



**WELLBORE INTEGRITY: MODIFYING AND CHARACTERIZING  
OIL WELL CEMENT TO ENHANCE WELLBORE LOGGING AND  
PREVENT PERFORATING DAMAGES IN HYDRAULIC  
FRACTURED WELLS**

A Thesis

Presented to

the Faculty of the Department of Civil and Environmental Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in Civil Engineering

By

Mohammad Amin Zomorrodian

December 2014

**WELLBORE INTEGRITY: MODIFYING AND CHARACTERIZING  
OIL WELL CEMENT TO ENHANCE WELLBORE LOGGING AND  
PREVENT PERFORATING DAMAGES IN HYDRAULIC  
FRACTURED WELLS**

---

Mohammad Amin Zomorrodian

Approved:

---

Chair of the Committee  
Cumaraswamy Vipulanandan, Professor, Civil  
and Environmental Engineering

Committee Members:

---

Robello Samuel, Adjunct Professor, Petroleum  
Engineering

---

Kalyana Babu Nakshatralla, Assistant  
Professor, Civil and Environmental  
Engineering

---

Suresh K. Khator  
Associate Dean  
Cullen College of Engineering

---

Roberto Ballarini  
Professor and Chairman  
Civil and Environmental Engineering

## **DEDICATION**

To my parents.

**WELLBORE INTEGRITY: MODIFYING AND CHARACTERIZING  
OIL WELL CEMENT TO ENHANCE WELLBORE LOGGING AND  
PREVENT PERFORATING DAMAGES IN HYDRAULIC  
FRACTURED WELLS**

A Thesis

Presented to

the Faculty of the Department of Civil and Environmental Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in Civil Engineering

By

Mohammad Amin Zomorrodian

December 2014

## **ABSTRACT**

Oil well cementing is considered as one of the foremost important and challenging operations in drilling. The main purpose of cement in wellbores is to provide zonal isolation, and support for casing. Properties of oil well cement should be taken into consideration to assure a high quality cementing job. The objective of this study was to investigate the effect of unconventional additives and contamination on oil well cement. In addition, self-healing oil well cement was developed to prevent perforation damages.

Laboratory results showed that polycarboxylate enhanced the rheology and reduced the fluid loss of cement by up to 96%. Nanoclay increased the compressive strength by up to 71%, and reduced the fluid loss by up to 64%. Salt and drilling fluid contamination altered the properties of cement particularly compressive strength and rheology. The proposed self-healing cement retained up to 22% of its initial mechanical strength and yielded zero permeability.

# TABLE OF CONTENTS

|                                                              |      |
|--------------------------------------------------------------|------|
| DEDICATION .....                                             | iv   |
| ABSTRACT .....                                               | vi   |
| TABLE OF CONTENTS .....                                      | vii  |
| LIST OF FIGURES .....                                        | xii  |
| LIST OF TABLES .....                                         | xvii |
| CHAPTER 1 INTRODUCTION .....                                 | 1    |
| 1.1 Objectives .....                                         | 2    |
| 1.2 Organization .....                                       | 2    |
| CHAPTER 2 BACKGROUND AND LITERATURE REVIEW .....             | 4    |
| 2.1 Oil well cementing.....                                  | 4    |
| 2.2 Oil well cement chemical composition and reactions ..... | 5    |
| 2.3 Properties of Oil Well Cement.....                       | 8    |
| 2.3.1 Density .....                                          | 8    |
| 2.3.2 Rheology.....                                          | 10   |
| 2.3.3 Fluid Loss .....                                       | 14   |
| 2.3.4 Mechanical Properties .....                            | 15   |
| 2.3.5 Thickening Time.....                                   | 16   |
| 2.3.6 Porosity and Permeability .....                        | 17   |

|                                      |                                                  |    |
|--------------------------------------|--------------------------------------------------|----|
| 2.3.7                                | Shrinkage and Expansion .....                    | 17 |
| 2.3.8                                | Electrical Properties .....                      | 18 |
| 2.3.9                                | Piezoresistivity .....                           | 20 |
| 2.4                                  | Admixtures of Oil Well Cement .....              | 20 |
| 2.4.1                                | Accelerators and Retarders .....                 | 21 |
| 2.4.2                                | Extenders.....                                   | 22 |
| 2.4.3                                | Weighting Agents.....                            | 23 |
| 2.4.4                                | Dispersants .....                                | 23 |
| 2.4.5                                | Fluid Loss Agents .....                          | 24 |
| 2.4.6                                | Lost-Circulation Control Agents .....            | 25 |
| 2.4.7                                | Specialty Additives.....                         | 26 |
| 2.5                                  | Summary .....                                    | 26 |
| CHAPTER 3 MATERIALS AND METHODS..... |                                                  | 28 |
| 3.1                                  | Types of Oil Well Cement and Drilling Fluid..... | 28 |
| 3.1.1                                | Modifying Oil Well Cement.....                   | 28 |
| 3.2                                  | Oil Well Cement Additives .....                  | 29 |
| 3.3                                  | Curing and Monitoring Cement Slurry.....         | 29 |
| 3.4                                  | Electrical Properties .....                      | 30 |
| 3.5                                  | Fluid Loss Test.....                             | 31 |
| 3.6                                  | Permeability Tests .....                         | 33 |

|                                                          |                                                                              |    |
|----------------------------------------------------------|------------------------------------------------------------------------------|----|
| 3.7                                                      | Gas Migration Evaluation .....                                               | 33 |
| 3.8                                                      | Rheological Measurements .....                                               | 34 |
| 3.9                                                      | Mechanical Properties and Piezoresistivity .....                             | 35 |
| 3.10                                                     | Summary .....                                                                | 36 |
| CHAPTER 4 BEHAVIOR OF SMART OIL WELL CEMENT .....        |                                                                              | 38 |
| 4.1                                                      | Sample Preparation .....                                                     | 38 |
| 4.2                                                      | RESULTS .....                                                                | 39 |
| 4.2.1                                                    | Rheological Properties.....                                                  | 39 |
| 4.2.2                                                    | Electrical Properties during Curing.....                                     | 42 |
| 4.2.3                                                    | Fluid Loss and Filter Cake Permeability.....                                 | 48 |
| 4.2.4                                                    | Mechanical Properties and Piezoresistivity .....                             | 51 |
| 4.2.5                                                    | Correlation between Electrical Resistivity and Compressive Strength<br>..... | 55 |
| 4.3                                                      | Summary .....                                                                | 57 |
| CHAPTER 5 BEHAVIOR OF CONTAMINATION ON OIL WELL CEMENT . |                                                                              | 59 |
| 5.1                                                      | Effects of Salt Contamination with Oil Well Cement.....                      | 59 |
| 5.1.1                                                    | Sample Preparation and Mixing .....                                          | 59 |
| 5.1.2                                                    | Rheology Behavior.....                                                       | 59 |
| 5.1.3                                                    | Fluid Loss .....                                                             | 60 |
| 5.1.4                                                    | Compressive Strength after 24 hours of curing.....                           | 61 |

|                                    |                                                                                             |    |
|------------------------------------|---------------------------------------------------------------------------------------------|----|
| 5.1.5                              | Electrical Properties .....                                                                 | 62 |
| 5.2                                | Effect of Bentonite Contamination on Oil Well Cement.....                                   | 64 |
| 5.2.1                              | Fluid Loss Results.....                                                                     | 64 |
| 5.2.2                              | Gas Migration Properties .....                                                              | 65 |
| 5.2.3                              | Mechanical Properties .....                                                                 | 66 |
| 5.2.4                              | Predicting the Effect of Bentonite on Calculated API Fluid Loss of Oil<br>Well Cement ..... | 67 |
| 5.3                                | Effect of Synthetic Based Drilling Fluid Contamination on Oil Well<br>Cement.....           | 75 |
| 5.3.1                              | Rheological Properties.....                                                                 | 75 |
| 5.3.2                              | Fluid Loss and Filter Cake Permeability.....                                                | 76 |
| 5.3.3                              | Compressive Strength and Ultrasonic Pulse Velocity .....                                    | 78 |
| 5.4                                | Summary .....                                                                               | 79 |
| CHAPTER 6 SELF-HEALING CEMENT..... |                                                                                             | 81 |
| 6.1                                | Sample Preparation .....                                                                    | 82 |
| 6.2                                | Rheology.....                                                                               | 83 |
| 6.3                                | Fluid Loss .....                                                                            | 84 |
| 6.4                                | Mechanical Properties .....                                                                 | 85 |
| 6.5                                | Permeability .....                                                                          | 87 |
| 6.6                                | Summary .....                                                                               | 88 |

|            |                                      |    |
|------------|--------------------------------------|----|
| CHAPTER 7  | CONCLUSIONS AND RECOMMENDATIONS..... | 90 |
| 7.1        | Conclusions .....                    | 90 |
| 7.2        | Recommendations .....                | 92 |
| 7.3        | Future Work .....                    | 93 |
| REFERENCES | .....                                | 94 |

## LIST OF FIGURES

|                                                                                                                                                          |    |
|----------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 2-1 - Schematic of wellbore cementing (Plank J. , 2011) .....                                                                                     | 5  |
| Figure 2-2 - Shear stress versus shear rate in Bingham plastic fluid .....                                                                               | 11 |
| Figure 2-3 - Shear stress versus shear rate in power-law fluids .....                                                                                    | 12 |
| Figure 2-4 - Shear stress vs. shear rate in Newtonian and different non-Newtonian fluids .....                                                           | 13 |
| Figure 2-5 - Schematic of fluid loss in the wellbore (BakerHughes, 2010) .....                                                                           | 14 |
| Figure 3-1 - HPHT filter press components .....                                                                                                          | 31 |
| Figure 3-2 - Schematic of fluid loss test.....                                                                                                           | 32 |
| Figure 3-3 - Standard viscometer used in this study.....                                                                                                 | 35 |
| Figure 3-4 - A hardened cement sample under indirect tensile test .....                                                                                  | 36 |
| Figure 4-1 - Effect of nanoclay on the rheology of oil well cement.....                                                                                  | 39 |
| Figure 4-2 - Effect of polycarboxylate on the rheology of 33% cement slurry .....                                                                        | 40 |
| Figure 4-3 - Effect of polycarboxylate on the rheology of 30% cement slurry .....                                                                        | 40 |
| Figure 4-4 - Effect of water to cement ratio on the rheology of oil well cement ..                                                                       | 41 |
| Figure 4-5 - Changes in normalized electrical resistivity in respect to initial resistivity during first 5 hours of curing, in 30% cement slurries ..... | 42 |
| Figure 4-6 - Changes in normalized electrical resistivity in respect to initial resistivity during first 5 hours of curing, in 38% cement slurries ..... | 43 |
| Figure 4-7 – Rate of changes in normalized electrical resistivity during first 5 hours of curing for water to cement ratio of 30% .....                  | 44 |
| Figure 4-8 – Rate of changes in normalized electrical resistivity during first 5 hours of curing for water to cement ratio of 38% .....                  | 44 |

|                                                                                                                                                                    |    |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 4-9 - Changes in normalized electrical resistivity during 30 days of curing for samples containing polycarboxylate with water to cement ratio of 30% .....  | 45 |
| Figure 4-10 - Changes in normalized electrical resistivity during 30 days of curing for samples containing polycarboxylate with water to cement ratio of 38% ..... | 46 |
| Figure 4-11 - Rate of change in normalized resistivity for 30% w-c ratio samples containing polycarboxylate .....                                                  | 47 |
| Figure 4-12 - Rate of change in normalized resistivity for 38% w-c ratio samples containing polycarboxylate .....                                                  | 47 |
| Figure 4-13 - Calculated API fluid loss of 38% cement samples containing nanoclay at 100 psi.....                                                                  | 48 |
| Figure 4-14 - Filter cake permeability of 38% cement samples containing nanoclay at 100 psi.....                                                                   | 49 |
| Figure 4-15 - Fluid loss of 30% and 38% with Polycarboxylate .....                                                                                                 | 50 |
| Figure 4-16 - Filter cake permeability of 30% w-c ratio slurries with polycarboxylate.....                                                                         | 50 |
| Figure 4-17 - Compressive strength of 38% w-c samples containing nanoclay after 24 hours of curing.....                                                            | 51 |
| Figure 4-18 - Compressive strength of samples with 30% and 38% w-c ratio containing polycarboxylate after 7 days of curing .....                                   | 52 |
| Figure 4-19 - Compressive strength of samples with 30% and 38% w-c ratio containing polycarboxylate after 30 days of curing .....                                  | 53 |
| Figure 4-20 - Piezoresistivity of 30% w-c slurries containing polycarboxylate after 30 days of curing .....                                                        | 54 |

|                                                                                                                                       |    |
|---------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 4-21 - Piezoresistivity of 38% w-c slurries containing polycarboxylate after 30 days of curing .....                           | 55 |
| Figure 4-22 - Correlation between ultimate change in normalized resistivity and ultimate compressive strength for 30% w-c ratio ..... | 56 |
| Figure 4-23 - Correlation between ultimate change in normalized resistivity and ultimate compressive strength for 38% w-c ratio ..... | 56 |
| Figure 5-1 - Effect of salt contamination on the rheology of oil well cement .....                                                    | 60 |
| Figure 5-2 - Effect of salt contamination on fluid loss of oil well cement.....                                                       | 61 |
| Figure 5-3 – Effect of salt contamination on 24 hour compressive strength of oil well cement.....                                     | 62 |
| Figure 5-4 - Effect of salt contamination on electrical resistivity of oil well cement during initial curing.....                     | 63 |
| Figure 5-5 - Effect of bentonite on the fluid loss in the 38% oil well cement .....                                                   | 65 |
| Figure 5-6 - Effect of bentonite on gas permeability of oil well cement.....                                                          | 66 |
| Figure 5-7 - Effect of bentonite contamination on 24 hour compressive strength of cement samples .....                                | 67 |
| Figure 5-8 - Calculated vs. predicted effect of bentonite on fluid loss of oil well cement at 100 psi .....                           | 68 |
| Figure 5-9 - Calculated vs. predicted effect of bentonite on fluid loss of oil well cement at 200 psi .....                           | 69 |
| Figure 5-10 - Calculated vs. predicted effect of bentonite on fluid loss of oil well cement at 300 psi .....                          | 69 |

|                                                                                                                         |    |
|-------------------------------------------------------------------------------------------------------------------------|----|
| Figure 5-11 - Calculated vs. predicted effect of bentonite on fluid loss of oil well cement at 400 psi .....            | 70 |
| Figure 5-12 - H parameter predicted using P-Q model vs. calculated values.....                                          | 71 |
| Figure 5-13 - Predicted vs. calculated values for G parameter.....                                                      | 72 |
| Figure 5-14 - Calculated vs. predicted fluid loss for oil well cement contaminated with bentonite at 100 psi .....      | 73 |
| Figure 5-15 - Calculated vs. predicted fluid loss for oil well cement contaminated with bentonite at 100 psi .....      | 74 |
| Figure 5-16 - Calculated vs. predicted fluid loss for oil well cement contaminated with bentonite at 100 psi .....      | 74 |
| Figure 5-17 - Calculated vs. predicted fluid loss for oil well cement contaminated with bentonite at 100 psi .....      | 75 |
| Figure 5-18 - Effect of SBM contamination on the rheology of oil well cement...                                         | 76 |
| Figure 5-19 - Effect of SBM contamination on fluid loss of cement at 100 psi....                                        | 77 |
| Figure 5-20 - Effect of SBM contamination on permeability of filter cake in cement samples .....                        | 77 |
| Figure 5-21 - Effect of SBM contamination on 24 hour compressive strength of cement samples .....                       | 78 |
| Figure 5-22 - Effect of SBM contamination on ultrasonic pulse velocity of cement samples after 24 hours of curing ..... | 79 |
| Figure 6-1 - Effect of AV-101 (catalyst) on the rheology of oil well cement containing 0.5% bentonite .....             | 83 |
| Figure 6-2 - Effect of catalyst on fluid loss of cement at 100 psi.....                                                 | 84 |

|                                                                                                                     |    |
|---------------------------------------------------------------------------------------------------------------------|----|
| Figure 6-3 - Tensile strength of cement after 24 hours of curing with and without catalyst .....                    | 85 |
| Figure 6-4 - 24 hour compressive strength of cement samples after curing and after exposure to fracking fluid.....  | 86 |
| Figure 6-5 - Formed polymer gel in cracked cement sample after being exposed to the fracking fluid .....            | 87 |
| Figure 6-6 - Permeability of cement samples after curing, after cracking and after exposing to fracking fluid ..... | 88 |

## LIST OF TABLES

|                                                                                              |    |
|----------------------------------------------------------------------------------------------|----|
| Table 2-1 - Temperature and pressure at different depths (Smith, 1990).....                  | 6  |
| Table 2-2 - API classification of oil well cements (Azar & Samuel, 2007).....                | 7  |
| Table 5-1 - Gas migration results for 38% cement slurries with and without<br>bentonite..... | 65 |
| Table 6-1 - Comparision between the rheology of water and proposed fracking<br>fluid.....    | 84 |

# **CHAPTER 1**

## **INTRODUCTION**

With the increased demand in energy, the big focus is on aligning the exploration and production of oil and gas products. The oil consumption has increased by 171% during the last four decades (Yahaba, 2010). Drilling and completion are major steps in oil and gas production and occur after the seismic investigations. The major conventional operations include drilling the well, placing the casing, cementing and completion of the wellbore (Devold, 2013).

Failure in drilling and completion operations can lead to failure of the wellbore and may also have disastrous environmental impacts. An oil well cementing failure which occurred in 2010 in the Gulf of Mexico caused the world's largest accidental marine oil spill in the history of petroleum industry in which a blowout led to a huge fire and oil spill in the gulf of Mexico (Garg & Gokavarapu, 2012). The petroleum industry has been funding innovative solutions to improve oil extraction and reduce the risks in oil and gas production.

Well cementing is one of the most critical operations in well drilling and completion. It consists of the procedure of placing cement between the casing and the formation surrounding the casing. The main purposes of cementing the wellbore is to provide isolation for the casing and liner strings, prevent corrosion and providing wellbore stability. Cement forms a strong, almost impermeable barrier between the casing and formation which prevents gas and fluids from

migrating through the wellbore and provides support for the casing (Azar & Samuel, 2007).

## **1.1 Objectives**

The objective of the study was to investigate the effects of selected additives and contamination on the behavior of smart oil well cement, and to develop a system to overcome cementing issues in production zones. The specific objectives are as follows:

- 1 Evaluate the effects of unconventional admixtures on the behavior of smart oil well cement.
- 2 Investigate the effects of drilling fluid and salt contamination on the properties of oil well cement.
- 3 Develop admixtures to provide self-healing properties for repairing the damages on oil well cement during completion operations.

## **1.2 Organization**

This thesis is categorized into seven chapters. Chapter 2 summarizes the basic concepts of oil well cement, its properties and chemical compositions and the utilization of additives in cementing. In chapter 3, the materials and methods used for evaluating various properties of oil well cement are discussed. Chapter 4 presents the effects of different conventional and unconventional additives and the water to cement ratio on the behavior of oil well cement. In chapter 5, the impacts of drilling fluid and salt contamination on the behavior of oil well cement are discussed. Also constitutive models are presented in this chapter to predict the behavior of contaminated cement. In chapter 6, a new admixture is presented

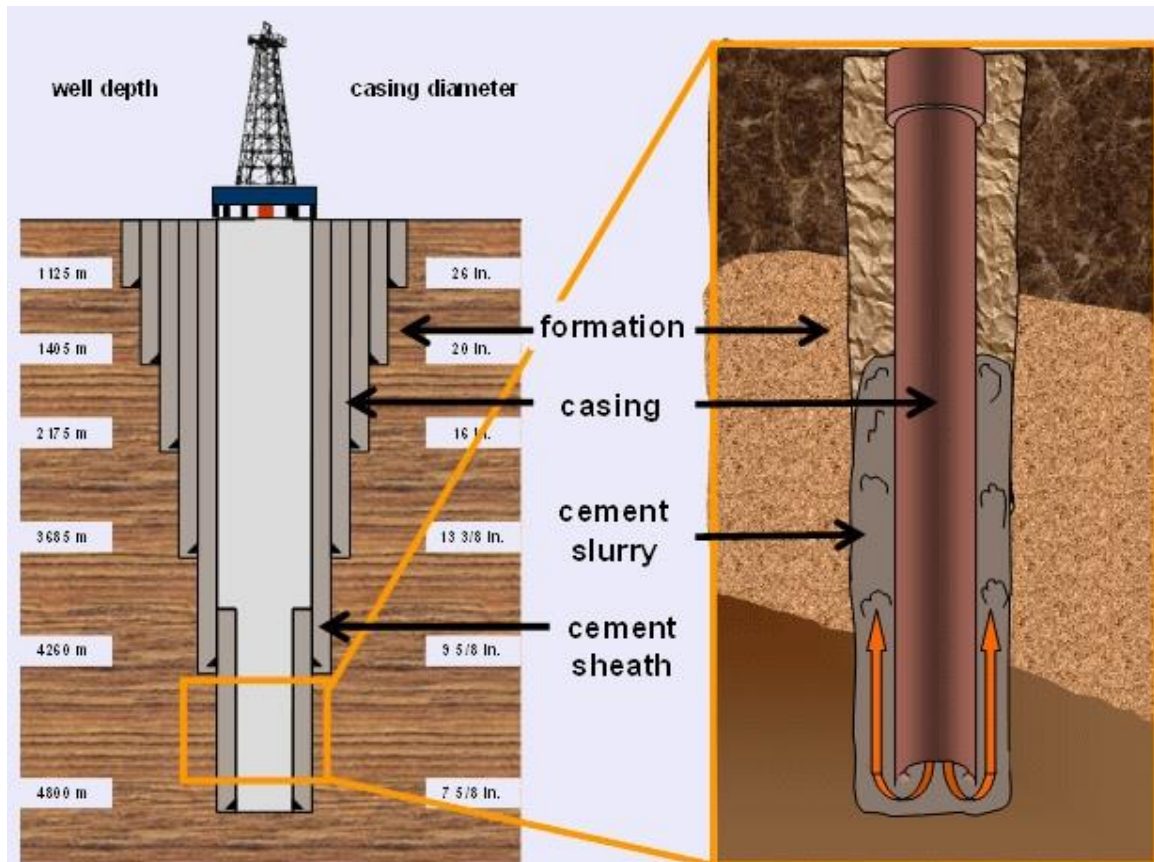
to provide well integrity by providing self-healing properties for oil well cement in hydraulic fractured wells. The conclusions and recommendations are summarized in chapter 7.

## **CHAPTER 2**

### **BACKGROUND AND LITERATURE REVIEW**

#### **2.1 Oil well cementing**

Oil well cementing is the process of placing cement around casing to fill and seal the annulus within the drilled hole. During the drilling process, drill bit cuts through the formation and is constantly being lubricated and cooled down by drilling fluids. The drilling fluid also provides stability for the wellbore. However, after drilling a certain section of the wellbore, drilling fluid cannot provide stability and prevent geological formation from collapsing. For this reason, drill bit is removed from the wellbore, casing is placed and cement is pumped. Cement will fill the area between casing and formation and after a certain time it forms hardened cement paste which yields high mechanical properties and low permeability (Azar & Samuel, 2007; Iverson, Darbe, & McMechan, 2008). Oil well cementing was first introduced in 1920s to overcome critical issues in regards to well integrity (Joshi & Lohita, 1997). The main objectives of developing cementing as an oil well completion operation were providing zonal isolation, prevent corrosion, reducing the risk of groundwater contamination, providing stability for the wellbore and supporting the casing. Fig 2.1 represents a schematic of cemented wellbore.



**Figure 2-1 - Schematic of wellbore cementing (Plank J. , 2011)**

Designing appropriate oil well cement depends on various factors such as wellbore geometry, bottomhole well pressure and temperature, type and properties of drilling fluid and formation properties. Different properties of liquid and hardened oil well cement should be taken into account such as rheology, fluid loss and mechanical properties which are discussed later in this chapter.

## **2.2 Oil well cement chemical composition and reactions**

Most cements used in oil and gas industry are modified Portland cement. It is produced from limestone and either clay or shale at around 3000 degree F. After the roasting step, the product is ground to a desired size. The size of cement particles defines the ratio of water required for mixture in such a way that

smaller size yields higher water to cement ratio. American Petroleum Institute (API) has defined 9 types of cements to be used for oil well cementing. This categorization is mainly based on applicability of cement in different pressures and temperatures. Temperature and pressure in the wellbore changes based on the drilled depth. Table 2.1 shows the profile of temperature and pressure for different well depths. Table 2.2 represents the classified API oil well cements and their application (Azar & Samuel, 2007).

**Table 2-1 - Temperature and pressure at different depths (Smith, 1990)**

| Depth<br>(ft) | Circulating Temperature<br>(F) | Static Temperature<br>(F) | Pressure<br>(psi) |
|---------------|--------------------------------|---------------------------|-------------------|
| 1000          | 80                             | 92                        | 700               |
| 6500          | 120                            | 158                       | 3850              |
| 9800          | 150                            | 198                       | 6160              |
| 14300         | 200                            | 252                       | 9655              |
| 18300         | 250                            | 300                       | 13285             |
| 21750         | 300                            | 341                       | 16650             |

**Table 2-2 - API classification of oil well cements (Azar & Samuel, 2007)**

| Class Type | Details                                                                                                                                                                                                                          |
|------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Class A    | For use up to 6000 ft depth, when special properties are not required                                                                                                                                                            |
| Class B    | For use up to 6000 ft depth, when conditions require moderate to high sulfate resistance.                                                                                                                                        |
| Class C    | For use up to 6000 ft depth, when conditions require high early strength.                                                                                                                                                        |
| Class D    | For use from 6000 ft to 10000 ft depth, under conditions of high temperatures and pressures.                                                                                                                                     |
| Class E    | For use from 10000 ft to 14000 ft depth, under conditions of high temperatures and pressures.                                                                                                                                    |
| Class F    | For use from 10000 ft to 14000 ft depth, under conditions of extremely high temperatures and pressures.                                                                                                                          |
| Class G    | Intended for use as a basic cement from surface to 8000 ft depth. Can be used with accelerators and retarders to cover a wide range of well depths and temperatures.                                                             |
| Class H    | A basic cement for use from surface to 8000 ft depth as manufactured. Can be used with accelerators and retarders to cover a wider range of well depths and temperatures                                                         |
| Class J    | Intended for use as manufactured from 12000 ft to 16000 ft depth under conditions of extremely high temperatures and pressures. It can be used with accelerators and retarders to cover a range of well depths and temperatures. |

Oil well cements mainly consist of four components:  $C_3A$  (tricalcium aluminate),  $C_4AF$  (tetracalcium alumino ferrite),  $C_3S$  (tricalcium silicate) and  $C_2S$  (dicalcium silicate) along with calcium sulfate (gypsum) and some alkali sulfates and lime. The first two main components,  $C_3A$  and  $C_4AF$ , mainly control the

rheological properties and the later components,  $C_3S$  and  $C_2S$ , develop the mechanical strength of cement. When cement is exposed to water  $C_3S$  and  $C_2S$  form C-S-H (calcium silicate hydrates) gel and CH (calcium hydroxide). This gel is the principal binder and provides strength to hardened cement (Patil & Deshpande, 2012). The chemical reactions:



are related to compressive strength of cement slurry during early and long term curing.

## 2.3 Properties of Oil Well Cement

Oil well cement should be designed based on the wellbore conditions and situations such as temperature, pressure and permeability of formation. During designing the oil well cement, different properties should be taken into account. These properties include slurry and hardened properties of cement such as density, rheology, fluid loss, mechanical properties. In this section, the important properties of oil well cement are discussed.

### 2.3.1 Density

During drilling and completion of wellbores, two different formation pressures should be taken into account: pore pressure and fracture pressure. Pore pressure is pressure of the fluids within the formation. It normally increases by increasing the depth of wellbore and is classified in three different categories (Azar & Samuel, 2007):

- Normal pressure if the pressure gradient is around 0.433psi / ft of depth
- Abnormal pressure if the pressure gradient is greater than 0.433psi / ft depth
- Subnormal pressure if the pressure gradient is lower than 0.433psi / ft depth

Fracture pressure is the pressure required to fracture the structure of a formation. If the formation is exposed to a pressure higher than the fracture pressure, the formation will break and lost circulation will happen (Rocka, et al., 2004).

Cement density defines the hydrostatic pressure of cement column in the wellbore. If the pressure is higher than the fracture pressure of wellbore, the formation may fracture. Also low density cement may allow the formation fluid to flow inside the borehole if the hydrostatic pressure is lower than pore pressure. The density of cement is presented in pound per gallon (ppg). Each pound per gallon equals  $0.12 \text{ g/cm}^3$  in SI unit. Neat cement slurry has a density from 14 to 18 ppg ( $1.67$  to  $2.15 \text{ g/cm}^3$ ). Additives can be used to increase or decrease the cement density. Also water to cement ratio can be modified to change the density of slurry. Densified cement has a density of 16 to 22 ppg ( $1.91$  to  $2.39 \text{ g/cm}^3$ ) and high water to cement ratio slurries have a density of 11 to 15 ppg ( $1.31$  to  $1.8 \text{ g/cm}^3$ ). Foamed cements can be designed to have densities of 4-7 ppg but they need careful control of annulus pressure to assure no gas or fluid migration in the wellbore (Azar & Samuel, 2007; McElfresh & Boncan, 1982; Allen & Sands, 1993).

### 2.3.2 Rheology

Rheology of cement is one of its most important properties. Rheology is the study deformation of materials whose behavior falls between solids and fluids which mainly includes determining the relationships between the flow rate (shear rate) and the shear stress in the fluid (Guillot, 2006). The rheological properties of oil well cement define the following (Shahriar, 2011):

- Pumpability and flowability
- Frictional pressure between cement, casing and formation
- Ability of slurry to transport cuttings
- Effects of pressure and temperature on placement of slurry

Shear rate is defined as the velocity difference between two plates in accordance with the distance between the two plates. The unit used for shear rate is  $\text{sec}^{-1}$ . The stress applied to the plates is called shear stress and is defined as force on the area of plate.

In general, fluids can be categorized in two different groups based on the rheological behavior: Newtonian and non-Newtonian. In the Newtonian fluids the shear stress is proportional to the shear rate. The slope of the line represents the viscosity of fluid and it does not depend on the flow condition but may depend of temperature and pressure (Guillot, 2006). An example of Newtonian fluids is tap water or thin motor oil.

The viscosity in non-Newtonian fluids depends on the shear rate and the duration the shear rate is applied. For some non-Newtonian fluids, a certain amount of shear stress is required to overcome the internal friction of the material

and start to flow. Different rheological models have been developed to predict the behavior of non-Newtonian fluids at different shear rates. The most common models include Bingham, Power law and Herschel-Bulkley models.

### 2.3.2.1 Bingham Model

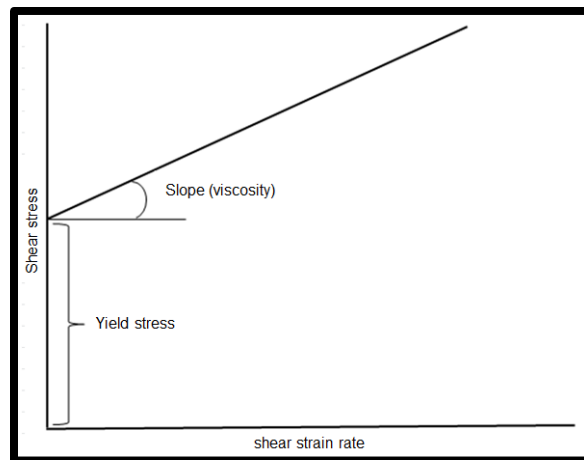
Bingham model takes into account the initial shear stress required for the fluid to flow. The parameters of Bingham plastic fluid include the following (Bingham, 1922):

- $\tau_0$  which is the value of shear stress at shear rate of zero ( $\dot{\gamma}=0$ )
- Plastic viscosity, which is the slope of the straight line,  $\mu_p$

The parameters of Bingham model:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \quad (2-2)$$

are represented in Fig 2.2.



**Figure 2-2 - Shear stress versus shear rate in Bingham plastic fluid**

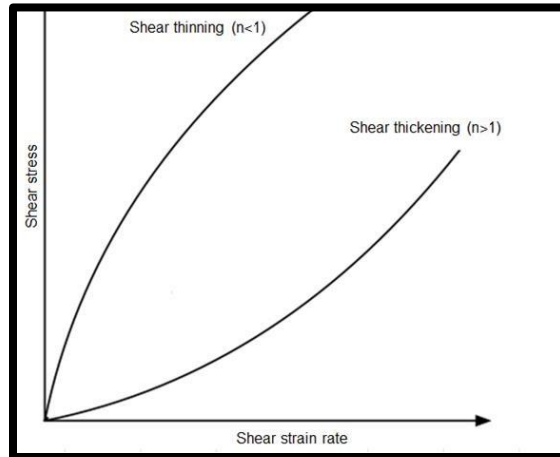
### 2.3.2.2 Power-Law Model

Power-law fluids flow immediately after applying shear stress and the relationship between shear stress and shear rate is not linear. The slope of the

shear stress vs. shear rate defines the apparent viscosity. Equation 2.3 describes the power-law model:

$$\tau = k \dot{\gamma}^n, \quad (2-3)$$

where  $k, n, \tau$  and  $\dot{\gamma}$  are consistency, power-law exponent, shear stress and shear rate. The exponent  $n$  defines whether the fluid is shear thinning or shear thickening as shown in Fig 2.3. The apparent viscosity in shear thinning fluids decreases by increasing the shear stress whereas in shear thickening fluids the apparent viscosity increases when shear rate increases.



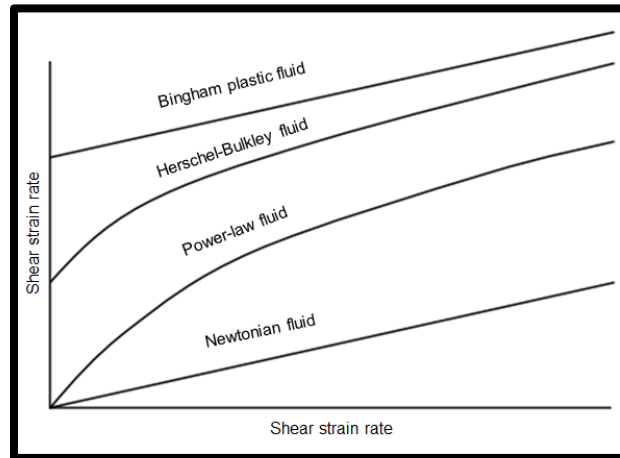
**Figure 2-3 - Shear stress versus shear rate in power-law fluids**

### **2.3.2.3 Herschel-Bulkley Model**

Herschel-Bulkley model combines the Bingham model and power-law model. It takes into account the required initial shear stress for the fluid to begin to flow in the equation:

$$\tau = \tau_0 + k \dot{\gamma}^n, \quad (2-4)$$

where  $k, n, \tau, \dot{\gamma}$ , and  $\tau_0$  are consistency, power-law exponent, shear stress, shear rate and yield stress. Fig 2.4 compares the different Newtonian and non-Newtonian fluids.



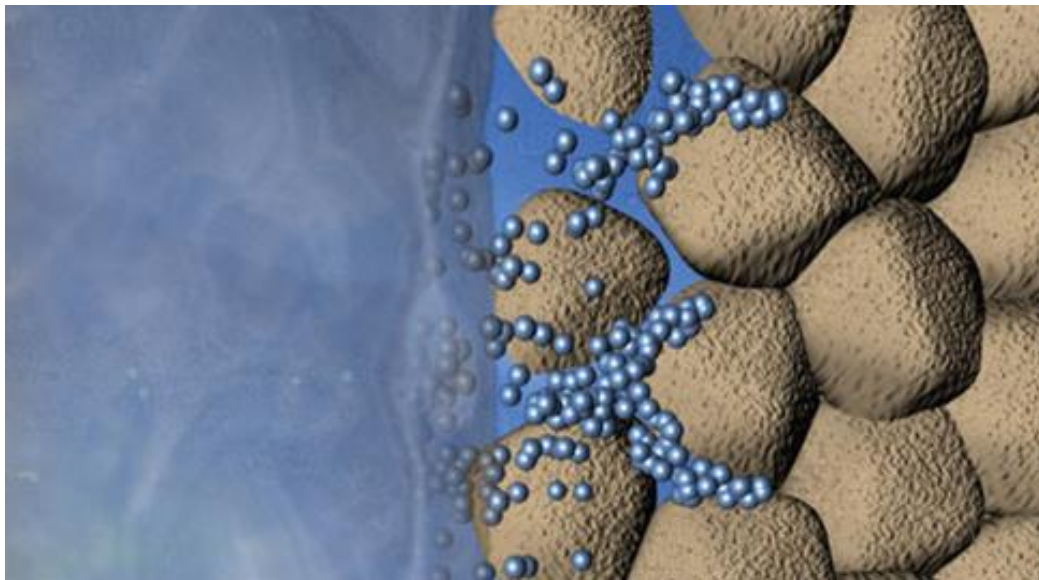
**Figure 2-4 - Shear stress vs. shear rate in Newtonian and different non-Newtonian fluids**

The rheological study of cement slurry includes investigating the shear stress shear vs strain rate, viscosity, yield point and gel strength. The rheological study for oil well cement is usually more complicated compared to conventional cement due to the high pressure and temperature in the wellbore. Normally certain additives are added to the slurry to modify its rheological behavior in certain conditions. Marinating an appropriate rheology for oil well cement is critical for providing pumpability and flowability for slurry and defining the friction when cement is pumped inside the casing or in the annulus. In addition, gel strength which is the static strength development during the transition between liquid and hardened states is another important factor for oil well cement. It defines the strength development and the ability of cement column to prevent gas and fluid from invading inside the wellbore (Sabins, Tinsley, & Sutton, 1982).

### 2.3.3 Fluid Loss

The formation around the wellbore may include permeable zones and natural fractures. During and after the placement of oil well cement, due to the difference between the hydrostatic pressure of slurry and pore pressure of formation, there is a chance for the leakage of the liquid phase of cement into the formation matrix. This phenomenon is called fluid loss. Fluid loss creates dehydrated masses of cement called filter cake, and impacts the properties of cement by reducing the water content of cement. Fluid loss also changes the volume of cement column and leads to hydrostatic pressure loss. The pressure loss may allow the formation fluids in the borehole and reduce the zonal isolation (Azar & Samuel, 2007; Bruckdorfer & Gleit, 1988; Bannister & Lawson, 1985).

Fig 2.5 represents the schematic of fluid loss.



**Figure 2-5 - Schematic of fluid loss in the wellbore (BakerHughes, 2010)**

Different factors affect the fluid loss of oil well cement such as density, gel strength development, formation permeability and pore pressure.

#### **2.3.4 Mechanical Properties**

One of the main objectives of cementing the wellbore is to provide support for casing. During and after the well drilling and completion processes, casing and the cement sheath are subjected to many pressures. The main processes that apply pressure on the hardened cement include drilling, perforation, stimulation, thermal cycling and production of the reservoir (Thiercelin, Dargaud, & Baret, 1998; Reddy, et al., 2005). If the pressure on the cement column exceeds its mechanical strength, there is a chance for developing microannuli and cracks which may permit formation fluids and gas inside the wellbore and lose the zonal isolating properties of cement. These phenomena could force well shutdown or result in high remedial expenses (Reddy, et al., 2005).

The conventional method for evaluating the mechanical properties of oil well cement is to measure the compressive strength of hardened samples. However, it has been shown that compressive strength is not the main parameter for investigating the mechanical resistance for cement (Myers, El Shaari, & Dillenbeck, 2005; McDaniel, Watters, & Shadravan, 2014). To assure efficient and long term isolation for the wellbore, other mechanical properties such as Young's modulus, Poisson's ratio, and flexural and tensile strength should also be taken into account. Several factors affect the mechanical properties of hardened oil well cement. These factors include the following (Azar & Samuel, 2007):

- Temperature: Increasing temperature accelerates the hydration of cement and results in higher compressive strength. Both bottom hole temperature and heat of hydration may affect the setting time of cement.
- Pressure: Increasing pressure may delay the setting time of cement and result in lower compressive strength. However, the effect of pressure is not as dominant as the effect of temperature.
- Water content: Increasing the water to cement ratio in slurry reduces the mechanical strength.
- Admixtures: Several additives can be added to cement to increase the bonding and rate of hydration in cement in order to increase the mechanical strength.

### **2.3.5 Thickening Time**

One the cement particles are exposed to water, the chemical reactions take place in slurry and hydration starts. In the hydration process, cement slurry transforms from liquid state to solid state. Thickening time is the duration that cement slurry stays in fluid state and is pumpable. Consistometer is usually utilized to investigate the thickening time of cement. Studying the thickening time is an important task in oil well cementing since cement must be flowable when pumped and excessive waiting time can cause a weak support and increase the wait on cement and risk of damage (Ramos, 1992). Temperature and pressure of the wellbore affect the thickening time as well as cement compositions. Retarder or accelerators can be added to cement to increase or decrease the thickening time, respectively (Shahriar, 2011).

### **2.3.6 Porosity and Permeability**

Porosity is determined as the fraction of pores or voids volume to total volume that can vary between 0 to 100%. In oil well cements, porosity affects the mechanical properties as well as the durability of cement sheath (Jenkins, 1966). In addition, high porosity may result in higher permeability and increase the risk of gas or fluid migration through the wellbore. Permeability is defined as the ability of material to allow gas or liquid to pass through it. Permeability is measured based on the flow rate of liquid or gas and is presented in  $\text{m}^2$  or Darcy unit. Different factors affect the porosity and permeability of oil well cement such as admixtures, water to cement ratio, temperature and pressure of curing and type of cement. (Shahriar, 2011). Assessing the porosity and permeability of oil well cement is critical to assure appropriate mechanical strength and zonal isolation for the wellbore.

### **2.3.7 Shrinkage and Expansion**

Shrinkage is defined as the reduction in the volume and is considered as a safety problem for oil well cement (Backe, et al., 1998). The gas migration takes place when the hydrostatic pressure of cement column starts to decline. Shrinkage increases the hydrostatic pressure drop and increases the chance of gas migration. In addition, shrinkage in hardened cement may develop microannuli and micro fractures which allow the gas and fluid to enter the wellbore from formation. Chemical shrinkage can be categorized as external shrinkage and total shrinkage. The external shrinkage is the change in the bulk volume of cement sheath causing microannuli between cement and formation.

The total shrinkage is the sum of chemical shrinkages and the contraction pores of cement (Backe, et al., 1998). Chemical shrinkage is directly related to the formation of Calcium Silicate as cement is exposed to water (Chenevert & Shrestha, 1991).

Expansion of oil well cement is significant to enhance the quality of cement sealing. It is important that expansion occurs after cement slurry is pumped in the annulus and formation of hardened cement structures starts.

Different factors affect the expansion and shrinkage of oil well cement, including wellbore temperature and pressure, water to cement ratio and cement additives. However, it has been shown that the water to cement ratio does not affect the shrinkage within the first 48 hours of curing of class G oil well cement (Justnes, et al., 1995). Some additives can be used in oil well cement to decrease the shrinkage. These additives are called extenders and reduce the risk of gas migration by expanding the cement slurry (Shahriar, 2011).

### **2.3.8 Electrical Properties**

Electrical resistivity is an intrinsic material property that defines the degree to which a material opposes the flow of electric current. Electrical resistivity is the reciprocal of the electrical conductivity and its SI unit is ohm.meter ( $\Omega \cdot m$ ). Ohm's law indicates that the ratio of voltage to electrical current in a material is equal to electrical resistance of the conductor. Electrical resistance can be calculated based on electrical resistivity, length and cross sectional area of the material (Lowrie, 2007) by using the equation:

$$R = \rho \frac{l}{A}, \quad (2-5)$$

in which R is resistance ( $\Omega$ ),  $\rho$  is electrical resistivity ( $\Omega \cdot m$ ), l is length of material (m), and A is the cross sectional area of the material ( $m^2$ ).

After cement is exposed to water, calcium (Ca) and hydroxyl (OH) ions get into solution. For a period of few tens of minutes, the concentration of  $Na^+$  and  $OH^-$  tends to increase to reach saturation. These two ions along with  $K^+$  and  $SO_4^{2-}$  contribute to decrease the resistivity of cement paste during the initial period of curing. While the structure of cement is building up and C-S-H is deposited in the pores, the porosity and availability of ions decrease which results in increment of electrical resistivity (Backe, Lile, & Lyomov, 2001; Topcu, Uygunoglu, & Hocaoglu, 2011). Cement slurry can be characterized based on the changes in electrical resistivity during the curing period. It can be used to find the initial and final setting, compressive strength, and rate of hydration and other characteristics of curing oil well cement (Backe, Lile, & Lyomov, 2001). In addition, electrical resistivity can be used as a sensing property to determine the contamination of cement with other materials in the wellbore (Zomorrodian & Vipulanandan, 2013).

Different factors can affect the electrical resistivity of oil well cement during curing such as water to cement ratio, admixtures, pressure and temperature of curing and moisture content. When curing cement slurry is contaminated with another material, the value and rate of change in electrical resistivity may be affected. This phenomenon happens due to the different electrical properties of

cement and the contaminating materials and also the alteration of cement hydration process caused by contamination.

### **2.3.9 Piezoresistivity**

The piezoresistive behavior is a change in electrical resistivity of a material when a mechanical strain is applied. Mechanical strain by changing the internal atomic spacing, changes the ability of electrons to flow through a piezoresistive material. Studies have been performed to evaluate the piezoresistive behavior of cement reinforced with fibers. These studies showed that fiber reinforced cement is capable of sensing its strain due to its piezoresistive behavior (Chung, 2002; Qizhao, Binyuan, Darong, & Zhuoqiu, 1996; Shi & Chung, 1999). Also it has been shown that in modified cementation materials the changes in electrical resistivity with applied stress is up to 50 times higher than the changes in mechanical strain (Vipulanandan & Garas, 2008). Hence, electrical resistivity in modified piezoresistive cement slurry can be used as an indicator to determine the applied stress on the cement sheath in the wellbore.

## **2.4 Admixtures of Oil Well Cement**

The characteristics of wellbores such as high temperature and pressure, permeability of formation can affect different properties of oil well cement. Hence, the oil well cement slurry must be designed to meet the desired properties such as thickening time, fluid loss, viscosity, free water and mechanical strength in wellbore conditions. In addition, oil well cement must have an appropriate initial

viscosity in order to be pumpable into the wellbore. The demanding requirements can be achieved by modifying water to cement ratio and the additives.

A variety of oil well cement additives are currently being used for oil and gas well cementing applications to provide appropriate placement of cement, zonal isolation for the wellbore and support for casing during the lifetime of the well.

In this section, a literature review of different oil well cement additives is presented. Some of the mentioned additives have multifunctional properties which means they can affect more than one property of oil well cement.

#### **2.4.1 Accelerators and Retarders**

Accelerator and retarder additives are used in oil well cement to increase or decrease the setting time of cement, respectively. Generally temperature increases the rate of hydration which results in early setting of cement. In shallow, low-temperature wells, accelerators are used in cement admixtures to increase the hydration rate and reduce the setting time of cement since too long setting times cause financial losses due to long weight on cement. In addition, too long setting time can cause segregation of particles or result in contamination of slurry.

One of the most common accelerators is calcium chloride ( $\text{CaCl}_2$ ). Other common accelerators are sodium chloride ( $\text{NaCl}$ ), sodium silicates, sodium metasilicate and silica fume (Heinold, Dillenbeck, & Rogers, 2002; Shahriar, 2011). The effectiveness of these additives depends on their concentration, curing temperature and pressure and their compatibility with other additives.

Unlike accelerators, retarders postpone the setting time of oil well cement. These additives are used in high temperature wells in order to slow the hydration, keep cement in pumpable state and prevent pre-mature setting. Too early setting time results in poor placement and may lead to improper zonal isolation and cement failure (Eoff & Doug, 1995). There is a large number of retarder additives for oil well cement such as lingosulfonates, hydroxyethylcellulose, hydroxycarboxylic acids, sugar, zinc oxide. Retarders mainly affect the hydration of cement by binding to calcium ions and preventing the development of ettringite crystals (Coveney & Humphries, 1996; Bermudez, 2007). In the past decade, nano-engineered cement admixtures have been studied and it has been shown that certain nano materials such as nanosilica can decrease the setting time of cement and increase the mechanical strength dramatically. It has been shown that nanosilica, by providing new nucleation sites for C-S-H, stimulates C-S-H development in the cement slurry and increase the rate of hydration and ultimate compressive strength (Thomas, Jennings, & Chen, 2009).

#### **2.4.2 Extenders**

Cement extenders are used to decrease the cement density and lower the hydrostatic pressure of cement column. Reducing the hydrostatic pressure is essential when the fracture pressure is low and there is a chance that cement causes fracture in the formation. Extenders exist in generally three different groups: water extender, low-density aggregate and gas. The most common extender is water but increasing the water to cement ratio results in lower mechanical properties of cement. Low-density aggregates are additives with

density lower than cement. One of the most common low-density additives used in cementing application is clay bentonite. It has lower density compared to cement and can be used to obtain a cement slurry with density of 10-12 ppg. Lower densities of cement can be achieved by using compressed gas. Cement integrated with gas is called foamed cement and may yield density as low as 4-7 ppg (Azar & Samuel, 2007; Samsuri, Junin, & Osman, 2001).

#### **2.4.3 Weighting Agents**

Weighting agents are used to increase the density of oil well cement to control the pressure in the wellbore during the pumping of cement. These additives have higher specific gravity compared to cement, and can be utilized to increase the density of cement to up to 25 ppg. Common weighting materials include hematite ( $\text{Fe}_2\text{O}_3$ ), hausmannite ( $\text{Mn}_3\text{O}_4$ ), iron ore and barite ( $\text{BaSO}_4$ ). The other method to create high density water is to use dispersants which allow less water to be used in cement while still pumpable (Azar & Samuel, 2007; Caritey & Brady, 2013).

#### **2.4.4 Dispersants**

Dispersants which are also known as thinners are used to control the viscosity and pumpability of cement slurry (Boughton, Pavlich, & Wahl, 1962). Most common dispersants are sulfonates such as polynaphthalene sulfonates and lingosulfonate. Generally by adding dispersants, the yield point and viscosity of cement reduces. Hence, lower water to cement ratio can be used in slurry. In addition, some additives such as bentonite increase the viscosity by absorbing

the pore water in cement slurry. In that case dispersants can be used to modify the negative effects of other additives on viscosity (Shahriar, 2011). Some dispersants such as lingsulfonate have retarding effect on cement and increase the setting. Hence when used in low temperature wells, they should be integrated with accelerators to provide appropriate setting time for cement.

Polycarboxylate is used in concrete industry as a superplasticizer to reduce the amount of water while maintaining slurry's flowability. The low water to cement ratio results in higher ultimate compressive strength of hardened cement (Heikal, Morsy, & Aiad, 2005).

#### **2.4.5 Fluid Loss Agents**

Fluid loss additives are used in oil well cement to prevent the pore water of cement to enter the permeable zones in the wellbore. They are known as a key additive for efficient cementing operations and can prevent altering the mechanical properties and excessive density of cement or annulus bridging caused by fluid loss. Fluid loss additives reduce water loss from slurry in three different means. First types of fluid loss additives absorb onto cement particles and reduce filter cake pores and its permeability which results in lower fluid loss. Second type of fluid loss additives plugs the pores in the filter cake through creating micelles or a polymer film. This results in forming a filter cake with lower permeability which prevents fluid loss in the wellbore. Third type of fluid loss additives binds the water molecules. This way a large amount of water is bound can cannot be released into the porous formation.

Fluid loss additives have become increasingly developed over time. First type of fluid loss additives was bentonite which plugs and reduces the permeability of filter cake (Nelson, 1990). Bentonite reduces the fluid loss but increases the viscosity of cement. In the late 1950's, cellulose based polymer started to be used commonly as fluid loss additives. The limitations of cellulose based fluid loss agents are based on their composition. For instance, usage of HEC based additives is generally limited by temperature and also they may lose efficiency in presence of sodium chloride. Carboxymethylhydroxyethylcellulose (CMHEC) on the other hand, is salt toralable and can be used in high temperatures but have extreme retarding properties (Mueller, 1992). Other types of additives such as polyvinyl alcohol (PVA) have appropriate fluid loss control in oil well cement. PVA reduces the permeability of filter cake by forming a polymer film in the filter cake (Plank, Lummer, Dugonjic-Bilic, & Sadasivan, 2009). By the advancement of nano technology, nano materials have been utilized in oil well cement to improve different properties. For instance, it has been shown that adding nanosilica reduces the fluid loss of oil well cement (Patil & Deshpande, 2012).

#### **2.4.6 Lost-Circulation Control Agents**

Lost circulation is the partial or complete loss of cement slurry into the formation. It occurs in fractured, vuggy or unconsolidated zones. Lost circulation can be prevented by adding bridging or plugging materials know as lost circulation agents. Granular materials such as coarse bentonite, gilsonite and

granular coal are among bridging agents. They can seal the fracture and stop cement from entering the formation (Michaux, Nelson, & Vidick, 1989).

#### **2.4.7 Specialty Additives**

In addition to conventional additives, specialty additives are implemented in oil well cementing in order to enhance different properties. For instance, carbon fiber can be used to increase the piezoresistivity of oil well cement and allow monitoring the pressures in the wellbore by measuring electrical resistivity (Vipulanandan & Garas, 2008; Vipulanandan, et al., 2014). Other types of additives can be used to modify special properties of the cement such as bonding to formation and casing and gas migration.

### **2.5 Summary**

Main objectives of cementing the oil well are to provide zonal isolation for the wellbore and support for the casing. Two basic criteria should be met when designing oil well cement. First it should have appropriate rheological properties to be easily pumpable to certain depths. Second, the cement sheath must provide low permeability, sufficient mechanical strength and adequate bonding with casing and formation throughout the life of the well. Due to the extreme conditions in the wellbore, designing oil well cement is generally much less tolerant compared to conventional cement. The high temperature and pressure in addition to different formation characterizations should be taken into account when designing oil well cement. Different properties are taken into consideration when designing cement slurry such as density, fluid loss, rheology, mechanical

strength, setting and thickening time, porosity and permeability, shrinkage and expansion.

Neat oil well cements are commonly limited by different factors. In order to modify cement slurry to achieve required properties in certain conditions additives can be used. Oil well cement additives impact different properties of oil well cement by affecting hydration process, molecular interactions in slurry, absorbing and binding water, provide acid attack resistance, plugging pores and reducing permeability, preventing gas migration and increasing the bonding between formation and casing with cement.

The efficiency of additives can be affected by different factors such as water to cement ratio, curing temperature and pressure and formation geology. In addition, some additives have multifunctional properties meaning that they affect more than one property in cement slurry. When designing cement slurry, enough attention must be paid to the integrated effects of additives and their compatibility.

## **CHAPTER 3**

### **MATERIALS AND METHODS**

This chapter describes the materials and laboratory experiments used in this study. Cement type, additives and admixtures and testing procedures for evaluating different properties of liquid and hardened cement slurry are discussed.

#### **3.1 Types of Oil Well Cement and Drilling Fluid**

Class H oil well cement was used in this study. The API suggested water to cement ratios ranging from 30% to 100% were used in samples. In studies which effect of certain additives or contamination was investigated, a control neat cement sample was used for evaluation.

Synthetic based drilling fluid was used in this study to evaluate its contamination effects on oil well cement. Vegetable oil based ester was used to prepare the drilling fluid sample with ester to water ratio of 3:2 and 1% chemical surfactant. Chemical surfactant was used in order to allow mixture of water and vegetable oil.

##### **3.1.1 Modifying Oil Well Cement**

In order to increase the sensing properties of oil well cement slurry, in cases that will be discussed later, 0.1% carbon fiber BWOC (by weight of cement) was used during the mixture of cement. The carbon fiber was prepared based on a certain procedure that assures the efficiency of 0.1% of it in improving sensing property.

### 3.2 Oil Well Cement Additives

This section describes the additives used and evaluated in this study. The order of mixing for each additive is presented further in this thesis.

**Polycarboxylate:** Polycarboxylate superplasticizer is liquid with a carboxylate group with  $\text{COO}^-$  which dissolves in water.

**Nanoclay:** Nanoclay is a white powder with particles of nanoscale dimensions.

**Bentonite:** Bentonite is a form of clay mainly consists of montmorillonite minerals and is used as extender agent in oil well cement.

**Acrylamide polymer gel components:** The polymer gel components include acrylamide polymer grout (AV-100), triethanolamine (AV-101) as activator and ammonium persulfate as catalyst (AV-102)

**Salt:** Sodium chloride (NaCl) or table salt is a colorless crystalline compound which occurs naturally in seawater and halite.

### 3.3 Curing and Monitoring Cement Slurry

For tests on hardened oil well cement and monitoring the curing process, slurries were placed in cylindrical molds with a diameter of 2 inches and a height of 4 inches. Two wires were placed in the molds vertically at a distance of 2 inches in order to measure the electrical resistance during curing.

Electrical resistance was measured using a LCR meter during the curing time. In order to minimize the contact resistance between the wires and the cement slurry, measurements were performed at 300 kHz.

For some tests, effect of condition of curing was evaluated. Two different conditions were taken into account: dynamic and static. For dynamic condition,

the slurry was placed in a mixer and a low RPM (150) was applied on the slurry for 3 hours. For static conditioning, the same slurry was placed in a mold for the same period of time. The difference between the rheology of the same sample cured in different condition was evaluated.

### 3.4 Electrical Properties

Electrical resistivity of the curing samples was measured using an API standard resistivity meter as shown in Fig 3.1. In order to measure the resistivity of hardened samples, the electrical resistance was measured during curing and was then converted to electrical resistivity by using equation 3.1:

$$R = \rho \frac{l}{A} = \rho k , \quad (3-1)$$

where  $\rho$  is the electrical resistivity (Ohm.meter), R is electrical resistance (Ohm), l is the length between the wires and A is the cross sectional area between the wires.

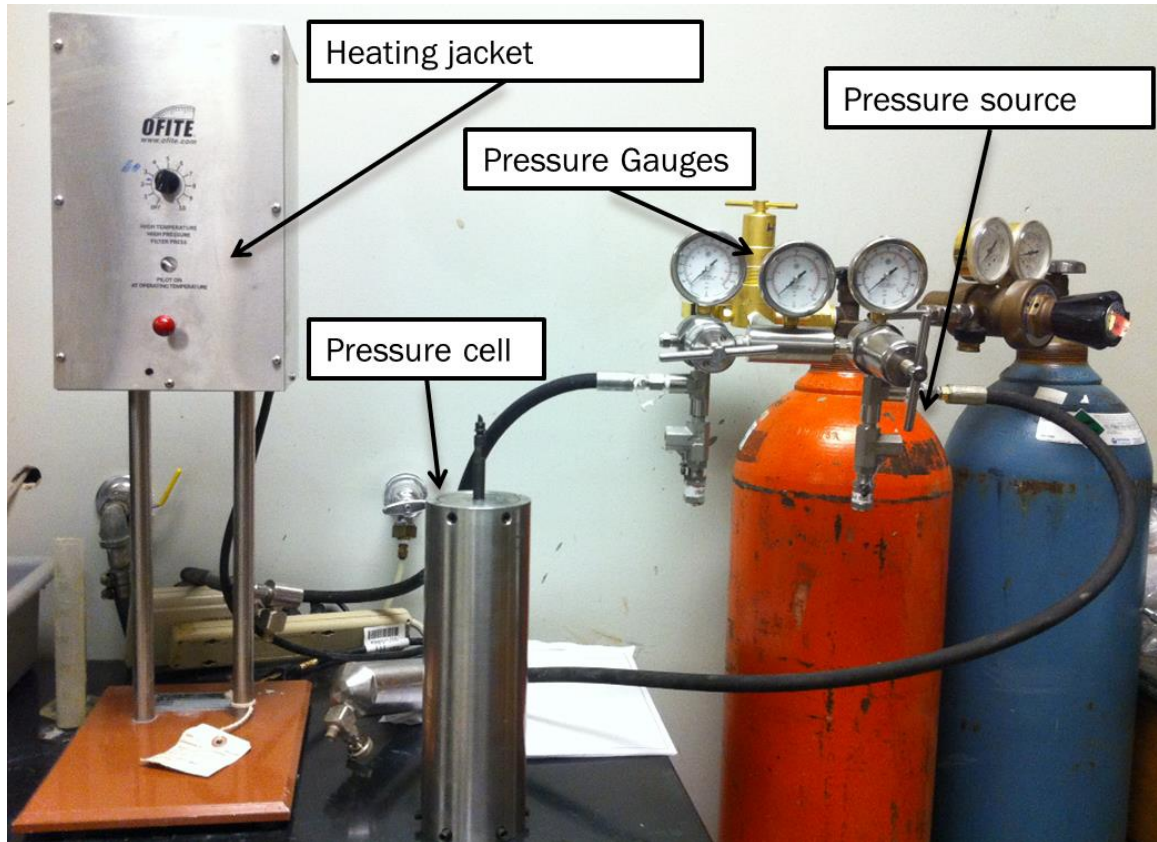
The distance and length of embedded wires may vary in different tests. In order to eliminate the possible caused errors on comparing different samples, the changes in electrical resistance was calculated in respect to initial resistance and the factor k was eliminated. Assuming same cross sectional area and distance between the wires during curing, the normalized change in electrical resistivity can be presented as:

$$\frac{R_n - R_0}{R_0} = \frac{\rho_n k - \rho_0 k}{\rho_0 k} = \frac{\Delta \rho}{\rho_0} , \quad (3-2)$$

in addition, the changes in electrical resistance at each time interval in respect to initial resistance were calculated.

### 3.5 Fluid Loss Test

Fluid loss tests were performed by using a HPHP filter press system. It consists of a HPHT pressure cell, heating jacket, pressure gauges and a pressure source as shown in Fig 3.1.



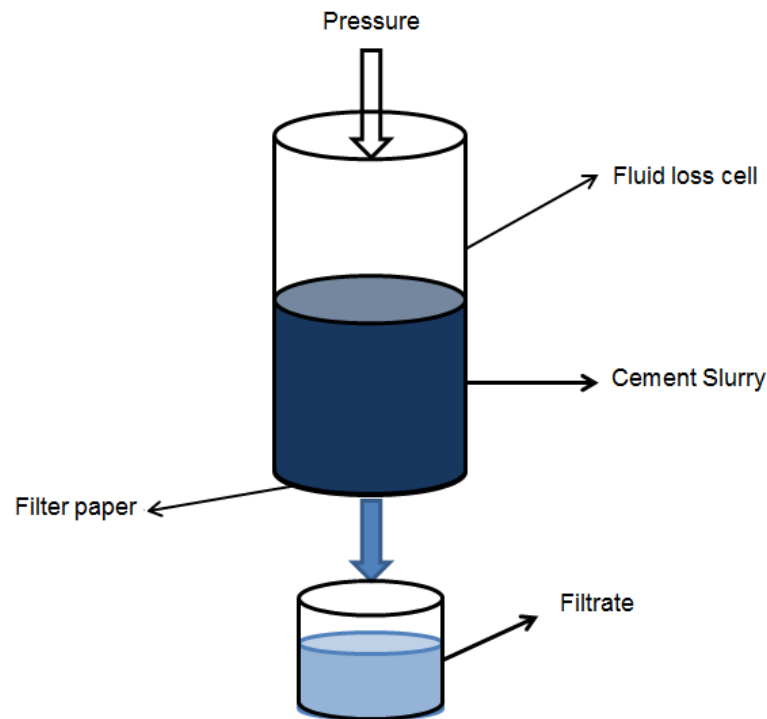
**Figure 3-1 - HPHT filter press components**

A filter paper that represents the permeable zones was placed at the bottom and top of the cell. Sample was poured in the cell and cell was placed in the hearing jacket. Pressure gauges were connected to the top and bottom of the cell. Desired pressure was defined by using the pressure gauges. After achieving the pressure, the screws on top and bottom of the cell were loosen by one fourth of a round. That would apply the pressure on the sample which results in water loss of the sample. The filtrate water was collected from the bottom of the sample

and the measurements were done every minute. This continued for 30 minutes unless blow out occurred in which case the test was stopped and the filtrate liquid was measured. Blow out occurs when applied gas passes through the sample and can be determined by increase in the back pressure (pressure at the bottom of the sample). Filter cake was removed after the test and its dimensions and weight was measured. A schematic of the filter press mechanism is shown in Fig 3.2. API fluid loss was calculated using:

$$FL = 2 \times Volume_{filtrate} \times \sqrt{\frac{30}{BlowOutTime(min)}}, \quad (3-3)$$

which takes into account the blowout time and filtrate volume to extrapolate the fluid loss at 30 minutes.



**Figure 3-2 - Schematic of fluid loss test**

### 3.6 Permeability Tests

Permeability tests were performed for filter cakes and hardened cement slurries by using filter press device. Sample was placed in the cell and a certain amount of water (100 mL) was poured on top of the filter cake. Fluid loss cell was closed and 100 psi pressure was applied on top of the sample. In case of hardened cement, acrylamide polymer gel was poured around the sample to ensure no water leakage between cement and the cell. The permeability was then calculated by using the equation:

$$k = \frac{Q \times \mu \times L}{P \times A}, \quad (3-4)$$

where K is the permeability (m<sup>2</sup>), Q is the flow rate (m<sup>3</sup>/sec),  $\mu$  is the viscosity of water (Pa.s), L: is the length of the filter cake (m), P is the applied pressure (N/m<sup>2</sup>), and A is the surface area of filter cake (m<sup>2</sup>). The calculated permeability results were then converted to mDarcy.

### 3.7 Gas Migration Evaluation

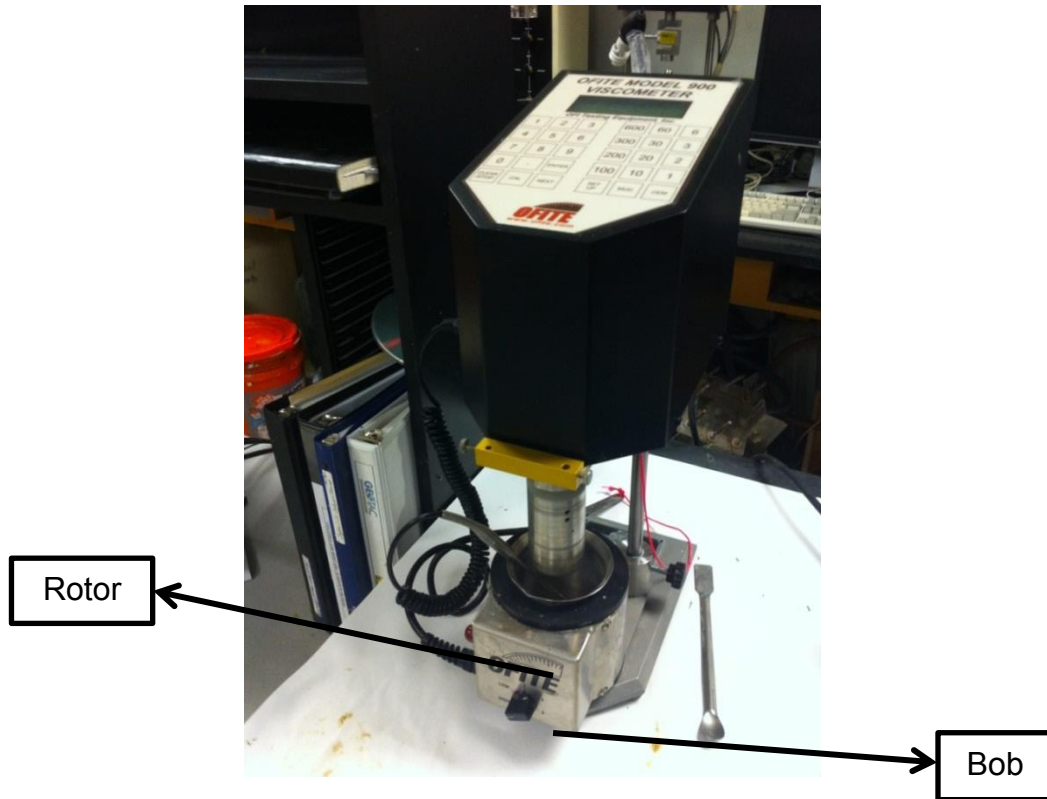
Ability of filter cake to prevent gas migration was evaluated by modifying fluid loss cell. Filter cake was placed in the cell and pressure gauges were attached to the cell. A storage tank was attached to the bottom of the cell. The storage tank was filled with 3 liter of water. Gas pressure was applied at the top of the sample and the back pressure (pressure at the bottom) was measured using pressure gauge. The outgoing gas entered the attached tank, applied pressure on the water in the tank and emptied it out. The time it was taken for the water tank to empty was used to calculate the flow rate of the gas. The gas permeability was then calculated based on the flow rate, viscosity of gas, length

of the filter cake, applied pressure, and the surface area of the filter cake. The flow rate of the gas through the sample defines the ability of filter cake to prevent gas migration in the wellbore during the initial stages of curing. Gas migration tests were done at 50 psi in room temperature.

### **3.8 Rheological Measurements**

Rheological measurements were performed by using a standard viscometer (OFITE model 900). The device is presented in Fig 3.3. This device consists of a rotor and a bob. The rotor applies shear rates inside the slurry. The bob is placed within few millimeters inside the rotor and is connected to a spring measures the related shear stress.

Slurry was poured in the cup and lifted up. Shear strain rates were defined on the device and the shear stress associated with each shear rate was measured. For lower shear strain rates, the time of measurement was higher in order to enhance the accuracy of measurements. Shear rates studied varied from 0.2 to 1020  $\text{sec}^{-1}$ . For gel strength measurements, slurry was kept in static condition in the cup for desired time (10 seconds, 1 minute or 10 minutes), and then a low shear strain rate was applied after conditioning and the shear stress was measured. The yield shear stress was calculated based on the viscosity and shear rates at higher shear strain rates.



**Figure 3-3 - Standard viscometer used in this study**

### **3.9 Mechanical Properties and Piezoresistivity**

Compressive strength and tensile strength of samples were investigated in this study by using GEOTAC Sigma-1 load tests system. This device has maximum load limit of 5000 pounds, hence for samples cured more than 24 hours a hydraulic compression machine with higher loading limit was used. In order to investigate the piezoresistivity of hardened cement, electrical resistance was measured during loading the samples and the changes in resistance with respect to initial resistance was calculated at various pressures. Changes in electrical resistance were then converted to electrical resistivity changes and the piezoresistivity of samples was investigated.

Indirect tensile tests were performed on hardened cement slurries in this study. Cement samples were fixed horizontally between two wood strips to

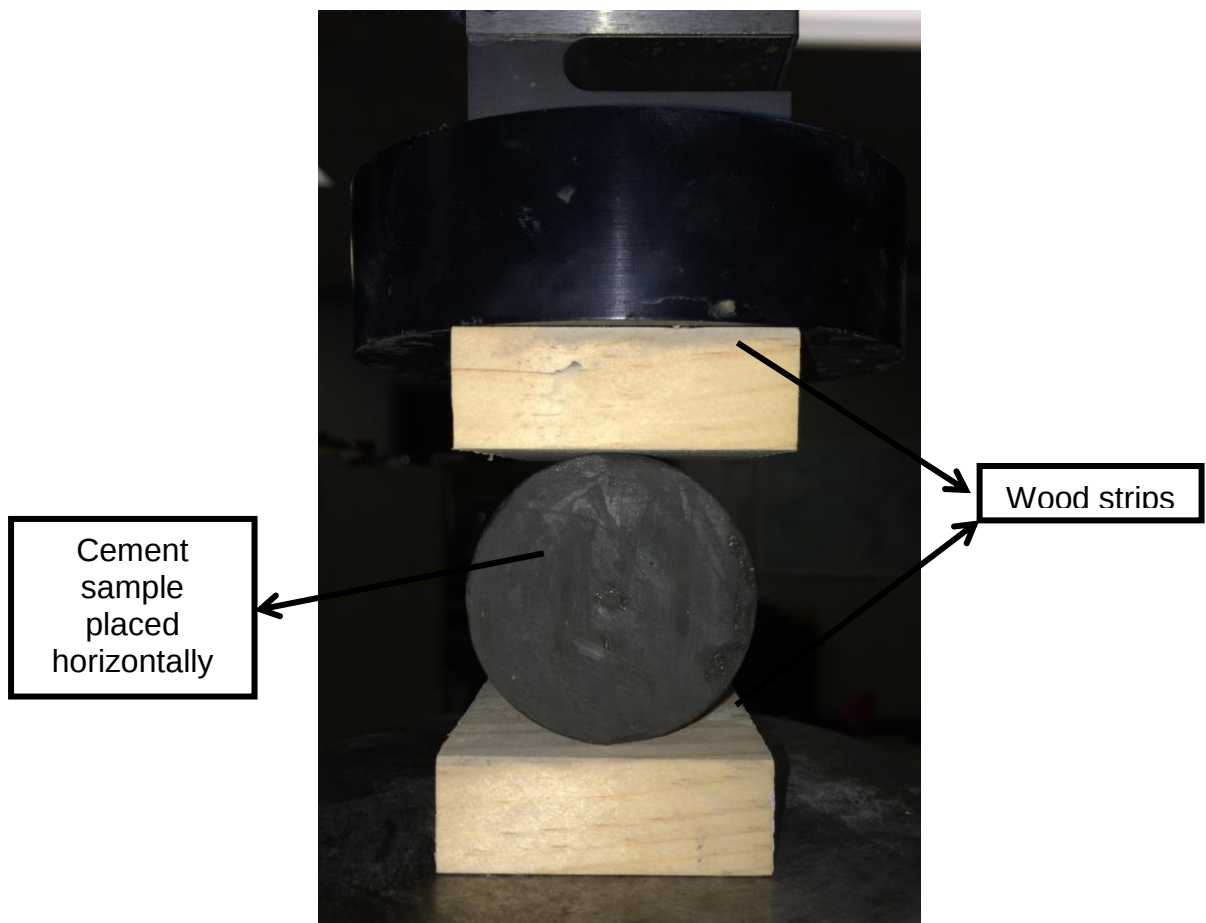
ensure evenly distributed force as shown in Fig 3.4. Compressive load was then applied and increased until samples cracked and increase in load was observed.

The tensile strength was then calculated using equation 3.4:

$$S_T = \frac{2F}{\pi hd}, \quad (3-5)$$

where  $S_T$  is tensile strength (psi),  $F$  is applied force at the time of failure (pound),

$H$  is the length of specimen loaded(in), and  $d$  is the diameter of specimen (in).



**Figure 3-4 - A hardened cement sample under indirect tensile test**

### **3.10 Summary**

This chapter described the methods and materials used in this study for investigating the properties of oil well cement:

1. Class H cement with water to cement ratio ranging from 30% to 100% was used. The cement was modified by 0.1% carbon fiber (BWOC).
2. Synthetic based vegetable oil was used to mix synthetic based mud.
3. Unconventional additives included polycarboxylate and nanoclay.
4. Salt, bentonite, and SBM was used in contamination studies.
5. The components of acrylamide polymer were used for developing self-healing oil well cement.
6. Electrical properties of cement were measured using a multimeter.
7. Filter press device was used to measure the fluid loss, and permeability.
8. Darcy law was used to calculate the water and gas permeability.
9. Rheological properties were investigated using a standard rheometer at room pressure.
10. The mechanical properties after 24 hours of curing were measured using GEOTAC Sigma-1 load. For longer curing times, a hydraulic compression machine with higher load limit was used.

## **CHAPTER 4**

### **BEHAVIOR OF SMART OIL WELL CEMENT**

The effect of three different additives on properties of oil well cement was investigated. The two additives included polycarboxylate and nanoclay. Also the effects of water to cement ratio on the rheology of oil well cement was evaluated. The results and discussions are presented in this chapter.

#### **4.1 Sample Preparation**

For evaluating the effects of polycarboxylate, the additive was added and mixed with the water until dissolved. Then cement was added to the mixture at a low speed. After cement was added, the slurry was mixed at a high speed. For nanoclay test, the additive was mixed with cement before adding the cement in to the water. Water-to-cement ratio for nanoclay study was 38%. For polycarboxylate water-to-cement ratios of 30%, 33%, and 38% were used. The amounts of additives used with respect to the weight cement were as follow:

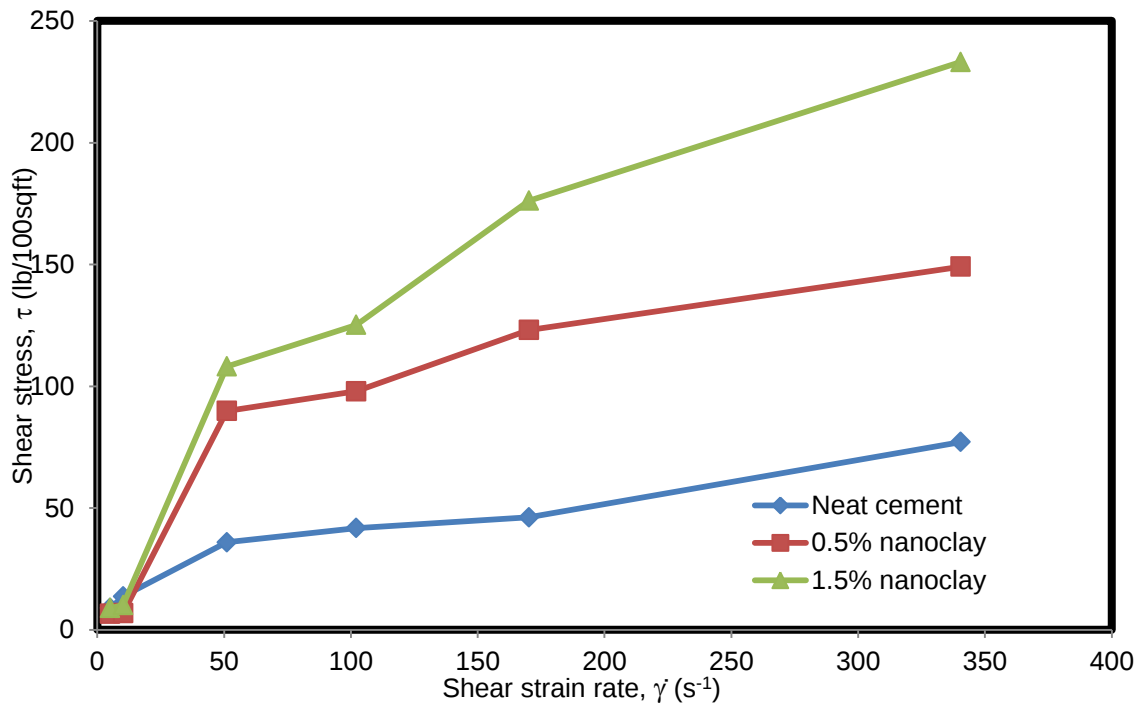
- Nanoclay: 0.5% and 1.5% by weight of cement (BWOC)
- Polycarboxylate: 0.3% and 0.6% by weight of cement (BWOC)

In a series of tests, the effects of water to cement ratio as well as curing conditions on the rheological properties of oil well cement were evaluated 5 minutes after mixing. For these tests, cement was mixed with water at water to cement ratios of 100%, 66%, 50%, 38% and 33%.

## 4.2 RESULTS

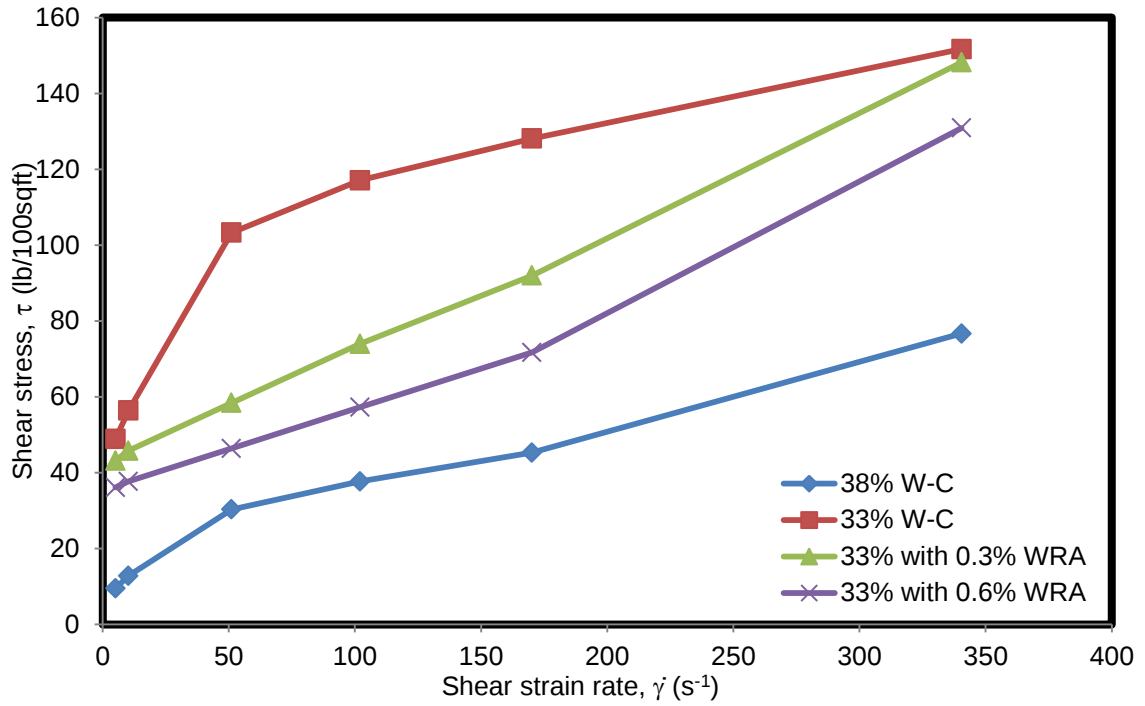
### 4.2.1 Rheological Properties

The effects of nanoclay on rheological properties of the oil well cement are shown in Fig 4.1. The addition of nanoclay increased the shear stress at both low and high shear strain rates.

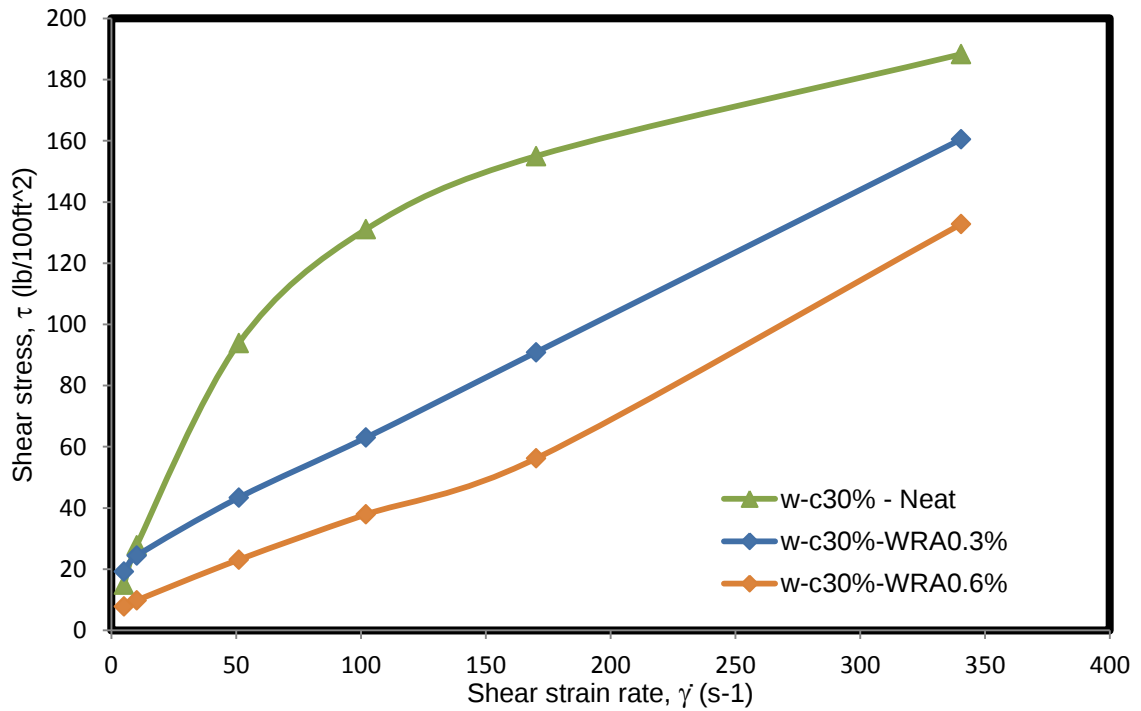


**Figure 4-1 - Effect of nanoclay on the rheology of oil well cement**

The effect of polycarboxylate on rheology of 30% and 33% oil well cement slurry is presented in Figs 4.2 and 4.3, respectively. It is observed that the addition of polycarboxylate reduces the rheology of cement slurry notably regardless of water to cement ratio. For this reason, this additive can be used to increase the pumpability of cement slurries with low water to cement ratio.

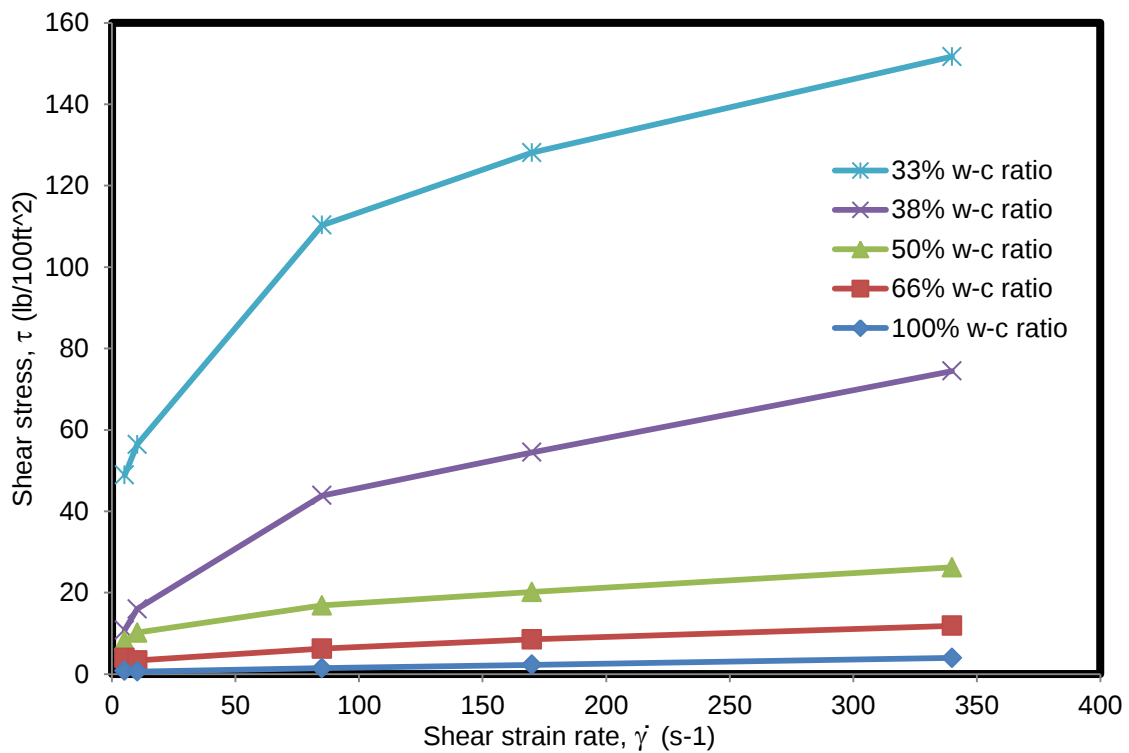


**Figure 4-2 - Effect of polycarboxylate on the rheology of 33% cement slurry**



**Figure 4-3 - Effect of polycarboxylate on the rheology of 30% cement slurry**

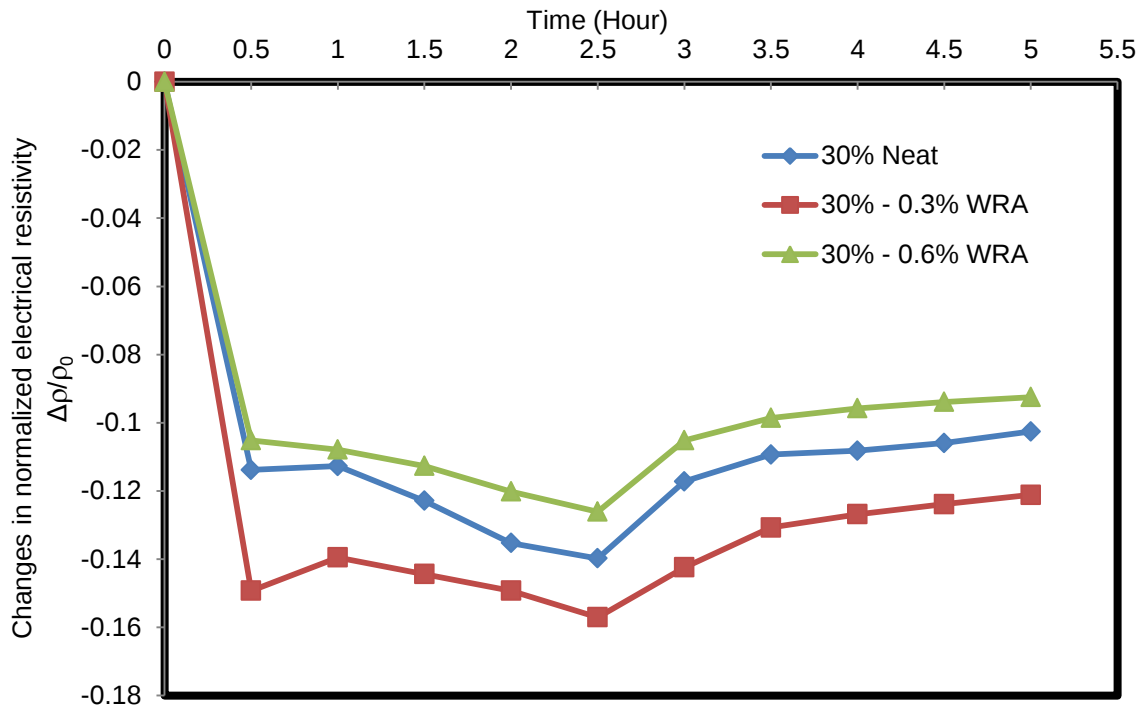
Fig 4.4 represents the effect of water to cement ratio on rheology of oil well cement. It was found that the shear stress decreased at all shear strain rates by increasing the water to cement ratio. This impact was more significant at higher shear strain rates. Shear stress decreased by 97% and 98% at shear strain rate of  $340 \text{ s}^{-1}$  and  $170 \text{ s}^{-1}$ , respectively, by increasing the water to cement ratio from 33% to 100%. The effect of polycarboxylate on rheology of cement indicates that this additive can be used to enhance rheology when cement slurries with lower water to cement ratios are used. In addition, nanoclay due to its increasing impact on rheology should be used with higher water to cement ratio.



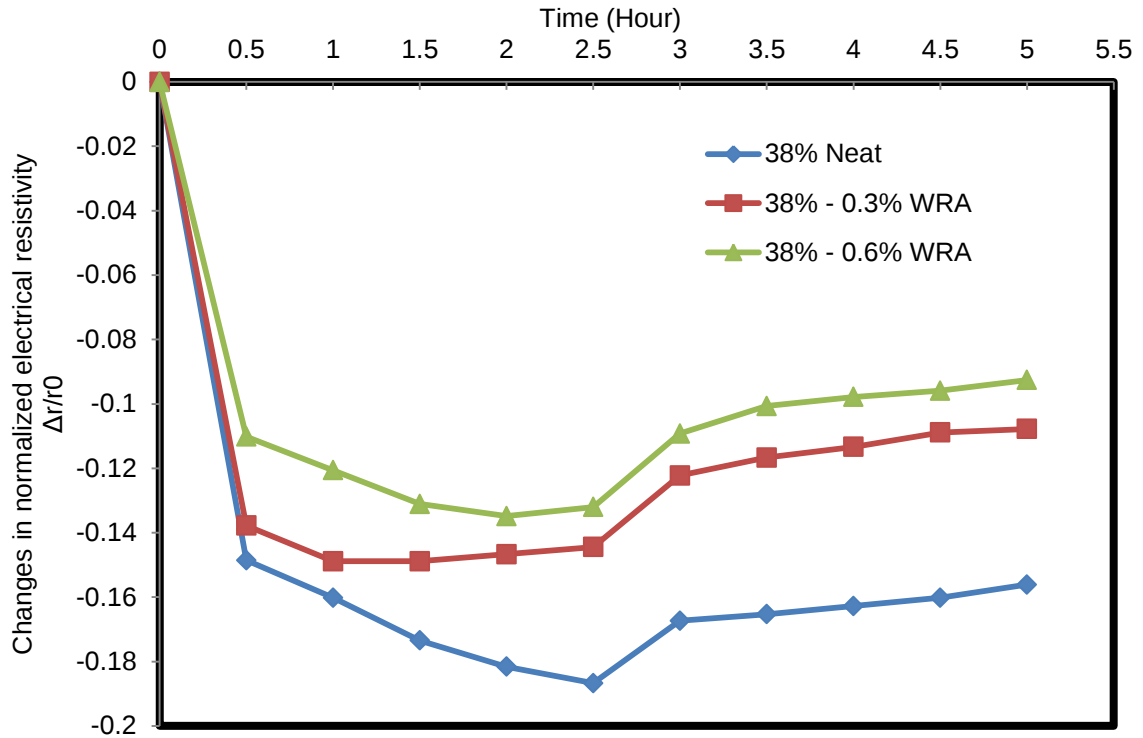
**Figure 4-4 - Effect of water to cement ratio on the rheology of oil well cement**

#### 4.2.2 Electrical Properties during Curing

The changes in normalized electrical resistivity of short term curing cement slurries containing polycarboxylate with water to cement ratio of 30% and 38% is presented in Fig 4.5 and 4.6. It is shown that electrical resistivity decreased up to first 2.5 hours of curing. The reason behind this is the release of cement particle ions into the pore water which increases the ability of water to flow electrons. The two major ions that contribute to decreasing the electrical resistivity of slurry in the initial curing time are  $\text{Na}^+$  and  $\text{OH}^-$ .

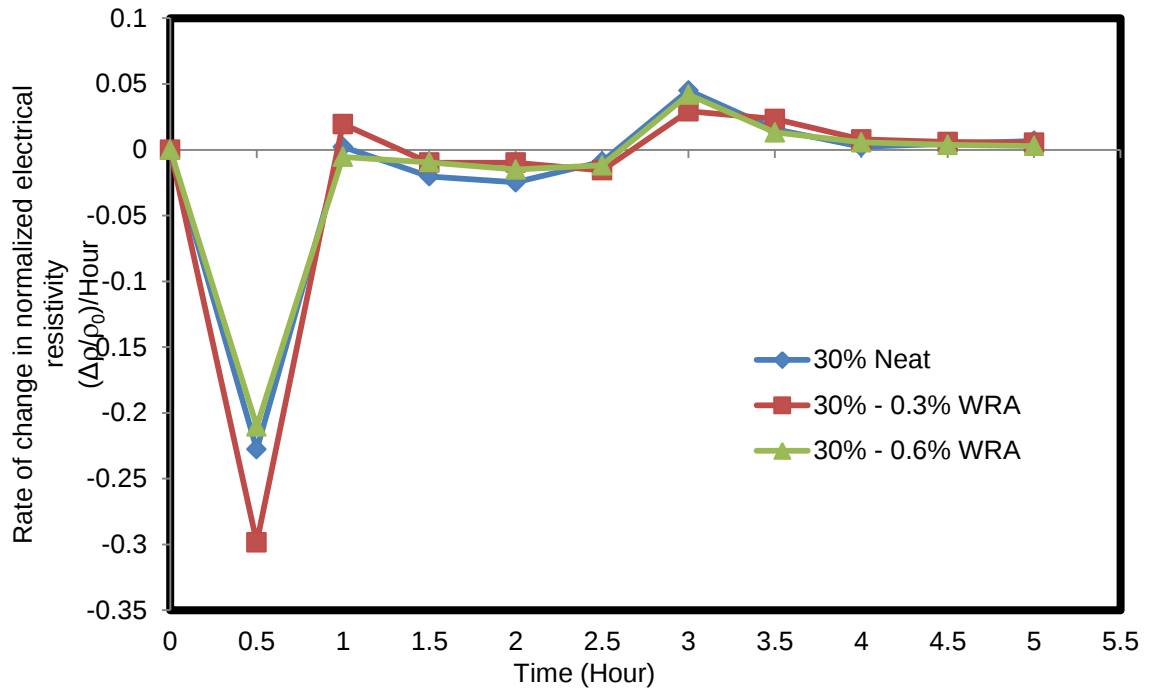


**Figure 4-5 - Changes in normalized electrical resistivity in respect to initial resistivity during first 5 hours of curing, in 30% cement slurries**

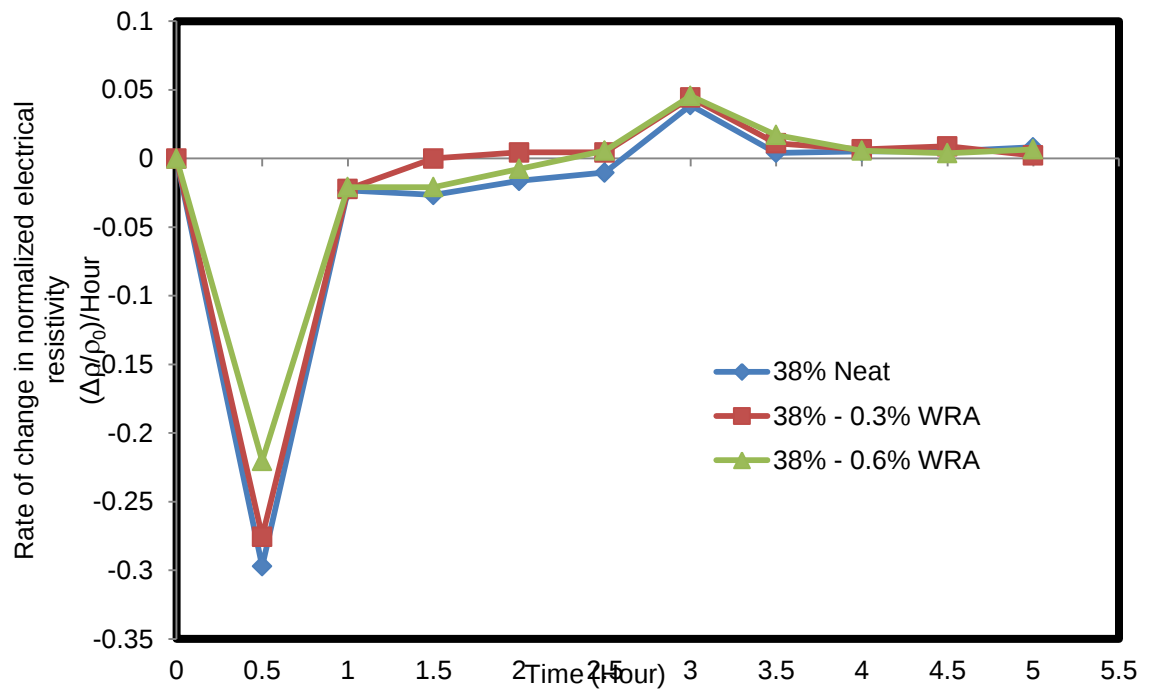


**Figure 4-6 - Changes in normalized electrical resistivity in respect to initial resistivity during first 5 hours of curing, in 38% cement slurries**

The rate of change in normalized electrical resistivity is shown in Figs 4.6 and 4.7 for samples with 30% and 38% water to cement ratio, respectively. It is observed that during the first 5 hours of curing, the changes in resistivity occur at the highest rate during the first 30 minutes after mixing. The initial change in electrical resistivity is due to the release of ions in the water. The high rate of change in electrical resistivity during the first 30 minutes of curing indicates that at this time the rate at which the ions are released in water is at its highest. Also the highest positive rate of change in resistivity happens after 2.5 hours of curing. The positive rate of change is due to the chemical reactions in the water-cement mixture which uses the ions and reduces the conductivity of the slurry.

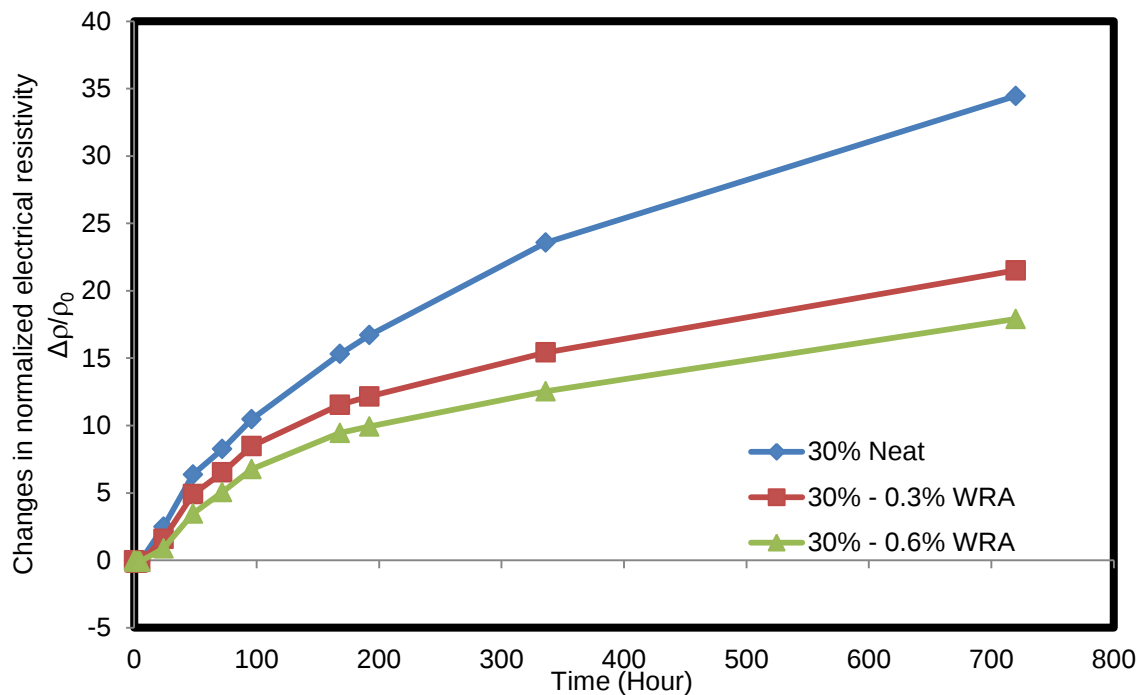


**Figure 4-7 – Rate of changes in normalized electrical resistivity during first 5 hours of curing for water to cement ratio of 30%**

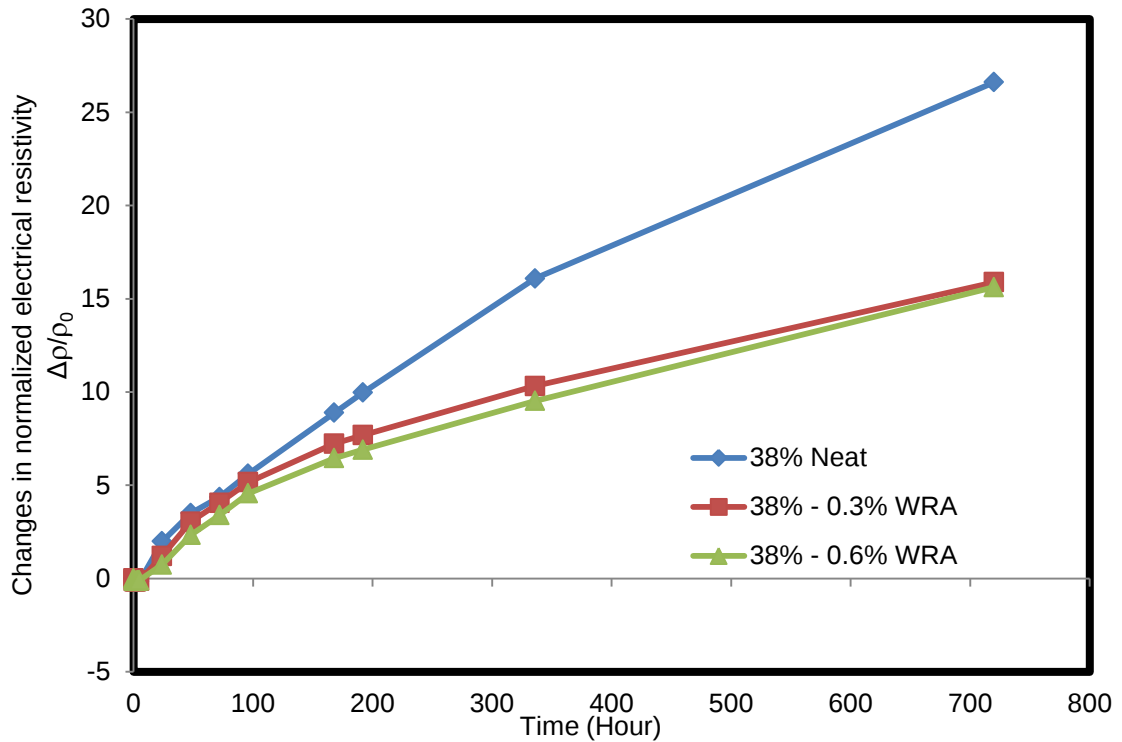


**Figure 4-8 – Rate of changes in normalized electrical resistivity during first 5 hours of curing for water to cement ratio of 38%**

The changes in normalized electrical resistivity during 30 days of curing for samples containing polycarboxylate with water to cement ratio of 30% and 38% are represented in Figs 4.8 and 4.9, respectively. It is observed that for both series of samples, the highest change in electrical resistivity occurred in samples with no polycarboxylate. Also the highest change in samples with water to cement ratio of 30% is 23% higher than 38% w-c ratio samples. Adding polycarboxylate decreased the maximum change in electrical resistivity by up to 48% which indicates its reducing effect on the chemical reactions between the ions.

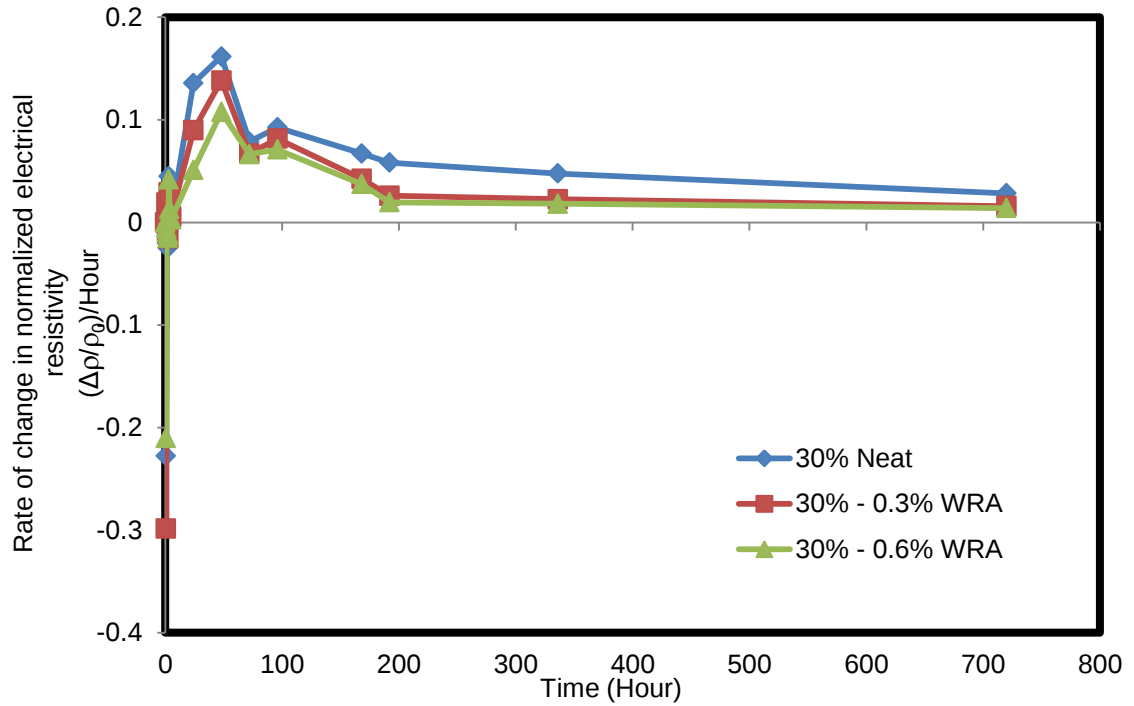


**Figure 4-9 - Changes in normalized electrical resistivity during 30 days of curing for samples containing polycarboxylate with water to cement ratio of 30%**

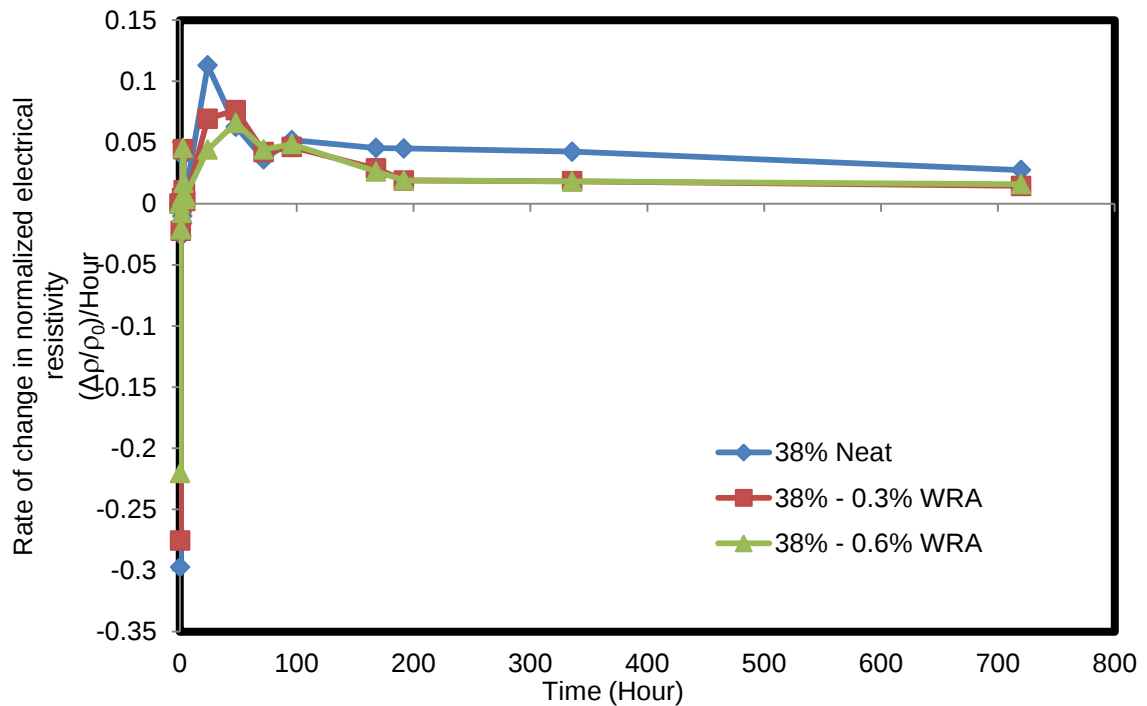


**Figure 4-10 - Changes in normalized electrical resistivity during 30 days of curing for samples containing polycarboxylate with water to cement ratio of 38%**

The rate of changes in normalized resistivity at various time intervals for 30% and 38% w-c ratio samples is presented in Figs 4.10 and 4.11. The maximum rate was  $0.16$  and  $0.11 \text{ hour}^{-1}$  for 30% and 38% w-c ratio specimens, respectively. In both series, neat cement samples showed higher rate of change in all time intervals. For neat 38% cement sample the maximum rate happened between 5 to 24 hours of curing while for all other specimens the maximum occurred between 24 to 48 hours after mixing.



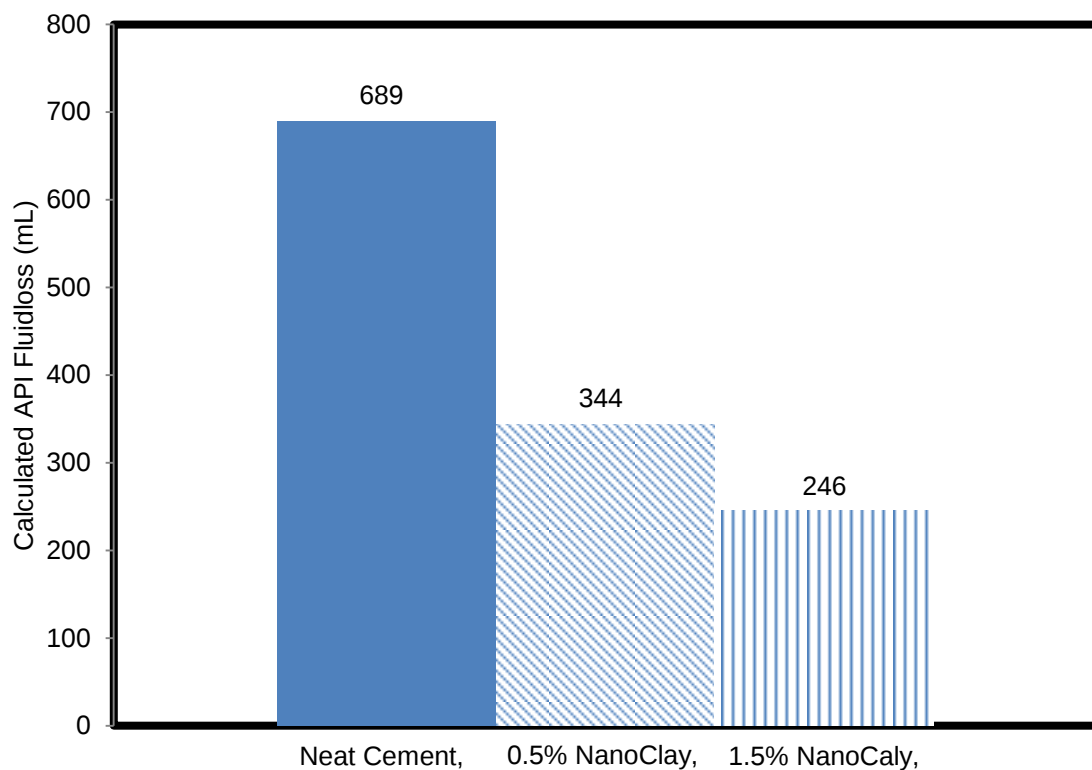
**Figure 4-11 - Rate of change in normalized resistivity for 30% w-c ratio samples containing polycarboxylate**



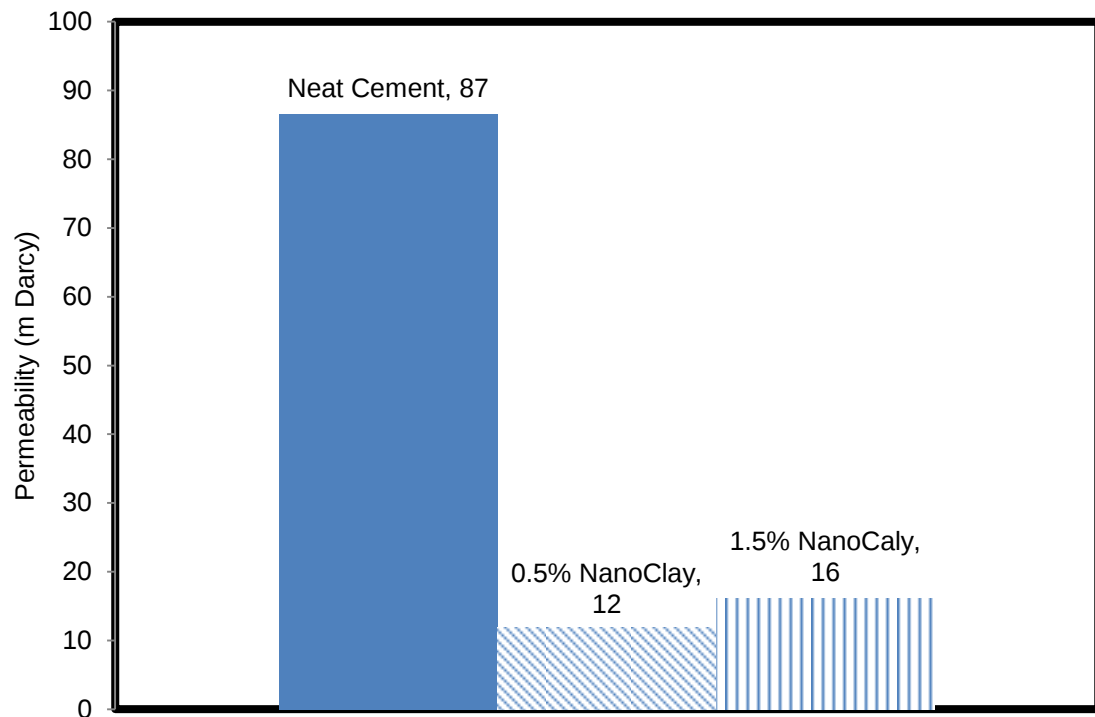
**Figure 4-12 - Rate of change in normalized resistivity for 38% w-c ratio samples containing polycarboxylate**

### 4.2.3 Fluid Loss and Filter Cake Permeability

Fig 4-13 represents the calculated API fluid loss of 38% w-c ratio cement samples containing nanoclay, and the filter cake permeability is shown in Fig 4.14. It was observed that by increasing the amount of nanoclay, the fluid loss decreased by up to 64%. Also adding nanoclay to slurry decreased the filter cake permeability by up to 86%. The lower permeability of filter cake for samples containing nanoclay is the main reason for lower fluid loss. Filter cake with lower permeability reduces the rate at which water is filtrated from the cement slurry and reduces the final fluid loss.

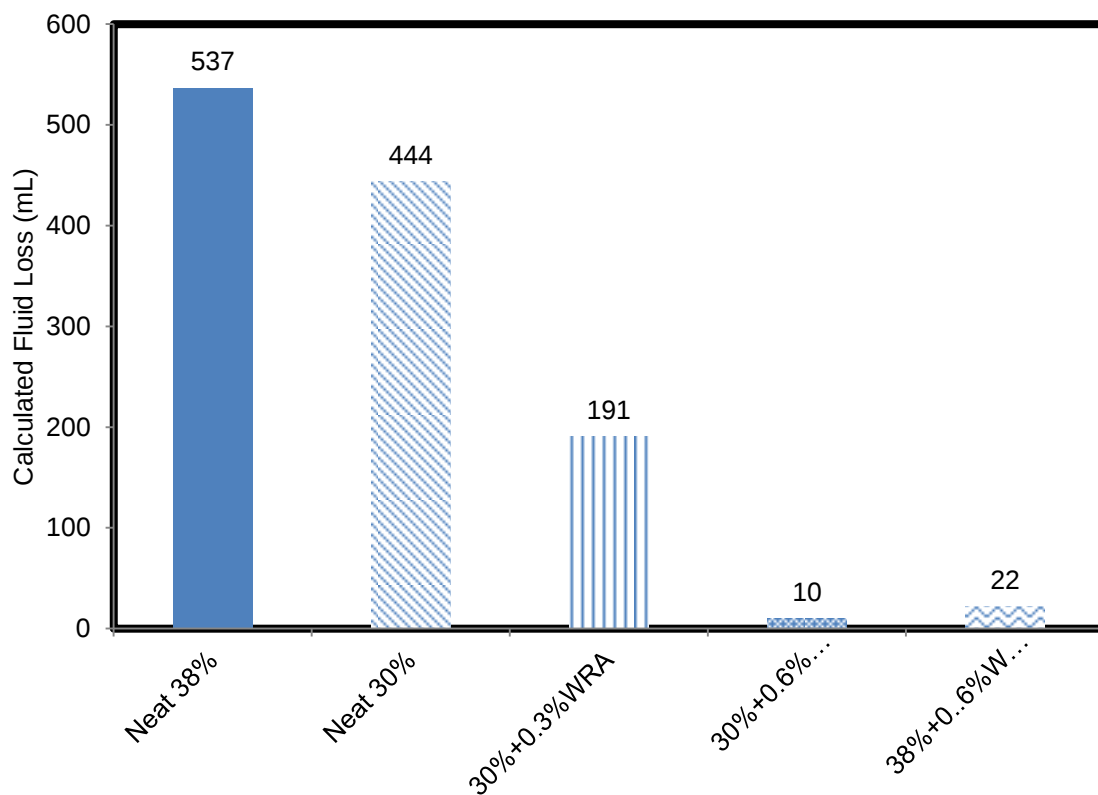


**Figure 4-13 - Calculated API fluid loss of 38% cement samples containing nanoclay at 100 psi**

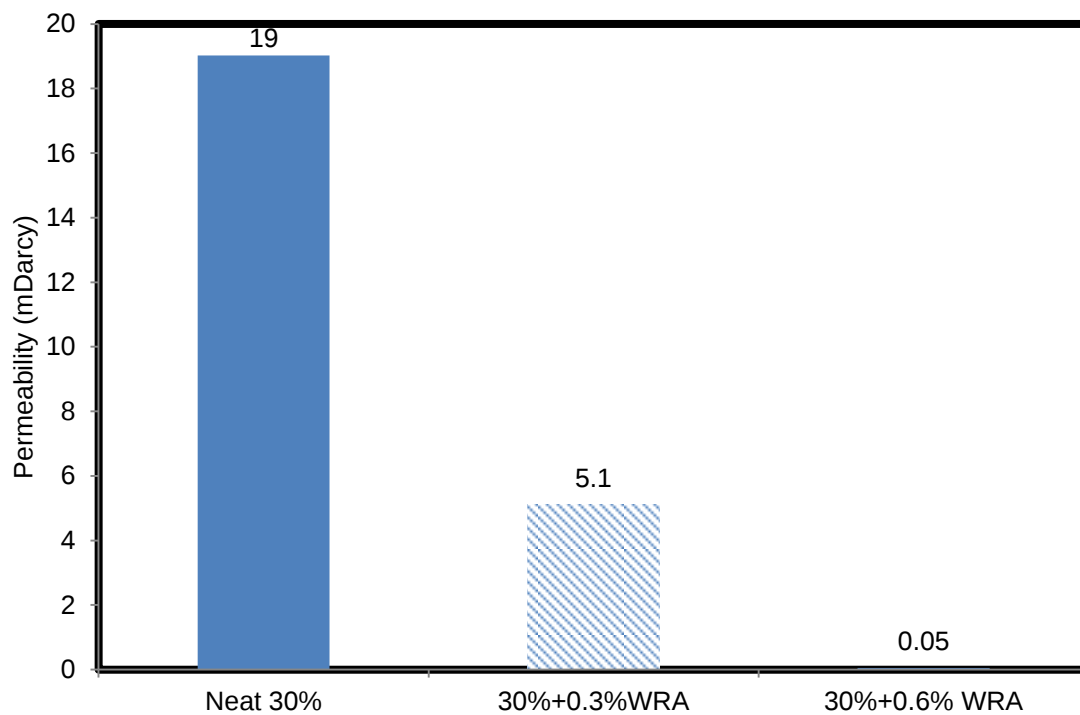


**Figure 4-14 - Filter cake permeability of 38% cement samples containing nanoclay at 100 psi**

The calculated API fluid loss and for samples with water to cement ratios of 30% and 38% is presented in Fig 4.15. It was found that adding polycarboxylate reduces the fluid loss significantly. The reason behind this phenomenon was investigated by calculating the permeability of filter cakes of the samples. Fig 4-16 illustrates the filter cake permeability of 30% cement samples with polycarboxylate. It is observed that adding polycarboxylate reduced the permeability of filter cake by up to 99%. Adding 0.6 polycarboxylate forms a thin layer of filter cake (6mm) with permeability of 0.05 mDarcy. The very low permeability of the formed layer does not allow the liquid to filtrate and reduces fluid loss by up to 96%.



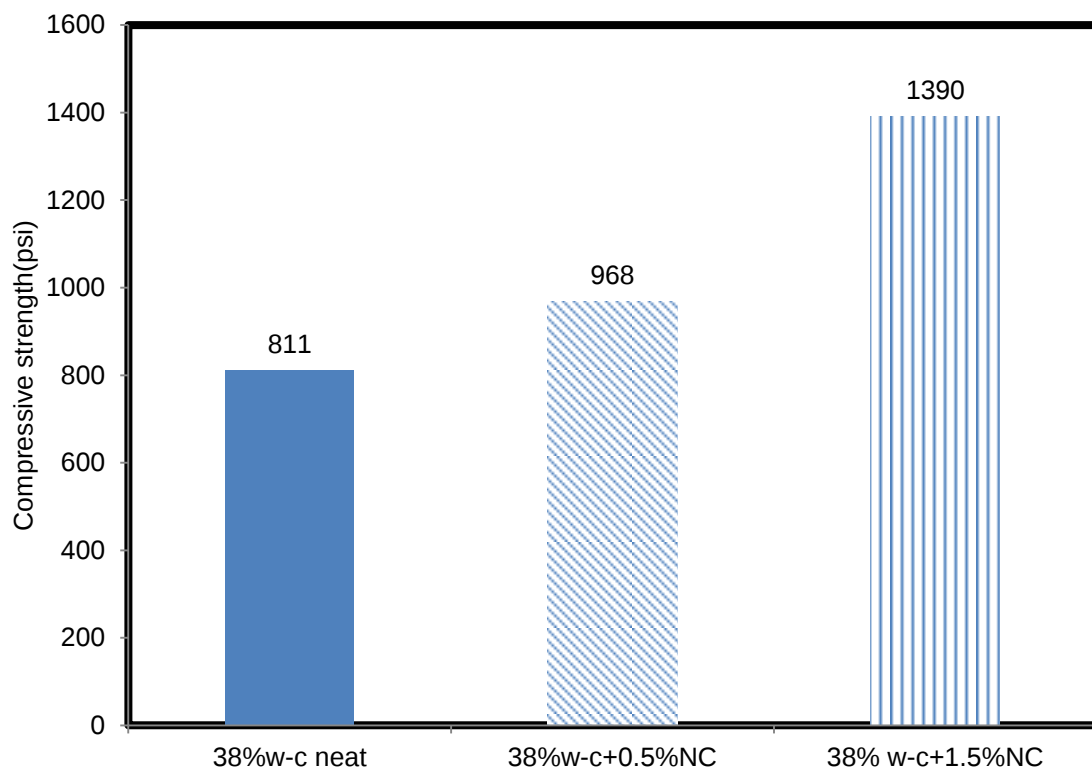
**Figure 4-15 - Fluid loss of 30% and 38% with Polycarboxylate**



**Figure 4-16 - Filter cake permeability of 30% w-c ratio slurries with polycarboxylate**

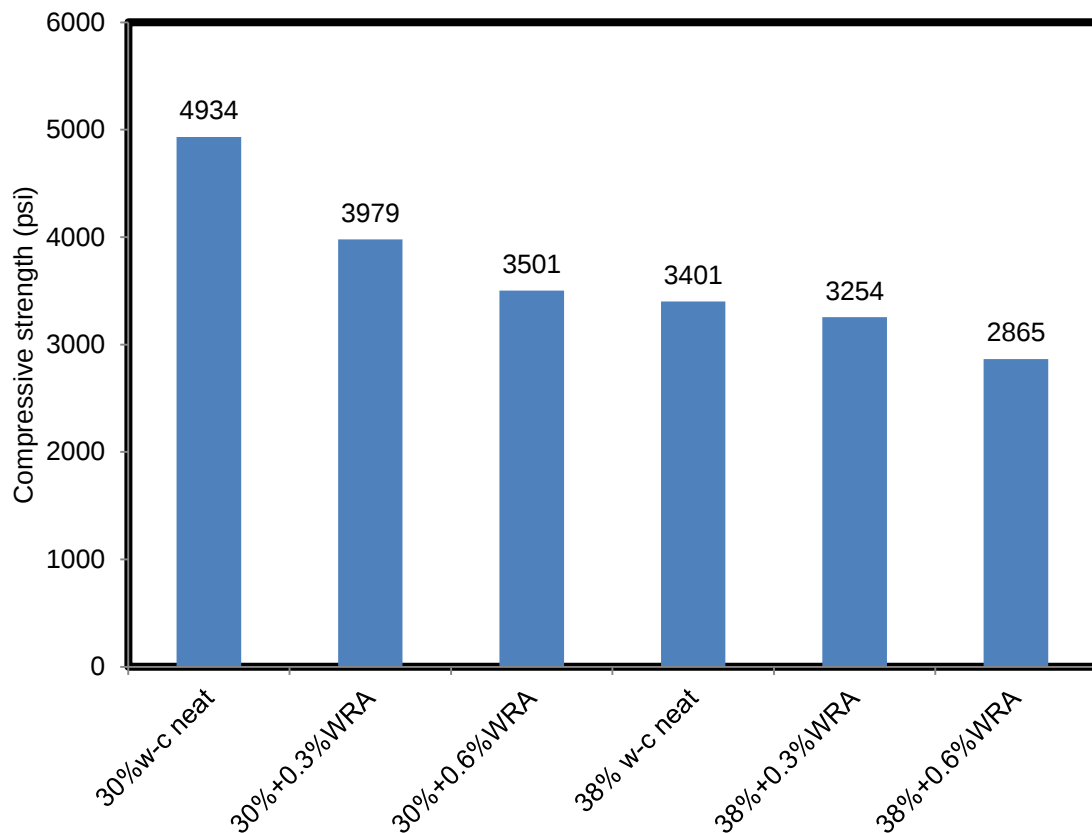
#### 4.2.4 Mechanical Properties and Piezoresistivity

The effect of nanoclay on ultimate 24 hour compressive strength of 38% w-c ratio slurries is presented in Fig 4-17. It is observed that adding 0.5% and 1.5% nanoclay increased the 24 hour compressive strength of samples by 19% and 71%, respectively. The nano size particles of nanoclay fill the voids in the cement paste and decrease the porosity. The decrement in porosity increases the compressive strength of hardened cement. In addition, nanoclay reduced the free water of cement samples which resulted in no segregation of cement particles.

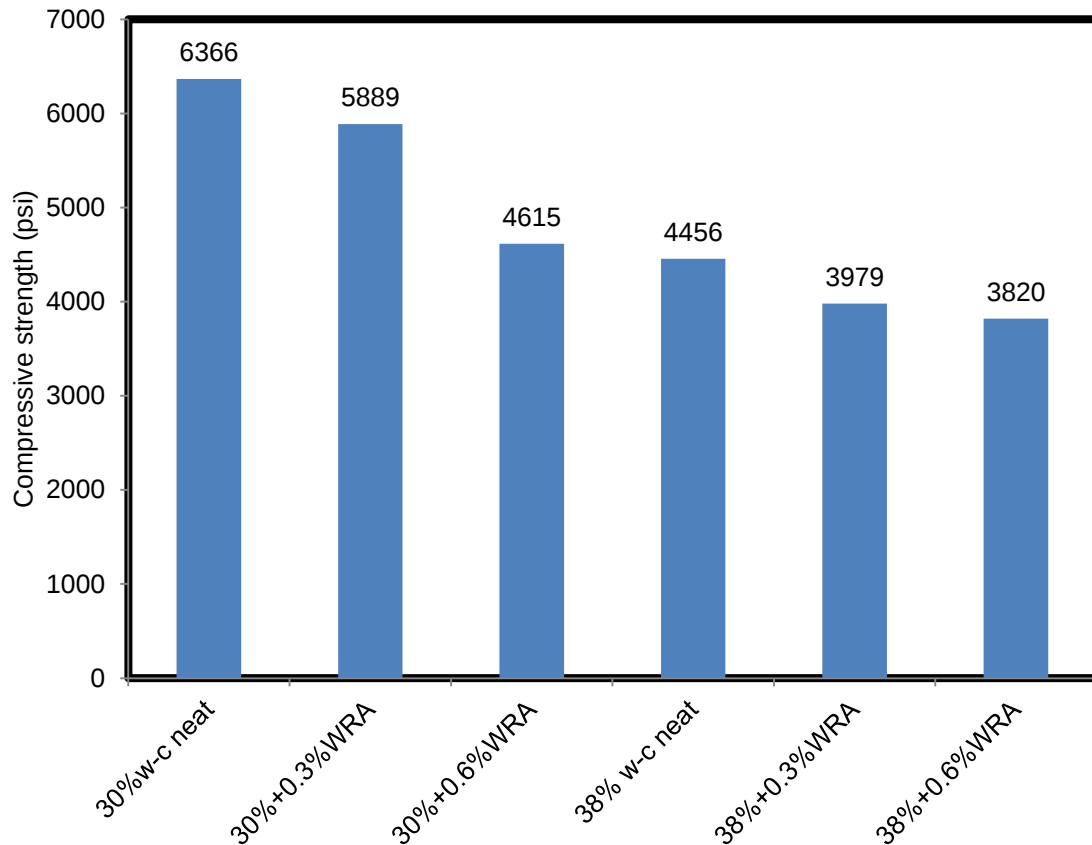


**Figure 4-17 - Compressive strength of 38% w-c samples containing nanoclay after 24 hours of curing**

The seven day and 30 day compressive strength of 30% and 38% w-c ratio slurries containing polycarboxylate are represented in Fig 4-17 and 4-18, respectively. Samples with lower water to cement ratio showed up to 29% higher compressive strength. This occurred due to lower capillary pore volume of samples with 30% w-c ratio compared to 38% w-c ratio samples. Adding polycarboxylate reduced the 7 day and 30 day compressive strength of samples by up to 29% and 28%, respectively. It should be noted that for low water to cement ratio, the effect of polycarboxylate in decreasing the ultimate compressive strength is 84% and 93% higher after 7 days and 30 days, respectively.



**Figure 4-18 - Compressive strength of samples with 30% and 38% w-c ratio containing polycarboxylate after 7 days of curing**



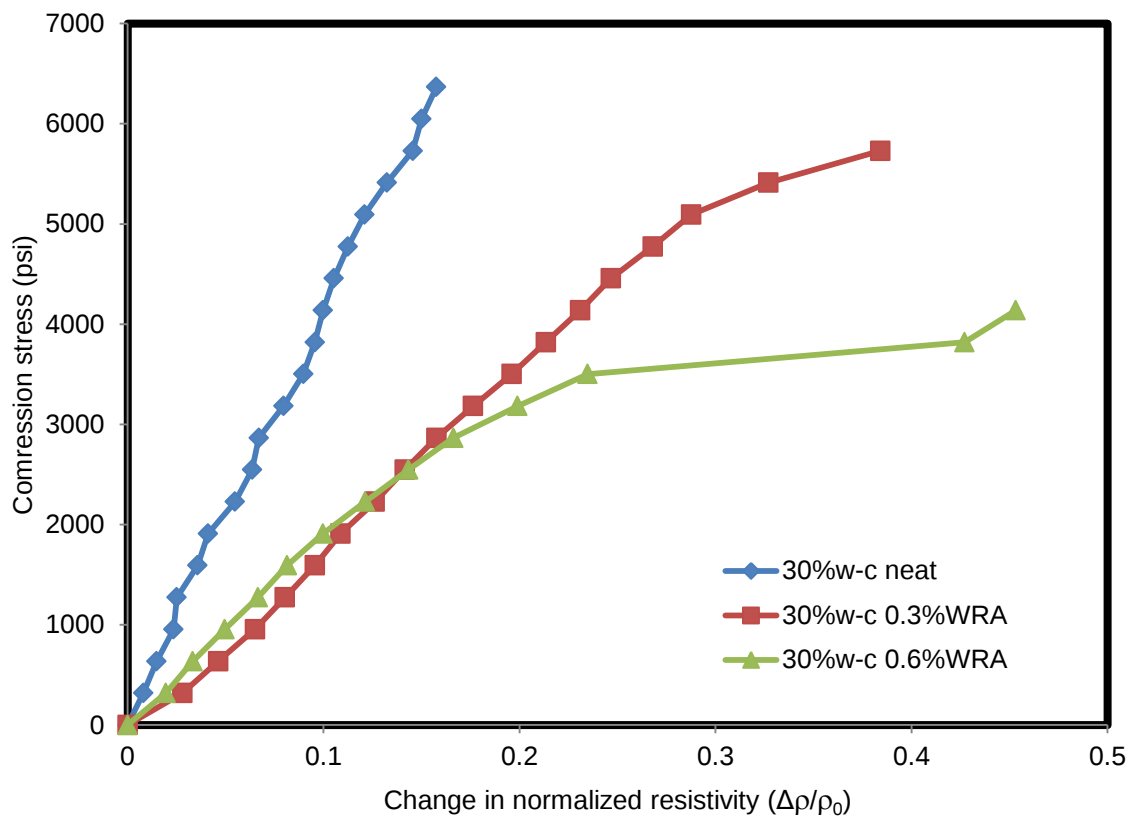
**Figure 4-19 - Compressive strength of samples with 30% and 38% w-c ratio containing polycarboxylate after 30 days of curing**

Fig 4-20 and 4-21 show the piezoresistivity behavior of 30 day cured cement samples with water to cement ratio of 30% and 38%, respectively. It is found that all modified oil well cement samples showed changes in electrical resistivity during axial loading which indicates piezoresistive behavior. Two of the samples showed a sudden increase in the electrical resistivity during compressive test, which occurred at the time that the cracking initiated.

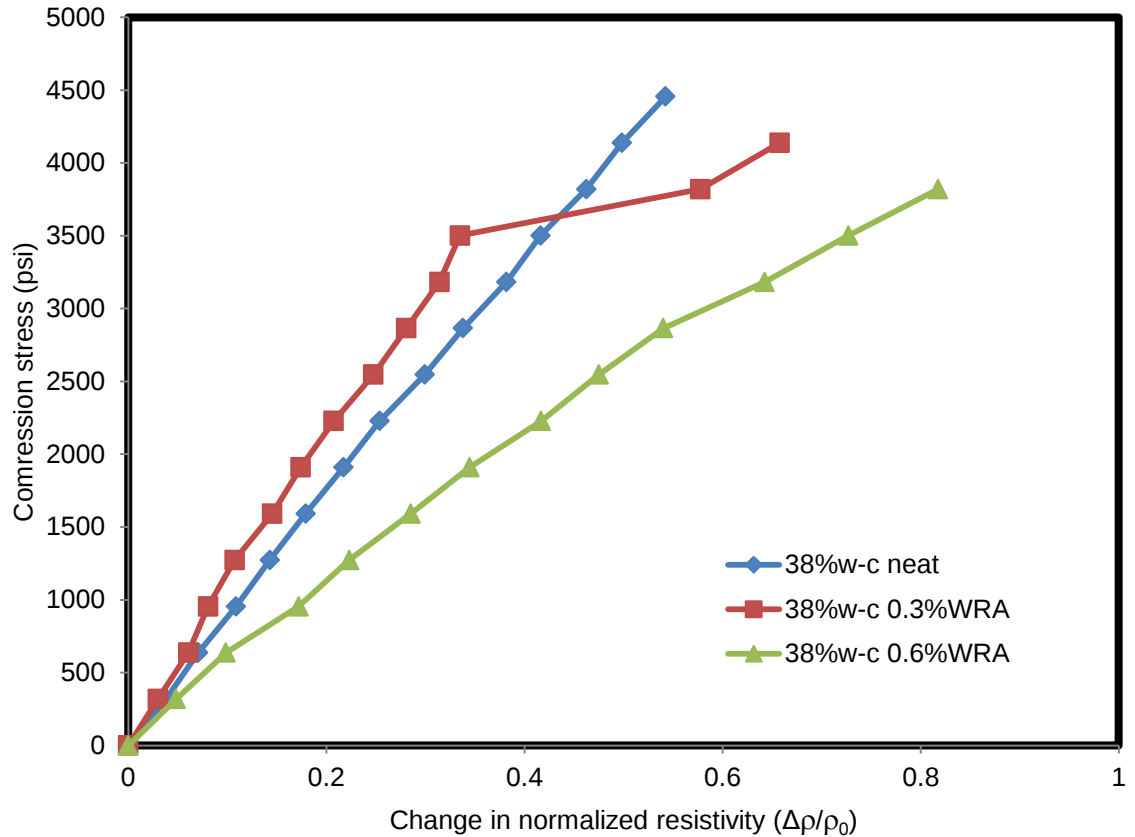
It was observed that adding polycarboxylate, while decreasing the compressive strength, increased the piezoresistive behavior of cement samples. In the samples with 38% w-c ratio, the initial piezoresistivity was higher in neat

sample compared to the sample containing 0.3% polycarboxylate. However, the final piezoresistivity of the sample containing 0.3% polycarboxylate was higher.

Cement slurries with higher water to cement ratio showed higher piezoresistivity compared to low water to cement ratio samples. The maximum change in normalized resistivity for 38% w-c ratio was 82% while the maximum change was 48% for 30% for slurries with water to cement ratio of 30%.



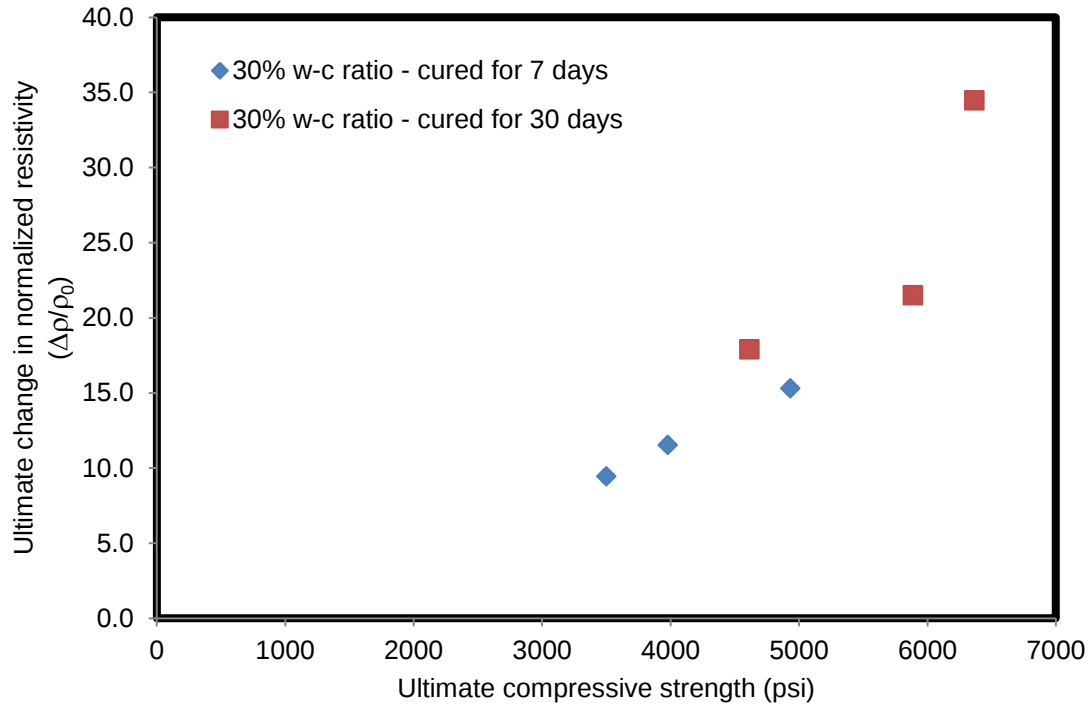
**Figure 4-20 - Piezoresistivity of 30% w-c slurries containing polycarboxylate after 30 days of curing**



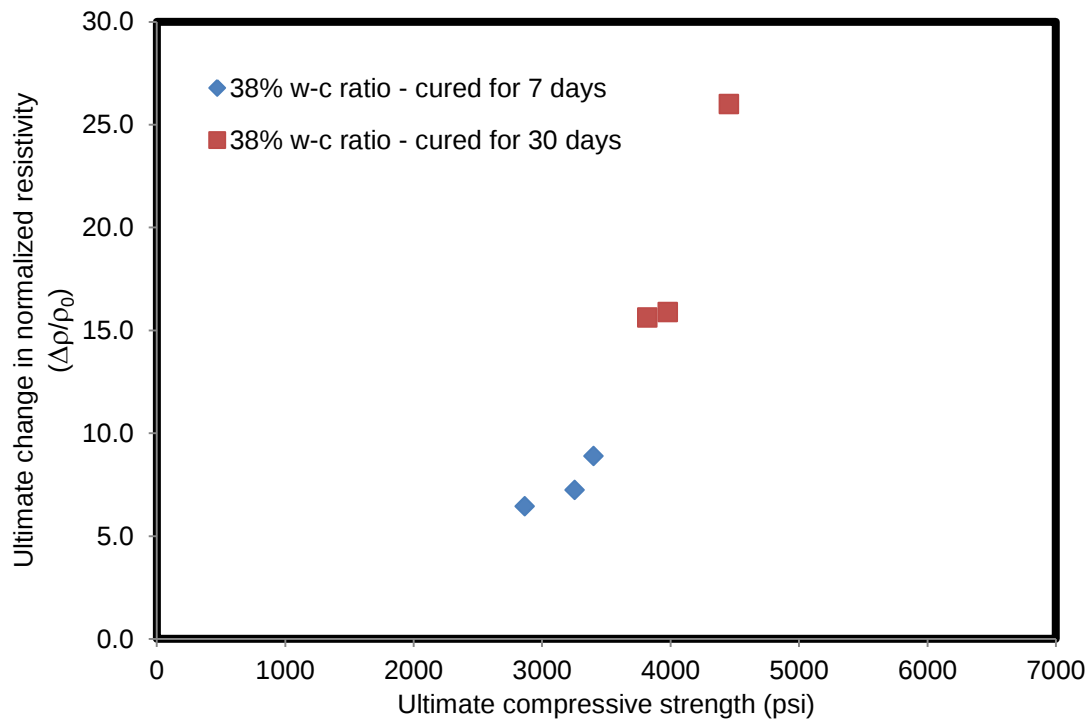
**Figure 4-21 - Piezoresistivity of 38% w-c slurries containing polycarboxylate after 30 days of curing**

#### 4.2.5 Correlation between Electrical Resistivity and Compressive Strength

Figs 4-22 and 4-23 represent the correlation between the ultimate changes in normalized electrical resistivity and ultimate compressive strength for 30% and 38% w-c ratio samples, respectively. It observed that changes in electrical resistivity are related to the compressive strength of samples. It was observed that cement slurries containing polycarboxylate showed lower ultimate change in normalized resistivity which indicates that adding polycarboxylate interacts with the chemical reactions of the ions in cement slurry which results in lower rate of hydration and ultimate compressive strength.



**Figure 4-22 - Correlation between ultimate change in normalized resistivity and ultimate compressive strength for 30% w-c ratio**



**Figure 4-23 - Correlation between ultimate change in normalized resistivity and ultimate compressive strength for 38% w-c ratio**

### 4.3 Summary

Laboratory tests were performed to evaluate the effect of different additives on properties of modified oil well cement. It was shown that adding nanoclay increases the rheology of oil well cement at low and high shear strain rates. Polycarboxylate can be used to decrease the rheology of oil well cement and can be used to cement slurries with low water to cement ratio in order to increase the pumpability. Also water to cement ratio plays a significant role in rheology of oil well cement.

- 1 Electrical measurements during curing indicated that electrical resistivity of curing samples decrease during up to 2.5 hours of curing and increase afterward. Also the highest negative rate of change in normalized resistivity occurred during the first 30 minutes of curing. It was noticed that adding polycarboxylate reduced the change in normalized electrical resistivity during curing by up to 48%.
- 2 Fluid loss tests indicated that adding 1.5% nanoclay decreased the fluid loss and the filter cake permeability by 64% and 86%, respectively. In addition, adding 0.6% polycarboxylate reduced the fluid loss 96%. Polycarboxylate reduced the fluid loss by forming a thin layer of filter cake with a permeability of 0.05 mDarcy which was 99% lower than the filter cake permeability of neat cement.
- 3 Mechanical tests showed that adding 1.5% nanoclay increased the 24 hour compressive strength of cement from 811 psi to 1390 psi. Cement slurries with water to cement ratio of 30% and 38% containing polycarboxylate showed up to 29% and 28% lower compressive strength after 7 days and 30

- days of curing, respectively. Sample with lower ultimate change in normalized resistivity showed lower compressive strength, which indicates that polycarboxylate interacts with the reaction of ions in the cement slurry and reduces the rate of hydration and ultimate compressive strength.
- 4 Piezoresistivity measurements indicated that the modified oil well cement has piezoresistive behavior. The piezoresistivity behavior of cement samples with 38% w-c ratio was higher compared to 30% w-c specimens. Also adding polycarboxylate increased the piezoresistivity of oil well cement for both 30% and 38% w-c samples.

## **CHAPTER 5**

### **BEHAVIOR OF CONTAMINATION ON OIL WELL CEMENT**

Behavior of oil well cement slurry contaminated with salt, water based drilling mud and synthetic based drilling fluid was investigated. This chapter represents the samples preparation, mixing order and laboratory tests results and analysis. In addition, two models were developed to predict the certain behavior of contaminated oil well cement and are presented in this chapter.

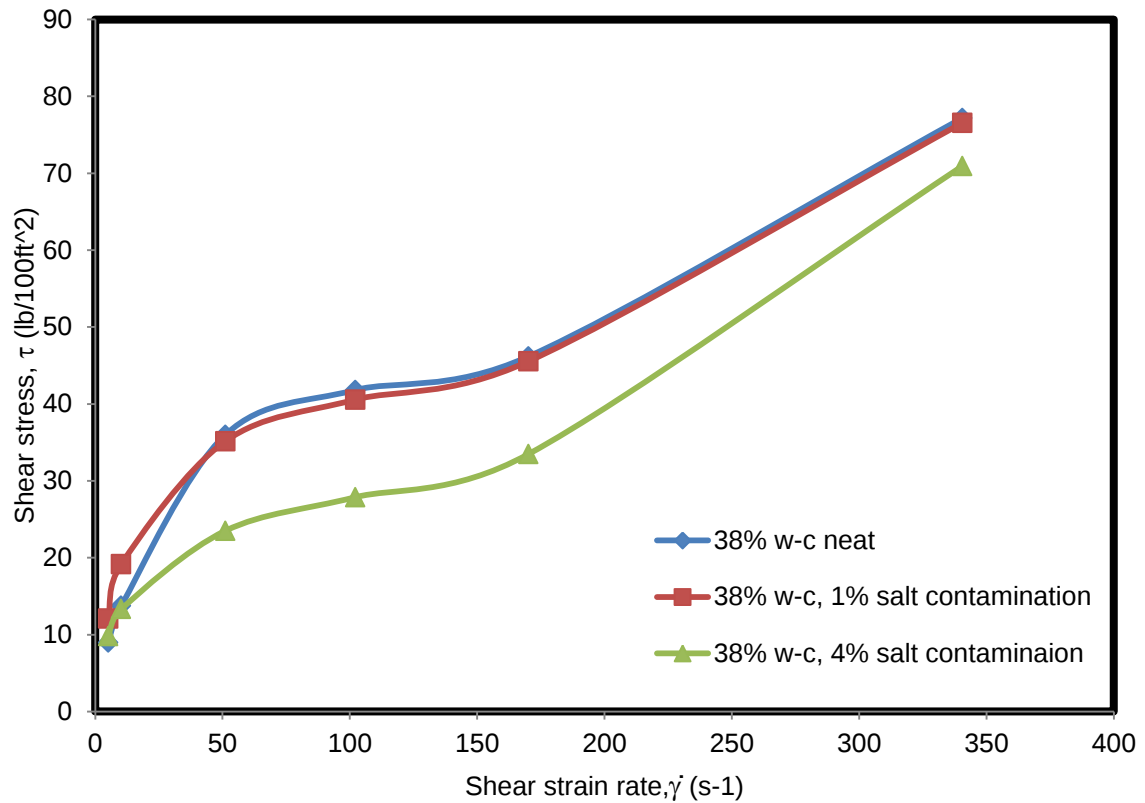
#### **5.1 Effects of Salt Contamination with Oil Well Cement**

##### **5.1.1 Sample Preparation and Mixing**

Oil well cement with water to cement ratio of 38% was used in this study. Contaminated samples were prepared by adding 1% and 4% salt (BWOC) to cement slurry 5 minutes after mixing. The effect of salt contamination was evaluated by comparing the properties of contaminated samples with the control sample containing no salt.

##### **5.1.2 Rheology Behavior**

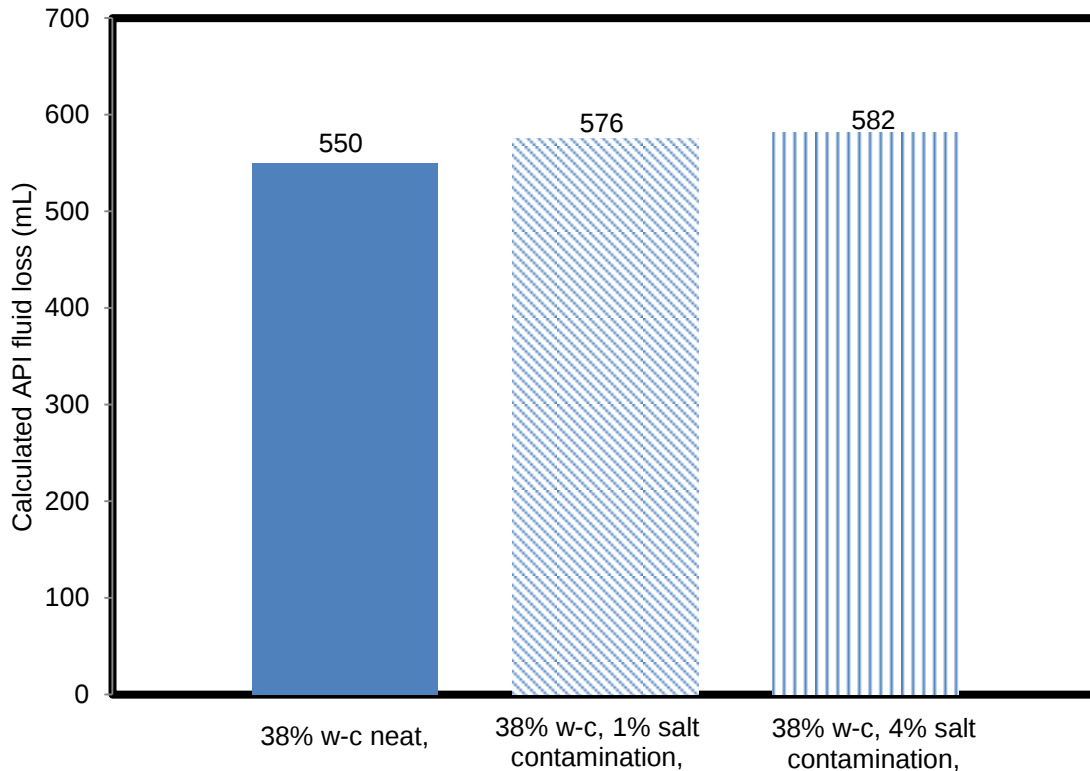
Fig 5.1 represents the rheological behavior of oil well cement contaminated with salt. It is observed that the rheology of oil well cement was not much altered by 1% salt, however increasing the salt content to 4% reduced the shear stress by up to 33%. This occurs due to the inclusion of salt in cement slurry which aids in dispersion and reducing the viscosity of the mixture.



**Figure 5-1 - Effect of salt contamination on the rheology of oil well cement**

### 5.1.3 Fluid Loss

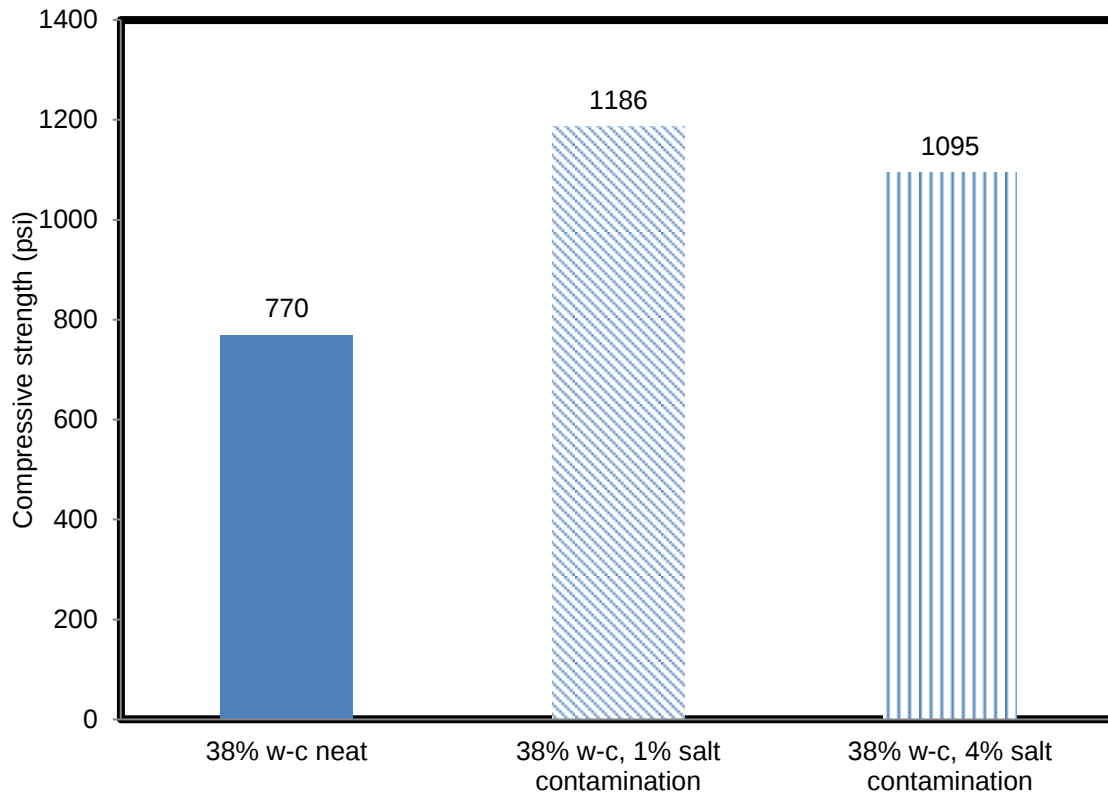
Fig 5.2 shows the effect of salt contamination on the fluid loss of oil well cement. The fluid loss increased by 5% and 6%, when salt contamination increased to 1% and 4%, respectively. The slight increase in the fluid loss may be due to the dispersing properties of salt in the cement slurry which allows more water to filtrate from samples when pressure is applied. It should be noted that the blowout time for all samples were identical.



**Figure 5-2 - Effect of salt contamination on fluid loss of oil well cement**

#### **5.1.4 Compressive Strength after 24 hours of curing**

Fig 5.3 represents the effect of salt contamination on compressive strength of cement slurry after 24 hours of curing. 1% concentration of salt increased the compressive strength of cement by 54%. Slurry containing 4% salt had 42% higher compressive strength compared to control samples. 4% salt concentration showed 8% lower compressive strength compared to 1% salt contaminated sample. The increase in the compressive strength was due to the accelerating effect of salt. Salt increases the rate of chemical reactions in the slurry which results in higher compressive strength.

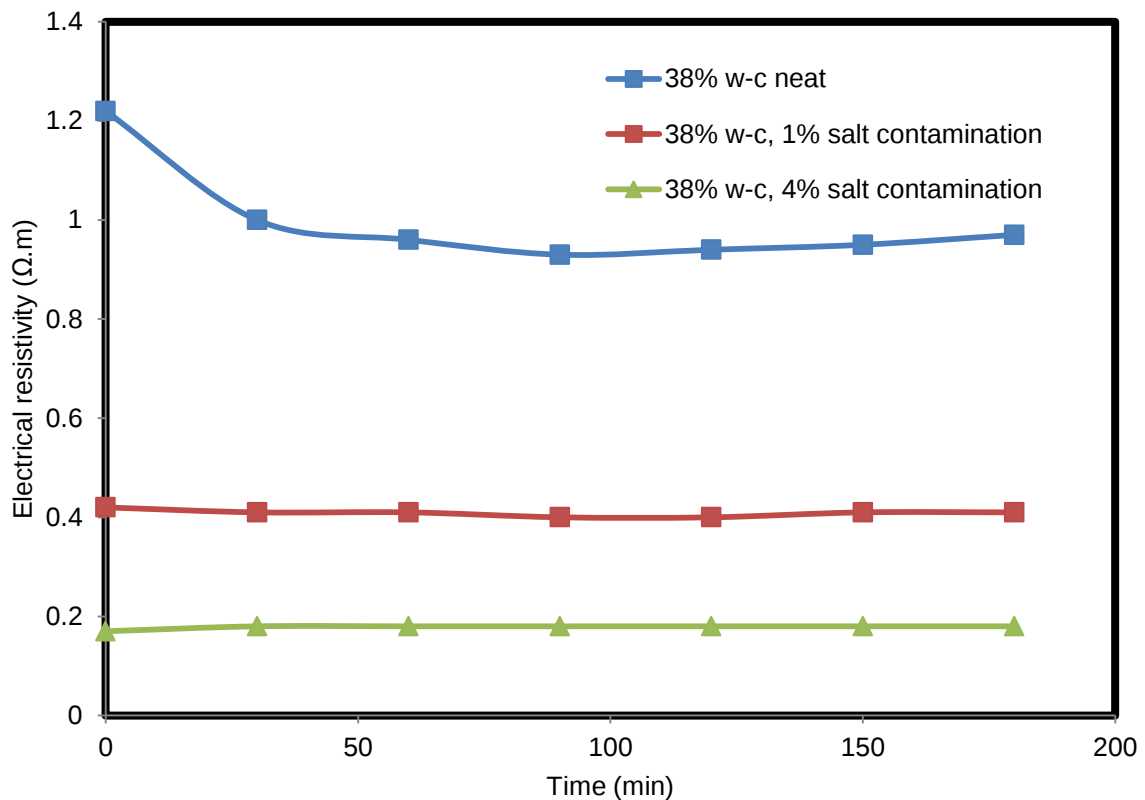


**Figure 5-3 – Effect of salt contamination on 24 hour compressive strength of oil well cement**

#### **5.1.5 Electrical Properties**

The electrical resistivity of samples during first 2.5 hours of curing is presented in Fig 5.4. It was observed that 1% and 4% salt contamination decreased the initial electrical resistivity by up to 66% and 86%, respectively. This is due to the release of sodium and chloride ions in the water. The ions increased the capability of water to transfer electrons, and reduced the electrical resistivity of the sample. The significant decrease in electrical resistivity can aid operators to determine salt contamination during cementing the wellbore by measuring electrical properties of cement.

Control samples showed 18% decrement in electrical resistivity during the first 30 minutes of curing, while no significant changes was observed during the initial curing for salt contamination samples. The initial reduction in the neat cement samples was due to the release of cement ions in the water. The reason that salt contaminated samples did not show a lower electrical resistivity initially was due to presence of sodium and calcium ions in the water. Due to the very high conductivity of salt water solution, the release of cement particle ions did not affect the electrical resistivity dramatically.



**Figure 5-4 - Effect of salt contamination on electrical resistivity of oil well cement during initial curing**

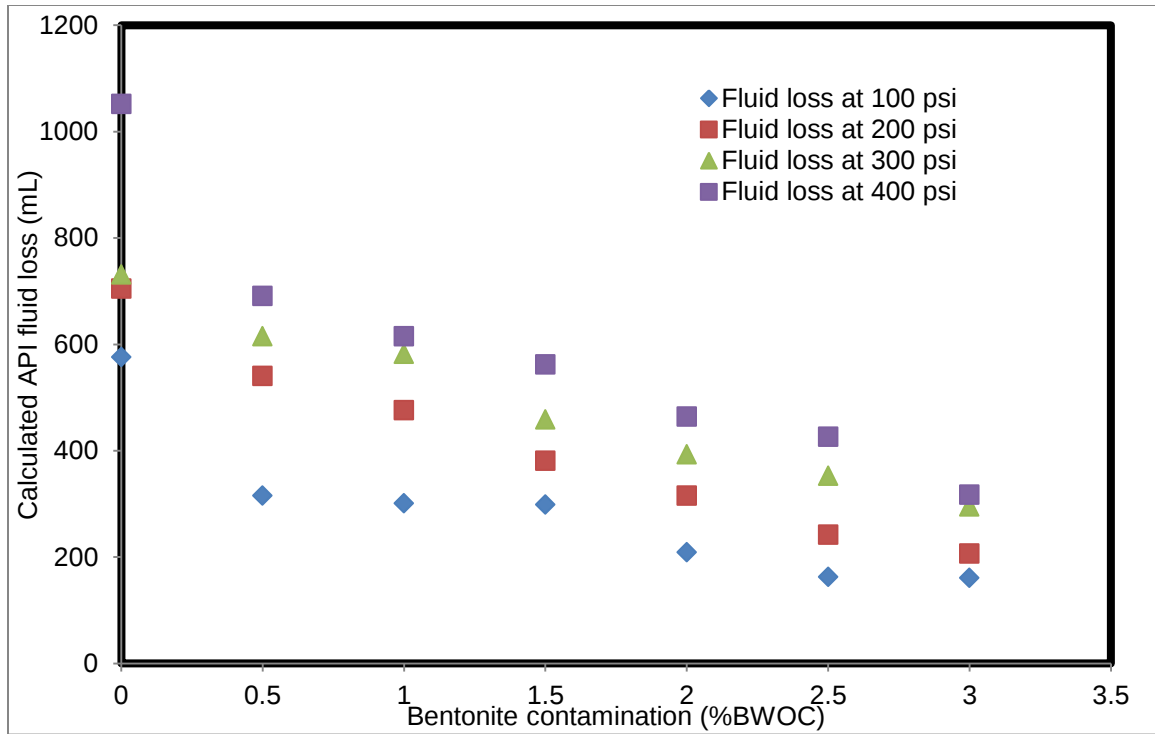
## **5.2 Effect of Bentonite Contamination on Oil Well Cement**

Water to cement ratio of 38% was used in this study for all samples. After mixing the cement with water, 0.5% to 3% bentonite was added to the slurry and the sample was mixed at a low rpm. The fluid loss was measured at 100, 200, 300 and 400 psi 5 minutes after mixing. In addition, gas migration property of filter cakes for samples including 0%, 0.5% and 2% bentonite was measured at 50 psi by measuring the gas flow rate and calculating the gas permeability. The measured data for contaminated samples was compared to the control cement sample containing no bentonite in order to evaluate the effect of bentonite contamination.

### **5.2.1 Fluid Loss Results**

The calculated fluid loss for oil well cement slurries contaminated with 0% to 3% bentonite is summarized in Fig 5.5. It was observed that increasing pressure resulted in up to 262% higher fluid loss. This occurred because higher pressure applies more force on the pore water in the cement slurry which increases the amount of the filtrated liquid. Also applying higher pressure reduced the blowout time which increases the calculated API fluid loss.

Samples with higher bentonite content showed lower fluid loss. Addition of 3% bentonite decreased the calculated API fluid loss by up to 259%. This is due to the effect of bentonite on absorbing the water in the cement slurry, which lowers the filtrate volume.



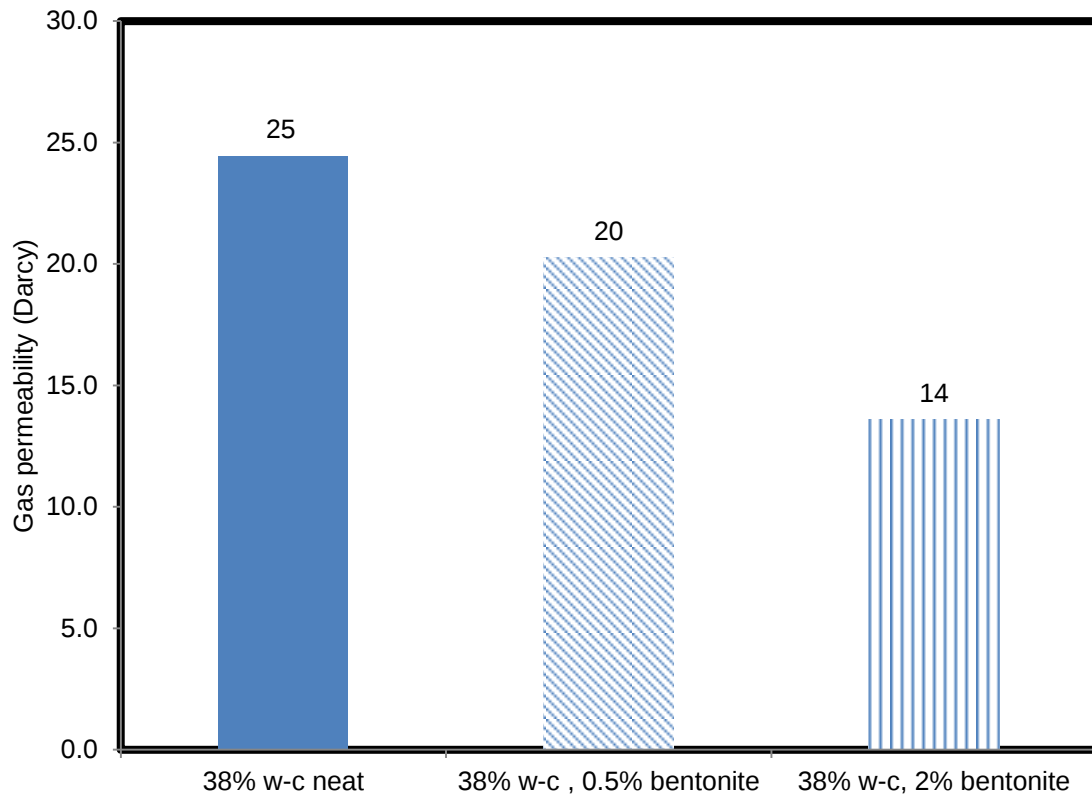
**Figure 5-5 - Effect of bentonite on the fluid loss in the 38% oil well cement**

### 5.2.2 Gas Migration Properties

Table 5-1 represents the measured data for gas migration tests. The calculated permeability is presented in Fig 5.6. It is shown that adding bentonite to cement reduced the gas permeability of filter cake. This can be explained based on the effect of bentonite particles in filling the pores in the filter cake which results in lower gas flow rate.

**Table 5-1 - Gas migration results for 38% cement slurries with and without bentonite**

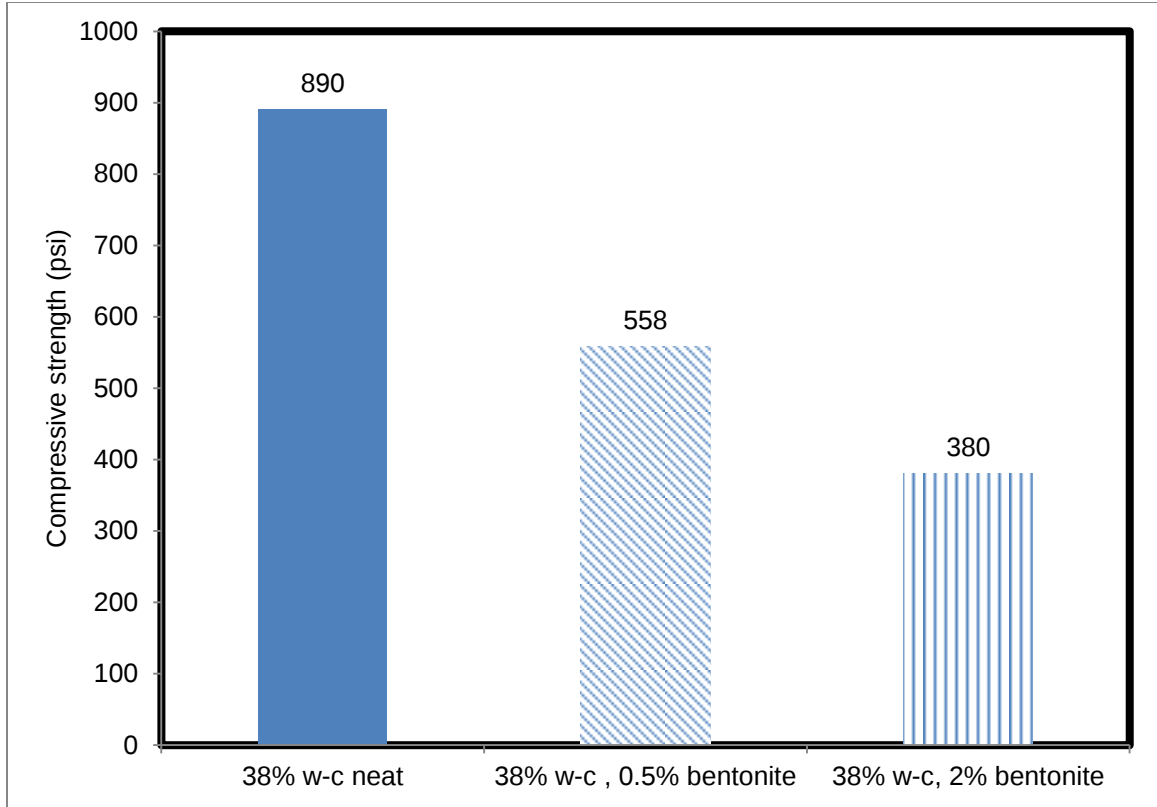
| Bentonite % | Top pressure (psi) | Flow rate (mL/s) | Bottom pressure (psi) |
|-------------|--------------------|------------------|-----------------------|
| 0           | 50                 | 103              | 20                    |
| 0.50%       | 50                 | 85               | 20                    |
| 2%          | 50                 | 57               | 20                    |



**Figure 5-6 - Effect of bentonite on gas permeability of oil well cement**

### 5.2.3 Mechanical Properties

Fig 5-7 shows the effect of bentonite contamination on oil well cement. It found from the results that 24 hour compressive strength of specimens containing 0.5% and 2% bentonite were 43% and 63% of sample with no added bentonite, respectively. Bentonite by adsorbing the water in the cement mixture reduces the hydration and lowers the rate of chemical reactions. This phenomenon consequently reduced the early compressive strength.



**Figure 5-7 - Effect of bentonite contamination on 24 hour compressive strength of cement samples**

#### **5.2.4 Predicting the Effect of Bentonite on Calculated API Fluid Loss of Oil**

##### **Well Cement**

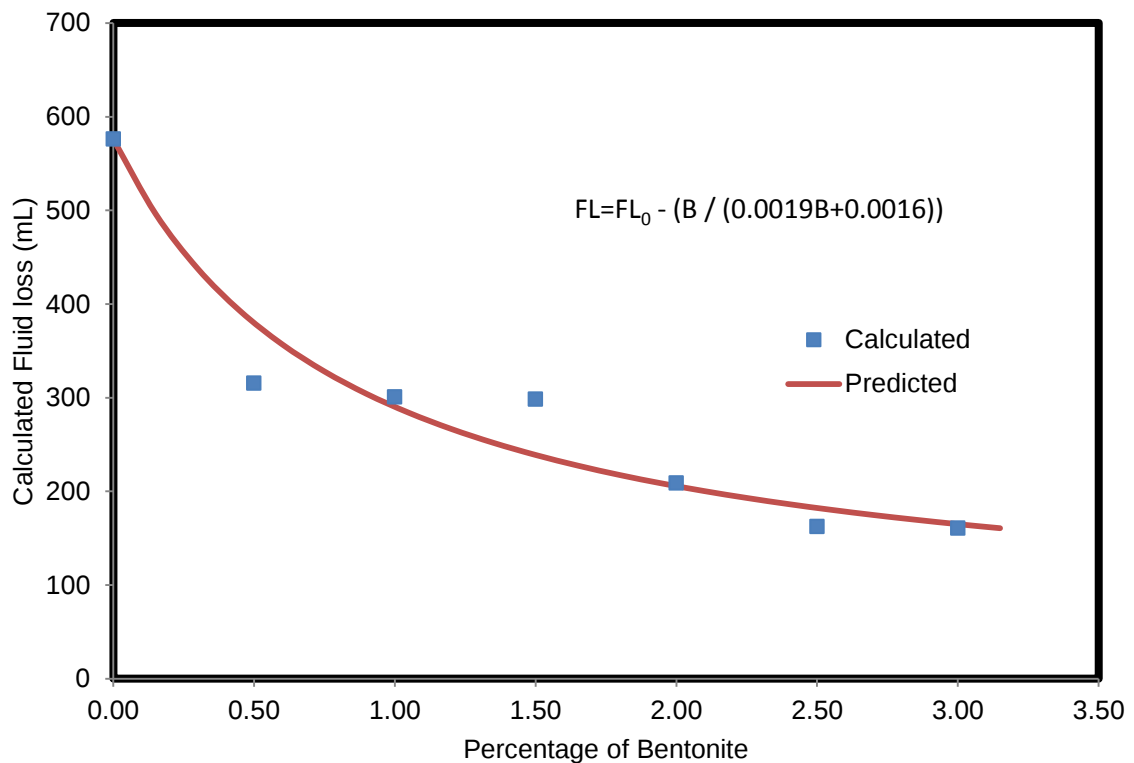
The fluid loss behavior of oil well cement contaminated with bentonite was modeled using a hyperbolic model based on percentage of bentonite contaminated:

$$FL = FL_0 - \frac{B}{(G \times B) + H} , \quad (5-1)$$

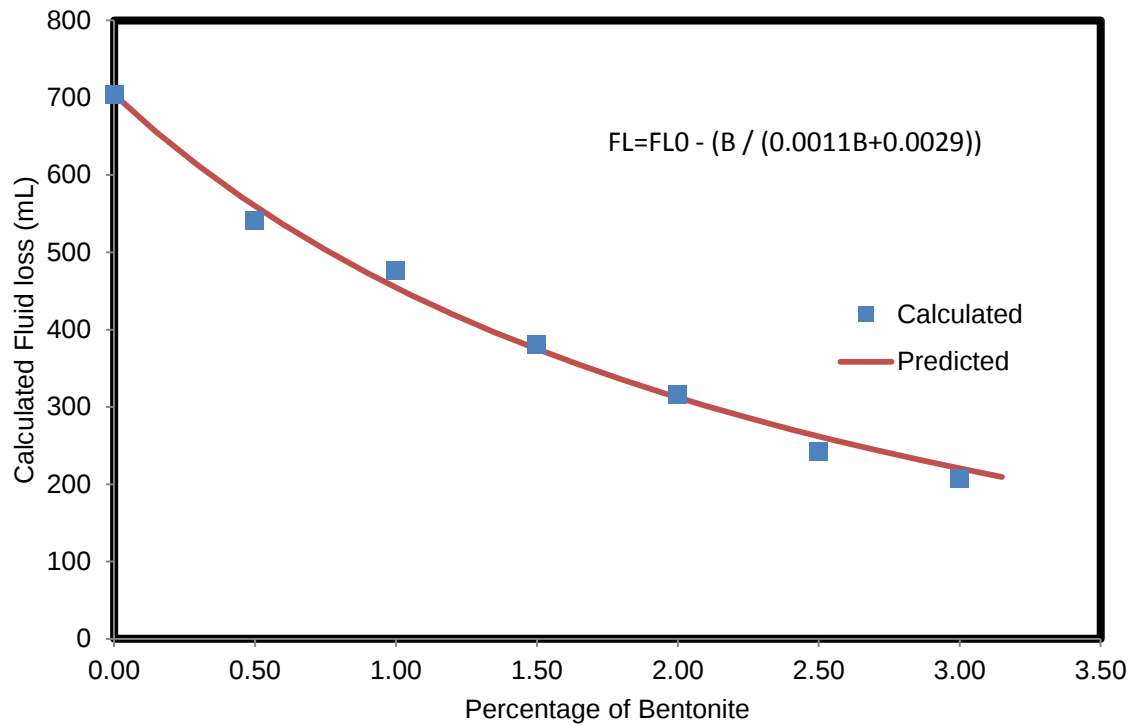
where:

FL is the predicted fluid loss,  $FL_0$  is the fluid loss of control sample at each pressure, B is the Percentage of bentonite, and G and H are Model constants.

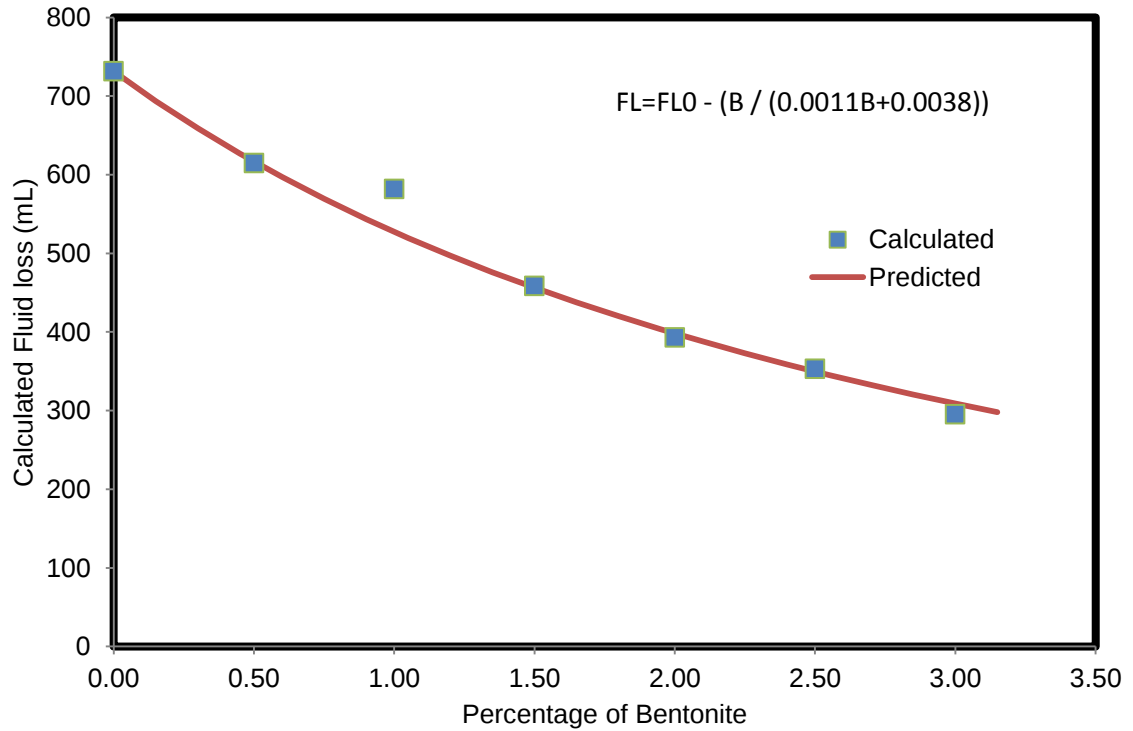
The model constants represent the pressure effect on the fluid loss and are discussed further in this section. Figs 5.8 through 5.11 represent the calculated fluid loss based on laboratory measurements vs. fluid loss predicted by using the developed hyperbolic model at 100, 200, 300, and 400 psi. It was shown that the model predicted the fluid loss at various pressures with high accuracy. This model was further developed to take into account the effect of pressure on fluid loss by relating the model constants (H and G) to different pressures applied.



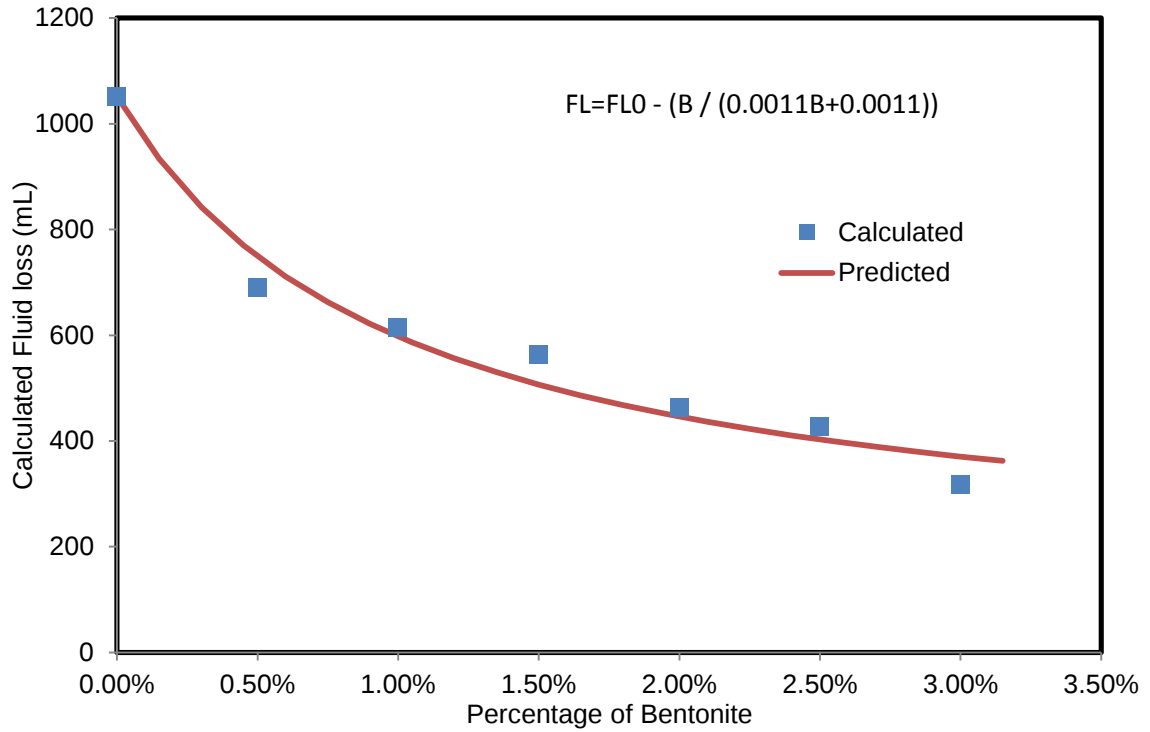
**Figure 5-8 - Calculated vs. predicted effect of bentonite on fluid loss of oil well cement at 100 psi**



**Figure 5-9 - Calculated vs. predicted effect of bentonite on fluid loss of oil well cement at 200 psi**



**Figure 5-10 - Calculated vs. predicted effect of bentonite on fluid loss of oil well cement at 300 psi**



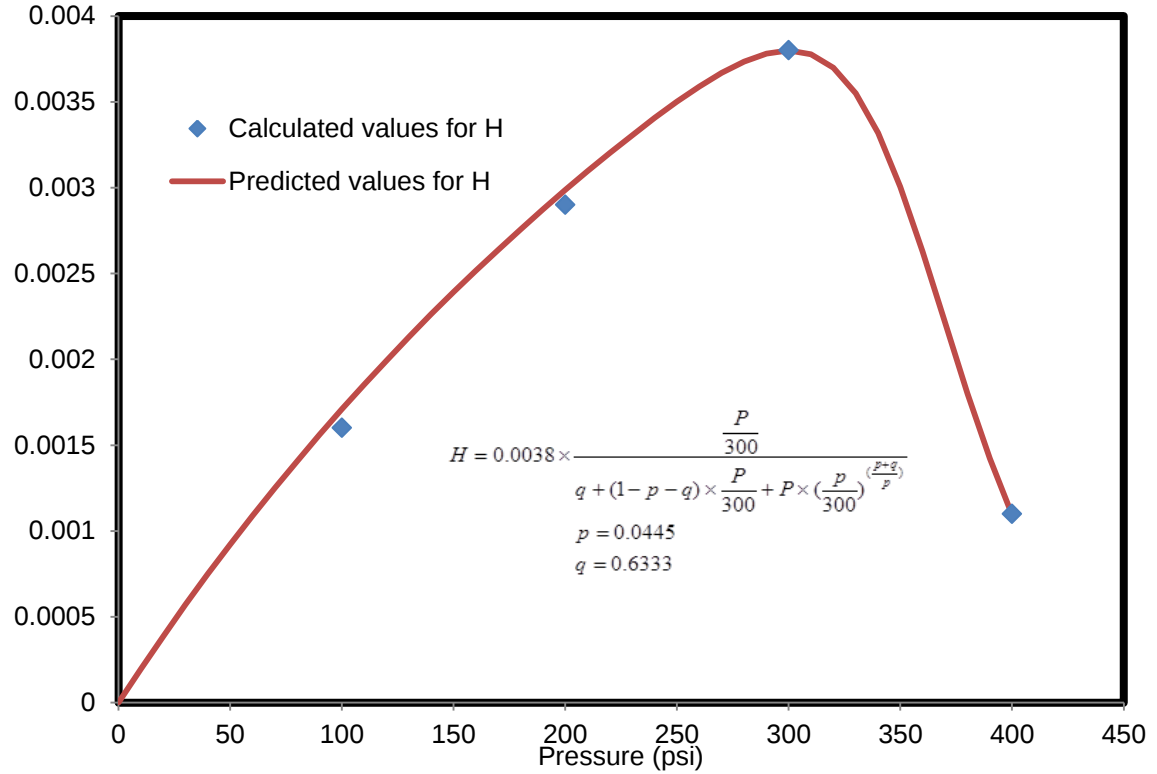
**Figure 5-11 - Calculated vs. predicted effect of bentonite on fluid loss of oil well cement at 400 psi**

In order to represent the effect of pressure on model parameters, two models were used. For H parameter, a P-Q based model was used to show the effect of pressure. P-Q model was used by Makarkia and Vipulanandan (Makarkia & Vipulanandan, 1992) to predict the behavior of polymer concrete and. The modified model used for predicting H parameter was:

$$H = H_c \times \left[ \frac{\frac{P}{P_c}}{q + (1 - p - q) \frac{P}{P_c} + p \left( \frac{P}{P_c} \right)^{\frac{(p+q)}{p}}} \right], \quad (5-2)$$

where H is the hyperbolic model parameter dependent on pressure,  $H_c$  is the peak value for H,  $P_c$  is the pressure at  $H_c$ , and p and q are the model parameters.

The predicted values for H parameter are compared to the calculated values and the results are represented in Fig 5.12.

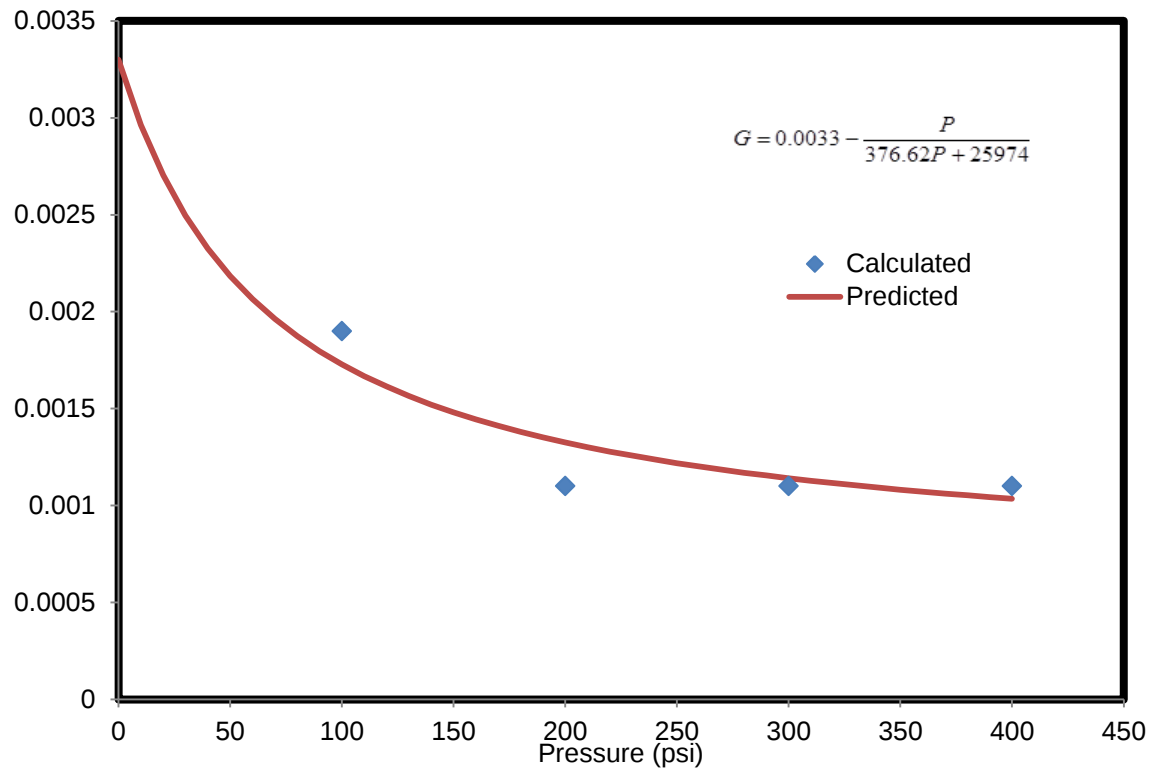


**Figure 5-12 - H parameter predicted using P-Q model vs. calculated values**

The G parameter was predicted using a hyperbolic model:

$$G = 0.0033 - \frac{P}{376.62P + 25974}, \quad (5-3)$$

where G is the hyperbolic model parameter and P is the pressure in psi. The comparison between the calculated and predicted values for G parameter is shown in Fig 5.13. It is shown that the model predicted the values for G parameter accurately.



**Figure 5-13 - Predicted vs. calculated values for G parameter**

A polynomial equation was then used for predicting the fluid loss of control samples at various pressures:

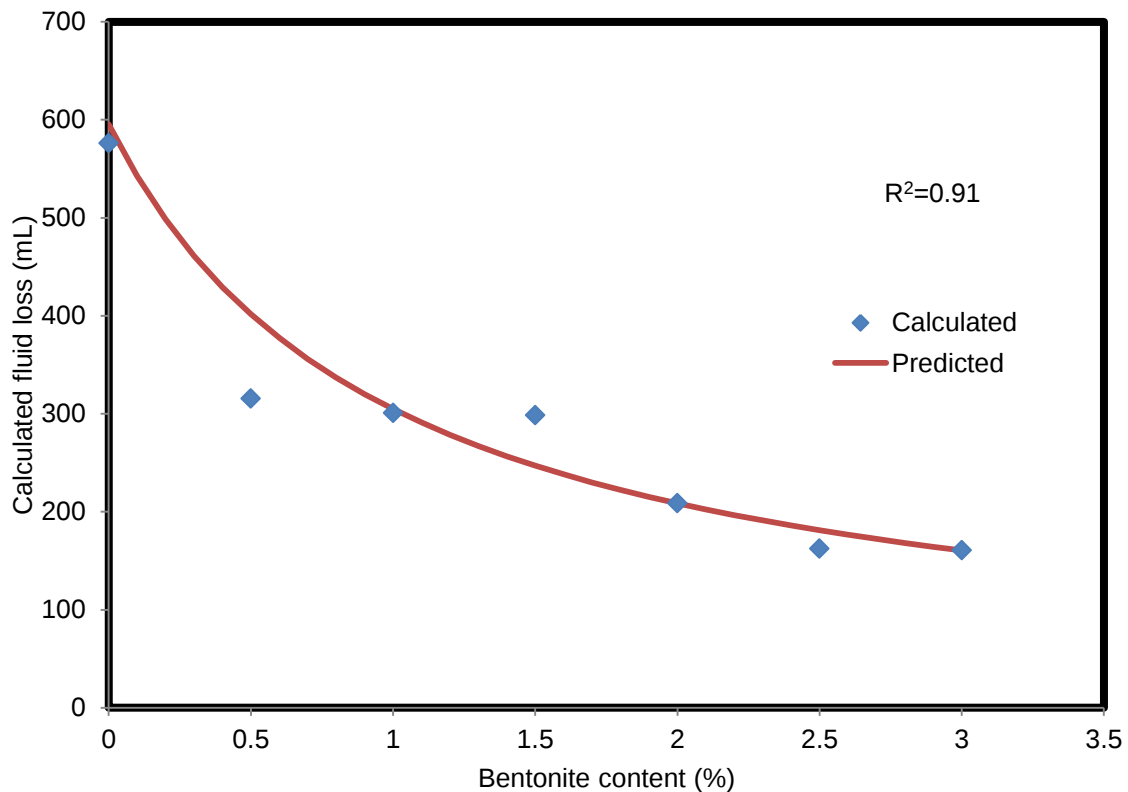
$$FL_0 = 0.0048P^2 - 0.9473P + 642, \quad \text{5-4}$$

where  $FL_0$  is the fluid loss of control samples containing no bentonite, and  $P$  is the applied pressure in psi.

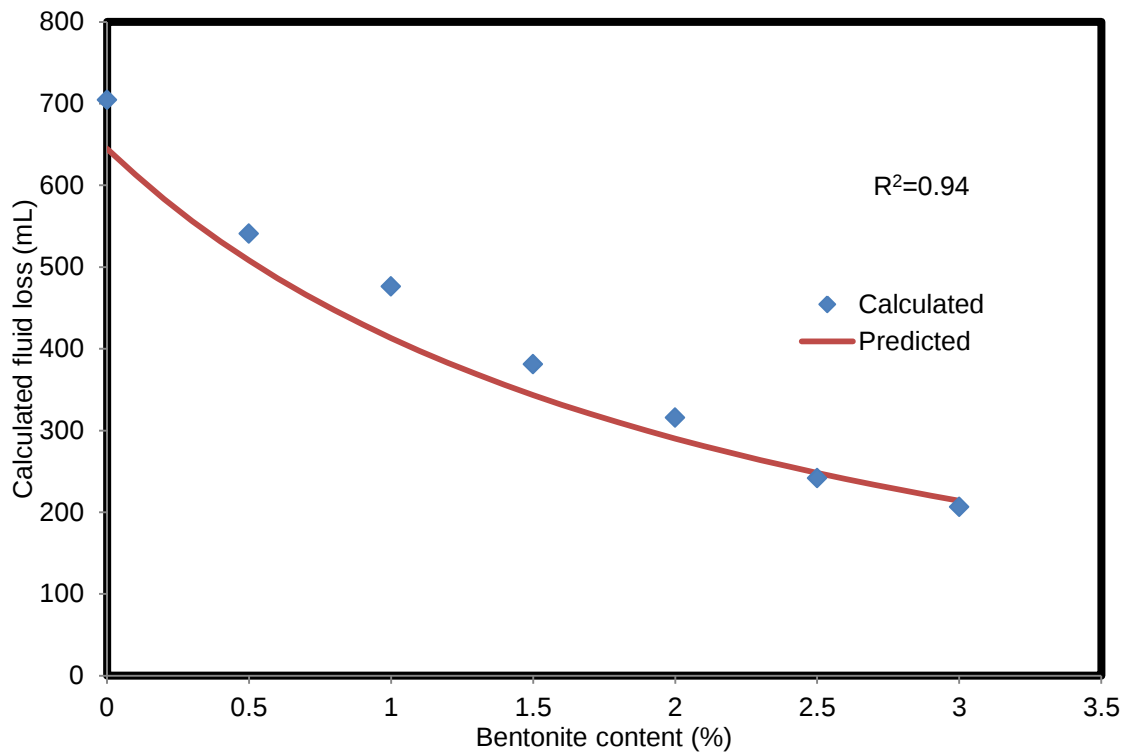
$FL_0$ ,  $H$  and  $G$  are the parameters of the hyperbolic model developed for predicting the effect of bentonite on fluid loss of oil well cement. The model was modified by replacing the pressure dependent parameters and the final was proposed:

$$FL = (0.0048P^2 - 0.9473P + 642) - \frac{B}{(0.0033 - \frac{P}{376.62P + 25974}) \times B + (0.0038 \times \frac{P}{300} + 0.633 + (0.322) \times \frac{P}{300} + 0.0445 \times (\frac{P}{300})^{(15.232)})} \quad 5-5$$

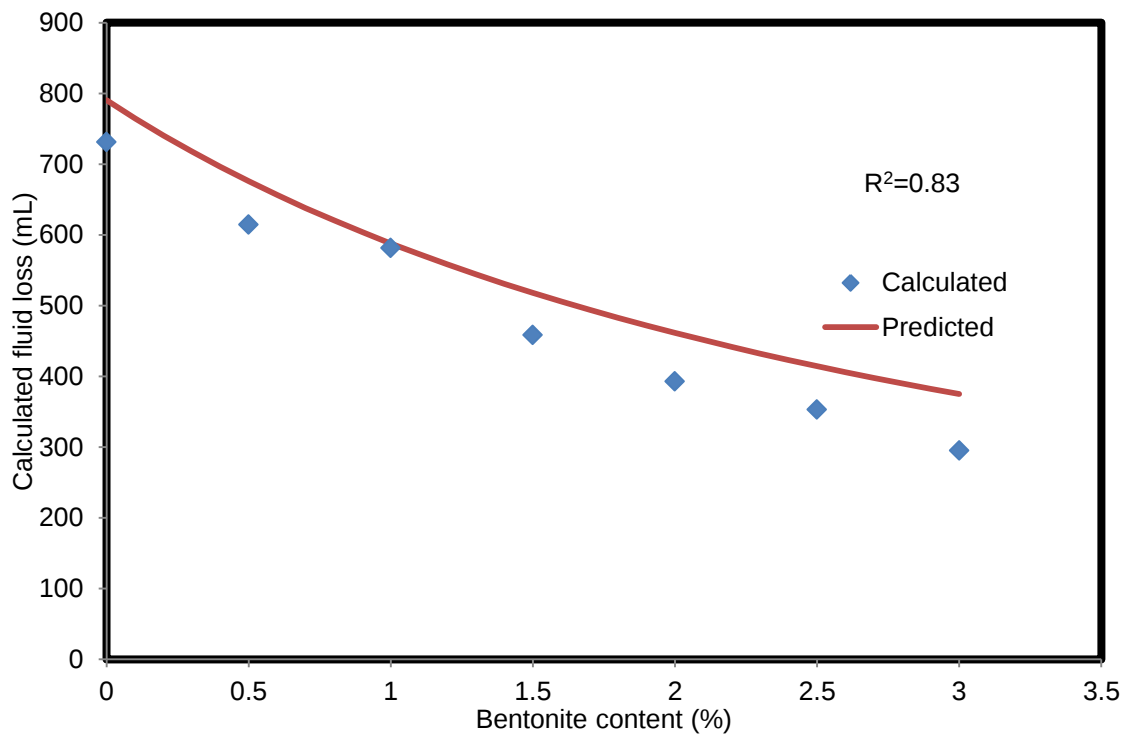
which takes into account the pressure and bentonite content to predict the calculated API fluid loss. Fluid loss was then predicted using the proposed model and the calculated fluid loss based on laboratory measurements was compared to the predicted fluid loss values to investigate the accuracy of the model. The calculated vs. predicted values for bentonite contaminated cement is presented in Figs 5.14 through 5.17.



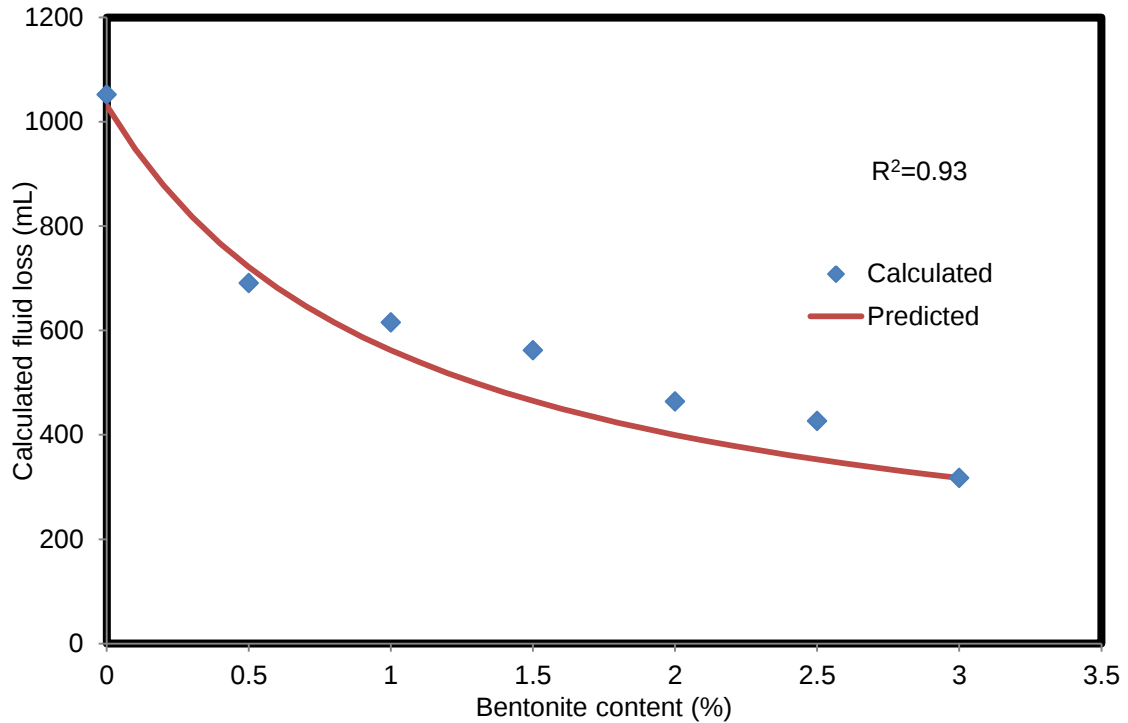
**Figure 5-14 - Calculated vs. predicted fluid loss for oil well cement contaminated with bentonite at 100 psi**



**Figure 5-15 - Calculated vs. predicted fluid loss for oil well cement contaminated with bentonite at 100 psi**



**Figure 5-16 - Calculated vs. predicted fluid loss for oil well cement contaminated with bentonite at 100 psi**



**Figure 5-17 - Calculated vs. predicted fluid loss for oil well cement contaminated with bentonite at 100 psi**

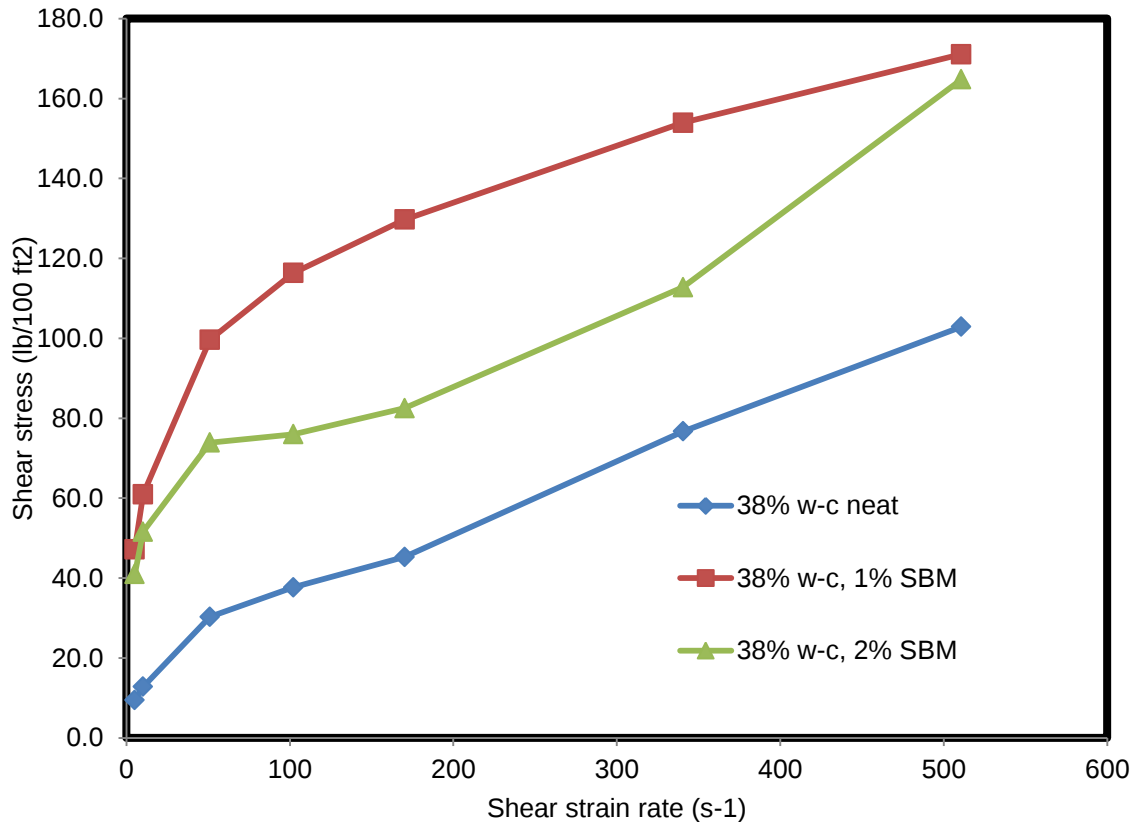
### **5.3 Effect of Synthetic Based Drilling Fluid Contamination on Oil Well Cement**

All cement specimens were mixed with water to cement ratio of 38%. The two types of cement samples included neat cement and contaminated cement with 1% and 2% SBM. Effects of SBM contamination were evaluated by comparing different properties of neat and contaminated slurries. Evaluated properties included rheology, fluid loss, filter cake permeability, 24 hour compressive strength, and ultrasonic pulse velocity.

#### **5.3.1 Rheological Properties**

Effect of SBM contamination on oil well cement slurry is shown in Fig 5.18. As represented, addition of SBM to cement increased the shear stress at all

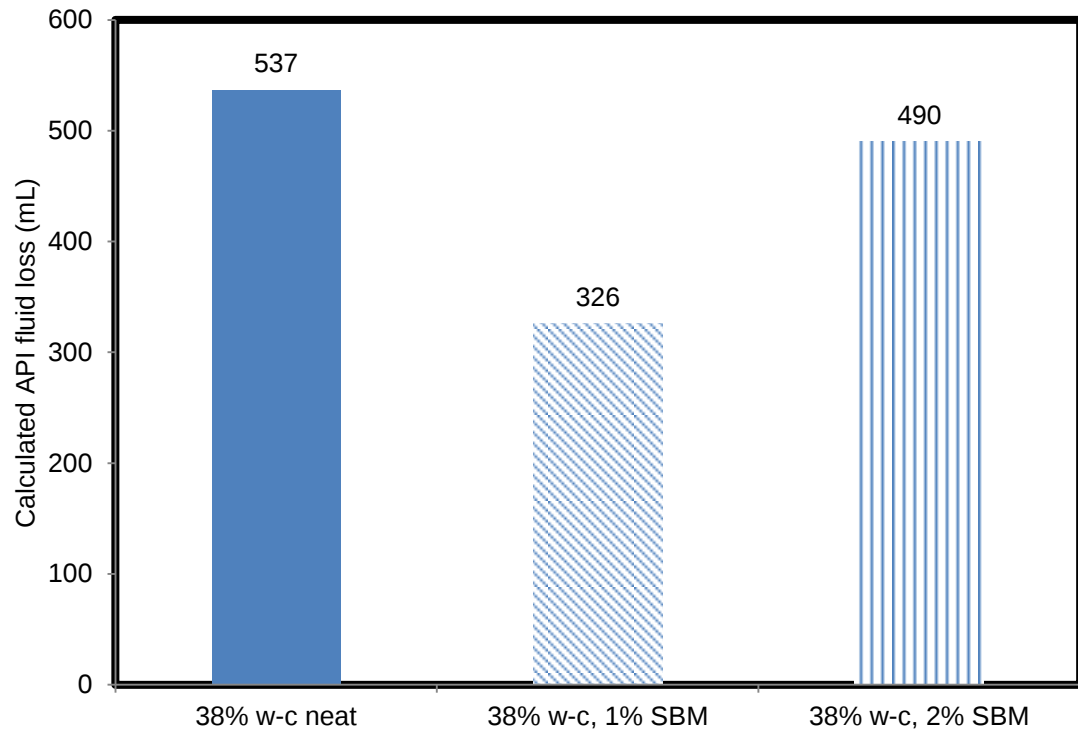
tested shear strain rates. 1% SBM increased the rheological properties more significantly compared to the 2% SBM.



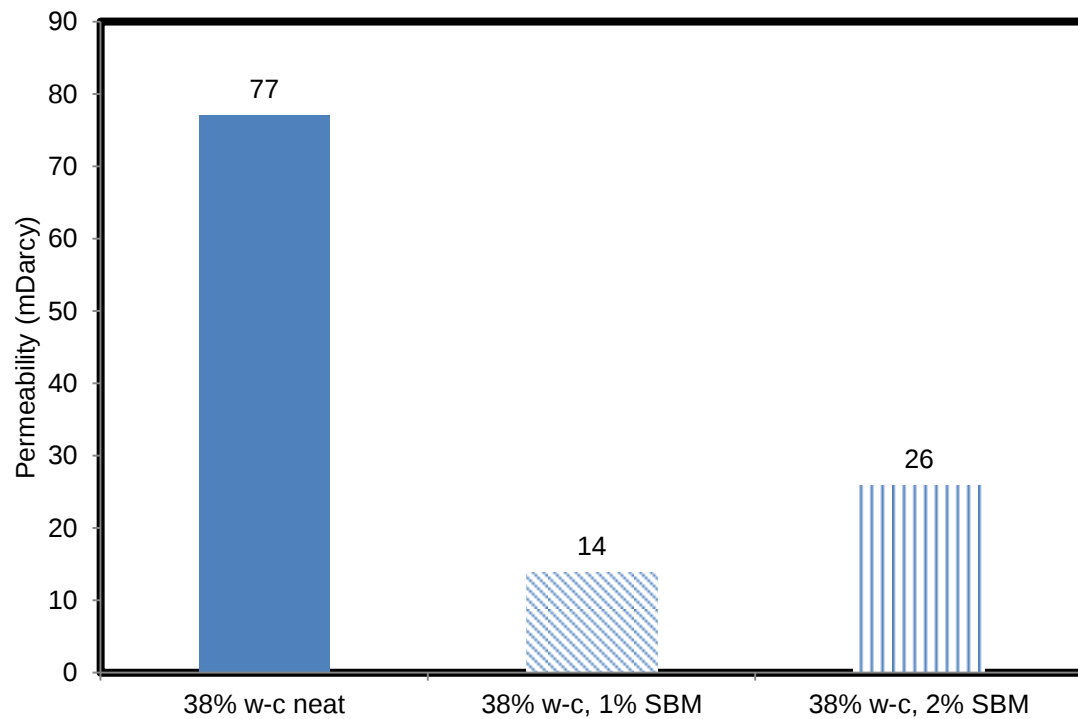
**Figure 5-18 - Effect of SBM contamination on the rheology of oil well cement**

### 5.3.2 Fluid Loss and Filter Cake Permeability

Fig 5.19 and 5.20 represent the effect of SBM contamination on fluid loss and filter cake permeability of oil well cement, respectively. It is shown that adding 1% and 2% SBM to cement slurries reduced the fluid loss by 39% and 9%, respectively. In addition, the filter cake permeability of cement was reduced by 82% and 66% when 1% and 2% SBM was added to the sample. The reduction in the permeability of the filter cake was the major reason for lower fluid loss in the contaminated samples.



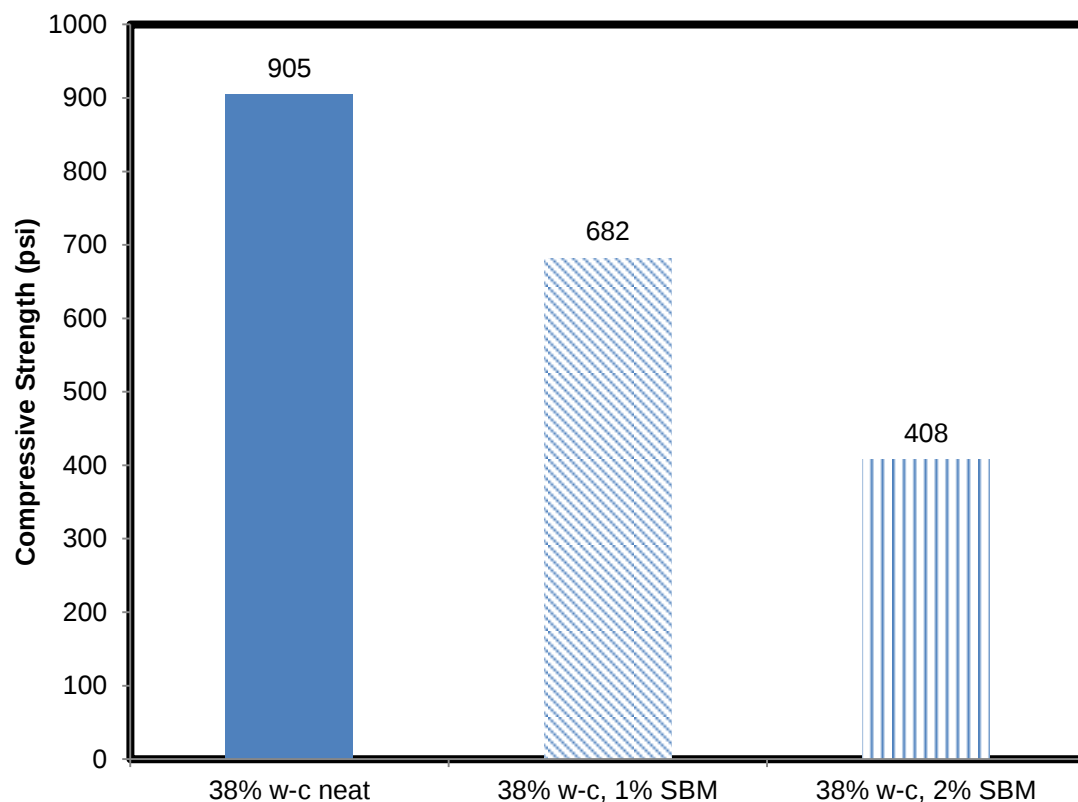
**Figure 5-19 - Effect of SBM contamination on fluid loss of cement at 100 psi**



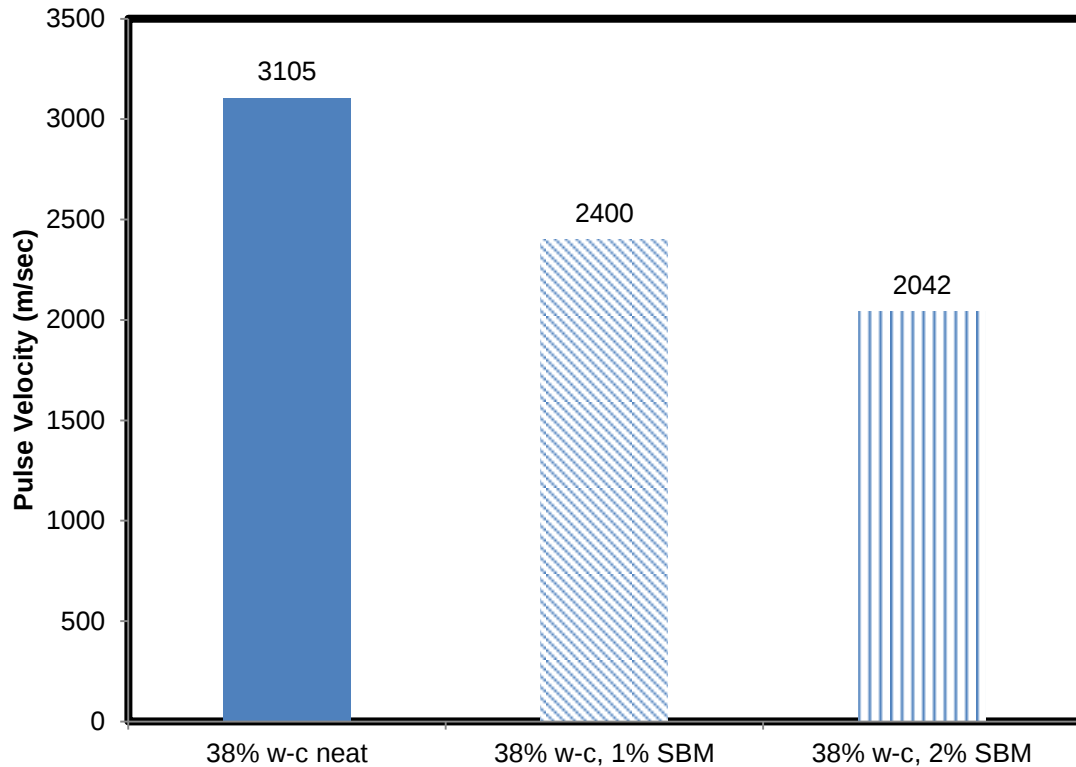
**Figure 5-20 - Effect of SBM contamination on permeability of filter cake in cement samples**

### 5.3.3 Compressive Strength and Ultrasonic Pulse Velocity

Fig 5.21 and 5.22 represent the compressive strength and ultrasonic pulse velocity of contaminated and uncontaminated samples after 24 hours. Adding 1% and 2% SBM, reduced the compressive strength of samples by 25% and 55%, respectively. The 1% and 2% SBM contamination also reduced the pulse velocity by 23% and 34%, respectively. The reduction in pulse velocity showed the increased porosity in the cement samples, which resulted in reduced compressive strength.



**Figure 5-21 - Effect of SBM contamination on 24 hour compressive strength of cement samples**



**Figure 5-22 - Effect of SBM contamination on ultrasonic pulse velocity of cement samples after 24 hours of curing**

## 5.4 Summary

In this chapter, the effects of salt, water based mud, and synthetic based mud was evaluated on different properties of oil well cement. Based on the tests results and analyses, the following observations are advanced:

- 1 Salt contamination increased the fluid loss as well as the compressive strength of cement. Salt also decreased the electrical resistivity of cement; hence measuring electrical resistivity of cement during cementing operations can enable the operator to determine the salt contamination.
- 2 Bentonite reduced the fluid loss of cement, while decreased the compressive strength by up to 63%. A hyperbolic model was developed to predict the effect of bentonite on fluid loss of cement at various pressures.

- 3 Synthetic based mud increased the rheology of cement, which leads to pumping issues. In addition, the compressive strength of SBM contaminated samples were up to 55% lower compared to uncontaminated samples. However, SBM reduced the fluid loss of slurries as well as water permeability of filter cake.

## CHAPTER 6

### SELF-HEALING CEMENT

Production zone cement sheath is subjected to high pressures induced by perforating charges to enable the hydrocarbons to enter the wellbore (Yao & Hua, 2007). This pressure may develop cracks and microannuli in the cement and negatively affect the wellbore integrity. Different self-healing cement systems have been developed to reduce the risk of cement failure in the wellbore. Traditionally, such systems utilize additives that are capable of swelling when exposed to certain fluids and shutting off the flow path in the cracked cement. The problem with these kinds of compositions is the long time it takes for self-healing process to take place. In addition, these additives swell only in presence of certain fluids which reduces the effectiveness of self-healing properties of cement (Reddy, Liang, & Fitzgerald, 2009; Browning, Duffy, Graugler, & Jones, 2012).

In this study, an oil well cement composition has been developed which is capable of self-healing cracks in cement in few minutes after being exposed to the hydraulic fracturing fluid. This technology utilizes acrylamide-based grout components as additives in cement and fracking fluid. After perforating operations, hydraulic fracturing fluids are used to stimulate the well into production by initiating or expanding fractures in the formation. Cracked cement in the perforating zone is exposed to the fracking fluid. This phenomenon was taken into consideration for proposing the self-healing technique. The three

components of the grout are found in cement and fracking fluid and once they are exposed to each other, the polymer gel forms.

Two series of laboratory tests were performed, first to ensure that the grout components have no negative effect on the rheology, fluid loss, and mechanical strength of cement and do not thicken the fracking fluid. Second series of tests evaluated the effectiveness of the proposed self-healing technique, by comparing the properties of damaged cement before and after exposing to fracking fluid. The second series of tests included the following two investigations:

- Measuring the permeability of cement after curing, after cracking under tensile stress, and after exposing the cracked sample to the proposed fracking fluid.
- Measuring the compressive strength of cement after 24 hours of curing, and after exposing the cracked sample to the proposed fracking fluid.

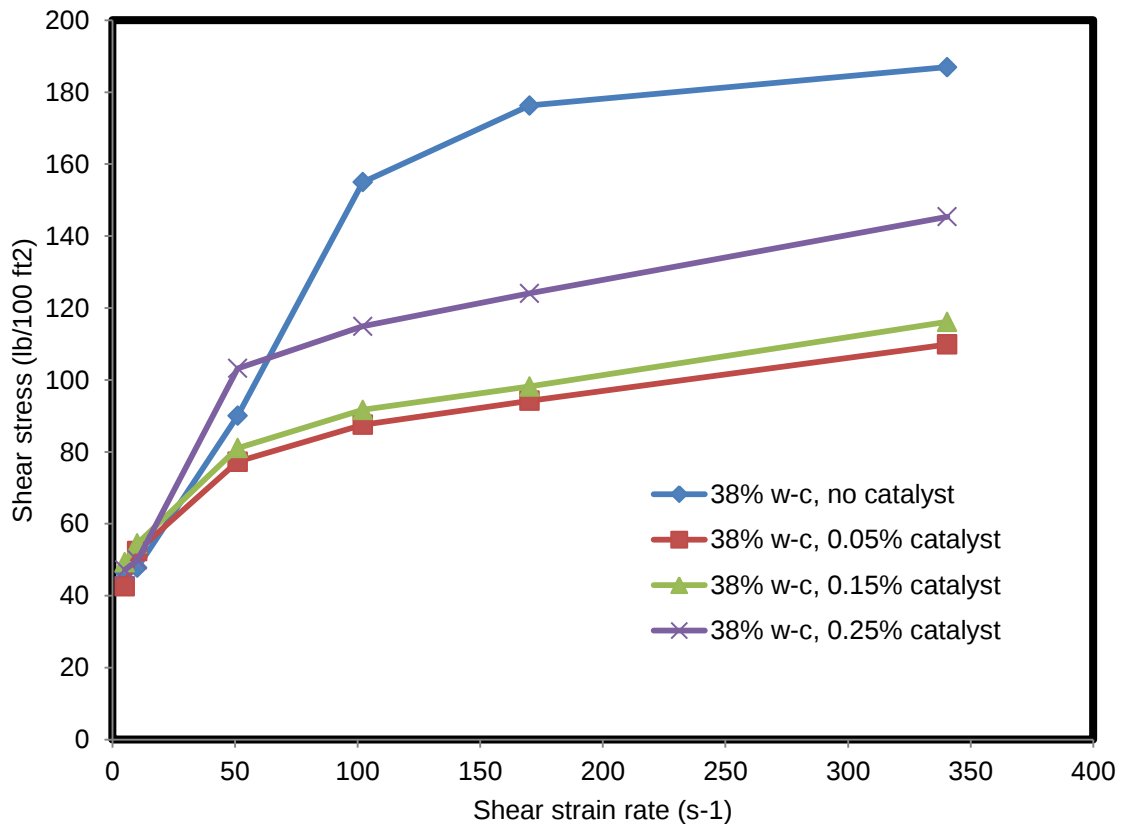
The results were then compared, and the effect of proposed technique to provide self-healing cement was investigated.

## **6.1 Sample Preparation**

API class H cement with water to cement ratio of 0.38, and 0.5% bentonite content (BWOC) was used in all specimens. AV-101 was solved in water and then added to the cement slurries. The cement samples included 0.0%, 0.05%, 0.15%, and 0.25% AV-10. A 7% water solution of AV-100 with 0.2% AV-102 was used as the fracking fluid.

## 6.2 Rheology

Figure 6.1 shows the rheology of cement with and without AV-101. Cement containing bentonite with no catalyst showed the highest rheology. Adding AV-101 reduced the shear stress by up to 44% and 41% at  $170.2 \text{ s}^{-1}$  and  $340.5 \text{ s}^{-1}$ , respectively.



**Figure 6-1 - Effect of AV-101 (catalyst) on the rheology of oil well cement containing 0.5% bentonite**

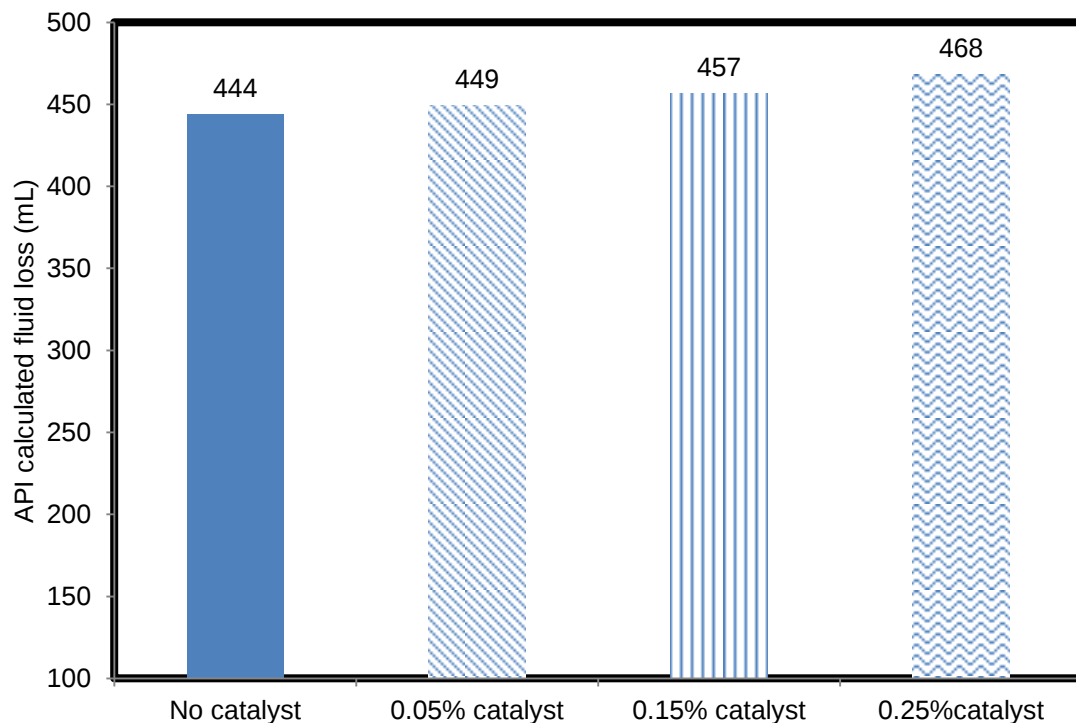
Table 6.1 represents the effect of grout components on the rheology of fracking fluid. Shear stress at 0 shear strain rate was extrapolated based on the behavior of material at higher shear strain rates. It was shown that AV-100 and AV-102 did not affect the rheology of water significantly.

**Table 6-1 - Comparison between the rheology of water and proposed fracking fluid**

| Rheological Property                                                                   | Tap Water | Proposed Fracking Fluid |
|----------------------------------------------------------------------------------------|-----------|-------------------------|
| Viscosity (cP)                                                                         | 0.95      | 1.2                     |
| Yield stress - Calculated shear stress at 0 shear strain rate (lb/100ft <sup>2</sup> ) | 0.0       | 0.0                     |

### 6.3 Fluid Loss

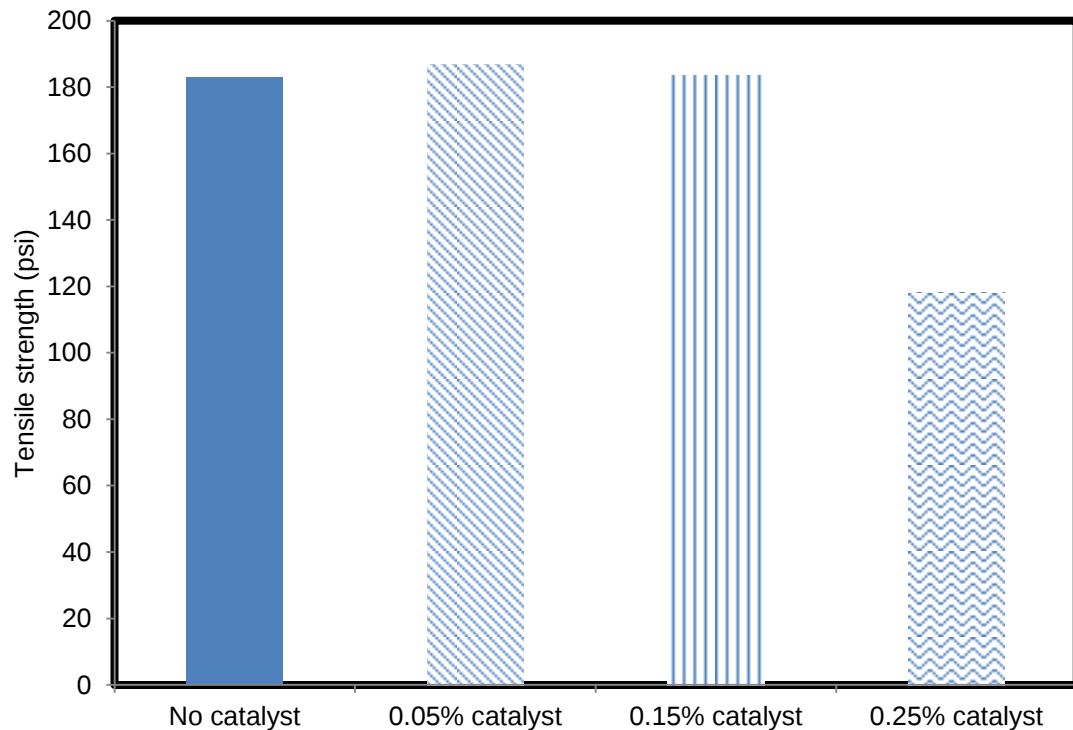
Fig 6.2 represents the fluid loss of cement samples with and without catalyst. It was shown that AV-101 did not affect the fluid loss of cement significantly. The maximum fluid loss occurred for the samples containing catalyst was 5% higher than the control sample.



**Figure 6-2 - Effect of catalyst on fluid loss of cement at 100 psi**

## 6.4 Mechanical Properties

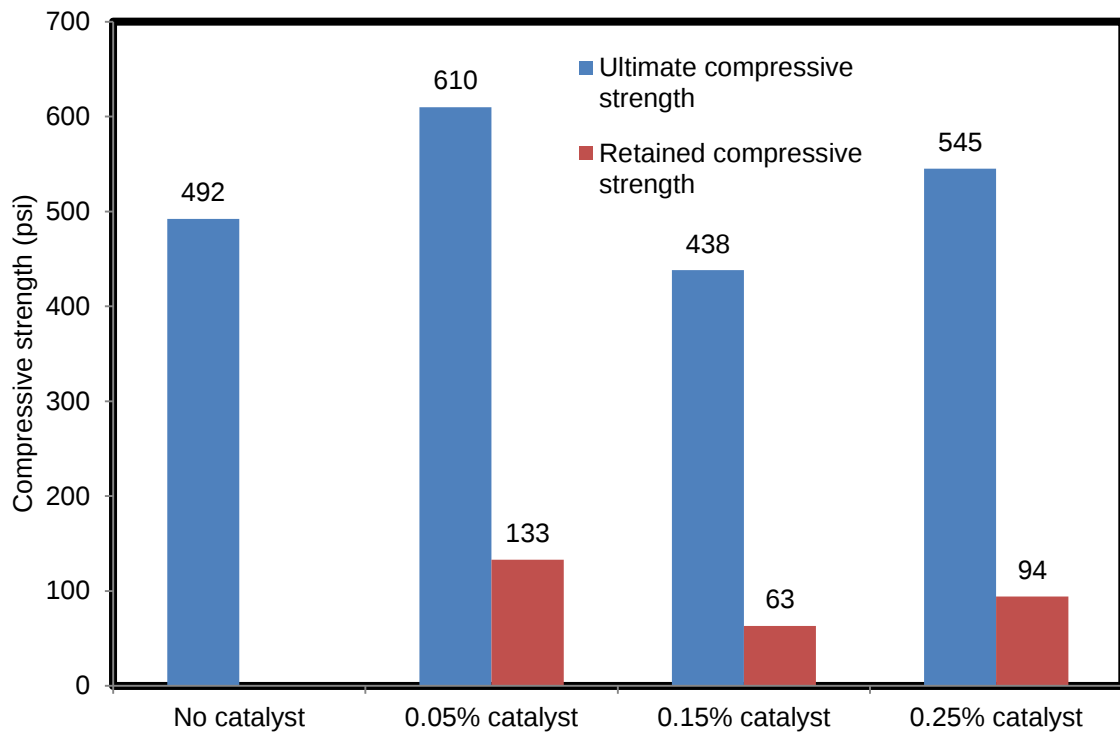
Fig 6.3 represents the split tensile strength of cement samples after 24 hours of curing. Adding up to 0.15% catalyst did not affect the tensile strength significantly; however it was shown that adding 0.25% catalyst reduced the tensile strength of cement by 35%.



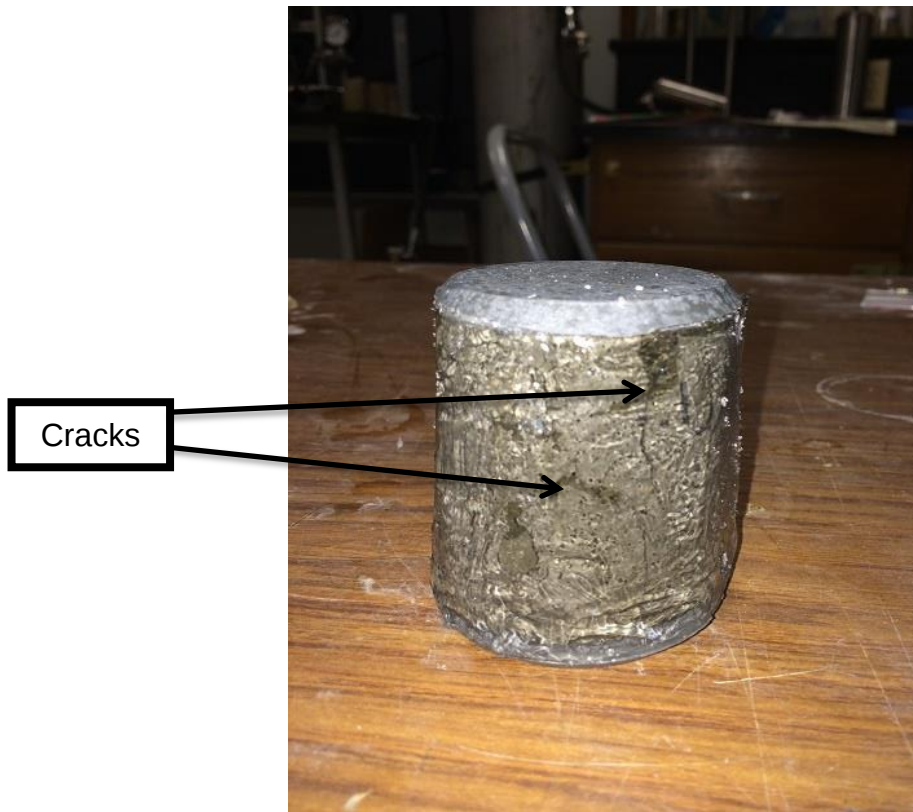
**Figure 6-3 - Tensile strength of cement after 24 hours of curing with and without catalyst**

Fig 6.4 represents the 24 hour compressive strength of samples at two stages, after curing and after exposing cracked cement to the proposed fracking fluid. Adding 0.05% and 0.25% catalyst to cement increased the compressive strength by 7% and 11%, respectively, while adding 0.15% catalyst decreased the compressive strength by 11%. The cracked samples retained up to 22% of their initial compressive strength after being exposed to the fracking fluid. Also,

the ultimate axial strain at the time of failure was higher than 1.0% for all self-healed samples which indicates the effectiveness of the polymer to increase the elasticity of cracked cement. The gelation time of the polymer varied between 45 to 75 minutes and was shorter for samples with higher concentration of AV-101. It should be mentioned that the difference in retained strength maybe due to the crack formations and not the AV-101 content, since the strength of the polymer gel is mainly dependent on AV-100 concentration. Fig. 6.5 shows the gel formed in a cracked cement sample after being exposed to the fracking fluid.



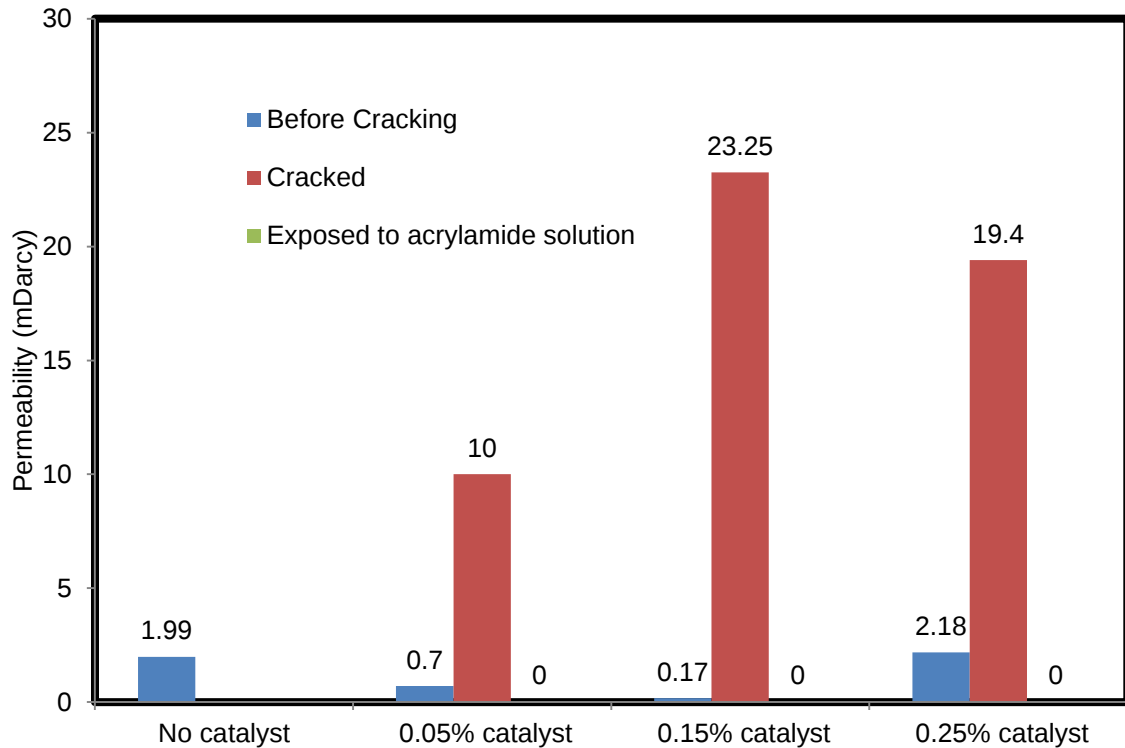
**Figure 6-4 - 24 hour compressive strength of cement samples after curing and after exposure to fracking fluid**



**Figure 6-5 - Formed polymer gel in cracked cement sample after being exposed to the fracking fluid**

## **6.5 Permeability**

Fig 6.6 represents the permeability of samples after curing, after cracking, and after exposure to the fracking fluid. It showed that the formed polymer gel decreased the permeability of all samples to zero. After cracks are induced in the sample, the proposed fracking fluid was injected in the cement. This results in formation of the polymer gel, which is impermeable. The impermeable gel fills the paths and does not allow water to pass through the sample. This results in zero water flow and water permeability.



**Figure 6-6 - Permeability of cement samples after curing, after cracking and after exposing to fracking fluid**

## 6.6 Summary

A self-healing cement system was proposed by using components of acrylamide polymer. The following observations were advanced in this study:

- 1 It was shown that addition of AV-101 to cement sample lowered the rheological properties of samples at both high and low shear rates. Also fluid loss of cement did not change significantly by adding the polymer component. AV-101 increased the compressive strength of samples by up to 10% and decreased the permeability by up to 91%.
- 2 Hardened cement samples retained up to 22% of their compressive strength and yielded zero permeability after exposure to fracking fluid.

- 3 Setting time of polymer gel was up to 77% shorter when the fracking fluid was injected in the samples. Also Higher concentration of AV-101 reduced the gelation time of polymer by 32%.

## CHAPTER 7

### CONCLUSIONS AND RECOMMENDATIONS

#### 7.1 Conclusions

This study focused on characterizing and developing smart oil well cement to provide wellbore integrity and enable the operators to manage the conventional issues related to well cementing operations. Additives such as polycarboxylate and nanoclay were evaluated. Also the properties of contaminated cement with salt, water based and synthetic based mud was investigated. In addition, measuring electrical properties of cement was proposed as a technique to characterize liquid and hardened slurry. In order to provide well integrity for hydraulic fractured wells, a cementing system was proposed to provide self-healing cement system. Based on the investigations of this study, the following conclusions can be drawn:

- 1 Nanoclay increased the rheology of oil well cement while decreased the fluid loss by up to 64%. The samples containing nanoclay showed lower filter cake permeability of up to 86%. In addition, nanoclay increased the 24 hour compressive strength of samples by up to 71%.
- 2 Polycarboxylate can be used as a superplasticizer in oil well cement. Laboratory tests showed that adding polycarboxylate decreased the rheology of oil well cement with water to cement ratio of 30% and 33%. Also adding polycarboxylate reduced the fluid loss and filter cake permeability of cement samples by up to 96% and 99%. A thin almost impermeable layer of filter cake was formed when 0.6% of polycarboxylate was used. However,

- polycarboxylate reduced the 7 day and 30 day compressive strength of samples by 16% and 14%, respectively.
- 3 Electrical measurements of curing cement showed that the electrical resistivity had a decreased trend during the first on hour of curing and had an increasing trend afterward. Cement samples with higher changes in normalized electrical resistivity at the time of compressive test showed higher mechanical properties.
  - 4 It was shown that cement samples including carbon fiber had piezoresistive behavior, which enables the operator to predict the amount of applied pressure on the cement column by measuring the electrical resistivity.
  - 5 It was shown that salt contamination decreased the rheology of cement while increased the 24 hour compressive strength by up to 54%. Also the electrical resistivity of salt contaminated samples was up to 86% percent lower compared to the control sample. Salt contamination did not affect the fluid loss significantly.
  - 6 Bentonite decreased the fluid loss at 100, 200, 300, and 400 psi. The calculated API fluid loss for samples including bentonite was up to 259% lower compared to control sample. Bentonite also reduced the gas permeability of samples by up to 44%. Adding 0.5% and 2% bentonite decreased the 24 hour compressive strength by 43% and 63%, respectively.
  - 7 A constitutive model was developed to predict the fluid loss of cement based on bentonite content and applied pressure.

- 8 Synthetic based mud contamination decreased the rheology and fluid loss of cement. Samples including 1% and 2% SBM showed 39% and 8% lower fluid loss, respectively. SBM contamination had negative impact on mechanical properties of cement slurry. 24 hour compressive strength of cement was 25% and 55% lower by adding 1% and 2% SBM, respectively.
- 9 The proposed self-healing cement restored up to 22% of initial compressive strength and yielded zero permeability. The components did not have significant negative effect of properties of liquid and hardened cement slurry.

## **7.2 Recommendations**

The following recommendations can be drawn from the study:

- 1 Measuring electrical resistivity during the curing of oil well cement enables the operator to predict curing stages as well as applied pressure on the cement column.
- 2 By implementing unconventional additives such as polycarboxylate and nanoclay, lower rheology and fluid loss can be achieved which aids in pumping cement and preventing lost circulation in cementing operations.
- 3 Contamination of oil well cement with drilling fluids may have disastrous results. Using an effective spacer and monitoring the cement may reduce the negative impacts of contamination.
- 4 Proposed self-healing technique can be used to provide wellbore integrity and reduce the damages of perforation on the cement column.

### **7.3 Future Work**

Based on the derived laboratory results in this study, the following future works can be performed to extend this work:

- 1 A numerical model can be developed to investigate and quantify the effects of bentonite and pressure on fluid loss of oil well cement.
- 2 A finite element model can be developed to predict the rheology of cement with unconventional additives at certain shear strain rates and evaluated using the present laboratory results.
- 3 A numerical model can be developed to investigate and quantify the piezoresistive behavior of modified oil well cement by using the present piezoresistivity results.
- 4 To extend the self-healing cement system, a model can be developed to quantify the effects of polymer components on retained mechanical strength and find the optimum amount based on conditions and objectives.

## REFERENCES

- Allen, T. E., & Sands, F. L. (1993). Why Control Cement Slurry Density. *SPE* 25324 (pp. 117 - 125). Signapore: Society of Petroleum Engineers.
- Azar, J. J., & Samuel, G. R. (2007). *Drilling Engineering*. Tusla: PennWell Corporation.
- Backe, K. R., Lile, O. B., & Lyomov, S. K. (2001). Characterizing Curing Cement Slurries by Electrical Conductivity. *SPE Drilling and Completion*, 201 - 207.
- Backe, K. R., Skalle, P., Lile, O. B., Lyomov, S. K., Justnes, H., & Sveen, J. (1998). Shrinkage of Oil Well Cement Slurries. *Journal of Canadian Petroleum Technology*, 37(09), 63-67. doi:<http://dx.doi.org/10.2118/98-09-06>
- BakerHughes. (2010). Max-Bridge - Costomized Bridging Technology. Baker Hughes. Retrieved 6 17, 2014, from [http://assets.cmp.bh.mxmccloud.com/system/a882c6a369f01211f9082c481a69ca73\\_30059-max-bridge\\_brochure-0810.pdf](http://assets.cmp.bh.mxmccloud.com/system/a882c6a369f01211f9082c481a69ca73_30059-max-bridge_brochure-0810.pdf)
- Bannister, C., & Lawson, V. (1985). Role of Cement Fluid Loss in Wellbore Completion. *SPE* 14433 (pp. 1-13). Las Vegas: Society of Petroleym Engineer.

- Bermudez, M. (2007). Effect of Sugar on the Thickening Time of Cement Slurries. *SPE Annual Technical Conference and Exhibition* (pp. 1 - 7). Anaheim: Society of Petroleum Engineers.
- Bingham, E. C. (1922). *Fluidity and Plasticity*. New York: McGraw.
- Boughton, L. D., Pavlich, J. P., & Wahl, W. W. (1962). The Use Of Dispersants In Cement Slurries To Improve Placement Techniques. Los Angeles: Society of Petroleum Engineers.
- Browning, R., Duffy, M., Graugler, D., & Jones, P. (2012). Effectiveness of self-Healing Cement Additives Based on Test Methodology Using Simulated Cement Sheath Cracks. Lexington: Society of Petroleum Engineers.
- Bruckdorfer, R., & Gleit, A. (1988). Static Fluid Loss Mode. *Society of Petroleum Engineers*, 1-20.
- Caritey, J.-P., & Brady, J. (2013). Performance of Thermal Cements with Different Weighting Materials. *SPE/IADC Drilling Conference* (pp. 1 - 9). Amsterdam: Society of Petroleum Engineers.
- Chenevert, M. E., & Shrestha, B. K. (1991). Chemical Shrinkage Properties of Oilfield Cements. *SPE Drilling Engineering*, 37 - 43.
- Chung, D. (2002). Piezoresistive Cement-based Materials for Strain Sensing. *Intelligent Material Systems and Structures*, 1-12.

- Coveney, P. V., & Humphries, W. (1996). Molecular Modelling of The Mechanism of Action of Phosphonate Retarders on Hydrating Cements. *Journal of Chemical Society*, 92, 831 - 841.
- Devold, H. (2013). *Oil and Gas Production Handbook, An Introduction to Oil and Gas Production, Transport, Refining and Petrochemical Insudtry*. Oslo: ABB Oil and Gas.
- Eoff, L. S., & Doug, B. (1995). High Temperature Synthetic Cement Retarder. *SPE International Symposium on Oilfield Chemistry - SPE 28957* (pp. 129 - 136). San Antonio: Society of Petroleum Engineers.
- Garg, T., & Gokavarapu, S. (2012). Lessons Learnt From Root Cause Analysis of Gulf of Mexico Oil Spill 2010. *SPE 163276* (pp. 1 - 11). Kuwait City: Society of Petroleum Engineers.
- Guillot, D. (2006). Rheology of Oil Well Cement. In G. E.B. Nelson (ED), *Well Cementing* (pp. 93-142). Texas: Schlumberger.
- Heikal, M., Morsy, M., & Aiad, I. (2005). Effect of Polycarboxylate Superplasticizer on Hydration Characteristics of Cement Pastes Containing Silica Fume. *CERAMICS SILIKATY*, 50(1), 5 - 14.
- Heinold, T., Dillenbeck, R. L., & Rogers, M. J. (2002). The Effect of Key Cement Additives on the Mechanical Properties of Normal Density Oil and Gas Well Cement Systems. *SPE 77867* (pp. 1 - 12). Melbourne: Society of Petroleum Engineers.

- Iverson, B., Darbe, R., & McMechan, D. (2008). evaluation of Mechanical Properties of Cements. *ARMA-08-293* (pp. 1 - 7). San Francisco: American Rock Mechanics Association.
- Jenkins, R. J. (1966). Accuracy of Porosity Determinations. *The Log Analyst*, 7(02).
- Joshi, R. C., & Lohita, R. P. (1997). *Advances in Concrete Technology, 2, Fly Ash in Concrete: Production, Properties and Uses*. Amsterdam: Gordon and Breach Science Publishers.
- Justnes, H., Loo, D., Reyniers, B., Skalle, P., Sveen, J., & Sellevold, E. J. (1995). Chemical Shrinkage of Oil Well Cement Slurries. *Advances in Cement Research*, 85-90.
- Lowrie, W. (2007). *Fundamentals of Geophysics*. Cambridge: Cambridge University Press.
- Makarkia, S., & Vipulanandan, C. (1992). Compressive Behavior of Glass-Fiber-Reinforced Polymer Concrete. *Journal of Materials in Civil Engineering*, 4(1), 91 - 105.
- McDaniel, J., Watters, L., & Shadravan, A. (2014). Cement Sheath Durability: Increasing Cement Sheath Integrity to Reduce Gas Migration in the Marcellus Shale Play. *SPE Hydraulic Fracturing Technology* (pp. 1-13). The Woodlands: Society of Petroleum Engineers.

- McElfresh, P. M., & Boncan, V. C. (1982). Applications of Foam Cement. *SPE 11203*. New Orleans: Society of Petroleum Engineers.
- Michaux, M., Nelson, E., & Vidick, B. (1989, April). Cement Chemistry and Additives. *Oilfield Review*. Schlumberger. Retrieved 6 23, 2014, from Slumberger:  
[http://www.slb.com/~media/Files/resources/oilfield\\_review/ors89/apr89/2\\_cement.pdf](http://www.slb.com/~media/Files/resources/oilfield_review/ors89/apr89/2_cement.pdf)
- Mueller, D. T. (1992). Performance Characteristics of Vinylsulfonate-Based Cement Fluid-Loss Additives. *SPE Rocky Mountain Regional Meeting* (pp. 609 - 617). Casper: Society of Petroleum Engineers.
- Myers, S. H., El Shaari, N. A., & Dillenbeck, R. L. (2005). A New Method to Evaluate Cement Systems Design Requirements for Cyclic Steam Wells. *SPE Western Regional Meeting*. Irvine: Society of Petroleum Engineers.
- Nelson, E. (1990). Well Cementing. New York: Elsevier Science Publishing Co.,Inc.
- Patil, R., & Deshpande, A. (2012). Use of Nanomaterials in Cementing Applicaions. *SPE 155607* (p. 4). Noordwijk: Society of Petroleum Engineers.
- Plank, J. (2011). *Oil Well Cementing*. Retrieved June 11, 2014, from Technische Universität München: <http://www.bauchemie-tum.de/master-framework/?p=Tief&i=13&m=1&lang=en>

Plank, J., Lummer, N. R., Dugonjic-Bilic, F., & Sadasivan, D. (2009).

Comparative Study of the Working Mechanisms of Different Cement Fluid Loss Polymers. *SPE International Symposium on Oilfield Chemistry* (pp. 1 - 26). The Woodlands: Society of Petroleum Engineers.

Qizhao, M., Binyuan, Z., Darong, S., & Zhuoqiu, L. (1996). Resistance Changement on Compression Sensible Cement Speciment under Different Stresses. *Wuhan University of Technology*, 11, 41 - 45.

Ramos, R. (1992). Thickening Time Measure To Simulate Cementing Operations on Deepwater Wells: Field Laboratory Validation. *Offshore Technology Conference* (pp. 751-756). Houston: Offshore Technology Conference.

Reddy, B. R., Liang, F., & Fitzgerald, R. (2009). Self-healing Cements that Heal without Dependence on Fluid Contact. Woodlands: Society of Petroleum Engineers.

Reddy, B., Santra, A. K., McMechan, D. E., Gray, D. W., Brenneis, C., & Dunn, R. (2005). Cement Mechanical Property Measurements Under Wellbore Conditions. *SPE 95921* (pp. 1-8). Dallas: Society of Petroleum Engineers.

Rocka, L. A., Falcao, J. L., Goncalves, C. J., Toledo, C., Lobato, K., Leal, S., & Lobato, H. (2004). Fracture Pressure Gradient in Deepwater. *IADC/SPE 88011* (p. 10). Kuala Lumpur: IADC/SPE Asia Pacific Drilling Technology.

- Sabins, F. L., Tinsley, J. M., & Sutton, D. L. (1982). Transition Time of Cement Slurries Between the Fluid and Set States. *Society of Petroleum Engineers*, 875 - 882.
- Samsuri, A., Junin, R., & Osman, A. M. (2001). The Utilization of Malaysian Local Bentonite as an Extender and Free Water Controller in Oil-Well Cement Technology. *SPE Asia Pacific Oil and Gas Conference* (pp. 1 - 5). Jakarta: Society of Petroleum Engineers.
- Shahriar, A. (2011). Investigation on Rheology of Oil Well Cement Slurries. *PhD Thesis*. Ontario, Canada: University of Western Ontario.
- Shi, Z.-Q., & Chung, D. (1999). Carbon Fiber-Reinforced Concrete for Traffic Monitoring and Weighing in Motion. *Cement and Concrete Research*, 435 - 439.
- Smith, D. (1990). *Cementing*. New York: Society of Petroleum Engineers Inc.
- Thiercelin, M., Dargaud, B., & Baret, J. (1998). Cement Design Based on Cement Mechanical Response. *SPE Drilling and Completion*, 266 - 273.
- Thomas, J., Jennings, H., & Chen, J. (2009). Influence of Nucleation Seeding on the Hydration Mechanisms of Tricalcium Silicate and Cement. *Journal of Physical Chemistry*, 4327 - 4334.
- Topcu, I. B., Uygunoglu, T., & Hocaoglu, I. (2011). Electrical Conductivity of Setting Cement Paste with Different Mineral Admixtures. *Construction and Building Materials*, 414 - 420.

Vipulanandan, C., & Garas, V. (2008). Electrical Resistivity, Pulse Velocity and Compressive Properties of Carbon Fiber Reinforced Cement Mortar.

*Materials in Civil Engineering*, 20, 93 - 101.

Vipulanandan, C., Krishnamoorti, R., Saravanan, R., Liu, J., Qu, Q., Narvaez, G.

G., Pappas, J. M. (2014). Development and Characterization of Smart Cement for Real Time Monitoring of Ultra Deepwater Oil Well Cementing Applications. *Offshore Technology Conference* (pp. 1 - 12). Houston: Offshore Technology Conference.

Yahaba, N. (2010). How Does a Decrease in Oil Production Affect the World Economy? *Asia Pacific Economy*, 5.

Yao, X., & Hua, S. D. (2007). Design of a Novel Composite Agent for Improving the Toughness of Oilwell Cement Sheath. Houston: Society of Petroleum Engineers.

Zomorrodian, M., & Vipulanandan, C. (2013, 02 08). Effect of Salt Contamination on the Fluid Loss, Early Strength and Piezoresistive Response of Class H Oil Well Cement. *Conference Poster*. Houston, Texas: Texas Hurricane Center.

