Spring 2018

New wellbore-integrity classification for gas migration problems and new cement formulations using Graphene Nano Platelets to prevent gas migration through cement

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Recommended Citation

Alkhamis, Mohammed Mousa M., "New wellbore-integrity classification for gas migration problems and new cement formulations using Graphene Nano Platelets to prevent gas migration through cement" (2018). *Masters Theses*. 7751.
https://scholarsmine.mst.edu/masters_theses/7751

NEW WELLBORE-INTEGRITY CLASSIFICATION FOR GAS MIGRATION PROBLEMS AND NEW CEMENT FORMULATIONS USING GRAPHENE NANO PLATELETS TO PREVENT GAS MIGRATION THROUGH CEMENT

by

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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

2018

Approved by

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PUBLICATION THESIS OPTION

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

Paper I: Pages 67 - 89, is to be submitted to The Science and Technology of Fuel and Energy, under the tittle ‘‘A New Classification of Well-Integrity Problems Related to Gas Migration’’.

Paper II: Pages 93 - 124, have been accepted as a conference paper by the Society of Petroleum Engineering under the title ‘‘New Cement Formulations Utilizing Graphene Nano Platelets to Improve Cement Properties and Long-term Reliability in Oil Wells”.

ABSTRACT

Gas migration, one of the primary problems related to the integrity of oil wells, is caused by cement failures. Gas migration can result in costly well repairs and may endanger personal, equipment, and result in severe operational difficulties and environmental issues. The ultimate objectives of this research were to provide a comprehensive review of the problem and to provide a solution to the problem using Graphene Nano Platelets (GNPs).

An intensive review was performed to understand the cement failures. The reasons behind these failures were analyzed and classified with respect to their locations in the wellbore. Recommendations and potential solutions for these problems were also suggested. A new classification was established and would work as a roadmap to understand the oil well cement failures and would help prevent their occurrence.

An intensive laboratory work was conducted to better understand the cement and the cement testing methodologies. In addition, GNPs were added to the cement to enhance its properties. The evaluation of the neat cement and the new cement formulations included testing their mineralogy by implementing X-ray diffraction (XRD) analysis, testing the mechanical properties of the set cement, testing the stability and rheology of the liquid slurry, and evaluating the chemical shrinkage of the cement. In addition, the effects of adding GNPs on the hydration process of the cement was studied using isothermal calorimeter. The findings of this investigation showed that GNPs played a key role in regulating the microstructure of the hydration products of the cement, which enhanced the toughness of the cement without affecting its stability and flow-ability. The GNPs also aided in controlling the propagation of micro cracks within the cement matrix.

ACKNOWLEDGEMENTS

In the name of Allah, the most Beneficent, the most Merciful.

I would like to express my sincere gratitude to Saudi Arabian Cultural Mission (SACM) for rewarding me full funded scholarship and for their friendly assistance throughout the study.

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 all the constructive feedback.

I also want to thank the NanoGraphene Inc. and Haliburton for providing me the nano particles and the cement and for their great technical support.

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.

Last but not least, a great thanks to my family. Words cannot express how grateful I am to them for all the support and encouragement.

Catalina mi vida, if it was not for you, I would not be able to achieve this. Thank you from all my heart.

TABLE OF CONTENTS

Page

PAPER

SECTION

LIST OF ILLUSTRATIONS

SECTION Page

PAPER I

PAPER II

LIST OF TABLES

SECTION Page

PAPER I

PAPER II

1. INTRODUCTION

1.1. STATEMENT AND SIGNIFICANCE OF THE PROBLEM

Cementing operations are recognized as one of the most essential aspects related to the integrity of oil and gas wells. Regardless the huge number of research and the great amount of field operations that have been conducted throughout the history world widely, the well-integrity failures are still occurring continuously within the life of wells from drilling phase to the abandonment of the well (Santos, 2015). The Norwegian standard defines well integrity as "application of technical, operational, and organizational solutions, to reduce risk of uncontrolled release of formation fluids throughout the life cycle of a well' (Norsok D-010., 2013). On 2010 the Gulf of Mexico evidenced one of the largest oil spill in the history of US waters (Macondo blowout), loss of well-integrity as an annulus cement failed to isolate the hydrocarbon is one of the causes of this tragic accident according to the investigations reports (Santos and Ribeiro, 2017). Losing zonal isolation can result in costly well repairs and may endanger personal, equipment, and result in severe operational difficulties and huge environmental issues, which may lead in the worst-case scenario to complete loss of the well (Bois et al., 2011). For these reasons, primary cement slurries designs must be optimized in such a way that accomplish short and long-term zonal isolation (Sauer, 1987).

(Rae, et al., 1989; Bois et al., 2011; Santos, 2015) and many other researchers divided well-integrity problems that face the oil and gas industry during and after the cementing operations into three categories according to their time of apparent: during cementing the well (within minutes), after the cement placement in the short-term (hours to days), and after the cement has been cured in the long-term (months to years). Figure 1.1 is an illustration of this categorization.

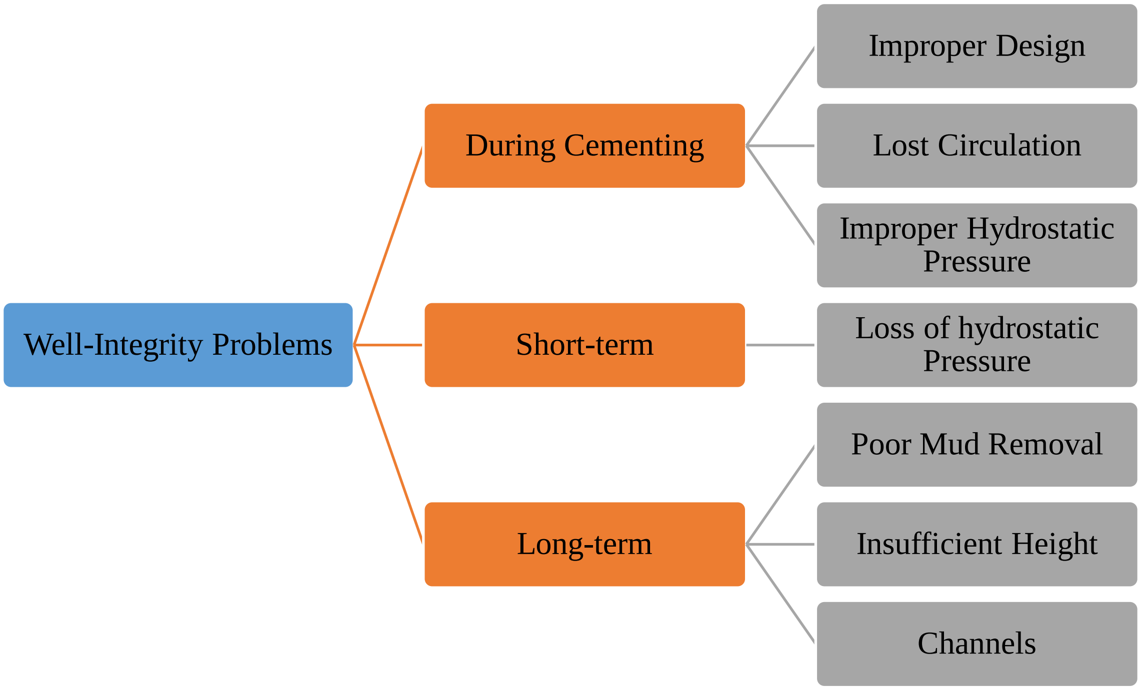

Figure 1.1. An illustration of well-integrity problems.

The first category is during the cement displacement process, which would occur within minutes; this may result in serious problems including blowouts like in the case of Macondo blowout. The control issues that may happen in this category could be because of inappropriate cement designing, failure in reaching the desired properties while mixing the cement slurry, lost circulation during the cement displacement, failure of casing float equipment, and improper hydrostatic pressure of the cement slurries or pre-flushes.

The second category is mainly after cement displacement process. It can happen within hours to days and it is related to the loss of hydrostatic pressure of the cement slurry during its initial hydration. This loss of hydraulic pressure may result in allowing the fluids especially gases to pass the cement barrier creating what is called channels.

The third category is after the cement has been cured (months to years). Generally, these problems caused by poor cementing practices such as poor selection of chemical agents for mud removal, poor centralization. In addition, insufficient cement height, which may lead to leakage and corrosion problems and the channels, might contribute to long-term cement failures.

This categorization can be found in many publications and it represent most of the cement failures related to gas migration. However, this categorization is too general and it does not state the failures clearly. In addition, a general categorization that depends on the time of apparent of each failure is not sufficient to recognize the connection between those failures and the consequences of each of them. These failures and more are still occurring continuously. Hence, a new classification that count for the locations of the failures, reasons behind them, and methods to mitigate them is essential. This work introduces a new classification of well-integrity failures that include many parameters such as the location of each failure, the causes of the failure, and potential solutions to avoid the failure. The solutions include utilizing unconventional additives such as the use of nanotechnology. Recently, carbon nanomaterials such as graphene, carbon nanotubes (CNTs), and carbon nanofibers (CNFs) have attracted many researchers due to their exceptional properties. This work also conducted an intensive laboratory evaluation of Portland cement and based on the evaluation, Graphene Nano Platelets (GNPs) were selected as an additive that has the potential to overcome many of those failures. The planner geometry of GNPs and their high aspect ratio (length to thickness) promoted them to act as platforms for Portland cement hydration products to grow with modified microstructure that enhance the toughness of the cement.

The primary objectives of this research were to provide a new classification of the cement failures that might compromise the wellbore-integrity and to provide a comprehensive study of GNPs as a solution to overcome those failures.

1.2. EXPECTED IMPACTS AND CONTRIBUTION

The new classification established herein can work as a guide for the oil and gas industry to better understand and evaluate cement systems prior to field jobs execution. The following information will have a strong impact on the oil and gas industry in the following manner:

- Considerations listed from this work will aid in optimizing the laboratory experiments to achieve reliable data.
- Complete mud removal is essential to achieve good bonding between the cement and its surroundings.
- Young modulus must be lowered and Poisson's must be increased to reduce the stresses induced in the cement sheath.
- It is essential to evaluate the initial state of stress in the cement sheath to know how much loading can be submitted to the cement before it fails.
- A huge assumption is made when evaluating cement failures is that each failure happens independent of other failures. For example, when analyzing

a micro annulus between the cement sheath and the formation, most of researches assume good bonding between the cement and the casing, which is not very true in all cases.

- It can be concluded from this review that the cement have to be: environmentally acceptable, with the desired density, suffers no excessive fluid loss, zero free fluids, achieve desired strength, low or no shrinkage, short transition time, can withstand high pressure and temperatures, resist downhole chemicals, and can achieve good bonding with the casing and the formation.
- Today the main focus in the industry is related to short-term properties, which is good for the place of the cement. However, the long-term properties are as important as short-term and even more.
- Cementing operations require the attention starting from designing the cement, the practices of placing the cement, up to providing long-term zonal isolation.

Results obtained from this research will promote using Nanotechnology to overcome the failures of Portland cement in providing zonal isolation. Failures related to gas migration, such as formation of micro-annuli, channels, and cracks, would be reduced when implementing GNPs.

- GNPs enhanced the overall performance of the cement and showed the potential in reducing the gas migration in oil and gas wells by stopping the propagation of micro cracks.

- GNPs modified the microstructure of the cement hydration crystals as the peaks of the hydration products varied.
- GNPs enhanced the mechanical properties (compressive and tensile strength) of the cement.
- GNPs reduced the shrinkage of cement by 30%. This reduction, especially at early ages, can help reduce the risk of gas migration through micro-annuli.
- The addition of small concentration of GNPs in this study did not affect the rheological properties significantly. However, the effect of time could have a significant effect on rheology.
- The cement systems tested in this study were stable and suffered less free fluids. In addition, the cement systems tested herein showed no significance sedimentation. This would help avoiding channels through the cement sheath.

1.3. OBJECTIVES

The main objective of this research was to classify the cement failures. Those failures that cost the oil and gas industry hundreds of wells throughout the history. In addition, to avoid the cement failures by introducing GNPs. Experimental tests were performed to evaluate the effects of adding these nanoparticles to the cement system. These experiments included analysis of x-ray diffraction patterns of both hydrated and anhydrate cement, density measurements, rheological behavior results, compressive strength results, tensile strength results, stability measurements, heat of hydration process, and the chemical shrinkage results. The following objectives were obtained in this research:

- A new classification that define the cement failures according to their locations in the wellbore.
- A guideline to several considerations crucial for future cement testing against cement failures.
- The importance of simulating downhole conditions on testing cement slurries.
- A comprehensive explanation of all the cement related problems that could result in gas migration.
- The effect of GNPs on the mechanical performance of the cement, which enhance the durability and reliability of the cement and makes it less likely to fail under harsh environments.
- The importance of XRD analysis in characterizing the cement and its additives.
- The ability of nanoparticles to act as a filler in the cement pore structure, hence minimizing the propagation of cracks within the cement sheath.
- The necessity of reducing cement shrinkage to maintain wellbore zonal isolation.

The results collected from this work provide a comprehensive knowledge and insight into the importance of simulating downhole conditions when testing cement. In addition, to the possibility of coupling the laboratory work with computerized models to evaluate the oil well cement behavior.

1.4. SCOPE OF THIS WORK

This research was divided into two Tasks: one was to review and understand the cement failures along with establishing a new classification of the failures. The second task was to conduct laboratory experiments to investigate the introduction of GNPs to Class-H Portland cement through a comprehensive evaluation. The evaluation included conducting lab experiments such as compressive and tensile strength tests to determine the effectiveness of using GNPs to improve cement mechanical properties. Figure 1.2 shows an illustration of the scope of this work.

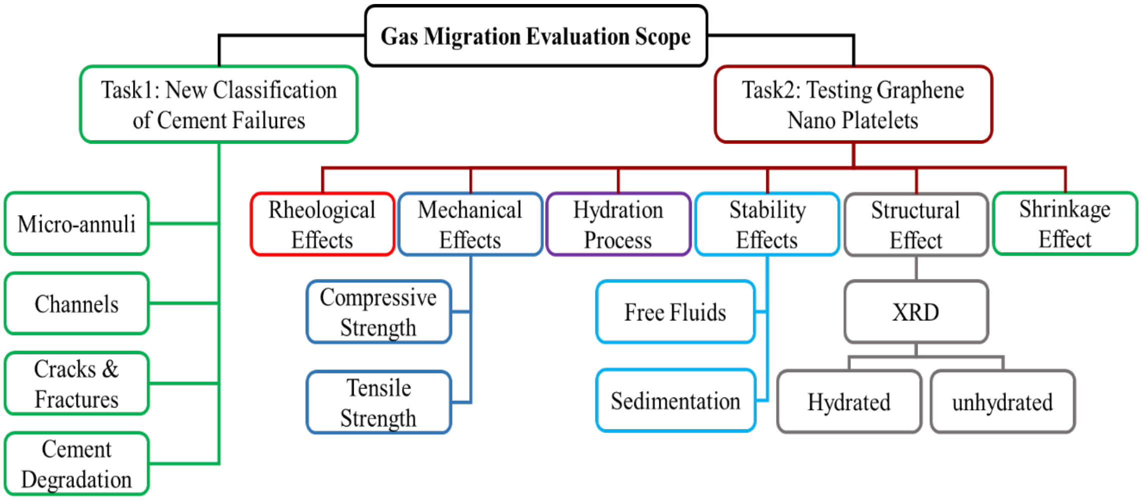

Figure 1.2. Scope of research.

2. BACKGROUND AND EXISTING TECHNOLOGIES

A sufficient cement design can be defined as a cement that can provide support for the casing, provide zonal isolation between the casing and the cement and between the cement and the formation, gains strength over time, easy to flow, and elastic and resilient to withstand several temperature and pressure cycles over the life of the well. To design such a cement the cement and the types of cement must be understood. In addition, the use of conventional (Normal-size), and unconventional (Nano-size) additives that are added to the cement system to enhance its properties and make the cement sheath reliable in all the phases of the well life from drilling, completion, production, to plug and abandonment, including stimulation operations must be analyzed.

2.1. CEMENT AND TYPES OF CEMENTS

Cement is a mineral powder manufactured through very precise processes. Historically, clays are known to be the first cementitious materials that have been used for constructions and building purposes followed by ordinary lime that hydrates to create a cementitious material that has been used to connect bricks and stones (Cementing Technology, 1984). Cement is used in residential constructions, civil structures, and other applications including the oil and gas industry to cement wellbores. Generally, in oil and gas wells, cement is mixed with water to form slurry, and then this slurry is pumped through the center of the casing and back up in the annulus between the casing and the formation. Types of cement in general can be classified into four major categories: (1) Natural cement,

(2) Pozzolan cement, (3) Blast furnace slag and slag cement, and (4) Portland and Portland compound cement (The Constructor, 2016).

2.1.1. Natural Cement. Natural cement is composed of natural cement rock of argillaceous clay and limestone that perform very well with a high degree of resistance and minimal shrinkage. This type of cement is cheap and set fast. It is used in decorating heritage structures and ecological construction projects (Vicat.com, 2017).

2.1.2. Pozzolan Cement. Pozzolanic cements were developed by the Romans using mineral substances of volcanic origin ash and it contains silicates of calcium, lime, iron, and aluminum. This type of materials exhibits high cementitious properties when mixed with lime (Cementing Technology, 1984).

2.1.3. Blast Furnace Slag and Slag Cement. Blast furnace slag and slag cement is a mixture of calcium silicate, aluminum silicate, and hydrated lime (Atashnezhad et al., 2017). These types of cement release a small amount of heat within the hydration process and they contain low-grade sulfates to allow these cements to work in harsh conditions such as sub-sea projects (Vicat.com, 2017).

2.1.4. Portland and Portland Compound Cement. Portland cement and Portland compound cement are mixture of lime, silica, alumina, and iron (Atashnezhad et al., 2017). These types of cement are commonly used in civil construction projects, industrial and commercial buildings, and in residential buildings (Vicat.com, 2017). Most of the drilling cements are made of Portland cement and that is why it is important to mention how it starts and what is its composition. Portland cement was first made by Joseph Aspdin in 1824 by burning powdered limestone and clay in his kitchen stove (Cement.org, 2017). Portland cement was named by Joseph Aspdin because the concrete produced from it looks alike the stone quarried on the Isle of Portland off the coast of England. It is verified that the first use of cement in the oil and gas industry was in 1903 in California when Union Oil Co. mixed and dumbed 50 sacks of Portland cement to shut off a water zone and drilling was continued after 28 days waiting on cement time of this operation.

Portland cement consists of five major compounds and a few minor compounds, mainly composed of tricalcium silicate, dicalcium silicate, tricalcium aluminate, tetra-calcium aluminoferrite, and gypsum. See Table 2.1 for weight percentages.

Table 2.1. Composition of Portland cement with chemical formula and weight percentage (De La Roij et al., 2012).

Cement Compound	**Weight Percentage**	**Chemical Formula**
Tricalcium silicate	50 %	Ca_3SiO_5 or $3CaO.SiO_2$
Dicalcium silicate	25 %	Ca_2SiO_4 or $2CaO.SiO_2$
Tricalcium aluminate	10 %	$Ca_3Al_2O_6$ or $3CaO.Al_2O_3$
Tetra-calcium aluminoferrite	10%	$Ca_4Al_2Fe_2O_{10}$ or $4CaO.Al_2O_3.Fe_2.O_3$
Gypsum	5 %	$CaSO_42H_2O$

2.2. PORTLAND CEMENT CLASSIFICATIONS

Before we discuss the manufacturing process of Portland cement, it is important to point out the difference between the types of Portland cements that are used for constructions and building and the classes of Portland cements that are utilized in oil well cements. In the U.S., many agencies study and write the specifications to manufacture Portland cements. Two of those agencies are (1) American Society for Testing and Materials (ASTM) and (2) American Petroleum Institute (API).

2.2.1. The American Society for Testing and Materials Standards. The American Society for Testing and Materials (ASTM) deals with cement for constructions and building use and it classifies the related cements into 8 types (Type I, IA, II, IIA, III, IIIA, IV, and V) (ASTM C 150/ C 150M). Since this research is focusing on oil well cement, we will not discuss the ASTM standards for Portland cement in details.

2.2.2. The American Petroleum Institute Specifications. The American Petroleum Institute (API) deals with cement that are used only in wells. Because of the conditions that are not encountered in constructions such as the wide ranges in pressure and temperature, the industry modified the specifications of constructions cement and adapted it to the oil well conditions. The API classifies the different types of Portland cement that are used in our industry into 8 classes (Classes A through H). The oil well cements are also available in moderate and highly sulfate resistant grades (MSR and HSR respectively) to prevent the deterioration of set cement downhole, which can happen due to the sulfate attack. In the next section a summary of those 8 classes of Portland cement (Applied Drilling Engineering, 1991). Table 2.2 lists the types of API cements.

2.3. PORTLAND CEMENT MANUFACTURING PROCESS

In the process of manufacturing Portland cement, there are raw materials, which are ground, mixed, and subjected to high temperature to produce the final product. This final product can hydrate when blended with water to have the desired cementitious properties. The manufacturing process of Portland cements includes (1) the raw materials, (2) the preparation of raw blends, (3) the burning operation, (4) the cooling process, and (5) the final grinding.

Table 2.2. API Cement Types.

Type	Depth [feet]	Note
API Class A	0 to 6000	Used when special properties are not required It is available only in ordinary grade O (ordinary grade includes magnesium oxide, sulfur trioxide, insoluble residue, tricalcium aluminate). This cement is similar to ASTM c 150, type I.
API Class B	0 to 6000	Used when conditions require moderate or high sulfate resistance. It is available in moderate sulfate resistance, which is similar to ASTM c 150, type II and high sulfate resistance.
API Class C	0 to 6000	Used when conditions require high early strength. It is available in ordinary O, moderate sulfate resistance which is similar to ASTM c 150, type III and high sulfate resistance.
API Class D	6000 to 10000	Used when conditions are moderately high temperatures and pressures. It is available in both moderate and high sulfate resistance.
API Class E	10000 to 14000	Used when conditions are high temperatures and pressures It is available in both moderate and high sulfate resistance
API Class F	10000 to 16000	Used when conditions are extremely high temperatures and pressures. It is available in both moderate and high sulfate resistance.
API Class G & H	0 to 8000	Used with additives such as accelerators to cover a wide range of temperatures and depths. It has no additions other than calcium sulfate or water, or both, shall be interground or mixed with the clinker during the manufacturing process of this cement. It is available in both moderate and high sulfate resistance.

2.3.1. The Raw Materials. The basic raw materials can found in quarries of calcareous and argillaceous rock in addition to sub products that have the same materials added whenever important. The composition of the final product will depend on the raw materials. We can divide the raw materials into two divisions (1) calcareous material and (2) argillaceous materials (Cementing Technology, 1984).

2.3.1.1. Calcareous materials. Calcareous material is material that contains calcium carbonate or calcium oxide such as:

- Limestone, which is a rock, formed generally by the accumulation of organic remains. Its basic component is calcium carbonate.
- Cement rock, which is a rock with similar composition to artificial cement.
- Chalk which is a soft, white, gray or buff limestone that composed mainly of marine shells.
- Marl, which is a loose, earthy deposit, contains an amount of calcium carbonate.
- Alkali waste, which is the waste of the chemical plants, which contains calcium oxide or calcium carbonate.

2.3.1.2. Argillaceous materials. Argillaceous materials are materials that contain clay or clay minerals such as:

- Clay, which is an earthy material that that is plastic when moist and hard when fired. In its composition, hydrous aluminum silicates in addition to other minerals.

- Shale which is a fossil rock formed by the consolidation of clay, mud or silt. It is composed of minerals essentially unalerted since deposition, it has a laminated structure or a finely stratified.
- Slate, which is a rock that is dense and fine-grained, produced because of compression of shales, clays, and other rocks.
- Ash, which is a byproduct of coal combustion, it has traces of silicate.

2.3.2. The Preparation of Raw Blends. In general, there are two main processes of blending the raw materials (1) the dry process and (2) the wet process. The difference between those processes is in the technique of separating the unwanted minerals from the raw materials (Cementing Technology, 1984).

2.3.2.1. The dry process. Dry process is cheaper than we process but on the negative side it is less controllable than the wet process. In this process, clay and limestone are fed into two different batteries of crushers. The crushing is important to downsize the raw materials into a size that is suitable for storage and blending before the final grinding stage. The size of the crushed materials depends on the milling machine used in this operation. After crushing the materials, the crushed products are stored in two different bins where the chemists will analyze the composition and mix the two different products to achieve the desired composition (Blending stockpiles are used sometimes for this step). Then the mixture will be pulverized to a mesh size of 100-200 to maximize the contact area between the particles (Cementing Technology, 1984).

2.3.2.2. The wet process. The wet process is more controllable process than the dry process but it requires more energy in order to vaporize the water in the kiln. The kiln is where we take the final blend of the dry and wet processes for the burning operation. In this process, the clay minerals are slurried so that pebbles will settle out while the limestone is crushed and stored in bins. The next step is to deliver the two material to a wet mill machine and when the desired composition is achieved, the mixture would be partially dried out and sent to the kiln (Cementing Technology, 1984).

2.3.3. The Burning Operation. The burning operation or the heat treatment is carried out in rotary kiln made of steel where the raw mixture is fed at a uniform ratio. The kiln is slightly inclined to the horizontal and the raw mixture is fed into the upper end of the kiln and heated gradually. This heating process includes:

- The evaporation of any free water present at a temperature of 100-degree C.
- Thermal decomposition of clay minerals (Dehydroxylation) at 300-650-degree C.
- Thermal decomposition of calcite at 800-950-degree C.
- At around 1250-1280-degree C some liquid starts to form.
- Above 1280-degree C the formation of further liquid and the formation of cementitious compounds (Cementing Technology, 1984).

2.3.4. The Cooling Process. The cooling process plays a major role in the quality of the clinker. Clinker is the product that we obtain from the rotary kiln. The cooling process can be (1) slow or (2) fast cooling.

2.3.4.1. The slow cooling method. The slow cooling allows the crystallization of the clinker components, which will ensure a better grinding. The final set cement tends to show higher compressive strength in the long term (Cementing Technology, 1984).

2.3.4.2. The fast cooling method. The fast cooling method might have glass within the product, which makes it harder to grind. The final set cement for this method develops high early strength but on the other hand, it might deteriorate with time (Cementing Technology, 1984).

2.3.5. The Final Grinding. After the clinker cools down, and stored in silos, the clinker is grinded and mixed with a small amount of gypsum (usually between 1.5 – 3%) to control the setting time of the cement.

The final product then will be sampled, analyzed, and stored. (Dowell book).

2.4. CEMENT HYDRATION PROCESS

The cement hydration process starts when water is added to the cement. Each of the compounds of the cement experiences hydration and participates in producing the final product. Generally, the calcium silicate (CS) is the only responsible of strength within the cement composition. With tricalcium silicate (C_3S) contributes in developing strength in the first days and dicalcium silicate (C_2S), which reacts slowly, contributes in developing strength at later times (De La Roij et al., 2012). Below are the equations for the hydration of C_3S and C_2S, respectively: (De La Roij et al., 2012).

Tricalcium Silicate + Water → Calcium Silicate Hydrate + Calcium Hydroxide + Heat

$$2\ Ca_3SiO_5 + 7\ H_2O \rightarrow 3\ CaO.2SiO_2.4H_2O + 3\ Ca(OH)_2 + 173.6\ kJ$$

Dicalcium Silicate + Water → Calcium Silicate Hydrate + Calcium Hydroxide + Heat

$$2\ Ca_2SiO_4 + 5\ H_2O \rightarrow 3\ CaO.2SiO_2.4H_2O + Ca(OH)_2 + 58.6\ kJ$$

At the early stages of the process, the C_3S rapidly reacts upon adding water to release calcium ions, hydroxide ions, and a large amount of heat. The pH rises over 12 due to the release of alkaline hydroxide (OH^-) ions. With a decrease in heat this process would continue slowly until the system get saturated. Then, the calcium hydroxide (CH) starts to crystalize while at the same time calcium silicate hydrate (C-S-H) begins to form (De La Roij et al., 2012).

The formed CH and C-S-H crystals provide “seeds” upon which more C-S-H can form. The C-S-H grow thicker forming a coat, which would make it hard for the water molecules to reach the anhydrate C_3S. The coat which grows thicker over time would make the production of C-S-H slower and slower (De La Roij et al., 2012).

The C_2S reacts with water in a similar way comparing to C_3S but in much slower manner. The other major compounds of Portland cement, tetra-calcium aluminoferrite, and tricalcium aluminate also react with water in a much more complicated reaction but do not contribute much to the strength. Another point that must be pointed out is that the hydration rate of each compound may be affected by changing the concentration of the other compounds, the process is not fully independence (De La Roij et al., 2012).

2.5. THE USE OF ADDITIVES IN THE CEMENT SYSTEM

Over the years, the operators of oil and gas fields tried many ways to avoid gas migration. Those ways include the use of annular backpressure, multistage cementing, and external casing packers (Drecq and Parcevaux et al., 1988). Although those techniques can meet some degree of success, they all have some limitations and that is why enhancing the cement slurry itself is essential.

Portland cement with its different classes are used in almost all oil well cementing jobs. However, the conditions such as pressure and temperature that the oil wells face are greatly different than normal conditions. This difference in conditions requires modifying Portland cement to meet the requirements. This can be achieved by adding chemical compounds called “additives” to the cement system to improve the performance of the cement.

To prevent gas migration, the design of the cement system must be optimized to overcome this problem. Designing a proper cement system require a full understanding to the applications where it will be utilized and therefore selecting the suitable additives that are required. For example, a weak formation requires a low-density cement to reduce the hydrostatic pressure hence weight-reducing additives can be added (Harms and Febus et al., 1985; Kulakofsky and Vargo et al., 2005; Al-Yami et al., 2010; Chengweng Wang et al., 2011). For wells that suffer from high gas migration it might be good to use a self-healing cement system in which the self-healing additive can plug the flow through the cracks that causes gas migration (Reddy, B et al., 2010; Browning et al., 2012). Another area of interest is the wells that severe from high pressure and high temperature cycles where fibers or expandable and flexible materials can be employed to shut the unwanted micro annuli (Le Roy-Delage et al., 2000; Iremonger et al., 2015). These and more applications where specific additives must be added to provide a long-term zonal isolation.

There are wide selections of additives that can be added to the cement system, each of those additives contribute in improving one or more property of the cement. In this section of the work some of those additives are presented, defined, and discussed. The additives that are presented here are classified per their size (1) conventional (Normal-size) additives and (2) unconventional (Nano-size) additives.

2.5.1. Conventional (Normal-size) Additives. Conventional or normal-size additives are additives that can be added to the cement system in its normal size to improve some of the properties of the cement. There are many types of conventional additives and some of them are categorized herein by their role in the cement system. This categorization includes some of the conventional additives that are used as (1) weighting additives, (2) weight-reducing additives, (3) fibers, (4) expandable and flexible additives, (5) accelerators, (6) retarders, (7) fluid loss control agents, and (8) self-healing additives.

2.5.1.1. Weighting additives. Weighting additives or heavyweight agents can be added to cement slurries to help hold high formation (pore) pressure and increase the density of the cement slurry due to its high specific gravity. Normally, these agents are added to the cement slurry where the application of the cement require density of 17 Ib/gal and higher. This high density can be achieved by reducing the water content in the cement or by adding weighting agent (Al-Yami et al., 2009). Some of the common weighting additives that are used in oil and gas wells are barite, hematite, hausmannite, and manganese tetroxide.

- Barite is has the advantage of being one of the cheapest products in the industry of oil and gas. Barite is used as weighting agent in both drilling fluids and cement slurries. It has a high surface area and requires high amount of water. Barite is dense sulfate mineral, soft with light gray color and occurs in nature as nonmetallic material (Petrowiki. 2017). It is widely used because of its high specific gravity and it is one of the most important fillers used in plastics, paints, rubber industries, and in addition to all these applications, it is used in some pharmaceutical formulations (Hang et al., 2007).
- Hematite is one of the most common used weighting agents in the oil and gas wells. It contains around 70% iron and has a specific gravity higher than barite. Hematite is a brick-red and it occurs in nature as a dull metallic luster (Petrowiki. 2017).

One of the biggest problems related to the use of hematite is settling which can be controlled by adding anti settling chemicals in the lab but in the field controlling hematite settling is not for sure (Al-Yami et al., 2009).

- Hausmannite has its unique properties that differs it from other weighting agents. The average particles size of this additive is relatively smaller than that of cement, which allows it to fit within the cement matrix, displacing entrained water, thus the result more stable slurry and lower viscosity. Hausmannite is byproduct mineral with a dark brownish-black color (Petrowiki. 2017).
- Manganese tetroxide shows low plastic viscosity values compared to barite. It has a spherical shape small particles and high specific gravity. These criteria make manganese tetroxide a very good weighting material compared to the others. It is believed that this additive shows lower plastic viscosity values due to the spherical shape of its particles, which reduce the friction in particle-to-particle interactions. It also can be mixed with hematite to improve gas migration resistance (Al-Yami et al., 2009).

2.5.1.2. Weight-reducing additives. Weight-reducing additives are mainly added to cement slurries that are used in the application of weak formations (lightweight cement applications) which require low-density cement to reduce the hydrostatic pressure. Back in history, conventional water-extended cements, with minimum densities of 11.5 to 12 Ib/gal, were the only cement slurries available for lightweight cement applications until the late 70’s when foamed cements and hollow spheres were introduced (Kulakofsky and Vargo et al., 2005).

The water-extended cement slurries are achieved by increasing the amount of water in a cement slurry to reduce its density. This addition of water can cause stability problems and to avoid these problems additional additives should be added such as bentonite, potassium silicates, fumed silica, and pozzolans. This kind of cement designs have the advantages of being inexpensive but on the other hand they are considered to have the lowest level of performance among all other cementing systems and as mentioned earlier the minimum density can be achieved is 11 Ib/gal (Kulakofsky and Vargo et al., 2005).

As alternatives to water-extended cement slurries, the industry is using weight-reducing additives such as adding gaseous phase to the cement and microspheres.

- Adding a gaseous phase to the cement slurry to form foamed cement is a way to reduce the cement slurry density. This gas can be nitrogen; the most commonly used in this type of cement, or compressed air. The main advantages introducing gaseous phase into the cement slurry are reducing the cement density, increase the slurry compressibility, good choice to avoid gas migration, increase set cement elasticity, good for overcoming outside stresses, and easy to change the density of the cement slurry as the well conditions change (Kulakofsky and Vargo et al., 2005).Foamed cement with its low-density and acceptable compressive strength is a good option to cement fragile formations providing zonal isolation and avoiding fallback problems (Harms and Febus et al., 1985). This choice was based on studying more than 60 cementing jobs were executed using foam cement. Foam cement can be created by stabilizing a gas (nitrogen) chemically and physically as microscopic cells within a tradition cement slurry. Nitrogen is a good choice because the nitrogen servicing equipment is more than capable of providing sufficient quantities of gas at suitable rates (Harms and Febus et al., 1985).

One thing must be mentioned is the importance of pre-job planning such as knowing the depth of the well, the locations of lost circulation zones, and the breakdown gradients of the weak formations, and on-job timing and execution of plans in addition to reliable equipment. Foamed cement provides adequate strength and permeability to stabilize, support, and protect the casing. It is great and cost effective system for shallow wells but when testing it using the cement bond logs, the results are difficult to be evaluated due to the unique physical properties that the foam cement developed when it is hardened (Harms and Febus et al., 1985). Although foamed cement has these benefits, it requires additional personal, equipment, and access to Nitrogen (Kulakofsky and Vargo et al., 2005).

- The use of microspheres is another method to reduce the density of cement in the oilfield. Microspheres have low specific gravity and can be solid plastic beads, hollow Pozzolanic spheres, and hollow engineered glass bubbles. Using microspheres, we can achieve a very low permeability, and a high strength to weight ratio cement in addition to a rapid compressive strength development that would reduce the waiting on cement time (Kulakofsky and Vargo et al., 2005). (Journal of Petroleum Technology et al., 2003) published a paper presenting the use of ultralight weight cement system, which is composed of ultralight weight hollow spheres developed by 3M. This stable glass spheres are made of soda lime borosilicate and it is non-deformable and insoluble in water. It provides the cement with sufficient strength and resiliency to hold critical cementing conditions. This type of cement has more compressive strengths comparing to foamed cement of the same density under confining pressures of 0-1500 psi. The tensile strengths of these cements are like those of foamed cement and it provides higher shear-bond values than conventional foamed cement.

The use of microspheres develops the cementing practices so use stage tool can be avoided. The stage tools is considered weak point, not well for long-term seal, and can fail causing serious delays and economic losses (Al-Yami et al 2010). Finally, it is important to have the microsphere blends with the highest standards of homogeneity, which might be a limitation in using microspheres to achieve low-density cement (Kulakofsky and Vargo et al., 2005).

2.5.1.3. Fibers. The use of fiber in cement slurries helps to combat lost circulation during cementation. The fibers main role is to build a high-performance bridging network around the thief zones, and their great advantage is that they are mostly compatible with the cementing system (Muhammed Ali et al., 2009).

Fibers are mostly used to ensure long-term wellbore integrity in well that are subjected to high pressure high temperature, steam injection wells, wells that are planned to have hydraulic fracturing operations, and well that suffer from corrosive gases such as carbon dioxide and hydrogen sulfide (Muhammed Ali et al., 2009). These types of applications require higher attention to the importance of tensile strength because in this kind of applications the stresses induced are radial due to the thermal expansion of the casing under the high temperature (Simon S et al., 2015).

Fiber based tensile strength-enhancing cement additive is a synthetic organic fiber for improving cement tensile strength. It has a less tensile strength comparing to other classes of fibers but can withstand the harsh conditions due to its flexibility. By having a flexible cement, we can mitigate the risk of having micro-annuli between the casing and the cement (Simon S et al., 2015). The fibers of medium length in the range of 1-3 mm are good for enhancing the tensile strength and minimizing rheological effects as fibrous materials when added to cement tend to increase the viscosity to numbers where the pumping becomes impossible and 0.5 % of fibers by weight of blend is the optimum amount. The cost of this material is one of the concerns that must be raised, as the use cheap fibers might not meet the requirements of this kind of applications.

2.5.1.4. Flexible and expandable additives. Flexible and expandable additives have been implemented in the oil and gas wells for more than 50 years to reduce the negative effects of bulk shrinkage, the casing expansion and contractions, enhance the mechanical properties, and resist corrosive gases (Muhammed Ali et al., 2009; and Jafariesfad et al., 2017).

Having flexibility in the cement sheath would reduce the effects of pressure and temperature cycles which would prevent initiating cracks within the cement sheath (Muhammed Ali et al., 2009) while adding expandable materials would limit the cement bulk shrinkage (Jafariesfad et al., 2017). Adding both materials minimize the de-bonding effects at the interface of each side of the cement sheath and help to withstand downhole stresses in gas wells, high pressure high temperature wells, plug and abandon applications, and multilateral wells (El-Hassan et al., 2005). Young’s modulus and Poisson’s ratio are key mechanical properties too, to get good cement sheath under pressure and temperature changes, linear expansion and low Young’s modulus in the cement system are required to maintain tight seal in the annulus (J. A-lthuwaini et al., 2010). Lowering Young’s modulus can be achieved by adding flexible materials (El-Hassan et al., 2005). In oil and gas field there are many expandable materials have been used. The two most commonly used are calcium oxide and magnesium oxide.

2.5.1.5. Accelerators. Accelerators are additives that can be added to the cement slurries to shorten the unnecessarily thickening time. Thickening time of the cement slurries depends mainly on the pressure and temperature, which they are subjected to. Reducing the thickening time means less wait on cement time, which means saving a lot of money especially in offshore wells. It is believed that the acceleration additives such as calcium chloride ($CaCl_2$), which is an inorganic salt, affects the rate of normal hydration but do not become integrated into new hydration products (Cementing Technology, 1984). However, these kind of additives have the potential to affect the set-cement permeability negatively (Peng et al., 2014). The most commonly used cement accelerators are calcium chloride, sodium chloride, seawater, and gypsum.

- Calcium chloride ($CaCl_2$) is the most effective accelerator. It is cheap and always acts as an accelerator. Calcium chloride in concentration up to 4% by the weight of cement is commonly used in wells having bottom hole temperature of 125-degree F. A ‘flash set’ can occur if more than 6% of calcium chloride was used and makes the reaction unpredictable (Cementing Technology, 1984).
- Sodium chloride is another effective accelerator but when used in low concentration about 5% by weight of mixing water for cements that do not contain bentonite (Applied Drilling Engineering, 1991). It is believed that using sodium chloride with high concentrations will retard the cement slurries instead of accelerating them (Cementing Technology, 1984).

- Seawater contains amounts of calcium chloride, sodium, and magnesium, which will all act as accelerators. Seawater is used for mixing cement on offshore locations. When seawater is used is better to be taken from open areas of the sea or ocean where the seawater is uniform unlike the shore seawater, which may be diluted with rivers fresh water. Temperature of the downhole is important too as if the temperature exceeded 160-degree F retarders may be needed to counteract the effects of seawater at higher temperatures (Cementing Technology, 1984).
- Gypsum can be mixed with Portland cement slurries to have a cement with short thickening time at low temperatures. This kind of additives should not be used at high temperatures for stability reasons. The temperature where we can add gypsum could be in the range of 140-degree C to 180-degree C.

2.5.1.6. Retarders. Retarders are chemicals that can be added to the cement slurries to delay the cement setting. These chemicals are added to the cement to allow enough time for the placement operation. There are cements classes such as Portland cement class E and class F considered as retarded cements where the retarding compounds could be lignin, gums, starches, weak organic, and cellulose derivatives. At some points these retarders are not compatible with other additives that could be added to control other properties and that is one of the reasons why API developed Portland cement classes H and G which as mentioned earlier contain no additives as manufactured (Cementing Technology, 1984). Retarders such as sodium chloride, lignosulfonates and derivatives, cellulose derivative, and polyhydroxy organic acids and sugar derivatives are used widely as retarders:

- Sodium chloride can function as a retarder when mixed with water and saturated with salt and can provide enough time to place cement like Portland cement class A, G, or H to depths between 10000 to 12000-feet at temperatures range of 230-260-degree F (Cementing Technology, 1984). When cementing through salt sections, slurries mainly are salt saturated and for most shale and clay sands lower salt concentrations are good since shale and clay sands are fresh water sensitive (Cementing Technology, 1984).
- Calcium lignosulfonates is one of the most common mud deflocculants and it has been found that at low concentrations this chemical can be an effective retarder for cement (Applied Drilling Engineering, 1991). It is applicable to all API classes of cement and it can be stabilized with organic acids, which allow them to be used under temperature as high as 300-degree F (Cementing Technology, 1984).
- Cellulose derivative or D8 main purpose is to reduce the fluid loss as a fluid loss agent but it has the ability to function as retarder. It is compatible with all types of cements. This retarder increase the viscosity of the cement slurry, which could an advantage in suspending the weighting agents but on the other hand, where turbulent flow is a must it is a disadvantage (Cementing Technology, 1984).
- Polyhydroxy organic acids and sugar derivatives is a retarder that the industry use for temperatures range of 200-400-degree F and it is effective in low concentrations as low as 0.2% by the weight of cement. It is also available in different types such as D109 a liquid retarder which is suitable for offshore locations where dry blending is impractical (Cementing Technology, 1984).

2.5.1.7. Fluid loss agents. Fluid loss agents are additives that can be added to the cement to work on controlling the filtration. The filtration happens generally near permeable zones where the water would be lost from the slurry causing several problems. It is important to limit the slurry water loss to avoid the increase in the slurry's viscosity, prevent the formation of annular bridges, and to minimize the effect on hydration of formation containing clay like shale (Applied Drilling Engineering, 1991). Failing to control the fluid loss could lead to low quality cement, higher density slurry, that could damage the formation, and the most important it can cause the cement to set before completing cement placement (Cheung and Beirute et al., 1985). The most commonly used fluid loss agents include latex, bentonite with dispersant, and various organic polymers.

2.5.1.8. Self-healing additives. Self-healing additives are expandable additives that expand to seal the cracks within the cement sheath. These self-healing additives can be activated upon contact with water or hydrocarbon or activated by contacting any fluid independent on the nature of the fluid.

- Designing a cement slurry containing self-healing additives activated by contacting specific fluids requires prior knowledge of the type of the fluids that may contact the cement during the productive lifetime of the well or after abandonment. Another compromising thing is the water absorption, as these additives absorb water from the slurry making it thicker and harder to pump. (Browning et al., 2012) tested different slurry recipes and proved the ability of elastomeric particles to swell and heal cracks when contact Kaydol white mineral oil. Particles size, crack size, and temperature of well fluids are still limitations.

- While tradition self-healing additives require contacting specific fluids, which hinder the self-healing effectiveness, (Reddy et al., 2010) presented a new cement composition with elastomeric additives that have the potential to heal cement cracks without the need for specific fluids to be activated. An extinction studies are required to investigate the availability of these materials in suitable particles sizes, physical properties, and chemical nature. For both types of self-healing additives even after shutting off the flow of a crack, it is still compromising when an increase in pressure differential occurred.

2.5.2. Unconventional (Nano-size) Additives. Although the conventional have been used and researched intensively in the century, these additives still fail in providing the cement with properties that provide full zonal isolation. The need of alternative method is necessary. Recently, one of the most active areas of research is the nanotechnology. Nanotechnology is a technology where substances with dimensions of 1 to 100 nanometers are used. It can be defined as the design, characterization, production, and application of materials, devices and systems by controlling the shape and size in the nanoscale (El-Diasty et al., 2015; M.F Fakoya and S.N Shah et al., 2017). The National Nanotechnology Initiative (NNI) described the nanotechnology as the manipulation of materials with at least one dimension sized from 1 to 100 nanometers. To better understand and visualize the Nano scale, the comparative size of nanometer to a meter is the same as that of a marble to the size of the earth (El-Diasty et al., 2015).

Many different materials can be downsized to the Nano-level, which would create significant changes in their physical and chemical properties (Deshpande et al., 2017). These materials include nickel nanoparticles, which improve the steam stimulation process by around 10% (El-Diasty et al., 2015). Ferric oxide nanoparticles, which have the potential to provide high-efficiency drilling practice and less formation damage (Mahmoud Omar et al., 2016). Nano silica, which improve the mechanical properties of cement and accelerate the hydration process (Patil, Rahul C et al., 2012). Nano magnesium oxide, which control the expansion in the cement sheath limiting the bulk shrinkage (Jafariesfad et al., 2017). Barite nanoparticles, which showed potential to reduce the cement fluid loss (Atashnezhad et al., 2017). Carbon nanomaterials, which improve the conductivity and the toughness of the cement (Shenghua Lv et al., 2013; and Sedaghat et al., 2014) .All of these materials and more have been studied in the past few years and proved the effectiveness of employing Nano materials in oil and gas industry.

In the oil and gas industry, the applications of nanotechnology have been growing in drilling and hydraulic fracture fluids, enhanced oil recovery, heavy oil viscosity reduction, logging operations, controlling formation fines, hydrocarbon detection, corrosion inhabitation, and oil well cementing (M.F Fakoya and S.N Shah et al., 2017).

This work focused on the enhancement that can be achieved in the cement system when introducing nanoparticles to the cement design.

Cementing the oil and gas wells has been discussed through this report, the importance of the cementing operation has been explained, and the conventional additives have been listed above with the importance and limitation of each of them. However, nowadays the industry nowadays is spending so much time in discovering unconventional ways to improve the cement design to meet the recent needs. From drilling deep offshore wells to drilling the long horizontal wells that are planned for hydraulic fractures ,which require cement able to withstand extreme high pressure and temperature, the industry is realizing the need of using unconventional sources to improve the cement. One of the unconventional ways is the use of nanotechnology, which is downsizing some conventional additives to Nano additives with new physical and chemical properties. Downsizing materials to Nano scales increases the surface area, thus an increase in the proportion of atoms on the surface of the particle, which increase the surface energy (El-Diasty et al., 2015). Figure 2.1 explains the increase in the surface area of the Nano materials.

Recently, carbon nanomaterials such as graphene nano platelets (GNPs), carbon nanotubes (CNTs), and carbon nanofibers (CNFs) have attracted many researchers due to their exceptional properties. This area of research needs additional experiments to investigate the influence of adding GNPs to the oil well cement. One of the objectives of this work is study GNPs and their effects on Portland cement class-H.

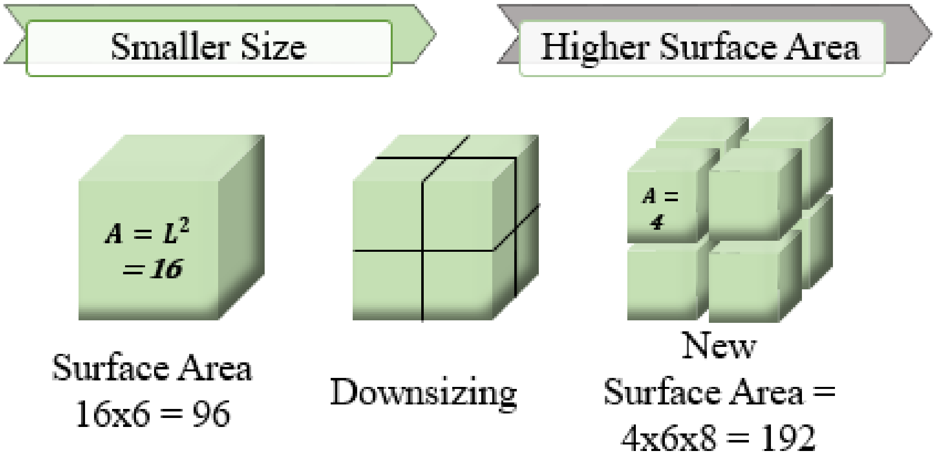

Figure 2.1. Effects of downsizing materials on surface area.

3. LITERATURE REVIEW

Hundreds of years were spent in studying the cement sheath, yet still cement failures are still unsolved. Several wells have not reached their full productive lifetime due to the unwanted gas migration. A numerus number of conventional additives have been implemented through the history to stop gas migration and that is why the industry is shifting to the use of nanotechnology to solve the problems related to cementing oil wells.

With this being said, it is essential after stating the problem and the conventional remediation to investigate the ability of unconventional solutions such as nanotechnology to provide solutions for cementing problems. Therefore, in this part of the research the work of other researchers in this area will be discussed and evaluated. The following investigation will include the effects of several nanoparticles on (1) rheological properties, (2) fluid loss, (3) mechanical properties, (4) porosity and permeability, (5) shrinkage, and (6) hydration process.

3.1. EFFECTS OF NANOPARTICLES ON RHEOLOGICAL PROPERTIES

As the aim is to cement wellbore it is a priority to make sure that the slurry is flow-able and thus it is important to study the rheological effects of adding nanoparticles to the cement system. For instant, adding silica nanoparticles to the cement system would slightly increases the rheological properties of the slurry (Patil and Deshpande et al., 2012) and adding iron nanoparticles to the cement system increases the viscosity (Vipulanandan, C et al., 2015). The simplest explanation of why the nanoparticles increases the viscosity of cement slurry is because of their high surface area (Santra et al., 2012). The concentration of nanoparticles in the Nano-fluids plays a major role too as nanoparticles tend to get close to each other when the concentration of the nanoparticles is higher (Bhuiyan et al., 2014). To better understand this phenomenon, two questions must be asked (1) what is Nano-fluid? (2) why nanoparticles tend to aggregate? and we will emphasize (3) the importance of dispersion.

3.1.1. What is Nano-Fluids? Nano-fluid is a colloidal mixture of nanoparticles dispersed in a base fluid (Bhuiyan et al., 2014). A colloid is a system of two substances one of them (dispersed) is finely divided and distributed in the other (dispersion medium) (Drew Myers, 2002).

3.1.2. Why Nanoparticles Tend to Aggregate? It is believed that the nanoparticles tend to get close to each other (aggregate) due to the interaction forces between the atoms and the molecules or what is called Van Der Waals forces (Drew Myers, 2002). The explanation of Van Der Waals forces simply is that particles in general tend to aggregate without the presence of an opposing repulsive interaction (Terence Cosgrove, 2010).

This would take us back to the importance of optimizing the concentration of nanoparticles in Nano-fluids as increasing the nanoparticles would increase the surface tension of the Nano-fluids (Bhuiyan et al., 2014). The result is the problem of aggregation that will held the potential properties of nanoparticles from exposing and enhancing the cement sheath (Patil and Deshpande et al., 2012) and conversely, might compromise some other important properties such as viscosity, compressive strength, and the hydration process. Therefore, to achieve a stable Nano-fluid it is important to pay attention to the dispersion and the effect of the size of the nanoparticles on the dispersion of the particles in the collide. Figure 3.1 shows the difference between stable and unstable colloid.

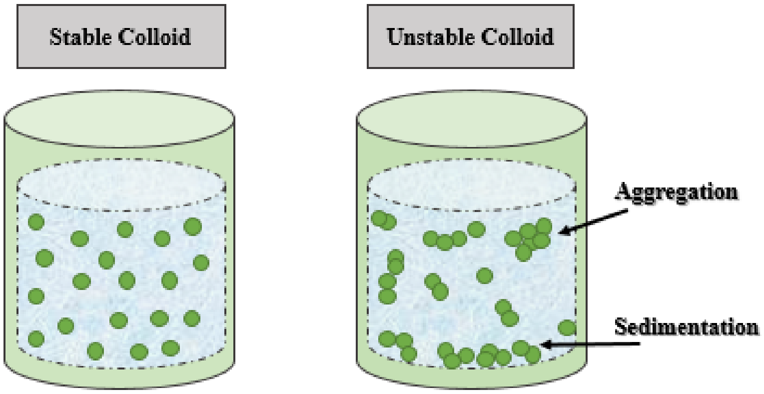

Figure 3.1. Examples of stable and unstable colloidal dispersion.

3.1.3. The Importance of Dispersion. It is important to stabilize the nanoparticles in the host fluids before any further investigation in the effects of Nano materials on cement and it is one of the challenges that the industry is facing (M.F Fakoya and S.N Shah et al., 2017). We can also prove the importance of dispersion as (Patil and Deshpande et al., 2012) mentioned in his research the possibility that the Nano silica particles entangled with the Nano latex, keeping the Nano silica de-aggregated and as a result helped using Nano silica as accelerator. In addition, (W. A. Khan et al., 2016) talked about a 40 % increase can be obtained if an efficient dispersion of carbon nanotubes in cement achieved. Many methods can be utilized to obtain a good dispersion. To highlight the importance of properly dispersing these nanomaterials, three methods to disperse the halloysite in water were used by (Deshpande and Patil et al., 2017) to get the best result and many tests can be done to test the stability of nanomaterials such as temperature effect (Jafariesfad et al., 2017). In addition to other tests such as pH test and salt test which will be discussed later in the section of evaluation of nanoparticles. It is essential too to study the effect of the size of the nanoparticles on their performance.

The effect of the size of the nanoparticles on their performance. Those systems of colloidal show a degree of size poly-dispersity (Terence Cosgrove, 2010). The size of the nanoparticles usually refers to the diameter of the nanoparticles and the range of sizes can be measured using Transmission Electron Microscope (TEM) or Zeta Potential measurements. Different sizes and aspect ratios play roles in the effectiveness of nanoparticles as (Pang et al., 2014) believes that the most effective Nano silica as accelerators were found to be related to the ones which have the smallest particle size in the range of 4 to 6 nanometers and with higher aspect ratios (Cigar-shape or string-of-pearls-shaped). Carbon nanotubes (CNTs) that have high aspect ratios, which means higher energies are required for crack to propagate and small diameters of carbon nanotubes helps both better distribution in the cement matrix and may involve different interaction with the cement matrix (Rahimirad et al., 2012). Also, the Nano magnesium oxide with the smaller particle size have larger reaction interface with water, resulting better limiting in bulk shrinkage (Jafariesfad et al., 2017).

3.2. EFFECTS OF NANOPARTICLES ON FLUID LOSS

As discussed earlier in this work the importance of controlling fluid loss to eliminate gas migration, the studies show that the nanoparticles has an effect on fluid loss specially Nano silica (Patil and Deshpande et al., 2012) believes that the ability of nanoparticles to fill the void spaces between cement particles is the reason behind the fluid loss enhancement. However, (Atashnezhad et al., 2017) claims that the reason of the enhancement is the ability of barite nanoparticles to plug the formation pores. In addition, high reactivity Nano magnesium oxide exhibited lower free fluid in comparison to the reference system (Jafariesfad et al., 2017).

3.3. EFFECTS OF NANOPARTICLES ON MECHANICAL PROPERTIES

Mechanical properties is another area where nanotechnology can be utilized to enhance the wellbore integrity (El-Diasty and Ragab, 2013). Today, the industry is showing great interest in extracting hydrocarbon from unconventional reservoirs and as this area is growing the need of enhancing the mechanical properties of the cement sheath is growing. Extracting oil and gas from unconventional reservoir may subject the well cement to significant stress levels such as high pressure and/or high temperature wells, deep-water wells, and storage gas wells. These wells require a cement sheath that is able to withstand these extreme conditions. Most of the results that have been reviewed showed a potential improvement in (1) compressive strength and/or (2) tensile strength, because of adding nanoparticles to the cement design. Carbon nanotubes, Graphene nano platelets, iron nanoparticles, Nano silica, magnesium oxide nanoparticles, barite nanoparticles, and Nano alumina are examples of promising nanoparticles in this area.

3.3.1. The Potential Improvement in Compressive Strength. Using 0.05% carbon nanotubes by mass to reinforce the cement sheath can increase the compressive strength up to 70% (Rahimirad et al., 2012) while (W. A. Khan et al., 2016) concluded that using 0.5% multi walled carbon nanotubes by weight of cement can increase the cement compressive strength to up to 15%. An increase in the cement compressive strength was observed when adding 1% iron nanoparticles to the cement system (Vipulanandan, C et al., 2015). When adding a small amount of magnesium oxide nanoparticles (less than 3%) a significant increase in compressive strength is observed (Jafariesfad et al., 2017). Nano silica also showed potential to increase the compressive strength of the cement (Patil and Deshpande et al., 2012; Lev V. Kim et al., 2013; Pang et al., 2014). (Lev V. Kim et al., 2013) believes that adding Nano silica with sizes range of 3-12 nm to the cement sheath can increase the compressive strength up to 72%. (Pang et al., 2014) believes that Nano silica can improve the two days' compressive strength of the cement by 30% and 136% for the seven days' compressive strength compared to the maximum results obtained by using calcium chloride as an accelerator. (Patil and Deshpande et al., 2012) tests results showed an increase of the cement compressive strength of three times his reference slurry. (Deshpande and Patil et al., 2017) in his tests compared a cement slurry that contains neat latex, which is an additive used in the industry to improve the fluid loss properties of cement to prevent gas migration, to a cement slurry that contains latex plus sub micronized alumina (200-400 nm). The results showed that the submicron alumina increased the compressive strength by around 2.5 times the compressive strength of the neat latex cement. These results proves the potential that nanoparticles have to improve the wellbore integrity in terms of compressive strength. More investigations have to be done to test other Nano materials such as barite nanoparticles to see if they improve the cement compressive strength or not.

3.3.2. The Potential Improvement in Tensile Strength. Halloysite nanoparticles, which are tubes of diameters size in the range of 30 to 70 nanometers and length of 1 to 1.3 microns, can be employed as a tensile strength enhancer and the enhancing is as high

77% (Deshpande and Patil et al., 2017). CNTs increases the tensile strength by 15% (De Paula et al., 2014). Also, GNP and CNF improved the tensile strength of cement by 10% (Peyvandi and Dahi, 2017). Conversely, the addition of magnesium oxide nanoparticles (MgO) to the cement system might reduce the tensile strength (Jafariesfad et al., 2017).

The effects of Nano MgO on compressive strength, tensile strength, and Young's modulus have to be investigated carefully as the addition of Nano scale expansive agent has a noticeable impact on the mechanical properties of cement. (Atashnezhad et al., 2017) stated the ability of barite nanoparticles to improve the mechanical properties of cement; however, this claim has to be proved with experiments.

3.4. EFFECTS OF NANOPARTICLES ON POROSITY AND PERMEABILITY

Porosity and permeability are other properties that nanoparticles can improve as the nanoparticles acts as a filler in the cement matrix, reducing the porosity of the cement (W. A. Khan et al., 2016) as this researcher proved the capability of multi walled carbon nanotubes to reduce the porosity. Likely, the permeability as the addition of Nano silica can reduce the permeability of the cement, providing more durable cement sheath (Pang et al., 2014).

3.5. EFFECTS OF NANOPARTICLES ON BULK SHRINKAGE

In 2016 Jafariesfad, used the expansion additive magnesium oxide but by downsizing its particles into Nano size to control the expansion performance of the additive, which would limit the bulk shrinkage of the cement sheath in oil wells. Limiting bulk shrinkage would help avoiding fluid migration and providing short and long-term isolation. The researcher proved that the development of expansive properties of Nano MgO could be controlled through heat treatment to produce the required expansion at the right time because if the expansion happened at early stages, when the slurry is still in fluid phase, the cement system will not be able to sustain the expansive forces. The right time for the expansion to occur is at the beginning of cement hardening phase.

Between the three versions of Nano MgO that the researcher tested, it can be concluded that the one with the high reactivity provides early expansion in the cement system, which eliminated bulk shrinkage for three weeks.

3.6. EFFECTS OF NANOPARTICLES ON HYDRATION PROCESS

It has been found that the nanoparticles have a huge impact in the cement hydration process. In this area, the silica nanoparticles took the attention of many researchers as Nano silica has the ability to accelerate the hydration process (Patil and Deshpande et al., 2012; Pang et al., 2014). Also, the high reactivity Nano MgO tested by (Jafariesfad et al., 2017) decreased the setting time of the system by 40% comparing to the reference system. Submicron alumina (200-400 nm) when added with latex to the cement design act as an accelerator at low temperature (Deshpande and Patil et al., 2017). Those materials succeeded to achieve early compressive strength under wide range of temperatures especially low temperature where accelerators are must to reduce the wait on cement time, which would lower the operational costs.

(Patil, Rahul C et al., 2012) added Nano silica particles to latex, an additive used widely on oil well cement to control fluid loss and help preventing gas migration. He tested the cement systems' compressive strength, thickening time, and fluid loss. His reference slurry contained neat latex and he compared it to cement slurry contains latex and micro-sized silica and cement slurry contains latex and Nano silica. The results of his work showed that Nano silica has the ability to improve the strength on the cement under different temperatures.

(Pang et al., 2014) investigated the feasibility of using different sizes and ratios of Nano silica as a cement additive to accelerate the hydration process of the cement at low temperatures. Traditionally, accelerators are common additives to cement in applications where temperature is very low, to reduce the wait on cement time but those additives have a negative potential to increase the cement permeability allowing fluids to migrate through the cement column. Nano silica particles on the other hand reduce the permeability and enhance the mechanical strength of the cement sheath. He revealed that the use on Nano silica as an accelerator is more effective the calcium chloride in lightweight cement and vice versa in regular weight cement.

Carbon nanomaterials, including carbon nanotubes (CNTs) and carbon nanofibers (CNFs), with their high aspect ratios (length to thickness), allow them to bond with the various cement hydrates. These carbon nanomaterials showed high potential to enhance mechanical properties of the cement. Their structure and Nano size abled those nanomaterials to fill the void spaces of the cement and stop the growth of micro cracks within the cement sheath (Peyvandi et al., 2017).

GNPs also offer distinctly high aspect ratios and high thermal and electrical conductivities; GNPs have been added to polymers, ceramics, and rubbers due to these characteristics (Wang et al., 2016). Nowadays, introducing GNPs to cementitious materials attracted many researchers.

4. NANOPARTICLES EVALUATION TESTS

In this section of the report, different methods to obtain nanoparticles are presented, then some main tests that are important to characterize the nanoparticles are discussed, next some important tests to ensure the stability of the nanoparticles in different environments are presented.

First, there are many different ways to produce nanoparticles some include chemical interfere, which known as bottom up methods and other include mechanical interfere, which known as top down methods. These different methods include:

- Chemical vapor deposition
- Plasma arcing
- Electrodeposition
- Sol-gel synthesis
- Ball milling
- The use of natural nanoparticles

Selecting the method of how the nanoparticles shall be produced depends on the material properties itself, the availability of the material, and some other factors which are out of the scope of this work.

Secondly, characterizing the nanoparticles, which include finding their range of sizes, their surface charge, and images of them. This kind of information about the nanoparticles would explain a lot about their behavior. Knowing the surface charge for example would help us predicting weather the particular nanoparticles would tend aggregate or not. There are many different tests and apparatus serve in this area including:

(1) transmission electron microscope (TEM), (2) Zeta potential and dynamic light scattering, and (3) pH test.

4.1. TRANSMISSION ELECTRON MICROSCOPE (TEM)

Transmission electron microscope is a very useful tool in this area as it can be used to study the shape and the dispersion of the nanoparticles and when matched with some software, it can be used to estimate the particles size distribution.

TEM utilizes a technique in which beams of electrons pass through the sample to form an image. The image then can be magnified on a screen with high resolution and studied to obtain the targeted information. See Figure 4.1 that shows the process of TEM.

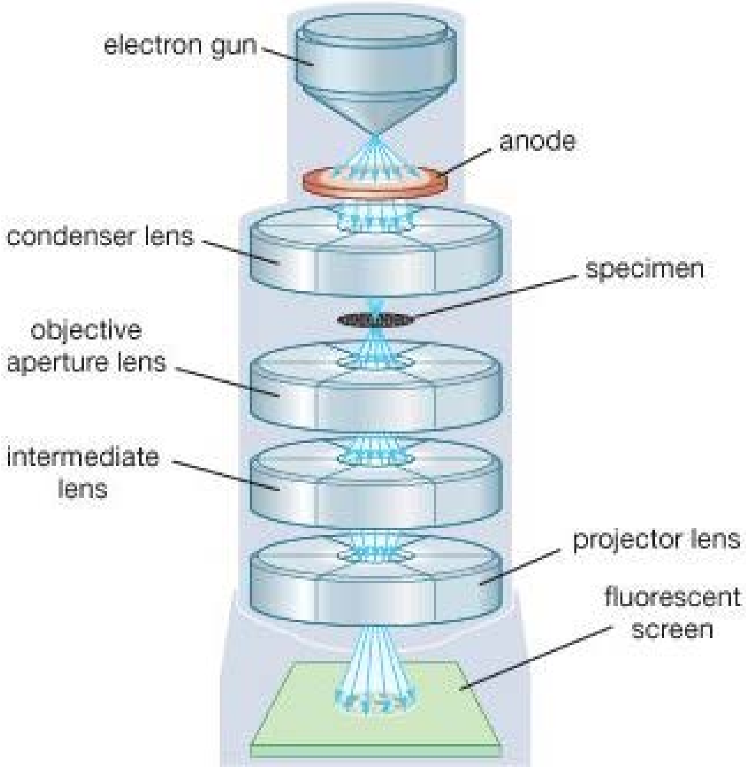

Figure 4.1. Process of taking image in TEM (Encyclopedia Britannica, Inc.).

The procedure is simple:

1) A small amount of the nanoparticles shall be mixed with water.
2) A drip of the mixture shall be placed on a screen.
3) The screen shall be placed in an isolated chamber until the water evaporated.
4) The dry particles on the screen can be tested.

4.2. ZETA POTENTIAL AND DYNAMIC LIGHT SCATTERING ANALYZER

The key of measuring the stability of colloidal dispersion is zeta potential measurements as it provide us with the charges of the nanoparticles and how strong those charges are. Mainly, this test to have an indication of the magnitude of the potential at the beginning of the diffuse double layer around the particles (the mV readings) (Jian Hang et al., 2007). Having this information would help identify weather the nanoparticles in the solution would aggregate or not. Figure 4.2 shows what we expect from Zeta potential measurement.

Lastly, it is important to test the nanoparticles before adding them to the cement system to ensure their effectiveness and to avoid any future problems. Testing the nanoparticles include testing their stability against (1) different pH values, (2) different salt concentrations, and (3) variety of temperatures.

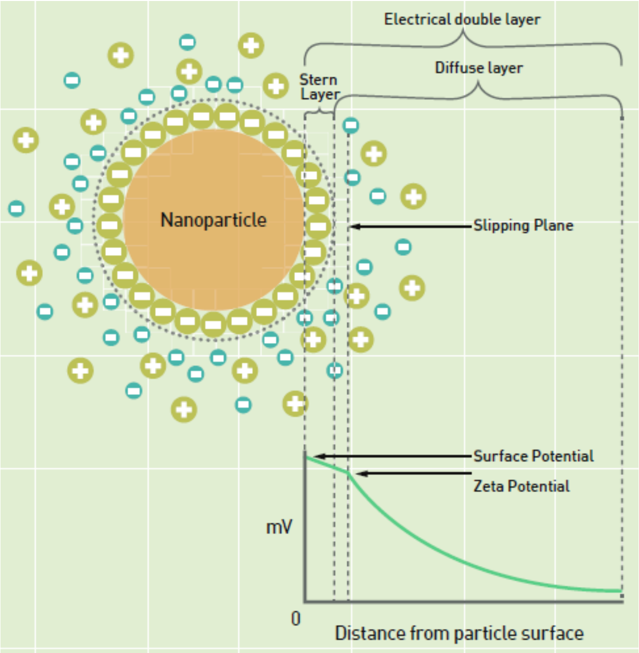

Figure 4.2. Zeta potential measurements (Malvern.com).

4.3. PH TEST

This test involves testing the nanoparticles in solutions of water with different pH values. The reason behind this test is to know the range of pH values where the nanoparticles will remain stable.

The procedure is simple:

- Multiple testing tubes shall be cleaned.
- Distilled water shall be added to the tubes.
- Sodium hydroxide or other additive to increase/reduce pH shall be added with different concentrations.
- The nanoparticles shall be added to the solutions.
- The stability can be indicated when the solution gets cloudy.
- pH indicator shall be used to record the pH value.

4.4. SALT TEST

Salt test is similar to pH test except that in this the concentrations of salt is one that has to be varied to test the ability of the nanoparticles to remain stable under wide range of salt concentration. This test is important, as nowadays most active projects are those in deep water, where the cement might face a high salinity environment.

4.5. TEMPERATURE TEST

This test is also similar to pH and Salt tests. However, here the temperature effects are to be studied. In this test the procedure steps are similar to those of pH test but here the temperature shall be changed to record to how extent the nanoparticles are able to remain stable.

5. CEMENT EVALUATION TESTS

To have a sufficient cement sheath that can provide support for the casing, provide zonal isolation, gains strength over time, easy to flow (pump-able), and elastic and resilient to withstand several temperature and pressure cycles over the life of the well, we must study and test the cement in the lab. API provides a recommended procedure for testing the oil well cement (API Specification 10) in addition to other recognized testing agencies such as (ASTM specifications) and some other non-standard procedures to test some properties of the cement.

The laboratory analysis and testing of the cement can be divided into four major sections: (1) testing the dry cement powders, (2) preparing the cement slurry, (3) testing the liquid cement slurries, and (4) testing the hard-set cements (Cementing Technology, 1984).

5.1. TESTING THE DRY CEMENT POWDER

Testing the dry cement powders involves the chemical analysis of the physical properties of the cement powders. In this stage of testing the cements, the tests are performed to ascertain the present of the chemical elements such as calcium, silicon, aluminum, and magnesium or the cement phase such as tricalcium aluminate, tricalcium silicate, dicalcium silicate, and tetracalcium alumina ferrite within the cement powders. There are three common methods to determine the elements present (1) flame atomic absorption spectrophotometry (2) energy dispersive analysis, and (3) wet chemical analysis (Cementing Technology, 1984). For the present of the cement phases and some other components in the cement powders, one of the following technique can be used (1) x-ray diffraction, (2) solubility tests, (3) thermogravimetric analysis, and (4) scanning electron microscopy (Cementing Technology, 1984).

5.1.1. X-Ray Diffraction.

X-Ray diffraction (XRD) yields quantitative results by relating the various peak areas obtained, to that of a calcium fluoride standard mixed with the cement powder sample. In this process, each compound has its own particular diffraction or 'fingerprint' at which the technician who is performing this experiment can determine which, and around how much, of each compound exists in the cement sample. The diffracted x-rays from the cement sample are detected by a proportional counter and the resultant signal are recorded in a strip chart recorder (Cementing Technology, 1984). The cement sample can be hydrated or unhydrated. For hydrated samples, the cement shall be ground to powder and sieved using 325 mesh. Figure 5.1 shows the XRD equipment and Figure 5.2 shows the related preparing equipment.

Figure 5.1. XRD equipment.

Figure 5.2. Samples of cement and the sieve (325 mesh).

5.1.2. Solubility Tests. Solubility tests are based on three basic information that can be utilized to perform simple test to estimate the present of the cement phases, which are:

- Tricalcium silicate and dicalcium silicate are soluble in a blend of methanol and salicylic acid.
- Tricalcium aluminate is soluble in a solution of cane sugar.
- Tetracalcium aluminate ferrite is in soluble in either of the solutions.

By carrying out a series of filtrations, the amounts of each phase can be determined gravimetrically using a standard laboratory apparatus (Cementing Technology, 1984).

5.1.3. Thermogravimetric Analysis. Thermogravimetric analysis records very precise changes in the weight of the cement powder sample when is heated. This method is used to identify effects like dehydration and de-carbonization, which would provide some information about the components in the cement sample (Cementing Technology, 1984).

5.1.4. Scanning Electron Microscopy. Scanning electron microscopy (SEM) and energy dispersive analysis, which can provide qualitive signs of the presence of contaminants within the cement powder.

5.2. PREPARING THE CEMENT SLURRY

American Petroleum Institute (API) stated important specific requirements and recommendations regarding preparing the cement slurry in laboratory scale including (1) the temperature of water and cement, (2) the mix water, (3) the mixing quantities, (4) the mixing devices and procedure, and (5) molding the slurry.

5.2.1. Temperature of Water and Cement. The temperature of the mix water shall be 23 ± 1 ˚C within 60 s before mixing and that applies to the cement powder too (API 10A 2010).

5.2.2. Mix Water. The water shall be distilled or deionized and it should be weighted in a clean, dry mixing container. No water shall be added to compensate for evaporation, wetting, etc. (API 10A 2010).

5.2.3. Mixing Quantities. For each class of Portland cement there is specific slurry components quantities see Table 5.1. The use of these components will result in mix-water percentages based on the mass of dry cement (API 10A 2010).

Table 5.1. Slurry Requirements.

Components	**Classes A & B [gr]**	**Class C [gr]**	**Classes D, E, F, H [gr]**	**Class G [gr]**
Mix water	355 ± 0.5	383 ± 0.5	327 ± 0.5	349 ± 0.5
Cement	772 ± 0.5	684 ± 0.5	860 ± 0.5	792 ± 0.5

5.2.4. Mixing Devices and Procedure. The mixing device shall be a one-liter size, bottom drive, and blade type mixer see Figure 5.3.

Figure 5.3. Examples of API mixers.

Prior to mixing, the cement shall be sieved and the mixing procedure is as follow:

1. The container shall be filled with water.
2. The mixer shall be switched on to 4000 ± 200 rpm.
3. The dry cement shall be added at uniform rate in less than 15 s.
4. The mixer shall be covered.
5. The speed shall be increased to 12000 ± 500 rpm for 35 ± 1 s.

5.2.5. Molding the cement slurry. After mixing the cement, the cement slurry shall be poured in molds in less than 5 min ± 15 s. The molds are standardized by API as cubes of 2 inches in length for compressive strength test as showed if Figure 5.4. The molds shall be placed curing bath at the desired temperature and pressure. In addition, some of the cement slurry shall be poured in cylindrical cells to be used in measuring other properties such as tensile strength and permeability. For shrinkage measurements some of the slurry shall be poured in a special curing molds where studying the shrinkage phenomena is applicable.

Figure 5.4. Example of API cubic mold.

5.3. TESTING THE LIQUID CEMENT SLURRIES

The second section of testing the cement is testing the liquid cement slurries which means test some properties of the cement while the cement is in liquid phase. This section includes many tests and procedures that are recommended by API to determine if a given cement composition is suitable for a given well conditions. The tests equipment required to perform some of these tests includes a mud balance, a rotational viscometer, a filter press, a consistometer, curing molds, and many other testing apparatus.

To make it easier for the reader, in the following section we explained the measurements that are needed to test in the cement slurries and then the equipment that are recommended to use. The measurements are (1) density, (2) rheological properties, (3) fluid loss, (4) thickening time, and (5) heat of hydration, and (6) setting time.

5.3.1. The Slurry Density. The slurry density is an important parameter in designing any cement system. Mostly the cement slurry is a target for the researcher when designing cement system for example, if the application requires a cement slurry of 16.5 lb./gal, the researcher will design a cement system with the appropriate additives to achieve this density. Then, a sample of the designed cement slurry will be tested in a mud balance to make sure that it has the desired density. The mud balance is an equipment that is used to measure the density of mud samples see Figure 5.5.

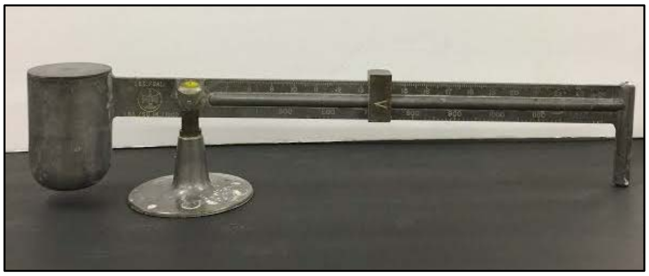

Figure 5.5. Example of mud balance.

The apparatus consists of a cup to be filled with mud sample and a movable rider to be adjusted to the position where it balance and the density can be determined. This mud balance is usually calibrated using fresh water, which has density of 8.33 lbm/gal. For cement density measurements, the same equipment is used but with some modifications as the entrained air in the sample is more difficult to remove than mud, and then the mud balance should be pressurized to reduce the effect of the entrained air.

5.3.2. The Rheological Properties. The rheological properties are important properties for the cement slurry design and it is important to be studied properly. During the cementing of oil and gas wells these rheological properties are not only the main factor affecting the annular displacement efficiency and the cement quality, they are also important in ensuring the safety of the cementing operation (He et al., 1999; Liu et al., 2001). The rheological properties can be obtained using rotational viscometer FANN 35 viscometer. Figure 5.6 shows the nomenclature of the rotational viscometer.

Figure 5.6. Example of viscometer.

The cement slurry is sheared at a constant rate between an inner bob and an outer rotating sleeve. There are six standard speeds in the rotational viscometer (3, 6, 100, 200, 300, and 600). The dimensions of the bob and the rotor are designed so that the dial reading at a rotor speed of 300 rpm (revolutions per minute) is equal to the apparent Newtonian viscosity in centipoise.

$$\mu_a(Newtonian\ Fluid) = \theta_{300} \tag{1}$$

At other rotor speeds, the apparent viscosity can be obtained using the following equation.

$$\mu_a = \frac{300\ \theta_N}{N} \tag{2}$$

Where, θ_N is the dial reading in degrees and *N* is the rotor speed in rpm (revolutions per minute).

The above equations are for fluids that follow Newtonians fluid behavior. For the non-Newtonian fluid, the viscometer can also be used to determine two parameters that follow Bingham plastic model which are plastic viscosity and yield point of the fluid. The plastic viscosity μ_P is in centipoise and is computed using the equation below:

$$\mu_P = \theta_{600} - \theta_{300} \tag{3}$$

Where, $\theta_{600}$is the dial reading at speed of 600rpm and $\theta_{300}$is the dial reading at speed of 300rpm. The yield point $\tau_y$is in lbf/100 ft^2 and is computed using this equation:

$$\tau_y = \theta_{300} - \mu_P \tag{4}$$

Gel-strength in units of lbf/100 ft^2 is another parameter that can be taken directly from the dial reading. This reading can be taken by letting the sample in static conditions for 10 seconds then turn on the viscometer at low speed usually 3rpm and noting the maximum dial deflection and it can be reported according to API as the initial gel strength or letting the sample in static for 10 minutes and report the value as 10 minutes-gel (Applied Drilling Engineering, 1991).

5.3.3. The Fluid Loss. The fluid loss from a cement slurry can be determined using an API filter press. Control the fluid loss of cement slurries is essential to reduce the dehydration of the slurry across the permeable zones of the well. In the test, the filtration rate is measured through a standard filter paper. The static fluid loss test is operated at pressure of 1000 psig and ambient temperature. Figure 5.7 shows the filtrate press test equipment. The mud cup is filled with mud or cement slurry samples and the pressure is applied through the pressure inlet and the volume collected in a 30-min time from the filtrate tube is doubled and reported as the standard water loss. This setup can be modified by adding a heating jacket or applying higher pressure to simulate the elevated temperature and pressure conditions of some wells.

The filtration rate increases with increasing temperature while pressure has less effect on the filtration rate (Applied Drilling Engineering, 1991). In addition, for high pressure high temperature (HPHT) the filter paper is one-half the area of the standard one so the volume of the water loss must be doubled before reported.

Figure 5.7. A filtrate press test equipment.

5.3.4. The Thickening Time. It is important to determine the thickening time of the cement before obtaining the rheological properties of the cement because it is important to simulate a given history of slurry pumping before making other tests since the cement thickens with time (Applied Drilling Engineering, 1991). The thickening time can be obtained using a cement consistometer see Figure 5.8.

Figure 5.8. An example of cement consistometer (Cement Test Equipment).

Depending on the desired temperature and pressure, a suitable consistometer is used to provide the slurry consistency B_c against time. the consistometer consists in general of rotating cylindrical slurry container equipped with a stationery paddle assembly, all in pressure chamber able to withstand pressures and temperatures similar to those encountered in the field. The cylindrical chamber rotates at speed of 150rpm during the test (Applied Drilling Engineering, 1991). The consistency is defined in terms of the torque T that exerted on the paddle by the cement slurry and the relation between the consistency and the torque is given by

$$B_c = \frac{T-78.2}{20.02} \tag{5}$$

Where, T is the torque and B_c is the slurry consistency in API consistency unit. The thickening time of the slurry is the time to reach 100 B_c which is the upper limit of pump-ability. The recommended placement time would be the thickening time minus one hour.

The consistometer can be also used to determine the minimum, maximum, normal, and free water content of the slurry.

5.3.5. The Cement Heat of Hydration. Earlier in this work, the entire hydration of the cement and the components involved in the hydration process were discussed in details. In this part of the work we mention an important device used in recording the hydration process at all stages since the liquid phase up to 144 hours. The device is Isothermal Calorimeter I-Cal 8000 see Figure 5.9. This device has 8 cells designed to test the cement hydration process using sensors to measure the heat flow generated by the hydration reaction of the cement. One reference sample and multiple testing samples.

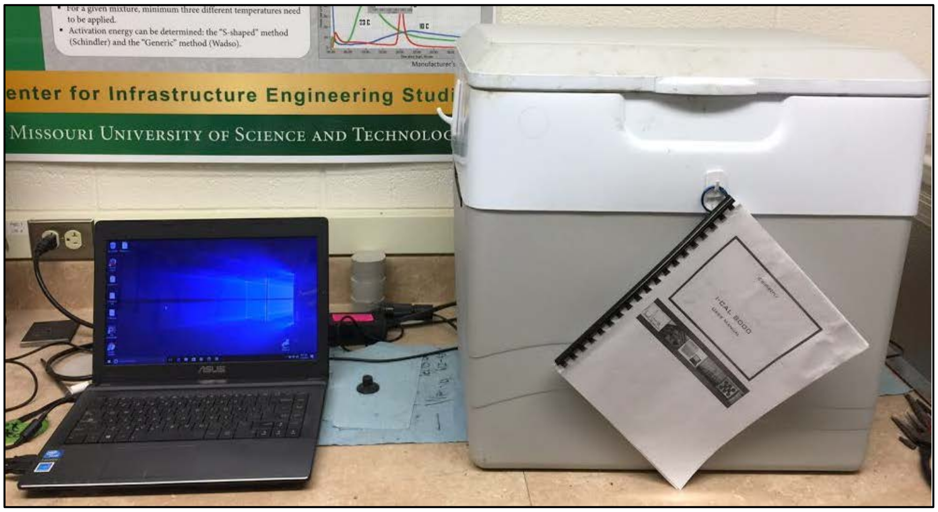

Figure 5.9. Isothermal Calorimeter I-Cal 8000.

5.3.6. The Setting-Time. The setting-time measurement is different than the thickening time as it is defined as the time taken for wet cement in a static condition to reach a conventional cohesive strength. It is a technique used by ASTM standards using Gilmore and Vicat needles (ASTM SC 2256-74, C 807-76 and C 191-74). Figure 5.10 shows the Vicat Apparatus.

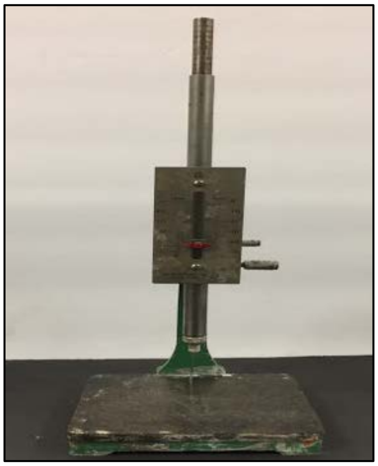

Figure 5.10. Vicat Apparatus.

5.4. TESTING THE HARD-SET CEMENT

The last section of testing the cement is testing the hard-set cement, which means testing the cement when it is already set. This section include testing many physical properties of a set cement such as (1) testing the compressive strength, (2) testing the tensile strength, (3) testing the bonding strength, (4) finding the permeability of the cement, (5) finding the porosity of the cement, and (6) testing the cement shrinkage

5.4.1. Testing the Compressive Strength. The compressive strength test determines the strength of the cement sheath. Compressive strength test simply measures the force needed to crush a sample of cement. After curing the cement sample in the molds for 8 hr ± 15 min and 24 hr ± 15 min it must be removed and placed in a hydraulic press where force will be exerted on the cube until failure see Figure 5.11. This is following the API recommendations. Depending on the class of cement used in the test, it must gain specific minimum strength after curing for 8 and 24 hours. However, this test can be modified with confining pressure around the sample to simulate the expected downhole pressures.

Figure 5.11. An example of hydraulic press testing machine.

For this test API recommends the use of 2” *2” *2” cubic molds which shall be cured in a water bath that is pressurized or under atmospheric pressure and under specific temperature depending on the class of cement to be used or the application.

5.4.2. Testing the Tensile Strength. The tensile strength is another parameter that has to be measured and enhanced to ensure the wellbore long-term integrity. When the tensile strength of the cement is exceeded, a radial crack may form along the cement sheath axis, which would create a high conductivity path for the fluids to migrate (Simon S et al., 2015). The tensile strength can be measured using the indirect tensile strength method which, is known as the Brazilian test see Figure 5.12.

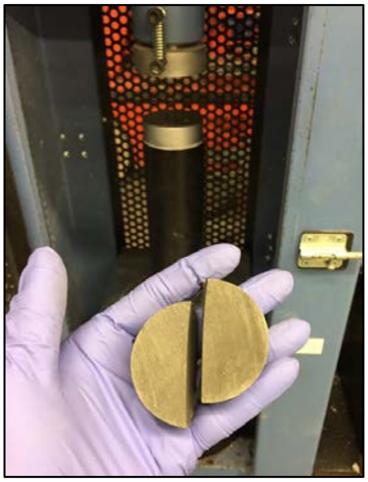

Figure 5.12. The Brazilian test.

The technique used in this test is applying compression force across the diameter of the cement cylindrical sample and stop when the failure occur. It is important to check if the failure crack is parallel to the load direction, otherwise the result is not reliable

(Simon S et al., 2015). The testing cylindrical shape specimens has to be cured in similar manners to those of compressive strength.

After determining the load required to initiate the fracture, the following equation can be used to find the tensile strength.

$$\sigma_T = \frac{2\,F}{\pi\,h\,D} \tag{6}$$

Where, F is the load, h and D are the height and the diameter of the specimen respectively.

5.4.3. Testing the Bonding Strength. Testing the cement bonding properties is conducted to ensure the ability of the cement to prevent the fluid communications between different layers. To prevent the formation of micro-annuli, good bonding at the interface of cement/formation and cement/casing must be achieved (Liu Xiangyu et al., 2015). The cement bonding can be categorized into more than one bonding properties, two of them will be presented in this work (1) shear bond and (2) hydraulic bond.

5.4.3.1. Shear bond. Shear bond is the bond between the casing and the cement that supports the casing in the hole (Carter and Evans, 1962). This bond can be measured using a “push out” shear bond test cell see Figure 5.13. (Carter and Evans, 1962; Liu Xiangyu et al., 2015). A mold is needed where a cylindrical rock sample is placed in the center and a plastic spacer is placed over the rock sample. Then, the cement slurry is poured between the rock and the mold wall. After the required curing time and under the targeted pressure, the mold is disassembled and the plastic cover is removed. Next, the cement sample with the rock in the center is flipped upside down and a load is applied on the rock until movement is initiated between the rock and the cement, which considered as the failure load. The shear bond can be obtained using the following equation (Liu Xiangyu et al., 2015).

$$\tau_{sb} = \frac{F}{A} \tag{7}$$

Where, τ_{sb} is the value of shear bond strength, F is the failure load, and A is the contact area. This setup can also be used to measure the bonding between the cement and the casing simply by replacing the rock with steel casing.

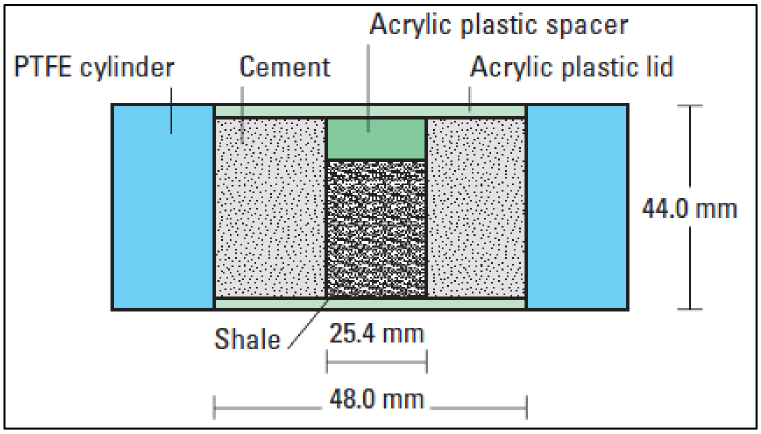

Figure 5.13. A schematic figure of a "push out" cell (Liu Xiangyu et al., 2015).

5.4.3.2. Hydraulic bond. Hydraulic bond is the bonds between the casing/cement and cement/formation interfaces that helps prevent fluid communication (Carter and Evans, 1962). Failure to achieve this bonding would result to the unwanted micro-annuli. It can be measured by cementing a pipe as a casing inside a wider pipe as the well hole then cementing the annulus between the two pipes. Next, is pumping gas or liquid from one hole at the side of the outer pipe and measure the pressure where leakage would happen as the hydraulic bond strength see Figure 5.14. (a) (Liu Xiangyu et al., 2015).

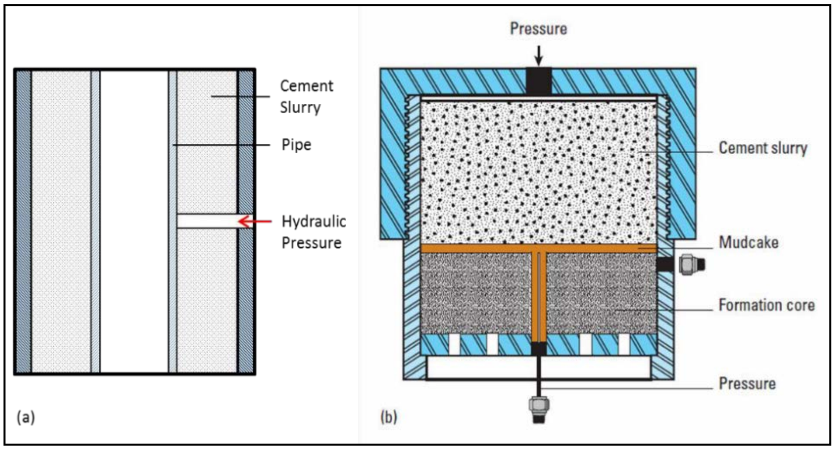

Figure 5.14. Hydraulic bond setup (Liu Xiangyu et al., 2015).

The sizes of the pipes (diameter and length) do not affect the hydraulic bonds strength; it is just a function of time (Carter and Evans, 1962).

Similar setup can be used to measure the hydraulic bonding between cement and formation as shown in Figure 5.14 (b).

5.4.4. Finding the Permeability of the Cement. Permeability generally defined in fluid mechanics and earth sciences as the ability of a porous media to allow fluids to pass through it, which is an important parameter when we talk about rocks and it is likely to have high permeability. However, when it comes to cement it is an undesirable property so to have a good zonal isolation it is essential to have the cement permeability as small as possible. Permeability can be measured using cement permeameter as shown in Figure 5.15 that is recommended by (API Rb10B, 2010). The test consists of core holder, where cement core is to be placed, and the permeability of the set cement will be measured by injecting fluid through the core at a given pressure differential across the length of the core (Drilling Book). The permeability can be obtained using the following form of Darcy's law.

$$k = 14{,}700 \frac{q \, \mu \, l}{A \, \Delta P} \tag{8}$$

Where, k is the permeability in milidarcy, q is the flow rate in mL/s, μ is the fluid viscosity in cp, L is the sample length in cm, A is the cross-sectional area of the sample in cm^2, and ΔP is the pressure differential in psi.

Figure 5.15. An example of Cement Permeameter (OFI Testing Equipment).

5.4.5. Finding the Cement Porosity. Porosity is defined as the available void spaces for fluid storage within the matrix. There several methods to measure the porosity of a sample such as Mercury Intrusion Porosimetry (MIP) and Helium Porosimeter see Figure 5.16.

Figure 5.16. Example of Helium Porosimeter (OFI Testing Equipment).

The Mercury Intrusion Porosimetry measures the pores by measuring the mercury volume that intrude the sample and similarly the Helium Porosimeter measures the volume of Helium that intruded the cement sample.

5.4.6. Testing the Cement Shrinkage. Cement shrinkage as we mentioned earlier is phenomena that has to be limited and controlled to ensure long-term isolation of the wellbore. There are several methods to measure the cement shrinkage over time such as (1) ring mold method and (2) membrane method.

5.4.6.1. Ring mold method. Ring mold method is used to measure the bulk shrinkage or bulk expansion while the cement sample has free access to water. This method is one of the methods recommended by API. It can performed under temperature as high as 88 ˚C and with or without pressure. This method is good to measure the effect of expansive materials in cement; however, the curing of the cement sample is different than that of API (B.R. Reddy et al., 2009).

5.4.6.2. Membrane method. Membrane (balloon) method is another good method for measuring cement shrinkage recommended by API. It measures the cement shrinkage or expansion while the cement sample is under impermeable conditions as the test slurry is placed in a balloon and kept under water in container by buoyancy forces. This method is good to measure the effect of expansive materials in cement (B.R. Reddy et al., 2009). This test measure the weight changes or the volume changes through tube connected to the container as shown in Figure 5.17.

Figure 5.17. The balloon test setup.

PAPER

I. A NEW CLASSIFICATION OF WELL-INTEGRITY PROBLEMS RELATED TO GAS MIGRATION

ABSTRACT

This paper provides a new classification of well-integrity problems related to gas migrations. It also updates the classification developed by Santos et al., 2015 based on the moment at which well-integrity issues manifest. (Rae, et al., 1989; Bois et al., 2011; Santos, 2015) and many other researchers divided well-integrity problems in a similar manner. This categorization can be found in many publications and it represent most of the cement failures related to gas migration. However, this categorization is too general and it does not state the failures clearly. In addition, a general categorization that depends on the time of apparent of each failure is not sufficient to recognize the connection between those failures and the consequences of each of them. These failures and more are still occurring continuously. Hence, a new classification that count for the locations of the failures, reasons behind them, and methods to mitigate them is essential. This work classifies well-integrity failures into four main types: micro-annuli at the interfaces on each side of the cement, channels through the cement sheath, fractures within the cement matrix, and cement degradation. Explanation of each of the problems, reasons behind each of them, and cement testing methodologies are summarized to clarify, understand, and prevent each of those problems in the future. In addition, considerations regarding testing cement against any of those failures are provided. This is intended to provide the industry with the latest

updates regarding these serious failures and to point out that full zonal isolation is achievable whenever reliable laboratory results are coupled with software modeling.

1. INTRODUCTION

Gas leakage, annular gas flow, gas migration, gas seepage, and many other terms are synonyms to a problem in oil wells. This problem that occur due to failure to achieve full zonal isolation may result to high maintenance costs and threats to surrounding communities and the environment. Gas migration can be flow between zones, flow into shallow sands, and/or flow to surface. Flow to surface would occur within minutes or hours after completing the well while flowing between zones may not be noticed until weeks or even months. Since 1903, where the first cement job was performed and until today, cements failures still occur. Regardless the huge number of research and the great amount of field operations that have been conducted throughout the history world widely, the well-integrity failures are still occurring continuously within the life of wells from drilling phase to the abandonment of the well (Santos, 2015). Gas migration is still reported through pressure build up. This pressure build up called “Sustained casing pressure (SCP)” and it can be a significant safety hazard. The Mineral Management Service of the US reported in 2003 that SCP affects more than 8,000 wells in the Gulf of Mexico (Rusch, 2004). The Norwegian standard defines well integrity as “application of technical, operational, and organizational solutions, to reduce risk of uncontrolled release of formation fluids throughout the life cycle of a well’ (Norsok, 2013). For these reasons, primary cement slurries designs must be optimized in such a way that accomplish short and long-term zonal isolation (Sauer, 1987).

During the drilling and completion phases of a well, cement is placed in the wellbore as a barrier between the casing and the formation. Figure 1 shows a cross-section of a wellbore. All casing strings must be cemented to protect and support the casing, and to isolate production zones. The cement must prevent the wellbore fluids from migrating in an annular flow path, which will allow the well to be utilized without any control problems. The main objective of cementing the annulus is to provide zonal isolation of the formations that have been penetrated by the wellbore. No fluid communication should happen during the life of the well among these various formations and the surface, no matter which fluids these formations are saturated with water, oil, or gas (Thiercelin, M.J et al., 1998).

Figure 1. A cross-section of a wellbore showing the role of the cement between the casing and the formation.

A good cement job is possible however; many considerations are to be taken into account to guarantee success. All the parameters related to cement job must be analyzed carefully starting by drilling practices including mud removal to selecting the most appropriate cement design and testing it simulating downhole conditions. In order to achieve that, the cement failures must be classified according to their features.

Today, the studies tend to work on avoiding these failures by dealing with each failure individually. This carries huge assumptions. For this reason, this work classifies well-integrity failures into four main types: micro-annuli at the interfaces on each side of the cement, channels through the cement sheath, fractures within the cement matrix, and cement degradation.

2. THE NEW CLASSIFICATION APPROACH

The new classification presented in Figure 2 classifies the possible cement failure intro four categories (1) the formation of micro-annuli at the interfaces on each side of the cement, (2) the creation of channels through the cement sheath, (3) the development of fractures within the cement matrix, and (4) cement degradation. This classification is based on the location of the failures in the wellbore. This paper explains the causes of these failures and the accomplished work regarding understanding and avoiding them. In addition, considerations regarding testing cement against these failures are listed.

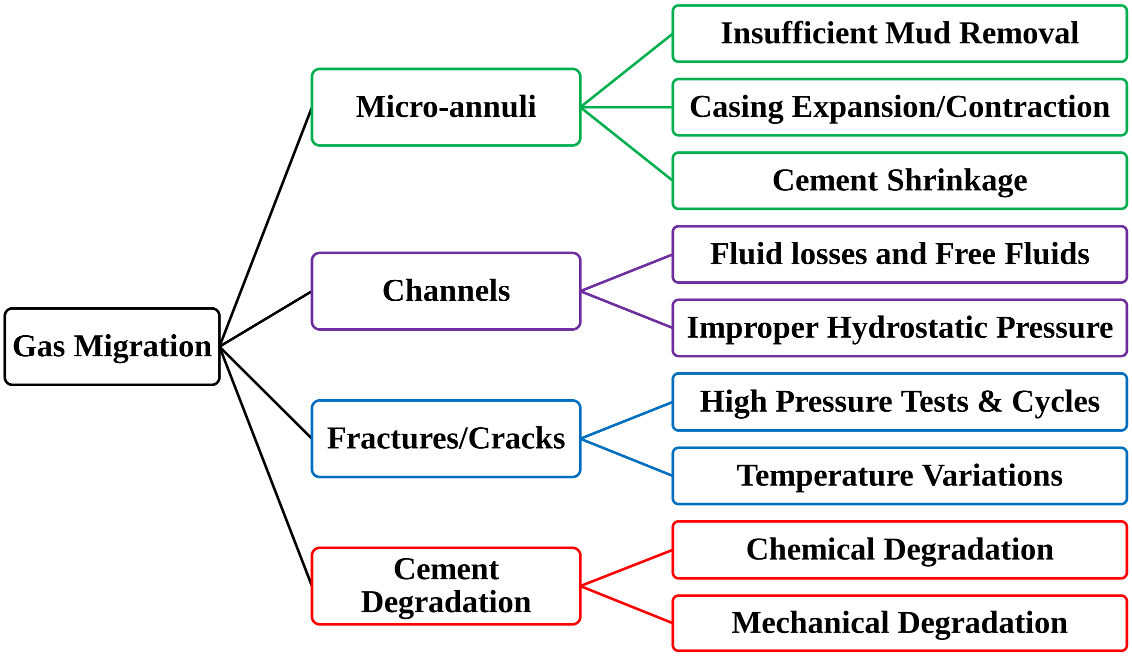

Figure 2. A new classification of gas migration related well-integrity problem**s.**

3. THE FORMATION OF MICRO-ANNULI

The formation of micro-annuli at the interface on each side of the cement sheath (between the cement and the casing and/or between the cement and the formation) must be studied and analyzed to understand the reasons behind these areas of potential gas leakages, so that we can avoid them (Bois et al., 2011). Micro-annuli can provide a path for the fluids especially gases to flow from high pressure layers to low pressure layers resulting an unwanted pressure build up (Rusch, 2004; Tahmourpour et al., 2010; Kupresan et al., 2014).

The formation of micro-annuli is mainly a result of de-bonding of the cement sheath from the casing and/or formation interface as shown on Figure 3. Therefore, it is important to achieve good bonding properties of cement-to-casing and cement-to-formation. Failing to maintain these bonding could lead to fluid communications between the layers of the formation and between the formation and the surface (Liu et al., 2015).

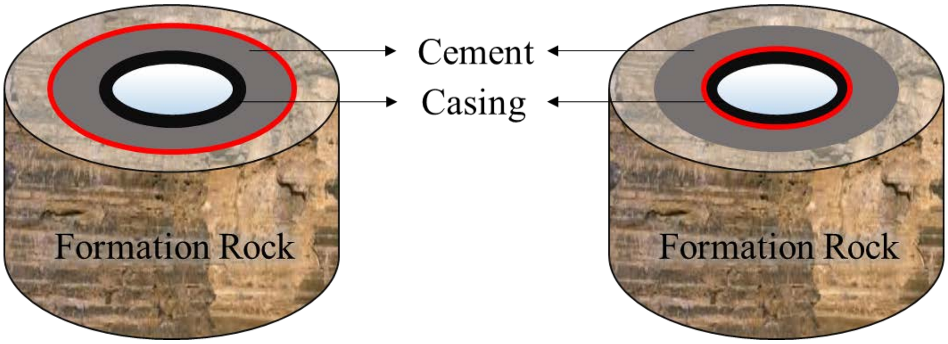

Figure 3. The location of micro annuli in the wellbore.

The reasons behind this undesired de-bonding are (1) insufficient mud removal, (2) casing expansions and contractions, and (3) cement shrinkage. Table 1 lists the time of occurrence of each of those reasons.

Table 1. Reasons behind formation of micro-annuli and time of occurrence.

The Reason behind the Failure	Time of Occurrence
Insufficient mud removal	During drilling and cementing of the well
Casing expansions and contractions	During any time of the life of the well
Cement shrinkage	During cementing to long-term

3.1. INSUFFICIENT MUD REMOVAL

To completely seal the wellbore, a great attention must be paid in removing the drilling fluids from the well. Insufficient mud removal could compromise short and long-term zonal isolation. Removing the mud before cementing the wells is not a new topic as in 1940 Jones and Berdine discovered the influences of the conditions of the drilling fluids, pipe movement during cementing, pipe centralization, flow rate, and difference of densities between fluids on mud removal along with the water pre-flushes. This path of research continued as in 1960’s Brice and Holmes presented the advantages of pumping a high-dispersed low-density slurry with low fluid losses. On the same period, Carter and Evans presented the effects of the type of the surfaces on the bonding between cement and casings. They concluded that the best bonding can be achieved by covering the pipe with resin-coated sand while the worst bonding was a result of oil coating. Other practices have to be considered, as on 1970’s the importance of centralization was the topic especially on deviated wells (Sauer, 1987). On 1979, Haut and Crook calculated the mud mobility factor (MMF) that measures the percentage of removed mud. By 1980’s until today, the industry started to combine all of the above considerations and more when removing the mud. Table 2 summarizes those considerations. It is essential to consider the importance of centralizing the casing, the volume of hole, and the type of casing. In addition, other practices such as circulating the well, pre-flushing the well, and the use of spacers must be along with the proper designs of those fluids.

Table 2. Considerations for efficient mud removal.

	Consideration	Notes	Reference
1	Centralization	Solids can settle on the low side of the hole	(Jones and Berdine 1940), (Sauer, 1987)
2	Borehole geometry	Important for volume calculations to ensure sufficient height of cement	(Haut and Crook 1979), (C. W. Sauer 1987)
3	Casing selection	The running speed of casing could also break the formation, creating loss circulation zones	(Carter and Evans, 1964), (Sauer, 1987)
4	Circulation the well and conditioning the mud	To thin the mud and break the gel particles left on the well	(Sauer, 1987)
5	Pre-flushes	The mechanical method is pre-flushing the fluids in a turbulent flow at a reasonable pump rate: • Restricted by well security. • Limited by the wide side of the annulus. The chemical method is pre-flushing in a laminar flow: • Pre-flushing by chemicals. • Protects the formation, avoids instability.	(Sauer, 1987), (Kelessidis et al., 1996), (Frigaard et al., 2001), (Foroushen et al., 2018)
6	Spacers	Important Spacers Properties: • Compatible with mud and cement. • Rheology and density. • Ability to change wettability of pipes and formations. • Contact time with fluids in the well and pump rates.	(Sauer, 1987), (Kelessidis et al., 1996), (J. Griffith et al., 1999), (Frigaard et al., 2001), (Yong Ma., et al 2007), (Foroushen et al., 2018)

3.2. CASING EXPANSIONS AND CONTRACTIONS

Casing expansion and contraction are another reason of the formation of micro-annuli. Casing expansion and contraction are results of internal pressure or thermal stress (Shakirah, 2008). An increase in the pressure and/or the temperature in the wellbore would expands the steel casing affecting the surrounding cement sheath negatively (Boukhelifa et al.,2005) or a decrease in mud density or temperature would contracts the casing (Bois et al., 2011). In addition, multiple changes in downhole conditions can cause the creation of micro-annuli (Thiercelin, M.J et al., 1998; Kupresan et al., 2014). This casing expansion and contraction effects must be reduced by increasing the shear and tensile bonding strength of the cement system (Liu et al., 2015). The effects of casing expansion may compromise the cement sheath, causing cement damages. These effects are discussed later on in this paper.

3.3. CEMENT SHRINKAGE

Back in 1900, Le Chatelier reported for the first time that Portland cement shrink up to 4.6% reduction in volume after setting time. Le Chatelier developed at that period a simple setup (the flask method) to estimate the cement shrinkage (Reddy et al., 2009). The flask method is simply a flask filled with a thin layer of cement, covered by water. The change in water volume through a tube connected to the flask is reported as volume shrinkage. Since that day, the importance of cement shrinkage became a topic of interest. Many studies have been conducted to explain cement shrinkage. The studies divided the cement shrinkage into two types:

1) The first one known as “chemical or hydration shrinkage” is the result of the chemical interaction between water and mineral compositions of Portland cement. This shrinkage happens because the products of this reaction is less in volume than the reactants, which might lead to formation of micro annuli especially at early ages (Beirute and Tragesser., 1973; and Backe et al., 1999). It is believed that one of the major factor affecting this shrinkage is the formation of calcium silicate crystals (ettringite). During cement hardening water adsorbs onto and absorbs within these crystals and as a result, the total volume of cement decreases (Chenevert and Shrestha., 1991).

2) The second type known as “bulk shrinkage” is related to the pore structure of the cement. During the hydration process, the cement losses its fluidity, and a capillary network is formed. This network initially contains water. The water is consumed by time thus increasing the capillary tension in the pores. As a result the pores contract (shrink in size) to relieve the tension which causes reduction in the external volume (Reddy et al., 2009). This pore contraction has the largest effect on shrinkage (Backe et al., 1999; and Jafariesfad et al., 2017).

3.3.1. How Cement Shrinkage Allows Gas Entry? The transition behavior of cement from liquid to solid is one of the factor that may allow gas entry. After mixing cement with water, the slurry develops static gel strength (SGS). The transition time starts when the cement slurry develops enough SGS to prevent transmission of full hydrostatic pressure and it ends when the slurry has enough solid properties to control percolation of gas through the cement column (Sabins et al., 1982). The shrinkage of a little importance until the start of transition period as the reduction in volume can be compensate by the movement of fluids. Gas enters the cement column when the hydrostatic pressure falls below the pore pressure of the formation. The hydrostatic pressure decline mainly caused by chemical shrinkage, so it is important to keep the shrinkage to minimum (Backe et al., 1999).

Cement Shrinkage is a serious phenomenon that can allow gas entry to the cement, resulting fluids communications between the layers of the formation and between the formation and the surface. It is essential to measure the cement shrinkage precisely and work on eliminating its effect. Many testing methods were developed to measure the cement shrinkage. The Le Chatelier flask method mentioned above is one of the very first methods. Although, this method is still in use, the volume of the slurry used in this method may compromise the results (Reddy et al., 2009). On the last 50 years, many attempts were conducted to build a setup able to measure the cement shrinkage precisely such as (Beirute and Tragesser., 1973; Chenevert and Shrestha., 1991; API TR 10TR2 1997; Backe et al., 1999; Goboncan and Dillenbeck, 2003; and Stormont et al., 2015). These researchers in addition to hundreds others who tried to modify the American Petroleum Institute (API) procedures (ring-mold, membrane, and cylindrical-sleeve). After reviewing those attempts to measure cement shrinkage, it can be concluded that many considerations are to be taken into account once testing the shrinkage of Portland cement. Table 3 lists the most important considerations of the testing.

The direction of shrinkage is also important. For instance, axial shrinkage may cause what is known as disking. When the cement exhibit axial shrinkage and cannot slide at its interfaces casing/formation, the disking occur as shown in Figure 4.

Table 3. Considerations when testing cement shrinkage.

	Consideration	**Note**	**References**
1	Data recording	The first 24 hours are the most important	(Beirute and Tragesser., 1973; Chenevert and Shrestha., 1991; and Reddy et al., 2009)
2	The accuracy of instrument	The variation in shrinkage might be very small	(Beirute and Tragesser., 1973)
3	The curing conditions (P & T)	High pressure/temperature increase shrinkage	(Beirute and Tragesser., 1973; Backe et al., 1999; and Reddy et al., 2009)
4	The conditions must remain constant	Depressurizing has huge impact	(Goboncan and Dillenbeck, 2003)
5	The permeability of formation	Weather cement will be exposed to water or not	(Reddy et al., 2009)
6	The confining environment	To determine the direction of shrinkage	(Goboncan and Dillenbeck, 2003; and Reddy et al., 2009)
7	The shear history of slurry	Shearing slurry reduce shrinkage	(Reddy et al., 2009)

Figure 4. The disking effect of axial cement shrinkage.

The cement design must be optimized. Starting from the water cement ratio as increasing water may increase cement shrinkage. Also, excessive decreasing in water content may dilute the cement particles, compromising the compressive strength (Chenevert and Shrestha., 1991). In addition, many additives can be used to compensate the shrinkage such as salt, bentonite, silica flour, sodium silicate, magnesium oxide, and calcium oxide. Table 4 lists additional considerations for designing cement slurries able to compensate shrinkage.

Table 4. Designing considerations to compensate shrinkage.

	Consideration	**Note**	**References**
1	The free water must be minimized	Free water increase shrinkage	(Chenevert and Shrestha., 1991)
2	Amount of water in slurry (water/cement ratio)	High water content means high shrinkage	(Chenevert and Shrestha., 1991; and Reddy et al., 2009)
3	The slurry yield	High yield less shrinkage effect	(Chenevert and Shrestha., 1991)
4	The amount of additives must be optimized	Excessive expansion could yield to gas leakage	(Goboncan and Dillenbeck, 2003)
5	Shortening transition time	This helps avoiding gas migration	(Backe et al., 1999; and Reddy et al., 2009)
8	The thermal behavior of the cement	This might affect the shrinkage	(Bois et al., 2011)

This shrinkage creates weak bond between either the cement sheath and the casing and/or the cement sheath and the formation (Wilcox et al., 2016). The shrinkage must be limited to avoid fluids migration and provide short and long-term isolation.

4. THE CREATION OF CHANNELS

The creation of channels through the cement sheath is a very critical problem that must be avoided because of its extreme dangerous, especially when hydrogen sulfide gas H_2S is involved (Drecq and Parcevaux et al., 1988). As the micro-annuli described above these channels allow the fluids to communicate within the layers of the formation and the surface.

Channels can be created within the cement slurry, as shown on Figure 5, because of mainly two reasons (1) cement fluid loss and free fluids and (2) Improper hydrostatic pressure. Channels are created due to those two reasons during the initial hydration process of the cement, specifically, when the hydrostatic pressure of cement fells below pore pressure of the formation.

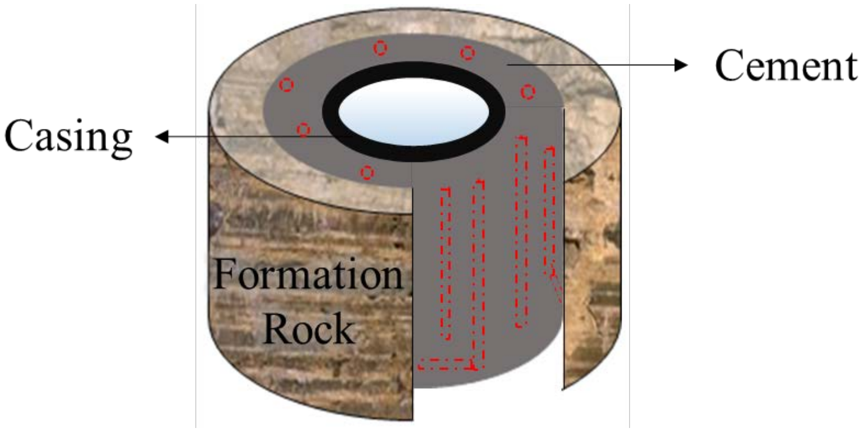

Figure 5. Gas migration through channel paths in cemented annulus.

4.1. CEMENT FLUID LOSS AND FREE FLUIDS

High cement fluid loss could allow the formation fluids to invade the cement slurry. This fluid influx would create paths, known as channels, for the gases to migrate between layers of formation and even to surface (J. Griffith et al., 1999). Cement fluid loss is the cement slurry loses water to porous formation. This water loss may lead to a high-density slurry that could damage the formation. Also, in this filtration the cement particles may plug the pores of the formation, building a cement filter cake. This cake will thicken as the displacement continues, increasing the required circulating pressure. Excessive cake thickness may bridge the annulus, blocking further displacement (Christian et al., 1976; and Baret., 1988)). The cement might set before completing cement placement, which causes an insufficient height column of cement (Cheung and Beirute et al., 1985).

The hydration of cement is the main parameter that control gas migration. As mentioned in the cement shrinkage section, the cement is a liquid that gains solid characteristics with time during a period called transition period. During this period, gas can enter the cement creating channels. Ideally, designing cement slurry that set immediately after displacement would eliminate the possibility of having channels within the set cement. However, designing such a slurry is not possible at least for now. Thus, dealing with fact that this transition period is happening, it seems the only way to mitigate the danger of having paths for gas through the cement sheath, is to shorten this period. Cement fluid loss must be controlled to avoid channeling through the cement sheath. The fluid loss controlling is not as simple as adding fluid loss additives. Fluid loss additives tie up the water required for hydration and release it slowly through the whole hydration process. However, part of the water needed for the hydration might be driven out, which would create micro capillaries. These micro capillaries may create a path for the gas to migrate in addition to the fact that many other properties of the cement would change, creating other failures (Christian et al., 1976) such as diluting the cement particles, which would affect the compressive strength of the cement negatively (Chenevert and Shrestha., 1991). The use of fluid loss additive, when optimized, will maintain the fluidity of slurry and will reduce the possibility of premature dehydration (Pavlich and wahl., 1962). Webster and Eikerts in 1979, proved the importance of minimizing the free fluids of cement. Free fluids are the fluids that separate from cement slurry when left at static conditions. Their work showed that controlling fluid loss alone would not stop the creation of channels. Controlling fluid loss has to be along with designing a zero free fluids cement system.

4.2. IMPROPER HYDROSTATIC PRESSURE

Improper hydrostatic pressure of the cement slurry during its initial hydration can also participate in creating channels through the cement sheath (Santos et al., 2015). In the wellbore, we have two pressure we have always to keep in mind pore pressure which is the pressure needed to keep the fluids in the formation and the fracture (parting) pressure which is the pressure if exceeded we can damage the formation. The column of fluids in the wellbore exerts the hydrostatic pressure and it must stay between the pore pressure and the fracture pressure (Drecq and Parcevaux et al., 1988). Failing to provide the correct hydrostatic pressure would increase the probability of having channels or damage the formation. The hydrostatic pressure can be controlled by the use of weighting agents and weight reducing agents.

5. THE DEVELOPMENT OF CRACKS AND FRACTURES

The development of fracture within the cement matrix is considered one of the long-term issues. In many cases, cement jobs were operated successfully and showed good sealing but eventually begin a pressure build up was observed (Tahmourpour et al., 2010). This pressure build up might be because of the development of fractures, cracks, and fissures within the cement matrix. The cement sheath deteriorates with time because of the post-cementing jobs such as pressure testing, producing, and stimulating (Ravi et al., 2002). Pressure and temperature oscillations also contribute in the development of fractures (Kupersan et al., 2014). In addition to over pressurize the casing or apply high thermal loads, which can badly damage the cement sheath (Goodwin and Crook, 1992; and Bois et al., 2011). Cracks and fractures are also related to chemical degradation as some chemicals when penetrate the cement pores expand causing cracks within the cement matrix (Brandl et al., 2011). This section discusses the effects of both pressure and temperature on the cement sheath.

5.1. CASING PRESSURE VARIATIONS

After cementing the casing string, it is subjected to pressure tests. These tests are important for determining the mechanical integrity of the casing. Excessive casing test pressures may compromise the cement sheath, causing radial cracks (Goodwin and Crook, 1992; Jackson and Murphey, 1993; Baukhelifa et al., 2005; and Bois et al., 2012). These tests also create shearing forces at the outer interface of the casing, hence cracking the inner cement (Thiercelin et al., 1998). It is important to point out that if these tests were conducted before cement-set, the chances of forming micro annuli are greater (Goodwin and Crook, 1992). The variations in pressure in the casing occur continuously because of replacing the mud (different density), pressure tests, and/or production operations. This pressure variation when it is positive (increase in pressure) would lead to radial cracks if the stiffness of the cement is higher than that of the formation or to shear damage if the cement is more flexible (Bois et al., 2012). If the pressure variation were negative (reduction in pressure), would form micro annuli. Figure 6 shows the difference between shear damaging and radial cracks. The changes in formation stresses also affect the cement sheath but this effect is out of the scope of this work.

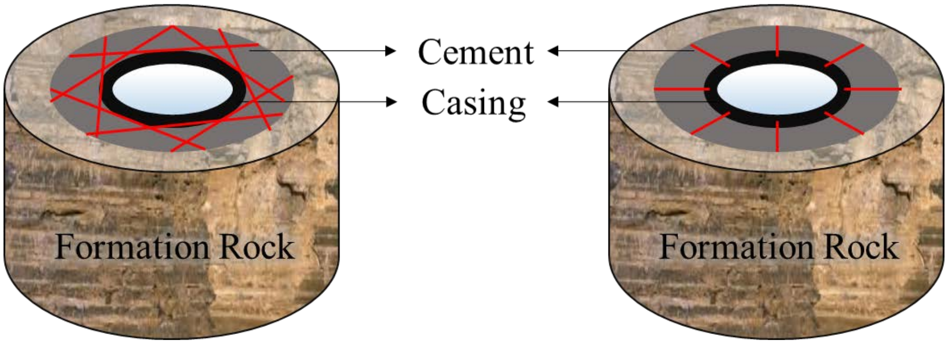

Figure 6. The difference between shear damaging (the left side) and radial cracks (right side).

5.2. TEMPERATURE VARIATIONS

During the production phase of the oil wells and if the well was used for steam injection operations, the cement in these wells is subjected to temperature changes. These temperature changes expand the casing, which may left the cement in a large deviatory state of stress. Excessive temperature changes may crack the cement. These cracks may occur due to cement failure in tension (Goodwin and Crook, 1992), or due to compressive failure (De Andrade et al., 2016). The major effects of these cracks are present when the casing contract back to its original state, the cracks would open and gas may flow (Saint-Marc et al., 2008). It is important not to shock the cement sheath with high temperature change. The reduction in temperature has to be as slow as possible. Many parameters have to be considered when designing cement system that can withstand pressure/temperature variations. Table 5. lists some of the main considerations.

Table 5. Mechanical integrity considerations.

	Consideration	**Note**	**Reference**
1	Cement stiffness	Elasticity properties	(Bois et al., 2012)
2	Formation stiffness	Elasticity properties	(Thiercelin et al., 1998; and Bois et al., 2012)
3	Cement thermal properties	Cement expanding and contraction under temperature variations	(Boukhelifa et al.,2005; and De Andrade et al., 2016)
4	Potential loadings on cement	To predict failures	(De Andrade et al., 2016)
5	The confining effect	Confining pressure act as a support	(De Andrade et al., 2016)
6	Cement flexibility	To withstand casing expansion	(Boukhelifa et al.,2005; Bois et al., 2012; and Giron et al., 2014)
7	Cement pore-pressure variations	Increase in pore pressure may increase micro annuli at the inner interface of cement	(Bois et al., 2012)

6. CEMENT DEGRADATION

Durable cement can be defined as a cement that preserve its properties including mechanical properties, and low hydraulic conductivity (porosity and permeability) with time (Lecolier et al., 2010). Cement degradation can be divided into two categories:

1) The chemical degradation: cement in oil wells is in contact with different types of fluids during the lifetime of the well to centuries after abandonment. This contact may degrade the cement. Thus, the durability of cement must be tested in presence of different corrosive fluids such as hydrogen sulfide (H_2S), carbon dioxide (CO_2), and high salinity water (brine).

2) The mechanical degradation: cement in oil wells is under compressive and tensile loadings during the life of the well and even after abandonment. These loadings may exceed the cement strength. The cement may fail under these loadings and cracks may occur compromising the zonal isolation. This degradation was discussed in the fractures/cracks section.

For chemical degradation, during cement hydration cement produces calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). C-S-H aids the strength of the cement while CH does not. Lowering cement permeability and reducing the CH content help increasing the resistance of set cement against chemical degradation (Brandl et al., 2011). Chemicals can affect cement through two ways. The first one by penetrating the cement sheath and expand causing cracks and the second way is by dissolving into the cement. Cement cannot withstand acidic conditions and C-S-H crystals would destabilize. When testing the durability of the cement, the downhole conditions must be taken into account as well as the nature of fluids that would contact the cement in place. In addition, the thermodynamic state, the composition of the fluids, and the changes that happen to those fluids must be analyzed as those fluids can modify the cement. Lab tests must simulate the downhole conditions to better state the degradation and avoid it.

During the production period of the wells, the deterioration of the cement might not be high but on the long-term, the cement degradation is very critical. This degradation may eliminate the role of Portland cement in the wells. An alternative to Portland cement for plug and abandonment must be designed (Lecolier et al., 2010).

7. CONCLUSIONS

This work has been done in an attempt to provide a guideline for the oil and gas industry when it comes to cementing operations. Many papers have been reviewed, many experimental setups have been evaluated, and many data and lab results have been analyzed to summarize the problems associated with cement in oil wells. This work classifies the cement failures based on their locations, define the reasons behind them, and list the considerations to overcome those failures. The main conclusions obtained from the studies that have been reviewed are summarized below:

- Cementing operations require attention starting from designing the cement, the practices of placing the cement, up to providing long-term zonal isolation.
- Complete mud removal is essential to achieve good bonding between the cement and its surroundings.

- The design of the cement should be comprehensive and must account for all types of failures. This work could be a roadmap to achieve that.
- Today the main focus in the industry is related to short-term properties, which is good for the place of the cement. However, the long-term properties are as important as short-term and even more.
- Young' modulus must be controlled and related to the formation Young's modulus in a way.
- It is essential to evaluate the initial state of stress in the cement sheath to know how much loading can be submitted to the cement before it fails.
- To perform a good evaluation of the state of stress in the cement sheath after it has set through the whole life of the well, the hydration process of the cement and the effect of time on cement must be understood and well analyzed.
- A huge assumption is made when evaluating cement failures is that each failure happens independent of other failures. For example, when analyzing a micro annulus between the cement sheath and the formation, most of researches assume good bonding between the cement and the casing, which is not very true in all cases.
- From gas flow point of view the gas has two options. Either to flow through the pores of the cement and face the resistance of tensile strength or to flow from the outside of the cement and face the resistance of compressive strength. Compressive strength is the strongest parameter of cement while tensile strength is the weakest so improving tensile strength of the cement is important especially at early ages.
- If mechanical degradation was combined with chemical degradation, the cement deterioration will be accelerated.

- It can be concluded from this review that the cement has to be:
    - Environmentally acceptable with desired density.
    - Suffers no excessive fluid losses with zero free fluids.
    - Achieve desirable strength and suffer low or no shrinkage.
    - Has short transition time.
    - Can resist downhole chemicals.
    - Can achieve good bonding with the surroundings.

The most important conclusion of this work is that the rules of thumbs days are over. Today, the industry can implement softwares to evaluate the cement sheath and discover its limitations. If the cement is a porous media that has a behavior described by rock mechanics laws and it seemed to be, then the industry has to use those laws as a reference to evaluate the initial state of effective stresses of the cement in downhole. Using softwares to build models that can predict the lifetime of the cement can be achieved effectively when coupled with accurate laboratory measurements. A setup that count for all the failures mentioned in this study is achievable and we are working on it now on our lab.

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II. NEW CEMENT FORMULATIONS UTILIZING NANO PLATELETS TO IMPROVE CEMENT PROPERTIES AND LONG-TERM RELIABILITY IN OIL WELLS

ABSTRACT

Cement is a major material component in the construction and sealing of hydrocarbon wells. Well leakage through cement is a problem that increases maintenance costs and poses threats to surrounding communities and the environment. This study focuses on reducing gas leakage potential and improving wellbore integrity by investigating Graphene Nano platelets (GNPs) as an additive that has the potential to improve cement durability by modifying the microstructure of the hydration products within the cement hence increasing the mechanical properties of Portland cement. GNPs offer distinctly high aspect ratios (length to thickness) and high thermal and electrical conductivities, which help enhance many properties of the cement. Experimental tests were conducted to evaluate the effects of introducing these nanomaterials to the cement system. The experimental tests include testing the mineralogy of the new cement formulations by implementing X-ray diffraction (XRD) analysis, testing the mechanical properties of the set cement, testing the stability and rheology of the liquid slurry, and evaluating the chemical shrinkage of the cement. In addition, the effects of adding GNPs on the hydration process of the cement was studied using isothermal calorimeter. The findings of this investigation show that adding GNPs to oil well cement systems improved the mechanical properties of the cement as the compressive and tensile strength of the cement increased by 10% and 30%, respectively by adding GNPs. The XRD analysis proved that GNPs

played a key role in regulating the microstructure of the hydration products. The GNPs also aided in controlling the propagation of micro cracks within the cement matrix. These results were obtained without affecting the cement stability and rheology significantly. The high surface area and aspect ratios of GNPs also played major role in reducing chemical shrinkage of the cement system. This work demonstrates that oil well cement can be enhanced dramatically by employing nanomaterials.

1. INTRODUCTION

During the drilling and completion phases of a well, cement is placed in the wellbore as a barrier between the casing and the formation. All casing strings must be cemented to protect and support the casing, and to isolate production zones. The cement must prevent the wellbore fluids from migrating in an annular flow path, which will allow the well to be utilized without any control problems. The main objective of cementing the annulus, which is presented between the casing and the formation, is to provide zonal isolation of the formations that have been penetrated by the wellbore. No fluid communication should happen during the life of the well among these various formations and the surface, no matter which fluids these formations are saturated with including water, oil, or gas.

Providing full zonal isolation for the life of the well is the main goal of primary cementing. Losing zonal isolation can result in costly well repairs and may endanger personal, equipment, and result in severe operational difficulties and huge environmental issues, which may lead in the worst-case scenario to complete loss of the well (Bois et al., 2011). For these reasons, primary cement slurries designs must be optimized in such a way that accomplishes short and long-term zonal isolation (Sauer, 1987).

Recently, one of the most active areas of research is nanotechnology. The National Nanotechnology Initiative (NNI) described nanotechnology as the manipulation of materials with at least one dimension sized from 1 to 100 nanometers. Nanotechnology can be defined as the design, characterization, production, and application of materials, devices and systems by controlling the shape and size in the nanoscale (M.F Fakoya and S.N Shah., 2017). To better understand and visualize the Nano scale, the comparative size of nanometer to a meter is the same as that of a marble to the size of the earth (El-Diasty et al., 2015).

The industry nowadays is spending so much time in discovering unconventional methods to improve the cement design to meet the recent needs such as drilling deep offshore wells and drilling long deviated horizontal wells that are planned for hydraulic fracturing. These needs require cement able to withstand extremely high pressures and temperatures. The industry is realizing the need of using unconventional sources to improve the cement. One of these unconventional ways is the use of nanotechnology, which downsizes some conventional additives to Nano additives with new physical and chemical properties (Deshpande et al., 2017). Downsizing materials to Nano scales increases the surface area of the materials, thus resulting in an increase in the proportion of atoms on the surface of the particle that increase the surface energy.

Many different nanomaterials can be used to enhance oil well cement including silica nanoparticles, magnesium oxide nanoparticles, alumina nanoparticles, iron nanoparticles, carbon nanotubes, and multiwall carbon nanotubes. These nanomaterials found their way in oil and gas industry as cement properties enhancers. Silica and alumina nanoparticles showed potential to accelerate the cement hydration process (Patil, Rahul C et al., 2012; Pang et al., 2014; and Deshpande and Patil et al., 2017). Magnesium oxide nanoparticles can be treated to control their expansion property and utilize it in limiting cement bulk shrinkage (Jafariesfad et al., 2016). Iron nanoparticles can increase the compressive strength of cement (Vipulanandan, C et al., 2015). Carbon nanomaterials, including carbon nanotubes (CNTs) and carbon nanofibers (CNFs), with their high aspect ratios (length to thickness), allow them to bond with the various cement hydrates. These carbon nanomaterials showed high potential to enhance mechanical properties of the cement. Their structure and Nano size abled those nanomaterials to fill the void spaces of the cement and stop the growth of micro cracks within the cement sheath (Peyvandi et al., 2017).

GNPs also offer distinctly high aspect ratios and high thermal and electrical conductivities; GNPs have been added to polymers, ceramics, and rubbers due to these characteristics (Wang et al., 2016). Nowadays, introducing GNPs to cementitious materials attracted many researchers.

This study investigates the introduction of GNPs to Class-H Portland cement through a comprehensive evaluation using these nanomaterials to enhance the toughness and the thermal conductivity of the oil well cement. The evaluation include conducting lab experiments such as compressive strength and tensile strength tests to determine the effectiveness of using GNPs to improve cement mechanical properties. The research also evaluates the impact of adding nanomaterials on cement shrinkage phenomenon. Improving the mechanical properties of cement and reducing the cement shrinkage, especially at early ages, will reduce the possibility of gas migration that could occur due to micro cracks in the oil well cement sheath and/or the micro annuli that can form between the cement and the formation or between the cement and the casing.

2. EXPERIMENTAL DESCRIPTION

2.1. EXPERIMENTAL MATERIALS

The cement systems used in this study were prepared using American Petroleum Institute (API) Class-H oil well cement and distilled water. The specific gravity of the cement was measured using gas Pycnometer to be 3.18 gm/cc. The chemical composition of Class-H cement are listed in Table 1. The compositions were obtained using X-ray fluorescence spectroscopy (XRF).

Table 1. The chemical composition of class-H cement.

Comp	**CaO**	**SiO_2**	**Fe_2O_3**	**Al_2O_3**	**SO_3**	**MgO**	**K_2O**	**SrO**	**TiO_2**	**Other**
Wt %	65.72	20.36	6.19	3.17	2.26	1.32	0.43	0.21	0.16	0.18

2.2. GRAPHENE NANO PLATELETS (GNPS)

The nanoparticles used in this study is Graphene Nano platelets (GNPs) provided by Nanographene Inc. Scanning electron microscope (SEM) and Transmission electron microscopy (TEM) images were provided by Nanographene Inc. as shown on Figure 1. It is a black-gray flake shaped particle. These Nano platelets offer distinctly high aspect ratios and high thermal and electrical conductivities. The properties of the nanoparticles are described in Table 2.

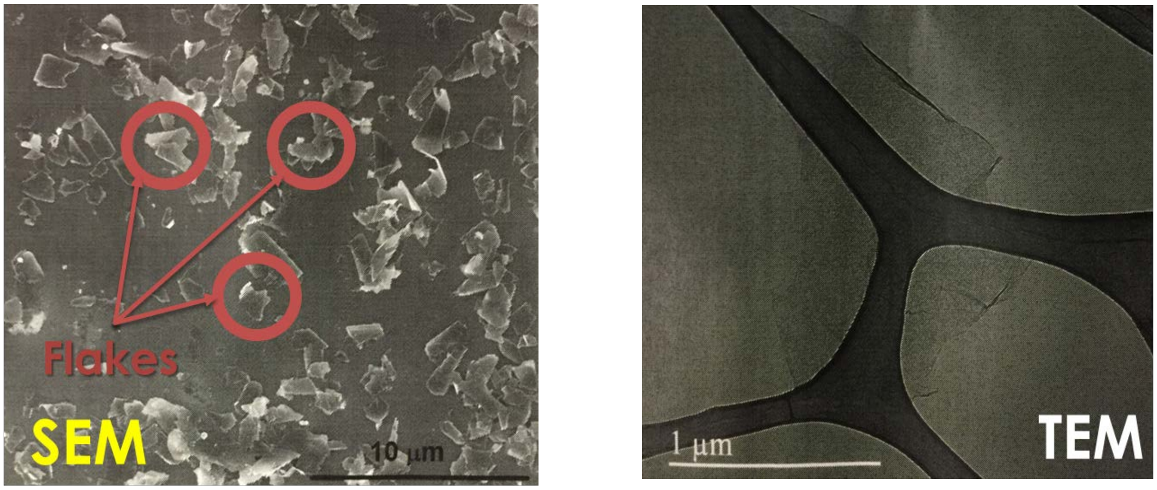

Figure 1. Shows SEM & TEM of GNPs (Provided by Nanographene Inc.).

Table 2. Properties of Nanoparticles As provided by Nanographene Inc.

Property	**Graphene Nano platelets**
Density	130 [kg/m^3]
Carbon Content	> 99.5 %
Thickness	< 3 nm
Flake Size	1.3-2.3 microns

2.3. CEMENT SLURRY

The cement systems studied in this work contained only Portland cement Class-H and the GNPs with no other additives. There was no need to add dispersant, anti-foam, or any other additives that are mostly added to the cement system when nanoparticles are used as additives. This might be due to the low concentrations of GNPs needed to enhance the cement.

2.4. CEMENT PASTE PREPARATION

All slurries were mixed at temperature of 24˚ C in a two speeds bottom-drive laboratory blender. For the reference slurry, the dry cement was added while mixing at low speed in around 15 seconds at a uniform rate then the blender was covered and the mixing continued for 35 seconds at high speed. For slurries containing nanoparticles, the dry nanoparticles were mixed at low speed in the mixing water for 10 seconds to disperse them prior to adding the cement (API RP 10B-2 2013). The addition of high concentration of nanoparticles (0.9%) required changing the second step of mixing to be at low speed for 50 seconds. (Pang and Boul et al., 2014) showed in their study that there is a very little effect of mixing speed on the hydration kinetics.

2.5. CEMENT PASTE FORMULATION

All cement systems had a water/cement ratio (WCR) of 0.38 in accordance to API specification 10A (API 2010). The mix designs are described in Table 3.

Table 3. Table of mixture.

Component	**MASS (Percentage By Weight of Cement BWOC)**				
Class-H Cement	100	100	100	100	100
Water	38	38	38	38	38
GNPs	0	0.1	0.3	0.6	0.9

3. EXPERIMENTAL METHODOLOGY

This section provides detailed description of each experiment conducted in this work along with the procedure and the required outcomes from each experiment. The experiments include X-ray diffraction for both hydrated and anhydrate cement, density, rheological behavior, compressive strength, tensile strength, stability, heat of hydration, and chemical shrinkage.

3.1. X-RAY DIFFRACTION MEASUREMENTS

X-ray diffraction is versatile, non-destructive analytical method that is utilized for identification and quantitative determination of phases of compounds. The identification can be accomplished by comparing the x-ray diffraction pattern of a specific sample (powder or solid) with known x-ray diffraction patterns. In this study, the phases of a sample of API Class-H cement was determined to help understanding the hydration process of the cement. In addition, several samples of hydrated cement (neat cement, 0.3% GNPs system, and 0.6% GNPs system) were prepared by grinding cured cement samples and sieved them using 325 mesh (recommended size for x-ray diffraction). The patterns of those samples were compared to study the effects of adding GNPs to the cement system. In addition, the hydration time effects on cement were studied by comparing the XRD patterns of sample cured at different ages. The tube of the diffractometer was operated at a current of 40 mA and a voltage of 45 KV. The scan range was set for 2θ of 5˚ to 70˚ using a step size of 0.01313 and time per step 97.92s. The obtained XRD patterns were analyzed using a commercial software supplied with the x-ray diffractometer.

3.2. DENSITY MEASUREMENTS

Density plays a major role in holding formation (pore) pressure, providing hydrostatic pressure, in the wellbore. The density of the slurries in this study were measured immediately after mixing the cement utilizing standard mud balance. The density values were recorded in lbm/gal and compared to neat cement reference slurry.

3.3. RHEOLOGY MEASUREMENTS

These measurements are important for this study as the addition of Nano-sized additives can decrease the workability of the cement slurry. For these measurements, the slurries were preconditioned before obtaining the rheological readings at room temperature and atmospheric pressure. An Ofite viscometer (model 800) was used to characterize the rheological behavior of the cement systems. The dial readings were taken in ascending order then in descending order with highest speed of 300 rpm. The ratio of the two readings at each speed was used to help qualify some of the slurries properties (API RP 10B-2 2013). The slurries rheological measurements were recorded as the average of the two dial readings at each speed.

3.4. COMPRESSIVE STRENGTH MEASUREMENTS

It determines the strength of the cement sheath. It is essential to determine the compressive strength of the cement to ensure the ability of the cement design to withstand downhole conditions. Compressive strength test simply measures the force needed to crush a sample of cement. For this test, all slurries were mixed and preconditioned prior to pouring them in 2” × 2” × 2” cubic molds. The molds then were placed in a curing bath at room temperature for 72 hours. Then, the set-cement cubes were carefully removed from the molds and wiped dry with a paper towel just before testing them to maintain their moisture content. The specimen height and width were measured using caliper and the minimum surface area was calculated. Any specimen with height less than 48 mm (1.9-inch) was discarded as recommended in API (API RP 10B-2 2013). Finally, the specimen were placed in a hydraulic press where force was applied until failure. The compressive strength results were calculated as force over area.

3.5. TENSILE STRENGTH MEASUREMENTS

Tensile strength is another parameter that has to be measured and enhanced to ensure the wellbore long-term integrity. When the cement tensile strength exceeded, a radial crack may form along the cement sheath axis, which would create a high conductivity path for the fluids to migrate (Iremonger et al., 2015). Herein, the tensile strength was measured using an indirect method that is known as the Brazilian test. The technique used in this test is applying compression force across the diameter of the cement cylindrical sample until failure occur. For this test, all slurries were mixed and preconditioned prior to pouring them in 2”× 4” cylindrical molds. The molds then were placed in a curing bath at room temperature for 7 days. Then, the set-cement cylinders were removed from the molds and sawed into three samples of 1” in thickness. The samples diameter and thickness were measured and documented. Then, the specimen were placed in a hydraulic press where force was applied until failure. It is important to check if the failure crack is parallel to the load direction, otherwise the result is not reliable (Iremonger et al., 2015).

3.6. STABILITY MEASUREMENTS

Two tests were conducted to determine the static stability of the cement slurries. Both free fluid and sedimentation tests were conducted. It is essential to combine both tests because free fluid may form with minimal sedimentation, and sedimentation may occur with no free fluid. For these tests, all slurries were mixed and preconditioned to simulate dynamic placement in a wellbore following the API procedures (API RP 10B-2 2013).

3.6.1. Free Fluid Test. Whenever the cement slurry is left to stand in a static condition for a period of time, some fluids may separate from the slurry. This fluids separation may affect the desired cement properties. In free fluids measurements, a 250-ml graduated cylinder was used. The slurries were poured into the cylinder, covered, and left in a vibration-less place for 2 hours in room conditions. Then, the volumes of the free fluids were measured and recorded as volume of free fluid. The volume fractions of the fluids were calculated using Equation. 1.

$$\varphi = \frac{V_{FF}}{V_i} \times 100 \tag{1}$$

Where, φ is the volume fraction of free fluid, expressed as a percentage; V_{FF} is the volume of free fluid, expressed in ml; and V_i is the initial volume of slurry, expressed in ml.

3.6.2. Sedimentation Test. The cement slurry can also experience particles sedimentation when left to stand in static conditions for a period of time. Settling can be discovered by comparing the density of different segments of the set cement (API RP 10B-2 2013). In sedimentation measurements, a tube of 1-inch inner diameter and 7.9-inch length was used. The slurries were poured into tubes, sealed, and cured in water bath for more than 24 hours. Then, the top covers were removed and the downgrade of the pastes were measured. The downgrade is the distance between the top of the set-cement and the top of the initial slurry. Then, the cement specimen were removed and 0.75-inch of the top and bottom were cut. Then, the middle parts were cut into at least four equally sized segments. The mass of each segment was measured in air and water to apply Archimedes Principle in calculating the relative density using Equation.2. The mass measurements were taken using the setup shown on Figure 2 to ensure accurate measurements.

$$d_{rel} = \frac{m_{air}}{m_{water}} \tag{2}$$

Where, d_{rel} is the relative density, expressed as fraction; m_{air} is the mass of the segment in air (dry mass), expressed in gm; and m_{water} is the mass of the segment in water (wet mass), expressed in gm.

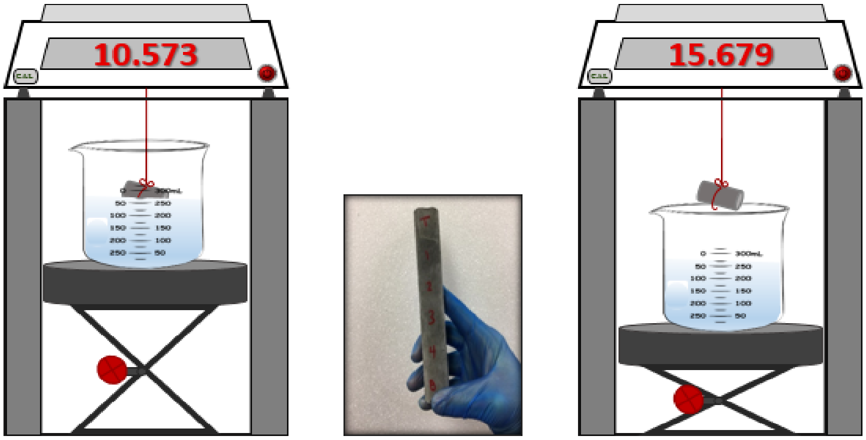

Figure 2. Shows a sedimentation sample and the setup used to measure the masses in air and in water.

Finally, the density variance between top and bottom segments of set-cement was calculated using Equation.3.

$$\Delta\rho = \rho_{bottom} - \rho_{top} \tag{3}$$

Where, $\Delta\rho$ is the change in density between top and bottom segments of set-cement, expressed gm/cc; ρ_{bottom} is the density of the bottom segment, expressed in gm/cc; and ρ_{top} is the density of the top segment, expressed in gm/cc.

3.7. HEAT OF HYDRATION MEASUREMENTS

Isothermal Calorimeter (I-Cal 8000) was used to measure the heat evolved from the chemical reactions of the cement. This method is one of the most effective methods to evaluate the effects of adding additives on the hydration process (Pang et al., 2014). For this test, samples of around 50 ± 2 gm of the slurries were poured and sealed in cups and transferred immediately to the calorimeter. The test was run for 72 hours and the data of the first hour were discarded for stabilization purposes. The temperature of the instrument was set to 24˚C and left for 24 hours to stabilize. The heat flow data were directly obtained from the instrument and the cumulative heat evolution measurements were determined by integrating the heat flow data.

3.8. SHRINKAGE MEASUREMENTS

There are two types of cement shrinkage. The first type is inner shrinkage also known as “chemical or hydration shrinkage”, which occurs during the cement hydration. Chemical shrinkage varies between 2.3 to 5.1% (Al-Yami et al., 2010). This shrinkage is the result of the chemical interaction between water and the mineral compositions of Portland cement. This shrinkage happens because the products of this reaction is less in volume than the reactants, which might lead to formation of micro annuli. The second type known as “bulk shrinkage” is related to the pore structure of the cement. During the hydration process, the cement losses its fluidity, and a capillary network is formed. This network initially contains water. The water is consumed by time thus increasing the capillary tension in the pores. As a result the pores contract (shrink in size) to relieve the tension which causes reduction in the external volume (Reddy et al., 2009). The shrinkages were measured for three days to analyze the effects of GNPs during the transition time of cement. For this test, the slurries were mixed, preconditioned, and poured in balloons. The balloons were placed in a glass container filled with water. The change in volume of the sample caused change in the level of the water in a tube connected to the top of the container. Figure 3 shows an illustration of the balloon test setup. The test was run for 72 hours.

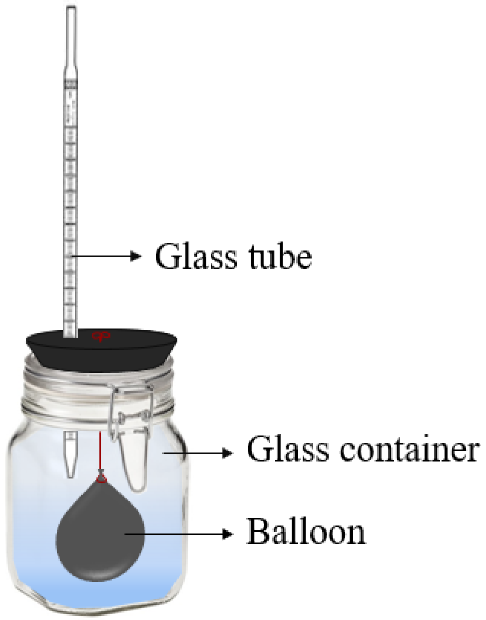

Figure 3. Shows an illustration of the balloon test setup.

4. RESULTS AND DISCUSSION

Laboratory tests were conducted at atmospheric pressure and 24˚C temperature to test and understand the behavior of the cement systems when the Graphene Nano platelets are introduced.

4.1. THE X-RAY DIFFRACTION RESULTS

The x-ray diffraction pattern of the cement powder is presented in Figure 4 The analysis of the pattern indicates the presence of the main crystalline phases, which are: Tricalcium silicate (alite or Ca_3SiO_5), Dicalcium silicate (belite or Ca_2SiO_4), Calcium Aluminoferrite (brownmillerite or Ca_2FeAlO_5), Ternesite ($Ca_5(SiO_4)_2(SO_4)$), and Magnesium oxide (periclase or MgO).

These compounds and many others are part of the complicated hydration process of Portland cement. Generally, the calcium silicate is the only compound responsible for strength within the cement composition. Tricalcium silicate (C_3S) contributes in developing strength in the first few days and dicalcium silicate (C_2S), which reacts slowly, contributes in developing strength at later times.

The hydration process starts upon adding water to the cement. At the early stages of the hydration process, the C_3S rapidly reacts upon adding water to release calcium ions, hydroxide ions, and a large amount of heat. The pH rises over 12 due to the release of alkaline hydroxide (OH-) ions. With a decrease in heat, this process would continue slowly until the system gets saturated.

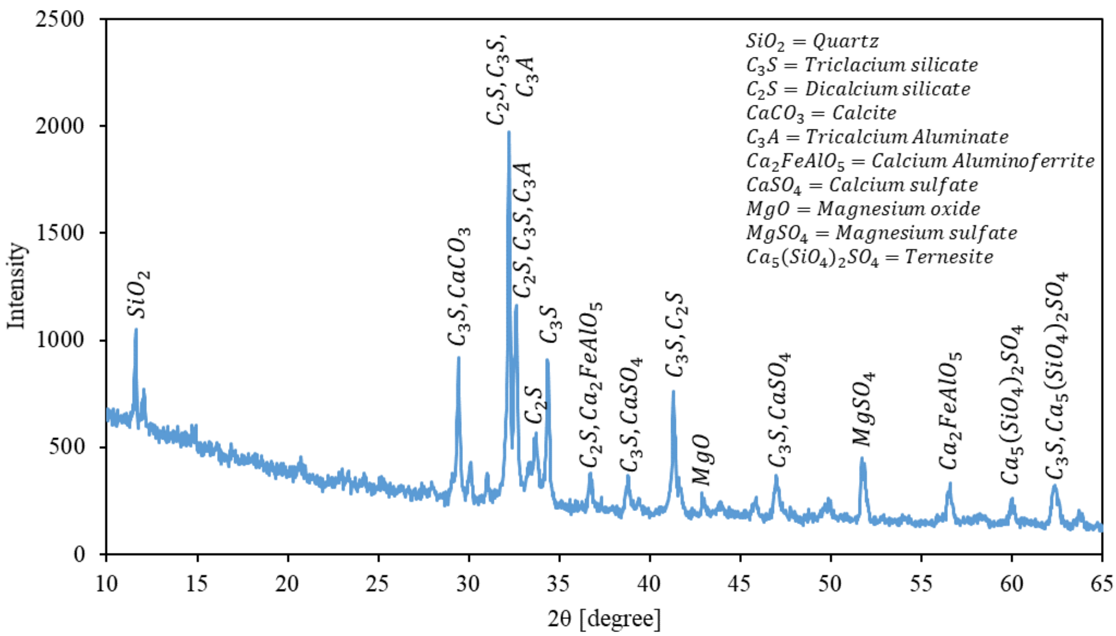

Figure 4. The mineralogical analysis of unhydrated Portland cement.

Then, the calcium hydroxide (CH) starts to crystalize while at the same time calcium silicate hydrate (C-S-H) begins to form, as shown in the chemical equation below (De La Roij et al., 2012).

Tricalcium Silicate + Water → Calcium Silicate Hydrate + Calcium Hydroxide + Heat

$$2\ Ca_3SiO_5 + 7\ H_2O \rightarrow 3\ CaO.2SiO_2.4H_2O + 3\ Ca\,(OH)_2 + 173.6\ \text{kJ}$$

The formed CH and C-S-H crystals provide “seeds” upon which more C-S-H can form. The C-S-H grows thicker forming a coat which would make it hard for the water molecules to reach the anhydrate C_3S. The coat grows thicker over time, which would make the production of C-S-H slower and slower. C_2S reacts with water in a similar way comparing to C_3S but in much slower manner, which is presented in the chemical equation below (De La Roij et al., 2012).

$$\text{Dicalcium Silicate + Water} \rightarrow \text{Calcium Silicate Hydrate + Calcium Hydroxide + Heat}$$

$$2\ Ca_2SiO_4 + 5\ H_2O \rightarrow 3\ CaO.2SiO_2.4H_2O + Ca\ (OH)_2 + 58.6\ kJ$$

This complex reaction forms different compounds such as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$ or AFt), monosulfunate ($Ca_4Al_2(OH)_2SO_4.H_2O$ or AFm), CH and C-S-H. Ettringite, monosulfunate, and calcium hydroxide would form in needle or rod-like crystals with disorder; the shape of the formed crystals determines the brittleness of the cement (Shenghua Lv et al., 2013).

It is believed that GNPs, when added to cement, control the microstructure of the mentioned crystals and regulate their growth to be flower-like shaped (Shenghua Lv et al., 2013; and Sedaghat et al., 2014). The GNPs behave like platforms for C_3S, C_2S, and C_3A to hydrate and grow. The growth of the hydration products such as CH and C-H-S would take place on the edges of the GNPs. This growth continues and is regulated by the nanoparticles. Figure 5 shows the XRD patterns of hydrated neat cement, hydrated cement + 0.3% GNPs, and hydrated cement + 0.6% GNPs. The GNPs peak is at $2\theta = 26.54^\circ$. It is not very clear due to the small concentration of GNPs added in the cement design. XRD analysis results demonstrate the effect of hydration time on the CH and AFt crystals, showing that they increase as time progresses, as shown on Figure 6.

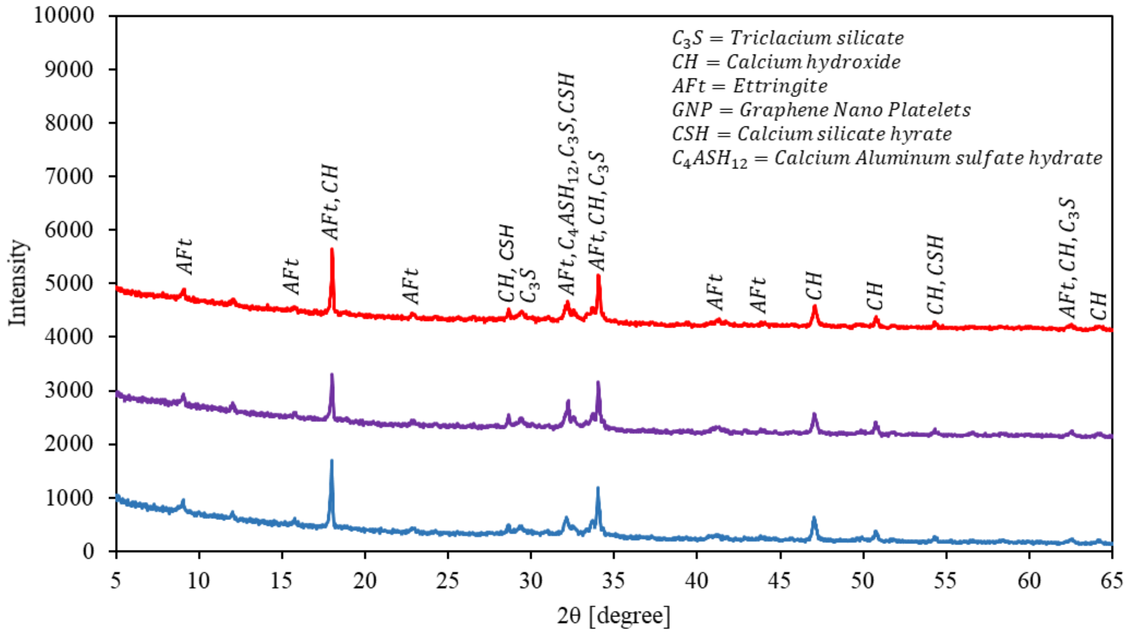

Figure 5. XRD patterns of hydrated cement and the addition of GNPs.

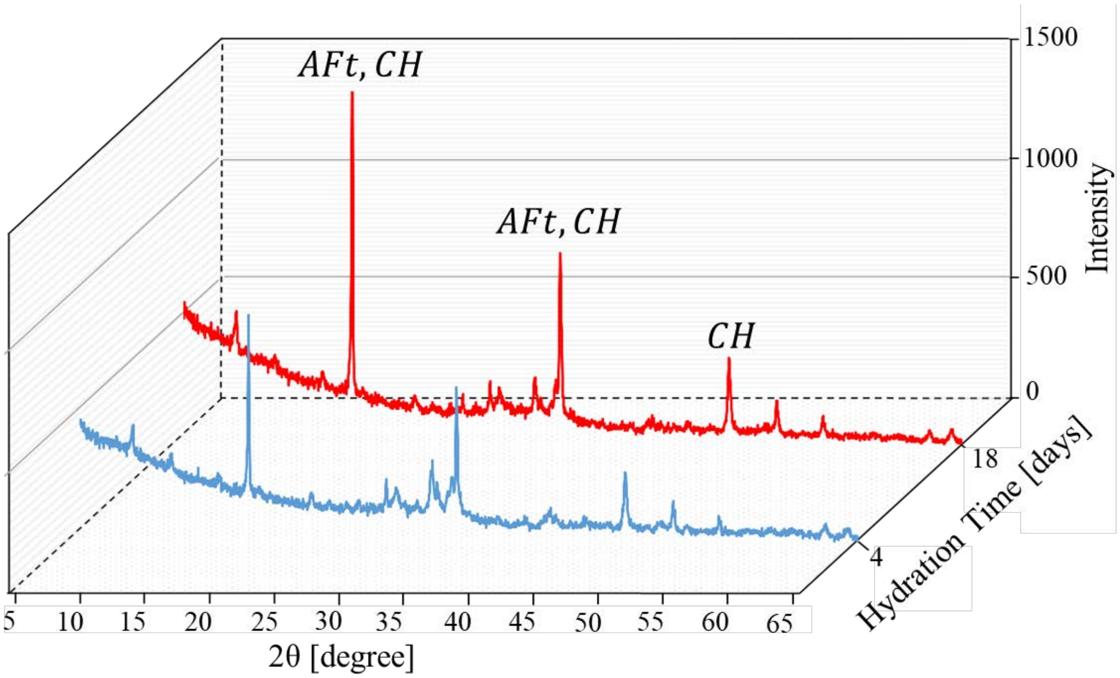

Figure 6. XRD patterns of hydrated cement shows the impact of hydration time.

4.2. DENSITY RESULTS

The density results of the neat cement system was around 16.8 ppg. The addition of 0.3% GNPs and 0.9% GNPs BWOC to the cement systems increased the density by 0.6% and 1.2%, respectively. Table 4 lists the average densities of all the slurries tested in this study.

Table 4. Effect of GNP on the density of the cement slurries.

Cement system	**Density ρ [lbm/gal]**
Neat cement	16.8
Cement + 0.1 GNP	16.8
Cement + 0.3 GNP	16.9
Cement + 0.6 GNP	17.0
Cement + 0.9 GNP	17.0

4.3. RHEOLOGICAL RESULTS

The rheological measurements of the cement systems are presented in Figure 7. The flow curves at temperature of 24˚C for the five cement designs are almost the same and very close to a straight line. The analysis of these results indicates that there is no significant change in the rheological behavior of the cement pastes when GNPs were added. However, there are effects of adding nanoparticles to the cement system but these effects are time dependent. In this study, rheological measurements were obtained for only fresh cement pastes. The effects of time have to be determined to understand the effects of adding GNPs to cement on the rheological properties.

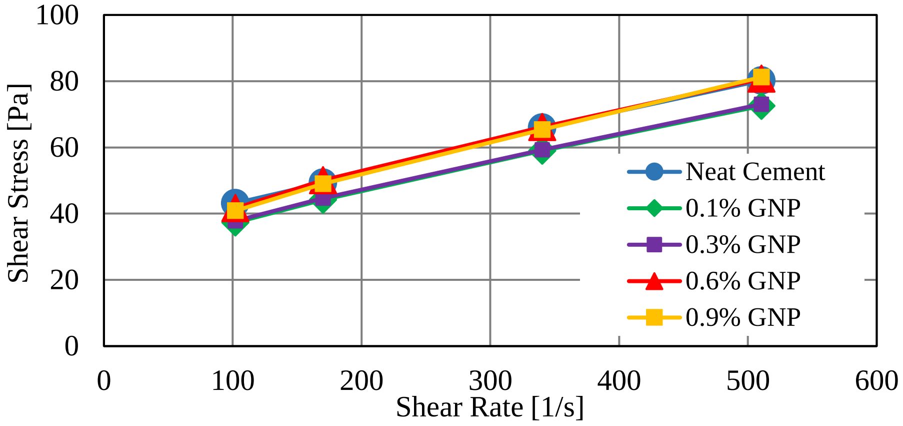

Figure 7. Flow curves at room temperature for the cement systems.

4.4. COMPRESSIVE STRENGTH RESULTS

The compressive strength of the cement sheath was affected positively by the addition of GNPs to the cement system. The laboratory results showed an increase in cement strength when adding nanomaterials in concentrations higher or equal to 0.3% of GNPs BWOC. Adding only 0.6% of GNPs BWOC increased the strength by around 10% when compared to reference system (neat cement). However, lowering the concentration of GNPs to 0.1% had an opposite effect on the cement strength. This might be due to the improper distribution of the nanoparticles through the cement paste, since the concentration of GNPs was low. Table 5 shows the increase in compressive strength measurements.

Table 5. Compressive strength of cement cured at 24˚c and atmospheric pressure.

Cement system	Maximum Load [kN]	Compressive Strength [psi]
Neat cement	65.6821	3816.5
Cement + 0.1 GNP	60.6707	3509.2
Cement + 0.3 GNP	67.9654	3919.6
Cement + 0.6 GNP	70.1449	4166.6
Cement + 0.9 GNP	70.9011	4211.7

As mentioned earlier, C_3S and C_2S are mainly responsible for compressive strength development (Patil and Deshpande, 2012; and De La Roij et al., 2012). Adding GNPs to the cement seemed to modify the formed hydrates and regulated the microstructure of the hydration crystals. This modification seemed to increase the degree of compaction, thus increasing the compressive strength.

4.5. TENSILE STRENGTH RESULTS

Tensile strength results are listed in Table 6. GNPs improved the flexibility of the cement systems. The addition of GNPs to the cement systems has increased the tensile strength, which is favorable in the oil wells cement. Using only 0.1% BWOC of GNPs, the increase in tensile strength was at least 20% compared to the reference system; the increase continued through all the tested concentrations. Based on both results compressive and tensile strengths, dosages between 0.3% and 0.6% of GNPs BWOC might be the optimum concentrations when considering both properties. Although, 0.9% of GNPs BWOC showed the highest values for both compressive and tensile strengths, there was an effect on the hydration process. This effect will be discussed in this paper later on .The results of XRD and compressive and tensile strength proved that GNPs enhanced the toughness of the cement.

Peyvandi et al. (2017) investigated the effects of graphite nano-sheets, with thickness of 6 to 8 nm, on the mechanical properties of the cement; they observed a small increase in compressional strength, and related it to an extra homogeneity of the slurry. This study also concluded that the addition of graphite nano-sheets improved the cement tensile strength by 10% by adding 0.2% of nanoparticles. These findings agree with the outcomes of this paper.

Table 6. Tensile strength of cement cured at 24˚c and atmospheric pressure.

Cement system	Curing Time [days]	Tensile Strength [psi]
Neat cement	7	343.5
Cement + 0.1 GNP	7	414.7
Cement + 0.3 GNP	7	420.4
Cement + 0.6 GNP	7	442.9
Cement + 0.9 GNP	7	491.8

4.6. STABILITY TEST RESULTS

Free Fluids Test results showed that the addition of GNPs to the cement system had a noticeable effect on the free fluids content. GNPs reduced the free fluids of the cement slurry in range of 50% to 72%. The maximum reduction in free fluids was observed in the slurry containing 0.9% GNPs BWOC, compared to the reference system. Table 7. Lists the volume of free fluids and the calculated free fluids content of each cement system. The results indicate that GNPs acted as a bridging agent between the cement particles, filled the pore spaces, and restricted the flow of free fluids. The reduction in free fluids helps keep the cement system properties, especially the effective density since the effective density decreases with increasing free fluids, which may led to reduction in the hydrostatic pressure, thus the formation of channels through the cement sheath (Webster and Eikerts., 1979).

Table 7. Free fluids of cement slurries at 24˚c and atmospheric pressure.

Cement system	V_{FF} [ml]	Free Fluids Content φ [Fraction]
Neat cement	5.7	2.28
Cement + 0.1 GNP	3.0	1.20
Cement + 0.3 GNP	1.8	0.72
Cement + 0.6 GNP	2.4	0.96
Cement + 0.9 GNP	1.6	0.64
API-10A Limits	/	5.90
*V_{ff} = Volume of collected free fluids.		

Sedimentation test results showed no significance settling in all the samples tested in this study. Table 8 presents the results of the sedimentation tests in addition to the downgrade. The results of both free fluids and sedimentation tests indicate that all the cement systems studied herein were stable and suffered no sedimentation. Thus, the addition of GNPs to the cement system did not compromise the properties of the cement. Generally, the stability of the cement slurry can be defined by zero free fluids and no significant settling (Al-Yami et al., 2010).

Table 8. Sedimentation of cement samples cured at 24˚c and atmospheric pressure.

Cement system	DOWNGRADE [mm]	$\Delta\rho$ [gm/cm^3]
Neat cement	3.33	0.027
Cement + 0.3 GNP	3.39	0.029
Cement + 0.6 GNP	3.20	0.032
Cement + 0.9 GNP	3.40	0.033
API Limits	5.00	0.060
*$\Delta\rho$ = change in specific density.		

4.7. HEAT OF HYDRATION

Upon adding water to Portland cement the reaction starts and heat is released as a result of this reaction. The amount of heat released is an indication of the rate of reaction. The heat flow curve of neat Class-H cement is presented in Figure 8. The curve in this figure can be divided into three periods; the first period is the induction period, where the cement slurry is movable, the second period is the acceleration period, where cement starts to set, a lot of heat is released in this period. Also, the microstructure of cement starts to build up in this period. This period is followed by the third period, which is the deceleration period. Less heat is released in this period. The heat of hydration process may takes around three days. However, the microstructure will keep building after three days but in a different manner.

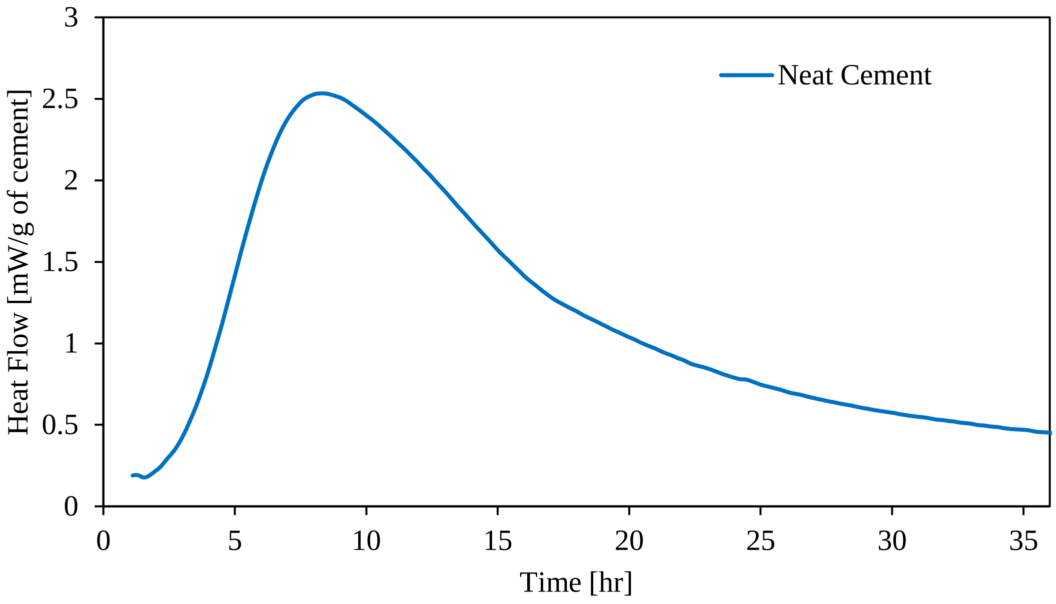

Figure 8. The heat flow of Class-H cement at 24˚C.

The heat flow curves of the cement designs, studied in this paper, are presented on the left side of Figure 9, showing the effect of adding GNPs to Class-H Portland cement. The heat flow curves of 0.1% and 0.3% of GNPs BWOC show increase on the height of the hydration peak but no changes in the position of the peak compared to the neat cement slurry. For 0.6% GNPs BWOC the heat flow curve is almost identical to the neat cement heat flow curve with no change in the height of the hydration peak.

The total heat released after 72 hours of neat cement and the slurries contained 0.3% and 0.6% GNPs BWOC are the same as shown on the right side of Figure 4.6, thus indicating no significant effect of adding 0.3% and 0.6% GNPs BWOC on the hydration process. However, the heat of hydration results indicated that adding 0.9% GNPs BWOC slightly accelerated the hydration process and reduced the setting time of the cement system. This could be due to the high surface area of the nanoparticles that would adsorb some of the water molecules, which might have speeded up the precipitation of CH required for breaking the acceleration period.

Generally, there are not many chemical effects of adding GNPs to Class-H Portland cement. The total heat of hydration released from all the slurries tested herein was almost the same except for the system containing 0.9% GNPs BWOC. The results presented here are based on the average of three runs. Those run were under temperature of 24˚C.

For the reaosn mentioned above in addition to the results obtained from free fluids tests and mechanical tests, a GNPs concentration between 0.3% to 0.6% BWOC was selected to be the optimum concentration that would enhance the cement properties without significantly affecting the setting time of the cement.

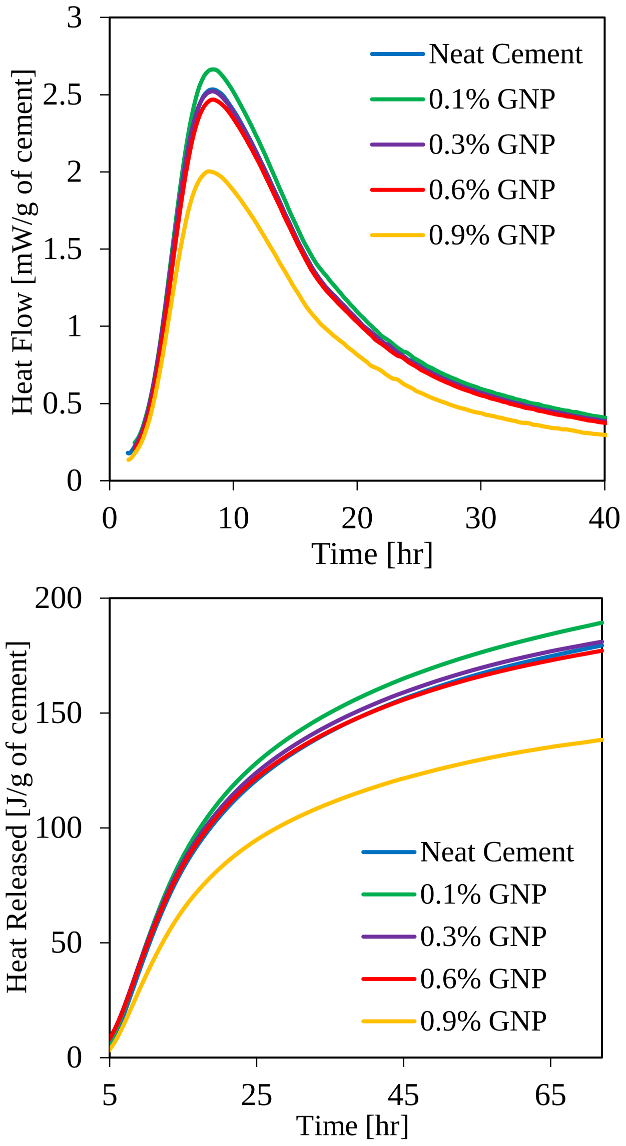

Figure 9. Effect of GNPs dosage (BWOC) on the hydration kinetics of Class-H cement at 24˚C.

4.8. SHRINKAGE TEST RESULTS

Shrinkage results indicated that the overall performance of cement slurries that contain GNPs reduced the overall shrinkage for the duration of the tests. For the slurry containing 0.3% GNPs BWOC, the reduction in shrinkage was around 15% compared to the neat reference slurry. For the slurry containing 0.6% GNPs BWOC, the reduction was around 30%. These results are shown in Figure 10.

The results show that the chemical shrinkage behavior of neat portland cement had two stages; a high chemical shrinkage stage followed by a slow stage. The first stage is the result of the chemical reaction between the water and the cement and the second stage is the result of free water flowing slowly back into the hardend cement. Since the free fluids were less in the slurries containing GNPs, a reduced shrinkage was observed. It seems that the high surface area of GNPs captured some of the available water from slurry and hence hindered, to some point, the formation of ettringite (AFt), that water adsorbs onto, and helped increase shrinkage at early ages (Chenevert and Shrestha., 1991).

The most important role of GNPs in these results can be seen in the first hours of the hydration process as the GNPs reduced the shrinkage during the transition period. The transition period of cement starts when the slurry develops static gel strength to prevent transmission of full hydrostatic pressure and ends when the cement has the ability to percolate the gas through its matrix (Sabins et al., 1982). Before this period the cement shrinkage is of little importance as the cement can sag and compensate the shrinkage. Controlling the chemical shrinkage is essential to mitigate gas migration that could happen due to loss of hydrostatic pressure. Early shrinkage could lead to micro annuli, which might cause loss of well control especially in high pressure zones (Beirute and Tragesser., 1973).

The importance of recording the chemical shrinkage from the mixing is reported in the literature since the shrinkage starts at that point. In this study, the dead time between mixing, filling the balloons, and sealing the setup was kept minimum. In addition, this time is similar or less than the time required to pump the cement in place. Finally, the addition of nanomaterials to the cement system seemed to fill the void spaces of the cement and helped reduce the shrinkage.

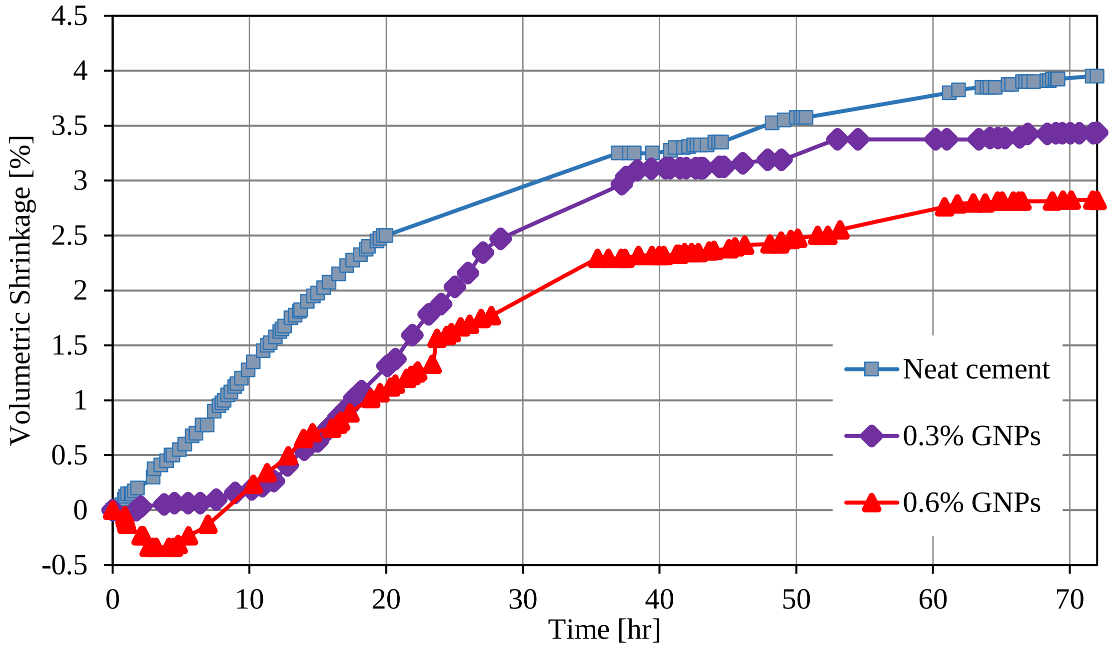

Figure 10. Effect of GNPs dosage (BWOC) on the shrinkage.

5. CONCLUSION

By studying the effects of adding GNPs to Class-H Portland cement, several findings were obtained in this study. These findings are based on the results of the analysis of x-ray diffraction patterns of both hydrated and anhydrate cement, density measurements, rheological behavior results, compressive strength results, tensile strength results, stability measurements, heat of hydration process, and the chemical shrinkage results. The main conclusions are summarized below:

- In general, GNPs enhanced the performance of the cement and showed the potential in reducing the gas migration in oil and gas wells by stopping the propagation of micro cracks.
- The results of XRD analysis proved that GNPs modified the microstructure of the cement hydration crystals as the peaks of the hydration products varied.
- The addition of small concentration of GNPs in this study did not affect the rheological properties significantly. However, the effect of time could have a significant effect on rheology.
- GNPs increased the compaction of the particles in the cement. Thus, the compressive strength increased by 10% compared to reference slurry.
- GNPs modified the microstructure of the hydration crystals, which enhanced the tensile strength by 30%.
- The cement systems tested in this study were stable and suffered less free fluids. In addition, the cement systems tested herein showed no significance sedimentation.
- The heat of hydration was investigated in this work. The GNPs in concentrations range of 0.1% to 0.6% did not affect the hydration process of the cement. However, the addition of 0.9% had a slight acceleration effect on hydration process.
- GNPs reduced the shrinkage of cement by 30%. This reduction, especially at early ages, can help reduce the risk of gas migration.
- Due to their thermal conductivity, the GNPs might have distributed the temperature through the cement uniformly, thus reducing the temperature

gradient of the cement sheath. The temperature gradient can create thermal cracks if the tensile stresses exceeded the tensile strain capacity of the cement. Additional experiments such as thermal diffusivity test are needed to further investigate the thermal conductivity impact of GNPs on the cement.

NOMENCLATURE

$kg/m^3 = Kilogram\,per\,meter\,cube.$

$nm = Nanometer.$

$kN = KiloNewton.$

$psi = Pounds\ per\ square\ inch.$

$lb/gal = Pounds\ per\ gallon.$

$°C = Degree\ celsius.$

$BWOC = By\,weight\ of\ cement.$

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

$V_i = Initial\ volume\ of\ cement, ml.$

$\varphi = Free\ fluids\ content, vol\%.$

$m = Mass\ of\ cement, gm, kg.$

$d_{rel} = Relative\ density, frac.$

$\rho = Gram\,per\ cubic\ centimeter, Pounds\ per\ gallon.$

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SECTION

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

This thesis provides a new classification that can work as a guide for the oil and gas industry to better understand and evaluate cement systems prior to field jobs execution. The major conclusions are obtained:

- Good cement can be achieved when cementing operations combines both a good cement design and carful execution.
- Complete mud removal is essential to achieve good bonding between the cement and its surroundings.
- The modulus of elasticity have a great impact on the durability of the cement.
- It is essential to evaluate the initial state of stress in the cement sheath to know how much loading can be submitted to the cement before it fails.
- A huge assumption is made when evaluating cement failures is that each failure happens independent of other failures. For example, when analyzing a micro annulus between the cement sheath and the formation, most of researches assume good bonding between the cement and the casing, which is not very true in all cases.
- It can be concluded from this review that the cement have to be: environmentally acceptable, with the desired density, suffers no excessive fluid loss, zero free fluids, achieve desired strength, low or no shrinkage,

short transition time, can withstand high pressure and temperatures, resist downhole chemicals, and can achieve good bonding with the casing and the formation.

- Long-term properties of the cement are as important as short-term properties, thus attention must be paid to how extent the cement can loaded. This can be achieved by combining laboratory results with computerized models.
- Cementing is an operation that require the attention from designing the cement, through the practices of placing the cement, to providing long-term zonal isolation.

Results obtained from this research will promote using Nanotechnology to overcome the failures of Portland cement in providing zonal isolation. Failures related to gas migration, such as formation of micro-annuli, channels, and cracks, would be reduced when implementing GNPs.

- GNPs enhanced the overall performance of the cement and showed the potential in reducing the gas migration in oil and gas wells by stopping the propagation of micro cracks.
- GNPs modified the microstructure of the cement hydration crystals as the peaks of the hydration products varied.
- GNPs enhanced the mechanical properties (compressive and tensile strength) of the cement.

- GNPs reduced the shrinkage of cement by 30%. This reduction, especially at early ages, can help reduce the risk of gas migration through micro-annuli.
- The addition of small concentration of GNPs in this study did not affect the rheological properties significantly. However, the effect of time could have a significant effect on rheology.

6.2. RECOMMENDATIONS

This study is only the start point to understand Portland cement. Although, this study was very intensive, still Portland cement and its reaction is very complicated. This work has to be extended until the optimum goal is achieved. Oil wells drilling and completion must be optimized. Below are some recommendations that may help to extend the knowledge in this topic:

1. Cement systems must be tested in a way that simulate downhole conditions. To accomplish that, a new testing model that simulate downhole conditions is essential.
2. More focus must be spent in modeling cement as a porous media following rock mechanics laws; hence, the durability of cement can be predicted.
3. Cement additives must be tested and optimized to ensure their ability to deliver their functions.
4. The drilling practices must be improved to guarantee the zonal isolation and the integrity of the cement sheath.

5. Determining the initial state of stress would help predicting to how extent the cement will withstand loadings, hence avoiding damaging the cement.
6. GNPs as an additive must be tested under different temperature to better evaluate its behavior.
7. The thermal conductivity of the cement with and without GNPs must be tested and analyzed to examine the ability of conductive materials to avoid thermal cracking in the cement sheath.
8. The porosity and permeability of new cement formulations presented here are to be tested. Nanomaterials have great impact on those properties.
9. Achieving good bonding between the cement and its surroundings are important. GNPs may help achieving better bonding. Laboratory experiments must be performed to prove this.

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