INVESTIGATION ON RHEOLOGY OF CEMENT PASTE AND CONCRETE AT HIGH TEMPERATURE

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By

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ABSTRACT

The objective of this research is to explore the important mechanisms that control the rheology of cement paste and concrete incorporating various chemical admixtures and subjected to high temperature and prolonged mixing time. The thesis also aimed at formulating recommendations for the effective use of chemical admixtures in high temperature environments. In order to achieve these objectives, the rheological properties of portland cement pastes incorporating various chemical admixtures were first investigated at different temperatures using both the conventional flow technique and the oscillatory shear technique. The results indicated that current technical data for chemical admixtures need to be validated for hot weather conditions; admixtures proven effective in mild weather may become ineffective at high temperature. For example, some water reducing and retarding admixtures acted as accelerators at high temperature, yet they have been recommended by manufactures for concrete in hot weather conditions.

The coupled effects of mixing time and ambient temperature on the rheology of portland cement paste incorporating superplasticizers were also investigated. Results suggested that polycarboxylate-based superplasticizers should be used at a dosage close to the saturation in order to ensure adequate rheological behaviour at high temperature and prolonged mixing time, while melamine sulfornate- and naphthalene sulfonate-based superplasticizers should be used at dosages beyond the saturation level.

The insights gained through these studies were then applied to study the rheology of fresh concrete incorporating various superplasticizers and subjected to prolonged mixing under high temperature. The test results indicated that the Bingham constants of concrete are significantly affected by changes in temperature, mixing time and admixture dosage. The relationship between the yield stress and plastic viscosity of concrete was investigated to develop a rational means for the objective assessment of the rheology of concrete mixtures in hot weather.

The coupled effects of the ambient temperature and mixing time on the compressive strength of concrete incorporating superplasticizers were also investigated. The results indicated that the compressive strength of concrete mixtures is temperature, mixing time and superplasticizer type dependent.

Furthermore, new equations were developed using genetic algorithms (GA) to predict the Bingham parameters (yield stress and plastic viscosity) of cement paste, the yield stress of concrete, and the oscillatory yield stress of cement paste considering various parameters including the ambient temperature, mixing time and superplasticizer type and dosage. The results indicated that the computed rheological parameters for cement paste and concrete compared well with corresponding experimental data. The GA equations thus developed captured well the effects of the various test parameters.

Keywords: rheology, cement paste, concrete, high temperature, mixing time, superplasticizer, yield stress, viscosity, thixotropy, compressive strength, slump loss, genetic algorithm, oscillatory rheology, modeling.

CO-AUTHORSHIP

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. Substantial parts of this thesis were either published in or submitted for publication to peer-reviewed technical journals and international conferences. The candidate carried out all experimental work, data analysis, modeling process, and writing the initial versions of all papers listed below. The contribution of his research advisor consisted of providing advice, and helping in the development of the final versions of publications:

- Al-Martini, S., and Nehdi, M. (2007), "Effect of Chemical Admixtures on Rheology of Cement Paste at High Temperature", *Journal of ASTM International*, 4(3), 1-17.
- Nehdi, M., and Al-Martini, S. (2007), "Effect of Temperature on Oscillatory Shear Behavior of Portland Cement Paste Incorporating Chemical Admixtures", *Journal of Materials in Civil Engineering*, ASCE, 19(12), 1090-1100.
- Al-Martini, S., and Nehdi, M. (2008), "Coupled Effects of Time and High Temperature on Rheological Properties of Cement Pastes Incorporating Various Chemical Admixtures", In press, *Journal of Materials in Civil Engineering, ASCE.*
- Al-Martini, S., and Nehdi, M. (2008), "Coupled Effects of High Temperature, Prolonged Mixing Time and Chemical Admixtures on Rheology of Fresh Concrete", In press, *ACI Materials Journal.*
- Al-Martini, S., and Nehdi, M. (2008), "Effects of High Temperature and Prolonged Mixing Time on Slump Loss and Compressive Strength of Concrete Incorporating Various Superplasticizers", Accepted for publication, *ICE Construction Materials Journal.*
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- Al-Martini, S., and Nehdi, M., (2008), "Genetic Algorithm-Based Yield Stress Equations for Concrete at High Temperature and Prolonged Mixing Time" Submitted, *Computers and Concrete Journal.*

- Al-Martini, S., and Nehdi, M. (2008), "Estimating Time and Temperature Dependent Yield Stress of Cement Paste Using Oscillatory Rheology and Genetic Algorithms", Submitted, *Cement and Concrete Research.*
- Al-Martini, S., and Nehdi, M. (2005), "Effect OF Chemical Admixtures and High Temperatures on Yield Stress and Plastic Viscosity of Cement Pastes", Conference of The Canadian Society of Civil Engineering, Toronto, paper GC-209, 10 p.
- Al-Martini, S., and Nehdi, M. (2005), "Effect of Chemical Admixtures on Oscillatory Rheology of Cement Paste in Hot Weather: Significance for High-Rise Building Construction", Proceedings of the 7th International Conference on Multipurpose High-Rise Towers and Tall Buildings", Dubai, paper IFHS-093, 11 p.
- Al-Martini, S., and Nehdi, M. (2007), "Rheological Properties of Cement Paste: Effect of Time and High Temperature", International Conference on Concrete under Severe Conditions: Environment and Loading, CONSEX, 07, France, 971-978.
- Al-Martini, S., and Nehdi, M. (2008), "Effects of High Temperature and Prolonged Mixing Time on Slump Loss and Compressive Strength of Concrete", 2nd Canadian Conference on Effective Design of Structures CCEDS II, Paper # 84, Canada.

DEDICATION

To my wife Dr. Reem Sabouni for her constant support and love. And to my parents Dr. Mohamad Martini and Dr. Ferial Halbouni; their love, support, and prayer have encouraged me throughout this work. Finally, I would like also to dedicate this work to my beloved son Eyad.

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Finally, I wish to express my sincere gratitude to my wife (Reem) and beloved son (Eyad).

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H'	Slope of the flow curve due to the sudden increase in rotational velocity,
γ	Oscillatory shear strain,
δ	Phase shift,
$\dot{\gamma}$	Shear rate,
γ_o	Amplitude of shear strain,
$\Delta\mu_{ct}$	Plastic viscosity increase with the time elapsed,
μ_p	Plastic viscosity,
$a, b, c,$	Model constants,
d, e, f	Model constants,
AAE	Average absolute error,
$c_{ap}, e_{ap}, c_{aT},$	Model constants,
e_{aT}, c_{aD}, e_{aD}	Model constants,
c_{bp}, e_{bp}, c_{bT}	Model constants,
$e_{bT}, c_{bD,}, e_{bD}$	Model constants,
D	Superplasticizer dosage,
f_{adm}	28-day compressive strength of concrete incorporating PCN, ML, or NS,
f_{PCN}	28-day compressive strength of concrete incorporating PCN,
G	Flow resistance,
G^*	Complex shear modulus,

G'	Shear modulus,
G''	Loss modulus,
GA	Genetic algorithms,
h	Height of the inner cylinder,
H	Viscosity factor,
ML	Melamine sulfonate-based high-range water-reducing admixture,
MR	Mid range water-reducing admixture,
N	Rotational speed,
NS	Naphthalene sulfonate-based high-range water-reducing admixture,
PC	Polycaraboxylate-based high-range water-reducing admixture,
PCN	A new generation of polycaraboxylate-based high-range water-reducing admixture,
R_i	Radius of the inner cylinder ,
R_o	Radius of the outer cylinder ,
Seg	segregation coefficient,
T	Ambient temperature,
t	Mixing time,
t^*	Time,
t'	Normalized time,
t_f	Time corresponding to dormant period,
T_R	Torque resistance,
T_t	Testing temperature,
V	Volumetric concentration of solute,

WR	water-reducing and retarding admixture,
W	Crowding effect,
σ	Oscillatory shear stress,
σ_o	Amplitude of shear stress,
τ	Shear stress,
τ_m	Measured shear stress,
τ_o	Yield stress,
$\tau_{0,c}(0,T)$	Initial yield stress of concrete (at zero time),
τ_p	Predicted shear stress,
Φ^*_1	Maximum packing density of a dry mixture,
Φ_i	Solid volume fraction of a constituent,
Ω	Angular velocity of the outer cylinder,
α	Experimental constant
ω	Angular velocity

Chapter 1

INTRODUCTION

1.1 General

Over the last few decades, the economic structure of the world in general and that of developing countries in particular has changed dramatically. Population has increased substantially and major economic functions generally drifted to large metropolitan areas. Hence, this era has been marked by a massive use of portland cement-based materials, which have become the basis of the majority of modern civil infrastructure.

For instance, some of the hot weather countries such as those in the Arabian Gulf have witnessed an extensive urbanization over the last decade. Billions of dollars have been invested in concrete construction and infrastructure projects. It is well known that high temperature has a negative effect on the performance of cement-based materials, particularly in their fresh state. Fresh cement-based materials at high temperature are more difficult to place due to the fast evaporation of mixing water and the acceleration of cement hydration reactions. Therefore, concrete having an adequate initial workability in hot weather regions can lose its workability rapidly, which can affect its mechanical properties and long-term durability.

Over the last decades, several types of new superplasticizers have been introduced to optimize the flow properties of cement-based products. Using such innovative materials, a

new generation of concrete, the so-called "self consolidating concrete" has emerged; this type of concrete is characterized by a high fluidity combined with a segregation resistance, and can be placed and consolidated under its own weight without or with minimum vibration. However the proper selection of superplasticizers has been principally based on a trial-and error process using tests such as Marsh flow or mini slump tests. For instance, the performance of superplasticizers when used in concrete subjected to special conditions such as prolonged mixing and high temperature are still largely unexplored. Indeed, superplasticizers have usually been developed in countries with mild temperature, and thus their technical data sheets provided by manufactures are not generally applicable for concrete in hot weather environments. Therefore, a fundamental understanding of the effects of extreme weather conditions on the performance of superplasticizers is needed. There is currently a lack of information on the effects of various superplasticizers on the rheology of fresh concrete as a function of the mixing time and ambient temperature.

Measuring the rheological properties of cement-based materials in the laboratory remains challenging since the equipment used to quantify the rheological properties of such materials is relatively costly, difficult to operate, and may not be suitable for use in construction sites due to its large size and/or complicated set up that is more suited for lab environments. The field tests commonly used for measuring the rheology of cement-based materials such as the slump, flow table, and L-box are empirical in nature. Moreover, there is a real need for the robotization of rheology measurements for cement-based materials, which requires the use of more fundamental tests.

1.2 Objectives and Scope

Concrete can be considered as a suspension in which cement paste is the medium and coarse and fine aggregates are the solid particles. Therefore, the rheological properties of cement paste affect the rheological behaviour of fresh concrete. Placing concrete at high temperature is a real challenge due to the acceleration of hydration reactions of cement and the fast evaporation of water, which causes a rapid loss of workability. Various chemical admixtures have been recommended to improve the fluidity of fresh concrete. However, such admixtures have generally been developed in countries with moderate temperature and they often lead to disappointing results when transposed to hot weather environments. Likewise, there is still a lack of information in the open literature regarding the effects of various chemical admixtures, especially the new generation superplasticizers, on the rheological properties of cement-based materials at high temperature. Hence, this research investigates the effects of commonly used chemical admixtures on the rheology of cement paste and concrete at high temperatures and prolonged mixing time.

The main objective of this study is to develop a better understanding of the important mechanisms that control the rheology of cement paste and concrete subjected to severe conditions such as high temperatures and/or prolonged mixing time, and to investigate the performance of chemical admixtures in mitigating workability problems of cement-based materials at high temperature.

This study also aims at establishing workability control charts for concrete incorporating various chemical admixtures at different temperatures and prolonged mixing times. These workability control charts can provide a tool for the objective assessment of

the rheology of fresh concrete allowing to reduce the incidence of errors when the workability of fresh concrete is evaluated solely based on visual inspection or empirical methods such as the slump test, thus providing a rational basis for the design of concrete mixtures under various temperatures and mixing times. There should be no difficulty in computerizing the entire process so that values of yield stress and plastic viscosity obtained automatically can be compared with specified values and then, on the basis of stored information, any necessary corrective action would be performed. Detailed objectives of this study are provided below:

1. Develop an improved understanding of the effects of the testing temperature on the rheological and viscoelastic properties of cement paste incorporating various admixtures.

2. Investigate the coupled effects of the ambient temperature and mixing time on the rheological properties of fresh cement paste and concrete incorporating various superplasticizers.

3. Explore the coupled effects of the ambient temperature and mixing time on the compressive strength of concrete incorporating various superplasticizers.

4. Develop a versatile model to predict the Bingham parameters of cement paste and concrete incorporating various superplasticizers and subjected to different mixing times and ambient temperatures.

5. Study the oscillatory rheology and formulate equations to predict the oscillatory yield stress of cement paste incorporating various superplasticizers and subjected to different mixing times and ambient temperatures.

1.3 Structure of Thesis

This thesis has been prepared according to the guidelines stipulated by the Faculty of Graduate Studies at the University of Western Ontario for an Integrated Article (formerly Manuscript). It has been divided into eleven chapters, eight of which have been written as self-contained documents and either published 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 following is a concise description of the contents of the thesis:

Chapter 2

Chapter 2 is divided into two parts. The first part summaries hot weather concreting problems and the current practice adopted to alleviate the adverse effects of hot weather on fresh concrete. The second part presents a brief background on the rheology and rheological parameters used to characterize materials. The rheology of cement paste and concrete is also briefly highlighted in this chapter.

Chapter 3

In this chapter, the rheological properties of portland cement pastes with a water-cement ratio (w/c) of 0.35 and 0.50 were investigated at different testing temperatures in the range of 20 to 45 °C using an advanced shear-stress/shear-strain controlled rheometer.

The influence of water reducing and retarding admixtures, polycarboxylate, naphthalene sulfonate and melamine sulfonate-based superplasticizers in addition to mid-range water reducing admixtures on the rheological properties of cement paste at various testing temperatures was investigated.

Chapter 4

In this chapter, the visco-elastic properties of portland cement pastes with a water-cement ratio (w/c) of 0.35 and 0.50 were investigated at different temperatures in the range of 20 to 45 °C through oscillatory rheological tests conducted using an advanced shear-stress/shear-strain controlled rheometer. The influence of water reducing and retarding admixtures, melamine sulfonate-based, polycarboxylate-based, and a new generation of polycarboxylate-based high-range water reducing admixtures on the oscillatory rheological properties of cement paste at various temperatures was also examined.

Chapter 5

This chapter investigates the combined effects of the ambient temperature and mixing time on the performance of polycarboxylate-, melamine sulfonate-, and naphthalene sulfonate-based high-range water-reducing admixtures used to enhance the flow of cement paste. Rheological parameters including yield stress, plastic viscosity, and thixotropy of cement pastes with a water/cement ratio of 0.38 were measured as a function of the superplasticizer dosage and ambient temperature (22-45 ^{o}C) over 20 to 110 minutes from the time of first contact between cement and water with 30 minutes between successive

measurements. The rheological tests were conducted using an advanced shear-stress/shear-strain controlled rheometer.

Chapter 6

The rheological properties of fresh concrete incorporating various superplasticizers were investigated as a function of the mixing time, ambient temperature, and admixture dosage. Three superplasticizers were used, namely, polycarboxylate-, melamine sulfonate-, and naphthalene sulfonate-based high-range water-reducing admixtures. Concrete mixtures were continuously agitated for up to 110 minutes using a drum concrete mixer under a controlled temperature ranging from 22 to 45 °C. The rheological testing was performed using a BML rheometer. The relationship between the yield stress and plastic viscosity was investigated in an attempt to develop a rational means for the objective assessment of the rheology of concrete mixtures in hot weather.

Chapter 7

The coupled effects of the ambient temperature and mixing time on the slump loss and compressive strength of fresh concrete incorporating superplasticizers were investigated. The concrete mixtures were made with ordinary portland cement (OPC) with a water/cement ratio of 0.38 and incorporating either a polycarboxylate-, melamine sulfonate-, or naphthalene sulfonate-based superplasticizer. Concrete mixtures were continuously agitated for up to 110 minutes under a controlled temperature ranging from 22 to 45 °C. The effect of such a mixing scheme on the slump loss and compressive strength of concrete at the ages of 12 hours, 1, 3, 7, and 28 days was investigated.

Chapter 8

In chapter 8, shear stress versus shear rate curves for cement pastes incorporating the various superplasticizers at different ambient temperatures and mixing times were predicted using genetic algorithms. Rheological equations were then derived from these curves using the Bingham model and employed to predict the yield stress and plastic viscosity of cement pastes. A parametric study was performed to evaluate the effects of the mixing time, ambient temperature, and superplasticizer dosage on the calculated yield stress and plastic viscosity.

Chapter 9

This chapter investigates the correlation between the flow behaviour of portland cement paste and concrete using the results of chapters five and six. The cement paste and concrete mixtures were subjected to prolonged mixing for up to 110 min at high ambient temperatures. The yield stress values of concrete and that of the corresponding cement paste were measured using concrete and cement paste rheometers. In this chapter, the genetic algorithms (GA) technique was also used to predict the yield stress of concrete considering various parameters, such as the mixing time, ambient temperature, and superplasticizer dosage. A parametric study was conducted to evaluate the ability of the GA equations thus developed to capture the effects of test parameters on the yield stress of concrete.

Chapter 10

A controlled shear stress/shear rate rheometer was used in this chapter to determine the viscoelastic behaviour of cement paste incorporating various superplasticizers and subjected to prolonged mixing at high ambient temperature. The yield stress from oscillatory shear stress tests was estimated using the intersection between the viscous part of the oscillatory shear strain/stress curve and the oscillatory shear stress axis. In this chapter, equations describing the variation of shear strain versus shear stress beyond the solid-fluid transition for cement pastes incorporating various superplasticizers at different ambient temperatures and mixing times were developed using genetic algorithms (GA). The yield stress of cement pastes was subsequently predicted using the developed equations by calculating the stress corresponding to zero strain. A parametric study was performed to evaluate the effects of the mixing time, ambient temperature, and superplasticizer dosage on the calculated yield stress.

Chapter 11

In this chapter, a summary of the thesis is provided along with the main conclusions, and recommendations for future research.

1.4 Original Contributions

This thesis is a comprehensive study on the effects of the temperature and time on the rheology of superplasticized cement paste and concrete. This work is a step towards formulating standards and specifications for using admixtures in hot weather concreting. The main contributions of the current study can be summarized as follows:

- Exploring the effects of several chemical admixtures on the rheology of cement paste and concrete subjected to high temperature and prolonged mixing. The results of this thesis revealed that technical data for chemical admixtures need to be validated for hot weather conditions because they have generally been developed in areas with mild temperatures; it has been demonstrated that admixtures proven effective in mild weather may not be effective when used in high temperature environments.

- Establishing workability control charts for concreting in hot environments. These charts can provide a means for the objective assessment of workability, allowing reducing the incidence of errors when concrete mixtures in hot environments are merely judged based on personal experience and visual inspection, or on empirical tools such as the slump test.

- New empirical equations for predicting the shear flow curve of cement paste mixtures incorporating various superplasticizers and subjected to prolonged mixing at various temperatures have been developed using the genetic algorithms approach.

- Similar equations for predicting the yield stress of fresh concrete mixtures incorporating various superplasticizers and subjected to prolonged mixing at various temperatures have been developed using the genetic algorithms approach.

- Also, equations for predicting the oscillatory shear strain-stress curves for the experimentally investigated cement paste mixtures (in the viscous region)

incorporating various superplasticizers and subjected to prolonged mixing at various temperatures have been developed using the genetic algorithms approach.

- The performance of various superplasticizers under high temperature and prolonged mixing has been quantified. Mechanisms for the difference in the behaviour of such superplasticizers have been proposed and explained.

- This thesis represents the first comprehensive attempt to mobilize flow and oscillatory rheology to explore the combined effects of time and temperature on the rheology of portland cement paste and concrete.

Chapter 2

LITERATURE REVIEW

2.1 Hot Weather Concreting

2.1.1 Introduction

Hot weather climates adversely affect the quality of fresh and hardened concrete through accelerating the rate of water evaporation and cement hydration (Al-Gahtani *et al.* 1998). Several standards and guidelines have specified a limit for the job site temperature, which if exceeded, concreting work is considered to be conducted under hot weather environment. For example, the upper limit of ambient temperature for the production of good quality concrete, as specified by The American Concrete Institute "Specification for Hot Weather Concreting", is 27 °C (ACI 305.1-06). The American Society for Testing and Materials (ASTM) "Standard Practice for Making and Curing Concrete Test Specimens in the Field" requires that concrete be mixed and initially cured at a temperature not exceeding 27 °C (ASTM C31 2002). In practice, strictly abiding by this limit is not an easy task and needs several precautions that are difficult to be implemented in-situ without additional high costs. Moreover, designing concrete mixtures is intricate since several interacting factors influence this procedure including concrete ingredients, placement, compaction, and curing, as well as the specific conditions of the construction site.

The temperature during a typical summer day in hot weather countries often exceeds the abovementioned specifications. For instance, Al-Gahtani *et al.* (1998) documented that

the summer daytime temperature in the vicinity of Dhahran in eastern Saudi Arabia are frequently in excess of 40 °C. The ACI Committee 305 for Hot Weather Concreting recommends that trial batches should be made at the highest expected job site temperature when designing concrete mixtures to evaluate the hot weather effects (ACI 305R-99).

2.1.2 Cement hydration

The hydration of cement starts immediately upon the contact of cement with water. A rapid evolution of heat takes place during the first minutes of hydration. Subsequently, the reactions are slowed down significantly for a period of time called the dormant or induction period, in which the thickness of hydration products around cement grains increases. The induction period typically lasts from 1 to 4 hours depending on the temperature, water to cement ratio (w/c), cement properties, and also admixtures. This period of time is necessary to transport, place and consolidate fresh concrete. The hydration reactions are then accelerated again because the layers of hydration products around cement grains collapse due to osmotic pressure, thus allowing further contact between cement and water. The acceleration usually lasts from 8 to 12 hours (Hewlett 1998). The hydration process may take up to a year during which the hydration rate is substantially slowed down with time, and the hydration products during this stage fill in the porous space densifying the hydrated cement paste (Hewlett 1998).

The rate of cement hydration accelerates with a rise in temperature. The increased rate of hydration with temperature brings about the stiffening of cement-based mixtures, which is generally referred to in concrete technology as "slump loss" (Soroka 1993). The accelerated slump loss reduces the time during which the fresh concrete remains workable

to allow for its placement. Such a slump loss is indeed one of the major problems in hot weather concreting, and is therefore discussed in more detail later in this chapter.

2.1.3 Potential concreting problems in hot weather

2.1.3.1 Increased water demand

Due to the high temperature in hot weather environments, mixing water evaporates rapidly from the fresh concrete surface. Consequently, concrete quickly loses its workability. To compensate for the water lost due to evaporation, additional amounts of water need to be added in order to achieve a desired slump (Soroka and Ravina 1998). However, increasing the water content is not recommended because it is known to be the main factor for reducing the concrete's compressive strength and causing durability problems (ACI 305R-99). Hasanain *et al.* (1989) investigated the evaporation rate of water from a freshly placed concrete surface cast at different times of a hot climate day. Their results indicated that the rate of water evaporation from freshly placed concrete surfaces depends mainly on the time of casting with the highest rate achieved at around noon time.

2.1.3.2 Slump loss and setting time

The already discussed rapid evaporation of water in addition to the acceleration of cement hydration at high temperature are the main reasons for the rapid stiffening of fresh concrete in hot weather regions. Sorka and Ravina (1998) reported that the increase of temperature from 20 to 40 ^{o}C has increased the rate of cement hydration about 2.5 times, which results in rapid slump loss of concrete.

El-Rayyes (1990) investigated the effect of the ambient air temperature on the time of initial and final setting of concrete mixtures made with a wide range of water-to-cement

ratio (w/c) and placed in extremely hot climates. The w/c ranged from 0.35 to 0.70. The concrete mixtures were initially prepared in a laboratory with a controlled temperature of 23 °C. After mixing, mortar was sieved from each concrete mixture and its initial and final setting times were measured in the lab at a temperature of 23 °C and outdoors at ambient temperatures ranging from 36 to 41 °C. El-Rayyes (1990) reported that the increase in the temperature from 23 to 41 °C reduced the initial and final setting time of concrete by about 25%.

2.1.3.3 Decreased 28-day compressive strength

As mentioned earlier, an extra quantity of water is required at high temperature to compensate for the fast evaporation of mixing water. However, adding extra water yields a higher w/c. Concrete placed under a high temperature can thus have a lower 28-day compressive strength than that placed under a moderate temperature. This is attributed to a higher w/c, higher concrete temperature at the time of placement or during curing, or both (ACI 305R-99). Al Gahtani *et al.* (1998) found that the compressive strength of concrete specimens prepared at a normal laboratory temperature, but cured under high temperature was about 6-20% less than that of the corresponding specimens prepared and cured at a normal temperature. They attributed these results to the fact that concrete strength is adversely affected by the acceleration of hydration at early ages when it is cured at high temperatures. High curing temperature produces a protective coating on the surface of hydrated cement grains, hindering the subsequent hydration and producing a non-uniform distribution of hydration products within the hardened cement paste matrix, thus leading to reduced compressive strength (Al Gahtani *et al.* 1998).

Gaynor *et al.* (1985) investigated the effect of the initial curing on the compressive strength of concrete. After mixing, some concrete specimens were initially air-cured for 16-20 hours at a temperature of 38 °C and then in a moist curing room at 23 °C and relative humidity of 95%, while other specimens were only cured in a moist curing room. The initial curing was intended to simulate poor initial curing for fresh concrete in hot weather. Their results showed that the 28-day compressive strength of specimens initially cured at 38 °C was about 11% less than that initially cured in a moist curing room.

2.1.4 Practices for mitigating hot weather concreting problems

To alleviate the harmful effects of hot weather on concrete, it is recommended to place concrete during time periods when the temperature is low and does not exceed the acceptable levels specified by standards. However, it is not always possible to abide by this recommendation, especially for large projects that dictate continuous concreting work even in periods of the day with high temperature to meet demanding schedules. Some of the practices applied in hot weather concreting are:

2.1.4.1 Using cooled mixing water

Although the mass of water used in mixing concrete is usually the least compared to that of aggregates or cement, cooled water can reduce the temperature of the entire concrete mixture, though this reduction is not substantial. For example, lowering the temperature of the mixing water by 2 °C can reduce the concrete temperature by approximately 0.5 °C (ACI 305R-99). The ACI 305R-99 report presents the expected reduction in the concrete temperature when replacing part of the mixing water having a temperature of 16 °C, 21 °C, 27 °C, or 32 °C with a cooled water having a temperature of 7 °C. It is reported that the

larger the amount of cooled water added as part of the mixing water, the more the concrete temperature is reduced. Moreover, the larger the difference in the temperature between the cooled water (7 °C) and the normal mixing water, the more concrete temperature is reduced.

2.1.4.2 Using ice as partial replacement for mixing water

Using ice as part of the mixing water has been a major means of reducing the fresh concrete temperature (ACI 305R-99). Crushed ice is placed in the concrete mixer as a part of the mixing water. Its portion should not exceed 75% of the total mixing water required. The larger the amount of ice added as part of the mixing water, the more is the reduction of the fresh concrete temperature that can be achieved (ACI 305R-99). The ACI report states that the concrete temperature can be decreased to 20-23 °C when replacing 75% of the mixing water with ice. This indicates that this practice is more effective than using cooled water alone. However, it is a costly option requiring additional equipment to be installed at ready mix concrete plants (ACI 305R-99).

2.1.4.3 Using proper ingredients

Concrete ingredients must be properly selected in order to achieve satisfactory performance of concrete under hot weather. In order to reduce the internal concrete temperature during hydration, the cement content should be kept as low as possible, but sufficient to meet workability, strength and durability requirements. In hot weather conditions, portland cement is often partially replaced by supplementary cementitious materials such as fly ash or blast furnace slag, which were found to reduce the early rate of

heat evolution, thus better controlling the rise in concrete temperature and the rate of slump loss.

Since aggregates represent 60-70% of the total volume of concrete, their temperature has a significant effect on the fresh concrete temperature. For example the temperature of concrete increases by about 17 °C when the aggregates temperature increases from 16 °C to 32 °C (ACI 305R-99). Therefore, all practical means should be employed to keep the aggregates as cool as possible, such as keeping the aggregates in a shaded storage.

2.1.4.4 Using chemical admixtures

Chemical admixtures are usually incorporated in concrete to reduce the amount of mixing water, while maintaining an adequate workability (Ramachandran *et al.* 1997). Several types of admixtures recognized by ASTM C494 can be used, including: water-reducing admixtures (Type A), retarding admixture (Type B), accelerating admixtures (Type C), water reducing and retarding admixtures (Type D), and water reducing and accelerating admixtures (Type E).

Water reducing admixtures are usually capable of reducing the quantity of mixing water required to produce concrete of a given workability by 5 to 15%. High-range water reducing admixtures (also called superplasticizers), on the other hand, are capable of reducing the quantity of mixing water by up to 30%. Superplasticizers are used for instance to produce the so-called 'self consolidating concrete (SCC)', which can be placed with little or no vibration. Self consolidating concrete (SCC) is a highly flowable concrete that can effectively fill formwork without the need for consolidating tools, and is useful, for example, for placing concrete in thin and heavily reinforced sections. Using concrete with

high flowability in hot weather environments may help to overcome the adverse effects of high temperature on slump loss (Soroka 1993). Superplasticizers allow a considerable increase in the initial slump of concrete, thus overcoming the subsequent slump loss, which is useful in hot weather conditions. However, these admixtures are usually developed in countries with mild climates and their behaviour can sometimes become different when used in hot climates. Therefore, such admixtures should be tested under high temperature before being recommended for hot weather concreting.

2.2 Rheology of Cement Paste and Concrete

2.2.1 Introduction

Rheology is defined as the science of flow and deformation of matter (Barnes *et al.* 1989). It investigates the relationship between force, deformation, and time. Broadly speaking, the matter can be everything from an elastic solid to a viscous liquid. Typically, rheology studies the deformation of those materials whose behaviour falls between solids and fluids (viscoelastic materials) (Barnes *et al.* 1989). The science of rheology can be employed for instance for achieving the following goals:

- To understand the interactions between different ingredients in a material, in order 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 design a processing equipment such as selecting the appropriate pump to provide enough power for a material to flow over a sufficient distance in pipelines. The relationship between the pump and flow in pipelines is governed by the rheological properties of the material.

If a force (F) is applied to the top of an element (Fig. 2.1), it will produce a shear stresses (τ) expressed in the following equation:

$$\tau = \frac{F}{A} \tag{2.1}$$

From the solid mechanics theory, the internal resistance to deformation can be determined knowing the rigidity modulus (G). As such, the relationship between the applied stress and the resulting strain is expressed in the following equation (Hibbeler 2005):

$$\tau = G\gamma \tag{2.2}$$

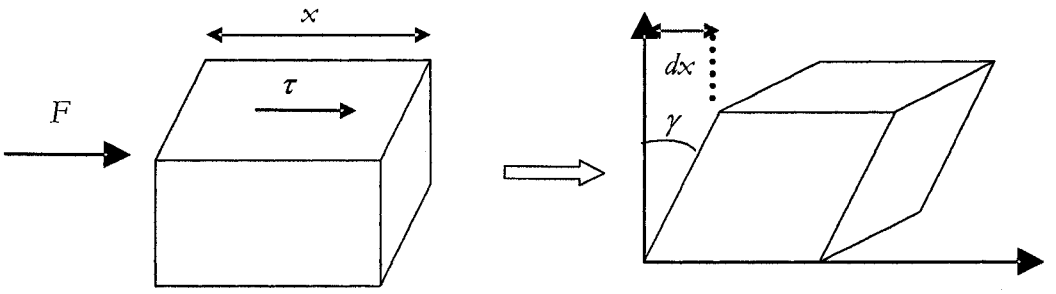

Figure 2.1: Description of the deformation of a solid element.

As shown in Fig. 2.1, the applied stress will lead to a deformation (*dx*) during the time period (*dt*) of the applied stress. This deformation can also be expressed in terms of an angle γ (shear strain). The change in shear strain per unit time is (Barnes *et al.* 1989):

$$\dot{\gamma} = \frac{d\gamma}{dt} \tag{2.3}$$

If the shear stress is divided by the rate of shear, the viscosity term (μ) can be obtained:

$$\mu = \frac{\tau}{\dot{\gamma}} \tag{2.4}$$

The previous equation is the Newtonian model, which is the simplest rheological model. The viscosity is physically defined as the measure of the resistance to flow (Macosco 1994).

Several means have been used to study the rheology of materials by inducing shear stress. Shearing a material using a two parallel plate geometry (Fig. 2.2) 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.

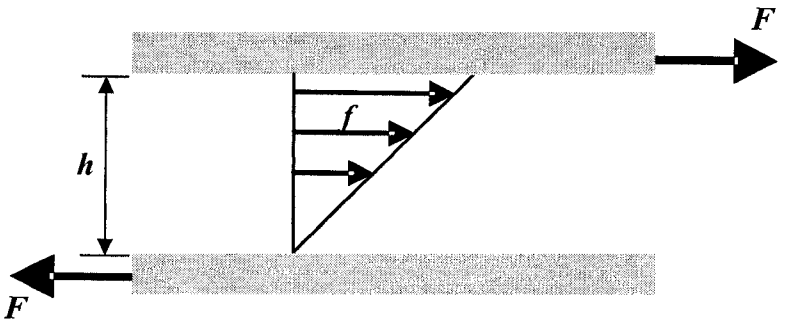

Figure 2.2-Sketch of the parallel plate geometry.

Using a coaxial cylinder geometry is another tool to measure the rheological properties of materials. It is the most commonly used geometry to study the rheological behaviour 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. A schematic representation of this geometry is shown in Fig. 2.3.

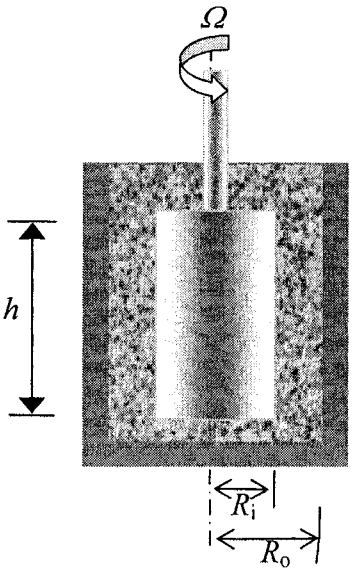

Figure 2.3-Sketch of coaxial cylinder geometry.

Assume that a Newtonian fluid fills the annular gap between the two cylinders and the inner cylinder is stationary, while the outer cylinder is rotating at a constant angular

velocity (Ω), the viscosity can be determined in the following equation (Ferguson and Kemblowski 1991):

$$\mu = \frac{T}{4\pi h\Omega}\left(\frac{1}{R_i^{\,2}} - \frac{1}{R_o^{\,2}}\right) \tag{2.5}$$

Where, T (Nm) is the torque resistance, $\boldsymbol{\Omega}$ is the angular velocity of the outer cylinder (rad/s), h is the height of the inner cylinder (m), R_i is the radius of the inner cylinder (m), and R_o is the radius of the outer cylinder (m).

2.2.2 Newtonian fluid

Generally, fluids can be classified into two groups: Newtonian and non-Newtonian. For Newtonian fluids (eg. water), the viscosity is independent of the shear rate and remains constant over the variation of the shear rate (Fig. 2.4). The Newtonian flow is the simplest. It occurs as soon as the stress is applied, and the shear stress increases linearly with the shear rate. These fluids maintain laminar flow during the applied shear stress. The characteristics of the Newtonian flow behaviour are summarized below (Barnes 1989):

- Viscosity does not change with the shear rate.
- Viscosity is independent of the time of shearing.
- Stresses in the 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.

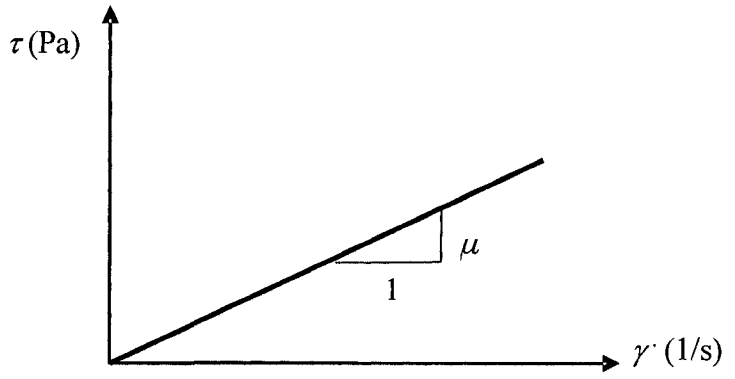

Figure 2.4: Shear stress versus shear rate curve for a Newtonian fluid.

Fluids that show a Newtonian flow behaviour have often low molecular weights. For example, water, glycerol, petrol, and oils are some fluids that show a Newtonian flow behaviour. Silicon oils are used as a calibration liquid for rheometers due to their reliability as a Newtonian liquid.

2.2.3 Non-Newtonian fluid

The other group of fluids is called non-Newtonian fluids. 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; this can be expressed as:

$$\mu = \mu(\dot{\gamma}, t) \tag{2.6}$$

The structure of time-dependent materials changes with time even if the applied shear rate is constant. Therefore, the viscosity of a flocculated suspension changes with time at a constant shear rate (Ferguson and Kemblowski 1991).

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. Bingham has accounted for this behaviuor by introducing a yield stress parameter in his equation (Bingham 1922):

$$\tau = \tau_o + \mu_p \dot{\gamma} \tag{2.7}$$

Where τ_0 is the yield stress (Pa) and μ_p is the plastic viscosity (Pa.s). 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. Roy and Asaga (1979) found that the yield stress of the same concrete varied when mixing techniques 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. Fluids with a non-Newtonian flow behaviour can be further classified as shear thinning or shear thickening fluids. The Power-Law is a two parameter model for describing pseudoplastic or shear-thickening behaviour in materials that show negligible yield stress and a varying differential viscosity. The Power-Law model describes these two phenomena in the following empirical equation (Ferguson and Kemblowski 1991):

$$\tau = K\dot{\gamma}^{n} \tag{2.8}$$

Where K is the consistency index and its unit is the viscosity unit (Pa.s). When the flow behaviour is shear thinning, $n < 1$, and $n > 1$ for shear thickening behaviour. For a Newtonian flow, n equals 1.

2.2.4 Yield stress

Viscoelastic materials are those that behave as a solid when the applied shear force is not large enough to overcome the internal friction in such materials. When the applied shear stresses become greater than the internal friction, viscoelastic materials start to flow driven by the force outcome from the difference between the applied and friction forces (Bingham 1922). The critical applied stress, beyond which a material starts to flow, is called yield stress and is equal to the internal friction. The material is said to be at its elastic limit when the applied stress is equal to the yield value (Bingham 1922).

The concept of yield stress has been highly debated among researchers. Bingham (1922) reported the existence of the yield stress and observed that a certain shear force is required to overcome the internal friction of a viscoelastic material to initiate the flow. Bingham further reported that if the shear stress of the flow is plotted against shear rate, a straight line for a given material is obtained, but it would not pass through the origin, and the yield value is the distance between the origin and the intersection of the line with the shear stress axis.

Barnes and Walter (1985) suggested that the yield stress is a myth and does not exist. They argued that the yield stress reported by previous researchers was merely the result of experimental limitations at low shear rates. They asserted that no one ever measured a yield stress, and they argued that new advanced instruments would spark off the existence of

yield stress. They stated that if a material flows when it is subjected to high stress, it would also flow, however slowly, under low stress.

Several researchers disagreed with the conclusions of Barnes and Walters. Hartnett and Hu (1989) took up the challenge and attempted to prove experimentally the engineering reality of the yield stress. They used a falling ball viscometer to experimentally test the conclusions of Barnes and Walters. The falling ball viscometer was used to determine the shear stress and shear rate of non-Newtonian fluids. The procedure to determine these parameters is explained in their paper. A nylon falling ball was placed in a falling ball viscometer containing an aqueous Carbopol solution. The downward movements were monitored by taking photographs for long periods of time in an attempt to demonstrate the absence of flow, i.e. the existence of yield stress. They reported that no measurable motion of the ball was observed for several months, indicating that the yield stress is an engineering reality, and is not dependent on the rheological model (Hartnett and Hu 1989). Astaria (1990) wrote an article to discuss the controversial conclusions of Barnes and Walters (1985), and Hartnett and Hu (1989). Astaria has adopted the idea of Hartnett and Hu (1989) regarding the engineering reality of yield stress. Evans (1992) stated that yield stress is an important engineering reality, although measuring an exact value of yield stress may be difficult due to equipment limitations. He suggested that the existence of an essentially horizontal region in a double-logarithmic plot of shear stress-shear rate is the most satisfactory proof for the existence of a yield stress.

The yield stress is influenced by the interparticle forces. Particles equally charged repel electrostatically each other. If the attraction forces become greater than the repulsion

forces, particles will remain together resulting in a highly flocculated material (Macosko 1994). Cement paste is normally flocculated and its yield stress is essentially the stress required to rupture the flocculated structure, initiating macroscopic flow (Dzuy and Boger 1983).

2.2.5 Viscosity

Once flow is initiated, a non-Newtonian particle suspension still tends to resist flow. The viscosity (μ) of a non-Newtonian fluid depends on the shear rate and this relationship can be represented by the following equation:

$$\mu = \frac{\tau}{\dot{\gamma}} \tag{2.9}$$

Where τ is the shear stress required for the material to flow, and $\dot{\gamma}$ is the shear rate. Viscosity is a measure of the resistance of a material to flow (Barnes *et al.* 1989).

When the volume fraction of a suspension becomes greater than 0.01, particles interact with each other, and start to enter the neighborhood of other particles, causing disturbance of the flow, which increases the viscosity (Macosko 1994). Hydrodynamic interaction forces are developed as a result of the relative motion of the neighboring particles (Macosko 1994). Bimodal suspensions (containing both colloidal and non-colloidal particles) display generally a non-Newtonian viscosity behaviour characterized by a competition between viscous forces and colloidal forces. When a bimodal suspension is sheared, the effects of viscous forces become more significant. The effect of viscous forces relative to colloidal forces increases with increasing the shear rate resulting in a variation of viscosity over the shear rate (Sengun and Probstein 1997). The apparent viscosity (the

viscosity at a certain shear rate) of bimodal suspensions may undergo a continuous decrease, known as shear thinning, when the shear rate increases until it reaches a stationary value termed the high shear rate limit relative viscosity when viscous forces become dominant (Sengun and Probstein 1997).

The viscosity of a suspension is largely influenced by the concentration of solids, and therefore several models have been developed relating the viscosity to the volume fraction of solids in the suspension (Φ). Einstein in 1911 developed a model relating the viscosity of dilute suspensions ($\Phi < 0.03$) to the particle phase volume (Barnes *et al.* 1989). Einstein's equation neglected the effect of the interactions between particles and did not account for the variations of size, shape, and particle distribution.

$$\mu = \mu_s(1 + 2.5\phi) \tag{2.10}$$

Where μ is the viscosity of the suspension and μ_s is the viscosity of the suspending medium (Barnes *et al.* 1989). The particle phase volume is defined as the ratio between the volume fraction of particles in the suspension and the entire volume of the suspension.

Ball and Richmond (1980) developed a model assuming that the effect of all the particles in a concentrated suspension is the sum of the effect of particles added sequentially (Barnes *et al.* 1989). Based on this assumption, Einstein equation can be written in a differential form:

$$d\mu = (5\mu/2)d\phi \tag{2.11}$$

Where $d\mu$ is the increment of viscosity corresponding to the addition of a small volume $d\Phi$. The viscosity of the final suspension can be obtained by integrating the phase volume between 0 and Φ and the resulting equation is:

$$\mu = \mu_s \exp(5\phi/2) \tag{2.12}$$

However, Ball and Richmond realized that the above equation did not account for the interaction between particles by neglecting the fact that when a particle is added to a relatively concentrated suspension it requires more space than its volume dΦ. Therefore, they replaced $d\Phi$ with $d\Phi/(1-W\Phi)$ and the equation becomes (Barnes *et al.* 1989):

$$\mu = \mu_s (1 - W\theta)^{-5/(2W)} \tag{2.13}$$

Where W represents the so called crowding effect. It can be observed that when $\Phi = 1/W$ the viscosity becomes infinite, and therefore $1/W$ is the maximum packing fraction (Φ_m).

Kreiger-Dougherty developed an equation for concentrated suspensions. The Kreiger-Dougherty equation accounts for the concentration, size distribution, and shape of particles and it takes the following form (Kreiger 1972):

$$\mu = \mu_s \left(1 - \frac{\phi}{\phi_m}\right)^{-[\mu]\phi_m} \tag{2.14}$$

Where Φ_m is the maximum volume fraction or maximum packing density of solids and μ is the intrinsic viscosity. The intrinsic viscosity is defined as the limiting value of viscosity when the concentration of particles in suspension approaches zero, and it takes into account the shape of particles. For example, the intrinsic viscosity for perfect spheres is 2.5, and it

is higher for other shapes (Szecsy 1997). Szecsy 1997 achieved limited success when he implemented the Kreiger-Dougherty equation to calculate the viscosity of fresh concrete. He tried to optimize the Kreiger-Dougherty equation to better suit his experimental results. Although the Szecsy optimized model gave a better prediction of concrete viscosity than the Kreiger-Dougherty equation, the predicted values were still far from the measured ones.

2.2.6 Shear thinning

Shear thinning materials, also called pseudoplastic materials, are characterized by a viscosity decrease with an increase of the shear rate (Barnes *et al.* 1989). For such materials, the exponent value of the power law model (Eq. 2.8) is less than 1 (n<1). In fluids containing particulate suspensions, laminar flow may orient the molecules or particles, reducing the resistance to flow (Reed 1995). Thus, the additional shear stress required to increase the shear rate by an increment decreases with increasing the shear rate. At rest, the particles of suspensions are flocculated. When sheared, the particles start to separate from each other, and shear thinning materials become less resistant to flow. The higher the shear rate, the more particles are separated, and therefore the less is the viscosity. Some suspensions have non-spherical particles which are arbitrarily arranged when suspensions are not disturbed. The non spherical particles will be oriented in the direction of flow and they become less resistant to flow resulting in decreasing viscosity. Cement suspensions can show shear thinning behaviour when it flows. The characteristic diagrams of shear stress-shear rate and viscsotiy-shear rate of shear thinning fluids are presented in Fig 2.5.

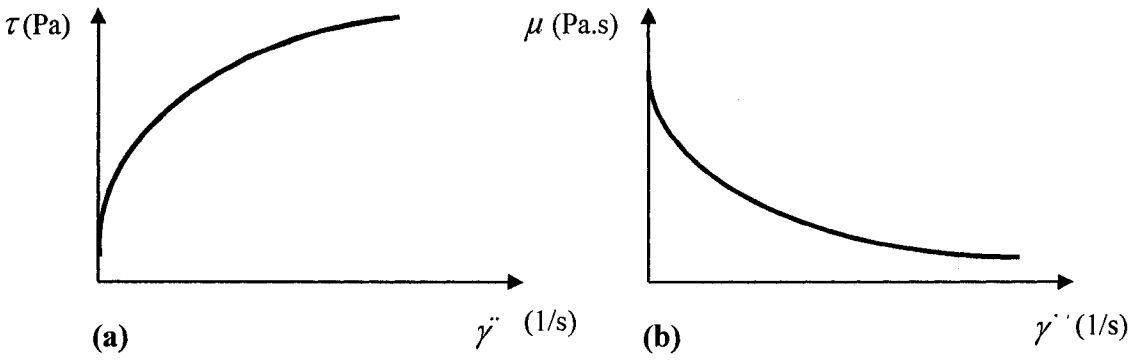

Figure 2.5-Typical shear thinning behaviour: (a) shear stress vs. shear rate, and (b) viscosity vs. shear rate.

2.2.7 Shear thickening

The shear thickening phenomenon, also called dilatancey, 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 dilatant materials increases with the increase of shear rate and the exponent value of the power law model (Eq. 2.8) is then higher than 1 (n>1). The microstructure of such materials will rearrange when sheared causing resistance to flow that increases with shear rate (Barnes *et al.* 1989). Figure 2.6 shows typical flow curves of a shear thickening fluid.

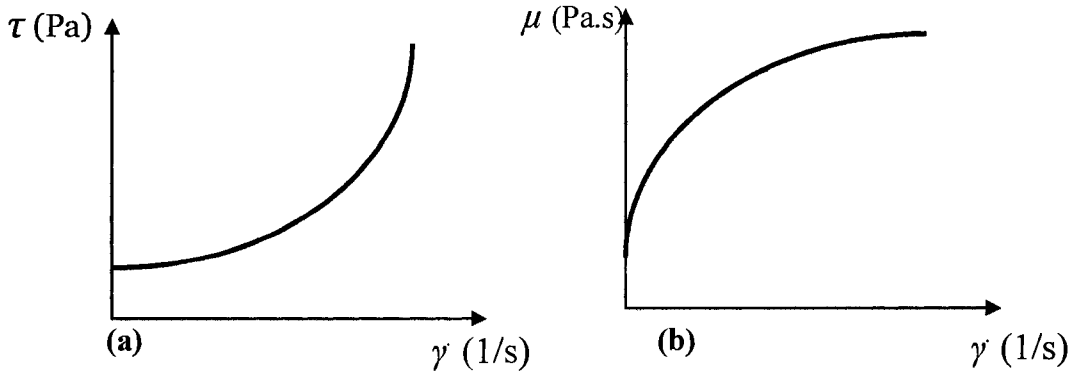

Figure 2.6-Typical shear thickening behaviour: (a) shear stress vs. shear rate, and (b) viscosity vs. shear rate.

2.2.8 Thixotropy

A thixotropic fluid is a fluid whose internal structure breaks down when sheared, and its internal structure will rebuild when the shear is discontinued. 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). The hysteresis loop is the standard test for the characterization of a thixotropic material. A hysteresis loop test is a shear sweep from low to high shear rate and back to low shear rate (Fig. 2.7). If a material is thixotropic, the resulting two curves (up and down curves) do not coincide, and the area enclosed between these two curves can be used to measure the degree of thixotropy. 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.

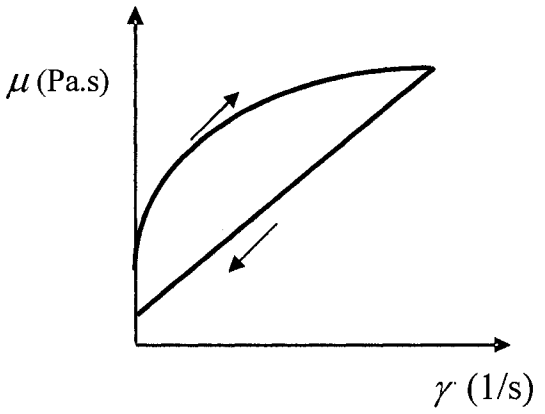

Figure 2.7-Typical hysteresis loop of a thixotropic fluid.

The opposite behaviour to thixotropy is called anti-thixotropy or rheopexy. Anti-thixotropy can 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).

Many materials such as cement paste can display thixotropic behaviour as well as rheopetic behaviour. The nature and explanation of the reversible structure breakdown associated with cement paste is further discussed in Chapter 3.

2.2.9 Cement paste and fresh concrete rheology

A cement powder is usually composed of a fraction of colloidal particles (less than 2 μm in diameter) and non-colloidal particles. Generally, about 20% by number of cement particles have a diameter less than 2 μm, i.e. colloidal fraction (Saak 2000). Cement based materials (cement paste and concrete) are viscolelastic materials, since they behave like solids below a certain stress, and like a plastic fluid beyond the yield stress. Concrete, for example, acts like a thick fluid and flows out of a concrete truck when enough energy is exerted on it. Cement paste can be considered as a suspension in which cement grains are the particles and water is the medium. Concrete can also be considered as a suspension, where the aggregates are the particles and cement paste is the medium.

The yield stress of portland cement suspensions is influenced by colloidal forces (i.e. Van der Waals attraction and electrostatic attraction/repulsion) (Sengun and Probstein 1997). The colloidal dispersion process is a result of the interaction forces between particles involving both repulsive and attractive interparticle forces (Lange 1989). A weak coagulation takes place in the material when there is a suitable balance between the attraction forces (van der Waals forces) and the electrostatic and steric repulsion forces

(Mewis 1979). When the repulsive forces are greater than the attractive forces, particles will disperse to form a system of separated particles, and when the attractive forces are dominant, particles will floc to form a low-density deformable network of touching particles that prevents mass segregation (Lange 1989).

Cement-based materials rheology depends on interparticle forces and the volume fraction of the suspension; they may follow the Newtonian law (viscosity is independent of shear rate) when their particles are fully dispersed, and they exhibit pseudoplastic, thixotropic behaviour (viscosity decreases with increasing shear rate) when their particles are flocculated (Yang *et al.* 1997). Chemical admixtures can be incorporated with cement paste to alter interparticle forces including attractive van der Waals forces, repulsive electrostatic and repulsive steric forces. Electrostatic repulsive forces develop when solute ions are attracted to medium particles to produce a system having particles with similarly charged particles. Steric forces, on the other hand, are developed by the attached macromolecules on the surface of particles. These charged macromolecules can have both repulsive electrostatic and steric repulsive forces. Although chemical admixtures have developed rapidly to improve the rheological properties of cement-based materials, the choice of the best admixture for a particular case is still a matter of trial and error using quality control tests such as Mini slump or Marsh flow tests.

2.3 Summary

Hot weather may create problems for concrete during its mixing, placement, and curing, which can adversely affect the properties of fresh and hardened concrete. Most of these problems are due to the acceleration of cement hydration and the fast evaporation of

mixing water at high temperature. The current practice to alleviate hot weather concreting problems such as adding cooled water or ice as part of the mixing water does not provide ideal solutions for hot weather concreting. Superplasticizers can provide a potential solution for hot weather concreting problems since they can improve the workability of cement-based materials while reducing the water to cement ratio. However, such superplasticizers have usually been developed in countries with mild temperature and their behaviour when incorporated in concrete at high temperature has not been fully explored. As such, a superplasticizer which behaves satisfactory when incorporated in concrete at mild temperate, may give disappointing performance when used in hot weather.

Rheological characterization is a tool that can evaluate the rheology of cement-based materials. By examining a suspension of cement particles in water and/or a suspension of aggregate particles in a cement paste, one can apply well established rheological theories. Hence, producing good quality concrete 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.

Cement-based materials are viscoelastic materials which do not flow if the applied shear stress is low and can not overcome the internal friction. They behave as solid-like materials when the applied stress is less than the yield stress and as a viscous fluid when the applied stress exceeds the yield stress. When it flows, cement paste follows a shear thinning behaviour due to the flocculated structure of its particles. The formation of flocs takes place due to the attractive (van der Waals) forces between neighboring colloidal

particles. Superplasticizers are usually incorporated in cement-based materials to improve their flow at the fresh state by deflocculating their particles. However, substantial research work is needed to develop fundamental knowledge for the effective use of superplasticizers in hot weather concreting.

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Chapter 3

EFFECT OF CHEMICAL ADMIXTURES ON RHEOLOGY OF CEMENT PASTE AT HIGH TEMPERATURE*

3.1 Introduction

Hot weather environments cause serious problems in the placement of fresh concrete due to the acceleration of cement hydration and faster water evaporation. Fresh concrete mixtures at high temperature tend to stiffen much faster with time compared to similar mixtures placed at moderate temperatures, and significant slump loss is usually experienced under high temperature (Soroka and Ravina 1998; and Thomas *et al.* 2003). This presents a real challenge in hot weather concreting because concrete does not remain workable long enough to allow time for its transporting, placement, compaction and finishing (Berge 1976).

The upper limit of ambient temperature to produce good quality concrete, as specified by ACI guidelines, is 27 °C (ACI 305.1-06). Likewise the ideal temperature of fresh concrete for its adequate placement ranges from 20-23 °C (El-Rayyes 1990). Practically speaking, achieving these criteria is often not an easy task in hot weather, and various precautions are needed during concrete mixing and placement to reduce its

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temperature. Such precautions are usually difficult to be implemented in-situ without high additional costs.

A study conducted by Hasanain *et al.* (1989) showed that the rate of water evaporation in hot weather is strongly related to the time of day at which concrete is being cast. For instance, the rate of evaporation in concrete cast during mornings was found to be much lower than that in concrete cast at noontime. Therefore, one of the common practices to overcome problems in hot weather concreting is to place concrete in early mornings or late afternoons when the temperature is moderate. However, this is not always a feasible solution, especially for large-scale construction projects. The economic importance of such projects and the associated strict construction schedules dictate continuous placing of concrete even at temperatures that exceed the maximum allowable limits. Generally, concrete is placed in hot weather regions, such as the Arabian Gulf, at temperatures often around 40 to 45 °C (Hasanain *et al.* 1989). To overcome the loss of concrete workability, additional mixing water is usually added to increase the fluidity of fresh concrete. However, this was found to cause significant reduction in the compressive strength of concrete and its long-term durability (Abbasi *et al.* 1992; Barnes *et al.* 1977).

Using cooled water for mixing concrete is one of the common practices to reduce fresh concrete temperature. However, since the amount of water used in mixing is relatively small, the effect of cooled water on reducing the temperature of fresh concrete mixtures during placing is insignificant (ACI 305R-99). Using ice as part of mixing water has also been a common means of reducing concrete temperature (ACI 305R-99), and proved to be more effective than using cooled water. However, it is a costly method; and at

a time when the concrete industry is striving to develop sustainable practices using energy efficient technologies and green materials, using ice in mixing concrete is against this trend.

Another method to reduce the temperature of fresh concrete in hot weather is chilling aggregates (Takeuchi *et al.* 1993). This can be done for instance by spraying liquefied carbonic acid gas at -78.5 °C on fine and coarse aggregates that are mixed in a special mixer. However, no major improvement in the workability of fresh concrete has been achieved using this technique (Takeuchi *et al.* 1993).

Efforts were also made to cool sand by injecting liquid nitrogen having a very low temperature (–196 °C) into a sand cooling apparatus. This dropped the sand temperature to well below the freezing temperature of water, causing a drop in the temperature of the entire concrete mixture. In this technique, the fresh concrete fluidity showed slight improvement (Kurita *et al.* 1990).

Chemical admixtures are also widely used to decrease water demand and improve concrete flowability, especially when placing concrete in highly congested reinforcement and hard-to-reach areas (Ramachandran *et al.* 1997). For instance, it was found that using a lignosulfonate-based set retarder at 0.25% by cement mass delayed the start of heat of hydration evolution by 1 to 1 ½ hour at a high temperature of 60 °C (Berge 1976).

Research was also conducted to study the effect of water-reducing and water reducing/retarding admixtures on improving concrete fluidity in hot weather at 33 °C (Ravina 1975). In this research, the amount of water needed to compensate for the slump

loss due to high temperature was measured. Four different water-reducing admixtures were used including polyhydroxy carbonic acid (ASTM Type D), modified lignin sulfonate (ASTM Type A), modified lignin carbohydrates (ASTM Type D), in addition to one retarding admixture. It was found that using the ASTM Type D admixture was effective at delaying setting, which is important to reduce the mechanical vibration needed for compaction and the occurrence of cold joints. On the other hand, these admixtures had the adverse effect of rapid change in the consistency of fresh concrete with time (Ravina 1975).

Research was conducted to study the possibility of decreasing the slump loss of concrete due to temperature rise using three superplasticizers (naphthalene sulfonate, naphthalene sulfonate modified with a retarding agent, and naphthalene sulfonate modified with twice the dosage of the same retarding agent) (Hampton 1981). It was found that in general, increasing the dosage of superplasticizers decreased the slump loss at high temperature, and that the naphthalene-based superplasticizer with a higher dosage of the retarding agent improved the fluidity of concrete at high temperature more efficiently than the naphthalene-based admixture alone. Also, lower dosages of the superplasticizer incorporating the retarding agent were needed to achieve results similar to that of the superplasticizer alone (Hampton 1981).

However, there is still a lack of information in the literature regarding the effect of various chemical admixtures on the rheological properties of fresh concrete at high temperature. Typically, research and development and technical data on chemical admixtures are developed in countries with cold or moderate climates. The products and the associated technical information are then exported to countries with hot weather

without adequate consideration of the local conditions. The field results in many occasions have been disappointing.

The rheological properties of cement paste play an essential role in the behaviour of fresh concrete. Therefore, the rheological properties of plain cement pastes having a w/c = 0.50 were investigated in this chapter at testing temperatures of 20, 40, and 45 °C. Moreover, cement pastes at a water/cement ratio (w/c) = 0.35 were tested at the same testing temperatures (20, 40 and 45 °C). These cement pastes incorporating various dosages of five different chemical admixtures, namely a gluconate acid-based water-reducing and retarding admixture (WRg), a polycarboxylate-based mid-range water-reducing admixture (MR), a polycarboxylate-based high-range water-reducing admixture (PC), a naphthalene sulfonate-based high-range water-reducing admixture (NS), and a melamine-based high-range water reducing admixture (ML). Experimental results allowed gaining a better understanding of the function of these admixtures at high temperature, which should lead to their effective use in the design of concrete mixtures under hot weather conditions.

3.2 Experimental Setup

CSA Type 10 (ASTM Type I) ordinary portland cement was used in all cement pastes investigated; its chemical and physical properties are shown in Table 3.1. Deionized distilled water was used for mixing, and its temperature was maintained at 19 ± 0.5 °C. Several cement pastes were made with a water/cement ratio (w/c) of 0.50 without admixtures to verify the reliability of the testing procedure and apparatus at different testing temperatures. The rheological properties of cement pastes without admixtures (w/c = 0.35) were also measured for testing temperatures of 20, 40, and 45 °C. This was done to

highlight the effect of the w/c on the rheology of cement paste at different testing temperatures by comparing the results to that of mixtures with w/c = 0.50. It should be noted that all cement pastes incorporating chemical admixtures were made with a w/c of 0.35. The rheological properties of the various cement pastes were investigated in detail at a moderate temperature of 20 °C and high testing temperatures of 40 and 45 °C.

Table 3.1-Properties of ordinary portland cement used

Chemical composition		Physical characteristics	
SiO_2 (%)	19.8		
CaO (%)	63.2	Loss on ignition (%)	2.5
Al_2O_3 (%)	5.0		
Fe_2O_3 (%)	2.4		
MgO (%)	3.3	Specific surface area, Blaine fineness (m^2/kg)	410
K_2O (%)	1.2		
SO_3 (%)	3.0		
Na_2O (%)	0.1		
TiO2 (%)	0.3	Specific gravity	3.17
CaCO3 (%)	--		
Equivalent alkalis (Na_2O + 0.658 K_2O)	0.80		
Tricalcium silicate (C_3S)	50.35		
Dicalcium silicate (C_2S)	18.8		
Tricalcium aluminate (C_3A)	9.2		
Tricalcium aluminoferrite	7.3		

3.3 Chemical Admixtures

Five different liquid chemical admixtures were used:

1. Gluconate acid-based water reducing and retarding admixture (WRg) that meets ASTM C 494 requirements for Type B retarding and Type D water-reducing admixtures. This admixture is intended to simultaneously delay the setting time of concrete and reduce the amount of mixing water required to get a designated slump value (Meyer and Perenchio 1979). It is believed to counteract the accelerating effect of temperature on cement hydration and improve cement paste rheological properties, which reduces the rate of slump loss of concrete (Meyer and Perenchio 1979; Fattuhi 1988). Its density is 1.22 g/cm^3 and concentration of solids is 47.0%. Five dosages of WRg (0.3%, 0.7%, 1.2%, 2.5% and 3.5% by mass of cement) were used in this chapter.

2. Polycarboxylate-based mid-range water-reducing admixture (MR) which meets ASTM C 494 requirements for Type A water-reducing admixture. Its density is 1.07 g/cm^3 and concentration of solids is 23.5%. Polycarboxylate is a synthetic organic polymer bearing carboxylic acid groups (Ramachandran *et al.* 1997). Five dosages of MR (0.3, 0.7, 1.2, 2.5, and 3.5%) were used.

3. Polycarboxylate-based high-range water-reducing admixture (PC) meeting ASTM C 494 requirements as a Type A water-reducing and Type F high-range water-reducing admixture. Its density is 1.05 g/cm^3 and concentration of solids is 38.0%. Three dosages of PC (0.3, 0.7, and 1.2%) by mass of cement were used in this chapter.

4. Naphthalene sulfonate-based high-range water-reducing admixture (NS) which complies with ASTM C-494 Type F high-range water-reducing admixture. Its density is 1.21 g/cm^3 and concentration of solids is 40.0%. Six dosages of NS (0.3, 0.7, 1.2, 2.5, 3.5, and 4.5%) were used in this chapter to investigate its effect on the rheological properties of cement paste at high temperature.

5. Melamine sulfonate-based high-range water-reducing admixture (ML) which complies with ASTM C 494 Type F high-range water-reducing admixture. Its density is 1.26 g/cm^3 and concentration of solids is 23.5%. Six dosages of ML (0.3, 0.7, 1.2, 2.5, 3.5, and 4.5%) by mass of cement were used.

3.4 Mixing Cement Pastes

A high-shear mixer with three variable speeds was used to adequately mix the cement paste components (Fig. 3.1(a)). The mixer consists of a bowl and a vertical shaft with two blades at two vertical levels. First, the mixing water was poured into the mixing bowl. Using a graduated needle, the specified quantity of liquid admixture was injected into the mixing water. Then the weighed quantity of cement powder was added to the water and manually stirred for one minute. The cement paste was subsequently mixed for one minute at low speed, then at high speed for another minute. The mixer was stopped for 1.5 minutes, during which the bowl was scraped with a rubber paddle to ensure homogeneity. Mixing resumed for another minute at high speed. The total time between the beginning of mixing and the start of rheological tests was seven minutes for all cement pastes. This mixing procedure was strictly followed for all cement pastes to avoid the effects of exogenous variables on the results (Roy and Asaga 1979; Williams *et al.* 1999).

3.5 Rheometer

An advanced rheometer (TA-Instruments AR 2000) was used throughout this investigation to measure the shear stress-strain rate data and consequently the rheological properties of cement pastes (Fig. 3.1(b)) (TA Rheology 2001). The rheometer has an advanced system for temperature control in the range of -5 to 100 ^{o}C. Instrument calibration was done using a certified viscosity standard mineral oil (a Newtonian oil) with a known viscosity of 1.40 Pa.s. The measured yield stress was zero and viscosity was 1.42 Pa.s with an error of 1.4%, which is less than the tolerated error of 4% specified by the manufacturer.

The geometry of the test accessory has a significant influence on the measured rheological properties of cement paste (Rahman and Nehdi 2003). The coaxial concentric cylinder geometry was considered suitable for this study and was thus used throughout this investigation. This geometry consists of a cylinder with a conical end that rotates inside a cylinder with a central fixed hollow. The gap between the rotating shaft and the hollow is 1 mm. The gap between the head of the conical end and the bottom of the hollow was set at 0.5 mm and kept constant for all experiments. The rheometer has an auto gap adjustment system which compensates for the expansion of the stainless steel coaxial cylinder when a wide temperature range is applied during an experiment, thus ensuring the gap to remain constant. To keep the w/c constant and prevent evaporation of water from tested cement paste samples due to temperature rise, a solvent trap cover was used.

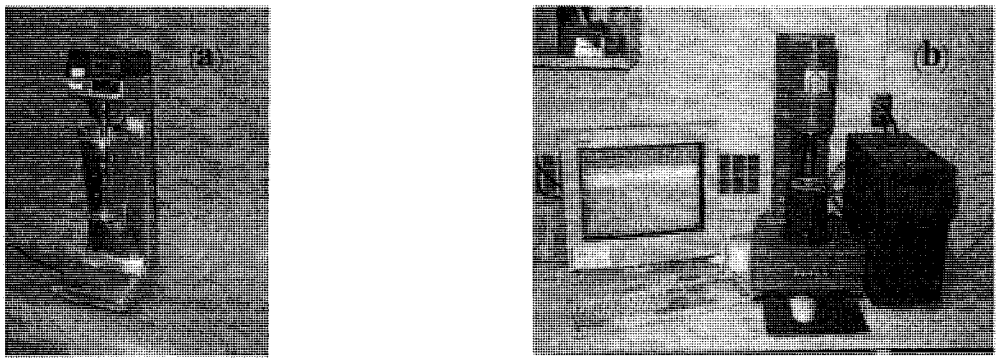

Figure 3.1-Illustration of, (a) cement paste mixer, and (b) rheometer used with coaxial cylinder geometry.

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 (e.g. Newtonian, Bingham, Herchel-Bulkley, Caisson, Modified Bingham, Sisko, and Williamson). The Bingham model was used throughout this study to calculate cement paste rheological properties, i.e. yield stress, viscosity, and thixotropy. It is however, understood that rheological data estimated may depend on the rheological model (Nehdi and Rahman 2004; Papo, 1988; Malek and Roy 1991).

3.6 Testing Procedure

After mixing, the cement paste sample was placed in the gap space of the coaxial cylinder. First, temperature was adjusted to the required level. Then, the cement paste sample was presheared at 70 s^{-1} for two minutes in order to break down the structure of the cement paste sample, creating uniform conditions before testing (Saak *et al.* 2001). The preshearing procedure was kept constant for all tested samples. Subsequently, a continuous sweep shear rate was applied by increasing the shear rate from 0 to 50 s^{-1} to produce the up-curve. The cement paste was maintained 15 s at a shear rate of 50 s^{-1}, and then the sample

was sheared from 50 s^{-1} to 0 s^{-1} to produce the down-curve. This procedure allowed producing a hysteresis loop, which is also used to characterize the thixotropy of cement paste (Saak 2000). A schematic representation of the testing procedure is illustrated in Fig. 3.2.

3.7 Rheological Parameters

Generally, cement paste is believed to follow a Bingham behaviour, which is represented by the following equation:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \tag{3.1}$$

Where τ, τ_0, μ_p, and $\dot{\gamma}$ are the shear stress, yield stress, plastic viscosity, and shear rate, respectively.

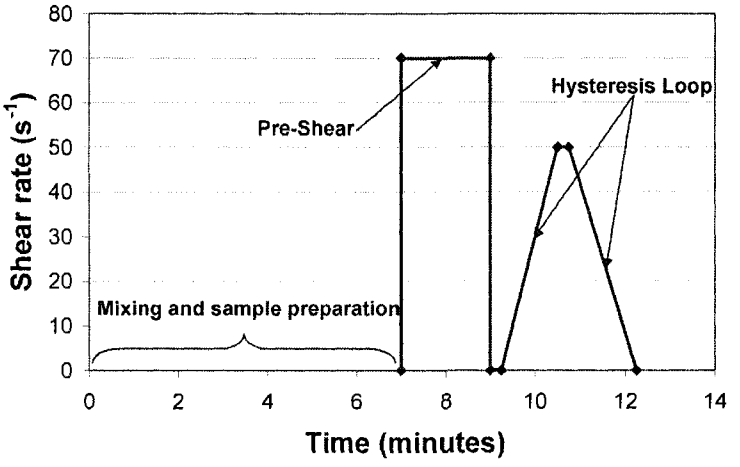

Figure 3.2-Shear rate history used in rheological tests.

The yield stress is the stress required for the cement paste to start flowing. It can be identified by the intercept of the flow curve (shear rate versus shear stress) with the shear stress axis. After overcoming the yield stress, viscosity indicates how the material can flow. Plastic viscosity is the slope of the fitted straight line of the flow curve to the Bingham model, and the apparent viscosity is the ratio between shear stress and shear rate at each shear rate on the flow curve. Therefore, the apparent viscosity at a specific shear rate is the slope of the flow curve at this point.

The yield stress and plastic viscosity were calculated from the shear rate-shear stress down-curve using the Bingham model. The down-curve was adopted because it better fits to the Bingham equation than the up-curve (Saak 2000; Eirich 1960). When a cement paste is sheared from 0 to 50 s^{-1}, breakdown in its structure occurs. Thus, the down-curve (unloading) will not usually follow the same path as the up-curve (loading). The down-curve is normally lower in shear stress values than that for the up-curve. Figure 3.3 shows a typical hysteresis loop for cement paste at high testing temperature. It can be observed that the down-curve (unloading) became higher than the up-curve during the loading process, which is contrary to normal hysteresis behaviour of cement paste at lower testing temperature. This reverse hysteresis behaviour in cement paste was also observed elsewhere (Saak 2000), and is sometimes called anti-thixotropy or rheopexy (Ferguson and Kemblowski 1991).

The reverse hysteresis loop indicates that the structure of the material stiffens as it is sheared at high temperature due to the mechanism of thixotropy build-up (Eirich 1960), likely as a result of accelerated hydration. The area enclosed between the up and down

curves was calculated and used to assess the degree of thixotropy (Saak 2000; Eirich 1960). In this chapter, negative thixotropy indicates the normal hysteresis behaviour of cement paste, while positive thixotropy refers to the reverse hysteresis behaviour.

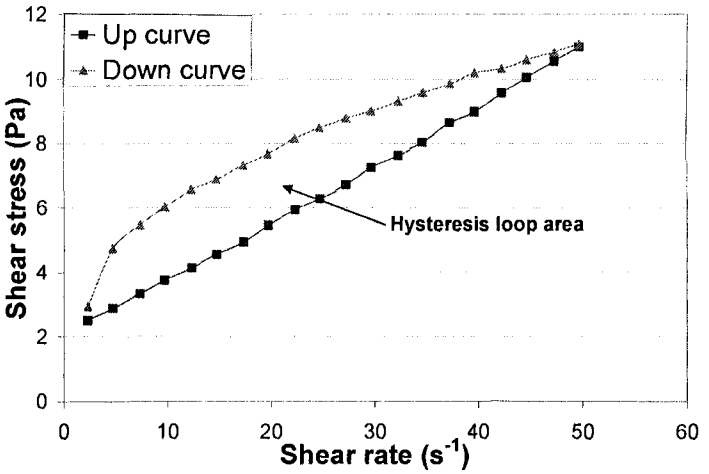

Figure 3.3-Typical hysterersis loop for cement paste at high testing temperature.

3.8 Analysis of Results

3.8.1 Reliability of rheometer at different testing temperatures

For further rheometer calibration and to ensure statistical repeatability of results, three sets (each set consists of four cement paste samples prepared at a w/c of 0.50), were tested at three different testing temperatures, i.e. 20, 40, and 45 °C. A new cement paste mixture was used for replicating each test since rheological properties of cement paste are time, temperature, and shear history dependent. As shown in Table 3.2, the averages of the measured plastic viscosities of the cement pastes at 20, 40, and 45 °C were 0.28, 0.29, and 0.42 Pa.s, respectively with standard deviations of 0.02, 0.02 and 0.04. The averages of the measured yield stress values were 6.48, 7.40 and 8.19 Pa with standard deviations of 0.15, 0.22 and 0.32 Pa at testing temperatures of 20, 40 and 45 °C, respectively. The standard

deviation values are relatively small, which confirms that the experimental procedure and the rheometer can produce repeatable measurements with acceptable accuracy.

Table 3.2-Repeatability of rheological measurements (cement pastes with w/c = 0.5)

Temperature °C	Plastic viscosity (Pa.s)			Yield stress (Pa)		
	Measured	Average	*SD*	Measured	Average	*SD*
20	0.27	0.28	0.02	6.41	6.48	0.15
	0.25			6.47		
	0.26			6.76		
	0.29			6.55		
40	0.30	0.29	0.02	7.17	7.40	0.22
	0.26			7.32		
	0.28			7.68		
	0.31			7.50		
45	0.52	0.42	0.04	8.51	8.19	0.32
	0.47			7.76		
	0.45			8.32		
	0.42			8.15		

Furthermore, it can be observed from the results that the yield stress and plastic viscosity values increased with the increase of testing temperature for both cement pastes with w/c = 0.35 and w/c = 0.50 (Fig. 3.4). This is likely due to the increase in the rate of hydration of cement at higher testing temperature. The increase of the yield stress between 20 and 40 °C was less significant than that between 40 and 45 °C (Fig. 3.4(a)). This suggests that the increase of yield stress versus temperature is not linear, which is in agreement with findings of Soroka (1993) who observed that the rate of slump loss increased with temperature. Similar to yield stress, the rate of increase in plastic viscosity between 40 and 45 °C was higher than that between 20 and 40 °C (Fig. 3.4(b)). It can be further observed that the rate of increase of yield stress and plastic viscosity for cement

pastes with w/c = 0.35 was higher than that for cement pasts with w/c = 0.50, especially when testing temperature exceeded 40 °C. Figure 3.4 also shows that when the w/c increased, the values of yield stress and plastic viscosity increased, likely due to the increase in the volume fraction of solids with the decrease of the w/c.

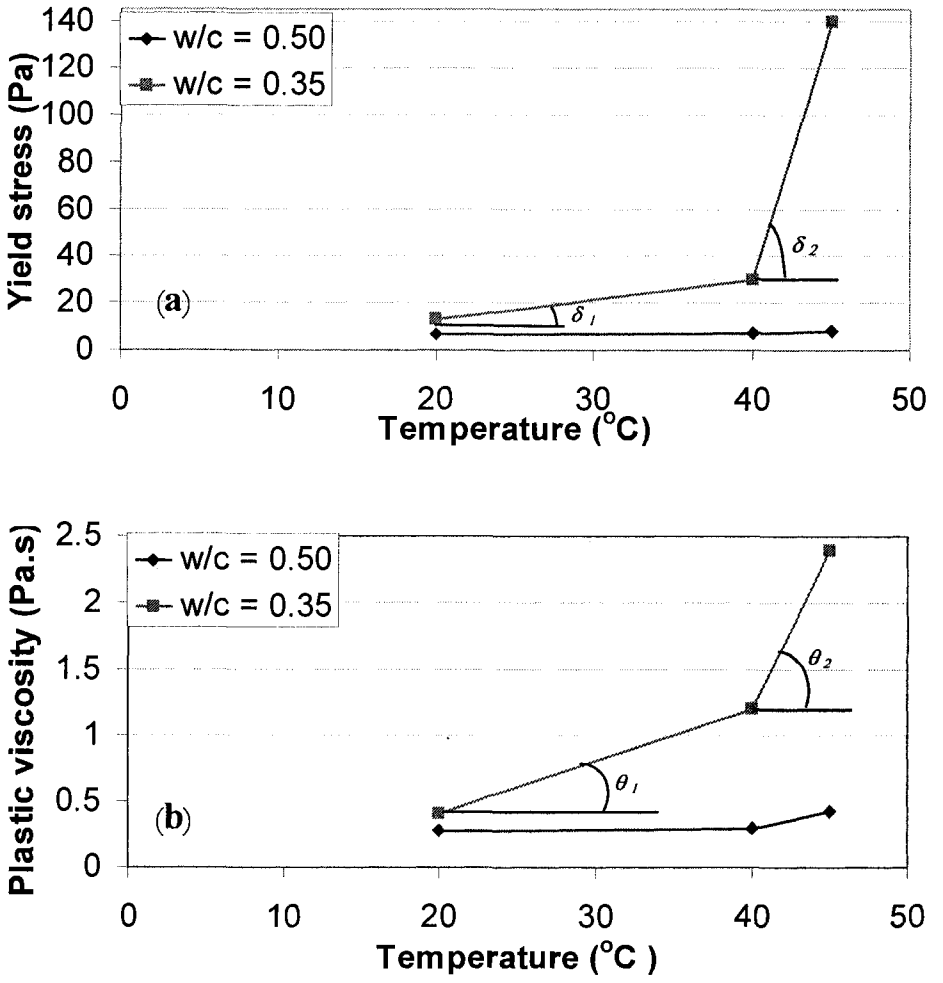

Figure 3.4-Effect of testing temperature on rheology of cement paste: (a) yield stress and (b) plastic viscosity.

3.8.2 Effect of admixtures on yield stress of cement paste at high testing temperature

The effect of various admixtures on the yield stress of cement paste at different testing temperatures is presented in Figs. 3.5, 3.6, and 3.7. A different scale is used for the

figure presenting results for the WRg due to the much higher yield stress values observed. Figure 3.5(a) illustrates yield stress values measured for cement pastes incorporating various dosages of a water-reducing and retarding admixture (WRg) at different testing temperatures. It can be observed that yield stress values generally decreased with the increase of the WRg dosage, and increased significantly with testing temperature increase. The rate of increase in yield stress became much higher when testing temperature exceeded 40 °C, but this increase was less significant at high WRg dosages. For example, at a dosage of 0.3% the increase in yield stress between 40 and 45 °C was about tenfold its value between 20 and 40 °C, whereas at a dosage of 2.5%, the increase in yield stress between 40 and 45 °C was only double of its value between 20 and 40 °C. Although the increase of WRg dosage from 0.7% to 2.5% reduced the yield stress value at 45 °C significantly, the difference in yield stress values for cement paste at 40 and 45 °C was still high at about threefold its value between 20 and 40 °C. At a higher WRg dosage of 3.5%, the yield stress of cement paste at high testing temperature dropped significantly and approached its value at the moderate testing temperature of 20 °C (Fig. 3.5(a)). Additionally, the saturation dosage at 20 and 40 °C was comparable at about 1.2%. However, no saturation dosage was reached when testing temperature was higher (45 °C) even when the dosage was 2.5 to 3.5%. It can be further observed that the yield stress of cement paste without WRg increased with an increased dosage of WR_g (0.3%) and then it decreased indicating that WRg worked as an accelerator at low dosages (Fig. 3.5(a)).

In Fig. 3.5(b), the effect of a mid-range water reducing admixture (MR) on the yield stress is presented. At 20 °C, yield stress decreased with the increase of MR dosage and reached a saturation dosage at about 1.2%. At 40 °C, no evident effect of the change of the

MR dosage was observed below a dosage of 2.5%, and then yield stress started to decrease beyond this dosage. At a dosage of 3.5%, yield stress became lower than the corresponding value at 20 °C. At 45 °C, yield stress steeply decreased with increasing MR dosage and again reached a value less than that at 20 °C at a dosage of 3.5%. It is observed that the MR admixture prevented yield stress from escalating to very high values at 45 °C, in contrast with the case of the WRg admixture.

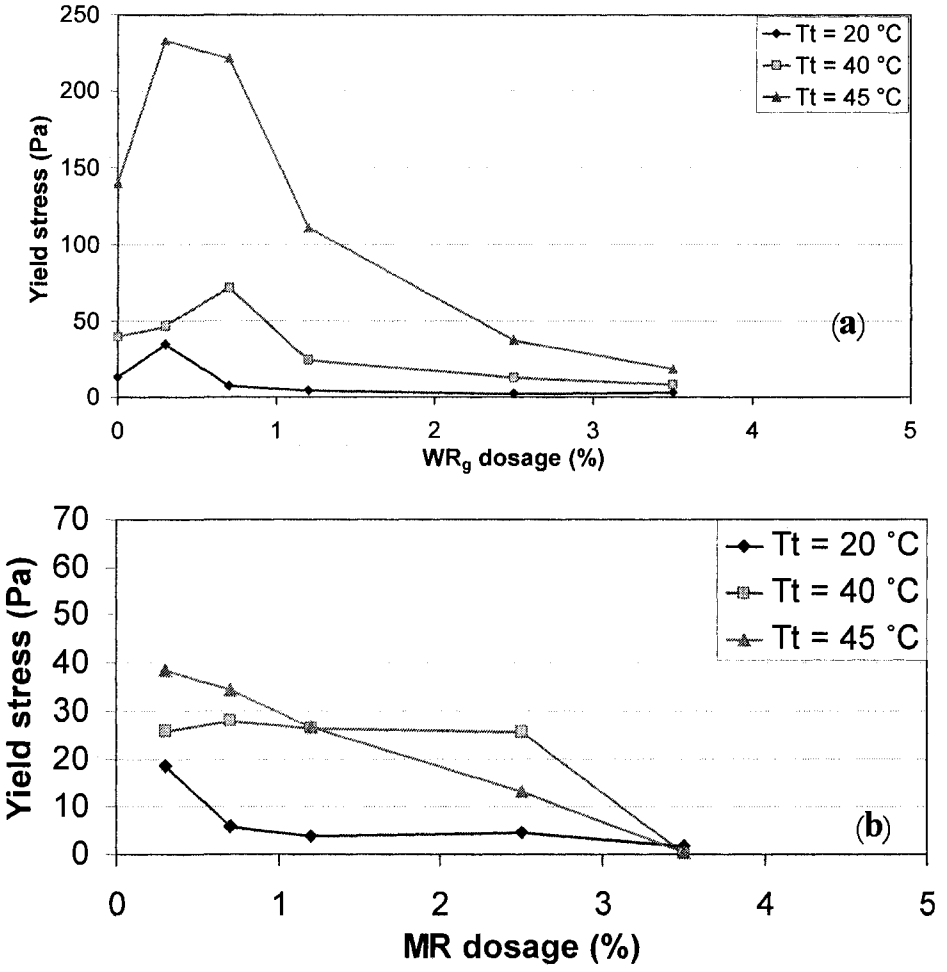

Figure 3.5-Yield stress of cement paste at various testing temperatures and different dosages of admixtures (a) WRg and (b) MR (w/c = 0.35; admixture dosage is in % of cement mass).

The effect of the PC dosage on yield stress with variation of testing temperature is presented in Fig. 3.6. It can be observed that yield stress at low PC dosage (0.3%) increased significantly with testing temperature. The difference in yield stress values between 40 and 45 °C was about double the corresponding value between 20 and 40 °C. At low dosages, the PC could not apparently offset the acceleration of hydration due to the increase of testing temperature. However, an increased PC dosage seemed to mitigate the acceleration of hydration due to higher temperature, and even neutralized it at a high dosage of 1.2% since yield stress at the various testing temperatures approached a value of zero (Fig. 3.6).

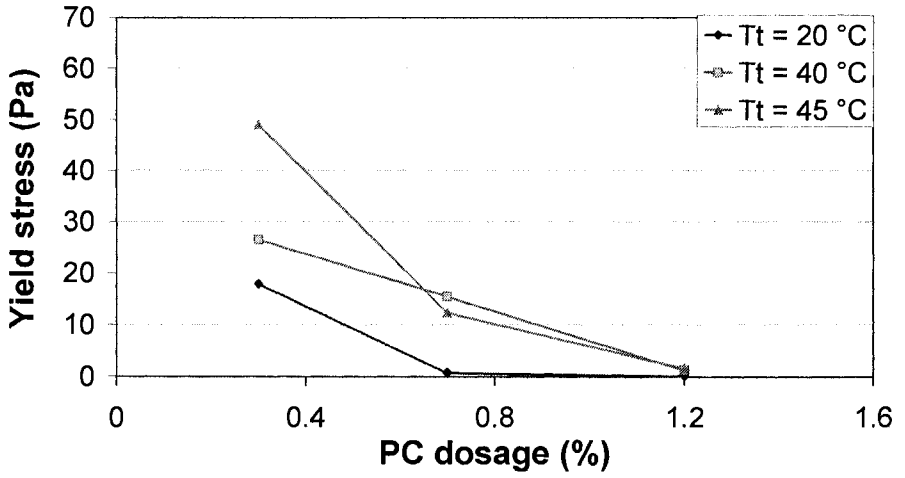

Figure 3.6-Yield stress of cement paste at various testing temperatures and different dosages of admixtures PC (w/c = 0.35; admixture dosage is in % of cement mass).

In Fig. 3.7(a), the effect of the naphthalene sulfonate-based superplasticizer on yield stress of cement paste at different testing temperatures is illustrated. The yield stress initially increased with higher NS dosage. After a threshold dosage (around 1.2% at 40 and 45 °C and 0.7% at 20 °C), yield stress started to drop significantly. This indicates that at low admixture dosages and high testing temperatures, the NS was not effective and rather

acted as an accelerator. This behaviour of the NS was also documented by other researchers (Ramachandran *et al.* 1997; Szecsy 1997).

As shown in Fig. 3.7(b), yield stress also initially increased with testing temperature and ML dosage up to about 1.2%, and then it started to decrease steeply at higher dosages until it reached a plateau (saturation dosage) at about a dosage of 3.5%, where no further decrease in yield stress could be achieved.

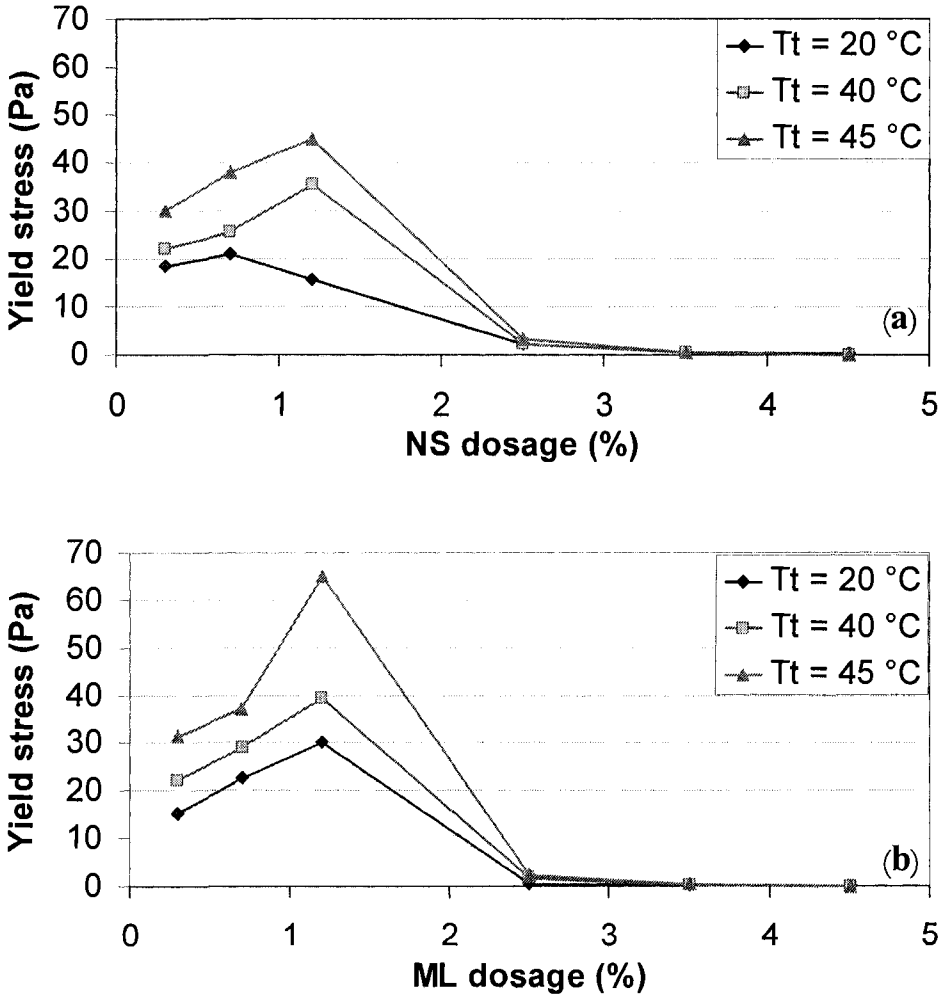

Figure 3.7-Yield stress of cement paste at various testing temperatures and different dosages of admixtures (a) NS and (b) ML (w/c = 0.35; admixture dosage is in % of cement mass).

ML acted as an accelerator at low dosage where it enhanced yield stress likely via acceleration of hydration at increased temperature, and it acted as a retarder at high dosages where it reduced yield stress and effectively offset the acceleration of hydration at high testing temperature. It was documented by others (Ramachandran *et al.* 1997) that ML acted as an accelerator below a dosage of 2% and as a retarder above this dosage.

3.8.3 Effect of admixtures on viscosity of cement paste at high testing temperature

Figure 3.8 illustrates the variation of plastic viscosity at different testing temperatures for cement pastes incorporating various dosages of WRg. Generally, plastic viscosity decreased significantly with the increase of the WRg dosage but reached a threshold value at a dosage of 0.7% at 20, 40, and 45 ^{o}C beyond which no significant reduction in plastic viscosity could be achieved. Tables 3.3 and 3.4 show that there were significant changes in the apparent viscosity at low and high shear rate when the testing temperature and WRg dosage changed. Generally, the apparent viscosity increased with the increase of testing temperature, and decreased when the WRg dosage increased. It can be further observed that the rate of increase in apparent viscosity at both high and low shear rate was much higher at a higher testing temperature for all cement pastes incorporating different WRg dosages. For instance, the apparent viscosity at low shear rate (5 s^{-1}) for cement paste at a WRg dosage of 0.3% increased fourfold between 40 and 45 ^{o}C, while the corresponding value at 40 ^{o}C was less than double that at 20 ^{o}C.

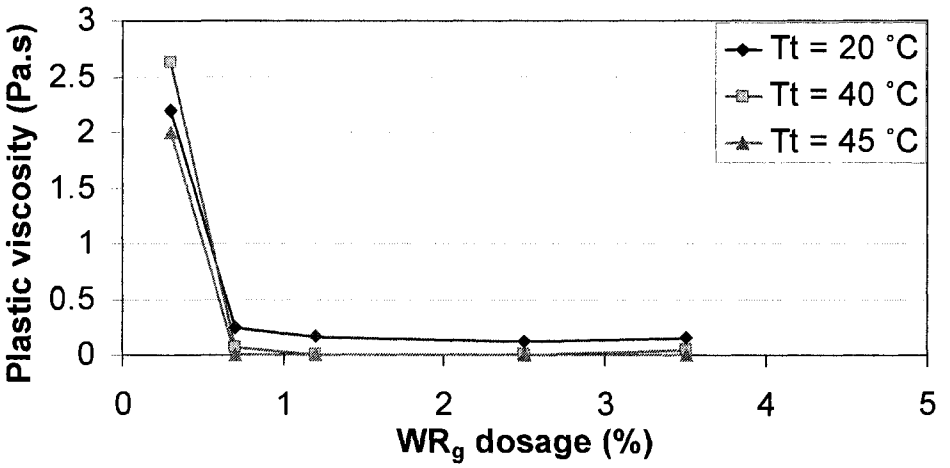

Figure 3.8-Plastic viscosity of cement paste at various testing temperatures and different dosages of WRg (w/c = 0.35; admixture dosage is in % of cement mass).

It can be argued that plastic viscosity measured from the down-curve of the hysteresis loop does not always truly represent the material property. This is because the slope of the line generated by fitting a cement paste flow curve to the Bingham model depends on the error of the fit, which is in some cases high, a behaviour also observed by Saak (2000). In this study, plastic viscosity was measured and analyzed because it is generally used to create mechanical models for the deformation behaviour of cement paste since it is very difficult to rely on apparent viscosity measurements at each shear rate point to formulate such models (Nehdi and Rahman 2004).

Figure 3.9 shows the effect of incorporating a mid-range water-reducing admixture (MR) on the plastic viscosity of cement pastes at various testing temperatures. It can be observed that at low dosages (0.3 and 0.7%) plastic viscosity increased at a relatively constant rate when testing temperature increased. Moreover, plastic viscosity decreased when the dosage of MR increased and reached a low value that was independent of testing

temperature at a dosage of 1.2%, likely due to the retarding effect of MR at high dosage. Some increase in plastic viscosity was observed for a dosage of 2.5% at 40 and 45 °C. Since this behaviour was not observed for the apparent viscosity, it could be attributed to the error associated with the fitting of cement paste flow curve to the Bingham model as discussed previously. Similar to plastic viscosity, the apparent viscosity at high and low shear rates increased with testing temperature and decreased when the MR dosage increased (Tables 3.3 and 3.4). It is further observed from Table 3.3 that at 40 °C and below a dosage of 2.5%, the apparent viscosity at low shear rate of cement pastes incorporating MR did not show any trend (increase or decrease), but decreased steeply beyond this dosage. A similar behaviour was also observed for yield stress. This indicates that it may be necessary to consider the specific site temperature when designing concrete mixtures incorporating MR for hot weather conditions.

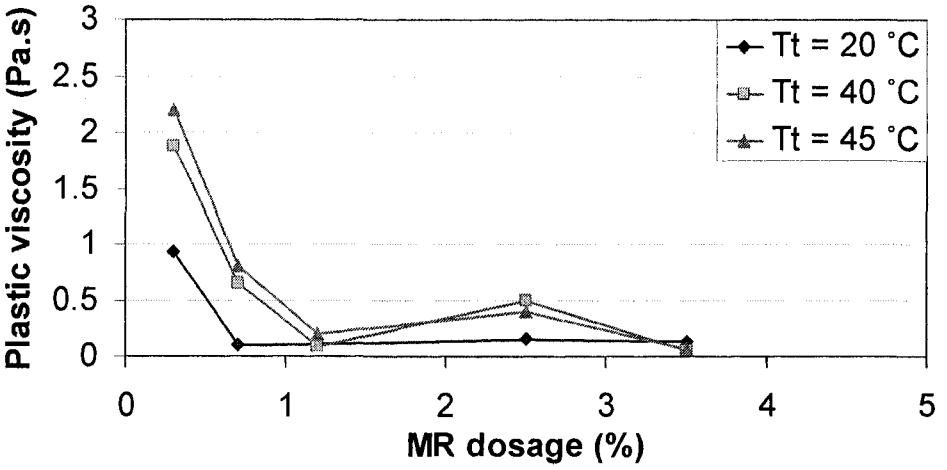

Figure 3.9-Plastic viscosity of cement paste at various testing temperatures and different dosages of MR (w/c = 0.35; admixture dosage is in % of cement mass).

Figure 3.10 shows the effect of the polycarboxylate-based superplasticizer on the plastic viscosity of cement pastes at different testing temperatures. At low PC dosage (0.3%), it can be observed that plastic viscosity increased when testing temperature increased due to accelerated hydration reactions. At higher dosage (0.7 and 1.2%), plastic viscosity dropped significantly at all testing temperatures. In general, the apparent viscosity decreased with an increase of the PC dosage for both low and high shear rates (Tables 3.3 and 3.4). Due to shear thinning behaviour, the apparent viscosity at high shear rate was smaller than that at lower shear rate for a specific testing temperature and PC dosage. Regardless of the shear rate, the apparent viscosity at 20 °C approached a zero value at a PC dosage of 1.2% (Tables 3.3 and 3.4). At 40 and 45 °C and PC dosage beyond 0.7%, apparent viscosity measurements at each PC dosage were comparable. From Fig. 3.10 and Tables 3.3 and 3.4, it appears that the apparent viscosity varied with testing temperature and PC dosage in a manner generally similar to that of plastic viscosity.

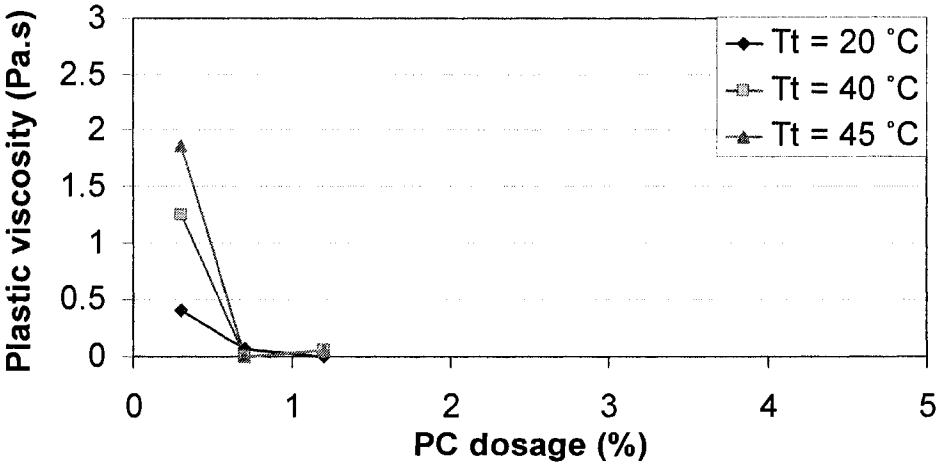

Figure 3.10-Plastic viscosity of cement paste at various testing temperatures and different dosages of PC (w/c = 0.35; admixture dosage is in % of cement mass).

In Fig. 3.11 the effect of the naphthalene sulfonate-based superplasticizer on plastic viscosity is presented. There appeared to be an initial increase in plastic viscosity with increasing NS dosage and testing temperature until a threshold dosage of about 0.7%, beyond which plastic viscosity decreased with increasing NS dosage. When the NS dosage and testing temperature varied, the effect on apparent viscosity at both high and low shear rates was similar to that observed for plastic viscosity (Tables 3.3 and 3.4). Again, as the NS dosage increased, the apparent viscosity increased until a dosage of 0.7% and 1.2% for high and low shear rates, respectively, after which it started to decrease. Moreover, the apparent viscosity at each NS dosage increased when testing temperature increased. The value of apparent viscosity at each NS dosage and testing temperature decreased at higher shear rates.

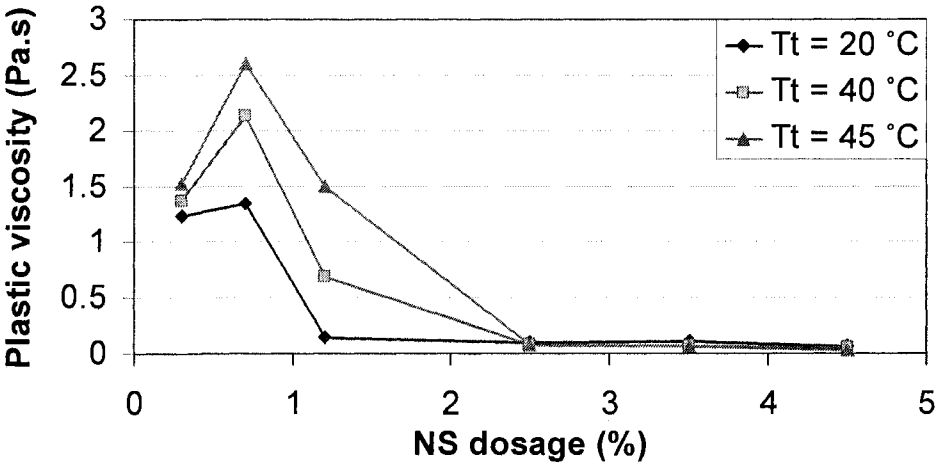

Figure 3.11-Plastic viscosity of cement paste at various testing temperatures and different dosages of NS (w/c = 0.35; admixture dosage is in % of cement mass).

As shown in Fig. 3.12, plastic viscosity increased with testing temperature and with the ML dosage up to a threshold level of 1.2% for testing temperatures of 40 and 45 °C, and 0.7% for 20 °C. Then, it started to decrease steeply until it reached a plateau (saturation dosage). The ML dosage also affected the apparent viscosity; an increase in dosage up to 1.2% increased the apparent viscosity at both low and high shear rates. However, the apparent viscosity decreased steeply beyond a ML dosage of 1.2% (Tables 3.3 and 3.4).

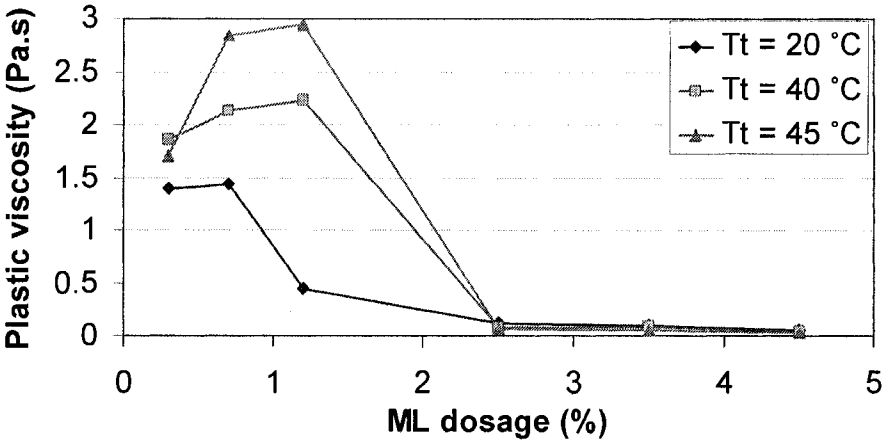

Figure 3.12-Plastic viscosity of cement paste at various testing temperatures and different dosages of ML (w/c = 0.35; admixture dosage is in % of cement mass).

Table 3.3-Apparent viscosity at low shear rate (5 s^{-1}) for cement pastes made with different admixtures (w/c = 0.35)

% of cement mass	T = 20 °C					T = 40 °C					T = 45 °C				
	WRg[a]	MR[a]	PC[a]	NS[a]	ML[a]	WRg[a]	MR[a]	PC[a]	NS[a]	ML[a]	WRg[a]	MR[a]	PC[a]	NS[a]	ML[a]
0.3	7.80	4.40	3.60	4.36	3.85	10.70	5.90	5.50	4.12	5.40	47.00	8.00	9.60	4.40	7.40
0.7	1.70	1.40	0.22	5.05	5.20	15.34	5.50	3.15	5.88	6.75	53.80	6.63	2.58	9.33	7.62
1.2	1.06	0.96	0.05	3.40	5.80	4.20	4.80	0.28	6.50	8.93	24.54	4.92	0.37	8.80	12.63
2.5	0.55	1.03		0.62	0.25	2.40	5.50		0.60	0.50	8.25	2.70		0.75	0.50
3.5	0.72	0.45		0.15	0.10	1.16	0.06		0.18	0.10	4.10	0.18		0.13	0.11
4.5				0.10	0.05				0.06	0.04				0.03	0.04

[a]WRg: water reducing and retarding admixture, PC: polycarboxylate-based high-range water-reducing admixture, MR: mid-range water-reducing admixture, NS: Naphthalene Sulphonate-based high-range water-reducing admixture, and ML: melamine sulfonate-based high-range water-reducing admixture.

Table 3.4-Apparent viscosity at high shear rate (45 s^{-1}) for cement pastes made with different admixtures (w/c = 0.35)

% of cement mass	T = 20 °C					T = 40 °C					T = 45 °C				
	WRg[a]	MR[a]	PC[a]	NS[a]	ML[a]	WRg[a]	MR[a]	PC[a]	NS[a]	ML[a]	WRg[a]	MR[a]	PC[a]	NS[a]	ML[a]
0.3	2.77	0.73	1.3	1.55	1.66	3.56	1.73	2.32	1.63	2.2	7	2.74	2.6	1.8	2.3
0.7	0.36	0.09	0.24	1.7	1.8	1.75	0.326	1.17	2.5	2.58	4	0.25	1.2	3.4	3.4
1.2	0.24	0.04	0.2	0.48	1.04	0.45	0.075	0.65	1.32	2.2	2.12	0.075	0.55	1.5	3.63
2.5	0.17		0.22	0.15	0.13	0.28		0.5	0.13	0.13	0.63		0.28	0.15	0.12
3.5	0.21		0.16	0.08	0.09	0.21		0.12	0.06	0.05	0.35		0.06	0.03	0.04
4.5				0.075	0.05				0.05	0.04				0.03	0.03

[a]WRg: water reducing and retarding admixture, PC: polycarboxylate-based high-range water-reducing admixture, MR: mid-range water-reducing admixture, NS: Naphthalene Sulphonate-based high-range water-reducing admixture, and ML: melamine sulfonate-based high-range water-reducing admixture.

3.8.4 Effect of various chemical admixtures on thixotropy

Figure 3.13 shows the effect of WRg on thixotropy of cement pastes. Thixotropy increased dramatically when testing temperature increased, especially when testing temperature exceeded 40 °C. Thixotropy was generally higher at a WRg dosage of 0.7% than that at a dosage of 0.3%, perhaps because the amount of stiffening upon relaxation for a dosage of 0.7% was higher due to a more effective particle dispersion than that for a dosage of 0.3%. Beyond a dosage of 0.7%, thixotropy values started to decrease gradually with the increase of the WRg dosage. Furthermore, the difference in thixotropy values between 40 and 45 °C for all WRg dosages were much higher than that between 20 and 40 °C.

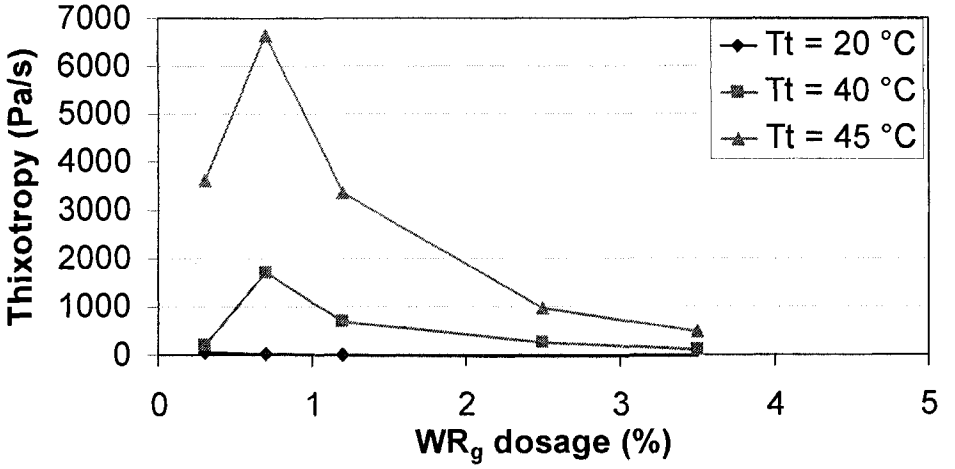

Figure 3.13-Thixotropy of cement paste at various testing temperatures and different dosages of WRg (w/c =0.35; admixture dosage is in % of cement mass).

In Fig. 3.14(a) thixotropy measurements for cement pastes made with a mid-range water-reducing admixture (MR) are illustrated. At 20 °C, thixotropy had negative values, indicating that the hysteresis loop had a regular behaviour. At high testing temperature (40

and 45 °C), thixotropy increased with the dosage of MR up to a dosage of 2.5% at which it started to drop and reached a low value at a dosage of 3.5%. This indicates that low dosages of the MR could not mitigate the increase in stiffening of cement pastes at high testing temperature, while it could achieve this goal at a high dosage (3.5%). It can be further observed that at a dosage of 2.5%, the thixotropy value at 40 °C was higher than that at 45 °C, which is consistent with that of yield stress.

The thixotropy behaviour for cement pastes incorporating the polycarboxylate-based superplasticizer is presented in Fig. 3.14(b). Due to its effective dispersing mechanism, PC could effectively mitigate the build-up of cement paste structure as a result of testing temperature increase, and thixotropy values were generally lower than those of mixtures incorporating the WRg and MR. At 20 °C, thixotropy reached negative values for all PC dosages indicating that cement paste thixotropy turned back to its normal hysteresis behaviour. At high testing temperatures of 40 and 45 °C, thixotropy increased slightly when the admixture dosage increased from 0.3 to 0.7%. However, thixotropy became negative for both testing temperatures when the PC dosage exceeded 1.2%, indicating that the hysteresis behaviour at high testing temperature became normal and that no significant effect of high early stiffening of cement paste is taking place.

The thixotropy behaviour of cement pastes made with NS is presented in Fig. 3.15(a). At 20 °C, thixotropy decreased with increasing NS dosage and reached negative values (normal behaviour) beyond a dosage of about 2%. Thixotropy increased dramatically up to a NS dosage of around 1.2% and 0.7% for 40 and 45 °C, respectively and then decreased until it reached a negative value at a dosage of about 2%. Moreover,

using high dosages of NS shifted the reverse hysteresis behaviour of cement paste back to its normal and delayed the stiffening of cement paste.

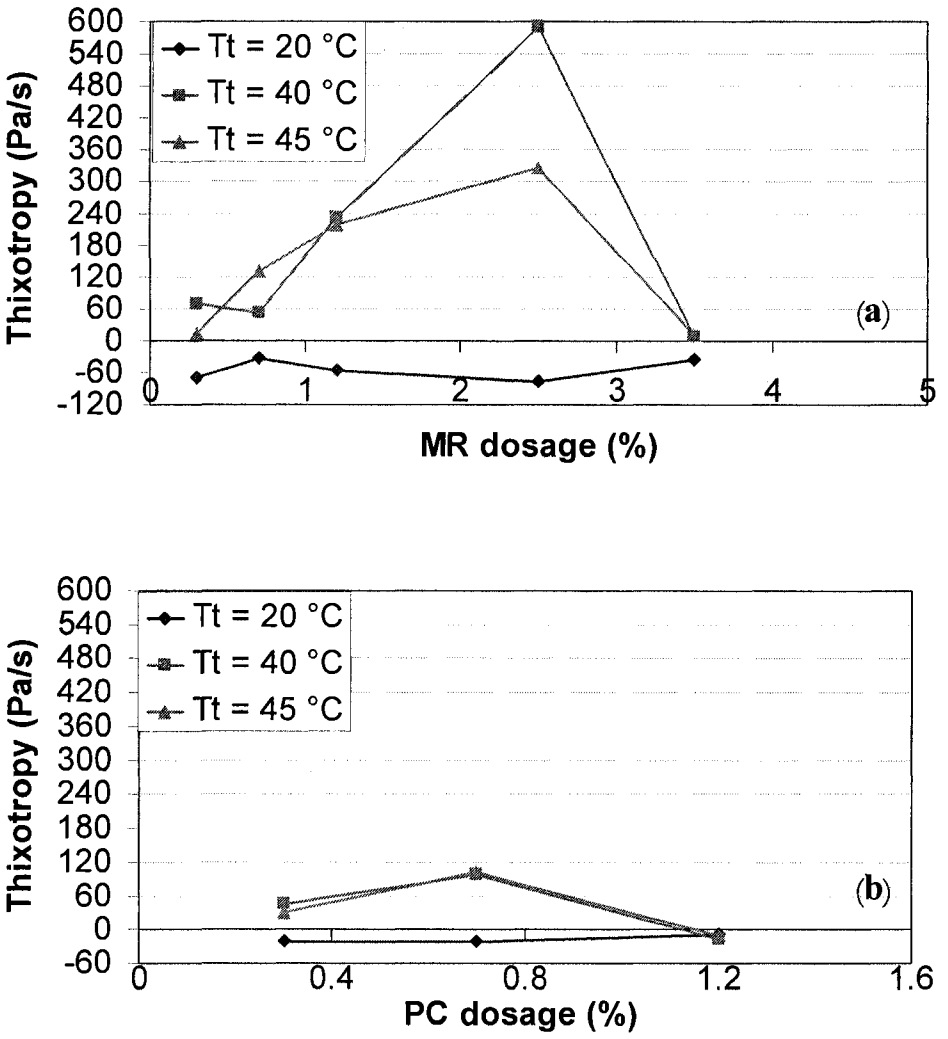

Figure 3.14-Thixotropy of cement paste at various testing temperatures and different dosages of (a) MR and (b) PC (w/c =0.35; admixture dosage is in % of cement mass).

The effect of the ML on thixotropy is shown in Fig. 3.15(b). It can be observed that thixotropy values increased at all testing temperatures with the increase of the ML dosage until a threshold dosage of 1.2% at which thixotropy started to decrease. At a dosage of

2.5%, thixotropy values became negative indicating that the reverse hysteresis loop has turned back to a regular behaviour.

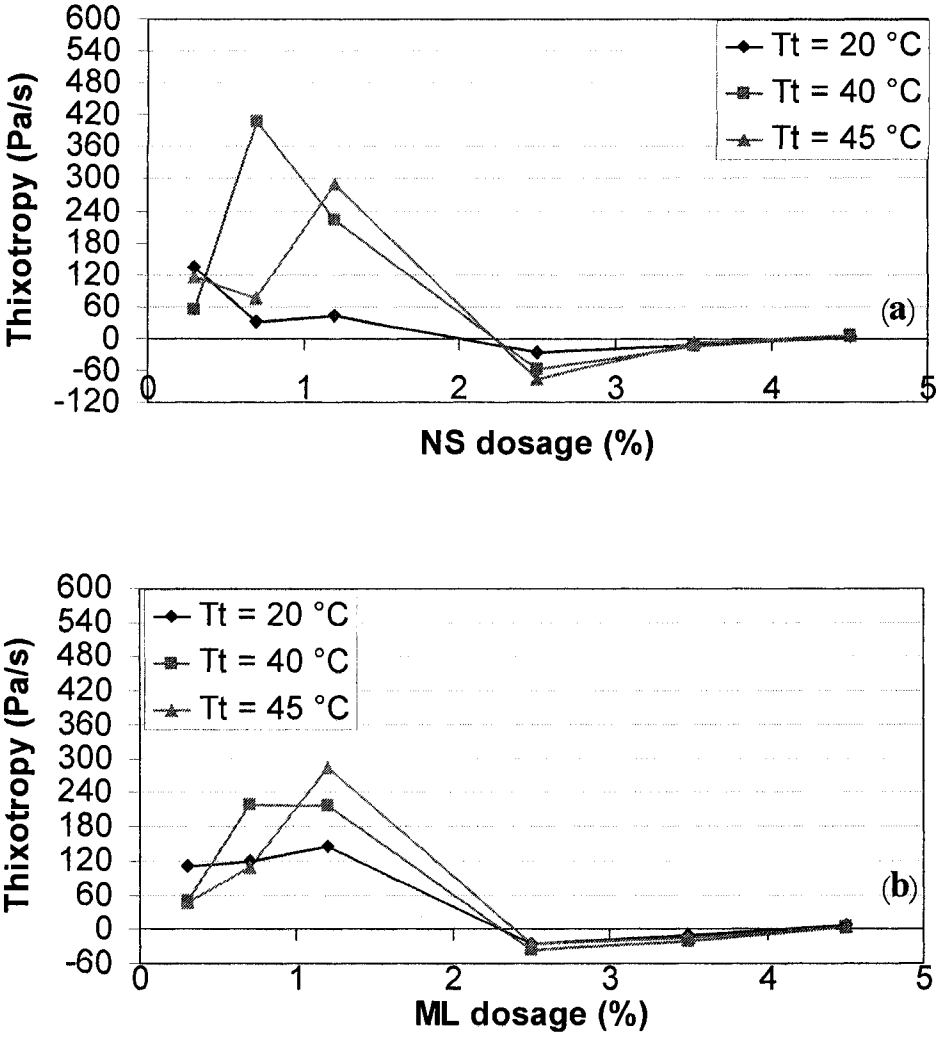

Figure 3.15-Thixotropy of cement paste at various testing temperatures and different dosages of (a) NS and (b) ML (w/c =0.35; admixture dosage is in % of cement mass).

3.9 Discussion

Rheological parameters at high testing temperature for cement pastes made with various dosages of five different admixtures were investigated in this chapter. Although the effects of plasticizers and temperature on the rheology of cement grouts were investigated previously (Domone and Thurairatnam 1988), it was attempted in the current chapter to determine the rheological properties of cement pastes incorporating various types of chemical admixture that can be used in hot weather concreting. Moreover, a larger range of temperature was investigated in this study to cover a wider scope of temperature that can occur in hot weather during placement of concrete.

The effects of various chemical admixtures and testing temperature on the rheological properties of cement paste were clearly depicted in measured yield stress and apparent viscosity values, especially at low shear rate (5^{-1}). It was observed that there was a strong agreement between the behaviour and trend of both yield stress and apparent viscosity at low shear rate (5^{-1}). Plastic viscosity did not always truly describe the effects of chemical admixtures and testing temperature on the rheological properties of cement paste at high testing temperature as discussed earlier. The thixotropy behaviour of cement paste at high testing temperature was also investigated. In general, it was observed that at low dosage of chemical admixtures, thixotropy increased with the increase in testing temperature. This is due to the build up in the structure of cement paste due to the acceleration of hydration reactions. It was also observed that there was a decrease in thixotropy when the dosage of admixtures increased. This is likely due to the delay in stiffening of cement paste induced by the dispersion effect action of chemical admixtures.

The differences in rheological results observed can be attributed to the various mechanisms by which each admixture affects the behaviour of cement paste. The gluconate acid-based WRg admixture showed a different behaviour than that expected. Instead of acting as a retarder at high testing temperature, it rather behaved as an accelerator. It was observed in previous work (Ravina and Soroka 1994) that using a water reducing and retarding admixture increased the slump loss when concrete was under prolonged mixing for up to 180 minutes at temperatures of 21 °C and 32 °C. Meyer and Perenchio (1979) investigated the reasons behind the rapid stiffening of cement paste when a water reducing and retarding admixture was incorporated and attributed this behaviour to the accelerated hydration of C_3A due to the presence of a water reducing and retarding admixture, resulting in rapid formation of fine ettringite crystals, which connected solid particles together.

Other studies suggested that adsorption could be one of the mechanisms by which a water reducing and retarding admixture operates (Ramachandran *et al.* 1997; Meyer and Perenchio 1979; Ravina and Soroka 1994). Adsorption of the admixture on the surfaces of unhydrated cement grains forms a barrier preventing water from reacting with cement grains, consequently, delaying the hydration process. A high temperature could break this layer, leading to accelerated hydration. This could be the reason why the WRg failed to operate as a retarder at high testing temperature. Therefore, it can be suggested that a WRg type D may act only as a water reducer at high temperature and could lose its retarding quality.

Moreover, lower water content is typically associated with smaller spacing between solid particles in the fresh mixture. Thus, hydration products can easily bridge the space

between cement particles due to the proximity of particles, resulting in a faster rate of hydration and stiffening is brought about earlier. This could be an additional reason why the WRg type D behaved as an accelerator at high testing temperature, which suggests that using WRg type D at very high temperature is not recommended.

The effect of the naphthalene sulfonate and melamine-based superplasticizers was found to be dosage-dependent; they tended to act as accelerators at low dosages and as retarders at high dosages. This behaviour was discussed by Ramachandran *et al.* (1997). It was found that at a dosage less than 2%, both ML and NS accelerated the hydration of C_3A and C_3S, while when the dosage exceeded 2%, they retarded the hydration of C_3A and C_3S. Therefore, it is argued that at high temperatures, these admixtures could be used effectively only at high dosages.

Due to its effective dispersing mechanism, the polycarboxylate-based superplasticizer deflocculates cement flocks and frees the entrapped water to fluidize the cement paste (Ramachandran *et al.* 1997). Therefore, it effectively enhanced the rheological properties of cement pastes at high temperature, and this admixture seemed to be effective for concrete in hot weather conditions.

The recommended dosages by manufacture for the studied admixtures are 0.20% ± 0.07%, 0.20 to 0.78%, 0.2 to 1%, 0.65 to 1.6%, and 0.6 to 1.5% for WRg, MR, PC, NS, and ML, respectively. By comparing these dosages with the results presented in this chapter, it can be observed that the recommended dosages are below those that seemed effective at high temperature, except for the PC which had a reasonable recommended range.

It should be noted that the effect of these admixtures on the rheology of cement paste at high temperature was investigated immediately after mixing. Their time dependent behaviour is critical for their performance in hot weather concreting. Chapter five will focus on the combined effect of temperature and time on the performance of these admixtures to formulate more realistic recommendations for field practice.

Further research is also needed to investigate the effect of possible hybrid blends of these admixtures at high temperature versus time and to assess compatibility between various admixtures and a wide scope of cementitious blends to optimize binder-admixture formulations for effective use in hot weather concreting applications. Such investigation should go beyond the classic flow behaviour to address volume change at high temperature and long-term mechanical strength and durability to make final recommendations for hot weather concreting.

3.10 Conclusions

The effects of various chemical admixtures on the rheological properties of cement paste at high testing temperature were investigated in this chapter. Five admixtures were used including a glocunic acid-based water-reducing and retarding admixture (WRg), a polycarboxylate-based mid-range water-reducing admixture (MR), a polycarboxylate-based high-range water-reducing admixture (PC), a naphthalene sulfonate-based high-range water-reducing admixture (NS), and a melamine-based high-range water-reducing admixture (ML). Various cement pastes were made incorporating different dosages of the admixtures. Their rheological properties were investigated at 20, 40, and 45 ^{o}C. The following conclusions can be drawn:

- Cement paste at high testing temperature can have a reverse hysteresis behaviour.
- Both yield stress and viscosity increased nonlinearly with testing temperature.
- The WRg used in this chapter acted as an accelerator at high testing temperature and is not recommended for concrete in hot weather conditions.
- The MR improved the rheological properties of cement paste at high testing temperature only at a dosage beyond 2.5% where both yield stress and apparent viscosity continuously decreased with the increase of MR dosage, while thixotropy approached a value of zero at a dosage of 3.5%.
- The PC effectively improved the rheological properties of cement paste at high testing temperature.
- NS and ML behaved as accelerators at low dosages but improved the rheological properties of cement paste at high dosages.
- Further research is needed to investigate the effects of these admixtures versus time and temperature, and to examine possible hybrid blends of these admixtures and their compatibility with binders used in hot weather concreting.
- It should be emphasized that the findings of this study are valid for the admixtures used herein. Other admixtures, even from the same category, may exhibit different behaviour, and thus should be investigated to validate the current results.

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Chapter 4

EFFECT OF TEMPERATURE ON OSCILLATORY SHEAR BEHAVIOUR OF PORTLAND CEMENT PASTE INCORPORATING CHEMICAL ADMIXTURES*

4.1 Introduction

The hydration of portland cement begins as soon as it comes in contact with water. It has been well established that the rate of hydration of cement is temperature dependent. Thus, concrete placed in high temperature environments tends to hydrate faster than that placed at moderate temperature, often resulting in rapid loss of workability and a reduction in the available time for its placement and handling. As specified by the American Concrete Institute (ACI) guidelines, the upper limit of ambient temperature to produce good quality concrete is 27 ^{o}C (ACI 305.1-06). However, in hot weather, concrete is usually placed under much higher temperatures. For example, in the Arabian Gulf, concrete is often placed at temperatures around 40 to 45 ^{o}C (El-Rayes 1990). High-range water reducing admixtures are usually added to concrete to reduce the amount of mixing water needed and to improve workability. These admixtures are mostly developed and tested in areas of the world with moderate temperature environments often without sufficient specifications for hot weather concreting. Therefore, comprehensive research to investigate

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the behaviour of such admixtures in hot weather should be conducted in order to develop adequate standards and specifications for hot weather environments.

The rheology of fresh concrete is strongly affected by the rheological properties of cement paste. Only limited research has been carried out to examine the effect of temperature on the rheology of cement pastes incorporating different chemical admixtures (Al-Martini and Nehdi 2007; Domone and Thurairatnam 1988). It has been observed that the rheological properties of cement pastes at high temperature depend on the type of admixture used. As such, it was found that some admixtures improved workability at high temperature, while others achieved opposite results. Moreover, the dosage of admixtures had an important effect since at low dosages some admixtures could act as accelerators, thus enhancing the thixotropic behaviour of cement paste at high temperature, but when their respective dosage exceeded certain threshold levels, such admixtures could act as retarders and reduce the extent of cement paste thixotropy as reverse hysterisis loops became normal at high dosage (Al-Martini and Nehdi 2007).

The behaviour of chemical admixtures is affected by cement constituents. Borner and Sarkar (1995) investigated the effect of a polynaphthalene sulfonate superplasticizer (PNS) on the fluidity of five types of cements with different constituents including ASTM Type I, II, III and V cements. They found that the amount of C_3A in the cement affects the fluidity of cement pastes significantly. Cements with low C_3A content displayed greater fluidity than those incorporating high C_3A content.

It is important to note that the rheological properties of cement paste are also strongly shear history dependent (Saak 2000). In flow tests, the cement paste microstructure is

broken down and consequently the measured yield stress will be significantly affected. Typically, flow curves (shear stress vsersus shear rate) are obtained and yield stress and viscosity as a function of shear rate are calculated (Williams *et al.* 1999). Although such tests can depict the rheological behaviour of cement paste at continuous shear flow, i.e. during its transportation, pumping, and placing, it fails to define rheological properties at very low shear rates. For instance, viscous properties obtained from flow curves generally do not apply to a quiescent cement paste in place in a casing column (Chow *et al.* 1988).

On the other hand, various empirical rheological models (e.g. Bingham, Herchel-Bulckley, Modified Bingham, and Casson) are used to estimate rheological parameters, i.e. yield stress and plastic viscosity, from experimental flow curves. Although yield stress measurements obtained using these models are generally considered to be reasonable, Nehdi and Rahman (2004a) found that the estimated cement paste rheological properties vary significantly when calculated using various models. Furthermore, there are several limitations associated with such models. In particular, the estimation of yield stress using a given analytical model is achieved by the extrapolation of shear stress-shear rate data corresponding to a zero shear rate. It was found by Yahya and Khayat (2001) that the Bingham model gave unfavorable fitting of experimental measurements for highly pseudoplastic cement grouts with very low w/c, while the fit was adequate for flowable grouts.

Oscillatory tests can effectively depict the behaviour of cement paste at very low shear strain/shear stress where cement paste behaves elastically as a solid. The principle underlying such tests is that when strain in cement paste is very low, the cement particles

stay in close contact with each other, and cement paste behaves in an elastic mode; it is able to recover elastically once the load is removed. At low oscillatory shear stress, the cement paste microstructure is undisturbed. By increasing the shear stress, strain will increase, resulting in increasing the distance between particles until a certain stress at which point they are separated from each other and start to flow. This stress is called the critical stress and is generally similar to the yield stress in flow tests (Schultz and Struble 1993; Chow *et al.* 1988). Therefore, oscillatory tests have the potential to provide more accurate information on the rheology of cement paste. Figures 4.1(a), 4.1(b), and 4.1(c) schematically illustrate cement paste without shearing, cement paste sheared below the critical stress, and cement paste sheared beyond the critical stress, respectively. The outer circles in the figures represent the growth in hydration products. Due to hydration, the volume fraction of the solids increases resulting in an increase in the shear modulus (Struble *et al.* 2000).

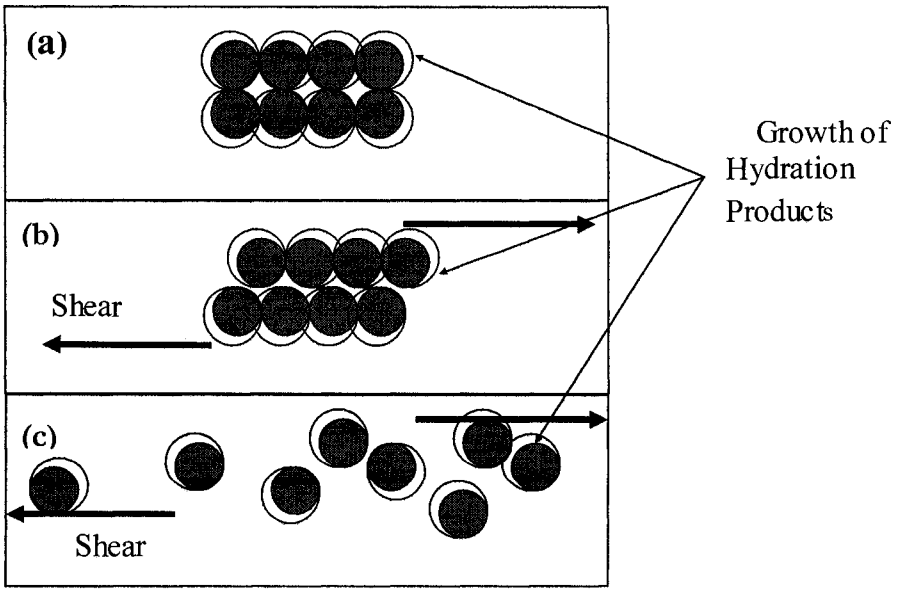

Figure 4.1-A schematic representation of (a) cement paste flocs without shear, (b) cement paste sheared below critical stress (elastic region), and (c), cement paste sheared above the critical stress (viscous region).

Although only a few studies in the literature (Saak 2000; Schultz and Struble 1993; Chow *et al.* 1988; Saasen and Marken 1991) used oscillatory tests to investigate the viscoelastic properties of cement paste, the effects of temperature and chemical admixtures on these properties using the oscillatory technique remain largely unexplored. In this chapter, the viscoelastic properties of cement paste at w/c = 0.35 and incorporating various dosages of four different chemical admixtures, namely water reducing and retarding admixture (WRp), melamine-based high-range water reducing admixture (ML), polycarboxylate-based high-range water reducing admixture (PC), and a new generation of polycarboxylate-based high range water reducing admixture (PCN) were tested at three different testing temperatures (20, 35, and 45 °C). Moreover, the rheological properties of cement pastes having w/c = 0.35 and 0.50 and not incorporating admixtures were also investigated at testing temperatures of 20, 35, and 45 °C. This was done to highlight the effect of the w/c on the rheology of cement paste at different temperatures. The results allowed gaining a better understanding of the function of these admixtures at high temperature, which should lead to their effective use in the design of concrete mixtures under hot weather conditions. This will also help in selecting adequate admixtures and dosages to overcome rheological difficulties, e.g., rapid loss of workability, pumping problems, acceleration of cement hydration, fast evaporation of mixing water, and forming of cold joints, which are often encountered during concrete construction in hot weather.

4.2 Principles of Oscillatory Shear Stress

Conventional flow tests are applied for routine measurement of viscosity parameters of cement paste using coaxial cylinders, parallel plates, and other devices. The major limitation of such tests is their incapability to accurately measure rheological properties at

low shear rates. For instance, yield stress cannot be measured directly and rheological models are used to estimate this parameter from experimental shear-stress shear-rate curves. The results obtained depend on the type of model and its assumptions (Nehdi and Rahman 2004a). Moreover, when cement paste flows, its microstructure is broken down and consequently the yield stress values measured are affected considerably. Therefore, variation of shear stress versus shear rate may not be optimal to investigate the effects of temperature and time on the rheology of cement paste (Struble *et al.* 2000). Oscillatory tests are considered to be more adequate for quantifying the viscoelastic properties of fluids (Chow *et al.* 1988; Saasen and Marken 1991). Hence, oscillatory stress sweep was used in this chapter to investigate the rheology of cement pastes at high temperature.

4.2.1 Apparatus

An advanced rheometer (TA-Instruments AR 2000) was used throughout this investigation to measure the dynamic rheological properties of cement pastes (Fig. 4.2) (TA Rheology Advanced Data Analysis 2001). The rheometer is provided with an advanced system for temperature control in the range of -5 to 100 °C. The geometry of the test accessory has a significant influence on the measured rheological properties of cement paste (Nehdi and Rahman 2004b). The coaxial concentric cylinder geometry was used throughout this study. This geometry consists of inner and outer cylinders; the inner cylinder rotates inside a central fixed hollow of the outer cylinder. The gap between the inner and outer cylinders is 1 mm. It is necessary to use such a narrow gap so that the shear rate remains constant across the gap, which is important especially in static flow studies to minimize the effect of error in rheological measurements caused by wall slip (Saak *et al.* 2001). The gap between the head of the conical end of the inner cylinder and the bottom of

the hollow was set at 0.5 mm and kept constant for all experiments. The rheometer has an auto gap system that compensates for the expansion of the stainless steel of the coaxial cylinder when a wide temperature range is applied during an experiment, thus ensuring the gap remains constant.

The cement pastes were mixed using a high-shear mixer with three variable speeds (Fig. 3.1(a)). The mixer consists of a bowl and a vertical shaft with two blades at two vertical levels, and has the capability of mixing the cement paste evenly and uniformly.

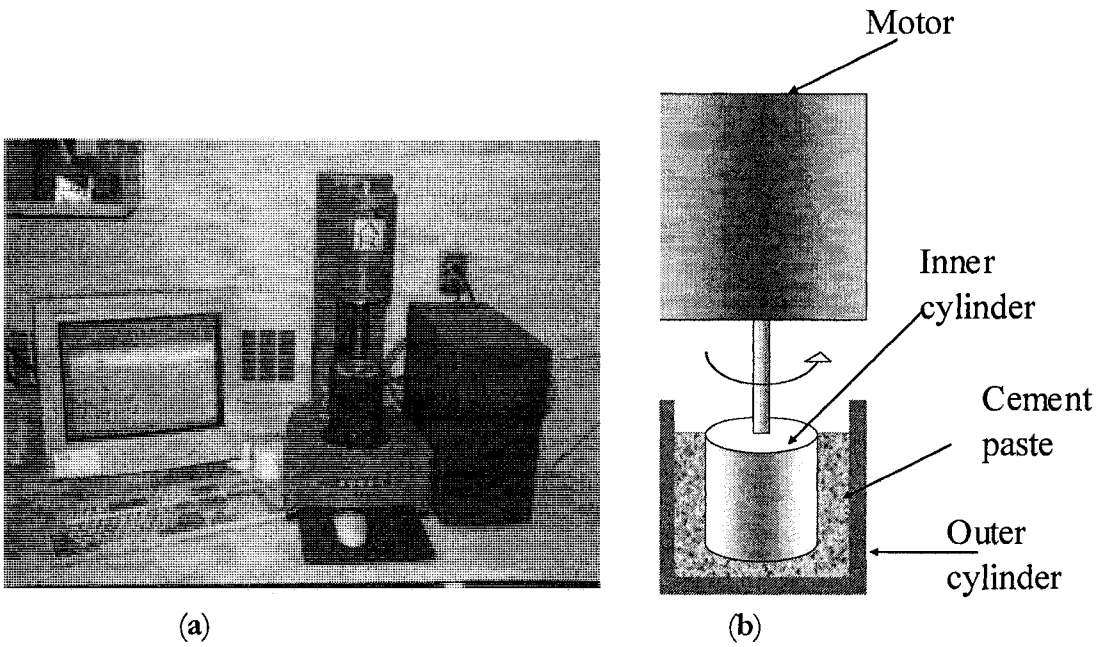

Figure 4.2- Illustration of instrument used: (a) cement paste rheometer; and (b) schematic diagram of rheometer.

4.2.2 Analytical aspects

The applied oscillatory stress can be illustrated as follows:

$$\sigma = \sigma_o \cos \omega t \qquad (4.1)$$

In the case of an ideal elastic solid, the resulting oscillatory strain will be completely in phase with stress and is expressed as follows:

$$\gamma = \gamma_0 \cos \omega t \tag{4.2}$$

The resulting oscillatory strain for a viscous fluid will be 90^0 out of phase with the stress, and is expressed in the following equation:

$$\gamma = \gamma_o \cos\left(\omega t - \frac{\pi}{2}\right) \tag{4.3}$$

Thus, the resulting oscillatory strain for a viscoelastic material such as cement paste is given by:

$$\gamma = \gamma_o \cos(\omega t - \delta) \tag{4.4}$$

When a viscoelastic material is subjected to a sinusoidal stress, the resulting sinusoidal strain will have a lag of δ with that of stress, which varies in the range of 0 to $\pi/2$ (Chow *et al.* 1988; Ferguson and Kemblowski 1991).

The complex behaviour of a viscoelastic material subjected to a sinusoidal stress wave is further expressed by the complex shear modulus (G^*) in the following equation (Ferguson and Kemblowski 1991; Barnes *et al.* 1989):

$$G^* = G' + iG'' \tag{4.5}$$

The real component (the shear modulus) in the above equation is calculated according to equation (4.6), and the imaginary component (the loss modulus) is calculated according to equation (4.7).

$$G' = \frac{\sigma_o}{\gamma_o}\cos\delta \tag{4.6}$$

$$G'' = \frac{\sigma_o}{\gamma_o}\sin\delta \tag{4.7}$$

For perfectly elastic solid materials, G'' is zero, therefore no loss occurs and equation (4.5) becomes:

$$G^* = G' \tag{4.8}$$

For perfectly viscous liquid materials, the shear modulus equals zero. Hence, there is no rigidity in the material as it becomes fluid, and equation (4.5) becomes:

$$G^* = iG' \tag{4.9}$$

The phase angle (δ), i.e. the lag between the applied stress and resulting strain, is expressed as follows:

$$\tan\delta = \frac{G''}{G'} \tag{4.10}$$

It is important to note that the phase angle is zero when the material is an elastic solid, and is $\pi/2$ when the material is a viscous liquid. The shear modulus was plotted versus oscillatory stress in a log-log scale throughout this chapter.

4.2.3 Materials

Canadian Standards Association (CSA 23.2) Type 10 (similar to ASTM Type I) ordinary portland cement was used in all cement pastes investigated. Its chemical and

physical properties are summarized in Table 3.1. Deionized distilled water was used to prepare the cement pastes and its temperature was maintained at 19 ± 0.5 °C.

The following four different types of liquid chemical admixtures were used:

1. Water reducing and retarding admixture (WRp). This admixture is based on phosphonic acid and carboxilic acid. WRp meets ASTM C 494 requirements for Type B retarding, and Type D water-reducing and retarding admixtures. Its density is 1.07 g/cm^3 and concentration of solids is 12.4%. WRp is believed to retard the setting time by controlling the hydration of portland cement, thus mitigating the acceleration of hydration of concrete due to high temperature, and improving workability in hot weather.

2. Melamine sulfonate-based high-range water reducing admixture (ML) complies with ASTM C-494 Type F high-range water-reducing admixture. Its density is 1.25 g/cm^3 and concentration of solids is 23.5%

3. Polycarboxylate-based high-range water-reducing admixture (PC) meeting ASTM C 494 requirements as a Type A water-reducing and Type F high-range water-reducing admixture. Its density is 1.05 g/cm^3 and concentration of solids is 38.0%. Polycarboxylate is a synthetic organic polymer bearing carboxylic acid groups (Ramachandran *et al.* 1997).

4. A new generation of polycarboxylate-based high-range water-reducing admixture (PCN). PCN meets ASTM C 494 requirements as a Type A water-reducing and Type F high-range water-reducing admixture. Its density is 1.1 g/cm^3 and

concentration of solids is 46.4%. Due to its very high dispersing capability caused by its long chain, there was no need to use a dosage higher than 1% by mass of cement.

Table 4.1 illustrates the admixtures investigated with the range of each used in this chapter. These admixtures are commonly used in the concrete industry and were recommended by manufacturers for concrete at high temperature.

Table 4.1-Variables used in the study and their range

Variables	WRp (%)	ML (%)	PC (%)	PCN (%)	W/C		Temp. (°C)
Range	0.7-4.0	0.3-3.0	0.3-1.2	0.3-1.0	0.35	0.50	20-45
Basis of Choice	Exp. Results	Exp. Results	Exp. Results	Exp. Results	Low fluidity of plain paste	High fluidity of plain paste	Covers the range of temperature in hot weather countries

4.3 Experimental Set-Up

Some cement pastes were prepared with a water/cement ratio (w/c) of 0.50 and not incorporating admixtures to validate the reliability of the testing procedure and apparatus in producing repeatable measurements at different testing temperatures. Cement pastes with w/c = 0.35 and without admixtures were also tested at 20, 35, and 45 °C to compare the effects of various admixtures and to highlight the effect of w/c on the rheology of cement paste at different temperatures. It should be noted that all cement pastes incorporating admixtures were made with w/c = 0.35. The calibration of the instrument was done using a certified viscosity standard Newtonian mineral oil with a known viscosity of 1.40 Pa.s at 25

°C. The measured viscosity was 1.42 Pa.s at 25 °C with an error of 1.4%, which is less than the tolerated error specified by the manufacturer (4%). The testing and mixing procedure were conducted according to the following steps:

- Using a graduated needle, the specified quantity of liquid admixture was injected into the mixing water.
- The weighed quantity of cement powder was added to the water and was manually stirred for one minute.
- The cement paste was subsequently mixed for one minute at low speed, then at high speed for another minute.
- The mixer was stopped for 1.5 minutes, during which the bowl was scraped with a rubber paddle to ensure homogeneity. Mixing resumed for another minute at high speed.
- After mixing, the cement paste sample was placed in the gap space of the coaxial cylinders, and the paste was covered with a solvent trap to prevent evaporation of water during testing.
- The temperature was adjusted to the required level over approximately one minute. Then, the cement paste sample was pre-sheared for two minutes by applying a shear rate sweep at 70 s^{-1} in order to break down the structure of the cement paste sample and create uniform conditions before testing (Saak *et al.* 2001).
- The cement paste sample was subsequently left undisturbed for 5 minutes in order to rebuild its broken structure due to the pre-shear procedure before the beginning of rheological measurements.

- Subsequently, a stress sweep procedure was performed by stressing the cement sample from 0.008 to 700 Pa and the resulting strain was recorded. The stressing rate was increased according to the following equation:

$$\sigma = 0.0069 \times e^{0.0254t} \tag{4.11}$$

The total time between the beginning of mixing and the start of rheological tests was 7 minutes for all cement pastes. This mixing procedure was strictly followed for all cement pastes to avoid the effect of exogenous variables on the results (Williams *et al.* 1999; Chow *et al.* 1988; Roy and Asaga 1979). The pre-shearing procedure was kept constant for all samples tested. This allowed applying higher shear stress, which resulted in less scatter of data and more reproducible measurements. Throughout rheological testing, the frequency of the oscillatory shear was maintained constant at 1 Hz.

The stress sweep technique helps to trace the dispersing effect of admixtures (Chen *et al.* 2006). If at low stress the shear modulus is very high (above 100 kPa), the cement particles are fully flocculated. In this case, the cement particles are insensitive to stress and will not yield. Conversely, the cement particles are fully dispersed when they exhibit very low shear modulus (less than 10 Pa).

4.4 Typical Viscoelastic Behaviour of Cement Paste

As shown in Fig. 4.3, the calculated shear modulus (G') and loss factor (G'') (Eqs. 4.6 and 4.7) for cement paste (w/c = 0.50) followed a plateau when the applied oscillatory stress was below the yield stress. This indicates that the phase shift angle was very small, and therefore the complex modulus was very close to the shear modulus. It could be observed that there is some instability in the figure at low levels of oscillatory stress. This

behaviour has been observed by others (e.g. Struble *et al.* 2000; Struble and Chen 2005; and Chen *et al.* 2006) and is not well understood. It is believed that it may be due to the fact that at extremely low oscillatory stress, the shear modulus readings are unstable, and become increasingly stable as the oscillatory stress increases. The linear region of the curve corresponds to the elastic behaviour of cement paste. In this region, the strain is very low and cement paste particles are in close contact with each other. Thus, G' in this region was not affected by microstructure breakdown, and cement paste behaved like a solid material. Further, in this region G' was higher than G'' which is in agreement with that observed by Struble *et al.* (2000). When the stress increased beyond the critical stress, a steep decline in the G' and G'' curves occurred due to the increase in strain, which became large enough so that little contact between cement particles existed and cement paste started to flow. The edge of the curve at which cement paste shifted from elastic to viscous behaviour is called the critical stress, which is equivalent to the yield stress in traditional flow experiments. This stress will be called the yield stress throughout this chapter. At a certain oscillatory stress, G'' became higher than G' which indicates that the paste microstructure became more liquid-like. It should be noted that this behaviour is typically observed in this chapter for all cement paste.

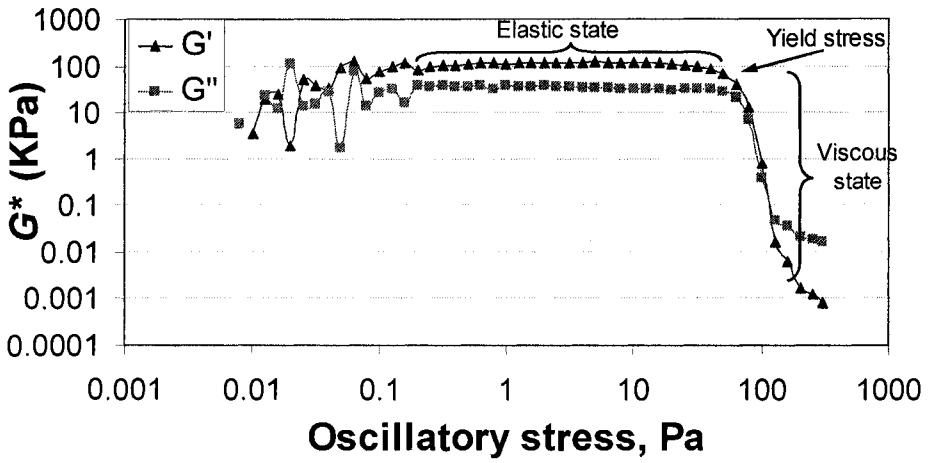

Figure 4.3-Shear modulus (*G'*), loss modulus (*G"*) as a function of oscillatory shear (w/c = 0.50).

4.5 Results and Discussion

4.5.1 Viscoelastic properties of cement paste at high testing temperature

To evaluate the viscoelastic properties of cement paste at high temperature, a sinusoidal stress was applied and the resultant strain was measured. Figures 4.4(a) and 4.4(b) present the relationship between temperature and shear modulus and temperature and yield stress, respectively, for cement pastes with w/c = 0.50 and w/c = 0.35 without admixtures. It can be observed from the figures that the shear modulus and yield stress values increased with the increase of testing temperature. This is likely due to the increase in the rate of hydration of cement particles at high temperature, which results in an increase of the bond strength between particles (Struble *et al.* 2000). It can be further observed that at w/c = 0.50, the rate of increase in both shear modulus and yield stress with testing temperature was almost linear. This increase was not linear at w/c = 0.35 and it was relatively less significant between 20 and 35 °C than that between 35 and 45 °C (Fig. 4.4). At a high testing temperature of 45 °C, the shear modulus and yield stress values for the

cement paste with w/c = 0.35 were much higher than that for w/c = 0.50. This could be attributed to the increase in the volume fraction of solids with the decrease of w/c from 0.50 to 0.35. As a result, the buildup in structure of the cement paste with w/c = 0.35 due to the increase of temperature was much faster than that for cement paste with w/c = 0.50.

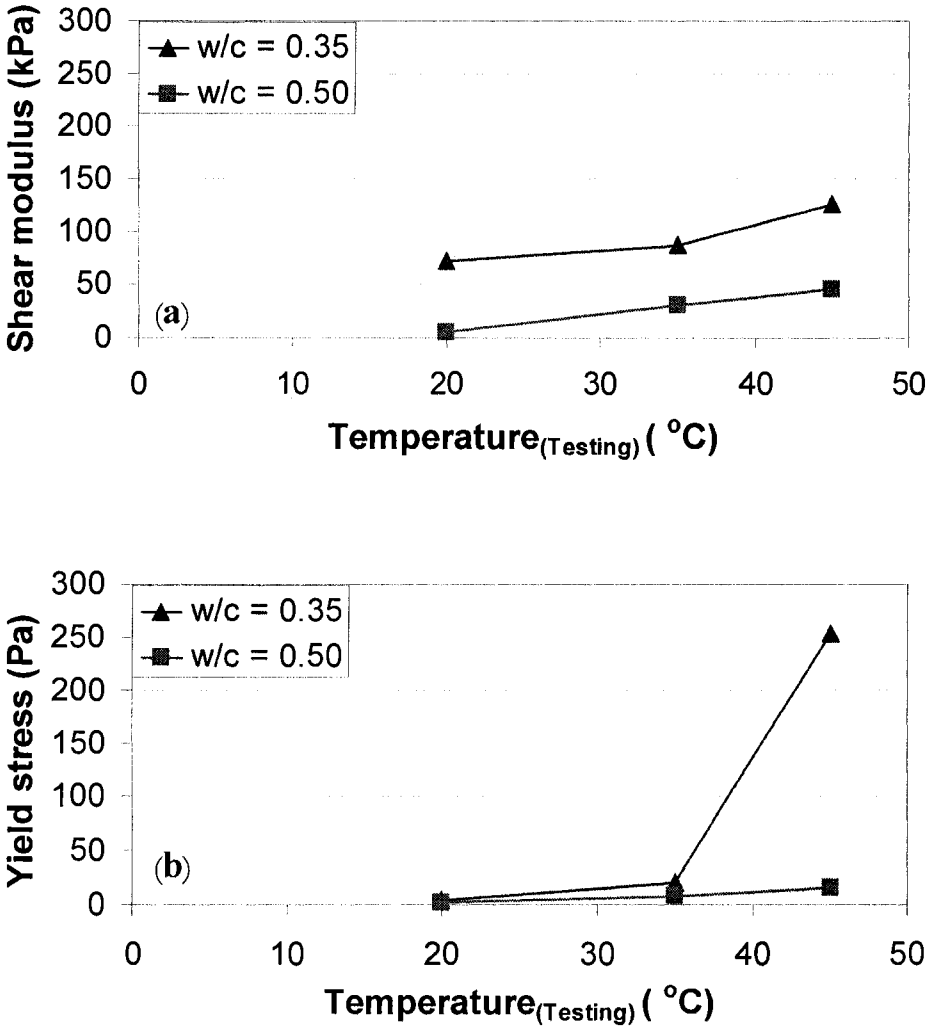

Figure 4.4-Effect of testing temperature on (a) shear modulus, and (b) yield stress.

This observation is in agreement with previous findings (e.g. Soroka 1993) who observed that the rate of slump loss increased with temperature. It is well known that the

increase of the shear modulus of a flocculated suspension with the increase of the solid volume fraction follows a power law (Sonntag and Russel 1987). The focus in this chapter was on the elastic region of the curve in which both oscillatory shear stress and strain are low since at higher stress the curve becomes nonlinear and it would be very difficult to interpret results (Saak 2000). The evolution of *G'* in the elastic region of the curve due to testing temperature variation is also illustrated in Fig. 4.5. It is shown that *G'* increased when the testing temperature increased. The figure also shows that yield stress increased with testing temperature, which indicates that more stress was needed to make cement paste flow. This was likely due to the fact that cement paste hydration accelerated significantly when temperature increased (Al-Martini and Nehdi 2007). It should be noted that the values of shear modulus and yield stress for each testing temperature in Fig. 4.5 can be depicted in Fig. 4.4 for cement pastes with w/c = 0.50.

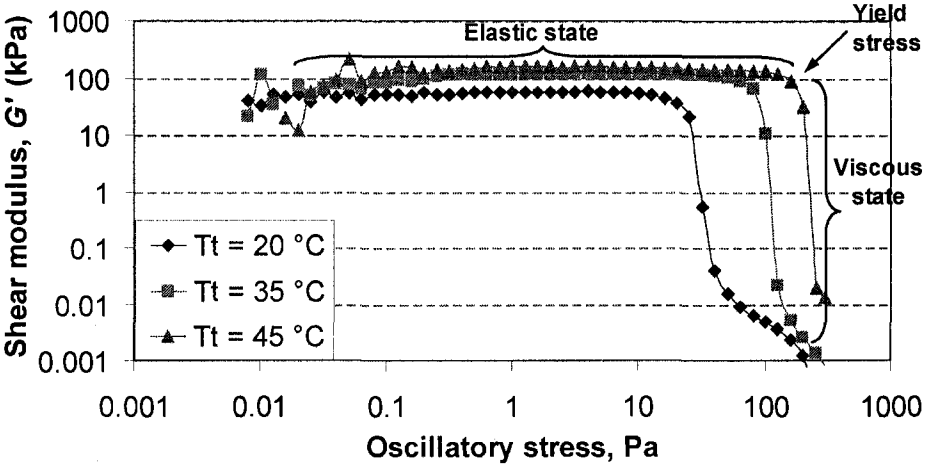

Figure 4.5-Typical shear modulus at different testing temperatures (w/c = 0.50).

4.5.2 Reliability of rheometer at different testing temperatures

For further rheometer calibration and to ensure statistical repeatability of results, three sets (each consists of four cement paste samples prepared at w/c of 0.50 without admixtures) were tested at three different testing temperatures (20, 35, and 45 °C). A new cement paste mixture was used for replicating each test, since rheological properties of cement paste are time, temperature, and shear history dependent.

As shown in Table 4.2, the standard deviation values are relatively small. The ratios of standard deviations of the observations and their means for the shear modulus are 5.7%, 1.25%, and 2% at 20, 35, and 45 °C, respectively. In the case of yield stress these ratios are 1.9%, 0.4%, and 0.2%, respectively. Therefore, the standard deviations of the results listed did not exceed 6%, which indicates that the experimental procedure and the rheometer can produce repeatable measurements with acceptable accuracy. As such, only one observation was taken for subsequent measurements.

Table 4.2-Repeatability of oscillatory shear measurements (cement pastes with w/c = 0.5)

Temperature	Shear modulus (G') (KPa)			Yield stress (Pa)		
°C	Measured	Average	*SD*	Measured	average	*SD*
20	5.80 6.57 5.93 6.31	6.06	0.35	2.01 2.10 2.05 2.09	2.06	0.04
35	31.54 30.65 30.90 31.22	31.08	0.39	8.00 7.98 8.03 8.05	8.02	0.03
45	45.11 47.35 45.80 46.20	46.12	0.94	15.95 15.92 15.99 15.97	15.96	0.03

4.5.3 Effect of temperature and chemical admixtures on shear modulus (G')

Shear modulus (*G'*) data from stress sweep experiments for cement pastes incorporating various admixtures with different dosages and testing temperatures are presented in Figs. 4.6 and 4.7. Figure 4.6(a) illustrates shear modulus values measured for cement pastes incorporating various dosages of a water reducing and retarding admixture (WRp) at different testing temperatures. It can be observed that the shear modulus generally decreased with the increase of the WRp dosage, and increased significantly with temperature increase. The rate of increase in shear modulus became much higher when testing temperature exceeded 35 °C, but this increase was less significant at high WRp dosages. For example, at a WRp dosage of 0.7% the shear modus values were 140 kPa and 100 kPa at 35 °C and 20 °C, respectively. Yet, the shear modulus value at 45 °C and at a higher dosage of 1.5% was 167 kPa. Therefore, a dosage of 0.7% was not tested at 45 °C because the shear modulus would reach very high values, which could damage the instrument. At a high WRp dosage of 3%, the *G'* values of cement paste at different temperatures were comparable. Beyond this dosage, there was no noticeable change in the shear modulus when testing temperature was 45 °C. This indicates that WRp at 45 °C had reached a saturation dosage of 3%. At 35 °C, the saturation dosage was 1.5%, which is half that at 45 °C. Moreover, at 35 °C the cement paste with 0.7% or 1.0% WRp dosage experienced full gellation where the shear modulus became very high and no drop in shear modulus was noticed at these two dosages.

As shown in Fig.4.6(b), the shear modulus increased with temperature and with the ML dosage up to 0.7%, then it started to decrease steeply until it reached a plateau (saturation dosage) beyond which no further decrease in shear modulus was achieved. The

effect of the ML depended on its dosage. At low dosage, it acted as an accelerator since it enhanced the effect of high temperature, while it acted as a retarder at high dosage since it effectively offset the acceleration of hydration at high temperature and its influence on the shear modulus. It has been previously reported that ML acted as an accelerator below a dosage of 2% and as a retarder above this dosage (Ramachandran *et al.* 1997).

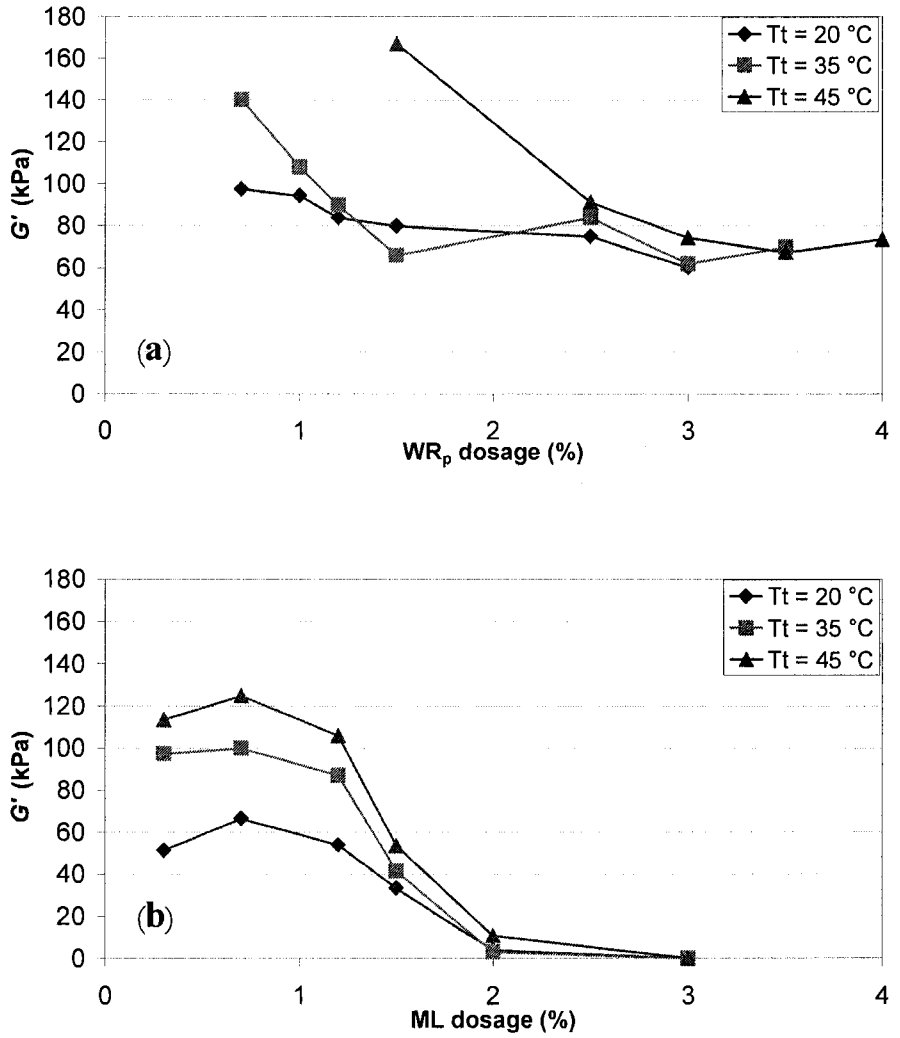

Figure 4.6-Shear modulus (*G'*) of cement pastes at various testing temperatures and different dosages of admixtures, (a) WRp and (b) ML (w/c = 0.35, admixture dosage is in % of cement mass).

The shear modulus results of cement pastes incorporating various dosages of PC are presented in Fig. 4.7(a). It can be observed that the shear modulus generally decreased with the increase of PC dosage, and increased significantly with temperature increase, especially when testing temperature exceeded 35 °C. For instance, at a PC dosage of 0.5% the increase in shear modulus between 35 and 45 °C was about eight times its value between 20 °C and 35 °C. It can be further noticed that at high testing temperature (45 °C) the dispersing capability of PC was not very effective when the dosage increased from 0.3% to 0.5%, while it was significantly effective at lower testing temperatures (35 °C and 20 °C). This indicates that at low dosages, the PC could not apparently offset the acceleration of hydration due to high temperature. However, an increased PC dosage seemed to offset the acceleration of hydration due to higher temperature, and even neutralized it at a high dosage of 1.2% since the shear modulus at the various testing temperatures approached a value of zero. The saturation dosages can be clearly depicted in this figure for all temperatures. At 20 °C and 35 °C the saturation dosage was similar (0.7%).

The rheological response of cement pastes incorporating a new generation of polycarboxylate high-range water reducing admixture is depicted in Figure 4.7(b). The dispersing ability of PCN was dosage and temperature dependent. At 45 °C, the cement paste with a dosage of 0.3% was flocculated (high shear modulus). However, this admixture was very effective at lower testing temperatures (20 °C and 35 °C) since the shear modulus values were relatively low for all dosages. Moreover, with increasing dosage, cement pastes incorporating PCN became progressively better dispersed at all temperatures than those incorporating a similar dosage of PC. The saturation dosage of PCN at 45 °C was 1.0%, while it was 1.2% for the PC.

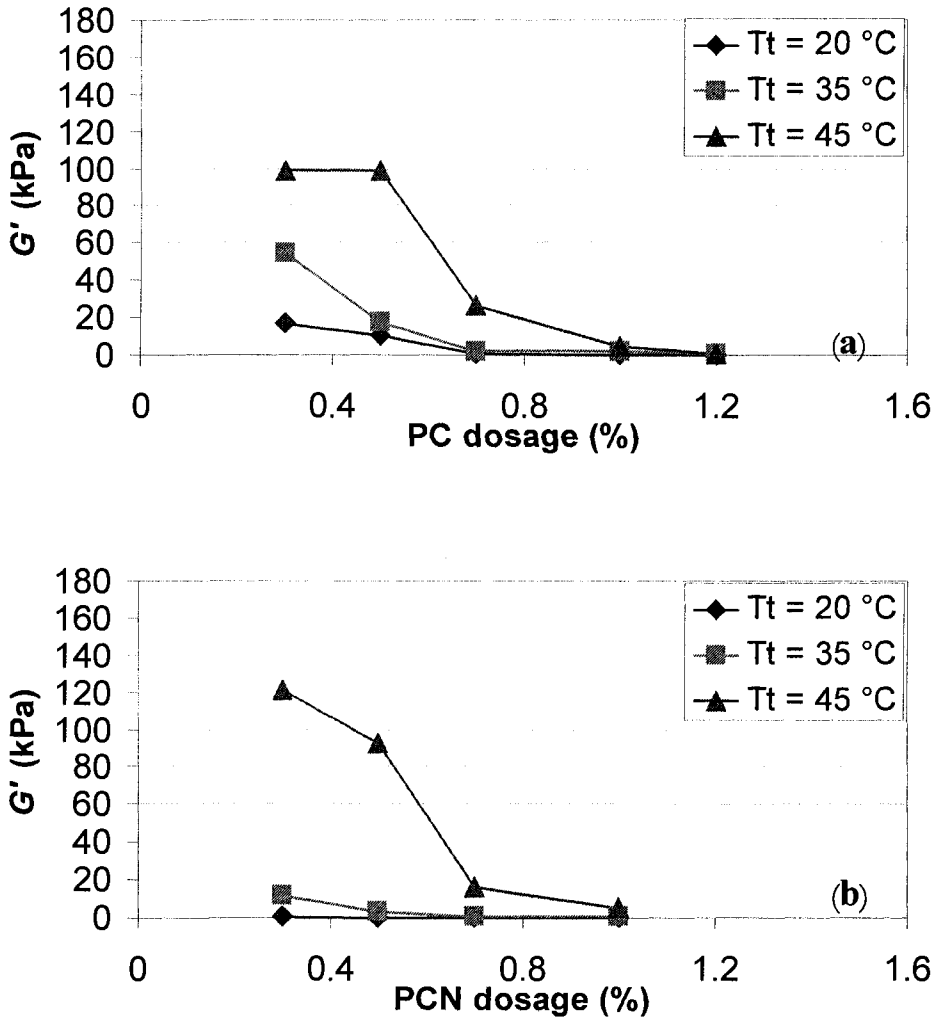

Figure 4.7-Shear modulus (G') of cement pastes at various testing temperatures and different dosages of admixtures, (a) PC and (b) PCN (w/c = 0.35, admixture dosage is in % of cement mass).

4.5.4 Effect of testing temperature and chemical admixtures on yield stress

Figure 4.8(a) presents the values of yield stress for cement pastes incorporating various dosages of a water reducing and retarding admixture (WRp) at different testing temperatures. The yield stress decreased significantly with increasing WRp dosage. Moreover, the higher the temperature the higher the saturation dosage. The WRp saturation dosages were 1.0%, 1.5%, and 2.5% at 20 °C, 35 °C, and 45 °C, respectively.

It should be noted that at 35 °C cement pastes with a dosage of 0.7% and 1.0% WRp did not yield, i.e. the shear modulus values exhibited a plateau and no steep drop of the shear modulus in the range of oscillatory stress investigated (0.3 to 700 Pa) was observed. As a result, Fig. 4.8(a) does not have values for the yield stress at these two dosages. This indicates that the cement pastes at these relatively low dosages of WRp were fully flocculated. Thus, these two dosages were not further tested at 45 °C.

In Fig. 4.8(b), the effect of the melamine sulfonate-based high-range water reducing admixture (ML) on yield stress of cement paste at different testing temperatures is illustrated. It is shown that yield stress increased with temperature and with the ML dosage up to 1.2%, then it started to decrease steeply beyond this dosage until it reached a plateau (saturation dosage), and the value of yield stress approached zero. The ML acted as an accelerator at low dosage since it enhanced the acceleration of hydration due to temperature rise, and acted as a retarder at high dosage where it effectively offset the effect of high temperature. For instance, at a low ML dosage of 0.3%, yield stress increased exponentially with temperature. The difference in the increase of yield stress between 35 and 45 °C was about double that between 20 and 35 °C. This is due to the acceleration in the rate of hydration at higher temperature.

The measured yield stress values for cement paste incorporating various dosages of a polycarboxylate-based high-range water reducing admixture (PC) at different testing temperatures are illustrated in Fig. 4.9(a). It is shown that yield stress decreased with the increase of the PC dosage, and increased significantly with temperature increase. Moreover, when testing temperature exceeded 35 °C, the rate of increase in yield stress

became much steeper. For example, at a dosage of 0.3%, the difference in yield stress values between 35 and 45 °C was about triple the corresponding value between 20 and 35 °C. At a high PC dosage of 1.2%, yield stress at various testing temperatures approached a zero value, indicating that very little energy is needed to transfer cement paste from its elastic state to a viscous state.

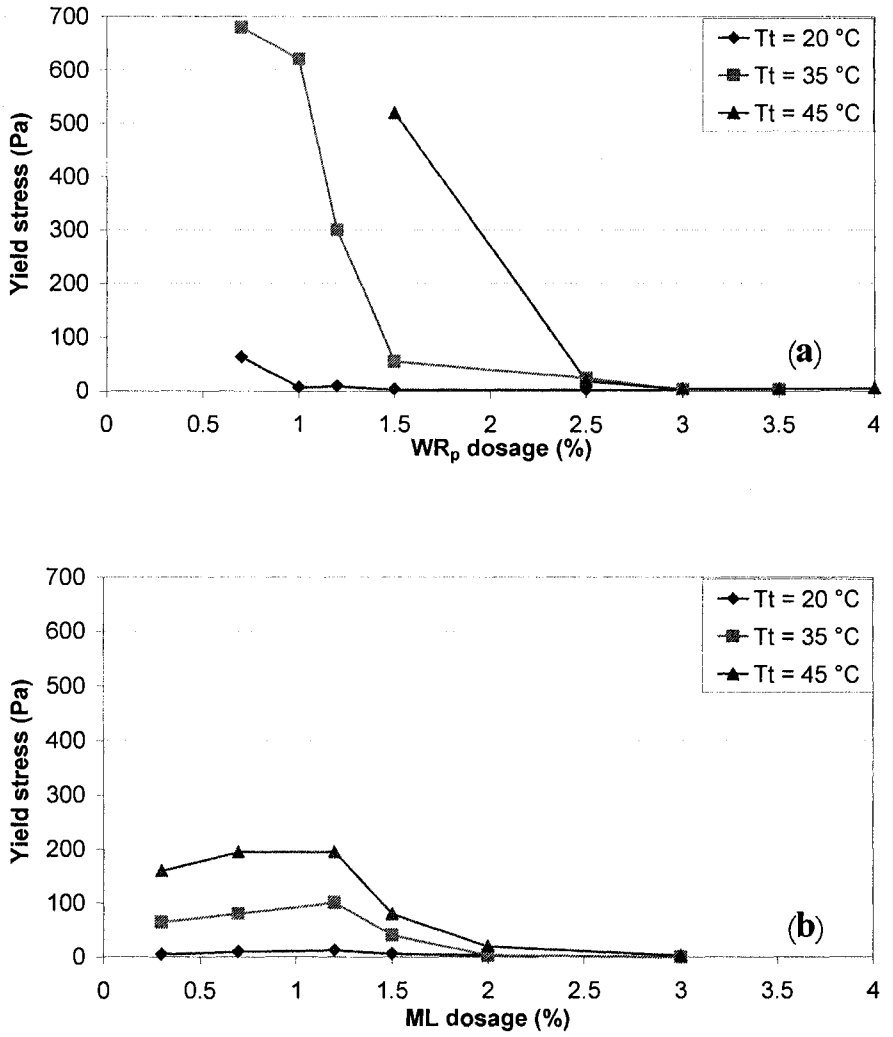

Figure 4.8-Yield stress of cement pastes at various testing temperatures and different dosages of admixtures, (a) WRp and (b) ML (w/c = 0.35, admixture dosage is in % of cement mass).

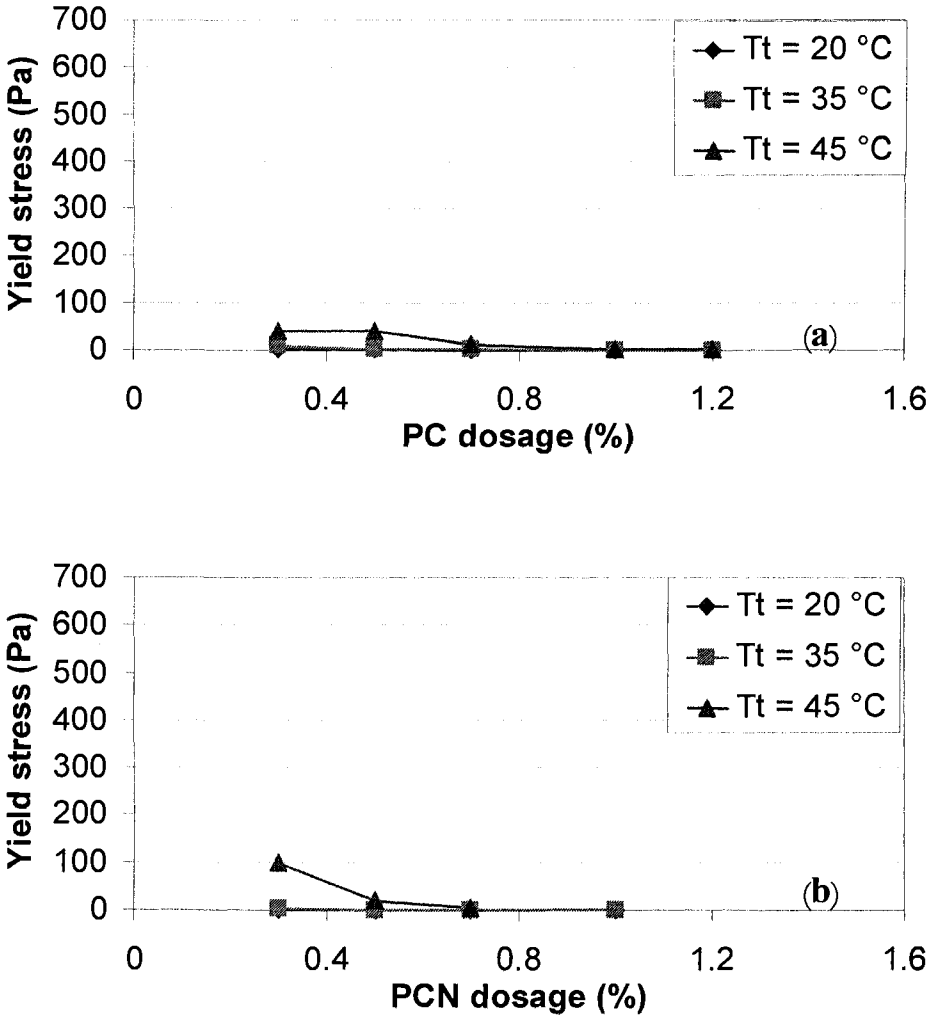

Figure 4.9-Yield stress of cement pastes at various testing temperatures and different dosages of admixtures, (a) PC and (b) PCN (w/c = 0.35, admixture dosage is in % of cement mass).

The dispersing behaviour of PCN is captured in Fig. 4.9(b). The yield stress steeply dropped with dosage increase at all testing temperatures investigated. At a low dosage (0.3%), the yield stress value at 45 °C was much higher than that at 20 °C and 35 °C. At a dosage of 0.7%, the yield stress values at all testing temperatures were comparable. The depicted saturation dosages were 0.5% and 0.7% at 35 °C and 45 °C, respectively. No saturation dosage was depicted at 20 °C and yield stress values were relatively low.

4.5.5 Comparison of admixtures

The oscillatory rheological testing of cement paste is an effective technique that allows comparing the effects of different chemical admixtures. It allows the designer of concrete mixtures in hot weather selecting the adequate admixture and dosage for a specific application. Therefore, a research program on the rheology of fresh concrete at different temperatures was conducted later considering the results of this investigation (Al-Martini and Nehdi 2008). For this purpose, shear modulus and yield stress values for cement pastes incorporating the investigated admixtures were plotted in Figs. 4.10 and 4.11, respectively.

Figure 4.10 (a, b, and c) shows shear modulus measurements for cement pastes incorporating various dosage of the WRp, ML, PC, and PCN admixtures at testing temperatures of 20, 35 and 45 °C. Results for the control mixture, i.e. cement pastes at w/c = 0.35 with no admixture, are also shown in these figures as solid horizontal lines. It can be observed that each admixture had a different effect on the rheology of cement paste at various temperatures. This is attributed to the mechanism by which each admixture influences the rheological properties of cement paste.

In general, the shear modulus decreased with the increase of admixtures dosage and threshold values were observed. Cement pastes with WRp had shear modulus values higher than that of the control mixture for corresponding testing temperatures at dosages below 2.5%, 1.2%, and 2% for testing temperatures of 20, 35 and 45 °C, respectively. This indicates that below these dosages, WRp has increased the rigidity of cement paste. The shear modulus decreased steeply with the increase of WRp dosages beyond such a threshold value at high testing temperature (35 °C and 45 °C), but could not decrease well

below that of the control mixture. Some studies have suggested that the mechanism by which a water reducing and retarding admixture operates could be adsorption (Ramachandran *et al.* 1997; Meyer and Perenchio 1979; Ravina and Soroka 1994), where a water reducing and retarding admixture particles are adsorbed on the surface of unhydrated cement grains forming a barrier preventing water from reacting with cement grains, consequently delaying the hydration process.

For ML, the shear modulus values for most dosages and at all temperatures were less than that of the control mixture (Fig. 4.10). However, at low dosages ML did not improve the viscoelastic properties of cement pastes since their rigidity increased. Beyond a dosage of 1.0%, ML became effective and the shear modulus started to decrease until it reached values well below that of the control mixture at all temperatures. Ramachandran *et al.* (1997) have observed a similar behaviour for ML. They documented that at dosages less than 2.0%, ML accelerated the hydration of C_3A and C_3S. They further argued that when the dosage exceeded 2%, ML retarded the hydration of C_3A and C_3S.

Due to the effective dispersing mechanism of polycarboxylate, cement pastes made with the PC and PCN had lower shear modulus values than that of the control mixture for all admixture dosages. Such admixtures consist of complex polymer carboxylate ether flexible molecules which wrap around cement particles and keep them separated. This deflocculates cement grains and frees the entrapped water to fluidize the cement paste (Ramachandran *et al.* 1997). These admixtures tended to decrease the shear modulus well below that of the control mixture even at relatively low dosages (0.3% - 1.2%). However, it

can be observed that PCN had a slightly better dispersing quality than that of PC due to its longer chain.

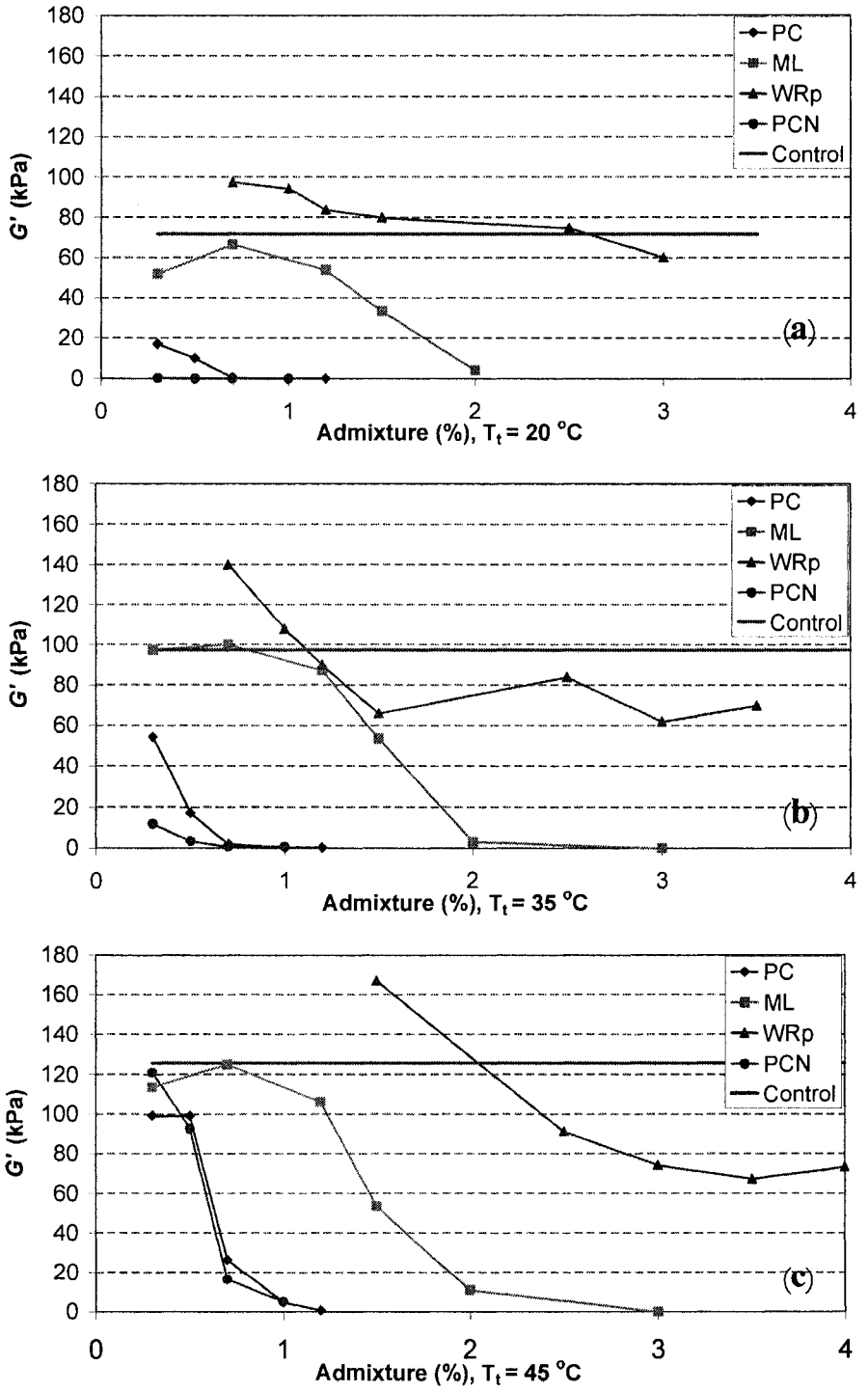

Figure 4.10-Shear modulus of cement pastes incorporating different admixtures at various testing temperatures, (a) $T_t = 20$ °C, (b) $T_t = 35$ °C, and (c) $T_t = 45$ °C (w/c = 0.35, admixture dosage is in % of cement mass).

Figures 4.11(a, b, and c) show the yield stress values versus the dosage of different admixtures at three testing temperatures (20, 35, and 45 °C) along with that of the control mixture. The cement paste with WRp admixtures did not yield below a dosage of 1.5% at 45 °C. Therefore, no yield stress value for this WRp dosages at this temperature was illustrated in the figure. This indicates the occurrence of gellation, which can be identified by high shear modulus and high yield stress values (Chen *et al.* 2006). The yield stress became lower than that of the control mixture only beyond threshold dosages of 1.5%, 2.5% and 2.5% at 20 °C, 35 °C, and 45 °C, respectively. The yield stress behaviour for ML, PC, and PCN was generally similar to that of the shear modulus as discussed above.

Table 4.3 presents the dosages recommended by manufacturers of the admixtures studied and the effective dosages identified in this study for each admixture and temperature investigated. In the light of the results presented, it can be observed that such recommended dosages are below those that seemed effective at high temperature, except for the PC which had a reasonable recommended dosage range (Table 4.3).

Table 4.3-Recommended admixture dosages by manufacturers and effective dosages found in this study at different testing temperatures

Admixture	Recommended dosage by manufacturer percent of cement mass (%)	Effective dosage percent of cement mass (%)		
		T = 20 °C	T = 35 °C	T = 45 °C
WRp	0.26 ± 0.065	1	1.5	2.5
ML	0.6 - 1.5	1.5	2	2
PC	0.2 - 1	0.5	0.7	1
PCN	0.13 - 0.39	0.3	0.7	0.7

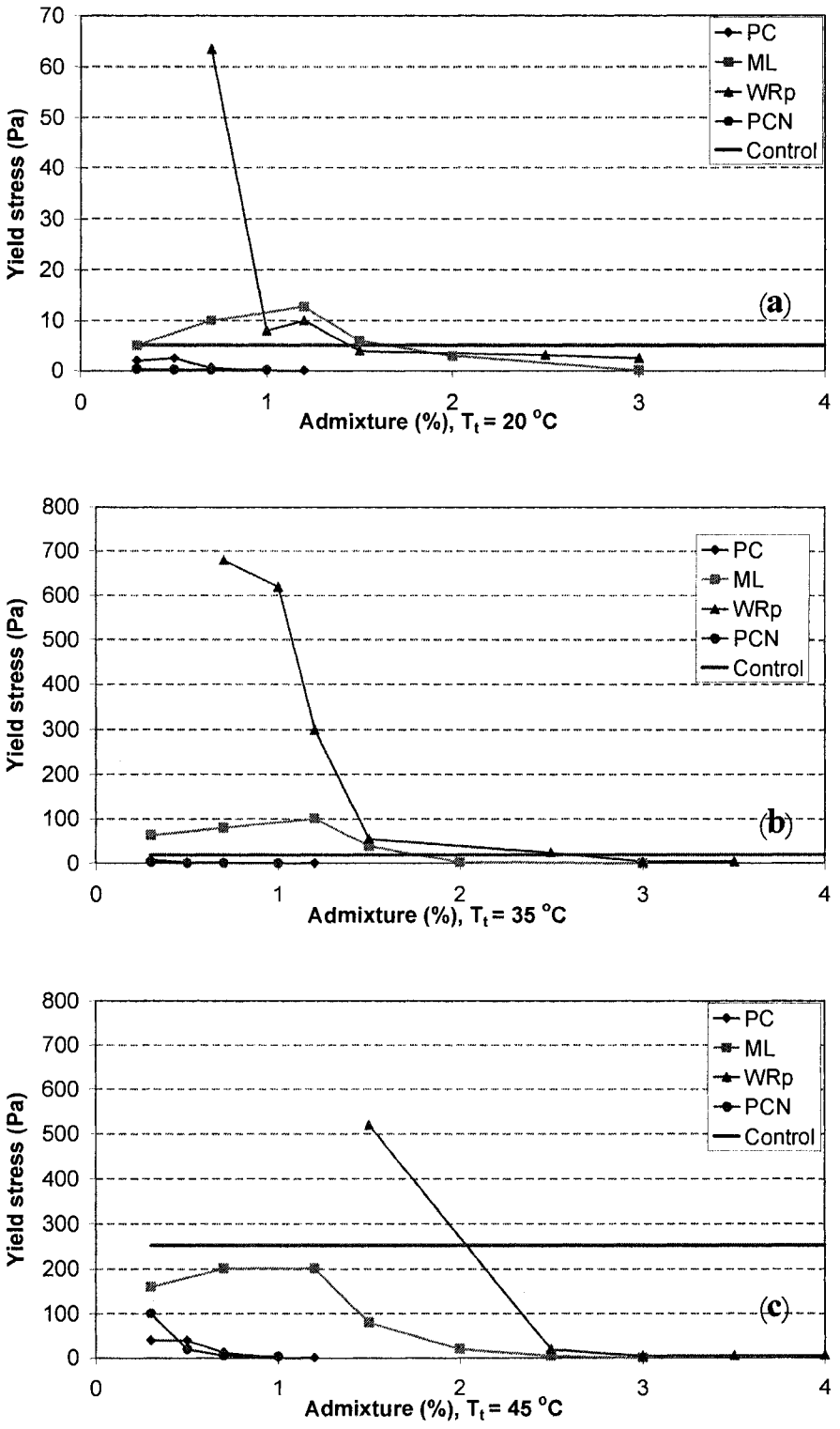

Figure 4.11-Yield stress of cement pastes incorporating different admixtures at various testing temperatures, (a) T_t = 20 °C, (b) T_t = 35 °C, and (c) T_t = 45 °C (w/c = 0.35, admixture dosage is in % of cement mass).

4.6 Conclusions

The effects of various chemical admixtures on the viscoelastic properties of cement paste at high testing temperature were investigated in this chapter. Four admixtures were used including a water reducing and retarding admixture (WRp), a melamine sulfonate-based high-range water reducing admixture (ML), a polycarboxylate-based high-range water reducing admixture (PC), and a new generation of polycarboxylate-based high-range water reducing admixture (PCN). Various cement pastes were made incorporating different dosages of the admixtures. Their viscoelastic properties were investigated at 20, 35, and 45 ^{o}C using oscillatory shear tests. This work is a step towards formulating standards and specifications for using admixtures in hot weather concreting. The following conclusions can be drawn:

- The yield stress and shear modulus values for the various cement pastes increased nonlinearly with the increase of temperature.
- WRp was effective only beyond a certain threshold dosage at each temperature. Below such threshold value, it acted as an accelerator of cement hydration.
- ML behaved as an accelerator at low dosages (below 2%), but improved the viscoelastic properties of cement paste at higher dosages.
- PC effectively improved the viscoelastic properties of cement pastes at high temperature. Both yield stress and shear modulus values decreased significantly with the increase of PC dosage.
- PCN achieved a slightly better dispersing behaviour than that of PC.
- The results indicate that technical data for chemical admixtures usually developed in areas with mild climate need to be validated for hot-weather

conditions. Admixtures proven effective in mild weather may become ineffective at high temperature.

- The results reported herein are valid for the particular admixtures and cement used. Other admixtures even from the same category may behave differently, and thus need separate investigation.

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Chapter 5

COUPLED EFFECTS OF TIME AND HIGH TEMPERATURE ON RHEOLOGICAL PROPERTIES OF CEMENT PASTES INCORPORATING VARIOUS SUPERPLASTICIZERS*

5.1 Introduction

Fresh concrete mixtures typically experience continuous stiffening and slump loss with time. At moderate temperatures, this stiffening and associated slump loss do not create real difficulties and concrete remains workable long enough for its handling and placement. However, hot weather environments cause serious problems in the placement of fresh concrete due to the acceleration of cement hydration and faster water evaporation. Thus, significant slump loss is usually experienced under high temperature (Soroka and Ravina 1998). The reactivity of cement constituents such as C_3A, C_4AF, and SO_3 is the main factor in concrete slump loss (Bornen and Sakar 1995) and is believed to be more rapid at high temperatures (Hewlett 1998). This constitutes a real challenge in hot weather concreting since concrete does not remain workable for the period of time required for its transporting, placement, compaction and finishing (Berge 1976).

Several researchers have investigated the fluidity of cement paste incorporating various chemical admixtures as a function of time. For instance, Bornen and Sakar 1995

* A version of this chapter is in the process of publication in the Journal of Materials in Civil Engineering ASCE. Parts of this chapter have also been published in the proceeding of the International Conference on Concrete under Severe Conditions: Environment and Loading CONSEX, 07, 2007.

evaluated the effect of the adsorption of a naphthalene sulfonate superplasticizer (NS) onto cement grains on the flow loss of cement pastes with w/c = 0.35 as a function of time. The adsorption of NS versus time was determined by measuring the change of sulfate ions concentration in the pore solution using inductively coupled plasma (ICP). Measurements of fluidity were conducted using a mini-slump test at 10, 30, 60, 90, and 120 minutes. It was observed that the addition of the superplasticizer improved the initial slump, and that the slump loss was strongly dependent on the admixture adsorption, which in turn, was related to the NS dosage and mixing time. For instance, little effect the admixture dosage on adsorption was found when the NS dosage increased from 0.5 to 1%, while significant adsorption was observed with an increased dosage from 1 to 2%. It was also reported that at a dosage of 2%, about 92% of NS was adsorbed within the first 10 minutes and marginal adsorption was observed from 10 to 120 minutes. Therefore, fluidity of cement pastes decreased sharply after 10 minutes of mixing.

The coupled effects of time and temperature on the variation of the rheological properties of highly flowable mortars with water-to-binder ratios of 0.42 and 0.53 were investigated by Petit *et al.* (2006). Polycarboxylate and polynaphthalene sulfonate high-range water-reducing admixtures were used in their investigation. The temperature varied from 10 to 30 °C. The mortars were mixed in a high shear mixer for 3 minutes, and then kept in the mixing bowl covered with a plastic sheet at isothermal conditions of the targeted test temperatures until the rheological test. The yield stress was found to increase in a linear fashion with time up to the end of the dormant period for the investigated admixtures and temperatures, except for the polycarboxylate admixture at 10 °C, which exhibited a sharp

reduction in yield value over 30% of the dormant period, and then the yield value increased linearly.

Yamada *et al.* (1998) investigated the effects of naphthalene sulfonate-based and polycarboxylate-based superplasticizers on the fluidity of portland cement paste. Fluidity was evaluated using a pipe with an inner diameter of 50 mm and a height of 51 mm by measuring the spread width of the paste on a plastic plate. The measurements were taken after 5 and 30 minutes from the start of mixing. The temperature at which tests were conducted in this study was not specified. The portland cement paste mixed with the polycarboxylate superplasticizer displayed no changes in fluidity with time. In the case of portland cement paste mixed with naphthalene sulfonate, fluidity decreased with time.

More recently, Li *et al.* (2004-a) developed numerical models in an attempt to quantitatively predict the workability of high-fluidity concrete for any time period and under any stress state. The influence of the admixture dosage, elapsed time, and temperature on the mean potential energy of cement particles was included in the model. The time dependence of the Bingham constants (yield stress and plastic viscosity) was investigated when concrete was standstill or under continuous agitation (mixing). Due to the lack of an appropriate test apparatus, it was not possible to conduct an experimental investigation to measure the rheological behaviour of fresh concrete and its variation with time. Thus, only numerical calculations were carried out using concrete mixture proportions obtained from other research work in the literature. As expected, both yield stress and apparent viscosity increased with the elapsed time and at higher temperature. However, the increase was more remarkable when the concrete mixture was under the

standstill condition than when it was under continuous agitation. When concrete is agitated, flocculated cement particles are dispersed and as a result, fluidity is improved, which explains the above behaviour.

The effect of superplasticizers on rheology of cement paste, particularly at high temperature, is still largely unexplored. Thus, there is a real need to investigate the effect of these admixtures on fresh cement paste subjected to prolonged mixing at high temperature. The objective of the present chapter was to evaluate the rheological parameters of cement pastes incorporating various superplasticizers at different mixing times and ambient temperatures. Hence, the rheological properties of cement pastes at a w/c = 0.38 and incorporating three different superplasticizers, namely, a new generation of polycarboxylate-based (PCN), melamine sulfonate-based (ML), and naphthalene sulfonate-based (NS) superplasticizers were studied at three different ambient temperatures: 22, 35 and 45 °C. The temperature of 22 °C represents concrete placed at moderate temperature conditions, while 35 and 45 °C are represent concrete placed at high and extreme temperature conditions, respectively. To study the effect of time, the cement paste mixtures were subjected to prolonged mixing for up to 110 minutes and rheological measurements were taken at 20 min and then at each half hour interval. The results allowed gaining a better understanding of the function of these admixtures at high temperature, which should lead to their effective use in the design of concrete mixtures under hot weather conditions.

5.2 Rheological Parameters

Generally, cement paste is believed to behave as a Bingham fluid (Tattersall and Banfill 1983). The yield stress τ_o described in equation (5.1) represents the stress required

for cement paste to start flowing. It is the intercept of the flow curve (shear rate vs. shear stress) with the shear stress axis. In order for cement paste to flow, the yield stress must be overcome. The viscosity μ indicates how fast the material can flow. Plastic viscosity μ_p is defined by the slope of the fitted straight line of the flow curve to the Bingham model shown in equation (5.1):

$$\tau = \tau_0 + \mu_p \dot{\gamma} \tag{5.1}$$

The shear rate-shear stress down curve was considered when calculating the yield stress and plastic viscosity using the Bingham model. It was argued (Ferguson and Kemblowski 1991) that the down curve was a better fit to the Bingham equation than the up curve. Because cement paste is sheared from zero to 50 s^{-1}, breakdown in its structure occurs. Therefore, the down-curve (unloading) will not follow the same path as the up-curve (loading).

5.3 Experimental Procedure

5.3.1 Materials

CSA Type 10 (similar to ASTM Type I) ordinary portland cement was used in all cement pastes investigated. Deionized distilled water was used for the mixing, and its temperature was maintained at 22 ± 0.5°C. The superplasticizers used in this chapter included: 1- a new generation of polycarboxylate-based superplasticizer (PCN) with dosages ranging from 0.1% to 1.3% by mass of cement; 2- melamine sulfonate-based superplasticizer (ML) with dosages ranging from 1.4% to 3% by mass of cement; and 3- naphthalene sulfonate-based superplasticizer (NS) with dosages ranging from 1.2% to 2.4% by mass of cement.

5.3.2 Apparatus

The mixer used in this study is a paddle mixer (Fig. 5.1(a)) with variable speed; the lowest speed (45 rpm) was used thoughout this study. The mixer consists of a bowl and a vertical shaft, which has the capability of mixing the cement paste evenly and uniformly. The mixer was placed in a temperature controlled chamber.

An advanced rheometer (TA-Instruments AR-2000) was used to measure the shear stress-strain rate data, and consequently the rheological properties of the cement pastes (Fig. 5.1(b)). The coaxial concentric cylinder geometry was considered suitable for this study and was thus used. The computer controlled rheometer used is equipped with a rheological data analysis software, which can fit the shear stress-strain rate data to several rheological models (e.g. Newtonian, Bingham, Herchel-Bulkley, Casson, Modified Bingham, Sisko, and Williamson). The Bingham model was selected to calculate cement paste rheological properties, i.e. yield stress and plastic viscosity. It is understood, however, that rheological data calculated can vary depending on the rheological model used (Nehdi and Rahman 2004).

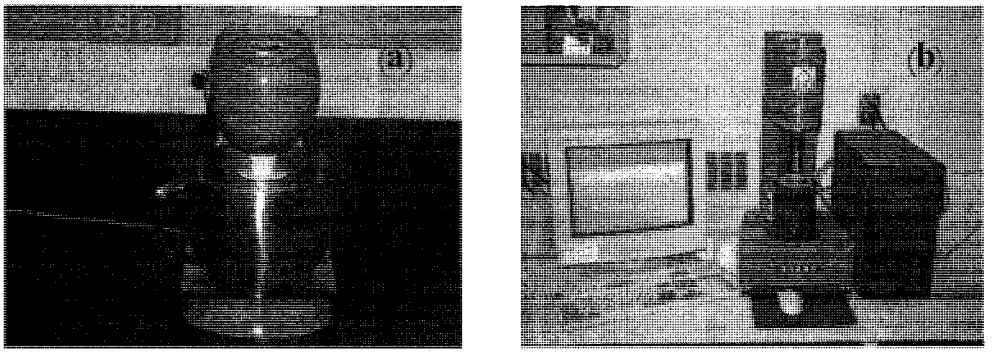

Figure 5.1-Illustration of (a) cement paste mixer, and (b) rheometer with coaxial cylinder geometry.

5.3.3 Procedure

For high temperature, the temperature controlled chamber was set to the required temperature (35 or 45 °C) 24 hours before the experiment; whereas, for the moderate temperature, the mixing was conducted under laboratory conditions at 22 °C. The weighed cement powder was placed inside the temperature controlled chamber to reach the desired ambient temperature at least 12 hours before the experiment.

The weighed cement powder was placed in the mixer bowl. Using a graduated needle, the specified quantity of liquid admixture was injected into the mixing water. The mixing water was then poured in the cement powder and manually stirred for one minute. The cement paste was subsequently mixed for 3 minutes. The mixer was stopped for 1 minute, during which the bowl was scraped with a rubber paddle to ensure homogeneity. Mixing resumed for another 16 minutes at a speed of 45 rpm. Then, the first cement paste sample was taken from the cement paste batch and placed into the gap of the coaxial cylinders for the first rheological test. The total time between the start of mixing and taking the first sample was 20 minutes. The cement paste batch was mixed for an additional 90 minutes. A new cement paste sample was taken and tested every half hour. This procedure was strictly followed for all cement pastes to avoid the effect of exogenous variables on the results. The prolonged mixing was intended to give an indication on the rheological behaviour for instance during continuous mixing of concrete in a concrete truck mixer for its hauling to a construction site.

The cement paste sample was placed in the gap space of the coaxial cylinders and pre-sheared at 70 s^{-1} for two minutes in order to break down the structure of the cement

paste sample and create uniform conditions before testing (Saak *et al.* 2001). Subsequently, a continuous shear rate sweep was applied by increasing the shear rate from 0 to 50 s^{-1} to produce the up curve, and the cement paste was maintained for 15 seconds at this shear rate before being sheared from 50 s^{-1} to 0 s^{-1} to produce the down curve. This procedure allowed the production of a hysteresis loop, which is also used to characterize the thixotropy of cement paste (Saak 2000). A schematic representation of the testing sequence is illustrated in Fig. 5.2. The focus of this research was to trace changes in the cement paste structure related to combined effects of elapsed time and ambient temperature in the presence of various superplasticizers during continuous mixing.

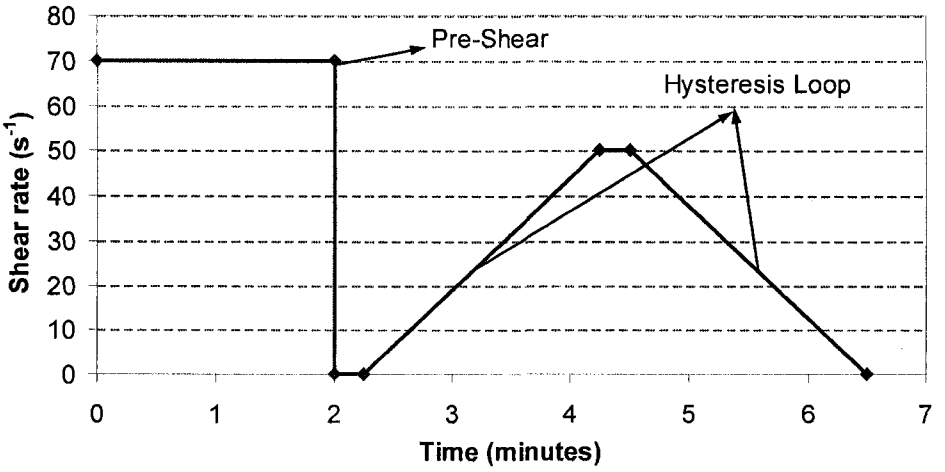

Figure 5.2-Shear rate history used in rheological tests.

5.4 Results and Discussion

5.4.1 Rheological properties at high temperature and prolonged mixing

Figure 5.3 shows the apparent viscosity versus shear rate flow curves obtained for cement pastes incorporating different dosages of PCN at 45 °C after 110 min of mixing. Shear thinning behaviour can be observed for the cement pastes prepared with PCN over

the full range of shear rate investigated and for all PCN dosages (Figs. 5.3(a)-5.3(b)). This is typical for agglomerated suspensions such as cement paste that exhibit a pseudoplastic behaviour (Eirich 1960), which has been attributed to the shear alignment of cement particles occurring with increasing shearing stress (Eirich 1960). Thus, at a low shear rate, attractive inter-particle forces are predominant over hydrodynamic forces exerted by the flow field and, therefore, the formation of flocs takes place. When the shear rate increases, the hydrodynamic forces become higher and overcome the attractive inter-particle forces leading to the break down of flocs into smaller particles. Consequently, the liquid entrapped within flocs is gradually released, thus decreasing viscosity (Barners *et al.* 1989; Ferguson and Kemblowski 1991).

Minimum apparent viscosity was reached and steric stabilization occurred when the saturation dosage (0.4%) of PCN was attained (Fig. 5.3(a)). However, higher PCN dosages beyond 0.4% (Fig. 5.3(b)) seemed to increase the apparent viscosity. The explanation of this phenomenon is linked to the primary mechanism, i.e. steric hindrance, by which PCN disperses cement particles. When the polycarboxylate polymer adsorbs on cement particles, repulsive interaction occurs due to elastic and mixing mechanisms. The elastic mechanism is a function of the polymer adsorption layer thickness, while the mixing mechanism depends on the density of the polymer adsorption layer (Yamada *et al.* 1998). 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. As such, the elastic component of the steric hindrance deploys repulsive forces when cement particles try to approach each other. On the other hand, the mixing term of the steric hindrance corresponds to the resistance occurring when two neighboring polymers approach each

other. Therefore, beyond the saturation dosage, this resistance will increase with the increase of the un-adsorbed PCN polymers, thus increasing viscosity (Yamada *et al.* 1998).

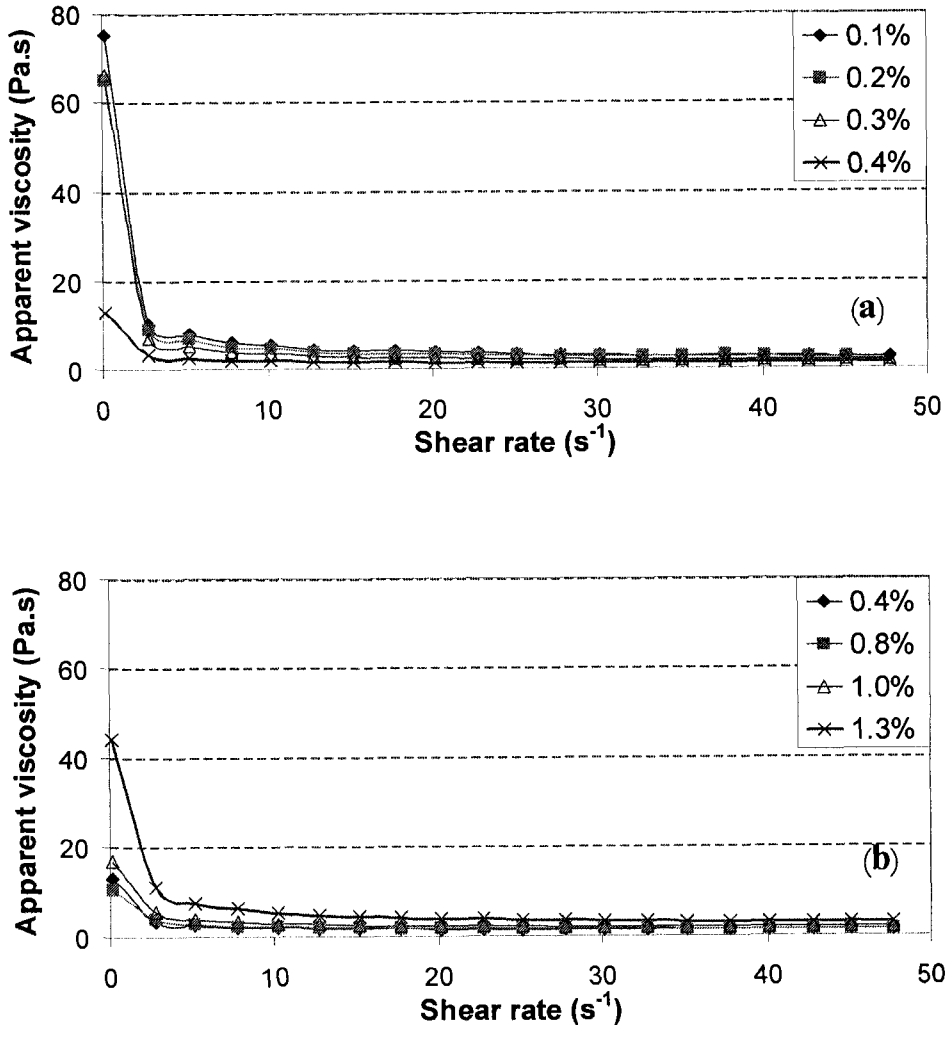

Figure 5.3-Apparent viscosity versus shear rate curves for cement pastes with different dosages of PCN mixed up to 110 minutes at a temperature of 45 °C [(a)- below the dispersant saturation dosage and (b)- above the dispersant saturation dosage].

Shear thinning behaviour was also observed for cement pastes mixed with ML. Minimum apparent viscosity was reached at a dosage of 2.8% (Fig. 5.4(a)). A change in the rheological behaviour from shear thinning to shear thickening of the cement paste was

observed at high dosage of NS (2.4%) (Fig. 5.4(b)). The apparent viscosity of the cement paste incorporating 2.4% of NS continuously increased with shear rate (Fig. 5.4(b)). A different scale was used in Fig. 5.4(b) to clearly visualize this behavior. Materials that exhibit such a behaviour are called dilatant (Hunter 2001). This phenomenon could be attributed to an increase of the liquid trapped in voids at higher shear rates. It is believed that particles can rub each other resulting in an increase in the resistance to flow while the shear rate increases (Hunter 2001). The dilatant behaviour of the cement paste mixed with 2.4% of NS could be explained by interactions between the molecules of the non adsorbed admixture in the water solution. A similar behaviour was observed by Papo *et al.* (2002) for cement pastes mixed with a polyphosphate admixture at 25 °C. This is also in agreement with findings of Cyr *et al.* (2000).

According to Hoffman (1998), shear thickening could be due to the disordered structure occurring at high concentration of suspensions. Due to this disordered structure, particles jam, causing more energy to dissipate. Therefore, hydrodynamic forces become higher than repulsive inter-particle forces and viscosity increases with higher shear rate. Another theory attributed this phenomenon to hydrodynamic clusters formed when shear forces become high enough to drive particles nearly into contact (Brady and Bossis 1985). This cluster jams the flow causing viscosity to increase when the shear rate increases.

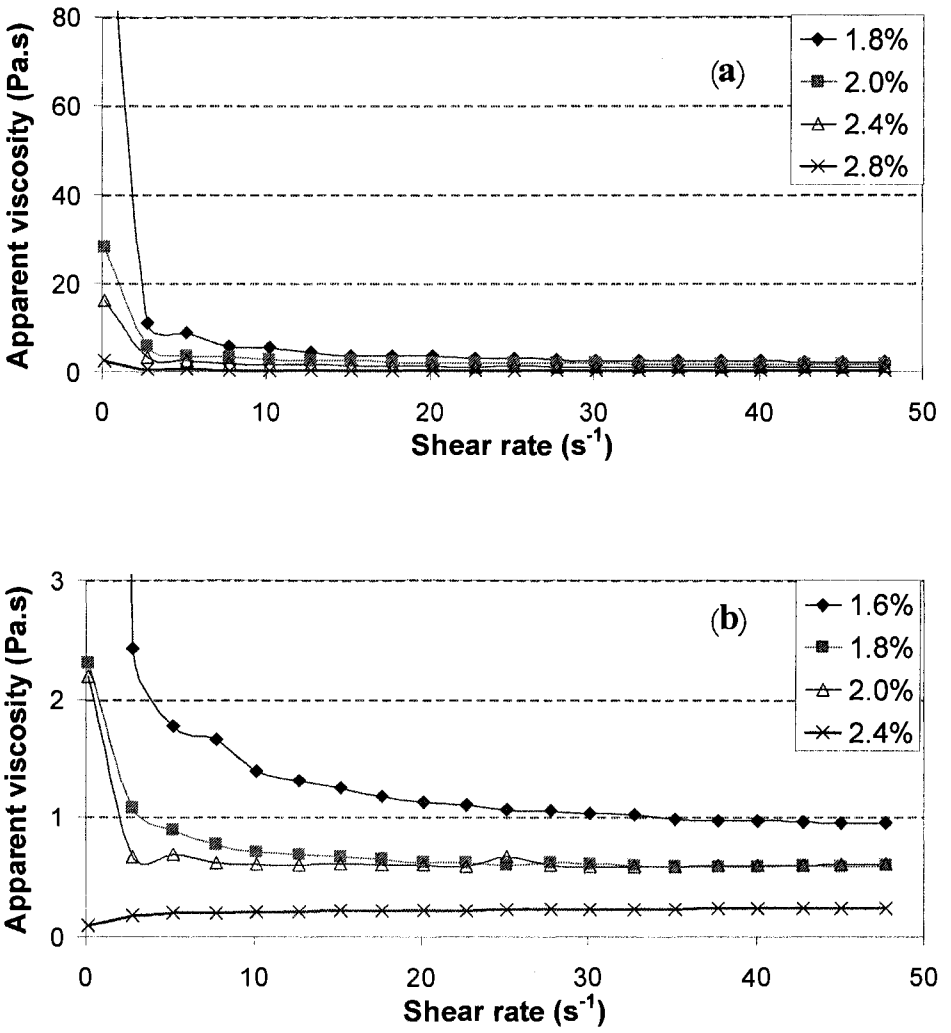

Figure 5.4-Apparent viscosity versus shear rate curves for cement pastes with different dosages of superplasticizers mixed up to 110 minutes at a temperature of 45 °C [(a)- ML and (b)- NS].

5.4.2 Coupled effects of admixture dosage, time, and temperature on yield value of cement pastes

The effect of the PCN dosage on the yield stress of cement pastes with variation in mixing time at different ambient temperatures is presented in Figs. 5.5(a)-5.5(c). the yield stress decreased with increasing PCN dosage up to a certain level, beyond which it started to increase. This critical dosage is commonly known as the saturation dosage. In practice, it is important to identify this dosage since an excess of admixture can cause bleeding, segregation and/or substantial retardation of the setting (Petit *et al.* 2005). The saturation dosage was depicted to be 0.4% at 22, 35, and 45 °C as evidenced in Figs. 5.5(a), 5.5(b), and 5.5(c), respectively.

It can be further observed that below the saturation dosage yield stress increased significantly as time elapsed. This increase was more significant at high temperatures (35 and 45 °C) than at a moderate temperature (22 °C). For example, at a PCN dosage of 0.1% and a temperature of 45 °C, the increase in yield stress between 50 min and 80 min was about 5 times the corresponding value between 20 min and 50 min, while that difference at the same dosage was minor at 22 °C. It can be concluded that at low dosage, the PCN could not offset the acceleration of hydration due to high temperature. However, an increased PCN dosage seemed to offset the acceleration of hydration due to high temperature, and even neutralized it at a dosage of 0.4% for all investigated temperatures.

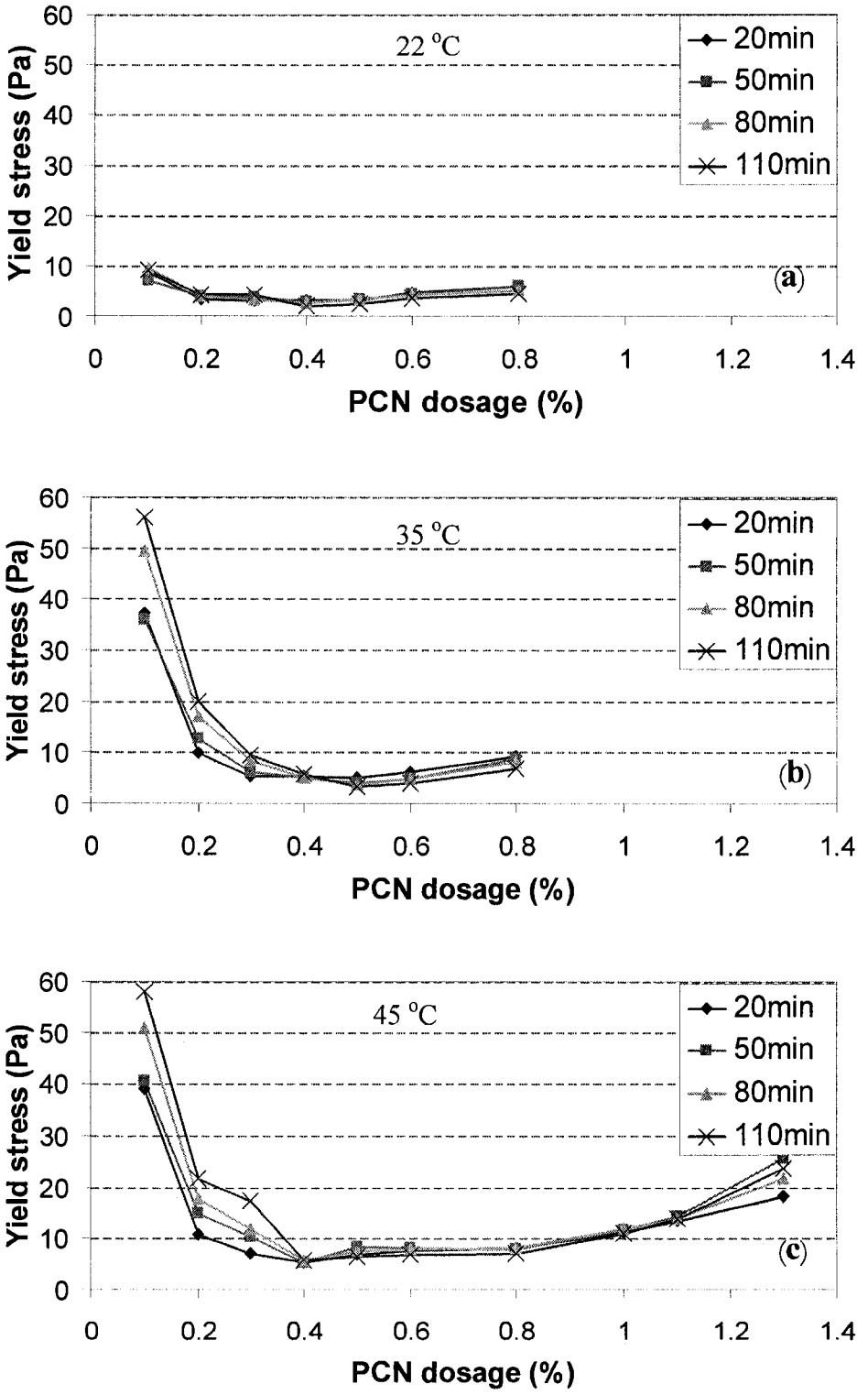

Figure 5.5-Variation in yield stress with time and superplasticizer dosage for cement pastes (w/c = 0.38) incorporating PCN [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

Figures 5.6(a, b, c) illustrate the effect on yield stress of the ML dosage and mixing time at three different ambient temperatures, namely 22, 35, and 45 °C. The yield stress decreased with increasing ML dosage at all temperatures. It can also be observed that yield stress increased with the increase of mixing time. Unlike for cement paste incorporating PCN, the increase in yield values with time occurred even at a moderate temperature (Fig. 5.6(a)). However, this increase in yield stress became gradually less significant with higher ML dosage until it reached negligible values for all investigated mixing times and ambient temperatures. Beyond the saturation dosage of 2.8%, no further decrease in yield stress was depicted.

Yield stress values of cement pastes incorporating different dosages of NS and mixed for 110 minutes at 22, 35, and 45 °C are presented in Figs. 5.7(a, b, c), respectively. Generally, NS behaved in a similar manner to that of ML (Figs. 5.6(a, b, c)). The observed NS saturation dosage was 1.8% at 22, 35, and 45 °C. Similar behaviour was reported by Petit *et al.* (2005) for high fluidity mortars incorporating NS and tested at different temperatures (12-30 °C).

It should be noted that at similar dosage, yield stress values for cement pastes made with NS were generally lower than that for cement pastes made with ML. This is likely attributed to the difference in adsorption mechanisms between ML and NS, despite the similarity in their dispersion mechanisms brought about by the negative charge build-up on cement grains (Hanehara and Yamada 1999). Indeed, NS has shown more adsorption than ML as documented elsewhere (Hanehara and Yamada 1999).

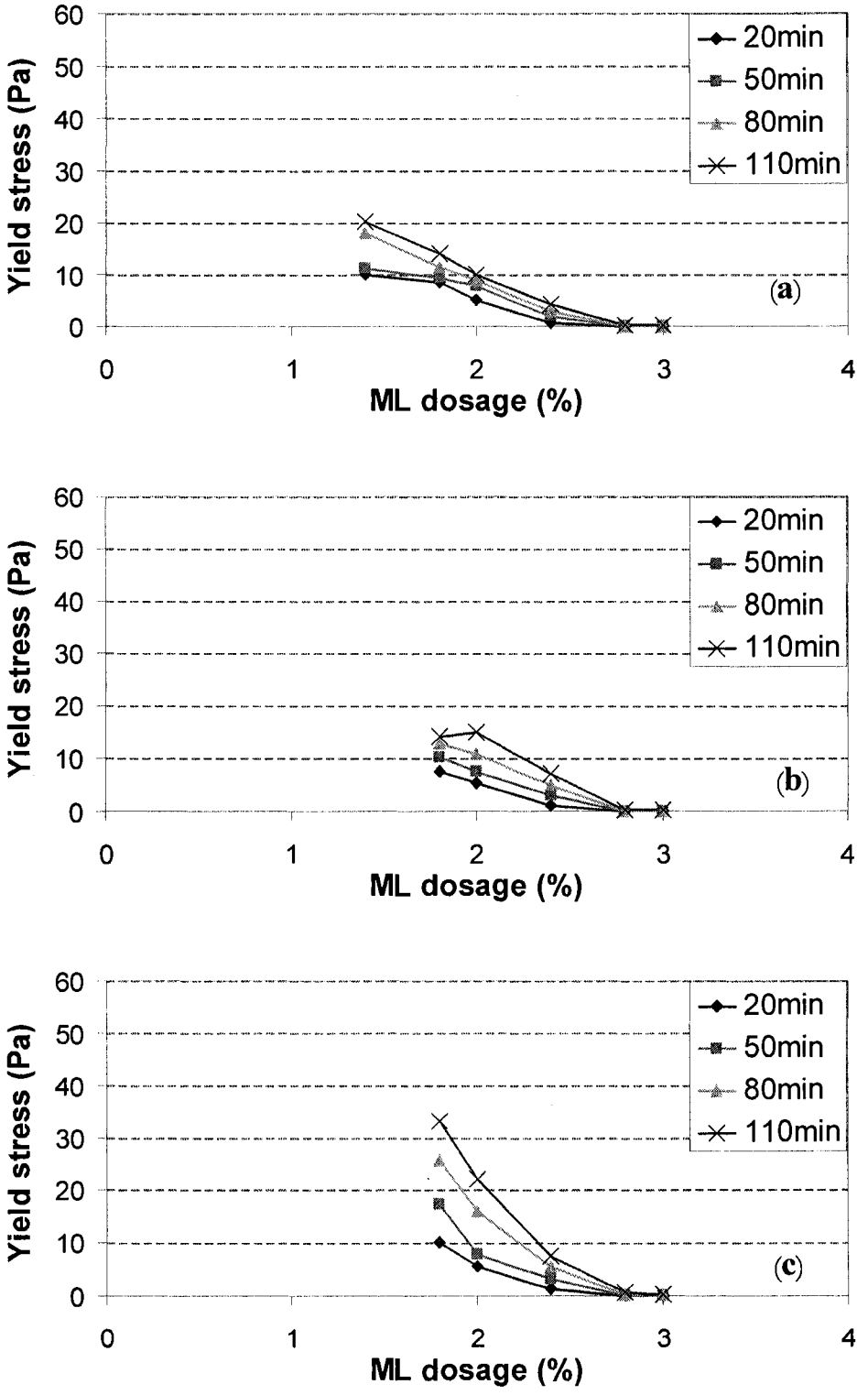

Figure 5.6-Variation in yield stress with time and superplasticizer dosage for cement pastes (w/c = 0.38) incorporating ML [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

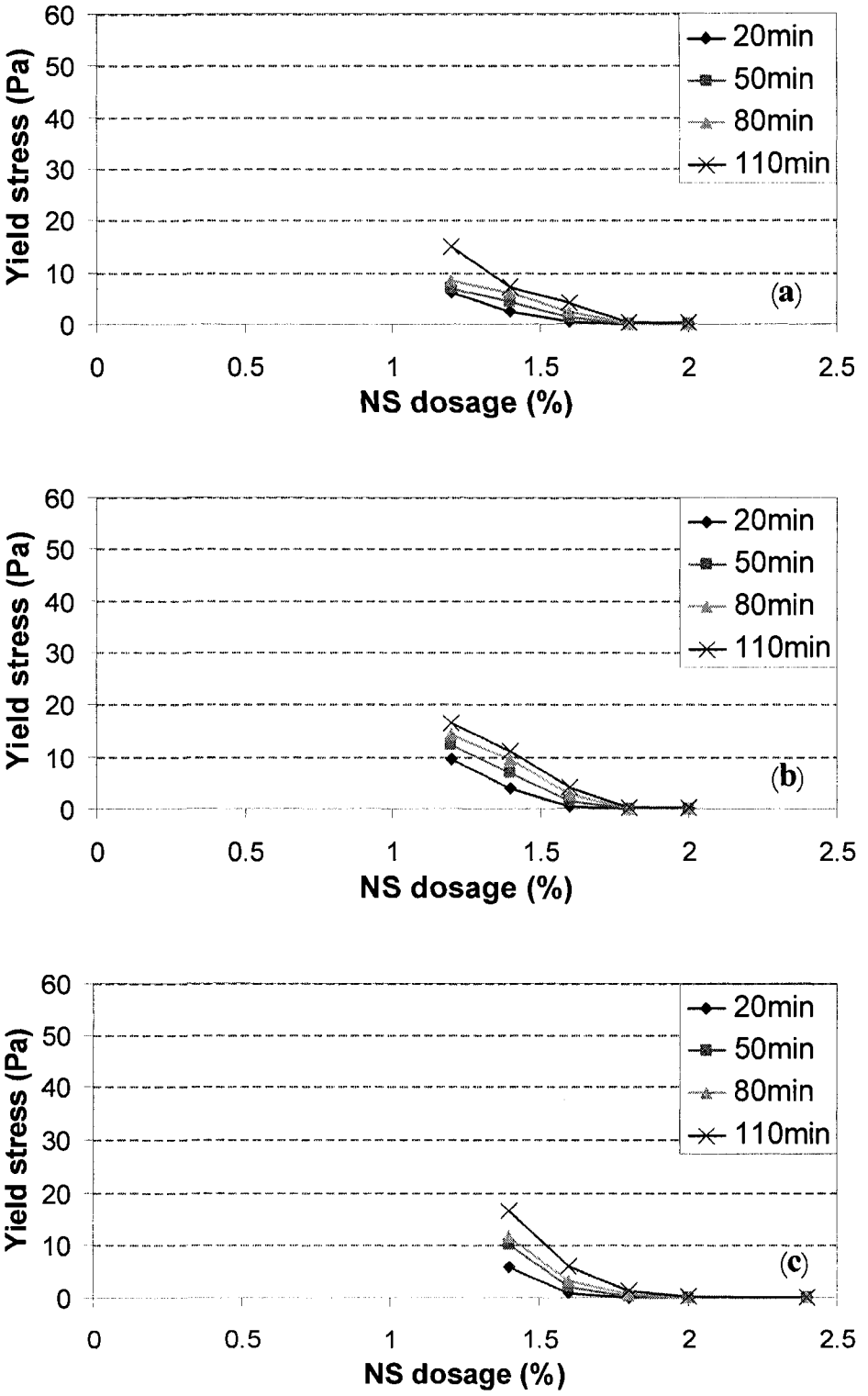

Figure 5.7-Variation in yield stress with time and superplasticizer dosage for cement pastes (w/c = 0.38) incorporating NS [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

As shown in Fig. 5.8, yield stress values for cement pastes incorporating different dosages of PCN (i.e. 0.3%, and the saturation dosage of 0.4%) at various ambient temperatures (22, 35, and 45 °C) increased linearly with time. The rate of increase in yield stress with time at high ambient temperatures (35 and 45 °C) and for dosages below the saturation dosage was much higher than that at moderate temperature (22 °C) (Figs. 5.8(a) and 5.8(b)). This indicates that concrete incorporating PCN placed at a moderate temperature will not likely encounter placement difficulties even if it is subjected to a relatively long distance of hauling. However, a significant increase in yield stress with time can be observed at high temperatures (35 and 45 °C). The hydration of cement is more rapid at higher temperature and the larger amount of hydration products raises the inter-frictional resistance of the cement paste particle assembly, which in turn increases yield stress (Li *et al.* 2004-b). Moreover, when cement hydrates, its surface energy increases and this lowers the dispersing effect of superplasticizers. Hydrated products generated around cement particles have high surface area, which further reduces the effectiveness of polymer adsorption (Yamada *et al.* 1998).

Conversely, at the saturation dosage, the evolution of yield stress with time at 45 °C was marginal (Fig. 5.8(b)). Cement hydration with an overdose of PCN is usually slow because some of the polymers are not adsorbed, which in turn keeps the density of the adsorbed layer constant for a certain time period (Li *et al.* 2004-b). This time depends on the ratio of the actual admixture dosage to the saturated adsorbed amount. Thus, the higher the PCN overdose, the longer the density of the adsorption layer remains constant.

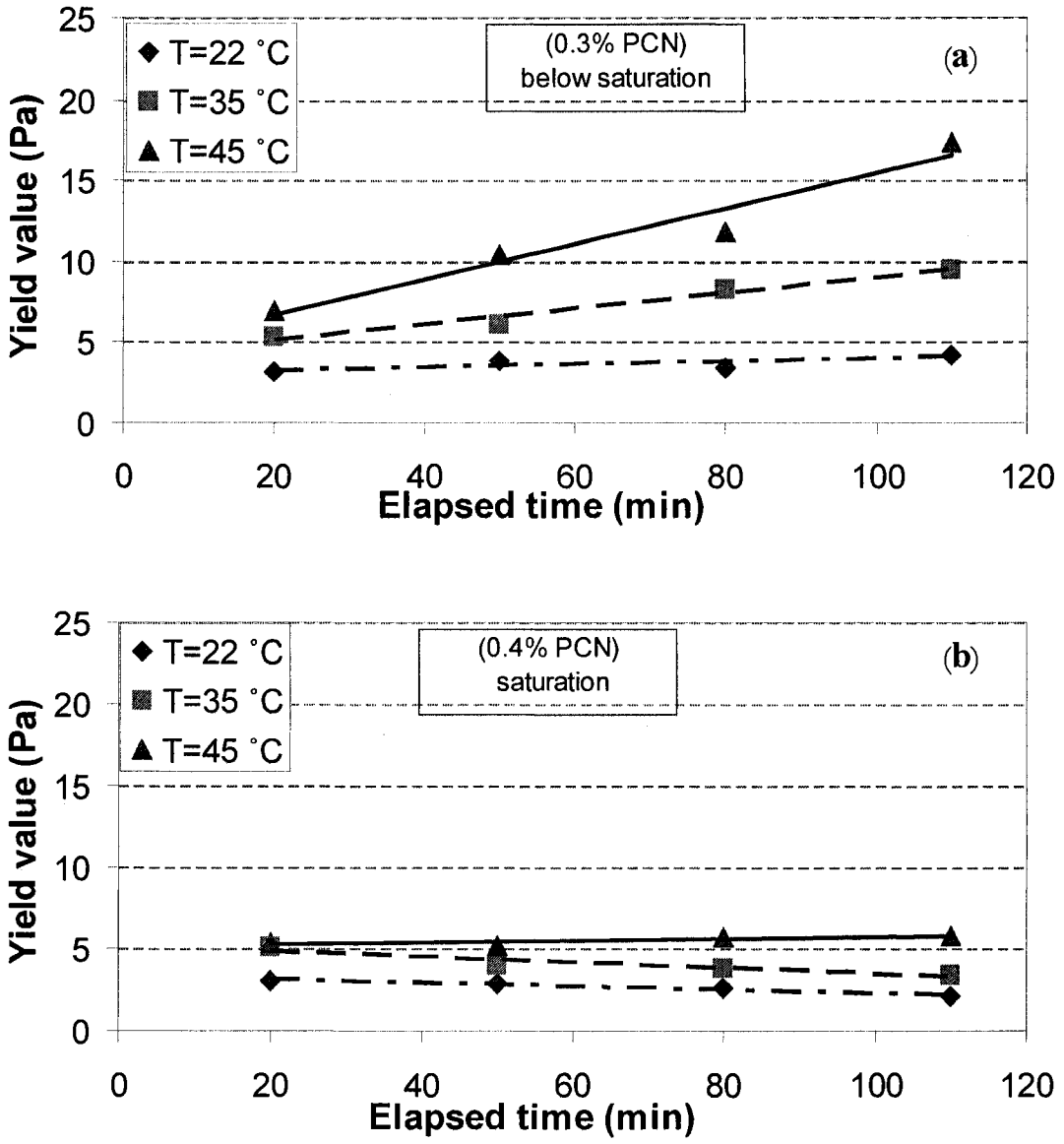

Figure 5.8-Variation in yield stress with time and temperature for cement pastes incorporating PCN [(a) at 0.3% and (b) at saturation dosage of 0.4%].

The evolution of yield stress values with time for cement pastes incorporating ML are illustrated in Figs. 5.9(a)-5.9(b). Below the saturation dosage, yield stress values increased linearly with time (Fig. 5.9(a)). As temperature increased, the rate of the increase in yield stress with time became more significant. Values of yield stress were comparable at 20 minutes for the three investigated temperatures, indicating that ML could initially

counteract the effects of high temperature in accelerating the hydration of cement. However, its effectiveness decreased with time at high temperatures. At the saturation dosage (2.8%), yield values dropped significantly and the increase in yield stress with time was marginal (Fig. 5.9(b)).

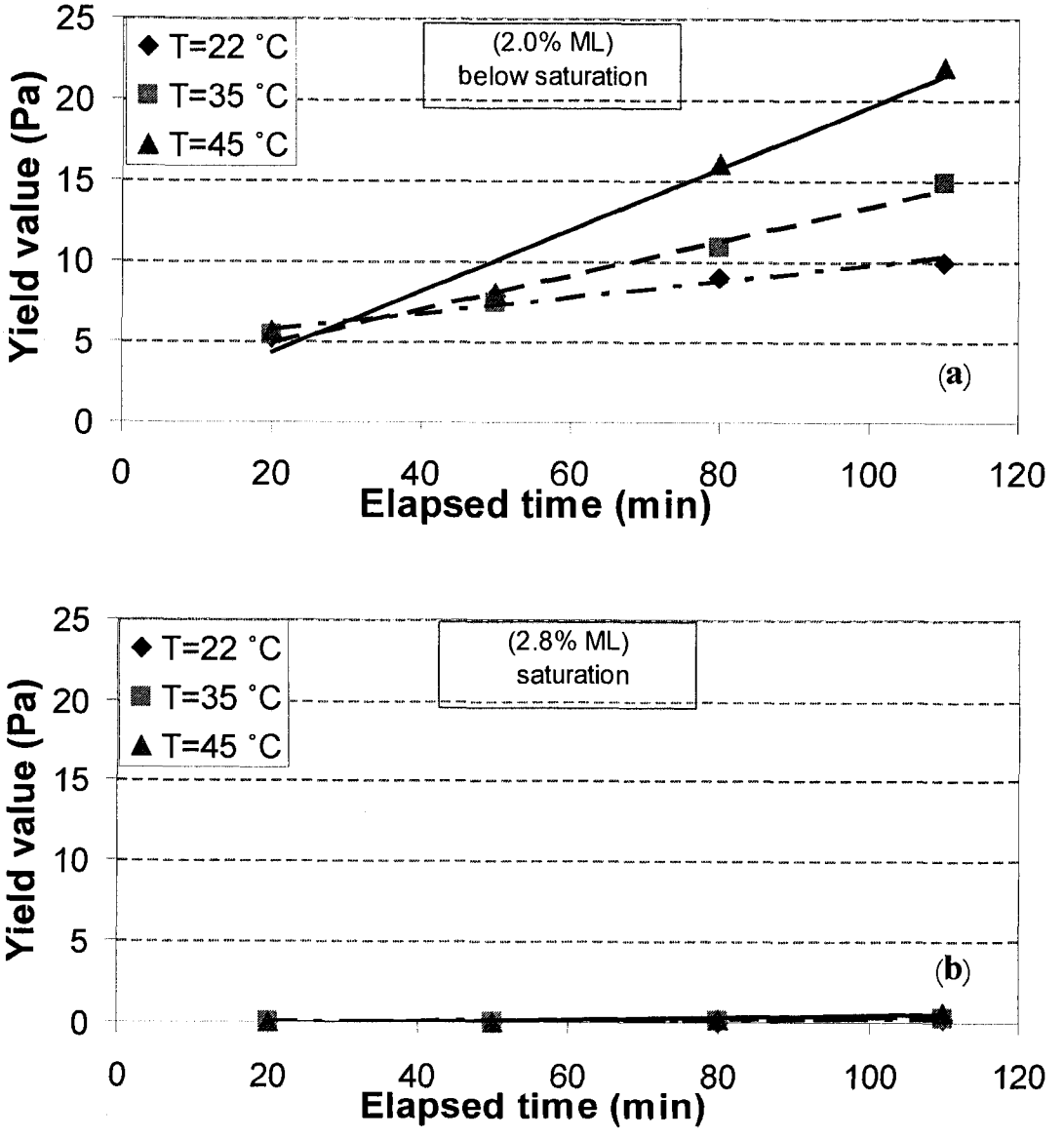

Figure 5.9-Variation in yield stress with time and temperature for cement pastes incorporating ML [(a) at 2.0%, and (b) at saturation dosage of 2.8%].

In Figs. 5.10(a)-5.10(b) the yield stress values versus time for cement pastes incorporating NS are presented. At a dosage of 1.4%, yield stress increased with time with a similar rate at different ambient temperatures. At the NS saturation dosage, cement pastes had small values of yield stress for all test temperatures up to 110 min of mixing.

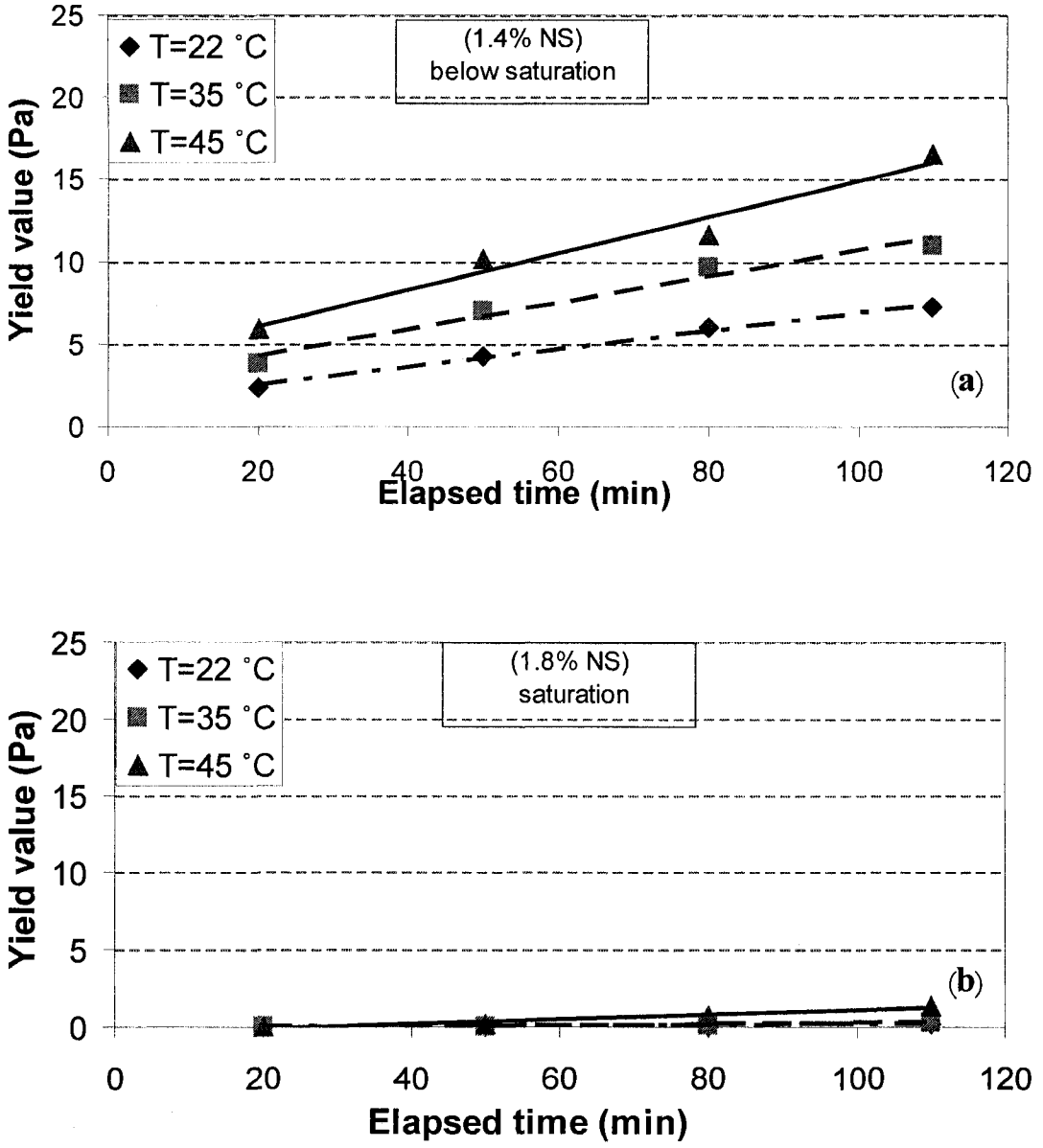

Figure 5.10-Variation in yield stress with time and temperature for cement pastes incorporating NS [(a) at 1.4%, and (b) at saturation dosage of 1.8%].

5.4.3 Coupled effects of admixture dosage, time and temperature on plastic viscosity of cement pastes

Plastic viscosity values for the various cement pastes were measured from the down flow curves and plotted in Figs. 5.11, 5.12, and 5.13. Figures 5.11(a)-5.11(c) show the effect of the PCN admixture dosage on plastic viscosity of cement pastes at various ambient temperatures and for different mixing times. As expected, viscosity became higher at higher temperature. It can be further observed that below the saturation dosage, plastic viscosity decreased with an increase of the PCN dosage and increased with an increase of the mixing time. The rate of viscosity increase with time was more pronounced when the PCN dosage was low and/or when the temperature was high, which is in agreement with yield stress results. Beyond the saturation dosage, plastic viscosity tended to increase with higher dosage and increased mixing times.

The plastic viscosity values for cement pastes incorporating ML at 22, 35 and 45 °C are illustrated in Figs. 5.12(a), 5.12(b) and 5.12(c), respectively. Plastic viscosity versus ML dosage, time, and temperature behaved in a similar manner to that of yield stress (Figs. 5.6(a)-5.6(c)).

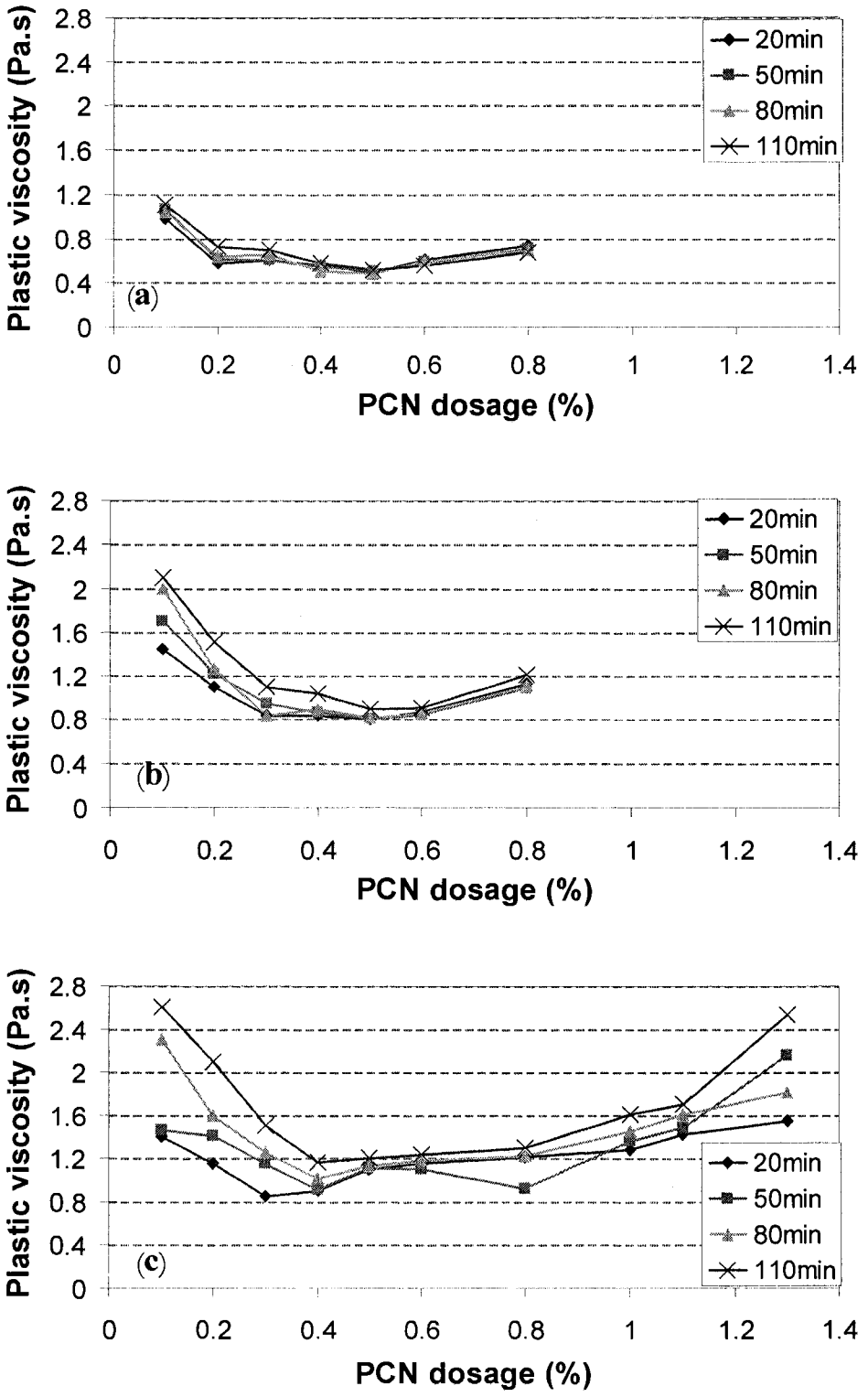

Figure 5.11-Variation in plastic viscosity with time and superplasticizer dosage for cement pastes (w/c = 0.38) incorporating PCN [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

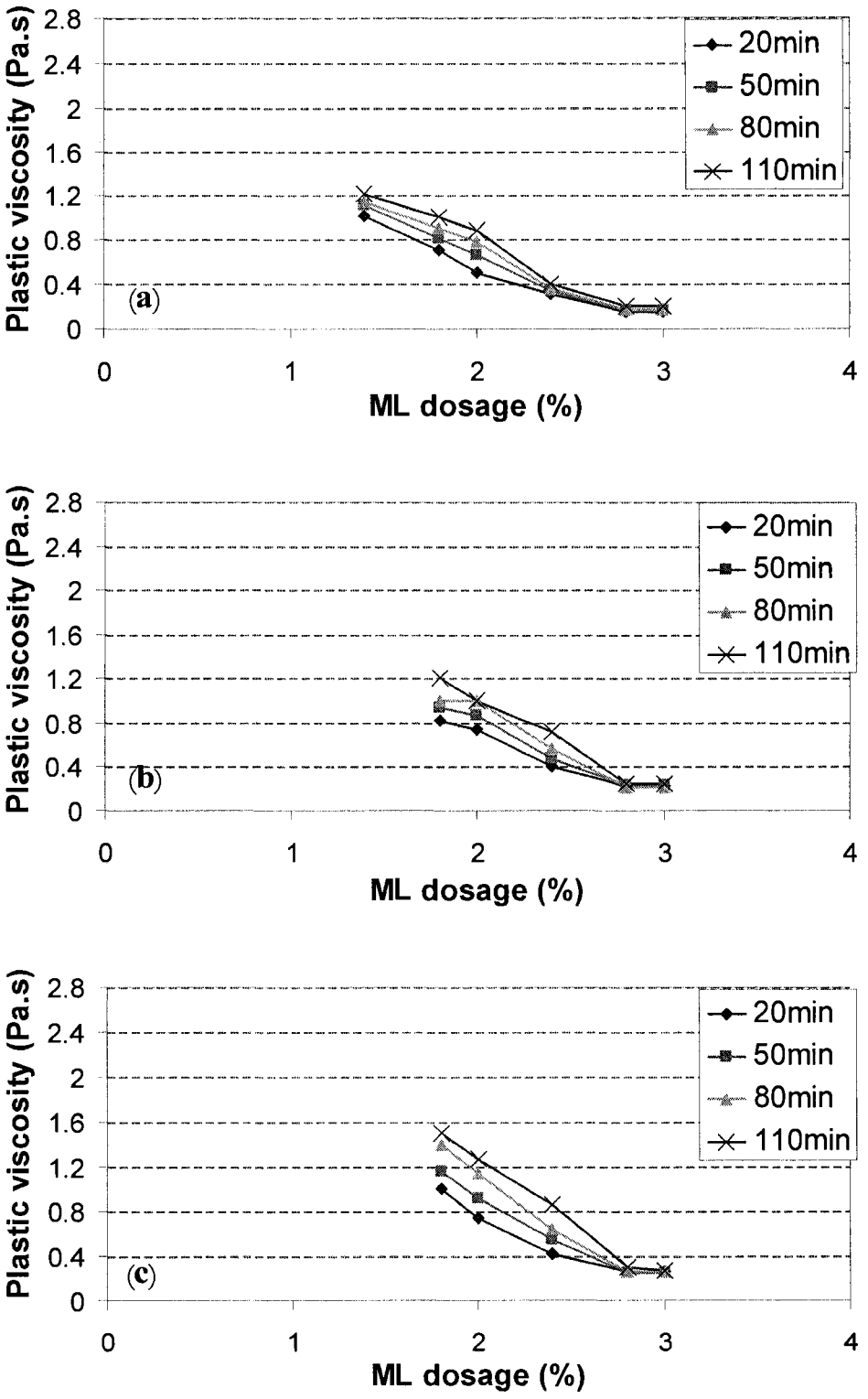

Figure 5.12-Variation in plastic viscosity with time and superplasticizer dosage for cement pastes (w/c = 0.38) incorporating ML [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

As shown in the figure, plastic viscosity decreased with the increase of the ML dosage and increased with temperature and time for a fixed ML dosage. At the saturation dosage, viscosity dropped dramatically and its values were comparable at all mixing times. Also, at high ML dosages, the effect of temperature on viscosity was not significant.

The effect of the NS dosage as a function of time and temperature on the plastic viscosity of cement pastes is presented in Figs. 5.13(a)-5.13(c). Plastic viscosity had a comparable trend to that of yield stress for cement pastes made with NS (Figs. 5.7(a)-5.7(c)). However, unlike yield stress, plastic viscosity at high NS dosages did not approach a zero value.

The relationship between mixing time and plastic viscosity for cement pastes incorporating PCN at three ambient temperatures (22, 35, 45 ^{o}C) is illustrated in Figs. 5.14(a)-5.14(b). It can be observed that plastic viscosity increased linearly with time for all PCN dosages and at all temperatures.

Figures 5.15(a) and 5.15(b) illustrate the relationship between measured viscosity and elapsed time for cement pastes incorporating various ML dosages. Again, similar to the results of yield stress, viscosity increased linearly with the elapsed time at all temperatures and ML dosages.

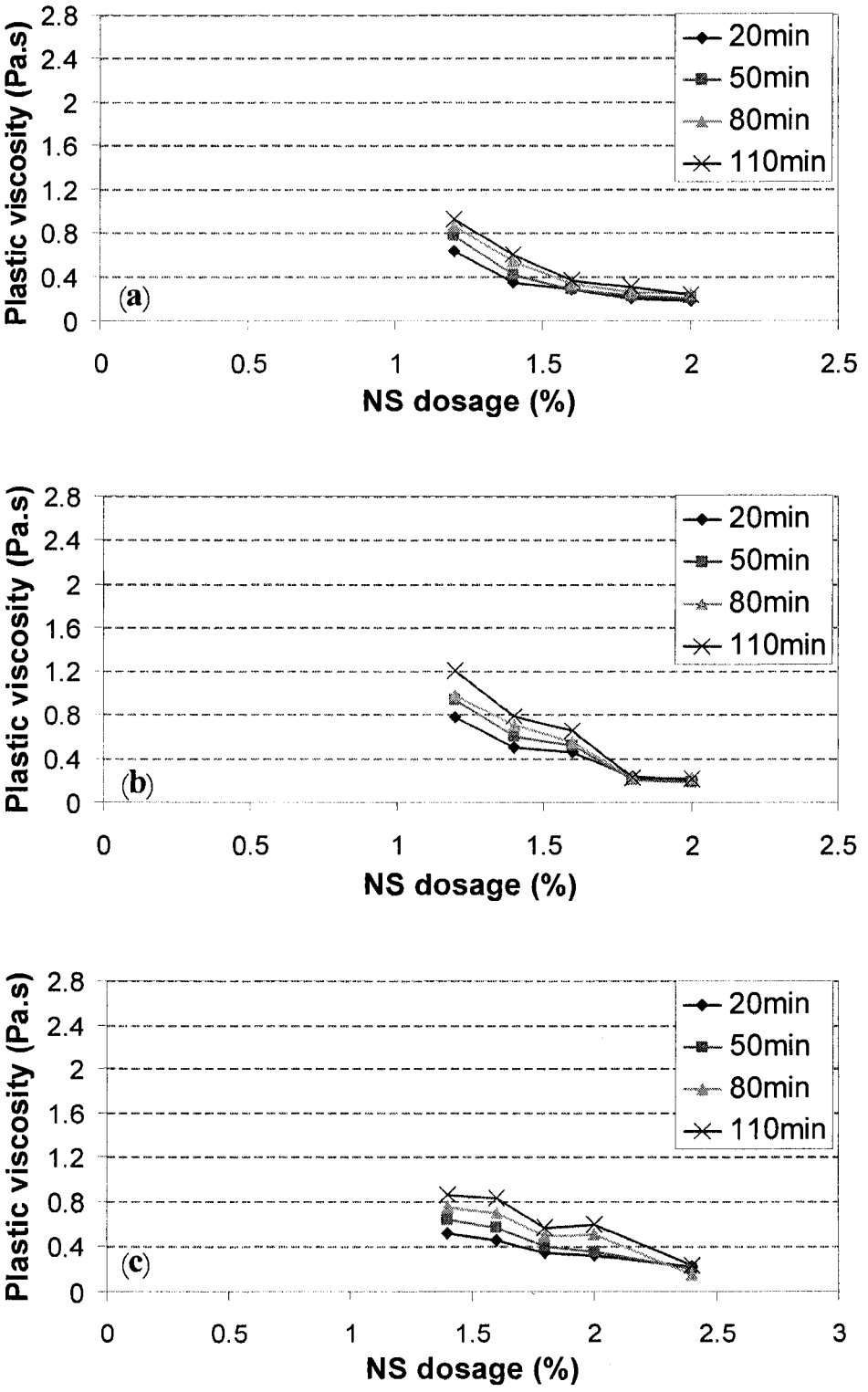

Figure 5.13-Variation in plastic viscosity with time and superplasticizer dosage for cement pastes (w/c = 0.38) incorporating NS [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

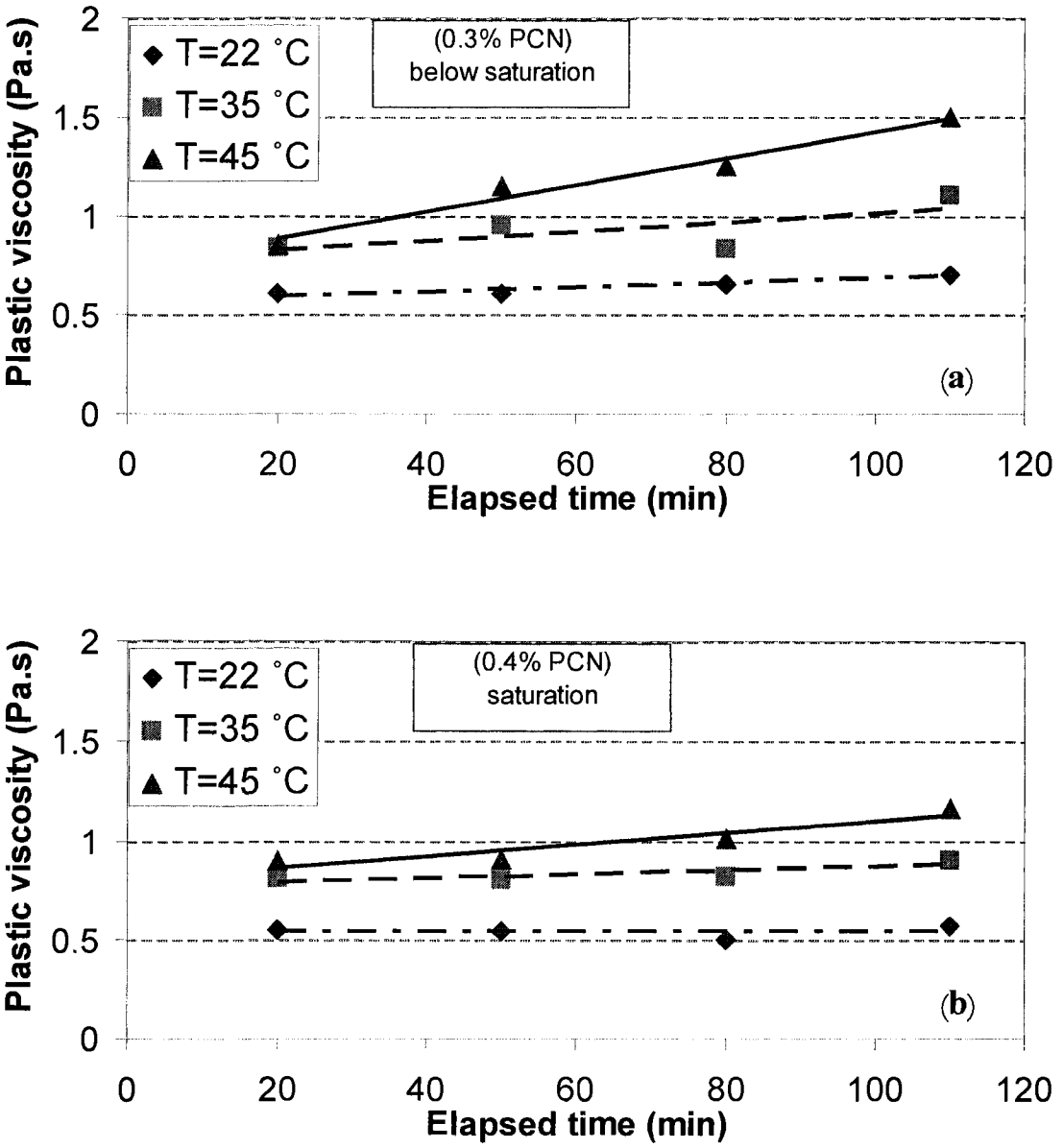

Figure 5.14-Variation in plastic viscosity with time and temperature for cement pastes incorporating PCN [(a) at 0.3% and (b) at saturation dosage of 0.4%].

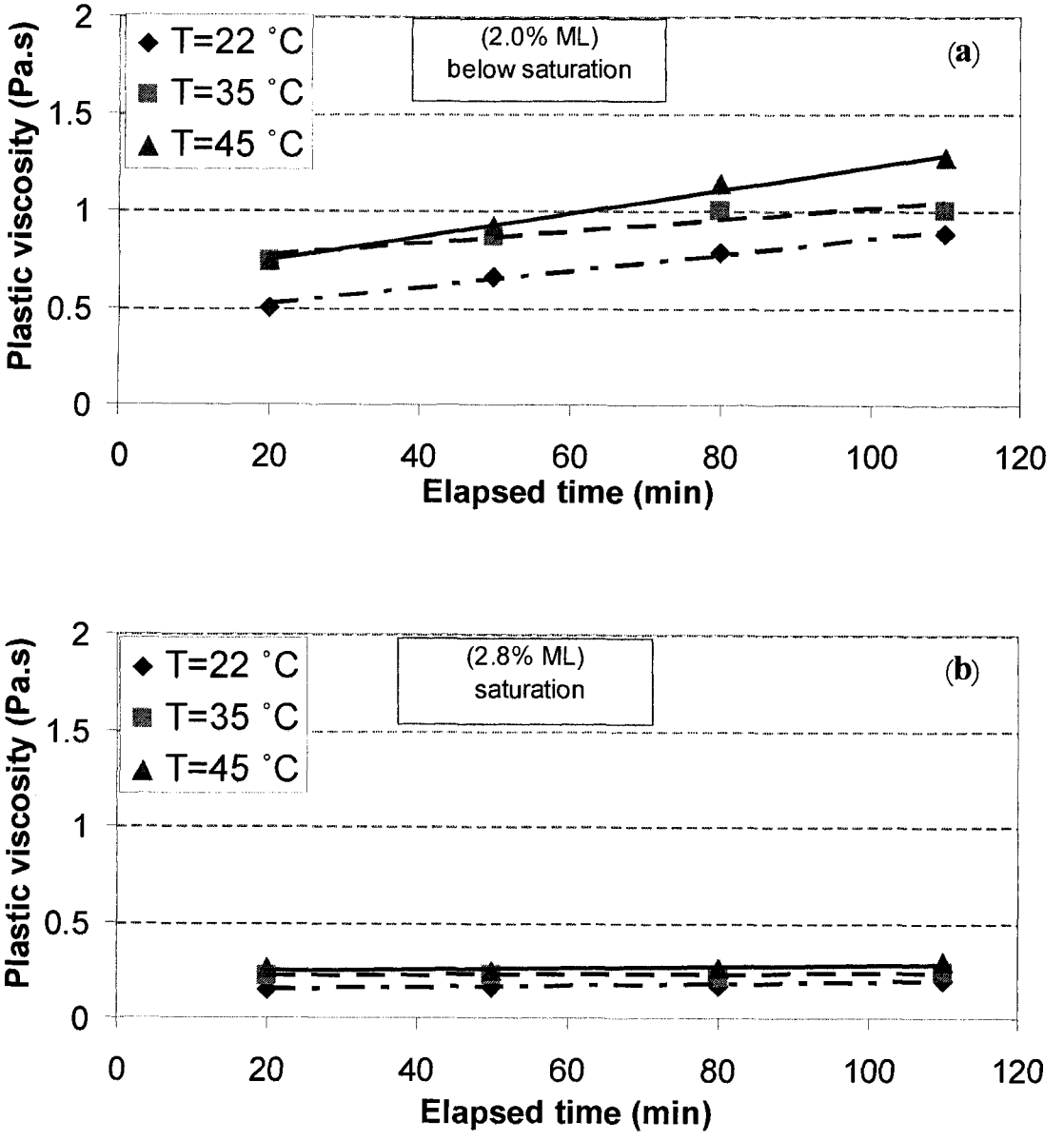

Figure 5.15-Variation in plastic viscosity with time and temperature for cement pastes incorporating ML [(a) at 2.0% and (b) at saturation dosage of 2.8%].

The effect of NS on plastic viscosity versus time and temperature is presented in Figs. 5.16(a)-5.16(b). At a dosage of 1.4%, viscosity increased linearly with time with a rate higher than that at the saturation dosage. The rate of viscosity increase was higher at 45 ^{o}C.

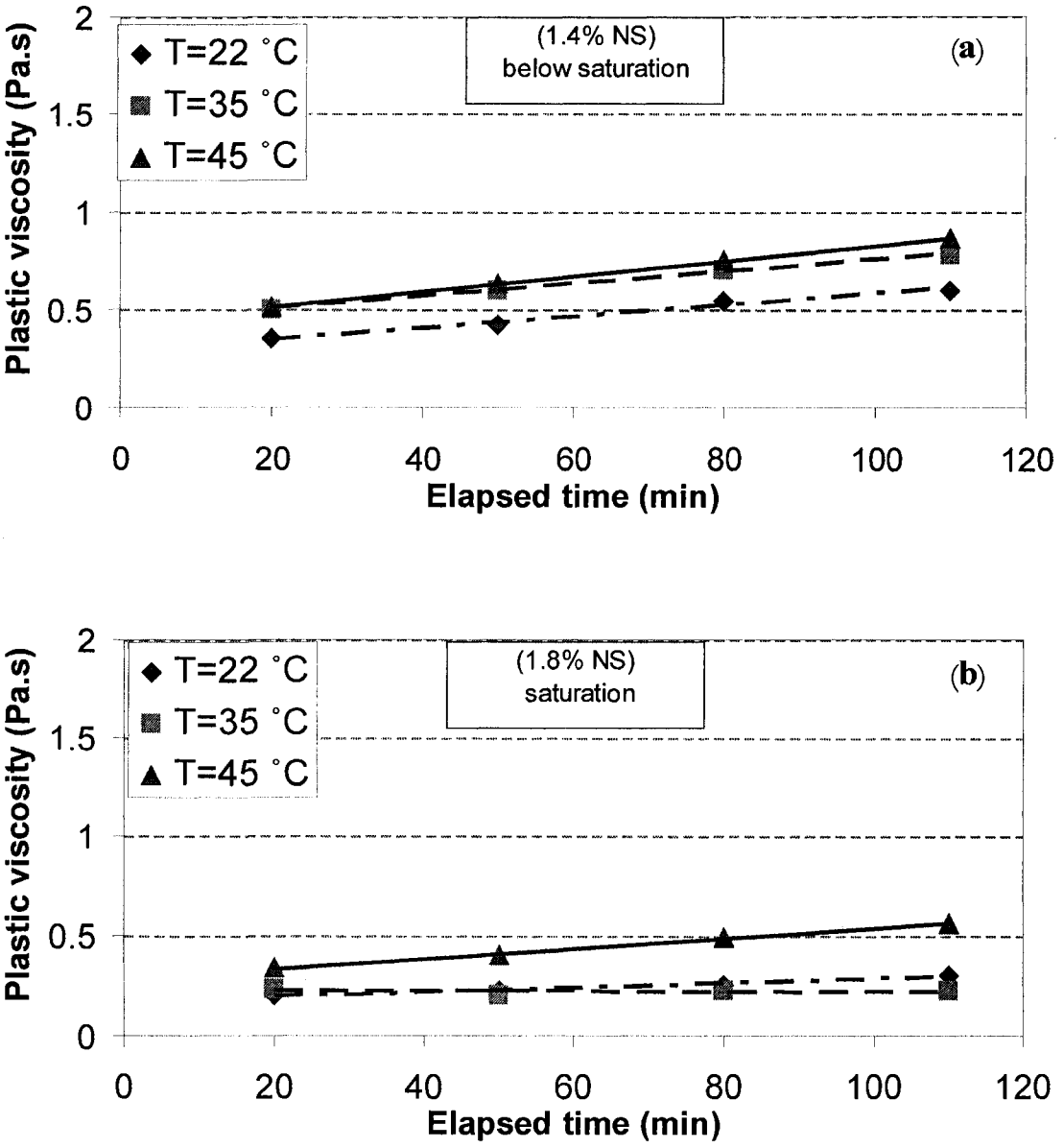

Figure 5.16-Variation in plastic viscosity with time and temperature for cement pastes incorporating NS [(a) at 1.4% and (b) at saturation dosage of 1.8%].

5.4.4 Coupled effects of temperature and time on thixotropy of cement pastes incorporating various superplasticizers

Changes in thixotropy due to ambient temperature and mixing time for cement pastes incorporating different dosages of various superplasticizers were calculated by integrating the enclosed hysteresis loop areas between the up and down parts of flow curves. The results in Figs. 5.17, 5.18, and 5.19 indicate the ongoing build up in the cement paste internal structure with time due to the hydration process. Figures 5.17(a), 5.17(b), and 5.17(c) illustrate the effect of the PCN dosage on thixotropy at 22, 35 and 45 ^{o}C, respectively. Generally, thixotropy increased with time and this increase was more remarkable at higher temperature. In accordance with the evolution of yield stress and plastic viscosity, thixotropy was inversely related to the PCN dosage below the saturation dosage and it was directly related to the PCN dosage beyond the saturation dosage.

As shown in the figure, at a fixed PCN dosage and time, thixotropy increased with temperature, which is related to the rapid change in cement paste structure due to the acceleration of hydration reactions. The stronger cement paste is structured, the more time is needed to recover the breakdown in its structure after it has been sheared, and therefore, a larger thixotropy is measured (Coussot *et al.* 2002).

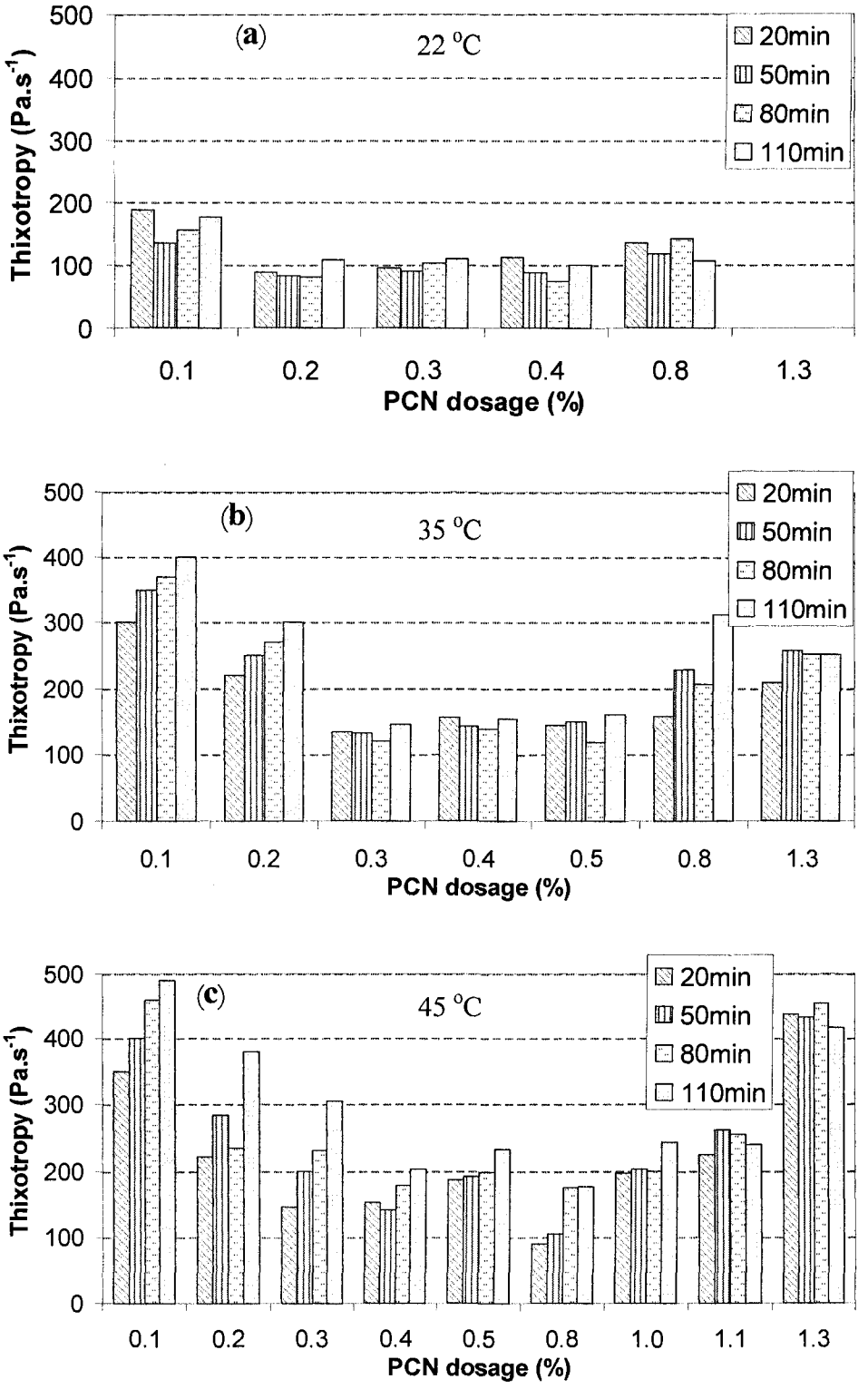

Figure 5.17-Thixotropy (integrated area between up and down flow curves) as a function of PCN dosage [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

The effect of the ML dosage on the thixotropy of cement paste as a function of time and temperature is presented in Figs. 5.18(a), 5.18(b), and 5.18(c) at 22, 35, and 45 °C, respectively. Thixotropy increased with higher temperature, indicating the rapid change in cement paste structure due to the acceleration of hydration reactions. Similar to yield stress and plastic viscosity, thixotropy decreased with the increase of the ML dosage and increased with time at all ambient temperatures. However, in the case of high admixture dosage (2.4% and 2.8%), the effect of time on thixotropy became small. As can be seen in Fig. 18(a), no clear trend for thixotropy versus time could be observed at 22 °C for a ML dosage of 2.4% and thixotropy maintained approximately similar values over 80 min of mixing. However, at 110 min a rapid growth in thixotropy occurred at both temperatures (35 °C and 45 °C).

Thixotropy results obtained for cement pastes incorporating NS as a function of time, temperature and NS dosage are presented in Figs. 5.19(a)-5.19(c). Contrary to the case of the PCN and ML admixtures, at low dosages, thixotropy increased slightly with an increase of dosage, and it decreased at high dosages.

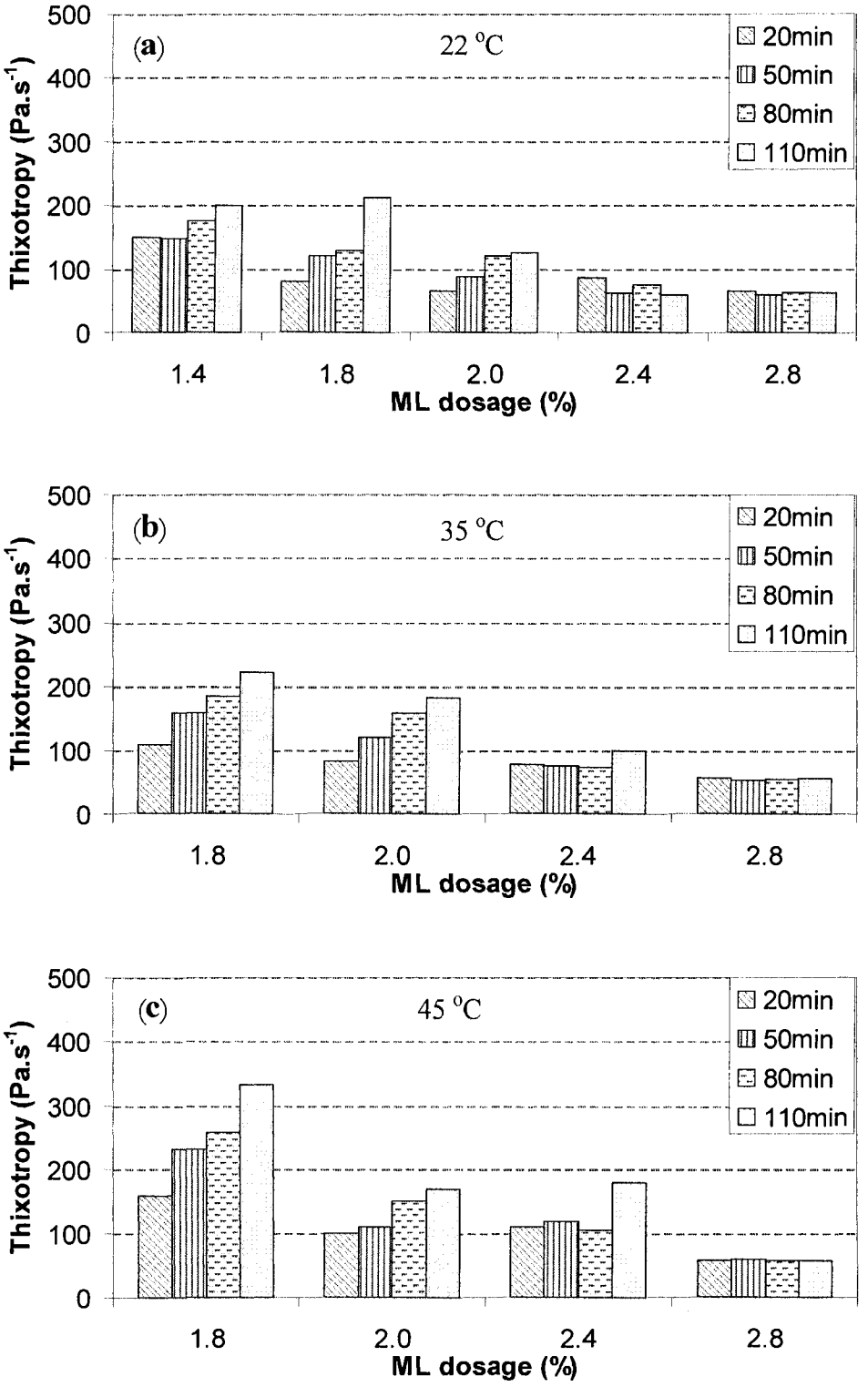

Figure 5.18-Thixotropy (integrated area between up and down flow curves) as a function of ML dosage [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

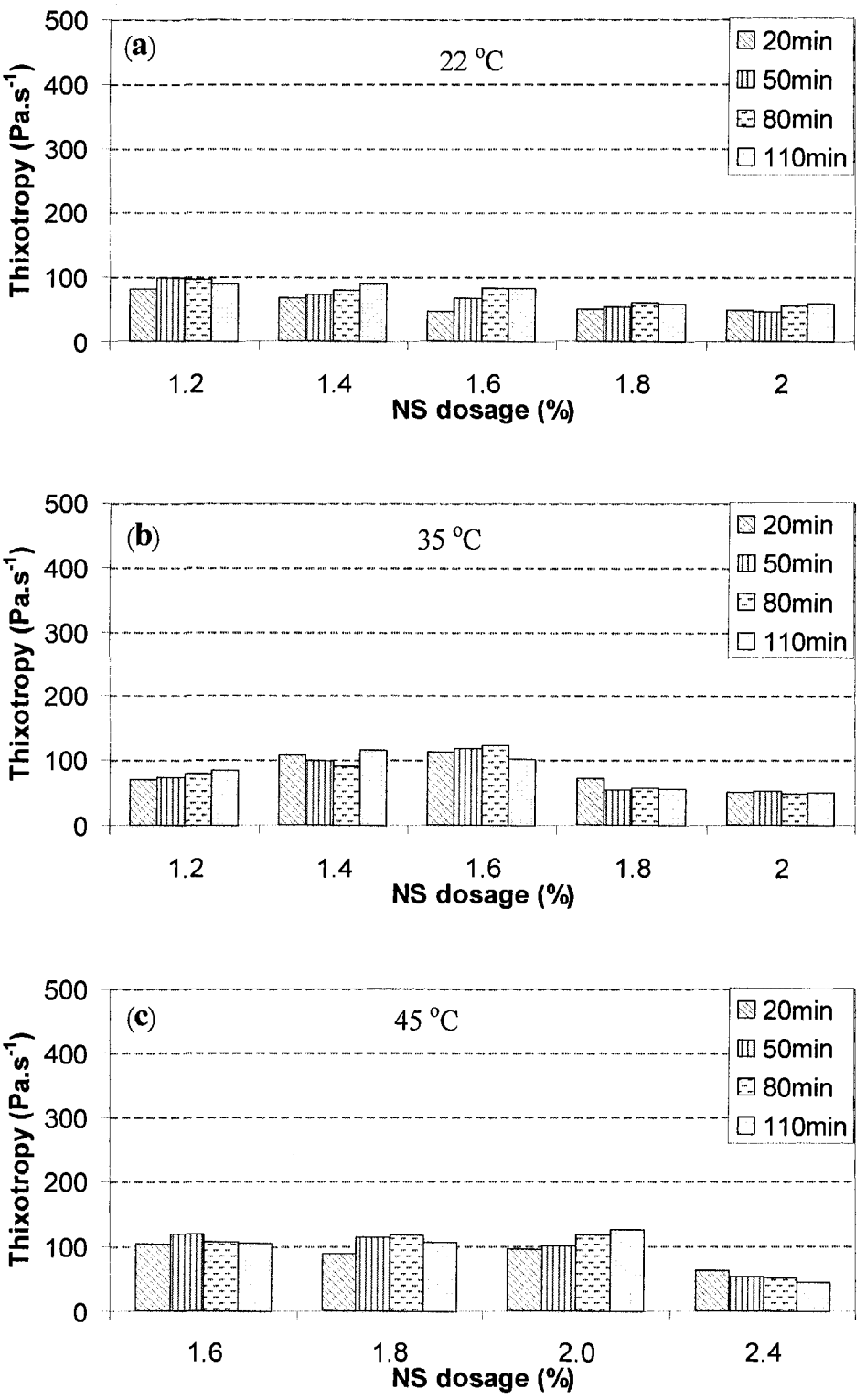

Figure 5.19-Thixotropy (integrated area between up and down flow curves) as a function of NS dosage [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

5.4.5 Discussion

Considering the above results, it can be argued that PCN was an effective dispersing agent since it achieved relatively low yield stress values using lower dosages compared to that of NS and ML. The high deflocculating ability of PCN is due to its dispersing mechanism, which involves both electrostatic repulsion and steric stabilization. In the case of NS and ML, the mode of action is achieved through electrostatic repulsion by adsorption of these admixtures on the surface of cement particles. The negatively charged ionized sulfonate groups on the adsorbed NS and ML molecules cause cement particles to deflocculate; the water trapped is released becoming available for fluidification (Rixon and Mailvaganam 1999). PCN has a similar electrostatic mechanism to NS and ML owing to its negatively charged carboxyl groups. However, it also has a steric hindrance mechanism due to its long flexible side chains attached to these polymers. Accordingly, cement particles will be prevented from coming close to each other and dispersion can be maintained at relatively low dosages (Rixon and Mailvaganam 1999).

Kim *et al.* (2000) found that the fluidity of cement paste prepared with NS depended mainly on the amount of free NS in the solution rather than on the amount of adsorbed NS. Based on their results and those of the present study, it could be argued that the NS adsorption rate increases with temperature, which will consequently decrease the amount of free NS. It was found by Kim *et al.* (2000) that the amount of NS adsorption was also a function of time; about 75% and 90% of NS were adsorbed on cement after 2 and 30 minutes, respectively.

It can be argued that at a low dosage (1.4%) and high temperature, NS was quickly adsorbed on cement grains. Thus, yield stress started to increase with temperature at 20 minutes after mixing (Fig. 5.10(a)). Conversely, at the saturation dosage, a sufficient amount of free NS is believed to be provided, and therefore values of yield stress for different temperatures at 20 minutes nearly coincided (Fig. 5.10(b)).

Yamada *et al.* (1998) found a direct relationship between polycarboxylate adsorption and fluidity of cement paste, and an inverse relationship between naphthalene sulfonate adsorption and cement paste fluidity. They also reported that naphthalene sulfonate was adsorbed in larger quantity than that of polycarboxylate. This was attributed to the different behaviour of the two admixtures versus hydration kinetics. The specific surface area of hydrated cement is greater than that of unhydrated cement, and that of hydrated superplasticized cement is higher than that of hydrated plain cement. The increase in specific surface area was found to be more significant in the case of naphthalene sulfonate than that for polycarboxylate. Accordingly, the addition of NS increases the specific surface of the early hydrates and a larger amount of NS needs to be adsorbed.

Comparing the thixotropy results as a function of time at a ML dosage of 2.4% with that of yield stress and plastic viscosity at the same dosage, it can be observed that yield stress and plastic viscosity at high temperatures (35 and 45 ^{o}C) increased continuously with time (Figs. 5.6(b)-5.6(c) and Figs. 5.12(b)-5.12(c)), while thixotropy did not change significantly up to 80 minutes and exhibited substantial increase at 110 minutes (Figs. 5.18(b)-5.18(c)). This suggests that there are two ranges of cement paste microstructure, namely short and long ranges. The long range is related to interaction between neighboring

flocs; while the short range is related to the interaction between particles forming the flocculent (Kim *et al.* 2000). Thus, yield stress occurs when shear stress is strong enough to separate pairs of flocs, while viscosity is a result of the energy required to move liquid into and out of the space between flocs (Hunter 2001). On the other hand, thixotropy accounts for the short range of forces. The increase of yield stress with time at high temperatures (35 and 45 ^{o}C) and a ML dosage of 2.4% (Figs. 5.6(b)-5.6(c)) can be attributed to the increase in the interaction forces between flocs. As long as thixotropy is concerned with the internal structure, its behaviour with time can be attributed to the increase of the electrokinetic potential of particles forming the flocculent at high temperatures (Hunter 2001).

Additionally, two mechanisms are likely involved in the bond between cement particles in the flocculent at high temperatures and for a prolonged mixing time. The first is the increase in the electrokinetic potential due to temperature increase. This mechanism tends to affect the dispersion of particles in the flocculent. The other mechanism increases the bond between particles due to ongoing hydration with time and its rate increases with temperature (Hewlett 1998). Accordingly, the increase of temperature enhances, on one hand, the electrokinetic potential favoring dispersion, and on the other hand, increases the hydration rate strengthening the bond between particles in the flocculent. The effect of the rate of hydration seems to be higher than that of the electrokinetic potential increase at low admixture dosages. Thus, forces due to the strengthened bond between cement particles in the flocculent at high temperature oppress the repulsive forces due to the increase in electrokinetic potential. This leads to an increase in thixotropy with temperature (Figs. 5.18(b)-5.18(c)). High admixture dosages can slow down the rate of hydration, making it equivalent to that of the electrokinetic potential for mixing times up to 80 minutes,

resulting in comparable values of thixotropy over this time period. At 110 minutes, the rate of hydration apparently became again higher than that of the electrokinetic potential, which explains the substantial increase in thixotropy at this dosage at 35 and 45 °C (Figs. 5.18(b)-5.18(c)).

5.5 Conclusions

The influence of ambient temperature and mixing time on the evolution of the rheological properties of cement pastes incorporating polycarboxylate-, melamine sulfonate-, and naphthalene sulfonate-based superplasticizers was investigated in this chapter. The comprehensive set of data thus developed allows drawing significant conclusions:

- Cement pastes incorporating PCN and ML displayed shear thinning behaviour at high temperatures and prolonged mixing time regardless of the superplasticizer dosage.
- The NS saturation dosage for cement paste at high temperature and prolonged mixing could be identified by the shift in the shear rate-viscosity curve from shear thinning to shear thickening when the NS dosage exceeded the saturation.
- The yield stress and plastic viscosity decreased with the PCN dosage up to the saturation dosage, but tended to increase beyond that level.
- The yield stress and plastic viscosity of cement pastes incorporating ML and NS decreased with the increase of superplasticizer dosage until a saturation dosage beyond which no significant decrease in yield stress could be achieved.

- PCN has displayed effective dispersing ability in the range of the investigated temperature, since it achieved low yield stress values using a relatively low dosage. However, at high dosages, NS and ML were more effective at decreasing yield stress, viscosity, and thixotropy versus temperature.
- For all superplasticizers tested, the evolution of yield stress and plastic viscosity versus time was linear regardless of the temperature.
- Regardless of the superplasticizer used, thixotropy increased with time and temperature below the superplasticizer saturation dosage.
- In accordance with the evolution of yield stress and plastic viscosity, thixotropy of cement pastes incorporating PCN decreased with the increase of the PCN dosage below the saturation dosage and it was directly related to the PCN dosage beyond the saturation dosage.
- It seems that to ensure adequate rheological behaviour at high temperature and prolonged mixing time, a PCN dosage close to the saturation dosage needs to be used, while ML and NS dosages beyond the saturation dosage are preferred. However, research on concrete mixtures is needed before the present results obtained on cement pastes can be transposed to full-scale field concreting. The results are also for the particular superplasticizers and cement used and need to be validated for other cements and superplasticizers even from the same category.

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Chapter 6

COUPLED EFFECTS OF HIGH TEMPERATURE, PROLONGED MIXING TIME, AND CHEMICAL ADMIXTURES ON RHEOLOGY OF FRESH CONCRETE*

6.1 Introduction

Ready mix concrete is subjected to continuous mixing and agitation for different periods of time during its hauling to construction sites. Although it is usually intended to minimize the hauling distance and time for economical purposes, this objective can not be achieved in many cases due to factors including traffic, distance to construction site, and delays in placing concrete (Ravina 1975). The resulting prolonged mixing is usually associated with a slump loss of concrete. Poor workability of concrete can create several problems including difficulty of concrete placement and compaction resulting in concrete having increased voids and lower mechanical strength and durability (Soroka and Ravina 1998). Excessive slump loss does not usually occur in moderate temperature concreting, but it becomes more significant in hot weather conditions. The preferable condition for placing concrete is generally when the ambient temperature ranges from 20 to 23 °C (El-Rayyes 1990). The ACI guidelines for hot weather concreting specify that ambient temperature is considered high beyond 27 °C (ACI 305.1-06).

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One of the common practices to alleviate hot weather concrete placement problems is using more mixing water, but this practice hinders the mechanical strength and durability of concrete (Abbasi *et al.* 1992). Chemical admixtures have been widely investigated as a potential means to reduce slump loss by increasing the initial fluidity of concrete. For instance, Ravina (1975) investigated the effects of polyhydroxy carbonic acid, modified ligin sulfonate, and ligin carbohydrate sulfonate-based high-range water reducing admixtures (HRWR) on the total amount of mixing water added to concrete during prolonged mixing (1 or 2 hours) at a temperature of 30 ^{o}C to compensate for the slump loss in order to regain the initial slump of 10 ± 1 cm. It was found that the chemical admixtures improved the concrete workability and reduced the total amount of mixing water needed to compensate for slump loss. The reduction in mixing water was a function of the admixture dosage i.e. the higher the dosage, the more was the reduction in the mixing water. For example, when the dosage increased from 0.15% to 0.50%, the mixing water decreased by about 6.0% (Ravina 1975).

Hampton (1981) studied the possibility of decreasing the rapid slump loss of concrete due to high temperature using a naphthalene sulfonate HRWR. The temperature ranged from 22-32 ^{o}C. Concrete was mixed at room temperature and a propane burner was placed under the mixer to reach higher temperature. Concrete was mixed in a rotating drum mixer for 2 minutes before the initial slump was taken. After 30 minutes of rest concrete was remixed for 2 minutes and the slump was taken again. This procedure was further repeated at 60 minutes. It was found that only marginal slump loss occurred when the concrete was mixed at a moderate temperature for up to 60 minutes. The slump loss was significant under a high temperature of 32 ^{o}C, but decreased when the admixture was added.

A few researchers investigated the fluidity of fresh concrete incorporating chemical admixtures and subjected to continuous agitation. For instance, Amziane *et al.* (2005) investigated the workability of fresh portland cement concrete mixtures under continuous agitation. The rheological properties of nine concrete mixtures with different additives and admixtures, i.e. slag, set retarder, high-range water reducing admixture (HRWRA), and viscosity-modifying admixture (VMA), were evaluated while they were still in a mixing truck. The mixing time ranged from 30 to 120 minutes after the first contact between cement and water. The temperature was recorded, although it was not considered as a test parameter, and it varied from 18 to 31 ^{o}C. The truck was used as a concrete rheometer to measure the rheological parameters (yield stress and plastic viscosity) of the nine fresh concrete mixtures. This was achieved using principles similar to that of a traditional rheometer. Accordingly, the rotational speed of the drum changed from high to low and the power consumption of the motor was measured at each rotational speed. The measured power was an indication of the torque exerted by a rheometer. The rheological properties of the nine concrete mixtures were also measured by a portable rheometer. The yield stress measured by the mixing truck correlated well with that of the rheometer. The plastic viscosity measured by the rheometer was more realistic than that measured by the mixing truck, and therefore a poor correlation was found between the two measurements. This was attributed to several sources of uncertainty in the precision of the measurements of the drum's rotational speed and torque.

Struble and Chen (2005) investigated the workability of concrete as a function of time by measuring the flow resistance (G), the viscosity factor (H), and slump. To study the behaviour of concrete in a ready-mix truck, some concrete mixtures were subjected to

continuous agitation, while other mixtures were tested without agitation to investigate how concrete would behave in a formwork. Only the slump test was performed on concrete mixtures not subjected to agitation because a severe stiffness was expected, which could damage the instrument. The effect of temperature was not investigated and the test temperature was maintained at 25 ^{o}C. A total of 8 concrete mixtures were prepared, two of which did not incorporate chemical admixtures with a water to binder ratio (w/b) of 0.54, while the rest of the mixtures included chemical admixtures with a w/b ranging from 0.35 to 0.45. Three chemical admixtures were used including a lingosulfonate water reducer, naphthalene sulfonate-, and carboxylate–based HRWR. The initial target slump was 200 mm. In order to provide continuous agitation for concrete, a standard rotating drum mixer at a low speed was used. The concrete mixtures were tested over a time span of 100 min. It was found that the investigated rheological properties (*G* and *H*) increased with time, while the slump decreased with time. The slump for a concrete mixture subjected to continuous agitation was found to be higher than that of a similar mixture without agitation. Li *et al.* (2004) developed numerical models in an attempt to quantitatively predict the workability of high-fluidity concrete for any time period and under any stress state. Polycarboxylate-based HRWR was used. In addition to the admixture dosage and elapsed time, the influence of temperature on the mean potential energy of cement particles was also included in the model (Li *et al.* 2004). They investigated the time dependence of the Bingham constants (yield stress and plastic viscosity) when concrete was under standstill and continuous agitation (mixing) conditions. Li *et al.* (2004) developed a model using concrete mixture proportions collected from the literature. Their results indicated that both the yield stress and apparent viscosity increased with time and temperature. However, the

increase was more remarkable when the concrete mixture was under the standstill condition than that under agitation (Li *et al.* 2004).

Using the slump test to assess the workability of fresh concrete has become inadequate, particularly for modern concrete mixtures incorporating chemical admixtures. Its main deficiency is that two fresh concrete mixtures having the same slump value may behave quite differently in the jobsite. This is due to the fact that the standard slump test is only related to the yield stress, while it is not possible to fully evaluate the concrete flow merely using a single parameter (Ferraris and de Larrard 1998). It is well established that the flow properties of fresh concrete at low shear rates approximate the Bingham model expressed in equation (6.1) (Tattersall 1991):

$$\tau = \tau_0 + \mu_p \dot{\gamma} \tag{6.1}$$

Where τ, τ_0, μ_p, and $\dot{\gamma}$ are the shear stress, yield stress, plastic viscosity, and shear rate, respectively.

According to equation (6.1), the shear stress should be measured at least at two different shear rates to estimate the Bingham constants. Physically, the yield stress represents the force required to initiate flow, while plastic viscosity is a measure of the resistance of the mass to an increase in the rate of flow.

Using a rheometer, fresh concrete can be characterized by two Bingham parameters (yield stress and plastic viscosity). Accordingly, the rheometer permits to differentiate between two fresh concrete mixtures that may have been wrongly judged identical by the standard slump test. This allows developing a more reliable control system; especially that

yield stress and viscosity respond differently to the various factors that concrete is subjected to, such as the ambient temperature, type and dosage of chemical admixtures, and mixing time.

Only a few studies in the literature (Hampton 1981; Struble and Chen 2005; Li *et al.* 2004) investigated the effect of the mixing time on the workability of fresh concrete incorporating superplasticizers. Hence, more information is needed regarding the coupled effects of the ambient temperature (including high temperatures) and prolonged mixing time on the rheological properties of concrete incorporating superplasticizers. Previous research by the present authors (Al-Martini and Nehdi 2007) showed that superplasticizers improved the rheological properties of cement paste under high temperatures. Therefore, this chapter aims at formulating recommendations for the effective use of chemical admixtures at high temperatures, which should enhance the rheological properties of fresh concrete in hot weather conditions. In this chapter, the rheological properties of fresh concrete with a w/c = 0.38 and incorporating three superplasticizers, namely, a new generation of polycarboxylate (PCN), melamine sulfonate (ML), and naphthalene sulfonate (NS)-based superplasticizers were studied at three different ambient temperatures: 22, 35 and 45 °C. The w/c was selected to be 0.38 because for a higher w/c the effect of superplasticizers on rheological properties is diminished, while very low w/c and high temperatures combinations need focus in future research. The superplasticizers selected for this study are commonly used in the concrete industry and were recommended by manufacturers for concrete at high temperature. The temperature of 22 °C represents concrete placed at moderate temperature conditions, while 35 and 45 °C are for concrete placed at high temperature conditions. To study the coupled effects of time and

temperature, the concrete mixtures were also subjected to prolonged mixing for up to 110 minutes from the time of mixing, and rheological measurements were taken at half hour intervals. Based on many trial batches, the selected time interval was found adequate to observe the changes in concrete rheological properties as a function of mixing time and ambient temperature. The prolonged mixing was intended to give an indication on the rheological behaviour for instance during continuous mixing of concrete in a transit mixer during its hauling to a construction site.

6.2 Experimental Program

6.2.1 Materials

CSA Type 10 (similar to ASTM C150 Type I) ordinary portland cement was used in all concrete mixtures investigated; its physical and chemical properties are shown in Table 3.1. Tap water was used for the mixing and its temperature was maintained at 22 ± 0.5 °C. The coarse aggregates were washed natural pea gravel with a nominal size of 10 mm, and the fine aggregates were well graded natural sand. Figure 6.1 shows the grain size distribution of fine aggregates. The absolute volume method described by the ACI Committee 211 Standard Practice for Selecting Proportions for Normal, Heavyweight and Mass Concrete (ACI 211.1-91) was used to calculate the concrete mixture proportions. The concrete mixtures had w/c = 0.38 and incorporated 475 kg/m^3 of cement, 895 kg/m^3 of fine aggregate and 800 kg/m^3 of coarse aggregate with no air entrainment. These proportions are typical for a flowable concrete mixture design (Bassuoni and Nehdi 2007). It should be noted that the superplasticizer dosages were chosen based on the results reported in previous chapters for cement pastes incorporating these superplasticizers.

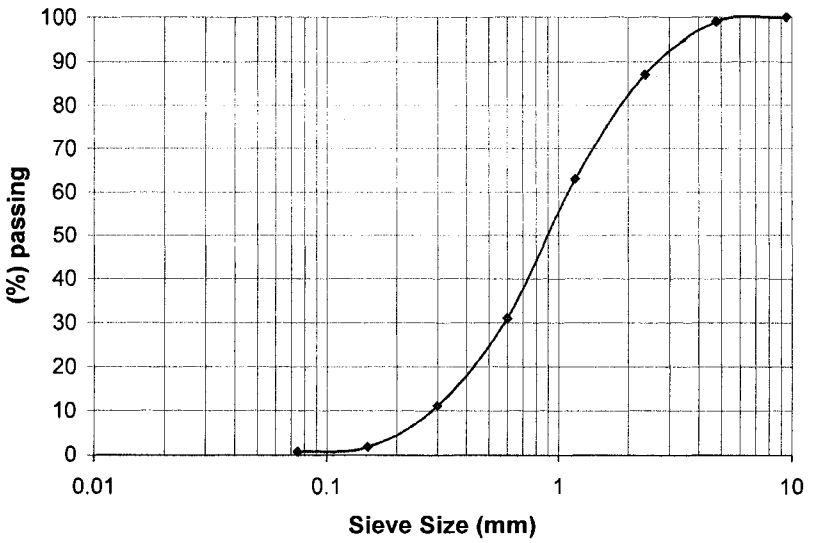

Figure 6.1-Grain size distribution of fine aggregates.

The following superplasticizers were used in this chapter: 1- A new generation of polycarboxylate-based superplasticizer (PCN); the dosage of PCN ranged from 0.4% to 1.7% by mass of cement. 2- Melamine sulfonate-based superplasticizer (ML); the dosage of ML ranged from 1.4% to 3.8% by mass of cement. 3- Naphthalene sulfonate-based superplasticizer (NS); the dosage of NS used in the chapter ranged from 1.2% to 3.0% by mass of cement.

6.2.2 Apparatus

A drum concrete mixer with a maximum capacity of 3 cu. ft. was used throughout this investigation. A temperature and relative humidity controlled walk-in environmental chamber was used for the preparation of the concrete mixtures. A BML rheometer (version 4) was used throughout this investigation to measure the rheological properties of fresh concrete. The rheometer has a coaxial cylinder system, which consists of outer and inner cylinders (Fig. 6.2(a)). As the outer cylinder rotates at variable angular velocity, the inner

cylinder measures the torque. The outer and inner cylinders have radii of 0.145 and 0.100 m, respectively. The radii of the outer and inner cylinders were designed in such a way to ensure an acceptable variation of shear rate across the gap and to accommodate large variations of concrete textures. As shown in Fig. 6.2(b), the inner cylinder is provided with vertical ribs to reduce the effect of wall slippage at the interfacial zone between the inner cylinder surface and fresh concrete. The BML rheometer is fully automated and the entire experimental process is controlled by a computer software called WinFresh (Viscometer 4 2000).

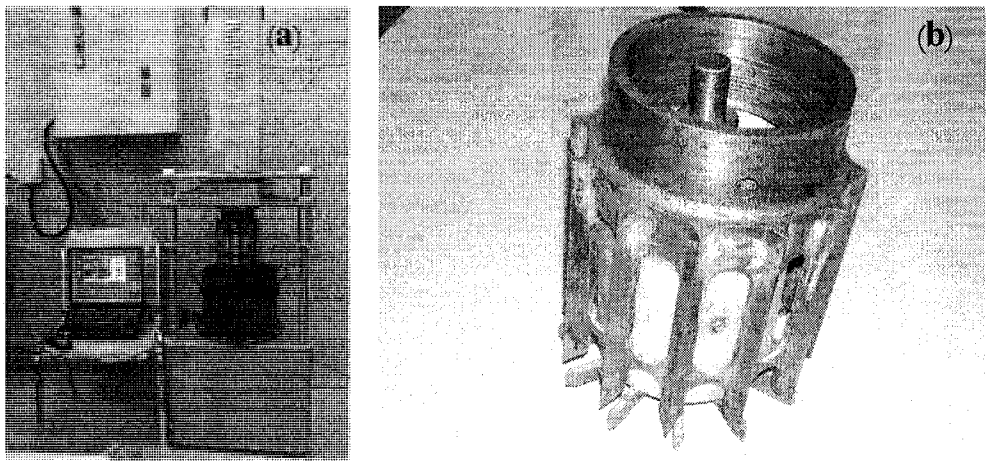

Figure 6.2-Illustration of the instruments used, (a) concrete rheometer with coaxial cylinders and (b) inner cylinder geometry.

The BML rheometer used in this study measures the torque resistance, T_R, of concrete at several rotational speeds. The torque resistance typically increases linearly with the increase of the flow rate. This relationship is expressed in the following equation:

$$T_R = G + HN \tag{6.2}$$

Where, T_R (Nm) is the torque resistance, G (Nm) is the flow resistance, H (Nm.s) is the viscosity factor, and N is the rotational speed (rev/s). Similar to yield stress, G is the intercept of the T_R-N line with the torque axis (y axis), and it represents the force necessary for concrete to start flowing; H is the slope of this line and is a measure of the resistance of the concrete to an increased speed of flow (Geiker *et al.* 2002). The WinFresh software (Viscometer 4 2000) that controls the rheometer uses the Riner-Rivlin equation (6.3) to convert the measured constants (G and H) to Bingham constants (τ_o and μ):

$$\Omega = \frac{T}{4\pi h\mu}\left(\frac{1}{R_i^2} - \frac{1}{R_o^2}\right) - \frac{\tau_o}{\mu}\ln\left(\frac{R_o}{R_i}\right) \tag{6.3}$$

Where, Ω ($\Omega = 2\pi . N$) is the angular velocity of the outer cylinder (rad/s), h is the height of the inner cylinder (m), R_i is the radius of the inner cylinder (m), and R_o is the radius of the outer cylinder (m).

6.2.3 Test procedure

The environmental chamber was set to the required temperature (35 or 45 °C) 24 hours before the experiment. For moderate temperature testing, the mixing was conducted in the lab environment, which had a controlled temperature of 22 °C. Both environmental chamber and lab had a relative humidity (RH) of 50%. The coarse and fine aggregates were oven dried. The weighed coarse and fine aggregates and cement powder were placed inside the environmental chamber to adjust their temperature to the required level at least 12 hours before the experiment.

The procedure used involved a continuous mixing of concrete incorporating superplasticizers. The mixing procedure in this investigation was tailored considering both the ASTM C 685-02 guidelines (Standard Specification for Concrete Made by Volumetric Batching and Continuous Mixing) and that reported by Ferraris and de Larrard (1998) for concretes incorporating superplasticizers. Before the start of mixing, the fine aggregates were placed in the mixer drum followed by the coarse aggregates. Then mixing started and aggregates were dry mixed for one minute. Subsequently, a third of the total quantity of the mixing water was poured into the mixer followed by adding the cement powder. After an additional one minute of mixing, the next third of the water was added and mixing continued for another three minutes. Using a needle, half of the specified quantity of liquid admixture was injected into the last third of the mixing water and was stirred evenly before pouring it gradually and uniformly in the concrete mixture. After another minute of mixing, the other half of the admixture was injected uniformly into the concrete batch. The slump test was conducted in accordance with the ASTM C 143-02 guidelines (Standard Test Method for Slump of Hydraulic-Cement Concrete) after 17 minutes of the start of mixing. The first concrete sample was then taken and placed into the container of the coaxial cylinder for the first rheological test. The total time between the beginning of the mixing and taking the first sample was 20 minutes. A new concrete sample was taken every half hour up to 90 minutes after the first sample. The concrete batch was mixed for a total of 110 minutes. This experimental procedure was strictly followed for all concrete mixtures to avoid the effect of exogenous variables on the results.

Figure 6.3 illustrates the rheological test sequence for fresh concrete mixtures. Only, the down-flow curve was adopted because the time needed to obtain equilibrium at each

shear rate is shorter when decreasing the shear rate (0.6-0.1 rev/s), and hence potential segregation during testing is decreased (Viscometer 4-02). As shown in Fig. 6.3, the rotational speed was decreased in a stepwise manner and not continuously. The duration of each shear rate stage was 3.5 sec so as to reduce the total time of testing. According to this procedure, the shear rate was not excessively high and the duration of the rheological test was not too long, so that the particles of the suspension would not be deformed. After the down-curve was completed, the rotational velocity was increased to the maximum level for a short period of time, and then reduced to 2/3 of the maximum rotational velocity to evaluate the development of segregation during testing.

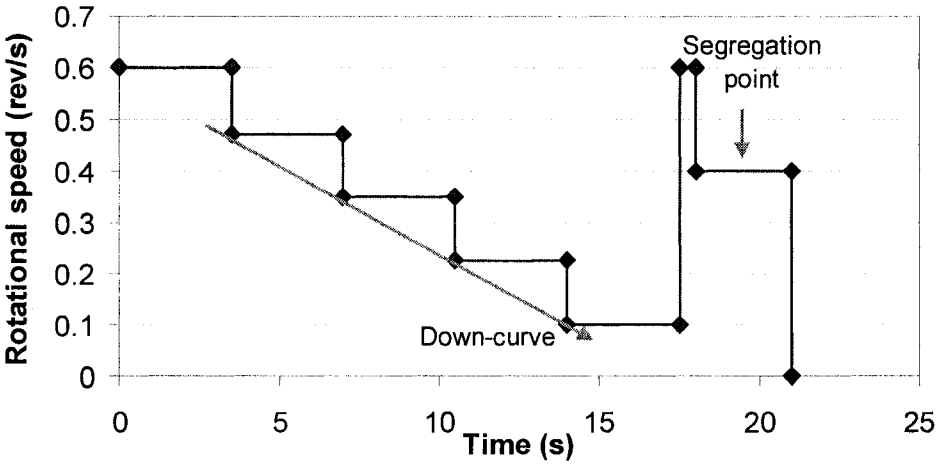

Figure 6.3-Measuring procedure used (rotational speed as a function of time).

The segregation coefficient (*Seg*) was defined according to this procedure as the relative change in the slope of the flow curve (plastic viscosity) due to the sudden increase in the rotational speed (Fig. 6.3), and is calculated according to the following equation (Viscometer 4-02):

$$Seg = \frac{H - H'}{H} \times 100\% \tag{6.4}$$

Where, H is the slope of the flow curve during testing, and H' is the slope of the flow curve due to the sudden increase in rotational velocity at the end of the test.

Using this procedure, fresh concrete was subjected to prolonged agitation in order to simulate the continuous mixing of concrete in a concrete truck mixer during its hauling to construction sites. The prolonged mixing was carried out in the environmental chamber to control the ambient temperature. It should be noted that each rheological test took 3 min from the time of filling the bowl of the rheometer to the time of emptying the concrete back into the concrete mixer.

Repeatability of the rheometer measurements was verified by measuring the rheological properties of four similar concrete mixtures incorporating 0.4% PCN at 22 °C after 20 and 50 min of mixing. The results in Table 6.1 indicates that the rheometer can produce repeatable measurements with acceptable accuracy.

Table 6.1-Repeatability of rheological measurements (concrete with w/c = 0.38 and 0.4% PCN)

Mixing time (min)	Plastic viscosity (Pa.s)			Yield stress (Pa)		
	Measured	Average	*SD*	Measured	Average	*SD*
20	14.8 15.2 14.3 14.5	14.7	0.4	35 36 34.5 35.7	35.3	0.68
50	15.9 16.2 15.5 16.3	15.9	0.36	205 202 200 204	202.7	2.2

6.3 Results and Discussion

6.3.1 Rheological properties of fresh concrete at high temperature and prolonged mixing

Figures 6.4-6.5 illustrate the influence of the admixture dosage on the rheological behaviour of fresh concrete mixed for up to 110 min at 45 °C. Figures 6.4(a) and 6.4(b) show results for fresh concrete incorporating PCN below and beyond the saturation dosage, respectively. Shear thinning behaviour was generally observed for fresh concrete at the various PCN dosages used and over the range of rotational speeds investigated. However, the shear thinning was more pronounced at low PCN dosages (e.g. 0.8%) as evidenced in Fig. 6.4(a). Shear thinning is a typical behaviour for fresh concrete, which is a pseudoplastic agglomerated suspension. This phenomenon could be explained by the shear alignment of molecules due to the increase in shear stress (Eirich 1960). Therefore, at low shear rate, the suspension of particles form flocs because the attractive interparticle forces are higher than the hydrodynamic forces exerted by the flow field. At high shear rate because the hydrodynamic forces overcome the attractive interparticle forces (Barners *et al.* 1989; and Ferguson and Kemblowski 1991), the flocs will break down into smaller particles, thus releasing the liquid entrapped. The measured torque decreased with the increase of the PCN dosage over the range of rotational speeds studied (Fig. 6.4(a)). The minimum torque was achieved at a PCN dosage of 1.5%, which is the saturation dosage at 45 °C, beyond which the measured torque increased (Fig. 6.4(b)). This is contrary to the traditional definition of saturation (Fig. 6.4(b)) since usually no significant decrease in the measured torque could be obtained beyond the saturation with a further increased

admixture dosage, but no significant increase in torque is usually experienced with conventional admixtures beyond the saturation dosage.

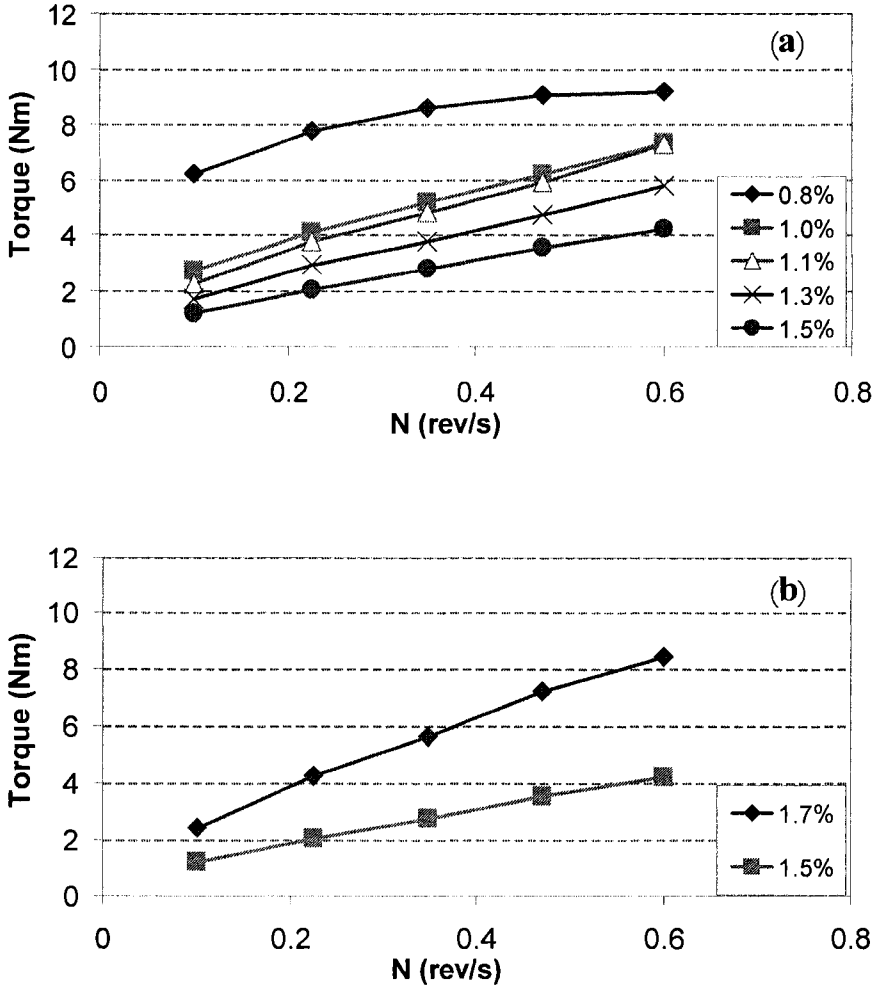

Figure 6.4-Torque versus rotational speed for concrete mixtures incorporating various superplasticizer dosages mixed for up to 110 minutes at a temperature of 45 °C [(a)-PCN below the dispersant saturation dosage and (b)-PCN above the dispersant saturation dosage].

The primary mechanism by which PCN disperses fresh concrete particles is steric hindrance. When PCN is mixed with concrete, it is adsorbed onto cement particles. This steric hindrance effect is related to two terms, namely, elastic and mixing terms. The

former depends on the thickness of the polymer adsorption layer, while the latter depends on the density of the polymer adsorption layer. The mixing term represents the resistance initiated when two neighboring polymer layers penetrate each other. The elastic term, on the other hand, represents the repulsive force related to polymer chains that is developed when two cement particles approach each other (Li *et al.* 2004). The fresh concrete is dispersed when the neighboring cement particles have a distance equal to or higher than double the polymer adsorption layer, and the repulsive force is the only deployed term in steric hindrance. When an overdose of PCN is used, some of the polymers are not adsorbed by cement particles. The density of the polymer layer increases, which increases the mixing term. As a result, polymers tend to penetrate each other developing resistance (Li *et al.* 2004). This explains the increase in the torque when the PCN dosage exceeded the saturation dosage.

Fresh concrete incorporating ML and mixed for 110 min at 45 ^{o}C also displayed a shear thinning behaviour (Fig. 6.5(a)). The shear thinning was more remarkable at low ML dosage (e.g. 2.8%). The minimum torque was observed at a ML dosage of 3.8%. Shear thinning was also observed for fresh concrete mixed with NS (Fig. 6.5(b)). Similar to PCN and ML, the shear thinning was more pronounced at a low NS dosage. However, at the high NS dosage of 3.0%, the behaviour shifted from shear thinning (curve slightly concave down) to shear thickening (curve slightly concave up) (Fig. 6.5(b)). Materials with such a behaviour are referred to as dilatant. According to Hunter (2001), the liquid trapped in the voids of such materials (dilatants) increases at higher shear rates. As a result, particles can rub each other causing an increase in the resistance to flow when the shear rate increases. The dilatant behaviour of the concrete mixed with 3.0% NS could be explained by

interactions between the molecules of the non-adsorbed superplasticizer in the water solution. A similar behaviour was observed by others (Papo *et al.* 2002) for cement pastes mixed with a polyphosphate superplasticizer at 25 °C.

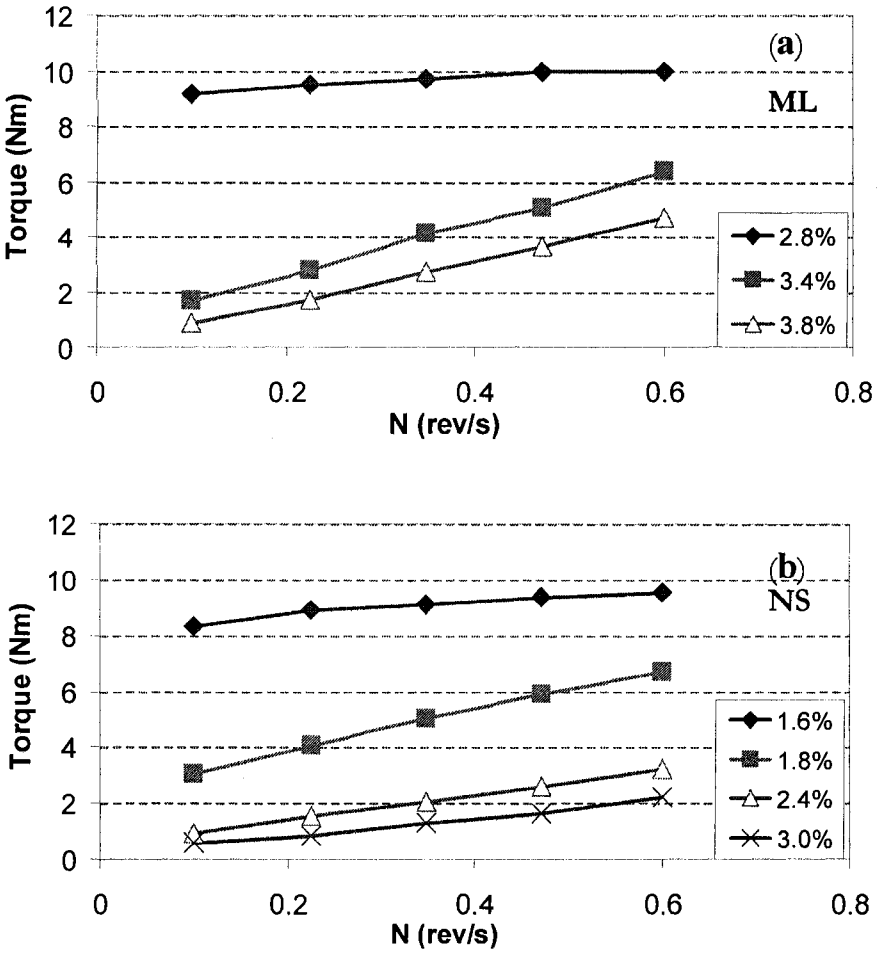

Figure 6.5-Torque versus rotational speed for concrete mixtures incorporating various superplasticizer dosages mixed for up to 110 minutes at a temperature of 45 °C [(a)-ML and (b)-NS].

Hoffman (1998) attributed this phenomenon (shear thickening) to the disordered structure occurring at high concentration of suspensions. Particles jam due to this disordered structure causing more energy to dissipate. Therefore, viscosity increases with

higher shear rate because hydrodynamic forces become higher than repulsive inter-particle forces. Another theory attributes the occurrence of shear thickening to hydrodynamic clusters formed when shear forces become high enough to drive particles nearly into contact (Brady and Bossis 1985). Thus, apparent viscosity (the slope at each point of the curve) increases when the shear rate increases because the clusters jam the flow (Brady and Bossis 1985).

6.3.2 Coupled effects of superplasticizer dosage, mixing time and temperature on yield stress of fresh concrete mixtures

The effect of the PCN dosage on the yield stress of fresh concrete at 22, 35, and 45 ^{o}C is presented in Figs. 6.6(a), 6.6(b), and 6.6(c), respectively. The higher the temperature, the higher was the PCN dosage required to reduce the yield stress significantly and to mitigate the accelerated rate of hydration due to high temperature. Surprisingly, the yield stress increased when the PCN dosage exceeded a certain dosage, referred to as the saturation dosage. The reason behind this unexpected behaviour has been already explained in the previous section. Moreover, the saturation dosage was lower at lower temperature. For instance, the saturation dosage was 0.8% at 22 ^{o}C, while it was 1.1% and 1.5% at 35 and 45 ^{o}C, respectively.

The yield stress results for fresh concrete incorporating ML at 22, 35, and 45 ^{o}C are presented in Figs. 6.7(a), 6.7(b), and 6.7(c), respectively. Similar to PCN, the yield stress generally dropped when the ML dosage increased for all mixing times and ambient temperatures. However, the yield stress value for concrete mixed for 110 min at 35 ^{o}C

increased when the ML dosage increased from 2.0% to 2.4% and it significantly dropped beyond this dosage (Fig. 6.7(b)).

This behaviour of ML was observed by the authors (Al-Martini and Nehdi 2007) for cement paste and they concluded that ML is dosage-dependent; it tended to act as an accelerator below a certain dosage and as a retarder beyond this dosage. Ramachandran *et al.* (1997) reported that at a dosage less than 2%, ML accelerated the hydration of C_3A and C_3S, while when the dosage exceeded 2%, ML retarded the hydration of C_3A and C_3S (Ramachandran *et al.* 1997). Therefore, it is argued that at high temperatures and prolonged mixing time, ML could be used effectively only at high dosages.

Unlike PCN, no increase in yield stress was observed beyond the ML saturation dosage. The saturation for ML can be defined as the dosage beyond which no significant decrease in the yield stress could be achieved with a further increase of the ML dosage. The saturation can be further distinguished (for prolonged mixing) as the dosage at which yield stress values at different mixing times were comparable (Figs. 6.7(a)-6.7(c)). The saturation dosage was shown to depend on the mixing time and temperature. At 22 °C, the observed saturation dosage was 2.4% at 20 and 50 min of mixing and 2.8% at 110 min. The depicted saturation dosage at 35 and 45 °C was 2.8% for concrete mixed up to 50 min, and 3.4% for a mixing time of 110 min. It should be noted that concrete mixtures at 45 °C and incorporating 1.8% and 2.4% of ML were not tested at 110 min of mixing because they became stiff (Table 6.2) and there was a risk of damaging the rheometer.

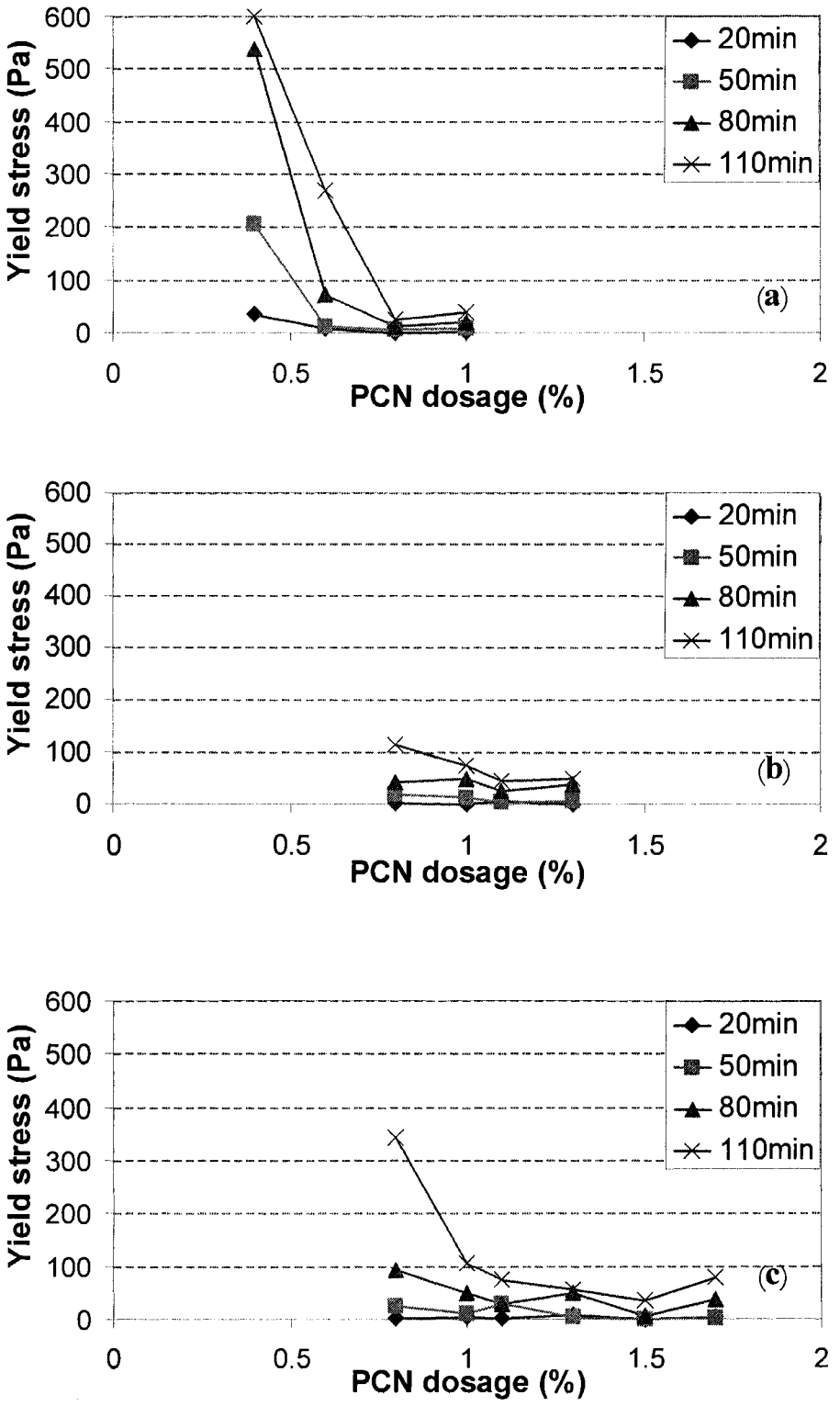

Figure 6.6-Variation of yield stress with time and superplasticizer dosage for concrete mixtures (w/c = 0.38) incorporating PCN [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

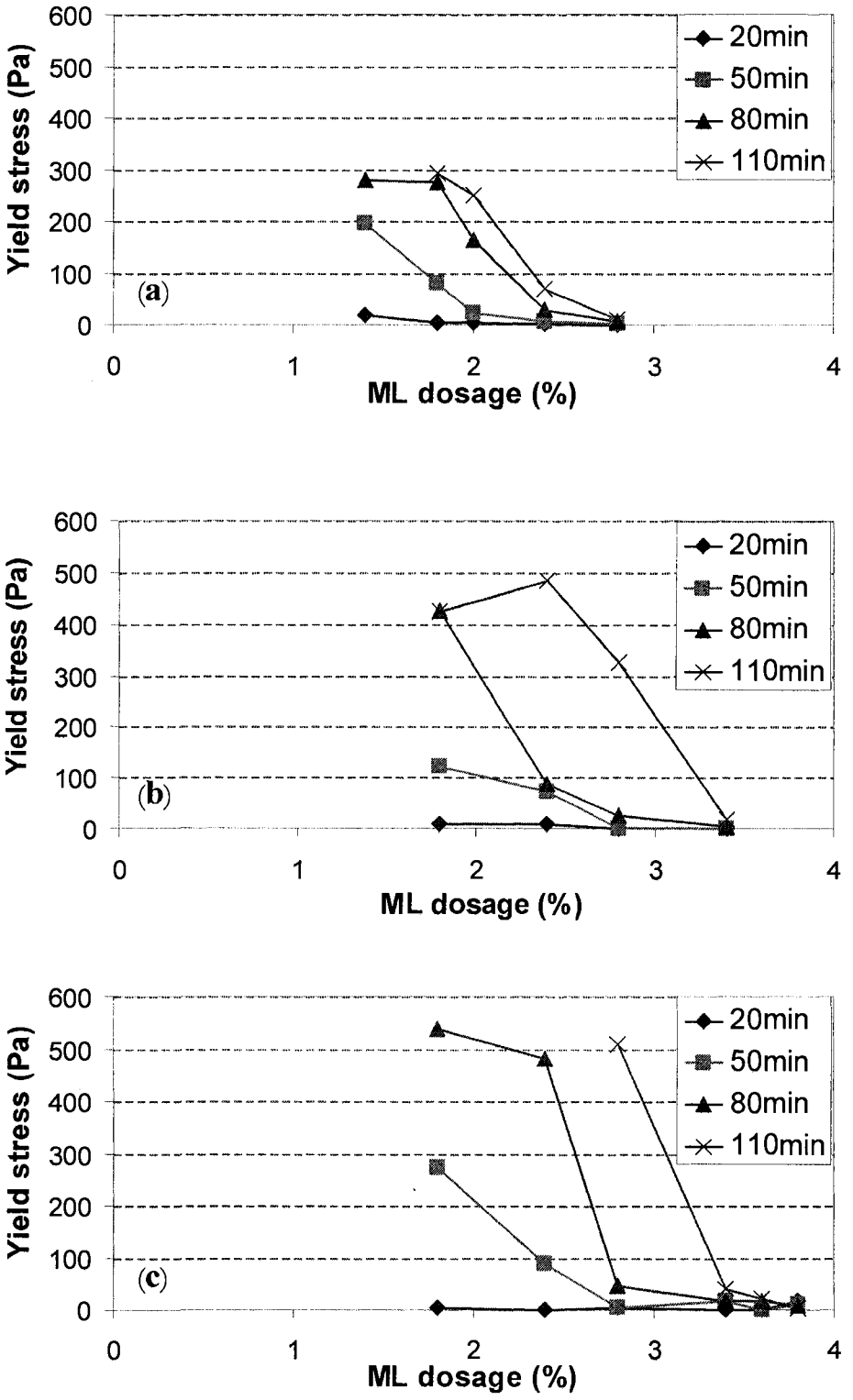

Figure 6.7-Variation of yield stress with time and superplasticizer dosage for concrete mixtures (w/c = 0.38) incorporating ML [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

Figures 6.8(a), 6.8(b), and 6.8(c) illustrate the coupled effects of NS dosage and mixing time on the yield stress of fresh concrete mixtures at three different temperatures (22, 35, and 45 °C). Generally, the yield stress decreased with increasing NS dosage at all temperatures. It can be further observed that the yield stress of concrete at 35 °C and 110 min of mixing time increased when the NS dosage increased from 1.2% to 1.4%. This behaviour for NS has also been reported by others (Ramachandran *et al.* 1997) and it was attributed to the same reason discussed above for ML. It can also be observed that yield stress increased with the increase of the mixing time. The observed saturation dosage was 2% at all test temperatures for up to 80 min of mixing, and it was 2.4% at all test temperatures at 110 min of mixing (Fig. 6.8).

6.3.3 Coupled effects of superplasticizer dosage, mixing time, and temperature on plastic viscosity of concrete mixtures

Figures 6.9(a), 6.9(b), and 6.9(c) present plastic viscosity values for fresh concrete mixtures as a function of time and PCN dosage at 22, 35, and 45 °C, respectively. In general, plastic viscosity increased with time for most concrete mixtures; however, no clear trend could be depicted versus the PCN dosage. For instance, it can be observed that plastic viscosity values for a PCN dosage of 0.4% at 22 °C and mixing time of 80 and 110 min were lower than that at 20 min and 50 min, which is contrary to the regular behaviour observed for the other concrete mixtures. It should be noted that the corresponding yield stress values for this mixture at 80 and 110 min were as high as 550 and 600 Pa, respectively (Fig. 6.6(a)). Moreover, the corresponding slump values were as low as 50 and 40 mm, respectively (Table 6.2). Thus, at these mixing times the mixture became stiff. When concrete stiffens, the torque values required for initiating flow (corresponding to

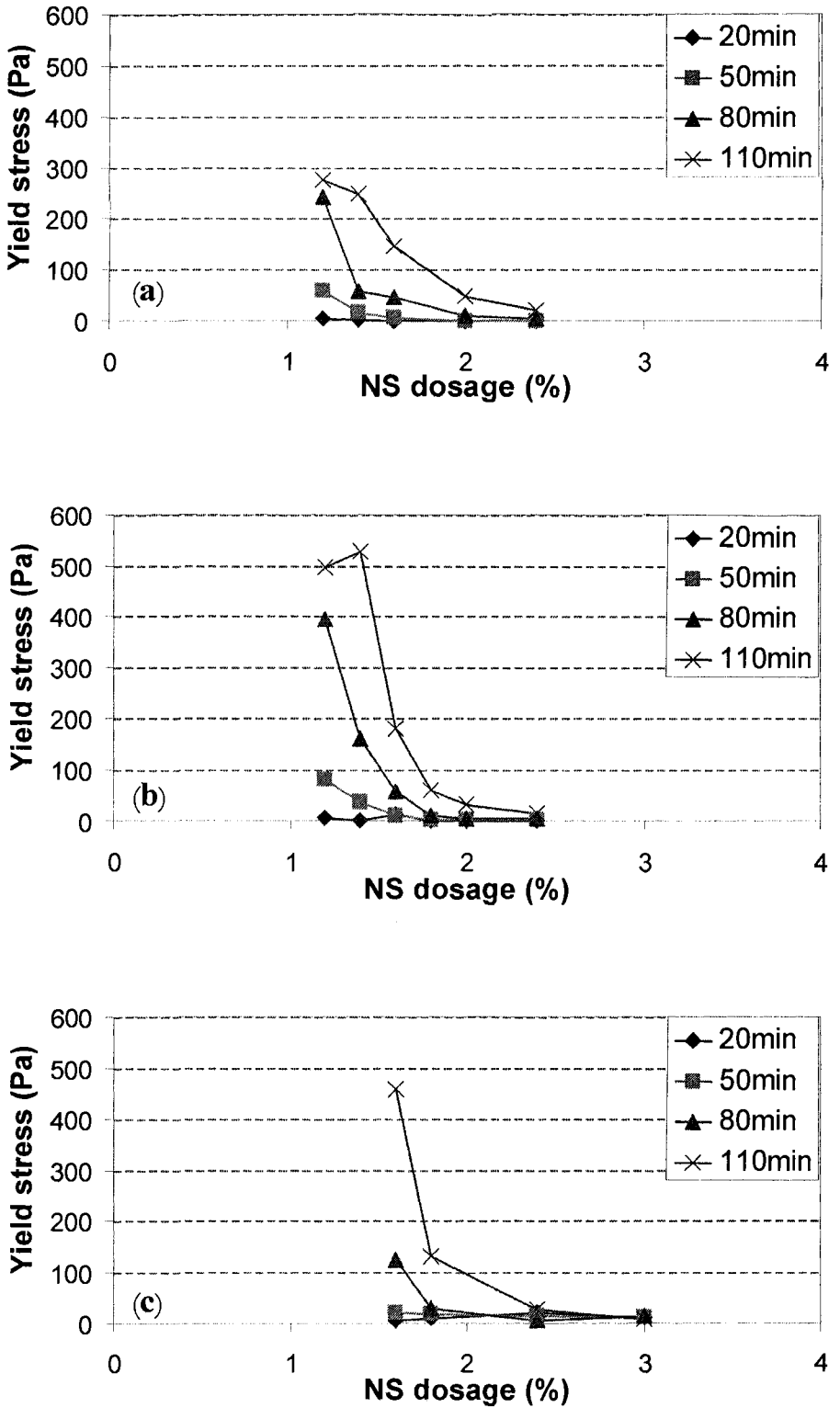

Figure 6.8-Variation of yield stress with time and superplasticizer dosage for concrete mixtures (w/c = 0.38) incorporating NS [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

yield stress) became very high. Since the torque-angular speed curve must pass through such points, the overall slope of this curve is decreased, which is exhibited by a decrease in viscosity. Such a reduction in viscosity is perceived as an artifact and not as a real physical effect (Nehdi *et al.* 1998).

Similar to the case of PCN, no clear trend of plastic viscosity versus ML dosage could be observed at different ambient temperatures and mixing times (Figs. 6.10(a)-6.10(c)). Plastic viscosity increased with the elapsed mixing time. However, some concrete mixtures mixed for 80 and 110 min showed lower viscosity values than that at 20 and 50 min (Figs. 6.10(a)-6.10(c)). Due to the prolonged mixing, a significant slump loss occurred (Table 6.2) and the yield values for these mixtures were high (Figs. 6.7(a)-6.7(c)). The reason behind this behaviour has been already explained. Plastic viscosity for concrete mixtures incorporating NS displayed similar behaviour to that of similar mixtures made with PCN and ML for the different ambient temperatures and mixing times investigated (Figs. 6.11(a)-6.11(c)). As shown in Table 6.2, some concrete mixtures went over time from flowable to stiff consistency. The slump values lower than 200 mm correspond to the conventional slump test, while those higher than 200 mm were measured using the slump flow test. Appendix A shows a summary of the concrete mixtures in this study.

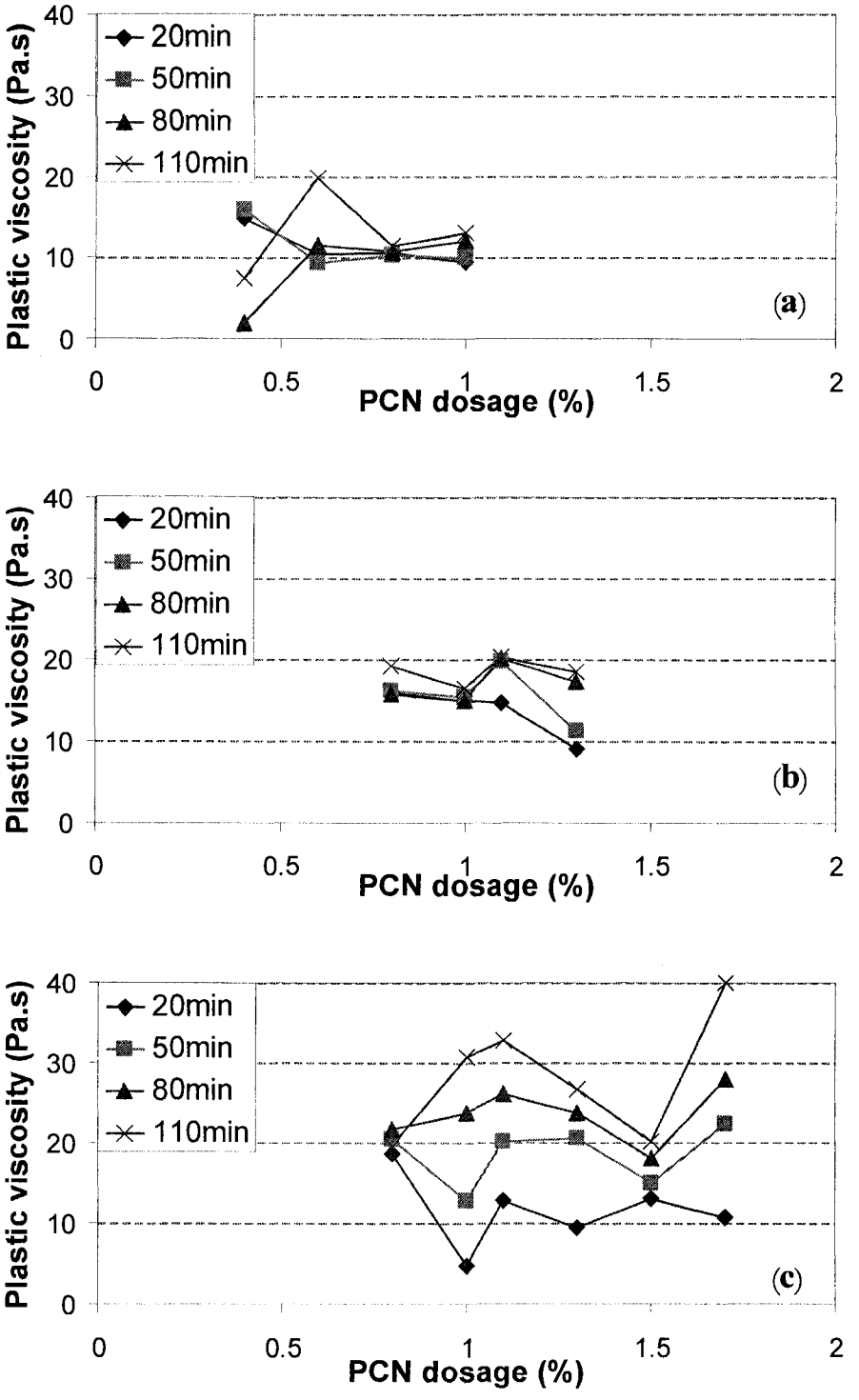

Figure 6.9-Variation of plastic viscosity with time and superplasticizer dosage for concrete mixtures (w/c = 0.38) incorporating PCN [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

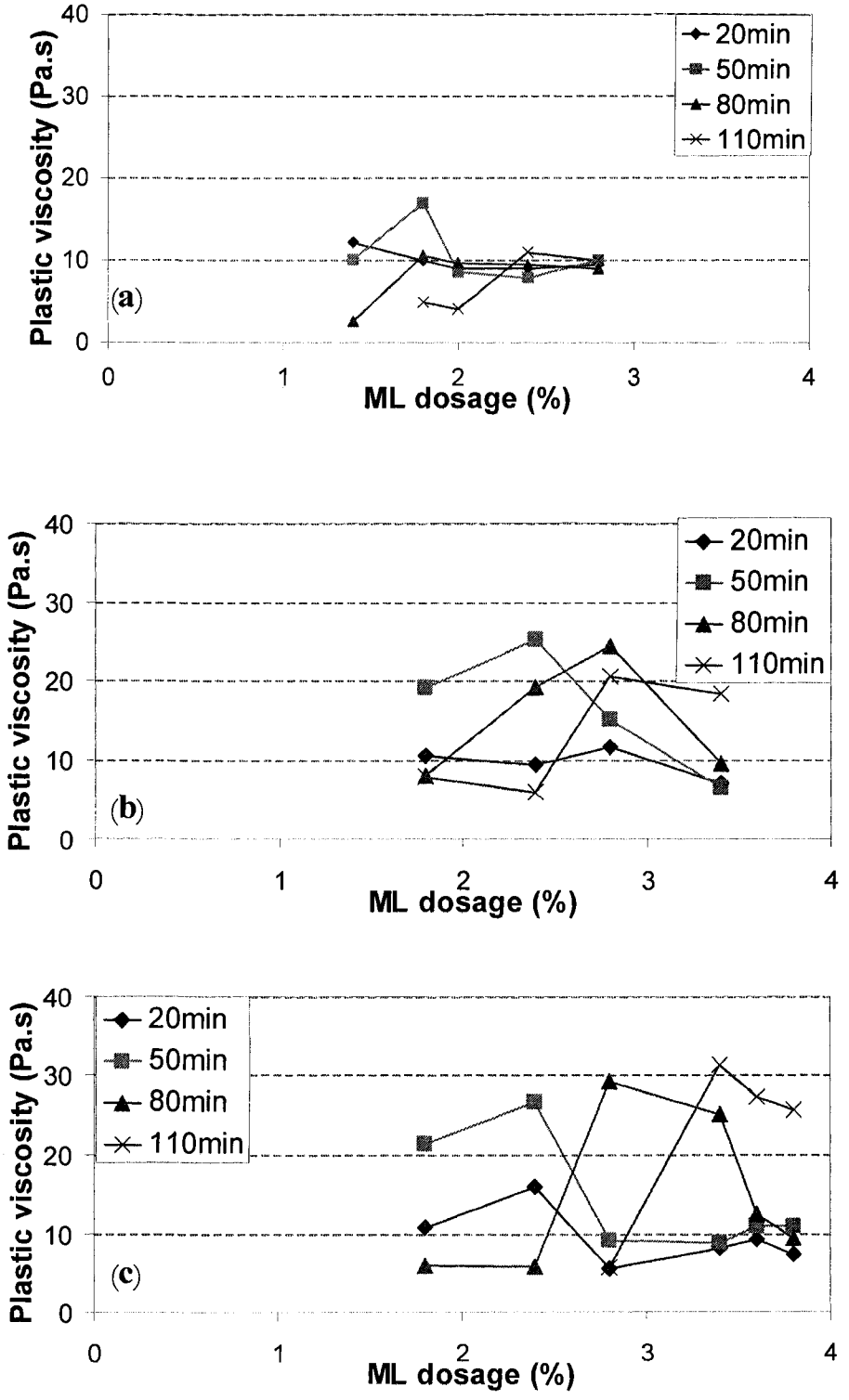

Figure 6.10-Variation of plastic viscosity with time and superplasticizer dosage for concrete mixtures (w/c = 0.38) incorporating ML [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

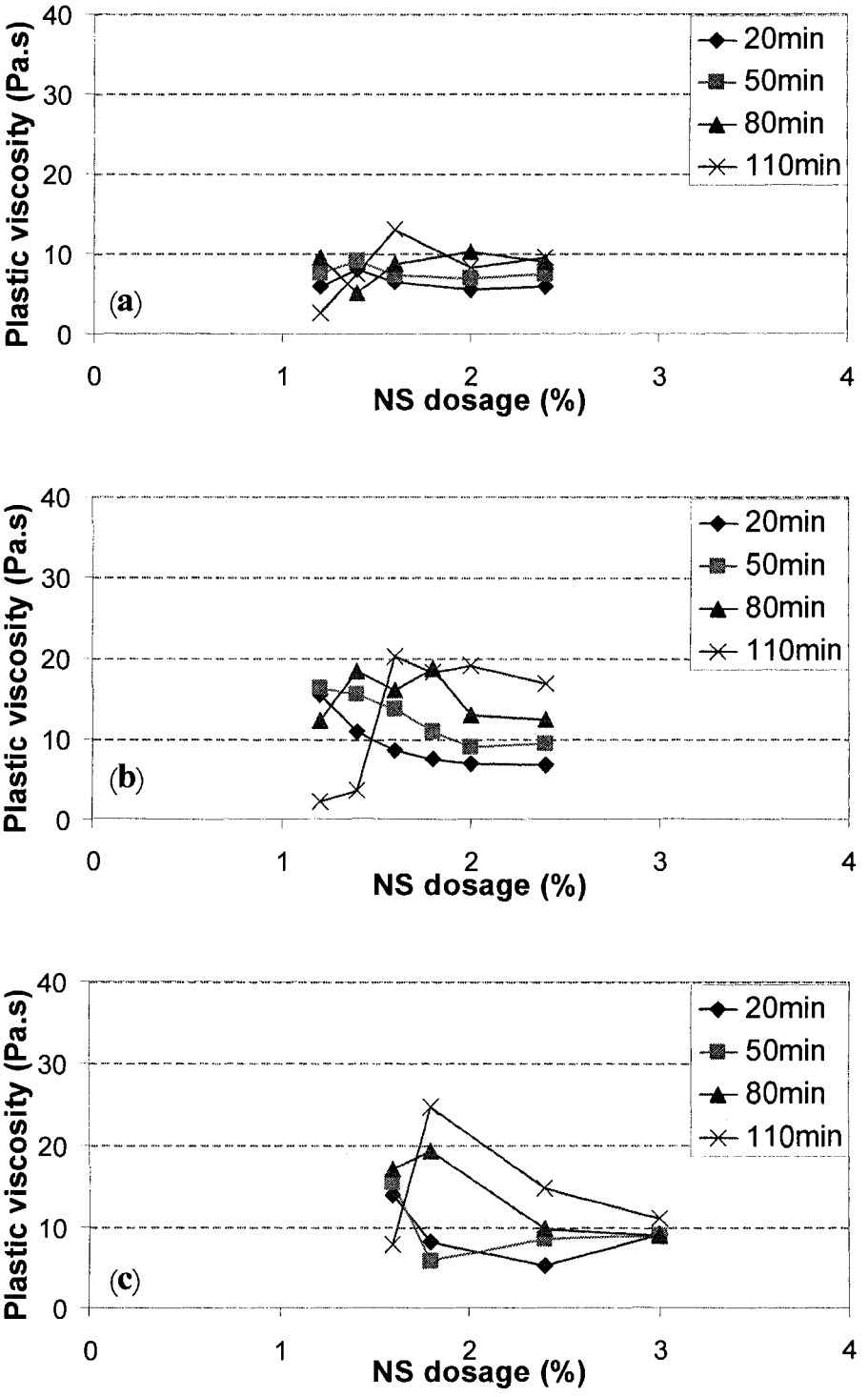

Figure 6.11-Variation of plastic viscosity with time and superplasticizer dosage for concrete mixtures (w/c = 0.38) incorporating NS [(a) at 22 °C, (b) at 35 °C, and (c) at 45 °C].

6.3.4 Discussion

The fresh concrete mixtures investigated in this chapter displayed progressive stiffening with time and temperature as indicated by a decrease in slump (Table 6.2) and an increase in yield stress (Figs. 6.6, 6.7, and 6.8). In the light of the above results, it can be argued that PCN was an effective dispersing agent for concrete under high temperature and prolonged mixing conditions; it reduced the yield stress of concrete mixtures significantly at considerably lower dosages compared to those of ML and NS. Although there is similarity between the behaviour of fresh concrete mixtures incorporating ML and NS, a relatively lower dosage of NS was needed to effectively reduce the yield stress. The difference between the performance of the various admixtures is attributed to the mechanism by which each admixture acts.

The mode of action of PCN involves both electrostatic repulsion and steric stabilization, which gives it a high deflocculating ability. Polycarboxylates consist of complex flexible molecules that wrap around cement particles and keep them separated. This can be effective at a relatively low w/c ratio. As hydration continues, the dispersing effect of polycarboxylates persists owing to its natural side chain and to the controlled adsorption over time that causes the remaining PCN molecules to overlap previously adsorbed ones. By the time the effectiveness of these last molecules ends, the concrete has usually been placed.

On the other hand, the adsorption of ML and NS on cement particles is the main mechanism by which they act (Rixon and Mailvaganam 1999). When ML or NS are added to a concrete mixture, their polymeric particles are adsorbed by cement grains giving them

the same charge. Consequently, cement particles start to repel away from each other and become more free to move (Rixon and Mailvaganam 1999). Over time, the surface charge of the particles diminishes because of the hydration crystals that nucleate on the surface. This causes the hydrating cement particles to flocculate and without further water addition, the concrete becomes no longer workable.

The data presented above allow assessing the relationship between concrete slump and Bingham constants, i. e. yield stress and plastic viscosity. The yield stress values for all concrete mixtures as a function of time and temperature were plotted versus the corresponding slump in Fig. 6.12(a). The slump is inversely correlated with yield stress in a curvilinear relationship and the data was fitted using a logarithmic trendline with a correlation coefficient of $R^2 = 0.90$. Previously published empirical studies have shown a correlation between yield stress and slump. For instance, Ferraris and de Larrard (1998) reported a simple linear relationship between slump and yield stress but slump was recognized by Struble and Chen (2005) to have a negative curvilinear correlation with the yield torque (G) with an exponential fit.

The marked scatter of data points in Fig. 6.12(b) shows the independence of slump and plastic viscosity for the studied concrete mixtures incorporating various admixtures at different ambient temperature and mixing time. Mori and Tanigawa (1990) reported that the slump value was mainly related to yield stress, while no correlation was observed between slump and plastic viscosity. Hu and de Larrard (1996) found that the loss of concrete workability was directly reflected by the increase in yield stress, however, plastic viscosity remained nearly constant. They concluded that the plastic viscosity cannot be

evaluated using the slump test. This is expected since slump characterizes fresh concrete in a rather static condition, while viscosity is a dynamic flow property (Tattersall 1991; and Eirich 1960). After flow has started, i.e. after the yield stress has been overcome, the flow behaviour of concrete is governed by the plastic viscosity. Thus, the different behaviours of two concretes having the same slump is likely due to the different values of plastic viscosity between the two concretes (Ferraris and de Larrard 1998).

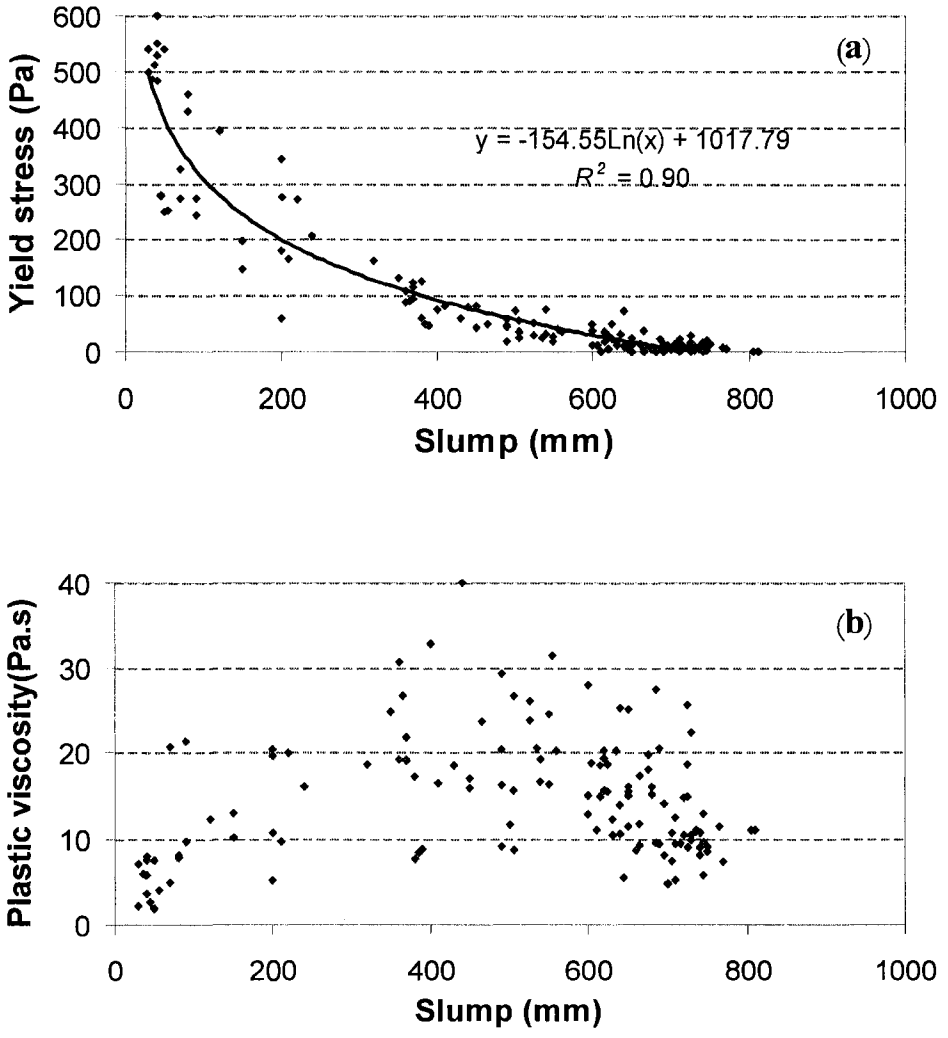

Figure 6.12-Relationship between: (a) yield stress and slump, and (b) plastic viscosity and slump.

The data in this chapter also allow establishing workability control charts for concrete incorporating various admixtures at different ambient temperatures and prolonged mixing time. These charts can provide a tool for the objective assessment of the rheology of fresh concrete, therefore reducing the incidence of errors when the workability of fresh concrete is evaluated solely based on visual examination (Tattersall 1991). Considering the results of Bingham constants (yield stress and plastic viscosity) for various concrete mixtures on one hand, and the associated slump measurements along with visual observation on the other hand, such bands can be created (Fig. 6.13). In Fig. 6.13(a) yield stress was plotted versus plastic viscosity for all mixtures incorporating the three admixtures investigated and tested at different ambient temperatures and mixing times. Moreover, the segregation index measured by the rheometer for each mixture was recorded and compared to a visual rating of segregation.

As shown in Fig. 6.13(a), concrete mixtures were classified as too fluid, satisfactory, marginally fluid, or low fluidity based on the factors already discussed. Concrete was considered too fluid when its slump flow was over 600 mm with observed segregation. It was realized that too fluid concrete had a segregation index ranging from 25 to 50%. The concrete mixtures with a slump flow higher than 450 mm and without any observed segregation have been classified as satisfactory. The segregation index for such mixtures ranged from 12 to 25%. The marginally fluid concrete mixtures had a slump between 120 mm to 450 mm with a segregation index from 5 to 15%. Such mixtures have shown good stability. Finally, the low fluidity mixtures had a slump below 120 mm and a segregation index lower than 5%.

Data points corresponding to low fluidity and marginally fluid concrete mixtures fell into two zones namely, the low fluidity zone and marginally fluid zone (Fig. 6.13(a)), with boundaries enveloping the data points of low fluidity and marginally fluid concrete mixtures investigated. It can be observed from the figure that beyond a certain value of yield stress, plastic viscosity decreased with the increase of yield stress due to the decrease in the slope of the torque-rotational speed curves for stiff mixtures explained earlier. Fluidity decreased significantly beyond this critical level of yield stress. It could be argued that this threshold value represents the boundary between satisfactory and marginally fluid zones. Below this critical level, plastic viscosity was positively correlated with yield stress. This is in agreement with the previous observation for concrete mixtures having low workability, where it was found that plastic viscosity artificially decreased with time elapsed, while yield stress increased.

Figure 6.13(b) shows only the data points corresponding to satisfactory concrete mixtures. Therefore, a different scale of yield stress was used in Fig. 6.13(b). A workability box, in which good workability concrete mixtures fell, was determined (Fig. 6.13(b)). Moreover, the data points were classified based on the ambient temperature corresponding to each point. The satisfactory points which lay outside the workability box that was surrounded by too fluid or marginally fluid data points were excluded. This workability box represents the values of plastic viscosity and yield stress combinations needed to have concrete mixtures with adequate workability and stability. Points that fell below this box were for concrete mixtures susceptible to segregation, while points that fell higher than the box were for concrete mixtures having low workability (Fig. 6.13(b)).

Three sub zones could be further recognized in this workability box. Zone (I) was for data points at 22 °C, zone (II) was for points at 35 °C, and zone (III) was for points at 45 °C (Fig. 6.13(b)). As shown in the figure, points corresponding to 22 °C were located mainly in the left bottom corner of the box (zone I), points corresponding to 35 °C were located between the two dashed lines (zone II), and points corresponding to 45 °C were located below and around the diagonal of the box (zone III).

These findings offer a rational basis for the design of concrete mixtures to meet workability requirements under various temperatures and mixing times. Attention should be paid to keeping plastic viscosity values as low as possible in order to ensure adequate flow. Similarly, a low yield stress will ensure that concrete is workable; however, concrete with very low yield stress is more susceptible to segregation. Based on the abovementioned discussion, it could be argued that it would be possible to computerize the entire process so that values of yield stress and plastic viscosity obtained automatically would be compared with specified values and then, on the basis of the stored information, any necessary corrective actions would be performed.

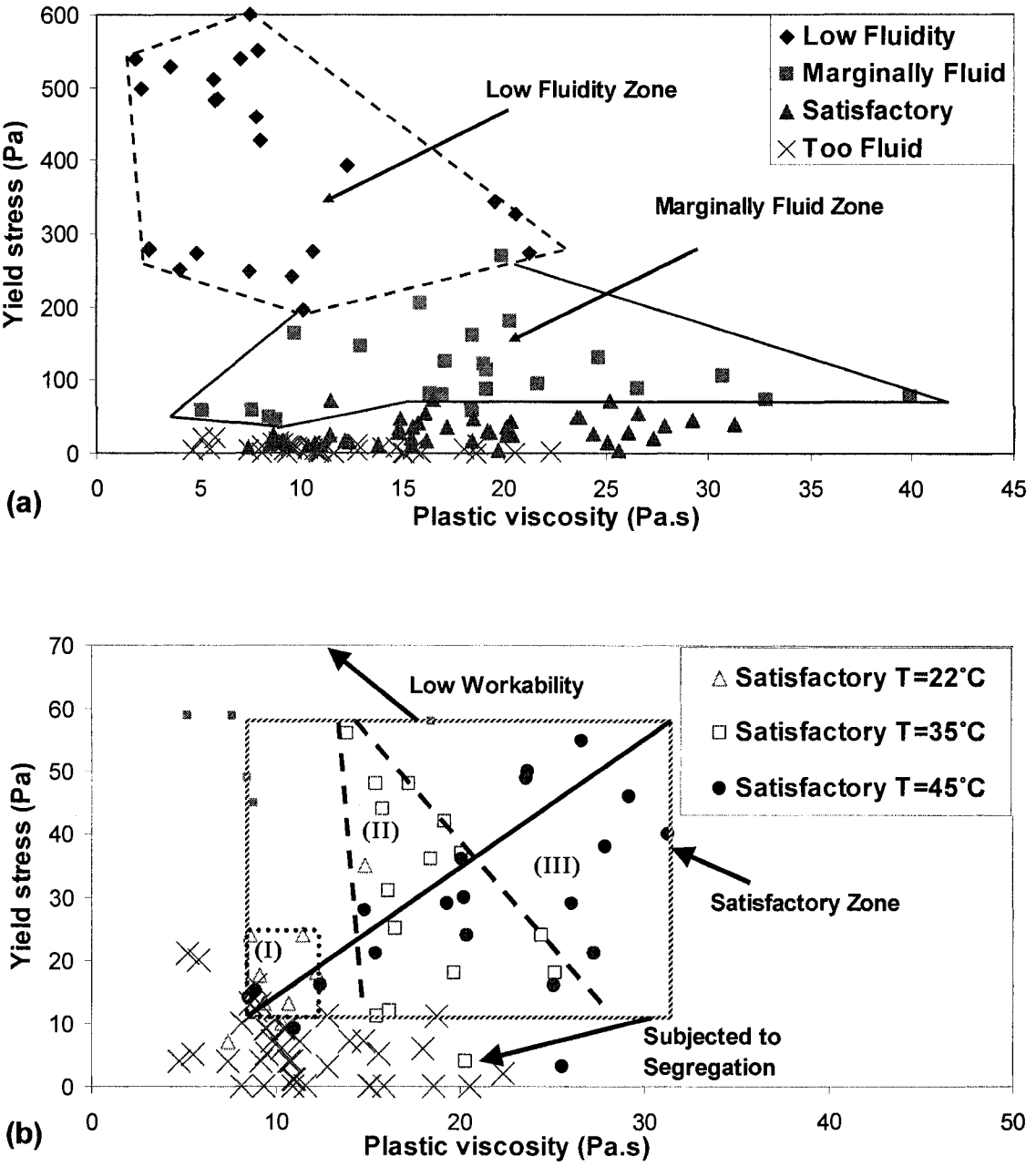

Figure 6.13-Plot of plastic viscosity versus yield stress for all concrete mixtures tested, showing suggested control charts, (a) for low fluidity and marginally fluid mixtures, (b) for satisfactory mixtures.

In summary, these results show that the rheological behaviour of fresh concrete under high temperature and prolonged mixing time is related to both the yield value and plastic viscosity. The results suggest that using only a simple empirical method, such as the slump test, is not adequate to fully characterize fresh concrete under prolonged mixing time and high temperature. Therefore, tests using the multiple-point principle are capable of giving the necessary information to design and control concrete mixtures under such conditions.

The workability control charts created in this chapter give an indication of the yield stress and plastic viscosity values needed for a particular job within the temperature range from 22 to 45 ^{o}C and hauling time up to 110 min. However, it should be emphasized that these control charts are only valid for the types of materials used in this investigation and therefore, further research should be conducted considering other types of materials in order to create more generalized control charts.

Table 6.2-Measured slump in mm for all concrete mixtures

Superplasticizer	Temperature °C	22				35				45			
	Dosage (%) \ Time (min)	20	50	80	110	20	50	80	110	20	50	80	110
PCN	0.4	615	240	50	40	–	–	–	–	–	–	–	–
	0.6	730	690	500)	220	–	–	–	–	–	–	–	–
	0.8	750	720	705	650	680	550	450	370	725	535	370	200
	1.0	700	650	605	535	650	630	600	540	640	600	465	360
	1.1	–	–	–	–	720	675	620	560	745	635	525	400
	1.3	–	–	–	–	625	590	555	530	745	690	525	505
	1.5	–	–	–	–	–	–	–	–	750	735	675	560
	1.7	–	–	–	–	–	–	–	–	740	730	600	440
ML	1.4	630	150	45	0.5	–	–	–	–	–	–	–	–
	1.8	620	450	280	70	640	370	80	40	735	90	30	0.5
	2.0	750	505	210	55	–	–	–	–	–	–	–	–
	2.4	745	600	500	370	715	640	360	35	650	365	40	5
	2.8	720	650	635	610	665	680	550	70	645	630	490	38
	3.4	–	–	–	–	705	705	685	615	740	725	650	555
	3.6	–	–	–	–	–	–	–	–	710	805	710	685
	3.8	–	–	–	–	–	–	–	–	770	810	745	725
NS	1.2	730	380	90	45	620	410	120	30	–	–	–	–
	1.4	700	490	200	50	610	505	190	40	–	–	–	–
	1.6	740	705	390	150	660	640	490	140	695	625	380	80
	1.8	735	723	610	450	740	680	605	430	745	670	590	350
	2	735	740	630	390	680	660	650	540	–	–	–	–
	2.4	745	740	710	660	690	670	660	620	710	750	730	725
	3	–	–	–	–	–	–	–	–	750	740	740	735

NOTE: Slump<200 mm is conventional slump and slump>200 is slump flow.

6.4 Conclusions

The assessment of the workability of fresh concrete mixtures in terms of the Bingham parameters, namely the yield stress and plastic viscosity, can provide a powerful tool for the control of concrete production in hot weather environments. The coupled effects of ambient temperature and mixing time on the evolution of the rheological properties of continuously agitated concrete mixtures incorporating polycarboxylate-, melamine sulfonate-, and naphthalene sulfonate-based high-range water reducing admixtures were investigated in this chapter. The following conclusions can be drawn based on the comprehensive set of data presented in this investigation:

- Shear thinning behaviour was identified for fresh concrete mixtures incorporating PCN or ML under prolonged mixing and high temperature.
- The rheological behaviour of fresh concrete mixtures incorporating NS and subjected to prolonged mixing at high temperature shifted from shear thinning to shear thickening behaviour when the NS dosage exceeded the saturation level.
- The increase of the PCN dosage up to the saturation decreased the yield stress however; beyond the saturation dosage, yield stress increased.
- The saturation dosage for fresh concrete mixtures incorporating NS and ML can be identified when no or a marginal decrease in yield stress was achieved beyond such a dosage.
- The saturation dosage for fresh concrete mixtures incorporating PCN varied with temperature.
- The saturation dosage for fresh concrete mixtures incorporating ML or NS varied with temperature and mixing time.

- Plastic viscosity did not show any evident trend with the change in admixture dosage.
- PCN was found to be an effective dispersing agent since it was able to achieve low yield stress values at relatively low dosages. However, at the saturation dosage, ML and NS were able to drop the yield stress values to lower levels than that achieved by PCN.
- The results show that PCN should be used at a dosage close to the saturation level to ensure adequate rheological behaviour of concrete at high temperature and prolonged mixing time. PCN dosages beyond the saturation were found to reduce workability.
- The slump had an inverse correlation with the yield stress in a logarithmic curvilinear mode, while no correlation was found between slump and plastic viscosity.
- The plots of yield stress versus plastic viscosity for all concrete mixtures investigated allowed to establish workability control charts for concreting in hot environments. These charts could provide a means for the objective assessment of workability, allowing reducing the incidence of errors when concrete mixtures in hot environments are merely judged based on personal experience and visual inspection, or on empirical tests such as the slump test.
- It should be emphasized that the present results are applicable only for the particular superplasticizers and materials used in this study and need to be extended for other superplasticizers, even from the same category, and other cements and aggregates types and sources using further experimental work.

6.5 References

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Chapter 7

EFFECTS OF HIGH TEMPERATURE AND PROLONGED MIXING TIME ON SLUMP LOSS AND COMPRESSIVE STRENGTH OF CONCRETE INCORPORATING VARIOUS SUPERPLASTICIZERS*

7.1 Introduction

The quality of concrete can be adversely affected during mixing, placing, and curing at high temperatures (Abbasi and Al-Tayyib 1983). The rate of water evaporation increases at high temperature resulting in a higher rate of slump loss. If a long hauling distance is required, concrete might reach the construction site having a low workability. The quality control engineer may reject such unworkable concrete. In hot weather countries, large quantities of concrete are being rejected each summer due to this problem causing project delays, and at times costly legal problems. To compensate for the slump loss during concrete hauling, more mixing water can be added. However, the compressive strength of concrete is greatly influenced by the water/cement ratio (w/c); high (w/c) was found to be the main cause for reducing the compressive strength of concrete in the field (Abbasi *et al.* 1992). The ideal ambient temperature for placing concrete ranges from 20 to 23 °C (El-Rayyes1990). The American Concrete Institute (ACI) Specifications for Hot Weather Concreting state that the ambient temperature at the concrete construction site should not

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exceed 27 °C (ACI 305.1-06). Thus, it is usually intended to carry out concreting work during time periods when the temperature is moderate. However, this practice is not always possible, especially for large-scale projects requiring continuous concreting. Hence, special precautions must be taken during high temperature periods of the day, which eventually adds extra costs. Even if adequate precautions were taken for the concrete to arrive at the construction site with good workability, curing under high temperatures, especially during the first 24 hours, can be problematic.

For instance, Barners *et al.* (1977) found that the curing temperature of concrete during the first 24 hours after casting is important. Their results showed that concrete specimens initially cured at high temperature (35 and 38 °C) exhibited lower strength at 7 and 28 days compared to that of similar specimens exposed to an early-age curing temperature below 30 °C. Ortiz *et al.* (2005) investigated the compressive strength of concrete mixed at different time periods of the hottest day of the summer of year 2000 in Spain. The reference mixture was mixed and early cured at a constant temperature of 20 °C, while the other mixtures were mixed and early cured in a climatic chamber. The thermal profile of the chamber was programmed according to the maximum and minimum temperatures recorded in the day investigated. The maximum temperature of that day was 38 °C, which was reached around noontime, while the minimum temperature was 23 °C recorded around midnight. The concrete mixing was performed at five different hours of that day including 10:00, 11:30, 13:00, 14:30, and 17:30. After mixing and casting, concrete specimens were cured for the first 24 hours in the climatic chamber, then demolded and stored in a curing room at a temperature of 20 °C and relative humidity of 95% until the date of compressive strength testing (7 or 28 days). Ortiz *et al.* (2005) found

that the compressive strength of concrete was very susceptible to the ambient temperature during the first 24 hours after casting; the concrete mixed in the evening had higher compressive strength at all ages than that mixed in the late morning or noontime. Their results also showed that the reference mixture had a higher compressive strength than that of the other mixtures. They attributed this behaviour to the "crossover effect", whereby the early-age compressive strength of concrete cured at high temperature during the first 24 hours, is higher than that initially cured at normal temperature, but the later-age compressive strength is lower Ortiz *et al.* (2005).

Ravina and Soroka (1994) investigated the coupled effects of temperature and prolonged mixing time on the compressive strength of concrete. Concrete was subjected to prolonged mixing for up to 180 min under the temperatures of 21 or 32 °C. After mixing, the concrete was cured for 24 hours at the same temperature of mixing, then in a standard fog-room at a temperature of 21 °C for the rest of the curing period. Water reducing and retarding admixtures were used. It was found that water reducing and retarding admixtures had speeded up, rather than delayed, the rate of slump loss. It was reported that the rise of temperature from 21 to 32 °C had accelerated the slump loss and increased the water demand. The compressive strength was found to increase linearly with the mixing time.

In practice, concrete is mixed for a wide range of time periods and also at different temperatures. Hence, the knowledge of the coupled effects of the mixing time and ambient temperature on the early-age behaviour of concrete is of great importance. The main objective of the present chapter is to investigate such coupled effects of the ambient temperature and mixing duration on the slump loss and compressive strength of concrete

incorporating polycarboxylate-based (PCN), melamine sulfonate-based (ML), and naphthalene sulfonate-based (NS) superplasticizers. The ambient temperature ranged from 22 to 45 °C, thus, covering temperatures encountered during summer seasons in hot weather countries. The concrete was continuously agitated for up to 110 min. The dosages of superplasticizers were chosen based on the research conducted by Nehdi and Al-Martini (2007) on cement pastes incorporating similar superplasticizers. The ultimate goal of the current research program was to explore the feasibility of producing concrete having good workability and strength at high ambient temperatures and prolonged mixing time.

7.2 Experimental Program

The mixing of concrete was performed at controlled temperatures (22, 35 and 45 °C). The reference temperature was chosen in the range of 20 to 23 °C to simulate moderate climates. In the present research, concrete was subjected to a prolonged mixing time under different ambient temperatures to simulate the hauling of concrete in a high temperature environment.

7.2.1 Materials and mixture proportions

Ordinary portland cement (CSA Type 10), coarse (nominal size of 10 mm) washed natural pea gravel, and natural sand were used as in chapter 6. The absolute volume method described by the ACI Committee 211 (Standard Practice for Selecting Proportions for Normal, Heavyweight and Mass Concrete) (ACI 211.2-98) was used to calculate the concrete mixture proportions. All mixtures were made with 475 kg/m^3 of cement, 895 kg/m^3 of fine aggregate and 800 kg/m^3 of coarse aggregate with no air entrainment. The water to cement ratio was constant for all mixtures (w/c = 0.38). The following liquid

superplasticizers were used in this study: 1- A new generation of polycarboxylate-based superplasticizer (PCN). The dosage of PCN ranged from 0.8% to 1.7% by mass of cement. 2- Melamine sulfonate-based superplasticizer (ML). The dosage of ML ranged from 1.8% to 3.4% by mass of cement. 3- Naphthalene sulfonate-based superplasticizer (NS). The dosage of NS used in the study ranged from 1.2% to 2.4% by mass of cement.

7.2.2 Preparation and testing of specimens

The coarse and fine aggregates along with the cement powder were placed inside an automated walk-in environmental chamber for a sufficient time period before mixing to adjust their temperatures to the required level. The batches of concrete were prepared according to the following procedure: the fine and coarse aggregates were introduced into the drum-mixer and dry mixed for one minute. One third of the mixing water was added while the mixer was running followed by adding the cement powder. Mixing continued for another one minute and the second third of the mixing water was added and mixing continued for three minutes. The remaining water, to which one half of the total dosage of superplasticizer had been previously injected and uniformly stirred, was then added and mixing continued for one minute. The remaining amount of liquid superplasticizer was subsequently added uniformly into the concrete batch while mixing for 14 minutes. Using a drum mixer, the concrete was continuously agitated for up to 110 minutes in order to simulate the continuous mixing of concrete in a truck mixer during its hauling to a construction site. The procedure used for mixing corresponds to the ASTM C 685-02 guidelines (Standard Test for Concrete Made by Continuous Mixing) and that reported by Ferraris and de Larrard (1997) for concretes incorporating superplasticizers. The slump test was conducted in accordance with the ASTM C 143-95 guidelines (Standard Test for

Slump of Hydraulic Cement Concrete). Mixing and preparation of test specimens took place in the lab environment (22 °C) for moderate temperature concreting, and in the temperature controlled walk-in environmental chamber (at 35 and 45 °C) to simulate hot weather concreting. Specimens for compressive strength were taken from the mixer after 20, 50, 80, and 110 minutes of mixing, and the slump test was conducted before taking each sample.

Immediately after the concrete had been cast and compacted, specimens were covered with plastic lids to prevent water evaporation and remained in the same environment of mixing for 24 hours. Subsequently, specimens were demolded and stored in a standard fog-room at a constant temperature of 22 °C and relative humidity of 95% until the date of compressive strength testing.

The compressive strength was determined on 100×200-mm cylinders at ages of 12 hours, 1, 3, 7, and 28 days. The 12 hours, 1 and 3-days compressive strengths were measured to study the effect of high temperature and prolonged mixing on the early-age compressive strength of concrete. Khan *et al.* (1995) reported that the early-age compressive strength behaviour of concrete can be depicted during the first 3 days after casting. The reported values of compressive strength are the averages of three replicate concrete specimens for each mixture at each testing date.

7.3 Results and Discussion

7.3.1 Effect of temperature and mixing time on slump loss of concrete incorporating various superplasticizers

The combined effects of temperature and mixing time on the slump loss of concrete mixtures incorporating different superplasticizers are illustrated in Figs. 7.1, 7.2, and 7.3. The dosages of superplasticizers in this figure are 0.8% and 1.0% for PCN, 2.4% and 2.8% for ML, and 1.6% and 1.8% for NS by mass of cement.

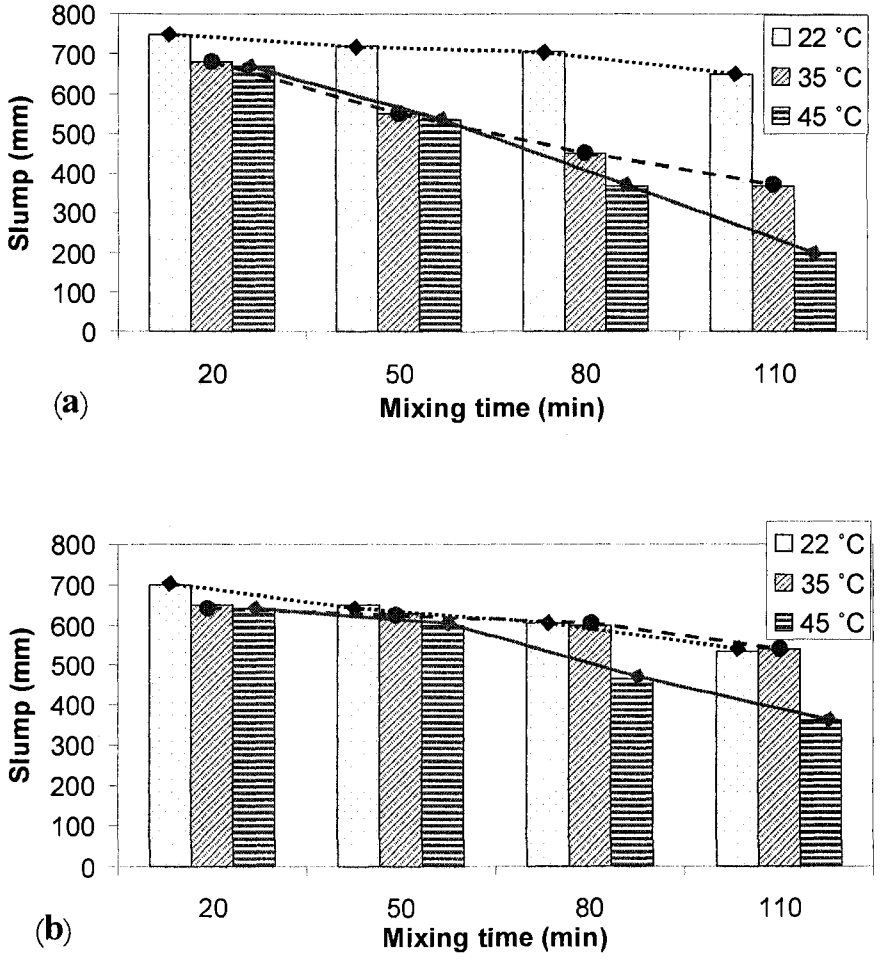

Figure 7.1-Effect of PCN on the slump loss of concrete mixtures subjected to various mixing times and temperatures: [at (a) 0.8% and (b) 1.0%].

The concrete mixtures incorporating these superplasticizer dosages were selected because they had similar initial slump flow at a temperature of 22 °C and a mixing time of 20 min (Figs. 7.1, 7.2, and 7.3), which allowed comparing the effects of the various superplasticizers on concrete slump loss. It was reported elsewhere that the slump loss is largely a function of the initial slump value, and that the higher the initial slump, the greater is the slump loss (Meyer and Perenchio 1979).

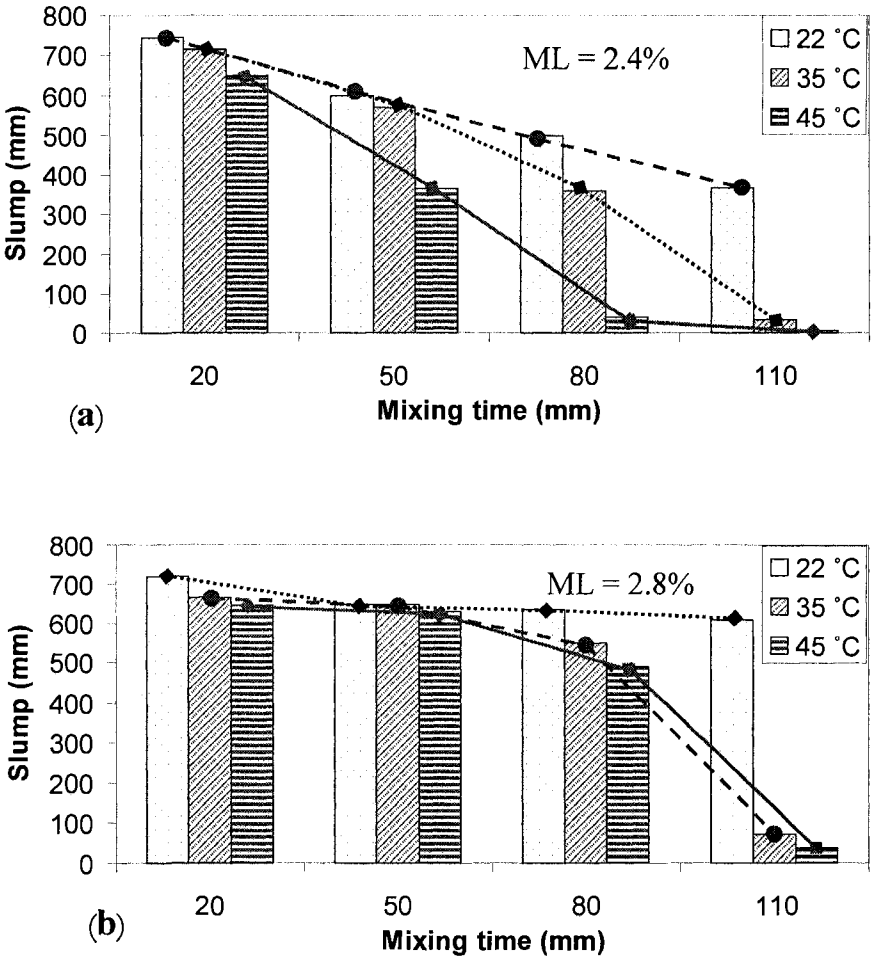

Figure 7.2-Effect of ML on the slump loss of concrete mixtures subjected to various mixing times and temperatures: [at (a) 2.4% and (b) 2.8%].

As shown in Figs. 7.1, 7.2, and 7.3, some concrete mixtures went over time from flowable to stiff consistency. The slump values lower than 200 mm correspond to the conventional slump test, while those higher than 200 mm were measured using the slump flow test.

The top of columns in Figs. 7.1, 7.2, and 7.3 were connected with lines for easier visualization of the rate of slump loss. The light dotted lines correspond to results at 22 °C, the thick dotted lines are for results at 35 °C, and the solid lines are for results at 45 °C. It can be observed in Fig. 7.1(a) that the slump flow of concrete made with PCN decreased with time in a quasi linear manner at all temperatures tested. As expected, the higher the temperature, the greater was the rate of slump loss (Fig. 7.1(a)). At a higher dosage of 1.0%, PCN retained higher slump flow over time even at high temperature; but the rate of slump loss was higher at the higher temperature (Fig. 7.1(b)). The rate of slump loss for concrete made with 2.4% ML increased at higher temperature (Fig. 7.2(a)). Likewise, at higher dosage (2.8%), ML better retained slump at all temperatures (Fig. 7.2(b)). Furthermore, concrete made with ML showed a higher rate of slump loss at high temperatures than that of similar concrete incorporating PCN.

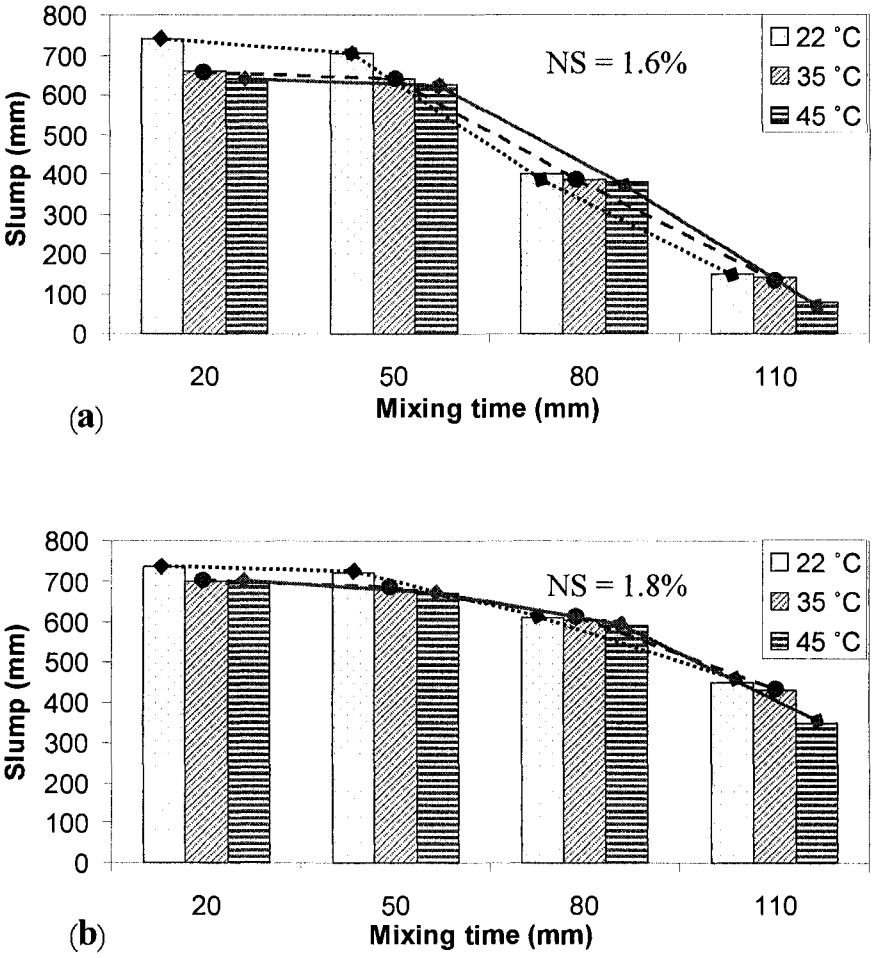

Figure 7.3-Effect of NS on the slump loss of concrete mixtures subjected to various mixing times and temperatures: [at (a) 1.6% and (b) 1.8%].

In comparison with the other superplasticizers, NS seemed to better retain slump when concrete was mixed for up to 50 min at high temperature (Figs. 7.3(a) and 7.3(b)). However, after 50 min, the slump of concrete made with 1.6% NS decreased sharply (Fig. 7.3(a)). At a higher dosage of 1.8%, the rate of slump loss after 50 min was relatively lower (Fig. 7.3(b)). It can be further observed in Figs. 7.3(a) and 7.3(b) that concrete made with NS and mixed for more than 50 min at moderate temperature experienced a higher slump loss than that of concrete made with PCN. Hence, special attention should be taken when

concrete made with NS superplasticizers is subjected to prolonged mixing, even at moderate temperature. This can become more critical in the case of cement-superplasticizer compatibility problems, which is beyond the scope of this chapter.

7.3.2 Effect of mixing time on compressive strength

Figure 7.4 illustrates the compressive strength values at different ages for cement mixture incorporating 0.8% PCN, 2.4% ML, and 1.6% NS made and initially cured at 22 °C and different curing ages for concrete mixtures. As expected, the compressive strength generally increased linearly with increased mixing time for all superplasticizers used. This trend has also been reported by Ravina and Soroka (1994). It can be observed that the compressive strength of concrete made with ML exhibited the highest rate of strength increase due to prolonged mixing, followed by that of concrete made with NS and PCN, respectively (Figs. 7.4(a), 7.4(b), 7.4(c)). This is probably due to the fact that prolonged mixing mitigated set-retardation effects, caused by the relatively high dosage of ML, and to less extent NS.

The relation between the mixing time and compressive strength at high temperatures (35 and 45 °C) also followed a linear trend. For the sake of brevity, only the slopes of the regression lines along with their coefficients of correlation are presented in Table 7.1. Again, the strength curves for concrete made with ML generally exhibited higher slopes than that of concrete made with the other superplasticizers. Based on the limited results of this study, it seems that a prolonged mixing time is particularly beneficial for the compressive strength gain of concrete mixtures incorporating a high dosage of melamine-sulfonate superplasticizers.

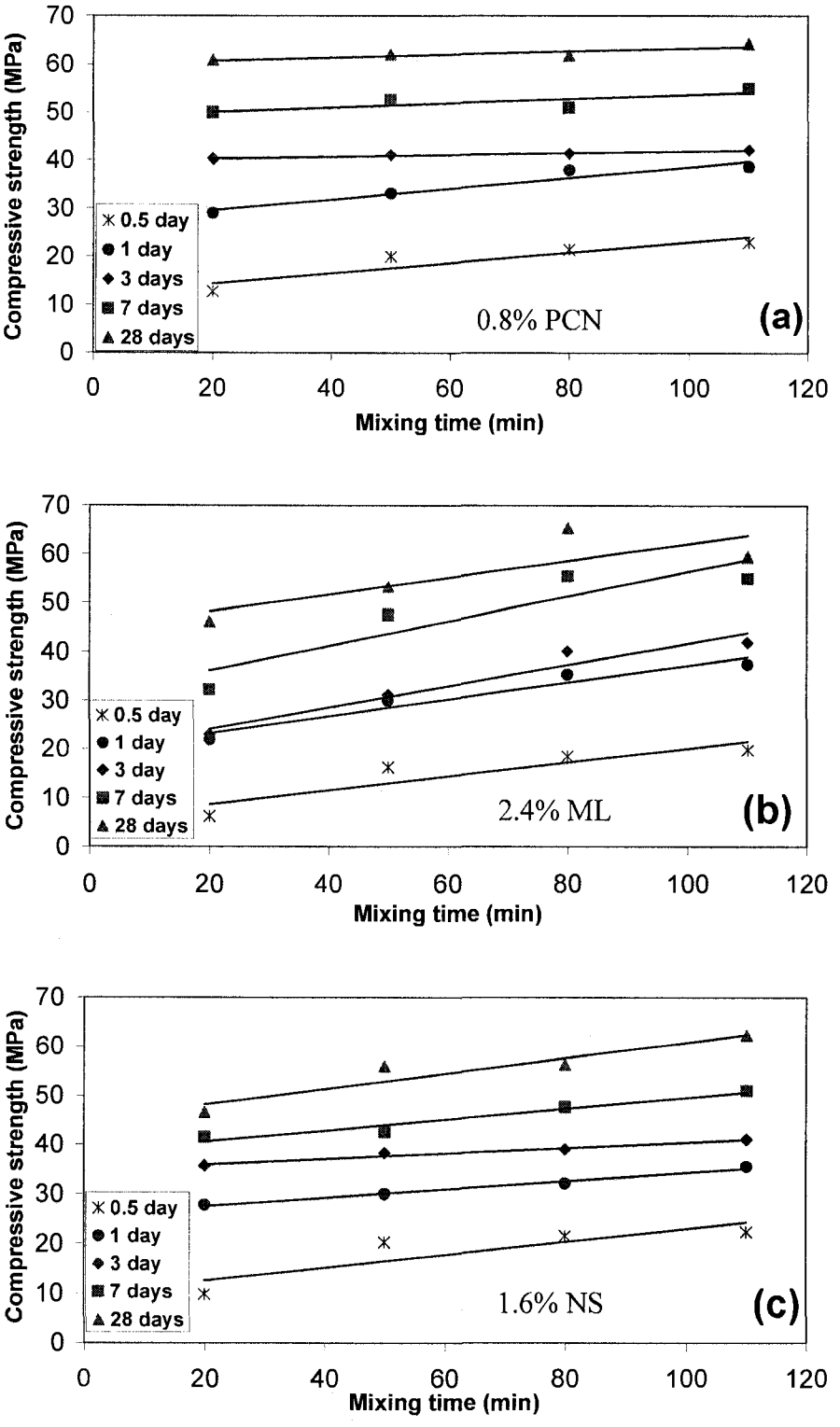

Figure 7.4-Relation between mixing time and compressive strength at different ages for concrete made at 22 °C with, (a) 0.8% PCN, (b) 2.4% ML, and (c) 1.6% NS.

Table 7.1-Slope values of regression lines for compressive strength versus mixing time data and their coefficients of correlation

Temperature	Superplasticizer	Age, days									
		0.5		1		3		7		28	
		Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2
35 °C	0.8% PCN	0.082	0.90	0.147	0.99	0.059	0.80	0.139	0.90	0.062	0.70
	2.4% ML	0.120	0.82	0.160	0.82	0.087	0.98	0.124	0.81	0.184	0.91
	1.6% NS	0.170	0.89	0.065	0.89	0.095	0.80	0.081	0.84	0.161	0.96
45 °C	0.8% PCN	0.110	0.92	0.080	0.90	0.072	0.88	0.018	0.70	0.014	0.70
	2.4% ML	0.140	0.90	0.170	0.81	0.255	0.84	0.225	0.78	0.245	0.97
	1.6% NS	0.086	0.98	0.110	0.83	0.126	0.88	0.130	0.97	0.171	0.82

7.3.3 Effect of temperature on compressive strength

The effect of temperature on the compressive strength of concrete mixtures incorporating 0.8% PCN, 2.4% ML, and 1.6% NS is plotted in Figs. 7.5 and 7.6. Relative values for each mixture made and early cured at 22, 35, and 45 °C are given in terms of that at 22 °C, i. e. strength ratio = (compressive strength at specific temperature/compressive strength at 22 °C). Data in Fig. 7.5(a) correspond to mixtures cured for 12 hours, and data in Figs. 7.5(b), 7.5(c), 7.6(a) and 7.6(b) are for mixtures cured for 1, 3, 7 and 28 days, respectively. A different scale is used in Fig. 7.5(a) presenting results for the very early-age compressive strength (12 hours) due to the much higher relative strength values at such a very early age.

Figures 7.5(a), 7.5(b) and 7.5(c) show that concrete subjected to high temperature (35 °C and 45 °C) during mixing and early-age curing attained greater early-age strength than that subjected to a moderate temperature (22 °C). Such an effect could be attributed to the well known acceleration of hydration reactions due to higher initial temperature after concrete placing. It can be further observed that the relative strength values for the very early-age compressive strength (at 12 hours) for specimens taken after 20 min of mixing were higher than the relative strength values of specimens taken after longer mixing time (Fig. 7.5(a)).

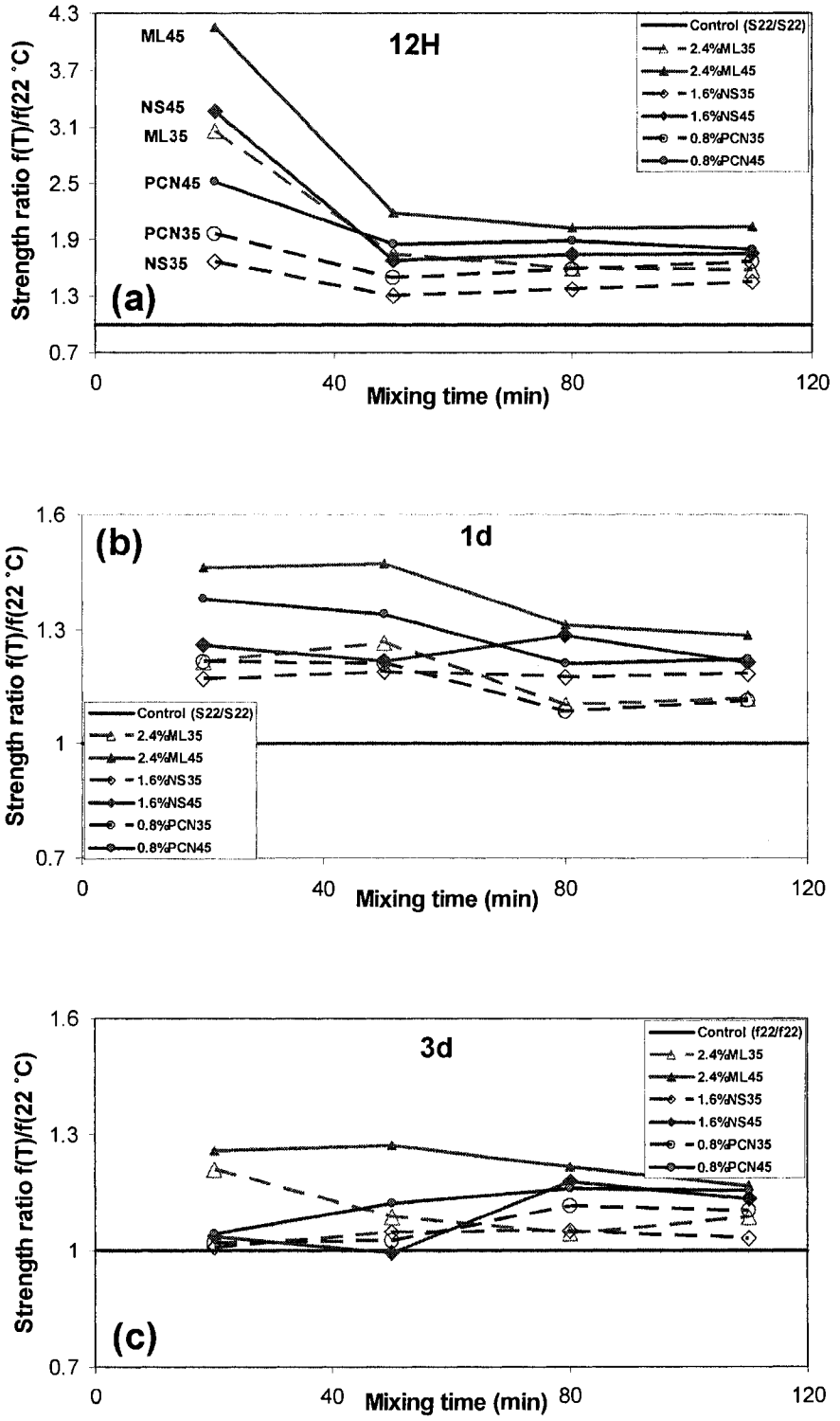

Figure 7.5-Relative strength of concrete mixed and early cured at 22, 35, or 45 °C, to that of concrete mixed and early cured at 22 °C, at (a) 0.5-day, (b) 1-day and (c) 3-days.

Figure 7.6(a) shows that the 7-day compressive strength did not seem to be adversely affected by the initial high temperature; 7-day strength values for mixtures and early cured at high temperatures were comparable to the corresponding values for mixtures made and early cured at moderate temperature. Similar observation was reported by Mouret *et al.* (1997). It can be further observed that the 28 day relative strength values at high temperature were lower than that subjected to the moderate temperature of 22 °C (Fig. 7.6(b)). Such an observation is in good agreement with findings of Kim *et al.* (1998).

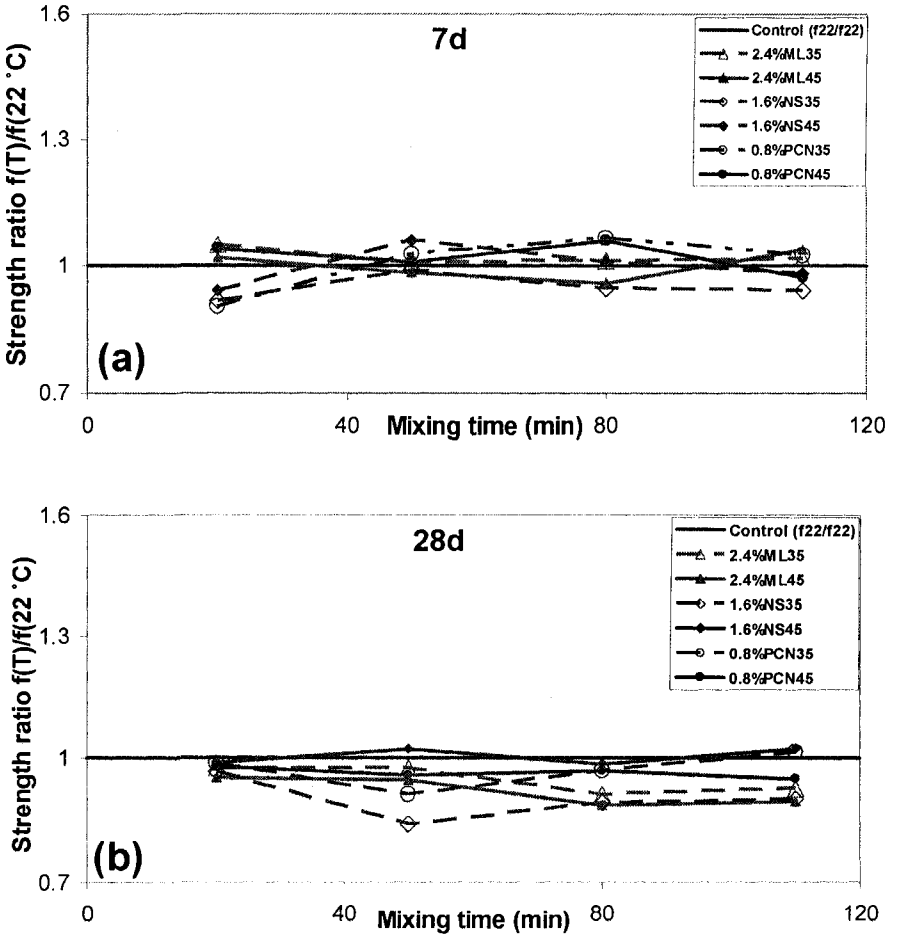

Figure 7.6-Relative strength of concrete mixed and early cured at 22, 35, or 45 °C, to that of concrete mixed and early cured at 22 °C, at (a) 7-days and (b) 28-days.

7.3.4 Effect of superplasticizer type on compressive strength

To further investigate the effect of the superplasticizer type on the compressive strength of concrete, the 28-day compressive strength data of concrete mixtures having high workability (slump flow higher than 650 mm) are displayed in Table 7.2. The slump flow values for each temperature differed within a range of 25 mm (Table 7.2). It can be observed that the superplasticizer dosage needed to obtain a target slump flow at each temperature varied from superplasticizer to another. Higher dosages were required for concrete mixtures incorporating ML than that incorporating NS, and the least dosages were needed when PCN was incorporated. As shown in Table 7.2, concrete mixtures made with ML or NS had lower 28-day compressive strength values than similar mixtures made with PCN. The reduction in strength shown in the last column of Table 7.2 was calculated according to the following equation:

$$\text{Reduction in Strength} = \left(1 - \frac{f_{adm}}{f_{PCN}}\right) \times 100 .$$

Where, f_{adm} = 28-day compressive strength of concrete incorporating PCN, ML, or NS and;

f_{PCN} = 28-day compressive strength of concrete incorporating PCN.

As shown in Table 7.2, the compressive strength values at 35 °C for concrete mixtures incorporating ML and NS were about 25% lower than that of similar mixtures incorporating PCN because PCN has better dispersion. This suggests that the compressive strength should also be considered when choosing the type of superplasticizer to be incorporated in concrete to achieve a target slump in high temperature environments. This aspect needs further investigation through a more comprehensive testing program.

Table 7.2-Effect of superplasticizer type on 28-days compressive strength for concrete mixtures having comparative slump flow

Temperature (°C)	Superplasticizer	Dosage (%)	Mixing time (min)	Slump flow (mm)	28 day compressive strength (MPa)	Reduction in strength (%) $(1-\frac{f_{admix}}{f_{PC}})\times 100$
22	PCN	0.6	20	730	56.0	0.0
	ML	2.4	20	745	46.2	17.5
	NS	2.0	20	735	46.5	17.0
35	PCN	0.8	20	680	60.0	0.0
	ML	3.4	20	705	43.6	27.3
	NS	2.0	20	680	50.0	26.7
45	PCN	1.5	20	750	61.3	0.0
	ML	3.4	20	740	47.0	23.3
	NS	1.8	20	745	53.5	12.7

7.3.5 Discussion

Based on the results of this chapter, high temperature and prolonged hauling time can have combined adverse effects on concrete slump, which is in agreement with earlier research (Ravina and Soroka 1994). Generally, concrete subjected to different temperatures and prolonged mixing time behaved differently depending on the type of superplasticizer used. Concrete mixtures incorporating PCN had the least slump loss over the investigated range of temperatures and mixing times. This indicates that PCN acted as an effective dispersing agent for concrete under high temperature and prolonged mixing conditions; it delayed the slump loss at considerably lower dosages compared to those of ML and NS. The discrepancy in the behaviour of various superplasticizers is mainly related to the way each superplasticizer disperses cement particles.

The effectiveness of PCN is due to its dispersing mechanism which involves both electrostatic repulsion and steric stabilization. The complex flexible molecules of polycarboxylates wrap around cement particles and keep them separated. Therefore, PCN can disperse cement particles effectively even at a relatively low w/c ratio. The dispersion capability of PCN usually persists over relatively longer time periods. This is due to its

natural side chains and a possible controlled adsorption over time which is claimed to cause remaining PCN molecules to overlap previously adsorbed ones.

On the other hand, the mode of action of ML and NS depends on the ML or NS adsorption on cement particles (Rixon and Mailvaganam 1999). When ML or NS are added to a concrete mixture, their polymeric particles are adsorbed onto cement particles giving them similar electric charge. Consequently, cement particles start to repel away from each other and become more free to move (Rixon and Mailvaganam 1999). Over time, the surface charge of the particles diminishes because of the hydration crystals that nucleate on their surface. This causes the hydrating cement particles to flocculate, and without further water addition, the concrete becomes no longer workable.

Longer mixing can result in a more homogeneous microstructure, which could be the reason behind the observed increase of compressive strength with increased mixing time. The increase in early-age compressive strength at high temperature reflects the acceleration of cement hydration reactions due to the initial high temperature. However, the rapid hydration due to the high early curing temperature can form shells around cement grains preventing hydration products to diffuse into the bulk cement matrix (Kim *et al.* 1998). The non-uniform diffusion of hydration products along with the difference in thermal expansion coefficients of concrete constituents can cause the porosity inside the cement paste to increase and micro-cracks to develop (Kim *et al.* 1998). As a result, the accelerated hydration rate at high temperatures increases the early-age strength of concrete, but eventually reduces the strength at later age due to the non-homogeneous diffusion of hydration products (Kim *et al.* 1998).

Furthermore, a change in the microstructure of concrete cast during the summer season was also reported (Mouret *et al.* 1997). In particular, the concentration of calcium hydroxide at the interface between the cement paste and aggregates increased at higher temperatures. Mouret *el al.* (1997) assumed that the transition zone might have been weakened by chemical phenomena when the temperature increased. Ortiz *et al.* (1979) also tried to explain the increased concrete compressive strength in the very early stages and its reduction at later ages due to higher curing temperature. They attributed this phenomenon to the assumption that rapid hydration at high temperature forms products with poor physical structure having more pores than that formed at moderate temperature. These pores would remain unfilled leading to lower mechanical strength than that of a less porous cement paste that hydrates slowly, but would eventually have a higher gel/space ratio (Ortiz *et al.* 2005). The observations above may explain the reduction in compressive strength for concrete made and early cured at high temperature observed in the present chapter.

The compressive strength data at 28-days were plotted versus corresponding slump values for all concrete mixtures investigated (Fig. 7.7). The total number of data points is 120, from which 48 correspond to PCN and 36 and 36 data points are for ML and NS, respectively. The concrete mixtures having a slump flow less than 400 mm are 8 mixtures incorporating PCN, 10 mixtures incorporating ML, and 12 mixtures incorporating NS (Fig. 7.7). Thus, only 16.5% of concrete mixtures incorporating PCN had slump values less than 400 mm, while 28% and 33% of mixtures incorporating ML and NS, respectively, had slump flow values less than 400 mm. This indicates some advantages of PCN over the other superplasticizers concerning slump retention.

It can be observed that most of the strength data fell between 50 and 70 Mpa. The graph was divided into four regions: region (1) is for strengths less than 50 Mpa, region (2) is for strengths from 50 to 60 Mpa, region (3) is for strengths between 60 and 70 Mpa, and region (4) is for strengths higher than 70 Mpa. It can be observed that all strength values below 50 Mpa correspond to high fluidity mixtures (slump flow higher than 600 mm). Only one data point had a strength higher than 70 Mpa, and it corresponds to concrete mixture incorporating 1.1% PCN; this mixture had a slump flow value of 400 mm (Fig. 7.7).

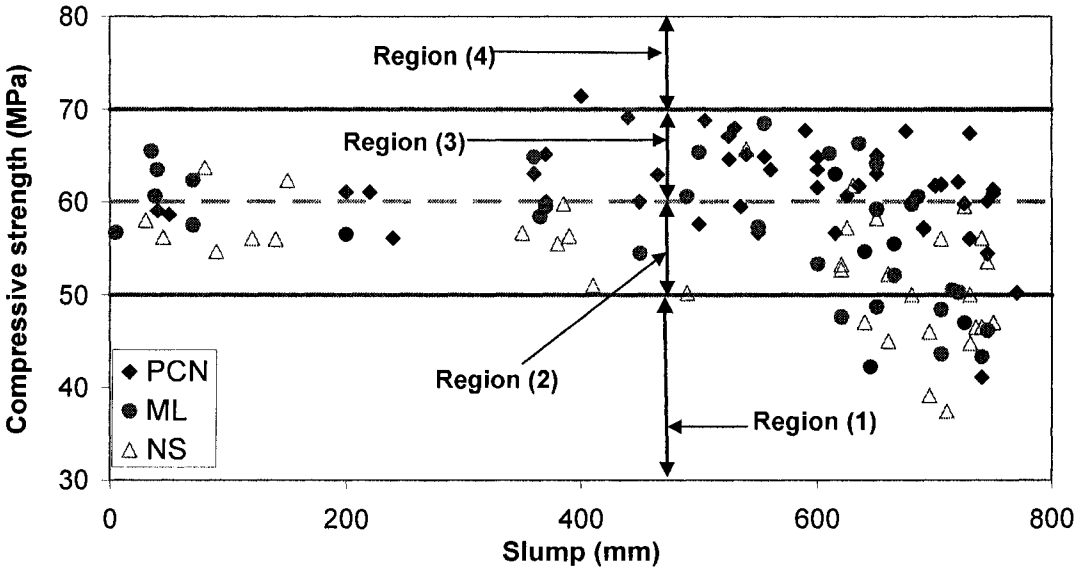

Figure 7.7-Slump versus 28-day compressive strength for concrete mixtures tested at different temperatures and mixing times showing the data corresponding to each superplasticizer investigated.

Data points were further classified in Table 7.3 based on compressive strength. Table 7.3 presents the percentage of data points related to each superplasticizer and located in one of the four strength regions, with respect to the total number of data points for the corresponding superplasticizer. It can be observed that only 2.0% of concrete mixtures

incorporating PCN had compressive strength values less than 50 Mpa, while 22.2% and 25.0% of mixture incorporating ML and NS, respectively, had compressive strength values less than 50 Mpa. Furthermore, 63.5% of concrete mixtures incorporating PCN had a strength higher than 60 Mpa, while only 36.1% and 11.0% of mixtures made with ML and NS, respectively, had compressive strength values higher than 60 Mpa. This also supports the previous observation on the effect of the selected superplasticizer, not only on slump los, but also on compressive strength.

Table 7.3-Percentage of 28-day compressive strength data points for each superplasticizer in each strength region

Superplasticizer	Total number of points	Percentage of total points for each superplasticizer (%)			
		< 50 MPa	50-60 MPa	60-70 MPa	>70 MPa
PCN	48	2.0	34.5	61.5	2.0
ML	36	22.2	41.7	36.1	0.0
NS	36	25.0	64.0	11.0	0.0

7.4 Conclusions

The present chapter explores how the mixing time and initial ambient temperature affect the slump loss and compressive strength of concrete. Based on the results obtained, the following conclusions can be drawn:

- As expected, the slump loss was accelerated with the rise of temperature.
- PCN was found to be able to retain higher slump at relatively low dosage over prolonged mixing at high temperature than the other superplasticizers considered in this study.
- A large decrease in slump was observed for concrete mixtures incorporating NS at all temperatures after 50 minutes of mixing. Therefore, care is needed when this superplasticizer is used in concrete subjected to prolonged mixing.

- Concrete initially subjected to high temperature attained higher early-age compressive strength than that of a similar concrete subjected to a moderate temperature.
- The concrete made and initially cured at high temperature achieved lower 28-day compressive strength than that of a similar concrete made and initially cured at moderate temperature.
- The results of this study indicate that compressive strength generally increased with longer mixing, thus suggesting that prolonged mixing is beneficial for the compressive strength gain of concrete, especially that incorporating ML.
- Results for concrete mixtures incorporating different superplasticizers and having similar slump values at each investigated mixing and early curing temperature indicated that the type of superplasticizer affected the 28-day compressive strength; the highest compressive strength values were obtained when PCN was used.
- It should be emphasized that the present results are applicable for the particular superplasticizers and materials (cement type and aggregates) used in this study and need to be extended for the other superplasticizers, cement types, and aggregates using further experimental work..

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Chapter 8

GENETIC ALGORITHM-BASED RHEOLOGICAL EQUATIONS FOR CEMENT PASTE AT HIGH TEMPERATURE AND PROLONGED MIXING TIME*

8.1 Introduction

The rheology of cement paste affects the flow behaviour of concrete. Thus, a fundamental knowledge of the rheology of concrete requires an appropriate understanding of the rheological properties of cement paste (Papo and Caufin 1988). As such, measuring the rheological parameters of cement paste can give an indication about the workability of fresh concrete. These parameters are usually estimated by conducting rheological tests such as conventional shear flow tests. Cement paste is a viscoelastic material which exhibits an infinite absolute viscosity until a sufficiently high shear stress is applied to initiate flow. This stress is referred to as the yield stress, above which cement paste shows a simple linear flow where the gradient of shear stress increases linearly with the shear strain rate. The slope of the shear stress-shear strain rate flow curve, which is called the plastic viscosity, is generally constant and independent of the shear strain rate. The flow of cement paste can be expressed using the Bingham equation (Eq. 8.1) (Asaga and Roy 1980):

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* A version of this chapter has been accepted for publication in the ICE Construction Materials Journal .

$$\tau = \tau_0 + \mu_p \dot{\gamma} \tag{8.1}$$

Where, τ(Pa) is the shear stress at shear rate $\dot{\gamma}$ (1/s), and τ_0 (Pa) and μ_p (Pa.s) are the yield stress and plastic viscosity values, respectively.

The yield stress is determined by extrapolation of the shear stress-shear rate curve corresponding to a zero shear rate, and the plastic viscosity is the slope of this curve. In order to determine the rheological parameters of cement paste, a Two-Point Workability Test can be used by applying a given shear rate and measuring the resulting shear stress. The measured Bingham values are influenced by various parameters, such as the mixing time, ambient temperature, superplasticizer type and dosage (Al-Martini and Nehdi 2008).

Petit *et al.* (2006) investigated the coupled effects of time and temperature on the rheological properties of highly flowable mortars. The temperature in their investigation ranged from 10 to 30 °C. After mixing, mortars remained in a standstill condition and the rheological parameters were measured over time (t) up to the end of the dormant period. They found that the yield stress increased linearly with time up to the end of the dormant period, and the slope of this function became higher with higher temperature. To eliminate the effect of temperature, a non-dimensional parameter (t') was introduced. This normalized t' (value between 0 and 1) is defined as the elapsed time after the contact of cement with water divided by the time (t_f) corresponding to the end of the dormant period ($t'=t/t_f$). The yield stress was found to increase linearly with the increase in the normalized time period (t'), independent of the mixture temperature; the slope of this line was found to depend on the mixture proportions. Plastic viscosity had a relationship with the normalized

time similar to that of the yield stress, and showed a linear and unique trend for each mixture.

The variation of the plastic viscosity and yield stress of cement paste with the elapsed time and temperature should be quantified. However, the methods of measuring these parameters are costly and time-consuming. A few researchers tried to develop equations to calculate the Bingham parameters of cement-based materials considering various conditions. For instance, Murata and Kikukawa (1992) developed equations to predict the plastic viscosity of cement paste considering the effects of temperature and elapsed time under standstill conditions. The temperature ranged from 10 to 30 °C and the time investigated was up to 3 hours with half hour intervals between tests. They introduced a viscosity equation valid only for cement paste immediately after mixing at 20 °C using the volumetric concentration of solute (V). Variations in the elapsed time and temperature were later accounted for by developing an experimental equation based on 25 cement paste samples, which calculates the increase in plastic viscosity with the time elapsed $\Delta\mu_{ct}$ (Pa.s/h) at a prescribed temperature. The plastic viscosity at a certain temperature and elapsed time was estimated by adding the value of the increase in viscosity due to the time elapsed to the initial plastic viscosity value calculated immediately after mixing at 20 °C.

The data presented in the present chapter were obtained from chapter five on cement paste mixtures incorporating polycarboxylate-, melamine sulfonate-, or naphthalene sulfonate-based superplasticizers. The cement paste mixtures were subjected to continuous mixing at various temperatures. This work is part of a large research program aiming at establishing correlations between the rheological parameters of cement pastes and that of

corresponding concretes with particular attention to problems arising from prolonged mixing under high temperature.

8.2 Experimental Work

8.2.1 Materials and mixture proportioning

CSA Type 10 (similar to ASTM Type I) ordinary portland cement was used in all cement pastes with a water to cement mass ratio (w/c) of 0.38. The following superplasticizers were used in preparing the cement pastes:

1- a new generation of polycarboxylate-based superplasticizer (PCN).The dosages of PCN ranged from 0.1% to 1.3% by mass of cement.

2- Melamine sulfonate-based superplasticizer (ML). The dosages of ML ranged from 1.4% to 3.0% by mass of cement.

3- Naphthalene sulfonate-based superplasticizer (NS). The dosages of NS used in the study ranged from 1.2% to 2.4% by mass of cement.

8.2.2 Experimental procedure

The effects of the mixing time and ambient temperature on the rheological parameters of cement pastes incorporating various superplasticizers were investigated. For high temperatures (35 and 45 ^{o}C) the mixing was carried out in a temperature controlled chamber, and for the moderate temperature (22 ^{o}C), the mixing took place in the controlled lab environment.

An advanced rheometer (TA-Instruments AR-2000) with a coaxial concentric cylinder geometry was used to measure the Bingham parameters of the cement pastes. The rheometer is fully automated and the entire experimental process is controlled by a software.

For each cement paste mixture, the first sample was taken for the first rheological test after 20 minutes from the start of mixing. Then, a new cement paste sample was taken and tested every half hour. The total time of mixing each cement paste mixture was 110 min. The prolonged mixing was intended to give an indication on the rheological behaviour of concrete subjected to continuous mixing in a concrete truck mixer during its hauling to a construction site. To ensure uniform conditions before testing, each cement paste sample was pre-sheared at 70 s^{-1} for two minutes in order to break down its structure (Saak *et al.* 2001). Subsequently, the shear rate was increased from 0 to 50 s^{-1} to produce the shear stress-shear strain rate up curve, and the cement paste was maintained for 15 seconds at this shear rate, and then it was sheared from 50 s^{-1} to 0 s^{-1} to produce the down curve. This procedure allowed for the production of a ysteresis loop, which can be used to characterize the thixotropy of cement paste (Saak 2000). A schematic representation of the testing sequence can be found in Fig. 5.2 .

8.2.3 Experimental results

Figure 8.1 shows a typical shear stress/shear rate down curve for cement paste. The flow curve was obtained by measuring the shear stress at a given shear rate. The data points in the curve can be fit to the Bingham equation (Eq. 8.1) as shown in the figure. The yield stress is the intersect of the Bingham line with the y-axis and the plastic viscosity is the

slope of this line (Fig. 8.1). The relationships between the Bingham parameters (yield stress and plastic viscosity) and test variables (mixing time, temperature and superplasticizer dosage) have been investigated in this chapter.

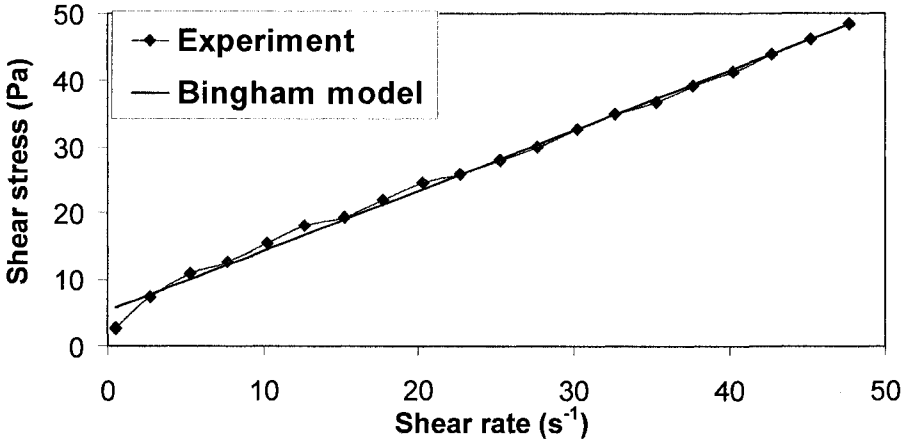

Figure 8.1-Example of shear stress versus shear rate (down curve).

The experimental results show that a linear function was generally representative of the relationship between yield stress/plastic viscosity and mixing time with a correlation coefficient (R^2) above 0.90. This relationship can be expressed as follows:

$$\tau_o / \mu_p = \alpha\, t + b \tag{8.2}$$

The power law generally gave a best fit for the relationship between yield stress/plastic viscosity and temperature with a correlation coefficient (R^2) above 0.90 for all cases and can be expressed as follows:

$$\tau_o / \mu_p = cT^d \tag{8.3}$$

The relationship between yield stress/plastic viscosity and superplasticizer dosage below the saturation dosage was generally governed by an inverse power function with a coefficient of correlation (R^2) above 0.90:

$$\tau_o / \mu_p = eD^{-f} \tag{8.4}$$

Where *a, b, c, d, e,* and *f* are model constants. Table 8.1 shows the ranges of the abovementioned experimental coefficients. A sample for these relationships is shown in Figs. 8.2 and 8.3 for some PCN results.

8.2.4 Database

The genetic algorithm technique employed in this investigation to model the Bingham yield stress and plastic viscosity must be trained using a relatively comprehensive and large number of representative data sets in order to become able to capture the relationship between the input and output parameters. The number of data points used to train the model was 660, 600, and 620 for PCN, ML and NS, respectively. Furthermore, 200 new data points unfamiliar to the model for each superplasticizer were used to test its performance. It should be noted that each flow curve consists of 20 data points.

Table 8.1-Range of model coefficients

Coefficient	PCN		ML		NS	
	τ_o	μ_p	τ_o	μ_p	τ_o	μ_p
a	0.001-0.5	0.001-0.01	0.002-0.5	0.001-0.01	0.005-0.1	0.001-0.01
b	3-37	0.4-2	0.5-10	0.1-2	0.5-2	0.1-0.5
c	0.02-0.3	0.02-0.2	0.3-10	0.01-1	0.004-0.1	0.001-1
d	0.001-2.5	0.5-1.5	0.1-4	0.3-1	0.1-1	0.1-1
e	1-4	0.3-2	1000-2500	2-20	1000-4500	1.5-60
f	0.3-2	0.3-1	2-10	1-5	1-5	1-5

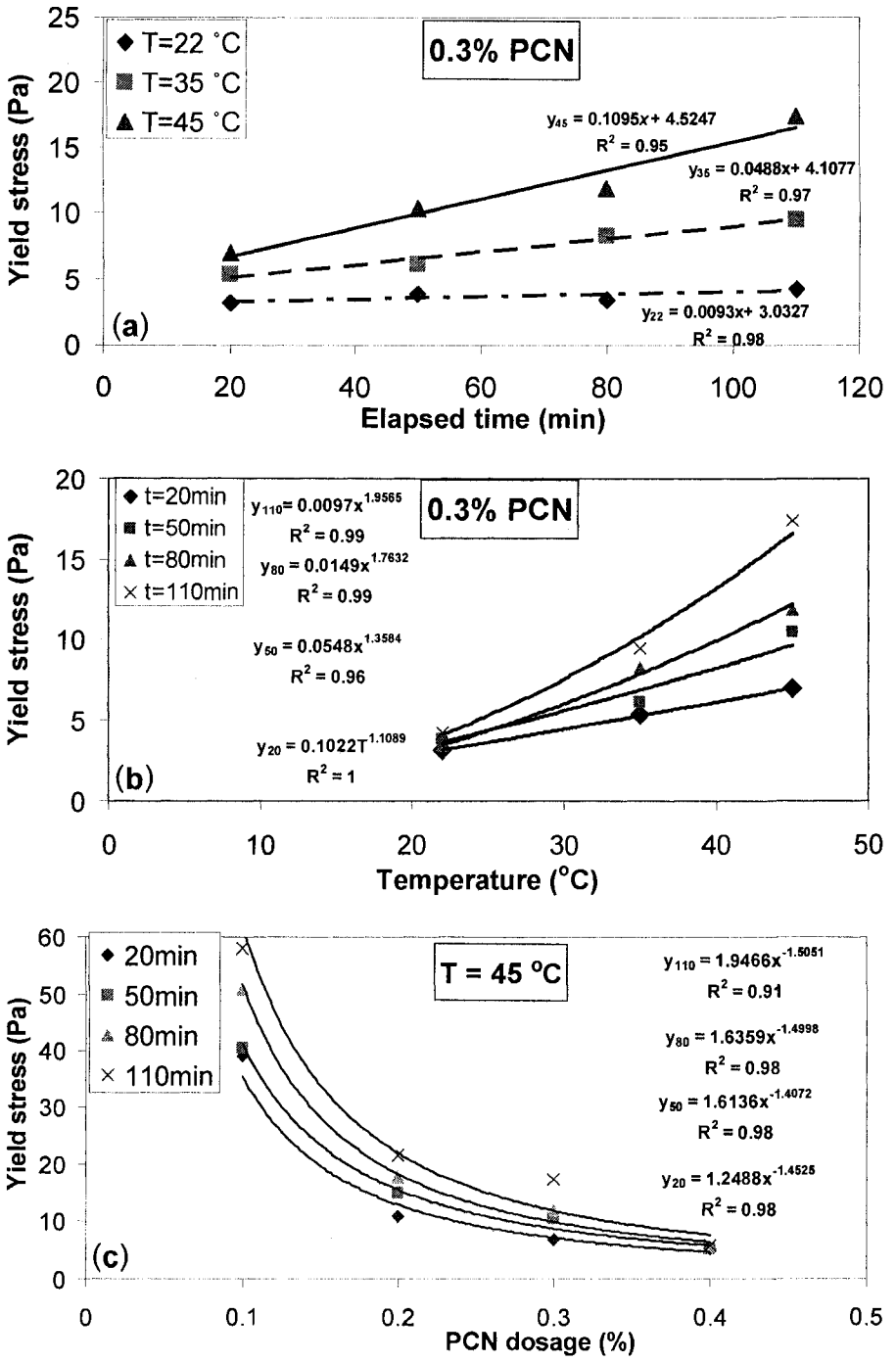

Figure 8.2-Variation in yield stress of cement paste as a function of: (a) mixing time (0.3% PCN at different temperatures), (b) ambient temperature (0.3% PCN at different mixing times), and (c) PCN dosage (at 45 °C and different mixing times).

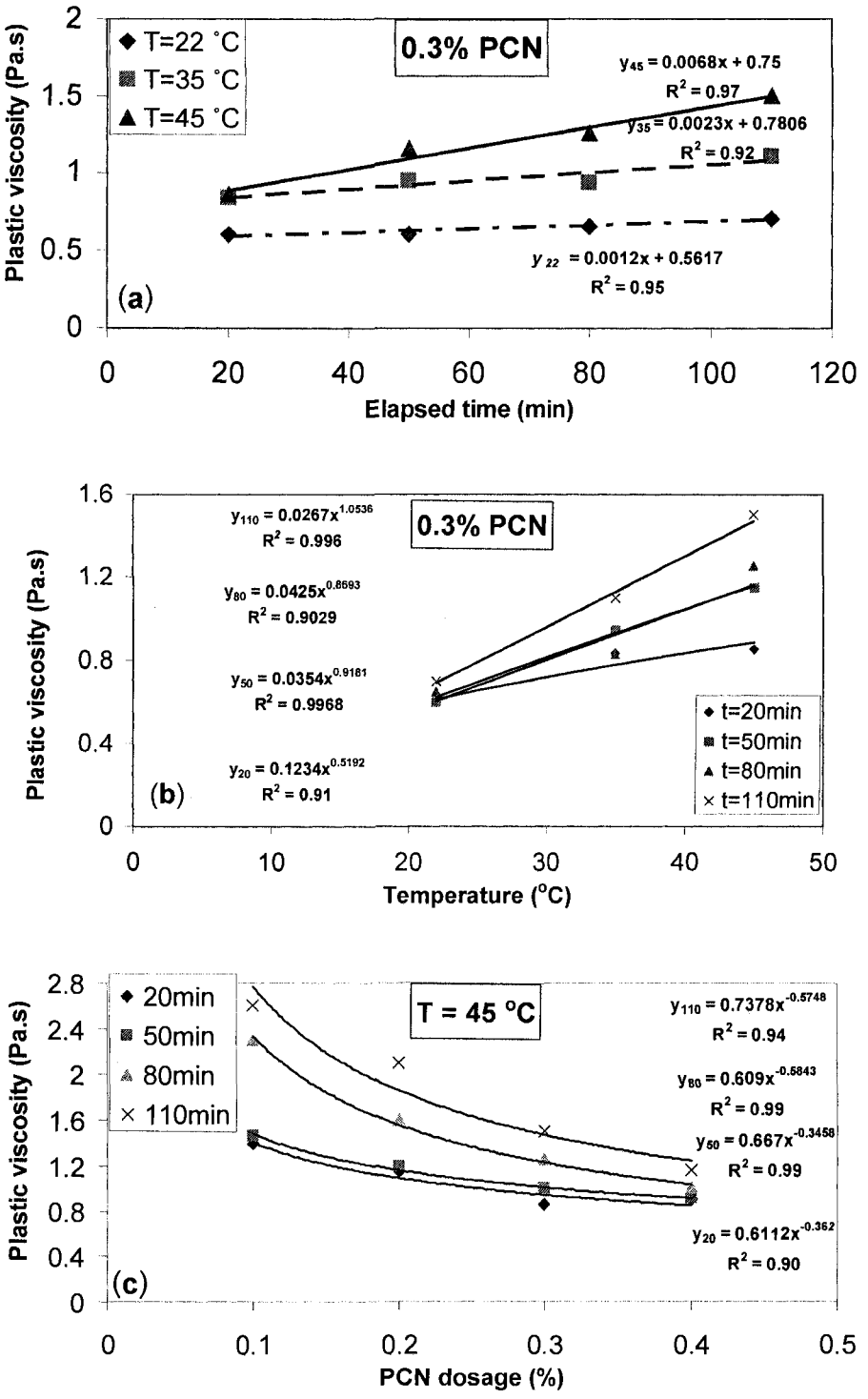

Figure 8.3-Variation in plastic viscosity of cement paste as a function of: (a) mixing time (0.3% PCN at different temperatures), (b) ambient temperature (0.3% PCN at different mixing times), and (c) PCN dosage (at 45 °C and different mixing times).

8.3 Genetic Algorithm Approach

The Genetic Algorithms (GA) method is a global optimization technique for high dimensional and nonlinear problems. It can be defined as a search technique based on the mechanism of natural selection and the natural genetics of biological evolution. The main characteristic of GA is its ability to provide optimum solutions to approximately formulated problems. GA starts the search of an optimum solution with an initial coded set of random solutions called population. The population includes a set of individuals called chromosomes; each chromosome represents a potential solution to the problem at hand. The process of GA optimization simulates the Darwinian evolution process to create populations from one generation to another. As such, GA evaluate each chromosome and selects the fittest individuals in the initial population and subsequently undergoes genetic operations including crossover, and mutation to produce a new generation having a genetic structure superior to that of the parents (Michalewicz 1996). This process is repeated for each population; after some number of generations the best chromosome representing an optimal solution is obtained and no significant further improvement can be achieved. The appropriate selection of some key parameters (selection method and pressure, recombination rate, mutation rate and number of individuals) is critical to have successful performance of GA. The following sections present a brief description of the selection, crossover, and mutation operators that constitute the general form of the GA search process.

8.3.1 Selection

The power of using Gas depends mainly on their ability to search a population of potential solutions based on selecting the fittest survival chromosomes. As such, the

selection method and pressure provide the driving force in a genetic algorithm towards promising solutions in the search space. Selection specifies how the genetic algorithm chooses parents for the next generation. This process simulates a natural selection of the best fit individuals that can adapt to changing environments and survive for reproduction in the forthcoming generations. The parents are chosen for the next generation based on their scaled fitness values. An individual can be selected as a parent more than one time and in this case it contributes its genes to more than one child. A variety of different selection methods are used to select the best fitted chromosomes. The most common ones are briefly explained below, while a thorough description can be found in Michalewicz (1996).

8.3.1.1 Roulette wheel selection

The roulette wheel is the simplest selection method in Gas which chooses parents by simulating the initial population as a roulette wheel divided into sections; each section in the roulette wheel corresponds to an individual where its area is proportional to the individual's expectation. The probability of selecting a certain individual for mating to produce more offspring for the next generation depends on its fitness value; the healthier individuals (higher fitness values) have higher probability to be selected. The construction of a roulette wheel process starts with calculating the fitness value $eval(v_i)$ for each chromosome v_i (I = 1, ……., *pop-size*), followed by finding the total fitness of the population $\left(F = \sum_{i=1}^{pop-size} eval(v_i)\right)$. The probability of selecting each chromosome (p_i) is then simply calculated by dividing its fitness value ($eval(v_i)$) by the total fitness of its population according to the following equation (Eq. 8.5):

$$p_i = \frac{eval(v_i)}{F} \tag{8.5}$$

The selection process is based on generating a set of random numbers equal to the desired generation size from the range of 0 to 1. The selection of chromosomes from the initial population to become parents in the new generation is carried out by spinning the roulette wheel *pop-size* times; each time the individual whose segment spans any of the random numbers is selected. Obviously, an individual could be selected more than once. A simple illustration of how the roulette wheel selection method works can be found in the following example. An initial population of 6 individuals along with their assigned fitness is presented in Table 8.2. It should be noted that the probability of each individual being selected is shown in the last raw of the table and is calculated using equation (8.5).

Table 8.2-Probability of selecting individuals using the roulette wheel selection method

Individual	1	2	3	4	5	6
Fitness value $eval(v_i)$	5	8	4	3	2	3
Selection probability (p_i)	0.2	0.32	0.16	0.12	0.08	0.12

It can be observed from the table that individual 2 has the highest fitness value, and consequently the highest selection probability (Table 8.2) indicating that it is highly expected to be selected for mating. This individual will occupy the largest interval on the selection line shown in Fig. 8.4. Then, a set of 6 random numbers is selected (0.94, 0.75, 0.18, 0.42, 0.9, 0.25) and each number is mapped over the selection line (Fig. 8.4). The selected individual is the one whose segment spans a random number. For this particular

example, the selected individuals for mating to generate a new generation are (1, 2, 2, 4, 6, 6). It can be observed that individuals 2 and 6 have been selected more than once.

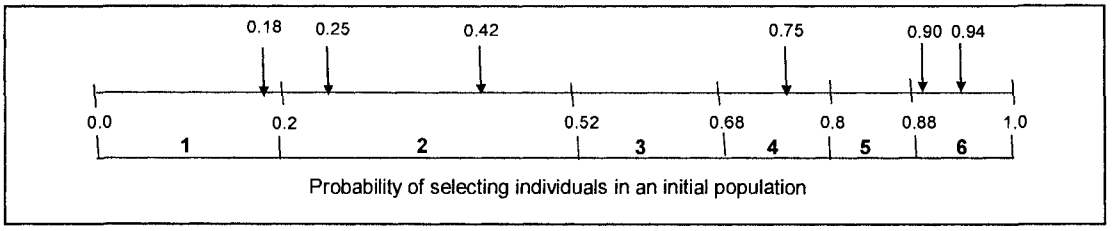

Figure 8.4-Selection using the roulette wheel method.

8.3.1.2 Tournament selection

Tournament selection choses randomly a group of individuals from an initial population. The number of individuals in each group is denoted as tournament size and it should be at least 2. The best individual of a group is chosen for mating with a selected parent from another group to produce a new generation of offspring. This process is repeated until selecting the desired number of individuals (parents).

8.3.2 Crossover (Recombination)

After the best individuals were selected from the initial population to become parents, the crossover operator is ready to be applied. Crossover is the basic operator that specifies how the genetic algorithm creates offspring for the next generation. This is performed on pairs of selected chromosomes (parents). The crossover operator combines genes (strings) from the two parents to form two new offspring hopefully having better genetic structures. The amount of exchanged genes is governed by the crossover rate, which is the ratio of the number of offspring created in each generation to the population size and therefore the crossover rate should be carefully chosen. Selecting a relatively high

crossover rate reduces the chances of a false optimum because it allows exploration in the large solution space. However, a too high value of recombination rate might result in a waste of time due to substantial computation effort in exploring unpromising regions of the solution space.

The following example illustrates the crossover operator on chromosomes (parents) v_1 and v_2. Each chromosome consists of 21 bits and the crossover point was randomly selected after the sixth gene.

V_1 = (000000|111110000010101),
v_2 = (110111|110110011000100).

The two created offspring are:

v_1' = (000000|110110011000100),
v_2' = (110111|111110000010101).

8.3.3 Mutation

Mutation is a background operator which randomly alters one or more genes positions in a chromosome producing new genes that were not present in the initial population. Assume that the sixth genes in v_1 and v_2 were selected for mutation. Thus, after mutation the chromosomes v_1 and v_2 will become:

v_1" = (000001111110000010101),
v_2" = (110110110110011000100).

If the mutation rate is too slow, many useful chromosomes might not be tested, and if the mutation rate is too high, there will be much random perturbation and consequently the

offspring will start losing resemblance to their parents resulting in an algorithm which is unable to learn from the history of the search (Goldberg 1989).

8.4 Modeling Methodology

The genetic algorithms approach was used in the present chapter as an optimization technique to develop equations for the shear flow of cement paste as a function of test parameters, i.e. mixing time, mixing temperature, superplasticizer type and dosage. Thus, an original form of the equation defining the overall flow behaviour of cement paste is required. Generally, cement paste is believed to behave as a Bingham fluid (Asaga and Roy 1980) and therefore, the Bingham equation was chosen in this study for GA optimization.

Using the method of separation of variables, both yield stress and plastic viscosity can be expressed as a function of the mixing time, ambient temperature and superplasticizer dosage according to the following equations:

$$\tau_o = \frac{(a_y t + b_y)(c_y T^{d_y})}{(e_y D^{f_y})} \tag{8.6}$$

$$\mu_p = \frac{(a_v t + b_v)(c_v T^{d_v})}{(e_v D^{f_v})} \tag{8.7}$$

Substituting these two equations in Eq. 8.1, the shear stress/shear rate curve of a cement paste at various mixing times, ambient temperatures, and superplasticizer dosages can be expressed as follows:

$$\tau_o = \frac{(a_y t + b_y)(c_y T^{d_y})}{(e_y D^{f_y})} + \frac{(a_v t + b_v)(c_v T^{d_v})}{(e_v D^{f_v})}\dot{\gamma} \tag{8.8}$$

Where, t is time (min), T is temperature (°C), and D is superplasticizer dosage (% by cement mass). The subscripts of the yield stress and plastic viscosity constants are represented by the letters (y) and (v), respectively.

Equation 8.8 was optimized using the genetic algorithms technique based on the experimental database. The optimum coefficients of this equation were determined so that the shear flow in Eq. 8.8 can be predicted with an acceptable margin of accuracy within the ranges of the tested mixing time, ambient temperature, and superplasticizer dosage. Previous work by the authors (Al-Martini and Nehdi 2007) showed that the studied superplasticizers had different effects on cement paste rheology, and therefore, a separate equation was developed for each superplasticizer. The constructed objective function measures how well the model's predicted output agrees with the corresponding experimentally measured data. The GA search process was terminated when the maximum number of generations was reached and a set of coefficients that best minimizes the objective function was found. The search was conducted within the range of coefficients presented in Table 8.1. The parameters used in genetic algorithm setting are presented in Table 8.3.

Table 8.3-Parameters used in genetic algorithm setting

Number of Individuals	70
Maximum Generations	5000
Selection Method	Roulette wheel selection
Selection Pressure	1.7
Recombination Rate	0.74
Mutation Rate	0.01

The three optimized equations are as follows:

For cement paste incorporating PCN:

$$\tau_{PCN} = \left[\frac{(0.0312t+3)\times(0.02T^{1.15})}{4D^{0.3}}\right] + \left[\frac{(0.0022t+0.64)\times(0.02T^{0.8})}{1.91D^{0.33}}\right]\times\dot{\gamma} \qquad (8.9)$$

For cement paste incorporating ML:

$$\tau_{ML} = \left[\frac{(0.0076t+0.51)\times(0.3T^{0.92})}{2500D^{2.1}}\right] + \left[\frac{(0.002t+0.223)\times(0.01T^{0.555})}{20D^{1.66}}\right]\times\dot{\gamma} \qquad (8.10)$$

For cement paste incorporating NS:

$$\tau_{NS} = \left[\frac{(0.0073t+0.5)\times(0.004T^{0.1})}{4500D^{3.6}}\right] + \left[\frac{(0.00073t+0.1)\times(0.001T^{0.636})}{60D^{2.4}}\right]\times\dot{\gamma} \qquad (8.11)$$

Using the above equations, the flow curves of cement pastes incorporating these superplasticizers can be predicted at a certain temperature and mixing time. It is important to note that the validity of these models remains within the range of the parameters tested (i. e. range of shear rate, temperature, mixing time, and superplasticizer type and dosage).

8.5 Results and Discussion

8.5.1 Performance of GA equations in predicting shear flow of cement paste

The acceptance/rejection of a GA model for cement paste shear flow is based on its ability to generalize its prediction to new cement paste mixtures not previously used in the model development, and thus unfamiliar to the model (i. e. the testing data points). Figures 8.5, 8.6, and 8.7 show a comparison between experimental and predicted shear flow curves

for cement pastes incorporating the three superplasticizers investigated. In Figs. 8.5-8.7 both training and testing data points are presented. Figures 8.5 (a, b, and c) exhibit the results for cement pastes incorporating PCN at 22, 35, and 45 °C, respectively. It can be observed that the data points predicted by the GA model are located on, or within a small range around, the equity lines. For cement pastes incorporating ML, the predicted versus measured data are presented in Figs. 8.6(a, b, and c) for 22, 35, and 45 °C, respectively. Again, the GA model proved its ability of predicting the shear flow for cement paste made with ML at different temperatures and mixing times, as proved by the data falling on, or within a narrow range of, the equity lines. The results of the GA model for NS mixtures are presented in Figs. 8.7(a-c). It can be observed that the model was able to calculate the shear flow of cement paste made with NS with satisfactory performance since the predicted and corresponding measured data points were also located close to the equity lines. It can be observed that the values of shear stress at 45 °C are lower than that at 22 and 35 °C. It should be noted that the minimum NS dosage experimentally tested at 45 °C was 1.6%, which is higher than that tested at 22 and 35 °C (1.2%); this dosage was chosen based on trial mixtures to avoid severe stiffening of cement pastes after the prolonged mixing time of 110 min at high temperature (45 °C).

The ability of each of the shear flow equations considered in this study to accurately estimate the shear flow curves of cement paste with variation of mixing time and temperature was evaluated using the average absolute error (*AAE*) (Eq. 8.12) along with the ratio of measured to predicted shear flow (τ_m/τ_p).

$$AAE = \frac{\left|\tau_m - \tau_p\right|}{\tau_m} \times 100 \tag{8.12}$$

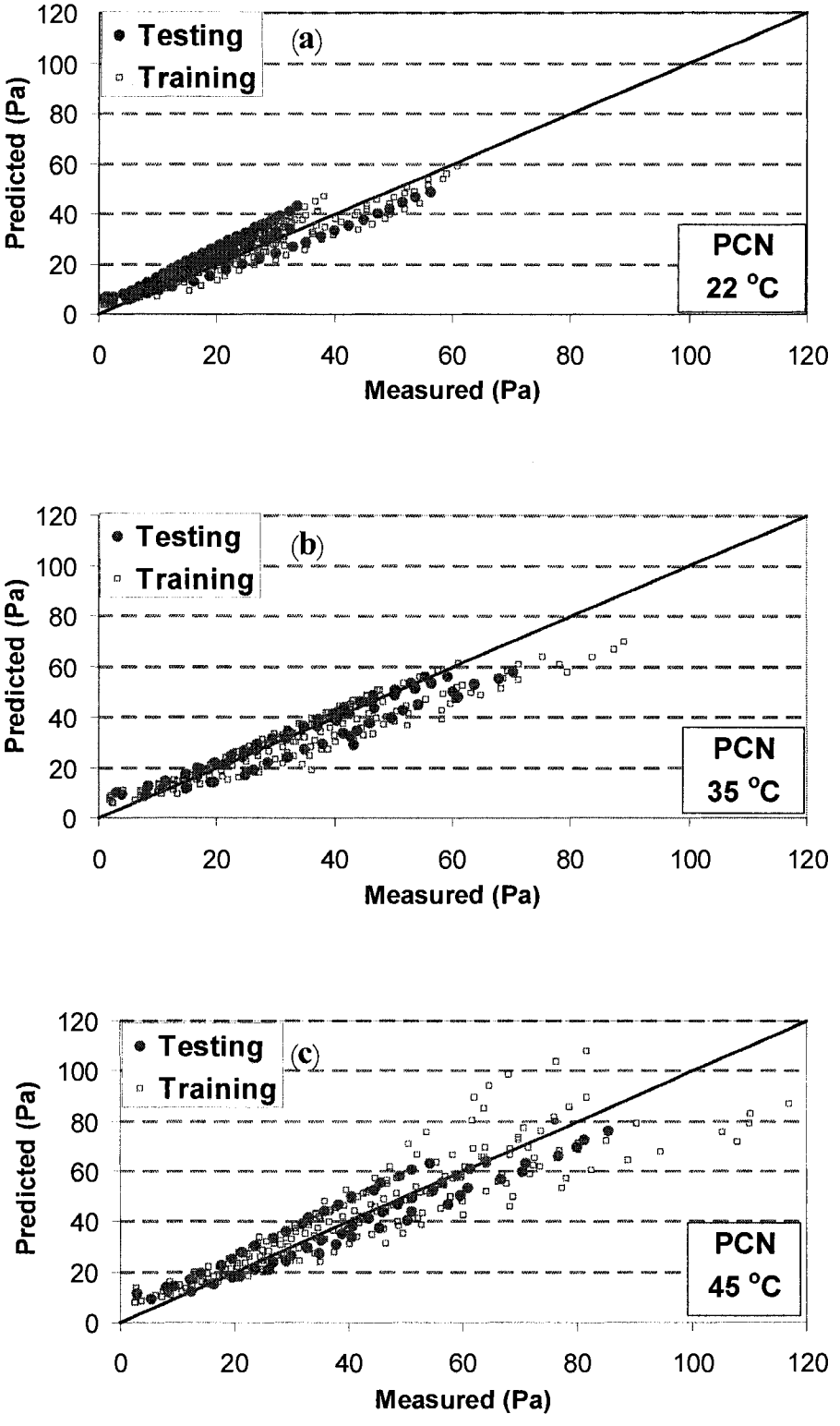

Figure 8.5-Measured versus predicted shear stress (τ) for cement pastes incorporating PCN at different temperatures and mixing times.

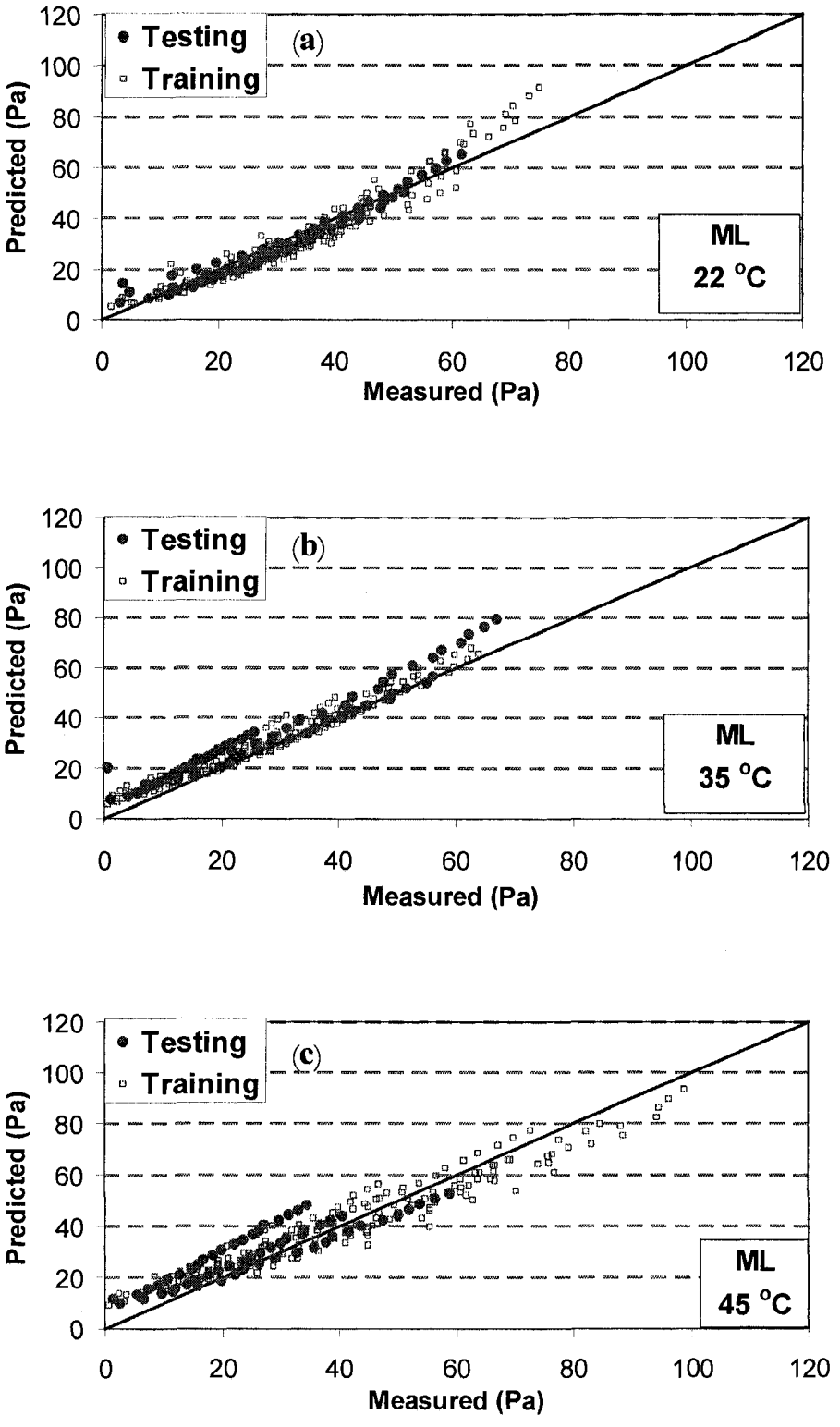

Figure 8.6-Measured versus predicted shear stress (τ) for cement pastes incorporating ML at different temperatures and mixing times.

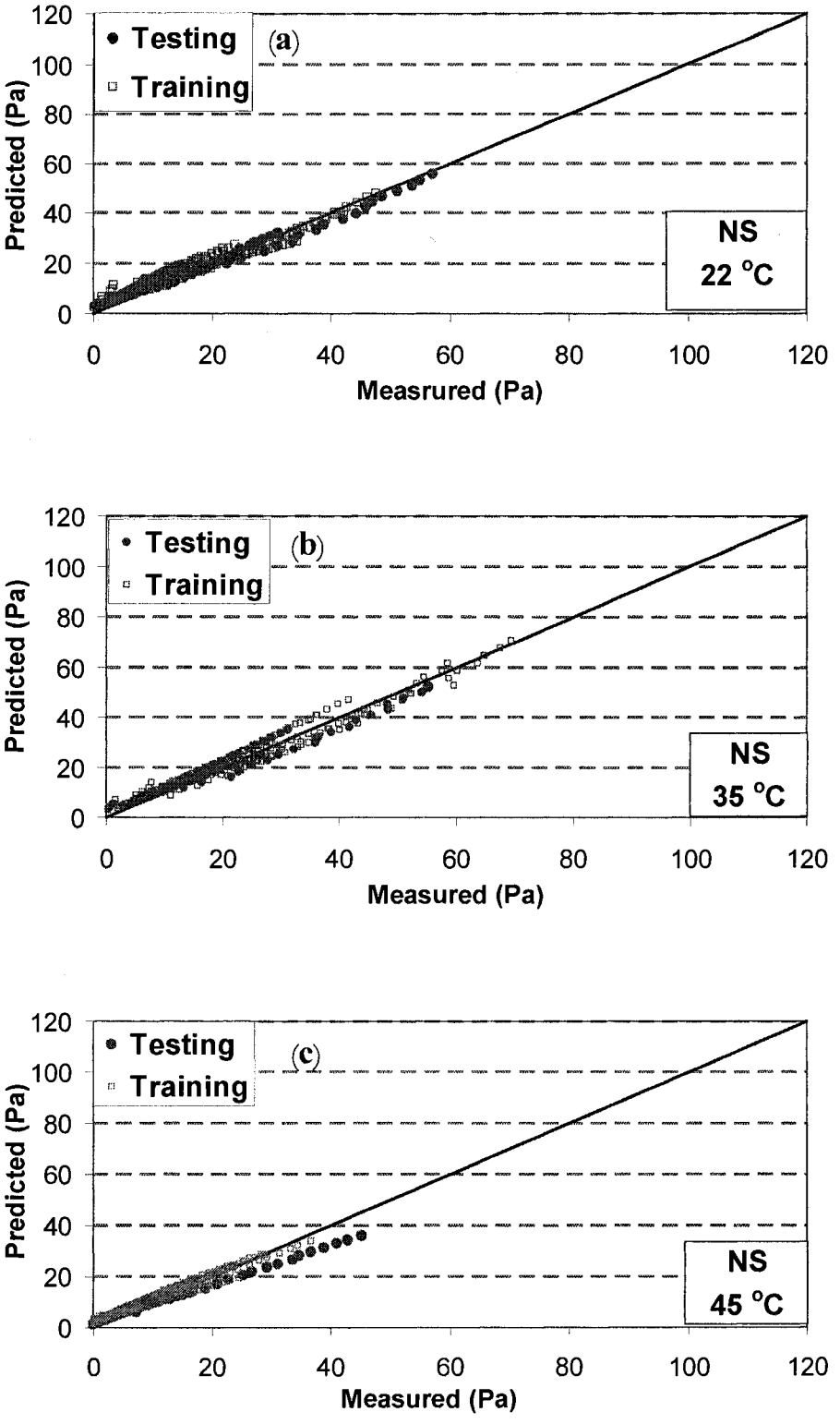

Figure 8.7-Measured versus predicted shear stress (τ) for cement pastes incorporating NS at different temperatures and mixing times.

The average, standard deviation (*SD*), and coefficient of variation (*COV*) of the measured to predicted shear flow ratio and average absolute error (*AAE*) for all testing shear flow/shear rate data investigated are presented in Table 8.4. The results indicate that the GA model was successful in learning the relationship between the different shear flow parameters for the various cement pastes.

Table 8.4-Performance of cement paste shear flow calculation equations for different superplasticizer dosage and temperature

Temperature (°C)	Superplasticizer	*AAE* (%)	$\tau_{(measured)}/\tau_{(calculated)}$ (All test points)		
			Average	*SD*	*COV* (%)
22	PCN	17	0.92	0.21	24
	ML	11	1.06	0.17	16
	NS	17	0.89	0.19	22
35	PCN	13	1.09	0.32	29
	ML	18	0.85	0.19	22
	NS	12	0.96	0.19	20
45	PCN	16	0.98	0.21	21
	ML	23	0.91	0.24	26
	NS	19	0.89	0.24	27

8.5.2 Performance of GA equations in predicting Bingham parameters of cement paste

The first term in Eqs. 8.9-8.11 calculates the yield stress values for cement pastes incorporating the various superplasticizers. Figures 8.8(a), 8.8(b), and 8.8(c) present the predicted yield stress values versus the corresponding measured ones for cement pastes incorporating PCN, ML, and NS, respectively. To validate the equations, the testing experimental data, which are unfamiliar to the GA model in the training process, were used and the *AAE* along with the average, standard deviation, and covariance of the ratio between predicted and experimental yield stress results are shown in Table 8.5. It can be observed that the *AAE* values were 37, 39, and 34, for PCN, ML, and NS, respectively. The errors are relatively higher than that for shear flow predictions. The reason for such higher

errors is likely due to the relatively higher variation of strain readings at low shear stress. It may be also attributed to errors associated with the way the yield stress is estimated using flow tests by extrapolating the shear stress-shear rate curve corresponding to a zero shear rate.

Table 8.5-Performance of cement paste yield stress and plastic viscosity calculation equations for different superplasticizers

Superplasticizer	*AAE* (%)	γ_o (measured)/γ_o (calculated) (All test points)			*AAE* (%)	μ_P (measured)/μ_P (calculated) (All test points)		
		Average	*SD*	*COV* (%)		Average	*SD*	*COV* (%)
PCN	37	1.01	0.41	40	11	1.03	0.14	14
ML	39	0.88	0.31	39	12	1.01	0.14	14
NS	34	0.86	0.36	42	9	1.05	0.13	12

The predicted plastic viscosity data (the second term in Eqs. 8.9-8.11) versus the corresponding experimentally measured values are plotted in Figs. 8.9(a-c). The plastic viscosity data of cement paste incorporating PCN are displayed in Fig. 8.9(a), and that made with ML and NS are shown in Figs. 8.9(b) and 8.9(c), respectively. It can be observed that the GA equations were able to predict the plastic viscosity with good accuracy since most of the points are located either on or within a narrow range of the equity lines. The *AAE* values along with the average, standard deviation, and covariance of the ratio of measured over predicted plastic viscosity data are shown in Table 8.5. It can be observed that the GA equations were more accurate in predicting the plastic viscosity than in predicting yield stress since the *AAE* values for viscosity are smaller than that for yield stress.

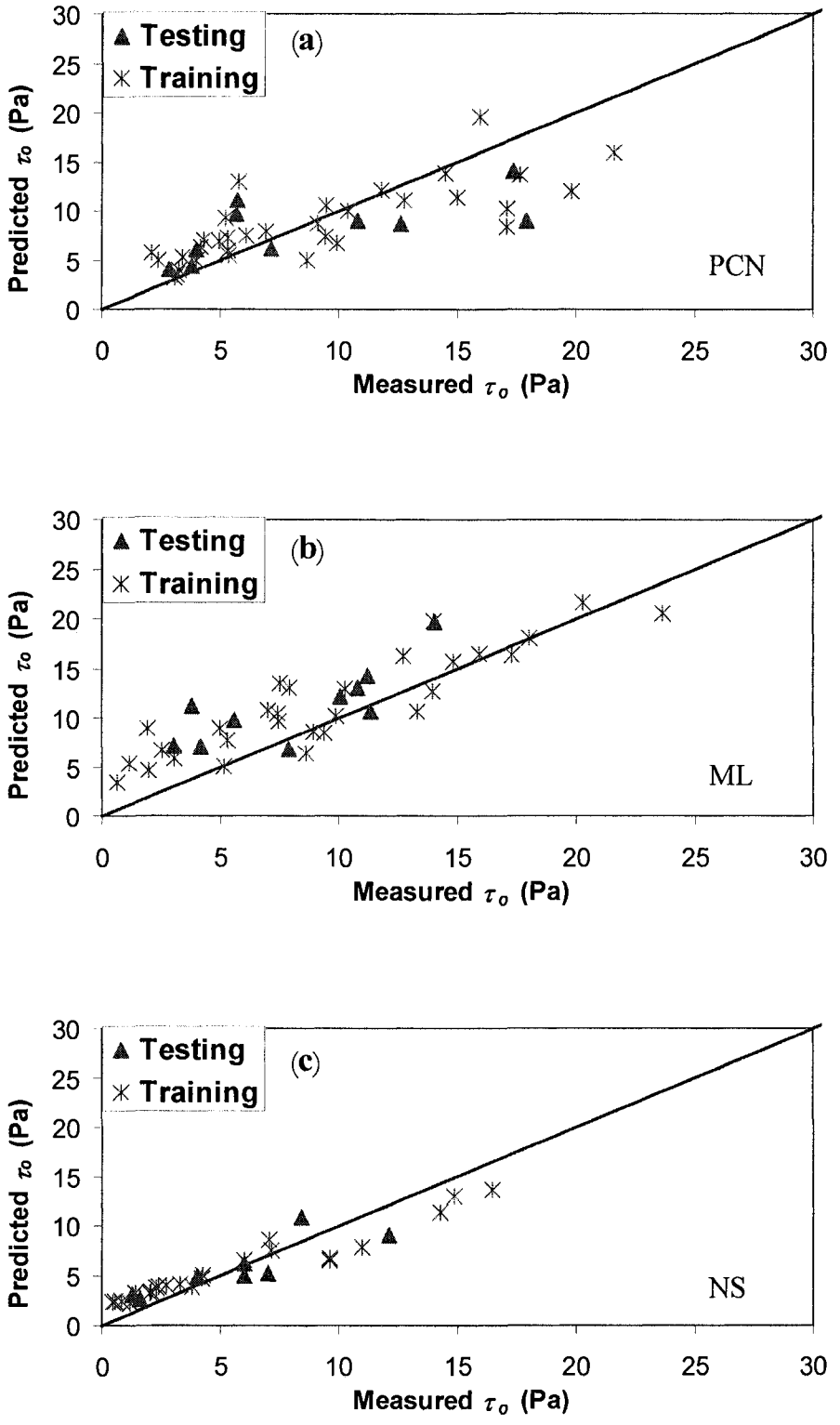

Figure 8.8-Measured versus predicted yield stress [(a) PCN, (b) ML, and (c) NS].

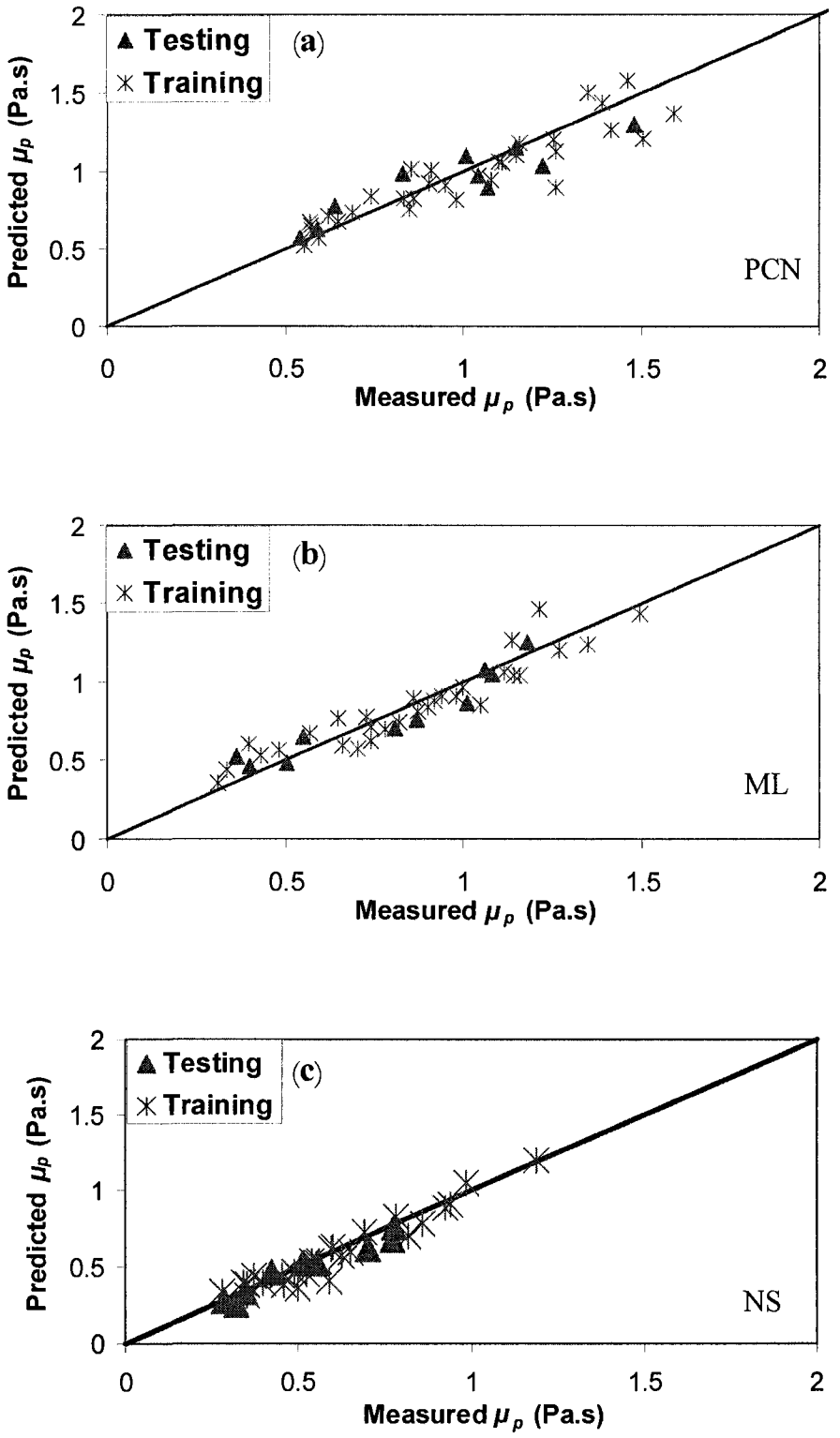

Figure 8.9-Measured versus predicted plastic viscosity [(a) PCN, (b) ML, and (c) NS].

8.5.3 Parametric study

Because the GA equations thus developed showed satisfactory performance and demonstrated the ability to predict the Bingham parameters of cement pastes incorporating various superplasticizers at different temperature and mixing time, it would be useful to investigate whether these equations have captured the effects of the various test variables. Therefore, the influence of the mixing time, ambient temperature, and superplasticizer dosage on the yield stress and plastic viscosity was examined. In this study, Eqs. 8.9-8.11 have been used to predict the Bingham parameters for data points unfamiliar to the model, but within the range of data used in the development of the model equations. The mixing time was varied in the range from 20 to 110 min and the temperature was varied in the range between 22 and 45 ^{o}C. Three cement paste mixtures were randomly selected from the experimental data to investigate the sensitivity of the GA equations to changes in the mixing time and temperature. These mixtures included cement pastes made with 0.3% PCN, 1.8% ML, and 1.6% NS.

Figure 8.10 illustrates the predicted Bingham parameters of the above mentioned mixtures using the GA equations along with the corresponding experimental results versus the elapsed mixing time. Two mixing times were not experimentally tested (50 and 100 min) but were included in the predictions. It can be observed that the variation of yield stress versus mixing time was reasonably estimated, and the predicted data were comparable to the corresponding measured values. It can also be observed that the cement paste with 1.8% ML exhibited the highest slope of yield stress variation versus mixing time among the other mixtures, which is in good conformity with the experimental results (Fig. 8.10(a)). The results of the GA-predicted plastic viscosity values were also located close to

the corresponding experimental values, which indicate that the plastic viscosity predicted by the GA model is sensitive to the change in the elapsed mixing time (Fig. 8.10(b)).

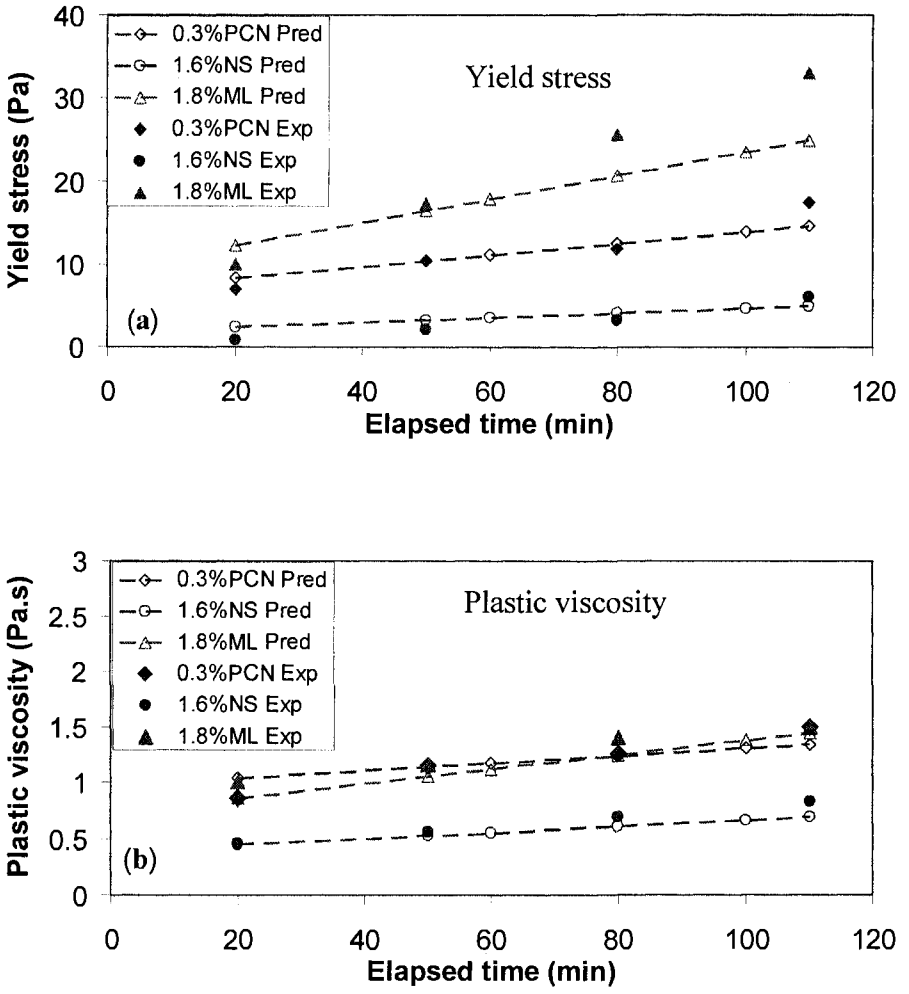

Figure 8.10-Variation in Bingham parameters of superplasticized cement pastes with elapsed time at a temperature of 45 °C: (a) yield stress, and (b) plastic viscosity.

The effect of the variation of temperature on the predicted yield stress and plastic viscosity is shown in Fig. 8.11. Additional data points not measured experimentally were also predicted by the GA model as shown in the figure. It can be observed that the predicted yield stress was reasonably sensitive to the change of temperature and increased

with the increase of temperature, reflecting the experimental trend. This is expected since the increase of temperature accelerates the rate of hydration of cement paste as discussed elsewhere (Al-Martini and Nehdi 2007). Moreover, most of the experimental data points are located in the vicinity of the corresponding predicted values (Fig. 8.11(a)). Similar to yield stress, the GA-predicted values of plastic viscosity also increased with temperature (Fig. 8.11(b)). The data in Fig. 8.11 indicate that the Bingham parameters predicted by the GA equations are sensitive to changes in cement paste temperature.

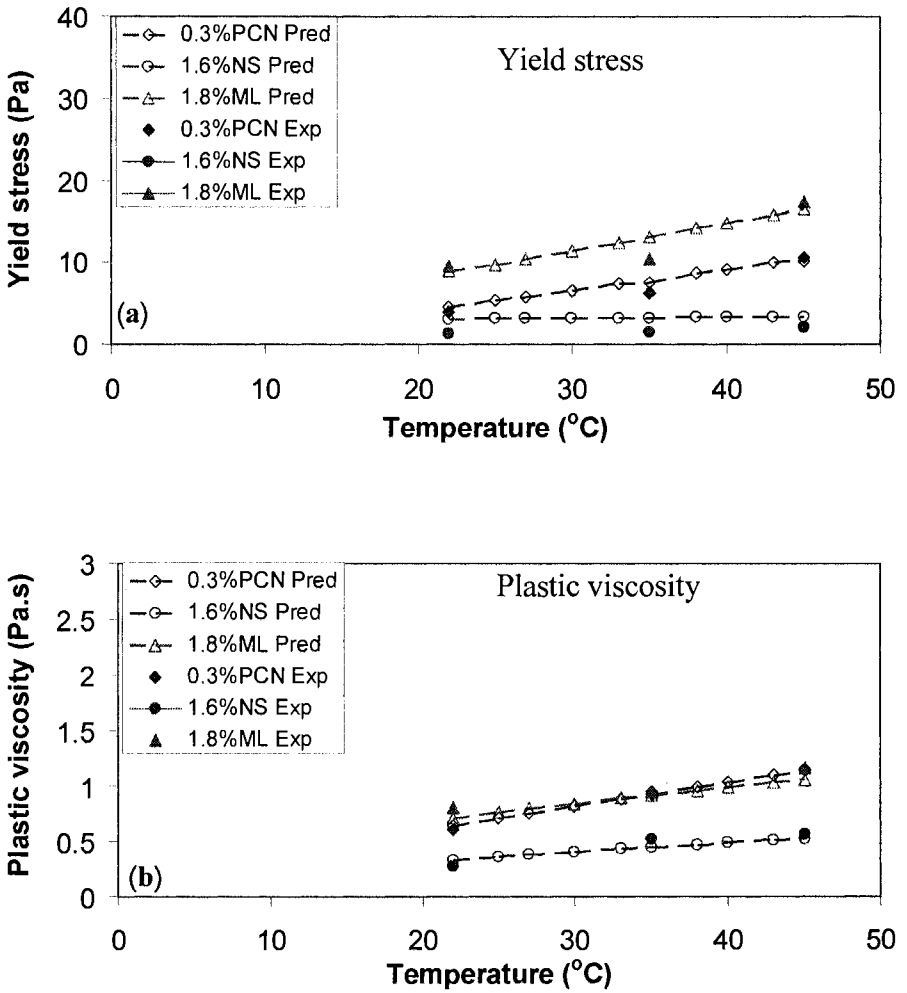

Figure 8.11-Variation in Bingham parameters of superplasticized cement pastes versus test temperature at 50 min of mixing time: (a) yield stress, and (b) plastic viscosity.

The influence of the superplasticizer dosage on the predicted yield stress and plastic viscosity is illustrated in Fig. 8.12. In this figure, the mixing time is 50 min and the temperature is 45 °C. Both experimental and predicted yield stress results decreased when the superplasticizer dosage increased as expected. It can be observed in Fig. 8.12(a) that the decrease in the predicted yield stress became marginal beyond a certain dosage for each superplasticizer; this dosage is denoted in the present paper as the theoretical saturation dosage, which was higher than that experimentally measured. An approximate estimation of the experimental saturation dosage can be found by the intersection of the two tangent lines to the ends of each curve for each superplasticizer (Fig. 8.12(a)). Using this approach, the saturation dosages can be depicted at 0.38% for PCN, 2.60% for ML, and 1.65% for NS, which are close to the corresponding experimentally determined values of 0.4%, 2.8%, and 1.8% for PCN, ML, and NS, respectively (Al-Martini and Nehdi 2008).

The effect of variation of the superplasticizer dosage on the plastic viscosity calculated by the GA equations is presented in Fig. 8.12(b). It can be observed that the plastic viscosity decreased when the superplasticizer dosage increased, which is in good agreement with experimental results. The experimental results of plastic viscosity shown in Fig. 8.12(b) are located relatively close to the corresponding GA-predicted values for all superplasticizers. This is expected since the *AAE* values of the predicted plastic viscosity are relatively small for all superplasticizers ($\leq$ 12%) as already discussed (Table 8.5).

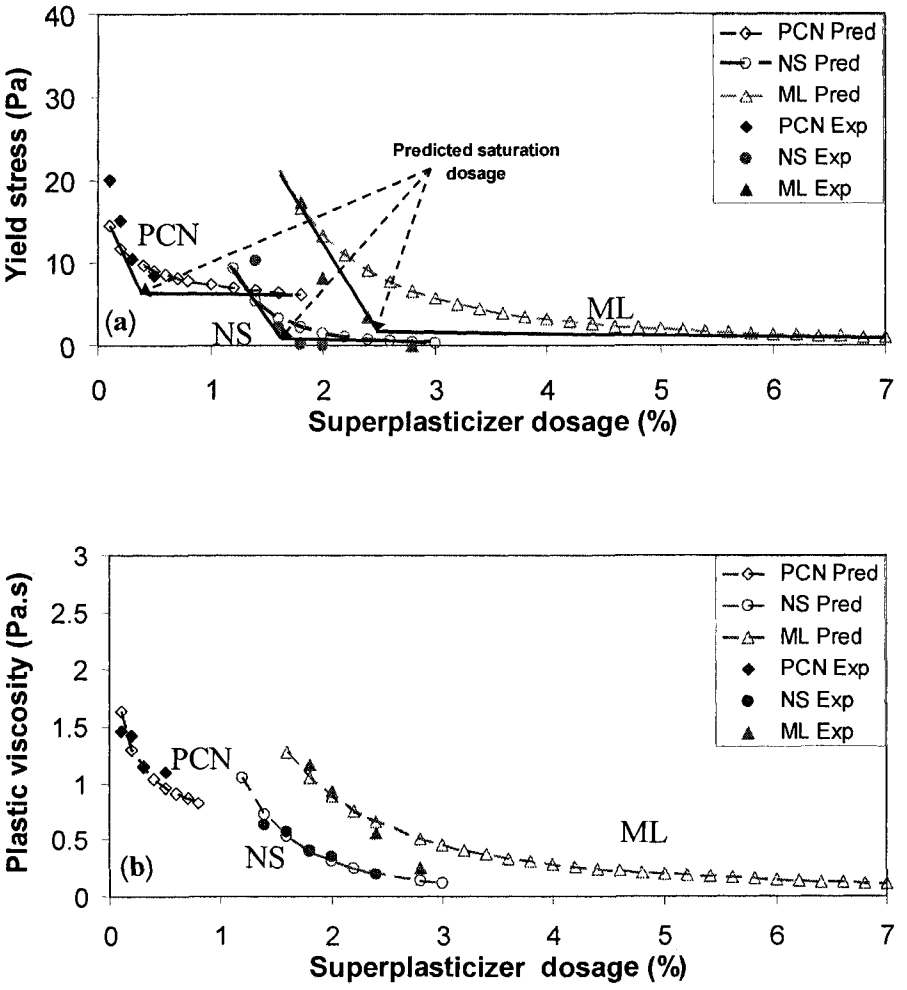

Figure 8.12-Variation of Bingham parameters of superplasticized cement pastes versus superplasticizer dosage at 45 °C and 50 min of mixing: (a) yield stress, and (b) plastic viscosity.

8.6 Conclusions

Empirical equations for predicting the shear flow curve of cement paste mixtures incorporating various superplasticizers and subjected to prolonged mixing at various temperatures have been developed in this chapter using the genetic algorithms approach. These flow curves were used to calculate the yield stress and plastic viscosity values for the various cement pastes investigated. The following conclusions can be drawn:

- The GA shear flow equations allowed predicting the yield stress and plastic viscosity of cement pastes incorporating PCN, ML, or NS with reasonable accuracy.
- The GA-based flow equations for cement paste developed in this chapter can depict the effect of the elapsed mixing time on the yield stress and plastic viscosity of cement pastes incorporating various superplasticizers and exposed to high temperature and prolonged mixing.
- The GA-based equations are sensitive to the increase in temperature and can capture the increase in yield stress and plastic viscosity with increased temperature.
- The GA-based equations are sensitive to the increase in superplasticizer dosage; both yield stress and plastic viscosity decreased in a curvilinear mode when the superplasticizer dosage increased.
- The approach suggested in this chapter to predict the superplasticizer saturation dosage gave satisfactory results when compared to corresponding experimental values.
- The GA-based approach for predicting the flow curve of cement paste incorporating various superplasticizers at different mixing time and temperature can allow developing a computational tool for predicting the Bingham parameters of cement paste. However, this demands extensive research to develop the proposed predictive equations beyond the limits of the material types and proportions, and ranges of test parameters used in the present study.

8.7 References

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Chapter 9

GENETIC ALGORITHM-BASED YIELD STRESS EQUATIONS FOR CONCRETE AT HIGH TEMPERATURE AND PROLONGED MIXING TIME*

9.1 Introduction

Proper understanding and controlling the rheological properties of fresh concrete can help ensuring its easy placement, consolidation and finishing, especially under severe field conditions such as prolonged hauling time and high temperature. Concrete is considered as a suspension in which aggregates are the particles and cement paste is the medium. Knowing the rheological properties of fresh cement paste may give an indication about the flow behaviour of fresh concrete. It is generally accepted that the flow of cement paste conforms well to the Bingham model (Asaga and Roy 1980). The behaviour of fresh concrete can also be described using the Bingham model in the following form (Tattersall 1991):

$$\tau = \tau_0 + \mu_p \dot{\gamma} \tag{9.1}$$

Where, τ (Pa) is the shear stress at shear rate $\dot{\gamma}$ (1/s) and τ_0 (Pa) and μ_p (Pa.s) are the yield stress and plastic viscosity values, respectively. Yield stress can be defined as the force needed to overcome the friction between solid particles, while the plastic viscosity

* A version of this chapter was submitted to the journal of Computers and Concrete for peer review and possible publication.

term is due to viscous dissipation resulting from the movement of water in the sheared material (Ferraris and de Larrard 1998).

The yield stress is an important rheological parameter that affects the flow behaviour of cement-based materials. It plays an essential role for example when it is required to place concrete easily without applying vibration. Therefore, the yield stress can be used as a quality control indicator for self leveling concrete (Yahia and Khayat 2001). Using a given rheological model (e.g. Bingham model), the yield stress can be determined from flow tests through extrapolation of the shear stress- shear rate curve to find the stress corresponding to zero shear rate.

The rheological properties of fresh concrete and cement paste are complex in different ways. Hence, measuring the rheological parameters of cement paste may not allow to accurately predict that of concrete. A few researchers attempted to investigate the correlation between the flow behaviour of cement paste or mortar and concrete, so that the fluidity of fresh concrete can be evaluated using simple tests on cement paste or mortar. For instance, Maruya *et al.* (2006) investigated the relationship between the yield stress of cement paste and slump flow of fresh concrete. Concrete having a water to cement ratio (w/c) of 0.35 was subjected to prolonged mixing for 60 min at 20 °C, and its slump flow was measured at 5, 30, and 60 min. The cement paste was prepared with the same w/c (w/c = 0.35) and the yield stress was also measured at 5, 30, and 60 min. It was found that the relationship between the slump flow of concrete and yield stress of cement paste was linear with a coefficient of correlation (R^2) of 0.62.

Struble and Chen (2005) tried to asses the correlation between the rheological properties of concrete and mortar. The concrete was continuously agitated in a mixer for up to 100 minutes at 25 °C and periodically sampled for rheological tests every 20 min. The mortar, on the other hand, was mixed only for a few minutes, rheologically tested, and then remained undisturbed in the rheometer until the next test; the rheological measurements were carried out every 20 min for up to 100 min. It was found that the relationship between the yield stress of mortar and that of concrete was fairly linear with a coefficient of correlation (R^2) of 0.70.

Several research efforts have been made to develop equations for predicting the yield stress of concrete. Some researchers tried to create empirical or analytical equations that relate the yield stress of concrete to its measured slump since in practice the slump test is routinely measured for quality control (Murata and Kikukawa 1992; Saak *et al.* 2004; and Wallevik 2006). Other researchers tried to create relationships between the yield stress of concrete and some of its physical properties. For example, Ferraris and de Larrard (1998) developed equations to calculate the yield stress of concrete as a function of the ratio between the volumetric fraction of solid materials and the maximum packing value of these solids (Φ_i/Φ^*_i). They found that the relative concentration of concrete solid components (cement, sand, or gravel) had different relationships with yield stress. Therefore, the yield stress equations proposed by Ferraris and de Larrard (1998) followed a linear form, in which the (Φ_i/Φ^*_i) for all concrete solid gradients were summed up. They developed two yield stress equations: the first was for concrete without superplasticizers, and the second was for concrete incorporating 1% by mass of binders of naphthalene-sulfonate (NS) superplasticizer.

More recently, Petit *et al.* (2007) developed equations to calculate the yield stress of concrete using the initial yield stress value (at zero time) of the corresponding mortar. They first investigated the coupled effects of time and temperature on the rheological properties of highly flowable mortars. The ambient temperature ranged from 10 to 30 °C and the changes in rheological properties of mortars were investigated over the dormant period. Thus, mortars remained in a standstill condition after being mixed and its rheological parameters were measured over time up to the end of dormant period. The time was normalized by dividing the elapsed time after the contact of cement particles with water (t) by the time, t_f, corresponding to the dormant period ($t'=t/t_f$). This non-dimensional parameter (t') that varies from 0 to 1 was used to eliminate the effect of temperature. They found that the yield stress of mortar increased linearly with the normalized time period (t'), and independently of the mixture temperature, but with different slopes for different mixtures. The same procedure was repeated on corresponding self-consolidating concrete (SCC) mixtures. It was found that the evolution of the yield stress of concrete with the normalized time (t') was exponential ($\tau_{o,c}(t') = \tau_{o,c}(0,T)e^{\alpha.t'}$), where $\tau_{o,c}(0,T)$ is the initial yield stress of concrete (at zero time), which depends on the test temperature, and α is an experimental constant depending on the type of concrete. A table with different values of this constant corresponding to different concrete mixtures at 20 °C was provided. Equations to predict the variation of yield stress of SCC using the measured initial yield stress of the corresponding mortar ($\tau_{o.m}(0,T)$) at a given temperature were also developed.

Measuring the rheological properties of fresh concrete is a difficult task usually requiring the use of a rheometer having a large gap to accommodate concrete aggregates.

Hence, the complicated methods used for this purpose are generally unsuitable for rapid quality control in field conditions. Therefore, it is important in the robotization of concreting operations to develop reliable equations for predicting its flow and deformation, in which various factors such as the mixing time, ambient temperature, and superplasticizer type and dosage are considered.

In this chapter, the correlation between the yield stress of concrete mixtures and that of corresponding cement paste mixtures was investigated to explore the possibility of using the cement paste rheology to predict the rheology of concrete made with a similar paste. Furthermore, equations for calculating the yield stress of fresh concrete as a function of the mixing time, ambient temperature, and superplasticizer dosage were developed using the genetic algorithm technique (GA). These equations have been ascertained to be applicable and reasonably accurate upon exploring their sensitivity to changes in the test parameters.

9.2 Experimental Work

9.2.1 Materials

The cement paste and concrete mixtures were prepared using ordinary CSA Type 10 portland cement and incorporating a new generation of polycarboxylate- (PCN), melamine sulfonate- (ML), or naphthalene sulfonate– (NS) based superplasticizers. All cement paste and concrete mixtures were made with a water to cement mass ratio (w/c) of 0.38. Washed natural pea gravel was used as coarse aggregate along with natural sand as fine aggregate. The concrete mixture proportions were calculated using the absolute volume method. Accordingly, all concrete mixtures were made with 475 kg/m^3 of cement, 895 kg/m^3 of fine aggregate and 800 kg/m^3 of coarse aggregate with no air entrainment.

9.2.2 Apparatus

The rheology of fresh concrete and cement paste were investigated using a BML rheometer and an AR-2000 rheometer, respectively. The cement paste rheometer measures the shear stress (τ) at different shear rates (γ), while the concrete rheometer measures the torque resistance (T_R) at several rotational speeds (N). For the cement paste, the relationship between shear stress and shear rate is fit to the Bingham model (Eq. 9.1). For concrete, the relationship between flow resistance and flow rate is typically linear and can be expressed using the following equation:

$$T_R = G + H N \tag{9.2}$$

Where, T_R (Nm) is the torque resistance, G (Nm) is the flow resistance, H (Nm.s) is the viscosity factor, and N is the rotational speed (rev/s).

Similar to the Bingham yield stress, G is the intercept of the T_R-N line with the torque axis (y), and it represents the force necessary for concrete to start flowing; H is the slope of this line and is a measure of the resistance of the concrete to an increased speed of flow (Geiker *et al.* 2002). Equations 9.3 and 9.4, which are based on the *Reiner-Riwlin Equation,* were used by the software that controls the concrete rheometer to convert the measured constants (G and H) to Bingham constants (τ_o and μ_p) (Wallevik 2006):

$$\mu = \frac{H\left(1/R_i^{\,2} - 1/R_o^{\,2}\right)}{8\pi^2 h} \tag{9.3}$$

$$\tau_o = \frac{G\left(1/R_i^{\,2} - 1/R_o^{\,2}\right)}{4\pi h \ln\left(R_o / R_i\right)} \tag{9.4}$$

Where, R_i is the radius of the inner cylinder (R_i = 0.10 m), R_o is the radius of the outer cylinder (R_o = 0.145 m), and h is the height of the inner cylinder (h = 0.20 m). A detailed description of the concrete rheometer and procedure implemented can be found in chapter six.

9.2.3 Experimental procedure

The concrete and cement paste mixtures were continuously mixed for up to 110 min to simulate the concrete mixing in a concrete truck mixer during concrete transportation to a construction site. For high temperatures (35 and 45 °C), the mixing was conducted in an environmental chamber, and for moderate temperature (22 °C) mixing took place in the lab under a controlled environment at 22 °C.

The rheology of fresh concrete and cement paste mixtures was measured after 20, 50, 80, and 110 minutes from the start of mixing. The testing scheme used for cement paste and concrete, can be found in chapter 5 and 6, respectively. Further details about the mixing and rheological test procedures can be found elsewhere (Al-Martini and Nehdi 2008-a; and Al-Martini and Nehdi 2008-b).

9.2.4 Experimental results

Figures 9.1(a) and 9.1(b) illustrate typical flow curves (only the down part of curves is shown) for fresh cement paste and concrete, respectively. The superplasticizer saturation dosage is traditionally defined as the dosage beyond which a higher dosage will not significantly decrease the yield stress. This definition was found to be valid for cement paste and concrete mixtures incorporating ML and NS (Al-Martini and Nehdi 2008-a; and Al-Martini and Nehdi 2008-b). However, the saturation dosage for cement paste and

concrete made with PCN was identified when the yield stress stopped decreasing and started to increase with further increase of the PCN dosage. An explanation of this phenomenon can be found elsewhere (Al-Martini and Nehdi 2008-a; and Al-Martini and Nehdi 2008-b). Based on experimental results, the yield stress of cement paste made with a particular superplasticizer also reflects the behaviour of this superplasticizer when it is incorporated in concrete made with a similar cement paste.

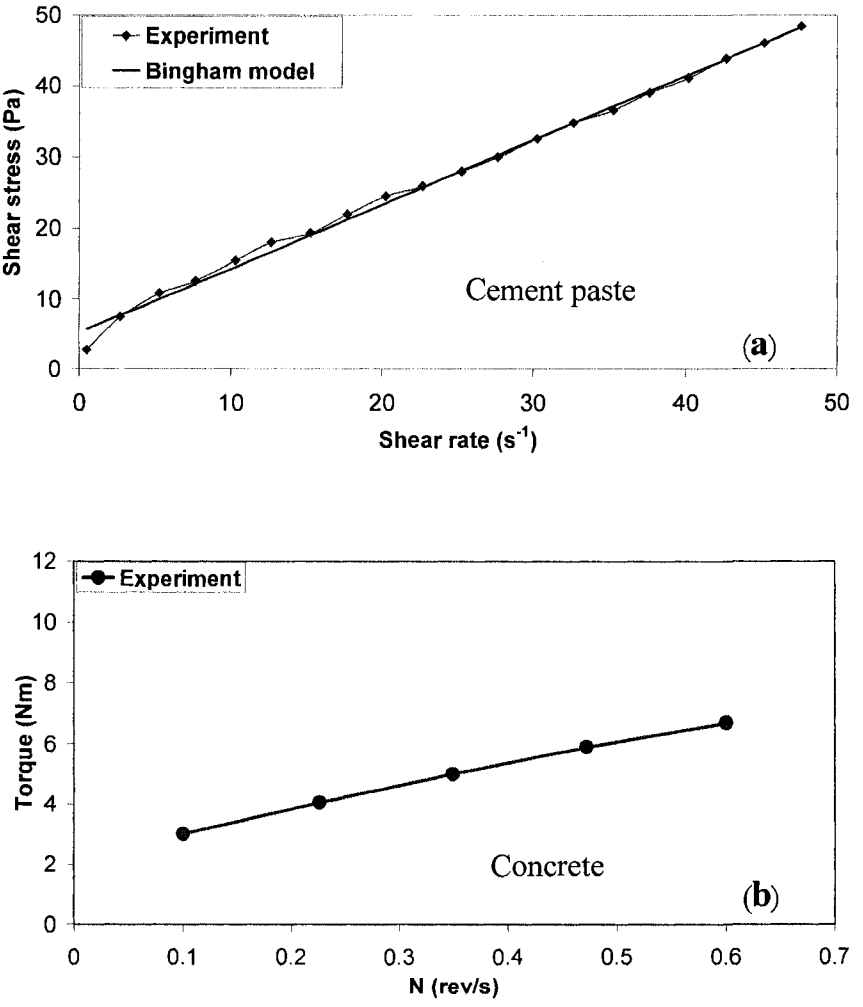

Figure 9.1-Flow curves: (a) shear stress versus shear rate (down curve for cement paste), and (b) torque versus rotational speed (down curve for concrete).

To evaluate the relationship between the rheology of fresh concrete and that of cement paste, the yield stress of concrete mixtures incorporating ML or NS was plotted versus that of corresponding cement paste mixtures (Fig. 9.2). It should be noted that this relationship could not be investigated for PCN, because the PCN saturation dosage for cement paste was much lower (0.4%) than that for the corresponding concrete (1.5%). As such, the rheology of concrete made with PCN could not be investigated at a dosage below 0.4% because it became very stiff, which could damage the instrument. Maruya *et al.* (2006) reported that polycarboxylate superplasticizers can also be adsorbed by aggregates in concrete. Therefore, more superplasticizer is needed for concrete than that for cement paste when evaluating the fluidity of concrete and cement paste. Several functions (such as linear, logarithmic, and polynomial) were tested to correlate the yield stress of concrete mixtures with that of corresponding cement paste mixtures; the linear function was found to give the best fit. Figure 9.2(a) shows that the yield stress of concrete made with ML increased linearly when the yield stress of its corresponding cement paste increased, however the correlation coefficient was low ($R^2 = 0.41$). Similar to ML, the yield stress of concrete mixtures incorporating NS correlated linearly with the yield stress of corresponding cement pastes, but the coefficient of correlation was also weak ($R^2 = 0.50$) (Fig. 9.2(b)).

Thus, it can be argued that measuring the yield stress of cement paste can give some indication about the rheological behaviour of concrete made with a similar paste. However, the rheology of concrete must be specifically explored to gain more accurate knowledge of its flow behaviour. As such, the equations developed by the authors in previous work (Al-Martini and Nehdi 2008-c) to predict the rheological properties of cement paste mixtures

subjected to prolonged mixing under various temperatures cannot be used to predict the yield stress of corresponding concrete mixtures, and therefore new equations for concrete need to be developed.

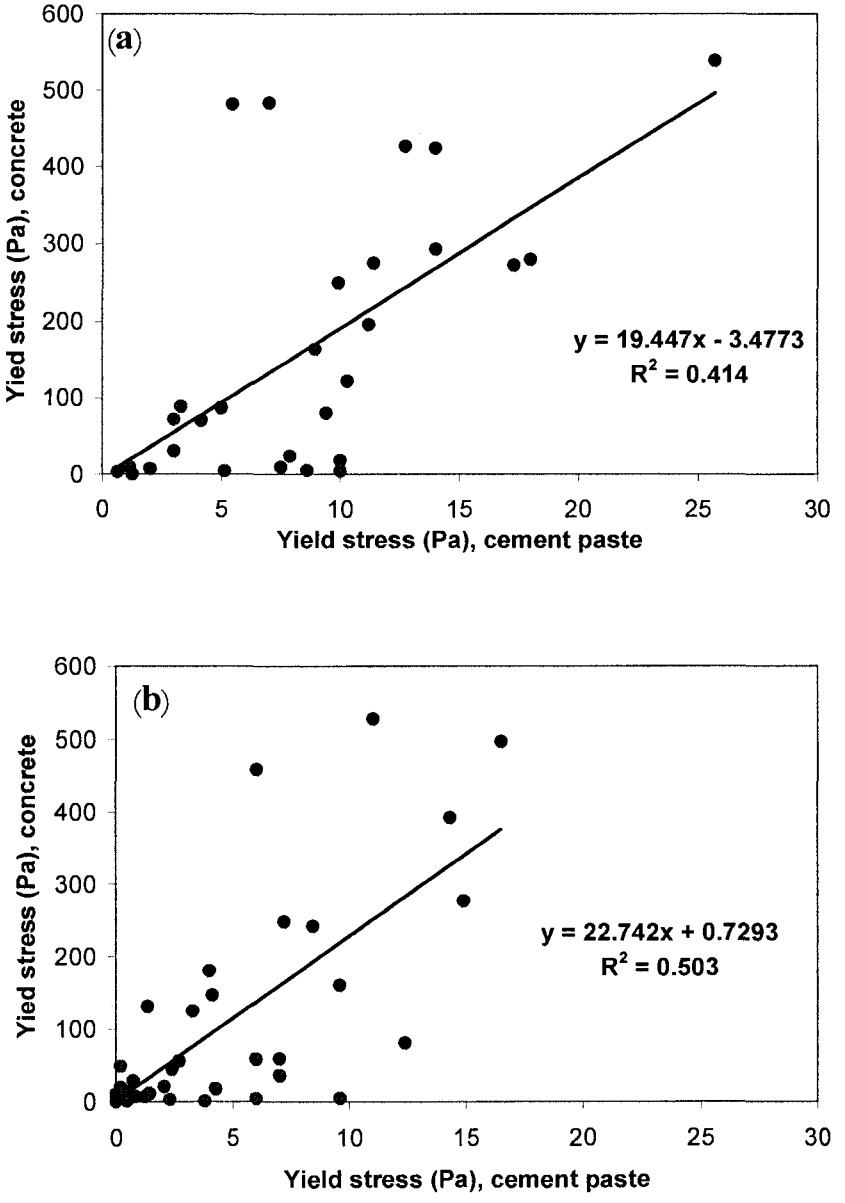

Figure 9.2-Correlation between yield stress of concrete and that of cement paste made with: (a) ML and (b) NS.

The yield stress versus elapsed time of fresh concrete mixtures incorporating 0.8% PCN, 1.8% ML, and 1.6% NS are plotted in Figs. 9.3(a), 9.3(b), and 9.3(c), respectively. It can be observed that the yield stress generally increased linearly with the elapsed time at the temperatures tested. The yield stress evolution with temperature generally followed power functions for the mixing times investigated (Figs. 9.4(a), 9.4(b), 9.4(c)). It should be noted that the rheology of concrete made with 1.8% of ML could not be investigated at 45 ^{o}C and 110 min because it became very stiff which could damage the instrument. The variation of yield stress of concrete mixtures at 45 ^{o}C as a function of the superplasticizer dosage is illustrated in Figs. 9.5(a), 9.5(b), and 9.5(c), for mixtures incorporating 0.8% PCN, 1.8% ML, and 1.6% NS, respectively. The yield stress decreased with increased superplasticizer dosage and an inverse power function governed this relationship. It should be noted that the relationships between yield stress and test variables were similar for all concrete mixtures investigated, and results for other concrete mixtures not discussed above will not be presented herein.

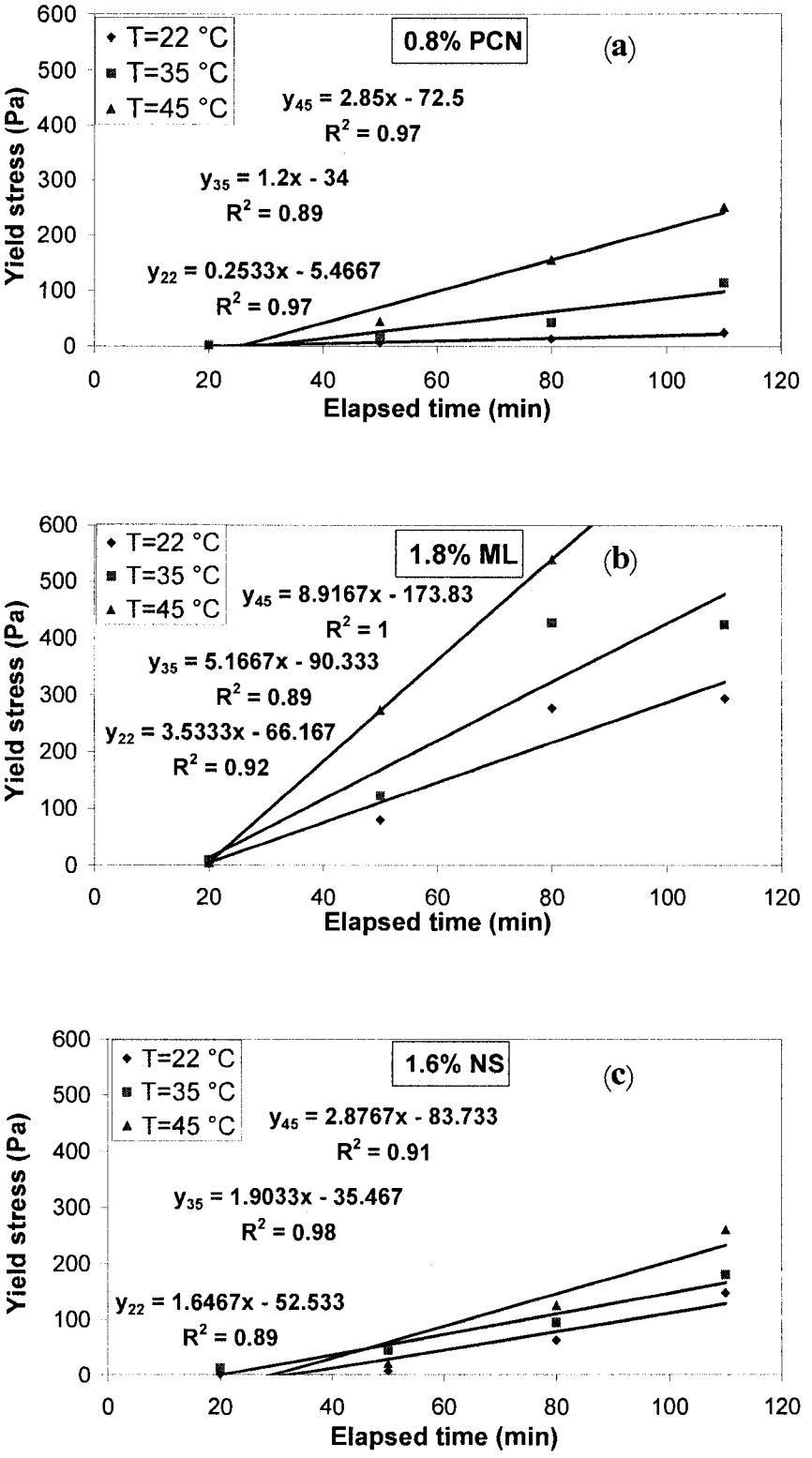

Figure 9.3-Typical variation in yield stress of concrete as a function of mixing time for different superplasticizers.

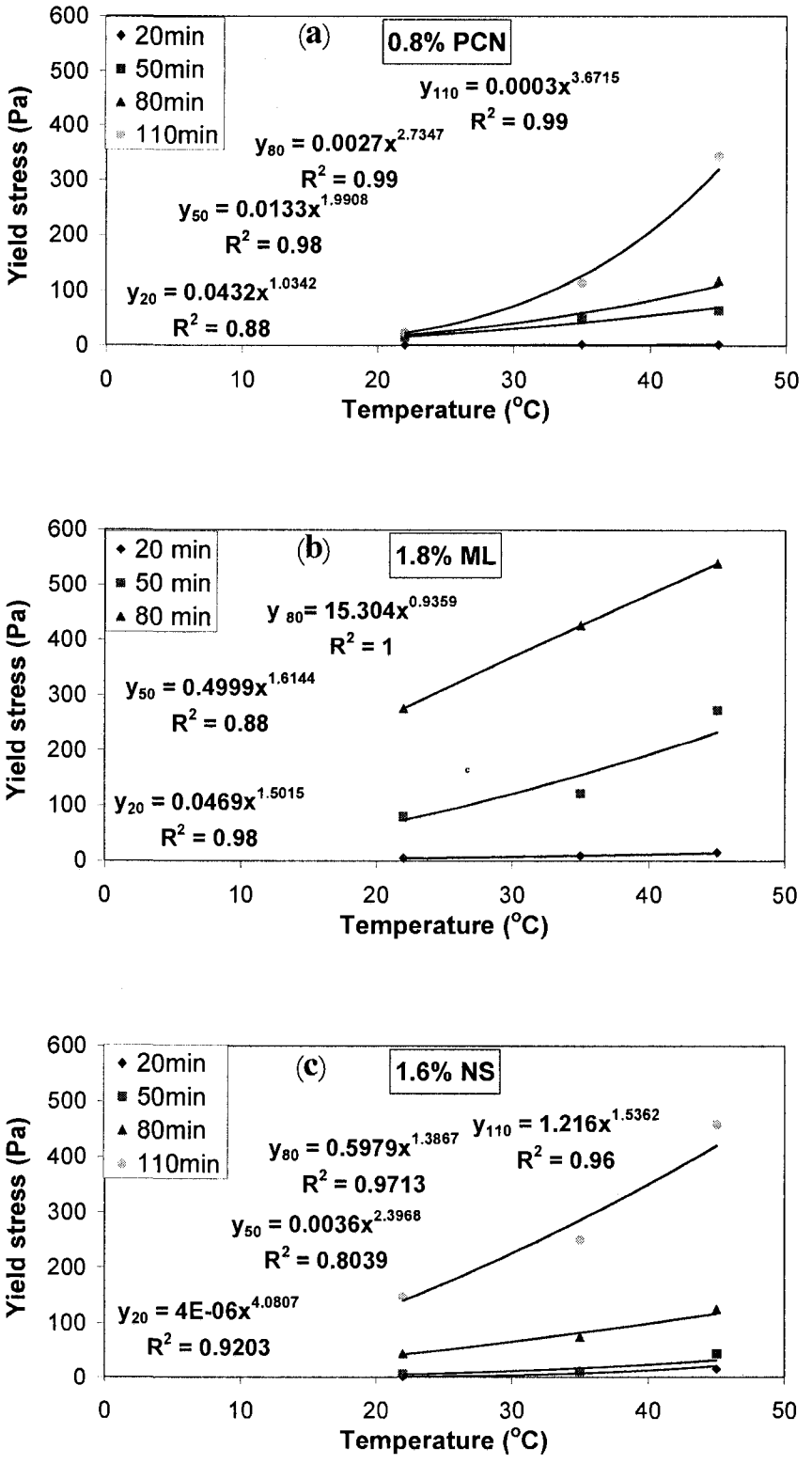

Figure 9.4-Typical variation in yield stress of concrete as a function of ambient temperature for different superplasticizers.

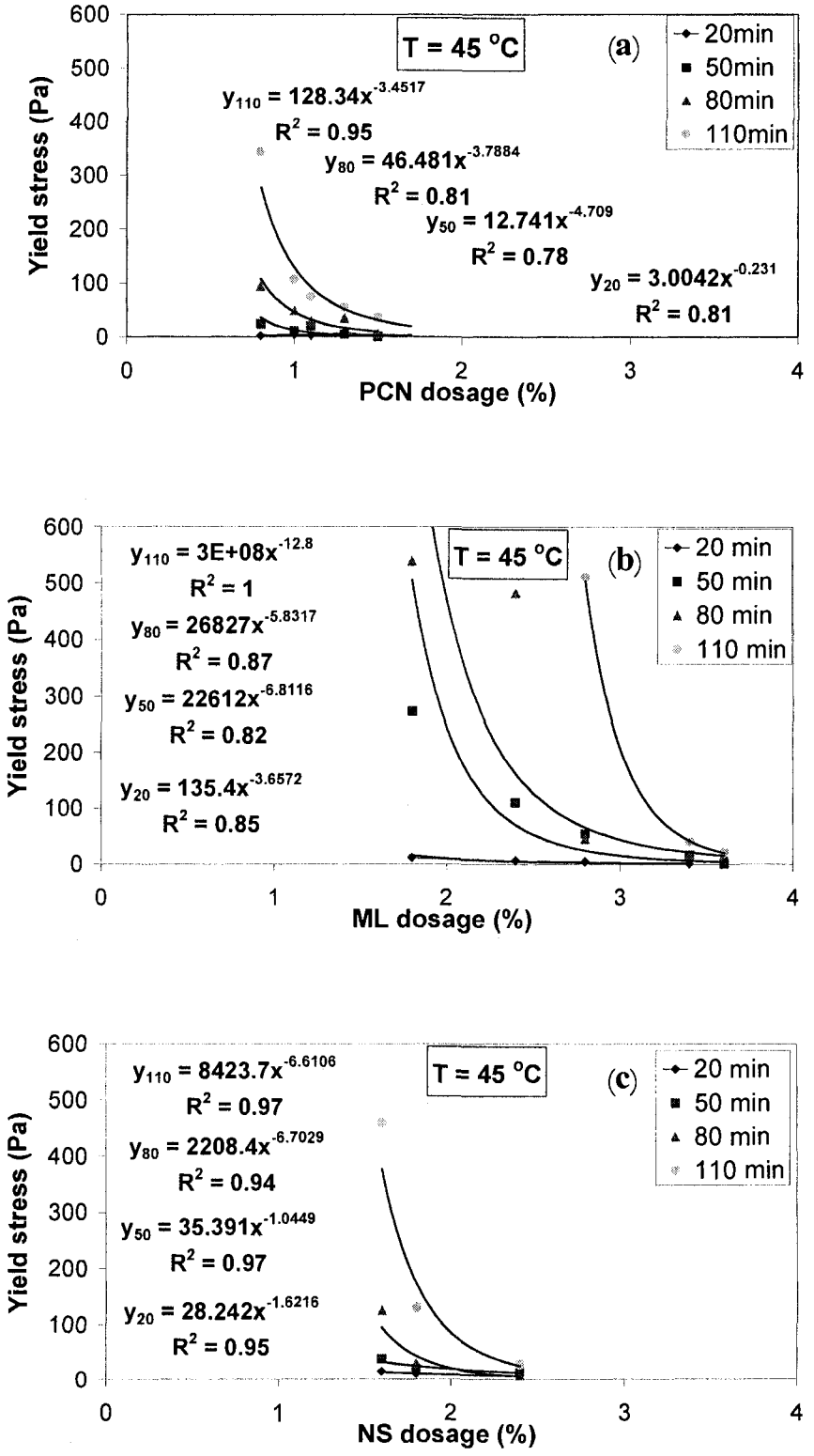

Figure 9.5-Typical variation in yield stress of concrete as a function of superplasticizer dosage for different superplasticizers.

9.3 Database

In order to develop genetic algorithm (GA) models able of capturing the relationships between the input and output parameters, they must be trained on a relatively large number of representative data sets. Data used in the training and testing of the GA models were obtained from the experimental program conducted by the present authors (Al-Martini and Nehdi 2008-b). In total, 120 concrete mixtures were tested (40 for each of the 3 superplasticizers). For each superplasticizer, 30 mixtures were used during the model training process, and the remaining 10 mixtures were used for testing the model. The GA-based equations were optimized to predict the Bingham yield stress for each concrete mixture. It must be noted that each flow curve consists of 5 data points (Fig. 9.1(b)). Hence, 150 data points (30 mixtures multiplied by 5 points each) for each superplasticizer were used for the training process, while 50 data points (10 mixtures multiplied by five points each) were used for testing.

9.4 Modeling Methodology

The genetic algorithm (GA) approach (see for example Michalewicz 1996) was used in this investigation to develop yield stress equations for fresh concrete mixtures incorporating various superplasticizers and subjected to prolonged mixing at various temperatures. For this goal, an original equation defining the overall flow behaviour of concrete must be used in the GA-based optimization process. Equation 9.2 was used in this chapter to create GA-based yield stress equations for fresh concrete.

The experimental results showed that the yield stress had a linear relationship with the mixing time, and therefore the relationship between the yield torque (yield torque is proportional to yield stress) and time can be expressed as follows:

$$G = a\ t - b \tag{9.5}$$

Based on the experimental results, the relationship between the yield torque of concrete and temperature can be generally fit to a power function as follows:

$$G = cT^{d} \tag{9.6}$$

The yield stress has an inverse power function with the superplasticizer dosage below the saturation dosage, and therefore the relationship between the yield torque and superplasticizer dosage can be written as follows:

$$G = eD^{-f} \tag{9.7}$$

Accordingly, the yield torque can be expressed as a function of the mixing time, ambient temperature, and superplasticizer dosage using the method of separation of variables:

$$G = \frac{(a\ t - b\ )(c\ T^{d}\ )}{(e\ D^{f}\ )} \tag{9.8}$$

Where *a, b, c, d, e,* and *f* are model constants. Table 9.1 shows the ranges of the abovementioned experimental coefficients.

Table 9.1-Range for model coefficients

Coefficient	PCN	ML	NS
a	0.1-4.0	0.1-10.0	0.3-5.0
b	0.1-150.0	1.5-200.0	10-200.0
c	0.0000007-1	0.0001-15	0.0001-2
d	0.5-5.0	0.8-4.0	0.1-2.0
e	0.4-500	10000-90000	20000-50000
f	1-5	1-15	0.9-10.0

Substituting Eq. 9.8 in the first term of Eq. 9.2, the flow curve can be obtained as follows:

$$T_R = \frac{(a\ t - b\ )(c\ T^d\ )}{(e\ D^f\ )} + HN \tag{9.9}$$

Where, t is time (min), T is temperature (°C), and D is superplasticizer dosage (% by cement mass). The second term in Eq. 9.9 (the viscosity factor, H) was considered as a constant for each flow curve and its value was taken from the measured slope of the flow curve considered.

Using the genetic algorithms approach, Eq. 9.9 was optimized and the optimum coefficients in this equation were determined so that the yield torque in Eq. 9.9 can be predicted with an acceptable accuracy within the ranges of the tested mixing time, ambient temperature, and superplasticizer dosage. A new equation was developed for each superplasticizer type, because previous work by the authors (Al-Martini and Nehdi 2008-b) showed that each superplasticizer behaved differently.

An objective function was constructed to measure how well the predicted yield torque data agree with the corresponding measured experimental values. The GA search process was terminated when the maximum number of generations was reached and then a

set of coefficients that minimizes the objective function was found. Table 9.2 shows the model parameters.

Table 9.2-Parameters used in genetic algorithm setting

Number of Individuals	70
Maximum Generations	10000
Selection Method	Roulette wheel selection
Selection Pressure	1.7
Recombination Rate	0.74
Mutation Rate	0.01

The optimized equations were converted to the Bingham yield stress through multiplying each by the conversion factor introduced in Eq. 9.4. The optimized equations are shown below:

For concrete incorporating a polycarboxylate superplasticizer:

$$\tau_{o\,PCN} = \left[\frac{(0.371t - 5.62)\times\left(10^{-7}T^{1.563}\right)}{500D^{2.93}} \times \frac{\left(1/R_i^{\,2} - 1/R_o^{\,2}\right)}{4\pi h \ln(R_o/R_i)}\right] \tag{9.10}$$

For concrete incorporating melamine-sulfonate superplasticizer:

$$\tau_{o\,ML} = \left[\frac{(1.5t - 29.3)\times\left(0.00079T^{1.5}\right)}{50000D^{2.5}} \times \frac{\left(1/R_i^{\,2} - 1/R_o^{\,2}\right)}{4\pi h \ln(R_o/R_i)}\right] \tag{9.11}$$

For concrete incorporating naphthalene-sulfonate superplasticizer:

$$\tau_{o\,NS} = \left[\frac{(0.43t - 8.5)\times\left(0.00007T^{0.1}\right)}{20000D^{4}} \times \frac{\left(1/R_i^{\,2} - 1/R_o^{\,2}\right)}{4\pi h \ln(R_o/R_i)}\right] \tag{9.12}$$

9.5 Results and Discussion

9.5.1 Validation of yield stress equations

The predicted yield stress data of fresh concrete mixtures is plotted versus the corresponding experimentally measured values in Fig. 9.6. The figure includes both training data (data used during the construction of the equations) as well as testing data (data not used during the construction of the equations and thus unknown to the model). The data points predicted by the GA model for PCN, ML, and NS are shown in Figs. 9.6(a), 9.6(b), and 9.6(c), respectively; they are located on or within small ranges around the equity lines.

The testing data, which are unknown to the GA model in the training process, were used to validate the yield stress equations (9.10-9.12). The ability of each of the yield stress equations to accurately estimate the yield stress of fresh concrete mixture with variation of the mixing time, temperature, and superplasticizer type and dosage was evaluated using the average absolute error (*AAE*) (Eq. 9.13) along with the ratio of the measured to predicted yield stress ($\tau_{o,m}/\tau_{o,p}$).

$$AAE = \frac{\left|\tau_{om} - \tau_{op}\right|}{\tau_{om}} \times 100 \tag{9.13}$$

The average, standard deviation (*SD*), and coefficient of variation (*COV*) of the measured-to-predicted yield stress ratio and average absolute error (*AAE*) for testing data are presented in Table 9.3. It can be observed that the *AAE* values were 36%, 28%, and 33% for PCN, ML, and NS, respectively. The results indicate that the GA model was able to learn the relationships between yield stress and the different testing parameters.

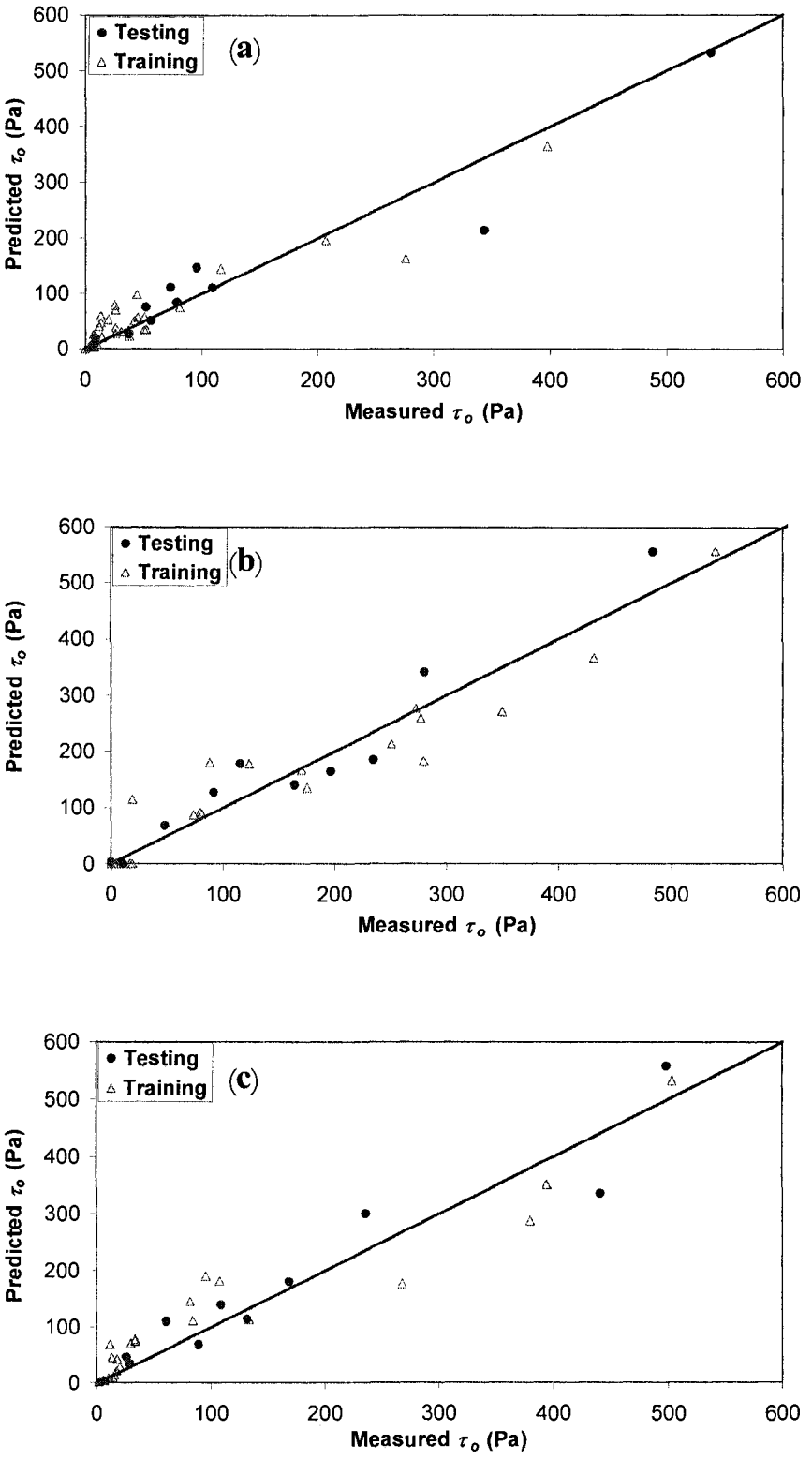

Figure 9.6-Measured versus predicted yield stress for concrete mixtures at different temperatures and mixing times and incorporating: (a), PCN, (b) ML, and (c) NS.

Table 9.3-Performance of calculation equations for the yield stress of fresh concrete mixtures incorporating different superplasticizers

Superplasticizer	*AAE* (%)	γ_o (measured)/γ_o (calculated) (All test points)		
		Average	*SD*	*COV* (%)
PCN	36	0.94	0.35	37
ML	28	0.92	0.25	27
NS	33	0.97	0.35	36

9.5.2 Parametric study

There is need to explore whether the GA-based equations thus developed have captured the effects of the various test variables on yield stress. Hence, the influence of the mixing time, ambient temperature, and superplasticizer dosage on the yield stress of fresh concrete was tested. Concrete mixtures made with 0.8% PCN, 1.8% ML, and 1.6% NS were selected from the experimental database to conduct the parametric study.

Figure 9.7(a) illustrates the sensitivity of the GA-based equations to change in the mixing time. It should be noted that the yield stress values at 60 and 100 min were not experimentally tested, but were predicted by the model (Fig. 9.7(a)). It can be observed from Fig. 9.7(a) that the GA equations were able to capture the effect of the mixing time on the yield stress of concrete; the predicted yield stress increased with the elapsed time. The experimental results used for comparison are reasonably located close to the corresponding predicted values (Fig. 9.7(a)).

To examine the sensitivity of the GA-based equations to the ambient temperature, the yield stress of the selected concrete mixtures was predicted at various temperatures and at 50 min (Fig. 9.7(b)). The yield stress of concrete at temperatures not tested experimentally was also predicted as shown in Fig. 9.7(b). It can be observed that the yield stress increased with the increase of temperature, indicating that the GA has captured the effect of temperature on the yield stress of concrete. It can also be observed in Fig. 9.7(b) that yield stress predictions were reasonably close to the corresponding experimentally measured values.

To evaluate whether the developed equations captured the effect of the superplasticizer dosage on yield stress, the yield stress of concrete at 50 min and 45 °C was calculated at varying superplasticizer dosages. Figure 9.7I illustrates the ability of the GA-based equations to capture the influence of the superplasticizer dosage on the yield stress values of fresh concrete mixtures; the yield stress decreased in a curvilinear trend with the increase of the superplasticizer dosage and the predicted values of yield stress are reasonably close to the corresponding experimental data (Fig. 9.7I). At a certain dosage, the decrease of yield stress became quasi linear and marginal for all superplasticizers tested (Fig. 9.7I). This critical dosage was depicted for each superplasticizer and compared to the corresponding saturation dosage measured experimentally. The predicted critical dosages were 1.4%, 3.2%, and 2.2%, for PCN, ML, and NS, respectively, and the corresponding experimentally measured saturation dosages were 1.5%, 2.8%, and 2.0% for PCN, ML, and NS, respectively (Al-Martini and Nehdi 2008-b). The saturation dosage for each superplasticizer was estimated reasonably well by the GA-based equations.

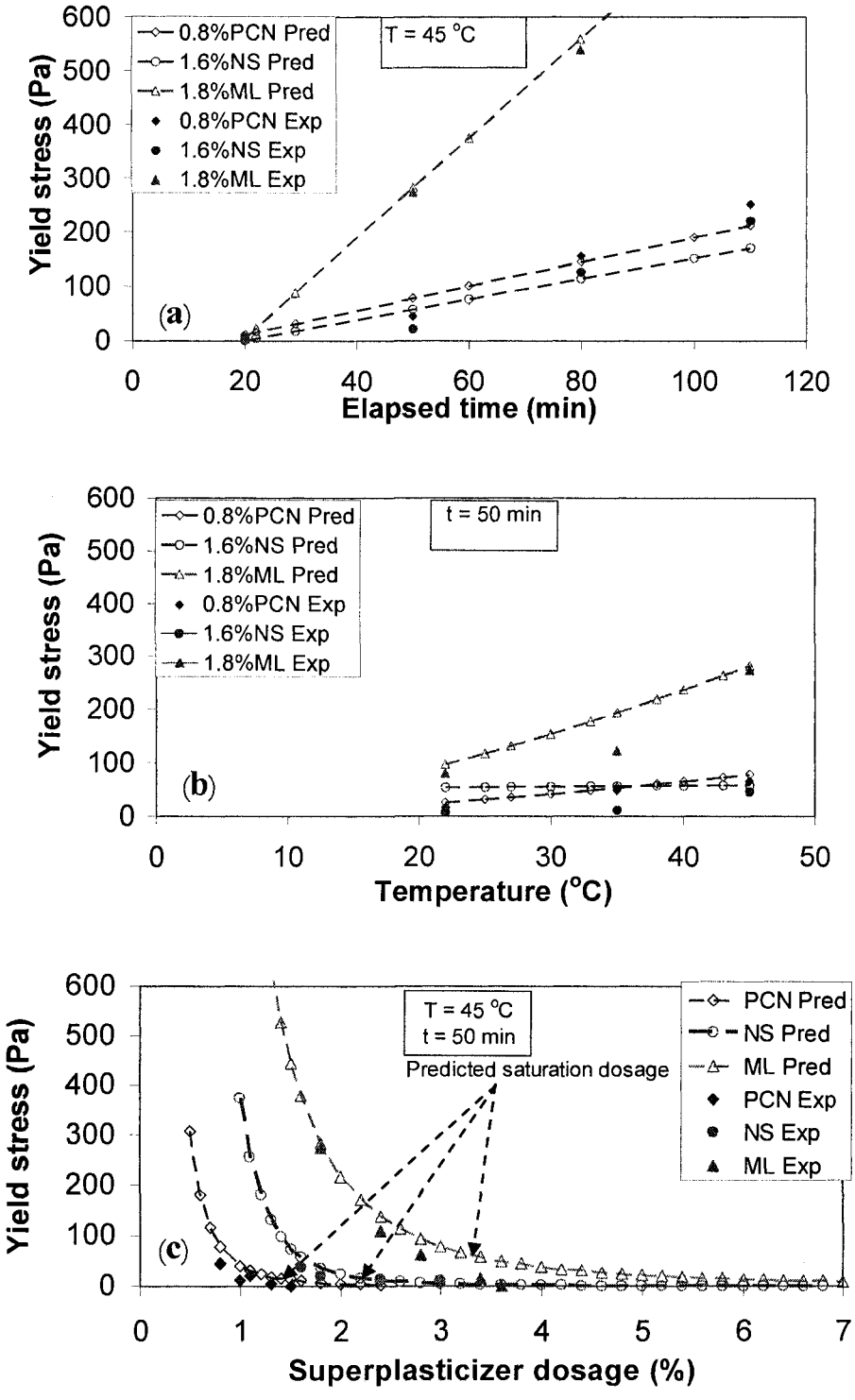

Figure 9.7-Variation in yield stress of superplasticized concrete mixtures versus: (a) elapsed time at 45 °C, (b) ambient temperature at 50 min, and (c) superplasticizer dosage at 45 °C and 50 min.

9.6 Conclusions

In this chapter, the correlation between the rheology of fresh concrete and that of cement paste mixtures was evaluated by measuring the yield stress of concrete and that of its corresponding cement paste. The concrete and cement paste mixtures incorporating various dosages of different superplasticizers, namely PCN, ML, or NS, and were subjected to prolonged mixing at high temperature. The results showed weak linear correlations between the yield stress of concrete and that of its corresponding cement paste, indicating that cement paste rheology cannot be used to accurately predict the rheology of concrete made with a similar paste.

The genetic algorithms technique was used to develop equations for predicting the yield stress of concrete. Three equations (a separate equation for each superplasticizer) were developed to calculate the yield stress of concrete at various mixing time, ambient temperature, and superplasticizer dosage. The calculated yield stress results using the proposed equations agreed well with corresponding experimental values. A sensitivity analysis for each equation to various test parameters was carried out and the following conclusions can be made:

- The GA-based equations captured the effect of the mixing time on the yield stress of concrete; the calculated yield stress increased with the elapsed time.
- The GA-based equations captured the effect of the ambient temperature on the yield stress of concrete, and the calculated yield stress increased with the increase of the ambient temperature.

- The GA-based equations also captured the effect of the superplasticizer dosage on the yield stress of concrete, and the calculated yield stress decreased in a curvilinear mode when the superplasticizer dosage increased.
- The saturation dosage for each superplasticizer was depicted from the calculated yield stress versus dosage curves; the depicted saturation dosages agreed well with corresponding experimental values.
- It should be empathized that the proposed yield stress equations for concrete are valid for the type of materials tested and within the range of parameters investigated. Therefore, the validity of these equations must be further verified by conducting additional experimental research in which different materials and test parameter ranges are used.

9.7 References

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Chapter 10

ESTIMATING TIME AND TEMPERATURE DEPENDENT YIELD STRESS OF CEMENT PASTE USING OSCILLATORY RHEOLOGY AND GENETIC ALGORITHMS*

10.1 Introduction

Oscillatory shear tests are a rheological technique capable of providing information on the properties of viscoelastic materials. Fresh cement paste is considered as a viscoelastic material since it has both elastic and viscous properties. In recent years, oscillatory shear tests have been given special attention by several researchers who studied the rheology of cement paste (Struble and Schultz 1993; Nehdi and Al-Martini 2007; Chen *et al.* 2006; Papo and Piani 2004; and Saak *et al.* 2001). Using this technique, the elastic and viscous behaviour of cement paste can be characterized and it can be determined whether cement particles are dispersed or flocculated (Min *et al.* 1993). This technique was used for instance to investigate the continuously changing cement paste structure during hydration, which could not be investigated effectively using conventional flow tests, because such tests cause changes in the microstructure of cement paste (Struble and Chen 2005).

Indeed, cement paste with flocculated cement particles is sensitive to the shear history, making the measurement of its yield stress a difficult task (Struble and Leit 1995).

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* A version of this chapter was submitted to the journal ofCement and Concrete Research for peer review and possible publication.

Conventional flow curves allow estimating the yield stress through extrapolation of the flow curve to determine the shear stress at zero strain (Struble and Leit 1995). One of the major drawbacks of this technique is the fact that yield stress is measured when cement paste is flowing (viscous state) after its structure has already been broken. Furthermore, the value of yield stress estimated using conventional flow curves depends on the rheological model used for its calculation since each model can fit the experimental shear stress–shear strain data differently (Nehdi and Rahman 2004). Conversely, an oscillatory shear test estimates the yield stress of cement pastes by depicting the shift point from its elastic to viscous state. This is done through subjecting the cement paste to a sinusoidal shear stress and measuring the corresponding strain. The applied oscillatory stress can be expressed as follows:

$$\sigma = \sigma_o \cos \omega t \tag{10.1}$$

For an ideal elastic solid, the resulting oscillatory strain will be in phase with the stress and is expressed as follows:

$$\gamma = \gamma_0 \cos \omega t^* \tag{10.2}$$

For a viscous liquid, the resulting oscillatory strain will be 90° out of phase with the stress, and is expressed in the following equation:

$$\gamma = \gamma_o \cos\left(\omega t^* - \frac{\pi}{2}\right) \tag{10.3}$$

Thus, the resulting oscillatory strain for a viscoelastic material such as cement paste is given by:

$$\gamma = \gamma_o \cos(\omega t^* - \delta) \tag{10.4}$$

In the equations above σ is the shear stress (Pa), σ_o is the amplitude of shear stress (Pa), ω is the angular velocity (1/s), t^* is time (s), γ is the shear strain, γ_o is the amplitude of shear strain, and δ is the phase shift. When a viscoelastic material is subjected to a sinusoidal stress, the resulting sinusoidal strain will have a lag of δ with that of stress, which varies in the range of 0 to $\pi/2$ (Chow *et al.* 1988; Ferguson and Kemblowski 1991).

At low shear stress, cement particles are typically in close contact with each other and cement paste behaves as a solid material, where its microstructure is not disturbed and can recover elastically (Schultz and Struble 1992). When the applied stress becomes sufficiently high and reaches a certain value, the strain becomes significant and cement particles begin to separate from each other, thus cement paste starts to flow. The critical stress at which the cement paste transforms from elastic to viscous state corresponds to the yield stress parameter of the Bingham equation:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \tag{10.5}$$

Where τ is shear stress (Pa), τ_o is the yield stress (Pa), μ_p is the plastic viscosity (Pa.s), and $\dot{\gamma}$ is the shear rate (s^{-1}).

In the present chapter, the oscillatory shear stress technique was applied to cement pastes incorporating various superplasticizers and subjected to prolonged mixing at high temperature. The objective is to find a methodology based on the experimental oscillatory shear stress test results to predict the yield stress of superplasticized cement pastes under various ambient temperatures and mixing times.

10.2 Experimental Procedure

The cement paste mixtures tested in this chapter are identical to those previously investigated in chapter five using the conventional flow curve technique. Ordinary portland cement Type I was used along with liquid superplasticizers including a polycarboxylate-based superplasticizer (PCN), melamine sulfonate-based superplasticizer (ML), and naphthalene sulfonate-based superplasticizer (NS). The water to cement ratio (w/c) was 0.38 and the dosages of superplasticizers ranged from 0.2-0.4% for PCN, 1.8-2.4% for ML, and 1.2-2.0% for NS by mass of cement.

The cement paste mixtures were subjected to prolonged mixing for up to 110 min at various ambient temperatures (22-45 ^{o}C). For the moderate temperature, the mixing took place in the lab environment with a controlled temperature of 22 ^{o}C, and for high temperatures (35 and 45 ^{o}C); the mixing was carried out in an environmental chamber with controlled temperature. The shear stress-shear strain and oscillatory shear tests were performed using an advanced rheometer (TA-Instruments AR-2000) with a coaxial concentric cylinder geometry. The first rheological measurement was taken at 20 min after the first contact between cement and water. Subsequently, a new cement paste sample from

the same mixture subjected to continuous mixing was tested every half hour for up to 110 min.

The flow test procedure is described in detail in chapter five. For the oscillatory shear test, the cement paste was subjected to a shear rate sweep from 0 to 70 s^{-1} for two minutes to create uniform conditions before testing by breaking down its structure (Saak *et al.* 2001). The cement paste sample was then left to rest for 5 min in order to rebuild its broken structure. Subsequently, a stress sweep was applied by stressing the cement paste sample from 0.008 to 500 Pa, and the resulting strain was recorded. The frequency of the oscillatory shear was maintained constant at 1 Hz throughout the rheological testing.

10.3 Experimental Results

Figure 10.1(a) shows a typical descending part of a conventional flow curve for cement paste. It is well established that cement paste reasonably follows a Bingham behaviour (Asaga and Roy 1980), and therefore the flow curve in Fig. 10.1(a) was fit to the Bingham equation (10.5). The yield stress (the parameter of concern in this chapter) is determined by extrapolation of the shear stress-shear rate curve corresponding to a zero shear rate, and the plastic viscosity is the slope of this curve as shown in Fig. 10.1(a).

Figure 10.1(b) illustrates a typical oscillatory shear strain/stress curve displayed only over a narrow range of oscillatory shear stress (less than 10 Pa) to clearly visualize the transition of cement paste from a solid-like material to a liquid-like material. The relationship between oscillatory shear strain and oscillatory shear stress can be divided into three regions as shown in Fig. 10.1(b). Region (1), the zone below the yield point, represents the elastic solid behaviour of fresh cement paste. The strain in this region is very

small (about 10^{-6}). The relationship between strain and stress is linear with a marginal slope (almost zero). At low stress, cement particles are flocculated due to mutual attraction forces exerted by a combination of van der Waals and electrostatic forces, and they stick together to form agglomerates. The elastic linear region of the oscillatory shear stress-shear strain curve indicates that at a small strain the structure of cement paste deforms without breakdown of its structure (Min *et al.* 1993).

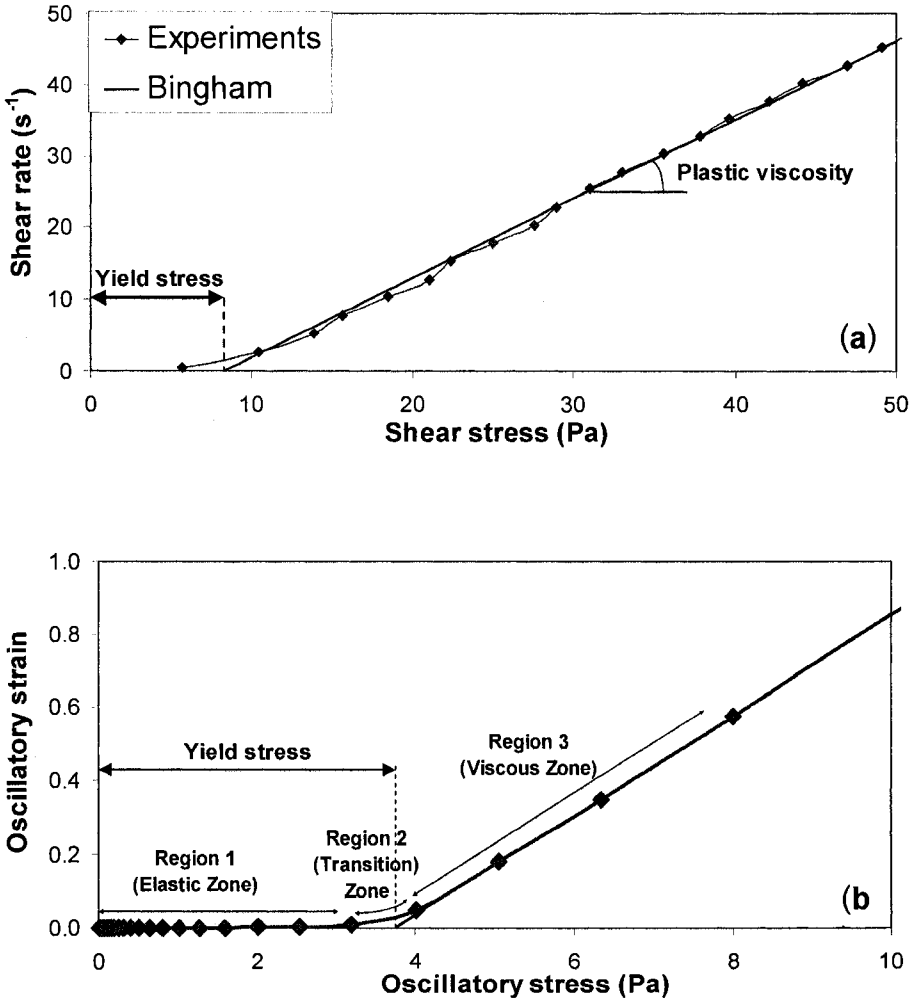

Figure 10.1-Typical rheological curves: (a) shear rate-shear stress flow curve (only down curve shown), and (b) oscillatory shear strain/stress curve.

In region 2 (transition zone), the relationship between the oscillatory shear strain and oscillatory shear stress follows a quasi curve-linear form, which represents the beginning of structure breakdown of cement agglomerates. This zone identifies the shift of fresh cement paste from an elastic to viscous state (the solid-liquid transition). The transition from solid-like to liquid-like behaviour can be observed across a remarkably narrow stress increment (usually 1 Pa or less).

In zone 3, the cement paste deforms greatly under the applied stress; the relationship between strain and stress is linear (Fig. 10.1(b)). The yield stress can be reasonably estimated as the intersection point between the linear viscous part of the strain-stress curve with the oscillatory stress axis as shown in Fig. 10.1(b).

The yield stress for cement pastes at different ambient temperatures and mixing times and incorporating ML are estimated using both conventional flow test (Bingham model) and an oscillatory shear tests (Fig. 10.2). It can be observed that the yield stress values estimated by the oscillatory shear test roughly correspond with that measured using the flow test since the data points are not closely located to the equity line. Struble and Schultz (1993) reported a similar observation for cement pastes at different w/c and stated that the value of yield stress determined using the oscillatory technique estimated better the yield stress than that using the flow curve technique.

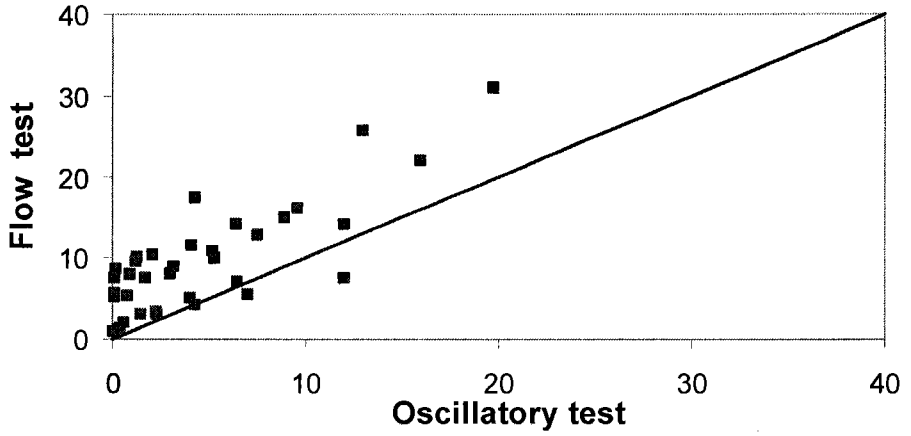

Figure 10.2-Yield stress value (in Pa) estimated from shear flow tests versus corresponding oscillatory shear tests data for cement pastes at different temperatures, mixing times, and ML dosages.

Figure 10.3 shows the effect of the mixing time and ambient temperature on the yield stress of cement pastes incorporating various superplasticizers as estimated using the oscillatory shear test. It can be observed that the yield stress increased with the increase of mixing time, which is in agreement with findings of previous work (Al-Martini and Nehdi 2008) using conventional flow tests (Fig. 10.3(a)). The yield stress of cement pastes also increased with the increase of temperature (Fig. 10.3(b)). The rate of this increase became higher at higher temperature, which reflects the acceleration of hydration reactions of cement at higher temperature (Al-Martini and Nehdi 2007).

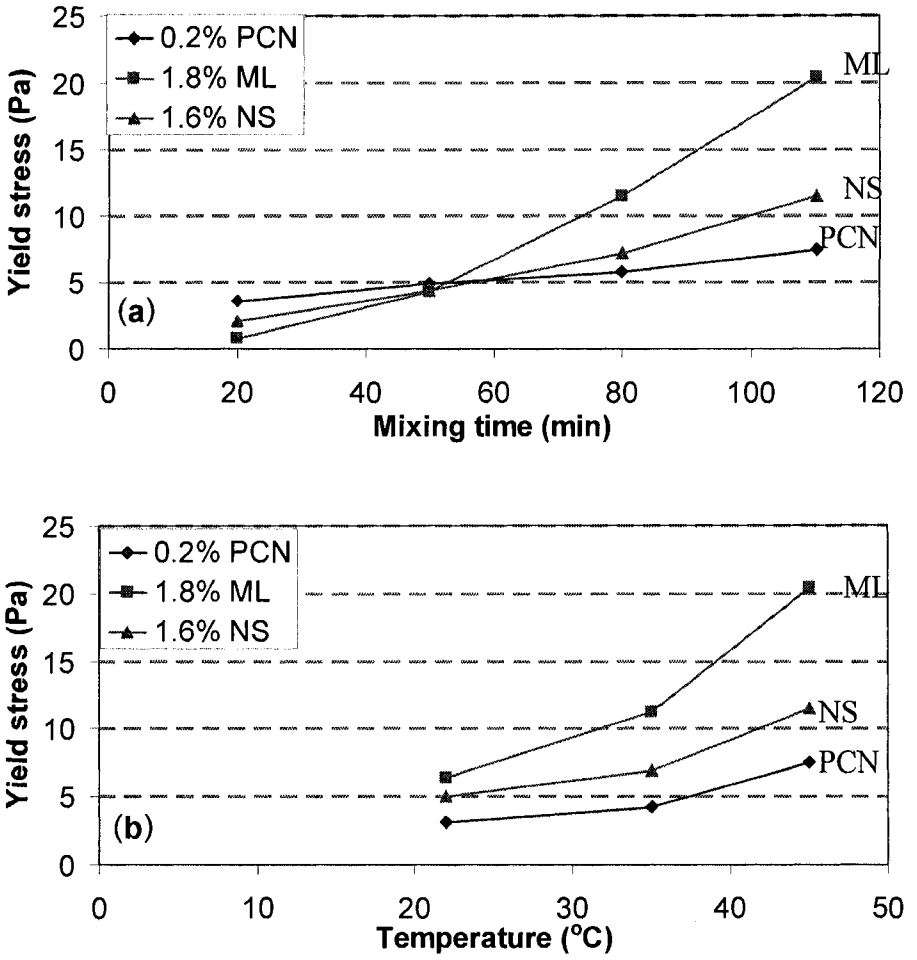

Figure 10.3-Variation of yield stress of cement pastes versus: (a) mixing time at 45 °C, and (b) temperature after 110 min of mixing.

10.4 Database

The genetic algorithm (GA) technique used in this chapter to model the yield stress of cement pastes must be trained using a relatively large and comprehensive number of representative data sets in order to become able to capture the relationships between the input and output parameters. In total, 108 cement paste mixtures were tested (36 mixtures for each superplasticizer used). For each superplasticizer, 26 mixtures were used during the training process, and the rest were used for testing the model. GA-based equations were optimized to predict the viscous part of the oscillatory shear strain-stress curve for each

cement paste mixture. Each oscillatory shear strain/stress curve consists of 10 points. For each admixture, the highest value of shear stress at the end of the transition zone between the linear and viscous parts of the curve for all experiments performed on this admixture was depicted. Taking advantage of the fact that the viscous region is linear, the ten data points for each admixture were chosen from the range after the highest value of shear stress depicted (the viscous part). Hence, 260 oscillatory stress-strain data points (26 mixtures multiplied by 10 points each) for each superplasticizer were used for the training process, while 100 data points (10 mixtures multiplied by ten points each) were used for testing.

10.5 Modeling Methodology

As mentioned earlier, the yield stress can be defined as the intersection between the viscous region of the oscillatory shear strain-stress line and the oscillatory shear axis. This linear relationship between oscillatory strain and stress was found to have the following form:

$$\gamma = a \times \tau - b \tag{10.6}$$

Where α, and b are experimental coefficients, which are functions of the mixing time (t), ambient temperature (T), and superplasticizer dosage (D) (Figs. 10.4-10.9). These relationships can be presented as follows:

$$a(t) = -c_{at} \times t + e_{at} \text{ (for all superplasticizers)} \tag{10.7}$$

$$a(T) = -c_{aT} \times T + e_{aT} \text{ (for all superplasticizers)} \tag{10.8}$$

$$a(D) = +c_{aD} \times D + e_{aD} \text{ (for all superplasticizers)} \tag{10.9}$$

$$b(t) = -c_{bt} \times t + e_{bt} \text{ (for PCN)} \tag{10.10}$$

$$b(t) = +c_{bt} \times t + e_{bt} \text{ (for ML and NS)} \tag{10.11}$$

$$b(T) = -c_{bT} \times T + e_{bT} \text{ (for all superplasticizers)} \tag{10.12}$$

$$b(D) = -c_{bD} \times D + e_{bD} \text{ (for all superplasticizers)} \tag{10.13}$$

where c_{at}, e_{at}, c_{aT}, e_{aT}, c_{aD}, e_{aD}, c_{bt}, e_{bt}, c_{bT}, e_{bT}, c_{bD}, and e_{bD} are experimental coefficients. Table 10.1 shows the experimental ranges of these coefficients for each superplasticizer; these ranges were used by the GA model in its search for optimum solutions. Using the method of separation of variables, the oscillatory shear strain-stress relationship (Eq. 10.6) can be expressed as follows:

For PCN:

$$\begin{aligned}\gamma = &\left[\left(-c_{at}t + e_{at}\right)\left(-c_{aT}T + e_{aT}\right)\left(c_{aD}D + e_{aD}\right)\right]\tau - \\ &\left[\left(-c_{bt}t + e_{bt}\right)\left(-c_{bT}T + e_{bT}\right)\left(-c_{bD}D + e_{bD}\right)\right]\end{aligned} \tag{10.14}$$

For ML and NS:

$$\begin{aligned}\gamma = &\left[\left(-c_{at}t + e_{at}\right)\left(-c_{aT}T + e_{aT}\right)\left(c_{aD}D + e_{aD}\right)\right]\tau - \\ &\left[\left(c_{bt}t + e_{bt}\right)\left(-c_{bT}T + e_{bT}\right)\left(-c_{bD}D + e_{bD}\right)\right]\end{aligned} \tag{10.15}$$

where t is time (min), T is temperature (°C), and D is superplasticizer dosage (% by cement mass).

The Genetic Algorithm (GA) technique (see Michalewicz 1996; and Goldberg 1989) was used to optimize the coefficients of equations 10.14 and 10.15 so that the viscous part of the experimental oscillatory shear strain/stress curves for various mixtures can be predicted with acceptable accuracy within the ranges of test parameters, i. e. mixing time, ambient temperature, and superplasticizer dosage. Separate equations were developed for different superplasticizers, because it was found in previous work by the authors (Nehdi and Al-Martini 2007) that these superplasticizers had different effects on the rheology of cement pastes.

Table 10.1-Range of model coefficients in equations 10.14 and 10.15

Coefficient	PCN		ML		NS	
	a	*b*	*a*	*b*	*a*	*b*
c_t	0.0001-0.001	-0.001-0.05	0.0001-0.005	-0.03-0.05	0.0007-0.009	0.0007-0.03
e_t	0.2-1	0.21	1-5	-10-2	0.1-0.9	0.001-2
c_T	-0.001-0.01	0.0001-0.05	-0.001-1	-0.0001-0.1	0.0007-0.04	0.0001-10
e_T	0.2-1	0.1-2	0.1-1	-8-3	0.1-1.5	0.001-10
c_D	20-200	50-400	100-1000	50-1000	10-100	2-300
e_D	0.01-0.5	0.5-2	0.2-2	1-20	0.1-1	0.1-10

The GA search process was terminated when the maximum number of generations was reached and then a set of coefficients that minimizes the objective function was found. Table 10.2 presents the parameters used in the genetic algorithm setting.

Table 10.2-Parameters used in genetic algorithm setting

Number of Individuals	70
Maximum Generations	10000
Selection Method	Roulette wheel selection
Selection Pressure	1.7
Recombination Rate	0.74
Mutation Rate	0.01

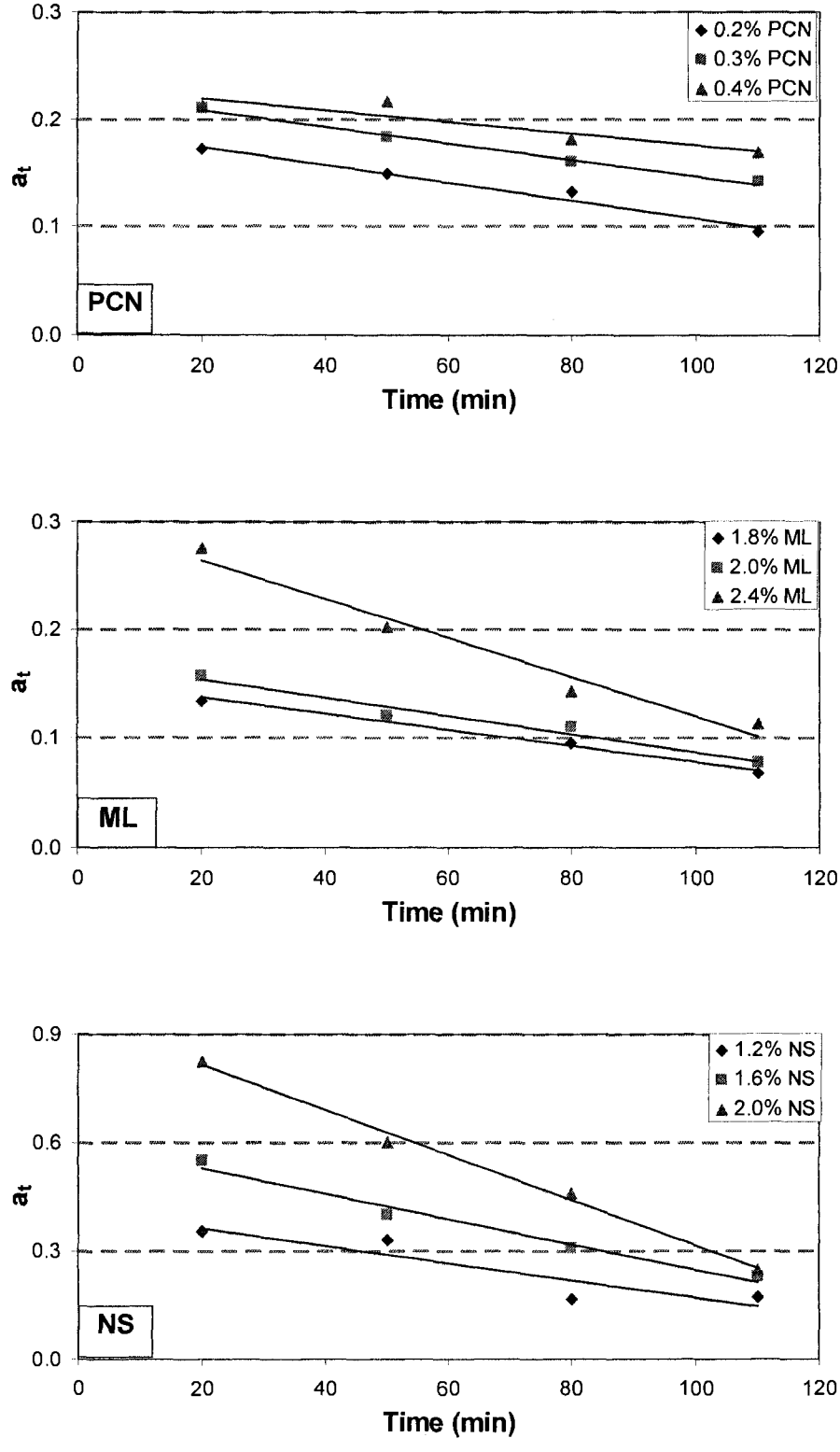

Figure 10.4-Experimental coefficient (a) of oscillatory shear strain/stress equations as a function of mixing time.

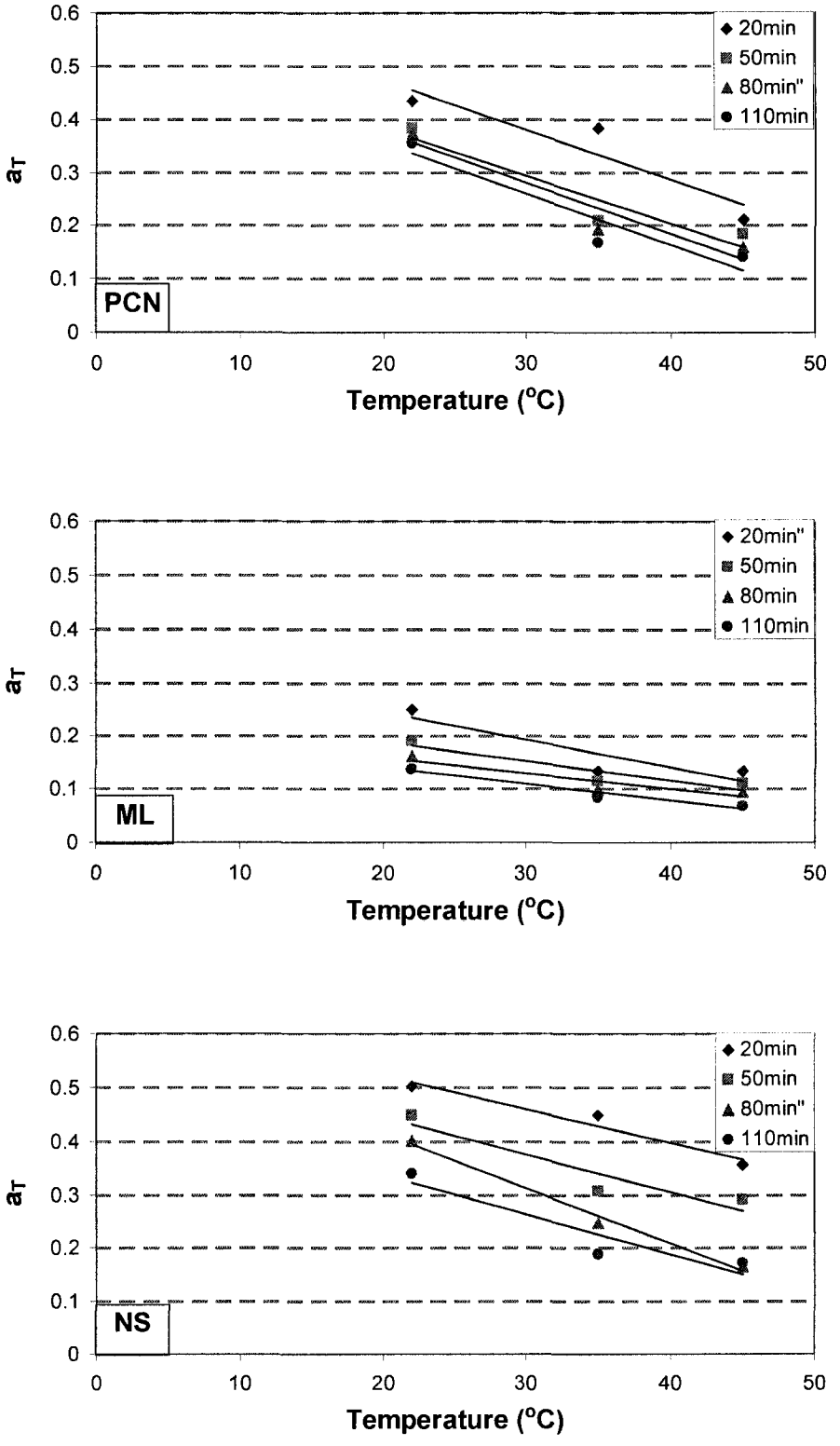

Figure 10.5-Experimental coefficient (*a*) of oscillatory shear strain/stress equations as a function of ambient temperature.

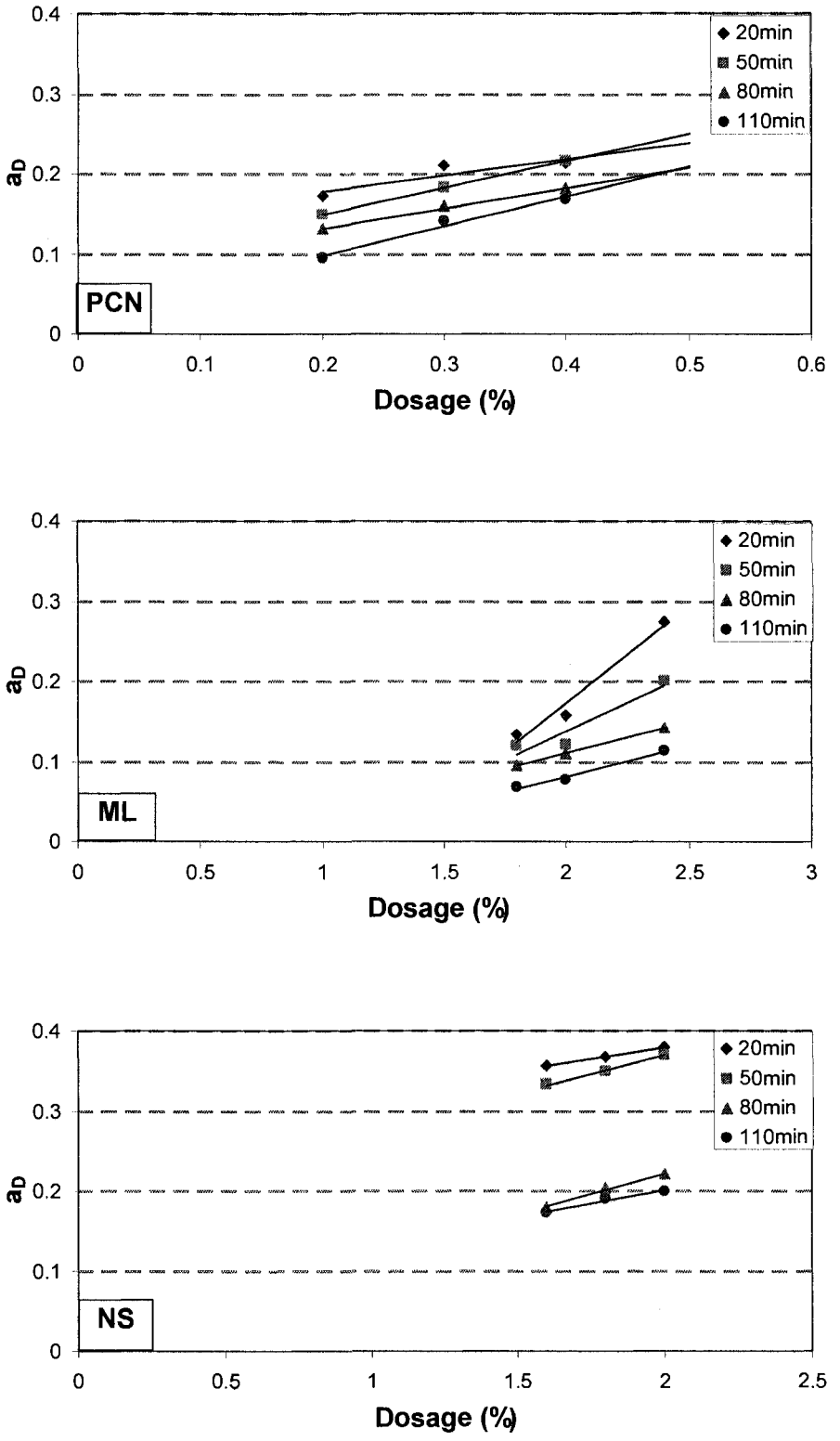

Figure 10.6-Experimental coefficient (a) of oscillatory shear strain/stress equations as a function of superplasticizer dosage.

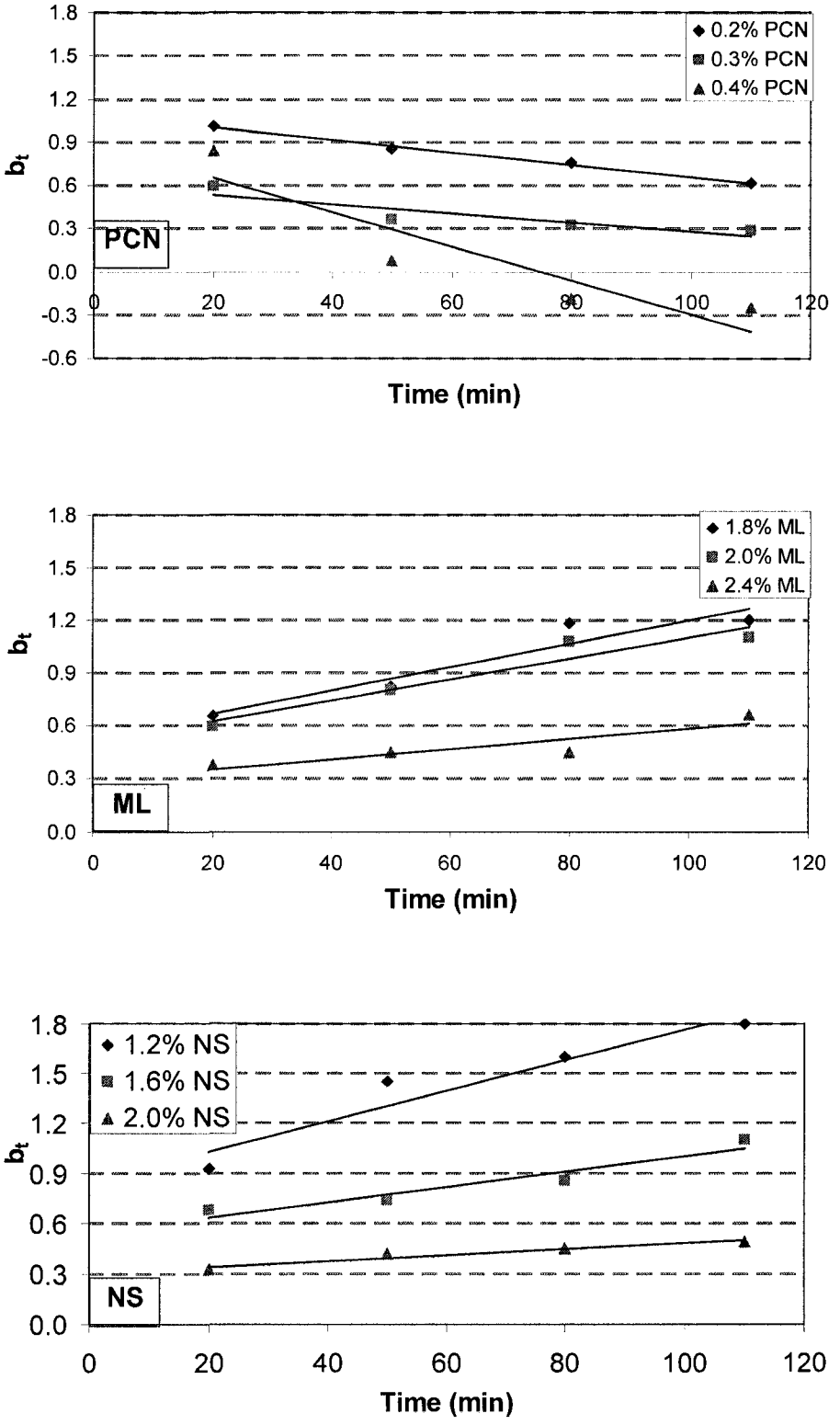

Figure 10.7-Experimental coefficient (*b*) of oscillatory shear strain/stress equations as a function of mixing time.

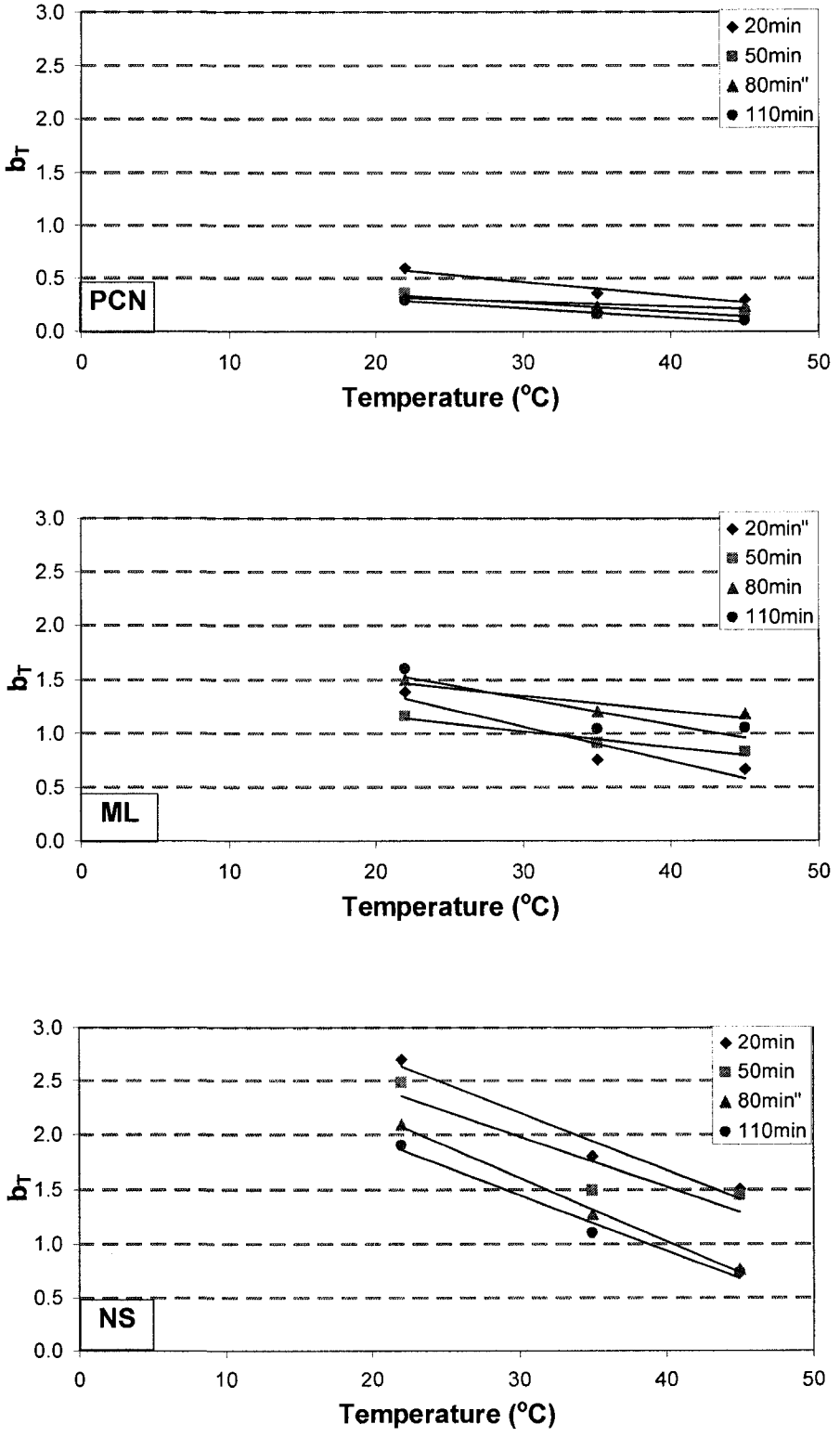

Figure 10.8-Experimental coefficient (*b*) of oscillatory shear strain/stress equations as a function of ambient temperature.

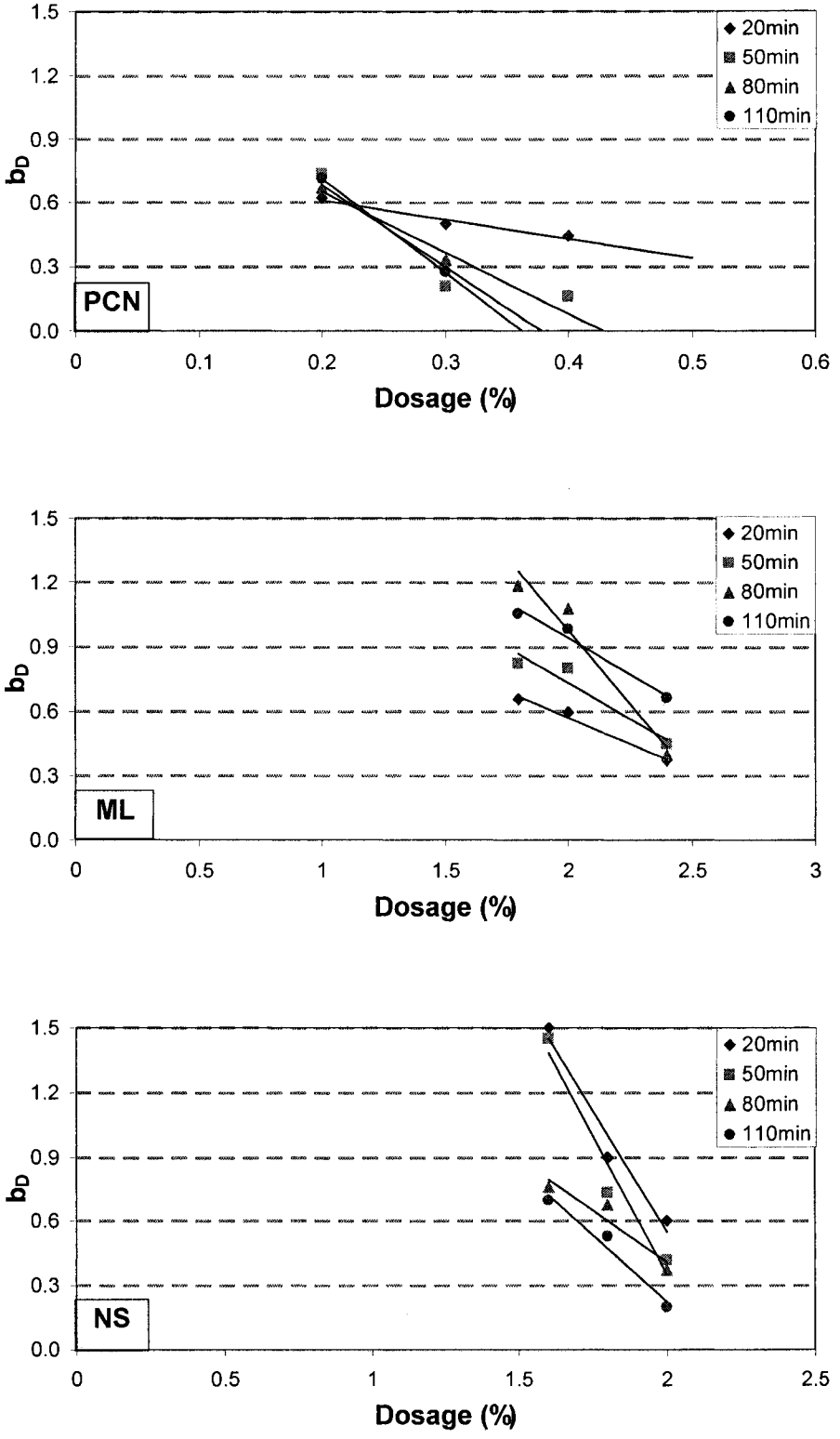

Figure 10.9-Experimental coefficient (*b*) of oscillatory shear strain/stress equations as a function of superplasticizer dosage.

The three optimized equations are as follows:

For cement pastes incorporating PCN:

$$\gamma_{PCN} = [(-0.001t+0.8)\times(-0.01T+0.66)\times(200D+0.41)]\tau - [(0.001t+0.21)\times(-0.0001T+2)\times(-400D+2)] \quad (10.16)$$

For cement pastes incorporating ML:

$$\gamma_{ML} = [(-0.005t+2.4)\times(-0.0065T+0.4)\times(126D-2)]\tau - [(0.021t-0.41)\times(-0.00001T-0.21)\times(-453D+6)] \quad (10.17)$$

For cement paste incorporating NS:

$$\gamma_{NS} = [(-0.0027t+0.861)\times(-0.018T+1.5)\times(71.4D-0.68)]\tau - [(0.009t+0.0011)\times(-0.0226T+0.001)\times(-188.6D+0.65)] \quad (10.18)$$

10.6 Results and Discussion

10.6.1 Validation of GA-based oscillatory shear strain/stress equations

The performance of the GA-based oscillatory shear strain-stress equations was assessed by examining their ability to predict experimental data not previously used during developing the model, and thus unfamiliar to the model. A comparison between the experimental and GA model-predicted oscillatory shear strain of cement paste in the viscous range is presented in Figs. 10.10-10.12, which shows both training and testing data points. The results for cement paste incorporating PCN at 22, 35, and 45 ^{o}C are illustrated

in Figs. 10.10(a), 10.10(b), and 10.10(c), respectively. It is shown that the data points predicted by the GA model are located on or within a small range around the equity lines. Similar to PCN, the predicted data points for ML are located close to the equity lines (Figs. 10.11(a), 10.11(b), 10.11(c)). The data points corresponding to NS are depicted in Figs. 10.12(a), 10.12(b), 10.12(c). Again the GA model proved to be able to predict the viscous part of the oscillatory shear strain/stress curve for cement paste made with NS. Figures 10.10-10.12 show that strain values are lower at higher temperature. This is due to the fact that cement paste gets stiffer (deforms less) with increasing temperature.

To further validate the ability of the GA-based oscillatory shear strain/stress equations developed in this chapter to accurately predict the strain values of cement pastes with variation of the mixing time and ambient temperature, the average absolute error (*AAE*) (Eq. 10.19) along with the ratio of measured to predicted shear strain (γ_m/γ_p) were calculated.

$$AAE = \frac{\left|\gamma_m - \gamma_p\right|}{\gamma_m} \times 100 \tag{10.19}$$

Table 10.3 presents the values of the standard deviation (*SD*) and coefficient of variation (*COV*) of the measured-to-predicted oscillatory shear strain ratio and average absolute error (*AAE*) for all testing data points. The results indicate that the GA model reasonably captured the relationship between the test parameters and oscillatory shear strain of cement pastes.

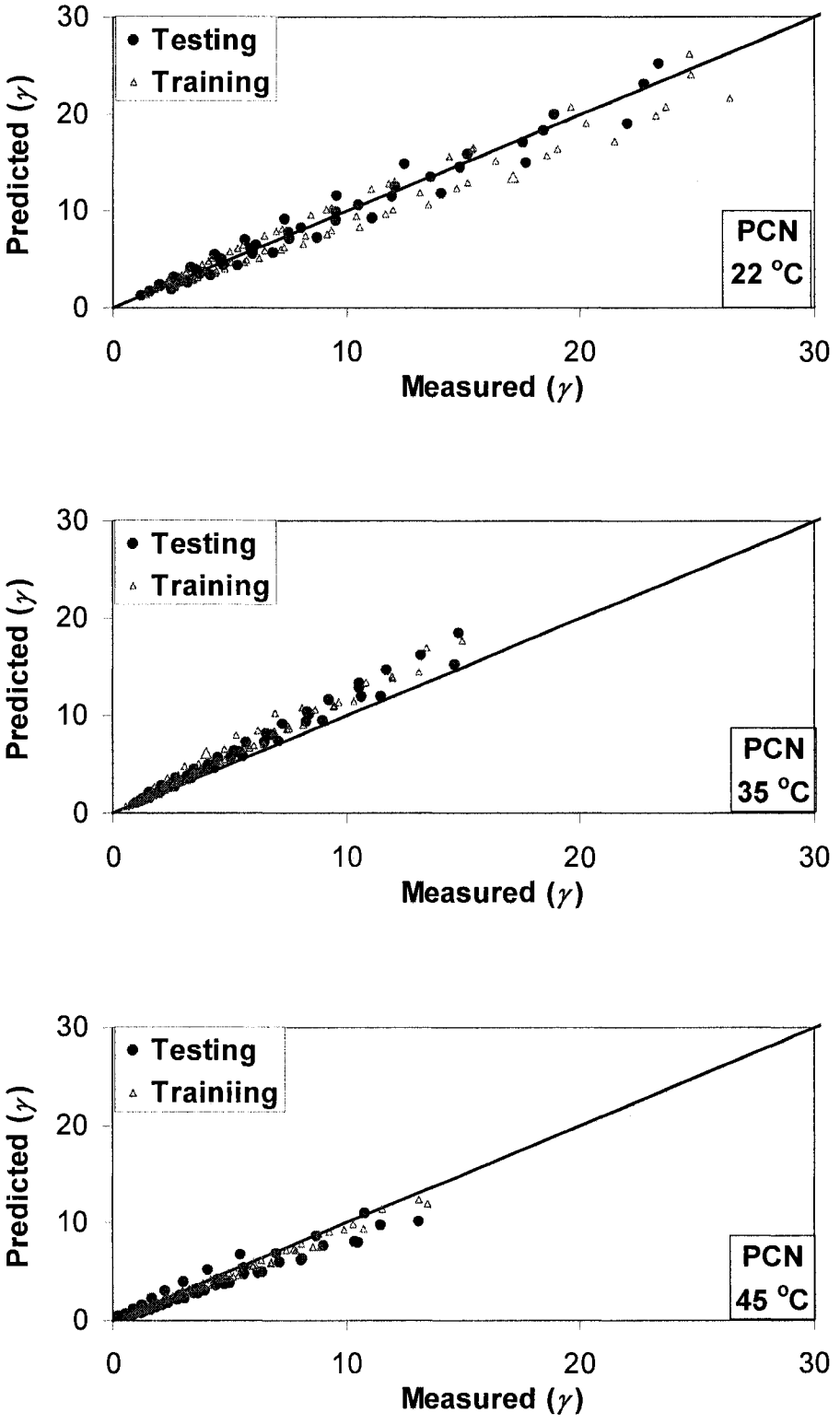

Figure 10.10-Measured versus predicted oscillatory strain for cement pastes incorporating PCN at different temperatures and times.

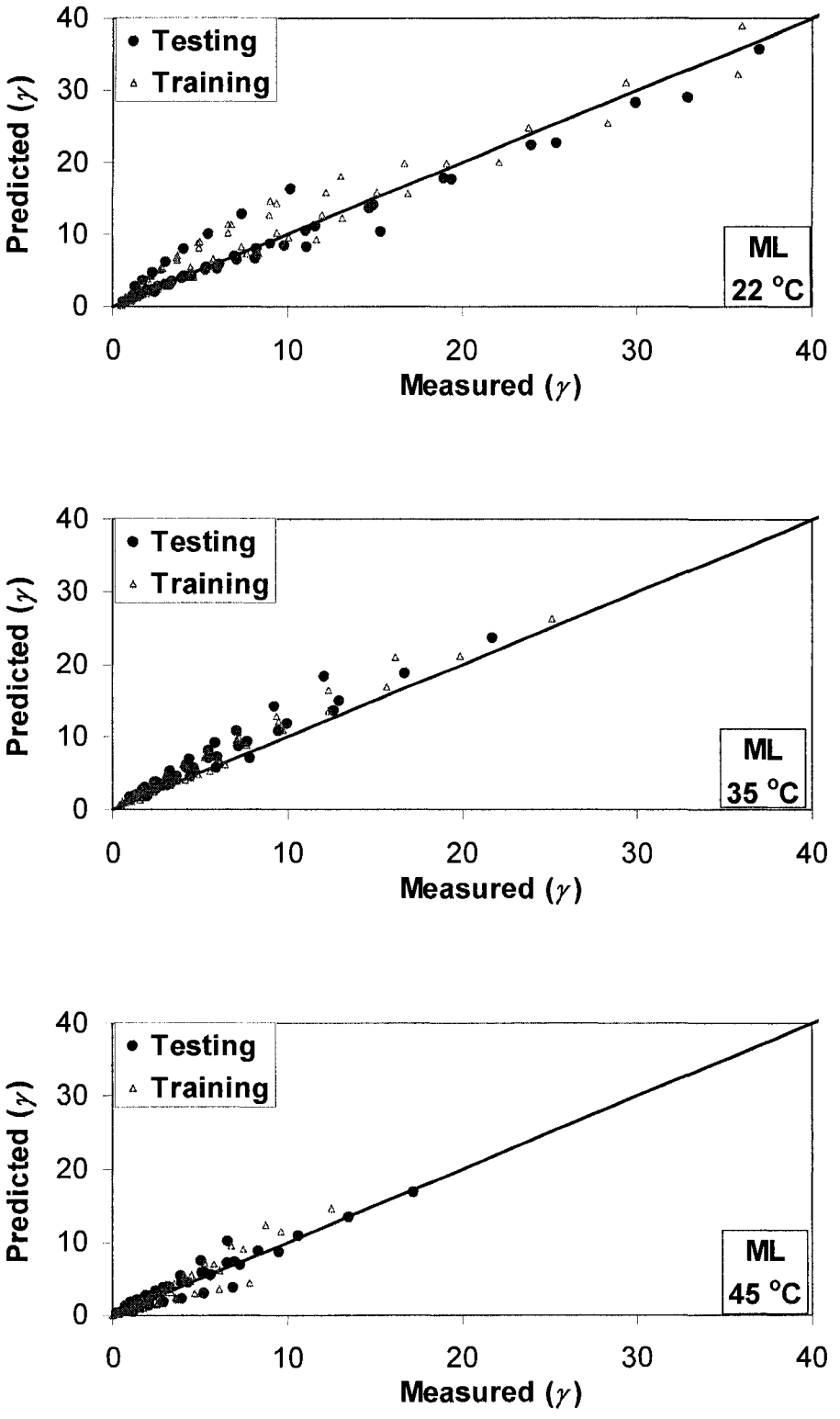

Figure 10.11-Measured versus predicted oscillatory strain for cement pastes incorporating ML at different temperatures and times.

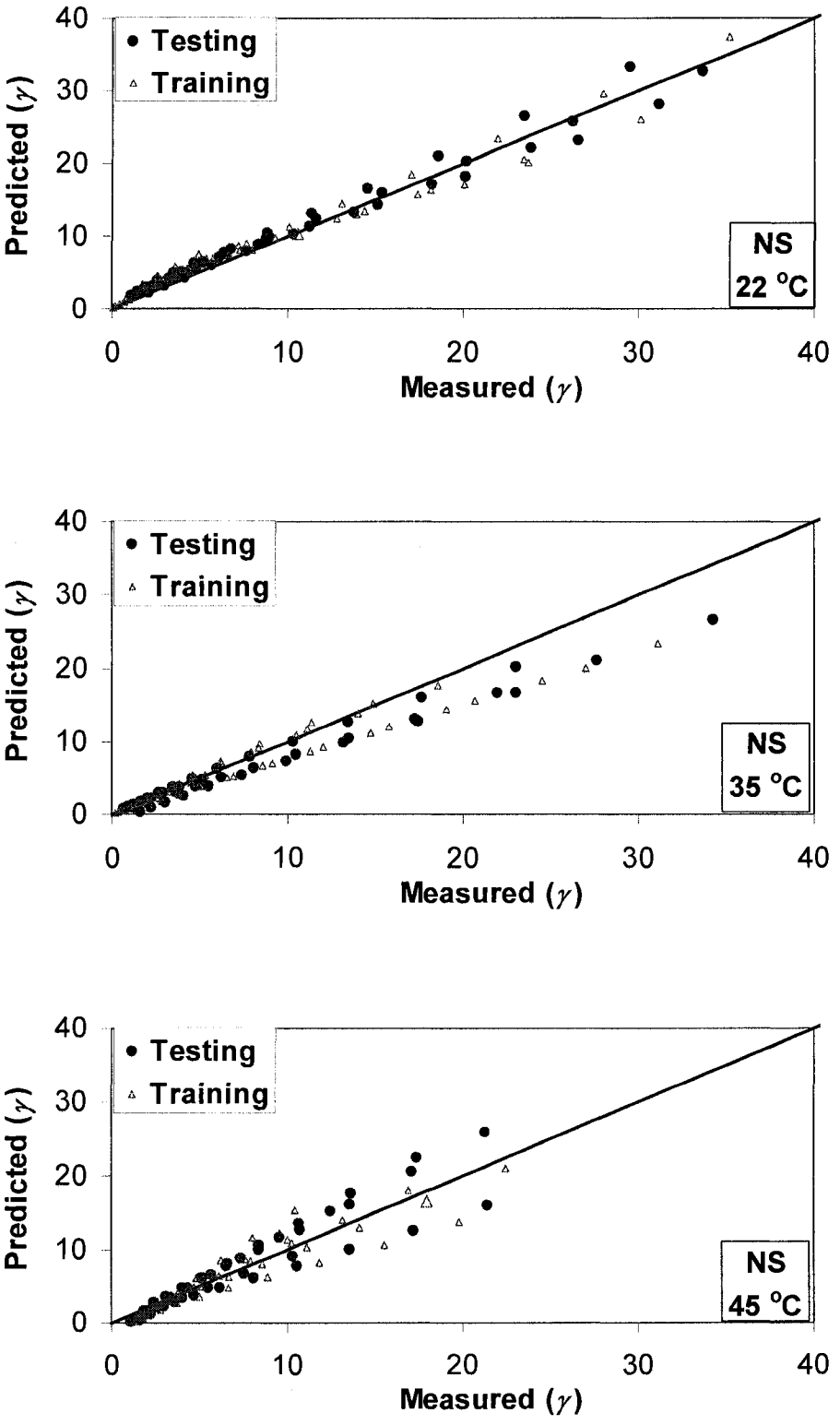

Figure 10.12-Measured versus predicted oscillatory strain for cement pastes incorporating NS at different temperatures and times.

Table 10.3-Performance of GA-based oscillatory shear strain equations of cement paste mixtures

Temperature (°C)	Superplasticizer	*AAE (%)*	$\gamma_{(measured)}/\gamma_{(calculated)}$ (All test points)		
			Average	*SD*	*COV (%)*
22	PCN	12	1.01	0.13	13
	ML	19	0.98	0.23	23
	NS	17	0.90	0.13	15
35	PCN	15	0.90	0.07	8
	ML	25	0.80	0.13	16
	NS	19	1.10	0.16	15
45	PCN	16	1.14	0.19	16
	ML	23	1.08	0.37	35
	NS	22	1.07	0.29	27

10.6.2 Performance of GA-based oscillatory shear strain equations for predicting yield stress of cement paste

As explained earlier, yield stress values were calculated using the developed equations by determining the stress corresponding to zero strain (the intersection of the strain/stress curve in the viscous range with the oscillatory shear stress axis). The predicted yield stress values versus the corresponding experimentally measured values are presented in Figs. 10.13(a), 10.13(b), and 10.13(c) for cement pastes incorporating PCN, ML, and NS, respectively. It is shown that the predicted and measured yield stress data points are located close to the equity lines.

The *AAE* along with the average, standard deviation, and covariance of the ratio between the predicted and experimental yield stress results for the testing data are shown in Table 10.4. It can be observed that the *AAE* values were less than 20% indicating that the equations predicted the yield stress with reasonable accuracy.

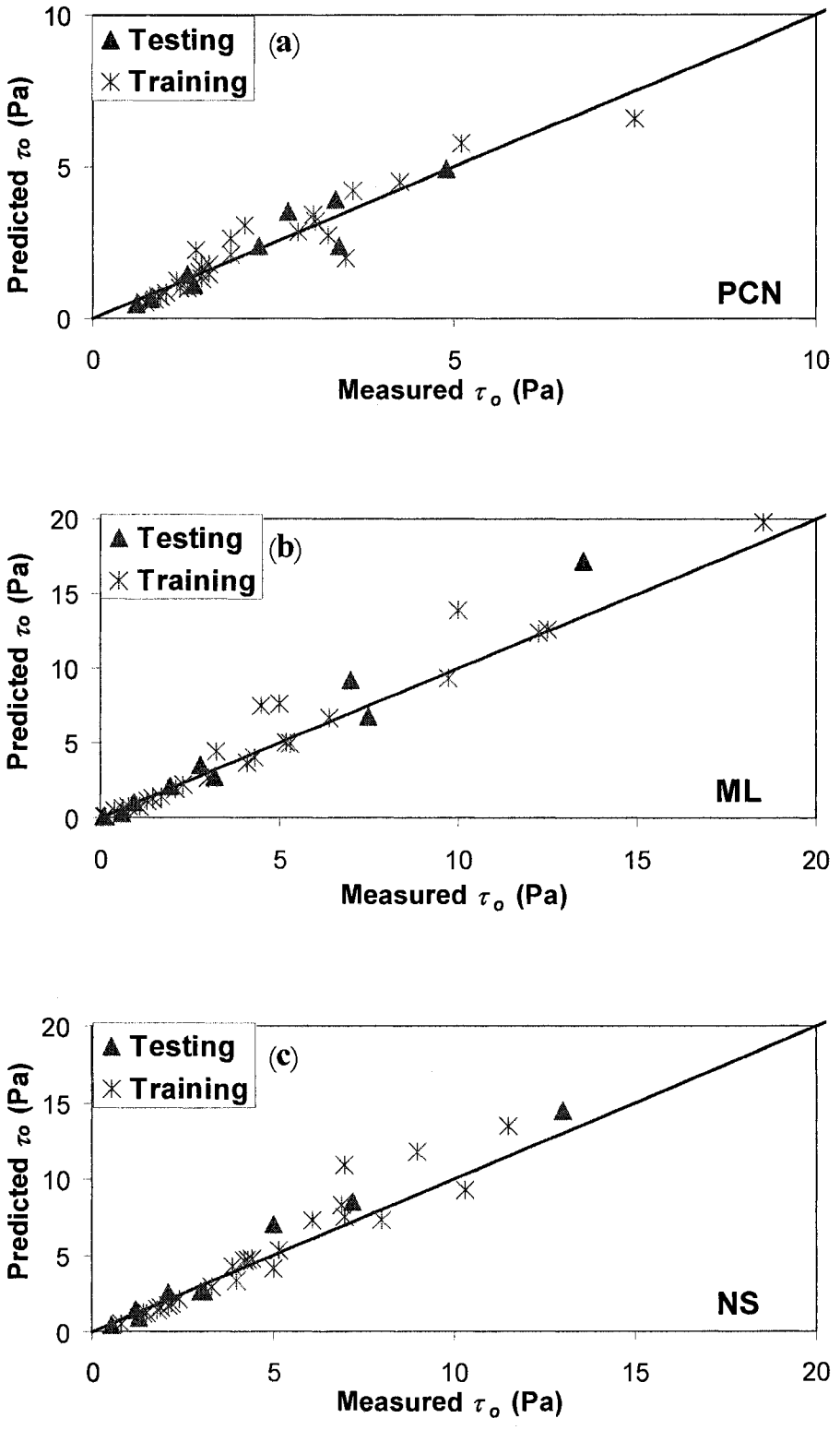

Figure 10.13-Measured versus predicted yield stress for cement paste mixtures at different temperatures and mixing times and incorporating: (a) PCN, (b) ML, and (c) NS.

Table 10.4-Performance of GA-based oscillatory shear strain equations in predicting yield stress of cement paste mixtures

Superplasticizer	*AAE* (%)	$\tau_{o(measured)} / \tau_{o(calculated)}$ (All test points)		
		Average	*SD*	*COV* (%)
PCN	16	1.09	0.22	21
ML	20	0.92	0.19	0.2
NS	19	1.05	0.21	20

It should be noted that cement paste rheology is time, temperature, and shear history dependent, and is hence affected by high variability. For instance, typical *AAE* for predicting yield stress in the literature include 28% for mortar (Ferraris and de Larrard, 1998) and 46% for concrete (Chidiac and Habibbeigi 2005). So, the predictions of the present GA model with an error lower than 20% are indeed reasonably accurate.

10.6.3 Parametric study

The GA–based oscillatory shear strain/stress equations displayed satisfactory performance in predicting the yield stress of cement pastes incorporating the superplasticizers investigated within the practical training range of test parameters. The ability of these equations to capture the effects of each input parameter on the yield stress of cement pastes is explored below. To examine the sensitivity of the developed equations to variation of the mixing time, one mixture for each superplasticizer was randomly selected from the experimental data, and the yield stress was calculated with changing only

the mixing time and maintaining the rest of the experimental parameters constant. To examine the sensitivity of the developed equations to the variation of temperature, the mixing time was kept constant and the ambient temperature was varied. Concerning the effect of the superplasticizer dosage, both the mixing time and ambient temperature were maintained constant and the yield stress values were calculated while only varying the superplasticizer dosage. It should be noted that some values of the parameters were not tested experimentally but were considered in the model calculations.

The cement paste mixtures investigated were made with 0.3% PCN, 1.8% ML, and 1.6% NS. The response of equations (10.16-10.18) in predicting the yield stress with variation of the experimental parameters is illustrated in Fig. 10.14 along with the corresponding experimental results. It can be observed that the predicted yield stress increased with the mixing time, which is in agreement with the trend of the experimental data (Fig. 10.14(a)). Furthermore, the predicted yield stress values were comparable to the experimentally measured values, which indicates that the GA-based oscillatory shear strain equations (10.16-10.18) have successfully captured the sensitivity of the yield stress to variation of the mixing time.

To investigate the sensitivity of the predicted yield stress to variations of the ambient temperature, the mixing time was fixed at 50 min and yield stress values were calculated while only varying the temperature. As shown in Fig. 10.14(b), the predicted yield stress values increased with the increase of temperature, which is in conformity with the experimental trend. The results of the experimental yield stress values were also located close to the corresponding ones predicted by the GA-based equations, indicating that the

yield stress predicted by the GA model was sensitive to the change in the ambient temperature (Fig. 10.14(b)).

The influence of the superplasticizer dosage on the predicted yield stress is illustrated in Fig. 10.14I. The yield stress was predicted while setting the mixing time at 50 min and the temperature at 45 ^{o}C and varying the superplasticizer dosage. It can be observed that the developed equations have also captured the effect of the superplasticizer dosage on yield stress; yield stress decreased as the dosage increased and the experimental data points are located close to the corresponding predicted values. As shown in Fig. 10.14I, beyond a certain superplasticizer dosage, the yield stress versus superplasticizer dosage curve became nearly a plateau where the decrease in the predicted yield stress with a higher dosage became marginal. The intersection of the two tangent lines to the ends of each curve was found to give an approximate estimate of the experimentally measured superplasticizer saturation dosage for cement pastes made with ML and NS. For pastes incorporating PCN, the predicted saturation dosage can be found at the intersection point between the tangent line of the top end of the curve with the x-axis (Fig. 10.14I). The saturation dosages were predicted at 0.37% for PCN, 2.45% for ML, and 1.6% for NS, which are reasonably close to those experimentally determined values, which were 0.4%, 2.8%, and 1.8% for PCN, ML, and NS, respectively (Al-Martini and Nehdi 2008).

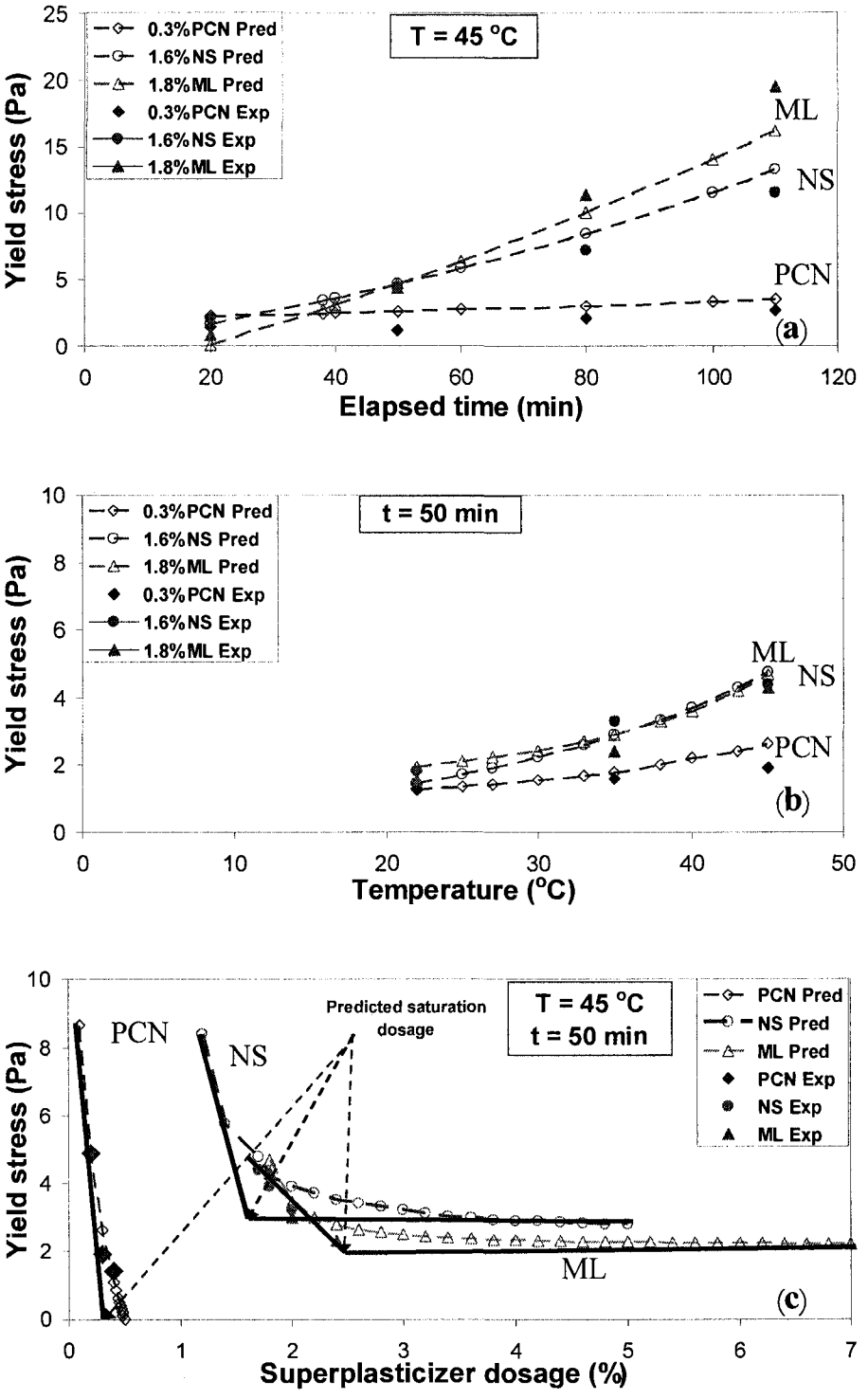

Figure 10.14-Variation in yield stress of superplasticized concretes versus: (a) elapsed time at 45 °C, (b) ambient temperature at 50 min, and (c) superplasticizer dosage at 45 °C and 50 min.

10.7 Conclusions

In this chapter, the oscillatory shear behaviour of cement pastes incorporating various superplasticizers and subjected to different mixing times and ambient temperatures was characterized using a controlled shear stress-strain rheometer. The behaviour of cement paste depended on the applied shear stress; at low shear stress levels, cement paste behaved as an elastic solid, while at higher stress range, it behaved as a linear viscous liquid. Cement paste shifts from a solid-like to a liquid-like behaviour in a narrow range of stress of usually less than 1 Pa. The yield stress of cement paste was estimated as the intersection of the linear curve with the shear stress axis in the viscous range. The oscillatory yield stress values did not agree well with corresponding values obtained using conventional flow curves. The yield stress estimated using the oscillatory shear technique varied with the mixing time, ambient temperature, and superplasticizer dosage. Genetic algorithm-based equations for predicting the oscillatory shear strain-stress curves for the experimentally investigated cement paste mixtures (in the viscous region) have been developed considering the various test parameters. The oscillatory shear strain calculated using the proposed equations agreed well with the corresponding experimental results and allowed to predict the oscillatory yield stress. The following conclusions can be drawn from this work:

- The GA-based oscillatory shear strain equations allowed predicting the yield stress of cement paste incorporating PCN, ML, or NS with reasonable accuracy.
- The GA-based oscillatory shear strain equations developed in this chapter can depict the effect of the elapsed mixing time on the yield stress of cement pastes incorporating various superplasticizers and exposed to various temperatures.

- The GA-based oscillatory shear strain equations were sensitive to the increase in temperature and captured the increase of yield stress with increasing temperature.
- The GA-based oscillatory shear strain equations were also sensitive to the increase in the superplasticizer dosage; yield stress decreased in a curvilinear mode when the superplasticizer dosage increased.
- The prediction of the superplasticizer saturation dosage using the approach suggested in this chapter gave satisfactory results when compared to corresponding experimentally measured values.
- It should be emphasized that the GA-based oscillatory shear strain equations thus developed are valid for the type of materials tested and within the range of parameters investigated in this study. Therefore, further experimental research is needed to validate these equations using different materials and ranges of test parameters.

10.8 References

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Chapter 11

SUMMARY, COCLUSIONS, AND RECOMMENDATIONS

11.1 Summary

Concrete mixed, transported, and placed under hot weather conditions encounters many problems, which can adversely affect its long-term properties and serviceability. Most of these problems are due to the increased rate of cement hydration and the fast evaporating of mixing water in freshly mixed concrete at high temperature. To alleviate these adverse effects, an effort is made to carry out construction during time periods when the temperature is moderate. However this cannot be an ultimate solution especially for projects whose economical importance and demanding construction schedule dictate continuous placing of concrete even under undesirable weather conditions. Had the concrete been placed at ideal temperatures, its curing may still take place under high temperatures. Concrete mixed, placed and/or cured at high temperatures normally reaches higher early compressive strengths, but generally achieves lower 28-day strength than that of concrete produced and cured at a moderate temperature.

One of the common practices to overcome the slump loss of fresh concrete at high temperature is to add more mixing water. This practice is known to reduce the concrete compressive strength. Chemical admixtures have been incorporated in concrete to obtain desired slump values at reduced water to cement ratios, thus improving the mechanical

properties and durability of concrete. These admixtures have generally been developed in countries with moderate temperature, and current technical information on their use in concrete has thus traditionally been developed for countries with mild climates. Hence, they may behave unsatisfactory when used in high temperature environments.

The current study aimed at formulating recommendations for the effective use of chemical admixtures at high temperature, which should enhance the rheological properties of cement-based materials in hot weather conditions. Chapter two summarized the concreting problems encountered in hot weather environments along with the main principles of cement-based materials rheology. Chapters three and four investigated the effects of various chemical admixtures on the rheological properties of cement paste at high temperature using the conventional flow curve and oscillatory shear test techniques, respectively. The combined influence of the ambient temperature and mixing time on the evolution of the rheological properties of cement pastes and concrete incorporating various superplasticizers was investigated in chapters five and six, respectively. Cement pastes and concrete mixtures were continuously agitated for up to 110 min to simulate prolonged mixing in a transit truck during transport to a construction site. Chapter seven explored how the mixing time and the early age ambient temperature affect the slump loss and compressive strength of concrete. In Chapter eight, empirical equations for predicting the shear flow curve of cement paste mixtures incorporating various superplasticizers and subjected to prolonged mixing at various temperatures were developed using the genetic algorithms approach. These flow curves were used to calculate the Bingham yield stress and plastic viscosity values for the various cement pastes investigated. Chapter nine evaluated the relation between the rheology of fresh concrete and that of corresponding

cement paste mixtures by correlating the yield stress results of concrete and that of its corresponding cement paste. Moreover, the genetic algorithms technique was used in chapter nine to develop equations for predicting the yield stress of concrete. Three equations (a separate equation for each superplasticizer) were developed to calculate the yield stress of concrete at various mixing time, ambient temperature, and superplasticizer dosage. The yield stress results calculated using the proposed equations agreed well with corresponding experimental values. In Chapter ten, the oscillatory shear behaviour of cement pastes incorporating various superplasticizers and subjected to different mixing times and ambient temperatures was characterized using a controlled shear stress-shear strain rheometer. Equations describing the variation of shear strain versus shear stress beyond the solid-fluid transition for cement pastes incorporating various superplasticizers at different ambient temperatures and mixing times were developed using genetic algorithms (GA). The yield stress of cement pastes was subsequently predicted using the developed equations by calculating the stress corresponding to zero strain. A parametric study was performed to evaluate the effects of the mixing time, ambient temperature, and superplasticizer dosage on the calculated yield stress values.

11.2 Conclusions

The results in chapter three showed that at high testing temperature, cement paste can have a reverse □ ysteresis behaviour. Both yield stress and plastic viscosity increased non-linearly with temperature. The two types of water reducing and retarding admixtures used in chapters three and four acted as accelerators at high temperature and were effective only beyond a certain threshold dosage. They are not therefore recommended for hot weather

concreting. The mid-range water-reducing admixture (MR) improved the rheological properties of cement paste at high temperature only at a dosage beyond 2.5% where both the yield stress and apparent viscosity continuously decreased with the increase of the MR dosage. The polycarboxylate-based superplasticizers (PC and PCN) effectively improved the rheological properties of cement paste at high temperature. Melamine sulfonate-based (ML) and naphthalene sulfonate-based (NS) superplasticizers behaved as accelerators at low dosages but improved the rheological properties of cement paste at high dosages. The behaviour of cement paste depended on the applied shear stress; at low shear stress levels, cement paste behaved as an elastic solid, while at higher stress range, it behaved as a linear viscous liquid. The results of chapters three and four indicated that engineering/technical data obtained on concrete made with chemical admixtures usually developed in areas with mild climate need to be validated for hot-weather conditions; commercial admixtures proven effective in mild weather may become ineffective at high temperature.

Chapters five and six showed that cement pastes and concretes incorporating PCN and ML under prolonged mixing and high temperature displayed shear thinning behaviour regardless of the superplasticizer dosage. The rheological behaviour of fresh cement paste and concrete mixtures incorporating NS and subjected to prolonged mixing at high temperature shifted from shear thinning to shear thickening behaviour when the NS dosage exceeded the saturation level. This phenomenon could be explained by the interactions between the molecules of the non adsorbed NS. The yield stress of cement paste and concrete mixtures decreased with the PCN dosage up to the saturation dosage, but tended to increase beyond that level. The explanation of this phenomenon is linked to the primary mechanism, i.e. steric hindrance, by which PCN disperses cement particles. The mixing

term of the steric hindrance corresponds to the resistance occurring when two neighboring polymers approach each other. Therefore, beyond the saturation dosage, this resistance will increase with the increase of the un-adsorbed PCN polymers, thus increasing the yield stress. The yield stress of cement paste and concrete mixtures incorporating ML or NS decreased with the increase of the superplasticizer dosage until a saturation dosage, beyond which no significant decrease in yield stress could be achieved. The results showed that to ensure adequate rheological behaviour at high temperature and prolonged mixing time, a PCN dosage close to the saturation dosage needs to be used, while ML and NS dosages beyond the saturation dosage are preferred.

No clear trend of concrete plastic viscosity versus superplasticizer dosage could be observed in chapter six. Chapter six showed that the slump of fresh concrete had an inverse correlation with the yield stress in a logarithmic curvilinear mode, while no correlation was found between the slump and plastic viscosity. Based on the results in chapter six, the assessment of the workability of fresh concrete mixtures in terms of the Bingham parameters, namely the yield stress and plastic viscosity, can provide a powerful tool for the control of concrete production in hot weather environments. The plots of yield stress versus plastic viscosity for all concrete mixtures investigated allowed to establish workability control charts for concreting in hot environments. These charts could provide a means for the objective assessment of workability, allowing reducing the incidence of errors when concrete mixtures in hot environments are merely judged based on personal experience and visual inspection, or based on empirical tests such as the slump test.

Experiments were conducted in chapter seven to investigate the effects of the mixing time, ambient temperature and superplasticizer type on the compressive strength of the concrete mixtures studied in chapter six. The results showed that concrete initially subjected to high temperature attained higher early-age compressive strength than that of a similar concrete subjected to a moderate temperature. The concrete made and initially cured at high temperature achieved lower 28-day compressive strength than that of a similar concrete made and initially cured at moderate temperature. The results of this study indicated that the compressive strength generally increased with longer mixing, thus suggesting that prolonged mixing is beneficial for the compressive strength gain of concrete. Results for concrete mixtures incorporating different superplasticizers and having similar slump at each investigated mixing time and early curing temperature indicated that the type of superplasticizer affected the 28-day compressive strength; the highest compressive strength values were obtained when PCN was used.

Chapter eight was devoted to developing equations that can predict the shear flow of cement paste considering various parameters including the mixing time, ambient temperature, and superplasticizer type and dosage. The results indicated that genetic algoriths (GA) based shear flow equations allowed predicting the yield stress and plastic viscosity of cement pastes incorporating PCN, ML, or NS with reasonable accuracy. The GA-based flow equations for cement paste developed in chapter eight could depict the effects of the elapsed mixing time and ambient temperature on the yield stress and plastic viscosity of cement pastes incorporating various superplasticizers. The GA-based equations also captured the effect of the superplasticizer dosage; both yield stress and plastic viscosity decreased in a curvilinear mode when the superplasticizer dosage increased. The approach

suggested in this chapter to predict the superplasticizer saturation dosage gave satisfactory results when compared to corresponding experimental values.

Results of chapters five and six showed weak linear correlations between the yield stress of concrete and that of its corresponding cement paste, indicating that cement paste rheology cannot be used to accurately predict the rheology of fresh concrete made with a similar paste. Additionally, measuring the rheological properties of fresh concrete is a difficult task usually requiring the use of a rheometer having a large gap to accommodate concrete aggregates. Hence, the complicated methods used for this purpose are generally unsuitable for rapid quality control in field conditions. Therefore, it is important in the robotization of concreting operations to develop reliable models for predicting its flow and deformation, in which various factors such as the mixing time, ambient temperature, and superplasticizer type and dosage are considered. Thus, new equations were developed in chapter nine to calculate the yield stress of concrete subjected to prolonged mixing under high temperature. Results of a parametric study showed that the GA-based equations captured the effect of the mixing time and ambient temperature on the yield stress of concrete; the calculated yield stress increased with higher temperature and longer mixing. The GA-based equations also captured the effects of the superplasticizer dosage on the yield stress of concrete; the calculated yield stress decreased in a curvilinear mode when the superplasticizer dosage increased. The saturation dosage for each superplasticizer was depicted from the calculated yield stress versus dosage curves; and predicted results agreed well with corresponding experimental values.

Chapter ten showed that oscillatory yield stress values for cement paste did not agree well with corresponding values obtained in chapter five on identical cement pastes using conventional flow curves. The yield stress estimated using the oscillatory shear technique varied with the mixing time, ambient temperature, and superplasticizer dosage. Genetic algorithm-based equations for predicting the oscillatory shear strain-stress curves for the experimentally investigated cement paste mixtures (in the viscous region) have been developed considering the various test parameters. The oscillatory shear strain calculated using the proposed equations agreed well with the corresponding experimental results and allowed to predict the oscillatory yield stress. The GA-based oscillatory shear stress-strain equations allowed predicting the yield stress of cement paste incorporating PCN, ML, or NS with reasonable accuracy. They could also depict the effect of the elapsed mixing time on the yield stress of cement pastes incorporating various superplasticizers and exposed to various temperatures. These GA-based equations also captured the increase of the yield stress with increasing temperature. They were also sensitive to the increase in the superplasticizer dosage; the yield stress decreased in a curvilinear mode when the superplasticizer dosage increased. The prediction of the superplasticizer saturation dosage using the approach suggested in this chapter gave satisfactory results when compared to corresponding experimentally measured values.

11.3 Recommendations and Future Work

- It should be emphasized that the experimental findings of this study are valid for the admixtures, cement and aggregates used herein. Other admixtures, even from the same category, may exhibit different behaviour, and thus should be investigated to validate the current results.

- It should be also emphasized that the GA-based equations thus developed are valid for the type 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.
- The mechanical properties and durability of hardened concrete are the main properties that control its use in the field. The effects of the ambient temperature, mixing time and superplasticizer type and dosage on the compressive strength of concrete have been investigated in this thesis. Thus, a logical next step would be to study the durability properties of concrete incorporating superplasticizers and subjected to prolonged mixing at high temperature to make final recommendations for hot weather concreting.
- Further research is also needed to investigate the effects of possible hybrid blends of various admixtures 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 use in hot weather concreting applications.

APPENDIX A

Mixtures Proportions for Cement Paste and Concrete Mixtures Tested

1- Concrete mixtures

Note:

1- All mixtures composition values are material weights given in kg
2- C = Type I portland cement
3- FA = Fine aggregate
4- CA = Coarse aggregate
5- S = Superplasticizer (% of cement mass)
6- A, B, C = 22, 35, 45 °C
7- 1, 2, 3, 4 = 20, 50, 80, 110 min
8- SP = Superplasticizer type

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
1PCNA0.4	PCN	895	800	475	0.38	0.4
2PCNA0.4	PCN	895	800	475	0.38	0.4
3PCNA0.4	PCN	895	800	475	0.38	0.4
4PCNA0.4	PCN	895	800	475	0.38	0.4
1PCNA0.6	PCN	895	800	475	0.38	0.6
2PCNA0.6	PCN	895	800	475	0.38	0.6
3PCNA0.6	PCN	895	800	475	0.38	0.6
4PCNA0.6	PCN	895	800	475	0.38	0.6
1PCNA0.8	PCN	895	800	475	0.38	0.8
2PCNA0.8	PCN	895	800	475	0.38	0.8

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
3PCNA0.8	PCN	895	800	475	0.38	0.8
4PCNA0.8	PCN	895	800	475	0.38	0.8
1PCNA1.0	PCN	895	800	475	0.38	1.0
2PCNA1.0	PCN	895	800	475	0.38	1.0
3PCNA1.0	PCN	895	800	475	0.38	1.0
4PCNA1.0	PCN	895	800	475	0.38	1.0
1PCNB0.8	PCN	895	800	475	0.38	0.8
2PCNB0.8	PCN	895	800	475	0.38	0.8
3PCNB0.8	PCN	895	800	475	0.38	0.8
4PCNB0.8	PCN	895	800	475	0.38	0.8
1PCNB1.0	PCN	895	800	475	0.38	1.0
2PCNB1.0	PCN	895	800	475	0.38	1.0
3PCNB1.0	PCN	895	800	475	0.38	1.0
4PCNB1.0	PCN	895	800	475	0.38	1.0
1PCNB1.1	PCN	895	800	475	0.38	1.1
2PCNB1.1	PCN	895	800	475	0.38	1.1
3PCNB1.1	PCN	895	800	475	0.38	1.1
4PCNB1.1	PCN	895	800	475	0.38	1.1
1PCNB1.3	PCN	895	800	475	0.38	1.3
2PCNB1.3	PCN	895	800	475	0.38	1.3

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
3PCNB1.3	PCN	895	800	475	0.38	1.3
4PCNB1.3	PCN	895	800	475	0.38	1.3
1PCNC0.8	PCN	895	800	475	0.38	0.8
2PCNC0.8	PCN	895	800	475	0.38	0.8
3PCNC0.8	PCN	895	800	475	0.38	0.8
4PCNC0.8	PCN	895	800	475	0.38	0.8
1PCNC1.0	PCN	895	800	475	0.38	1.0
2PCNC1.0	PCN	895	800	475	0.38	1.0
3PCNC1.0	PCN	895	800	475	0.38	1.0
4PCNC1.0	PCN	895	800	475	0.38	1.0
1PCNC1.1	PCN	895	800	475	0.38	1.1
2PCNC1.1	PCN	895	800	475	0.38	1.1
3PCNC1.1	PCN	895	800	475	0.38	1.1
4PCNC1.1	PCN	895	800	475	0.38	1.1
1PCNC1.3	PCN	895	800	475	0.38	1.3
2PCNC1.3	PCN	895	800	475	0.38	1.3
3PCNC1.3	PCN	895	800	475	0.38	1.3
4PCNC1.3	PCN	895	800	475	0.38	1.3
1PCNC1.5	PCN	895	800	475	0.38	1.5
2PCNC1.5	PCN	895	800	475	0.38	1.5

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
3PCNC1.5	PCN	895	800	475	0.38	1.5
4PCNC1.5	PCN	895	800	475	0.38	1.5
1PCNC1.7	PCN	895	800	475	0.38	1.7
2PCNC1.7	PCN	895	800	475	0.38	1.7
3PCNC1.7	PCN	895	800	475	0.38	1.7
4PCNC1.7	PCN	895	800	475	0.38	1.7
1MLA1.4	ML	895	800	475	0.38	1.4
2MLA1.4	ML	895	800	475	0.38	1.4
3MLA1.4	ML	895	800	475	0.38	1.4
4MLA1.4	ML	895	800	475	0.38	1.4
1MLA1.8	ML	895	800	475	0.38	1.8
2MLA1.8	ML	895	800	475	0.38	1.8
3MLA1.8	ML	895	800	475	0.38	1.8
4MLA1.8	ML	895	800	475	0.38	1.8
1MLA2.0	ML	895	800	475	0.38	2.0
2MLA2.0	ML	895	800	475	0.38	2.0
3MLA2.0	ML	895	800	475	0.38	2.0
4MLA2.0	ML	895	800	475	0.38	2.0
1MLA2.4	ML	895	800	475	0.38	2.4
2MLA2.4	ML	895	800	475	0.38	2.4

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
3MLA2.4	ML	895	800	475	0.38	2.4
4MLA2.4	ML	895	800	475	0.38	2.4
1MLA2.8	ML	895	800	475	0.38	2.8
2MLA2.8	ML	895	800	475	0.38	2.8
3MLA2.8	ML	895	800	475	0.38	2.8
4MLA2.8	ML	895	800	475	0.38	2.8
1MLB1.8	ML	895	800	475	0.38	1.8
2MLB1.8	ML	895	800	475	0.38	1.8
3MLB1.8	ML	895	800	475	0.38	1.8
4MLB1.8	ML	895	800	475	0.38	1.8
1MLB2.4	ML	895	800	475	0.38	2.4
2MLB2.4	ML	895	800	475	0.38	2.4
3MLB2.4	ML	895	800	475	0.38	2.4
4MLB2.4	ML	895	800	475	0.38	2.4
1MLB2.8	ML	895	800	475	0.38	2.8
2MLB2.8	ML	895	800	475	0.38	2.8
3MLB2.8	ML	895	800	475	0.38	2.8
4MLB2.8	ML	895	800	475	0.38	2.8
1MLB3.4	ML	895	800	475	0.38	3.4
2MLB3.4	ML	895	800	475	0.38	3.4

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
3MLB3.4	ML	895	800	475	0.38	3.4
4MLB3.4	ML	895	800	475	0.38	3.4
1MLC1.8	ML	895	800	475	0.38	1.8
2MLC1.8	ML	895	800	475	0.38	1.8
3MLC1.8	ML	895	800	475	0.38	1.8
4MLC1.8	ML	895	800	475	0.38	1.8
1MLC2.4	ML	895	800	475	0.38	2.4
2MLC2.4	ML	895	800	475	0.38	2.4
3MLC2.4	ML	895	800	475	0.38	2.4
4MLC2.4	ML	895	800	475	0.38	2.4
1MLC2.8	ML	895	800	475	0.38	2.8
2MLC2.8	ML	895	800	475	0.38	2.8
3MLC2.8	ML	895	800	475	0.38	2.8
4MLC2.8	ML	895	800	475	0.38	2.8
1MLC3.4	ML	895	800	475	0.38	3.4
2MLC3.4	ML	895	800	475	0.38	3.4
3MLC3.4	ML	895	800	475	0.38	3.4
4MLC3.4	ML	895	800	475	0.38	3.4
1MLC3.6	ML	895	800	475	0.38	3.6
2MLC3.6	ML	895	800	475	0.38	3.6

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
3MLC3.6	ML	895	800	475	0.38	3.6
4MLC3.6	ML	895	800	475	0.38	3.6
1MLC3.8	ML	895	800	475	0.38	3.8
2MLC3.8	ML	895	800	475	0.38	3.8
3MLC3.8	ML	895	800	475	0.38	3.8
4MLC3.8	ML	895	800	475	0.38	3.8
1NSA1.2	NS	895	800	475	0.38	1.2
2NSA1.2	NS	895	800	475	0.38	1.2
3NSA1.2	NS	895	800	475	0.38	1.2
4NSA1.2	NS	895	800	475	0.38	1.2
1NSA1.4	NS	895	800	475	0.38	1.4
2NSA1.4	NS	895	800	475	0.38	1.4
3NSA1.4	NS	895	800	475	0.38	1.4
4NSA1.4	NS	895	800	475	0.38	1.4
1NSA1.6	NS	895	800	475	0.38	1.6
2NSA1.6	NS	895	800	475	0.38	1.6
3NSA1.6	NS	895	800	475	0.38	1.6
4NSA1.6	NS	895	800	475	0.38	1.6
1NSA2.0	NS	895	800	475	0.38	2.0
2NSA2.0	NS	895	800	475	0.38	2.0

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
3NSA2.0	NS	895	800	475	0.38	2.0
4NSA2.0	NS	895	800	475	0.38	2.0
1NSA2.4	NS	895	800	475	0.38	2.4
2NSA2.4	NS	895	800	475	0.38	2.4
3NSA2.4	NS	895	800	475	0.38	2.4
4NSA2.4	NS	895	800	475	0.38	2.4
1NSB1.2	NS	895	800	475	0.38	1.2
2NSB1.2	NS	895	800	475	0.38	1.2
3NSB1.2	NS	895	800	475	0.38	1.2
4NSB1.2	NS	895	800	475	0.38	1.2
1NSB1.4	NS	895	800	475	0.38	1.4
2NSB1.4	NS	895	800	475	0.38	1.4
3NSB1.4	NS	895	800	475	0.38	1.4
4NSB1.4	NS	895	800	475	0.38	1.4
1NSB1.6	NS	895	800	475	0.38	1.6
2NSB1.6	NS	895	800	475	0.38	1.6
3NSB1.6	NS	895	800	475	0.38	1.6
4NSB1.6	NS	895	800	475	0.38	1.6
1NSB1.8	NS	895	800	475	0.38	1.8
2NSB1.8	NS	895	800	475	0.38	1.8

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
3NSB1.8	NS	895	800	475	0.38	1.8
4NSB1.8	NS	895	800	475	0.38	1.8
1NSB2.0	NS	895	800	475	0.38	2.0
2NSB2.0	NS	895	800	475	0.38	2.0
3NSB2.0	NS	895	800	475	0.38	2.0
4NSB2.0	NS	895	800	475	0.38	2.0
1NSB2.4	NS	895	800	475	0.38	2.4
2NSB2.4	NS	895	800	475	0.38	2.4
3NSB2.4	NS	895	800	475	0.38	2.4
4NSB2.4	NS	895	800	475	0.38	2.4
1NSC1.6	NS	895	800	475	0.38	1.6
2NSC1.6	NS	895	800	475	0.38	1.6
3NSC1.6	NS	895	800	475	0.38	1.6
4NSC1.6	NS	895	800	475	0.38	1.6
1NSC1.8	NS	895	800	475	0.38	1.8
2NSC1.8	NS	895	800	475	0.38	1.8
3NSC1.8	NS	895	800	475	0.38	1.8
4NSC1.8	NS	895	800	475	0.38	1.8
1NSC2.4	NS	895	800	475	0.38	2.4
2NSC2.4	NS	895	800	475	0.38	2.4

Mixture	SP	Compositions (kg/m^3)				
		FA	CA	C	w/c	S (%)
3NSC2.4	NS	895	800	475	0.38	2.4
4NSC2.4	NS	895	800	475	0.38	2.4
1NSC3.0	NS	895	800	475	0.38	3.0
2NSC3.0	NS	895	800	475	0.38	3.0
3NSC3.0	NS	895	800	475	0.38	3.0
4NSC3.0	NS	895	800	475	0.38	3.0

2- Cement paste mixtures

Mixture	SP	w/c	S (%)
1PCNA0.1	PCN	0.38	0.1
2PCNA0.1	PCN	0.38	0.1
3PCNA0.1	PCN	0.38	0.1
4PCNA0.1	PCN	0.38	0.1
1PCNA0.2	PCN	0.38	0.2
2PCNA0.2	PCN	0.38	0.2
3PCNA0.2	PCN	0.38	0.2
4PCNA0.2	PCN	0.38	0.2
1PCNA0.3	PCN	0.38	0.3
2PCNA0.3	PCN	0.38	0.3
3PCNA0.3	PCN	0.38	0.3
4PCNA0.3	PCN	0.38	0.3
1PCNA0.4	PCN	0.38	0.4
2PCNA0.4	PCN	0.38	0.4
3PCNA0.4	PCN	0.38	0.4
4PCNA0.4	PCN	0.38	0.4
1PCNA0.5	PCN	0.38	0.5
2PCNA0.5	PCN	0.38	0.5
3PCNA0.5	PCN	0.38	0.5

Mixture	SP	w/c	S (%)
4PCNA0.5	PCN	0.38	0.5
1PCNA0.6	PCN	0.38	0.6
2PCNA0.6	PCN	0.38	0.6
3PCNA0.6	PCN	0.38	0.6
4PCNA0.6	PCN	0.38	0.6
1PCNA0.8	PCN	0.38	0.8
2PCNA0.8	PCN	0.38	0.8
3PCNA0.8	PCN	0.38	0.8
4PCNA0.8	PCN	0.38	0.8
1PCNB0.1	PCN	0.38	0.1
2PCNB0.1	PCN	0.38	0.1
3PCNB0.1	PCN	0.38	0.1
4PCNB0.1	PCN	0.38	0.1
1PCNB0.2	PCN	0.38	0.2
2PCNB0.2	PCN	0.38	0.2
3PCNB0.2	PCN	0.38	0.2
4PCNB0.2	PCN	0.38	0.2
1PCNB0.3	PCN	0.38	0.3
2PCNB0.3	PCN	0.38	0.3
3PCNB0.3	PCN	0.38	0.3
4PCNB0.3	PCN	0.38	0.3

Mixture	SP	w/c	S (%)
1PCNB0.4	PCN	0.38	0.4
2PCNB0.4	PCN	0.38	0.4
3PCNB0.4	PCN	0.38	0.4
4PCNB0.4	PCN	0.38	0.4
1PCNB0.5	PCN	0.38	0.5
2PCNB0.5	PCN	0.38	0.5
3PCNB0.5	PCN	0.38	0.5
4PCNB0.5	PCN	0.38	0.5
1PCNB0.6	PCN	0.38	0.6
2PCNB0.6	PCN	0.38	0.6
3PCNB0.6	PCN	0.38	0.6
4PCNB0.6	PCN	0.38	0.6
1PCNB0.8	PCN	0.38	0.8
2PCNB0.8	PCN	0.38	0.8
3PCNB0.8	PCN	0.38	0.8
4PCNB0.8	PCN	0.38	0.8
1PCNC0.1	PCN	0.38	0.1
2PCNC0.1	PCN	0.38	0.1
3PCNC0.1	PCN	0.38	0.1
4PCNC0.1	PCN	0.38	0.1
1PCNC0.2	PCN	0.38	0.2

Mixture	SP	w/c	S (%)
2PCNC0.2	PCN	0.38	0.2
3PCNC0.2	PCN	0.38	0.2
4PCNC0.2	PCN	0.38	0.2
1PCNC0.3	PCN	0.38	0.3
2PCNC0.3	PCN	0.38	0.3
3PCNC0.3	PCN	0.38	0.3
4PCNC0.3	PCN	0.38	0.3
1PCNC0.4	PCN	0.38	0.4
2PCNC0.4	PCN	0.38	0.4
3PCNC0.4	PCN	0.38	0.4
4PCNC0.4	PCN	0.38	0.4
1PCNC0.5	PCN	0.38	0.5
2PCNC0.5	PCN	0.38	0.5
3PCNC0.5	PCN	0.38	0.5
4PCNC0.5	PCN	0.38	0.5
1PCNC0.6	PCN	0.38	0.6
2PCNC0.6	PCN	0.38	0.6
3PCNC0.6	PCN	0.38	0.6
4PCNC0.6	PCN	0.38	0.6
1PCNC0.8	PCN	0.38	0.8
2PCNC0.8	PCN	0.38	0.8

Mixture	SP	w/c	S (%)
3PCNC0.8	PCN	0.38	0.8
4PCNC0.8	PCN	0.38	0.8
1PCNC1.0	PCN	0.38	1.0
2PCNC1.0	PCN	0.38	1.0
3PCNC1.0	PCN	0.38	1.0
4PCNC1.0	PCN	0.38	1.0
1PCNC1.1	PCN	0.38	1.1
2PCNC1.1	PCN	0.38	1.1
3PCNC1.1	PCN	0.38	1.1
4PCNC1.1	PCN	0.38	1.1
1PCNC1.3	PCN	0.38	1.3
2PCNC1.3	PCN	0.38	1.3
3PCNC1.3	PCN	0.38	1.3
4PCNC1.3	PCN	0.38	1.3
1MLA1.4	ML	0.38	1.4
2MLA1.4	ML	0.38	1.4
3MLA1.4	ML	0.38	1.4
4MLA1.4	ML	0.38	1.4
1MLA1.8	ML	0.38	1.8
2MLA1.8	ML	0.38	1.8
3MLA1.8	ML	0.38	1.8

Mixture	SP	w/c	S (%)
4MLA1.8	ML	0.38	1.8
1MLA2.0	ML	0.38	2.0
2MLA2.0	ML	0.38	2.0
3MLA2.0	ML	0.38	2.0
4MLA2.0	ML	0.38	2.0
1MLA2.4	ML	0.38	2.4
2MLA2.4	ML	0.38	2.4
3MLA2.4	ML	0.38	2.4
4MLA2.4	ML	0.38	2.4
1MLA2.8	ML	0.38	2.8
2MLA2.8	ML	0.38	2.8
3MLA2.8	ML	0.38	2.8
4MLA2.8	ML	0.38	2.8
1MLA3.0	ML	0.38	3.0
2MLA3.0	ML	0.38	3.0
3MLA3.0	ML	0.38	3.0
4MLA3.0	ML	0.38	3.0
1MLB1.8	ML	0.38	1.8
2MLB1.8	ML	0.38	1.8
3MLB1.8	ML	0.38	1.8
4MLB1.8	ML	0.38	1.8

Mixture	SP	w/c	S (%)
1MLB2.0	ML	0.38	2.0
2MLB2.0	ML	0.38	2.0
3MLB2.0	ML	0.38	2.0
4MLB2.0	ML	0.38	2.0
1MLB2.4	ML	0.38	2.4
2MLB2.4	ML	0.38	2.4
3MLB2.4	ML	0.38	2.4
4MLB2.4	ML	0.38	2.4
1MLB2.8	ML	0.38	2.8
2MLB2.8	ML	0.38	2.8
3MLB2.8	ML	0.38	2.8
4MLB2.8	ML	0.38	2.8
1MLB3.0	ML	0.38	3.0
2MLB3.0	ML	0.38	3.0
3MLB3.0	ML	0.38	3.0
4MLB3.0	ML	0.38	3.0
1MLC1.8	ML	0.38	1.8
2MLC1.8	ML	0.38	1.8
3MLC1.8	ML	0.38	1.8
4MLC1.8	ML	0.38	1.8
1MLC2.0	ML	0.38	2.0

Mixture	SP	w/c	S (%)
2MLC2.0	ML	0.38	2.0
3MLC2.0	ML	0.38	2.0
4MLC2.0	ML	0.38	2.0
1MLC2.4	ML	0.38	2.0
2MLC2.4	ML	0.38	2.4
3MLC2.4	ML	0.38	2.4
4MLC2.4	ML	0.38	2.4
1MLC2.8	ML	0.38	2.8
2MLC2.8	ML	0.38	2.8
3MLC2.8	ML	0.38	2.8
4MLC2.8	ML	0.38	2.8
1MLC3.0	ML	0.38	3.0
2MLC3.0	ML	0.38	3.0
3MLC3.0	ML	0.38	3.0
4MLC3.0	ML	0.38	3.0
1NSA1.2	NS	0.38	1.2
2NSA1.2	NS	0.38	1.2
3NSA1.2	NS	0.38	1.2
4NSA1.2	NS	0.38	1.2
1NSA1.4	NS	0.38	1.4
2NSA1.4	NS	0.38	1.4

Mixture	SP	w/c	S (%)
3NSA1.4	NS	0.38	1.4
4NSA1.4	NS	0.38	1.4
1NSA1.6	NS	0.38	1.6
2NSA1.6	NS	0.38	1.6
3NSA1.6	NS	0.38	1.6
4NSA1.6	NS	0.38	1.6
1NSA1.8	NS	0.38	1.8
2NSA1.8	NS	0.38	1.8
3NSA1.8	NS	0.38	1.8
4NSA1.8	NS	0.38	1.8
1NSA2.0	NS	0.38	2.0
2NSA2.0	NS	0.38	2.0
3NSA2.0	NS	0.38	2.0
4NSA2.0	NS	0.38	2.0
1NSB1.2	NS	0.38	1.2
2NSB1.2	NS	0.38	1.2
3NSB1.2	NS	0.38	1.2
4NSB1.2	NS	0.38	1.2
1NSB1.4	NS	0.38	1.4
2NSB1.4	NS	0.38	1.4
3NSB1.4	NS	0.38	1.4

Mixture	SP	w/c	S (%)
4NSB1.4	NS	0.38	1.4
1NSB1.6	NS	0.38	1.6
2NSB1.6	NS	0.38	1.6
3NSB1.6	NS	0.38	1.6
4NSB1.6	NS	0.38	1.6
1NSB1.8	NS	0.38	1.8
2NSB1.8	NS	0.38	1.8
3NSB1.8	NS	0.38	1.8
4NSB1.8	NS	0.38	1.8
1NSB2.0	NS	0.38	2.0
2NSB2.0	NS	0.38	2.0
3NSB2.0	NS	0.38	2.0
4NSB2.0	NS	0.38	2.0
1NSC1.4	NS	0.38	1.4
2NSC1.4	NS	0.38	1.4
3NSC1.4	NS	0.38	1.4
4NSC1.4	NS	0.38	1.4
1NSC1.6	NS	0.38	1.6
2NSC1.6	NS	0.38	1.6
3NSC1.6	NS	0.38	1.6
4NSC1.6	NS	0.38	1.6

Mixture	SP	w/c	S (%)
1NSC1.8	NS	0.38	1.8
2NSC1.8	NS	0.38	1.8
3NSC1.8	NS	0.38	1.8
4NSC1.8	NS	0.38	1.8
1NSC2.0	NS	0.38	2.0
2NSC2.0	NS	0.38	2.0
3NSC2.0	NS	0.38	2.0
4NSC2.0	NS	0.38	2.0
1NSC2.4	NS	0.38	2.4
2NSC2.4	NS	0.38	2.4
3NSC2.4	NS	0.38	2.4
4NSC2.4	NS	0.38	2.4

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