixed in the blender for 10 seconds at low speed. Then an alkaline activator was added in the mixture while mixing at low speed for 10 seconds. Mixing continued for 30 seconds at high speed.

Table 3. Optimum mix design of Class C flyash-based geopolymer cement (Ahdaya and Jani 2018)

Total Water	AA/FA	Flyash	Na2SiO3/NaOH	NaOH Solution	Na2SiO3 Solution	Water
33%	0.4	600 gm	1	120 gm	120 gm	193.2 gm

After mixing all the cement slurries were poured into a 2 * 2 in. cylindrical mold and the placed inside a water bath at atmospheric pressure and 110^{o}F. The cement paste was allowed to set for 3 days before each experiment to gain 40% of its full strength (Neville 2012). The cement cores were strong enough to avoid breaking during demolding but were also weak enough to allow quick chemical reactions due to CO_2 attack (Qingyun

Li et al. 2015). This shorter curing period can resemble the cement already containing CO_2 that is used in wells drilled in a reservoir (Garnier et al. 2010).

2.3. EXPERIMENTAL SETUP AND PROCEDURE

A specially designed setup (Figure 1) was used to create an in-situ CO_2 environment. Two accumulators, water bath, CO_2 cylinder and a syringe pump were used in this experimental setup. Syringe pump was used to increase the pressure of CO_2 to the desired value. Pressure gauges were installed to monitor pressure changes. One pressure relief valve was installed to bleed of CO_2 pressure at the end of the experiment. This experiment was repeated 12 times, in which 6 experiments were conducted at 500 psi pressure while other were conducted at 1500 psi CO_2 pressure at 110^{o}F for 3,7 and 14 days. The procedure followed for each experiment is described below:

1. A total of six samples were prepared for each run. Out of six, three samples were fully immersed in water inside accumulator 2 for the CO_2 exposure. Water is used rather than saline (1% NaCl) to provide more extreme conditions as CO_2 is more soluble in water (Spycher and Pruess 2005).
2. Accumulator 2 was kept inside the water bath to provide temperature. Temperature was kept constant at 110^{o}F for all the experiments.
3. CO_2 was first injected inside accumulator 1 from CO_2 cylinder. Pressure of CO_2 was increased to desired level (500 and 1500 psi) using syringe pump.
4. Pressurized CO_2 was injected inside accumulator 2 to create CO_2 environment for cement cores. After the exposure time, pressure was reduced slowly to avoid breaking of cement due to sudden pressure drop.

5. Samples were taken out of the accumulator 2 and dried gently before any further experiments.

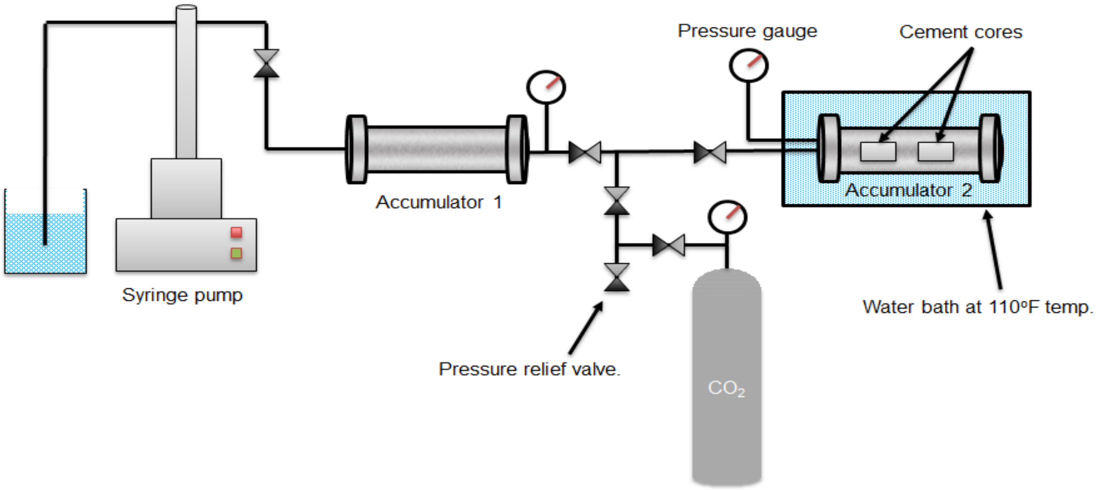


Figure 1. Experimental setup

2.3.1. HPHT Exposure Conditions. Two types of exposure conditions were used in this research to mimic the effect of increasing CO_2 partial pressures, CO_2 physical state on both types of cement. At 500 psi and 110°F, CO_2 will behave like gas, while at 1500 psi and 110°F CO_2 will be in supercritical state. In both exposure conditions, CO_2 will dissolve in water and reduce the pressure. Thus, pressure was regularly increased to desired value.

2.3.2. pH of Water. pH of water was measure by pH meter before the injection of carbon dioxide inside the setup. After the exposure time pH of water was again measured to see the changes.

2.3.3. Visual Degradation. Exposed cores were compared with unexposed cores in terms of color change, texture change, and other visual changes.

2.3.4. Density. Change in the bulk density of cores was measured before and after the exposure. First, the dry weight of the core was measured, then the core was submerged in water to measure its weight inside the water. The below mentioned equations were then used to calculate the bulk density.

The density of every segment was calculated using the following equations:

$$\rho = \frac{Wt_a}{Volume} \tag{1}$$

$$V = \frac{Wt_a - Wt_w}{\rho_w} \tag{2}$$

Where ρ is the density in gm/cm^3, Wt_a is the weight in air in gm, Wt_w is the weight in water in gm, and ρ_w is the water density in gm/cm^3.

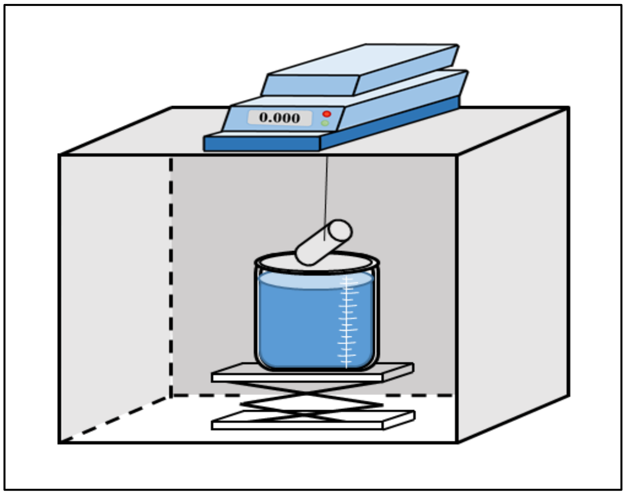


Figure 2. Mass measurement setup

2.3.5. Compressive Strength. To measure the compressive strength, force was applied axially on the cores till it failed or was crushed. Compressive strength of exposed and unexposed cores was measured in order to see the reduction in strength due to CO_2 exposure. First every core was wiped dry using paper towels to maintain their moisture content. Then, a Vernier caliper was used to measure the diameter and height of each core, and the minimum surface area was calculated. Uniaxial force was applied on the cores inside the hydraulic press until they broke. That force was divided by the contact area to calculate the compressive strength of the specimens.

3. RESULTS AND DISCUSSION

Cement cores were exposed to CO_2 at two different CO_2 partial pressures 500 and 1500 psi at 100 deg F in static condition. The results from each test is discussed and compared between Portland cement and Geopolymer cement.

3.1. pH OF WATER

Injected carbon dioxide is dissolved in water to form carbonic acid, as stated in Equation (1). This reduces the pH of water. Figure 3 and 4 shows pH of water before and the injection 500 and 1500 psi CO_2 for both types of cement cores. The reduction of pH was observed in Figure 3 and 4. Water is used in this research to provide a more aggressive environment, Since CO_2 is more soluble in water than in brine (Spycher and Pruess 2005, Rimmele and Barlet-Gouedard 2008). In both cases, pH was reduced to around 6.8-7, whereas Portland cement has a pH above 12.5 (Taylor et al. 1997, Neville et al. 2012, Rendell et al. 2002). This will cause equilibrium in the system, which will lead to diffusion of carbonic acid inside the cement matrix (Qingyun li et al. 2015).

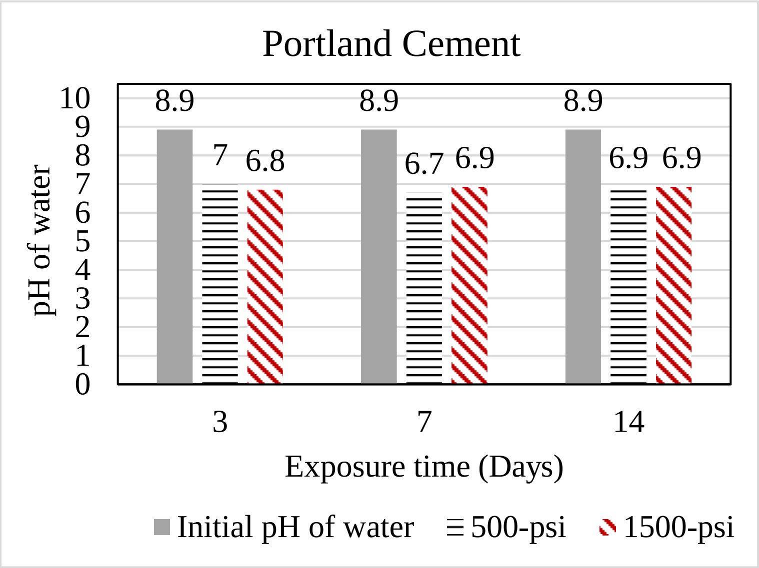


Figure 3. pH of water before and after the injection of 500 psi and 1500 psi of CO_2 pressure for Portland cement

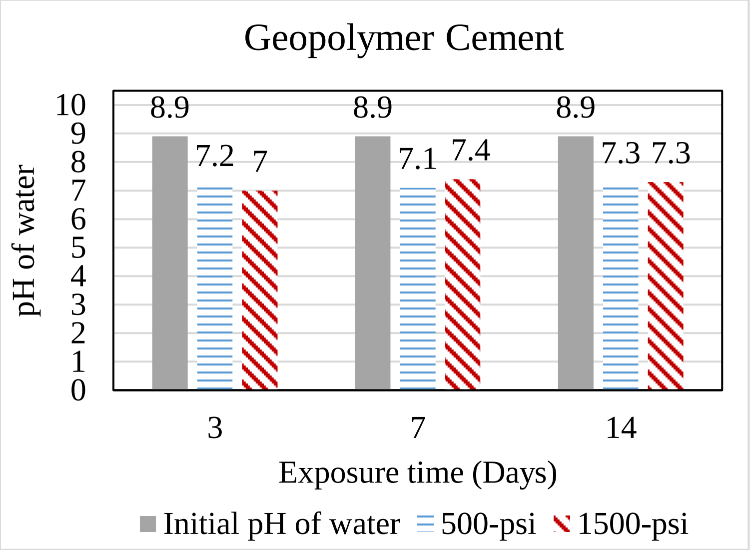
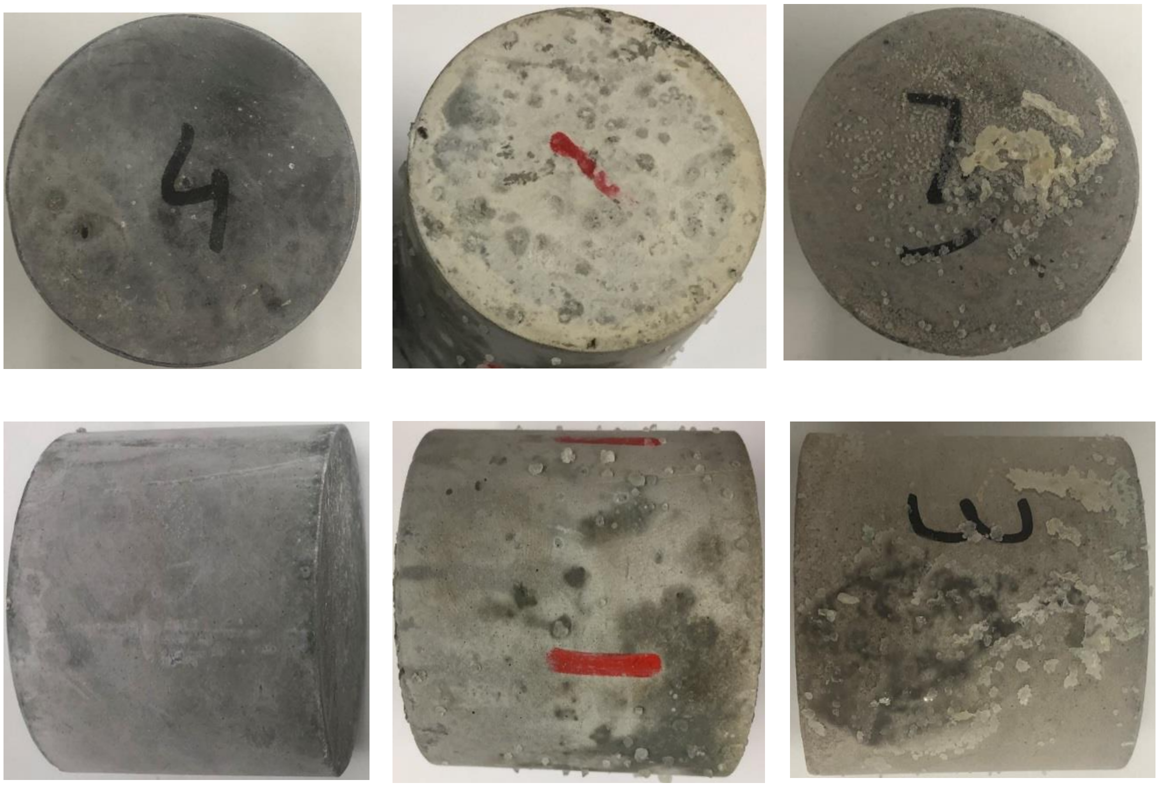


Figure 4. pH of water before and after the injection of 500 psi and 1500 psi of CO_2 pressure for Class C flyash-based geopolymer cement

3.2. VISUAL DEGRADATION

3.2.1. Portland Cement. Millimeter-sized precipitates of calcium carbonate ($CaCO_3$) were observed on the surface of cores. Figure 5 shows the comparison between surfaces of Portland cement cores after exposure to CO_2 partial pressures of 500 psi and 1500 psi. The amount of precipitates increases with an increase in pressure. The same effect was observed in previous studies as well (G. Rimmele and Barlet-Gouedard 2008).



(a) **(b)** **(c)**

Figure 5. Images of the surface of Portland cement before and after 14 days of CO_2 exposure (a) unexposed cores (b) after 500 psi exposure (c) after 1500 psi exposure

3.2.2. Geopolymer Cement. Almost no change in the surfaces of geopolymer cement cores was observed before and after exposure to both pressures (Figure 6). At 1500 psi, only a small amount of precipitates was observed. This suggest that geopolymer cement does not react with CO_2 or carbonic acid.

(a) **(b)** **(c)**

Figure 6. Images of the surface of geopolymer cement before and after 14 days of CO_2 exposure (a) unexposed cores (b) After 500 psi exposure (c) after 1500 psi exposure

3.3. DENSITY OF CEMENT

Due to pH inequilibrium between cement pore water (pH = 13) and the aqueous solution (pH = 6) carbonic acid (H_2CO_3) diffuses inside the cement matrix and dissolves portlandite ($Ca(OH)_2$) to form calcium carbonate ($CaCO_3$). Shen et al. (1989) showed that formation of $CaCO_3$ leads to volume expansion, as the molar volume of $CaCO_3$ is higher than $Ca(OH)_2$. This will increase the density of the material, as available pore space inside the cement matrix is filled by $CaCO_3$.

Figure 7, 8, 9 and 10 shows difference in density observed in Portland and geopolymer cement cores after CO_2 exposure. Figure 7 and 8 shows results of Portland cement for 500 and 1500 psi CO_2 exposure. Figure 9 and 10 represents geopolymer cement results for 500 and 1500 psi CO_2 exposure. At 500 psi and 110 However, no significant increase in density was observed in Portland cement or Geopolymer cement after CO_2 exposure (Figure 7, 8, 9 and 10). In 2014, Zhang and Talman observed the same behavior for the Class G neat Portland cement as the density remained unchanged. However, Barlet-Gouedard and Rimmele (2006) observed that density was increased from 16 ppg to 18 ppg after the first week of exposure in CO_2 saturated water. This is probably due to the higher temperature (90°C) and higher pressure (4061 psi) conditions used in their experiments. Class C flyash-based geopolymer cement showed the same result as Portland cement before and after the exposure.

3.4. COMPRESSIVE STRENGTH OF CEMENT

Strength measurement is considered an indirect method of ensuring well integrity. Longer exposure of cement to CO_2 environment leads to dissolution of the main cement binding phases ($Ca(OH)_2$ and C-S-H), and the dissolution of carbonation product $CaCO_3$ (As shown earlier in the chemical reactions). This will decrease the compressive strength of the cementitious material and can jeopardize the effectiveness of well plugging.

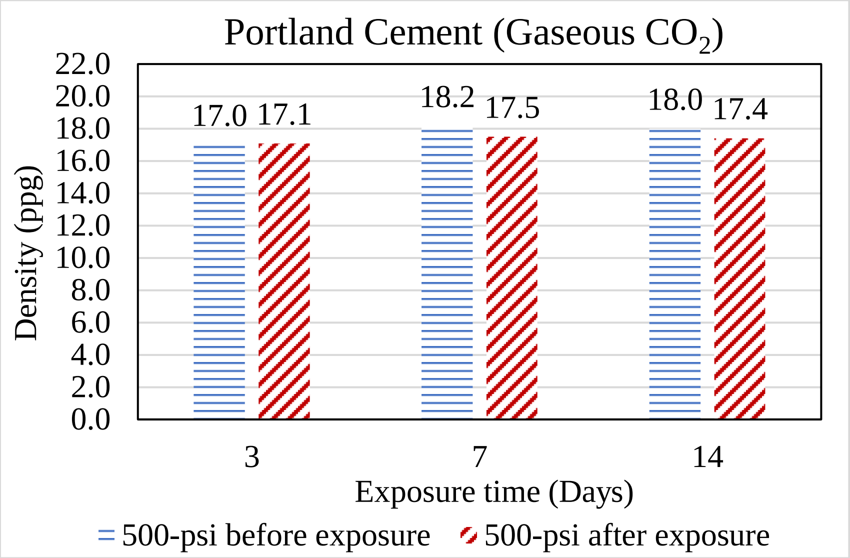


Figure 7. Changes in the density of Portland cement before and after 500 psi CO_2 exposure for 3, 7, and 14 days

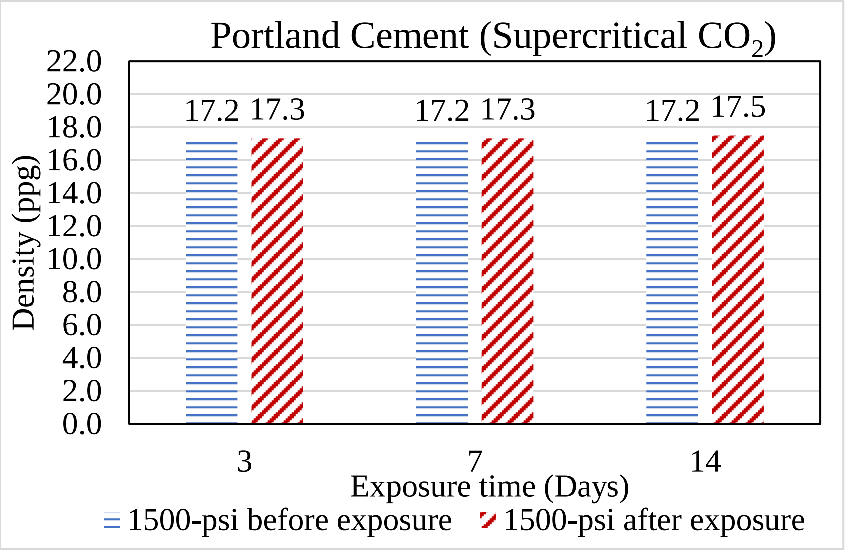


Figure 8. Changes in the density of Portland cement before and after 1500 psi CO_2 exposure for 3, 7, and 14 days

$CaCO_3$ has a higher molar volume than $Ca(OH)_2$. Thus, formation of $CaCO_3$ will cause volum expansion, since there is less available space, it will result in higher stress, which could result in micro cracks inside the cement matrix and ultimately lead to

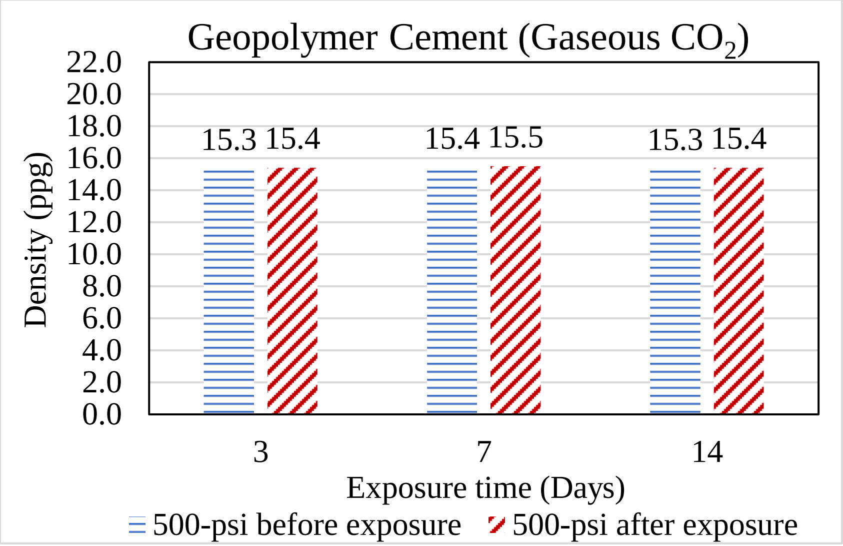


Figure 9. Changes in the density of class C flyash-based geopolymer cement before and after 500 psi CO_2 exposure for 3, 7, and 14 days

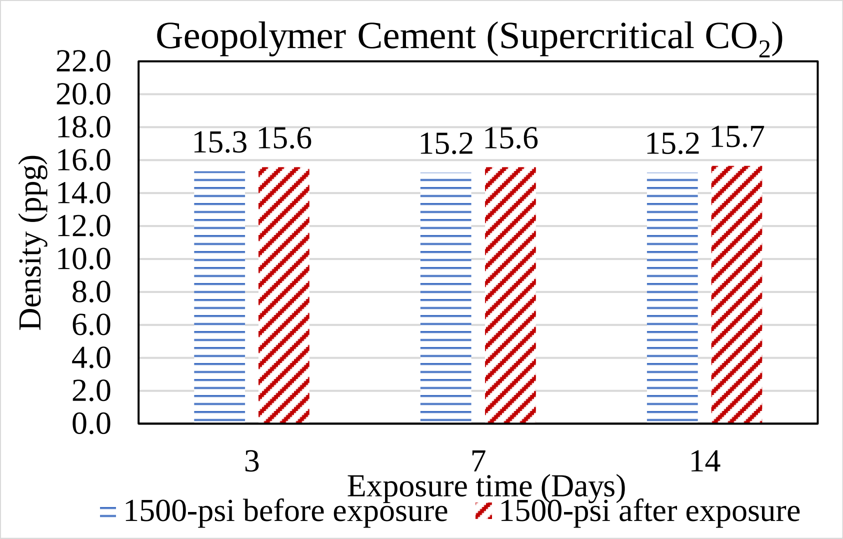


Figure 10. Changes in the density of class C flyash-based geopolymer cement before and after 1500 psi CO_2 exposure for 3, 7, and 14 days

reduction of strength. Table 4 below shows compressive strength of Portland cement and geopolymer cement without any exposure at different durations. It is clear from the Table 4 that Class C flyash-based geopolymer has very low compressive strength compared to

Class H neat Portland cement. In this research, the mix design for geopolymer from our previous study was used. All the experiments in that study were conducted at room temperature and atmospheric pressure. Experiment was performed to investigate the effect of curing temperature on the strength of Class C flyash-based geopolymer cement. It was found that with an increase in curing temperature, the strength of Class C flyash-based geopolymer was decreased. However, it was still above the acceptable API range of 500 PSI for well plugging purposes. Comparisons were made between the strength of exposed and unexposed cores; unexposed cores were kept in the water bath at all times, whereas exposed cores were kept inside the water bath for the first three days and then kept inside the accumulator for CO_2 exposure.

Table 4. Compressive strengths of both cement without CO_2 exposure cured in 110^{o}F and atmospheric pressure for different durations

Total Curing time (Days)	6	10	17
Cement type	Strength (psi)	Strength (psi)	Strength (psi)
Portland Cement	5111	5850	6773
Geopolymer Cement	1464	1628	1733

Compressive strengths of Portland cement and geopolymer cement were measured after the exposure. The strength results of cement cores after exposure of 500 and 1500 psi CO_2 pressure for 3, 7, and 14 days were then plotted in graph with the strength results of cement cores without exposure (Figure 11, 12, 13, and 14). Portland cement clearly shows strength reduction after exposure to CO_2 environment (Figure 11 and 13). Geopolymer cement shows very less strength reduction than Portland cement (Figure 12 and 14). The strength reduction percentages were calculated from these graphs and plotted to further analyze effects of increased CO_2 partial pressure, exposure time, and physical state of CO_2 on both types of cement.

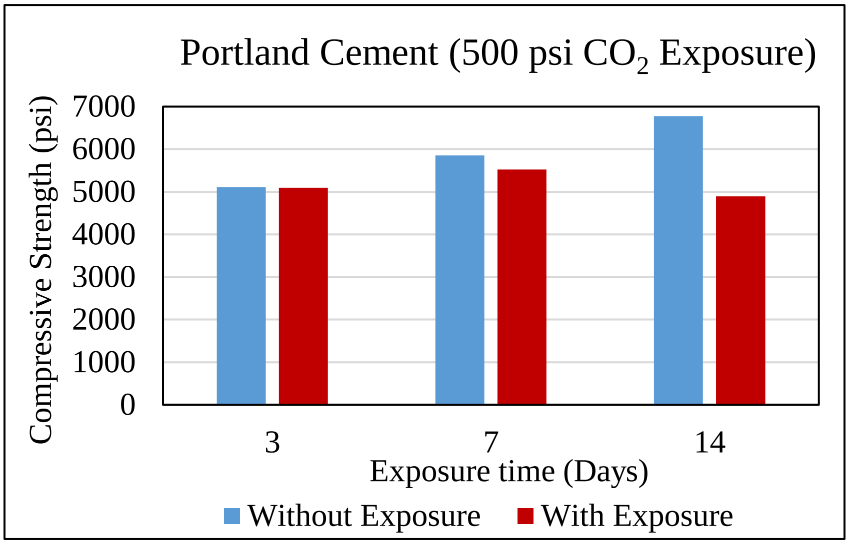


Figure 11. Compressive strength of Portland cement before and after 500 psi CO_2 exposure for 3, 7, and 14 days

Figure 15 and 16 shows that increased CO_2 partial pressure increases the strength reduction percentage in both kinds of cement. Increased pressure changes physical state of the CO_2 and changes the solubility in water. Figure 15 shows that a 41.54% reduction in strength was observed at a 1500 psi CO_2 partial pressure whereas only a 27.77% reduction was observed at a 500 psi CO_2 partial pressure after 14 days of exposure. Thus, degradation of the cement from exposure to CO_2 depends on the CO_2 partial pressure, which was confirmed by many past studies. These results give us an idea that an increase in the CO_2 injection pressure inside the geological reservoir will effectively changes the cement's integrity.

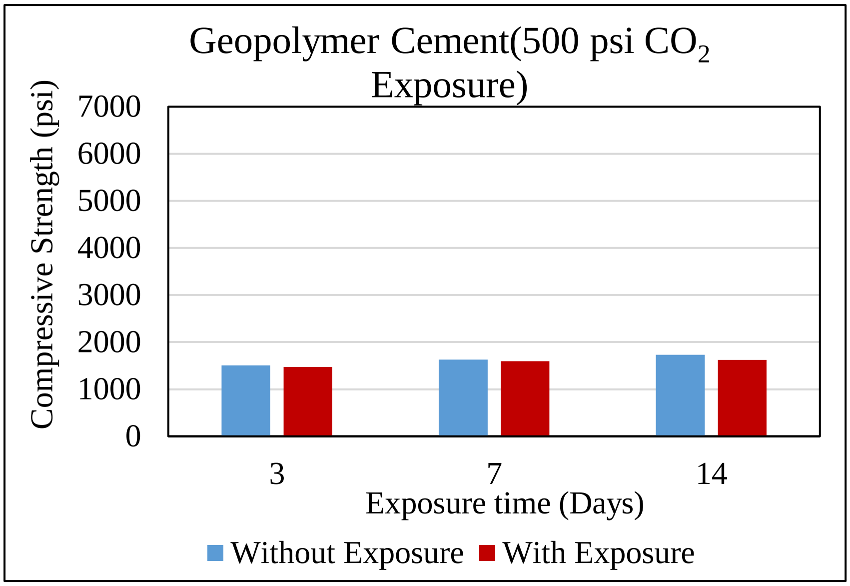


Figure 12. Compressive strength of geopolymer cement before and after 500 psi CO_2 exposure for 3, 7, and 14 days

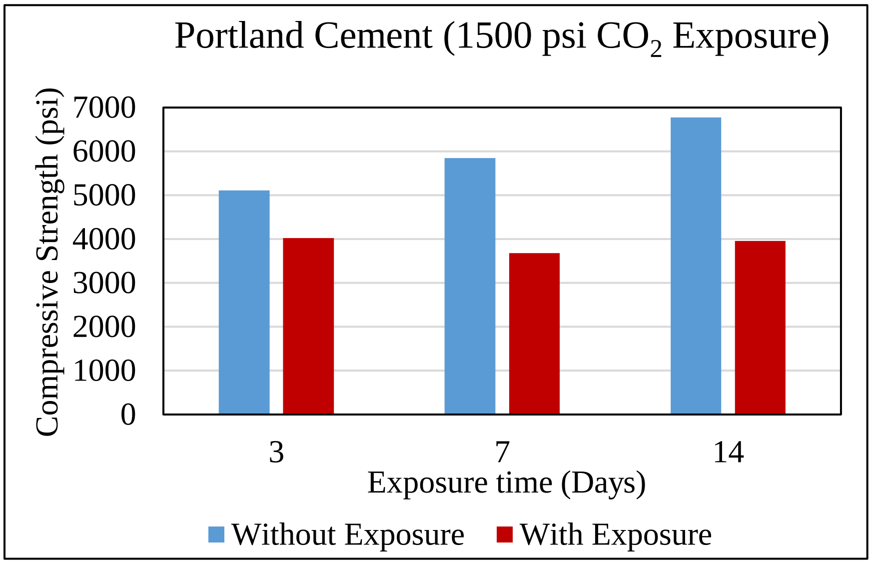


Figure 13. Compressive strength of Portland cement before and after 1500 psi CO_2 exposure for 3, 7, and 14 days

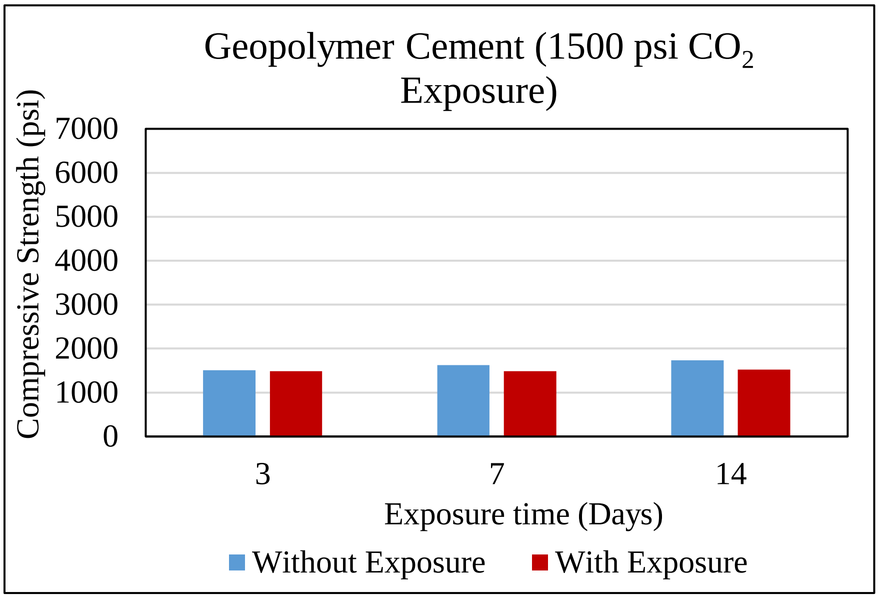


Figure 14. Compressive strength of geopolymer cement before and after 1500 psi CO_2 exposure for 3, 7, and 14 days

Referring to the results of Portland cement after CO_2 exposure in figure 15, it was observed that there was no significant reduction in geopolymer cement strength at 500 psi pressure after 3, 7 and 14 days of exposure and at 1500 psi pressure after 3 days of exposure (Figure 16). However, after 7- and 14-days of 1500 psi CO_2 exposure, geopolymer showed little reduction in strength (Figure 12). However, it was still less than Portland cement, as only a 12.06% reduction of strength was observed after 14 days of exposure compared to 41.54% in case of Portland cement. This shows that carbon dioxide does not affect geopolymer cement significantly.

After that, the effect of exposure time on the compressive strength of both types of cement was observed. It can be seen in Figure 17 and 18 that the duration of CO_2 exposure

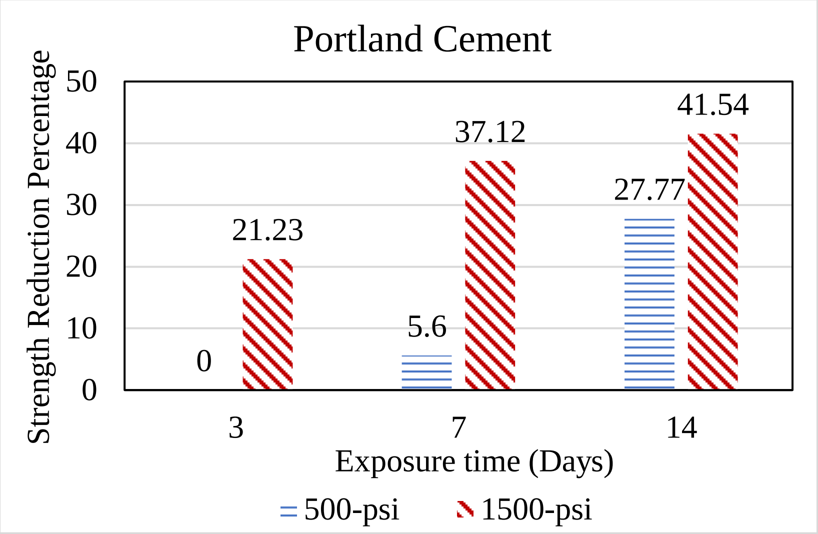


Figure 15. Effect of increased CO_2 partial pressure on the reduction of Portland cement's strength after 3, 7 and 14 days of CO_2 exposure

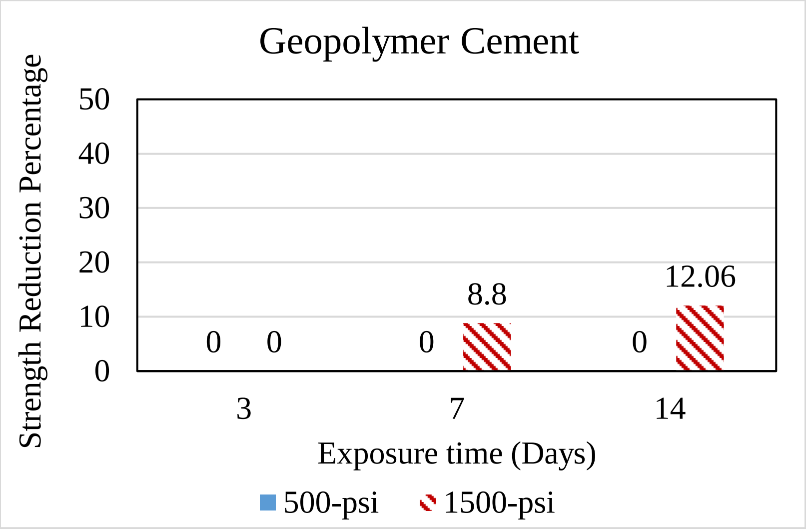


Figure 16. Effect of increase in CO_2 partial pressure on reduction of Class C flyash-based geopolymer cement strength after 3, 7 and 14 days of CO_2 exposure

affects the integrity of cement, as a huge amount of strength was lost in both cements when they were exposed for 14 days compared to 3 days. For the Portland cement the possible explanation is that after long-term exposure, precipitated $CaCO_3$ starts dissolving along with the main binding phase C-S-H, leaving amorphous silica in the structure (as explained in Equation 3 and 4). Amorphous silica is highly porous and lacks structure. Thus, it can cause a reduction of strength. Results for geopolymer show a very low reduction of strength (Figure 18). Figure 19 shows that the physical state of CO_2 also affects the cement's integrity. Gaseous CO_2 has less of an effect on strength than supercritical CO_2. In a geological reservoir, CO_2 will be in a supercritical state, and thus strength reduction will be greater.

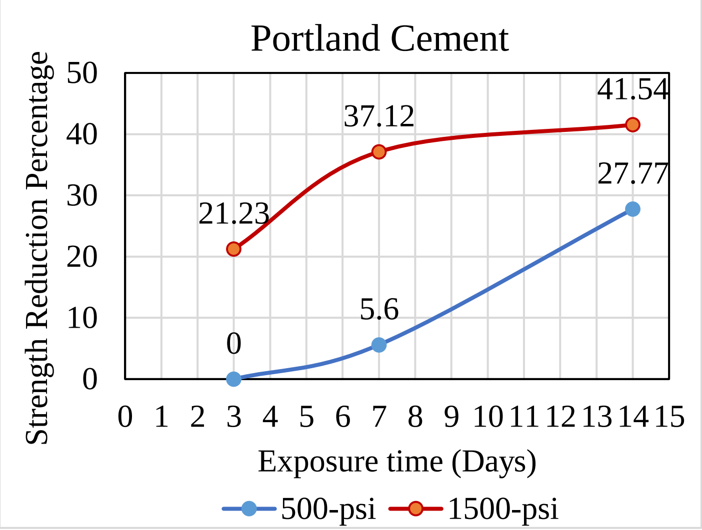


Figure 17. Effect of exposure time on reduction of Portland cement strength after 3, 7, and 14 days of CO_2 exposure

In 2006, Barlet-Gouedard and Rimmele observed a 33% reduction for Class G cement samples inside CO_2 saturated water. A 28% reduction in strength was observed by Moroni and Santra in 2009. Tarco and Asghari (2010) observed a 19.35% reduction of strength in CO_2 saturated brine. Qingyun (2015) observed a 93% reduction in compressive

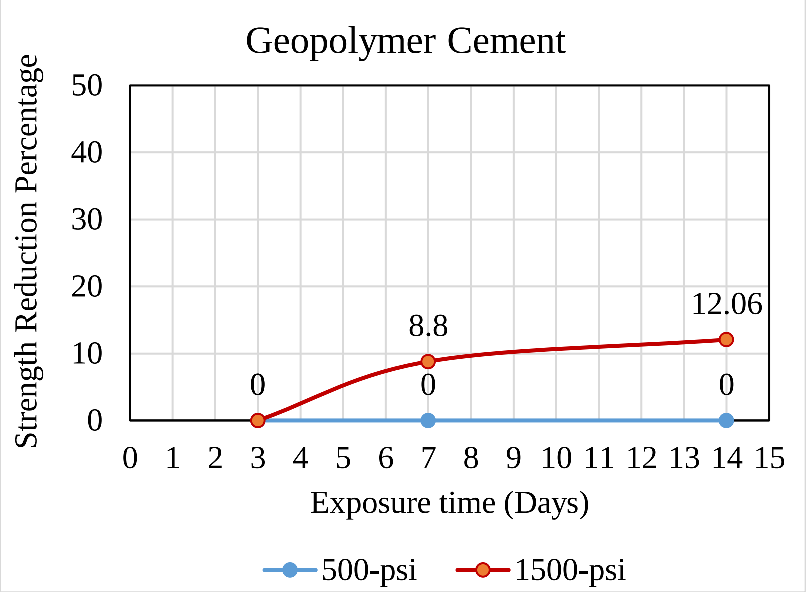


Figure 18. Effect of exposure time on reduction of Class C flyash-based geopolymer cement strength after 3, 7, and 14 days of CO_2 exposure

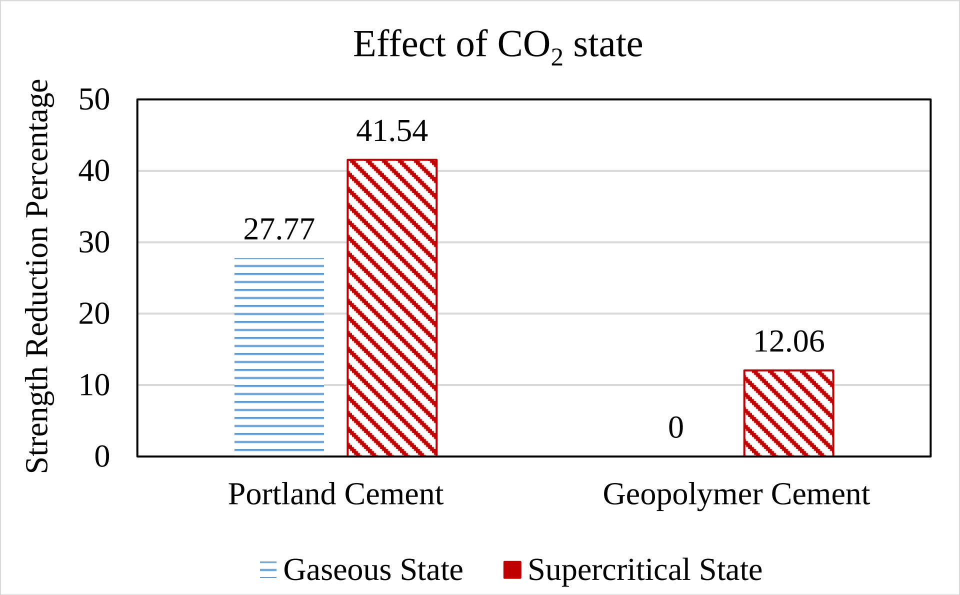


Figure 19. Effect of CO_2 physical state on reduction of Portland cement and Class C flyash-based geopolymer cement strength after 14 days of CO_2 exposure

strength. These studies compared the strength of samples before and after exposure; however, our comparison was performed between the same age samples with and without exposure. Also, previous studies used different CO_2 exposure conditions (pressure and temperature), curing time, curing condition and different types of cement than our experiment. Thus, comparison between our work and past studies was not possible.

4. CONCLUSIONS

A new cement class C flyash-based geopolymer cement was proposed for use in carbon capture and storage wells for the purpose of reducing the leakage of carbon dioxide into the atmosphere. Negligible visual degradation and minimal reduction in strength of geopolymer cement compared to Class H Portland cement suggest that it can be possible alternative to Portland cement for carbon dioxide storage operations. However, there is still much more work to do in this area. The following conclusions were made from this work:

- CO_2 dissolved in water to form carbonic acid, which decreased the pH of water to 6.8-7 and caused an inequilibrium in pH between cement and CO_2 saturated water leading to diffusion of CO_2 inside the cement matrix.
- No significant change in the density was observed in either type of cement, as was similarly observed by Zhang and Talman in 2014. However, Barlet-Gouedard and Rimmele in 2006 observed density changes after the first week of exposure which was probably due to the higher temperature (90°C) and higher pressure (4061 psi) conditions used in their experiments.
- Almost negligible change in the surface of the geopolymer cement cores was observed after exposure when compared to Class H Portland cement.

- Compressive strength of geopolymer was very low compared to Class H Portland cement due to higher curing temperature. Although it was above the acceptable API range, it became necessary to determine the formulation of Class C flyash-based geopolymer cement for higher temperature applications.
- Increased CO_2 partial pressure led to a higher strength reduction in both types of cement. 42% of Portland cement's strength was reduced after 14 days of 1500 psi CO_2 exposure. However, only 12% of geopolymer cement's strength was reduced after 14 days of 1500 psi CO_2 exposure.
- Geopolymer cement's compressive strength did not reduce after 500 psi CO_2 exposure for 3, 7 and 14 days. However, in case of Portland cement exposure of 500 psi CO_2 pressure reduced 5.6% strength after 7 days and 27.77% strength after 14 days.
- Longer duration of CO_2 exposure led to greater compressive strength reduction in both types of cement. Again, this effect was lower in geopolymer cement compared to class H Portland cement.

REFERENCES

Ahdaya, M., Jani, P., Imqam, A. et al., (2018). The Development of New Formulation of Geopolymer Cement for Wellbore Integrity Improvements. IPTC 19393 MS-2018.

API Specification 10A/ISO 10426-1, Specification for Cements and Materials for Well Cementing, Twenty-third Edition.

Barlet-Gouedard, V., Rimmele, G., Goffe, B., & Porcherie, O. (2006, January 1). Mitigation strategies for the risk of CO_2 migration through wellbores. Society of Petroleum Engineers. doi:10.2118/98924-MS

Barbara G. Kutchko, Brian R. Strazisar, Nicolas Huerta, Gregory V. Lowry, David A. Dzombak, and Niels Thaulow, CO_2 Reaction with Hydrated Class H Well Cement under Geologic Sequestration Conditions: Effects of Flyash Admixtures; Environmental Science & Technology 2009 43 (10), 3947-3952 DOI: 10.1021/es803007e.

Barbara G. Kutchko, Brian R. Strazisar, Gregory V. Lowry, David A. Dzombak, and Niels Thaulow; Rate of CO_2 Attack on Hydrated Class H Well Cement under Geologic Sequestration Conditions; Environmental Science & Technology 2008 42 (16), 6237-6242 DOI: 10.1021/es800049r

Gielen, D, “The future role of CO_2 capture and storage. Results of the IEA-ETP model”, Report Number EET/2003/04, Paris November 2003.

Garnier, A., Laudet, J.-B., Neuville, N., Le Guen, Y., Fourmaintraux, D. M., Rafai, N., Shao, J. F. (2010, January 1). CO_2-Induced Changes in Oilwell Cements under Downhole Conditions: First Experimental Results. Society of Petroleum Engineers. doi:10.2118/134473-MS

Gaëtan Rimmelé, Véronique Barlet-Gouédard, Olivier Porcherie, Bruno Goffé, Fabrice Brunet, Heterogeneous porosity distribution in Portland cement exposed to CO_2-rich fluids, Cement and Concrete Research, Volume 38, Issues 8–9, 2008, Pages 1038-1048, ISSN 0008-8846, https://doi.org/10.1016/j.cemconres.2008.03.022.

Liwei Zhang, David A. Dzombak, David V. Nakles, Steven B. Hawthorne, David J. Miller, Barbara Kutchko, Christina Lopano, Brian Strazisar, Effect of exposure environment on the interactions between acid gas (H_2S and CO_2) and pozzolan-amended wellbore cement under acid gas co-sequestration conditions, International Journal of Greenhouse Gas Control, Volume 27, 2014, Pages 309-318, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2014.06.030.

Marchetti, C., 1977. On geoengineering and the CO_2 problem. Clim. Change 1 (1), 59e68.

Moroni, N., Santra, A. K., Ravi, K., & Hunter, W. J. (2009, January 1). Holistic Design of Cement Systems to Survive CO_2 Environment. Society of Petroleum Engineers. doi:10.2118/124733-MS.

Neville, A. M. Properties of Concrete; Fifth ed.; Prentice Hall: Upper Saddle River, NJ, 2012.

Nelson, E. B. Well Cementing; Schlumberger Educational Services: Sugar Land, TX, 1999.

N. Spycher, K. Pruess, CO_2-H_2O mixtures in the geological sequestration of CO_2. II. Partitioning in chloride brines at 12–100 °C and up to 600 bar, Geochimica et Cosmochimica Acta 69 (13) (2005) 3309–3320.

Qingyun Li, Yun Mook Lim, Katharine M. Flores, Kelly Kranjc, and Young-Shin Jun; Chemical Reactions of Portland Cement with Aqueous CO_2 and Their Impacts on Cement's Mechanical Properties under Geologic CO_2 Sequestration Conditions; Environmental Science & Technology 2015 49 (10), 6335-6343 DOI: 10.1021/es5063488.

Rendell, F.; Jauberthie, R.; Grantham, M. Deteriorated Concrete: Inspection and Physicochemical Analysis; Thomas Telford: London, 2002.

Sarmiento, J.L. and Gruber, N., "Sinks for anthropogenic carbon" 30-36, Physics today, 2002.

Stefan Bachu, D. Brant Bennion, Experimental assessment of brine and/or CO_2 leakage through well cements at reservoir conditions, International Journal of Greenhouse Gas Control, Volume 3, Issue 4, 2009, Pages 494-501, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2008.11.002.

Santra, A. K., Reddy, B. R., Liang, F., & Fitzgerald, R. (2009, January 1). Reaction of CO_2 with Portland cement at Downhole Conditions and the Role of Pozzolanic Supplements. Society of Petroleum Engineers. doi:10.2118/121103-MS.

Tarco, J. C., & Asghari, K. (2010, October 1). Experimental Study of Stability and Integrity of Cement in Wellbores Used for CO_2 Storage. Society of Petroleum Engineers. doi:10.2118/142004-PA.

SECTION

2. CONCLUSIONS AND RECOMMENDATIONS

2.1. CONCLUSIONS

This research started with comprehensive review of experimental and field studies that had been conducted earlier. Proposed Class C flyash geopolymer cement was then optimized for the oil well cementing purposes and compared with Portland cement. Lastly, Performance of Portland cement and geopolymer cement in CO_2 environment was compared. The concluding remarks from the comprehensive review was described below:

- Portland cement used to cast wells will get two kinds of CO_2 exposure depending upon nature and mobility of fluids.
- Injected CO_2 underground dissolves in formation water to form carbonic acid which reacts with Portland cement. This process alters the chemistry of Portland cement which can lead to change of mechanical properties.
- Alteration of mechanical properties can lead to risk of CO_2 leakage from the storage reservoir.
- Additives like Pozzolans were added with the cement to obtain CO_2 resistant cement. However, an optimum quantity of Pozzolans are recommended with cement.
- Flyash is best known pozzolan among all due to ready availability and easy mixing capacity with the cement. It is mainly recommended to be used with Portland cement for CO_2 storage purposes.

- Cement containing flyash also degrades in CO_2 environment due to availability of Portland cement constituents which reacts with CO_2.
- A non-Portland cement, Class C flyash based geopolymer was recommended to be used as a potential alternative to Portland cement.

An experimental study was conducted to obtain formulation of geopolymer cement which can work as an oil well cement. API tests were conducted on different ratios of alkaline activator to flyash, sodium silicate to sodium hydroxide ratios at three different sodium hydroxide concentrations. Established formulation was compared with Portland cement. The obtained conclusions are listed below:

- Sodium hydroxide concentrations and plastic viscosity has inverse relationship; as concentration of NaOH increases, plastic viscosity will decrease slightly
- Concentration of NaOH positively affect the compressive strength for the AA/FA ratio 0.2 but unusual trend was observed in the case of AA/FA ratio 0.4
- Fluid loss from the slurry decreased with increasing sodium silicate to sodium hydroxide ratios.
- The optimized geopolymer cement has higher compressive strength, lower fluid loss, no free fluid than Portland cement. Rheological behavior is same as Portland cement.
- Geopolymer cement can be used as an oil well cement and provide better well sealing than Portland cement.

Finally, Geopolymer cement and Portland cement were exposed to CO_2 environment at two different CO_2 partial pressures for different durations. The change in density, compressive strength, and surface texture was compared.

- No change in density was observed for both cements after the CO_2 exposure
- Millimeter sized $CaCO_3$ crystals were observed on the surface of Portland cement which in the case of geopolymer cement was not present
- Geopolymer cement was found to gain very low compressive strength compared to Portland cement due to higher curing temperature.
- Increase in CO_2 partial pressure lead to higher strength reduction in both types of cement.
- No strength reduction was observed at 500 psi CO_2 exposure in geopolymer cement.
- Longer duration of CO_2 exposure lead to higher compressive strength reduction in both types of cement but again very low in geopolymer cement compared to Class H Portland cement.
- Negligible degradation visually, very low strength reduction of geopolymer cement compared to Class H portland cement suggest that it can be possible alternative to Portland cement for carbon dioxide storage operations.

2.2. RECOMMENDATIONS

This work proposed an alternative to Portland cement which is class C flyash-based geopolymer cement to use in CO_2 storage wells. Experimental studies were also conducted to optimize geopolymer slurry for oil well cementing operations and to analyze the performance of geopolymer cement in CO_2 environment. However, there is still a lot of work to do in this area which is mentioned below:

- Optimize geopolymer slurry to obtain a formulation that can work at higher temperature and pressure.
- SEM, XRD, TGA analysis of Class C flyash-based geopolymer after CO_2 exposure to better understand mineralogical and chemical changes due to CO_2.
- CO_2 exposure at higher pressure and temperature with wet scCO_2 and CO_2 saturated brine. Brine was recommended to use, as exposure of CO_2 saturated water is more severe than CO_2 saturated brine.

BIBLIOGRAPHY

American Petroleum Institute. Worldwide Cementing Practices; API: Dallas, TX, 1991

Andrew Duguid, George W. Scherer, Degradation of oil well cement due to exposure to carbonated brine, International Journal of Greenhouse Gas Control, Volume 4, Issue 3, 2010, Pages 546-560, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2009.11.001.

Brandl, A., Cutler, J., Seholm, A. J., Sansil, M., & Braun, G. (2010, January 1). Cementing Solutions for Corrosive Well Environments. Society of Petroleum Engineers. doi:10.2118/132228-MS.

Barbara G. Kutchko, Brian R. Strazisar, Nicolas Huerta, Gregory V. Lowry, David A. Dzombak, and Niels Thaulow; CO_2 Reaction with Hydrated Class H Well Cement under Geologic Sequestration Conditions: Effects of Flyash Admixtures. Environmental Science & Technology 2009 43 (10), 3947-3952, DOI: 10.1021/es803007e.

Garnier, A., Laudet, J. B., Patil, S., Patil, R., Ravi, K., & Ferreira, L. (2012, January 1). Effect of Acid Gas on Cement Sheath Integrity: Experimental Findings. Society of Petroleum Engineers. doi:10.2118/160890-MS.

Liwei Zhang, David A. Dzombak, David V. Nakles, Steven B. Hawthorne, David J. Miller, Barbara Kutchko, Christina Lopano, Brian Strazisar, Effect of exposure environment on the interactions between acid gas (H_2S and CO_2) and pozzolan-amended wellbore cement under acid gas co-sequestration conditions, International Journal of Greenhouse Gas Control, Volume 27, 2014, Pages 309-318, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2014.06.030

Nelson, E. B. Well Cementing; Schlumberger Educational Services: Sugar Land, TX, 1990

Nelson, E.B., Guillot, D., Well cementing, 2nd Edition, Schlumberger, Sugar Land (2006), 3-5.

Stefan Bachu, D. Brant Bennion, Experimental assessment of brine and/or CO_2 leakage through well cements at reservoir conditions, International Journal of Greenhouse Gas Control, Volume 3, Issue 4, 2009, Pages 494-501, ISSN 1750-5836, https://doi.org/10.1016/j.ijggc.2008.11.002.

Taylor, H. F. Cement Chemistry; Thomas Telford: London, 1997

VITA

Priyesh Parimal Jani was born in Ahmedabad, India. He received his bachelor’s degree in petroleum engineering from Pandit Deendayal Petroleum University, Gandhinagar, Gujarat, India. After graduation, Priyesh worked as Drilling Operation Engineer in John Energy Ltd., Gujarat, India from August 2014 – December 2016. He started at Missouri University of Science and Technology during the spring semester of 2017 to work under the supervision of Dr. Abdulmohsin Imqam. He received the Master of Science degree in Petroleum Engineering from Missouri University of Science and Technology in May 2019.