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## Investigation on Rheology of Oil Well Cement Slurries

Anjuman Shahriar, *University of Western Ontario*

Supervisor: Dr. Moncef Nehdi, *The University of Western Ontario*

A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Civil and Environmental Engineering

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INVESTIGATION ON RHEOLOGY OF OIL WELL CEMENT SLURRIES

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by

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Graduate Program in Engineering Science  
Department of Civil and Environmental Engineering

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
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The School of Graduate and Postdoctoral Studies  
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London, Ontario, Canada

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requirements for the degree of  
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## ABSTRACT

The rheology of oil well cement (OWC) slurries is generally more complicated than that of conventional cement paste. In order to contend with bottom hole conditions (wide range of pressure and temperature), a number of additives are usually used in the OWC slurries, which exhibit different characteristics depending on the combination of admixture used. The objective of this research is to develop a fundamental understanding of the important mechanisms that affect the rheology of OWC slurry incorporating various chemical and mineral admixtures. The partial replacement of OWC using different mineral admixtures, offers both environmental and economic benefits.

The mechanisms underlying the effects of chemical admixtures on the rheology of OWC slurry were investigated at different temperatures using an advanced shear-stress/shear-strain controlled rheometer. The compatibility and interactions between the binder and chemical admixtures were explored. It was found that the rheological properties of OWC slurries are highly dependent on the temperature, water/cement ratio, and the admixture used. Coupled effects of temperature and chemical admixtures had a substantial effect on the flow properties of the slurries. The results indicated that current technical data for chemical admixtures need to be validated for oil well cementing; admixtures proven effective in normal cementing work at moderate temperature may become ineffective for oil well cementing at high temperature.

The coupled effects of temperature and supplementary cementing materials (SCMs) on the rheology of OWC slurry were also investigated. Because of differences in their chemical compositions and the mechanisms by which they act, OWC slurries incorporating SCMs exhibit different rheological behaviour than those prepared with pure OWC. It was found that not all SCMs act in similar manner when used as partial replacement for cement. For example, fly ash, owing to its spherical particle shape, reduces the water demand when used. On the other hand, silica fume increased the water demand because of its higher surface area. Results suggested that new generation polycarboxylate-based high-range water reducing admixtures (PCH) improved the rheological properties of all slurries at all temperature tested. However, lower PCH dosage was found to be less efficient in reducing the yield stress or plastic viscosity of OWC slurries when metakaolin (MK) or rice husk ash (RHA) were used

as partial replacement for OWC. PCH was found to enhance the shear thickening behaviour of OWC slurries and the intensity of this behaviour varied with the type and amount of SCM. Such a phenomenon was amplified with metakaolin, reduced by SF, unchanged with FA and showed irregular behaviour with RHA.

Furthermore, new equations were proposed using multiple regression analysis (MRA) and design of experiments (DOE) to predict the Bingham parameters (yield stress and plastic viscosity) of cement slurries prepared in combination with or without SCMs considering various parameters including the ambient temperature, chemical admixture type and dosage, and superplasticizer type and dosage. An artificial neural network (ANN) model was developed to predict the rheological properties of OWC slurries. The results indicated that the predicted rheological parameters for OWC slurries were in good agreement with corresponding experimental results. However, the ANN-based model performed better than the MRA-based model or DOE-based model in predicting the rheological properties of OWC slurries.

**Keywords:** oil well cement, rheology, cement slurry, high temperature, superplasticizer, yield stress, viscosity, thixotropy, fly ash, metakaolin, silica fume, rice husk ash, multiple regression analysis, artificial neural network, design of experiment, modeling.

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This thesis has been prepared in accordance with the specifications of Integrated Article (Formerly Manuscript) format stipulated by the Faculty of Graduate Studies at The University of Western Ontario. All the experimental works were conducted in the Advanced Concrete Technology Laboratory at the University of Western Ontario by the author under the supervision of Prof. Moncef Nehdi. Major portions of the work outlined in this thesis have been published or are under review (see list below) for possible publication in peer-reviewed technical journals and conferences. The author carried out all experimental work, data analysis, modeling process, and writing of the initial draft of all papers listed below. The contribution of her research advisor consisted of providing guidance and supervision, and helping in the development of the final versions of the publications.

### **Refereed Journal Publications**

1. **Shahriar, A.,** and Nehdi, M. (2010) Effect of chemical admixture on rheology of oil well cement slurries. Accepted in Construction Materials, ICE, Jul 2010, 40 p, (ID: COMA-D-10-00023R1).
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3. **Shahriar, A.,** and Nehdi, M. (2011) Modeling rheological properties of oil well cement slurries using artificial neural networks and multiple regression analysis. Submitted to Construction & Building Materials.

4. **Shahriar, A.,** and Nehdi, M. (2011) Artificial intelligence model for rheological properties of oil well cement slurries incorporating supplementary cementitious materials. Submitted to *Advances in Cement Research*.
5. **Shahriar, A.,** and Nehdi, M. (2011) Optimization of Rheological Properties of Oil Well Cement Slurries Using Experimental Design. Submitted to *Cement and Concrete research*.
6. **Shahriar, A.,** and Nehdi, M. (2008) Effect of supplementary cementitious materials on rheology of oil well cement slurries. *Proc. of Annual Conference - Canadian Society for Civil Engineering*, Vol. 3, 10-13 Jun, 1494-1502 (Ph.D. Work)

## **DEDICATION**

I dedicate this thesis to my parents, Salma Begum and Md. Amjad Hossain who have always been a great encouragement for this great achievement, and to my twin baby girls, Saniya and Sabrina and to my husband, Shahria Alam who make my life meaningful and enjoyable.



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## LIST OF NOTATIONS

$\dot{\gamma}$	Shear rate
$\mu$	Viscosity
$\tau$	Shear stress
$\mu_p$	Plastic viscosity
$\tau_0$	Yield stress
$\eta$	Constant slope for Newtonian model
$\mu_\alpha$	Viscosity at infinite shear rate
$W_{ji}^l$	The connection strength between neurons $i$ and $j$ in layers $l$ and $l-1$ , respectively
$a, b$	Model constant
$a, b, c, d, e, f, g,$ and $h$	Regression coefficient
$a_1$ to $a_9$	Model coefficient
AAE	Average absolute error
$a_0$ and $b_0$	The overall mean of the total effect estimates of all factors for yield stress and plastic viscosity, respectively
ANN	Artificial neural network
ANOVA	Analysis of variance
API	American Petroleum Institute
Avg.	Average
$b_1$ to $b_9$	The contribution of the corresponding factor to the response
BWOC	By weight of concrete
BWOW	By weight of water
$c$	Regression constant
CCD	Central composite design
$D_A$	Dosage of admixture
$E_{st}$	System error
$f$	Activation function
FA	Fly ash
HCR	Hydroxylated carboxylic acid-based retarding admixture
HSR	High sulphate-resistant
$I$	Identity matrix

$J$	Jacobian matrix
$J^T$	Transpose matrix of $J$
$K$	Consistency
LSM	Lignosulphonate -based mid-range water reducing admixture
MK	Metakaolin
MRA	Multiple regression analysis
MSR	Moderate sulphate resistant
$n$	Power law exponent
OWC	Oil well cement
$P$	No of training pattern
PCH	New generation polycarboxylate-based high-range water reducing admixture
PCM	Polycarboxylate-based mid-range water reducing admixture
$Prob$	Probability
PV	Plastic viscosity
$R^2$	Correlation coefficient
RA	Rheoplastic solid admixture
RHA	Rice husk ash
SCM	Supplementary cementitious material
$SD$	Standard deviation
SF	Silica fume
SRA	Phosphonate-based set retarding admixture
$T$	Temperature
$T$	Temperature
$Temp$	Temperature
$t_{pk}$ and $o_{pk}$	The predicted output and provided target of pattern $p$ at output unit $k$ , respectively
w/c	water-to-cement ratio
$X_i^{l-1}$	Input at each neuron $J^l$ in layer $l$ in ANN
$Y_j^l$	Output from ANN
YS	Yield stress
$\varepsilon$	Noise or error observed in the responses
$\theta_j^l$	A threshold value assigned to neuron $j$ in layer $l$
$\mu$	Learning rate



## *Chapter 1*

# **INTRODUCTION**

### **1.1 Introduction**

Petroleum production and exploration has a paramount influence on the global economic structure. The world's oil consumption has been increasing day by day. It grew by 171% during the period from 1965 to 2008 (Yahaba, 2010). Over the last two decades, the amount of oil consumption per year has exceeded the amount of newly found oil reserves. Therefore, with time, the possibility of an ultimate decrease in oil production is becoming a realistic scenario. However, the exact amount of undiscovered oil reserves is not well known. Hence, it is difficult to predict when the ultimate decrease in oil production will initiate and affect the overall global economy. The human culture and modern technological society are very much dependent on the earth's oil and chemical feedstock. A significant decrease in oil production may trigger substantial economic hardship, such as a recession or depression due to higher energy prices, unless cost-effective and competitive alternative energy sources will be put in place.

Improper oil and gas well design and well cementing can jeopardise oil production. Oil spills such as the recent Gulf of Mexico deepwater horizon oil spill are some of the causes of oil loss from the global reserve. Besides economic losses, oil spills cause environmental disasters particularly in marine habitats because of toxic substances. The oil industry has been spending billions of dollars to invent more technologically advanced materials and equipment to improve oil extraction and to minimize loss of oil and gas. Nonetheless, the fact remains that it is virtually impossible to solve every new problem that may arise.

Well cementing is the process of placing a cement slurry in the annulus space between the well casing and the geological formations surrounding the well bore in order to provide zonal isolation in oil, gas, and water wells. The goal is to exclude fluids such as water or gas to move from one zone to another zone in the well. Incomplete zonal isolation and/or a weak hydraulic seal between the casing and the cement and between the cement and the formations, may cause oil spills and the well may never run at its full producing potential

(Calvert, 2006). The appropriate cement slurry design for well cementing is a function of various parameters, including the well bore geometry, casing hardware, formation integrity, drilling mud characteristics, presence of spacers and washers, and mixing conditions. The rheological behaviour of oil well cement (OWC) slurries must be optimized to achieve an effective well cementing operation.

Over the last few decades, several types of new chemical admixtures such as superplasticizers, retarders, viscosity modifying admixtures, etc. have been introduced to optimize the flow properties of cement-based products. Early age and hardened properties of cement based systems are highly depended on the type and dosage of chemical admixtures used. The proper selection of chemical admixtures is mainly based on a trial and error procedure using tests such as the Marsh cone flow, mini slump test, and other rheological tests. The performance of chemical admixtures is strongly influenced by the chemical and physical properties of the cement. Most of the commercial chemical admixtures have been used with Ordinary Portland cement and for general purpose use. Therefore, the technical data sheets provided by the manufacturers are not generally applicable for oil well cementing. In order to contend with bottom hole conditions (wide range of pressure and temperature), a special class of cements called OWCs, specified by the American Petroleum Institute (API) (API Specification 10A, 2002) are usually used in the slurry composition. The interactions of OWC with different types of admixtures and the associated cement-admixture compatibility at high temperature are still largely unexplored.

This high cement production to meet the needs of modern urbanization and other industrial purposes is both an ecological and economic concern. The production of one ton of cement releases about one ton of CO<sub>2</sub> into the atmosphere and consumes a substantial amount of energy. In the wake of a potential energy crisis, the threat of global warming, and the increasing cement consumption of a rapidly growing world population, the uses of supplementary cementitious materials (SCMs) are being encouraged considering their significant environmental and economic benefit and their potential as a sustainable solution. Most of these SCMs are recycled industrial by-products that save fossil fuels, preserve cement raw materials, and reduce hazardous emissions into the atmosphere due to cement production. Moreover, some of these materials impart to the cement-based systems improved early age behaviour, superior workability, strength, and durability. The mechanisms

underlying these improvements imparted by SCMs are still a matter of controversy. Over the last few decades, a number of researches have been conducted to characterize the influence of SCMs in ordinary concrete. However, very scant information can be found on the rheological properties of oil well cement slurries when SCMs are used as partial replacement for oil well cement.

The rheological properties of cement-based materials determine the quality of the hardened cementitious matrix and help predicting its end use performance and its physical properties during and after processing. Measuring the rheological properties of cement-based materials in the laboratory remains a challenging task. The rheological properties are affected by numerous factors including the water-to-cement ratio (w/c), size and shape of cement grains, chemical composition of the cement and the relative distribution of its components at the surface of grains, presence and type of additives, compatibility between cement and chemical admixtures, mixing and testing procedures, etc. Moreover, slip at the slurry-shearing surface interface during rheological tests, particle-particle interactions, chemical reactions, non-homogeneous flow fields, and human errors can make the rheological experiments difficult to reproduce. Above all, the equipment used to properly quantify the rheological properties of cement-based materials is relatively expensive, difficult to operate, and may not be suitable for use in construction sites because of its large size and/or complicated set up.

## **1.2 Objective and Scope of the Study**

Cement slurry can be considered as a composite suspension of cement and supplementary cementitious materials in water, one or multiple chemical admixtures, fillers, etc. Oil well cement (OWC) slurries are pumped between the well bore and the steel casing inserted in the well to seal off all strata of the formation, except those that have oil so that gases and water do not contaminate the oil bearing strata. OWCs are sometimes pumped to depths in excess of 6000 m (20000 ft). At such depths, the temperature may rise up to 205°C (400°F), but is normally reduced by the circulation of cooler drilling mud (Orchard, 1962). The cement slurry may also be subjected to very high pressures reaching over 200 MPa (30000 psi) (Joshi and Lohita, 1997) depending on the height and density of the column of material above it. Thus, oil/gas well cementing operations face additional challenges in contrast to common cementing work above ground. In addition to the high pressure and temperature, the

OWC must be able to contend with weak or porous formations, corrosive fluids, etc. A number of additives have been used to alter the chemical and physical properties of the OWC slurry as required for flow-ability and stability of the slurry and the long term performance of wells. The conventional admixtures which have been developed in countries with mild climates for cementing jobs above ground, may lead to inadequate results when exposed to high temperatures. Likewise, there is still a lack of information in the open literature regarding the effects of various chemical admixtures, such as new generation superplasticizers, on the rheological properties of cement-based materials at high temperature. Hence, this research investigates the effects of a number of conventional chemical admixtures along with new-generation chemical admixtures on the rheology of oil well cement slurries.

Mineral and chemical admixtures play an important role in controlling the physical and chemical properties of cement slurries and hardened cementitious systems. However, not all minerals and supplementary cementitious materials act in the same way on the rheological properties, primarily because of their different physical and chemical properties. Typically, published research has been conducted on ordinary portland cement. There is still a lack of information regarding the coupled effects of chemical and mineral admixtures at high temperature on the rheology of oil well cement slurries.

The present study attempts to develop a better understanding of the important mechanisms that controls the rheology of OWC slurry subjected to severe conditions such as high temperature, and to investigate the performance of various chemical admixtures in controlling the rheological behaviour of oil well cement slurries.

The present study also undertakes the task of clarifying the mechanisms of various SCMs in controlling the OWC slurry rheology at high temperature. The knowledge thus gained could ultimately allow the optimization of blended oil well cements, leading both to ecological and economic benefits.

The specific objectives of this study are provided below:

1. Develop an improved understanding of the effects of temperature on the rheological properties of oil well cement slurries incorporating various chemical admixtures.

2. Investigate the coupled effects of supplementary cementitious materials and new generation chemical admixtures on the rheological properties of oil well cement slurries.
3. Develop a versatile model to predict the Bingham parameters of oil well cement slurries incorporating various chemical admixtures and subjected to various temperatures.
4. Develop a design chart to identify the influence of adjusting oil well cement slurry mixture variables, such as the type of dosage of chemical and mineral admixture, on rheological properties, such as yield stress and plastic viscosity, and to simplify the test protocol and number of experiments required to achieve an optimum balance amongst various parameters involved in slurry rheology tailoring.

### **1.3 Organization of Dissertation**

This thesis has been prepared according to the guidelines specified by the Faculty of Graduate Studies at the University of Western Ontario for an Integrated Article (formerly Manuscript) format. It has been divided into nine chapters, six of which have been written as self-contained documents and have been either accepted or submitted for possible publication in various peer-reviewed technical journals and international conferences. Related literature and necessary background to each subject have been included in each corresponding chapter. The subsequent sections provide in sequence a concise description of the contents of each chapter in order to address the objectives of the study presented in Section 1.2.

### **Chapter 2**

In Chapter 2, the basic concepts involved in oil well cementing, the chemical and physical properties of oil well cements and the role of related additives and chemical admixtures are discussed. Although mechanical properties and durability aspects are not a part of the present investigation, the chapter provides a review on the mechanical properties of hydrated OWC slurries and their durability, and critically examines state-of-the-art practice, and identifies future research directions and technology development needs.

### **Chapter 3**

Chapter 3 is divided into two parts. The first part presents a brief theoretical background on the rheology and rheological parameters used to characterize materials. The second part presents the rheology of oil well cement slurries, time-independent rheological models, the effect of time and temperature, and the current practice for rheological tests and equipment.

### **Chapter 4**

In this chapter, the rheological properties, including yield stress, plastic viscosity, thixotropy and gel strength of Class G API oil well cement slurries having w/c of 0.35, 0.44, and 0.50 were investigated at different temperatures in the range of 23 to 60°C using an advanced shear-stress/shear-strain controlled rheometer. The interactions of Class G OWC with different types of admixtures such as a new generation polycarboxylate-based high-range water reducing admixture (PCH), lignosulphonate-based mid-range water reducing admixture (LSM), polycarboxylate-based mid-range water reducing admixture (PCM), phosphonate-based set retarding admixture (SRA), hydroxylated carboxylic acid-based retarding admixture (HCR) and a rheoplastic solid admixture (RA) have been investigated and discussed.

### **Chapter 5**

In this chapter, the interactions of Class G oil well cement and four different types of SCMs including metakaolin (MK), silica fume (SF), rice husk ash (RHA), and class F fly ash (FA) on the rheological properties of oil well cement slurries have been investigated. The flow properties of Class G oil well cement slurries at w/c=0.44 and incorporating those SCMs along with a new generation polycarboxylate-based high-range water-reducing admixture were tested at different test temperatures (23, 45 and 60°C). A series of flow tests using an advanced rheometer were carried out to determine optimum dosage of admixture.

### **Chapter 6**

This chapter is divided into two parts. In the first part, an artificial neural networks (ANN)-model was developed to predict the shear stress versus shear rate flow curves for OWC slurries. The slurries were prepared using class G oil well cement with a water-cement ratio

(w/c) of 0.44, and incorporating three different chemical admixtures, namely a new generation polycarboxylate-based high-range water reducing admixture, polycarboxylate-based mid-range water reducing admixture, and a lingsulphonate-based mid-range water reducing admixture. The flow curves developed using the ANN-model have been employed to predict the Bingham parameters (yield stress and plastic viscosity) of OWC slurries. A parametric study was performed to evaluate the performance of the ANN-model in predicting the rheological behaviour of OWC slurries with variation of temperature and type and dosage of the admixture.

In the second part, multiple regression analysis (MRA) was employed to develop equations for the shear stress of OWC slurries as a function of the shear rate, dosage of chemical admixture, and temperature. Subsequently, the Bingham model was used to determine the rheological properties including yield stress and plastic viscosity. A parametric study was conducted to evaluate the ability of the MRA equations thus developed to capture the effects of test parameters on the yield stress and plastic viscosity. Finally, the performance of both the ANN and MRA models was compared.

## **Chapter 7**

In chapter 7, the shear stress versus shear rate curves for OWC slurries incorporating the various supplementary cementitious materials (metakaolin, silica fume, rice husk ash and fly ash) and a new generation polycarboxylate-based high-range water reducing admixture (PCH) at various temperatures were predicted using an artificial neural network model. A sensitivity analysis was performed to evaluate the effects of mixture variables, such as dosage of PCH, type and dosage of SCM, and test variables such as time, on the predicted yield stress and plastic viscosity of oil well cement slurries. Model predictions were validated using experimental data.

## **Chapter 8**

In this chapter, a second order  $2^k$  central composite response surface model was developed to evaluate the effects of temperature, superplasticizer dosage, and dosage of SCM on the rheological properties of OWC slurries using a statistical design approach and design of

experiments. This model was used to evaluate the two-way interaction of parameters that had a significant influence on the rheological properties of OWC slurries.

## **Chapter 9**

Chapter 9 presents a summary of the study along with the main conclusions obtained based on the research program undertaken. A few recommendations for future research have also been formulated.

### **1.4 Original Contributions of Thesis**

This thesis provides a comprehensive study on the effects of conventional chemical admixture and supplementary cementitious materials on the rheological properties of oil well cement slurries subjected to high temperature. This work is a step towards formulating guidelines and specifications for using these admixtures in oil well cementing.

The main contributions of the current study can be summarised as follows:

1. The study explored the effects of conventional chemical admixtures which have been developed in countries with moderate temperatures for cementing jobs above ground. The results of this study reveal that not all the admixtures tested may be suitable for oil well cementing work because they may lead to disappointing results when exposed to high temperature. However, a new generation polycarboxylate-based high-range water-reducing admixture, a polycarboxylate-based mid-range water reducing admixture and hydroxylated carboxylic acid-based retarding admixture improved OWC slurry fluidity at all temperatures tested. Likewise, the results of this thesis indicate that technical data for chemical admixtures need to be revised for oil well cementing applications considering the extreme down-hole environment.
2. This study explored the effects of supplementary cementitious materials, such as metakaolin (MK), silica fume (SF), rice husk ash (RHA) and fly ash (FA) in tailoring the rheological properties of OWC slurries. This work is a contribution towards a more fundamental understanding of the mechanism of the tested SCMs in changing the rheology of oil well cement slurries at high temperature, which should help in



selecting adequate admixtures and their effective dosages to overcome difficulties encountered during the construction of oil and gas wells.

3. A versatile model has been developed to learn the relationships between different shear flow parameters for various OWC slurries using artificial intelligence. The model can successfully predict the rheological properties of OWC slurries within the range of tested admixture dosages and temperatures investigated.
4. A set of empirical equations using multiple regression analysis has been developed to predict the shear flow behaviour of OWC slurries prepared using chemical and mineral admixtures and subjected to high temperature.
5. Isoresponse curves and contour charts have been created, which can simplify the test protocol and reduce the number of experimental tests required to achieve an optimum balance amongst the various parameters involved and to gain a better understanding of trade-offs between key mixture parameters such as the superplasticizer dosage and type and content of supplementary cementitious materials.

### **1.5 Reference**

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*Chapter 2***STATE-OF-THE-ART REVIEW ON OIL WELL CEMENTS****2.1 Introduction**

Oil well cementing is the process of placing a cement slurry in the annulus space between the well casing and the geological formations surrounding to the well bore. When a certain section of the depth of an oil or gas well has been drilled successfully, the drilling fluid cannot permanently prevent the well bore from collapsing. Therefore, oil well cementing was introduced in the late 1920s (Joshi and Lohita, 1997) with a number of objectives: (i) protecting oil producing zones from salt water flow, (ii) protecting the well casing from collapse under pressure, (iii) protecting well casings from corrosion, (iv) reducing the risk of ground water contamination by oil, gas or salt water, (v) bonding and supporting the casing, and (vi) providing zonal isolation of different subterranean formations in order to prevent exchange of gas or fluids among different geological formations. In addition to their exposure to severe temperature and pressure, oil well cements (OWCs) are often designed to cope with weak or porous formations, corrosive fluids, and over-pressured formations.

The appropriate cement slurry design for well cementing is a function of various parameters, including the well bore geometry, casing hardware, formation integrity, drilling mud characteristics, presence of spacers and washers, and mixing conditions. The rheological behaviour of OWC slurries must be optimized to achieve effective well cementing operation. Strict control of the hardened cement mechanical properties and durability during the service life of the well are very important criteria, especially under such severe environments. Thus, a special class of cements called oil well cements (OWCs), has emerged and is specified by the American Petroleum Institute (API) (API Specification 10A, 2002). A number of additives have also been used to alter the chemical and physical properties of the OWC slurries as required for the flowability, and stability of the slurry and long term performance of wells.

Substantial research has been conducted to improve the efficiency of oil well production by improving the physical and mechanical properties of OWC slurries. This chapter discusses the basic concepts involved in oil well cementing, the different types of OWCs, and their chemical and physical properties. An insight into the additives that can modify the behaviour of the OWC systems and allow successful slurry placement between the casing and the formation, rapid compressive strength development, and adequate zonal isolation during the lifetime of the well is also provided. Furthermore, research on the rheology, mechanical properties and durability of OWCs under severe environmental exposure is critically examined, and technology development needs and future research directions are identified. This critical review paper should provide a concise yet in-depth source of information to assist professionals understanding oil-well cementing projects.

## **2.2 Basic Cementing Process**

A typical oil/gas well can be several thousand meters in depth, less than a meter in diameter (Lafarge, 2009), and is usually constructed using a metal casing surrounded by a special cement slurry mix that fills the annulus space between the outer face of the tubing and the wall formation of the hole. OWCs are sometimes pumped to depths in excess of 6000 m (20000 ft). At such depth the temperature may rise up to 205°C (400°F), but is normally reduced by the circulation of cooler drilling mud (Orchard, 1962). The cement slurry may also be subjected to very high pressures reaching over 200 MPa (30000 psi) (Joshi and Lohita, 1997) depending on the height and density of the column of material above it. Thus, oil/gas well cementing operations face additional challenges in contrast to common cementing work above ground. Contaminations from the formations can pose additional problems. Thus, OWC slurries are pumped between the well bore and the steel casing inserted in the well to seal off all strata of the formation, except those that have oil so that gases and water do not contaminate the oil bearing strata.

After drilling the well to the desired depth, the drill pipe is removed and a longer string of casing is run into the well until it reaches its bottom. The circulatable completion fluids such as drilling mud must be removed and replaced with a hardened cement to ensure intimate contact and bonding of the cement with the casing and formation surfaces. Sufficient cement slurry is pumped down the inside of the casing and forced up the outside of the casing

through the annular space between the casing and subterranean bore hole wall (Powers et al., 1977; Detroit et al., 1981) using two-plug cementing method (Calvert, 2006; Oilfield Glossary, 2009). Pressure is applied above plugs by an aqueous displacement fluid to displace any remaining cement slurry (Detroit et al., 1981). Two types of cementing plug (top and bottom) are typically used on a cementing operation to allow the cement slurry to pass through the casing and to reduce the contamination of cement slurries by other fluids that remain inside the casing prior to pumping cement slurry (Oilfield Glossary, 2009). Typically, the cement slurry is brought much higher than the production zones into the well bore to exclude undesirable fluids from the well bore so as to protect fresh water zones and corrosion of the casing (Calvert, 2006). After the cementing process, a curing time is allowed for the slurry to harden before beginning completion work or drilling to a deeper horizon. The set cement slurry forms a low permeability annulus and isolates the productive zone of the well from the rest of the formation. Figure 2.1 is a schematic representation of a cemented well.

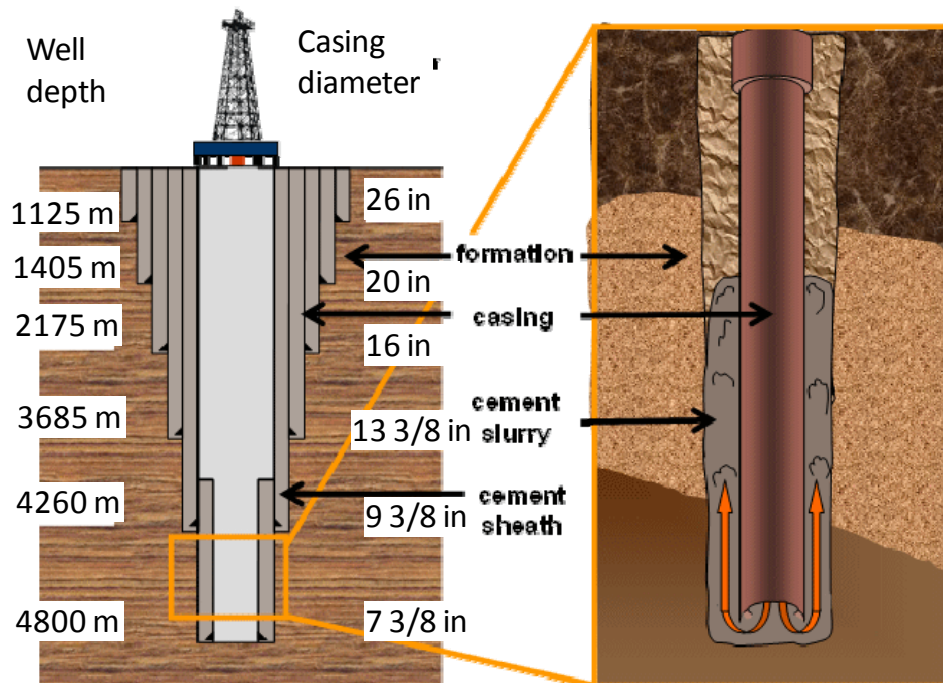


Figure 2.1 Schematic representation of a cemented well (Plank 2011)

## **2.3 Oil Well Cements**

The productivity of an oil well is significantly affected by the quality of cementing between the well casing and the surrounding strata. Cement slurry flowability and stability are major requirements for successful oil well cementing. The properties of oil well cement slurries depend on its mixture design and the quality of its components. Because the cement is the most active component of the slurry and usually has the greatest unit cost, its selection and proper use are important in obtaining an effective, yet economical material meeting the expected service life performance of the well.

Type I/II ordinary portland cements can provide adequate strength and durability for common applications (US Department of Transportation, 2009). However, some demanding applications may require the use of other cements to meet specific performance criteria. For instance, the need for high-early strength cements in pavement repairs, the use of blended cements with aggregates susceptible to alkali-aggregate reactions, and the use of oil well cements in the exploration and production of oil and gas in onshore as well as offshore wells are examples of such applications. Although slightly modified Type I, II and III portland cements can be used for cementing around the steel casing of gas and oil wells having depths not exceeding 1800 m (6000 ft), deeper wells usually require special oil well cements (Popovics, 1992).

### ***2.3.1 Classification of Oil Well Cements***

Oil-well cements are usually made from portland cement clinker or from blended hydraulic cements. OWCs provide a base ingredient in the slurry mix that is pumped into the interior metal casing of the well and forced back toward the surface from the base of the borehole filling the annulus (Powers et al., 1977, Detroit et al., 1981, Calvert, 2006). Initially, only one or two types of oil well cement were available. As oil/gas wells became deeper and subjected to more adverse environments, the more stringent performance criteria could not be satisfied by those cements. With the advent of the API Standardization Committee in 1937, improved OWCs were developed (Smith, 1987). The API Specifications for Materials and Testing for Well Cements (API Specification 10A, 2002) include requirements for eight classes of OWCs (classes A through H). OWCs are classified into grades based upon their  $C_3A$  (Tricalcium Aluminate) content: Ordinary (O), Moderate Sulphate Resistant (MSR), and

High Sulphate Resistant (HSR). Each class is applicable for a certain range of well depth, temperature, pressure, and sulphate environments. Class A, Class G and Class H are the three most commonly used oil well cements. Class A is used in milder, less demanding well conditions, while Class G and H cements are usually specified for deeper, hotter and higher pressure well conditions (Lafarge, 2009). Conventional types of portland cement incorporating suitable additives have also been used.

The chemical composition of cement is what distinguishes one type of oil well cement from another and determines the suitability of the cement for specific uses. The chemical composition of OWC is slightly different from that of regular portland cement. OWCs usually have lower  $C_3A$  contents, are coarsely ground, may contain friction-reducing additives and special retarders such as starch, sugars, etc, in addition to or in place of gypsum (Popovics, 1992). The key features of commonly used OWCs are summarized in Table 2.1 (API Specification 10A, 2002; Michaux and Nelson, 1990; Nelson et al., 2006; Lafarge, 2009; Halliburton, 2009).

API Class G and H are by far the most commonly used OWCs today. The chemical composition of these two cements is similar. The basic difference is in their surface area. Class H is coarser than Class G cement and thus has a lower water requirement (Table 2.1). The chemical composition and physical properties of typical class G and H cement are illustrated in Table 2.2 (API Specification 10A, 2002; Michaux and Nelson, 1990; Nelson et al., 2006).

A cement that is ground too fine should not be used as oil well cement. Microfine cements and ultra-fine (blain surface  $> 9000 \text{ cm}^2/\text{gm}$ ) portland cements cannot be used for primary cementing because it does not develop sufficient compressive strength to hold the casing in downhole condition and it does not generally have adequate sulphate resistance. However, microfine cement is a good option for oil well repairing since typical OWCs can not be used because of their larger particle size and the subsequent difficulty to penetrate in extremely small cracks/channels (Kumar et al., 2002).

Table 2.1 Key features of API Oil Well Cement (API Specification 10A, 2002; Nelson and Michaux, 2006; Lafarge, 2009; Halliburton, 2009)

Cement Class	A	B	C	D	E	F	G	H
Recommended w/c, % mass fraction of cement	46	46	56	38	38	38	44	38
Recommended range of depth, m (ft)	0 to 1830 (0 to 6000)	0 to 1830 (0 to 6000)	0 to 1830 (0 to 6000)	1830 to 3050 (6000 to 10000)	3050 to 4270 (10000 to 14000)	3050 to 4880 (10000 to 16000)	0 to 2440 (0 to 8000)	0 to 2440 (0 to 8000)
Availability	O* grade, compatible with ASTM C 150, Type I Portland Cement	MSR** and HSR*** grades, Comparable with ASTM C 150, Type II	O*, MSR** and HSR*** grades, similar to ASTM C 150, Type III	MSR** and HSR*** grades	MSR** and HSR*** grades	MSR** and HSR*** grades	MSR** and HSR*** grades	MSR** and HSR*** grades
Cost	Lower cost	Lower cost	More costly than ordinary portland cement	More costly than ordinary portland cement	More costly than ordinary portland cement	More costly than ordinary portland cement	...	...
Other features	Intended for use when special properties are not required	(1) Intended for use when conditions require moderate or high sulphate-resistance (2) lower C <sub>3</sub> A content than Class A	(1) Intended for use when conditions require high early strength (2) The C <sub>3</sub> S content and surface area are relatively high	(1) Required under conditions of moderately high temperatures and pressure (2) Retarded cement and retardation is achieved by reducing C <sub>3</sub> S and C <sub>3</sub> A, and increasing the particle size of the cement grains.	(1) Required under conditions of high temperatures and pressure (2) Retarded cement and retardation is achieved by reducing C <sub>3</sub> S and C <sub>3</sub> A, and increasing the particle size of the cement grains.	(1) Required under conditions of extremely high temperatures and pressures (2) Retarded cement and retardation is achieved by reducing C <sub>3</sub> S and C <sub>3</sub> A, and increasing the particle size of the cement grains.	(1) Basic well cement. (2) Thickening Times controllable with additives to prevent loss of circulation up to 250° F (~120° C)	(1) Basic well cement (2) Surface area is coarser than that of Class G (3) Thickening Times controllable with additives to prevent loss of circulation up to 450° F (~230° C)

\*O: ordinary, \*\* MSR: moderate sulphate resistant, \*\*\* HSR: high sulphate-resistant

### 2.3.2 Other Types of Oil Well Cements

In addition to API class OWCs, other cements can also serve the purpose for well cementing. For instance grey cement, which is a mineral mixture of chalk (Dusseault et al., 2009), and limestone containing silica and alumina (Portland Grey Cement, 2009) having cementitious properties when exposed to water, can be used for cementing oil wells. Hardened grey cement was found to be stronger and stiffer than hardened conventional OWCs (Dusseault et al., 2009). It is non-shrinking and has higher resistance to tension. Moreover, it has been claimed that grey cement is less costly than API Class G cement, provides a better final product since it reduces leakage behind the casing, improves the cement squeeze success ratio, provides better thermal well completion, and better resists acid attack and osmotic drying (Dusseault et al., 2009). Expansive cements have also performed adequately as well cements (Kosmatka, 1990). Latex and monomer-modified cementitious systems have been used for oil-well and geo-thermal cementing, respectively (Ramachandran, 1984). Moreover, a product known as Ceramicrete, which is a chemically bonded phosphate ceramic is claimed to provide a tight bond to the earth materials and casings in the presence of drilling fluids or hydrocarbons (Argonne National Laboratory, 2003). The hardened Ceramicrete is not affected by severe down-hole conditions and is stable in a wide range of adverse chemical environments. It has low thermal conductivity and can be pumped at a very low viscosity. For this reason, it is particularly useful for drilling in permafrost regions (Argonne National Laboratory, 2003).

Table 2.2 Chemical and physical properties of API Class G and Class H OWC (API Specification 10A 2002; Michaux and Nelson, 1990; Nelson et al., 2006)

Chemical Component (%)	Physical Properties
Magnesium oxide (MgO) ≤6.0	Maximum free fluid content, % 5.9
Sulphur Trioxide (SO <sub>3</sub> ) ≤3.0	Thickening Time (Schedule 5: 52°C and 35.6 MPa) ≤120 minutes
Loss on Ignition ≤3.0	Compressive strength at 8 hours @ 38 °C and atmospheric pressure 2.1 MPa
Insoluble Residue ≤0.75	
C <sub>3</sub> S (For MSR) 48-58	Compressive strength at 8 hours @ 60 °C and atmospheric pressure 10.3 MPa
C <sub>3</sub> S (For HSR) 48-65	
C <sub>3</sub> A (For MSR) ≤8.0	Soundness (automotive expansion), % ≤0.8
C <sub>3</sub> A (For MSR) ≤3.0	Consistency (52°C, 35.6 MPa and 15-30 minutes) ≤30 Bc
C <sub>4</sub> AF+2 C <sub>3</sub> A ≤24	
Equivalent Alkali (Na <sub>2</sub> O) ≤0.75	



## **2.4 Admixtures for Well Cementing**

Oil well cementing is generally less tolerant to errors than conventional cementing work. Thus, the OWC slurry must be carefully designed to meet demanding requirements such as a predictable thickening time (set time), fluid loss control, consistency, low viscosity, low free fluid, adequate strength, high sulphate resistance and overall high durability. OWC slurries must have a particularly low viscosity to be pumped into great depths. The down-hole high temperatures and pressures compel severe requirements on the setting behaviour of OWCs. OWC slurries usually incorporate Class G or H or other adequate cements, water, and chemical admixtures. They are formulated to provide the required physical properties at the conditions of pressure and temperature of the hole as well as the nature of the geological formations. However, they often have to contend with weak or porous formation, corrosive fluids, and over pressured formation fluids.

A wide variety of cement admixtures are currently available to enhance the OWC slurry properties and achieve successful placement between the casing and the geological formation, rapid compressive strength development, and adequate zonal isolation during the lifetime of the well. The effect of these admixtures depends on a number of OWC parameters, such as the particle size distribution and chemical composition of the cement, distribution of silicate and aluminate phases, reactivity of hydrating phases, gypsum/hemihydrate ratio, total sulphate content, free alkali content, and the quantity and specific surface area of the initial hydration products. The temperature, pressure, admixture dosage, mixing energy, mixing sequence, and water/cement ratio also have a significant effect on the behaviour of admixtures in OWC slurries (Nelson et al., 1990; Nelson et al., 2006).

### ***2.4.1 Types of Admixtures Used in OWC Slurries***

Typical admixtures for OWC slurries can be categorized into eight groups: set accelerators, set retarders, extenders, weighting agents, dispersants, fluid-loss control agents, lost circulation control agents, and other specialty additives (antifoam agents, fibers, etc.). The OWC slurry may incorporate retarders or accelerators to control the setting behaviour, weighting agents are light-weight systems to increase the density of the OWC slurry system, and extenders to lower the density of the cement system and increase its yield. Similarly,

different admixtures are used as dispersants or viscosifiers to control the viscosity of the slurry. For instance, fluid loss additives are used to control the loss of the aqueous phase of the OWC slurry to the geological formation and to maintain constant water to solid ratio in cement slurries, while lost circulation control agents are used to control the loss of the cement slurry to weak or regular formations. A detailed review of cement additives has been provided by Nelson et al. (1990 and 2006). In addition to chemical admixtures, a number of mineral additives such as fly ash, silica ( $\alpha$ -quartz and condensed silica fume), diatomaceous earth, gilsonite, powdered coal (Nelson et al. 1990; Nelson et al., 2006), etc, have been used to alter certain properties of OWC slurries. A new generation of engineered cement set control (ECSC) additive has been developed and successfully used to cement long casing sections. The ECSC overcomes the well integrity problems due to huge temperature differential exist between the bottom and the top of a long cement column (Moradi et al., 2006; Sorgard and Viali, 2007).

## **2.5 Density of OWC Slurries**

The density of neat cement slurry, i.e., mixture of water and cement, varies from 1773 kg/m<sup>3</sup> (110 lb/ft<sup>3</sup>) to 1965 kg/m<sup>3</sup> (123 lb/ft<sup>3</sup>) depending on the API Class of the cement and the water/cement ratio (w/c). Higher density cement slurry may be required to control well fluids subjected to high bottomhole formation pressures. It is desirable to increase the density of OWC slurries to minimize the diffusion of heavy drilling muds. Usually bentonite and organic gums are used to prevent segregation of the heavy constituents from the cement slurry (Ramachandran, 1984). In other cases, lower density cements may be required to prevent lost circulation during well cementing.

Density altering additives (weighting agents or extenders) are used to achieve specific density requirements. Weighting agents add weight to the slurry to achieve higher density, while extenders are low specific gravity materials that are used to reduce the slurry density and to increase slurry yield. For instance, Barite, sand and microsand have relatively high specific gravity and are finely divided solid materials used to increase the density of a drilling mud or OWC slurry. Barite (BaSO<sub>4</sub>) is the most commonly available weighting agent in oil/ gas well cementing, with a minimum specific gravity of 4200 kg/m<sup>3</sup> (262 lb/ft<sup>3</sup>) (Oilfield Glossary, 2009) and its particle size distribution is predominantly in the range of 3

to 74 microns (0.0012 to 0.0087 in) (Barite, 2009; Ariffin, 2009). Hematite, calcium carbonate, siderite, ilmenite, manganese tetraoxide (Nelson et al., 2006), sand and microsand (Halliburton, 2009) are other types of weighting agents, but only barite and hematite have related API/ISO standards (Oilfield Glossary, 2009). Barite was reported as less efficient weighting agent compared to ilmenite, hematite or manganese tetraoxide (Nelson et al., 1990; Nelson et al., 2006). However, ilmenite plant dust was found to be less favorable than that of barite because a change in consistency with time was observed before initial setting for slurries weighted with ilmenite plant dust (Saasen and Log, 1996). Typical properties of these weighting agents are illustrated in Table 2.3 (Saasen and Log, 1996; Oilfield Glossary, 2009) and the concentration of ilmenite, hematite and barite usually required to achieve a given slurry density are plotted in Figure 2.2. Table 2.4 (Nelson et al., 1990; Nelson et al., 2006) summarizes general information regarding the performance characteristics of commonly used extenders.

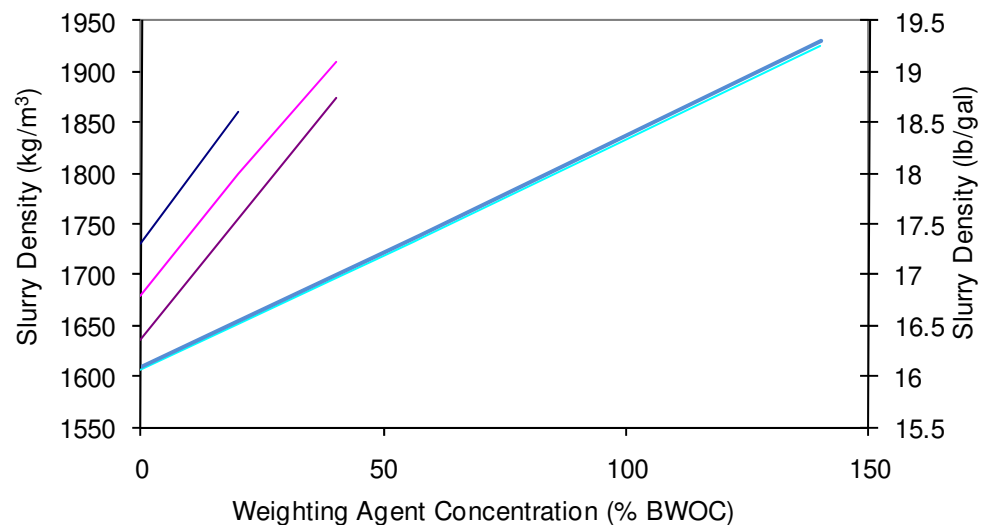


Figure 2.2 Densification of cement slurries with various weighting agents (PNS: Polynepthalylene Sulfonate) (Nelson et al. 1990, 2006).

Table 2.3 Typical properties of common weighting agents used in well cementing (Saasen and Log, 1996; Oilfield Glossary, 2009; Nelson et al., 2006)

Material	Density (S.G) g/cm <sup>3</sup>	Additional water requirement (L/kg)	Typical maximum slurry density (S.G) (gm/ cm <sup>3</sup> )
Barite	4.33	0.20	2.28
Hematite	5.05	0.019	2.64
Ilmenite	4.45	0.00	>2.40
Manganese tetraoxide	4.84	...	2.64
Siderite	3.80	...	...

Table 2.4 Summary of properties of extenders used in OWC slurries (Nelson et al., 1990; Nelson et al., 2006)

Extender	Slurry densities obtainable (lb/gal)	Other features
Bentonite (clay based extenders)	11.5-15	Assists fluid loss control. Hardened OWC system becomes less resistant to sulphate water and corrosive fluids because of increase in permeability
Fly ash	13.1-14.1	Resists corrosive fluids.
Sodium Silicates	11.1-14.5	Required in low percentages. Ideal for sea water mixing. Provides sufficient viscosity to allow the use of large quantities of mix water without excessive free water separation
Microspheres	8.5-15.0	Good compressive strength, low permeability, thermal stability, and insulating properties
Silica Fume	≥11	Possible to obtain low-density cement systems with a high rate of compressive strength development, improves fluid loss control
Foamed Cement	6.0-15.0	Excellent strength and low permeability

## 2.6 Setting Time and Thickening Time of OWC Slurries

As mentioned above, OWCs are subjected to a wide range of pressure and temperature, which has a major effect on the time required for their setting and hardening. The setting time is an important requirement in oil-well cementing. A premature setting can have disastrous consequences due to loss of circulation in the well, whereas too long setting times

can cause financial losses due to lost productivity, in addition to possible segregation of the slurry or contamination by fluids. OWC slurries must also harden rapidly after setting. A slow setting behaviour can be achieved by adjusting the composition of the cement and or by adding retarders. Constituents of the cement slurry and their percentage can affect the hardening time. For example, the setting time can usually be increased by reducing the proportion of tricalcium aluminate ( $C_3A$ ). Setting times of up to 4 hours at a temperature of  $93^\circ\text{C}$  ( $200^\circ\text{F}$ ) and 6 hours at a temperature of  $21^\circ\text{C}$  ( $70^\circ\text{F}$ ) can be achieved with a portland cement with no  $C_3A$  (Ramachandran, 1984). Retarders can increase setting times up to  $6\frac{1}{2}$  hours at a temperature of up to  $104^\circ\text{C}$  ( $220^\circ\text{F}$ ) (Ramachandran, 1984). For oil well construction, it is generally desirable to maintain the setting time of the cement slurry fairly constant over the temperature range of  $60^\circ\text{C}$  ( $140^\circ\text{F}$ ) to  $104^\circ\text{C}$  ( $220^\circ\text{F}$ ).

Accurate control of the thickening time, i.e. the time after initial mixing at which the cement can no longer be pumped, is crucial in the oil well cementing process. It is important to simulate the well conditions (temperature, pressure, etc.) as precisely as possible in determining the thickening time. There are some other factors that affect the pumpability of the slurry, but are very difficult to simulate during determining the thickening time of the slurry, such as fluid contamination, fluid loss to formation, unforeseen temperature variations, unplanned shutdowns in pumping, etc. (Hallibutton, 2009).

The thickening time is usually controlled by using retarders. The addition of carbohydrates such as sucrose can significantly extend the thickening time or even prevent setting completely (Bentz et al., 1994). But these are not commonly used in well cementing because of the sensitivity of the degree of retardation to small variations in concentration (Nelson et al., 1990; Bermudez, 2007). It was found that the sugar acts as a retarder of cement slurries when added in small concentrations and as an accelerator when added in high concentration (Bermudez, 2007). Lignosulfonates and hydroxycarboxylic acids are retarders that are believed to perform well for OWCs with low  $C_3A$  contents (Nelson et al., 1990). The mechanism by which these chemicals and others act as retarders is not well understood and is still a matter of controversy, but it is known that retarders bind to calcium ions (Taylor, 1997) and are able to inhibit the growth of ettringite crystals (Coveney and Humphries, 1996). A multiphase, multicomponent model for the hydration of OWC in the presence of retarders was proposed by Billingham et al. (Billingham et al., 2005). It was found that the chemical

actions of the retarders contribute to slowing the initial rate of hydration reactions and the sudden crystallization of ettringite. Other retarders used in well cementing include cellulose derivatives, organophosphonates and inorganic compounds such as acids and salts of boric, phosphoric, hydrofluoric, and chromic, zinc oxide (ZnO) and Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), sodium chloride (concentrations greater than 20% BWOW) (Nelson et al., 1990; Nelson et al., 2006). The thickening time of OWC slurries was also found to increase with the addition of polyvinyl alcohol (PVA) latex (Lu et al., 2005; Ding et al., 2001). Thickening time was found to be almost independent of temperature when the ECSC additive was used in the slurry, and the slurry allowed efficient and reliable cementing of long cement columns with a large temperature differential between the top and the bottom (Moradi et al., 2006; Sorgard and Viali, 2007).

Unlike retarders,  $\text{CaCl}_2$ ,  $\text{NaCl}$ , and sodium silicates are used to shorten the setting time and offset the set delay caused by other additives such as dispersants and fluid loss control additives. The accelerating effect of such chemicals depends on their chemical nature, concentration, curing temperature and other constituents of the cement slurry. Figure 2.3 illustrates the effect of  $\text{NaCl}$  on the thickening time of OWC slurries (Nelson et al., 1990; Nelson et al., 2006). Salts of carbonates, aluminates, nitrates, sulphates, thiosulphates, as well as alkaline bases such as  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{NH}_4\text{OH}$  accelerate the setting time (Nelson et al., 1990; Nelson et al., 2006). Glycerin contents of 26% by volume or less were also found to accelerate the hydration process of Class G OWC slurries (Saasen et al., 1991).

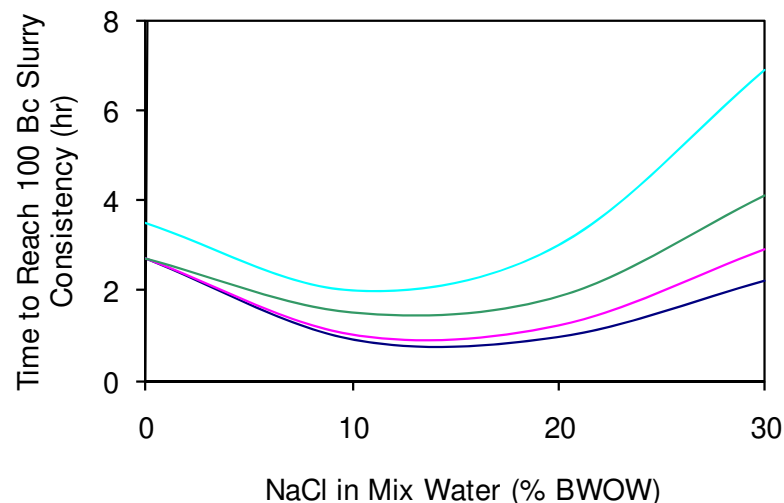


Figure 2.3 Effect of  $\text{NaCl}$  on thickening time (Nelson et al. 1990, 2006).

The criterion for evaluating the setting time of OWCs is different than that for other conventional cements. The setting time for OWCs is usually measured in terms of the change in viscosity/consistency at elevated temperature. The initial setting/thickening time is measured using a consistometer in terms of Bearden units of consistency ( $B_C$ ). At a consistency of 30  $B_C$ , a slurry is considered to be too viscous to be pumped, and this is usually the maximum consistency requirement during the 15 to 30 min stirring period for all classes of OWC (API Specification 10A, 2002). The time at which the consistency of an OWC slurry reaches 30  $B_C$  corresponds to the time of initial set of the cement. The time to reach 100  $B_C$  is referred as the thickening time of the cement slurry (API Specification 10A, 2002) and is usually expected to be slightly larger than that to reach 30  $B_C$  (Saasen and Log, 1996).

## **2.7 Hydration of Oil Well Cement**

The setting and hardening of an OWC slurry are the result of a series of simultaneous and consecutive reactions between water and the constituents of the cement. Vlachou and Piau (1997) studied the microstructural and chemical evolution of Class G OWC slurry from the first minutes after mixing the cement powder with water until the beginning of setting. Based on scanning electron microscopy (SEM) and X-ray Diffraction (XRD), it was concluded that the form and structure of the hydration products were a function of experimental conditions, such as hydration time since mixing, stirring conditions (Vlachou and Piau, 1997), temperature (Justnes et al., 1995), chemical composition of cement and additive used (Vidick, 1989) etc. The slurry hydrated under continuous stirring showed constant viscosity and adequate fluidity over several hours. The formation of small spheres of hydration particles of the aluminate phases had no influence on the flow curve probably because these particles created no bonds between them and they moved freely into the inter-particle spaces. Subsequently, the slurry thickened rapidly with the multiplication of hydrated crystals and the start of setting processes (Vlachou and Piau, 1997). On the other hand, slurries hydrated at rest showed a much more increase of viscosity during the first hours, after which the evolution process slowed down (Vlachou and Piau, 1997). It was reported that in case of slurries hydrated at rest, an over-saturation of ions in the grain neighborhood leads to the formation of aluminate hydration crystals of colloidal size (Vlachou and Piau, 1997). These

crystal cover the surface of the grains and the hydration reaction eventually slows down. On the other hand, ions dispersed all over the sample volume and dissolution continues until saturation in case of slurries hydrated under stirring. The chemical composition of cement and additives used can affect the evolution of the chemical composition of the liquid phase of the cement paste (Michaux et al., 1989, Vidick et al., 1989). X-ray diffraction and scanning electron microscopy showed that a neat cement slurry changes from CSH(II), C<sub>2</sub>SH<sub>2</sub>, C<sub>3</sub>S<sub>2</sub>H<sub>3</sub> to dicalcium silicate hydrate (C<sub>2</sub>SH) when the temperature exceeds 110°C and the microstructure of hardened slurry changes from a three-dimensional fiber network to a blank-block or mass block for different curing temperature conditions (Zhang et al., 2008). On the other hand, the major products of cement slurry with silica sands changes into C<sub>5</sub>S<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>S<sub>6</sub>H (> 150°C), C<sub>5</sub>S<sub>5</sub>A<sub>0.5</sub>H<sub>5.5</sub>, C<sub>3.2</sub>S<sub>2</sub>H<sub>0.8</sub> or other kinds of calcium silicate hydrate at high curing temperatures and the microstructures are transformed into a fiber network, rough frame network, short-parallel-needle fiber or mass block structure (Zhang et al., 2008). Different cements show different sensitivity to additives, thus exhibiting different behaviours when mixed with the same additives (Vidick et al., 1989; Jupe et al., 2007). According to Justnes et al. (1995) only about 10% hydration is necessary for a plain API class G cement slurry with w/c = 0.5 to retain its shape at atmospheric pressure. Even though, changes in the hydration of C<sub>3</sub>S with pumping time of cement slurries could not be correlated, it was found that the largest changes in pumping time as a function of temperature occurred in a temperature interval where ettringite/monosulphate decomposes and crystalline hydro garnet started to be formed (Jupe, 2005).

## **2.8 Mechanical Properties of Hydrated OWC Slurry**

Myers et al. (2005) argued that compressive strength is not the main parameter in well cement slurry design rather elasticity and tensile strength of the cement system is more important for casing support and zonal isolation. However, an effective and long term zonal isolation requires the consideration of other mechanical properties such as the flexural strength, shear strength and elastic properties (Young's modulus and Poisson's ratio), particularly when wells are subjected to anisotropic earth stresses. Such properties are especially important in the case of multilateral junction cementing, which has evolved as an economic means for increasing reservoir productivity and reducing development plan costs (Blanco et al., 2002). Various models have been developed to quantify stresses induced in



cement sheaths. In most instances, such models tend to predict that failure usually occurs under tensile stresses rather than under compressive stresses (Goodwin and Crook, 1992; Heinold et al., 2002).

The mechanical properties of hardened OWC slurry are affected by a number of factors and depend on the chemical composition of its constituents, temperature, curing regime etc. The compressive strength decreases with the addition of MgO, while the shear bond strength increases with the addition of MgO (Buntoro and Rubiandini, 2000). The addition of 3 to 5% by weight of cement (BWOC) of neat MgO as an expanding additive provides an excellent shear bond and acceptable compressive strength in geothermal and oil well cements at high temperatures of up to 250°C (Buntoro and Rubiandini, 2000; Saidin et al., 2008). For a cement slurry composed of 35% silica flour and 3% MgO BWOC, 3 days of curing result in higher shear bond strength and compressive strength as shown in Figure 2.4 (a, b). Microsilica (also called condensed silica fume), because of its high degree of pozzolanic activity, has allowed the introduction of low-density cement systems with higher rate of compressive strength development (Carathers and Crook, 1987). However, not all grades of microsilica improve slurry stability and mechanical properties of hardened cement system.

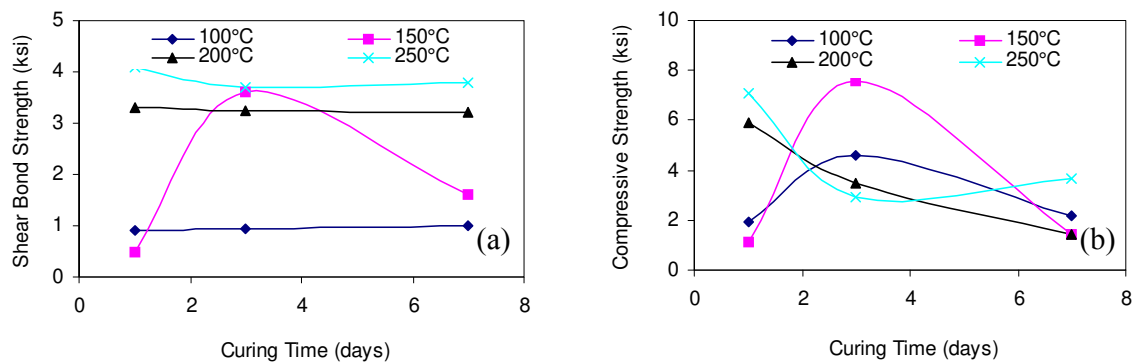


Figure 2.4 Effect of time on (a) shear bond strength behavior, and (b) compressive strength behavior of portland cement system containing 35% silica flour and 3% BWOC of neat magnesite at various temperature (Buntoro and Rubiandini, 2000).

Cement slurries prepared using densified microsilica neither improves the slurry stability nor the set cement permeability and mechanical properties (Daou, F. and Piot, 2008). Mechanical properties are not only dependant on the type of additives, but also on the slurry density. Thus, additives which are known to improve the flexural and tensile strength of hardened cementitious materials in low to medium density systems may not be as effective in higher density systems (Heinold et al., 2002). It has been found that incorporating polymeric latex particles improved the tensile strength and toughness of hydrated cementitious materials (Isenburg and Vanderhoff, 1974). Fibre-reinforced cement-based systems have been proven to be useful in various cementing applications. An increase in flexural strength and in energy absorption before fracture can be achieved by incorporating relatively small amounts of polymer latex together with short fibers. Approximately 0.8% by volume of a styrene-butadiene copolymer latex added to a glass fiber-reinforced Class G OWC improved the energy to fracture by a factor of four due to an enhancement of the interfacial shear strength between fibers and the cementitious matrix (Pafitis, 1995). It was reported that combined addition of fibers and latex increased both the strength and fracture energy to values greater than that found by the incorporation of either fibers or latex alone (Pafitis, 1995). On the contrary, a decrease in compressive strength was observed with increasing amount of fiber in latex modified cement since the increased amount of fiber led to an increase in the porosity and permeability of the hydrated OWC (Trabelsi and Al-Samarraie, 1999). Ultra lightweight slurries with densities from 9 to 11 ppg provide adequate mechanical properties (flexible and tension strengths) and resistance to H<sub>2</sub>S and CO<sub>2</sub> (Mata et al., 2006). The inert fibers, added to ultra lightweight slurries, improve the mechanical properties of the cement by creating a network across the loss zone during cementing in highly permeable and depleted formation, and the created net provide additional stability to resist tensile stresses (Garduño et al., 2006). Cestari et al. (2008 and 2009) studied the kinetic parameters of HCl interaction with an epoxy-modified cement slurry and a standard cement slurry and found that the epoxy-modified cement slurry have good potential to be used in environmental-friendly oil well operations. Portland cement and polyurethane nonionic composites was found to provide improved the mechanical properties compared with the slurry prepared using only Portland cement (Nascimento et al., 2008). Fiber-toughening agent, consisted of carboxylated nitrile rubber particles at 5.5% BWOC and a polypropylene fiber at 0.2% BWOC, was found to significantly increase both the elasticity and the toughness of set cement (Yao and Hua,

2007). A high performance light weight (HPLW) slurry along with an engineered fiber material (EFM) resulted in improved zonal isolation and less reservoir damage by reducing the hydrostatic pressure in the annulus and artificially increasing the fracture pressure during placement, and cost savings by avoiding remedial cementing and non productive time (Tranquini et al., 2007).

## **2.9 DURABILITY of HARDENED OWC SLURRIES**

Cement-based materials are subjected to deterioration under aggressive environments. The extreme temperature cycling of the well bore results in severe mechanical damage and ultimate failure of the cement sheath, potentially leading to microannulus (Saidin et al 2008). The rate of deterioration is generally aggravated at high temperature and pressure such as in the case of oil and gas bores. A strict control of cement reactivity and mechanical properties during the life cycle of the well is thus very important. The oil well cemented system should meet a wide range of short-term criteria such as free water, thickening time, filtrate loss, development of strength, shrinkage, etc., in addition to various long-term requirements including resistance to chemical attack, thermal stability and mechanical integrity of the cement sheath (Ravi et al., 2002).

### ***2.9.1 Porosity and Permeability***

The volume and size distribution of pores affect not only the mechanical strength of cement-based materials, but also its durability. The porosity and pore size distribution of a hardened OWC slurry depends on a number of factors such as the w/c ratio, degree of hydration, type of cement, mixing conditions, chemical admixtures and mineral additives, etc. High temperature has a drastic effect on the pore structure and compressive strength of cement-based materials. The total porosity is more than doubled when the curing or casting temperature increases from 20°C to 1000°C (Komonen and Penttala, 2001; 2004). Based on experimental results, Komonen and Penttala (2001) argued that exposure to a temperature from 50°C to 120°C can be as detrimental to the residual strength of a cement paste with a low water cement ratio as exposure to a temperature of 400-500°C. Justnes et al. (1995) studied the change in porosity and pore size distribution as a function of time during the setting period for a plain API Class G cement with a w/c ratio = 0.5 at both 20°C and 60°C. It was found that although there was enough liquid volume to allow gas intrusion and

percolation to occur, the pore entries were so small (1.0-1.6  $\mu\text{m}$  in diameter) that gas could enter only as small bubbles or when dissolved without disruption of the matrix. Polymeric latexes were found to improve the ability of the hardened OWC to prevent migration of reservoir fluids from one zone to another by decreasing permeability and preventing gas migration through the set slurry in the semi-solid state (Nakayama and Beaudoin, 1987; Su et al., 1991). It was reported that the increased amount of fiber in latex modified cement led to an increase in the porosity and permeability of the hydrated OWC (Trabelsi and Al-Samarraie, 1999). Light weight cement systems cured for 7 days at 185°F and 3000 psi exhibited lower permeability and porosity (Moulin and Revil, 1997).

### ***2.9.2 Shrinkage, Expansion and Dimensional Stability***

The expansion of OWC slurries is important to improve the quality of the well cementing sealing. Expansion should take place after pumping cement slurry into the annulus and the process should begin after the formation of the hardened cement structure starts but not after the formation of a rigid crystalline structure, as it can cause fracturing and adversely affect the porosity. On the other hand, if the expansion takes place too early, i.e. when the suspension is in a liquid state, the quality of formation isolation get worsens. The well casing is in an expanded state during the initial setting of the cement slurry due to the heat of hydration. Subsequent internal temperature reduction resulting from mud circulation may cause the casing to contract and destroy the cement/casing bond partially or entirely (Buntoro and Rubiandini, 2000). Expanding additives can overcome this problem as they tend to expand after the initial set, thus maintaining the bond between formation, cement and casing during pressure and temperature changes. Gypsum and gypsum containing substances can be used as expanding additives (Agzamov et al., 2001). The addition of gypsum with high-alumina binders, high-alumina slags, or anhydrous calcium sulfoaluminate makes the resultant cement quick solidifying and late expansive (Agzamov et al., 2001). The slurry mixing time and type of additive used have a significant influence on the expansion of the hydrated cement. Mixing OWC with CaO additives for three hours, which simulates cement slurry pumping into the well, ceases the expansion, whereas MgO does not change the cement expansion after the same treatment at a temperature of 80°C (Agzamov et al., 2001). Expansion is reduced by 30% and 70% when the pressure is increased up to 50 MPa and 100 MPa, respectively for cement with a CaO additive (Agzamov et al., 2001). In the case of

chromate aluminate cements, expansion is reduced by 25% with the addition of NaCl, and by 30% when the pressure increases from 10 to 100 MPa (Agzamov et al., 2001).

Gas leakage into and through the cemented annulus in oil and gas wells can cause environmental problems and compromise well safety. It is believed that a low shrinkage of the OWC slurry reduces the risk of gas migration (Backe et al., 1999; Backe, 1998). Shrinkage or expansion of a hydrating OWC slurry is dependant on the chemical composition and dosage of the constituents of the slurry, temperature and pressure. Chemical shrinkage, the volume reduction associated with the reaction between cement and water in a hydrating cement system, may be divided into two parts: external shrinkage and total shrinkage. The external shrinkage is the bulk volume change of cement slurry leading to a possible microannulus between the cement and the wellbore, whereas the total shrinkage is the sum of the external shrinkage and the contraction of pores of the slurry. The total chemical shrinkage of a given cement system can be reduced by increasing the slurry yield (Chenevert and Shrestha, 1991) or by decreasing the amount of water by adding sodium chloride, silica flour, bentonite, or sodium silicate (55) (Chenevert and Shrestha, 1991). Both the total and external chemical shrinkage of hardening Class G cement slurries seem to be independent of the w/c ratio at the early stage (during the first 48 hrs) (Justnes et al., 1995). The use of an extender reduces the shrinkage and the risk of gas migration provided that the mechanical strength development of the cement slurry is satisfactory (Backe, 1998). The external and total shrinkages of a neat Class G cement slurry cured at 20°C and atmospheric pressure were found to be about 1.0 ml/100g cement and 2.2 ml/100 g cement, respectively after 48 hours (Justnes et al., 1995). Human hair fibers reduces the plastic shrinkage cracks area of mortar by a remarkable percentage up to 92% and are claimed to commercially use in oil and gas well (Al-Darbi et al., 2006).

### ***2.9.3 Corrosion and Acid Attack***

Corrosion of hydrated OWC and the exterior wall of the well casing is common in oil wells. CO<sub>2</sub> corrosion was found to be the dominant mechanism of OWC deterioration in the form of carbonic acid leaching intensified by high temperature (Krilov et al., 2000). Yang et al. (2001) reported that the unconsolidated phase and diffusional effect as a result of the action of the formation water solution matrix Ca(OH)<sub>2</sub> with Ca(OH)<sub>2</sub> are the basic reasons causing

this form of corrosion while according to Zhang et al. (2009) the cement corrosion by CO<sub>2</sub> occurs by the destruction of the microstructure formed by the original hydration products of oil well cement and is affected by CaCO<sub>3</sub>, with different crystal structure, which is produced by the chemical reaction between CO<sub>2</sub> and the original hydration products.

Pyrite (FeS<sub>2</sub>), a common constituent of reservoir rocks, can be easily oxidized to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and sulphate ions (SO<sub>4</sub><sup>2-</sup>) by exposure to moderately oxidizing conditions, including de-oxygenated injection or process water or steam. Pyrite oxidation causes excessive degradation of well cements and replacement of cement by structurally less stable products such as calcium sulphates (Hutcheon, 1998). Sulfuric acid may also cause the corrosion of the well tube and subsequent casing leak, which may lead to a failure of the casing due to cement collapse, tubing corrosion or both (Hutcheon, 1998).

The durability of hardened OWC to acid exposure has not been well studied. About 40% of the world's remaining gas reserves contain more than 2% of CO<sub>2</sub> and/or more than 100 ppm of H<sub>2</sub>S (Lecolier, 2006). Therefore, a comprehensive investigation of the durability of OWC exposed to CO<sub>2</sub> and H<sub>2</sub>S is of paramount importance to optimize oil/gas well production and special attention has to be provided to the design of the well system including the casing and cementing materials subjected to corrosive gases.

The subsurface conditions that may exist in CO<sub>2</sub> sequestration sites can damage the cement that makes the primary plug in abandoned wells. Duguid et al. (2004 and 2005) conducted experiments at ambient pressure and various temperatures (20°C, 23°C and 50°C) with the pH adjusted using HCl. Extensive degradation was observed in these experiments due to the continuous flow of acidified, carbonated brine. These results showed that lower pH and higher temperature cause faster degradation and temperature had more effect on degradation rates than pH (Duguid et al., 2004 and 2005). The rate of mass loss of the hardened OWC slurry usually slows down with time. Duguid et al. (2004) found that cement slurry containing bentonite deteriorated at a faster rate than that of a neat Class H cement slurry. Even a short exposure to carbonated brine can damage the sealing properties of the cement in an abandoned well (Duguid et al., 2004). Light-weight cement slurries are usually more resistant to acid attack and the resistance also improves when latex is used in the formulation as shown in Table 2.5 (Moulin and Revil, 1997). It was reported that hardened OWC

deteriorated and lost its integrity under a hostile downhole environment (high reservoir temperature >180°C, sour gas: 22% CO<sub>2</sub> and 150 ppm H<sub>2</sub>S) after prolonged exposure (Krilov et al. 2000). Geothermal conditions (bottom hole temperature >250°C) (Sasaki et al., 1986) may result in well bore cement systems deterioration with loss of compressive strength and increasing permeability in a relatively short period of time (Gallus et al., 1979). According to Jacquemet et al. (2005) the presence of a H<sub>2</sub>S-CO<sub>2</sub> mixture induced carbonation of the cement and sulfidation of iron bearing phases (steel and C<sub>4</sub>AF) coupled with a pH decrease at elevated pressure and temperature (500 bar and 200°C). It was reported that reactive power cement (RPC) formulation, optimized according to the grain size distribution of Class G cement and two different types of silica particles (silica sand and silica fume) and other classical additives such as lignosulfonate derivatives (retarder), polynaphthalene sulfonate (dispersant) and acrylic polymer (fluid loss agent), reduced the deteriorating effect of H<sub>2</sub>S sulfur gas (Noik and Rivereau, 1999).

Table 2.5 Acid- resistant light-weight cement formulations (Moulin, E., and Revil, 1997)

	Cement 1	Cement 2	Cement 3	Cement 4
Density kg/m <sup>3</sup> (lbm/gal)	1440 (12)	1896 (15.8)	1440 (12)	1896 (15.8)
Latex (gal/sk)	-	-	1.25	1.6
Weight loss, %				
In 1 hr	1.0	3.7	0.3	2.8
In 4 hrs	4.3	21.0	0.9	7.7

#### ***2.9.4 Sulphate Attack***

Sulfate ions chemically combine with tricalcium aluminate in an expansive reaction and can cause cement distress. This process depends on the C<sub>3</sub>A content of cement, the type and concentration of sulphate ions, permeability of the cementitious matrix, and temperature. The degradation process decreases with increasing temperature and can be mitigated by reducing the permeability of the hydrated cement (Morales et al., 2003). The sulphate degradation process requires a certain incubation period before the cementitious matrix pores become filled with ettringite. It was reported that specimens prepared with Class A and Class G API oil well cements showed insignificant expansion during the first 240 days when exposed to solutions containing sulphates concentration ranging from 0 to 30000 ppm and temperatures

of 32 and 84°C (Morales et al., 2003). Pore blocking additives, dispersants and low w/c can improve the sulphate resistance and durability performance of Class A cement (Morales et al., 2003).

## **2.10 CONCLUSIONS**

Research on oil well cementing has been reviewed in this paper along with existing studies conducted on rheology, additives, mechanical properties and durability of oil/gas well cements. A successful oil well cementing should satisfy two basic criteria: (a) it should be easily pumpable for a sufficient time to allow proper placement of the slurry in the well bore subjected to extreme levels of temperature and pressure, and (b) the cement slurry should develop and maintain sufficient mechanical strength to support and protect the casing, and must have low permeability and adequate durability to ensure the long-term isolation of the producing formation. With the advent of API oil well cements, achieving these goals has become easier than before when only one or two Portland cements were available for well cementing. Chemical admixtures and mineral additives play an important role by altering the chemical and physical properties of the oil/gas well cement slurry and maintaining the proper rheology necessary for the placement of the cement slurry in typically deep well bores. The appropriate oil/gas well cement slurry design is a function of many parameters including the well bore geometry, casing hardware, formation integrity, drilling mud characteristics, presence of spacers and washers, and mixing conditions. An adequate rheological characterization of the slurry is required to optimize cementing properties. Though cement slurry rheology is a widely studied subject, correlations between rheological properties and the chemical, microstructural and mechanical behaviour of the slurry after setting have not yet been fully defined. The oil/gas well cement should meet various long-term requirements such as resistance to chemical attack by CO<sub>2</sub>, acids and sulphates, thermal stability and mechanical integrity of the cement sheath. There is an opportunity for researchers to develop novel oil/gas well cementitious systems that have stable rheology and appropriate setting properties under high temperature and pressure, and excellent durability in much adverse environments including CO<sub>2</sub>, acid and sulphate attack. This warrants further dedicated research.



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## *Chapter 3*

# **RHEOLOGY OF OIL WELL CEMENT SLURRIES**

### **3.1 Introduction**

The word “Rheology” originates from the Greek word “reo”, meaning flow. Rheology is the study of the deformation and flow of materials. Typically, rheology studies the deformation of those materials whose behaviour falls between solids and fluids (viscoelastic materials) (Barnes et al., 1989). The study of rheological properties attempts to determine the intrinsic fluid properties; mainly viscosity, which is necessary to determine the relationships between the flow rate (shear rate) and the pressure gradient (shear stress) that causes the movement of a fluid (Guillot, 2006). The science of rheology can be employed for instance for achieving the following goals:

- To understand the interactions between different ingredients in a material to get an insight into its structure.
- To control the quality of a raw material by measuring its rheological properties. The acceptance/rejection of a product can be determined based on rheological results.
- To evaluate the mixability and pumpability of a slurry.
- To determine the frictional pressure when a slurry flows in pipes and annuli.
- To evaluate the capability of a slurry or paste to transport large particles (e.g., some lost circulation materials and fibres).
- To evaluate how the surrounding temperature profile affects the placement of a slurry or paste.
- To design a processing equipment such as selecting the appropriate pump to provide sufficient power for a material to flow over a certain distance in pipelines. The relationship between the pump and flow in pipelines is governed by the rheological properties of the material.

Fluid movement may be compared to a large number of platelets moving parallel to one another at different velocities (Guillot, 2006) (Fig. 3.1). In this simple flow geometry, the

velocity of the fluid particles varies linearly from one plate to another and the shear rate (or velocity gradient) can be mathematically described as:

$$\text{Shear rate} = \frac{\text{The velocity difference between 2 platelets}}{\text{The distance between 2 platelets}}$$

Or

$$\frac{dv}{dx} = \frac{v_1 - v_2}{L} \quad (3.1)$$

Where,  $x$  is an axis parallel to the plates. The dimensions of equation 3.1 are

$$\frac{\text{length} \times \text{time}^{-1}}{\text{length}} = \text{time}^{-1}$$

Therefore, the unit of shear rate is  $\text{sec}^{-1}$  and is represented by  $\dot{\gamma}$ .

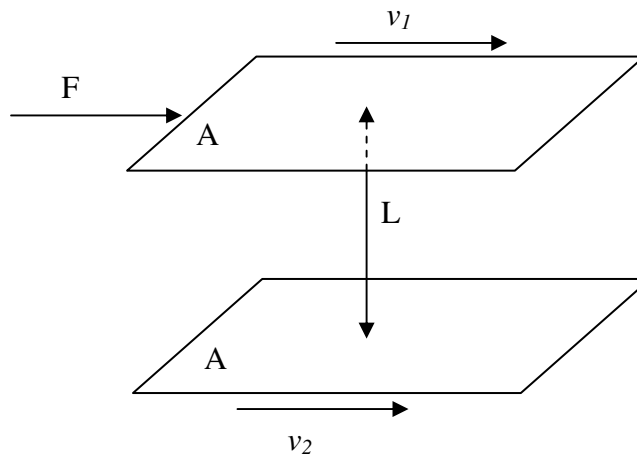


Figure 3.1 Flow between parallel plates

The force  $F$ , applied to the top of an element causes shear stresses ( $\tau$ ) expressed in the following equation:

$$\tau = \frac{F}{A} \quad (3.2)$$

The viscosity,  $\mu$ , of a fluid is the ratio of the shear stress,  $\tau$ , to the shear rate,  $\dot{\gamma}$ . In common oilfield units, the unit of viscosity is the centipoises (cp) and in SI unit, it is the Pascal-sec (Pa.s).

$$\mu = \frac{\tau}{\dot{\gamma}} \quad (3.3)$$

There are several ways to study the rheology of materials by inducing shear stress. Shearing a material using a two parallel plate geometry (Fig. 3.2) has been used to measure the viscosity of liquids. However, this geometry has encountered difficulty when used to test materials with low viscosity, since it is hard to hold such a material between the two plates.

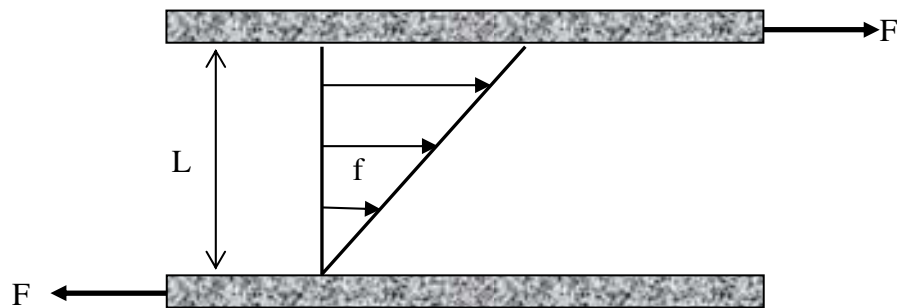


Figure 3.2 Illustration of the parallel plate geometry.

The coaxial cylinders geometry is the most commonly used tool to measure the rheological properties of fluids because the sample can be easily placed in the gap between two cylinders, and the material is sheared by rotating one of the cylinders. Figure 3.3 is a schematic representation of the coaxial cylinders geometry.

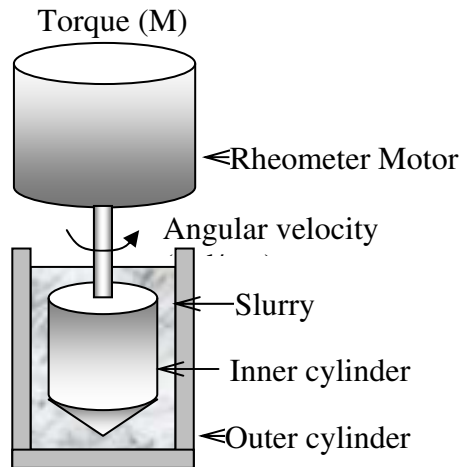


Figure 3.3 Schematic representation of coaxial concentric cylinders with cylindrical conical end geometry.

### 3.1.1 Newtonian Fluid

Generally, fluids can be classified into two groups: Newtonian and non-Newtonian. Newtonian fluids (Fig. 3.4) comply with the Newtonian model represented by equation 3.3, in which the shear stress,  $\tau$ , is proportional to the shear rate,  $\dot{\gamma}$ . The slope of the line is the viscosity,  $\mu$ , of the fluid which does not depend on the flow condition (e.g., shear rate, time of shearing) but depends on temperature and pressure (Guillot, 2006). Stresses in a Newtonian fluid will suddenly reach zero upon stopping the shearing. However, whatever is the period of the resting time, when the shearing starts again, the viscosity is as previously measured (Barnes, 1989).

Fluids that show a Newtonian flow behaviour have often low molecular weights. Common Newtonian fluids are water, gasoline, etc. Silicon oils are used as a calibration liquid for rheometers due to their reliability.

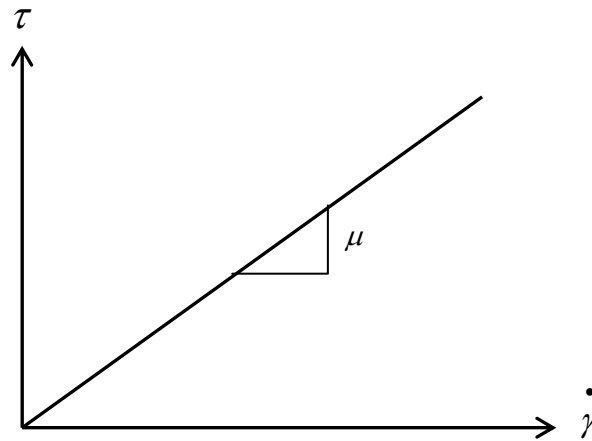


Figure 3.4 Shear stress-shear rate relationship for a Newtonian fluid.

### 3.1.2 Non-Newtonian Fluid

Unlike Newtonian fluids, the viscosity of non-Newtonian fluids depends on the applied shear rate and the time during which the shear rate is applied, i.e., the shear stress-shear rate relationship differs from a straight line that goes through the origin.

A certain level of stress must first be overcome before a non-Newtonian fluid starts to flow. The presence of a critical stress means that under static conditions, a non-Newtonian fluid essentially acts as a solid and will continue acting as a solid until the stress reaches the shear force needed to overcome the internal friction of the material. The Bingham plastic model was introduced to account for this distinguishing characteristic of non-Newtonian fluids (Bingham 1922):

Two parameters describe the Bingham plastic model :

- The value of  $\tau$  for  $\dot{\gamma} = 0$ ,  $\tau_0$
- The slope of the straight line, plastic viscosity ,  $\mu_p$  (Fig. 3.5).

$$\tau = \tau_0 + \mu_p \dot{\gamma} \quad , \text{ when } \tau > \tau_0 \quad (3.4)$$

$$\dot{\gamma} = 0, \text{ when } \tau \leq \tau_0 \quad (3.5)$$

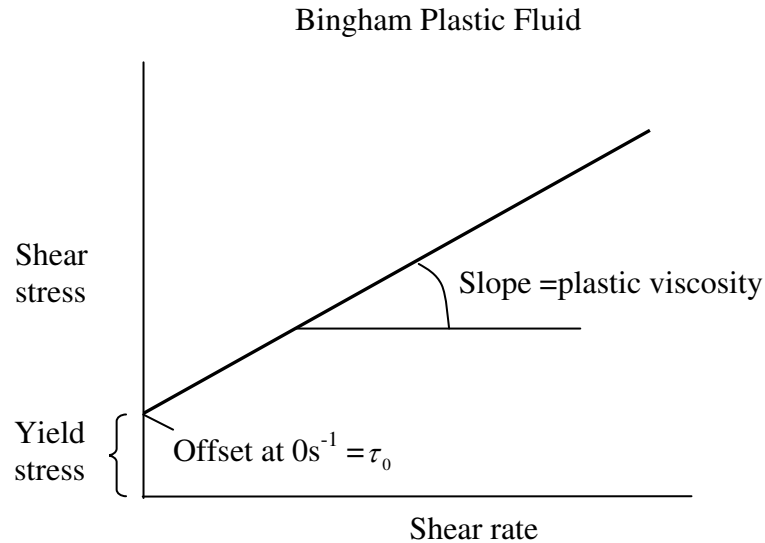


Figure 3.5 Shear stress-shear rate relationship for a Bingham plastic fluid.

The measured yield stress value may vary for a given material if the test conditions change. For example, Nehdi and Rahman (2004) found that the yield stress of cement paste varied if the type of the geometry used in the rheological test changed.

The fact that the viscosity depends on the shear rate means that the tested sample does not have a constant viscosity. Thus, the viscosity of a non-Newtonian fluid is measured at a specified shear rate and is called apparent viscosity. Power-law fluids include pseudo-plastic fluids which flow immediately when a pressure gradient is applied. However, unlike Newtonian fluids, the relationship between shear stress and shear rate is not linear (Fig. 3.6). The Power-law fluids pass through the origin and are described by the following formula:

$$\tau = k \dot{\gamma}^n \quad (3.6)$$



where,  $\tau$ ,  $k$ ,  $\dot{\gamma}$  and  $n$  represent the shear stress, consistency, shear rate, and power law exponent, respectively. The exponent  $n$  describes the shear thinning and shear thickening behaviour. Cement pastes or slurries are considered as shear thinning when  $n < 1$  and shear thickening when  $n > 1$ .

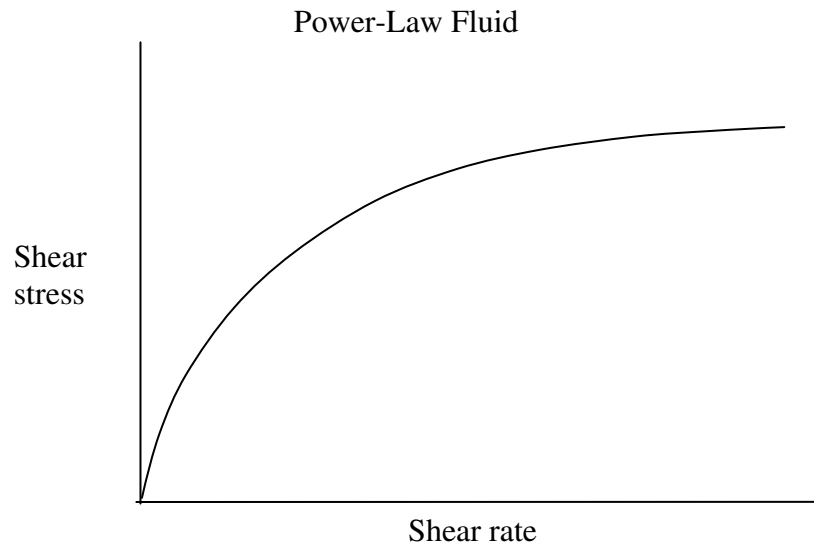


Figure 3.6 Shear stress-shear rate relationship for a Power-law with  $n < 1$ .

A fluid becomes shear-thinning when the apparent viscosity decreases with the increase in shear rate, i.e. when the slope of the shear stress vs. shear rate flow curve decreases with the shear rate (Fig 3.7).

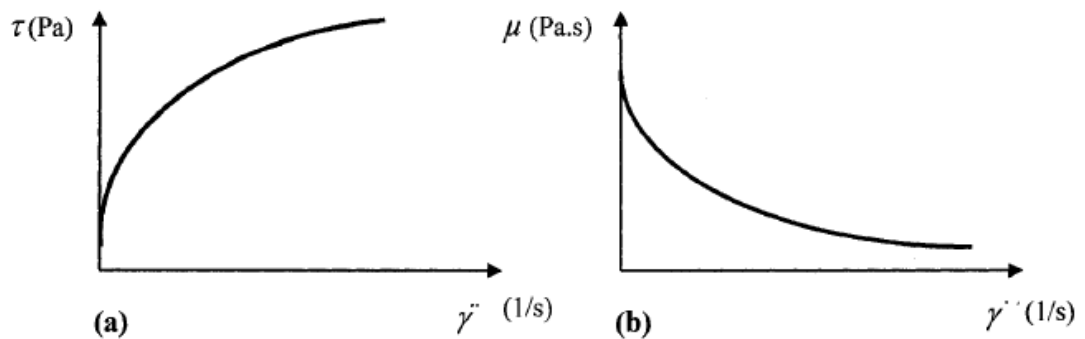


Figure 3.7 Typical shear thinning behaviour: (a) shear stress vs. shear rate, and (b) viscosity vs. shear rate.

The shear-thickening phenomenon is often associated with suspensions of irregularly shaped particles in which the liquid exhibits an increase in volume when it is sheared. The viscosity of shear-thickening materials increases with the increase of shear rate (Fig. 3.8). The microstructure of such materials will rearrange when sheared causing resistance to flow that increases with shear rate (Barnes *et al.*, 1989).

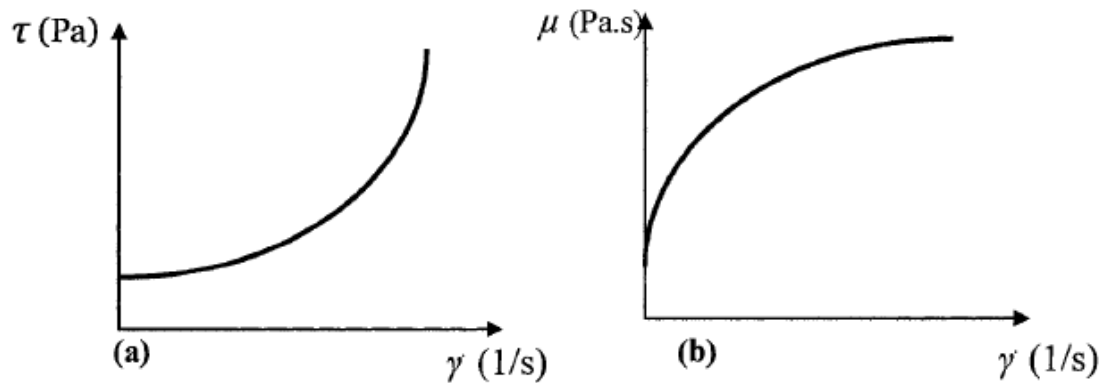


Figure 3.8 Typical shear thinning behaviour: (a) shear stress vs. shear rate, and (b) viscosity vs. shear rate.

A Herschel-Bulkley fluid combines Power-law and Bingham plastic behaviours of fluids through the following formula:

$$\tau = \tau_0 + k \dot{\gamma}^n \quad (3.7)$$

where,  $\tau$ ,  $\tau_0$ ,  $k$ ,  $\dot{\gamma}$  and  $n$  represent the shear stress, yield stress, consistency, shear rate, and power law exponent, respectively. The model assumes that below the yield stress ( $\tau_0$ ), the slurry behaves as a rigid solid, similar to the Bingham plastic model.

### 3.1.3 Thixotropy

Thixotropy is a gradual decrease of the viscosity under shear stress followed by a gradual recovery of structure when the stress is removed. Thixotropic fluids show both a shear thinning and time-dependent behaviour (Mewis, 1979). Thixotropy is due to the structure degradation resulting from rupturing flocs or linked particles when the material is sheared. When the shearing stress is removed, the material structure rebuilds again and is eventually restored to its original condition (Barnes *et al.*, 1989). A quantitative measurement of thixotropy can be attempted in several ways. The most apparent characteristic of a thixotropic system is the hysteresis loop, which is formed by the up-and down-curves of the flow curve. If a material is thixotropic, the resulting two curves (up and down curves) do not coincide, and the degree of thixotropic behaviour, measured by the area of the hysteresis loop, indicates a breakdown of structure (and hence shear thinning) that does not reform immediately when the stress is removed or reduced (Fig. 3.9). It should be noted that two successive tests are needed to determine whether a material is thixotropic or not; a material is thixotropic when a loop is also obtained in the second test. In thixotropic cement slurries, the down curve of the hysteresis loop is displaced to the right of the up-curve. The viscosity values of cement slurries in the down curve were found lower than those in the up-curve at a constant shear rate. The opposite behaviour to thixotropy is called anti-thixotropy or rheopexy. The reverse hysteresis indicates that the structure of the materials stiffens as it is sheared at high temperature due to the mechanism of thixotropy build up, likely as a result of accelerated hydration. Antithixotropy can also be encountered for systems whose rate of structure recovery is accelerated by, for example vibration, and therefore the build-up of structure due to such an effect is greater than the structure break down due to shearing. This phenomenon is also denoted as negative thixotropy, because the measured down-curve becomes higher than the up-curve, leading to a negative value of the enclosed area between these two curves (Mewis, 1979).

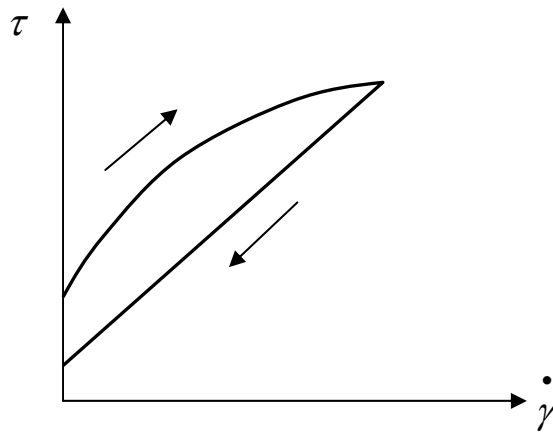


Figure 3.9 Typical hysteresis loop of a thixotropic fluid.

### 3.2 Rheology of Oil Well Cement Slurries

The rheological properties of an oil well cement (OWC) slurry determines the quality of the final product and helps predicting its end use performance and physical properties during and after processing. Rheological measurements can determine the flow properties of the cement slurry such as its plastic viscosity, yield point, frictional properties, gel strength, etc. Rheology studies the flow of fluids and deformation of solids under stress and strain. In shear flows, imaginary parallel layers of liquid move over or past each other in response to a shear stress to produce a velocity gradient, referred to as the shear rate, which is equivalent to the rate of increase of shear strain (Douglas et al., 1995). In extensional flows, elements flow towards or away from each other. Elongational or stretching flows are seldom found in cement systems (Banfill, 2003). However, it may be possible to experience some elongation at the entry or exit of a pipe. The rheological properties of OWC slurries are important in assuring that the slurries can be mixed at the surface and pumped into the well with minimum pressure drop. The rheological properties of the cement slurry also play a critical role in mud removal. A proper flow regime must be maintained for complete removal of the mud from the well bore (Nelson, 1984).

The flow regime of a cement paste or slurry can change with time, temperature, pretreatment, application of shear, type of application, type of dispersion, physical and chemical

characteristics of solid and liquid ingredients, the addition of special surface-active agents, and the extent of grinding and mixing. The rheological behaviour of the cement slurry also depends on a number of factors including the water-cement ratio, size and shape of cement grains, chemical composition of the cement and the relative distribution of its components at the surface of cement grains, presence of additives, mixing and testing procedures, etc. (Guillot, 1990; Guillot, 2006). The concentration and shape of solid particles has a significant effect on the rheological properties of an OWC slurry. The yield stress and plastic viscosity of cement paste usually increase as the cement becomes finer (Berg, 1979) and/or as the particle concentration increases (Barne et al., 1989).

The rheology of OWC slurries is generally more complicated than that of conventional cement paste. In order to contend with bottom hole conditions (wide range of pressure and temperature), a number of additives are usually used in the OWC slurries and the slurry shows different characteristics depending on the combination of admixture used. Sulfonates (polynaphthalene sulfonate, lignosulfonates) are the most commonly used cement dispersants. Lignosulfonates should not be used at lower temperature because of its retardation effect (Nelson et al 1990, Nelson et al. 2006).

It has been observed that the flow of OWC slurries follows the Bingham plastic model almost perfectly (Guillot, 1990). It was found that the viscosity of a Class G cement slurry decreases with the addition of a lignosulfonate dispersant as illustrated in Table 3.1 (Guillot, 1990). The yield value of the cement slurry decreased with increasing concentration of the dispersant (Michaux and Defosse, 1986). Glycerin acts as a slurry viscosifier and it was found that the associated increase in viscosity at lower shear rates is significantly lower than that at higher shear rates (Saasen et al., 1991). The shear thinning characteristics of Class G OWC slurry incorporating glycerin is illustrated in Fig. 3.10. Moreover, the incorporation of sub-micron size polymer latex (Nakayama and Beaudoin, 1987; Su et al., 1991) and replacement of cement by polymer powder (Chougnnet et al., 2006) can lead to a significant reduction in the OWC slurry viscosity, and therefore can improve mixability and pumpability. Rheological and hydraulic properties of foams (complex mixtures of gasses and liquids or slurries) are largely influenced by foam quality, liquid-phase viscosity, temperature, and pressure. It was found that unlike conventional aqueous foams, low-quality cement foams have a lower viscosity than the base fluid, and the viscosity increases as the

cement foam quality (gas volumetric fraction) increases from 10% to 30% (Ahmed et al., 2009). The viscosity of low-quality cement foam increased slightly after expansion or removal of pressure (Ahmed et al., 2009).

Table 3.1 Rheological parameters for Class G cement slurries with and without a dispersant (Guillot, 1990)

Fluid	Plastic Viscosity (mPa)	Yield Stress (Pa)
Neat Class G cement slurry	27.0	14.0
Dispersed Slurry	25.0	2.4

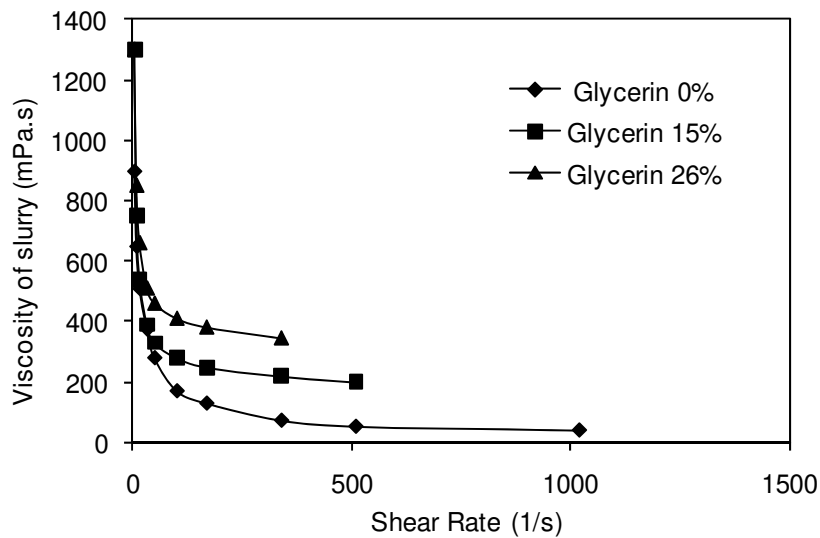


Figure 3.10 Viscosity of slurry as a function of the shear rate (Saasen et al., 1991).

The viscosity of OWC slurries exhibits a time-dependent behaviour which is difficult to characterize. However, for practical oilfield purposes, cement slurries are invariably represented by time-independent models as mentioned in the subsequent section. However, it is difficult to capture all possible trends of flow behaviour using a single rheological model (Yahia and Khayat, 2001). The performance of rheological models usually varies with the

test geometries, gap between shearing surfaces and their friction capacity, which makes the measurements more complicated (Nehdi and Rahman, 2004).

### ***3.2.1 Time-Independent Rheological Models***

Though there are qualitative and quantitative discrepancies between the rheological results for cement paste reported by different researchers, it is worthwhile to present the most commonly used rheological models to describe the rheological behaviour of cement slurries. These rheological models are usually mathematical expressions (Guillot, 1990; Banfill, 2003; Nehdi, 1998) of the shear stress or usually viscosity as a function of the shear rate. Figure 3.11 shows examples of slurry flow curves used in the petroleum industry (Guillot, 1990). Various rheological models used to describe cement slurry rheology are summarized in Table 3.2.

Existing time-independent rheological models allow fitting shear stress, shear strain rate and viscosity experimental data to specific trends using rheological data analysis software. However, no model is free from statistical error (Nehdi and Rahman, 2004). The Bingham plastic model and the power law model are widely used to describe the rheological properties of cement slurries (Guillot, 1990). The Bingham plastic model includes both yield stress,  $\tau_0$  and a limiting viscosity,  $\mu_p$  at finite shear rates, which the Power law model fails to consider. However, the Bingham plastic model tends to overestimate the shear stress at both low and high shear rates in a manner opposite to that of the power law model (Guillot, 1990). It was argued that friction pressures of cement slurries are better described by a modified form of the theoretical Bingham plastic friction pressure equations (Shah and Sutton, 1990).

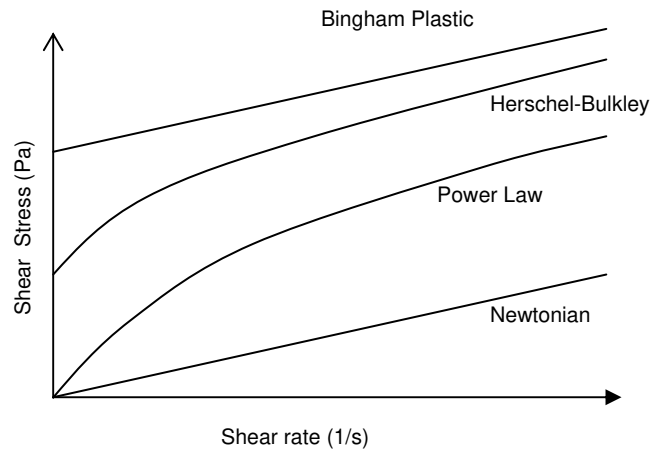


Figure 3.11 Examples of flow curves used in the petroleum industry (Guillot, 1990).

Table 3.2 Various time-independent rheological models for cement slurries

Model	Main Equation	Model	Main Equation
Newtonian Model	$\eta = \frac{\tau}{\dot{\gamma}}$	Vocadlo Model	$\tau = \left[ \tau_0^{1/n} + k^{1/n} \times \sqrt{\dot{\gamma}} \right]^n$
Bingham Plastic Model	$\tau = \tau_0 + \mu_p \times \dot{\gamma}$	Herschel-Bulkley Model	$\tau = \tau_0 + k \times \dot{\gamma}^n$
Modified Bingham Model	$\tau = \tau_0 + \mu_p \times \dot{\gamma} + c \dot{\gamma}^2$	Sisko Model	$\mu = \mu_\alpha + k \dot{\gamma}^{n-1}$
Power Law Model	$\tau = k \times \dot{\gamma}^n$	Williamson Model	$\mu = \frac{\mu_0}{1 + \left( k \dot{\gamma} \right)^n}$
Casson Model	$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\mu_p} \times \sqrt{\dot{\gamma}}$		

$\tau$  = shear stress,  $\dot{\gamma}$  = strain rate,  $\eta$  = constant slope for Newtonian model,  $\tau_0$  = yield stress,  $\mu_p$  = plastic viscosity,  $c$  = regression constant,  $k$  = consistency index,  $n$  = power law index,  $\mu_\alpha$  = viscosity at infinite shear rate,  $n$  = constant.



### 3.2.2 Effect of Time, Temperature and Pressure on Rheology of Cement Slurry

Temperature has a drastic effect on the rheological behaviour of cement slurries, which depends on the type of cement and admixtures used. The consistency, viscosity or plastic viscosity of cement slurries usually decreases with an increase in temperature as shown in Figure 3.12 (a, b). Limited experimental studies at higher temperatures suggest that cement slurry stability is problematic at higher temperature (Guillot, 1990). Pressure has a negligible effect on the flow behaviour of cement slurries because of the low compressibility and viscosity-pressure dependence of water. But the flow behaviour of cement slurries becomes increasingly sensitive to pressure at higher solid-liquid ratio (Guillot, 1990).

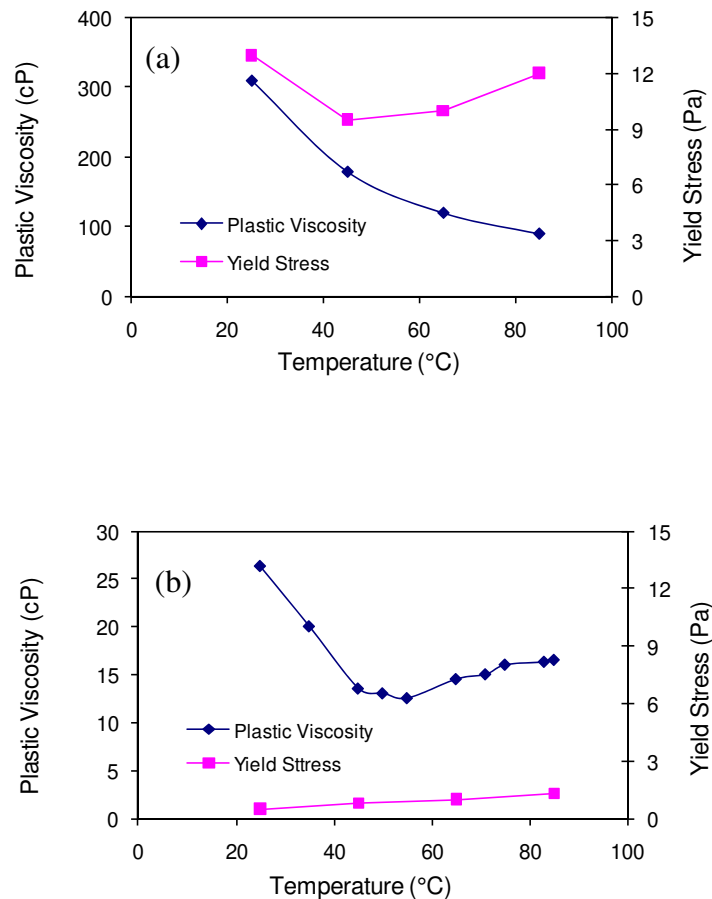


Figure 3.12 Temperature dependence of plastic viscosity and yield stress of a cement slurry with (a) cellulose derivatives and (b) a dispersant and a latex (Guillot, 1990).

The pressure and temperature dependence of the rheological properties of OWC slurries have not been well characterized because of the limitations of the standard oilfield testing equipment and API specifications for the determination of rheological properties, which limit the maximum temperature for measurements to 88°C at atmospheric pressure (Guillot, 1990; API RP 10B-2, 2005). However, Kellingray et al. (1990) used a modified pressurized consistometer to obtain rheological information of OWC slurries at high temperature and high pressure. The maximum temperature and pressure used in their experiments were 119°C (246°F) and 81.1 MPa (11800 psi), respectively.

It was concluded that compared to temperature effects, pressure had negligible effects on the rheological properties of cement slurries as shown in Figure 3.13(a, b). Ravi and Sutton (1990) investigated the effect of temperature and pressure on the plastic viscosity and yield point of class H cement slurries using a high pressure, high-temperature rheometer and developed a correlation to calculate the equilibrium temperature for plastic viscosity and yield point. Both plastic viscosity and yield stress were found to decrease with the increase in temperature. However, plastic viscosity reached a constant value beyond the equilibrium temperature whereas there was no evidence for yield stress to attain a constant value beyond a certain temperature (Ravi and Sutton, 1990). The equilibrium temperature of the slurry for plastic viscosity and yield stress need not be the same and was found to be dependent on the slurry composition (Ravi and Sutton, 1990).

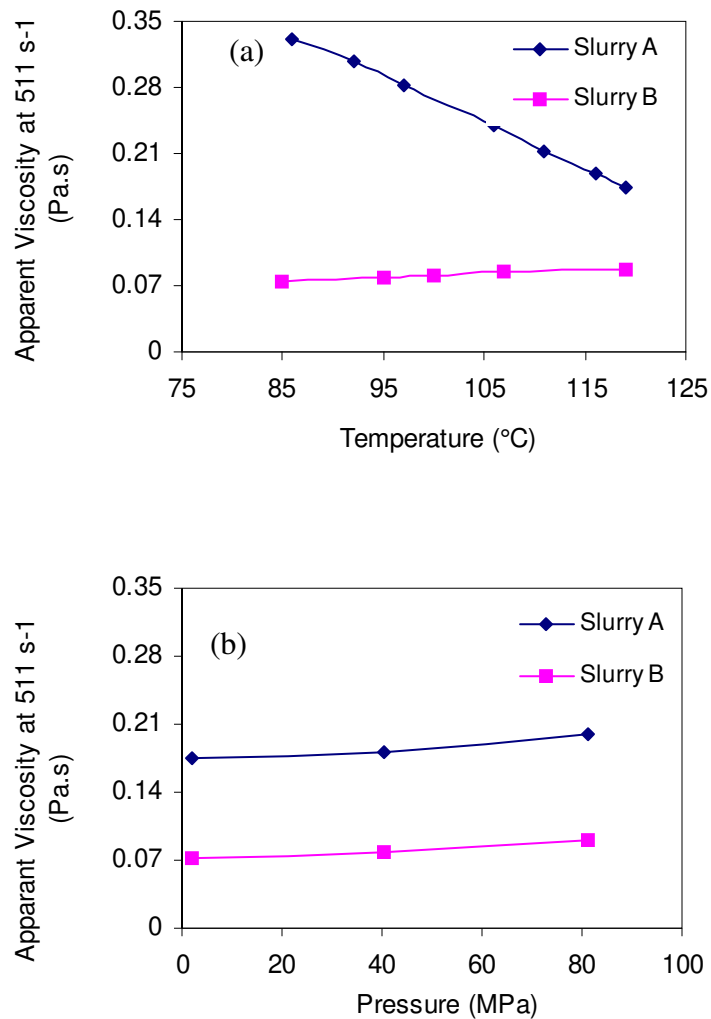


Figure 3.13 Effect of (a) temperature, and (b) pressure on the apparent viscosity of oil well cement slurries (Kellingray et al., 1990). Slurry A prepared using cement, silica flour, fluid loss aid (cellulose derivatives), dispersant (naphthalene sulphonate), and retarder (Calcium lignosulphonate) whereas Slurry B prepared using cement, silica flour and retarder (calcium lignosulphonate).

### 3.2.3 Equipment and Testing Methods for Rheology of OWC Slurries

Coaxial cylinder viscometers have been used for the evaluation of the rheological properties of OWC slurries. If the slurry rheological properties are well characterized, the friction pressure drop and the flow regime in the annulus of the oil well can be predicted with reasonable accuracy. Rheological measurements of cement slurries suffer from several

limitations including slip at the walls of the measuring device (Saak et al., 2001; Banfill and Kitching, 1991; Guillot 1990), migration of the particles due to centrifugal forces (Guillot, 1990; Denis and Guillot, 1987), shear induced migration (Coussot and Piau, 1995) or gravity induced migration known as settlement/sedimentation, and plug flow (Banfill, 2003; Guillot, 1990). A review of the literature concerning these effects is provided elsewhere (Banfill, 2003; Guillot, 1990). Similar problems have also been encountered in the case of pile-flow viscometers and vane rheometers.

More satisfactory results can be obtained by introducing devices in the measurement geometries to keep the paste homogeneous. These include angled blades (interrupted helical impeller) to lift particles (Bhatty and Banfill, 1982), re-circulating pumps to provide a circulation of the fluid through the sample cup and around the rotor-stator assembly (Meeten, 1990), blades with interlocking fingers (Vlachou and Piau, 2000) and more conventional mixers (Nachbaur et al., 2001). A modified cone and plate geometry was found efficient against settlement error, especially for relatively liquid suspensions with weak structures (Piau, 1997). Vlachou and Piau (2000) found that a modified parallel-plate geometry attached to commercial rotational rheometers reduced the settlement and slippage of OWC slurry particles at the walls and allowed to study the settling process of the cement slurries as a function of the intensity of the shear.

Most conventional rheometers limit the maximum temperature for measurements too much lower than the actual bottom hole temperature and limit the pressure to only atmospheric levels. Such measurements may lead to poor predictions of OWC slurry properties in the actual oil bore, which in turn can increase the risk of cementing failures. Kellingray et al. (1990) used a modified high-temperature and high-pressure consistometer to investigate the OWC slurry rheology under simulated bottom hole conditions. A number of rheometers capable of withstanding high temperature and pressure have been developed. However, research studies in this area are still needed to further refine the testing equipment and procedures. Though OWC slurry rheology is a widely studied subject, correlations between chemical, microstructural and mechanical behaviour of the slurry before and after setting have not yet been clearly defined, and thus require more dedicated research.

### 3.3 Conclusions

The rheological properties of cement-based materials determine the quality of the hardened cementitious matrix and help predicting its end use performance and its physical properties during and after processing. Measuring rheological properties of cement based materials in the laboratory remain a challenging task. The rheological properties are affected by numerous factors including the w/c, size and shape of cement grains, chemical composition of the cement and relative distribution of its components at the surface of grains, presence and type of additives, compatibility between cement and chemical admixtures, mixing and testing procedures, etc. Moreover, slip at the slurry-shearing surface interface, particle-particle interactions, chemical reactions, non-homogeneous flow fields, and human errors can make the rheological experiments difficult to reproduce. Above all, the equipment used to quantify the rheological properties of cement based materials is relatively expensive, difficult to operate, and may not be suitable for use in construction sites because of its large size and/or complicated set up.

Rheological characterization is a tool that can evaluate the rheology of cement-based materials. By examining a suspension of cement particles in water, one can apply well established rheological theories. Hence, producing good quality paste or slurry incorporating superplasticizers at high temperature can be achieved by controlling its rheological properties. Yield stress, viscosity and the degree of thixotropy are crucial parameters that affect the rheology of cement-based materials.

For the particular case of the petroleum industry, cement slurries are pumped down to several thousand meters into the ground to anchor and seal the casing to the borehole of oil or gas wells. Thus, an accurate characterization of the rheology of cement slurries is critical. However, oil well cement slurry rheology is more complicated than that of cement paste. In order to contend with bottom hole conditions (wide range of pressure and temperature), a special class of cements called oil well cements (OWCs), specified by the American Petroleum Institute (API) (API Specification 10A, 2002) and various additives are usually used in the slurry composition. Among the eight (8) different types of available OWC, Class G and H cements are usually specified for deeper, hotter and higher pressure well conditions. A thorough review of the types of admixtures used in the petroleum industry and the

rheology of oil well cement (OWC) slurries has been provided in the literature (e.g. Nelson *et al.*, 2006, and Guillot, 2006). But comparing the effects of different admixtures on the rheological properties of oil well slurries at different temperatures remains largely unexplored and substantial research work is needed to develop fundamental knowledge for the effective use of superplasticizers in oil well cementing.

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## Chapter 4

# COUPLED EFFECTS OF CHEMICAL ADMIXTURES AND TEMPERATURE ON RHEOLOGICAL PROPERTIES OF OIL WELL CEMENT SLURRIES\*

### 4.1 Introduction

Chemical admixtures play an important role in controlling the early-age physical and chemical properties of cement slurries, and subsequently those of the hardened cementitious system. However, admixtures are associated with some shortcomings including variation of the initial slump, rapid loss of fluidity of cement slurries, and binder-admixture compatibility problems. Cement slurries prepared with various kinds of admixtures using the same type of cement can exhibit large variations in flow. The rheological properties of cement slurries can be strongly affected by a number of factors including the water-cement ratio (w/c), size and shape of cement grains, chemical composition of the cement and relative distribution of its components at the surface of grains, presence of additives, interactions between the cement and chemical admixtures, mixing and testing procedures, time and temperature, etc.

For the particular case of the petroleum industry, cement slurries are pumped down to several thousand meters into the ground to anchor and seal the casing to the borehole of oil or gas wells. Thus, an accurate characterization of the rheology of cement slurries is critical. However, oil well cement slurry rheology is more complicated than that of cement paste. In order to contend with bottom hole conditions (wide range of pressure and temperature), a special class of cements called oil well cements (OWCs), specified by the American Petroleum Institute (API) (API Specification 10A, 2002) and various additives are usually used in the slurry composition. Among the eight (8) different types of available OWC, Class G and H cements are usually specified for deeper, hotter and higher pressure well conditions (Lafarge, 2010). A thorough review of the types of admixtures used in the petroleum industry and the rheology of oil well cement (OWC) slurries has been provided in the literature (e.g. Nelson *et al.*, 2006, and Guillot, 2006). But comparing the effects of different admixtures on the rheological properties of oil well slurries at different temperatures remains largely unexplored.

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The objective of this study is to investigate the interactions of Class G OWC with different types of admixtures and the associated cement-admixture compatibility. A series of flow tests using an advanced rheometer were carried out to determine the optimum dosage of admixtures at various temperatures. Pressure has been found to have a less significant influence on the rheological properties of OWC slurries compared to that of temperature (Guillot, 2006, Ravi and Sutton, 1990, and Kellingray *et al.*, 1990). Therefore, the rheological properties of cement slurries having w/c of 0.35, 0.44, and 0.50 were investigated at temperatures of 23, 45, and 60°C but at ambient pressure. Moreover, the flow properties of cement slurries with a w/c of 0.44 and incorporating various dosages of six different chemical admixtures were investigated at the same temperatures. The admixtures included a new generation polycarboxylate-based high-range water reducing admixture (PCH), lignosulphonate-based mid-range water reducing admixture (LSM), polycarboxylate-based mid-range water reducing admixture (PCM), phosphonate-based set retarding admixture (SRA), hydroxylated carboxylic acid-based retarding admixture (HCR) and a rheoplastic solid admixture (RA). The rheological tests were performed as per the American Petroleum Institute (API) recommended procedure using an atmospheric rheometer. However, pertinent data could not be found in the open literature to compare it to the rheological properties of slurries prepared with Class G oil well cement and the admixtures used for this study. The present study allowed gaining an improved understanding of the effect of chemical admixtures on the rheology of OWC slurries at high temperature. This should contribute to the selection of adequate admixtures and their effective dosages to overcome difficulties encountered during the construction of oil and gas wells including the rapid loss of workability, pumping problems, acceleration of cement hydration, fast evaporation of mixing water and zonal isolation.

#### **4.2 Rheology of Cement Slurries**

The rheological properties of cement-based materials determine the quality of the hardened cementitious matrix and help predicting its end use performance and its physical properties during and after processing. To characterize the rheology of a cement slurry, rheological parameters such as the yield stress, apparent viscosity, plastic viscosity, shear thinning, or shear thickening behaviour need to be studied. The yield stress indicates the minimum effort needed for a material to start flowing. Below the yield stress, cement slurries behave like a solid. The apparent viscosity is the slope of the straight line connecting the origin and any point on the shear stress-shear strain rate flow curve, i.e. it is the viscosity at a particular shear rate. If the points on the flow curve are fitted to a straight line, the slope of such a straight line represents the plastic

viscosity. Usually the plastic viscosity of a cement slurry is evaluated using the linear portion of the down-curve of the hysteresis loop. For a nonlinear flow curve, shear-thinning or shear-thickening behaviour may be observed. Shear thinning is when the apparent viscosity decreases with the increase in the shear rate, i.e. when the slope of the shear stress vs. shear rate flow curve decreases with the shear rate. Shear thickening is when viscosity of the cement slurry increases with the shear rate.

For fluids such as cement slurries, viscosity exhibits a time-dependent behaviour, which is difficult to characterize. However, for practical oilfield purposes, cement slurries are invariably represented by time-independent models. It has been observed that it is difficult to capture all possible trends of flow behaviour using a single rheological model (Yahia and Khayat, 2001). The performance of rheological models usually varies with the test geometries, gap between shearing surfaces and their friction capacity, which makes calculations of various rheological models complicated (Nehdi and Rahman, 2004).

Existing time-independent rheological models allow fitting shear stress, shear rate and viscosity data to specific trends using rheological data analysis software. However, no model is free from statistical error. The Bingham plastic model and the Power law are widely used to describe the rheological properties of cement slurries (Guillot, 2006). The Bingham plastic model includes both yield stress,  $\tau_y$  and a limiting viscosity,  $\mu_p$  at finite shear rates, which the Power law model fails to consider. Therefore, the Bingham plastic model (equation 1) was used in this study to calculate the yield stress and plastic viscosity from the shear rate-shear stress down-curve.

$$\tau = \tau_0 + \mu_p \dot{\gamma} \quad (4.1)$$

Where,  $\tau$ ,  $\tau_0$ ,  $\mu_p$ , and  $\dot{\gamma}$  represent the shear stress, yield stress, plastic viscosity, and shear rate, respectively.

The down-curve was chosen since it better fits to the Bingham plastic model than the up-curve. The down-curve is normally lower in shear stress values than the up-curve because of the breakdown in the slurry structure due to shear flow. The degree of thixotropic behaviour measured by the hysteresis loop, which is the area enclosed by the up and down curves (Saak, 2000), indicates a breakdown of structure. Conversely, a reverse hysteresis loop indicates that the structure of the material stiffens when sheared due to a mechanism of thixotropy build-up (Eirich,

1960). The reverse hysteresis behaviour is called anti-thixotropy or rheopexy (Ferguson and Kemblowski, 1991).

### 4.3 Materials

Cement slurries used in this study were prepared using a high sulfate-resistant API Class G oil well cement with a specific gravity of 3.14. The chemical and physical properties of this cement are summarized in Table 4.1. De-ionized distilled water was used for the mixing, and its temperature was maintained at  $23\pm 1^\circ\text{C}$  using an isothermal container. A number of conventional chemical admixtures along with new-generation admixtures were used and their effects on the rheological properties of cement slurries at different temperatures were evaluated. These admixtures include:

- (1) A new generation polycarboxylate-based high-range water reducing admixture (PCH), meeting ASTM C494 requirements as a Type A water-reducing and Type F high-range water reducing admixture was used at selected dosages of 0.25%, 0.50%, 0.75% and 1.0% by weight of cement.
- (2) Mid-range water reducing admixture (LSM) which is a lignosulphonate-based admixture meeting the ASTM C494 requirements as a Type A water reducing and Type F high-range water-reducing admixture. Four dosages of LSM, namely 0.5%, 1.0%, 1.5% and 2.0% by weight of cement were used in this study.
- (3) Polycarboxylate-based mid-range water reducing admixture (PCM) meeting the ASTM C494 requirements as a Type A water reducing and Type F high-range water reducing admixture. Four dosages of PCM, namely 0.25%, 0.50%, 0.75%, and 1.0% by weight of cement were used in this study.
- (4) Set-retarding admixture (SRA) meeting the ASTM C 494 requirements for Type B, retarding, and Type D, water reducing and retarding admixture. It is an organic phosphonate-based admixture commonly used in the petroleum industry. The dosages used were 0.3%, 0.6%, 1.0%, and 1.5% by weight of cement.
- (5) Hydroxylated carboxylic acid-based retarding admixture (HCR) complying with the ASTM C494 requirements for Type B, retarding, and Type D, water reducing and retarding admixture.

Four dosages of HCR (0.5%, 1.0%, 2.0%, and 3.0%) by weight of cement were used to examine the effect of HCR on the rheological properties of cement slurries at high temperature.

(6) Rheoplastic admixture (RA) is a solid admixture especially designed for cementitious grouts to reduce the required mixing water and produce flowable, pumpable, thixotropic, non-segregating high-strength cement slurry. Three dosages of RA (2.0%, 4.0%, and 6.0%) were used in this study.

Table 4.1 Chemical and physical properties of API Class G OWC

Chemical Component (%)		Physical Properties	
Silica (SiO <sub>2</sub> )	21.6	Fineness 45µm sieve	92.4% passing
Alumina (Al <sub>2</sub> O <sub>3</sub> )	3.3	Blaine (Spec. Surf.)	385 m <sup>2</sup> /kg
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> )	4.9	Thickening Time (Schedule 5)	110 minutes
Calcium Oxide, Total (TCaO)	64.2	Compressive strength at 8 hours @ 38 °C	2.1 MPa
Magnesium Oxide (MgO)	1.1	Compressive strength at 8 hours @ 60 °C	10.3 MPa
Sulphur Trioxide (SO <sub>3</sub> )	2.2		
Loss on Ignition	0.60		
Insoluble Residue	0.30		
Equivalent Alkali (as Na <sub>2</sub> O)	0.41		
C <sub>3</sub> A	<1		
C <sub>3</sub> S	62		
C <sub>2</sub> S	15		
C <sub>4</sub> AF+2 C <sub>3</sub> A	16		

#### 4.4 Apparatus

The cement slurry preparation is very important because of the influence of the shear history of the mixture on its rheological properties (Orban *et al.*, 1986). The cement slurries were prepared using a variable speed high-shear blender type mixer with bottom drive blades as per the ANSI/API Recommended Practice 10B-2.

A high accuracy advanced rheometer (TA instruments AR 2000) (Fig. 4.1(a)) was used to measure the rheological properties of cement slurries. The rheometer is capable of continuous shear rate sweep, stress sweep and strain sweep. The geometry of the test accessory and the gap

and friction capacity of its shearing surfaces have a significant influence on the measured rheological properties (Nehdi and Rahman, 2004). The coaxial concentric cylinder geometry was considered suitable for this study because of the typically low viscosity of cement slurries. The geometry consists of a cylinder with a conical end that rotates inside a cylinder with a central fixed hollow as shown in Fig. 4.1(b). The radius of the inner solid cylinder is 14 mm. This inner solid cylinder rotates inside a fixed hollow cylinder of 15 mm radius. The gap between the head of the conical end and the bottom of the hollow cylinder was set to 0.5 mm for all experiments. It is required to use such a narrow gap in order to maintain a constant shear rate across the gap, which is important, especially in case of static flow studies to minimize the error caused by wall slip in rheological measurements (Saak et al., 2001). The rheometer has an auto gap system which compensates for the expansion of the stainless steel of the coaxial concentric cylinders under a wide range of temperatures, thus keeping the gap constant during experiments. The rheometer has a smart swap technology for temperature control in the range of  $-10^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  in the case of the concentric cylinder system. The device keeps the temperature constant during the entire time span of the rheological test through a water circulation system. A solvent trap was used to prevent evaporation from the tested cement slurry sample by covering the top of the hollow cylinder. This solvent trap has an adequate mechanism to allow rotation of the shaft without any interference.

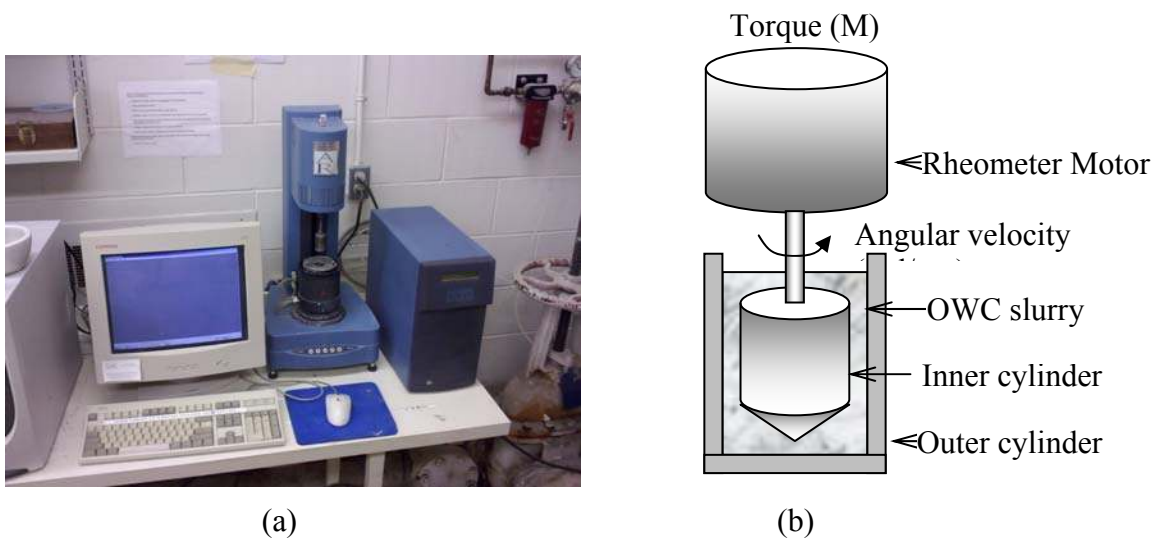


Figure 4.1 Illustration of, (a) advanced rheometer with coaxial cylinder geometry, and (b) coaxial concentric cylinder with cylindrical conical end geometry.

The rheometer was calibrated using a certified standard Newtonian oil with a known viscosity of 1.0 Pa.s and yield stress = 0 Pa at 20°C. The measured yield stress was 0 Pa and viscosity was 1.009 Pa.s with an error of 0.9%, which is less than the tolerated error of 4% specified by the manufacturer. This computer controlled rheometer is equipped with rheological data analysis software, which can fit the shear stress-strain rate data to several rheological models. The Bingham model was used throughout this study to calculate the rheological properties of cement slurries.

## **4.5 Experimental Procedure**

### ***4.5.1 Mixing and Preparing Cement Slurry***

The cement slurries were prepared using a high-shear blender type mixer with bottom driven blades according to the following procedure. First, the weighed amount of cement and the solid admixture (if any) were dry mixed in a bowl by hand using a spatula for about 30 sec. The mixing water was subsequently poured into the blender. Then the required quantity of liquid admixture was added into the mixing water using a needle, and the mixing started at a slow speed for 15 sec so that chemical admixtures could be thoroughly dispersed in the water. The cement-solid admixture was added to the liquids (liquid admixture and water) over a period of 15 sec. Manual mixing was conducted for 15 sec and a rubber spatula was used to recover material sticking to the wall of the mixing container to ensure homogeneity. Finally, mixing resumed for another 35 sec at high speed. This mixing procedure was strictly followed for all cement slurries. All mixing was conducted at a controlled ambient room temperature of  $23\pm 1^\circ\text{C}$ . The prepared slurry was then placed into the bowl of a mixer for preconditioning over 20 minutes at the test temperature (23°C, 45°C, or 60°C) at a speed of 150 rpm. The total time between the beginning of mixing and the start of the rheological tests was kept constant to avoid the effect of exogenous variables on the results. The rheometer set-up was also maintained constant for all slurries. The concentric cylinder test geometry was kept at the test temperature so as to avoid sudden thermal shock of the slurry.

### ***4.5.2 Rheometric Tests***

After mixing and preconditioning, the cement slurry sample was placed in the coaxial cylinder of the rheometer. The temperature of the rheometer was adjusted to the required level. The sample was then subjected to a stepped ramp or steady state flow and viscosity measurements were taken



at 20 different shear rates starting from 5.11 to 511  $\text{s}^{-1}$  after a continuous rotation of 10 sec at each speed. Subsequently, the data were measured at a descending shear rate from 511 to 5.11  $\text{s}^{-1}$  to obtain the down flow curve. The hysteresis loop thus produced was used to characterize the thixotropy of the cement slurry (Saak, 2000). A schematic representation of the viscometric testing program is illustrated in Fig. 4.2. To check the reproducibility of the test results, three sets of cement slurry were tested at three different temperatures. Neat cement slurries were prepared at a w/c of 0.44 but without chemical admixtures. The rheological properties of cement slurry are time, temperature, and shear history dependent. Therefore, each test was performed with a new cement slurry at 20 min after mixing. Figure 4.3 represents the generated data for the reliability tests and reveals that the experimental procedure and the rheometer can produce repeatable measurements with a relative error of about 10%.

#### ***4.5.3 Gel Strength***

Cement slurries create a particulate structure leading to gel formation when allowed to remain static. Static gel strength is an important factor related to the annular fluid migration. It is a measure of the attractive forces between the particles in a fluid under static or non-flow conditions. Conversely, yield strength is an indication of the attractive forces under flowing conditions. Gel strength also represents the thixotropic properties of the slurry. A gel formation is usually measurable even if the static period is short. After determining the rheological properties, the same slurry sample was used to determine the initial and final gel strength. For this purpose, the slurry sample was preconditioned at a shear rate of 511  $\text{s}^{-1}$  for a period of 1 minute to disperse the gel already formed. The sample remained static for 10 sec and then a shear rate of 5.11  $\text{s}^{-1}$  was applied. The maximum observed shear stress reading immediately after turning on the rheometer was recorded as the initial gel strength, also called the 10-sec gel strength. The slurry sample was subsequently kept static for 10 min and the peak shear stress was recorded again at a shear rate of 5.11  $\text{s}^{-1}$  and referred as the 10-min gel strength.

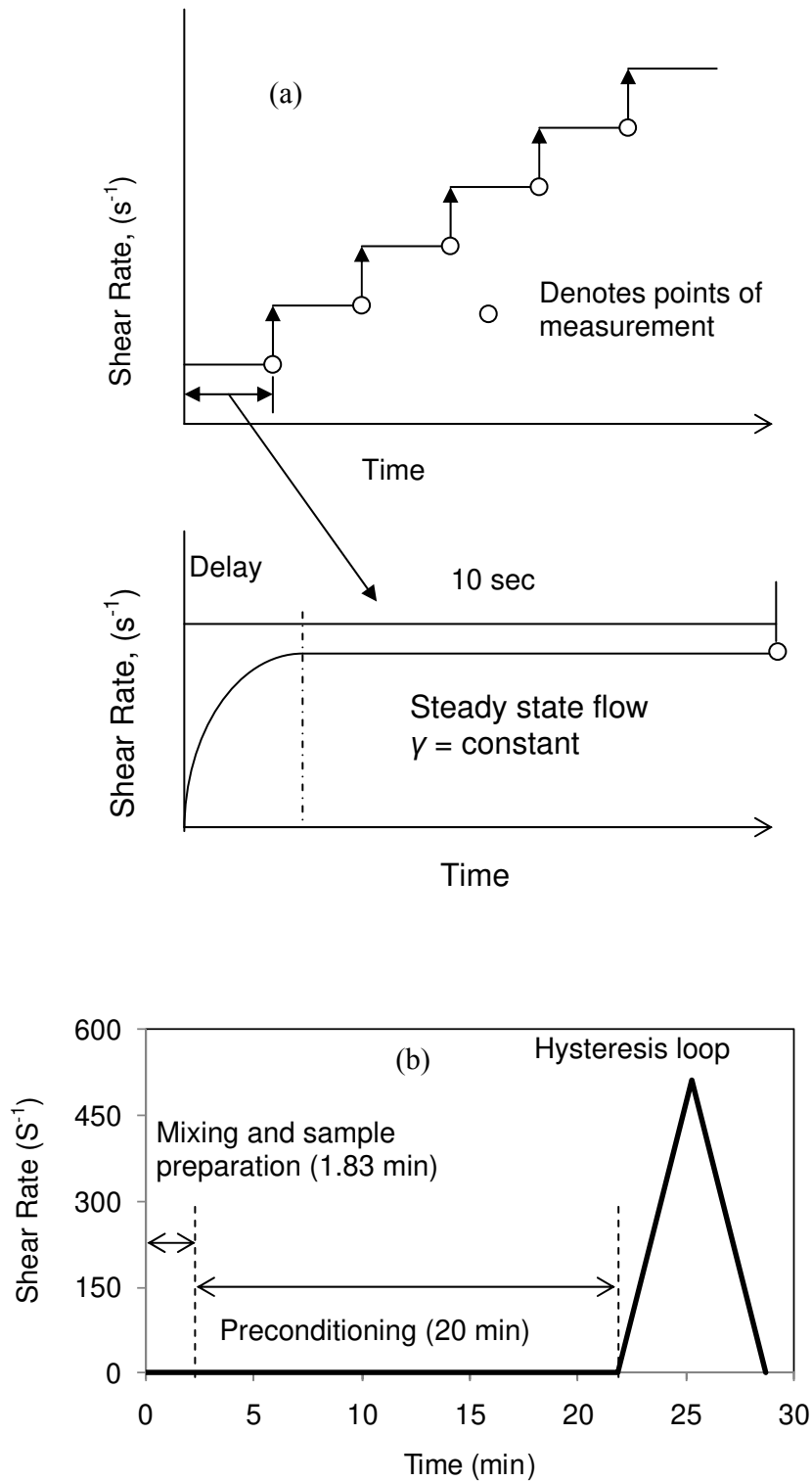


Figure 4.2 (a) Schematic representation of stepped ramp, and (b) rheometer test sequence (shear rate history used in rheological tests).

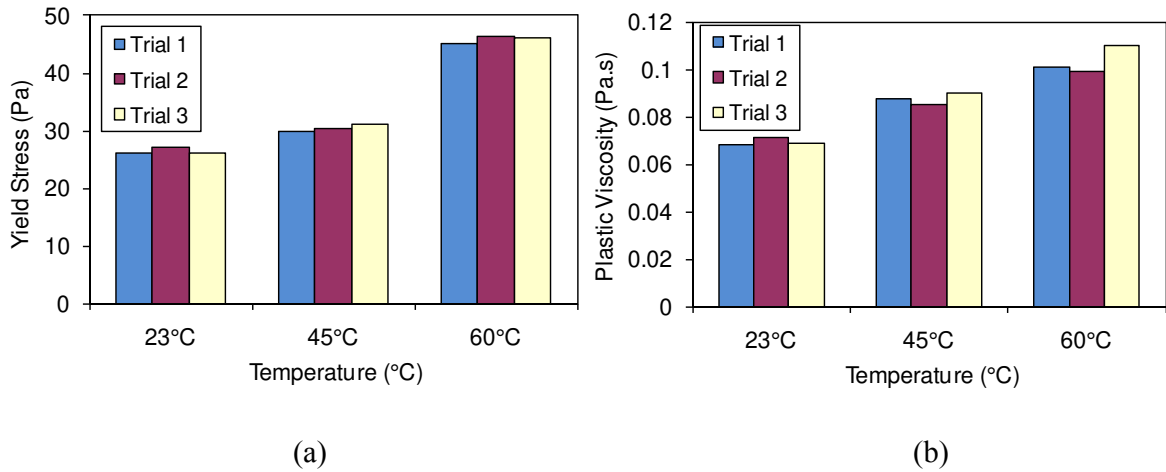


Figure 4.3 Generated (a) yield stress, and (b) plastic viscosity from Bingham model.

## 4.6 Results and Discussion

### 4.6.1 Effect of W/C and Temperature on Rheological Properties

In order to examine the effects of the w/c and temperature on oil well cement slurry rheology, neat cement slurries were prepared without any chemical admixtures. Cement slurries with different w/c at various temperatures showed significantly different rheological properties. However, regardless of the w/c and temperature, all slurries exhibited non-Newtonian and shear thinning behaviour as shown in Fig. 4.4.

Figure 4.5 illustrates typical hysteresis loops for cement slurries with a w/c of 0.44 at different temperatures. The area enclosed by the upper and lower curves of the hysteresis loop quantifies the degree of structure breakdown in the slurry due to shear flow and is an indication of thixotropy. The hysteresis loop area for cement slurries at 23°C was found to be smaller than those at higher temperatures, which implies that less structure exists in cement slurries at lower temperature. This is likely due to the increase in the rate of hydration of the cement at higher temperature. Smaller hysteresis loop area indicates the presence of less structure, which also generally results in improved flow properties. At 60°C, sudden occurrence of high shear stress in

the very low shear rate region may be associated with the formation of a gel structure network formed at such high temperature.

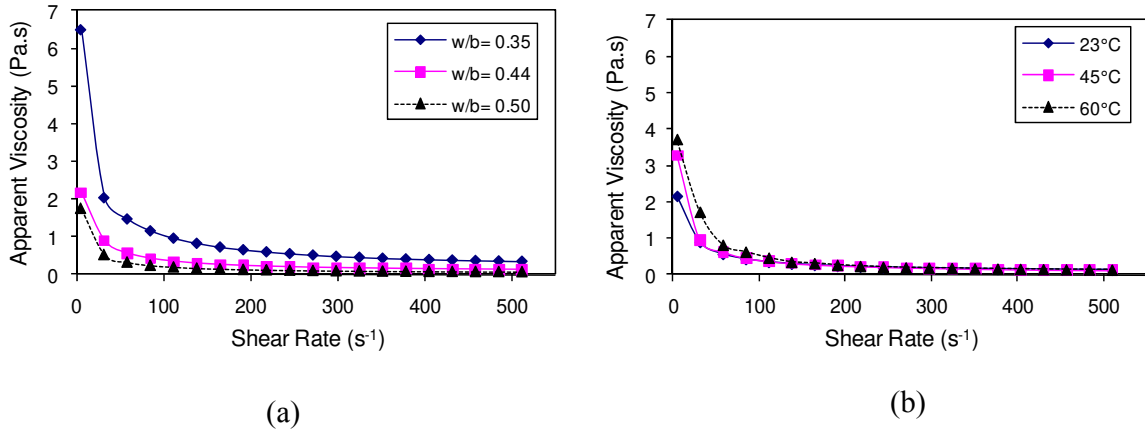


Figure 4.4 Variation of apparent viscosity (a) with variable w/c, and (b) at different temperatures.

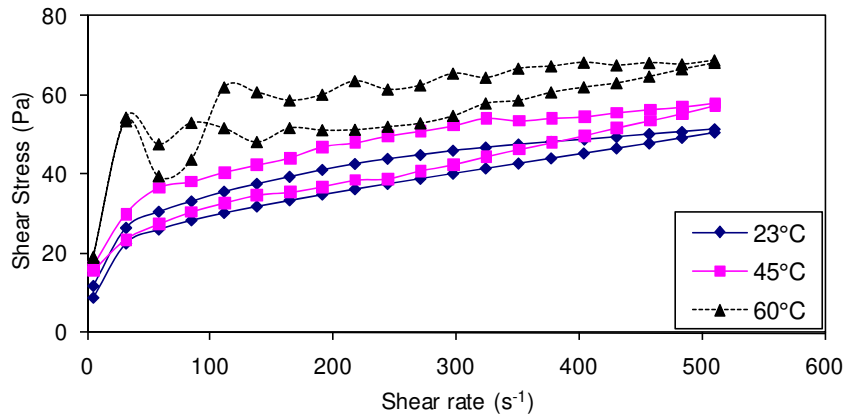


Figure 4.5 Hysteresis loop for an oil well cement slurry with w/c = 0.44.

The effect of the w/c on the yield stress with variation of temperature is illustrated in Fig. 4.6(a). As expected, the yield stress decreased with increasing w/c due to the decrease in the volume fraction of solids. Moreover, yield stress values increased with the increase of temperature, which indicates that more energy was required to make the cement slurry flow, likely due to the increase in the rate of cement hydration at higher temperature. The effect of temperature was more significant at lower w/c. As observed in Fig. 4.6, for a w/c of 0.35, the yield stress increase

between 23°C and 45°C was less significant than the corresponding values between 45°C and 60°C.

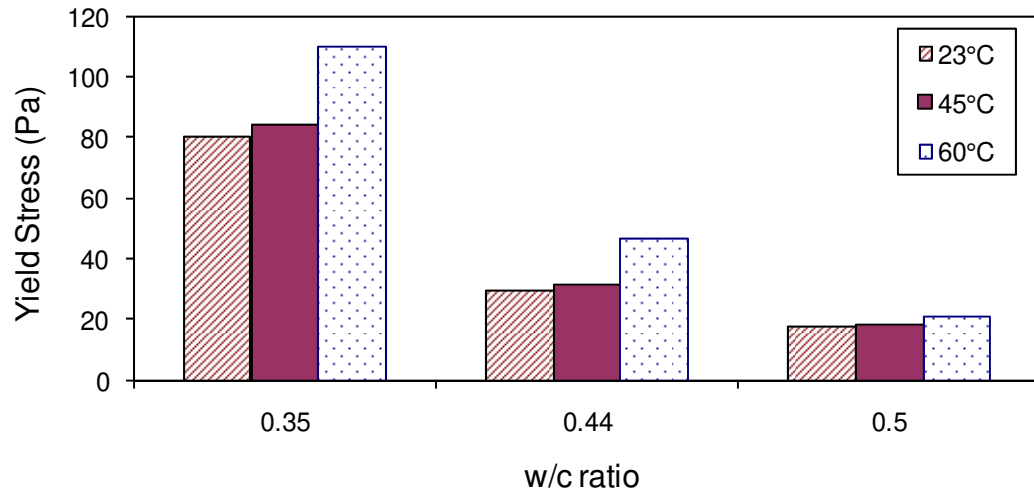


Figure 4.6 Variation of yield stress oil well cement slurry with temperature and w/c.

The plastic viscosity of slurries versus the temperature and w/c was determined using the slope of the linear portion of the down-curve of the hysteresis loop. The effect of the w/c and temperature on the plastic viscosity of OWC slurries is illustrated in Fig. 4.7.

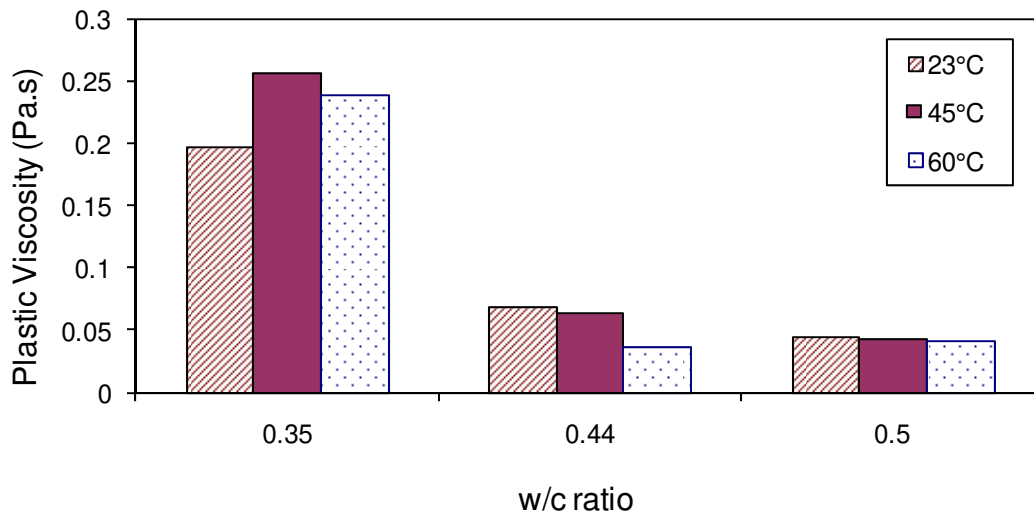


Figure 4.7 Variation of plastic viscosity of cement slurry with temperature and w/c.

Plastic viscosity decreased with increasing w/c at a nonlinear rate. It showed a sharp drop at all temperatures when the w/c increased from 0.35 to 0.44 and the subsequent decrease was not significant. Plastic viscosity also decreased with increasing temperature for the slurries with a w/c of 0.44 and 0.50, but it did not follow a consistent pattern when the w/c was 0.35.

#### ***4.6.2 Coupled Effects of Temperature and Chemical Admixtures on Yield Stress***

A steady state shear rate sweep was applied to cement slurries at various temperatures and the resultant flow curve was used to determine the yield stress and plastic viscosity using the Bingham plastic model. Figure 4.8(a) illustrates the yield stress values for OWC slurries incorporating various dosages of PCH at different temperatures. It can be observed that yield stress decreased significantly with increasing PCH dosage regardless of the temperature. The rate of decrease in yield stress was steeper at higher temperature. The differences between yield stress values measured at different temperatures (23°C, 45°C, and 60°C) decreased with higher dosage of PCH. This is likely due to the fact that a higher PCH dosage offset the acceleration of hydration due to higher temperature. This behaviour was also observed in earlier research (Nehdi and Al-Martini, 2007, Al-Martini, 2008). Moreover, the higher the temperature, the higher was the admixture saturation dosage (Fig. 4.8(a)). The observed saturation dosages were 0.30%, 0.50%, and 0.75% at 23°C, 45°C, and 60°C, respectively.

As shown in Figure 4.8(b), the yield stress increased with the LSM dosage up to 1.0% at 23°C, then decreased slightly beyond that dosage. At 45°C and 60°C, the yield stress increased gradually with increasing LSM dosage up to 1% then reached a plateau. The increase of yield stress with increasing admixture dosage may be due to the fact that the admixture was rather acting as an accelerator; a behaviour also observed elsewhere (Nehdi and Al-Martini, 2007). Yield stress increased sharply with increasing temperature (Fig. 4.8(b)). For instance, at a LSM dosage of 1%, the yield stress at 45°C and 60°C was 1.15 and 1.86 times higher than that at 23°C, respectively, which is likely due to the acceleration in the rate of hydration at higher temperature.

The effect of the PCM dosage on the yield stress at different temperatures is presented in Fig. 4.8(c). It is shown that yield stress increased significantly with temperature increase and decreased with the increase of the PCM dosage. It is also shown that at 60°C, yield stress values decreased steeply with PCM up to a dosage of 0.75%, and then the decrease became less significant. At 45°C, the yield stress values decreased continuously with increasing PCM dosages

until it reached a plateau (saturation dosage), beyond which no significant decrease in yield stress was observed. The depicted PCM saturation dosages were about 0.50%, 0.75%, and 1.00% at 23°C, 45°C, and 60°C, respectively.

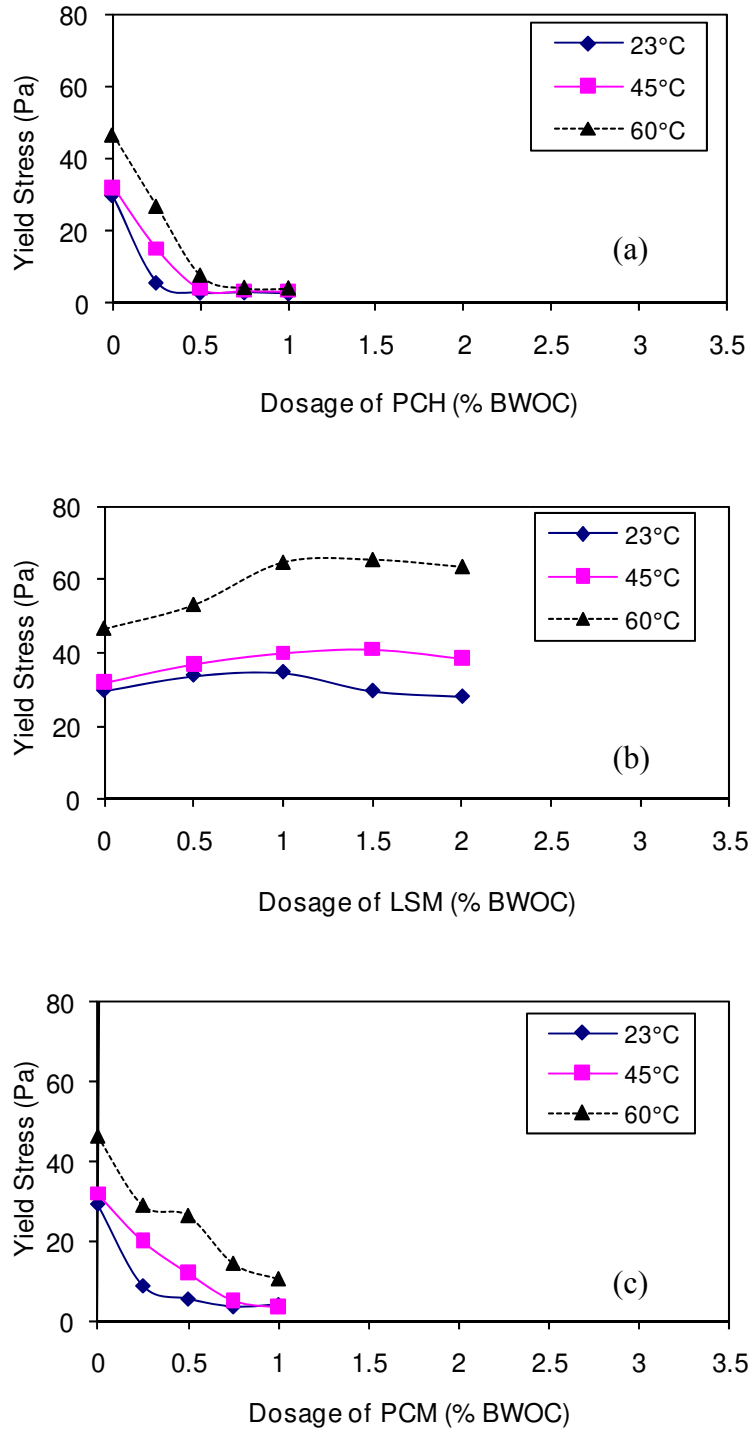


Figure 4.8 Yield stress of oil well cement slurries at various temperatures and different dosages of admixtures, (a) PCH, (b) LSM, and (c) PCM ( $w/c = 0.44$ ).

The effect of the set retarding admixture (SRA) on the yield stress of cement slurries at different temperatures is shown in Fig. 4.9. Generally, the yield stress increased significantly with temperature increase and decreased with the increase of the SRA dosage, except at 60°C and low SRA dosage (Fig. 4.9). Yield stress-SRA dosage curves at various temperatures were found to be nearly parallel to each other, which implies similar slurry behaviour at all temperatures investigated, though higher energy was needed to initiate flow of cement slurries at higher temperature.

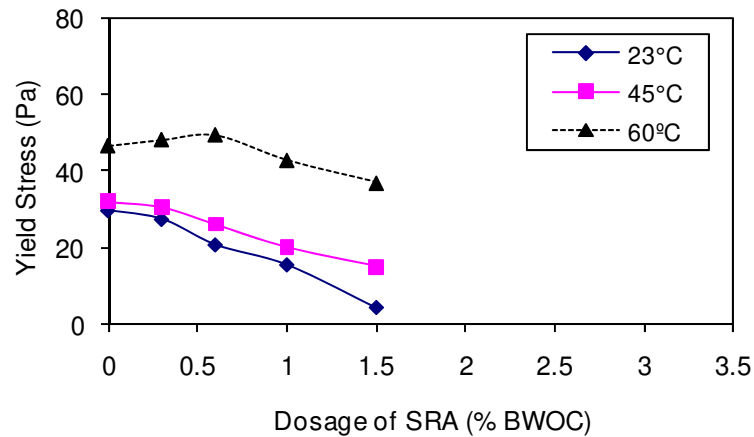


Figure 4.9 Yield stress of oil well cement slurries at various temperatures and different dosages of SRA admixtures (w/c = 0.44).

The yield stress values of cement slurries incorporating various dosages of HCR are presented in Fig. 4.10(a). Yield stress values increased significantly with increasing temperature and decreased slightly with increasing admixture dosage. At 23°C, the yield stress showed a sharp drop when the dosage increased from 0.50% to 1.00%. Beyond this dosage, there was no noticeable change in yield stress. At 60°C a gradual decrease in yield stress with increasing HCR dosage was observed.

Figure 4.10(b) illustrates the measured yield stress values at different temperatures for OWC slurries incorporating various dosages of the rheoplastic admixture (RA). Generally, yield stress values increased with higher temperature and higher RA dosage for a RA dosage below 2.0%. Beyond this dosage, yield stress values dropped significantly with RA dosage. At higher RA dosages (6%), yield stress values became comparable at all the temperatures investigated.



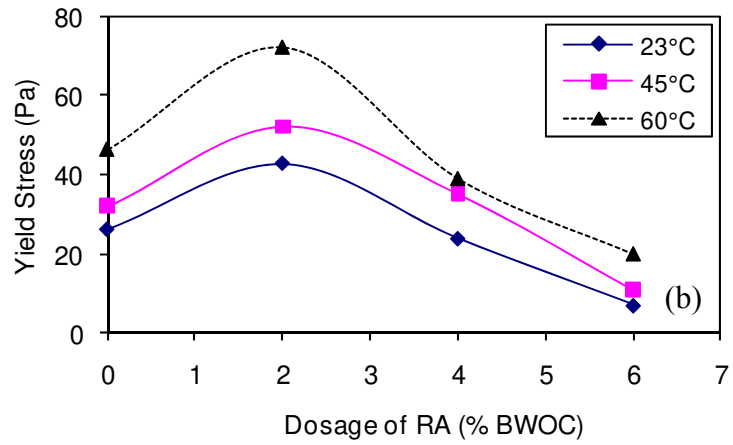
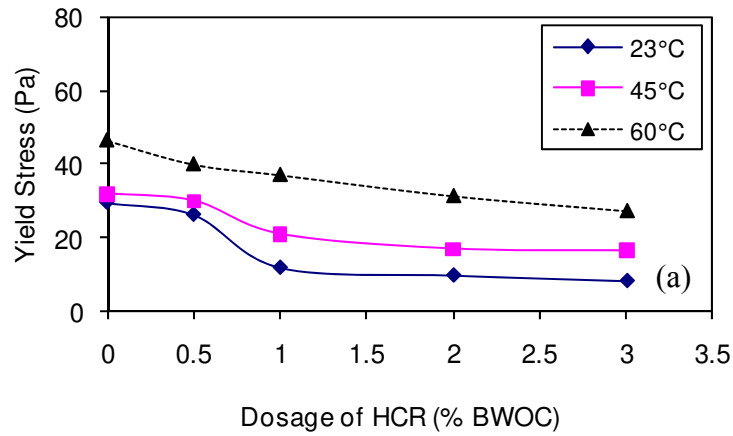


Figure 4.10 Yield stress of oil well cement slurries at various temperatures and different dosages of admixtures, (a) HCR, and (b) RA (w/c = 0.44).

### ***4.6.3 Coupled Effects of Temperature and Chemical Admixtures on Plastic Viscosity***

The plastic viscosity at different temperatures of OWC slurries incorporating different dosages of various admixtures was determined from the slope of the shear stress-shear strain down curve and is illustrated in Figs. 4.11, 4.12 and 4.13. The measured plastic viscosity does not always truly represent the material properly and sometimes could be misleading because of the high error involved in the fitting curve to the Bingham model (Saak, 2000). However, plastic viscosity was measured and presented in this section because it is very difficult to create mechanical models for the deformation behaviour of cement paste using the apparent viscosity at each shear rate point (Nehdi and Rahman, 2004).

Figure 4.11(a) illustrates the plastic viscosity at different temperatures for cement slurries incorporating various dosages of PCH. Generally, the plastic viscosity gradually decreased with increased PCH dosage up to a dosage of almost 0.50%, and then it tended to slightly increase beyond this dosage. It can be observed that plastic viscosity increased at a relatively constant rate with increasing temperature up to a dosage of 0.75%, and then tended to decrease.

Figure 4.11(b) presents the plastic viscosity values at different temperatures for cement slurries incorporating various dosages of LSM. The plastic viscosity at 23°C did not show a significant variation with LSM dosage. At 45°C, the plastic viscosity decreased significantly with increasing LSM dosage. It can be further observed that at high temperature (60°C) the dispersing capability of LSM was not effective and the plastic viscosity continuously increased with increasing dosage of up to 1.5%.

The plastic viscosity values at various temperatures for cement slurries incorporating various PCM dosages are presented in Fig. 4.11(c). At lower PCM dosage and at 23°C, the plastic viscosity decreased with increasing PCM up to a dosage of 0.50%, beyond which plastic viscosity showed a sharp increase. At 45°C, plastic viscosity decreased gradually with increasing PCM dosage up to 0.50% and then followed a plateau beyond which no further decrease was observed. Plastic viscosity decreased with increasing PCM dosage at 60°C except at a dosage of 0.5% where a sharp increase in plastic viscosity was observed. This sudden jump in plastic viscosity value at 60°C could be attributed to the error associated with the fitting of flow curve to Bingham model.

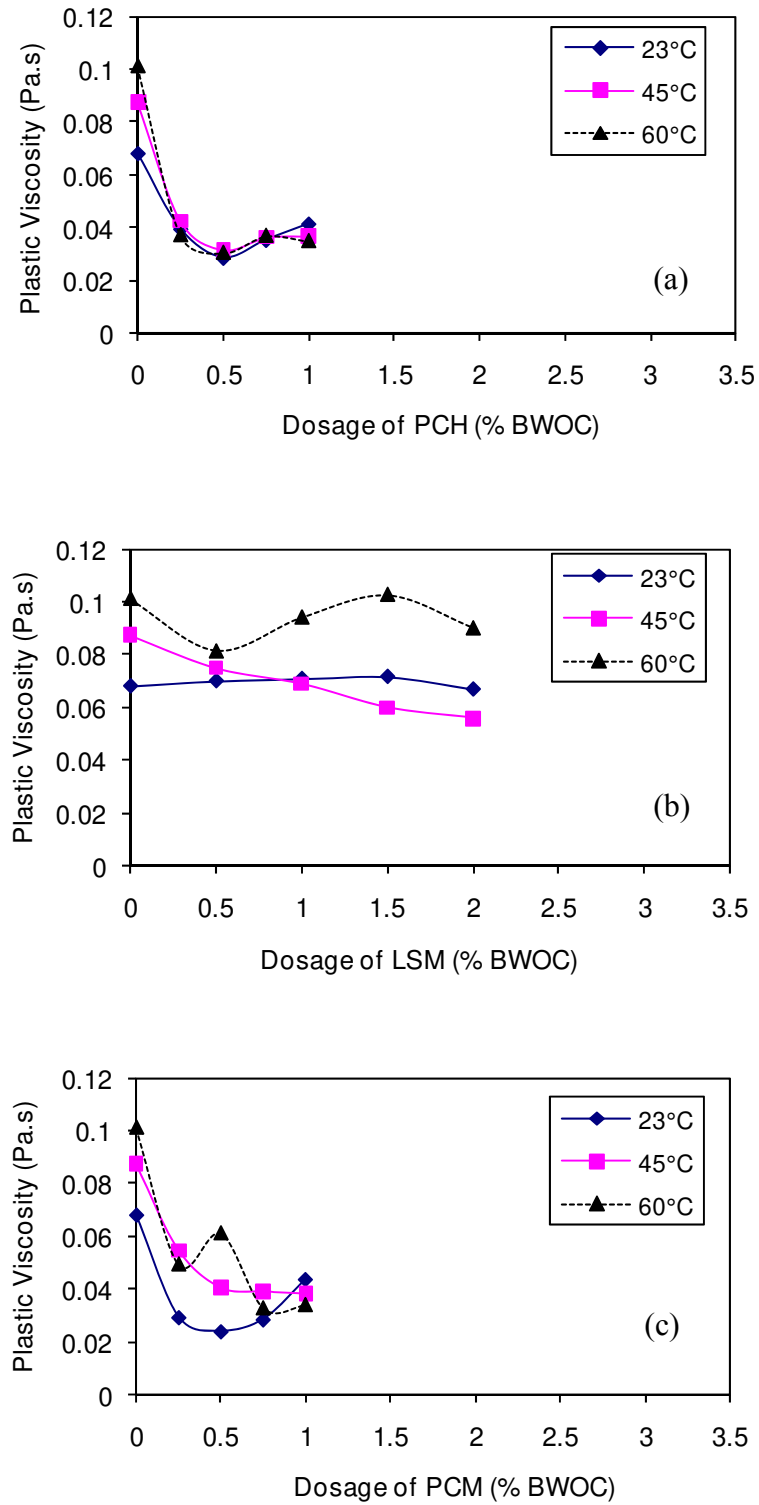


Figure 4.11 Plastic viscosity of oil well cement slurries at various temperatures and different dosages of admixtures, (a) PCH, (b) LSM, and (c) PCM (w/c = 0.44).

As shown in Fig. 4.12(a), the plastic viscosity generally increased with temperature increase, and decreased with increased SRA dosage, except at 60°C where plastic viscosity increased up to 0.6% SRA dosage and then decreased at higher dosage. Figure 4.12(b) shows that at 23°C plastic viscosity values increased up to about 0.50% HCR dosage, beyond which it decreased until it reached a plateau. At 45°C and 60°C, plastic viscosity generally decreased gradually with increasing HCR dosage.

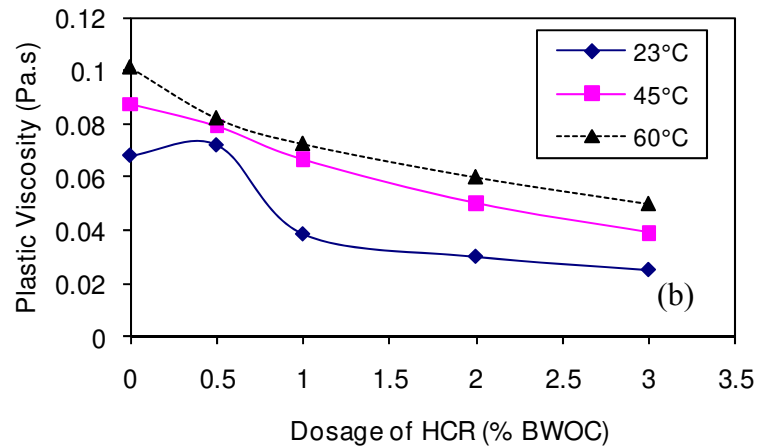
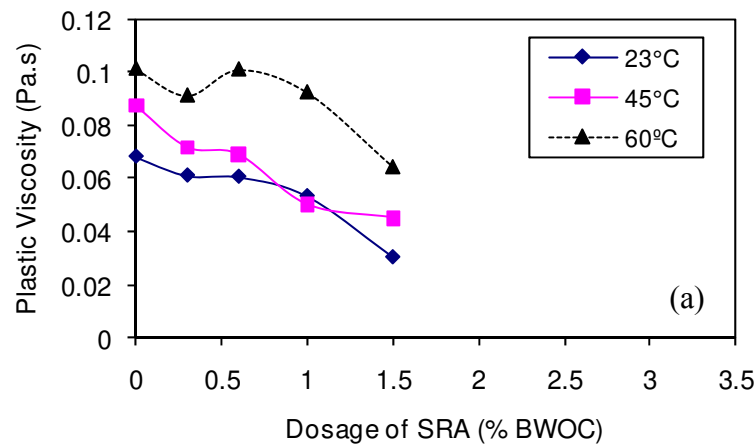


Figure 4.12 Plastic viscosity of oil well cement slurries at various temperatures and different dosages of admixtures, (a) SRA, and (b) HCR ( $w/c = 0.44$ ).

The plastic viscosity at different temperatures for cement slurries incorporating various dosages of RA is illustrated in Fig. 4.13). It is shown that plastic viscosity decreased with the increase of RA dosage, and increased significantly with temperature increase at low RA dosage. However, plastic viscosity values at all temperatures tested reached comparable values as the RA dosage increased.

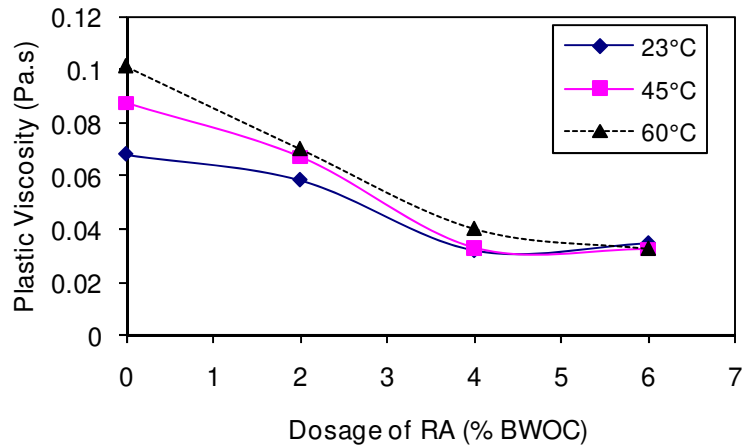


Figure 4.13 Plastic viscosity of oil well cement slurries at various temperatures and different dosages of RA admixtures ( $w/c = 0.44$ ).

#### 4.6.4 Coupled Effects of Temperature and Chemical Admixtures on Apparent Viscosity

The apparent viscosity results of OWC slurries at a shear rate of  $258 \text{ s}^{-1}$  are presented in Figs. 4.14, 4.15 and 4.16. A shear rate of  $258 \text{ s}^{-1}$  was chosen since it was the mean shear rate used in the experimental program. Figure 4.14(a) illustrates the apparent viscosity at different temperatures for cement slurries incorporating various dosages of PCH. It can be observed that the apparent viscosity decreased with increased PCH dosage at all investigated temperatures, and increased with temperature increase in a manner generally similar to that of yield stress. However, apparent viscosity values at different temperatures reached comparable values at higher PCH dosage. The observed saturation dosages were 0.30%, 0.50%, and 0.75% at 23°C, 45°C, and 60°C, respectively.

As shown in Fig. 4.14(b), the apparent viscosity increased gradually with LSM dosage up to 1.0% and this increase was more significant at higher temperature. Apparent viscosity of cement slurries with LSM appeared to follow the same trend as that of yield stress.

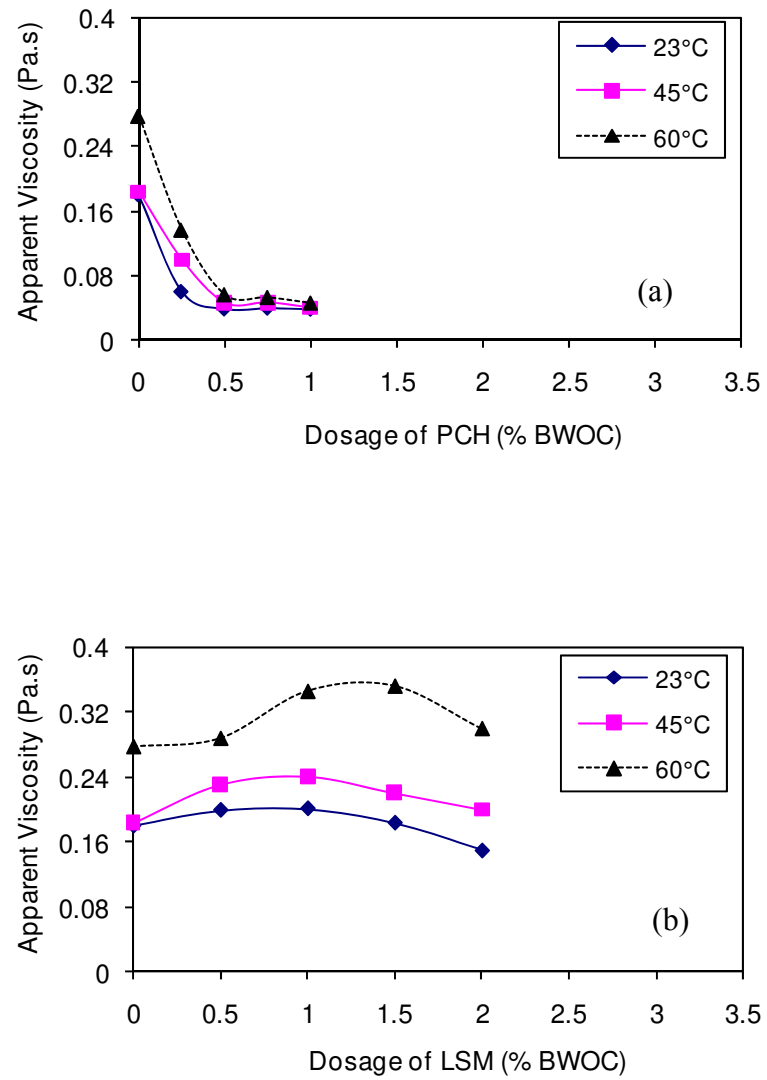


Figure 4.14 Apparent viscosity of oil well cement slurries at various temperatures and different dosages of admixtures, (a) PCH, and (b) LSM (w/c = 0.44).

Apparent viscosity values of OWC slurries incorporating various PCM dosages is presented in Fig. 4.15(a). It can be observed that the apparent viscosity generally decreased with the increase of PCM dosage, and increased significantly with temperature increase. At 60°C, no significant change in apparent viscosity was evident between dosages of 0.25 and 0.5%, but beyond this level the apparent viscosity decreased sharply. A sharp decrease in apparent viscosity was observed at low dosage at 45°C and 60°C. A similar trend was observed in the case of yield stress for OWC slurries prepared using PCM. At 23 and 45°C, the apparent viscosity decreased with the increase in SRA dosage (Fig. 4.15(b)). But at 60°C, a dosage below 0.6% could not effectively offset the acceleration of hydration due to high temperature. However, an increased dosage beyond that level was effective and led to a significant decrease in the apparent viscosity.

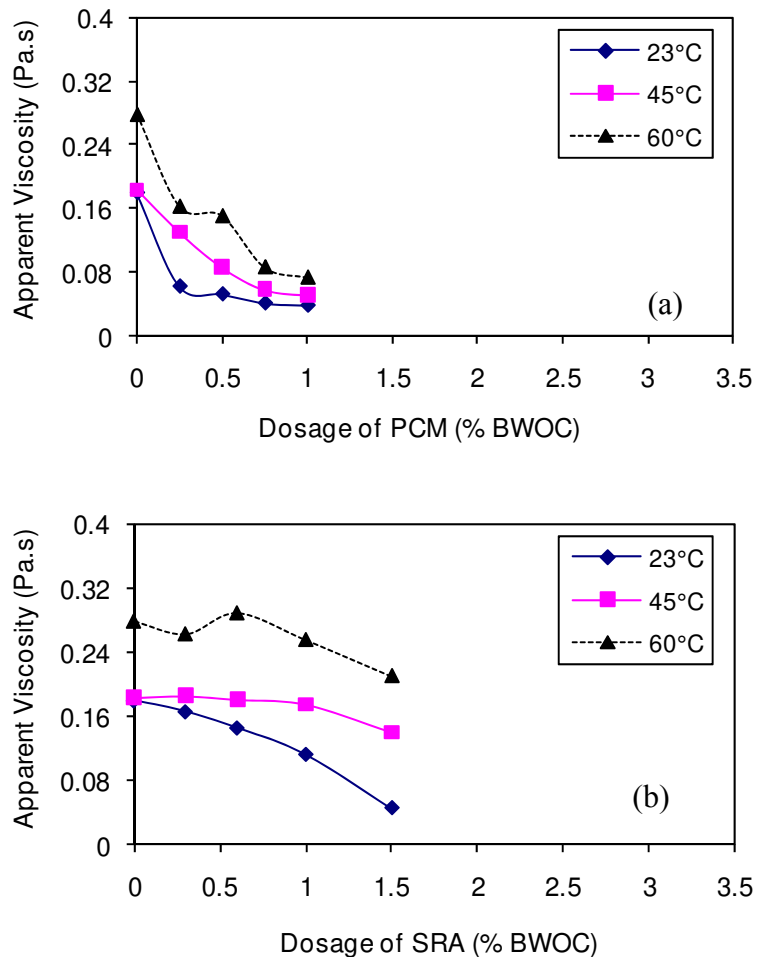


Figure 4.15 Apparent viscosity of oil well cement slurries at various temperatures and different dosages of admixtures, (a) PCM, and (b) SRA(w/c = 0.44).

HRC had little effect on the apparent viscosity below a dosage of 0.5% (Fig. 4.16(a)). As the dosage increased, the apparent viscosity gradually decreased with the HCR dosage and reached a plateau at all temperatures tested. The effect of RA on the apparent viscosity at different temperatures is illustrated in Fig. 4.16(b). It is shown that the apparent viscosity increased with the temperature and also with the RA dosage up to a dosage of 2.0% at all temperatures tested, then it started to decrease markedly beyond this dosage. It appears that RA acted as an accelerator at low dosage and as a retarder and dispersant at higher dosage.

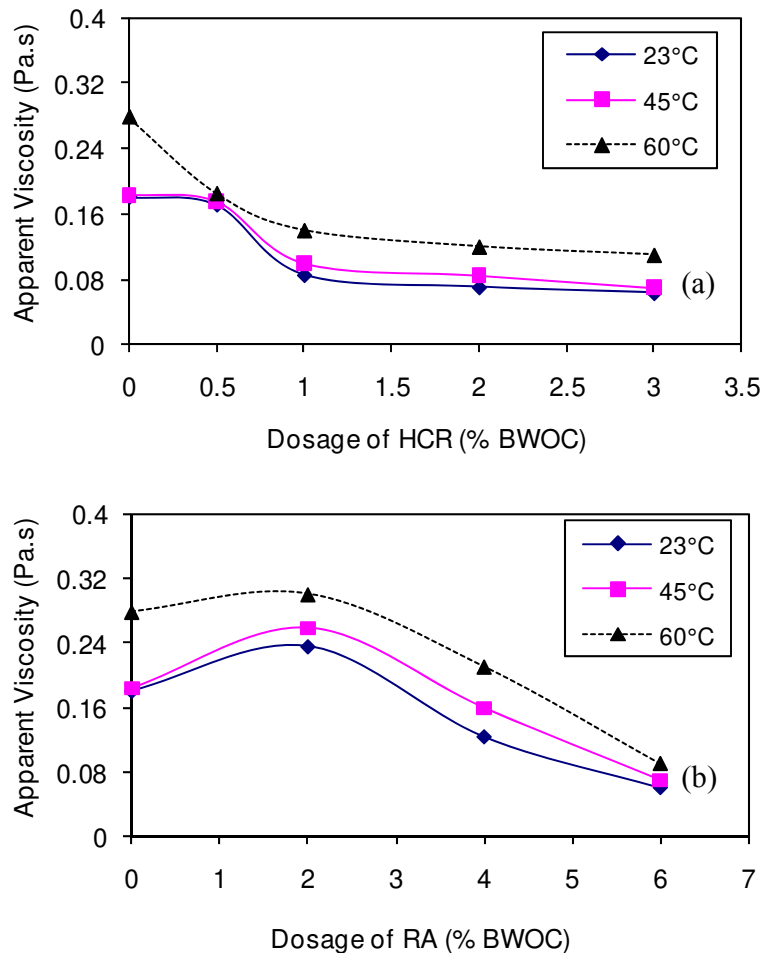


Figure 4.16 Apparent viscosity of oil well cement slurries at various temperatures and different dosages of admixtures, (a) HCR, and (b) RA(w/c = 0.44).



#### ***4.6.5 Coupled Effects of Temperature and Chemical Admixtures on Thixotropy***

The thixotropy at different temperatures of OWC slurries incorporating different dosages of various admixtures was determined by the area enclosed between the up and down-curves of the hysteresis loop and is presented in Figs. 4.17 and 4.18. A different scale was used so as to better predict the degree of thixotropy for each admixture. The thixotropy behaviour of cement slurries incorporating PCH is presented in Fig. 4.17(a). Generally, OWC slurry thixotropy was negative for all test temperatures. However, at 23°C, thixotropy was positive at a PCH dosage of 0.75% indicating that structure breakdown occurred due to the effective dispersing mechanism. Table 4.2 shows that the degree of thixotropy was generally lower for slurries prepared with PCH than that with other admixtures at all the temperatures investigated.

Figure 4.17(b) illustrates the effect of LSM on the thixotropy of OWC slurries. At 23°C, thixotropy increased up to a dosage of 1%, and then started to decrease, which is consistent with the trend of yield stress. At higher temperatures of 45°C and 60°C, thixotropy increased dramatically with LSM dosage up to 1.5%, likely due to the buildup of structure as a result of accelerated hydration at higher temperature. Thixotropy started to decrease beyond the dosage of 1.5%. However, at 60°C cement the slurry exhibited anti-thixotropy (negative value) for a dosage of 0.5%, which means that the material stiffened with increased shear at high temperature, a behaviour also observed elsewhere (Eirich, 1960).

Moreover, at 23°C, thixotropy increased up to a PCM dosage of 0.75% and then started to drop at a dosage of 1% (Fig. 4.17(c)). At higher temperatures (45°C and 60°C), the OWC slurry thixotropy shifted from positive to negative values, indicating that stiffening of the OWC slurry occurred at higher temperatures. However, thixotropy still approached lower values with the increase of PCM dosage. Low PCM dosages failed to mitigate the stiffening of cement slurries at high temperature, whereas it was more effective at a dosage of 0.75%.

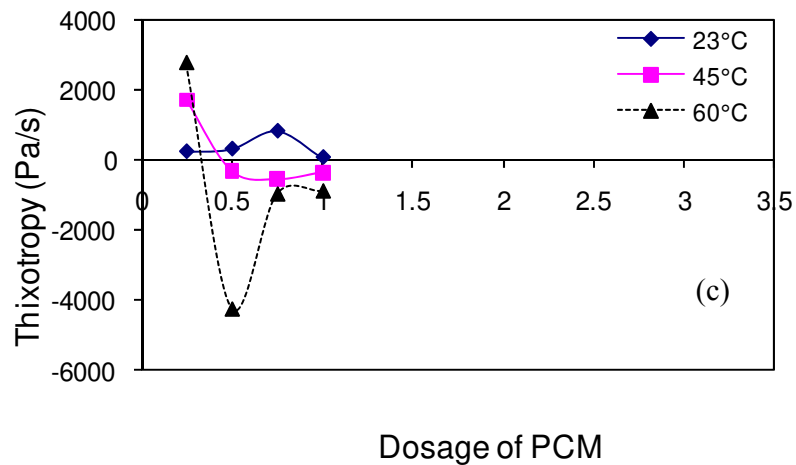
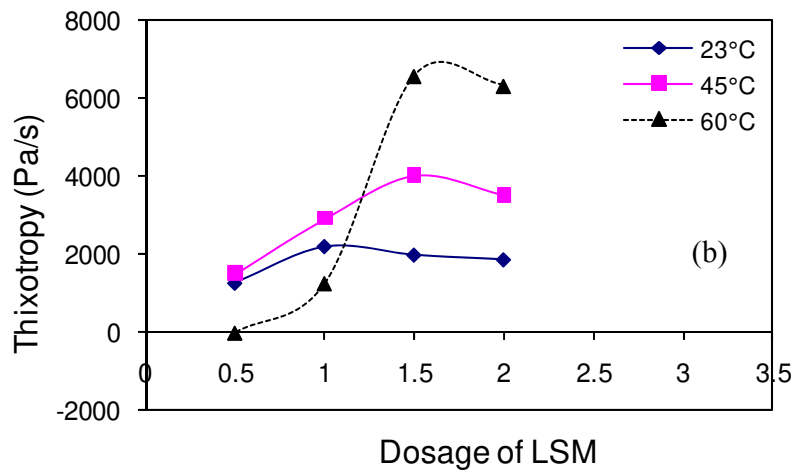
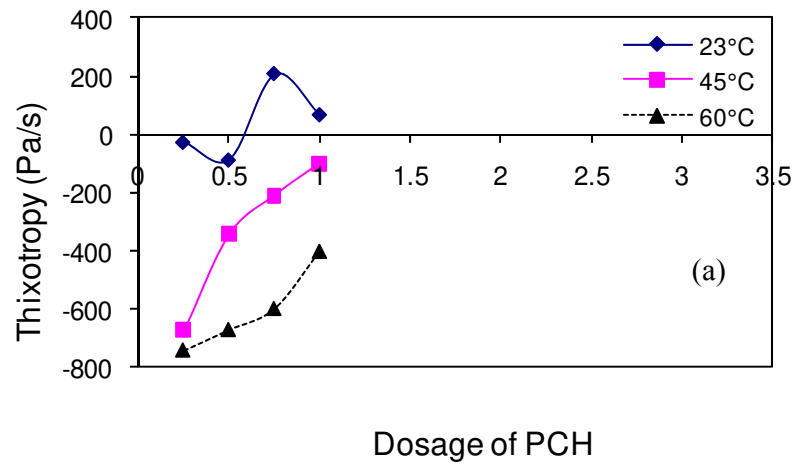


Figure 4.17 Thixotropy of oil well cement slurries at various temperatures and different dosages of admixtures, (a) PCH, (b) LSM, and (c) PCM ( $w/c = 0.44$ ).

Table 4.2 Thixotropy of oil well cement slurry incorporating different admixtures

Admixture	% BWOC	Thixotropy (Pa/s)			Admixture	% BWOC	Thixotropy (Pa/s)		
		23°C	45°C	60°C			23°C	45°C	60°C
PCH*	0.25	-27.2	-673.1	-742.5	SRA*	0.3	1899.5	3571.7	4027.4
	0.5	-87.6	-343.5	-670.9		0.6	1448.4	2027.5	6131.8
	0.75	207.7	-210.7	-598.6		1	-1463.1	1000.9	6660.5
	1	67.2	-100.0	-400.8		1.5	-21.2	512.7	-2253.3
LSM*	0.5	1248.3	1491.5	-38.6	HCR*	0.5	1200.3	1350.0	1934.1
	1	2192.2	2899.8	1232.4		1	-700.7	-940.9	-1350.4
	1.5	1970.9	4005.4	6551.3		2	-560.9	-760.6	-870.9
	2	1850.6	3509.1	6300.2		3	-300.1	-269.6	-430.3
PCM*	0.25	229.5	1688.9	2741.1	RA*	2	1942.8	4321.8	5000.3
	0.5	302.9	-322.6	-4254.5		4	-1944.0	879.7	4120.5
	0.75	798.0	-566.1	-990.3		6	560.5	700.4	750.7
	1	69.4	-367.3	-902.3		-	-	-	-

\*PCH: new generation polycarboxylate-based high-range water reducing admixture, LSM: lignosulphonate-based mid-range water reducing admixture, PCM: polycarboxylate-based mid-range water reducing admixture, SRA: phosphonate-based set retarding admixture, HCR: hydroxylated carboxylic acid-based retarding admixture, and RA: rheoplastic solid admixture.

The effect of the SRA on thixotropy is presented in Fig. 4.18(a). At 23°C, thixotropy decreased with increasing SRA dosage and became negative beyond a dosage of 0.75%. At 45°C, thixotropy decreased gradually with the SRA dosage, which is consistent with the findings of yield stress. Conversely, thixotropy increased significantly with the SRA dosage at 60°C up to a dosage of 1%, and then decreased until reaching a negative value at a dosage of about 1.5%.

It was also observed that at relatively low HCR dosage, the higher the temperature, the higher was the degree of thixotropy (Fig. 4.18(b)). Thixotropy shifted from positive to negative with increased HCR dosage at all test temperatures, indicating increased stiffening of the slurry. Thixotropy also decreased with relatively higher HCR dosages. It showed a comparable pattern at all investigated temperatures, which is consistent with the findings of yield stress.

Fig. 4.18(c) represents the effect of the RA on the thixotropy of OWC slurries. At 23°C, thixotropy decreased with increasing RA dosage and became negative at a dosage of about 4%. Beyond this dosage, the reverse hysteresis turned back to normal. At 45°C and 60°C, thixotropy generally decreased with increasing RA dosage.

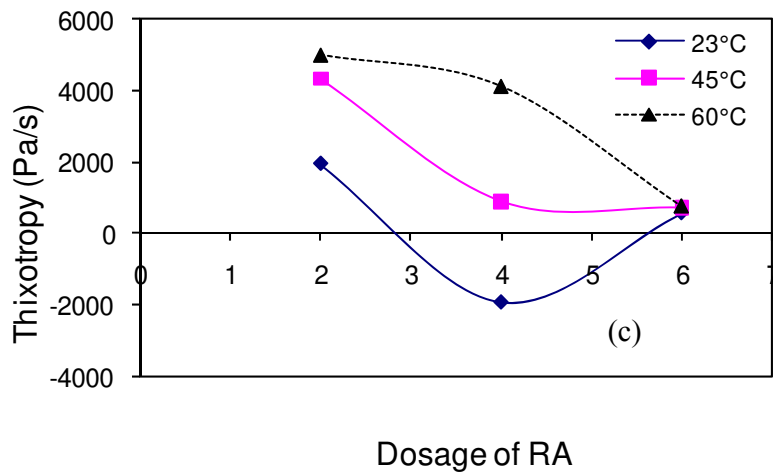
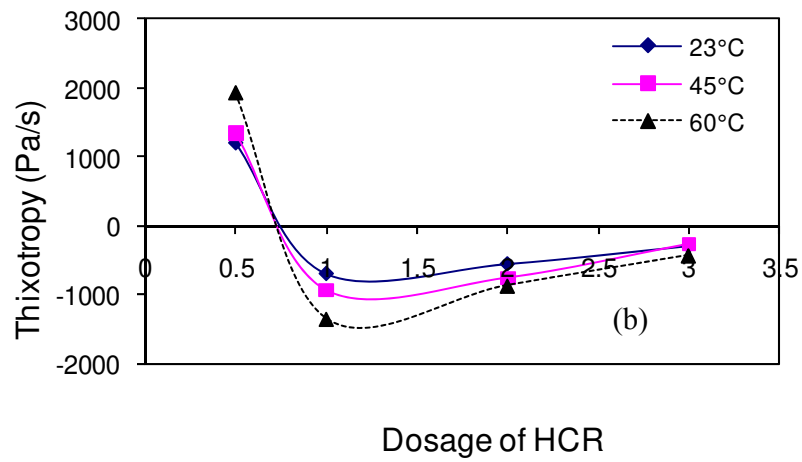
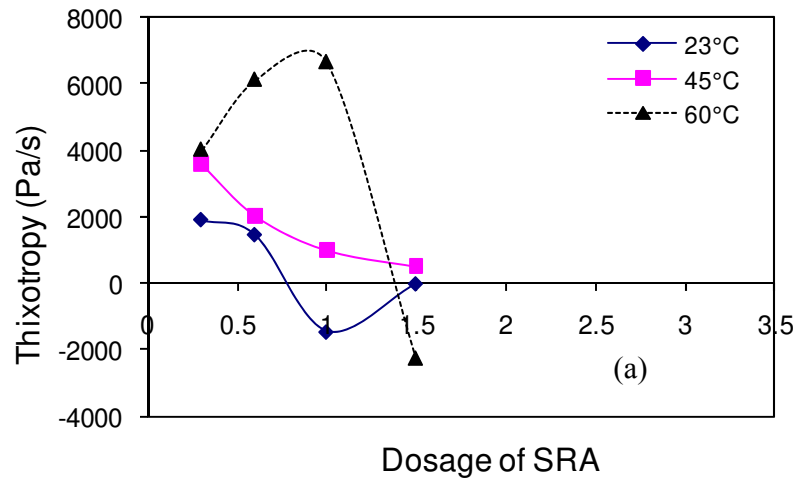


Figure 4.18 Thixotropy of oil well cement slurries at various temperatures and different dosages of admixtures, (a) SRA, (b) HCR, and (c) RA ( $w/c = 0.44$ ).

#### ***4.6.6 Effect of Temperature and Chemical Admixtures on Gel Strength***

It can be observed that the 10-sec gel strength, 10-min gel strength, and shear stress at low and high shear rates of  $5.11 \text{ s}^{-1}$  and  $511 \text{ s}^{-1}$  of neat cement slurries increased with decreasing w/c (Fig. 4.19) likely due to increased solid ratio. Figure 4.20 illustrates the effect of temperature on the rheological properties of a neat OWC slurry with w/c=0.44. At 23°C both gel strength values at 10-sec and 10-min were lower than the yield stress, regardless of the w/c. However, the rate of change of those properties with increasing temperature was not similar. Indeed, the 10-min gel strength was found to be higher than the yield stress at 45°C and 60°C for all w/c values tested. At 60°C, the 10-min gel strength was 1.94 times the yield stress, whereas the ratio was 0.67 and 1.13 at 23°C and 45°C, respectively. The higher value of the 10-min gel strength at 45°C and 60°C is due to the higher rate of hydration and subsequent stiffening of the slurry at increased temperature.

Table 4.3 represents the effects of the dosage of various admixtures and temperature on the 10-sec gel strength, 10-min gel strength, yield stress, and thixotropy. In general, the gel strength increased with increasing temperature for all admixtures and dosages used in this study. For PCH, PCM and HCR, both the 10-sec and 10-min gel strength decreased with increasing admixture dosage. Also, the higher the temperature the higher was the gel strength. For LSM, SRA and RA, the gel strength increased with the dosage up to a threshold level, beyond which the gel strength started to decrease. At all the temperatures investigated, the values of gel strength were generally lower for slurries prepared with PCH than those incorporating the other admixtures. Generally, the trends of gel strength in Table 4.3 were in general agreement with those of the yield stress and thixotropy.

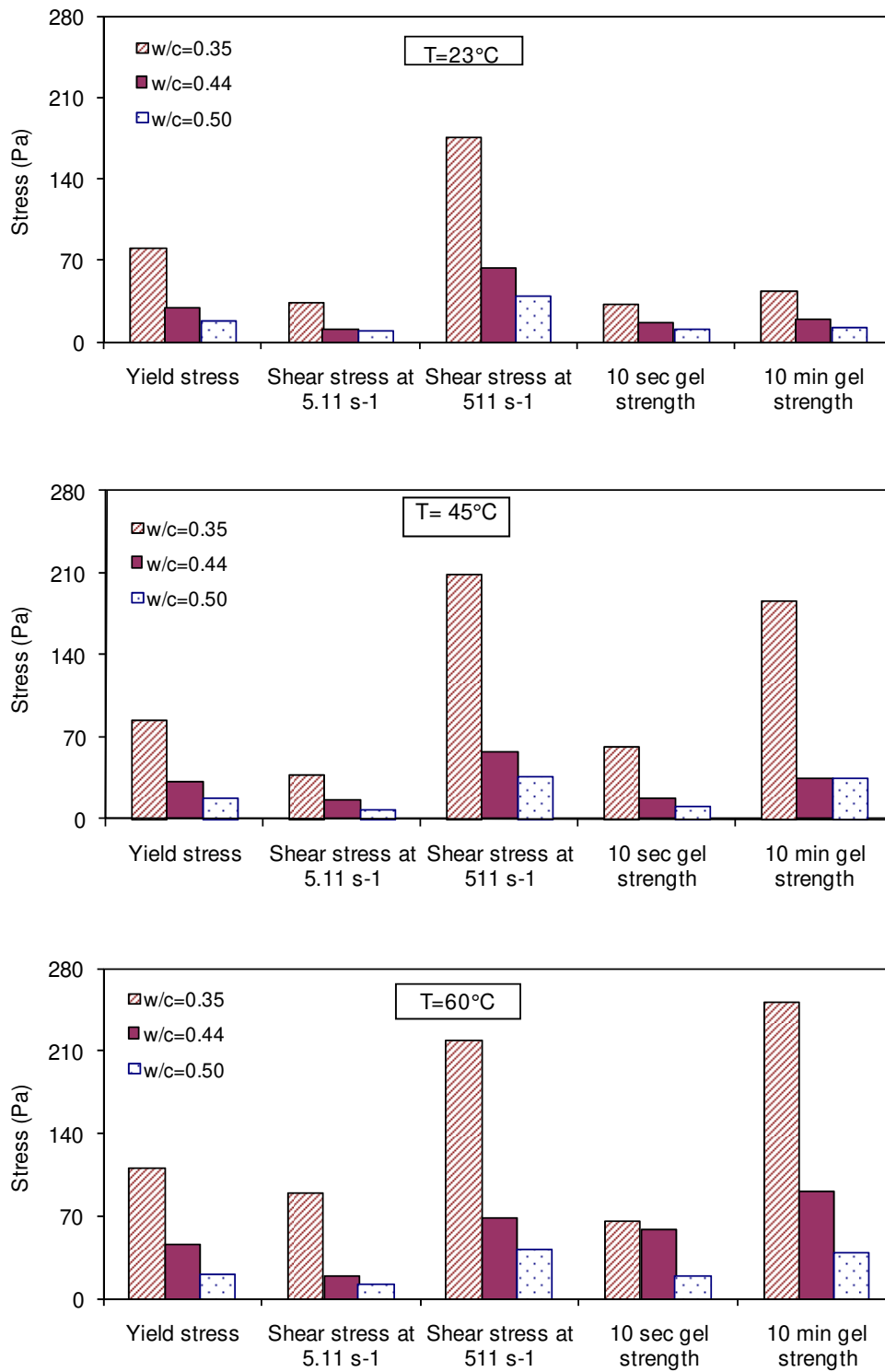


Figure 4.19 Variation of rheological properties of cement slurries with water cement ratio and temperature (a) at 23°C, (b) at 45°C, and (c) at 60°C.

Table 4.3 Gel strength and yield stress of oil well cement slurries incorporating different admixtures

Admixture	% BWOC	23°C			45°C			60°C		
		10-sec gel strength	10-min gel strength	Yield stress	10-sec gel strength	10-min gel strength	Yield stress	10-sec gel strength	10-min gel strength	Yield stress
		Pa	Pa	Pa	Pa	Pa	Pa	Pa	Pa	Pa
PCH	0.00	16.27	19.85	29.62	18.01	35.27	31.95	59.01	90.13	46.43
	0.25	4.04	5.19	5.62	11.20	18.79	15.00	17.88	77.21	26.65
	0.50	2.09	3.48	2.85	3.17	6.66	3.99	5.40	24.70	7.53
	0.75	2.67	5.17	2.95	1.85	5.28	3.56	1.88	15.17	4.15
	1.00	1.77	5.54	2.61	1.33	3.17	3.40	1.51	10.64	4.01
LSM	0.00	16.27	19.85	29.62	18.01	35.27	31.95	59.01	90.13	46.43
	0.50	21.94	25.31	33.74	22.57	31.33	37.00	30.81	63.51	52.92
	1.00	22.70	34.27	34.60	26.19	34.95	40.00	41.84	77.83	64.41
	1.50	19.33	30.66	29.52	35.05	43.81	41.00	42.40	97.33	65.17
	2.00	15.32	26.01	28.17	34.11	42.87	38.57	40.32	90.26	63.23
PCM	0.00	16.27	19.85	29.62	18.01	35.27	31.95	59.01	90.13	46.43
	0.25	6.19	7.10	8.95	13.79	18.81	20.11	18.90	198.50	29.06
	0.50	3.77	5.27	5.61	8.83	14.32	12.15	16.42	60.24	26.47
	0.75	3.74	5.42	3.66	3.73	7.85	5.27	10.83	31.72	14.47
	1.00	2.70	5.08	4.20	3.16	6.96	3.65	6.93	20.95	10.60
SRA	0.00	16.27	19.85	29.62	18.01	35.27	31.95	59.01	90.13	46.43
	0.30	13.54	17.98	27.29	16.93	25.13	30.55	29.98	69.81	48.08
	0.60	13.10	20.20	20.58	14.00	20.76	26.59	29.50	71.46	49.23
	1.00	9.86	24.62	15.31	11.24	23.01	20.08	25.17	42.63	42.64
	1.50	3.46	11.05	4.07	7.67	21.34	15.77	20.56	77.86	36.78
HCR	0.00	16.27	19.85	29.62	18.01	35.27	31.95	59.01	90.13	46.43
	0.50	15.19	19.01	26.33	15.01	29.93	30.87	29.56	73.59	39.95
	1.00	7.65	21.69	12.07	10.45	23.04	21.00	15.64	55.10	37.06
	2.00	5.42	14.45	10.06	7.77	20.77	17.48	9.11	41.18	31.33
	3.00	3.99	11.11	8.50	5.58	18.56	16.50	7.67	34.65	27.25
RA	0.00	16.27	19.85	29.62	18.01	35.27	31.95	59.01	90.13	46.43
	2.00	29.80	36.39	47.37	40.82	95.58	52.11	67.35	140.79	71.19
	4.00	20.40	29.47	24.52	26.15	70.64	35.03	28.67	100.52	39.01
	6.00	8.02	18.27	7.01	15.04	45.37	10.95	17.79	54.23	19.99

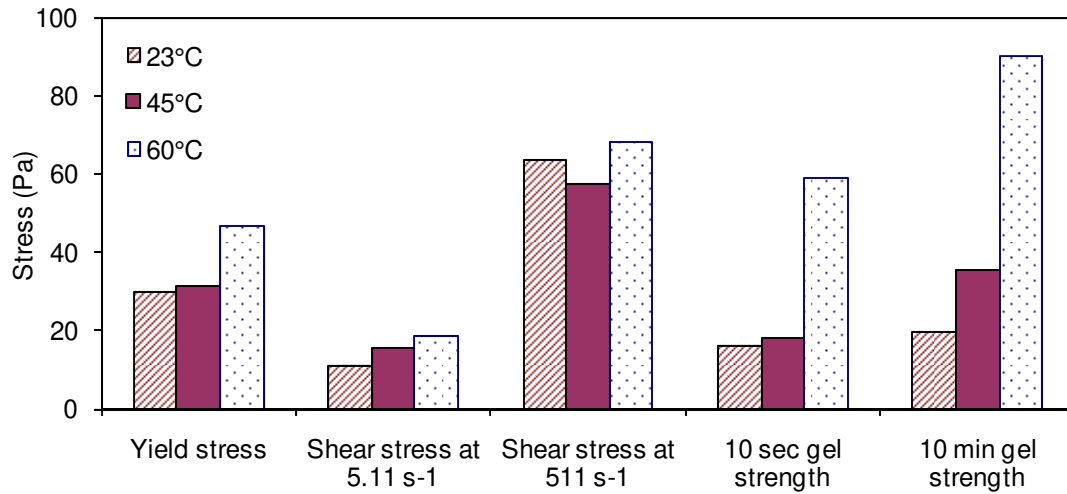


Figure 4.20 Variation of rheological properties of oil well cement slurries with temperature at w/c = 0.44.

#### 4.6.7 Comparison of Effects of Various Admixtures on Rheology of Oil Well Cement Slurries

Rheological data were taken at 20 different shear rate levels starting from 5.11 to 511 s<sup>-1</sup> and then at descending shear rates from 511 to 5.11 s<sup>-1</sup>. The maximum shear rate was chosen as 511 s<sup>-1</sup> because shear rates above this value were reported to provide inconsistent results (ANSI/API RP 10B-2, 2005). It should be noted that the data corresponding to the shear rate of 5.11 s<sup>-1</sup> was discarded and the Bingham plastic model was fitted between 11 to 511 s<sup>-1</sup> to calculate yield stress and plastic viscosity. This is because shear rate data at/or below 10.2 s<sup>-1</sup> can be affected by slippage at the wall of the coaxial cylindrical rheometer (Guillot, 2006) and do not provide reproducible results (ANSI/API RP 10B-2, 2005, Guillot, 2006). Due to differences in their chemical compositions and the mechanisms by which they act, the different chemical admixtures led to various effects of the rheological properties of OWC slurries that influence the properties of cement slurries.

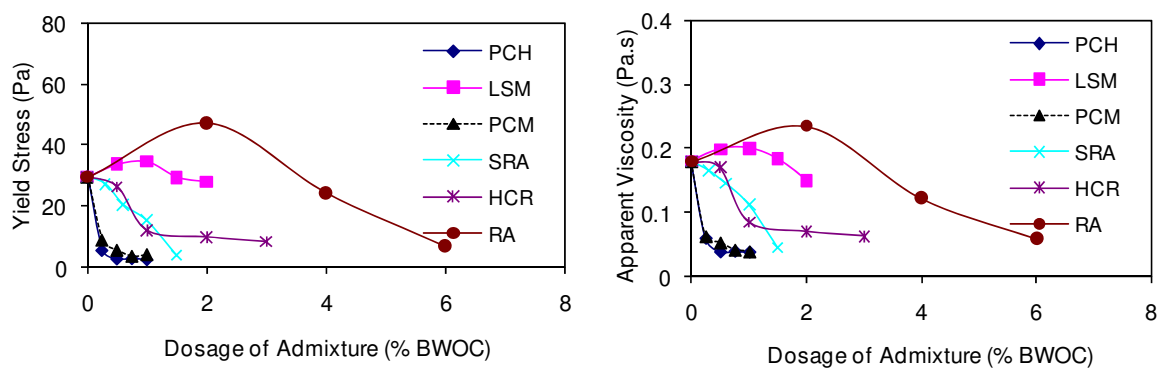
The effects of various dosages of the different chemical admixtures explored in this study on the rheological properties of OWC slurries at a w/c of 0.44 are presented in Figs. 4.21 to 4.23. Figure 4.21 shows yield stress and apparent viscosity values for OWC slurries incorporating PCH, LSM, PCM, SRA, HCR and RA admixtures at temperatures of 23°C, 45°C, and 60°C. Agreement between the behaviour and trend of yield stress and apparent viscosity can be observed. An OWC



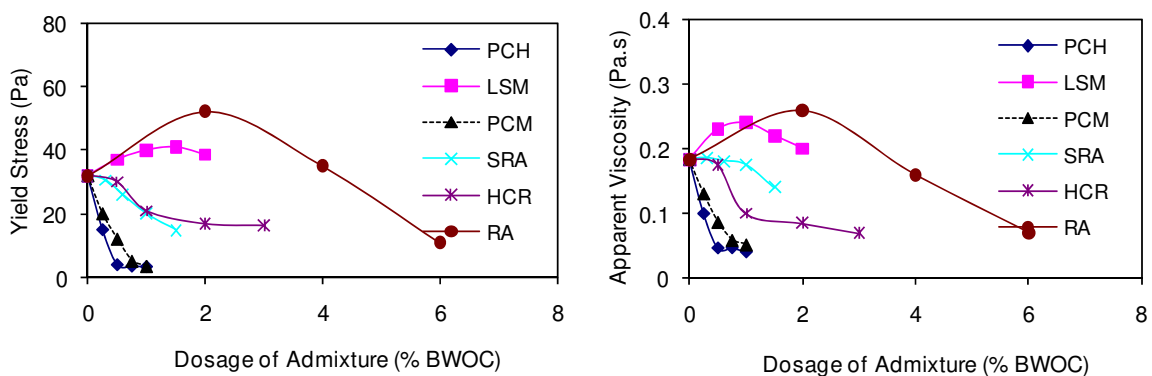
slurry with a w/c of 0.44 and incorporating no admixture was considered as a control mixture. It can be observed that the admixtures had diverse effects on the rheology of OWC slurries at various temperatures. The study reveals that both yield stress and apparent viscosity increased with temperature increase. However, the rate of increase of yield stress and apparent viscosity is not linear, which is in agreement with previous findings (Al-Martini, 2008, Nehdi and Al-Martini, 2007, Soroka, 1993).

For PCH, PCM and HCR, the yield stress and apparent viscosity decreased with the increase of admixture dosage, and saturation dosages could be observed. Results plotted in Fig. 4.21 reveal that PCH was generally more effective at reducing the yield stress and apparent viscosity than the other admixtures. Due to the effective dispersing mechanism of polycarboxylate, OWC slurries made with PCH had lower yield stress and apparent viscosity values than that of the control mixture for all admixture dosages and test temperatures. The polycarboxylate-based admixture, is composed of a backbone chain of complex polymers with carboxylate groups and grafted polyethylene oxide ( $9\text{OCH}_2\text{CH}_2$ )<sub>n</sub>, PEO) side chains. These polymers adsorb on to the hydrating cement grains and a portion of the grafted side chains is oriented into the solution. Because of the comb like structure of the polymers, the polyethyleneoxide (PEO) side chains interact favorably with the aqueous medium and stretch into the solution. The increased osmotic pressure resulting from the approach of cement grains towards each other and overlapping of adsorbed layers of the dispersant induce steric repulsive forces between the cement particles, thus fluidizing the cement slurry (Volpert, 2005, Nelson *et al.*, 2006).

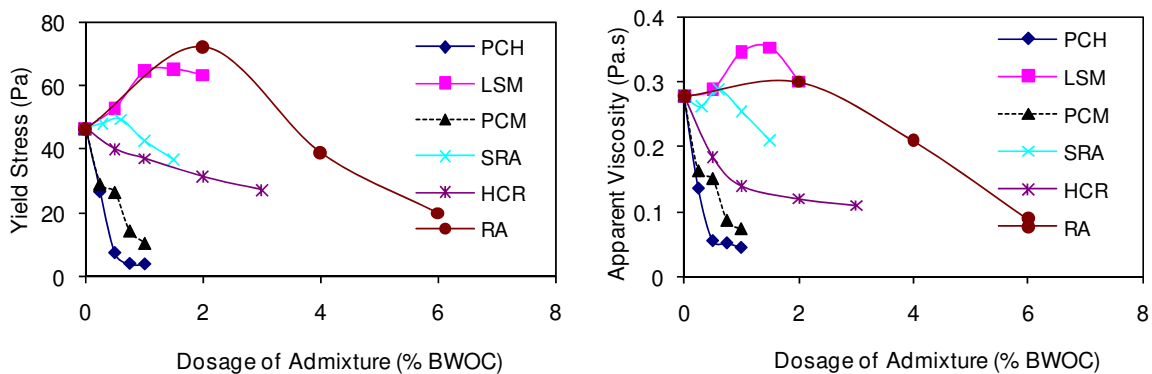
At relatively low dosages, LSM did not improve the rheological properties of cement slurries, but rather acted as an accelerator. However, at dosages above 1%, LSM started to act as a dispersant at 23°C and the yield stress values and apparent viscosity became lower than that of the control mixture. Depending on the lignosulphonate retarder's carbohydrate content and chemical structure (e.g. molecular weight distribution and degree of sulphonation) and the type of cement, it is generally effective to a bottom hole temperature of about 122°C (Nelson *et al.*, 2006). However, in the present study both at 45°C and 60°C, the yield stress and apparent viscosity values were generally higher than that of the control mixture. They only exhibited a decreasing trend beyond a dosage of 1.5%.



(a)



(b)



(c)

Figure 4.21 Yield stress and apparent viscosity of oil well cement slurries incorporating different admixtures at various temperatures, (a)  $T=23^{\circ}\text{C}$ , (b)  $T=45^{\circ}\text{C}$ , and (c)  $T=60^{\circ}\text{C}$  ( $w/c = 0.44$ ).

The effects of PCM and HCR were found to be similar to that of PCH, but somewhat less significant. At 23°C and 45°C, the yield stress and apparent viscosity started to decrease with increasing SRA dosage. But at 60°C, both values increased slightly at SRA dosage below 0.50%. At higher dosages, SRA effectively offset the acceleration of hydration and the yield stress and apparent viscosity started to decrease. For the rheoplastic admixture RA, it was found that the yield stress and apparent viscosity increased up to 2% RA and then decreased beyond that level since RA could effectively offset the acceleration of hydration at such a high dosage. It can be concluded that, the effect of LSM, SRA and RA on yield stress and apparent viscosity was dosage-dependent as observed elsewhere (Ramachandran *et al.*, 1997).

Figure 4.22 illustrates the effects of different admixtures and temperatures (23°C, 45°C, and 60°C) on the 10-sec and 10-min gel strength of OWC slurries. The 10-sec and 10-min gel strength followed a similar trend to that of yield stress and apparent viscosity. However, there exists no simple correlation between the values of yield stress and gel strength. Depending on the admixtures dosage and temperature, the ratio of the 10-sec gel strength to yield stress was found to be in the range of 0.50 to 1.37, whereas the range was found to be 0.67 to 7 for the 10-min gel strength to yield stress ratio.

Figure 4.23(a, b, and c) illustrates the effect of different admixtures on the plastic viscosity of OWC slurries at different temperatures (23°C, 45°C, and 60°C) along with that of the control mixture. It was reported that plastic viscosity of cement slurries generally decreases with an increase in temperature (Ravi *et al.*, 1990 and Ramachandran *et al.*, 1997). But it is not possible to provide such a conclusion based on the current study. In order to evaluate the reproducibility of test results, some selected tests were performed several times and the results were reproducible within a variability of 5%. At 23°C, plastic viscosity decreased with increased admixture dosage up to a certain level and then started to increase in the case of PCH, PCM, and RA at associated dosages of 0.50%, 0.50% and 4.0%, respectively. Plastic viscosity gradually increased with increased dosage in the case of LSM, whereas it decreased with increased SRA dosage. In the case of HCR, plastic viscosity generally decreased with increased dosage. At 45°C, admixtures showed almost similar behaviour in terms of plastic viscosity except for LSM. At 60°C, slurries incorporating PCH did not exhibit a regular behaviour and plastic viscosity increased with increased admixture dosage. In the case of PCM, SRA and HCR, plastic viscosity increased up to a certain limit and then started to decrease at associated critical dosages of 0.50%, 0.75% and 0.50%, respectively. However, it was not possible to provide a simple correlation of the effect of

chemical admixtures and temperatures on the plastic viscosity based on the present study, which was also noted previously (Nehdi and Al-Martini, 2007, Al-Martini, 2008).

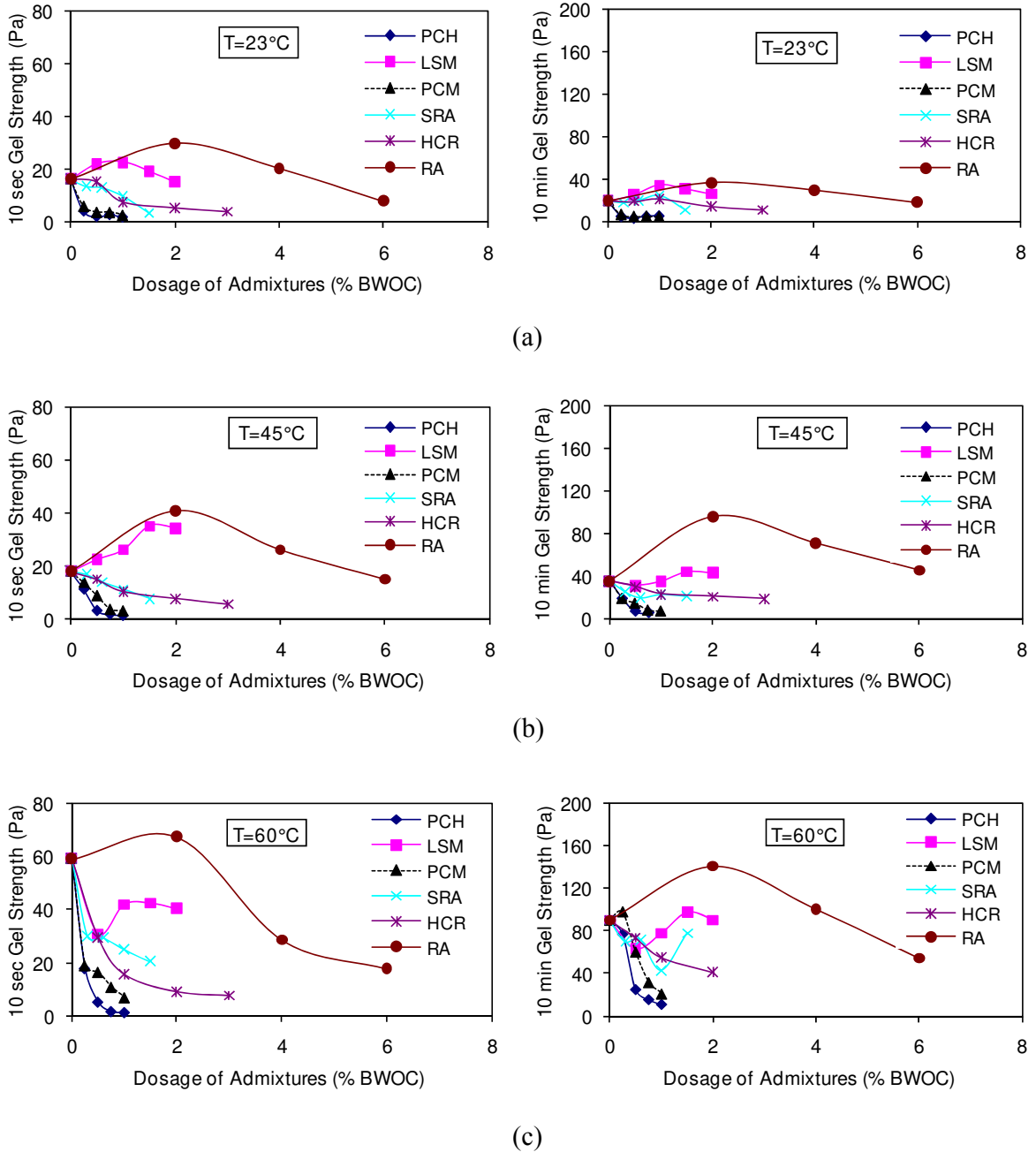
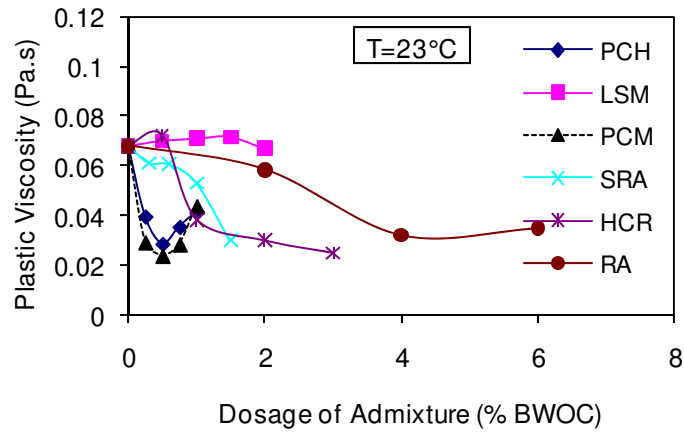
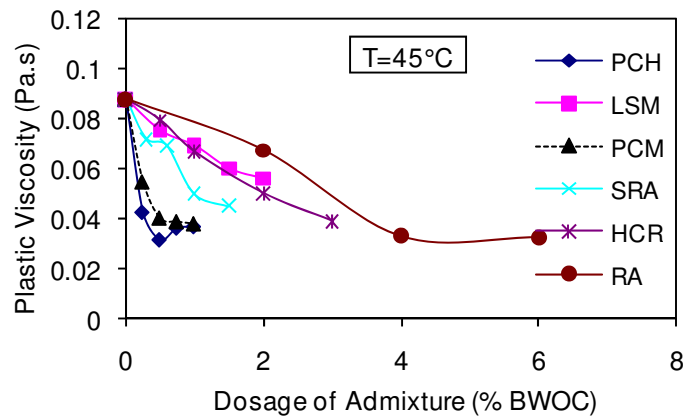


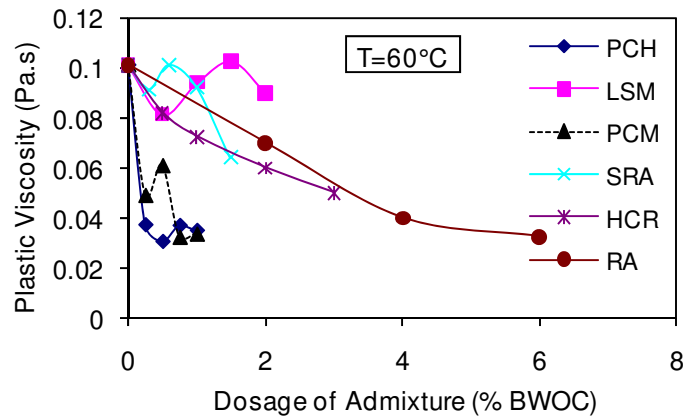
Figure 4.22 10-sec and 10-min gel strength of oil well cement slurries incorporating different admixtures at various temperatures, (a)  $T=23^{\circ}\text{C}$ , (b)  $T=45^{\circ}\text{C}$ , and (c)  $T=60^{\circ}\text{C}$  ( $w/c = 0.44$ ).



(a)



(b)



(c)

Figure 4.23 Plastic Viscosity of oil well cement slurries incorporating different admixtures at various temperatures (a)  $T=23^{\circ}\text{C}$ , (b)  $T=45^{\circ}\text{C}$ , and (c)  $T=60^{\circ}\text{C}$  ( $w/c = 0.44$ ).

Thixotropy measurements of OWC slurries showed that at lower dosage of admixtures (except for LSM), the higher the temperature the higher was the degree of thixotropy. This is probably because at lower dosages the admixtures are not effective enough to disperse the structures formed as a result of the acceleration of hydration at higher temperature. Thixotropy values were observed to decrease with increasing admixture dosage, indicating that higher dosages reduced the degree of stiffening. Similar findings were also observed in previous work (Nehdi and Al-Martini, 2007, Al-Martini, 2008) using ordinary Portland cement pastes.

As mentioned earlier, the rheology of OWC slurries depends on a number of factors, such as cement hydration kinetics (Saak, 2000), supporting liquid rheology (Nelson *et al.*, 2006), inter-particle forces (Saak, 2000, Nelson *et al.*, 2006), and solid volume fraction (Nelson *et al.*, 2006). A number of chemical admixtures such as plasticizers/water reducer (dispersants), retarders, weighting agents, extenders, etc, have been used to modify the rheological properties of OWC slurries for proper placement in deep and narrow oil well annulus. Most water reducing admixtures retard the cement hydration rate in addition to acting as a deflocculant due to electrostatic repulsion (Ramachandran *et al.*, 1997, Saak, 2000, Nelson *et al.*, 2006), steric repulsion, or both (Nelson *et al.*, 2006). Moreover, the performance of chemical admixtures also depends on other factors including the type of cement and its fineness, nature and amount of calcium sulfates and soluble alkali sulfates, C<sub>3</sub>A content and distribution of aluminates and silicate phases at the surface of cement grains (Vidick *et al.*, 1987), reactivity of cement phases (Michaux and Nelson, 1992), time, mixing energy and mixing method, water temperature, w/c, etc.

The mechanisms by which chemical admixtures act are still a matter of controversy. It was documented that the combined effect of adsorption and nucleation are responsible for the hydration retardation induced by admixtures (Ramachandran *et al.*, 1997 and Nelson *et al.*, 2006). Admixtures inhibit the contact of cement grains with water by adsorbing on to the surface of cement grains and the hydration products throughout the hydration process and thereby delay the hydration process. Retarders may also adsorb onto the nuclei of hydration products and can inhibit the further hydration. But at higher temperature, this layer can break down and the rate of hydration is accelerated. This may be one reason why LSM, SRA and RA seem to increase the yield stress and viscosity at high temperature.

Moreover, at lower dosage the adsorbed layer of admixture might not be sufficiently effective to act as a barrier to prevent the contact of water and cement grains, which promotes the acceleration of hydration reactions. This could be the reason why relatively higher yield stress

and viscosity values were observed at low dosages of LSM, SRA and RA. Moreover, lower water content reduces the space between solid particles. Hence, hydration products can easily come in closer contact with each other, resulting in faster rate of hydration reactions and earlier stiffening. This could probably be another reason why LSM, SRA and RA acted as accelerators up to a certain dosage.

It was documented that a portion of the chemical admixture is consumed by the initial hydration products if it is added in the mixing water during the pre-induction period, and thus does not contribute effectively to reducing the slurry viscosity and yield stress (Michaux and Nelson, 1992, Hanehara and Yamada, 1999, Nelson *et al*, 2006). This could also have contributed to getting increased yield stress and viscosity for slurries incorporating LSM, SRA and RA.

#### **4.7 Conclusions**

The rheological properties of OWC slurries are affected by numerous factors including the w/c, size and shape of cement grains, chemical composition of the cement and relative distribution of its components at the surface of grains, presence and type of additives, compatibility between cement and chemical admixtures, mixing and testing procedures, etc. Moreover, slip at the slurry-shearing surface interface, particle-particle interactions, chemical reactions, non-homogeneous flow fields, and human errors can make the rheological experiments difficult to reproduce. However, during the present tests, every effort was made to minimize experimental error by strictly following a consistent mixing and testing procedure. The effect of the w/c and temperature on the rheological properties of OWC slurries incorporating various chemical admixtures was studied using an advanced rheometer. Six admixtures were used in this study including a new generation polycarboxylate-based high-range water reducing admixture (PCH), lignosulphonate-based mid-range water reducing admixture (LSM), polycarboxylate-based mid-range water reducing admixture (PCM), phosphonate-based set retarding admixture (SRA), hydroxylated carboxylic acid-based retarding admixture (HCR), and a rheoplastic solid admixture (RA). The coupled effects of the temperature and type and dosage of admixture on yield stress, plastic viscosity, apparent viscosity, and gel strength were studied. Based on the experimental results, the following conclusions can be drawn:

- The rheological properties of OWC slurries are highly dependent on temperature; they generally increased nonlinearly with temperature increase. This is mainly due to the dependence of the formation of hydration products on temperature.

- As expected, the viscosity of OWC slurries decreased significantly with the increase of the w/c.
- The rheological properties of OWC slurries depended on the type of admixture used. PCH, PCM, and HCR improved fluidity at all test temperatures and for all dosages used, while slurries incorporating LSM required more energy to initiate slurry flow since the yield stress increased at all dosages tested.
- The admixture dosage had a significant effect on the slurry rheology. At lower dosages LSM, SRA and RA acted as accelerators, thus enhancing the thixotropic behaviour of OWC slurries. This was more pronounced at higher temperature. However, beyond certain threshold dosages, such admixtures became effective dispersants and reduced the extent of cement slurry thixotropy.
- PCH was found to be more effective at improving the rheological properties of OWC slurries at all test temperatures even at relatively lower dosages compared to the other admixtures tested.

It should be noted that the findings reported in this study are valid for the cement and admixtures used herein. Other cement/admixture combinations can exhibit different characteristics. Even admixtures from the same category could behave differently, and thus need to be investigated separately.

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*Chapter 5***EFFECT OF SUPPLEMENTARY CEMENTITIOUS MATERIALS  
ON RHEOLOGY OF OIL WELL CEMENT SLURRIES\*****5.1 Introduction**

The use of supplementary cementitious materials (SCMs) has received increased attention over the last few decades. Mineral and chemical admixtures play an important role in controlling the physical and chemical properties of fresh and hardened cementitious systems. Partial replacement of cement using SCMs is increasingly perceived as a sustainable solution. It reduces the cement factor thus reducing CO<sub>2</sub> emission from cement production, and mitigates disposal of various industrial by products. A large number of industrial and naturally occurring materials including fly ash, volcanic ash, ground granulated blast furnace slag, silica fume, Zeolite, diatomaceous earth, metal powder, and rice husk ash can be used as partial replacement for cement.

Due to differences in their chemical and physical properties, SCMs have diverse effects on the rheological, mechanical and long-term durability performance of cementitious systems. For the particular case of the petroleum industry, cement slurries are pumped to several thousand meters into the ground to anchor and seal the casing to the borehole of oil or gas wells. Thus, an advanced characterization of the rheology of oil well cement slurries is critical. However, the investigation of oil well cement slurry rheology is more complicated than that of cement paste. In order to contend with the bottom-hole conditions (wide range of pressure and temperature), various additives are usually used in the slurry composition. A thorough review of the different types of admixtures used in the petroleum industry and the rheology of oil well cement is available in the open literature (Nelson et al., 2006; Guillot 2006).

A number of studies (e.g. Janotka et al., 2010; Golaszewski et al., 2005; Vikan and Justnes, 2003; Sabir et al., 2001; Zhang and Han, 2000; Sybert and Reick 1990; Ivanov and Roshavelov, 1990; Saasen and Log, 1996; White et al., 1985) used supplementary

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\* Part of this chapter has been published in the proceeding of the Canadian Society of Civil Engineering Conference, 2008.

cementitious materials (FA, SF, MK and RHA) either in conventional portland cement paste or slurries. However, very scant information can be found on the rheological properties of oil well cement slurries incorporating SCMs as partial replacement for cement. Moreover, the coupled effects of temperature, chemical admixtures and mineral admixtures on the rheological properties of oil well cement slurries remain largely unexplored.

In this study, the flow properties of Class G oil well cement slurries with a water to cement ratio (w/c) of 0.44 and incorporating four different SCMs including metakaolin (MK), silica fume (SF), rice husk ash (RHA), and class F fly ash (FA) along with a new generation polycarboxylate-based high-range water reducing admixture (PCH) were tested at different temperatures (23, 45 and 60°C). Their behaviour was compared to that of a control slurry without admixtures. A series of flow tests using an advanced rheometer were carried out to determine the optimum dosage of admixtures. The effect of pressure has been ignored in this study since previous research (Guillot, 2006) indicated that it has an insignificant effect on the rheological properties of cement slurries compared to that of temperature.

The present study allowed gaining an improved understanding of the effect of SCMs on the rheology of oil well cement slurries at high temperature, which should help in selecting adequate admixtures and their effective dosages to overcome difficulties encountered during the construction of oil and gas wells.

## **5.2 Principles of Flow Properties**

Rheological properties control the flow, workability, pumpability, finishing, and other characteristics of cementitious slurries and mortar. Workability is the energy required to handle and finish a cementitious mixture, whereas pumpability is better represented by fundamental properties such as yield stress. The rheological properties of cement-based materials are not only shear rate and shear history dependent, but also time dependent, which is difficult to characterize. However, for practical oilfield purposes, cement slurries are usually represented by time-independent models. It has been observed that it is difficult to capture all possible trends of flow behaviour using a single rheological model (Yahia and Khayat, 2001). The performance of rheological models usually varies with the

test geometries, gap between shearing surfaces and their friction capacity, which makes the measurements even more complicated (Nehdi and Rahman, 2004).

Existing empirical and time-independent rheological models (e.g. Bingham, Herschel-Bulckley, Modified Bingham, Casson, etc.) allow fitting shear stress, shear rate and viscosity data to specific trends using rheological data analysis software. However, no model is free from statistical error. The estimated rheological properties can vary significantly when calculated using various models (Nehdi and Rahman, 2004). The Bingham plastic model and the Power Law model are widely used in the petroleum industry to describe the rheological properties of cement slurries (Guillot, 2006). The Bingham plastic model includes both yield stress,  $\tau_y$  and a limiting viscosity,  $\mu_p$  at finite shear rates, which the Power Law model fails to consider. Therefore, the Bingham plastic model (equation 5.1) was used in this study to calculate the yield stress and plastic viscosity from the shear rate-shear stress experimental down-curve. The down-curve (unloading) does not usually follow the same path as that of the up-curve because of the structural breakdown of the cement paste/slurry with the increase of shear rate. However, it was argued that the down-curve better fits the Bingham model than the up-curve (Ferguson and Kenblowski, 1991)

$$\tau = \tau_0 + \mu_p \dot{\gamma} \quad (5.1)$$

where,  $\tau$ ,  $\tau_0$ ,  $\mu_p$ , and  $\dot{\gamma}$  represent the shear stress, yield stress, plastic viscosity, and shear rate, respectively.

To characterize the rheology of cement slurry, rheological parameters such as the yield stress, apparent viscosity, plastic viscosity, shear thinning, or shear thickening behaviour need to be studied. The yield stress indicates the minimum effort needed for a material to start moving and is the intercept of the flow curve (shear stress vs. shear rate) with the shear stress axis. Below the yield stress, a material behaves like a solid. The plastic viscosity is the slope of the fitted straight line of the flow curve. Usually the plastic viscosity of cement slurry is evaluated using the linear portion of the down curve of the hysteresis loop. For a nonlinear flow curve, shear-thinning or shear-thickening behaviour may be observed and the assumption of constant plastic viscosity is not valid. In such case, Herschel-Bulkley's model (equation 5.2) becomes more suitable.

$$\tau = \tau_0 + k \dot{\gamma}^n \quad (5.2)$$

where,  $\tau$ ,  $\tau_0$ ,  $k$ ,  $\dot{\gamma}$  and  $n$  represent the shear stress, yield stress, consistency, shear rate, and power law exponent, respectively. The model assumes that below the yield stress ( $\tau_0$ ), the slurry behaves as a rigid solid, similar to the Bingham plastic model. The exponent  $n$  describes the shear thinning and shear thickening behaviour. Cement pastes or slurries are considered as shear thinning when  $n < 1$  and shear thickening when  $n > 1$ . A fluid becomes shear thinning when the apparent viscosity decreases with the increase in shear rate, i.e. when the slope of the shear stress vs. shear rate flow curve decreases with the shear rate. Shear thickening is when viscosity of the cement slurry increases with the shear rate.

### 5.3 Materials

Cement slurries tested in this study had a w/c = 0.44 and were prepared using a high sulphate resistant API Class G oil well cement (OWC) with various dosages of SCMs including metakaolin (MK), silica fume (SF), rice husk ash (RHA) and Class F fly ash (FA). The chemical and physical properties of the cement and SCMs are summarized in Table 5.1. Deionized distilled water was used for the mixing, and its temperature was maintained at 23±1°C using an isothermal container. The mixture composition of the slurries are provided in Table 5.2. A new generation polycarboxylate-based high-range water reducing (HRWR) admixture (PCH) meeting ASTM C 494 requirements as a Type-A water-reducing and Type-F high-range water-reducing admixture was used at dosages from 0.25 % to 2.5% by mass of binder for MK, SF, RHA, and FA.

Table 5.1 Properties of materials used

Properties	API Class G Oil Well Cement	Metakaolin	Silica Fume	Rice Husk Ash	Class F fly Ash
Silica (SiO <sub>2</sub> ) (%)	21.6	53.5	85	91.3	60
Alumina (Al <sub>2</sub> O <sub>3</sub> ) (%)	3.3	42.7	0.1	0.4	21
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> ) (%)	4.9	1.3	0.1	0.5	4.88
Calcium Oxide, Total (TCaO) (%)	64.2	0.09	0.4	0.6	6.26
Magnesium Oxide (MgO) (%)	1.1	0.07	–		
Sulphur Trioxide (SO <sub>3</sub> ) (%)	2.2		3	0.5	0.26
Loss on Ignition (%)	0.60	1.5	6	3.7	0.22
Insoluble Residue (%)	0.30		–		
Equivalent Alkali (as Na <sub>2</sub> O) (%)	0.41		1.5	1.4	
Fineness % passing 45µm sieve	92.4	99.5	97.2	80.9	90
Mean particle size (µm)		4.5	0.17	30.4	15.9
Specific surface area <sub>2</sub> (m <sup>2</sup> /kg)	385 (Blaine)	15000 (BET)	15000 (BET)	3040 (BET)	
Specific gravity	3.14	2.6	2.22	2.05	2.03

Table 5.2 Composition of cement slurry

	MK (% by mass)	SF (% by mass)	RHA (% by mass)	FA (% by mass)	Oil well Cement (% by mass)	PCH (% by mass)
Case 1	5-15	–	–	–	85-95	0-2.5
Case 2	–	5-15	–	–	85-95	0-2.5
Case 3	–	–	5-15	–	85-95	0-2.5
Case 4	–	–	–	5-15	85-95	0-2.5

## 5.4 Apparatus

The particle size distribution of the cement, SF, MK, RHA and FA was determined using a Malvern Mastersizer 2000 laser diffraction particle size analyzer. The cement slurry preparation is very important because of the influence of the shear history of the mixture on its rheological properties (Orban *et al.*, 1986). The cement slurries were prepared using a variable speed high-shear blender type mixer with bottom drive blades as recommended by the ANSI/API Recommended Practice 10B-2 (ANSI/API RP 10B-2, 2005).

A high accuracy advanced rheometer (TA instruments AR 2000) (Fig. 4.1(a)), capable of continuous shear rate sweep, stress sweep and strain sweep was used throughout this study to measure the rheological properties of cement slurries. Because of relatively the low viscosity of cement slurries, the coaxial concentric cylinder geometry was considered suitable for this study. The geometry consists of a cylinder with a conical end that rotates inside a cylinder with a central fixed hollow as shown in Fig. 4.1(b). The radius of the inner solid smooth cylinder is 14 mm. This smooth inner solid cylinder rotates inside a fixed hollow cylinder of 15 mm in diameter. The gap between the head of the conical end and the bottom of the hollow cylinder was set to 0.5 mm for all experiments. Such a narrow gap is necessary in order to maintain a constant shear rate across the gap to minimize the error caused by wall slip in rheological measurements (Saak *et al.*, 2001). The rheometer features an auto gap in order to compensate for the expansion of the stainless steel of the coaxial concentric cylinders under a wide range of temperatures, thus keeping the gap constant during experiments. The device keeps the temperature constant during the entire time span of the rheological test through a water circulation system. In order to prevent evaporation from the tested cement slurry, a solvent trap was used to cover the top of the hollow cylinder. This solvent trap has an adequate mechanism to allow rotation of the shaft without any interference.

The rheometer was calibrated using a certified standard Newtonian oil with a known viscosity of 1.0 Pa.s and yield stress of 0 Pa at 20°C. The measured yield stress was 0 Pa and viscosity was 1.009 Pa.s with an error of 0.9%, which is less than the tolerated error of 4% specified by the manufacturer. The rheometer is computer controlled and equipped with a rheological data analysis software, which can fit the shear stress-strain rate data to several rheological models. The Bingham and Herschel-Bulkley's models were used throughout this study to calculate the rheological properties of cement slurries.



## 5.5 Experimental Procedure

### 5.5.1 *Mixing and Preparation of Oil Well Cement Slurry*

A number of oil well cement slurries were prepared with a  $w/c = 0.44$  and not incorporating any chemical admixture or SCM in order to check the reliability of the testing procedure and the apparatus at different test temperatures. The cement slurries were prepared using a high-shear blender with bottom drive blades according to the following procedure. First, the weighed amount of cement and the SCM (if any) were hand mixed dry in a bowl for about 30 sec using a spatula. The mixing water was then poured into the blender and the required quantity of PCH (if any) was added into the mixing water using a needle. The mixing started at a slow speed for 15 sec. The cement-solid admixture was then added over a period of 30 sec. Manual mixing was conducted for 30 sec and a rubber spatula was used to recover material sticking to the wall of the mixing container to ensure homogeneity. Finally, mixing resumed for another 35 sec at high speed.

The mixing procedure was strictly followed for all cement slurries and mixing was conducted at ambient room temperature. The prepared slurry was then placed in the bowl of a mixer for preconditioning for 20 minutes at the specific test temperature at a speed of 150 rpm. The total time between the beginning of mixing and the start of the rheological test was kept constant to avoid the effect of exogenous variables on the results (Williams et al., 1999; Chow et al., 1988; Roy and Asaga, 1979). The rheometer set-up was also maintained constant for all slurries. The concentric cylinder test geometry was also conditioned at the test temperature so as to avoid sudden thermal shock to the slurry.

### 5.5.2 *Rheometric Tests*

After mixing and preconditioning, the cement slurry sample was placed in the coaxial cylinder of the rheometer and the slurry was covered with a solvent trap to prevent evaporation of water during testing. Temperature was adjusted to the required level. The sample was then subjected to a stepped ramp or steady state flow and viscosity measurements were taken at 20 different shear rates starting from 5.11 to 511  $s^{-1}$  after a continuous rotation of 10 sec at each speed. Then, the slurry sample was subjected to a descending shear rate from 511 to 5.11  $s^{-1}$  to obtain the down flow curve. The hysteresis

loop thus produced is used to characterize the thixotropy of cement paste (Saak, 2000). A schematic representation of the viscometric testing program is illustrated in Fig. 5.1.

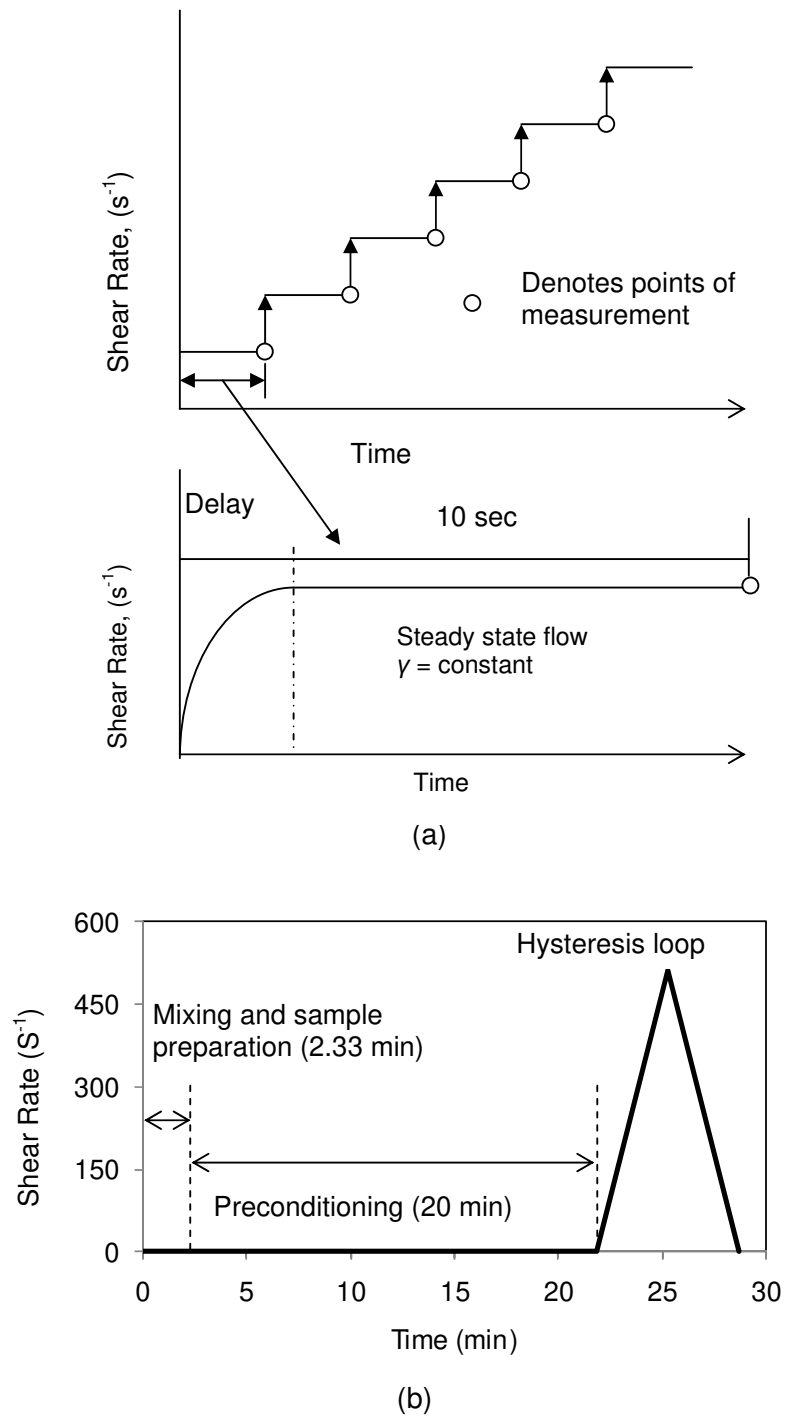


Figure 5.1 (a) Schematic representation of stepped ramp, and (b) rheometer test sequence (shear rate history used in rheological tests) for OWC-SCM slurry

## 5.6 Results and Discussion

### 5.6.1 Reliability of Rheometer and Rheometric Test

To ensure statistical repeatability of results, three sets of neat cement slurry (each consists of three different cement slurry samples) with  $w/b=0.44$  were tested at 23, 45 and 60°C. Another three sets of similar cement slurries with a  $w/b$  of 0.44 and incorporating 5% SCM but without chemical admixture were also tested. The rheological properties of cement slurry are time, temperature, and shear history dependent. Therefore, each test was performed on a new cement slurry at 21.5 mins after first contact between cement and water. Table 5.3 presents the data generated for the reliability study. The standard deviation values are relatively small, which reveals that the experimental procedure and the rheometer can produce repeatable measurements with satisfactory accuracy. In the case of neat cement slurries (Table 5.3(a)), the percentage of coefficient of variation (ratio of standard deviation to the mean) for the yield stress is 1.02, 1.72, and 0.83%, at 23°C, 45°C and 60°C, respectively. For plastic viscosity, the corresponding values are 1.71%, 4.62% and 5.81%, respectively. In the case of cement slurries incorporating SCM (Table 5.3(b)), the percentage of coefficient of variation for yield stress is 1.27%, 5.59%, 1.02%, and 4.07%, for MK, FA, SF and RHA, respectively. For plastic viscosity the corresponding values are 4.35%, 3.69%, 2.36% and 1.53%, respectively.

Table 5.3a Reliability of flow test using neat cement slurry at  $w/c=0.44$

Temp	Yield Stress				Plastic Viscosity			
	Estimated	Avg	<i>SD</i> *	<i>COV</i> **	Estimated	Avg.	<i>SD</i> *	<i>COV</i> **
23°C	26.62				0.068			
	27.01	26.66	0.27	1.02	0.071	0.06	0.0012	1.71
	26.35				0.069			
45°C	31.15				0.064			
	30.87	30.65	0.53	1.72	0.060	0.06	0.0028	4.62
	29.92				0.057			
60°C	46.43				0.035			
	45.55	46.09	0.38	0.83	0.031	0.03	0.0019	5.81
	46.28				0.032			

\* *SD* : Standard deviation, \*\* *COV*: Co efficient of variation

Table 5.3b Reliability of flow test using cement slurry with SCM at 60°C with w/c=0.44

SCM	Yield Stress				Plastic Viscosity			
	Estimated	Avg	<i>SD</i> *	<i>COV</i> **	Estimated	Avg.	<i>SD</i> *	<i>COV</i> **
MK	90.05				0.215			
	88.71	88.68	1.13	1.27	0.225	0.2263	0.0098	4.35
	87.29				0.239			
FA	22.97				0.076			
	23.41	22.32	1.25	5.59	0.081	0.0800	0.0030	3.69
	20.57				0.083			
SF	70.53				0.234			
	69.25	69.55	0.71	1.02	0.226	0.2270	0.0054	2.36
	68.88				0.221			
RHA	13.17				0.315			
	12.35	12.49	0.51	4.07	0.322	0.3213	0.0049	1.53
	11.95				0.327			

\* *SD* : Standard deviation, \*\* *COV*: Co efficient of variation

### 5.6.2 Effect of Type and Dosage of SCMs on Rheological Properties of OWC Slurries

In order to examine the effect of the type of SCM on OWC slurry rheology, cement slurries were first prepared with a water binder ratio of 0.44, but without any chemical admixture. After preconditioning, cement slurries were tested at three different test temperatures and the rheological properties are presented in Figs 5.2-5.5.

The effect of different SCMs on the yield stress of OWC slurries having w/c = 0.44 at different test temperatures, namely 23, 45 and 60°C are presented in Figs. 5.2(a-c) and 5.3(a-d). Figure 5.2 reveals that the yield stress gradually increased with the addition of MK and SF. This could be due to the increase in water demand by the addition of fine powders like MK and SF (mean particle sizes of 4.5 and 0.17  $\mu\text{m}$ , and specific surface of 15000 and 15000  $\text{m}^2/\text{kg}$ , respectively). However, the yield stress values for OWC-SF slurries were found to be greater than those of OWC-MK slurries, a behaviour also observed by others for ordinary Portland cement (OPC) (Caldarone et al., 1994; Caldarone and Gruber, 1995; Ding and Li, 2002). It was found that MK provided better workability than did SF for the given mixture proportions (Ding and Li, 2002) and less HRWR admixture was required for concrete mixtures modified by MK than SF mixtures (Caldarone et al., 1994; Caldarone and Gruber, 1995). Yield stress decreased with

increasing dosage of RHA. Similar behaviour was reported by Laskar and Talukder (2008) for concrete using OPC and different levels of RHA. It should be noted that the RHA was not ground to fine particle size after combustion. It can also be observed that unlike MK and SF, yield stress decreased with increased addition of FA which is in agreement with the findings of other researchers on OPC (Lange et al., 1997; Laskar and Talukdar, 2008). The replacement of cement by FA slows down the rate of hydration and extends the dormant period. This is likely due to the coarser particle size and lower surface area of FA, in addition to its spherical shape which reduces frictional forces among angular particles due to a “ball bearing” effect. It is also well known that the spherical particle shape of fly ash particles helps reducing the water demand to obtain a similar fluidity to that of mixtures made without any fly ash. Other studies suggested that among all 3D shapes, spheres give the minimum surface area for a given volume (Polya and Szego, 1951) resulting in lower water retention and subsequently lower water demand for a particular workability due to a higher particle packing density (Sakai et al., 1997, Yijin et al., 2004). White et al. (1985) suggested that particle size and shape are key factors for controlling the rheological properties FA based OWC slurries.

It should be noted that at similar dosage, yield stress values for cement slurries made with SCM and without any chemical admixtures at all test temperatures followed the following order: SF>MK>RHA>FA.

It can be observed that for all types and dosage of SCMs, yield stress increased non-linearly with the increase of temperature (Fig. 5.3). This is likely due to the increase of the rate of hydration reactions at higher temperature. Similar findings were observed for neat cement pastes by other researchers (Al-Martini, 2008; Nehdi and Al-Martini, 2007; Soroka, 1993). The increase was more substantial for SF and MK, perhaps due to their higher fineness. Figure 5.3(a,b) shows that yield stress for OWC slurries incorporating MK and SF was higher than that of the control mix without SCM for all MK and SF proportions tested. An opposite trend was observed when OWC was partially replaced with RHA or FA; the higher the RHA or FA dosage, the lower was the yield stress value (Fig. 5.3(c, d)). However, the yield stress for OWC slurries incorporating RHA was slightly higher than that of FA slurries irrespective of the test temperature and proportion of RHA or FA (Fig. 5.2 and 5.3(c, d)). This is due to the higher specific surface of RHA and its irregular particle shape versus the spherical shape of FA.

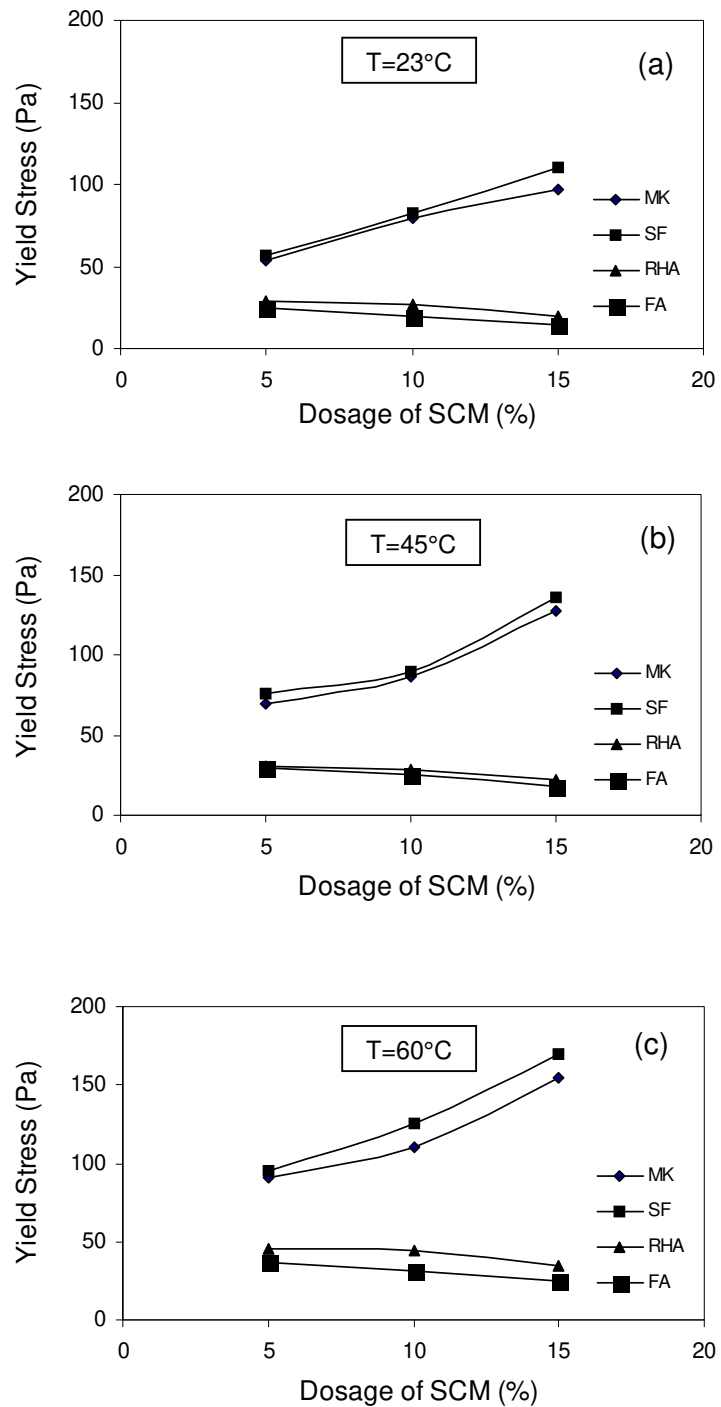


Figure 5.2 Variation of yield stress of OWC slurries with type and dosage of SCM at (a) 23°C, (b) 45°C and (c) 60°C.

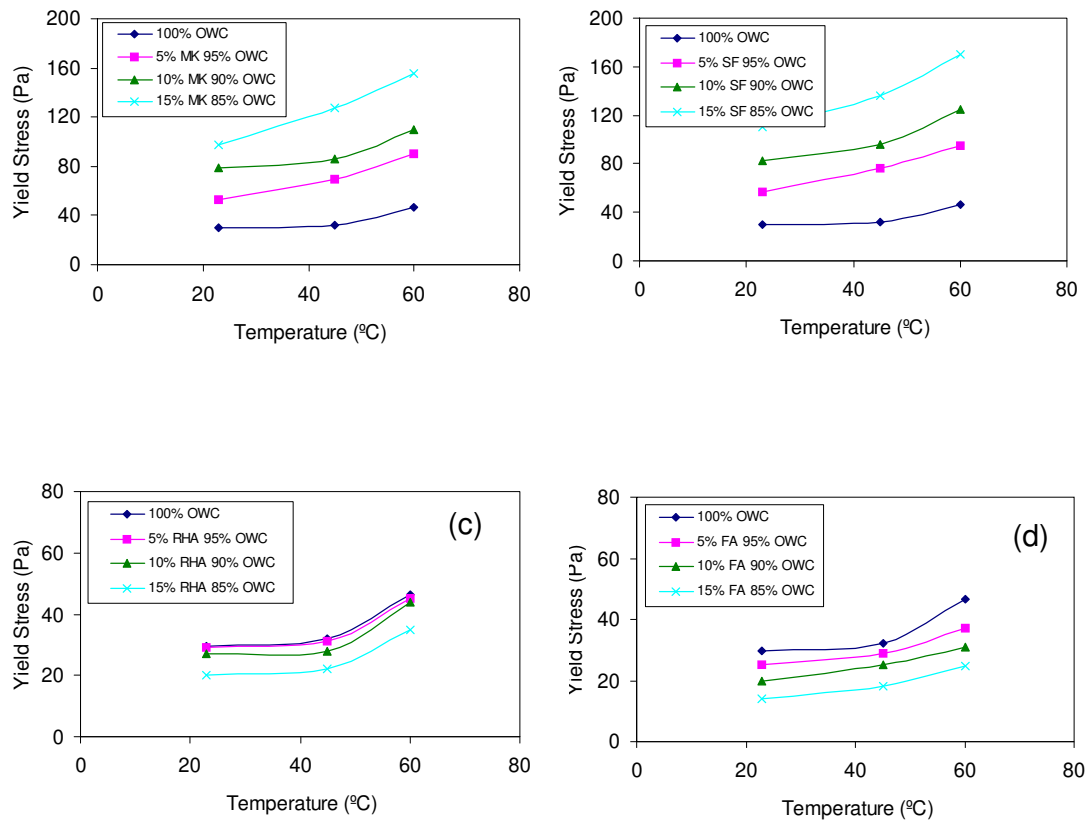


Figure 5.3 Variation of yield stress with temperature for OWC slurries prepared by partial replace of OWC by (a) MK, (b) SF, (c) RHA, and (d) FA.

Figures 5.4 and 5.5 show the effect of the partial replacement of OWC by SCM and that of temperature, respectively, on the plastic viscosity of OWC slurries. The plastic viscosity of OWC slurries generally followed the same trend as that of yield stress for all the SCMs tested, except for RHA. In the case of MK and SF, plastic viscosity values increased with the dosage of MK or SF used and decreased with the FA content at all temperatures tested. Conversely, plastic viscosity values increased with the addition of RHA as partial replacement of OWC. It can be observed that for all SCMs, plastic viscosity increased with temperature, but the increase was more substantial for MK (Fig. 5.5(a)).

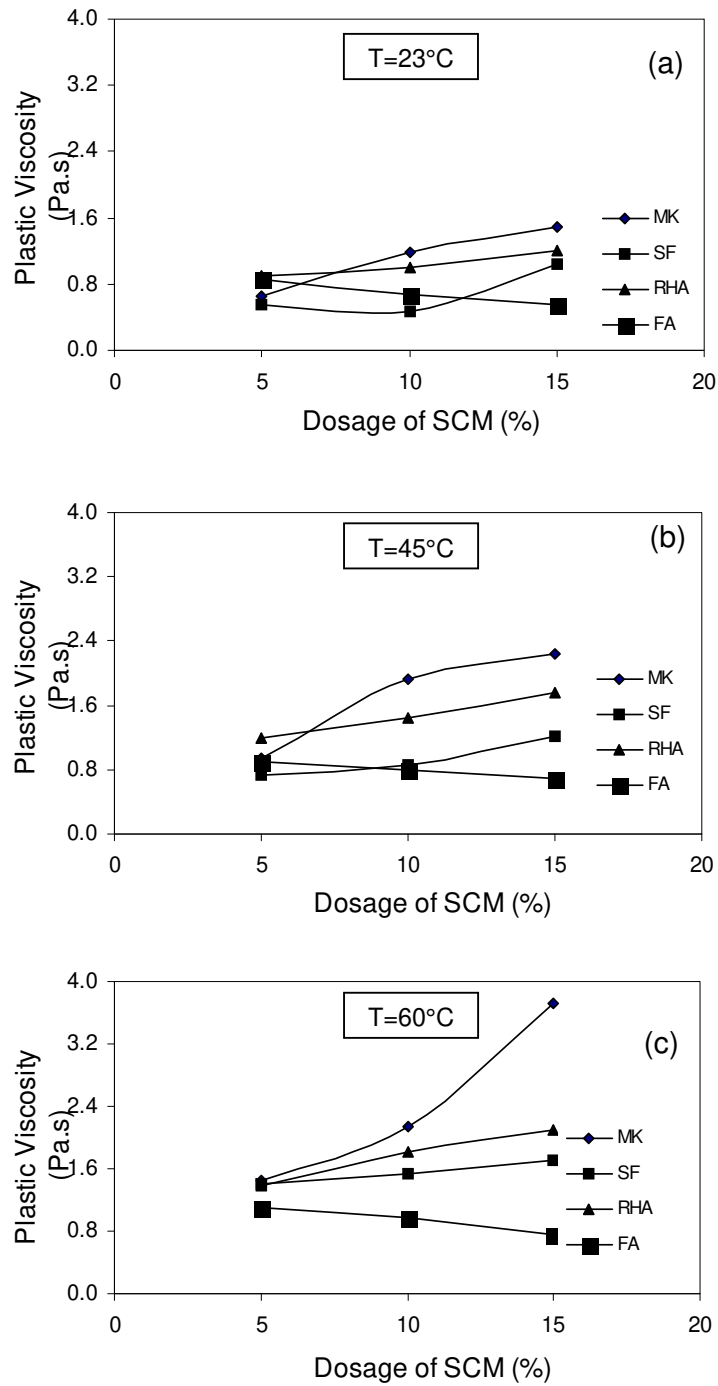


Figure 5.4 Variation of plastic viscosity of OWC slurries with type and dosage of SCM at (a)  $23^{\circ}\text{C}$ , (b)  $45^{\circ}\text{C}$  and (c)  $60^{\circ}\text{C}$ .



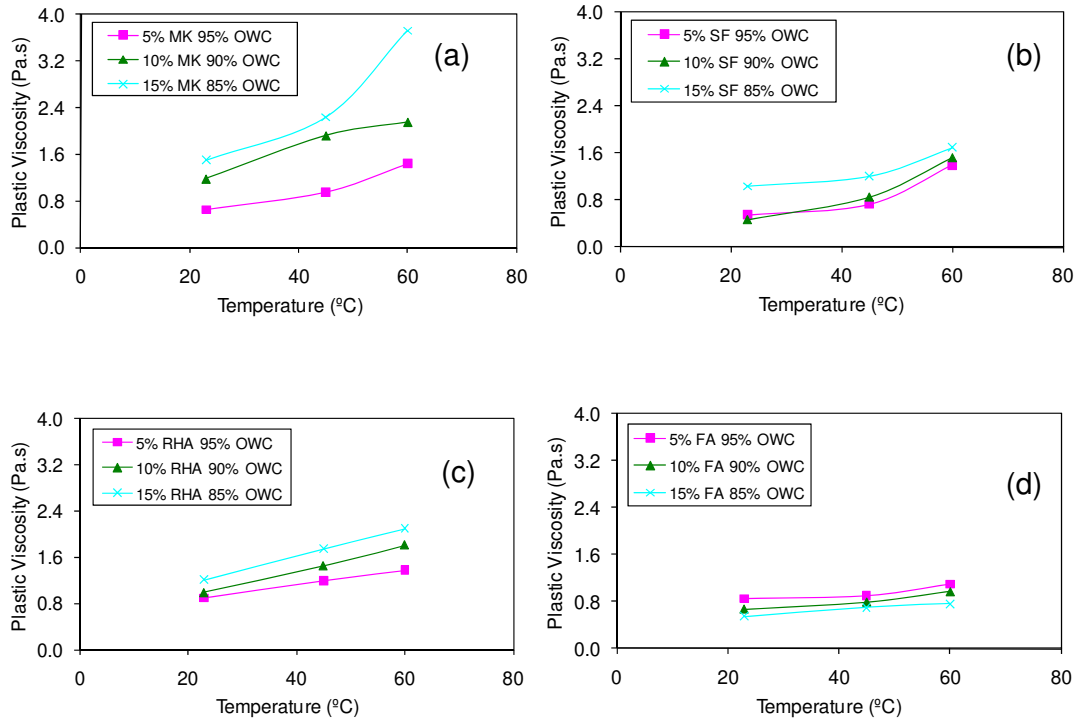


Figure 5.5 Variation of plastic viscosity with temperature for OWC slurries prepared by partial replace of OWC by (a) MK, (b) SF, (c) RHA, and (d) FA.

### 5.6.3 Coupled Effect of SCMS and PCH Dosage on Yield Stress of OWC Slurries

Figure 5.6 illustrates the variation of yield stress of OWC slurries incorporating varying dosages of SCMs and PCH at a w/b ratio of 0.44. Different scale has been used to represent results for FA and RHA due to much lower yield stress values than those for MK and SF.

It can be observed that for all SCMs, yield stress generally decreased with PCH addition and this decrease was generally gradual until reaching a saturation dosage. However, for each SCM, the saturation dosage depended on the SCM dosage and temperature. The saturation dosage of PCH using different SCMs at different temperature is illustrated in Table 5.4. It can be further observed from Fig. 5.6 that regardless of the dosage of SCM and PCH, the higher the temperature, the higher was the yield stress, which is due to the higher rate of hydration reactions at higher temperature. Yield stress decreased with PCH addition for all SCMs, yet the dosages required were higher in the case of SF and MK.

The coupled effects of MK and PCH dosage on the yield stress of OWC slurries with variation of temperature is presented in Figs. 5.6(a-c). The higher the amount of MK, the higher was the saturation dosage of PCH. Lower dosage of PCH was found to be less efficient in reducing the yield stress at higher dosage (15%) of MK and the phenomenon is more significant at higher temperature (Figs. 5.6(b-c)). Similar behaviour was observed in case of SF. It can be observed that at lower dosage of PCH, the increase in yield with dosage of SF is more significant at higher temperature (Fig. 5.6(e-g)) probably because of at higher temperature lower dosage of PCH fails to offset the higher rate of structural build up due to higher acceleration rate.

Figures 5.6(g-i) illustrate the variation of yield stress with the addition of RHA and PCH for OWC slurries at test temperatures. The yield stress value of OWC slurries incorporating RHA started to decrease steeply at a PCH dosage higher than 0.25% until it reached a plateau (saturation dosage) beyond which no significant reduction was visible. At 45° and 60°C the yield stress initially increased with PCH dosage up to 0.25% regardless of the RHA addition level. Subsequently, yield stress showed a significant reduction at dosages higher than 0.25%

FA was used up to 15% by mass as partial replacement for OWC and the coupled effects of FA and PCH on yield stress of oil well cement slurries at different temperatures are presented in Figs. 5.6(j-l). At 23°C and low dosage of PCH (0.25% PCH), yield stress for the OWC slurry incorporating 5% FA was slightly greater than that of the control OWC slurry prepared without any SCM. The saturation dosage of PCH for OWC slurries incorporating FA was found to become higher than that of the control mixture even though FA addition generally reduced the yield stress. This can be due to active adsorption of PCH by un-burnt carbon in FA. It was reported that un-burnt carbon in FA is responsible for loss of workability due to adsorption of high-range water reducing admixture molecules (Park et al., 2005).

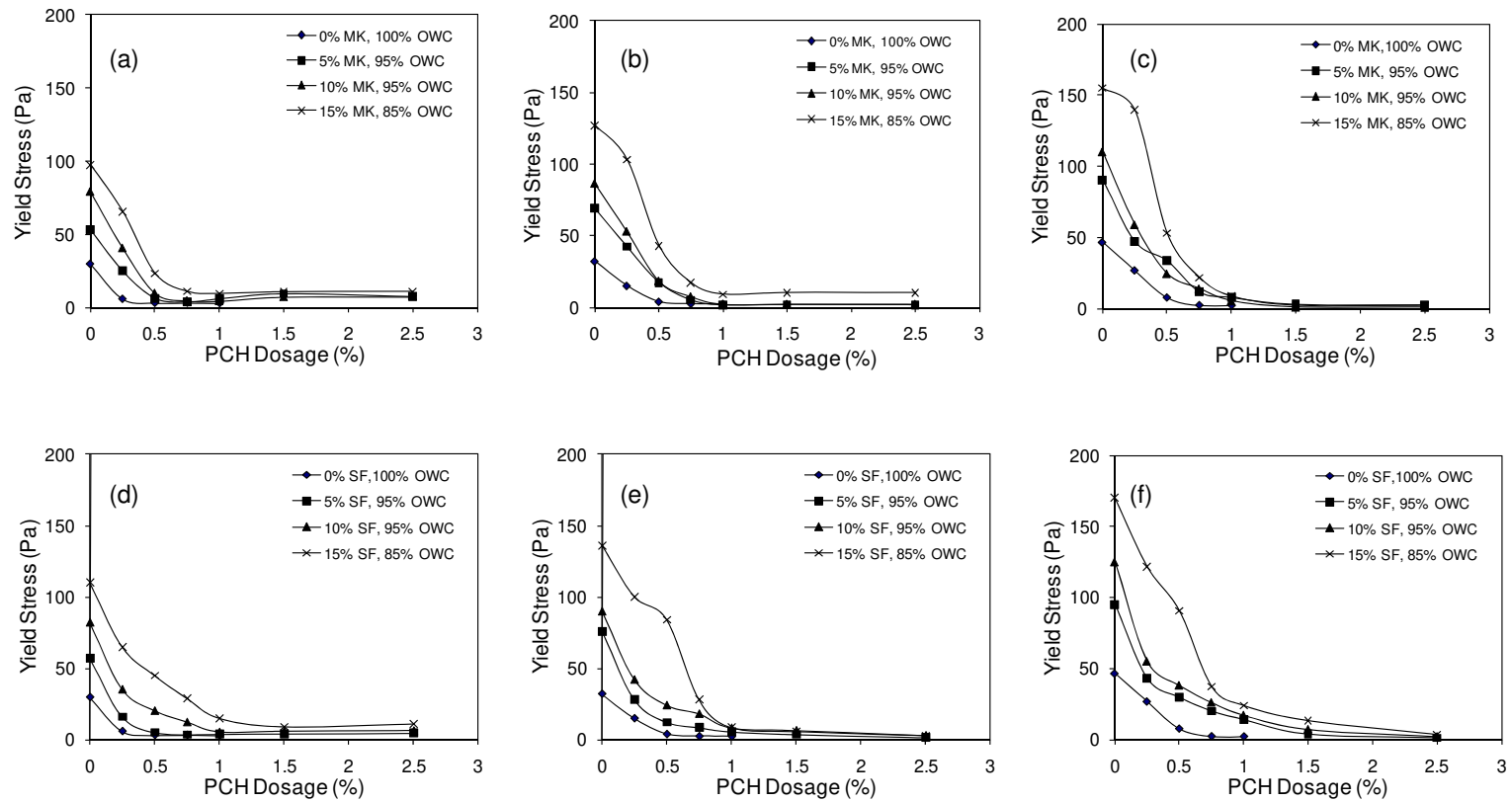


Figure 5.6 Variation of yield stress with dosage of PCH and SCM for OWC slurries incorporating MK [(a) at 23°C; (b) 45°C; and (c) 60°C], SF [(d) at 23°C; (e) 45°C; and (f) 60°C].

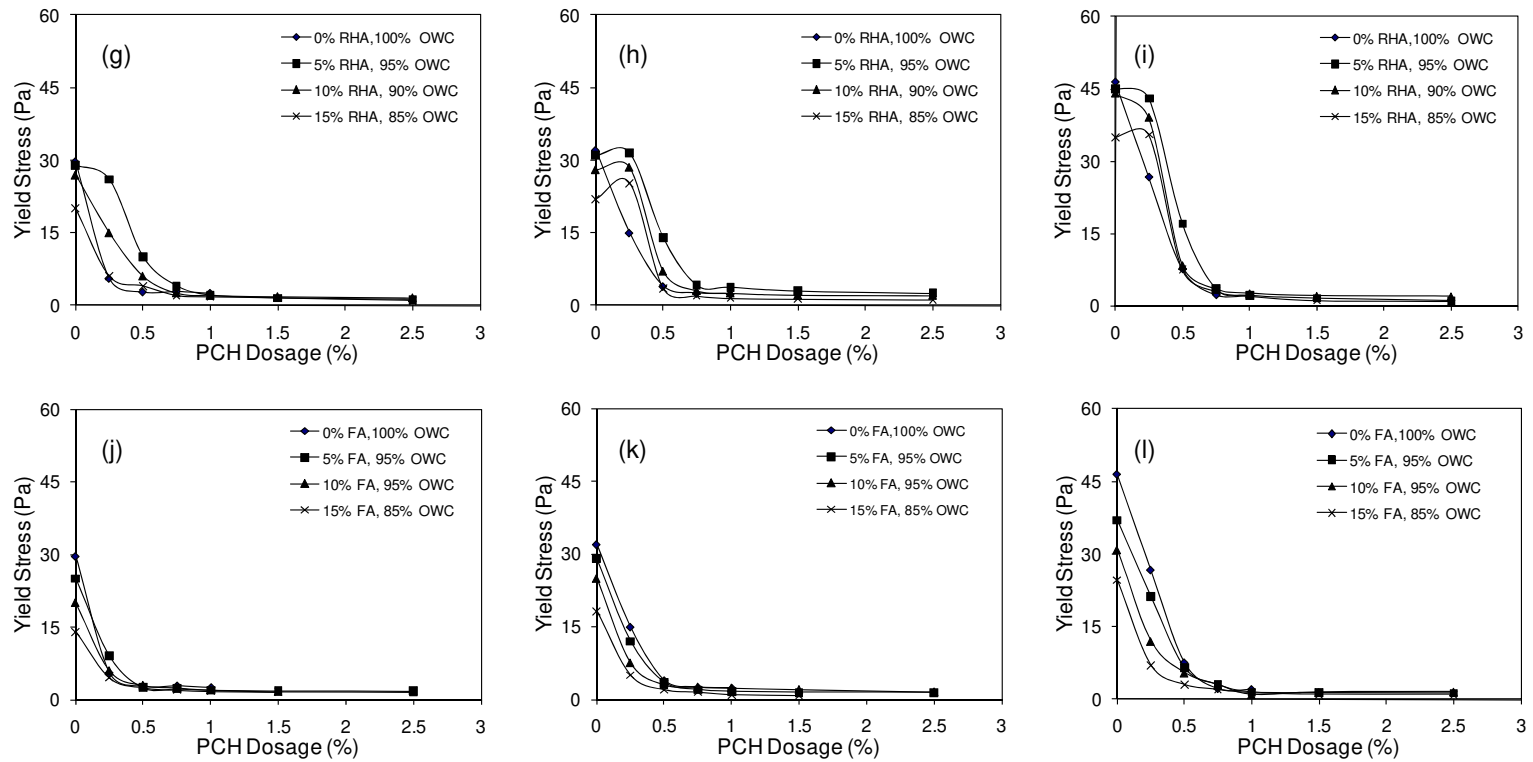


Figure 5.6 Variation of yield stress with dosage of PCH and SCM for OWC slurries incorporating RHA[(g) at 23°C; (h) 45°C; and (i) 60°C], and FA [(j) at 23°C; (k) 45°C; and (l) 60°C].

Table 5.4 Saturation dosage of SCM used at different temperature

	Addition level	Temperature		
		23°C	45°C	60°C
Control Mix		0.3	0.5	0.75
MK	5	0.75	1	1
	10	1	1	1.5
	15	1	1	1.5
SF	5	0.75	1	--
	10	1	1.5	--
	15	1.5	1.5	--
FA	5	0.5	0.75	1
	10	0.75	0.75	1
	15	0.75	1.0	1
RHA	5	1.5	1.5	1.5
	10	1	1.5	1.5
	15	1	1.5	1.5

#### ***5.6.4 Coupled Effects of SCMS and PCH Dosage on Viscosity and Shear Thinning/Thickening Behaviour of OWC Slurries***

Plastic viscosity values of the OWC slurries were measured as the slope of the down flow curve of the hysteresis loop and plotted in Fig. 5.7. In general, plastic viscosity was found to increase with the increase of test temperature and to decrease with the increase of PCH dosage. Figures 5.7(a-c) illustrate the plastic viscosity values for OWC slurries incorporating various dosages of MK and PCH at different temperatures. It can be observed that below the saturation dosage plastic viscosity of all slurries decreased with the dosage of PCH at 23°C. Beyond the saturation dosage, plastic viscosity of OWC slurries with 5% and 10% MK tended to increase, whereas, the value continued to decrease in the case of the slurry prepared with 15% replacement of OWC by MK.

Figures 5.7(d-f) show the coupled effects of SF and PCH on the plastic viscosity of OWC slurries. It can be observed that at 23°C the plastic viscosity continued to decrease up to the saturation dosage, then the value started to increase with PCH dosage. Similar behaviour was observed by Al-Martini (2008). Yamada et al. 1998 suggested that this phenomenon is linked to steric hindrance: the primary mechanism by which PCH disperses cement particles. When the polycarboxylate polymer adsorbs on cement particles, repulsive interaction occurs due to elastic and mixing mechanisms. Cement particles can be regarded as a dispersed medium when the distance between two particles

is equal to or higher than double the thickness of the polymer adsorption layer. The elastic component of the steric hindrance deploys repulsive forces when cement particles try to approach each other. On the other hand, when two neighbouring polymers approach each other the mixing term of the steric hindrance corresponds to the resistance among them. Therefore, beyond the saturation dosage, these resistances increase with the increase of the un-adsorbed PCH polymers and increase plastic viscosity. (Yamada et al., 1998). At 45°C, plastic viscosity values were found to continue its decreasing trends with PCH dosage, whereas some increase in the plastic viscosity was observed at PCH dosage of 1.5% for OWC slurry prepared with 15% addition of SF at 60°C.

The plastic viscosity of OWC slurries incorporating RHA showed a opposite trend to that of yield stress. It can be observed that plastic viscosity increased at a relatively constant rate with the addition of RHA (Figs. 5.7(g-i)) and this effect was more pronounced at higher temperature. Plastic viscosity appeared to increase at lower dosage of PCH and then started to decrease with increasing PCH dosage. The effect of FA and PCH dosage on plastic viscosity was illustrated in Figs. 5.7(j-l). It can be observed that plastic viscosity increased with temperature and decreased with FA dosage. It can also be observed that plastic viscosity values followed the same trend as that of yield stress and decreased with the addition of PCH dosage.

Figures 5.8 and 5.9 present the down flow curves and apparent viscosity, respectively, for OWC slurries incorporating 5% SCM with varying PCH dosages ranging from 0% to 1.5% at 60°C. The same level of partial replacement of OWC by various SCMs by mass was used in order to have a better understanding of the effect of individual SCMs with the variation of PCH. It is depicted in Fig. 5.8 that the shear stress of the slurries increased with increasing shear rate and decreased with increasing dosage of PCH for all the SCMs tested. It can be observed in Fig. 5.9(a) that the apparent viscosity gradually decreased with increasing shear rate for OWC slurries incorporating 5% MK (Fig. 5.9(a)) and SF (Fig. 5.9(b)) at all PCH dosages tested (0% to 1.5%). This phenomenon is called shear thinning/pseudoplastic behaviour, which is typical for agglomerated suspensions such as cement pastes and slurries (Eirich 1960). Cement slurries incorporating 5% RHA exhibited shear thickening behaviour at PCH dosage of 1.5% (Fig. 5.9(c)). In the case of FA, a change in the rheological behaviour from shear thinning to shear thickening was observed at a PCH dosage beyond 1% (Fig. 5.9(d)). Such slurries are called dilatant. The

apparent viscosity of the OWC slurries incorporating PCH dosages of 1% and 1.5% increased gradually with the increase of the shear rate.

Cyr et al. (2000) argued that the dispersing mechanisms of superplasticizers are responsible for the shear thickening behaviour. They used the Herschel-Bulkley equation (equation 5.2) to characterize the rheological properties of cement pastes. Cement slurries testing results demonstrate that Bingham model is not appropriate for describing cement slurries' shear thinning or thickening behaviour because of distortion of flow curve by decreasing or increasing of viscosity with increasing shear stress (Skripkiūnas and Daukšys, 2004). Even though the Bingham model has been used throughout the present study to characterize the rheological properties of OWC slurries, the Herschel-Bulkley model has been used in this section to identify the shear thinning or shear thickening behaviour of OWC slurries as a function of chemical and mineral admixtures. The variation of the exponent  $n$  with the dosage of PCH is presented in Fig. 5.10. It can be observed in Fig. 5.10 that the exponent  $n$  varies with the admixture dosage. Regardless of the SCM type, all OWC slurries showed shear thinning behaviour at lower dosages of PCH. Then, the exponent continued to increase with increased dosage of PCH and the slurry behaviour changed from shear thinning to shear thickening.

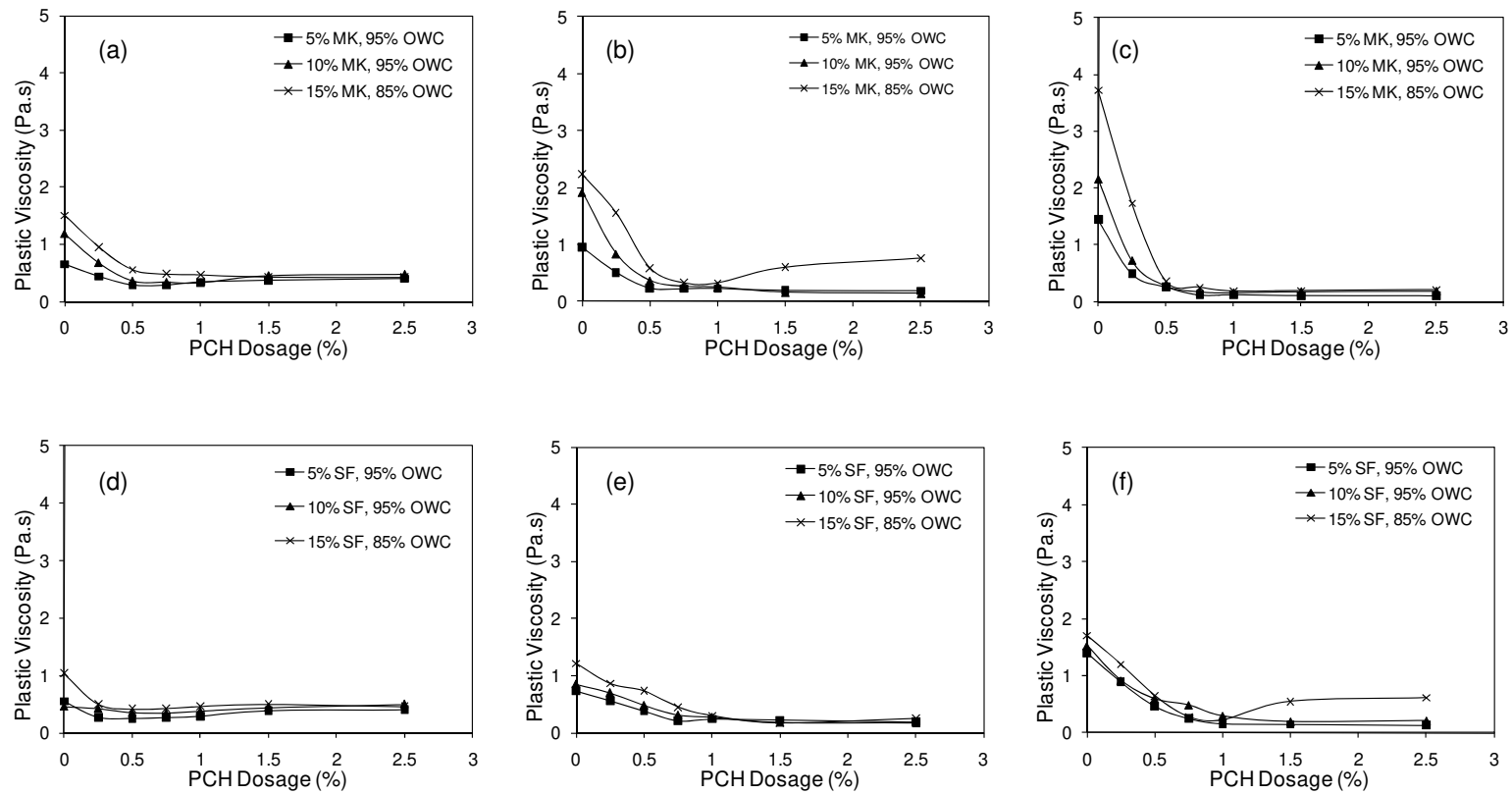


Figure 5.7 Variation of plastic viscosity with dosage of PCH and SCM for OWC slurries incorporating MK [(a) at 23°C; (b) 45°C; and (c) 60°C], SF [(d) at 23°C; (e) 45°C; and (f) 60°C].



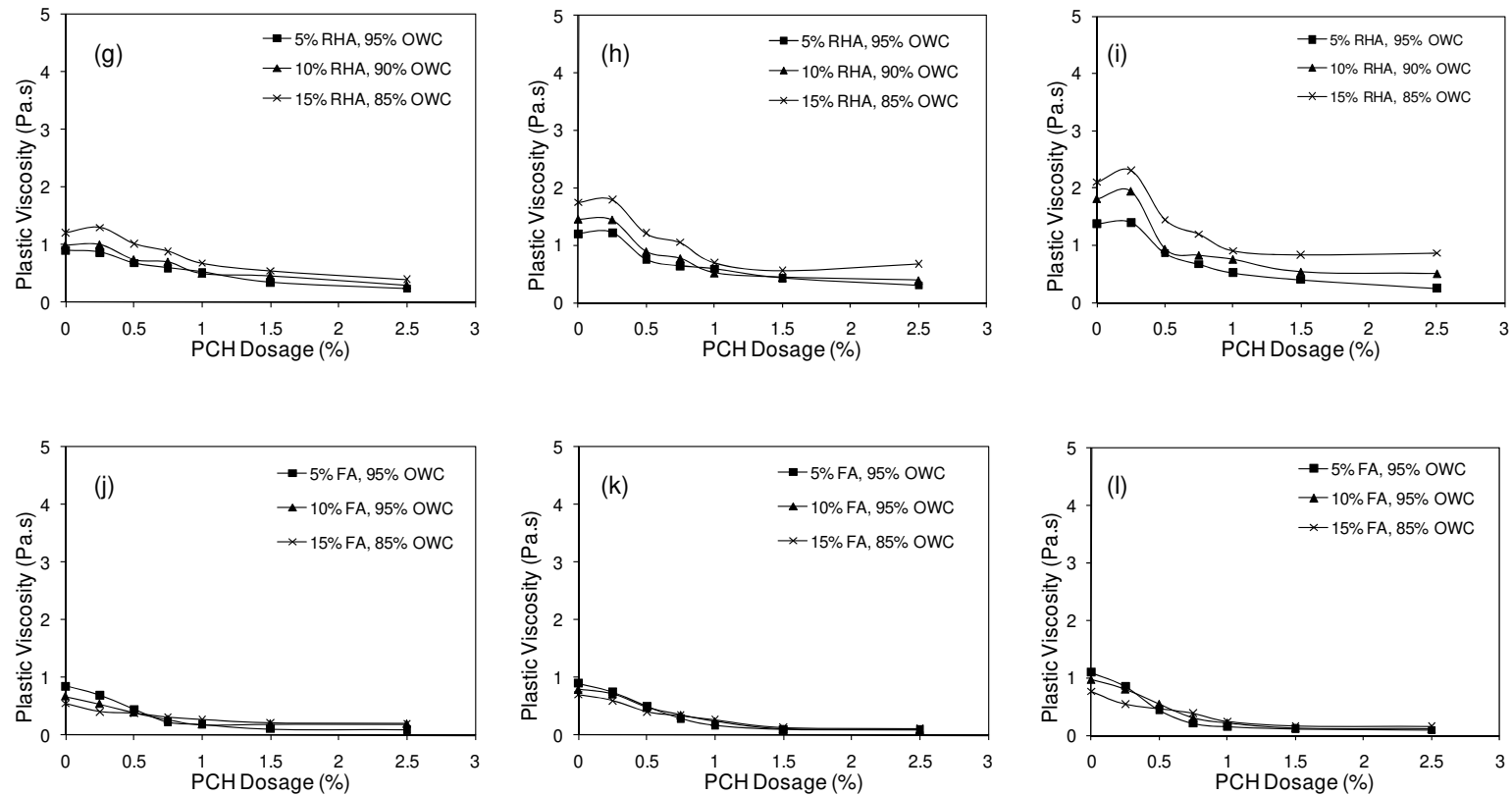


Figure 5.7 Variation of plastic viscosity with dosage of PCH and SCM for OWC slurries incorporating RHA [(g) at 23°C; (h) 45°C; and (i) 60°C], and FA [(j) at 23°C; (k) 45°C; and (l) 60°C].

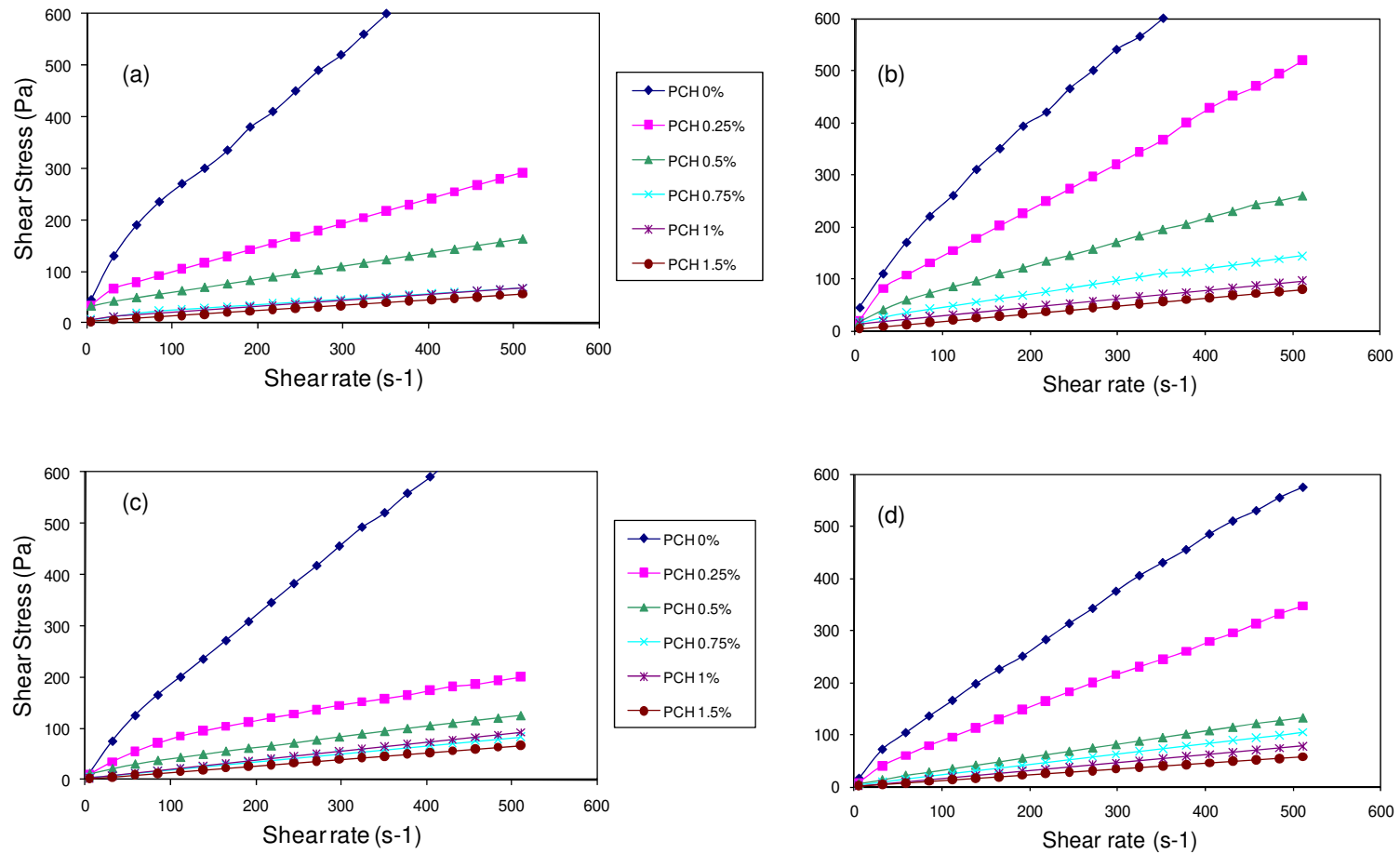


Figure 5.8 Flow curve of oil well cement slurry incorporating 5% of SCMs and different dosage of PCH Admixture at 60°C, (a) MK; (b) SF; (c) RHA; and (d) FA.

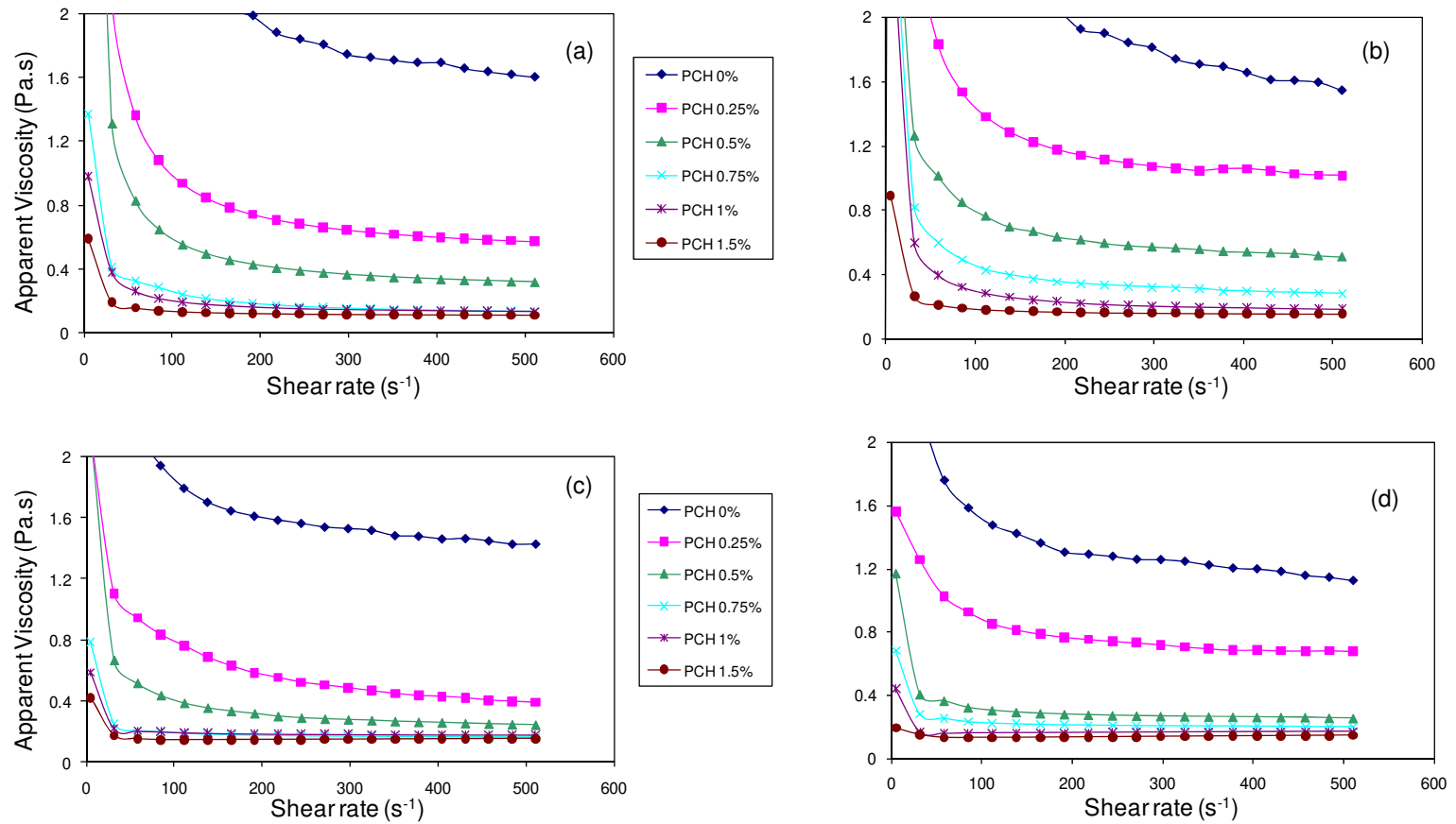


Figure 5.9 Apparent viscosity curve of oil well cement slurry incorporating 5% of SCMs and different dosage of PCH Admixture at 60°C, (a) MK; (b) SF; (c) RHA; and (d) FA.

The degree of shear thinning or shear thickening also depended on the type and dosage of SCM used. It can be observed that the degree of shear thickening increased with the dosage of PCH at higher MK content. However, the OWC slurry incorporating 5% MK showed shear thinning behaviour at each dosage of PCH. The slurries reverted from shear thinning to shear thickening at PCH dosages of 1.0% and 0.75% for 10 and 15% replacement of OWC by MK, respectively. The  $n$  value did not show significant changes with the dosage of SF dosage and shear thinning behaviour persisted for each SF content regardless of the PCH dosage (Fig. 5.10(b)). It can also be observed that, the higher the amount of SF, the lower is the value of  $n$  which implies that addition of SF reduces the dilatancy of oil well cement slurries. Similar finding was observed by Daukšys et al. (2008) for cement slurries prepared with microsilica addition. Addition of RHA as partial replacement of OWC reduced the value of  $n$  up to a PCH dosage of 0.5%. But when the dosage of PCH > 0.5%, it was observed that the  $n$  value increased with the dosage of RHA, except for the slurry prepared with 15% RHA and PCH dosage greater than 1.5%. In the case of FA, the value of the  $n$  exponent increased with the dosage of PCH and the slurry behaviour changed from shear thinning to shear thickening at a PCH dosage of 1% (Fig. 5.10(d)). It can be further observed in Fig. 5.10(d) that the value of  $n$  did not show significant changes with the FA replacement level at PCH dosages of up to 0.75%, beyond which the degree of shear thickening increased with higher replacement of OWC by FA.

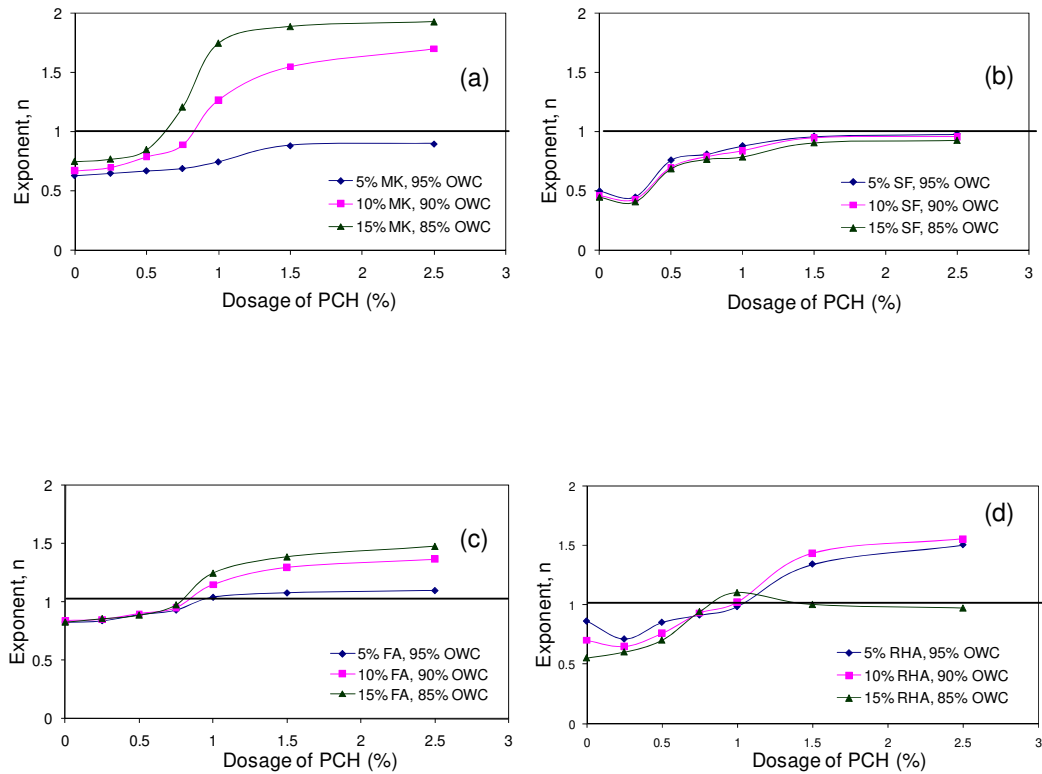


Figure 5.10 Variation of exponent  $n$  with dosage of PCH and SCMs at 60°C, (a) MK; (b) SF; (c) RHA; and (d) FA.

## 5.7. Discussion

Various studies reported the effects of temperature and high-range water reducers (e.g. Nehdi and Al-Martini, 2007; Al-Martini and Nehdi, 2009; Domone and Thurairatnam 1988) and mineral admixtures (Rahman and Nehdi, 2003; Nehdi and Rahman, 2004; Laskar and Talukdar, 2008; Nelson et al., 2006; Ferraris et al., 2001) on the rheology of cement paste, grout and concrete. Those studies were mostly carried on ordinary Portland cement. However, similar data could not be found in the open literature to compare the rheological properties of slurries prepared with API Class G oil well cement, along with the effect of SCMs and chemical admixtures. The effects of various type and dosage of SCMs on the rheology of OWC slurries having a w/c of 0.44 were investigated in the present study using a high accuracy advanced rheometer (TA instruments AR 2000). Rheological data were taken at 20 different shear rate levels starting from 5.11 to 511 s<sup>-1</sup>

and then at descending shear rates from 511 to  $5.11 \text{ s}^{-1}$ . However, the data corresponding to the shear rate of  $5.11 \text{ s}^{-1}$  was discarded while fitting the data to the Bingham plastic model or Herschel-Bulkley model to calculate the rheological properties. This is because, data at/or below  $10.2 \text{ s}^{-1}$  can be affected by slippage at the wall of the coaxial cylindrical rheometer (Guillot, 2006) and do not generally provide reproducible results (ANSI/API RP 10B-2 2005, Guillot 2006).

The rheology of OWC slurries depends on a number of factors including the type of cement and its fineness, nature and amount of calcium sulphates and soluble alkali sulphates,  $C_3A$  content and distribution of aluminates and silicate phases at the surface of cement grains (Vidick et al., 1987), reactivity of cement phases (Michaux and Nelson, 1992), cement hydration kinetics (Saak, 2000), supporting liquid rheology (Nelson et al., 2006), inter-particle forces (Saak, 2000; Nelson et al., 2006), solid volume fraction (Nelson et al., 2006), mixing energy and mixing method, type and dosage of chemical admixture, water temperature, w/c, etc. Considering the results discussed above, it can be concluded that OWC slurries incorporating SCMs exhibit different rheological behaviour than that prepared with pure OWC. This could be due to differences in their physical properties, chemical compositions, and the mechanisms by which they act. The particle shape and surface area play significant role in controlling the rheological behaviour of OWC slurries. The slurries prepared with larger fraction of spherical particles should have lower viscosity which is evident in case of slurries prepared with FA. But in case of SF, yield stress and viscosity was found to be greater with increasing amount of SF, probably because of higher surface area which increases the water demand to produce a similar fluidity to that of mixtures made without any SF. The OWC slurries prepared with RHA showed a different behaviour than that expected. Instead of increasing the yield stress, the values were found to decrease gradually with the increasing replacement level of RHA. Similar findings were also observed by Laskar and Talukdar (2008), while others (Habeeb and Fayyadh, 2009; Cordeiro et al., 2009; Nehdi et al., 2003) found that the replacement of cement by RHA resulted in increased water demand and reduced concrete workability. This discrepancy is due to the various fineness, specific surface and carbon contents of the RHA used in each study. In order to achieve the similar consistency (slump) to that of concrete made without RHA, more superplasticizer had to be used with partial replacement of OPC by RHA (Habeeb and Fayyadh, 2009 and Cordeiro et al., 2009). Laskar and Talukdar (2008) argued that finer RHA particles fill

into spaces between larger cement particles, which results in improved packing particle density and reduces frictional forces, thereby reducing yield stress.

The plastic viscosity of OWC slurries generally followed the same trend as that of yield stress for all the SCMs tested, except for RHA. Laskar and Talukdar (2008) argued that the fineness and shape of RHA play a critical role in increasing the plastic viscosity of OWC slurry. Any deviation from a spherical shape generally entails an increase in plastic viscosity for the same phase volume (Nehdi et al., 1998). Moreover, the higher the fineness the more is the number of contacts among particles, and consequently the higher is the resistance to flow.

The mechanisms by which PCH acts are still a topic of continuing research. It was argued that PCH form a comb like structure by adsorbing on to hydrating cement grains due to the orientation of a portion of the grafted side chains of polyethylene oxide (PEO) into the solution. The comb-like structure of the polymers helps the PEO side chains to interact favourably with the aqueous medium and to stretch into the solution. The increased osmotic pressure resulting from the approach of cement grains towards each other and overlapping of adsorbed layers of the dispersant induce steric repulsive forces between cement particles, thus fluidizing the cement slurry (Volpert, 2005; Nelson et al., 2006). The performance of PCH varied with the type and dosage of SCM used. This is due to differences in the chemical compositions and physical properties of the SCMs, the chemical composition of PCH itself and the mechanisms by which it acts. Generally, PCH improved the rheological properties of OWC slurries at all temperatures tested. However, higher the temperature, higher was the yield stress. This phenomenon is possibly due to the breakdown of the layer which was formed by PCH adsorption onto the surface of cement grains and the growth of hydration products due to the higher rate of hydration reactions.

Shear thinning behaviour was observed for OWC slurries with a PCH dosage of up to 0.5% for all the SCMs tested. Shear thinning behaviour is attributed to the shear alignment of cement particles in the direction of flow with an increase of shear stress (Eirich 1960). The formation of particulate flocs takes place at low shear rates because of higher inter-particle attractions. Hydrodynamic forces exerted by the flow field become predominant over the inter-particle attractive forces with the increase of shear stress.

Thus, flocs breakdown into smaller particles, which eventually releases the liquid entrapped within the flocs and decreases viscosity (Ferguson and Kemblowski 1991). All OWC slurries prepared without PCH, irrespective of the SCM used, showed shear thinning behaviour (Figs. 5.9 and 5.10). However, increasing the PCH dosage increased the value of the  $n$  exponent in the Herschel-Bulkley model, and the slurry behaviour shifted towards shear thickening (Fig. 5.10). It was observed in previous studies that the use of superplasticizers gives cement pastes a shear thickening behaviour (Cyr et al., 2000). Al-Martini and Nehdi (2009) observed that the use of PCH seemed to increase the apparent viscosity beyond the saturation dosage. However, such a relation between the saturation dosage and shear thickening could not be made in this study on OWC. It has been found that the degree of shear thickening also depends on the type and dosage of SCM used. MK was found to amplify this phenomenon, whereas SF was found to attenuate and suppress the shear thickening behaviour, which was also observed by others (Cyr et al., 2000) for OPC pastes. In the case of FA, PCH dosages of up to 0.75% were found to have insignificant effect on the  $n$ -value. When the PCH > 0.75, shear thickening behaviour persisted and the corresponding  $n$ -value slightly increased with the increase in the FA proportion. RHA used as partial replacement for OWC led to shear thinning behaviour up to a PCH dosage of 0.75%.

Barnes (1989) argued that the intensity of shear thickening is function of the particle shape, particle size, and particle size distribution. Irregular shaped particles tend to show shear thickening behaviour more easily, which could be one reason why the addition of MK as partial substitution for OWC intensified the shear thickening behaviour. Shear thickening behaviour could be attributed to the disordered structure of highly concentrated solid suspensions (Hoffman, 1998). This disordered structure dissipates more energy due to particle jamming, resulting in higher hydrodynamic forces than repulsive inter-particle forces, and hence viscosity increases with increasing shear rate (Hoffman, 1998). According to Bossis and Brady (1989), shear thickening could be due to the formation of hydrodynamic clusters, which occurs when shear forces are strong enough to drag particles virtually into contact. These clusters jam the particle flow and become larger and larger. As a consequence, the viscosity increases with increase in shear rate. The increase of shear rate enhances the disorder between cement particles as well as within the polymer chain of superplasticizers. Steric hindrance by which PCH disperses cement particles could be linked to the shear thickening phenomenon (Al-Martini and



Nehdi, 2009). When polycarboxylate polymers adsorb on to the hydrating cement grains, repulsive interaction occurs as a consequence of elastic and mixing mechanism. The elastic and mixing mechanisms are a function of the thickness and density of the polymer adsorption layer, respectively (Yamada et al., 1998). In order to be dispersed, the distance between two cement particles should be equal to or higher than double the thickness of the polymer adsorption layer. When cement particles try to approach each other, the elastic component of the steric hindrance exhibits repulsive forces. On the other hand, the mixing component of the steric hindrance produces resistance when two neighbouring polymers approach each other (Yamada et al., 1998). As a consequence, the resistance of the mixing component of the steric hindrance increases with the increase of PCH dosage. This is possibly the reason why the exponent  $n$ -value increased with the increase on PCH dosage and the slurry behaviour converged towards shear thickening.

## 5.8 Conclusions

The effects of various mineral admixtures with and without the presence of a new generation polycarboxylate-based high-range water reducing admixture (PCH) on the rheological behaviour of API Class G oil well cement slurries were investigated at 23, 45, and 60°C. First, OWC slurries incorporating various SCMs were tested without the use of PCH. Subsequently, PCH was used to prepare OWC slurries incorporating different SCMs. Based on the experimental results, the following conclusions can be drawn:

- The FA and RHA used in the present study reduced yield stress, which can have a positive influence on the pumpability of OWC slurries. However, MK and SF increased yield stress when used as partial replacement for API Class G OWC.
- The plastic viscosity of OWC slurries increased with the incorporation of MK, SF and RHA as partial replacement for OWC and decreased with the addition of FA.
- Regardless of type and dosage of SCM, both yield stress and plastic viscosity of OWC slurries were found to increase nonlinearly with the increase of temperature.
- At a given dosage, yield stress values for OWC slurries incorporating SCMs and without any chemical admixtures followed the following order: SF>MK>RHA>FA at all test temperatures.

- PCH, a new generation polycarboxylate-based high-range water reducing admixture, effectively reduced the yield stress and plastic viscosity of OWC slurries prepared with or without SCM addition at all temperatures tested.
- PCH was found to enhance the shear thickening behaviour of OWC slurries and the intensity of this effect varied with the type and amount of SCM (amplified with metakaolin, reduced by SF, unchanged with FA, and showed an irregular behaviour with RHA).

It should be noted that the findings reported in this study are valid for the cement, supplementary cementitious materials and chemical admixtures used herein. Other cement/admixture combinations can exhibit different characteristics. Even admixtures from the same category but from different source could behave differently, and thus need to be investigated separately.

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*Chapter 6***MODELING RHEOLOGICAL PROPERTIES OF OIL WELL CEMENT SLURRIES USING MULTIPLE REGRESSION ANALYSIS AND ARTIFICIAL NEURAL NETWORKS\*****6.1 Introduction**

The recent oil spill in the Gulf of Mexico and the associated environmental and economic impact has put renewed emphasis on the importance of oil well cementing operations. The rheological properties of oil well cement (OWC) slurries are important in assuring that such slurries can be mixed at the surface and pumped into the well with minimum pressure drop, thereby achieving effective well cementing operation. The rheological properties of OWC slurries depend on various factors including the water-cement ratio (w/c), size and shape of cement grains, chemical composition of the cement and relative distribution of its components at the surface of grains, presence and type of additives, compatibility between cement and chemical admixtures, mixing and testing procedures, time and temperature, etc. The interactions among the above mentioned factors play a vital role in altering the rheological properties of OWC slurries. Moreover, a wide range of bottom-hole pressure and temperature makes the characterization of the rheology of OWC slurries more challenging than that of normal cement paste. Therefore, a clear understanding of this complex behaviour is important in order to successfully predict the rheological properties of OWC slurries.

Much work has been conducted over the last few decades to investigate the rheological behaviour of cementitious systems such as cement paste, mortar, grout, slurry and concrete. A number of shear stress-strain rate relationships have been developed for cement slurries. However, there exists no model that explains the interactions among the materials used for preparing such slurries and test conditions such as temperature, shear rate, etc. The power-law, Bingham, and Herschel-Bulkley models are the most commonly used in the well cementing industry (Guillot, 2006). Such models are comprised of empirical expressions derived from the analysis of limited experimental data and/or based

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\* A part of this chapter has been under review for publication in ASCE Journal of Materials in Civil Engineering, 2010. Another part has been submitted to Construction & Building Materials, 2011.



on simplifying assumptions (El-Chabib and Nehdi, 2005). Moreover, they do not have true predictive capability outside the experimental domain and/or when different materials are used (El-Chabib et al., 2003), and do not explain the interactions among test parameters.

Artificial neural networks (ANNs) are powerful computational tool that allow overcoming the difficulty of assessing the complex and highly nonlinear relationships among model parameters through self-organization, pattern recognition, and functional approximation. ANN simulates the structure and internal functions of the biological brain. Unlike conventional models, ANN does not assume a model structure between input and output variables. It rather generates the model based on the database provided for training the network. An ANN solves problems by creating parallel networks and the learning of those networks, rather than by a specific programming scheme based on well-defined rules or assumptions (Bruni et al., 2006).

On the other hand, multiple regression analysis (MRA) is a statistical method to learn about the analytical relationship between several independent or predictor variables (input variables) and a dependent or criterion variable (output variable) (Statsoft, 2010). The relations may be linear or nonlinear, and independent variables may be quantitative or qualitative. MRA explains the effects of a single input variable or multiple variables on the output variable with or without considering the effects of other variables (Cohen et al., 2003).

Temperature has been found to have drastic effects on the rheological behaviour of cement slurries. Its effect also depends on the type of cement and admixtures used. Thus, it was argued that it would be difficult to find a general model that can represent the temperature dependency of cement slurry rheology (Guillot, 2006). Ravi and Sutton (1990) developed a correlation to calculate the equilibrium temperature for plastic viscosity and yield stress of Class H cement slurries using a high-pressure, high-temperature rheometer. It was found that both plastic viscosity and yield stress increased with the increase in temperature. However, plastic viscosity reached a constant value beyond the equilibrium temperature, whereas there was no evidence for yield stress to attain a constant value beyond a certain temperature. Using the Bingham plastic model, Ravi and Sutton (1990) developed equations to represent the variation of rheological parameters with temperature where the yield stress and plastic viscosity values were measured at 80°F (27°C) and limited to a maximum temperature,  $T_{max}$ . Their equations below were developed using cement systems containing specific additives, and are thus dependent on the slurry composition.

$$\mu_p(T) = a + (b \times T) + (0.00325 \times T^2) \quad (6.1)$$

Where,  $\mu_p$  is in mPa.s and  $T$  is in °F; and  $a = 65.0729 + 1.3054 \times \mu_p$  at 80°F; and  $b = 1.0734 - 0.00381 \times \mu_p$  at 80°F.

Currently, there is need to create a reliable method for predicting the rheological performance of OWC slurries and relating its composition (admixture type, dosage, etc.) and test conditions (e.g. shear rate, temperature) to the expected rheological properties. In this framework, ANN and MRA have been used in the present study to develop models to predict the shear stress of OWC slurries at a given shear rate, as a function of the temperature and admixture dosage. The ability of the models thus developed to evaluate the sensitivity of rheological properties to the variation of shear rate, admixture dosage, and test temperature was investigated. Hence, a shear stress-shear rate curve for OWC slurries can be predicted at different temperatures prior to fitting the data to conventional rheological models. Consequently, the rheological properties of OWC slurries can be predicted as a function of mixture composition and test conditions for the first time.

## 6.2 Experimental Program

### 6.2.1 Materials

OWC slurries used in this study were prepared using a high sulphate-resistant API Class G OWC with a specific gravity of 3.14. Deionized distilled water was used for the mixing, and its temperature was maintained at  $23 \pm 1^\circ\text{C}$  using an isothermal container. Three different chemical admixtures including a new generation polycarboxylate-based high-range water reducing admixture (PCH), polycarboxylate-based mid-range water reducing admixture (PCM) and mid-range lignosulphonate based water reducing admixture (LSM) were used to prepare the OWC slurries with a  $w/c = 0.44$ . Their dosages are presented in Table 6.1.

### 6.2.2 Apparatus

The OWC slurries were prepared using a variable speed high-shear blender type mixer with bottom drive blades as per the ANSI/API Recommended Practice 10B-2 (2005). A high accuracy advanced rheometer (TA instruments AR 2000) (Fig. 4.1(a) (Chapter 4)) was used to measure the rheological properties of the slurries. The rheometer is capable of continuous shear rate sweep and stress sweep. The coaxial concentric cylinder

geometry was considered suitable for this study because of the typically low viscosity of OWC slurries. The geometry consists of a cylinder with a conical end that rotates inside a cylinder with a central fixed hollow as shown in Fig. 4.1(b) (Chapter 4). The rheometer is equipped with a rheological data analysis software, which can fit the shear stress-strain rate data to several rheological models. The Bingham model was used throughout this study to calculate the rheological properties of cement slurries, i.e. yield stress and plastic viscosity.

Table 6.1 Chemical admixtures used for preparing oil well cement slurries

Type of admixture	Abbreviation	Dosages % BWOC*
New generation polycarboxylate-based high-range water reducing admixture	PCH	0.25, 0.50, 0.75, and 1.00
Polycarboxylate-based mid-range water reducing admixture	PCM	0.25, 0.50, 0.75, and 1.00
Mid-range lignosulphonate based water reducing admixture	LSM	0.5, 1.0, 1.5 and 2.0

\* BWOC: by weight of cement

### 6.3 Experimental Procedure

The cement slurries were prepared using a high-shear blender type mixer with bottom driven blades as per the ANSI/API Recommended Practice 10B-2 (ANSI/API RP 10B-2, 2005) at a controlled ambient room temperature of  $23 \pm 1^\circ\text{C}$ . The prepared slurry was then placed into the bowl of a mixer for preconditioning over 20 minutes at the test temperature ( $23^\circ\text{C}$ ,  $45^\circ\text{C}$ , or  $60^\circ\text{C}$ ) at a speed of 150 rpm. The total time between the beginning of mixing and the start of the rheological tests was kept constant to avoid the effects of exogenous variables on the results. The rheometer set-up was also maintained constant for all tested slurries. The concentric cylinder test geometry was maintained at the test temperature so as to avoid sudden thermal shock of the slurry.

After mixing and preconditioning, the cement slurry sample was placed in the coaxial cylinder of the rheometer. The temperature was adjusted to the required level and the sample was then subjected to a stepped ramp or steady state flow where rheological measurements were taken at 20 different shear rates starting from  $5.11 \text{ s}^{-1}$  up to  $511 \text{ s}^{-1}$  after a continuous rotation of 10 sec at each level. Subsequently, the data were measured

at a descending shear rate from  $511 \text{ s}^{-1}$  to  $5.11 \text{ s}^{-1}$  to obtain the down flow curve. A schematic representation of the viscometric testing scheme is illustrated in Fig. 4.2 (chapter 4).

#### 6.4 Experimental Results

Typical shear stress-shear rate down curves of the hysteresis loop for OWC slurries prepared using a new generation polycarboxylate-based high-range water reducing admixture (PCH) at  $60^\circ\text{C}$  are presented in Fig. 6.1. The down-curve better fits the Bingham plastic model than the up-curve (Ferguson and Kemblowski, 1991, Al-Martini and Nehdi, 2009), therefore the shear rate–shear stress down curve was considered in calculating the rheological properties (yield stress and plastic viscosity) using the Bingham plastic model (equation 6.2). The rheological parameters thus calculated are highly dependent on the temperature and admixture dosage as can be observed in Figs. 6.2 and 6.3.

$$\tau = \tau_0 + \mu_p \dot{\gamma} \quad (6.2)$$

Where,  $\tau$ ,  $\tau_0$ ,  $\mu_p$ , and  $\dot{\gamma}$  represent the shear stress, yield stress, plastic viscosity, and shear rate, respectively.

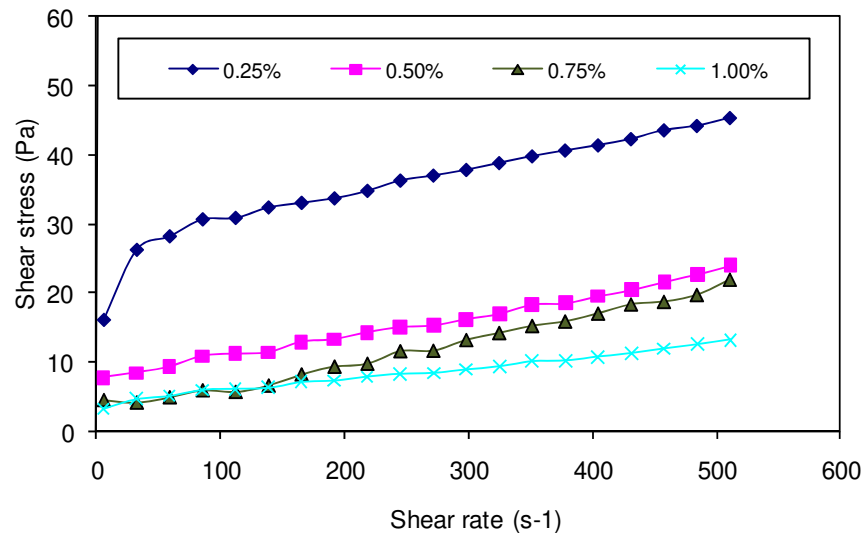


Figure 6.1 Shear stress-shear rate down curve for OWC slurries prepared using different dosage of PCH at  $60^\circ\text{C}$ .

In this study, two different approaches: MRA and ANN have been used to predict the shear stress as a function of test variables (temperature, admixture dosage and shear rate). The predicted flow curve allows in turn predicting the rheological properties of OWC slurries. Hence model predictions and corresponding experimental data can be compared.

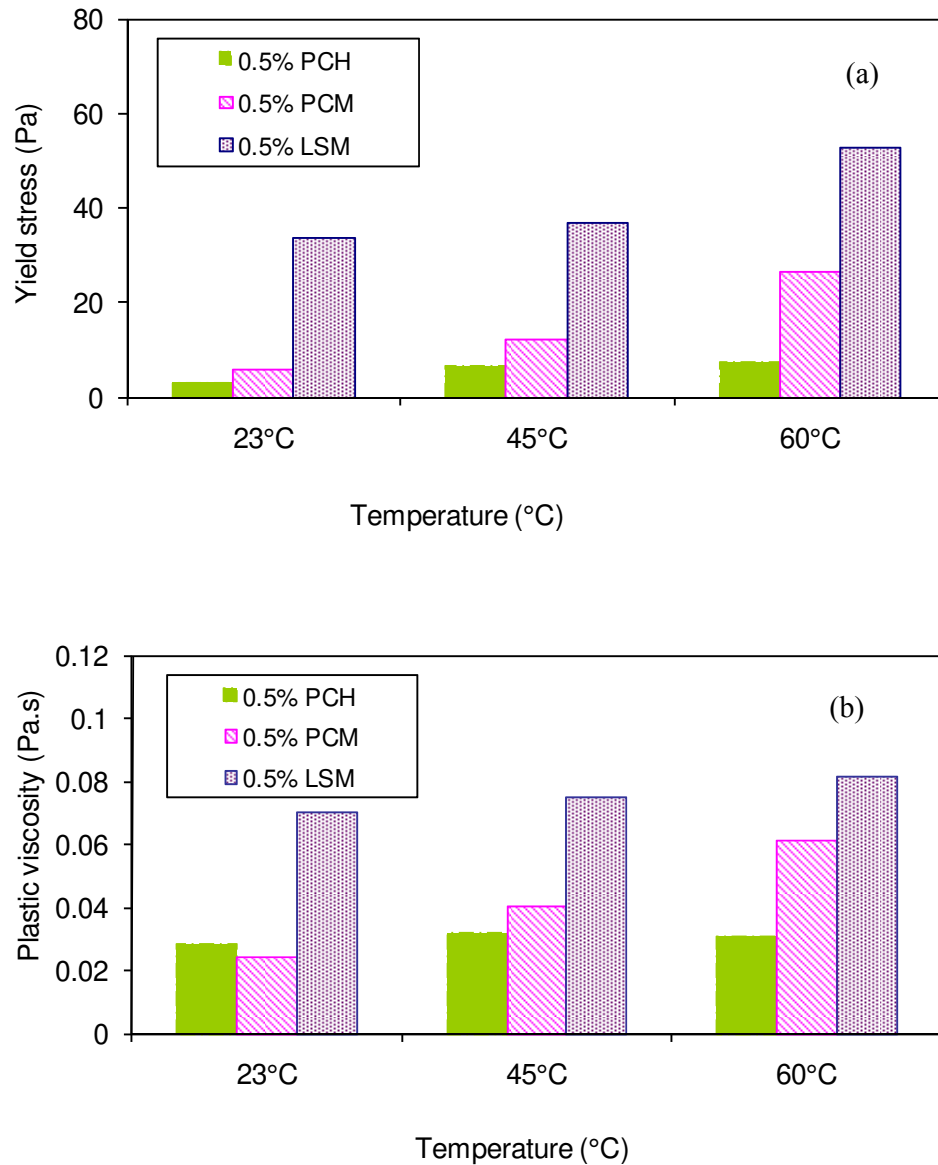


Figure 6.2 Effect of temperature on (a) yield stress, and (b) plastic viscosity of OWC slurry prepared using different admixtures (0.5% BWOC).

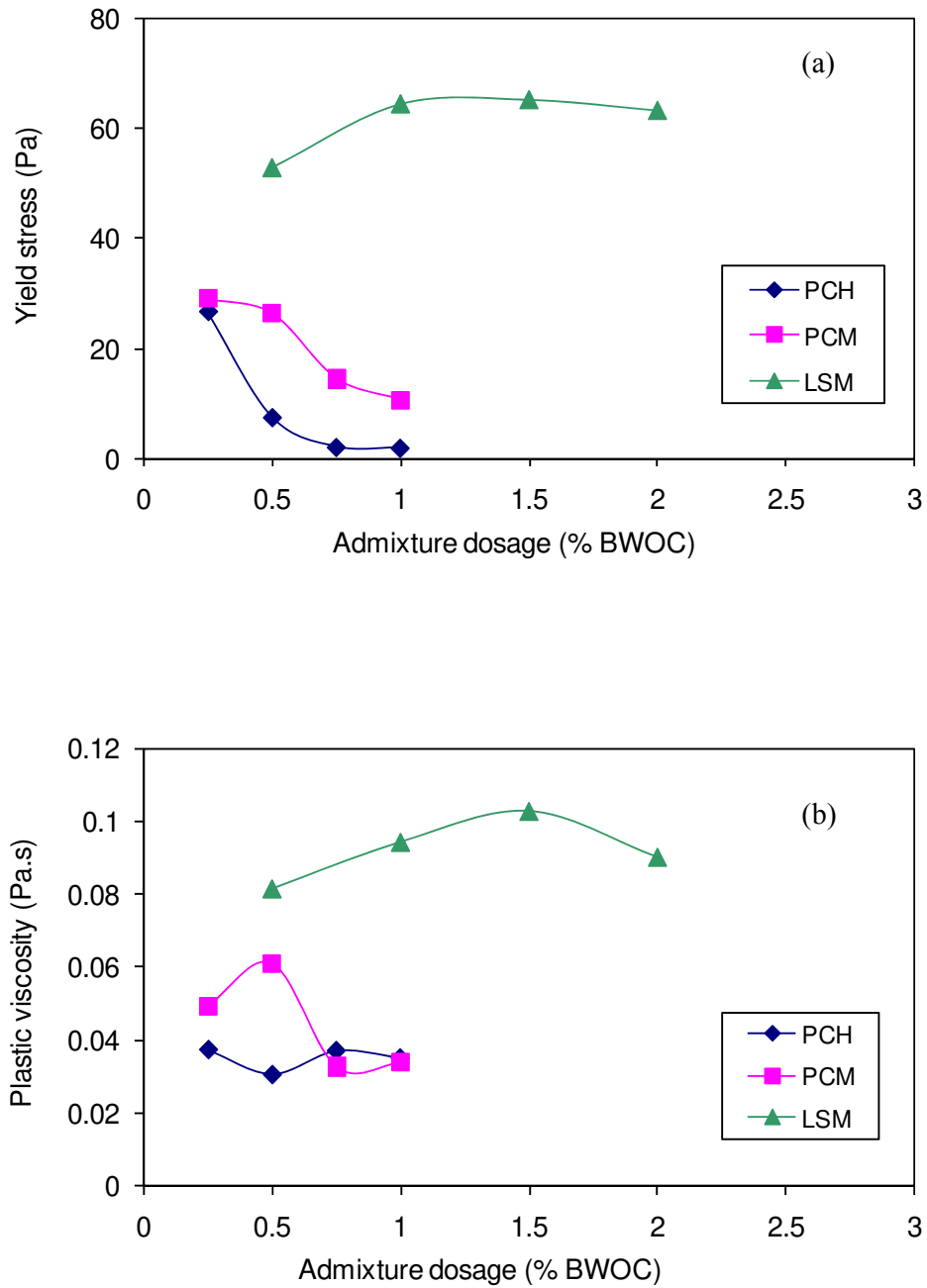


Figure 6.3 Effect of admixture dosage on (a) yield stress, and (b) plastic viscosity of OWC slurry prepared using different admixtures at 60°C.

## 6.5 Artificial Neural Networks Approach

ANNs simulate the structure and internal functions of the biological brain. An ANN is capable of learning the mapping between a set of input data and its corresponding output. Through training, it creates memory capable of predicting output when presented with a new set of data within the practical range of the input used in the training process. Among various kinds of ANNs, the feed-forward back-propagation learning algorithm is the most commonly used in engineering applications, for instance in modelling the behaviour of cement based materials. A neural network consists of a number of layers (an input layer, one or more hidden layers, and an output layer) of several interconnected linear or nonlinear processing units (neurons). Each processing unit receives multiple inputs from the neurons in the previous layer through the weighted connection, and after performing appropriate computation, transfers its output to other processing units or as a network output using an assigned transfer (activation) function as shown in Fig. 6.4.

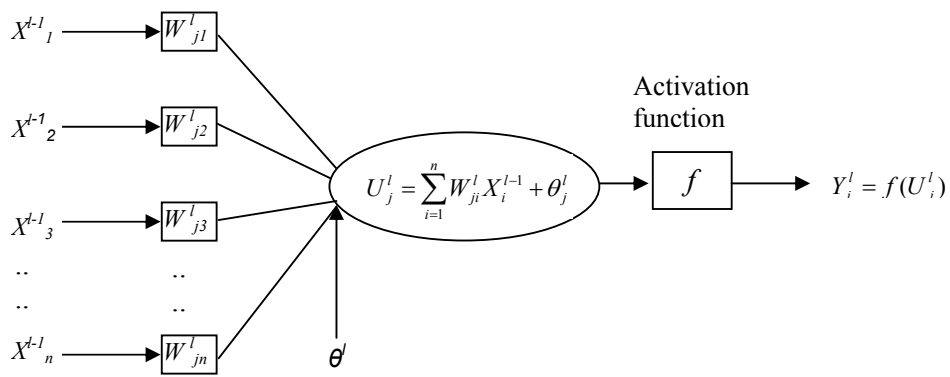


Figure 6.4 Simplified model of artificial neural network.

For a particular network, weight or connection strength is the backbone which controls the performance of the network. Randomly set initial weights are modified through network training until the network stabilizes. Each neuron  $J$  in layer  $l$  receives input  $X_i^{l-1}$  from the connected neurons in layer  $l-1$  and forms a single net input  $U_j^l$ , which is modified by the nonlinear activation function  $f$  to produce an output value  $Y_j^l$ :

$$U_j^l = \sum_{i=1}^n W_{ji}^l X_i^{l-1} + \theta_j^l \quad (6.3)$$

$$Y_j^l = f(U_j^l) \quad (6.4)$$

where  $W_{ji}^l$  is the connection strength between neurons  $i$  and  $j$  in layers  $l$  and  $l-1$ , respectively,  $n$  is the number of neurons in layer  $l-1$ , and  $\theta_j^l$  is a threshold value assigned to neuron  $j$  in layer  $l$ .

Because of the differentiability requirement needed in the back-propagation technique, the nonlinear log-sigmoid function presented in equation (6.5) is the most commonly used activation function. This function generates an output between 0 and 1 as the neuron's net input can have any value from negative to positive infinity (Demuth et al., 2008).

$$f_j^l = \frac{1}{1 + e^{-(U_j^l - \theta_j^l)}} \quad (6.5)$$

The generalized delta rule, developed by Rumelhart et al. (1986) is generally used as a learning mechanism in back-propagation neural networks. In this approach, the connection strength or weights are updated at a rate of  $\eta_k$ , known as the learning rate, in the direction in which the total network error decreases rapidly (towards the solution weights by correcting the errors). An iteration of this algorithm can be described as follows:

$$W_{ji}^{k+1} = W_{ji}^k - \eta_k \frac{\partial E^k}{\partial W_{ji}} \quad (6.6)$$

where,  $W_{ji}^k$  is a weight vector of current weights,  $\eta_k$  is the learning rate and  $E^k$  is the  $k^{\text{th}}$  error term. The selection of the learning rate is case sensitive and usually ranges from 0.0 to 1.0. A very high rate of learning may lead to rapid training, but it may not converge to a stable solution. A very low rate of learning, on the other hand, increases the training time and the algorithm takes too long to converge (El-Chabib and Nehdi, 2005).

The momentum is used to stabilize the weight trajectory. In this process, the weight is modified based on the current error correction to weights, plus some portion of the previous weight change shown in equation (6.7):

$$W_{ji}^{k+1} = W_{ji}^k + \delta W_{ji}^k + \alpha \delta W_{ji}^{k-1} \quad (6.7)$$



where,  $\alpha$  is the momentum term. The value of the momentum should always be less than 1.0. The network becomes completely insensitive to the local gradient and, therefore, fails to learn properly when  $\alpha=1$  (Demuth et al., 2008).

Over-fitting leads to a precise prediction of the training patterns yet can also cause poor generalization of new patterns. On the other hand, a premature training may cause unsatisfactory performance because of not adequately learning the embedded relationships between inputs and outputs. The training continues until it converges to a desired minimum error between its predicted outputs and the desired targets provided in the training process. The duration of training can be determined by (a) limiting the number of iterations, called training epochs, (b) setting a desired minimum error, or (c) monitoring the trend of error improvement so that training will be stopped when no or little improvement in the training error is reported over a given number or epochs. In each iteration, the error (as shown in equation 6.8) is compared with the convergence tolerance; if it is not met, the iteration continues and the calculated system error is back propagated to the network to adjust the weights and thresholds in a gradient search for the desired minimum system error (El-Chabib and Nehdi, 2005).

$$E_{st} = \frac{1}{P} \sum_{p=1}^P \sum_{k=1}^K (t_{pk} - o_{pk})^2 \quad (6.8)$$

where,  $E_{st}$  is the system error,  $p$  is a training pattern,  $P$  is the number of training patterns assigned to one epoch, and  $t_{pk}$  and  $o_{pk}$  are the predicted output and provided target of pattern  $p$  at output unit  $k$ , respectively.

The construction of a successful neural network requires considering three important steps: selection of database, network architecture, and network training and testing.

### **6.5.1 Selection of Database**

Although ANNs have been successfully used in predicting complex nonlinear relationships and in modeling various aspects in cement and concrete research, their efficiency depends on the quality of the database used for training (El-Chabib et al., 2003). In order to account for the primary aspects that influence the input-output relationship of rheological properties of OWC slurries and capture the practical range of key input parameters (shear rate, admixture dosage and temperature), the network should be trained using a large and comprehensive set of reliable experimental data. In order to

train the model, 190 data points were used for each of the three admixtures tested (PCH, PCM and LSM). Fifty new data points unfamiliar to the model, but within the range of training data, were used to test the performance of the network. It should be noted that each flow curve consists of 20 data points at equal shear rate intervals starting from 5.11 to 511 s<sup>-1</sup>. Table 6.2 presents the ranges, mean values, and standard deviations of all input and output variables in the final database.

Table 6.2 Range, average (*Avg.*), and standard deviation (*SD*) of input and output variables

	Training Data			Testing Data		
	<i>Range</i>	<i>Average</i>	<i>SD*</i>	<i>Range</i>	<i>Average</i>	<i>SD*</i>
Shear rate (s <sup>-1</sup> ), $\dot{\gamma}$	5.11-511	258	155	5.11-511	257.9	157.52
Temperature, °C	23-60	42.9	15.2	23-60	42.67	18.61
Dosage of PCH and PCM, %	0.25-1.0	0.63	0.28	0.25-1.0	0.60	0.27
Dosage of LSM, %	0.5-1.0	1.27	0.56	0.5-1.0	1.21	0.56
Shear stress (PCH), $\tau$	1.97-45.3	15.43	9.27	2.01-44.97	16.1	9.50
Shear stress (PCM), $\tau$	3.23-53.53	22.75	12.0	3.36-51.9	23.74	11.88
Shear stress (LSM), $\tau$	10.81-144.9	67.23	27.26	14.89-140.69	68.21	27.60

\* *SD*: Standard Deviation

### 6.5.2 Network Architecture

In this study, a feed-forward back propagation neural network was developed to predict the rheological parameters of OWC slurries. There are no generally accepted rules/guidelines to select the architecture or topography of a network. The topography and training parameters obtained through trial and error for the ANN model thus developed are presented in Fig. 6.5 and Table 6.3.

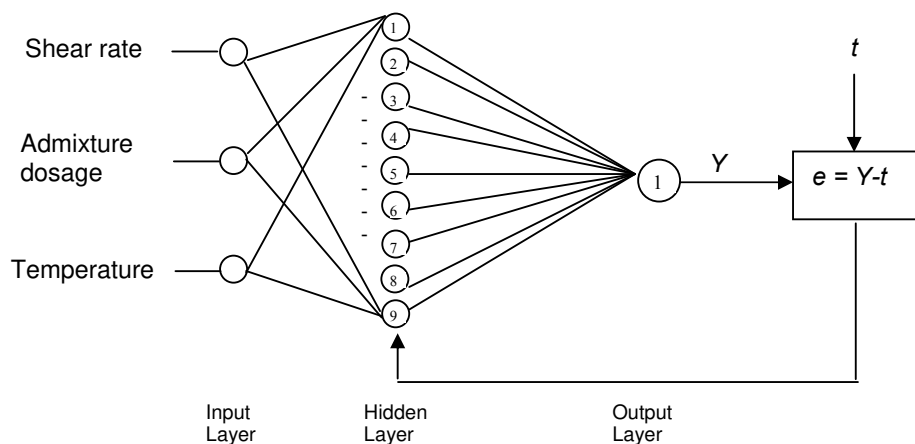


Figure 6.5 Architecture of developed ANN model.

Table 6.3 Topography and training parameters for the developed ANN model

Number of input nodes	3
Number of output nodes	1
Number of hidden layers	1
Number of nodes in hidden layers	9
Activation function input-hidden layers	Log-sigmoid
Activation function hidden-output layers	Linear
Distribution of weights	Gaussian
Momentum coefficient	0.03
Learning rate	0.05
Convergence	$5E^{-8}$

The model parameters were selected based on the lowest training and testing error. For example, in order to determine the optimum number of hidden nodes, the network performance was evaluated by changing the number of hidden nodes alone and keeping all other parameters unchanged. It can be observed in Fig. 6.6 that the addition of more hidden nodes consistently improved the performance of the ANN in the training process. However, in testing the model, its performance improved up to node number 9, but the average absolute error (*AAE*) started to increase thereafter. Therefore, nine hidden nodes

were used in this study to develop the ANN model. It should be noted that different network architectures can provide satisfactory performance for the same application.

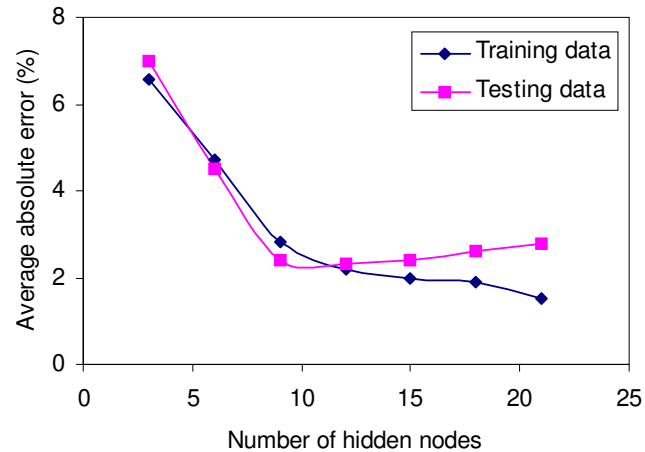


Figure 6.6 Selection of number of hidden layer nodes for slurries prepared using LSM.

### 6.5.3. Training Process

Training a feed-forward back-propagation neural network in order to predict the rheological properties of OWC involves teaching the network the relationships between the input parameters (admixture dosage, temperature and shear rate) and the overall cement slurry rheology. The success of the training process depends on (a) the selection of network parameters, (b) the algorithm used for learning, and (c) the validation of the model using experimental data available for training along with new testing data unfamiliar to the model. Specialized commercial computer software (Demuth et al., 2008) was used. Supervised training was implemented in this study by providing the network with sets of data (inputs/targets) and the network was instructed what to learn. Parameters such as the learning rate and convergence tolerance used for the ANN are presented in Table 6.3. A training pattern consists of an input vector of 3 elements including the admixture dosage, temperature and shear rate, and a corresponding output vector consisting of shear stress. The unipolar log-sigmoid (logsig) function and linear function were assigned as the transfer function for the processing units in the input-hidden layers and the hidden-output layers, respectively. A full connection between the processing units in adjacent layers was adopted. No connection is permitted between neurons in the same

layer. After completion of each learning process, the average sum-squared of all errors was calculated and back-propagated through the Levenberg-Marquardt (Demuth et al., 2008) algorithm to adjust the weights or connection strengths between the processing units. The Levenberg-Marquardt algorithm makes the leaning process faster and is based on the Jacobian matrix  $J$  that contains the first derivative of the network errors of corresponding weights. An iteration of the algorithm can be expressed as:

$$W^{k+1} = W^k - [J^T J + \mu I]^{-1} J^T e \quad (6.9)$$

where  $W^k$  is a vector of current weights,  $\mu$  is a leaning rate,  $J$  is the Jacobian matrix,  $J^T$  is the transpose matrix of  $J$ ,  $I$  is the identity matrix, and  $e$  is a vector of network errors. This iterative process continues until the network converges and a set of weights that minimizes the system error to the desired level or the maximum number of iterations (epochs) has been reached.

## 6.6 Multiple Regression Analysis

In the MRA-based approach, the dependent variables yield stress and plastic viscosity were correlated to the independent variables; i.e. shear rate, admixture dosage, and test temperature using first (linear) and then second (polynomial) order regression models. It was found that no substantial improvement was achieved by the polynomial regression. Therefore, the linear regression-based approach was used to observe the effect of temperature, admixture dosages and shear rate on shear stress. As a consequence, the shear stress values versus shear rate, admixture dosage and test temperature, were predicted using the following relationship:

$$\tau = a + b \dot{\gamma} + c D_A + d T + e \dot{\gamma} D_A + f \dot{\gamma} T + g D_A T + h \dot{\gamma} D_A T \quad (6.10)$$

where,  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ ,  $f$ ,  $g$ , and  $h$  are regression coefficients, and  $\tau$ ,  $\dot{\gamma}$ ,  $D_A$  and  $T$  are the shear stress, shear rate, dosage of admixture and temperature, respectively.

In order to perform the regression analysis, a total of 240 data points from down curves of the hysteresis loops were used for each of the three admixtures tested (PCH, PCM and LSM). Each data point consists of 3 input variables including shear rate, dosage of admixture and temperature, and one output parameter: shear stress. The least square approach was followed to estimate the coefficients of the model parameters. The

interaction between the considered three input parameters and the output parameter were also accounted for during the regression analyses and expressed in terms of  $t$  and probability ( $Prob.>|t|$ ) values. The probability value indicates the probability that the result obtained in a statistical test is due to chance rather than to a true relationship between the parameters (Genentech, 2010; Montgomery, 2009). The effects of the input parameters on the output parameters are considered highly significant when  $t$  values are high and probability values are low. The parameter is often considered nonzero and significantly influences the response of the model when the probability values are less than 5% (Sonebi, 2001; Health and Income Equity, 2010).

### 6.7 Model Performance

The developed models using the ANN and MRA techniques predicted the shear stress of the OWC slurries and the acceptability/rejection of the model was evaluated using the average absolute error ( $AAE$ ) given by equation 4 and the correlation coefficient ( $R^2$ ).

$$AAE = \frac{1}{n} \sum_{i=1}^n \frac{|\tau_{measured} - \tau_{predicted}|}{\tau_{measured}} \quad (6.11)$$

where  $\tau_{measured}$  and  $\tau_{predicted}$  are the experimentally measured shear stress value of OWC slurries and the corresponding data predicted by the model, respectively, and  $n$  is the total number of data points.

#### 6.7.1 Validation of ANN and MRA-Based Models

The artificial neural network model shown in Fig. 6.5 was trained using 190 training (input/target) patterns for each of the admixtures investigated, and tested using 50 patterns of new data points unfamiliar to the network and not used in the training process.

Figures 6.7, 6.8 and 6.9 illustrate the performance of the ANN in predicting the shear stress of OWC slurries incorporating PCN, PCM, and LSM, respectively. After successful completion of the training process, the network performance in predicting the shear stress of OWC slurries incorporating PCH was investigated and the results are presented in Fig. 6.7(a). It can be observed that all data points are located on or in the vicinity of the equity line with an  $AAE$  of 3.43%. For cement slurries incorporating PCM, the relationship between measured and predicted shear stress is presented in Fig. 6.8(a). The model was successfully trained to predict the shear flow with an  $AAE$  of 3.17%. Similarly, Fig. 6.9(a)

represents the performance of the ANN model in predicting the shear stress of cement slurries incorporating LSM. It can be observed that the model was able to predict the shear stress of the cement slurries satisfactorily since the measured and corresponding predicted data points are located along the equity line with an *AAE* of 2.82%.

The acceptance/rejection of the ANN model depends primarily on its performance in predicting the shear stress of new sets of unfamiliar data within the range of input variables of training patterns. In order to validate the developed model, the network was presented with 50 new sets of data which were not used in training the network. In this case, only input vectors of shear rate, dosage of admixture and temperature were presented to the network and no information or knowledge about the corresponding shear stress was provided. The response of the neural network is presented in Figs. 6.7(b), 6.8(b) and 6.9(b) for OWC mixtures made with PCH, PCM and LSM, respectively. The model predictions are accurate since the testing points are located slightly over or under the equity line but within the cluster of training data with an *AAE* of 2.76, 2.77 and 2.81% for slurries with PCH, PCM and LSM, respectively.

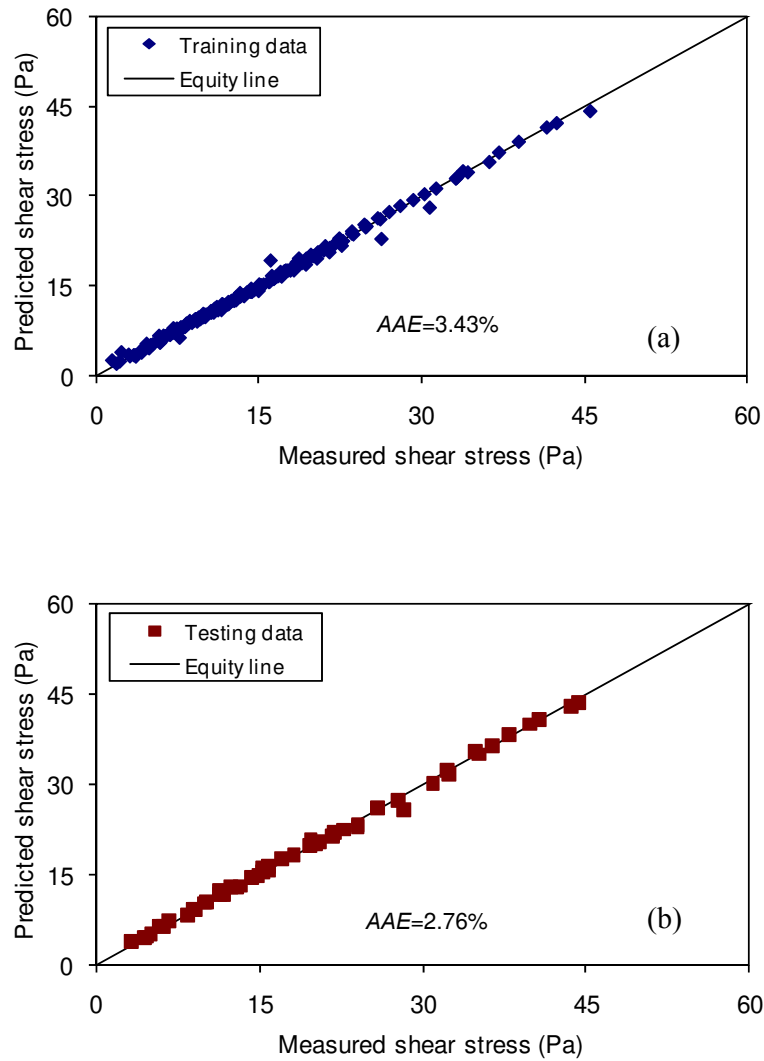


Figure 6.7 Measured versus predicted shear stress for OWC slurries incorporating PCH  
(a) Training data and (b) Testing Data



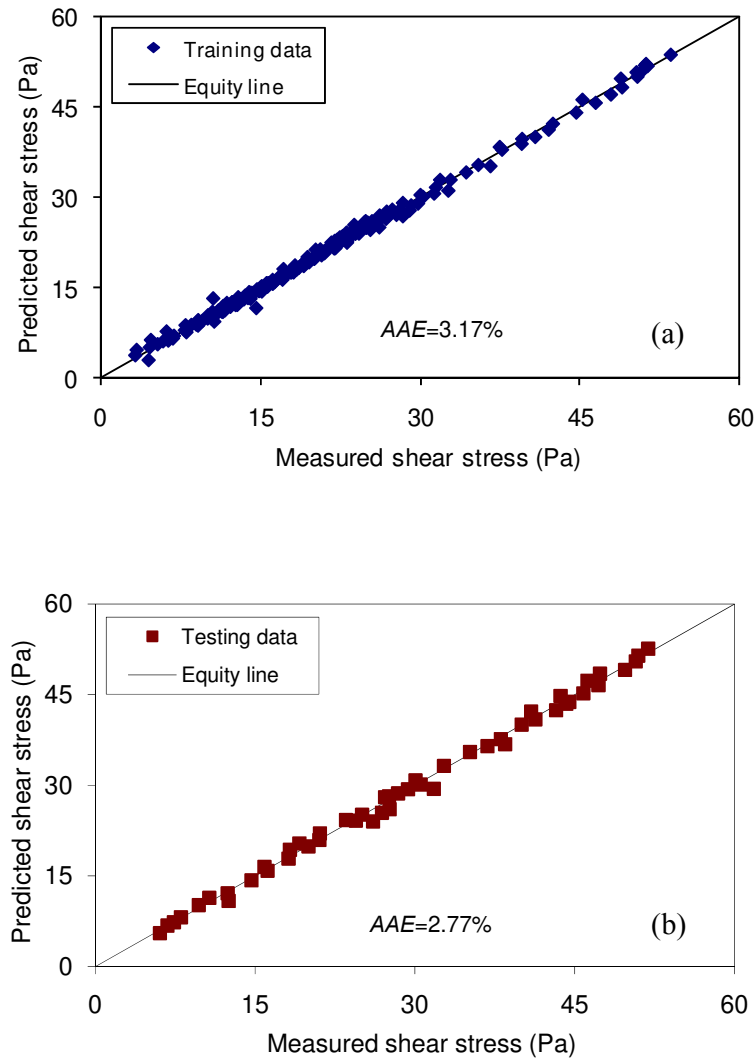


Figure 6.8 Measured versus predicted shear stress for OWC slurries incorporating PCM  
(a) Training data and (b) Testing Data

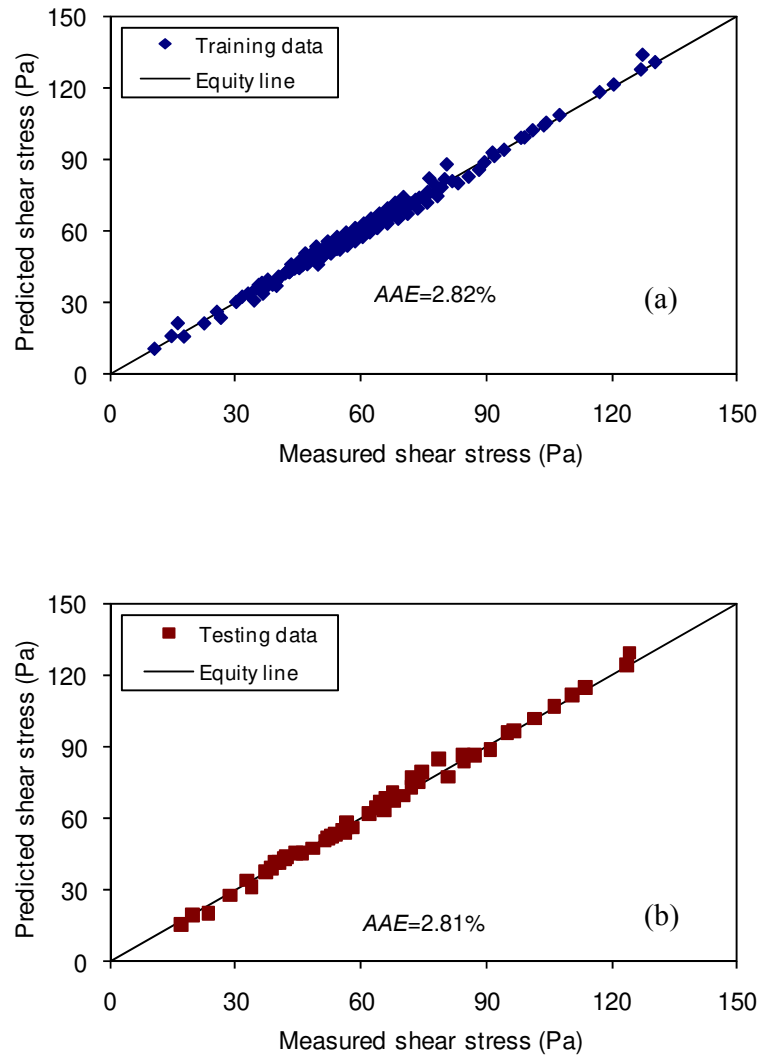


Figure 6.9 Measured versus predicted shear stress for OWC slurries incorporating LSM  
(a) Training data and (b) Testing Data

Figure 6.10 (a, b, c) represents the performance of models using the MRA technique in predicting the shear stress of OWC slurries incorporating PCH, PCM and LSM, respectively. All data points are located on or in the vicinity of the equity line with an *AAE* of 4.83, 6.32 and 5.05% for slurries with PCH, PCM and LSM, respectively.

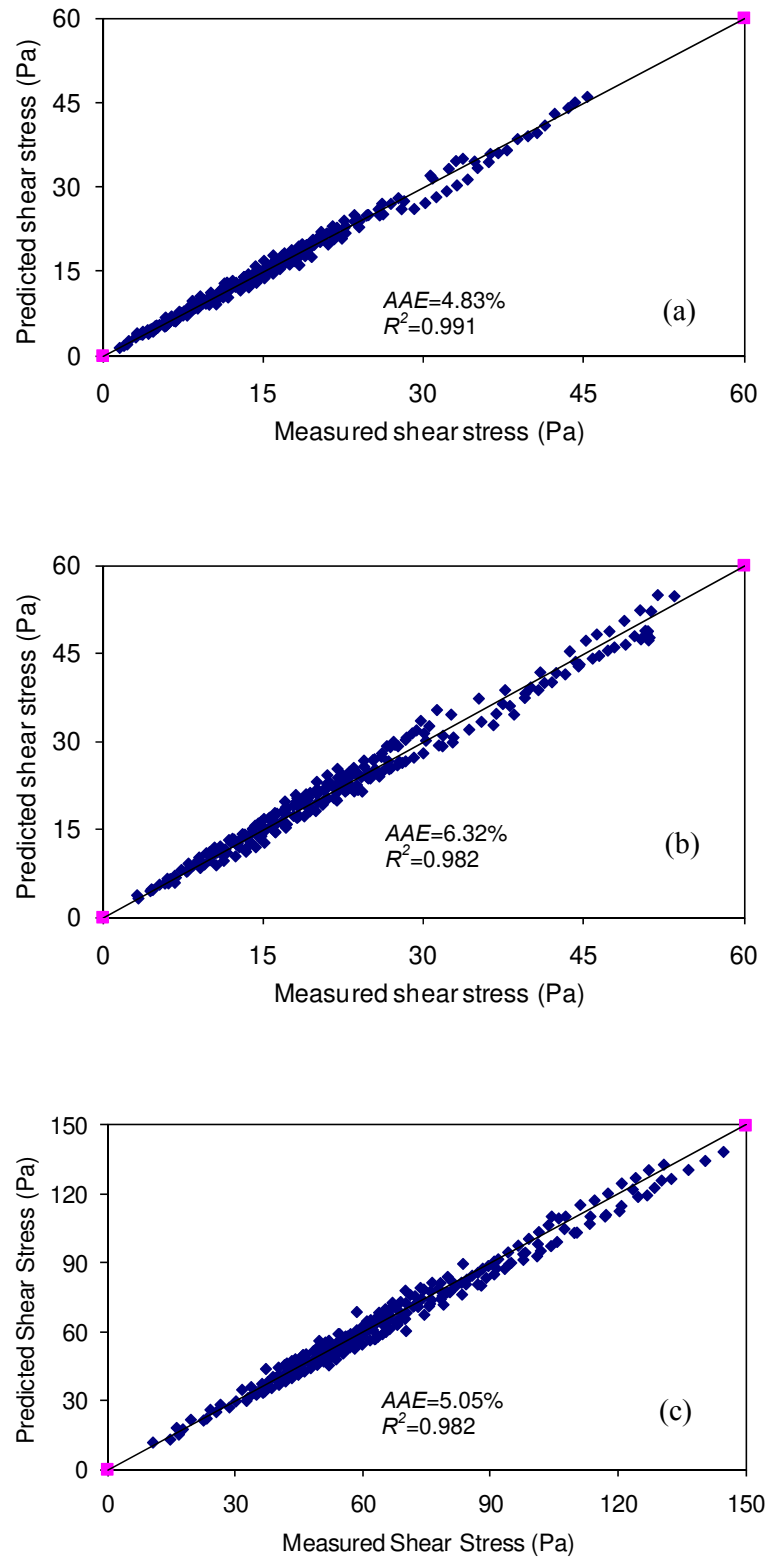


Figure 6.10 Measured versus MRA-model predicted shear stress for OWC slurries incorporating (a) PCH, (b) PCM, and (c) LSM.

Table 6.4 reveals the relative importance of various parameters as well as their interactions in predicting the shear stress of OWC slurries prepared with PCH, PCM and LSM. It can be observed that the probabilities of the derived coefficients of all the parameters for PCH and PCM are limited to 3.9%. This implies that there is less than 3.9% chance, or 96.1% confidence limit, that the contribution of a given parameter to the tested response exceeds the value of the specified coefficient. In case of LSM, the probabilities of the derived coefficients of all the parameters are limited to 4.9%. Negative coefficients suggest that an increase of the given parameter results in a reduction of the measured response. Moreover, the value/coefficient of the parameter represents the importance of the given parameter on the response value. The higher the coefficient of the parameter, the greater is its influence. For example, an increase in temperature increases the shear stress for all the admixtures tested, and an increase in the dosage of the admixture reduces the shear stress in the case of PCH and PCM, but increases the response value in the case of LSM, which is in good agreement with the experimental results. Moreover, the admixture dosage was found to have more influence on the model response than that of the other parameters. The presence of interactions with coupled terms specifies that the influence of the parameter on a particular response is quadratic (Sonebi, 2001).

The derived statistical models using the multiple regression analysis approach for shear stress of OWC slurries incorporating PCH, PCM and LSM have been selected based on the lowest average absolute error (*AAE*) and the highest correlation coefficient/determination coefficient ( $R^2$ ); they are given in Equations (6.12), (6.13) and (6.14), respectively.

$$\tau = 5.0 - 0.013\dot{\gamma} - 5.075D_A + 0.279T + 0.076\dot{\gamma}D_A + 0.001\dot{\gamma}T - 0.256D_A T - 0.002\dot{\gamma}D_A T \quad (6.12)$$

$$\tau = 5.0 - 0.022\dot{\gamma} - 8.849D_A + 0.429T + 0.085\dot{\gamma}D_A + 0.002\dot{\gamma}T - 0.220D_A T - 0.002\dot{\gamma}D_A T \quad (6.13)$$

$$\tau = 0.122\bar{\gamma} + 4.909D_A + 0.869T - 0.068\bar{\gamma}D_A - 0.072D_A T + 0.002\bar{\gamma}D_A T \quad (6.14)$$

The accuracy of the ANN- and MRA-based models thus developed was further evaluated by comparing the ratio of the measured-to-predicted values of the shear stress of OWC slurries. The maximum, minimum and average of the shear stress values, standard deviation (*SD*), and coefficient of variation (*COV*) and the average absolute error (*AAE*) for all the data are presented in Tables 6.5 and 6.6. The results reveal that both the ANN

and MRA have successfully learned to map between input parameters (shear rate, dosage of respective admixture, temperature) and corresponding output (shear stress). The proposed models satisfactorily predicted the shear stress with acceptable error. However, the *AAE* of the models developed using the ANN approach was found to be lower than that of MRA-based models. The better performance of the ANN-based model was also supported by the higher correlation coefficient ( $R^2$ ) than that provided by the MRA-based models.

### ***6.7.2 Performance of ANN and MRA in Predicting Rheological Properties Of OWC Slurries***

Based on the satisfactory performance of the developed ANN and MRA models in predicting the shear stress of OWC slurries, the down flow curve for a particular mixture was predicted by changing the shear rate and keeping the admixture dosage and temperature unchanged. Subsequently, the yield stress and plastic viscosity were determined from the model predicted down flow curve using the Bingham plastic model. The yield stress was obtained by extrapolating the shear stress-shear rate curve corresponding to a zero shear rate, and the plastic viscosity was the slope of the curve. One slurry mixture for each of the admixtures was randomly selected from the testing data and used to develop the down flow curve at different temperatures (23°C, 45°C, and 60°C). These OWC mixtures were made with 0.5% of each admixture.

Table 6.4 Model Parameters

	PCH ( $R^2 = 0.991$ )			PCM ( $R^2 = 0.982$ )			LSM ( $R^2 = 0.982$ )		
	<i>Coeff.</i>	<i>t</i>	<i>Prob.&gt; t </i>	<i>Coeff.</i>	<i>t</i>	<i>Prob.&gt; t </i>	<i>Coeff.</i>	<i>t</i>	<i>Prob.&gt; t </i>
Intercept	5.000	-	-	5.000	-	-	0.000	-	-
$\bar{\gamma}$	-0.013	-2.076	0.039	-0.022	-3.439	0.001	0.122	7.395	< 0.0001
$\bar{D}_A$	-5.075	-2.329	0.021	-8.849	-4.026	< 0.0001	4.909	2.723	0.0148
$\bar{T}$	0.279	10.323	< 0.0001	0.429	15.696	< 0.0001	0.869	12.073	< 0.0001
$\bar{\gamma} \times \bar{D}_A$	0.076	6.860	< 0.0001	0.085	7.633	< 0.0001	-0.068	-4.395	0.00158
$\bar{\gamma} \times \bar{T}$	0.001	7.765	< 0.0001	0.002	10.683	< 0.0001	0.000	-1.003	0.174
$\bar{D}_A \times \bar{T}$	-0.265	-4.407	< 0.0001	-0.220	-3.619	0.000	-0.072	-1.901	0.0495
$\bar{\gamma} \times \bar{D}_A \times \bar{T}$	-0.002	-7.329	< 0.0001	-0.002	-8.514	< 0.0001	0.002	5.921	< 0.0001

Table 6.5 Performance of ANN-based model in predicting the shear stress of cement slurries prepared with different chemical admixtures

Type of admixture	AAE (%)		$\tau_{measured}/\tau_{predicted}$					
	Training	Testing	Average		SD <sup>1</sup>		COV <sup>2</sup> (%)	
			Training	Testing	Training	Testing	Training	Testing
PCH	3.43	2.76	0.984	0.988	0.058	0.040	5.88	4.09
PCM	3.17	2.77	0.998	1.001	0.062	0.040	6.18	4.01
LSM	2.82	2.81	1.000	1.000	0.042	0.041	4.23	4.11

<sup>1</sup>SD: standard deviation, <sup>2</sup>COV = SD / Average \* 100

Table 6.6 Performance of MRA-based model in predicting the shear stress of cement slurries prepared with different chemical admixtures

Type of admixture	AAE (%)	$\tau_{measured}/\tau_{predicted}$				
		Maximum	Minimum	Average	SD <sup>1</sup>	COV <sup>2</sup> (%)
PCH	4.83	1.165	0.805	1.006	0.062	6.128
PCM	6.32	1.203	0.864	0.999	0.073	7.348
LSM	5.05	1.167	0.854	1.018	0.059	5.804

<sup>1</sup>SD: standard deviation, <sup>2</sup>COV = SD / Average \* 100

Figure 6.11 (a, b) represents the predicted yield stress and plastic viscosity values, respectively for OWC slurries incorporating 0.5% of PCH, PCM, and LSM at different temperatures, along with the corresponding experimentally measured values. Both the yield stress and plastic viscosity values predicted by the ANN- and MRA-based models followed a similar trend to that of the experimental data. In addition to test temperatures (23°C, 45°C and 60°C), rheological parameters were also determined at 35°C and 52°C in order to predict the model's response within the range of the input data. It can be observed that the yield stress for OWC slurries incorporating PCH was generally lower than that for slurries made with PCM and LSM. This is in agreement with findings for cement pastes (Al-Martini and Nehdi 2007, Al-Martini 2008). Both the yield stress and plastic viscosity were found to be sensitive to the change in temperature; the higher the temperature the higher was the yield stress, which is in good agreement with experimental results.

The effect of the admixture dosage at different temperatures on the predicted rheological parameters of OWC slurries is illustrated in Fig. 6.12. Some admixture dosages not used in experiments were also included in model predictions. Both experimental and predicted values of yield stress decreased with PCH and PCM dosage. In the case of LSM, the predicted yield stress values increased with the dosage up to 1.5% and then started to decrease, which is in good conformity with experimental results. It can be observed that the variation of yield stress with admixture dosage was reasonably estimated for all the admixtures considered and its predicted values were comparable to the corresponding measured data.

Moreover, the plastic viscosity of OWC slurries was found to be sensitive to the change of temperature and admixture dosage (Fig. 12(b)). The plastic viscosity values predicted by both the ANN- and MRA-based models showed irregular behaviour, which may be associated with the error involved in fitting the curve to the Bingham model. It was argued (Al-Martini and Nehdi, 2007) that plastic viscosity measured by fitting the down flow curve of the hysteresis loop to the Bingham model does not always truly represent the material properties because of the error associated with fitting the curve, which could be sometimes high as observed by Saak (2000).

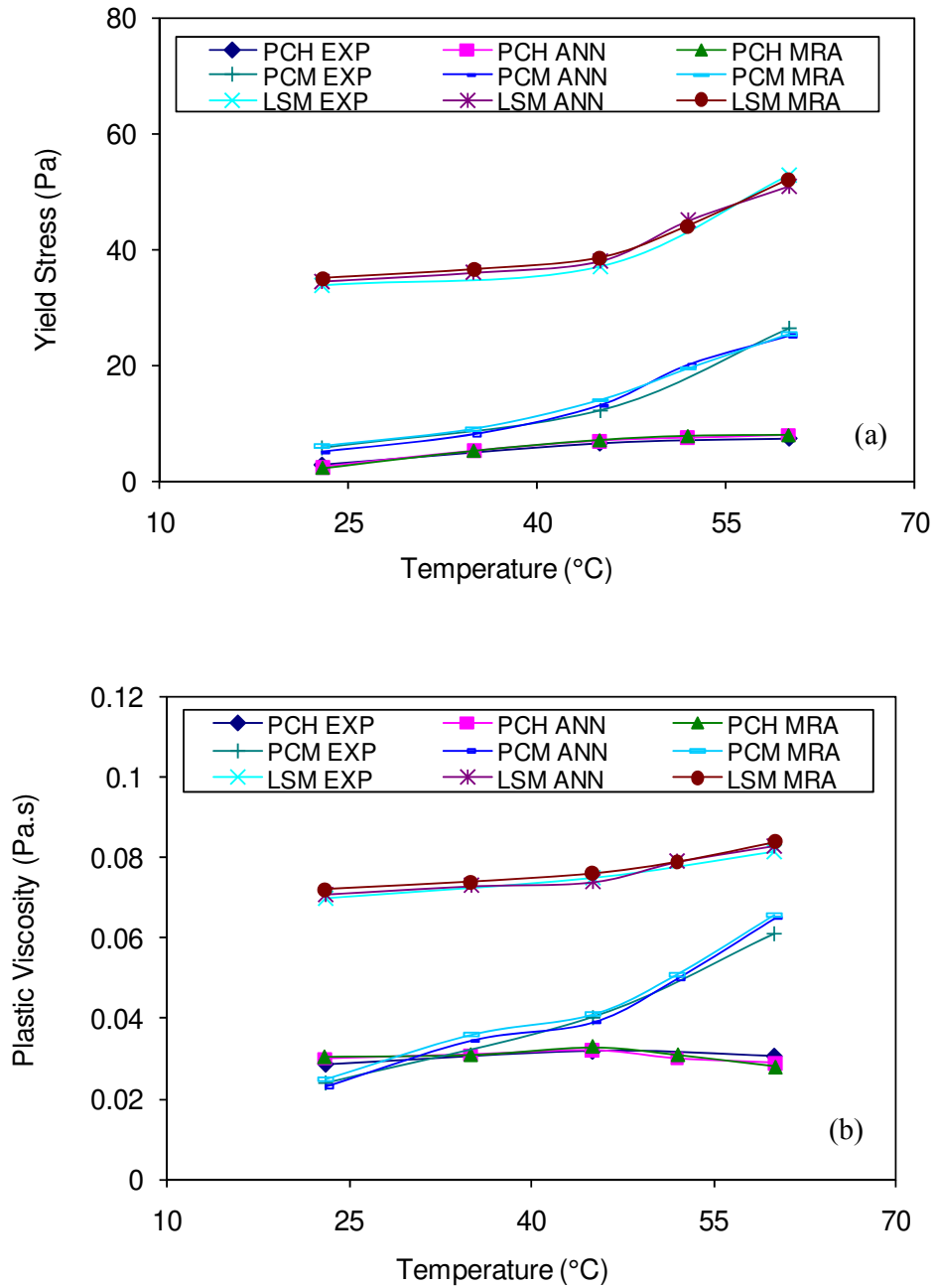


Figure 6.11 Variation of (a) yield stress, and (b) plastic viscosity of OWC slurries at different temperatures (Dosage of admixture = 0.5% BWOC).



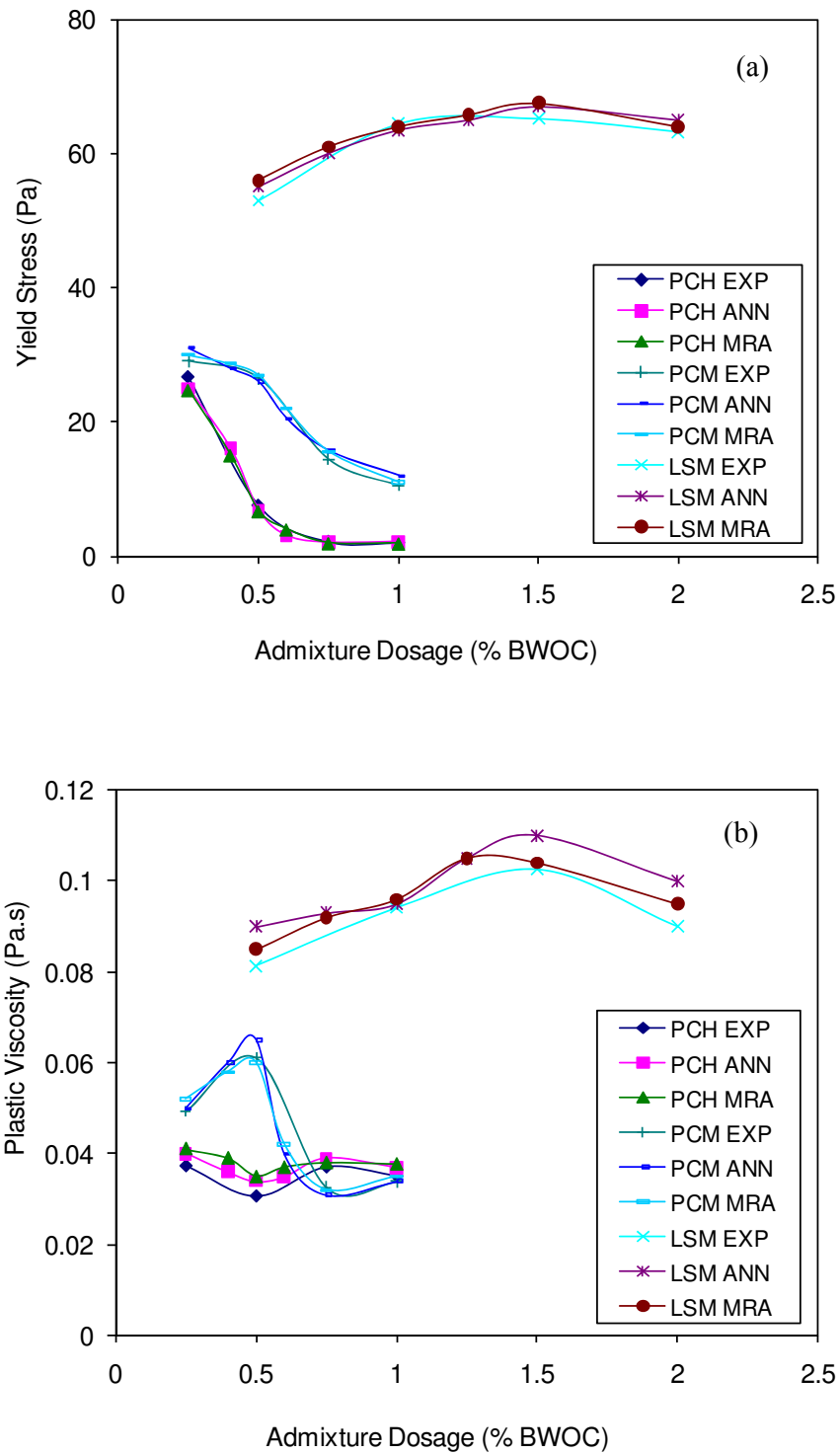


Figure 6.12 Variation of (a) yield stress, and (b) plastic viscosity of OWC slurries with admixture dosage and at a temperature of 60°C.

Figures 11 and 12 reveal that the models were able to recognize and evaluate the effects of the admixture dosage and temperature on yield stress and plastic viscosity. The *AAE* of the ANN model predictions was in the range of 1.4 to 15.6% and 0.7 to 11.8% for yield stress and plastic viscosity, respectively, and that for the MRA model was in the range of 1.2 to 17.5% and to 1.3 to 14.5% for yield stress and plastic viscosity, respectively; depending on the admixture dosage and temperature tested. The higher values of *AAE* are usually associated with the lower yield stress and plastic viscosity values since small prediction errors may result in high *AAE* in such cases.

## 6.8 Conclusion

In this chapter, the relationships amongst the shear stress, shear rate, temperature, admixture type and dosage for OWC slurries have been analyzed. The rheological properties of OWC slurries were modeled using a feed-forward back-propagation artificial neural network and multiple regression analysis. The models were then used to develop flow curves, which were used to calculate the yield stress and plastic viscosity values for OWC slurries with different admixtures and at different test temperatures. Based on this study, the following conclusions can be drawn:

- The ANN model developed in this study was able to learn the relationships between different shear flow parameters for various OWC slurries and successfully predicted their rheological properties of slurries used in the training process. It also demonstrated satisfactory performance when input parameters (shear rate, temperature, and dosage of admixture) unfamiliar to the ANN were used. The results prove that the ANN model is a powerful tool to quantitatively predict the rheological properties of OWC slurries within the range of tested admixture dosages and test temperatures.
- The MRA-based models were able to predict the rheological properties of OWC slurries with adequate accuracy.
- The flow curves developed using the ANN- and MRA-based models allowed predicting the Bingham parameters (yield stress and plastic viscosity) of OWC slurries with an acceptable accuracy and were found to be in good agreement with experimental results.

- The models proposed by both approaches were found to be sensitive to the effects of temperature increase and admixture dosage on the rheological properties of OWC slurries.
- The ANN-based model performed relatively better than the MRA-based model in predicting the rheological properties of OWC slurries.
- The proposed ANN- and MRA-based models can be extended and used to limit the number of laboratory trial mixtures and develop OWC slurries with suitable rheological properties, thus saving time and reducing the cost of OWC slurry design for specific applications.

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*Chapter 7***ARTIFICIAL INTELLIGENCE MODEL FOR RHEOLOGICAL  
PROPERTIES OF OIL WELL CEMENT SLURRIES  
INCORPORATING SCMs<sup>1</sup>****7.1 Introduction**

The world's production of portland cement is forecast to continue increasing throughout the next 40 years, from the 2.8 billion tons of 2009 to around 3.8 billion tons by 2030, and 4.4 billion tons by 2050 (Cement Technology Roadmap, 2009). Cement production is not only highly energy-intensive, but also causes global ecological problems by consuming substantial amounts of natural resources. Producing one ton of cement emits approximately one ton of carbon dioxide (CO<sub>2</sub>) mainly due to the calcination of raw materials and combustion of fuels. Growing concerns for reducing CO<sub>2</sub> emissions and reduction /recycling of waste materials have stimulated the usage of supplementary cementitious materials (SCMs). Such materials include fly ash, silica fume, ground granulated blast furnace slag, natural pozzolans, metakaolin, etc. Because of differences in their physical and chemical properties, not all SCMs act similarly when used as partial replacement for cement. For instance, owing to its spherical particle shape and relatively low specific surface, fly ash reduces the water demand when used as partial replacement for portland cement. Conversely, silica fume tends to increase the water demand due to its very high surface area.

OWC slurries are complex mixtures consisting of cement, water and a number of chemical and mineral additives. In the petroleum industry, cement slurries are pumped to several thousand meters into the ground to anchor and seal the casing to the borehole of oil or gas wells. They have to achieve specific rheological properties under stringent temperature and pressure conditions. Thus, an advanced characterization of the rheology of OWC slurries is critical. In order to contend with extreme bottom-hole conditions, various chemical and mineral additives are usually used in the slurry composition. Interactions amongst the

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<sup>1</sup> A version of this chapter has been accepted in *Advances in Cement Research*, 2011.

different ingredients used cause wide variation in the rheological properties, which depend on the specific materials and proportions used.

Many studies have been performed over the last few decades to investigate the rheological behaviour of cementitious systems such as, cement paste, mortar, grout, slurry and concrete. Determining the rheological properties of OWC slurries in-situ is not always practical. Extensive rheological testing requires sophisticated equipment not suitable for on-site operation, and is labour intensive and time consuming. Therefore, there is a need for models that can predict the rheological properties of OWC slurries with adequate accuracy. A number of shear stress-strain rate relationships have been developed for rheological properties of cement based systems, among which the power-law, Bingham, and Herschel-Bulkley models are the most commonly used in the well cementing industry (Guillot 2006). However, there exists no model that can account for interactions among the materials used for preparing such slurries and test conditions such as temperature. Such models are comprised of empirical expressions derived from the analysis of limited experimental data and/or based on simplifying assumptions (El-Chabib and Nehdi, 2005). Moreover, they do not have true predictive capability outside the experimental domain and/or when different materials are used (El-Chabib et al., 2003; 2005) and do not explain the interactions among test parameters.

Artificial neural networks (ANNs) are a powerful computational tool capable of solving complex and highly nonlinear functions through self-organization, pattern recognition, and functional approximation. ANNs simulate the structure and internal functions of the biological brain through computing. The use of ANNs in the field of civil engineering has increased over the last decades because of its ability to map between a set of input data and a corresponding output, and to perform global optimization for complex, nonlinear, and noisy problems. In this study, an ANN model has been developed for predicting the rheological properties of OWC slurries and relating the slurry composition (type and dosage of SCM, dosage of chemical admixture, etc.) and test conditions (e.g. shear rate, temperature) to the predicted rheological properties.

Four different mineral admixtures including metakaolin (MK), silica fume (SF), rice husk ash (RHA) and class F fly ash (FA) were used as partial replacement for API class G OWC in

this study. An ANN based model has been developed to predict the shear stress at a given shear rate as a function of the temperature, SCM type and dosage, and chemical admixture dosage. The ability of the ANN model to evaluate the sensitivity of the rheological properties to variations of the shear rate, admixture dosage, and test temperature was investigated. The shear stress-shear rate curve for OWC slurries could be predicted at different temperatures prior to fitting the data to conventional rheological models. Hence, for the first time, the rheological properties of OWC slurries could be predicted as a function of the mixture composition and test conditions. The ANN model would help designers selecting optimum OWC-SCM combinations considering the predicted rheological performance. It can be extended in future research to also account for mechanical strength and durability.

## **7.2 Materials and Apparatus**

OWC slurries were prepared using a high sulphate-resistant API Class G OWC with a specific gravity of 3.14, along with a new generation polycarboxylate-based high-range water reducing admixture (PCH) and different dosages of various SCMs including MK, SF, RHA and FA. The chemical and physical properties of the cement and SCMs are summarized in Table 5.1 (Chapter 5). Details of the mixture compositions of the slurries tested are provided in Table 5.2 (Chapter 5). Deionized distilled water was used for the mixing, and an isothermal container was used to maintain its temperature at  $23\pm 1^\circ\text{C}$ .

The cement slurries were prepared using a variable speed high-shear blender type mixer with bottom drive blades as per the ANSI/API Recommended Practice 10B-2 (ANSI/API RP 10B-2). A high accuracy advanced rheometer (TA instruments AR 2000) (Fig. 4.1), was used throughout this study to measure the rheological properties of OWC slurries. The rheometer is computer controlled and equipped with a rheological data analysis software, which can fit the shear stress-strain rate data to several rheological models. The Bingham model was used throughout this study to calculate the rheological properties. It is worth mentioning that rheological data depend on the type of rheological model used for fitting the experimental data (Nehdi and Rahman, 2004).



### 7.3 Experimental Procedure

The coupled effects of temperature, PCH dosage and type and amount of SCMs on the rheological properties of OWC slurries were investigated. The mixing of slurries was conducted at a controlled ambient room temperature of  $23\pm 1^\circ\text{C}$ . The prepared slurry was then placed in a temperature controlled chamber for preconditioning at the specific test temperature (23, 45, or  $60^\circ\text{C}$ ) and continually agitated at 150 rpm over 20 minutes. The rheometer set-up was maintained constant for all tested slurries. The concentric cylinder test geometry was preconditioned at the test temperature so as to avoid sudden thermal shock of the slurry. After mixing and preconditioning, the OWC slurry sample was placed in the coaxial cylinder of the rheometer. Once the temperature has been adjusted to the required level, the sample was sheared to a stepped ramp of steady state flow from  $5.11\text{ s}^{-1}$  to  $511\text{ s}^{-1}$  with 10 sec at each strain rate level. Subsequently, data were measured at a descending shear rate from  $511\text{ s}^{-1}$  to  $5.11\text{ s}^{-1}$  to obtain the down flow curve. A schematic representation of the viscometric testing scheme is illustrated in Fig. 5.1 (Chapter 5).

### 7.4 Experimental Results

Figure 7.1 illustrates typical shear stress-shear rate down curves for OWC slurries incorporating 5% SCM and different dosages of PCH at  $60^\circ\text{C}$ . The experimental results reveal that the Bingham model (Eq. 1) fits the shear stress-shear rate down curve with a correlation coefficient ( $R^2$ )  $> 0.95$ .

$$\tau = \tau_0 + \mu_p \dot{\gamma} \quad (7.1)$$

where,  $\tau$ ,  $\tau_0$ ,  $\mu_p$ , and  $\dot{\gamma}$  represent the shear stress, yield stress, plastic viscosity, and shear rate, respectively. The down-curve better fits the Bingham plastic model than the up-curve (Ferguson and Kembrowski, 1991; Al-Martini and Nehdi, 2009), therefore the shear rate–shear stress down curve was considered in calculating the rheological properties (yield stress and plastic viscosity).

The Bingham parameters (yield stress and plastic viscosity) are very much dependent on test variables as observed in Figs. 7.2 to 7.4. In this study, artificial neural networks have been

used to predict the shear stress as a function of test variables (temperature, SCM and PCH dosage, and shear rate). The predicted flow curve allows in turn to predict the rheological properties of OWC slurries using the Bingham or similar models.

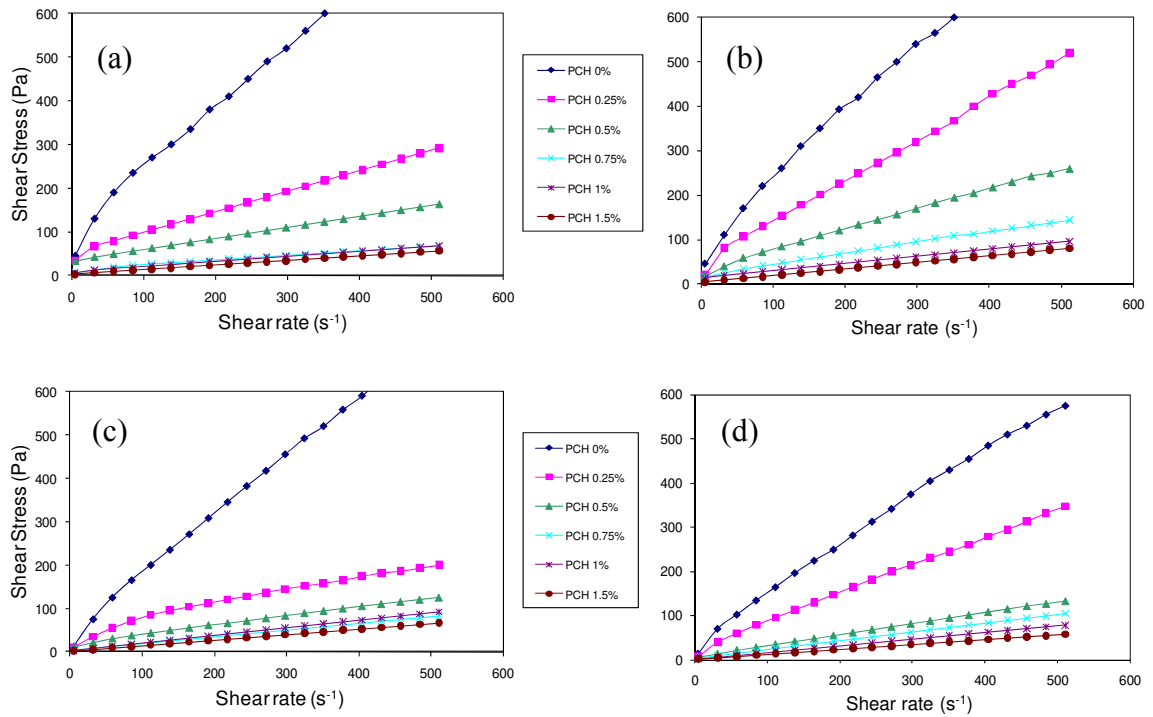


Figure 7.1 Flow curve of oil well cement slurry incorporating 5% of SCMs and different dosage of PCH Admixture at 60°C, (a) MK; (b) SF; (c) RHA; and (d) FA.

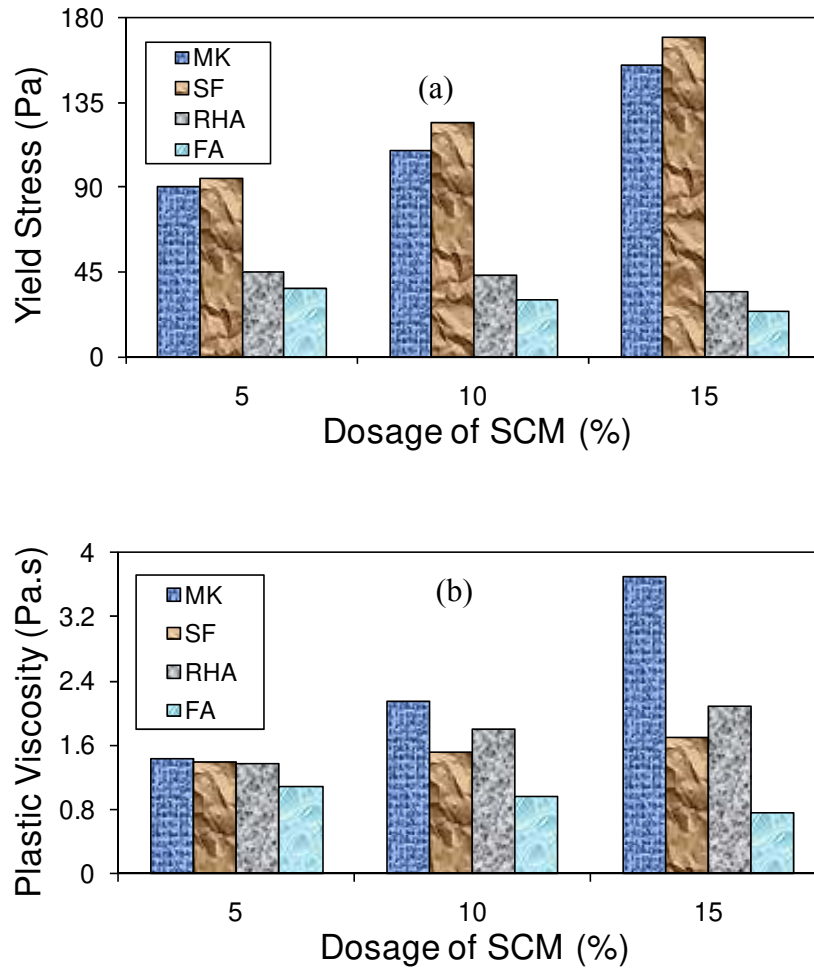


Figure 7.2 Variation of rheological properties of OWC slurries with type and dosage of SCM but without PCH at 60°C; (a) yield stress and (b) plastic viscosity.

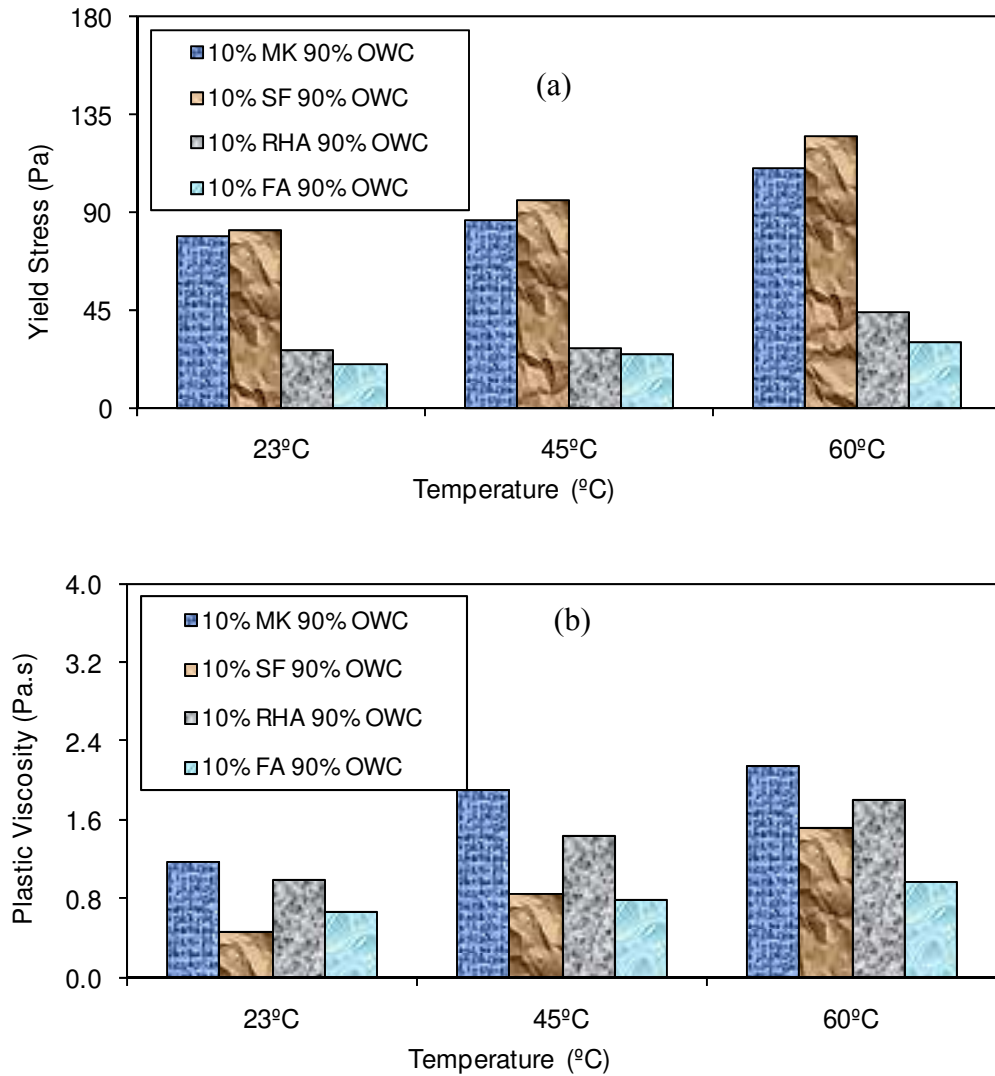


Figure 7.3 Variation of rheological properties with temperature for OWC slurries prepared by 10% replacement of OWC by SCM (MK, SF, RHA, and FA); (a) yield stress and (b) plastic viscosity.

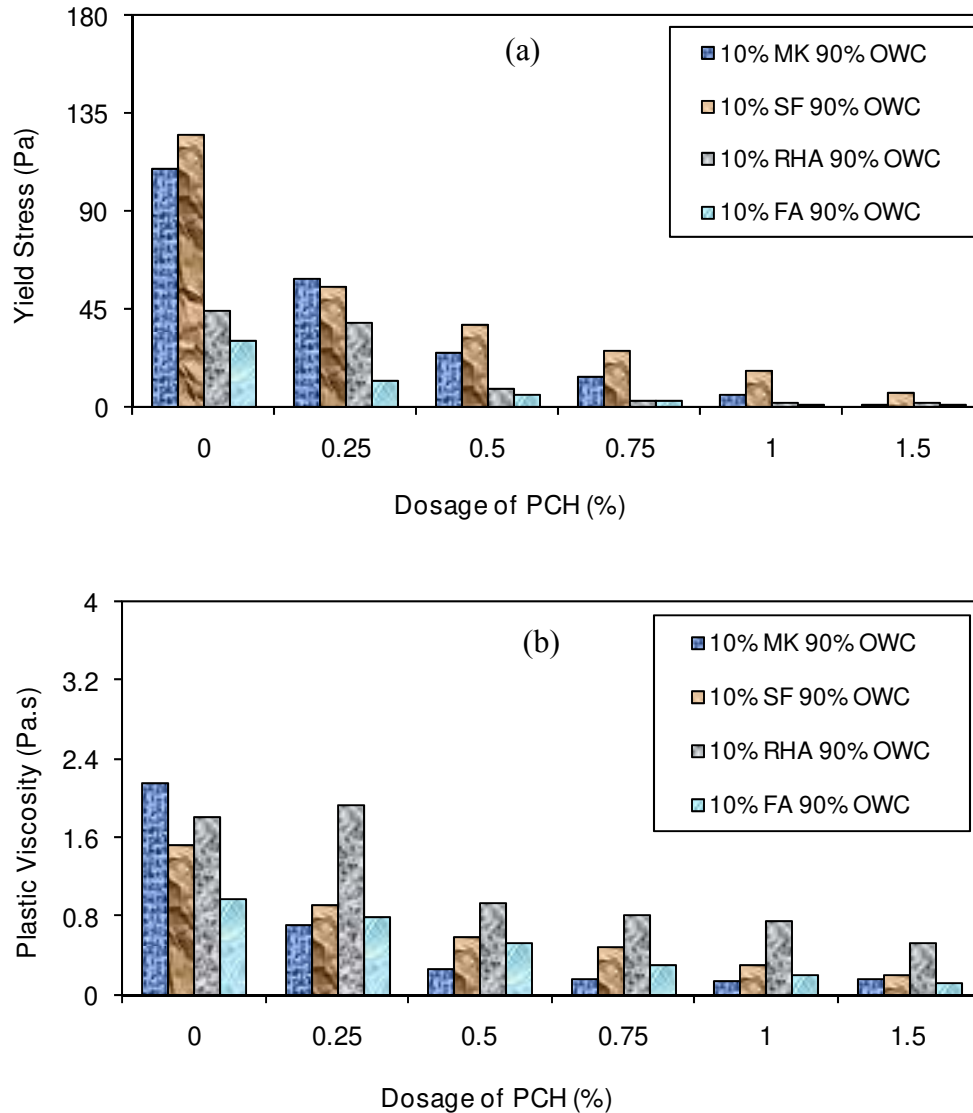


Figure 7.4 Variation of rheological properties with dosage of PCH for OWC slurries prepared by 10% replacement of OWC by SCM (MK, SF, RHA, and FA) at 60°C; (a) yield stress and (b) plastic viscosity.

## 7.5 Artificial Neural Network Approach

Artificial neural networks (ANNs) is a powerful computational tool that simulates the biological structure of neurons and the internal functions of the brain. An ANN is capable of learning the mapping between a set of input data and its corresponding output. Through training, it becomes capable of predicting an output when presented with a new set of data within the practical range of the input used in the training process. The feed-forward back-

propagation learning algorithm is the most commonly used in engineering applications, especially in modelling the behaviour of cement-based materials. ANNs are constructed of several linear or nonlinear processing units (neurons) arranged in an input layer, one or more hidden layers, and an output layer, and are often connected to neurons in other layers. Each processing unit receives multiple inputs from the neurons in the previous layer through the weighted connection, and after performing appropriate computation, transfers its output to other processing units or as a network output using an assigned transfer (activation) function as shown in Fig. 6.4 (Chapter 6).

There exists a number of network such as Hopfield network (Hopfield, 1982), Boltzmann machines (Ackley et al., 1985), the Kohonen network (Kohonen, 1982), and the multilayer feed-forward back-propagation neural network (Rumelhart et al., 1986). Among these the feed-forward back-propagation learning algorithm is the most commonly used in engineering applications, especially in modelling the behaviour of cement based materials.

Feed-Forward Back-Propagation Neural Network performs nonlinear transformation for functional approximation problems, recognize logic functions, and subdivide the pattern space for classification. It consists of a number of layers (input layer, hidden layer(s) and output layers) and processing units (neurons) in each layer. The neurons in one layer are fully connected between the processing units in adjacent layers with different weight but no backward connection is allowed and no connection exists between neurons in the same layer. The selection of the optimum number of hidden layers and the processing units (neurons) depends on the complexity of the problem. To date there are no well established rule to determine the suitable number of hidden layers and neurons (El-Chabib and Nehdi, 2005; Elbahy et al., 2010). These numbers are usually determined by trial and error. Fewer neurons than the optimum number results in fewer connection in the network which eventually reduces the ability of the network to implement nonlinear transformation for functional approximation. A premature training may cause unsatisfactory performance because of not adequately learning the embedded relationships between inputs and outputs. Over-fitting may not only lead to a precise prediction of the training patterns, but can also cause poor generalization of new patterns. The training continues until it converges to a desired minimum error between its predicted outputs and the desired targets provided in the training process. The duration of training can be determined by (a) limiting the number of iterations,

called training epochs, (b) setting a desired minimum error, or (c) monitoring the trend of error improvement so that training will be stopped when no or little improvement in the training error is reported over a given number or epochs. In each iteration, the error (as shown in equation 7.2) is compared with the convergence tolerance; if it is not met, the iteration continues and the calculated system error is back propagated to the network to adjust the weights and thresholds in a gradient search for the desired minimum system error (El-Chabib and Nehdi, 2005).

$$E_{st} = \frac{1}{P} \sum_{p=1}^P \sum_{k=1}^K (t_{pk} - o_{pk})^2 \quad (7.2)$$

where,  $E_{st}$  is the system error,  $p$  is a training pattern,  $P$  is the number of training patterns assigned to one epoch, and  $t_{pk}$  and  $o_{pk}$  are the predicted output and provided target of pattern  $p$  at output unit  $k$ , respectively.

The construction of an effective neural network requires considering three important steps: selection of database, network architecture, and network training and testing (El-Chabib et al., 2003).

### **7.5.1. Selection of Database**

The success of ANNs mostly depends on the quality of the database used for training (El-Chabib et al., 2003; Elbahy et al., 2010). The database should be large enough for the training process and should provide complete information about the relationships between the inputs and output. In order to account for the primary aspects that influence the input-output relationship of rheological properties of OWC slurries and capture the practical range of key input parameters (shear rate, dosage of SCM and PCH, and temperature), the network should be trained using a large and comprehensive set of reliable experimental data. The database comprised of a total of 900 patterns for each of the four SCMs tested (MK, SF, RHA and FA). Among which 780 patterns (660 for training and 120 for cross-validation) were used for training the network. One hundred and twenty (120) new data points unfamiliar to the model, but within the range of training data, were used to test the performance of the network. It should be noted that each flow curve consists of 20 data points at equal shear rate intervals starting from  $511 \text{ s}^{-1}$  to  $5.11 \text{ s}^{-1}$ . Each data pattern consists

of an input vector containing the four input parameters and an output vector containing the corresponding shear stress value for this input vector. The input parameters are the shear rate, dosage of SCM, dosage of PCH and test temperature. Table 7.1 presents the ranges, mean values, and standard deviations of all input and output variables in the final database.

Table 7.1 Range, average (Avg.), and standard deviation (SD) of input and output variables

	Training Data			Testing Data		
	Range	Average	SD*	Range	Average	SD*
Shear rate ( $s^{-1}$ ), $\dot{\gamma}$	5.11-511	258	153.6	5.11-511	257.9	157.52
Dosage of SCM, %	5-15	10.00	4.08	0-15	11.2	4.14
Dosage of PCH, %	0.25-1.5	0.80	0.43	0.25-1.5	0.76	0.48
Temperature, °C	23-60	42.67	15.2	23-60	42.67	18.61
Shear stress, $\tau$	2.17-1057	164.01	159.42	4.54-978.74	247.34	226.49

\* SD: Standard Deviation

### 7.5.2. Network Architecture

In this study, a feed-forward back propagation neural network was developed to predict the rheological parameters of OWC slurries. As mentioned earlier, there are no rules/guidelines to select the architecture or topography of a network. A trial and error method has been used to obtain the topography and training parameters for the ANN model. The topography and training parameters thus developed are presented in Fig. 7.5 and Table 7.2. A network that consists of one input layer, one hidden layer and one output layer was found to be most appropriate.



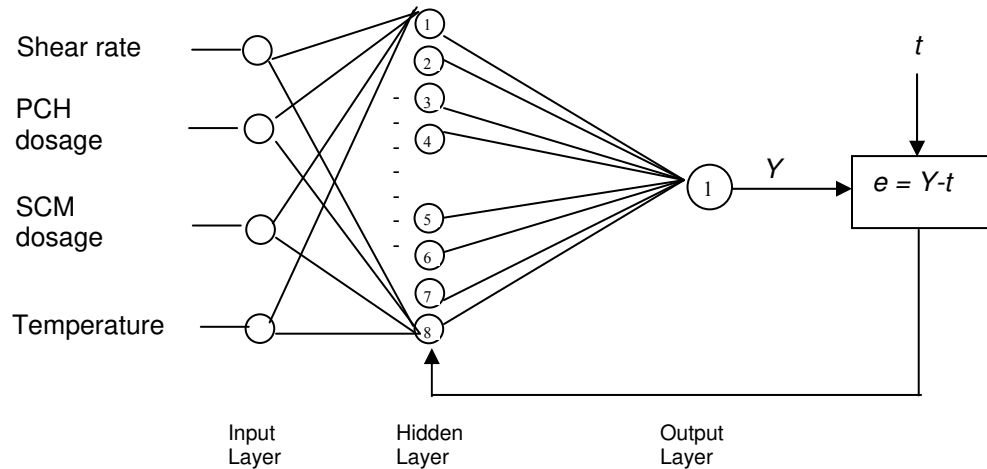


Figure 7.5 Architecture of developed ANN model.

The model parameters were selected based on the lowest training and testing error. For example, in order to determine the optimum number of hidden nodes, the network performance was evaluated by changing the number of hidden nodes alone and keeping all other parameters unchanged. It can be observed in Fig. 7.6 that the performance of the ANN was found to improve with the addition of more hidden nodes in the training process, whereas in the testing process of the model, its performance improved up to node number 8, but the average absolute error (AAE) started to increase thereafter. Therefore, eight hidden nodes were used in this study to develop the ANN model. It should be noted that different network architectures can provide satisfactory performance for the same application.

Table 7.2 Topography and training parameters for the developed ANN model

Number of input nodes	4
Number of output nodes	1
Number of hidden layers	1
Number of nodes in hidden layers	8
Activation function input-hidden layers	Log-sigmoid
Activation function hidden-output layers	Linear
Distribution of weights	Gaussian
Momentum coefficient	0.03
Learning rate	0.05
Convergence	$5E^{-8}$

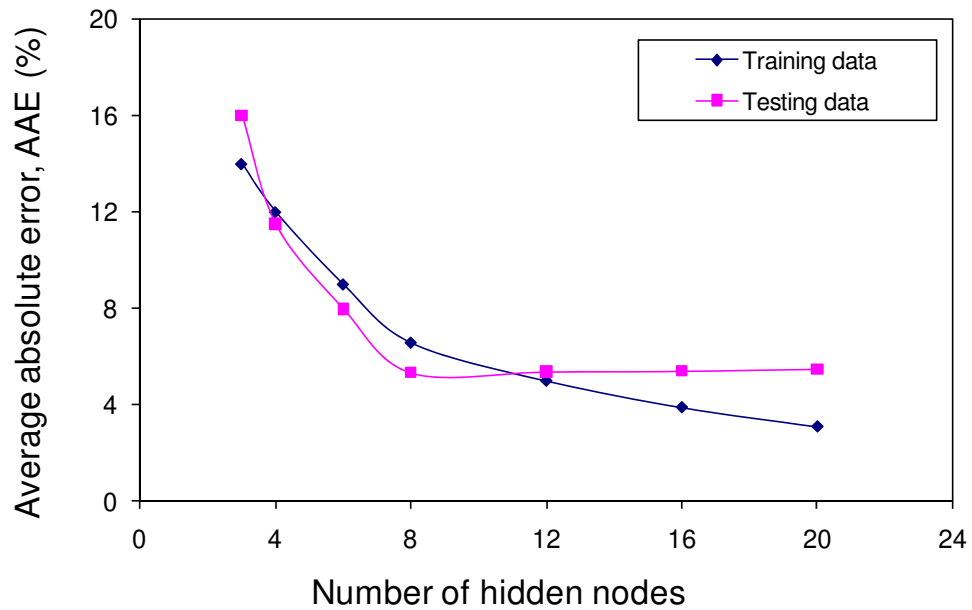


Figure 7.6 Selection of number of hidden layer nodes for OWC slurries prepared by partial replacement of RHA.

### 7.5.3. Training Process

Training a feed-forward back-propagation neural network involves teaching the network the relationships between the input parameters (shear rate, dosage of SCM, dosage of PCH, temperature) and the overall cement slurry rheology, and is usually performed in two stages: (i) feed-forward and (ii) back-propagation. The data flows from the input processing units to predict the desired network output. The obtained output is then compared with the predefined output and the difference is calculated. The error is then back propagated if the difference is greater than the predefined tolerance.

The success of the training process depends on (a) the selection of network parameters, (b) the algorithm used for learning, and (c) the validation of the model using experimental data available for training along with new testing data unfamiliar to the model. Specialized commercial computer software (Demuth et al., 2008) was used. Supervised training was implemented in this study by providing the network with sets of data (inputs/targets) and the

network was instructed what to learn. Parameters such as the learning rate and convergence tolerance used for the ANN are presented in Table 7.2. A training pattern consists of an input vector of 4 elements including the shear rate, dosage of corresponding SCM, dosage of PCH and temperature, and a corresponding output vector consisting of shear stress. The unipolar log-sigmoid (logsig) function and linear function were assigned as the transfer function for the processing units in the input-hidden layers and the hidden-output layers, respectively. The neurons were fully connected to the neurons in adjacent layers but no backward connection exists between neurons. No connection is permitted between neurons in the same layer as well. After completion of each learning process, the average sum-squared of all errors was calculated and back-propagated through the Levenberg-Marquardt (Demuth et al., 2008) algorithm to adjust the weights or connection strengths between the processing units. The Levenberg-Marquardt algorithm makes the leaning process faster and is based on the Jacobian matrix  $J$  that contains the first derivative of the network errors of corresponding weights and biases (Nehdi et al., 2001). An iteration of the algorithm can be expressed as:

$$W^{k+1} = W^k - [J^T J + \mu I]^{-1} J^T e \quad (7.3)$$

where  $W^k$  is a vector of current weights,  $\mu$  is a leaning rate,  $J$  is the Jacobian matrix,  $J^T$  is the transpose matrix of  $J$ ,  $I$  is the identity matrix, and  $e$  is a vector of network errors. This iterative process continues until the network converges, the mean square error (MSE) of the cross validation dataset increases, and a set of weights that minimizes the system error to the desired level, or the maximum number of iterations (epochs) provided for early stopping has been reached. Over fitting reduces the ability of the network to correctly predict the output of the unfamiliar data. Therefore, the network is considered generalized when the MSE of the cross validation data is minimized. Figure 7.7 represents the graphical representation of change in MSE value of the training and cross validation data patterns in the training process.

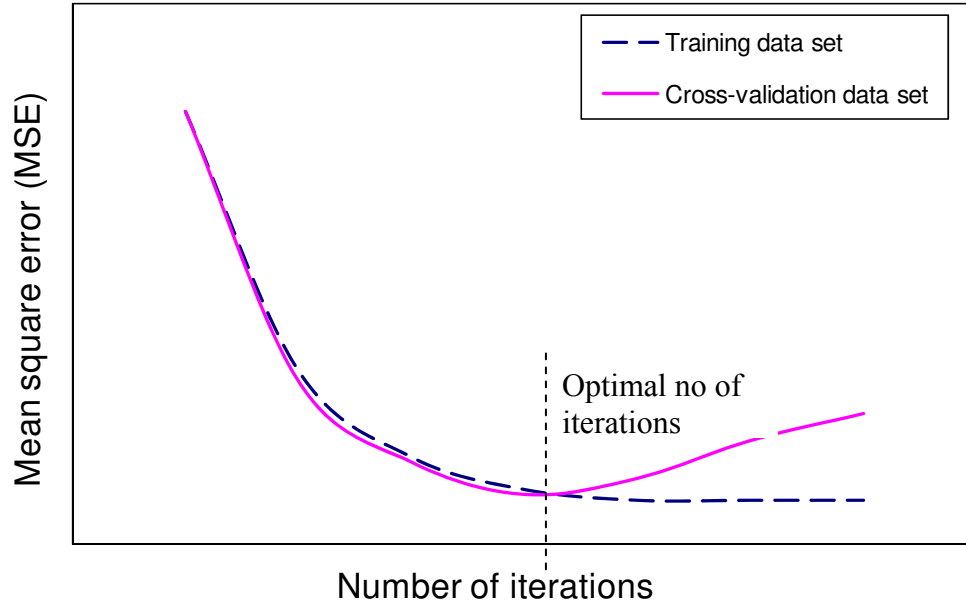


Figure 7.7 Graphical representation of the change in MSE of the training and cross-validation data set in training process.

## 7.6 Results and Discussion

A successful ANN is able to predict the corresponding output for new input parameters not previously used in the network training, but within the range of training patterns. The success of the training process must be evaluated and the quality of the model response to training patterns should be analyzed before testing the ANN to determine its ability to predict the output for new sets of input parameters involved in the rheology of OWC and SCM system.

### 7.6.1 Validation of ANN Model Using Training Data

The network model shown in Fig. 7.5 was trained using 780 training (input/target) pairs for each of the SCMs investigated, then tested using 120 pairs of data points unfamiliar to the network. The ANN model predicted the shear stress of the OWC slurries and the acceptability/rejection of the model was evaluated using the average absolute error (*AAE*) given by equation 7.4.

$$AAE = \frac{1}{n} \sum_{i=1}^n \frac{|Y_{measured} - Y_{predicted}|}{Y_{measured}} \quad (7.4)$$

where  $Y_{measured}$  and  $Y_{predicted}$  are the shear stress value of OWC slurries measured experimentally and the corresponding data predicted by the ANN, respectively, and  $n$  is the total number of data points.

Figures 7.8-7.11 illustrate the response of the ANN in predicting the shear stress of OWC slurries when OWC was partially replaced by MK, SF, RHA, and FA, respectively. The ANN model was capable of accurately predicting the shear stress corresponding to each set of input data. After successful completion of the training process, the network performance was checked with the input data set and the response in predicting the shear stress of OWC slurries incorporating MK were presented in Fig. 7.8(a). All data points were located on or in the vicinity of the equity line with an *AAE* of 5.44%. Fig. 7.9(a) represents the performance of the ANN model in predicting the shear stress of OWC slurries incorporating SF. The model was able to predict the shear stress of the cement slurries satisfactorily since the measured and corresponding predicted data points are located along the equity line with an *AAE* of 5.79%. For OWC slurries made with RHA as, the relationship between measured and predicted shear stress is presented in Fig. 7.10(a). The model was successfully trained to predict the shear flow with an *AAE* of 6.58%. Similarly, the network performance for OWC slurries with FA was found satisfactory with an *AAE* of 5.21% (Fig. 7.11(a)).

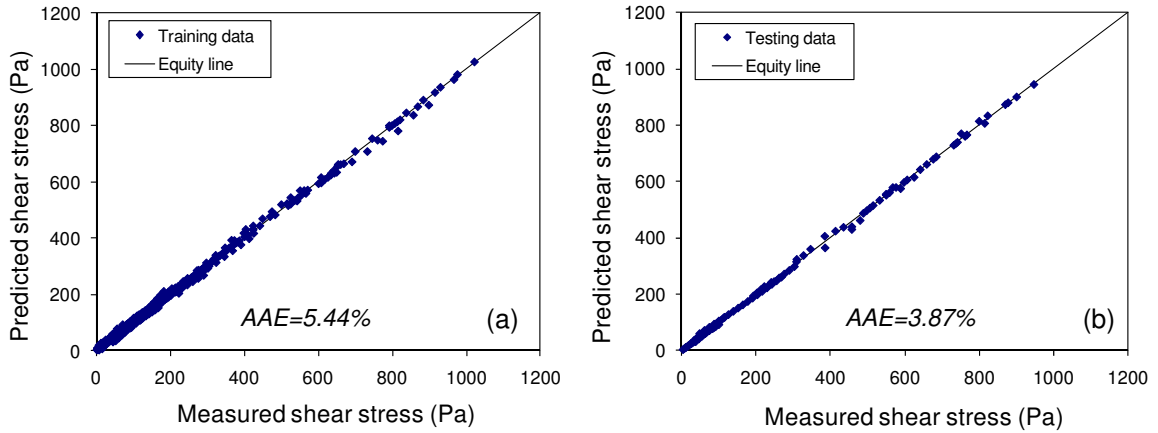


Figure 7.8 Measured versus predicted shear stress for OWC slurries at different temperature and dosage of PCH when MK was used as SCM to prepare slurries (a) Training data and (b) Testing Data.

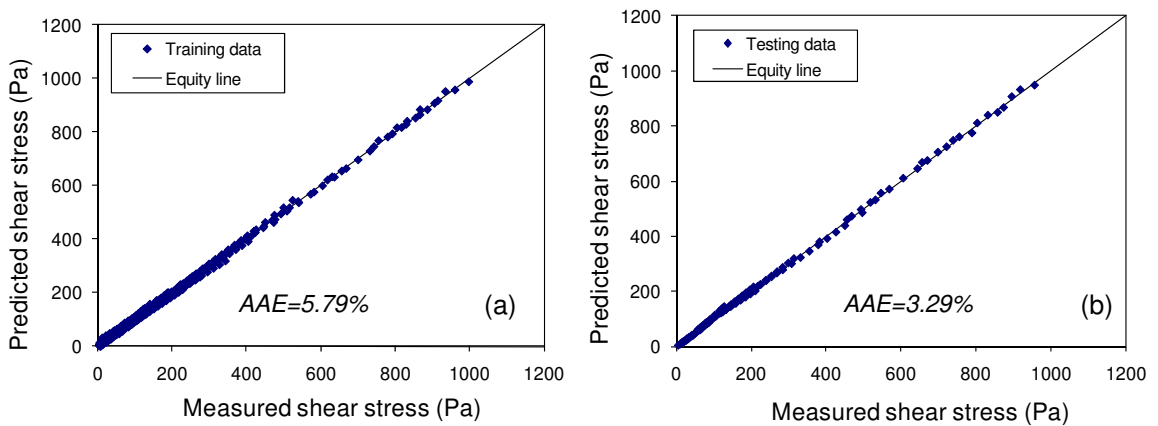


Figure 7.9 Measured versus predicted shear stress for OWC slurries at different temperature and dosage of PCH when SF was used as SCM to prepare slurries (a) Training data and (b) Testing Data.

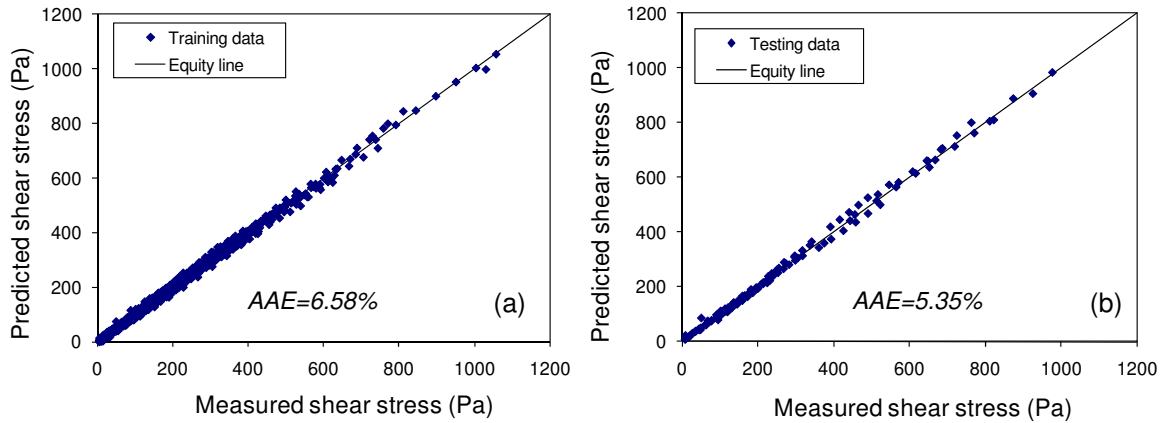


Figure 7.10 Measured versus predicted shear stress for OWC slurries at different temperature and dosage of PCH when RHA was used as SCM to prepare slurries (a) Training data and (b) Testing Data.

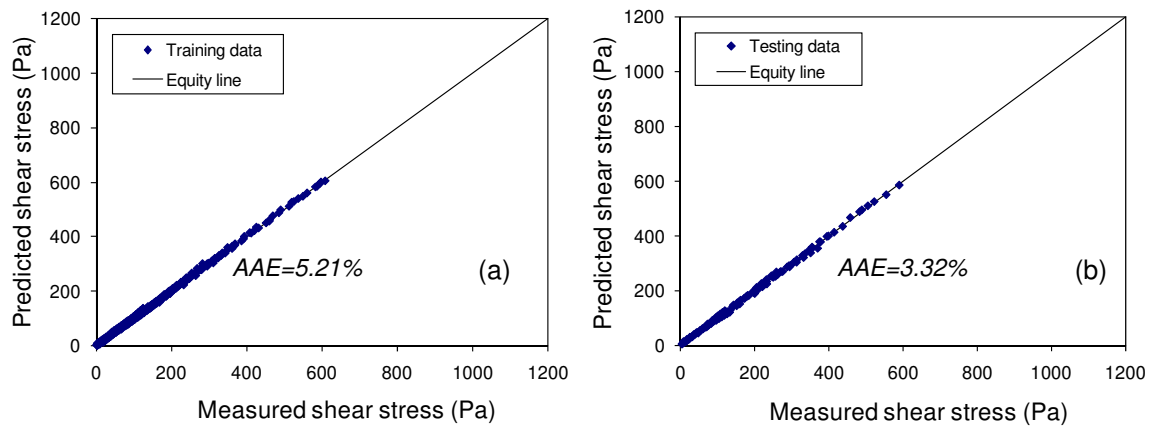


Figure 7.11 Measured versus predicted shear stress for OWC slurries at different temperature and dosage of PCH when FA was used as SCM to prepare slurries (a) Training data and (b) Testing Data.

### 7.6.2 Validation of ANN Model Using Test Data

The performance of the ANN model to predict the shear stress of new sets of unfamiliar data within the range of input variables of the training patterns determines the acceptance/rejection of the ANN. In order to validate the developed model, the network was

presented with 120 new sets of input data, which were not used during the training process. In this case, only an input vector of shear rate, dosage of admixture and temperature was presented to the network and no information or knowledge about the shear stress was provided. The response of the neural network is presented in Figs.8 (b), 9(b). 10(b) and 11(b) for OWC slurries incorporating MK, SF, RHA, and FA, respectively. The model predictions were appropriate since the testing points are located slightly over or under the equity line but within the cluster of training data with an *AAE* of 3.87, 3.29, 5.35, and 3.32% for slurries with MK, SF, RHA, and FA, respectively.

The average, standard deviation (*SD*), and coefficient of variation (*COV*) of the measured and predicted shear stress of OWC slurries and the average absolute error for all the testing and training data are presented in Table 7.3. The results reveal that the ANN model predicted the shear stress of OWC slurries incorporating SCMs with acceptable error.

Table 7.3 Performance of ANN in predicting the shear stress of cement slurries prepared with different supplementary cementitious materials

Type of admixture	<i>AAE</i> (%)		$Y_{measured}/Y_{predicted}$					
			<i>Average</i>		<i>SD</i> <sup>1</sup>		<i>COV</i> <sup>2</sup> (%)	
	Training	Testing	Training	Testing	Training	Testing	Training	Testing
MK	5.44	3.87	0.978	0.997	0.011	0.040	1.12	4.21
SF	5.79	3.29	1.013	1.001	0.080	0.110	7.89	10.99
RHA	6.58	5.35	0.983	0.989	0.012	0.089	1.22	8.99
FA	5.21	3.32	1.029	1.004	0.140	0.052	13.60	5.10

<sup>1</sup>*SD* :standard deviation, <sup>2</sup> $COV = SD / Average * 100$

### 7.6.3 Sensitivity Analysis of ANN in Predicting Rheological Properties of OWC slurries

The ANN model thus developed showed satisfactory performance in predicting the shear stress of OWC slurries incorporating MK, SF, RHA or FA. In order to examine the ability of the developed model to capture the effects of the individual input parameters on the desired output shear stress as well as on other rheological parameters such as yield stress and plastic viscosity, an attempt has been made to use the trained ANN to develop the down flow curve by randomly selecting one database pattern from the training data and subsequently creating other database patterns by changing the shear rate from 511 s<sup>-1</sup> to 5.11 s<sup>-1</sup> and keeping all other input parameters such as the PCH dosage, level of SCM and temperature unchanged.



The predicted shear stress versus shear rate curve thus obtained can be used to predict rheological properties such as the yield stress and plastic viscosity using the Bingham plastic model.

The sensitivity of the proposed model to temperature was first evaluated and one slurry mixture incorporating 10% for each of the SCMs with a PCH dosage of 0.5% was selected and used to develop the down flow curve by changing the shear rate from  $511 \text{ s}^{-1}$  to  $5.11 \text{ s}^{-1}$  for each of the temperature considered. The yield stress and plastic viscosity were determined using the Bingham plastic model. The yield stress was obtained by extrapolating the shear stress-shear rate curve corresponding to a zero shear rate, and the plastic viscosity was the slope of the curve. In addition to test temperatures ( $23^{\circ}\text{C}$ ,  $45^{\circ}\text{C}$  and  $60^{\circ}\text{C}$ ), rheological parameters were also determined at  $35^{\circ}\text{C}$  and  $52^{\circ}\text{C}$  in order to predict the model's response within the range of input data.

Figure 7.12 illustrates the predicted yield stress and plastic viscosity values for OWC slurries when OWC was replaced by 10% SCM at different temperatures. A different scale was used so as to better predict the variation of experimental and model-predicted data for each SCMs. Both yield stress and plastic viscosity values predicted by the ANN followed the same trend as that of the experimental data. The yield stress and plastic viscosity were found to be sensitive to the change in temperature; the higher the temperature the higher was the yield stress and plastic viscosity, which is in good agreement with experimental results.

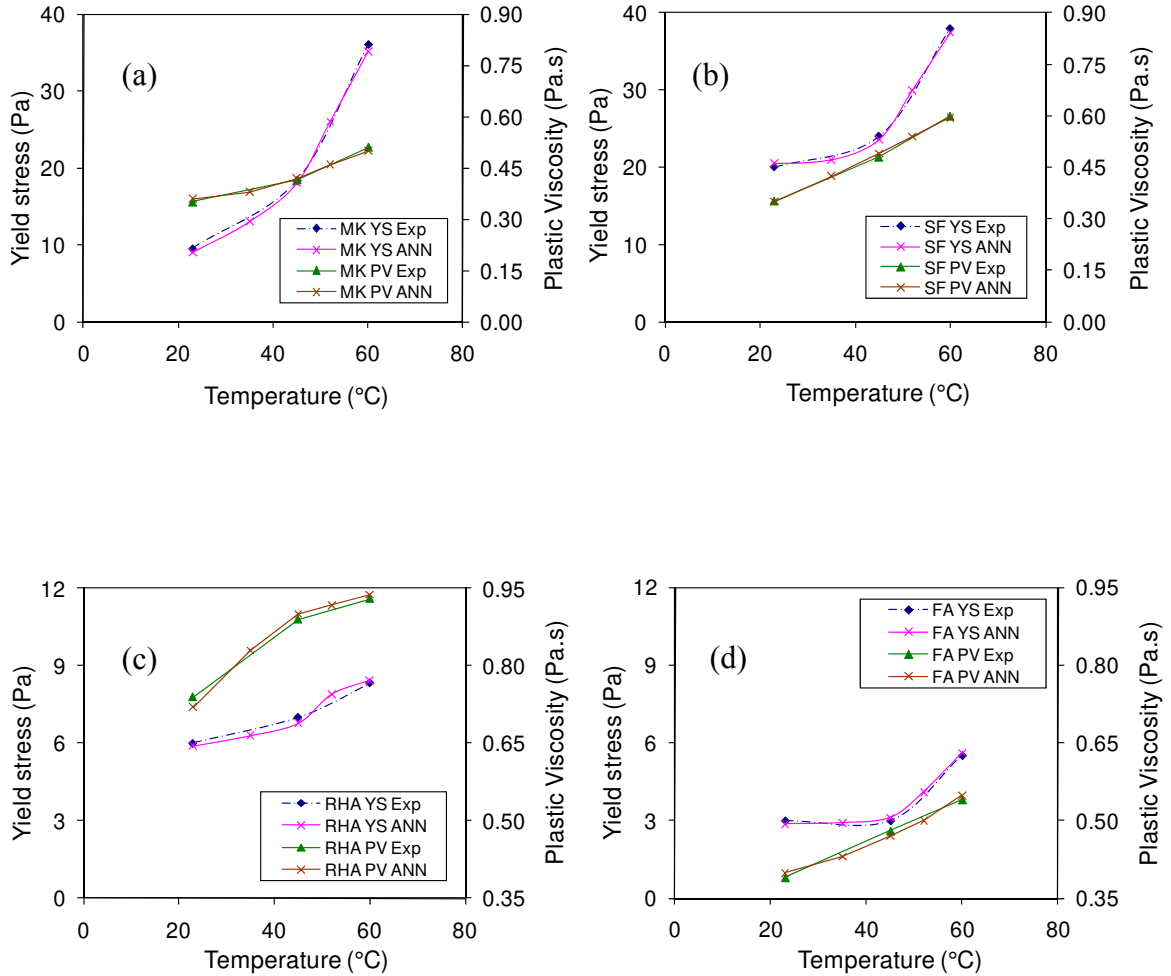


Figure 7.12 Variation of rheological properties with temperature for OWC slurries prepared with 10% replacement of OWC by (a) MK, (b) SF, (c) RHA, and (d) FA with 0.5% PCH.

In order to evaluate the sensitivity of the proposed model to the effect of the dosage of SCM on the predicted rheological parameters of cement slurries, input parameters such as the shear rate and dosage of SCM were varied from  $511 \text{ s}^{-1}$  to  $5.11 \text{ s}^{-1}$ , and 5 to 15%, respectively, while the temperature and PCH dosage were kept constant at  $60^\circ\text{C}$  and 0.5%, respectively. Figure 7.13 illustrates the variation of yield stress and plastic viscosity of OWC slurries at a temperature of  $60^\circ\text{C}$ . SCM dosages (7 and 12%) not used in experiments were also included in ANN model predictions. The yield stress was found to decrease when the API Class G OWC was partially replaced by FA and RHA and to increase when replaced by SF and MK, which conforms to findings of the experimental investigation. The plastic viscosity of OWC

slurries was found to increase with the incorporation of MK, SF and RHA as partial replacement for OWC and to decrease with the use of FA, which is in accordance with the experimental results.

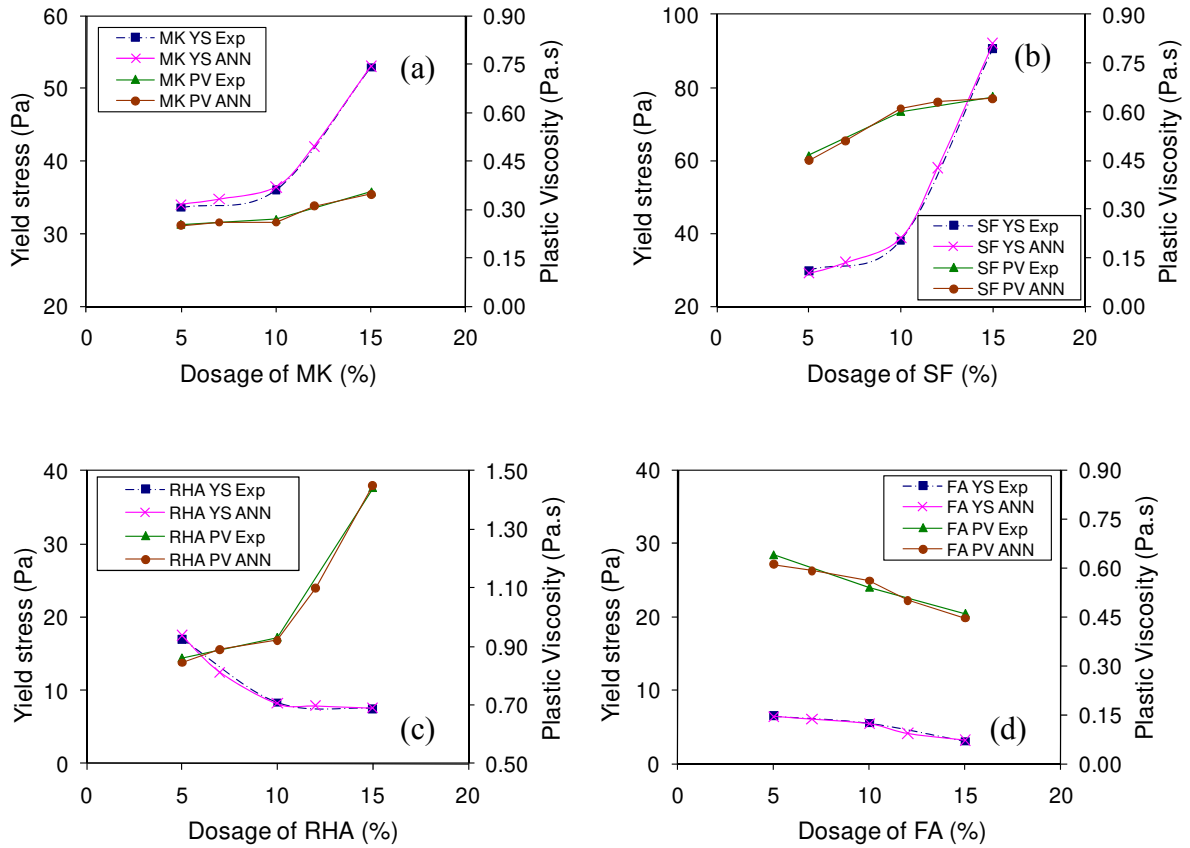


Figure 7.13 Variation of rheological properties with dosage of SCM for OWC slurries prepared by partial replacement of (a) MK, (b) SF, (c) RHA, and (d) FA at 60°C and with 0.5% PCH.

Figure 7.14 reveals the sensitivity of the ANN model to the PCH dosage for OWC slurries incorporating 10% SCM at 60°C. Predicted values of yield stress decreased with higher PCH dosage, which is in good conformity with experimental results. It can be observed that the variation of yield stress with admixture dosage was reasonably estimated for all PCH dosages considered and the predicted values were comparable to the corresponding measured data. Moreover, the plastic viscosity of OWC slurries was found to be sensitive to the PCH dosage. Plastic viscosity was found to decrease with higher PCH dosage for all the SCM

considered, except when OWC was replaced by MK. In the case of MK, plastic viscosity continued to decrease up to a PCH dosage of 1% and then started to increase, which is in good agreement with the experimental findings.

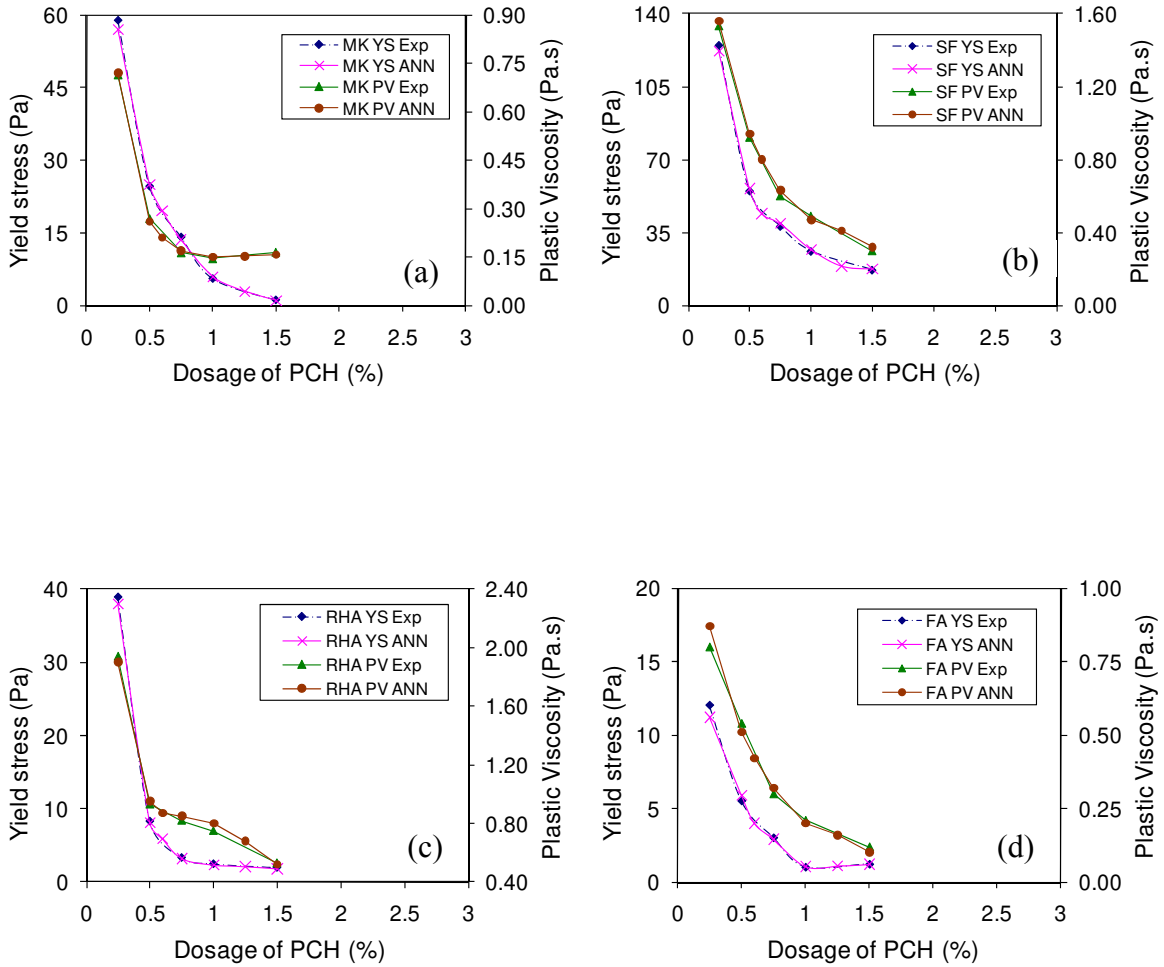


Figure 7.14 Variation of rheological properties of OWC slurries with dosage of PCH at 60°C and 10% replacement of OWC by (a) MK, (b) SF, (c) RHA, and (d) FA.

Figures 7.12 to 7.14 illustrate that the ANN-model was able to recognize and evaluate the effects of temperature, dosage of SCM and PCH on yield stress and plastic viscosity of OWC slurries with an *AAE* in the range of 1.11 to 8.07% and 0.92 to 15.87% for yield stress and plastic viscosity, respectively. The higher values of *AAE* are usually associated with the

lower yield stress and plastic viscosity values since small prediction errors may result in high *AAE* in such cases.

## 7.7 Conclusion

The relationships amongst the shear stress, shear rate, temperature, type and dosage of supplementary cementitious material, and dosage of PCH admixture for OWC slurries have been analyzed and the rheological properties were modeled using a feed forward back-propagation artificial neural network. The model was then used to develop flow curves, which were used to calculate the yield stress and plastic viscosity values for OWC slurries with different SCMs and at different test temperatures. Based on this study, the following conclusions can be made:

- The feed-forward back-propagation ANN architecture that resulted in optimum performance was selected based on a trial-and-error approach.
- The trained ANN accurately learnt the relationships between the different shear flow parameters for various OWC slurries incorporating SCMs such as metakaolin, silica fume, rice husk ash and fly ash, and successfully predicted the rheological properties of OWC slurries used in the training process.
- The ANN model also showed satisfactory performance in predicting the rheological properties when input parameters (shear rate, temperature, and dosage of SCM and PCH admixture) unfamiliar to the neural network were used as input.
- The flow curves developed using the ANN model allowed predicting the Bingham parameters (yield stress and plastic viscosity) with an acceptable accuracy and were found to be in good agreement with experimental results.
- The neural network proved to be a powerful tool to quantitatively predict the rheological properties of OWC within the range of tested admixture dosages and test temperatures.

- A sensitivity analysis was performed to study the effects of individual input parameters on the rheological properties of OWC slurries. Irrespective of the type and dosage of SCM used, the ANN model successfully captured the rheological behavior of OWC slurries with variation of input parameters.
- The ANN model was found to generalize its predictions beyond the training data to new slurries incorporating different dosages of admixtures (PCH and SCM) and considering different temperatures within the practical range of training data.
- Based on the performance of the developed ANN-model, it can be used to develop OWC slurries with desirable rheological properties without the need for an exhaustive number of trial batches as in the case in current practice.
- The predictive capability of the ANN model is limited to data located within the boundaries of the training range. However, the model can be retrained to a wider data range of input variables when new experimental data becomes available.

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*Chapter 8***OPTIMIZATION OF RHEOLOGICAL PROPERTIES OF OIL WELL CEMENT SLURRIES USING EXPERIMENTAL DESIGN****8.1 Introduction**

The rheology of oil well cement (OWC) slurries affects the primary oil well cementing job. Thus, a fundamental knowledge of the rheology of OWC slurry is necessary to evaluate the mix-ability and pump-ability of the slurry, optimize mud removal and slurry placement, and to predict the effect of wellbore temperature on slurry placement (Guillot, 2006). The rheology of cement slurries is complex since it is a manifestation of various interactions between the cement particles, water and other constituents, time and temperature. Cement slurries are visco-elastic materials that exhibit properties characteristic of both elastic solids and viscous fluids.

To characterize the rheology of a cement slurry, rheological parameters such as the yield stress, apparent viscosity, plastic viscosity, shear thinning, or shear thickening behaviour need to be studied. The Bingham plastic model and the Power law are widely used to describe the rheological properties of cement slurries (Guillot 2006). The Bingham plastic model includes both yield stress,  $\tau_y$  and a limiting viscosity,  $\mu_p$  at finite shear rates. The yield stress indicates the minimum effort needed for a material to start moving and is the intercept of the flow curve (shear stress vs. shear rate) with the shear stress axis. Below the yield stress, a material behaves like a solid. Yield stress is the contribution of the skeleton, i.e. it is a manifestation of friction among solid particles (Ferraris and Larrard, 1998). Plastic viscosity governs the flow after it is initiated and is the contribution of suspending liquids resulting from viscous dissipation due to the movement of water in the sheared material (Ferraris and Larrard, 1998, Laskar and Talukdar 2008). Plastic viscosity is the slope of the fitted straight line of the flow curve. The plastic viscosity of a cement slurry is usually evaluated using the linear portion of the down curve of the hysteresis loop.

Supplementary cementitious materials (SCMs) are increasingly being used considering their significant sustainability and economic benefits. Moreover, chemical admixtures play an

important role in controlling the early-age and hardened properties of cement based systems. However, because of their different physical and chemical properties, not all SCMs act in a similar manner with respect to rheological properties. For example, owing to its spherical particle shape, fly ash (FA) reduces the water demand when used as a partial replacement for cement. Conversely, silica fume (SF) increases the water demand by adsorbing water due to its very high surface area. Indeed, rheological parameters can exhibit an increase or decrease depending on the type of cement, time and temperature, admixture used, particle shape and size distribution, type, replacement level, and loss on ignition of the SCM used.

A number of researches have been performed over the last few decades to characterize the properties of cement based materials incorporating SCMs. Nonetheless, information regarding the influence of SCMs on the rheological properties of OWC slurries is less abundant. For instance, the current knowledge on metakaolin (MK) is generally centered on its pozzolanic behaviour and effect on cement hydration and concrete properties. It was reported that MK had adverse effects on the workability of concrete (Sabir et al. 2001). Golaszewski et al. (2005) performed Two-Point Workability tests on modified mortar and found that the addition of MK had lower influence on yield stress than on plastic viscosity. The degree of such an influence depends on the type of cement, properties of the superplasticizer, and the metakaolin content. The effects of other SCMs, such as SF and FA, on the rheological properties were also investigated. It was found that MK had less influence on rheological properties than SF and FA.

It was argued that there exists a threshold value of SF partial replacement for cement, beyond which both yield stress and plastic viscosity of concrete increase with increasing SF content (Tattersall, 1991). Faroug et al. (1991) observed that yield stress increased up to a 20% SF replacement level and then started to decrease. Plastic viscosity was found to decrease up to 10% SF and then it started to increase at higher levels of SF (Faroug et al., 1991). Park et al. (2005) found that both yield stress and plastic viscosity exhibited steep increases with the increase in condensed SF up to 15% replacement level. Nehdi et al. (1998) found that SF, when used as partial replacement for cement, increased the amount of superplasticizer needed to maintain a constant workability. Similar finding was also observed by Ferraris et al. (2001) who reported that the replacement of cement by SF significantly increases the high range water reducing (HRWR) admixture dosage at a given yield stress and plastic viscosity.

Laskar and Talukdar (2008) studied the effect of RHA on the rheological properties of Ordinary Portland Cement (OPC) concrete and found that yield stress decreased and plastic viscosity increased when RHA was used as partial replacement for OPC. Nehdi et al. (2003) found that the replacement of cement by RHA resulted in increased water demand and reduced concrete workability. However the water requirement for all RHA samples tested was lower than that of SF mixtures despite that some RHAs had higher surface area than that of SF.

The flow behaviour of pure FA paste is similar to that of cement paste (Sybert and Reick 1990). Sybert and Reick (1990) found that rheological properties vary linearly when cement is partially replaced by FA. A small change in the FA ash properties can cause large changes in the flow properties. Bunn et al. (1990) investigated the effect of temperature on FA ash slurry rheology and found that the apparent viscosity decreased with increasing temperature. Ferraris et al. (2001) found that partial replacement of cement by FA led to a decrease in the HRWR admixture dosage at a given yield stress and plastic viscosity. Tattersall (1991) found that yield stress decreased moderately, while the plastic viscosity decreased slightly when FA was used as partial replacement for cement. Banfill (1994) found that both yield stress and plastic viscosity decreased with the increase in FA content. Laskar and Talukdar (2008) report that the addition of increasing levels of up to 30% FA led to a decrease in the yield stress of concrete, then yield stress slightly increased up to a 50% FA level. The plastic viscosity was found to exhibit an irregular behaviour. It increased up to 10% FA and then decreased gradually up to 30% FA. Beyond this level, change in plastic viscosity was not significant (Laskar and Talukdar, 2008).

A number of researches (e.g. Menezes et al., 2010; Yahia and Khayat, 2002; Sonebi, 2001, 2002, 2010; Nehdi et al., 1997, Khayat et al., 1999) used statistical approaches to select mixture proportioning for cementitious systems. For example, Al-Darbi et al. (2006) used factorial design of experiments to evaluate the effects of human hair fibers on the reduction of shrinkage cracking of mortar considering the cement/sand ratio, water/cement ratio, and human hair fibers content as design parameters. These statistical methods provide greater efficiency and confidence in the results obtained, and could optimize the tested systems with a minimum number of experiments. Using this approach in the oil well cementing and petroleum industry is fairly new. For instance, Cestari et al. (2009) used  $2^3$  full-factorial

design to study the effects of temperature and HCL concentration on the adsorption of HCL onto API class A cement slurries.

The present study aims at evaluating the effects of temperature, superplasticizer dosage, and the type and level of SCM partial replacement for cement on the rheological properties of OWC slurries using a statistical approach and design of experiments. The statistical model thus developed could be used to evaluate the effects of experimental parameters and their interactions on the rheological properties of OWC slurries. It can also be used for tailoring OWC slurry mixtures to meet specific rheological requirements.

The optimization of OWC slurries often requires a number of trial batches to achieve adequate rheological properties. This is usually labor intensive and time consuming. A factorial experimental design approach was used in this study to determine the influence of temperature and key mixture design parameters such as the superplasticizer dosage and type and level of SCM used as partial replacement for cement, along with interactions between these parameters on the rheological properties of OWC slurries. A predictive model has been developed, which can simplify the test protocol required to achieve an optimum balance among various parameters for achieving a specific rheological performance of OWC slurries.

## **8.2 Materials**

The OWC slurries tested in this study for developing a predictive statistical model were prepared using a high sulphate-resistant API Class G OWC with a specific gravity of 3.14. De-ionized distilled water was used for the mixing, and its temperature was maintained at  $23\pm 1^\circ\text{C}$  using an isothermal container. The incorporated SCMs included MK, SF, RHA, and low calcium FA with an OWC partial replacement level ranging from 5 to 15%. The chemical and physical properties of the cement and SCMs are summarized in Table 5.1 (Chapter 5). A new generation polycarboxylate-based high-range water reducing admixture (PCH) was used as the chemical admixtures to prepare the OWC slurries at a water-to-cement mass ratio (w/c) of 0.44.

### 8.3 Test Procedure

The OWC slurries were prepared using a variable speed high-shear blender type mixer with bottom drive blades as per the ANSI/API Recommended Practice 10B-2 (2005) at a controlled ambient room temperature of  $23\pm 1^\circ\text{C}$ . The prepared slurry was then placed into the bowl of a mixer for preconditioning (at 150 rpm) over 20 minutes at the specific test temperature ( $23^\circ\text{C}$ ,  $45^\circ\text{C}$ , or  $60^\circ\text{C}$ ). The total time between the beginning of mixing and the start of the rheological tests was kept constant for all slurries to avoid the effects of exogenous variables on the results.

A high accuracy advanced rheometer (TA instruments AR 2000) (Fig. 4.1 (Chapter 4)), capable of continuous shear rate sweep, stress sweep and strain sweep was used throughout this study to measure the rheological properties of cement slurries. The rheometer set-up was also maintained constant for all tested slurries. The concentric cylinder test geometry was maintained at the test temperature so as to avoid sudden thermal shock of the slurry. The cement slurry sample was placed in the coaxial cylinder of the rheometer after mixing and preconditioning. The sample was subjected to a stepped ramp or steady state flow once the temperature of the rheometer was adjusted to the required level, and rheological measurements were taken at 20 different shear rates starting from  $5.11\text{ s}^{-1}$  up to  $511\text{ s}^{-1}$  after a continuous rotation of 10 sec at each level. The data were also measured at a descending shear rate from  $511\text{ s}^{-1}$  to  $5.11\text{ s}^{-1}$  to obtain the down flow curve. The schematic representation of the viscometric testing scheme illustrated in Fig. 5.1 (Chapter 5) has been used in this study.

### 8.4 Experimental Results

The Bingham plastic model (equation 8.1) was used in this study to calculate the yield stress and plastic viscosity from the shear rate-shear stress down-curve. The down-curve was chosen since it better fits to the Bingham plastic model than the up-curve (Ferguson and Kenblowski 1991).

$$\tau = \tau_y + \mu_p \dot{\gamma} \quad (8.1)$$

Where,  $\tau$ ,  $\tau_y$ ,  $\mu_p$ , and  $\dot{\gamma}$  represent the shear stress, yield stress, plastic viscosity, and shear rate, respectively.

The effect of the type and dosage of SCM on the yield stress and plastic viscosity of OWC slurries at different test temperatures, namely 23, and 60°C are presented in Figs. 8.1 and 8.2, respectively. It is revealed that the Bingham parameters (yield stress and plastic viscosity) are very much dependent on test variables such as the temperature, type and level of SCM and PCH dosage. For instance, the yield stress was found to increase with the addition of MK or SF and to decrease with the incorporation of RHA or FA. Incorporating FA caused the plastic viscosity of OWC slurries to decrease, while this value increased with the addition of other SCMs. Due to such variations, individual statistical models have been developed for each of these SCMs.

Figure 5.6 (Chapter 5) illustrates the variation of yield stress of OWC slurries incorporating varying dosages of SCMs and PCH at a w/b ratio of 0.44. Different scales have been used to represent results for FA and RHA due to their much lower yield stress values compared to those for MK and SF. It can be observed that for all SCMs used, yield stress generally decreased with PCH addition and this decrease was generally gradual until reaching a saturation dosage. However, for each SCM, the saturation dosage depended on the SCM dosage and temperature. It can be further observed from Fig. 5.6 that regardless of the dosage of SCM and PCH, the higher the temperature, the higher was the yield stress, which is due to the higher rate of hydration reactions at higher temperature. Yield stress decreased with PCH addition for all SCMs, yet the dosages required were higher in the case of SF and MK. Plastic viscosity values of the OWC slurries were measured as the slope of the down flow curve of the hysteresis loop and plotted in Fig. 5.7 (Chapter 5). In general, plastic viscosity was found to increase with the increase of test temperature and to decrease with the increase of PCH dosage.

### 8.5 Factorial Design Approach

A second order  $2^k$  central composite response surface model was used in this study to evaluate the influence of two different levels for each variable on the rheological properties of OWC slurries. The three experimental parameters for the rheological model are the PCH dosage, type and level of SCM, and temperature. Considering the nonlinear interactions between the variables, a second order central composite design (CCD) was selected to quantify the predicted responses (yield stress and plastic viscosity) for each SCM used using the following relationships:

$$\tau_0 = a_0 + \sum_{i=1}^3 a_i x_i + \sum_{i=1}^3 a_{ii} x_i^2 + \sum_{i<j} a_{ij} x_i x_j + \varepsilon \quad (8.2)$$

$$\mu_p = b_0 + \sum_{i=1}^3 b_i x_i + \sum_{i=1}^3 b_{ii} x_i^2 + \sum_{i<j} b_{ij} x_i x_j + \varepsilon \quad (8.3)$$

where,  $a_0$ ,  $a_i$ ,  $a_{ii}$ ,  $a_{ij}$ ,  $b_0$ ,  $b_i$ ,  $b_{ii}$ , and  $b_{ij}$  are regression coefficients, and  $\tau_0$ ,  $\mu_p$ ,  $\varepsilon$ ,  $x_1$ ,  $x_2$  and  $x_3$  are yield stress, plastic viscosity, noise or error observed in the responses, temperature, level of SCM, and dosage of PCH, respectively.

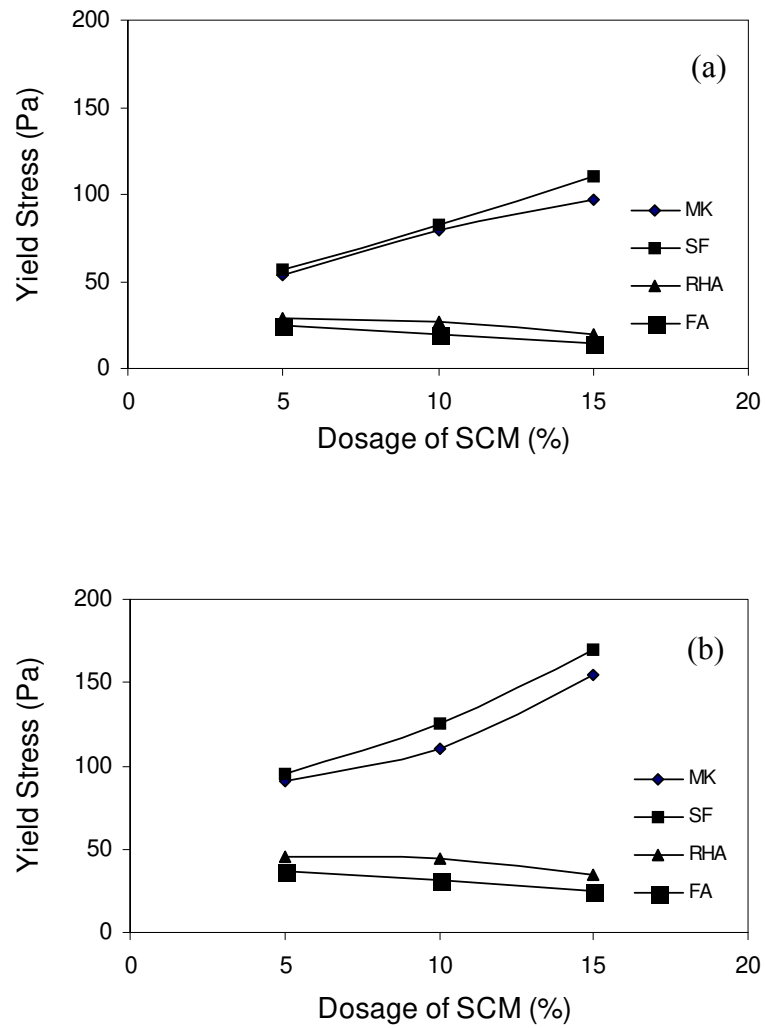


Figure 8.1 Variation of yield stress of OWC slurries with type and dosage of SCM at (a) 23°C, and (b) 60°C.



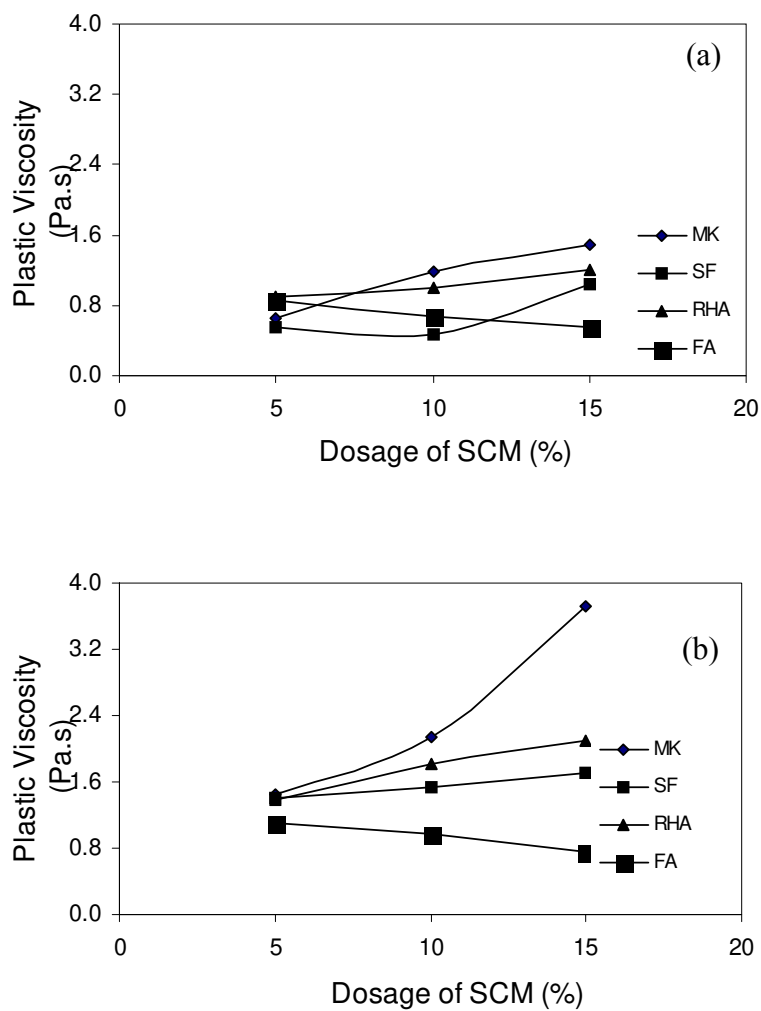


Figure 8.2 Variation of plastic viscosity of OWC slurries with type and dosage of SCM at (a) 23°C, and (b) 60°C.

This two-level factorial design requires a minimum number of tests. In this study  $k = 3$ ; thus the total number of factorial points is  $2^3 = 8$ . The error in predicting the responses increases with the distance from the center of the modeled region (Montgomery, 2009). Therefore, the use of the models is limited to the area bounded by the coded values ranging from  $-\alpha$  to  $+\alpha$ . In order to provide a reasonably consistent and stable variance of the predicted response, the model needs to be rotatable. CCD is made rotatable by the choice of  $\alpha$ , which in turn depends on the number of slurries in the factorial design. It has been reported (Montgomery, 2009) that  $\alpha = (n_f)^{1/4}$  produces a rotatable central composite design where  $n_f$  is the number of points used in the factorial portion of the design. In the present study, the two values of  $\alpha$  were chosen as  $\pm 1.68$ , and the coded variables of the mixtures ranged between -1.68 to +1.68 as summarized in Table 8.1. Parameters were carefully selected to carry out CCD to evaluate the effect of each factor at five different levels in codified values of  $\pm\alpha$  (axial points),  $\pm 1$  (factorial points), and center point.

Table 8.1 Coded and absolute values for investigated parameters

Parameter	-1.68	-1	Center point	+1	+1.68
Dosage of PCH (%)	0.00	0.25	0.88	1.50	1.92
Dosage of SCM (%)	1.60	5.00	10.00	15.00	18.50
Temperature (°C)	10.50	23.00	41.50	60.00	72.50

The results of single replication for yield stress and plastic viscosity from a total of 40 mixture combinations of OWC slurry for each type of SCM were considered in the experimental design of OWC slurries to calculate the coefficients of the regression equations. Iterations were conducted until reliable statistical models were obtained for yield stress and plastic viscosity as a function of the PCH dosage, level of SCM, and temperature. Five replicate center points were used to calculate the noise or degree of experimental error for the modelled responses. Then six different slurry mixtures (Table 8.2) were used to verify the accuracy of the model. The coded factors of variables are calculated as follows:

$$\text{Coded factor} = (\text{Absolute value} - \text{Factor mean}) / (\text{Range of the factorials values} / 2) \quad (8.4)$$

$$\text{Coded value of dosage of PCH} = (\text{Absolute value} - 0.875) / 0.625 \quad (8.5)$$

$$\text{Coded value of dosage of SCM} = (\text{Absolute value}-10)/ 5 \quad (8.6)$$

$$\text{Coded value of temperature} = (\text{Absolute value}-41.5)/ 18.5 \quad (8.7)$$

Table 8.2 Coded and absolute values for mixture proportions used in validation models

Mix	Dosage of PCH		Dosage of SCM		Temperature	
	Absolute	Coded	Absolute	Coded	Absolute	Coded
46	60	1.00	5	-1	1	0.20
47	45	0.19	15	1	1.5	1.00
48	50	0.46	7.5	-0.5	0.5	-0.60
49	23	-1.00	10	0	1	0.20
50	30	-0.62	12.5	0.5	0.75	-0.20
51	60	1.00	15	1	1.25	0.60

## 8.6 Discussion

The yield stress and plastic viscosity of OWC slurries resulting from the experimental program were analysed using a statistical software package (Design-Expert 8.0.3, 2010). The statistical analysis involved the fitting of mathematical equations to the experimental results to get the entire response surface of yield stress and plastic viscosity for each of the SCMs used. Subsequently, validation of the model was carried out through an analysis of variance (ANOVA).

The second order response surface model for the yield stress and plastic viscosity of OWC slurries using CCD with two-level factorial design of three independent variables (temperature (Temp), level of SCM (SCM) and PCH dosage (PCH)) is as follows:

$$\begin{aligned} \tau_0 = & a_0 + a_1 \times \text{Temp} + a_2 \times \text{SCM} + a_3 \times \text{PCH} + a_4 \times \text{Temp} \times \text{SCM} + a_5 \times \text{Temp} \times \text{PCH} \\ & + a_6 \times \text{SCM} \times \text{PCH} + a_7 \times \text{Temp}^2 + a_8 \times \text{SCM}^2 + a_9 \times \text{PCH}^2 + \varepsilon \end{aligned} \quad (8.8)$$

$$\begin{aligned} \mu_p = & b_0 + b_1 \times \text{Temp} + b_2 \times \text{SCM} + b_3 \times \text{PCH} + b_4 \times \text{Temp} \times \text{SCM} + b_5 \times \text{Temp} \times \text{PCH} \\ & + b_6 \times \text{SCM} \times \text{PCH} + b_7 \times \text{Temp}^2 + b_8 \times \text{SCM}^2 + b_9 \times \text{PCH}^2 + \varepsilon \end{aligned} \quad (8.9)$$

where,  $a_0$  and  $b_0$  denote the overall mean of the total effect estimates of all factors for yield stress and plastic viscosity, respectively; coefficients  $a_1$  to  $a_9$  and  $b_1$  to  $b_9$  refer to the contribution of the corresponding factor to the response, which is calculated as one half of the corresponding factor effect estimates; and  $\varepsilon$  is the random error term representing the effects of the uncontrolled variables.

The least square approach was used to estimate the coefficients of the model parameters. Power transformation of the corresponding responses (yield stress or plastic viscosity) was used to accommodate large differences between minimum and maximum values of the response variable. A maximum-to-minimum ratio of less than 3 usually has less influence on the power transfer, whereas transformation is required when the ratio is greater than 10 (Design-Expert 8.0.3, 2010). Different transformation factors have been used in this study based on a Box-Cox plot (Montgomery 2009). The interaction between the considered three input parameters and the responses were also accounted for during the regression analyses and expressed in terms of  $t$  values and probability ( $Prob.$ )  $>|t|$  values. The probability value indicates the likelihood that the result obtained in a statistical test is due to chance rather than to a true relationship between the parameters (Genentech, 2010; Montgomery, 2009). The effects of the input parameters on the output parameters are considered highly significant when  $t$  values are high and probability values are low. The parameter is often considered nonzero and significantly influences the response of the model when the probability values are less than 5% (Montgomery, 2009).

The ANOVA of derived statistical models for yield stress and plastic viscosity of OWC slurries prepared using SCM (MK, SF, RHA and FA) is presented in Tables 3 and 4, respectively. The coded coefficient and ( $Prob.$ )  $>|t|$  values provide a comparison of the effects of various parameters as well as their interactions on the modelled responses. ANOVA is used to test the significance of the model regression; and  $t$  test values based on student's distribution are used to identify the significant variables and second order interactions of the variables involved. The ( $Prob.$ )  $>|t|$  value of the model term is considered significant when the values are less than 0.05, and insignificant when the value is greater than 0.10. A negative coefficient indicates that an increase of a given parameter causes a reduction of the measured response. For example, increasing the temperature and MK dosage increased the yield stress of OWC slurries, whereas an increase in the PCH dosage reduced the yield stress value

(Table 8.4). A higher coefficient signifies greater influence on the response and vice versa. The presence of parameter interactions with coupled terms (e.g.  $Temp \times Temp$ ) indicates that the influence of the parameter is quadratic. The effects of second order interaction between parameters (e.g. Temp-SCM, Temp-PCH or SCM-PCH) on rheological properties are discussed later in this text.

The derived quadratic models for the yield stress and plastic viscosity of OWC slurries incorporating four different SCMs (MK, SF, RHA and FA) as partial replacement for OWC are presented in Table 8.5, where Temp, SCM and PCH are given in coded values. Comparing the values of the model coefficients in Table 8.5, it can be deduced that the yield stress of OWC slurries increased with temperature and decreased with higher PCH dosage for all SCMs used. Moreover, the addition of SCM can increase or decrease the yield stress value depending on the type of SCM. The yield stress of OWC slurries increased in the case of MK and SF addition, and decreased in the case of RHA and FA. Likewise, plastic viscosity increased with the increase of temperature, irrespective of the type of SCM used.

The significance of the derived models was evaluated by comparing the  $F$  test values (Table 8.6) to the  $F_{0.05, \nu_1, \nu_2}$  values tabulated in the Fisher distribution (Montgomery, 2009), where  $\nu_1$  and  $\nu_2$  are the degree of freedom of the model and model error, respectively. For a 95% confidence interval, the  $F_{0.05, 9, 5}$  value is 8.81. All the  $F$  values presented in Table 8.6 were at least six fold higher than the tabulated values, which implies that the developed models are significant in describing the coupled effects of temperature, PCH and SCM. The  $(Prob.) > F$  value indicates that there is only 0.01% chance that such a "Model F-Value" could occur due to noise.

The average measured response of the five replicate slurries for each SCM along with the estimated errors with 95% confidence intervals for each response are presented in Table 8.7. The estimated errors provide information about the relative experimental errors and repeatability of the test results for yield stress and plastic viscosity of OWC slurries incorporating SCMs.

Table 8.3 ANOVA of yield stress for OWC slurries with different SCMs

	Metakaolin		Silica Fume		Rice hush ask		Fly ash	
	$R^2=0.962$		$R^2=0.954$		$R^2=0.961$		$R^2=0.972$	
	Coefficient	(Prob.)> t	Coefficient	(Prob.)> t	Coefficient	(Prob.)> t	Coefficient	(Prob.)> t
Intercept	1.7670		2.5510		1.1890		0.6890	
A-Temp	0.1900	0.0026	0.4350	< 0.0001	0.3470	< 0.0001	0.0470	< 0.0001
B-SCM	0.4690	< 0.0001	0.7340	< 0.0001	-0.3800	< 0.0001	-0.0590	< 0.0001
C-PCH	-1.5720	< 0.0001	-1.3790	< 0.0001	-1.2490	< 0.0001	-0.2150	< 0.0001
AB	-0.0160	0.8157	-0.0630	0.3772	-0.0400	0.4320	-0.0070	0.3261
AC	-0.6550	< 0.0001	-0.3120	0.0007	-0.0760	0.2165	0.0200	0.0239
BC	-0.3930	< 0.0001	-0.5190	< 0.0001	-0.0120	0.8480	0.0060	0.4991
A <sup>2</sup>	0.1180	0.2662	0.2590	0.0190	0.0370	0.6270	-0.0340	0.0025
B <sup>2</sup>	0.4380	< 0.0001	0.2140	0.0413	-0.1480	0.0478	0.0140	0.1575
C <sup>2</sup>	1.2960	< 0.0001	0.5710	< 0.0001	0.7990	< 0.0001	-0.0940	< 0.0001

Table 8.4 ANOVA of plastic viscosity for OWC slurries with different SCMs

	Metakaolin		Silica Fume		Rice hush ask		Fly ash	
	$R^2=0.932$		$R^2=0.968$		$R^2=0.959$		$R^2=0.952$	
	Coefficient	(Prob.)> t	Coefficient	(Prob.)> t	Coefficient	(Prob.)> t	Coefficient	(Prob.)> t
Intercept	-0.3700		0.8900		1.2350		0.2660	
A-Temp	0.0510	0.0031	0.0110	< 0.0001	0.0840	< 0.0001	0.0630	< 0.0001
B-SCM	0.2200	< 0.0001	0.0120	< 0.0001	0.1100	< 0.0001	-0.0480	< 0.0001
C-PCH	-0.2500	< 0.0001	-0.0520	< 0.0001	-0.2670	< 0.0001	-0.2290	< 0.0001
AB	0.0520	0.0111	0.0000	0.8984	0.0020	0.8848	-0.0320	0.0046
AC	-0.0470	0.0491	-0.0100	< 0.0001	0.0000	0.9958	-0.0390	0.0037
BC	-0.0620	0.0108	-0.0080	0.0009	-0.0200	0.1338	0.0460	0.0009
A <sup>2</sup>	0.0020	0.9521	0.0050	0.0542	-0.0280	0.1024	0.0350	0.0329
B <sup>2</sup>	0.1600	< 0.0001	-0.0010	0.7720	-0.0270	0.0962	-0.0140	0.3517
C <sup>2</sup>	0.1400	< 0.0001	0.0220	< 0.0001	-0.0480	0.0084	0.1550	< 0.0001

Values of "Prob > |t|" less than 0.0500 indicate model terms are significant.

Values greater than 0.1000 indicate the model terms are not significant.

Table 8.5 Derived quadratic models for the yield stress and plastic viscosity of OWC slurries incorporating four different SCMs

MK	$\tau_0 =$	$1.767 + 0.19 \times Temp + 0.469 \times MK - 1.572 \times PCH - 0.655 \times Temp \times PCH - 0.393 \times MK \times PCH + 0.438 \times MK^2 + 1.296 \times PCH^2$	(8.10)
	$\mu_p =$	$-0.37 + 0.051 \times Temp + 0.22 \times MK - 0.25 \times PCH + 0.052 \times Temp \times MK - 0.047 \times Temp \times PCH - 0.062 \times MK \times PCH + 0.16 \times MK^2 + 0.14 \times PCH^2$	(8.11)
SF	$\tau_0 =$	$2.551 + 0.435 \times Temp + 0.734 \times SF - 1.379 \times PCH - 0.312 \times Temp \times PCH - 0.519 \times SF \times PCH + 0.259 \times Temp^2 + 0.214 \times SF^2 + 0.571 \times PCH^2$	(8.12)
	$\mu_p =$	$0.89 + 0.011 \times Temp + 0.012 \times SF - 0.052 \times PCH - 0.01 \times Temp \times PCH - 0.008 \times SF \times PCH + 0.005 \times Temp^2 + 0.022 \times PCH^2$	(8.13)
RHA	$\tau_0 =$	$1.189 + 0.347 \times Temp - 0.38 \times RHA - 1.249 \times PCH - 0.148 \times RHA^2 + 0.799 \times PCH^2$	(8.14)
	$\mu_p =$	$1.235 + 0.084 \times Temp + 0.11 \times RHA - 0.267 \times PCH - 0.028 \times Temp^2 - 0.027 \times RHA^2 - 0.048 \times PCH^2$	(8.15)
FA	$\tau_0 =$	$0.689 + 0.047 \times Temp + 0.059 \times FA - 0.215 \times PCH - 0.02 \times Temp \times PCH - 0.034 \times Temp^2 - 0.094 \times PCH^2$	(8.16)
	$\mu_p =$	$0.266 + 0.063 \times Temp - 0.048 \times FA - 0.229 \times PCH - 0.032 \times Temp \times FA - 0.039 \times Temp \times PCH + 0.046 \times FA \times PCH + 0.035 \times Temp^2 + 0.155 \times PCH^2$	(8.17)

Table 8.6 ANOVA for significance of regression models

		SS	DF	F Value	(Prob.) > F	R <sup>2</sup>
MK	YS	87.300	9	97.550	<0.0001	0.962
	PV	3.580	9	53.060	<0.0001	0.932
SF	YS	74.920	9	81.730	<0.0001	0.954
	PV	0.074	9	118.240	<0.0001	0.968
RHA	YS	46.030	9	98.240	<0.0001	0.961
	PV	2.090	9	92.100	<0.0001	0.959
FA	YS	1.230	9	136.730	<0.0001	0.972
	PV	1.610	9	77.500	<0.0001	0.952

Table 8.7 Repeatability of test results based on 5 replicate center points

	MK		SF		RHA		FA	
	YS (Pa)	PV (Pa.s)	YS (Pa)	PV (Pa.s)	YS (Pa)	PV (Pa.s)	YS (Pa)	PV (Pa.s)
Mean	7.55	0.37	17.91	0.42	4.16	0.77	2.53	0.29
Estimated error (95% confidence limit)	0.21	0.01	0.31	0.01	0.11	0.02	0.19	0.01
COV (%)	7.31	8.09	8.68	6.77	5.69	7.14	6.36	7.99

YS : yield stress, PV : plastic viscosity, COV = coefficient of variation



### 8.6.1 Accuracy of The Proposed Model

The proposed models were used to predict the yield stress and plastic viscosity of OWC slurries and the acceptability/rejection of such models was evaluated using the average absolute error (*AAE*) (given by equations 18 and 19) and by comparing the predicted-to-measured values obtained with six randomly selected mixes for each group of SCM.

$$AAE = \frac{1}{n} \sum_{i=1}^n \frac{|\tau_{measured} - \tau_{predicted}|}{\tau_{measured}} \quad (8.18)$$

$$AAE = \frac{1}{n} \sum_{i=1}^n \frac{|\mu_{p\,measured} - \mu_{p\,predicted}|}{\mu_{p\,measured}} \quad (8.19)$$

where  $\tau_{measured}$ ,  $\mu_{p\,measured}$ ,  $\tau_{predicted}$ , and  $\mu_{p\,predicted}$  are the experimentally measured yield stress and plastic viscosity values of OWC slurries and the corresponding data predicted by the model, respectively, and  $n$  is the total number of mixtures used in verification for each group of SCM. The maximum, minimum and average of the predicted-to-measured values for yield stress and plastic viscosity, standard deviation (*SD*), coefficient of variation (*COV*) and *AAE* for all the mixtures used in the validation of the models are presented in Tables 8.8 and 8.9, respectively. The results reveal that the ratio between the predicted and measured values ranged from 0.97 to 1.04, and 0.97 to 1.12, respectively, for yield stress and plastic viscosity of OWC slurries incorporating SCMs, which indicates an excellent accuracy of the proposed models in predicting the yield stress and plastic viscosity of OWC slurries prepared using different SCMs.

Table 8.8 Performance of proposed model in predicting the yield stress of cement slurries prepared with different SCM

Type of admixture	AAE (%)	$\tau_{measured}/\tau_{predicted}$				
		Maximum	Minimum	Average	SD <sup>1</sup>	COV <sup>2</sup> (%)
MK	8.85	1.17	0.87	0.99	0.11	10.89
SF	12.48	1.19	0.88	0.99	0.13	12.74
RHA	6.48	1.05	0.92	0.97	0.02	2.35
FA	7.64	1.13	0.93	1.04	0.08	8.24

<sup>1</sup>SD: standard deviation, <sup>2</sup> COV =  $SD / Average * 100$

Table 8.9 Performance of proposed model in predicting the plastic viscosity of cement slurries prepared with different SCM

Type of admixture	AAE (%)	$\tau_{measured}/\tau_{predicted}$				
		Maximum	Minimum	Average	SD <sup>1</sup>	COV <sup>2</sup> (%)
MK	13.50	1.26	0.90	1.12	0.13	11.46
SF	7.91	1.10	0.86	0.98	0.09	9.70
RHA	7.11	1.15	0.99	1.08	0.06	5.97
FA	5.47	1.06	0.88	0.97	0.06	6.36

<sup>1</sup>SD: standard deviation, <sup>2</sup> COV =  $SD / Average * 100$

### 8.6.2 Isoresponse of The Proposed Model

The proposed quadratic models thus obtained can be used to evaluate the effect of different parameters/variables on the rheological properties of OWC slurries with SCM partial replacement for OWC. The response surface methodology was used to draw the isoresponse surface and contour diagrams for yield stress and plastic viscosity of SCM based OWC slurries from the parameters under study (temperature, level of SCM, PCH dosage) over the experimental domain. The models also permit optimizing the effects of the parameters involved.

For example, the effect of temperature and MK dosage on yield stress and plastic viscosity of OWC slurries at two different PCH dosages (0.25 and 0.75%) are presented in Figs. 8.3 and 8.4, respectively. Both yield stress and plastic viscosity increased with the MK addition and decreased significantly with increasing PCH dosage. Yield stress and plastic viscosity tended to increase with the increase of temperature regardless of the MK level. However, the effect of temperature was more pronounced at higher MK dosage. For a particular dosage of PCH (0.25%), the increase in temperature from 23 to 60°C caused an increase in yield stress of 1.9

and 2.2 times when OWC was partially replaced by 5% and 15% MK, respectively. The increase in temperature from 23 to 60°C resulted in 1.17 and 1.61 times increase in plastic viscosity when the OWC replacement level was 5% and 15%, respectively.

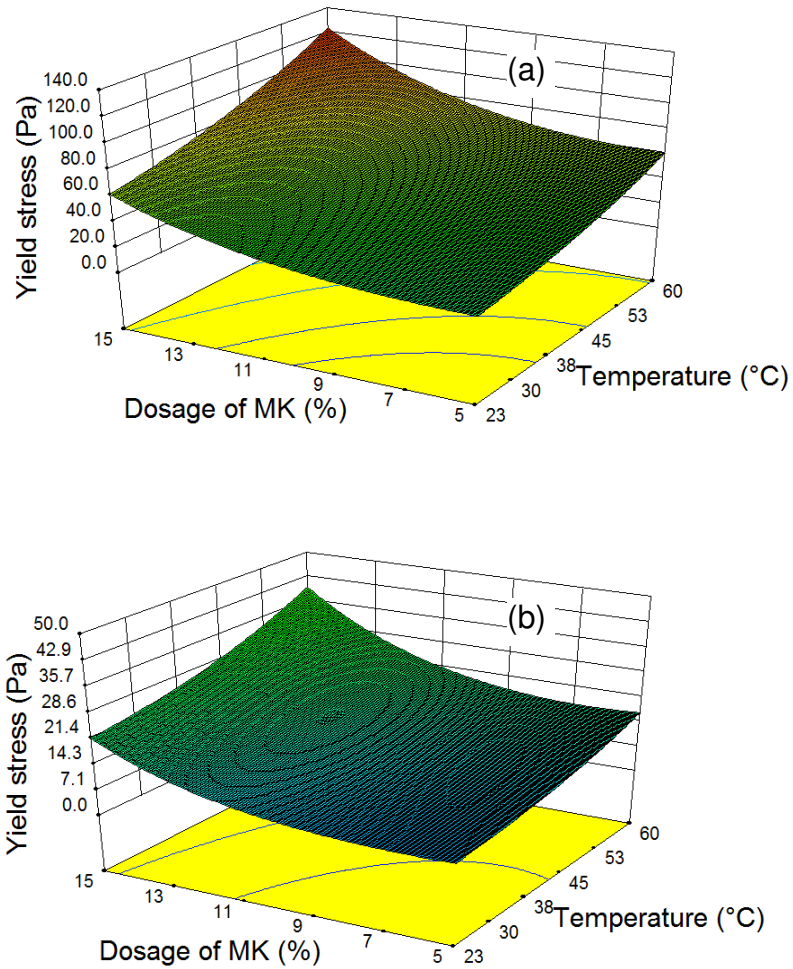


Figure 8.3 Response surface of yield stress of OWC slurries prepared by MK with PCH dosage of (a) 0.25% and (b) 0.75%.

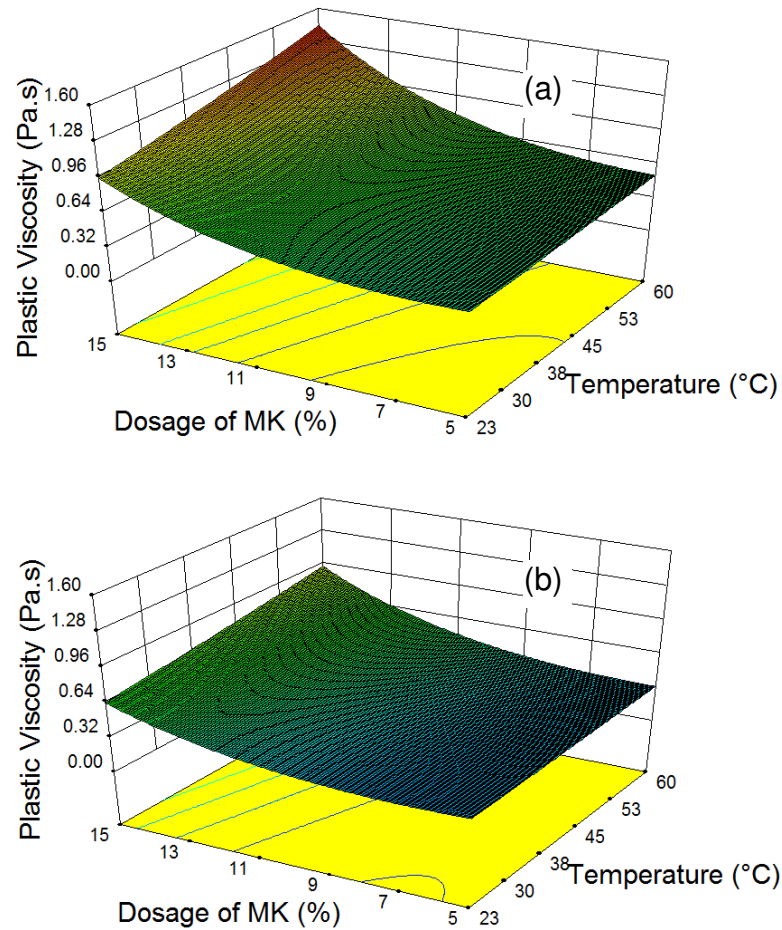


Figure 8.4 Response surface of plastic viscosity of OWC slurries prepared by MK with PCH dosage of (a) 0.25% and (b) 0.75%.

#### 8.6.2.1 Yield stress

Equations 8.10, 8.12, 8.14 and 8.16 in Table 8.5 show the effect of temperature, PCH dosage and level of SCM on the yield stress of OWC slurries with partial replacement of OWC by MK, SF, RHA, and FA, respectively. It can be observed that not all SCMs used acted similarly on the rheological properties of OWC slurries. Because of their different physical

and chemical properties, SCMs exhibited completely different behaviour at a given temperature and PCH dosage. However, yield stress was influenced, in order of magnitude, by the PCH dosage, dosage of SCM and temperature. The PCH dosage was found to have highest effect on the yield stress, which is due to its steric and electrostatic repulsions induced among cement particles, which is responsible for their deflocculation. Increasing level of SCM resulted in increased yield stress in the case of MK and SF, whereas yield stress values decreased with the addition of RHA and FA.

Figures 8.5-8.8 illustrate yield stress isoresponse curves for OWC slurries with increasing temperature and PCH dosage, when OWC was partially replaced by MK, SF, RHA and FA, respectively at two different levels (5% and 15%). The yield stress was found to decrease significantly with the increase of PCH dosage for all SCMs tested. Regardless of the type and dosage of SCM, the higher the temperature, the higher was the value of yield stress for a particular dosage of PCH, which is due to the higher rate of hydration at higher temperature. For a given PCH dosage and temperature, the yield stress was found to increase when the MK level increased from 5 to 15% (Fig. 8.5(a,b)). Similar behaviour was observed for SF (Fig. 8.6(a,b)). This is likely due to the associated increase in the water demand induced by the addition of high surface area MK and SF. It was reported that SF has the ability to immobilize a significant amount of water due to inherent hydrogen bonds on its surface (Winhab, 2000).

Comparing Figs. 8.5(a,b) and 8.6(a,b), it can be observed that the yield stress values of OWC-SF slurry were greater than those of the OWC-MK slurry, a behaviour also observed by others (Caldarone et al., 1994, Caldarone and Gruber, 1995, Ding and Li, 2002). It was found that MK provided better workability than did SF for a given mixture proportions (Ding and Li, 2002) and less HRWR admixture was required for concrete mixtures modified by MK than that of SF mixtures (Caldarone et al., 1994, Caldarone and Gruber, 1995). Unlike MK and SF, RHA was found to gradually reduce the yield stress value with an increasing replacement level (Fig. 8.7(a,b)). A similar finding was also observed by Laskar and Talukdar (2008), while others (Habeeb and Fayyadh, 2009, Cordeiro et al., 2009, Nehdi et al., 2003) found that the replacement of cement by RHA resulted in increased water demand and reduced concrete workability. This discrepancy appears to be due to differences in the average particle size of the RHA used. Yield was also found to decrease with increased

addition of FA (Fig. 8.8(a,b)). This is due to the spherical shape of FA, which reduces frictional forces among angular cement particles due to the so called “ball bearing” effect.

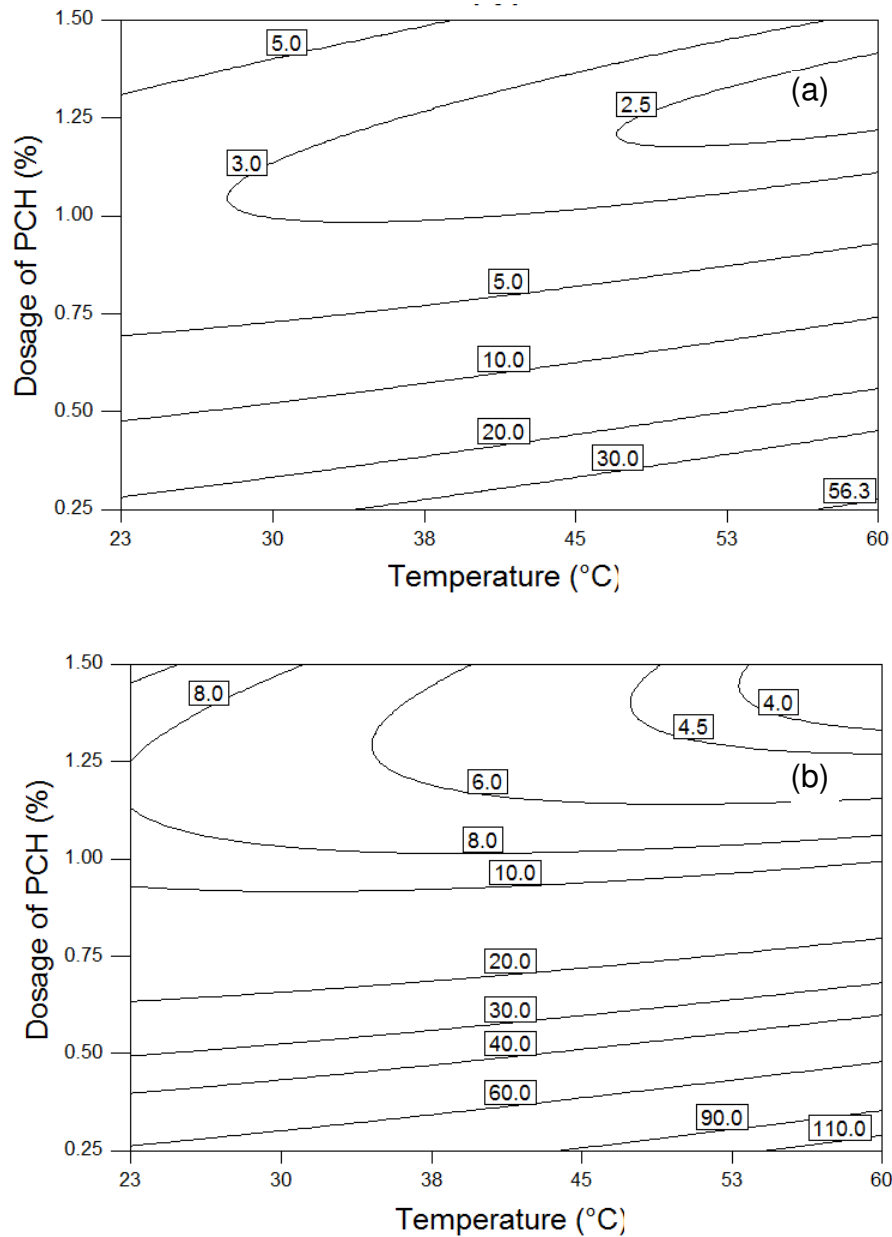


Figure 8.5 Variation of yield stress with dosage of PCH and temperature for OWC slurries incorporating MK ((a) 5% replacement level; and (b) 15% replacement level).

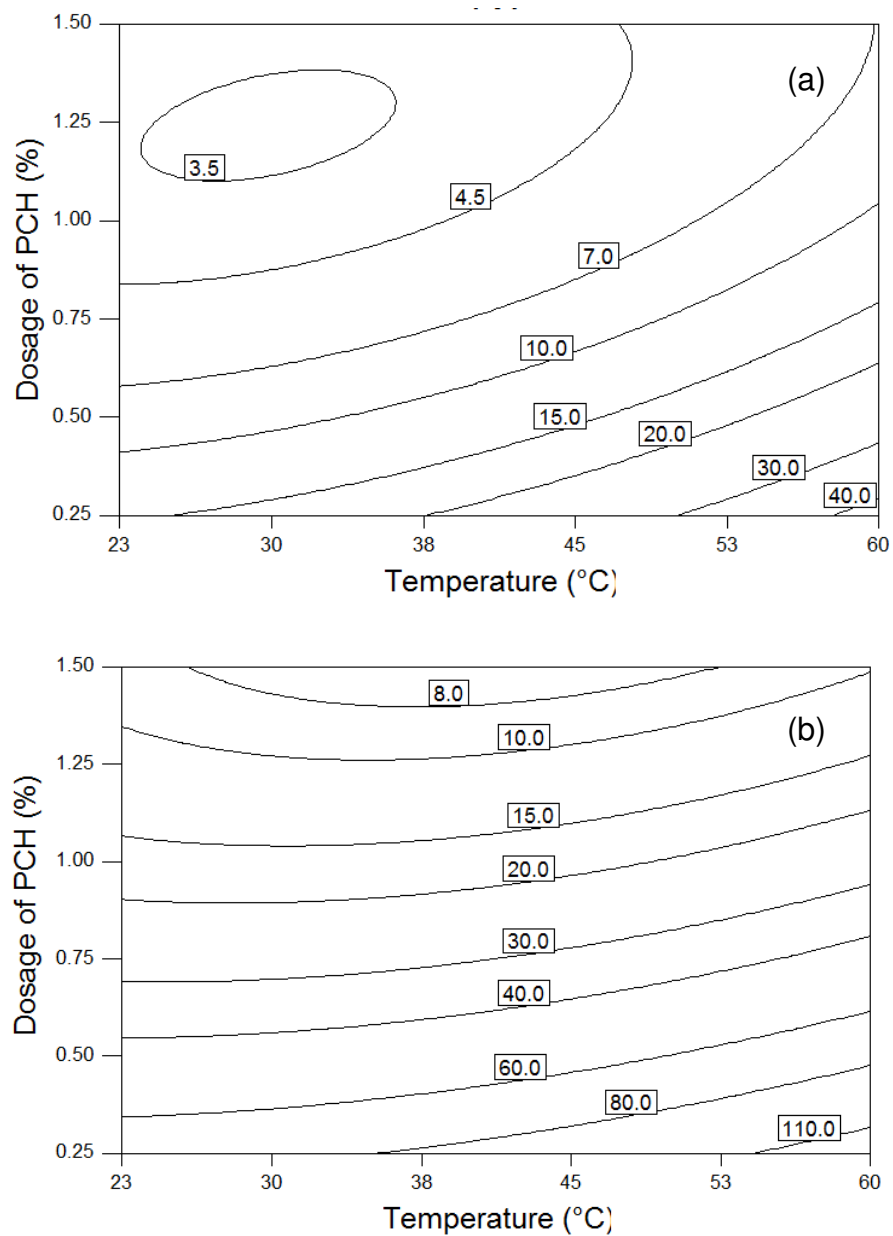


Figure 8.6 Variation of yield stress with dosage of PCH and temperature for OWC slurries incorporating SF ((a) 5% replacement level; and (b) 15% replacement level).

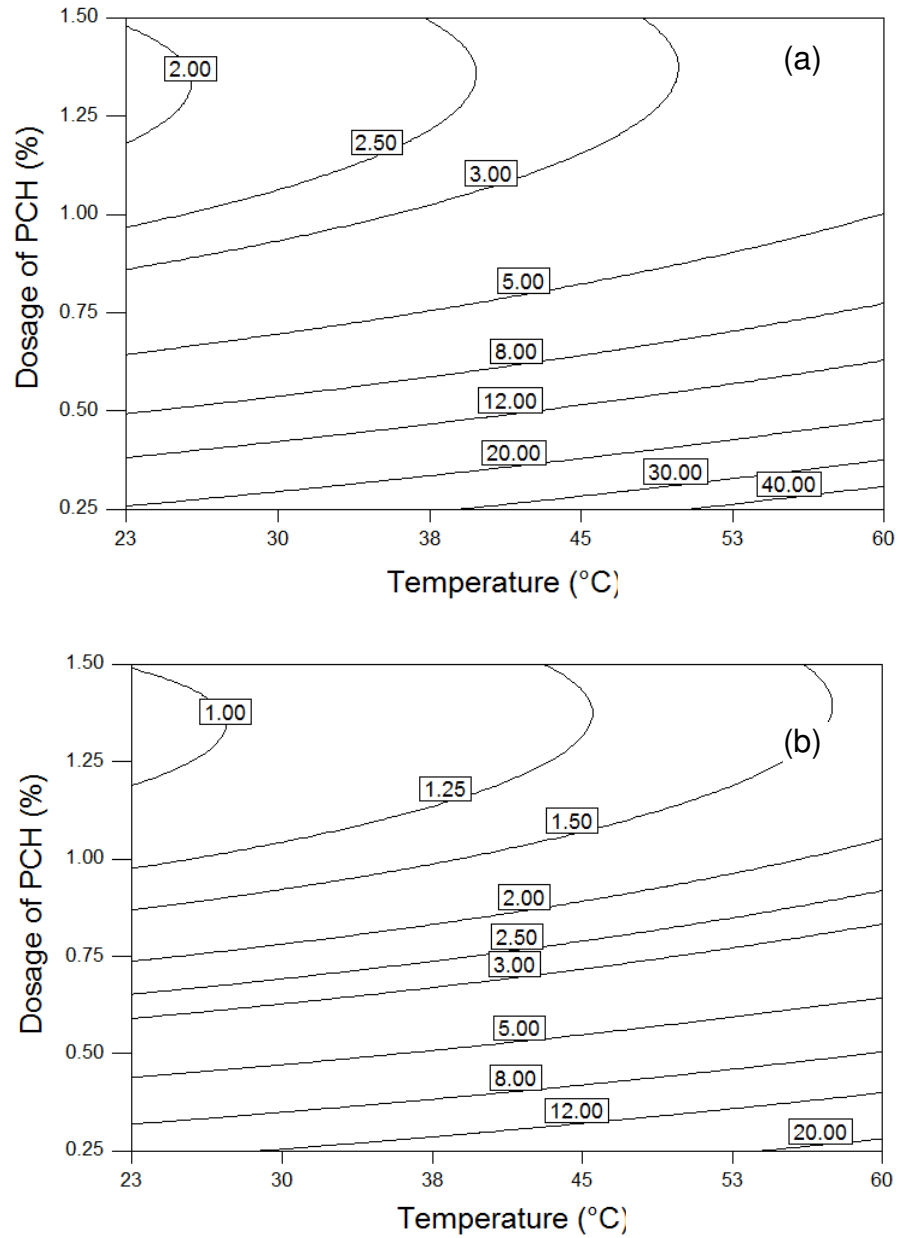


Figure 8.7 Variation of yield stress with dosage of PCH and temperature for OWC slurries incorporating RHA ((a) 5% replacement level; and (b) 15% replacement level).



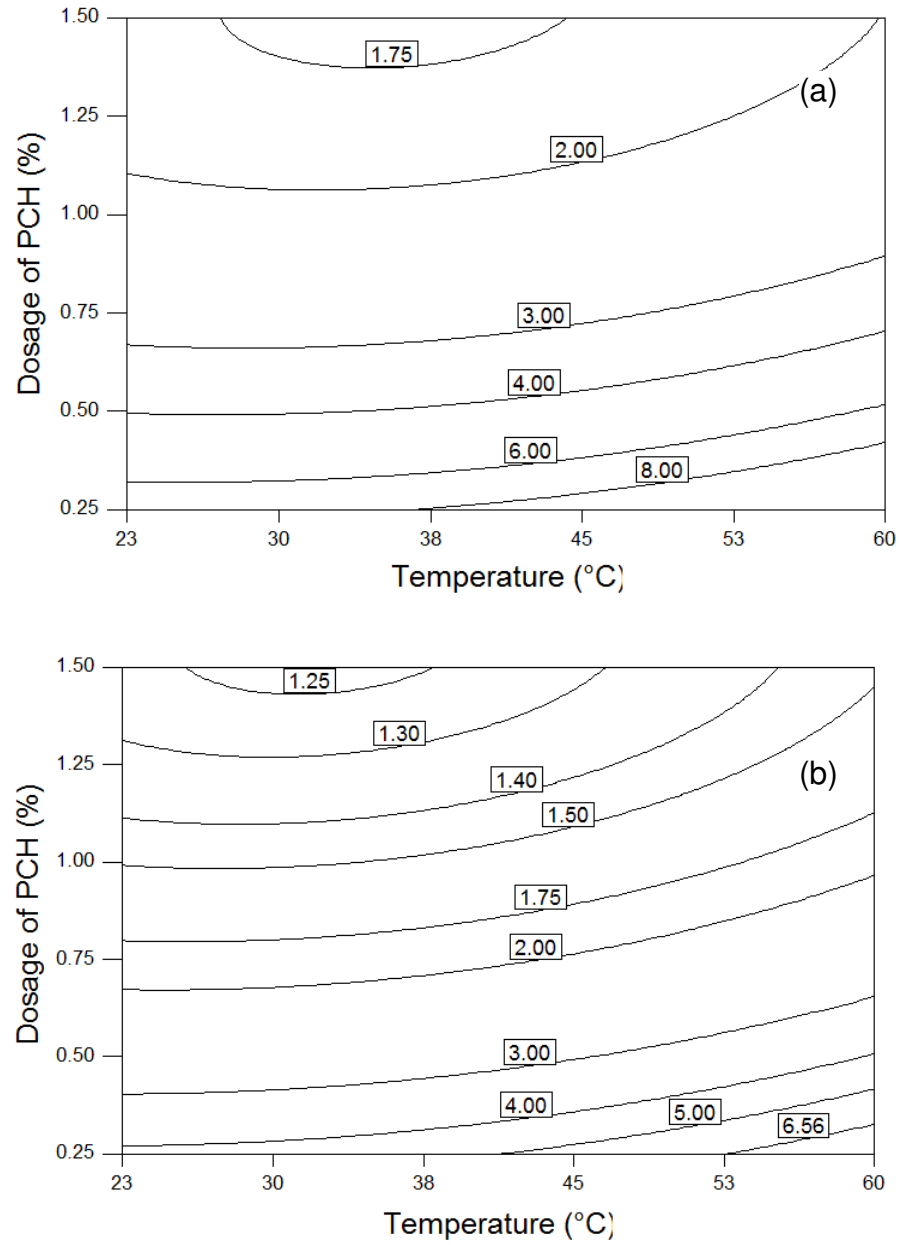


Figure 8.8 Variation of yield stress with dosage of PCH and temperature for OWC slurries incorporating FA ((a) 5% replacement level; and (b) 15% replacement level).

### 8.6.2.2 Plastic viscosity

Eqs. 8.11, 8.13, 8.15 and 8.17 in Table 8.5 describe the effect of temperature, PCH dosage and level of the corresponding SCM on the plastic viscosity of OWC slurries with partial replacement of OWC by MK, SF, RHA, and FA, respectively. The PCH dosage had the greatest influence on plastic viscosity. Temperature and the SCM replacement level influence the plastic viscosity value in different order depending on the SCM considered. Temperature was more influential for FA, while the SCM dosage was more significant for MK, SF and RHA. However, the degree of influence varied with the type of SCM used.

Figures 8.9 to 8.12 represent isoresponse curves for the plastic viscosity of OWC slurries with increasing temperature and PCH dosage, when OWC was partially replaced by different SCMs at two different levels (5% and 15%). An increase in PCH dosage led to a decrease in plastic viscosity values for all SCMs considered. An increase in temperature induced an increase in plastic viscosity values. It can also be observed that for a particular PCH dosage and at a particular temperature, plastic viscosity increased with the increase of MK, SF and RHA, whereas the value decreased with increasing FA level. Table 8.10 represents a comparison of plastic viscosity values for a particular PCH dosage (0.25% and 1%) at two different levels of SCM (5% and 15%) at a temperature of 60°C. For a particular dosage of PCH and SCM, the plastic viscosity of OWC-RHA slurries was higher than that of the other slurries investigated. This is probably because of the irregular and flaky shape of RHA particles and the absorption of more PCH by the un-burnt carbon content of RHA.

Table 8.10 Comparison of plastic viscosity values for PCH dosages of 0.25% and 1% at two different levels of SCM (5% and 15%) at 60°C

SCM	5%		15%	
	0.25% PCH	1% PCH	0.25% PCH	1% PCH
MK	0.51	0.235	1.25	0.55
SF	0.56	0.25	0.86	0.32
RHA	1.10	0.56	1.59	0.78
FA	0.76	0.26	0.56	0.17

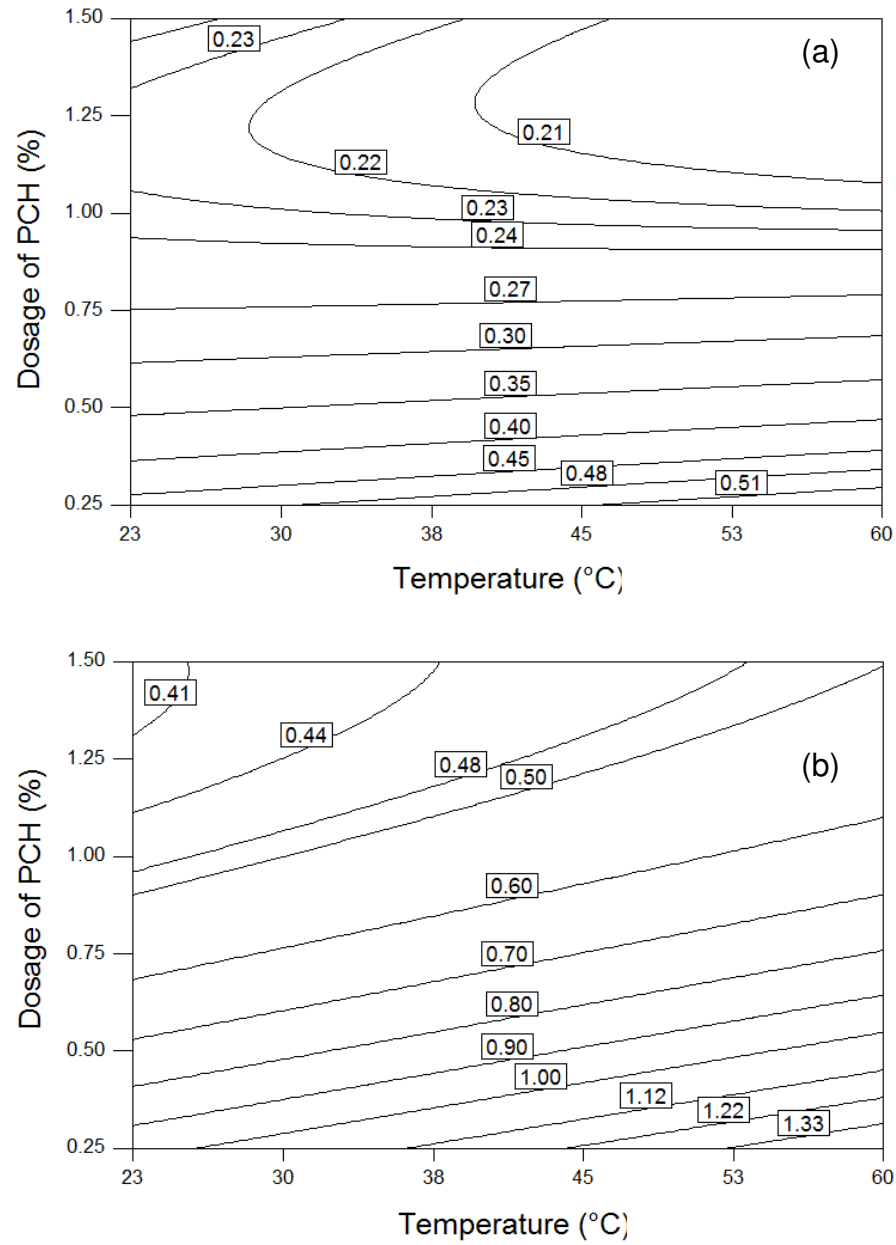


Figure 8.9 Variation of Plastic viscosity with dosage of PCH and temperature for OWC slurries incorporating MK ((a) 5% replacement level; and (b) 15% replacement level).

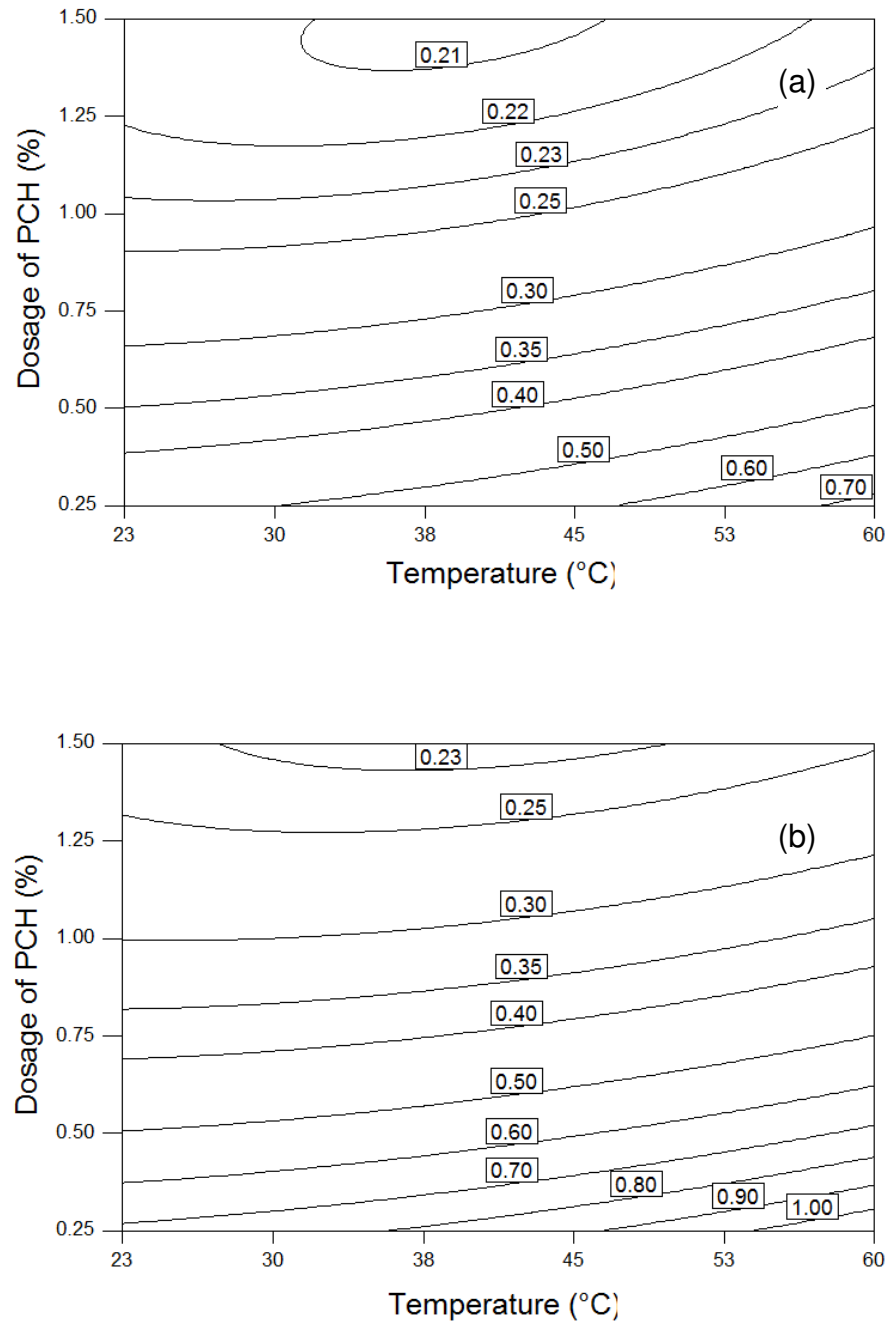


Figure 8.10 Variation of plastic viscosity stress with dosage of PCH and temperature for OWC slurries incorporating SF ((a) 5% replacement level; and (b) 15% replacement level).

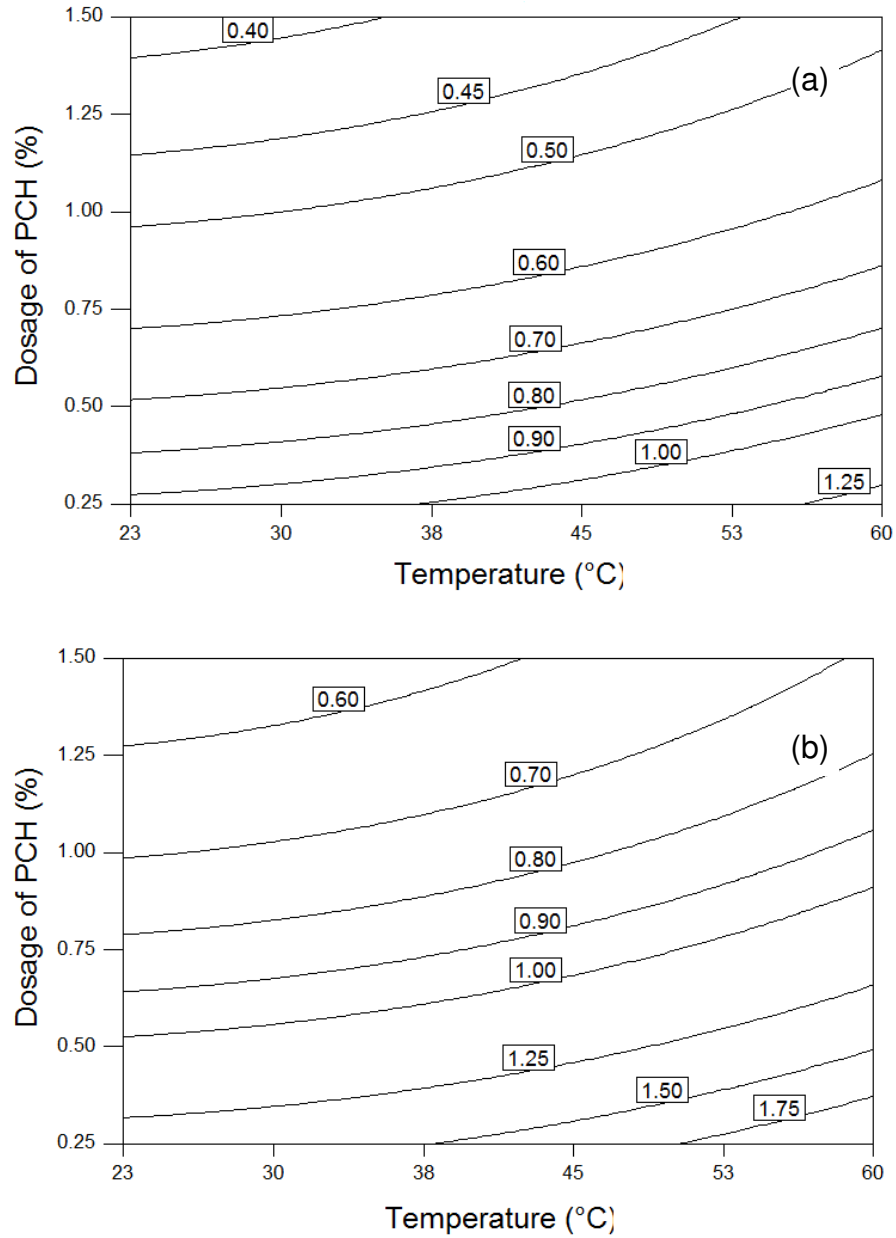


Figure 8.11 Variation of plastic viscosity stress with dosage of PCH and temperature for OWC slurries incorporating RHA ((a) 5% replacement level; and (b) 15% replacement level).

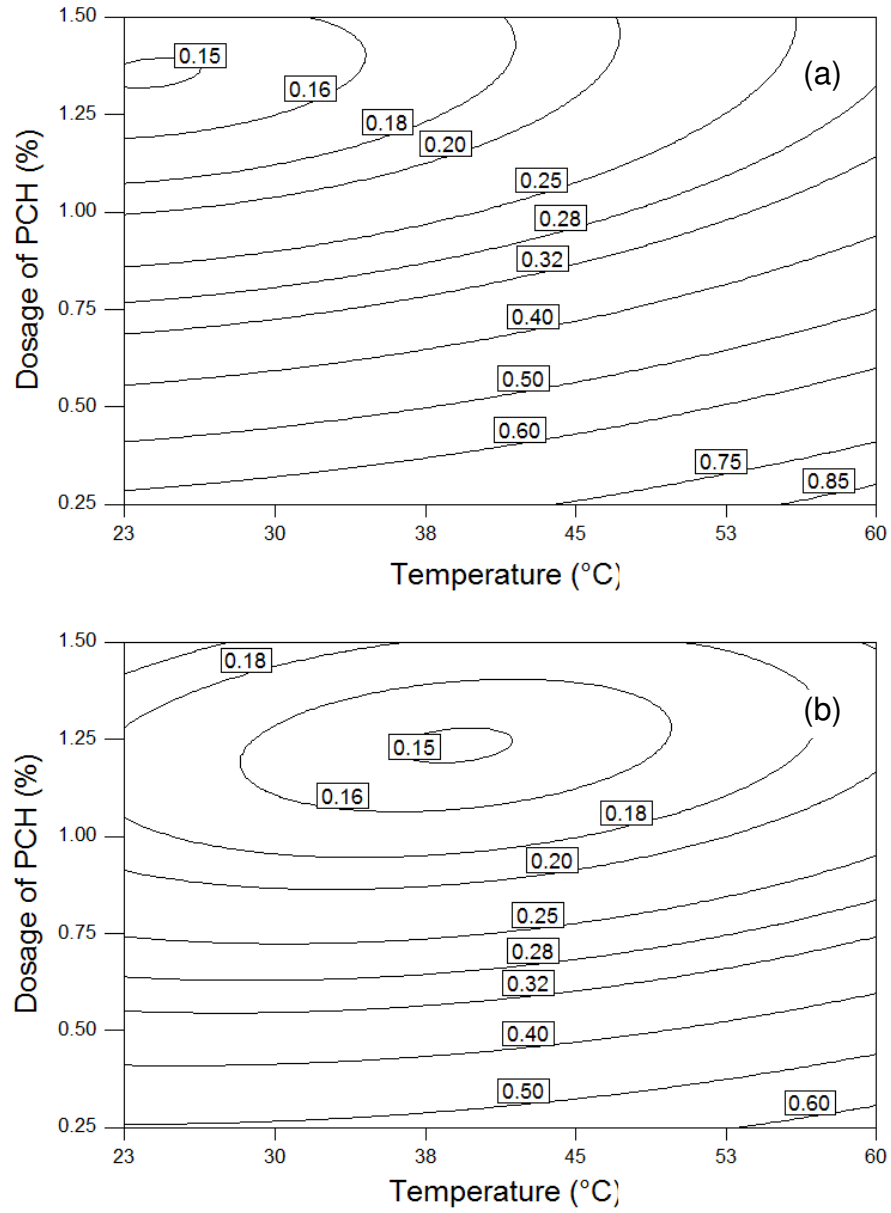


Figure 8.12 Variation of plastic viscosity stress with dosage of PCH and temperature for OWC slurries incorporating FA ((a) 5% replacement level; and (b) 15% replacement level).

### 8.6.2.3 Trade off between dosage of PCH and SCM

The proposed statistical model can be used to generate contour responses showing the influence of PCH dosage and level of SCM on the rheological properties of OWC slurries. Figure 8.13 illustrates the effect of the PCH dosage and SCM on the yield stress of OWC slurries at 60°C. It can be observed that for given PCH and SCM dosages, the use of FA as partial replacement for OWC resulted in the lowest yield stress. For example, for a PCH dosage of 0.75% and SCM of 10%, the yield stress values were 10, 25, 7 and 2.6 Pa for MK, SF, RHA and FA, respectively.

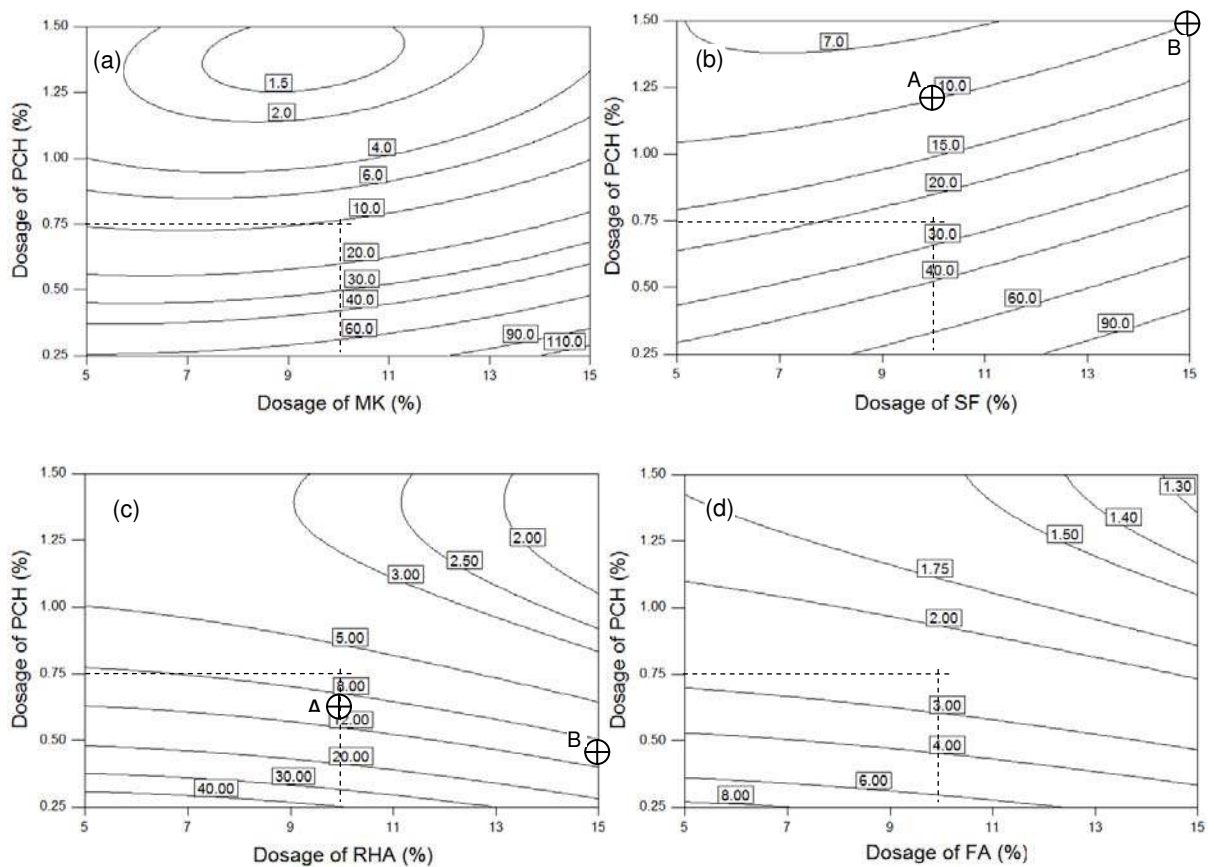


Figure 8.13 Isoresponse curve of yield stress of OWC slurries incorporating (a) MK, (b) SF, (c) RHA, and (d) FA as replacement of OWC at 60°C.

For OWC slurries made with MK, to maintain the yield stress at about 10 Pa, the PCH dosage is expected to increase from 0.75 to 0.95% when the amount of MK is increased from 10 to 15% (Fig. 8.13(a)). A yield stress of 10 Pa with OWC-SF slurry can be obtained with a PCH dosage of 1.2% and 10% SF (point A) or PCH dosage of 1.49% and 15% SF (point B) (Fig. 8.13(b)). It is observed in the figure that, increasing the dosages of RHA and FA reduced the yield stress value. The combination of PCH and RHA dosages can be 0.625 and 10% (point A) or 0.4 and 15% (point B) for a yield stress value of 10 Pa as observed in Fig. 8.13(c). Hence, several PCM-SCM combinations are possible to achieve a given yield stress.

Figure 8.14 illustrates the effect of PCH dosage and SCM on plastic viscosity of OWC slurries at 60°C. Similar to yield stress, different combinations of PCH and SCM are possible to obtain a given plastic viscosity. Figure 8.14(a) suggests that in order to produce a plastic viscosity of 0.5 Pa.s at 60°C, it is possible to use 0.5% PCH and 10% MK (point A), or 1.5% PCH and 15% MK (point B). Similarly, a slurry can have the same plastic viscosity value with a combination of 0.5% PCH and 5% SF (point A) or 0.7% PCH or 15% SF (point B) (Fig. 8.14(b)). Other possible combinations that lead to the same plastic viscosity values are 1.35% PCH and 5% RHA (point A on Fig. 8.14(c)) or 0.5% PCH and 15% FA (point A on Fig. 8.14(d)). The difference in PCH requirement is probably due to the difference in particle shape, surface area and carbon contents of the SCMs used in each study. For the particular PCH dosage of 0.75%, an increase of OWC replacement level by MK from 5 to 10% led to an increase in plastic viscosity from 0.28 to 0.37 Pa.s. At a similar PCH dosage, plastic viscosity increased from 0.37 to 0.45 Pa.s when the SF dosage increased from 5 to 10%. On the other hand, increasing the FA dosage led to a decrease in plastic viscosity from 0.5 to 0.42 Pa.s at a similar PCH dosage. Thus, an optimum OWC slurry having the desired yield stress and plastic viscosity value can be obtained by number of combinations of PCH and SCM depending on the type of SCM. Other mechanical strength and durability considerations have to be taken into consideration in the final selection of the OWC slurry mixture.



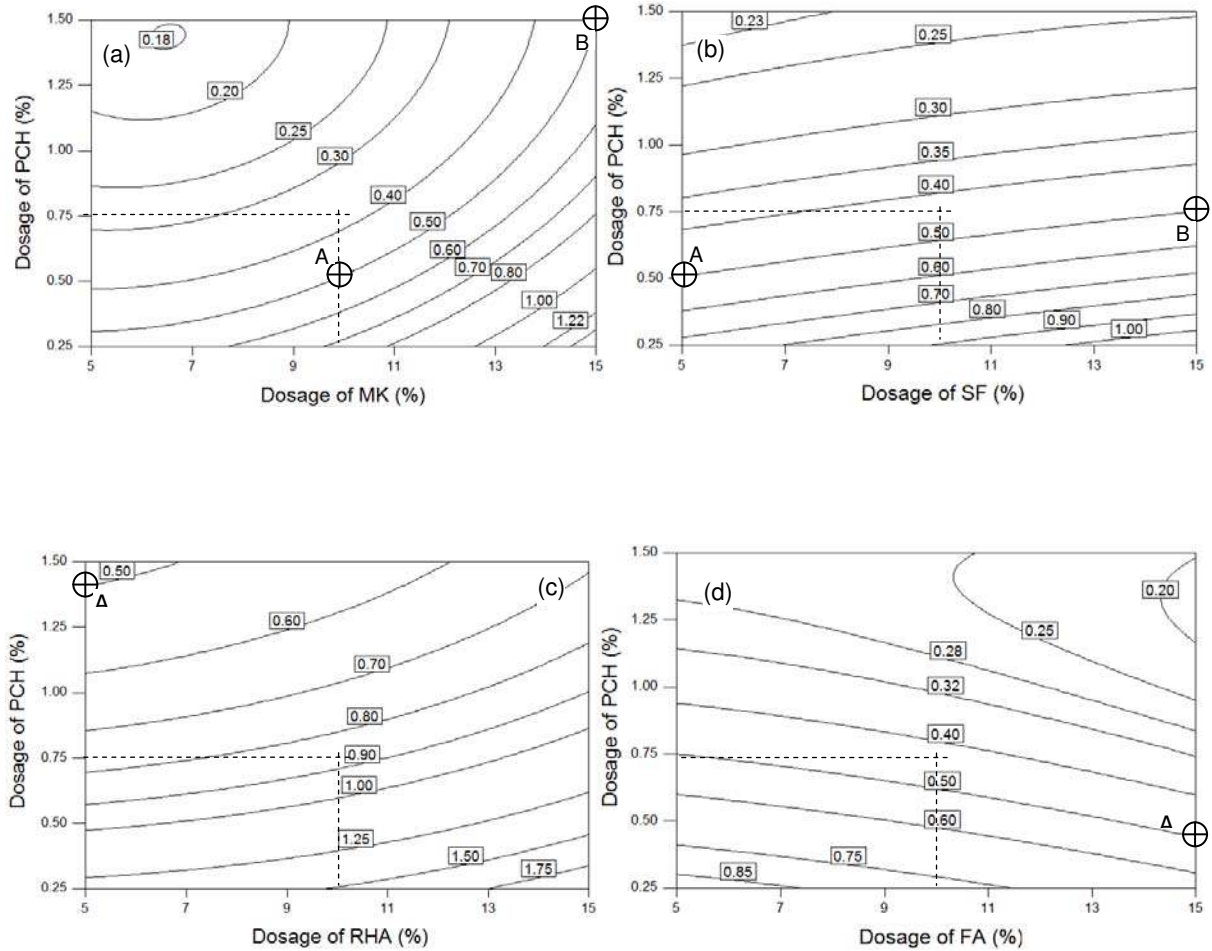


Figure 8.14 Isoresponse curve of plastic viscosity of OWC slurries incorporating (a) MK, (b) SF, (c) RHA, and (d) FA as replacement of OWC at 60°C.

## 8.7 Conclusion

A second order  $2^k$  central composite response surface model was developed to study the influence of temperature and key mixture parameters such as the PCH dosage, type and level of SCM and interactions between these parameters on the slurry rheological properties. Based on this work, the following conclusions can be drawn:

1. The proposed statistical models are capable of determining the influence of key parameters on the rheological properties of OWC slurries and can be used to predict

the influence of the various parameters on yield stress and plastic viscosity of OWC slurries.

2. The derived models reveal that the measured yield stress and plastic viscosity of OWC slurries are influenced by the PCH dosage, replacement of OWC by different types and dosages of SCMs, temperature and several coupled effects of these parameters.
3. The PCH dosage had the greatest influence on the yield stress and plastic viscosity of OWC slurries. An increase in the PCH dosage led to significant reduction in yield stress and plastic viscosity values.
4. Yield stress and plastic viscosity values are also affected by the type and dosage of SCM used as partial replacement for OWC. The yield stress increased with increasing dosage of MK and SF and decreased with increasing dosage of RHA and FA.
5. Plastic viscosity increased with the addition of MK, SF and RHA and decreased with increasing amount of FA.
6. At a given SCM dosage, the yield stress of OWC slurries without any chemical admixture follows the order: SF>MK>RHA>FA at all test temperatures.
7. Temperature had a significant influence on the rheological properties of OWC slurries. Both yield stress and plastic viscosity increased with increasing temperature. However, the degree of influence varied with the type and dosage of SCM used.
8. The response contours provide an effective means for selecting optimum combinations of PCH and SCM at different temperatures to produce a given yield stress and plastic viscosity. Several mixture proportions of OWC slurries with similar rheological properties are possible by varying the type and level of SCM and dosage of PCH.
9. The proposed statistical model can reduce the number of trial mixtures needed to optimize OWC slurries with tailor-made rheological properties using different SCMs, and thus can simplify the test protocol and saves time and cost.

10. The proposed model for OWC slurries is valid for OWC partial replacement levels by SCMs ranging from 5 to 15% by MK, SF, RHA or FA and PCH dosages ranging from 0.25 to 1.5% at different temperatures ranging from 23 to 60°C.
11. Although the model is based on a given set of materials and focused only on the Bingham properties of OWC slurries, it is possible to study other properties such as the thickening time, fluid loss, compressive strength, etc. The model can easily be extended to include such properties, along with other materials such as ground granulated blast furnace slag, limestone powder, diatomaceous earth, and different types of additives such as accelerators or retarders, fluid loss control additives, viscosity modifying admixtures, etc.

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## Chapter 9

### SUMMARY AND CONCLUSIONS

#### 9.1 Summary

Oil wells are drilled up to depths of thousands of meters. The productivity of oil wells is affected by the well cementing quality. The rheology, stability, and durability of the cement slurry used are major requirements for successful oil well cementing. In particular, the rheological behaviour of OWC slurries must be optimized to achieve an effective well cementing operation. The rheological properties of an OWC slurry determine the quality of the final product and help predicting its end use performance and physical properties during and after processing.

Rheological tests can determine the flow properties of the cement slurry such as its plastic viscosity, yield point, gel strength, thixotropic behaviour, etc. The rheology of cement slurries is a manifestation of the interactions between cement particles, water and other constituents, which makes its characterization difficult. Cement slurries are visco-elastic materials; they exhibit properties characteristic of both elastic solids and viscous fluids. To characterize the rheology of a cement slurry, rheological parameters such as the yield stress, apparent viscosity, plastic viscosity, shear thinning, or shear thickening behaviour have been studied. The Bingham plastic model and the Power law are widely used to describe the rheological properties of cement slurries (Guillot, 2006). The Bingham plastic model includes both yield stress,  $\tau_0$  and a plastic viscosity,  $\mu_p$  at finite shear rates. The yield stress indicates the minimum effort needed for a material to start moving and is the intercept of the flow curve (shear stress vs. shear rate) with the shear stress axis. Below the yield stress, a material behaves like a solid. Yield stress is the contribution of the skeleton, i.e. it is manifestation of friction among solid particles (Ferraris and Larrard, 1998). The plastic viscosity governs the flow after it is initiated and is the contribution of suspending liquids resulting from viscous dissipation due to the movement of water in the sheared material (Ferraris and Larrard, 1998; Laskar and Talukdar, 2008).



Oil well cement slurries are usually subjected to high levels of pressure and temperature depending on the height and density of the column of material above, which makes the characterization of their rheological properties even more complicated than that of normal cement pastes or grouts. A number of admixtures have thus been developed to alter the chemical and physical properties of OWC slurries as required for flowability, stability of the slurry, and long-term performance of wells. The conventional admixtures which have been developed in areas with moderate temperatures for cementing work above ground, may lead to disappointing results when exposed to high temperature during oil well cementing. Uses of supplementary cementing materials are also being encouraged in the petroleum industry as a sustainable solution. Mineral and chemical admixtures play an important role in controlling the physical and chemical properties of both fresh cement slurries and hardened cementitious systems. However, very scant information can be found on the rheological properties of oil well cement slurries when SCMs are used as partial replacement for cement. Moreover, the coupled effects of temperature, chemical admixtures and mineral admixtures on the rheological properties of oil well cement slurries remain largely unexplored.

The current study aimed at formulating recommendations for the effective use of chemical and mineral admixtures in oil well cements at high temperature, which should enhance the rheological properties of cement slurries in oil well cementing operations. Chapters two and three summarize the basic concepts involved in oil well cementing, the chemical and physical properties of oil well cements and the effects of related additives and chemical admixtures on oil well cement slurry rheology. Chapter four investigated the effects of various chemical admixtures on the rheological properties of cement slurries at high temperature using an advanced shear-stress/shear-strain controlled rheometer. The combined influence of the chemical admixtures and supplementary cementitious materials on the rheological properties of OWC slurries was investigated in Chapter five. An artificial neural network model was developed to simulate the influence of various types and dosages of chemical admixtures on the flow behaviour of OWC slurries in Chapter six. Empirical equations for predicting the shear flow curve of OWC slurry mixtures incorporating various superplasticizers at various temperatures were developed using multiple regression analysis and presented in Chapter six. These flow curves were used to calculate the Bingham yield stress and plastic viscosity values for the various OWC slurries investigated. The coupled effects of chemical

admixtures and supplementary cementitious materials were also modeled using artificial intelligence in Chapter seven. A parametric study was performed to evaluate the effects of temperature, and dosage of chemical admixtures and supplementary cementitious materials on the calculated yield stress and plastic viscosity values. Chapter Eight was devoted to developing empirical equations and response surface models using a statistical design approach and design of experiments to evaluate the effects of the dosage of chemical admixture, dosage and type of supplementary materials on the rheological properties of OWC slurries at different temperatures.

## **9.2 Conclusions**

The experimental results in chapter four demonstrated that the rheological properties of OWC slurries are highly dependent on temperature; both yield stress and plastic viscosity increased nonlinearly with temperature. The rheological properties of OWC slurries also depended on the type of admixture used. The new generation polycarboxylate-based high-range water reducing admixture (PCH), polycarboxylate-based mid-range water reducing admixture (PCM) and hydroxylated carboxylic acid-based retarding admixture (HCR) improved fluidity at all test temperatures and for all dosages used, while slurries incorporating a lignosulphonate-based mid-range water reducing admixture (LSM) required more energy to initiate slurry flow since the yield stress increased at all dosages tested. The admixture dosage had a significant effect on the slurry rheology. At lower dosages, the phosphonate-based set retarding admixture (SRA), HCR and rheoplastic solid admixture (RA) acted as accelerators, thus enhancing the thixotropic behaviour of OWC slurries. This was more pronounced at higher temperature. At lower dosage, the adsorbed layer of admixture might not be sufficiently effective to act as a barrier to prevent the contact of water and cement grains, which promotes the acceleration of hydration reactions. This could be the reason why relatively higher yield stress and viscosity values were observed at low dosages of LSM, SRA and RA. Beyond certain threshold dosages, such admixtures became effective dispersants and reduced the extent of cement slurry thixotropy. However, PCH was found to be more effective at improving the rheological properties of OWC slurries at all test temperatures, even at relatively lower dosages, compared to the other admixtures tested.

Thixotropy measurements of OWC slurries showed that at lower dosage of admixtures (except for LSM), the higher the temperature the higher was the degree of thixotropy. The explanation of the phenomenon is that, at lower dosages, the admixtures are not effective to disperse the structures formed as a result of the acceleration of the cement hydration reactions at higher temperature. Thixotropy values were observed to decrease with increasing admixture dosage, indicating that higher dosages reduced the degree of stiffening. The results of chapter four indicated that the conventional admixtures, which have been developed in countries with moderate temperature for cementing jobs above ground, may lead to disappointing results when exposed to high temperature and need to be validated before formulating recommendations specific to oil well cementing.

Chapter five substantiated that rheological properties of OWC slurry are largely dependent on the type and dosage of supplementary cementitious materials (SCM) used. However, regardless of the type and dosage of SCM, both yield stress and plastic viscosity of OWC slurries were found to increase nonlinearly with the increase of temperature. The fly ash (FA) and rice husk ash (RHA) used in the present study reduced yield stress, which can have a positive influence on the pump-ability of OWC slurries. However, metakaolin (MK) and silica fume (SF) increased yield stress when used as partial replacement for API Class G OWC. At a given dosage, yield stress values for OWC slurries incorporating SCMs and without any chemical admixtures followed the following order: SF>MK>RHA>FA at all test temperatures. The slurries prepared with a larger fraction of spherical particles should have lower viscosity, which is evident in the case of slurries prepared with FA. But in the case of SF, yield stress and viscosity were found to be greater with increasing SF amount, likely because of higher surface area, which increases the water demand to produce a similar fluidity to that of mixtures made without SF. The OWC slurries prepared with RHA showed a different behaviour than that expected. Instead of increasing yield stress, the values were found to decrease gradually with the increasing replacement level of RHA.

PCH was found to enhance the shear thickening behaviour of OWC slurries and the intensity of this effect varied with the type and amount of SCM (amplified with metakaolin, reduced by SF, unchanged with FA, and showed an irregular behaviour with RHA). The explanation of this phenomenon is linked to the primary mechanism, i.e. steric hindrance by which PCH disperses cement particles. When polycarboxylate polymers adsorb on to the hydrating

cement grains, repulsive interactions occur as a consequence of the elastic and mixing mechanisms. The elastic and mixing mechanisms are a function of the thickness and density of the polymer adsorption layer, respectively (Yamada et al. 1998). In order to be dispersed, the distance between two cement particles should be equal to or higher than double the thickness of the polymer adsorption layer. When cement particles try to approach each other, the elastic component of the steric hindrance exhibits repulsive forces. On the other hand, the mixing component of the steric hindrance produces resistance when two neighbouring polymers approach each other (Yamada et al. 1998). As a consequence, the resistance of the mixing component of the steric hindrance increases with the increase of PCH dosage. This is possibly the reason why the exponent  $n$ -value increased with the increase on PCH dosage and the slurry behaviour converged towards shear thickening.

The measured plastic viscosity does not always truly represent the material properly and sometimes could be misleading because of the high error involved in fitting the flow curve to the Bingham model (Saak, 2000). However, plastic viscosity was measured and presented in this thesis because it is very difficult to create mechanical models for the deformation behaviour of cement paste using the apparent viscosity at each shear rate point (Nehdi and Rahman, 2004). It was reported that plastic viscosity of cement slurries generally decreases with an increase in temperature (Ravi *et al.*, 1990 and Ramachandran *et al.*, 1997). But such a conclusion cannot be supported based on the current study and data reported in chapter four. In order to evaluate the reproducibility of test results, some selected tests were performed several times and the results were reproducible within a variability of 5%. At 23°C, plastic viscosity decreased with increased admixture dosage up to a certain level and then started to increase in the case of PCH, PCM, and RA at associated dosages of 0.50%, 0.50% and 4.0%, respectively. Plastic viscosity gradually increased with increased dosage in the case of LSM, whereas it decreased with increased SRA dosage. In the case of HCR, plastic viscosity generally decreased with increased dosage. At 45°C, admixtures showed almost similar behaviour in terms of plastic viscosity, except for LSM. At 60°C, slurries incorporating PCH did not exhibit a regular behaviour and plastic viscosity increased with increased admixture dosage. In the case of PCM, SRA and HCR, plastic viscosity increased up to a certain limit and then started to decrease at associated critical dosages of 0.50%, 0.75% and 0.50%, respectively. However, it was not possible to provide a simple correlation of the effect of

chemical admixtures and temperatures on the plastic viscosity based on the present study, which was also noted previously for ordinary cement pastes (Nehdi and Al-Martini, 2007, Al-Martini, 2008). In chapter five, regardless of the type and dosage of SCM, plastic viscosity values for OWC slurries were found to increase nonlinearly with the increase of temperature. The plastic viscosity of OWC slurries increased with the incorporation of MK, SF and RHA as partial replacement for OWC and decreased with the addition of FA.

Chapter six was devoted to developing a predictive model to simulate the influence of various types and dosages of chemical admixtures and SCMs on the flow behaviour of OWC slurries using Artificial Neural Networks. The ANN model developed in this study was able to learn the relationships between different shear flow parameters for various OWC slurries and successfully predicted the rheological properties of slurries used in the training process. It also demonstrated satisfactory performance when input parameters (shear rate, temperature, and dosage of admixture) unfamiliar to the ANN were used. The results prove that the ANN model is a powerful tool to quantitatively predict the rheological properties of OWC slurries within the range of tested admixture dosages and test temperatures.

Empirical equations for predicting the shear flow curves of OWC slurry mixtures incorporating various superplasticizers at various temperatures were also developed using multiple regression analysis and presented in Chapter six. The flow curves developed using the ANN- and MRA-based models allowed predicting the Bingham parameters (yield stress and plastic viscosity) of OWC slurries with an acceptable accuracy and were found to be in good agreement with experimental results. However, the ANN-based model performed relatively better than the MRA-based model in predicting the rheological properties of OWC slurries. The ANN-based model also captured the coupled effects of chemical admixture and supplementary cementitious materials in chapter seven. A sensitivity analysis was performed to study the effects of individual input parameters on the rheological properties of OWC slurries. Irrespective of the type and dosage of SCM used, the ANN model successfully captured the rheological behaviour of OWC slurries with the variation of input parameters. The model was also found to generalize its predictions beyond the training data to new slurries incorporating different dosages of admixtures and SCMs and considering different temperatures within the practical range of the training data.

A statistical design approach based on a second order central composite response surface model was developed in chapter eight to predict the rheological properties of OWC slurries with addition of SCMs such as: metakaolin silica fume, rice husk ash or fly ash. Optimization of OWC slurry often requires a number of trial batches to achieve adequate rheological properties, which is labour intensive, time consuming and thus costly. A factorial design approach was used in this study to determine the influence of temperature and key mixture parameters such as the dosage of superplasticizer, type and amount of SCMs and their interactions on the relevant rheological properties. The proposed model can simplify the test protocol and reduce the number of required tests to achieve an optimum balance among the various parameters involved and to gain a better understanding of trade-offs between key mixture parameters such as the dosage of superplasticizer and amount of supplementary cementitious materials.

### **9.3 Recommendations For Future Research**

It should be noted that the findings reported in this study are valid for the oil well cement, supplementary cementitious materials and chemical admixtures used herein. Other cement/SCM/admixture combinations can exhibit different characteristics. Even admixtures from the same category, but from different source, could behave differently, and thus need to be investigated separately.

The prediction capability of the developed ANN model are valid for the types of materials tested and within the range of parameters investigated in this study. However, the model can be retrained to a wider data range of input variables when new expanded data becomes available.

The multiple regression analysis and design of experiments based models are also valid for the types of materials tested and within the range of parameters investigated in this study. Therefore, further experimental research is needed to extend the proposed predictive equations beyond the limits of the material types and proportions, and ranges of test parameters used in the present study.

Further research is also needed to investigate the effects of possible hybrid blends of various chemical admixtures and mineral admixtures (supplementary cementitious materials) at high

temperature versus time and to assess the compatibility between various admixtures and a wide scope of cementitious blends to optimize binder-admixture formulations for effective and sustainable use in oil well cementing applications.

Pressure also plays an important role, though of usually less importance than that of temperature, on the rheology of oil well cements. It is recommended that the present work be extended and validated using advanced rheological testing that captures both the effects of temperature and pressure variations.

The mechanical properties and durability of hardened cementitious materials are critical for its end use in the field. The rheological properties of cement-based materials determine the quality of the hardened cementitious matrix and help predicting its end use performance and its physical properties during and after processing. The effects of temperature, chemical admixture, type and dosage of supplementary cementitious materials on the rheological properties of oil well cement slurries have been investigated in this thesis. Thus, a logical next step would be to study the mechanical properties and long-term durability properties of hardened oil well cementitious matrices incorporating conventional chemical admixtures and supplementary cementitious materials and subjected to high temperature and pressure to make final recommendations for oil well cementing.

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## **Publications:**

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### *Publication in Preparation*

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