Faculty of Science and Engineering
Department of Civil Engineering

Study on plastic and mechanical properties of plastic stabilized returned plastic concretes containing supplementary cementitious materials

Sarvesh Mali

This thesis is presented for the Degree of
Master of Philosophy
of
Curtin University

April 2016

Declaration

To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature:

Date: 18th April 2016

ABSTRACT

The growing concern for the ready-mix concrete industry is the disposal of returned unused concrete. In a plastic state, the concrete is a perishable product, and the disposal of any unused concrete provides a set of challenges. An increase in environmental regulations requires the industry to implement the best practices that effectively reduces the amount of by-product materials require disposal. However, little is known about the most effective parameters for recycling of returned plastic concrete without adversely affecting its properties. The present research has conducted laboratory trials to establish an optimal process for stabilizing returned plastic concretes using set retarding admixture called “stabilizer.” Three types of cement, widely used in the construction industry in Australia, are used in this research. First is the ordinary Portland cement (OPC), while the rest are blended cement containing 25% class F fly ash and 65% slag as partial replacement of OPC.

The study designed a control process to determine the stabilizer dosage and its influence on above three cement pastes. Later, the stabilizer dosage is applied in the concretes to evaluate the effect of stabilizer on plastic and mechanical properties of the concrete made by above three types of cement. The study is conducted in five phases. In first three phases, the setting time of OPC, flowability, and heat of hydration of above three cement grouts containing different stabilizer dosages are evaluated and a saturation dosage of stabilizer to hold the setting of cement and cementitious grouts for an extended period (24hrs and more) is established. Later, in Phase 4, the predicted stabilizer dosage was added to concretes made with above three types of cement to evaluate the plastic and harden properties of fresh concretes, stabilized concretes and blend of fresh concretes with 10%, 25% and 50% stabilized concretes. Finally, the feasibility of upgrading of low-grade stabilized concretes to higher grade concretes evaluated in the fifth phase of this study.

The results indicate that the retardation of stabilized blended cement grouts containing slag and fly ash is higher than the OPC grout. The OPC grout lost the fluidity faster than the blended cement grouts containing slag and fly ash. The effect of stabilizer dosages on hydration temperature of three cement grouts shows that with an increase in stabilizer dosages the hydration temperature decreases, indicating the slow setting of the cement grouts. The results showed that the initial slump values are within the tolerance except it is higher when stabilizer dosage is added after an hour, but the final slump is within the tolerance of control concrete. After stabilization of the concretes, the initial and final setting time of stabilized concretes is increased to more than 24 hours. The initial and final setting time of the blended concrete containing fresh concrete and 10%, 25% and 50% stabilized concretes are similar to those of fresh concrete for all cement types. The compressive strength and drying shrinkage compared to the control concrete is not affected by stabilizing the concretes. Results also show that the stabilized lower grade concretes can easily be upgraded to a higher grade by blending the stabilized concretes with fresh concretes, indicating not only the ability of stabilizer to stabilize the returned plastic concretes for 24 hrs, but also to upgrade its strength for efficient reusing capabilities.

ACKNOWLEDGEMENT

I would like to express the deepest gratitude to Dr. Faiz U. Shaikh as my research and thesis supervisor for his continuous support, thoughtful advice and encouragement throughout my research program. Without his incredible patience, guidance and persistent help this thesis would not have been accomplished.

I express my appreciation to Chairperson Dr. Ranjan Sarukkalige and co-supervisor Hamid Nikraz for their input to serve as the thesis committee

I would also like to extend my thanks to the Head of the civil engineering department Mr. Andrew Whyte and the secretary of the civil engineering department for their assistance during my study.

Finally, I would like to thank my parents, my wife, and my daughter for the moral supports, their confidence, prayer, and their love during all these years. Moreover, also all friends for their kind support at various point during my study at Curtin University.

TABLE OF CONTENTS

4.2 Setting time without stabilizer

LIST OF ACRONYMS

AS	Australian Standard
ASTM	American Society for Testing Materials
C_3A	Tricalcium Aluminates
C_4AF	Tetracalcium alumino- ferrite
C_2S	Dicalcium Silicate
C_3S	Tricalcium Silicate
CH	Calcium Hydroxide
CAH-	Calcium Aluminate hydrate
CSH	Calcium Silicate Hydrate
FA	Fly Ash
GB	General blended cement (75% OPC and 25% fly ash)
GP	General Portland Cement
ISM	Blended Cement (85%OPC and 15% slag)
LH	Low heat cement (35% OPC and 65% slag)
LTR	Long- Term Retarder
NRMCA	National ReadyMixed Concrete Association
OPC	Ordinary Portland cement
PBTC	Phosphonobutane tricarboxylic acid
GGBS	Ground Granulated iron Blast-furnace Slag
SCM	Supplementary Cementitious Materials

LIST OF NOTATIONS

MPa	Megapascal = N/m^2 (1Newton per square meter)
μƐ-	Shrinkage measured in microstrain

LIST OF TABLES

LIST OF FIGURES

LIST OF PUBLICATIONS

1. Shaikh, F.U.A., and Mali, S. (2015) Properties of stabilized recycled plastic concrete made with three types of cement. **Structural concrete** (DOI: 10.1002/suco.201500111)

2. Mali, S., Ahmed, S.F.U. and Nikraz, H., **Properties of plastic concrete reuse using extended set retarding admixtures, In the Proceedings of Concrete 2011, the annual conference of the concrete Institute of Australia**, Perth, Australia, 2011.

CHAPTER I

INTRODUCTION

1.1 Background

The annual global production of cement is 4.1 billion tons (U.S Geological Survey, 2016), calculated for concrete assuming it contains on average 11% cement. The annual global production of concrete is approximately 11 billion cubic meters. Australian cement industry produces 9 million tons of cement and approximately 24 million cubic meters of concrete. Every year a substantial amount of ready-mixed concrete is returned to concrete plant due to many reasons, such as surplus production, rejected concrete due to quality issues and trial batches. It is estimated that the amount of concrete waste is approximately 3% of total concrete production (Nielsen and Glavind, 2007) and with increasing use of concrete the generation of such waste concrete is also expected to increase; this significant waste stream must be disposed or recycled. There are many ways of handling waste products generated from Ready Mix concrete plants. Reclaimed aggregates have already used in many countries for manufacturing of low-grade concrete. The common practices include 1) Using concrete wash water pits or settling ponds at job sites or RMC plants for retaining disposed washout dumped directly from mixer trucks, of which the cementitious slurry is increasingly expensive to dispose . 2) Using a series of settling ponds to recover washout that is relatively clean and free from solids for washing the inside of concrete truck mixer drums this is one of the most common methods used in Australia. 3) Using CO_2 to neutralize alkaline cement-based wastewater (pH about 12) for reuse or for discharging into public sewers this process is used on few of the environmentally friendly project in Australia. 4) Using mechanical reclaimer units to recycle or reuse cement-based wastewater. 5) Using chemical stabilizing admixture systems or agents that temporarily stop the cement hydration process so that the wash water can be reused for making concrete (Leong, 2006).

Lobo and Mullings (2003) found that the slurry water with significantly higher solids content increased the water demand and accelerated the setting time. The effects were more pronounced with an increase in the age of the slurry paste and increase in the solids content. Concrete mixes containing higher water contents due to the use of higher solids in recycled slurry had an associated reduction in strength and increase in drying shrinkage and rapid chloride permeability. The stabilizing admixture was effective in overcoming the negative effects of age and higher solids content in the wash water.

The alternate practice used in the ready-mix industry to recycle concrete is to allow the returned concrete to harden and later crush the hardened concrete using the mechanical crusher. The problem of recycling the hardened concrete is the consumption of energy required to operate the mechanical crusher which liberates carbon dioxide. Where recycling is not possible or practical, to comply with environmental regulation, hardened concrete, sufficiently drained solid sludge and treated wastewater is disposed of in a landfill or into drainage systems. The complexity and stringency of regulations by different environmental legislations or laws about the quality of solid and liquid waste entering into the industrial waste stream have significantly increased the cost of disposing of returned concrete. Therefore, disposing of returned concrete has become a significant issue for the ready-mix concrete industry (Environchem Services, 1993), which increase the manufacturing cost of the concrete. Therefore, the industry is becoming increasingly interested in finding suitable alternatives to recycling the returned concrete.

The only way to avoid the costly disposal of such wet concrete is through reuse the concrete on the same day or next day. The reuse of wet concrete after a certain holding period can only be used if it maintains required workability, because with an increase in holding time the workability of wet concrete decreases due to continuing hydration of cement. One of the recent advances in concrete technology is the emerging development of a chemical admixture that can be used to reduce or possibly eliminate the need for the disposal of waste water and returned concrete (Lobo et al., 1995 and Kinney, 1998). This effect is possible because an extended set retarding admixture can suspend the setting time and hydration reaction of cement or cementitious material and thus hold the plastic concrete from setting for several hours. This admixture is also known as a ‘long-term retarder’ and as a ‘stabilizer’ which is the term used in this thesis. By extending the setting time and hydration of returned plastic concrete using a stabilizer, the returned concrete can be added to fresh concrete in limited amount without adversely affecting the properties of fresh concrete (Ramchadran, and Mailvaganam, 1992). Various hydration controlling admixtures are available in the market to control the cement hydration (Soroka and Ravina, 1998). Set retarding admixtures or retarder is one of such admixtures that slows down the cement hydration and is used in hot weather concreting. The use of admixtures is defined in the ASTM C494. There are two kinds of retarders, defined as Type B (Retarding Admixture) and Type D (Water-Reducing and Retarding Admixture). The main difference between these two is the water-reducing characteristic in Type D that gives higher compressive strength by lowering w/cm ratio. Retarding admixtures slow the rate of setting of concrete. By slowing the initial setting time of the concrete mixture, concrete can stay in its fresh state longer before it gets hardened.

The use of retarders to delay the hydration reaction of cement in concrete especially in hot weather concrete is a long practice (Soroka and Ravina, 1998) and the mechanism of different retarders to delay the setting of cement is well understood (Soroka and Ravina, 1998; Bhatty and Banfill, 1984; Peschard et al., 2006). There are also many studies where researchers have used different types of retarding admixtures to evaluate the effect on various properties of OPC concrete. For example, Al- Shamis et al. (1993) studied the influence of set retarding admixtures and micro silica on the setting time of cement paste and reported that both initial and final setting times increased with increase in retarding admixture dosages. They also reported that the set-retarder had no significant influence on the initials setting time of cement paste at high temperature e.g. at 40 and 50°C, however, little at a final setting time at those temperatures. In another study, Baskoca et al. (1998) studied the effect of retarder on the setting time, compressive and flexural strength of ordinary Portland cement (OPC) concrete at various agitation periods. They also reported an increase in setting time of concrete due to the addition of retarder and with increasing retarder dosage the setting time also increased. They also observed no compressive and flexural strength loss of stabilized concrete. Dias et al. (2010) found that the concrete with retarder overdose eventually reacceded or exceeded their corresponding 28-day strength. Hence, the overdose of retarder not appreciably affected the concrete strength gain.

Another stabilizing admixture system was introduced in the market in the early nineties, which consist of two phases: stabilization and activation. The stabilizer phase slows or stops the hydration of individual cement grains. It acts like high range retarder and it differs from conventional retarder because it also prevents the hydration of tricalcium aluminates (C_3A), whereas a conventional retarder does not. The activation phase allows the hydration process to proceed normally. The activating admixture acts as an antidote for the stabilizer and neutralizes the retarding effect (Lobo, 1995). Essentially it is an accelerator, and typically an accelerator can be used as an antidote for the stabilizer. Preliminary tests and field trials show that the physical properties of stabilized/activating concrete, such as strength, freeze-thaw durability, creep, corrosion resistance were as good as or better than those of the control untreated concrete (Borger et al., 1994). Paolini and Khurana (1998) and Lobo et al., (1995) have reported a comprehensive study where the stabilizer was used to stabilize the OPC concrete at a different time e.g. the same-day stabilized and the long-haul stabilized. Various properties of concrete were measured e.g. workability, setting time, unit weight, compressive and flexural strengths, elastic models, shrinkage, freeze-and-thaw and chloride permeability. The study showed that all the above properties of various stabilized OPC concrete were comparable and in some cases superior to the reference concrete. Senbetta and Bury (1992) have reported the economic benefit to this process of stabilizing concrete are realized in material saving and the reduction of the costs associated with disposal of by-product materials and plant influent. However, the effective use of this admixture requires specialized training of plant personnel so that the strength and durability-related properties of stabilized concrete will not be compromised.

To increase the sustainability of partial concrete replacement of cement with supplementary cementitious materials (SCM) in concrete is a common practice in the concrete industry at present time. The use of SCM in concrete also improves its mechanical and durability properties. However, it depends on the type of SCM, and its amount is a partial replacement of OPC, curing types, etc. The commonly used SCMs are class F fly ash, slag, and silica fumes. However, the fly ash and slag are used in relatively large quantity in concrete than the silica fume due to their availability and low cost. Australia and in many countries fly ash and slag are often blended with ordinary Portland cement (OPC) to produce commonly used general-purpose blended (GB) cement containing 75% OPC and 25% class F fly ash and low heat (LH) cement containing 35% OPC and 65% slag, along with commonly used general-purpose Portland (GP) cement. While the concretes containing fly ash and slag are widely used in construction industry, the effect of stabilizer on the plastic and harden mechanical properties of those returned concretes are still not known. The Very limited study is available on the reuse of plastic ordinary Portland cement (OPC) concrete using extended set retarding admixtures (Paolini and Khurana, 1998: Lobo et al., 1995). While the use of GB and LH cement is a common practice in the construction industry, no such study on concretes made with GB and LH cement is reported so far and a comprehensive study on the effect of stabilizer on properties of stabilized concrete made by GB and LH cement is urgently needed. Therefore, this study evaluates the plastic and harden properties of 24 hours stabilized concrete made by GB cement (i.e. containing fly ash) and LH cement (i.e. containing slag) and compared with that of controlled concrete (without stabilizer) and OPC concrete.

1.2 Significance

For returned plastic concrete to recycle efficiently and without any adverse impact on its quality, the industry would benefit from the knowledge of the parameters for optimal use of stabilizer (admixtures). However, the literature reviewed provides very little insight on it. Colin et al. (1995) and Kinney (1989) investigated the effects of stabilizer for reusing returned plastic concrete. The limitations of those studies were that the studies only used the OPC cement, and there was no proposal for the dosage of the stabilizer. Another researcher, e.g. Rickert and Thielen (2004) conducted research on the effects of stabilizer on the cement compounds (C_3A, C_3S, C_4AF). The limitations were that the effect of stabiliser was not studied on the concrete.

The present study has extended the above limitations through establishing a stabilizer dosage for stabilizing the OPC concrete by systematically establishing optimal processes and evaluating various plastic and mechanical properties. The use of supplementary cementitious materials (SCM) as partial replacement of cement in concrete is a common practice in construction industry e.g. containing fly ash and slag. Despite their increasing use in concrete, the effect of stabilizer on the plastic and mechanical properties of plastic concrete containing SCM is rarely studied. This study has also evaluated the effect of stabilizer on the plastic and mechanical properties of SCM modified concretes. This study further improved the sustainability of sustainable SCM modified concretes through reuse of such plastic concretes and upgrading of low-grade SCM modified stabilized concrete to a higher grade.

1.3 Scope and objectives:

The aim of this research is to experimentally evaluate the effect of stabilizer (extended set retarding admixture) on the plastic and mechanical properties of stabilized concretes made with ordinary Portland cement (OPC) , low heat cement (LH) comprising of 35% OPC and 65% slag; blended cements (GB) comprising of 75%OPC and 25% fly ash. To achieve the aim the specific objectives are as follows:

- Evaluate the effect of various stabilizer dosages on flowability, setting time and heat of hydration of OPC cement and blended cement grouts.

- Evaluate the effect of stabilizer on plastic and mechanical properties of stabilized concretes produce by above three types of cement.
- Evaluate the feasibility of using stabilizer to convert the lower grade stabilized concrete to higher grade concrete produced from above three types of cement.

Two commonly used blended cement containing 35% OPC and 65% slag; 75% OPC and 25% fly ash are used along with ordinary Portland cement (OPC) to produce three types of concretes in this study. Vicat apparatus test method is used to measure the initial and final setting time of above three cement pastes, while Marsh cone method is used in the evaluation of flowability of above three cement stabilized grouts with varying dosage of stabilizer to determine the holding time of the cement grout. Thermocouples are used to monitor the time taken by the above three cement grouts during their hydration to reach peak temperature due to different stabilizer dosages. Slump test is used to measure the workability of concretes. Penetration resistance apparatus is used to measure the initial and final setting time of concrete while the compressive strength and shrinkage of above-stabilized concrete are measured at 7, 28 and 56 days.

1.4 Organization of thesis:

The thesis is composed of five chapters as follows:

Chapter 1: This chapter contains relevant sections including the background, Scope, and objectives of this research.

Chapter 2: This chapter provides a literature review on setting and hydration of the cement or cementitious materials. It gives an understanding of setting time and hydration of cement or cementitious material, and the effect of water reducing admixture and stabilizer with different types of cement and supplementary cementitious materials (SCM). The effect of this stabilizer on the cement and cementitious particles physically and chemically are studied. During the use of stabilizer to recycle the concrete in the plastic stage the understanding of the effect on cement or cementitious materials is required and forecasting the setting time is very important.

Chapter 3: The chapter explains the process flow (Phase) of the experiments to study the effect of stabilizer on cement and cementitious grout and concrete. In addition to the normal process control factors that affects the uniform production of concrete, there are several additional processing factors that need to be considered when stabilized concrete is mixed with the fresh material to produce a blended concrete. Since it was not possible to study all of these factors, the first step in planning the experiment is to identify the most important processing factors.

Chapter 4: The principal objective of this chapter is to review the results achieved in different phases of the experiment. The effect of stabilizer through tests on the cement or cementitious grout and concrete are discussed. The key performance of the cement and cementitious grout and concrete are reviewed and discussed.

Chapter 5: This chapter concludes and gives an overview of the results of the experimental work and provides recommendations for future work.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction

This chapter provides a literature review of setting and hydration of the cement or cementitious materials. It gives an understanding of setting time and hydration of cement or cementitious material, and the effect of water reducing admixture and stabilizer with different types of cement and supplementary cementitious materials (SCM). In concrete technology, the stabilizer is also known as a long-term retarder, which on account of their composition is capable of inhibiting the setting and hydration of cement or cementitious materials for several days. The effect of this stabilizer on the cement and cementitious particles are studied. During the use of a stabilizer for use in recycling the concrete in the plastic stage the understanding of the effect on cement or cementitious materials is required and forecasting the setting, time is very important.

Contrary to the water reducing admixture, retarding admixtures, accelerating admixture, air entraining admixtures and superplasticiser where a wide range of knowledge has been gained concerning identification and more action in cement paste, mortar, and concrete. However, knowledge concerning stabilizer is still inadequate. Depending on the temperature and the time of addition, inverse reactions can occur with particular cement. For example, the retarder may suddenly act as setting accelerators and/or severely impair the strength development of concretes (Rickert and Thielen, 2004). In practice, this can lead to costly concrete removal and cleaning work, the loss of mixing truck drum, or even the destruction of entire bridge spans.

2.2 Cement and SCM Setting Time

Setting time is the term used to describe the stiffening of the cement paste. Broadly speaking, setting refers to a change form of fluid to a rigid state. This period starts when concrete loses its plasticity, becoming unworkable, and it is complete when it possesses enough strength to support loads with acceptable and stable deformation (Pinto, 1999). At the end of the setting period, concrete continuously gains strength with time in the subsequent hardening period (Pinto, 1999; Reinhardt and Grosse, 2004). Rheological properties of fresh concrete vary steadily within the initial and final setting times with consequent decrease in workability, as well as an increase in energy consumption at the subsequent consolidation (Kruml, 1990).

The setting is mainly caused by a selective hydration of C_3A and C_3S and is accompanied by temperature rise in the cement paste; initial set corresponds to a rapid rise, and final set corresponds to the peak temperature. The initial and final set should be distinguished from the false set which sometimes occur within a few minutes of mixing with water (ASTM C451).

Time of setting is defined as the point in time at which penetration resistance reaches specified values. ASTM C 403 identifies initial and final time in terms of penetration resistance as follows:

Initial Time of Set 3.5 MPa

Final Time of Set 27.6 MPa

Typically to a concrete contractor, the initial setting time refers to the time at which a concrete surface can bear the weight of an individual with minimal indentation. When water comes into contact with hydraulic cement, a chemical reaction called hydration occurs. This reaction combines water with cement forms chemical compounds, which increases the strength of the material and changes it from a plastic, moldable material to a solid capable of withstanding substantial loads. The setting time of cement and cementitious material varies. The setting time test report of national concrete pavement technology center bu Wang et al., 2007 below explains the variations in setting time:

Set Time Tests according to ASTM C 403, the initial set time of a cement-based material is defined as the time when the tested specimen exhibits 3.5 MPa (500 Psi) penetration resistance. The final setting time is defined as the time when the penetration resistance reaches 27.6 MPa (4000 Psi). Figure 2.1 illustrates that the penetration resistance of a tested specimen is a function of time, and it can be well-fitted by a power function curve. The setting times are determined from this solidification curve. The mortar samples made with different types of cement and fly ash replacements displayed different penetration resistance values at any given time.

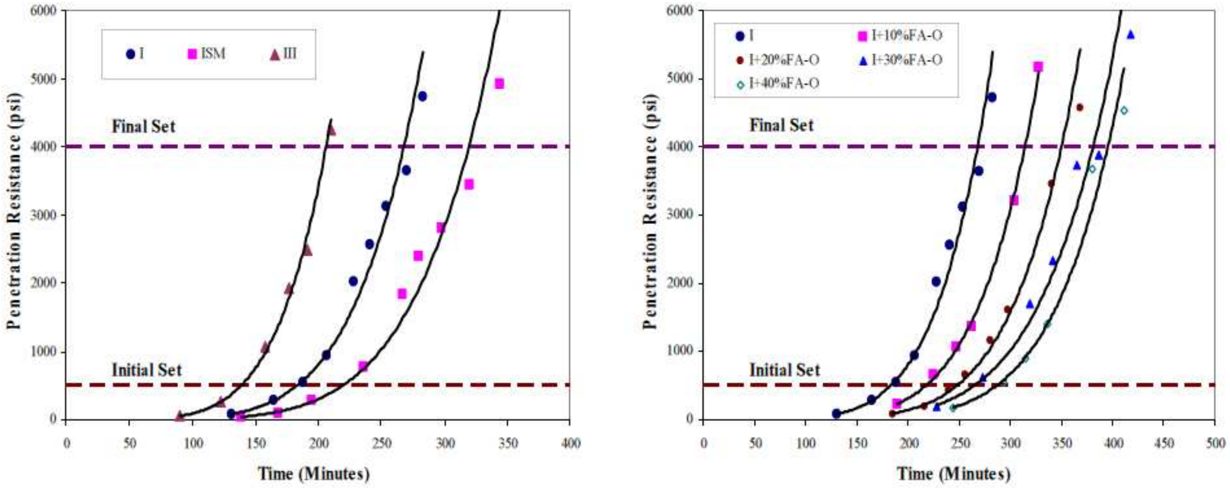


Figure 2.1 Determination of set times (reproduced from Wang et al., 2007)

Figure 2.2 show the setting times of different types of cement under different curing conditions. For all curing conditions, mortars made with Type III cement (High early strength cement) have the lowest initial and final setting times due to their higher surface area. Since hydration occurs at the surface of un-hydrated cement particles, finely ground cement will have a higher rate of hydration which, in turn, results in shorter setting times. ISM- Blended cement (85%OPC+15% slag) has longer set times compared to Type I cement (Ordinary Portland cement) and Type III cement due to slag replacement. At 20ºC, there are 36 and 48 minutes of delay for the initial and final set times, respectively. This result is consistent with the research results from Hogan and Meusel (1981), which indicate a 10- 20-minute delay for each 10% addition of slag. The curing temperature has the same effect on the setting times for all different mortars. The setting times decrease when the curing temperature increases. The setting times of Type I- cement increase about 3.4 and 5.5 hours for the initial and final setting times, receptively. These increases were about 2.6 and 4.1 hours for the Type III cement.

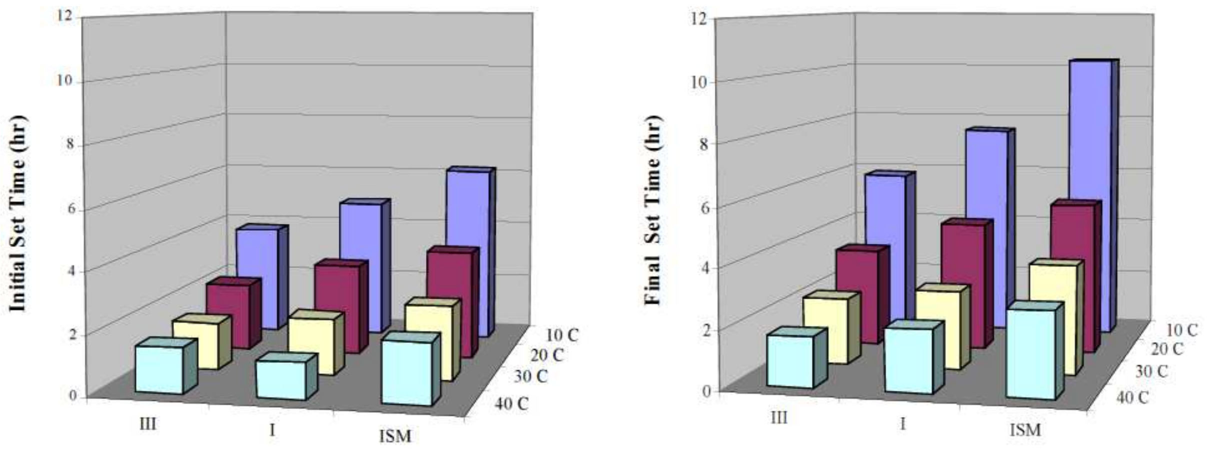


Figure 2.2 Effect of cement type and temperature onset times (reproduced from Wang et al., 2007)

Figures 2.3and 2.4 show the typical effects of class C fly ash (from different sources) fly ash replacement levels and temperature on concrete setting times. The addition of fly ash increased both initial and final setting times regardless of curing temperature. The increased setting times are due to the hydration retardation effect of fly ash. Setting times also increase as the temperature decreases. The effect of the temperature is more apparent for high fly ash replacement levels. For 40% fly ash (source O), the setting times increase to 6.3 and 9.3 hours for initial and final setting times, respectively. When the curing temperature decreases from 40ºC to 10ºC, for 10% fly ash replacement level, the setting times only increases by 4.1 and 6.3 hours for initial and final setting times..

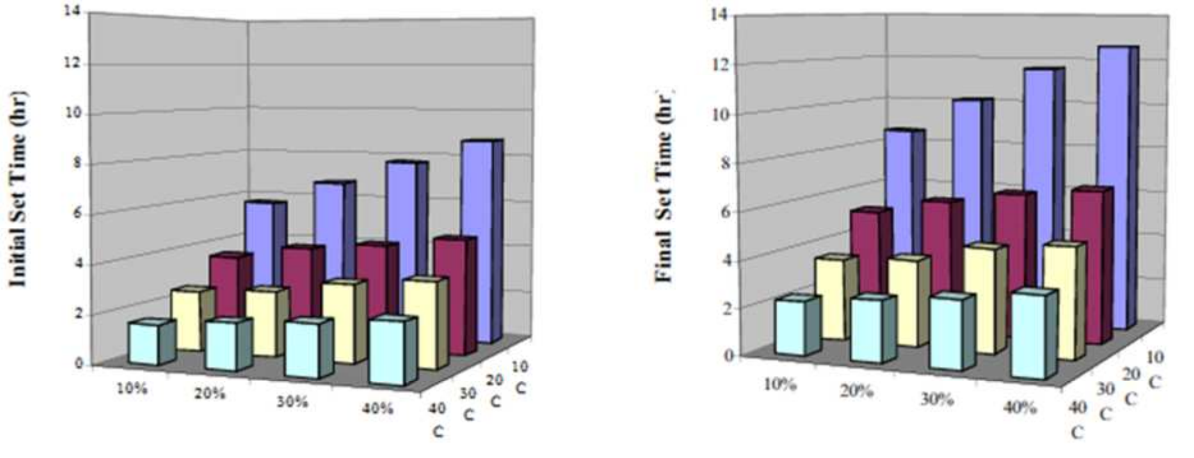


Figure 2.3 Effect of fly ash replacement and temperature onset times (source O) (reproduced from Wang et al., 2007)

Figure 2.4.shows that the setting times are also different for cement with Class C fly ash from different sources. The cement with fly ash from source O has shorter set times compared to

cement with other fly ashes; this may be caused by the different chemical composition and physical properties of different fly ashes.

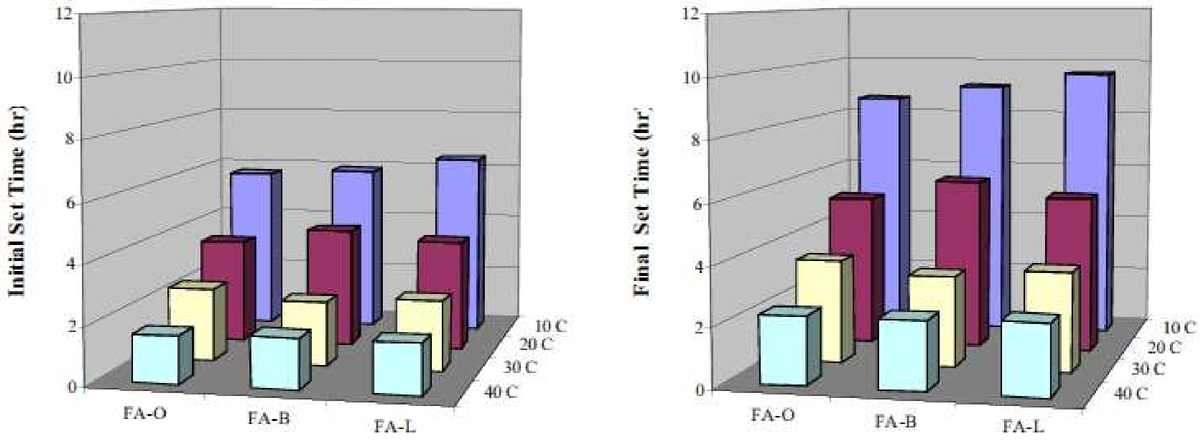


Figure 2.4: Effect of fly ash type and temperature onset times (reproduced from Wang et al., 2007)

Among other factors, the initial and final setting time are influenced by:

- Cementitious material chemistry
- Cementitious material fineness
- Cementitious material content
- Water to cementitious materials ratio
- Concrete and ambient temperatures
- Curing Temperature
- Admixture types
- Fly ash, GGBS and pozzolan properties

2.3 Cement and SCM Hydration

Cement hydration is a complex process and can be influenced by several factors. This section discusses the heat of hydration and factors that influence the rate and amount of heat liberated from hydration of the cement or cementitious materials.

2.3.1 Heat of Hydration

As shown in Figure 2.5 cement hydration process is typically divided into five stages. As soon as cement is mixed with water, a period of rapid heat evolution (stage1) occurs and lasts about fifteen to thirty minutes. The rapid reactions result from ions dissolving in water and reacting between C_3A. This stage is normally not captured by the calorimeter test due to its short reaction time. The heat evolution curves are generally measured begin with the dormant periods of cement hydration (stage 2). During the dormant period, cement hydration ceases, little heat is generated, and the concrete is flowable. As, ion dissolution continues with time the ion concentration of C_3S and C_2S increase in the concrete system. This period lasts less than five hours. At the end of the dormant period, the significant hydration starts again due to C_3S and C_2S hydration (stage 3). This period of cement hydration is called the acceleration period. Concrete temperature increases rapidly during this period. As time increases, the rate of heat generation gradually slows (stage 4). In this phase, the thickness of the hydrate layers that covers un-hydrated cement particles increases and the surface are of un-hydrated parts decreases. The layer of cement hydrates acts as the diffusion area, which governs the permeability of water and dissolved ions. Finally, cement hydration reaches the steady state (stage 5). Both stages 4 and 5 are known as the diffusion control phase.

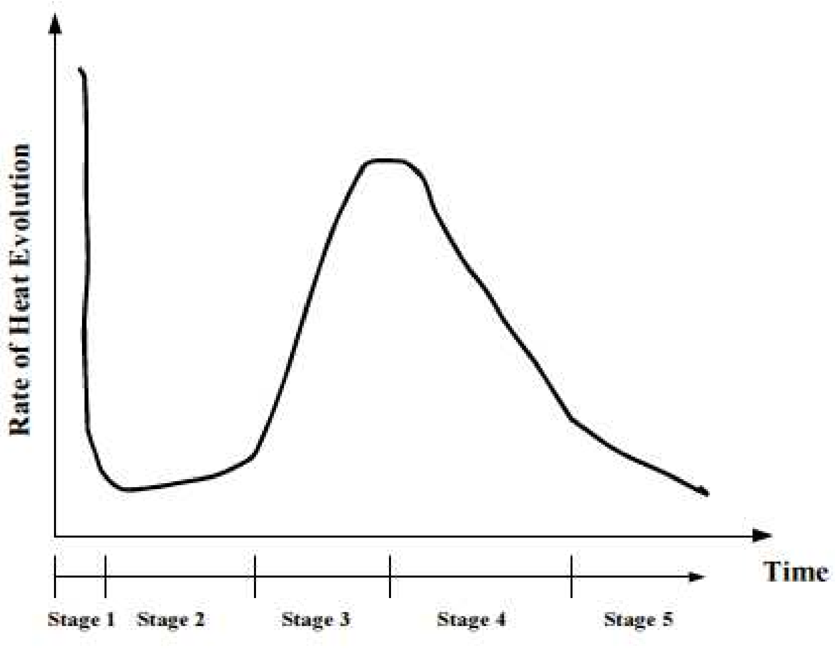


Figure 2.5 Cement hydration process (Reproduced from PCA 2006)

2.3.2 Factors affect the Heat of Hydration

The rate and amount of the heat liberated greatly depends on the chemical and physical properties of the cement, water/cement ratio, supplementary cementitious materials (SCM), chemical admixtures and curing conditions. These factors are discussed in the following sections and as discussed in section 2.2.

2.3.2.1 Cement Type

The heat generation rates of different types of cement under the same condition, which can be measured as a rise in temperature, vary significantly. In Figure 2.6, the temperature rise for Type III- High early strength cement is about 45^0 C. However, the increase for Type IV- the Low heat of hydration cement is only 25^0. The difference in heat generation rate is mainly due to the chemical composition and the fineness of various type of cement.

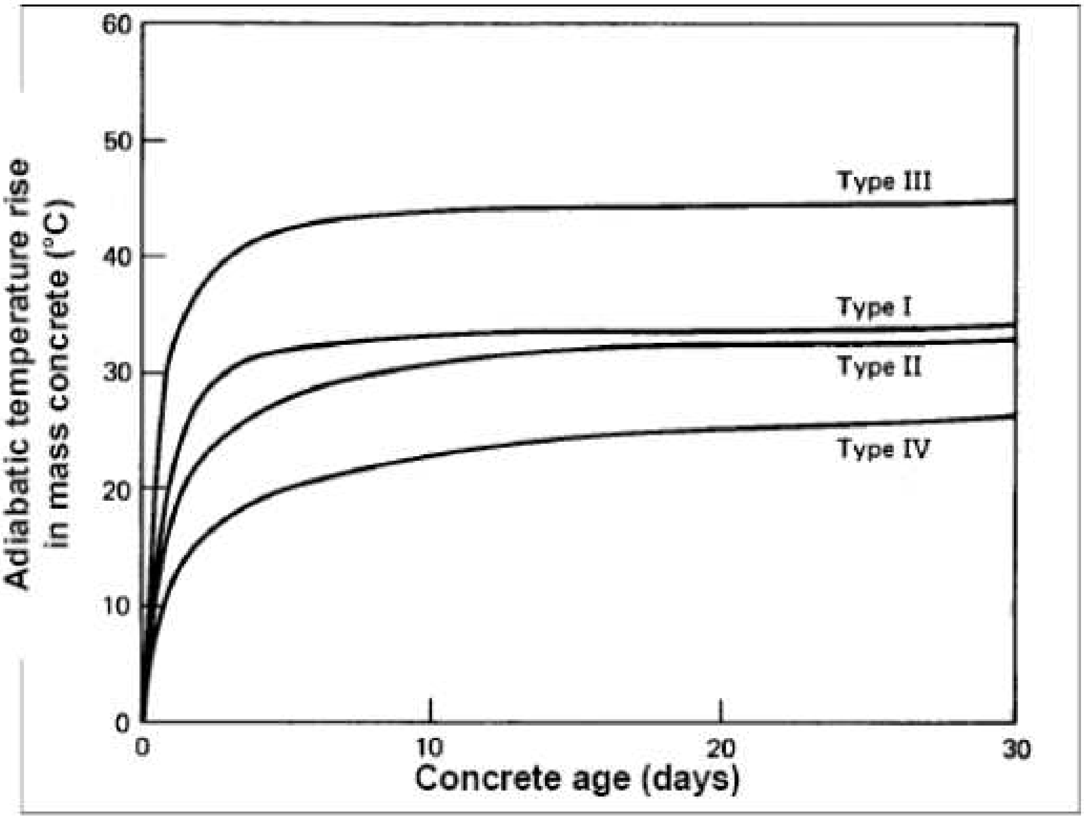


Figure 2.6 Temperature increase of mass concrete under adiabatic conditions (reproduced from Mindess and Young, 1981)

The effect of chemical compositions can be identified by evaluation the rate of hydration of individual compounds and their percentage in the cement. Each chemical compounds shows a different hydration rate and total liberated heat. The hydration characteristics of cement compounds are listed in Table 1.

Table 2.1 Hydration characteristics of cement compounds (Mindess, 2003)

Compounds	**Reaction Rate**	**Amount of heat liberated**	**Contribution to cement heat liberation**
C_3S	Moderate	Moderate	High
C_2S	Slow	Low	Low
$C_3A + C\ S\ H_2$	Fast	Very High	Very High
$C_4AF + C\ S\ H_2$	**Moderate**	**Moderate**	**Moderate**

The rate of hydration reaction of pure cement compounds is given in Figure 2.7a. It can be seen that C_3A reacts the fastest, followed by C_3S and C_2S. The presence of gypsum slows the early age reaction of C_3A. The hydration rate of the compounds in typical cement is plotted in Figure 2.7b. The figure shows that C_3S and C_2S react more rapidly than they do in their pure pastes. C_4AF falls between total liberated heat is also high.

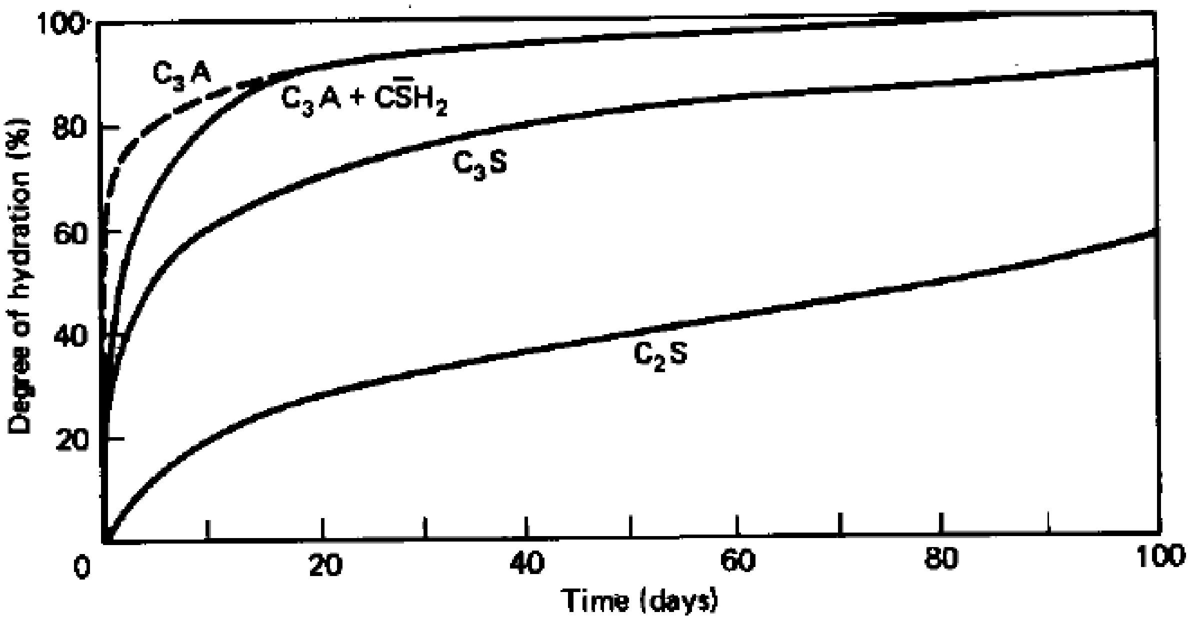


Figure 2.7a Hydration rate of cement compounds—in pastes of pure compounds (reproduced from Mindness and Young, 1981)

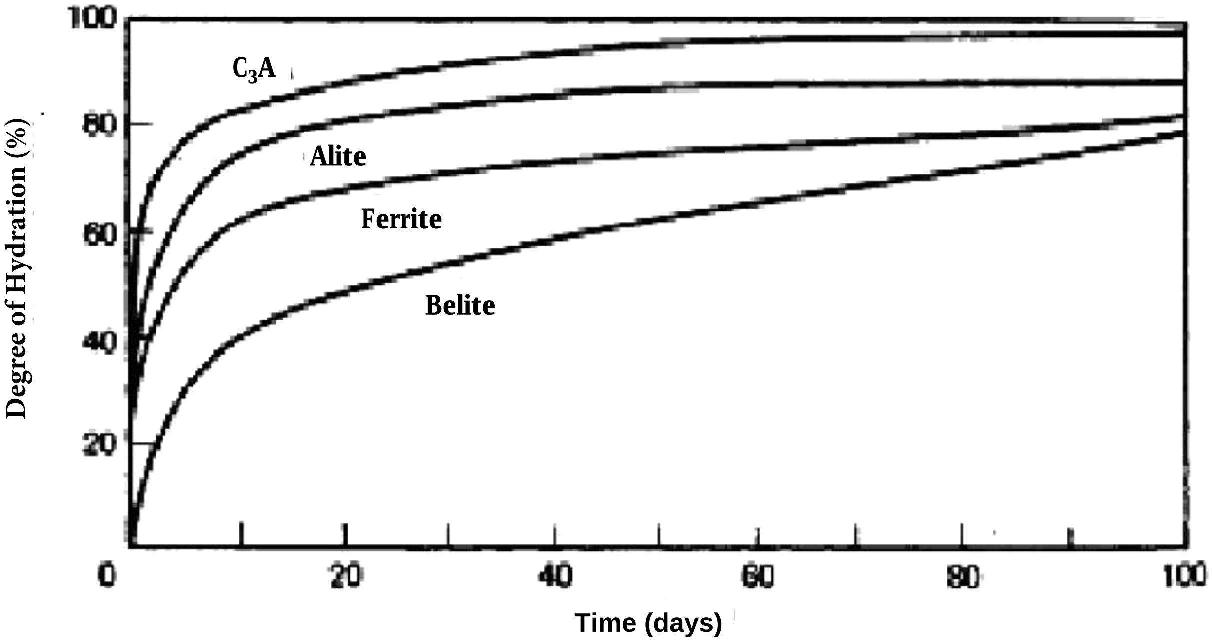


Figure 2.7b Hydration rate of cement compounds—in type I cement paste (reproduced from Mindess and Young, 1981)

Lerch and Bough (1934) studies the effect of C_3A and C_3S on the heat of hydration of pastes. Figure 2.8 indicates that C_3A content significantly increased the rate and amount of generated heat. The total heat is almost doubled when the C_3A increases from 0 to 20%. Regardless of the C_3A content, the reaction is stable after sixteen hours. Figure 2.9 shows the effect of C_3S which is similar to C_3A.

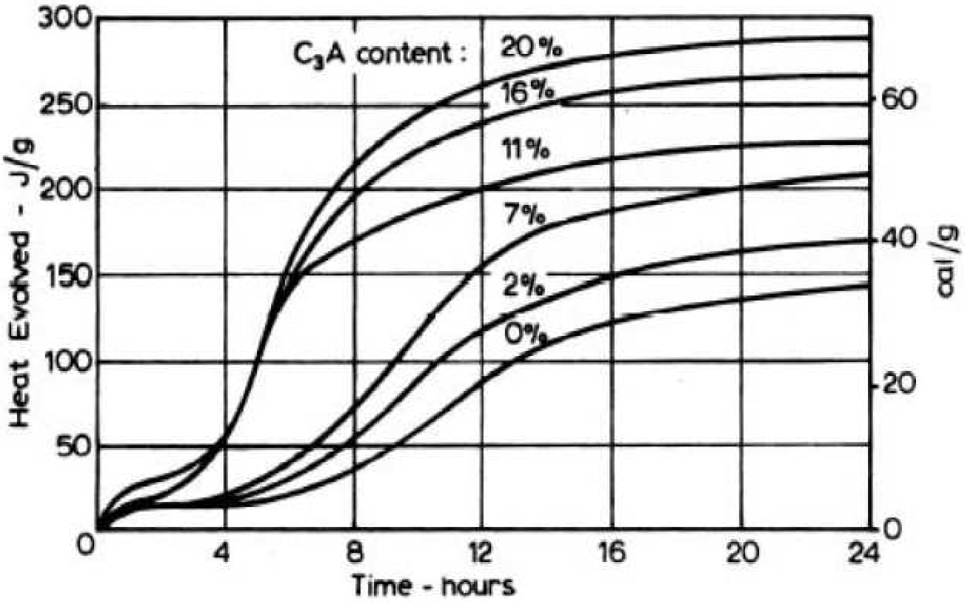


Figure 2.8: Effect of C_3A content (C_3S ≈constant) on heat of hydration (reproduced from Lerch and Bogue, 1934)

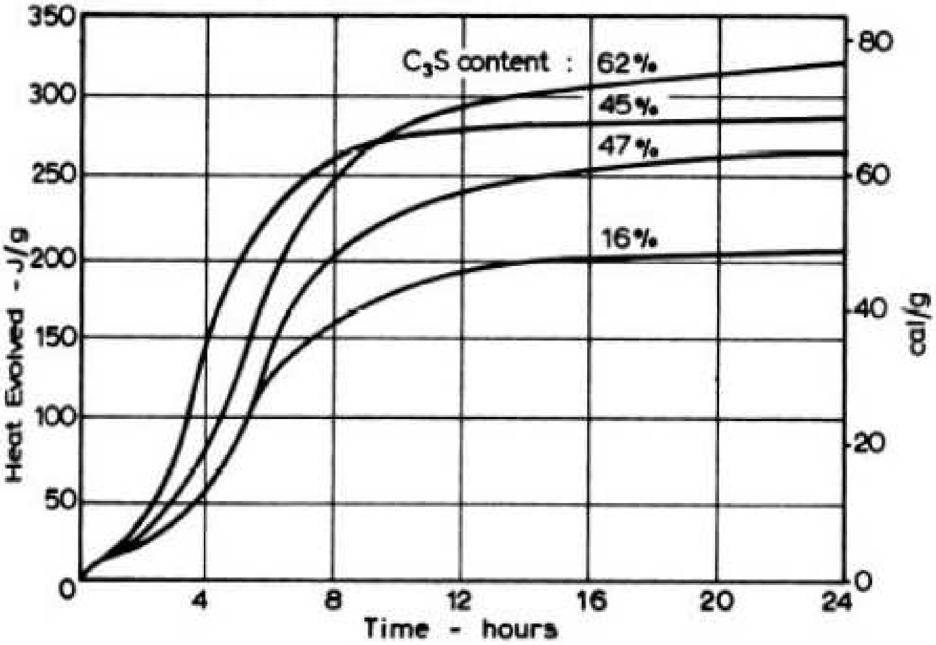


Figure 2.9 Effect of C_3S content (C_3A ≈constant) on heat of hydration (reproduced from Lerch and Bogue, 1934)

2.3.2.2 Sulphate Content

During the final process of cement production, a small amount of gypsum is added and inter-ground with the clinker to control the early reaction of tricalcium aluminate. With a low or over dosage of sulfate, the cement will have false or flash setting. The proper amount of sulfate required for cement varies with cement composition and fineness.

Lerch (1946) conducted a series of test to study the effect of gypsum on hydration in terms of the heat liberation. He found that heat liberated in 30 minutes was reduced by increasing SO_3 content regardless of the content of C_3A, Figure 2.10. This finding could be explained by the theory that alumina is less soluble in lime-gypsum solution than in limewater (Lerch et al. 1929). Adding gypsum saturates the solution more quickly, and the reaction of C_3A is retarded. Therefore, the heat of hydration is reduced.

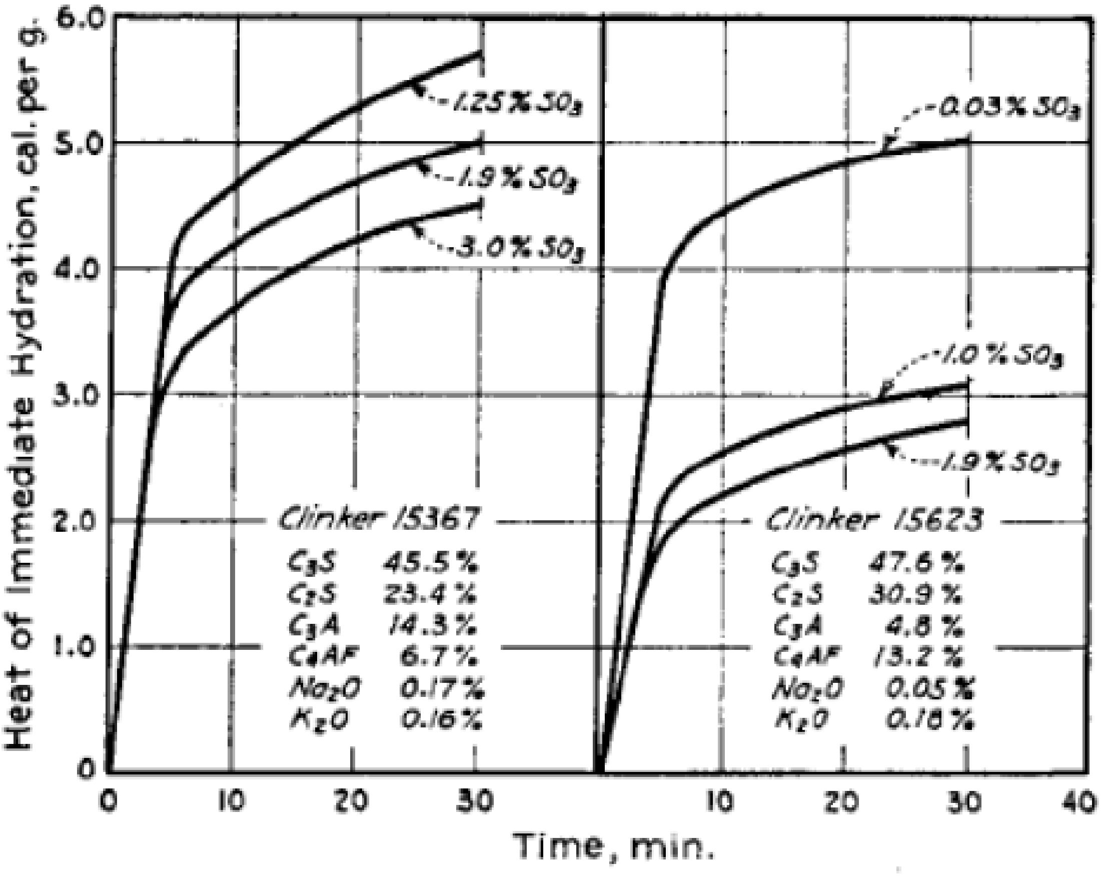


Figure 2.10 Heat of immediate hydration with SO_3 varied (reproduced from Lerch et al. 1946)

2.3.2.3 Fineness

Fineness is another factor that can affect the hydration of cement. The fineness of cement affects the placeability, workability, and water content of the concrete mixture. It is normally measured in terms of specific surface area. The average Blaine fineness of modern cement ranges from 3,000 to 5,000cm^2/g. Although cement with different particle distribution might have the same specific area, the specific surface area is still considered to be the most useful measure of cement fineness.

Since hydration occurs at the surface of cement particles, finely ground cement will have a higher rate of hydration. It has a higher specific surface area, which means there is more area in contact with water. The finer particles will also be more fully hydrated than coarser particles. However, the total heat of hydration at very late ages is not significantly affected. Figure 2.11 shows how the fineness increases the early age heat of hydration for two different types of clinkers.

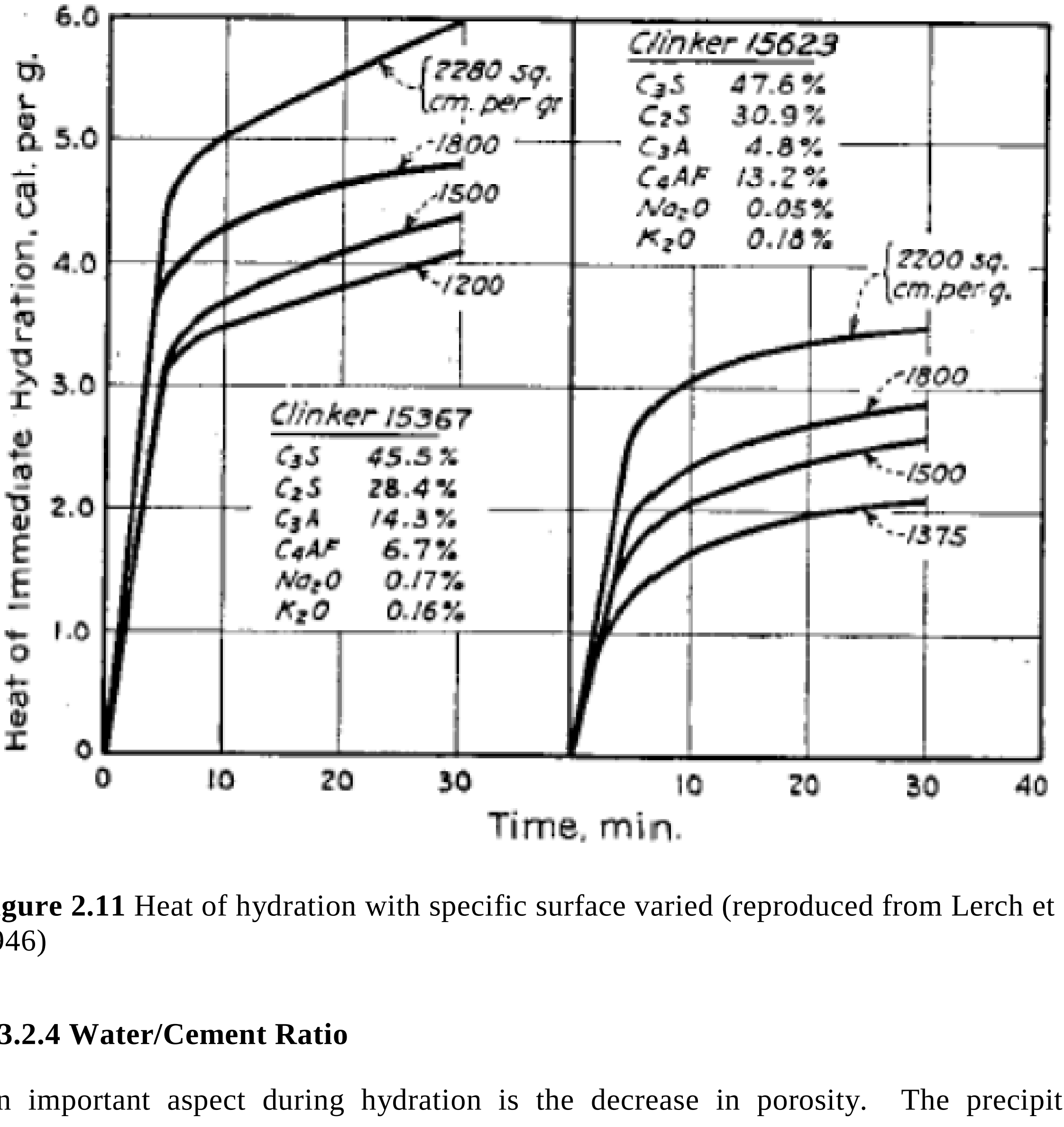


Figure 2.11 Heat of hydration with specific surface varied (reproduced from Lerch et al. 1946)

2.3.2.4 Water/Cement Ratio

An important aspect during hydration is the decrease in porosity. The precipitated hydration products, which have lower specific gravities and larger specific volumes, cause cement grains to expand continuously as cement hydration proceeds. However, the volume of the hydration product is less than the total volume of the cement and water that reacted to form it. The hydration product will not fill the volume made available for it. If external water is available, the cement will hydrate continuously until either the cement is completely hydrated or until the available space with the paste is completely filled. Complete hydration of cement is assumed to require a water/cement ratio of about 0.4 (Van Breugel, 1997). According to Young et al., hydration will stop when the amount of water is not enough to form a saturated C-S-H gel. A minimum w/c ratio of 0.42 is required for complete hydration. If external water is not available, the cement paste will dry as hydration proceeds. Additionally, when the internal relative humidity drops below about 80%, hydration stops.

Cement with high w/c ratio has more water and microstructural space available for hydration of cement, which in turn results in a higher ultimate degree of hydration. Since the heat of hydration is directly related to the degree of hydration, the heat generation is affected by the w/c ratio, Figure 2.12. The rate of heat evolution at early ages is not significantly affected by the w/c ratio. However, consistent with the findings of Byfors (1980), the heat evolution rate starts to decrease as the w/c ratio decreases after a certain time. In Figure2.12, the total heat liberated increase more than 100KJ/Kg when the w/c changes from 0.3 to 0.7.

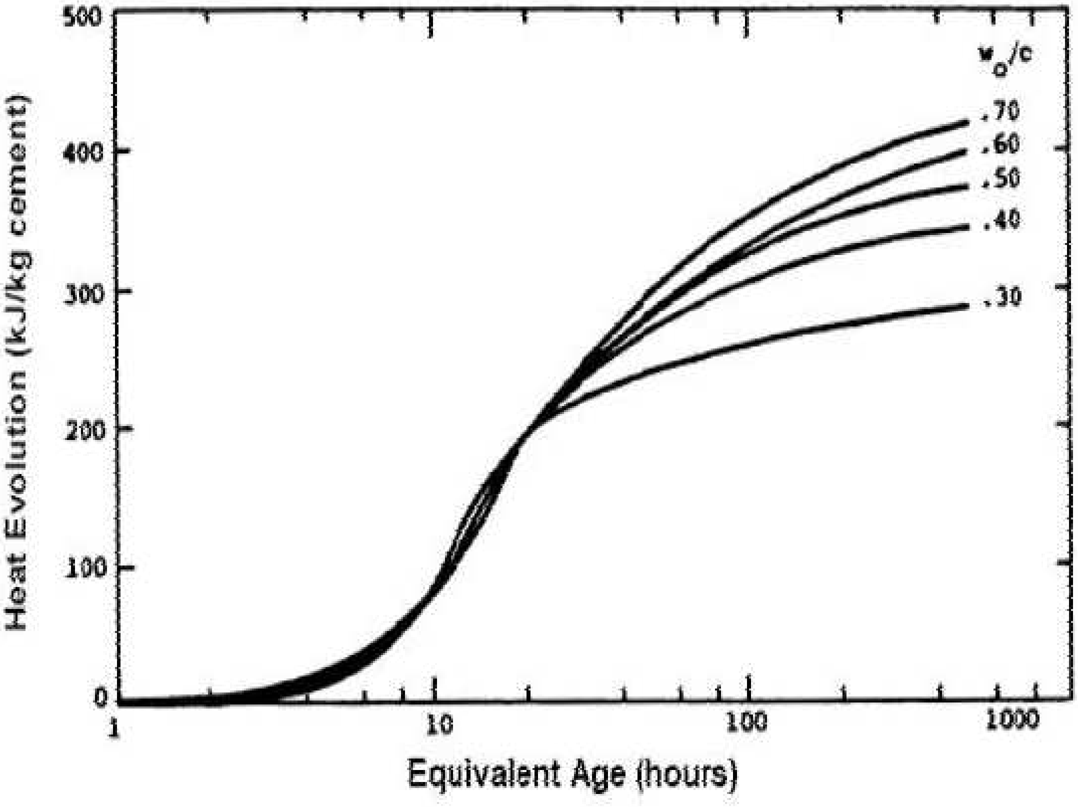


Figure 2.12 Effect of w/c ratio on the heat evolution (RILEM 42-CEA 1981)

2.3.2.5 Curing and Initial Temperature

Environmental temperature differs with seasons and time. Therefore, the effect of environmental temperature needs to be considered. Some investigators have studied the effect of curing temperature on cement hydration, Figure 2.13. Cement hydration is accelerated at early ages under high environmental temperature but decelerated later on. The initial hydration under high temperatures forms "shell" a coating layer of hydration. The shell is denser with increasing temperature. Cement hydration under lower temperature is higher than cement hydration under higher temperature. Blended cement with fly ash is similar to OPC. The initial reaction temperature has a similar effect on the rate of cement hydration. The higher the initial reaction temperature, the higher the hydration rate at an early age. However, at a later age, the hydration under lower initial reaction temperature could be higher.

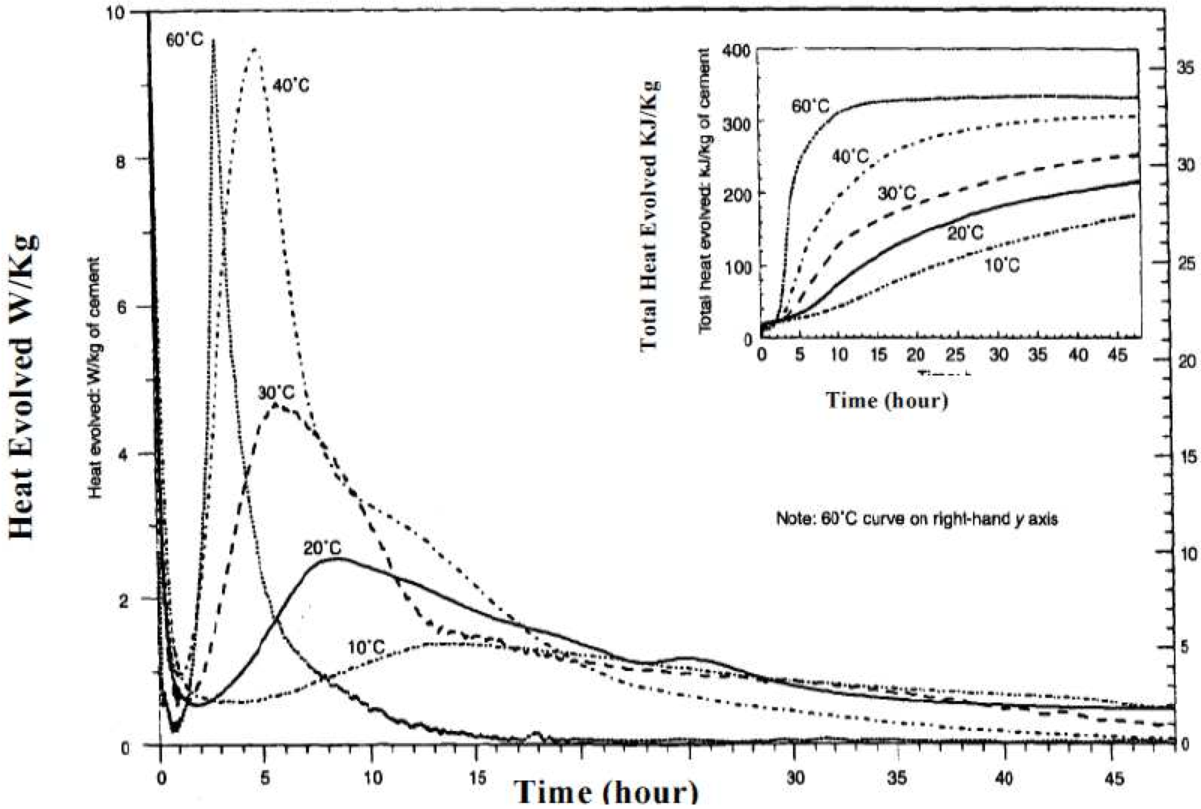


Figure 2.13: Effect of curing temperature on hydration (reproduced from Escalante-Garcia et al. 2000)

2.3.2.6 Supplementary Cementitious Materials

Supplementary Cementitious Materials concrete normally displays slow hydration, accompanied by low temperature, slow setting, and low early age strength. This effect is more pronounced as the proportion of SCMs in the blended cement increases and when the concrete is cured at a low temperature. The properties of the SCM concrete are caused by the reduction of the cement content and also by the pozzolanic reaction. It is accepted that the silicate and aluminate phase of SCMs react with $Ca(OH)_2$ produced by cement hydration to form calcium silicate and aluminate hydrates (Lea 1970). This reaction is known as the pozzolanic reaction (Equation 1)

$A1/S+CH+H_2O \rightarrow CSH, A1\text{-phase}$ (Eqn. 1)

The pozzolanic reaction is slower than C_3S hydration; however, the reaction rate is similar to C_2S. As a result, the pozzolanic reaction produces less heat than the cement hydration.

Fly Ash

Various researchers have studied the effect of fly ash on cement hydration. Crow et al. (1981) determined that adding a low-calcium fly ash reduces the heat of hydration of cement. Some high calcium Class C fly ash with self-cementitious properties may react very quickly with water, releasing excessive heat just like normal OPC hydration (Joshi et al. 1997). The total heat of hydration of fly ash normally depends on the content of CaO. Schindler (2003) recommended the total heat be equal to 1,800 times the percent of CaO. Figure 2.14a shows that the addition of fly ash not only decreases the maximum heat generation rate but also postpones the peak of hydration. As the fly ash ratio increases, the peak becomes wider. Figure 2.14b shows that the retardation of cement hydration mainly occurs during the dormant and acceleration periods. When cement and fly ash mix with water, the Ca^{2+} ion in pure solution is removed by the fly ash, which reacts like a Ca sink. The depressed Ca^{2+} concentration delays the nucleation and crystallization of CH and C-S-H, retarding hydration (Langan et al. 2002).

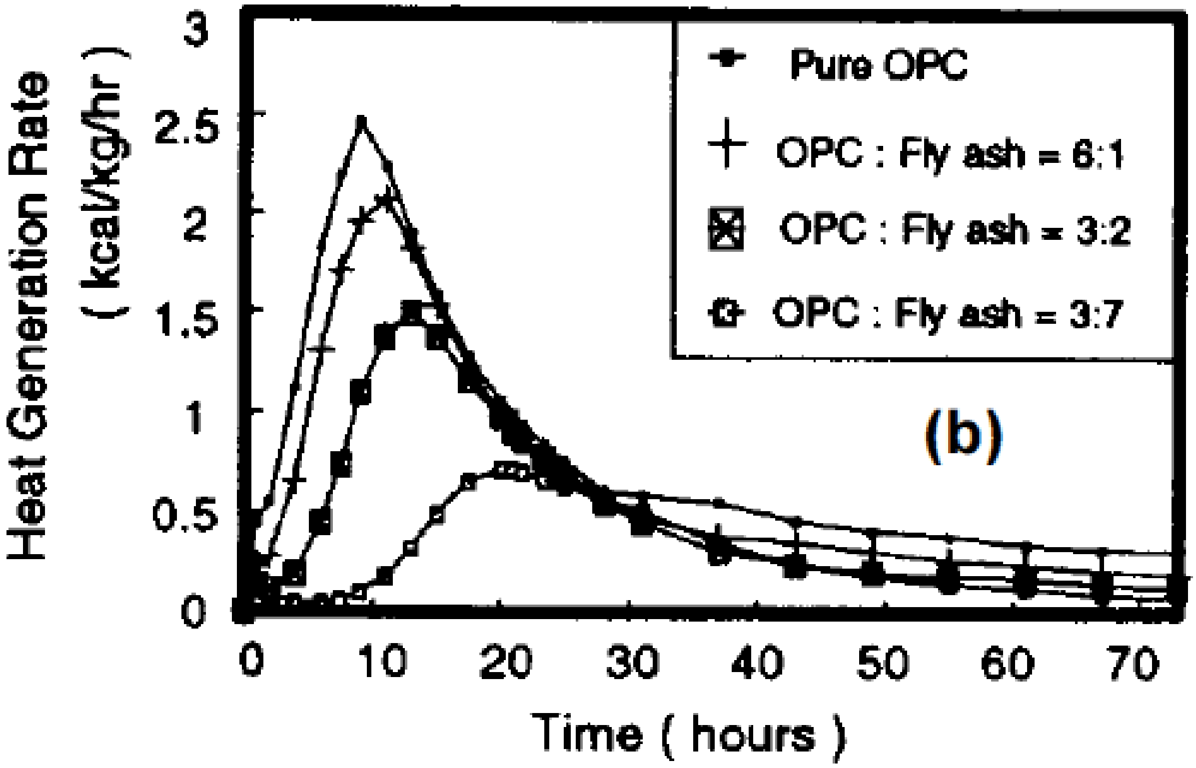


Figure 2.14a Effect of Class F fly ash on heat generation (reproduced from Kishi and Maekawa, 1995)

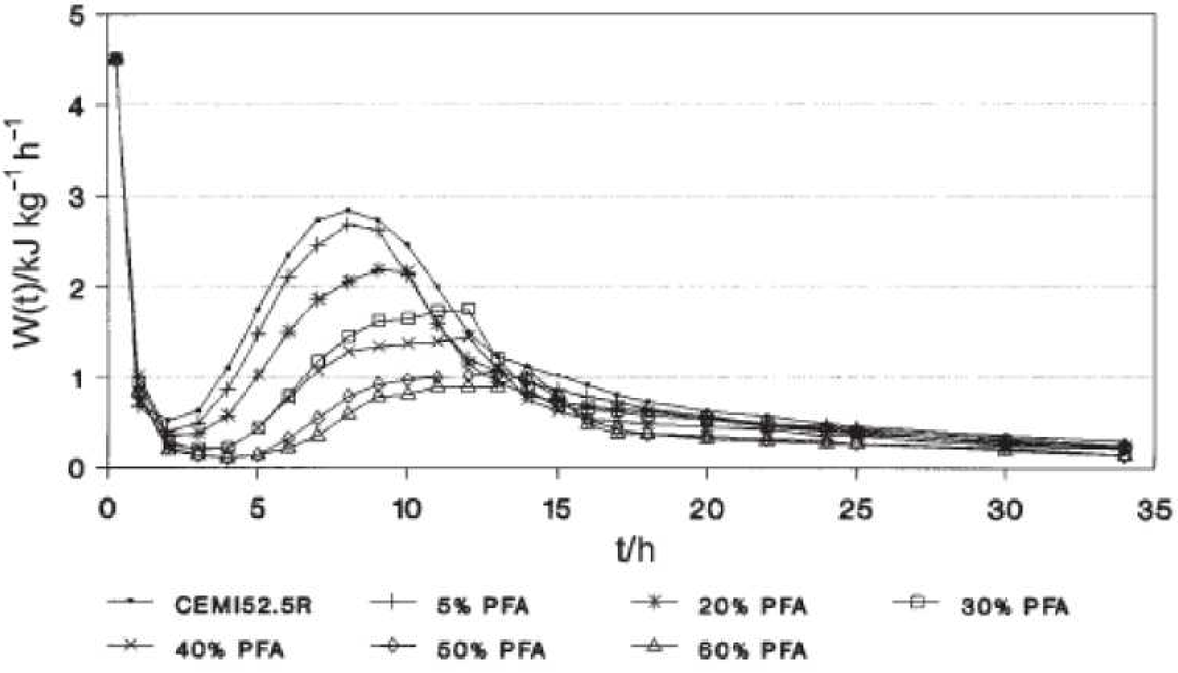


Figure 2.14b Effect of Class C fly ash on heat generation (reproduced from Nocuñ-Wczelik, 2001)

GGBF/ Slag

Figure 2.15 shows the effect of different levels of slag on the heat generation ratio. There are two peaks for slag blended cement; first is caused by cement hydration and second is due to slag reaction. The slag blended cement reaches the first peak at the same time as the pure OPC, indicating that adding slag into concrete will not delay the reaction of cement. The second peak is unaffected by the amount of replacement slag. Kishi et al. (1994) explained that the slag reacts independently as long as sufficient $Ca(OH)_2$ is released from the cement hydration.

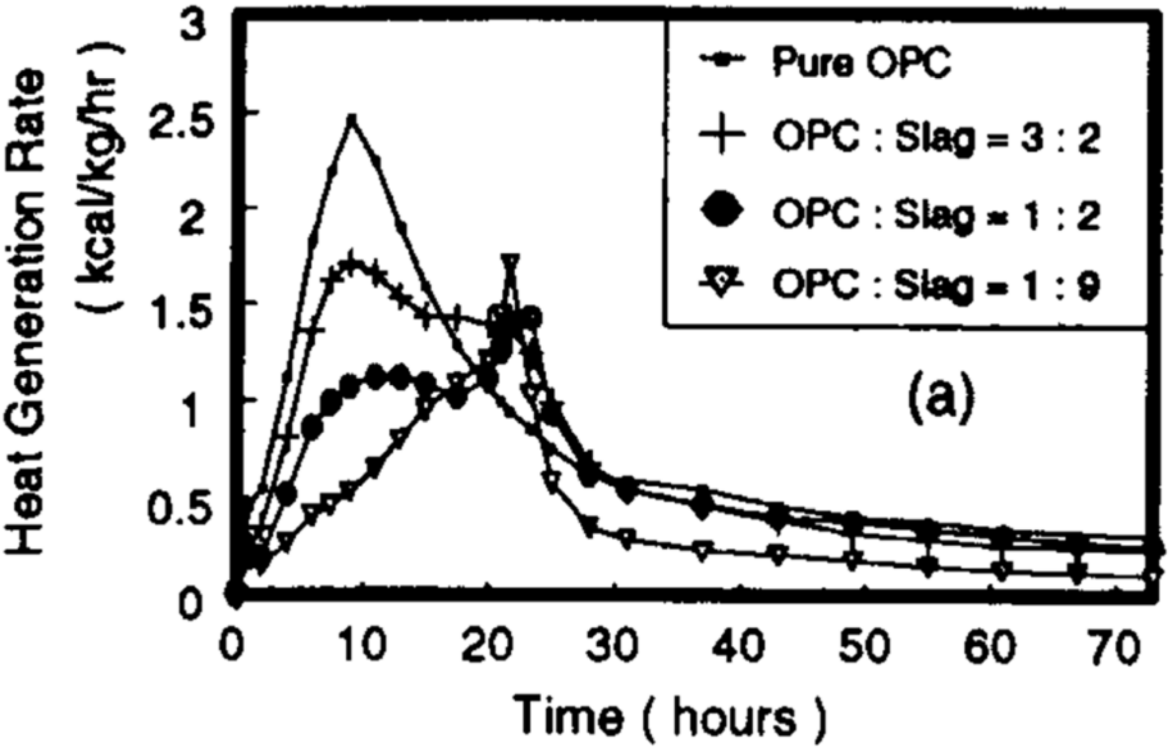


Figure 2.15 Effect of slag on hydration (reproduced from Kishi and Maekawa, 1994)

However, Hogan and Meusel (1981) found that the setting time of slag blended cement is delayed; there is a ten to twenty-minute delay for each 10% addition of slag. On the other hand, Uchikawa (1986) found that the peak of cement hydration was accelerated due to the finely ground slag's consumption of Ca^{2+} in the liquid phase when the fineness of the slag was increased, Figure 2.16

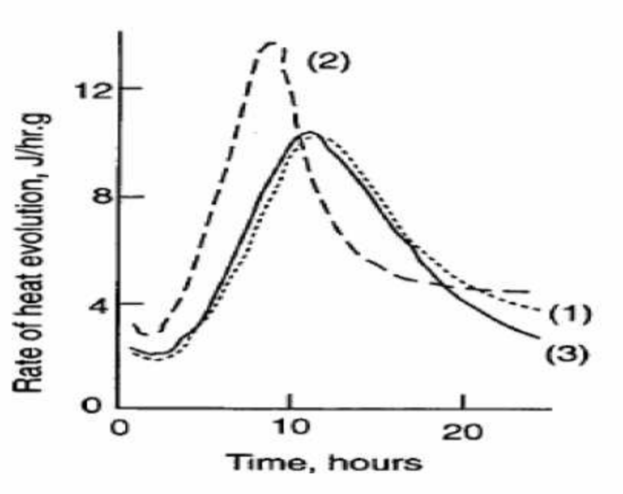


Figure 2.16 Heat evaluation at 20°C (1) 40% coarse slag (400 m2/Kg) (2) 40% fine slag (592 m2/Kg) (3) OPC (reproduced from Uchikawa 1986)

Ma et al. (1994) studied the hydration of blended cement containing 65% slag at different temperature ranging from 10^0C to 55^0C. In this study, the total heat of blended cement during the first 20hours was significantly increased. The test results also showed that temperatures less than 40^0C have little effect on the total heat. However, the total heat increases rapidly with a temperature above 40^0C, Figure 2.17. Consistent with the findings of Klierger et al. (1994), these results indicate that the slag blended cement has low reactivity at room temperature and is strongly heat activated.

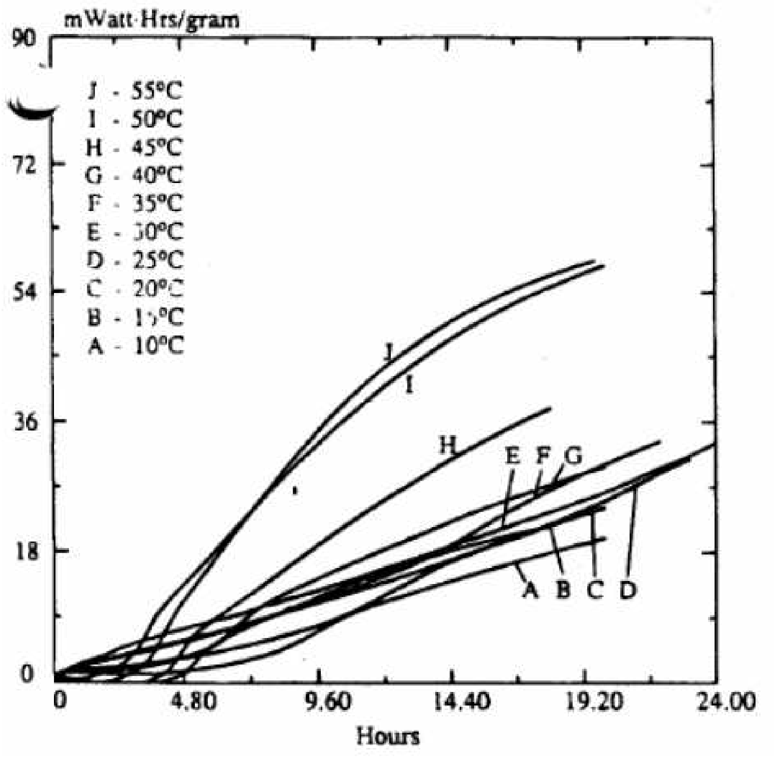


Figure 2.17 Total heat of blended cement with slag at different temperatures (reproduced from Ma et al. 1994)

2.4 Existing Test Methods for Heat of Hydration

Cement hydration is an exothermal process. The measurement of the heat is a convenient way to monitor and quantify the hydration reaction. There are four major types of calorimeters used in cement science and technology; adiabatic calorimeters, semi-adiabatic calorimeters, isothermal calorimeters, and solution calorimeters. Except for these four major types of calorimeters, other methods are developed to monitor the heat generation process.

2.4.1 Adiabatic and Semi-adiabatic Calorimeters

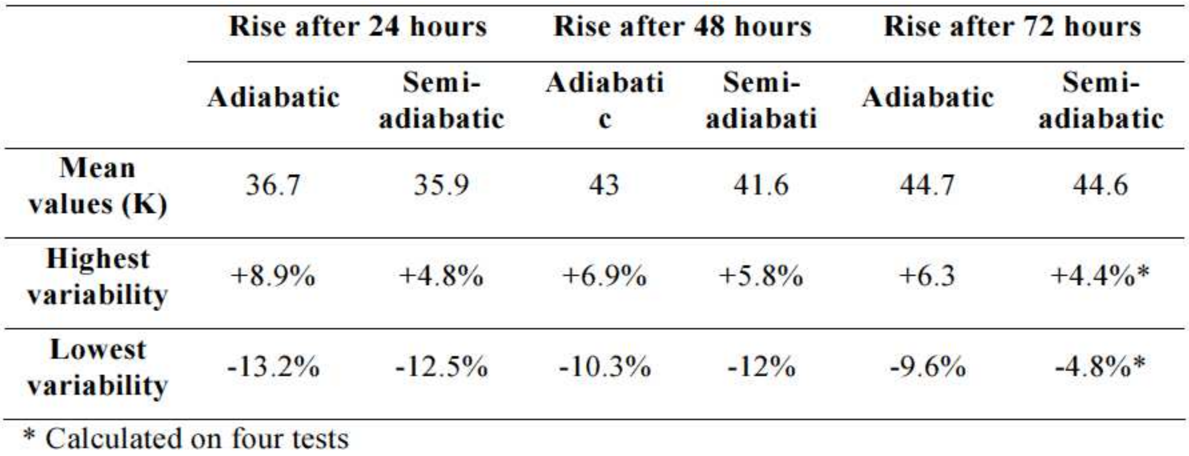
Since it is impossible to achieve an adiabatic environment, the calorimeter is considered to be adiabatic as long as the temperature loss in the sample is not greater than 0.02K/h. The heat loss is prevented by controlling the temperature of the surrounding environment. The insulating material could be water, air, and heated containers. Water insulation is the most popular way.

Adiabatic heat measurements are most convenient for producing a continuous heat of hydration curve under curing conditions close to mass curing. Moreover, also adiabatic hydration curves are the most suitable starting points for temperature calculation in hardening structures. One major drawback of an adiabatic calorimeter is that the effect of the curing temperature on the rate of hydration is measured implicitly. The activation energy is required to convert the results to the isothermal reference temperature. The results can also be affected by the assumption of the thermal properties of the materials. The advantage is that the heat evolution of an actual concrete mixture can be determined. Ballim (2004) conducted the adiabatic calorimeter test to obtain the rate of heat evolution and used this as an input to calculate the concrete temperature. De Schutter (1995) and Tanaka et al. (1995) performed the adiabatic test to estimate the heat of hydration of slag blended cement.

The semi-adiabatic calorimeter is similar with the adiabatic calorimeter. However, it allows a certain amount of heat loss to the environment. The maximum heat loss should be less that 100J/(h.K). The calculated adiabatic curve from the semi-adiabatic test is lower than the curve from the true adiabatic test. Since the temperature development is lower than the sample in adiabatic test due to heat loss, the semi-adiabatic method is suitable for pastes, mortars, and concrete samples. It has been widely used for determining the maximum heat of hydration of concrete.

The “Round-Robin” test program had been conducted by RILEM to compare the performance of different types of calorimeters. Fourteen different organizations participated in the program to compare the adiabatic curves and predicted adiabatic temperature curves from semi-adiabatic calorimeter and to find the main factors that affect the results from different calorimeters. All tests used the same materials and mix proportion. It is found that, for the adiabatic test, 50% of the adiabatic temperature rise variations are in a narrow range of the only 2K and that the specimen size and the environment do not significantly affect the temperature rise. For the semi-adiabatic test, the mean temperature rises are 2%-3% lower than the adiabatic tests. This indicates that the semi-adiabatic calorimeter could be used to predict the adiabatic temperature rise. Table 2.2 shows the summary of the test results.

Table 2.2 Variability of adiabatic and semi-adiabatic test results (reproduced from. Morabito, 1998)



	Rise after 24 hours		Rise after 48 hours		Rise after 72 hours	
	Adiabatic	Semi-adiabatic	Adiabatic	Semi-adiabati	Adiabatic	Semi-adiabatic
Mean values (K)	36.7	35.9	43	41.6	44.7	44.6
Highest variability	+8.9%	+4.8%	+6.9%	+5.8%	+6.3	+4.4%*
Lowest variability	-13.2%	-12.5%	-10.3%	-12%	-9.6%	-4.8%*

* Calculated on four tests

2.4.2 Isothermal Calorimeter

Isothermal Calorimeter is usually used for paste samples. These tests are conducted at a constant temperature. The heat of cement hydration is directly measured by monitoring the heat flow from the specimen. The total heat evolution can be determined by summating the measured heat over time. The disadvantage is that the duration of this test is normally limited to seven days due to the signal *sensitivity* limitations. Beyond this point, it is hard to distinguish the signal from its background. Also, the isothermal tests do not take into account the cement reactivity change due to the change of temperature. It is hard to predict the temperature increase of concrete from these results since the conditions in the real structure where the temperature continually changes are not reflected.

Isothermal Calorimeter is more widely used for studying the reaction of the kinetics of pure cement pastes. Many researchers have applied this method to study the cement heat signature. Ma et al. (1994) conducted the isothermal calorimeter tests to study the hydration behavior of blended cement containing fly ash, silica fume, and granulated blast furnace slag over the temperature range of 10°C to 55°C. The relationship between the blended cement reactivates, and the curing temperature was established. Xiong and Breugel (2001) used the 3114/3236 TAM Air isothermal calorimeter to determine the kinetics of cement hydration processes at different temperatures and applied the results to the numeric simulation model. Some other researchers also used this method to determine the activation energy of the cement.

2.4.3 Solution Calorimeter

ASTM C 186, Standard test method for the heat of hydration of hydraulic cement, describes the test of measuring cement heat of hydration using a solution calorimeter. This test consists of determining the heat of the solution of hydrated and the un-hydrated cement by dissolving the samples in a mixture of acids. The difference between those two measured heats of solution values is the heat of hydration of cement. This test is normally used for cement paste and perfume after 7 and 28 days of hydration, and the test results are comparable to the values obtained from the conduction calorimeter. The disadvantage of the test is that only small paste samples are used not a mortar or concrete samples.

2.4.4 Other Test Methods

Except for the four major types of calorimeter discussed above the un-thermostated heat, conduction calorimeter can also be used to monitor the heat evolution rate. Wadson (2004) developed a 14 channel un-thermostated calorimeter based on the similar theory as the isothermal calorimeter. The performance of this calorimeter is governed by the ambient temperature stability and the heat capacity balance between each sample and its reference. Wadson (2004) stated that the output could be used to quantify the retardation, detect cement-admixture incompatibility and investigate the hydration disturbance.

Other than the calorimeter method, there are other simple tests used to test the sample temperature. These tests include Dewar bucket, coffee cup and so on. The Dewar test can be used to monitor temperature development with time for both paste and mortar samples. The size of the sample depends on the size of the Dewar. The quality of the insulation could vary for different Dewar. The Dewar test is easy and cheap. However, only the temperature can be obtained using the test. The environment conditions can influence the test results.

For this research, Coffee cup method was used (Wang et al., 2007); “Coffee cup is an easy test to conduct with grout samples. Together with a thermocouple, it gives the temperature of the test sample and reference grout. The temperature difference between the sample and reference grout and shape of the curves will be analysed. It is good method to check the compatibility of materials, and it works well for cement with SCM or admixtures.

The “coffee cup” calorimeter test methodology can be used to:

- Uses of reference grout sample and other samples with different combinations and proportions of cement, SCM, and admixtures.
- Determine set time with a change in the slope of the heat curve.
- These tests can be done as part of a cement shipping requirement.
- This will work better when doing combinations of SCM or admixtures with cement or change of cement supplier.
- The temperatures shown on the hydration curves are meaningless; it is more the temperature difference and shape of the curves that make the results relevant.
- Set retarders can be tested. Some perform very uniform with only a retardation effect and not much change in hydration curve. Others have a significant effect on the hydration curve besides retardation.
- A temperature of 10 degrees made a compatible mix into an incompatible one.
- A good method to look at the compatibility of materials.
- Can be used to test overdose of admixture.
- At different temperatures, the effects may be totally different.
- All are done with grout samples.
- When you do this with concrete, the tests turn too noisy due to the presence of aggregates.

2.5 Chemical Admixture

Chemical admixtures are added to modify the setting time and reduce the water requirement of the concrete mix. Chemical admixtures may significantly change the cement hydration rate, and therefore the heat generation. AS 1478.1-2000 classified the chemical admixtures into the following twelve types:

Air-entraining AEA

Water-reducing WR

Set-retarding Re

Set-accelerating Ac

Water-reducing and set-retarding WRRe

Water-reducing and set-accelerating WRAc

High range water-reducing HWR

High range water-reducing and set-retarding HWRRe

Medium-range WR, normal setting MWR

Special purpose, normal setting SN

Special purpose accelerating SAc

Special purpose retarding SRe

NOTES: Special purpose admixtures are admixtures having claimed performance attributes outside the range of this Standard. Such attributes include but are not restricted to anti-washout, air detraining and corrosion inhibiting. Compliance with the provisions of this Standard gives some assurance that the admixture does not have a detrimental effect on the concrete.

Descriptions and Types of Admixture

Air-entraining admixture (Type AEA)

An admixture used for entraining air as discrete, non-coalescing, small bubbles. These admixtures are used to entrain moderate amounts of air, usually not more than 13% by volume of the mortar fraction of the concrete. The term does not apply to admixtures that produce foamed or cellular concrete of low density and has thermal insulating properties.

Water-reducing admixture (Type WR)

Water reducers are defined as admixtures that decrease the requirement of water to achieve a given workability. They sometimes accelerate or retard the concrete setting. When a water reducer is used without changing the mix proportion, the heat of hydration and temperature rise of concrete at an early age may increase. Using a water reducer can decrease the cement content at a given strength and slump, which in turn result in the reduction of heat generation and temperature rise (Massazza et al.1980).

Set-retarding admixture (Type Re)

Set-retarder is an admixture that delays the setting and initial hardening of concrete. The ingredients of the retarder are similar to that of the water reducers. Ben-Bassat (1995) states that “the heat of hydration and temperature rise of concrete containing retarder are less at an early age, and they are equal to about 3-7 days.

Set-accelerating admixture (Type Ac)

Set-accelerator is used to speed up the strength gain at early ages and reduce the setting time. Accelerating admixtures are normally used in a cold environment or where the early gain of strength and short time are required. An accelerator can increase the rate of heat evolution at the setting stage. Depending on the chemical composition of the accelerators, the rate of heat liberation in the hardening stage may also increase. (Nagataki 1995)

Water-reducing and set retarding admixture (Type WRRe)

Water-reducing and set retarding admixture that combines the properties of a water-reducing admixture with those of a set retarding admixture.

Water-reducing and set-accelerating admixture (Type WRAc)

An admixture that has both a water-reducing and set-accelerating function in concrete.

High range water-reducing admixture (Type HWR)

High-range water-reducing agents (superplasticizers) are a new class of water-reducing agents. The workability of high-range water-reducing agents increases more often than normal water-reducing agents. The use of superplasticizers mildly retards the setting of concrete, which in turn can reduce the heat generation in the setting period. However, super plasticizers do not affect the total heat of concrete. Figure 2.18 show that the adding of super plasticizers reduces the adiabatic temperature at an early age.

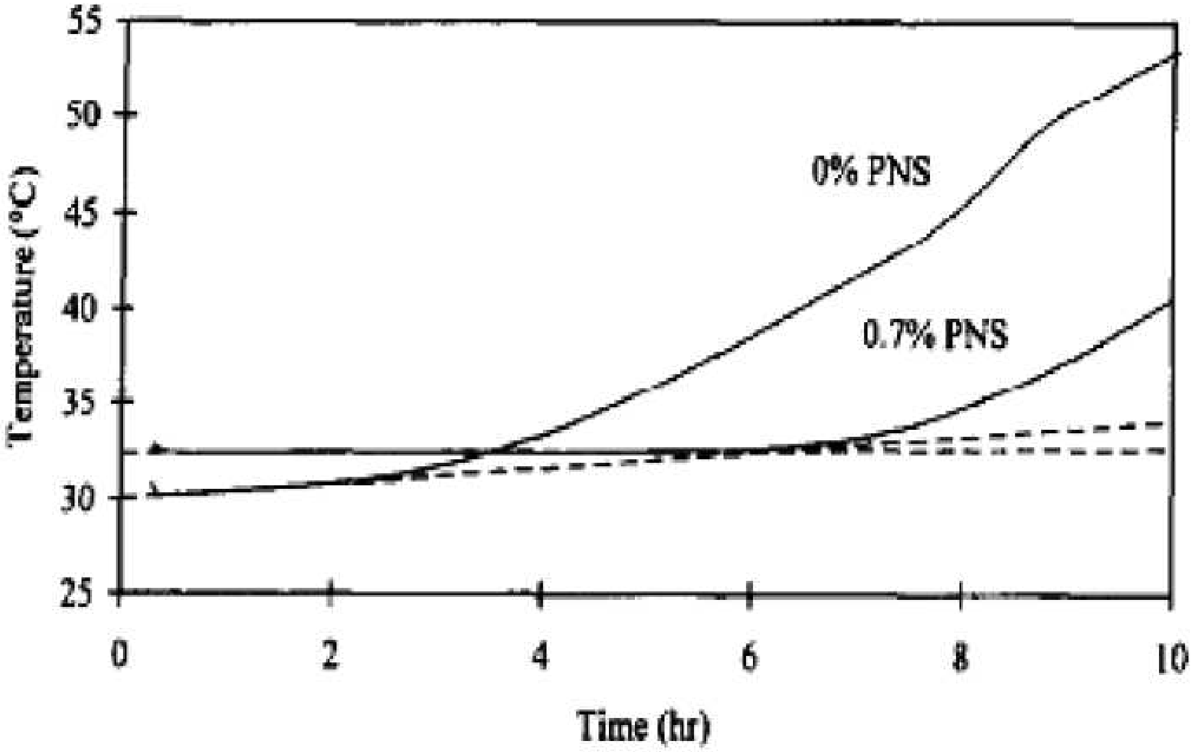


Figure 2.18 Effect of Superplasticizer on cement hydration (reproduced from Jolicoeur et al. 1998)

High range water-reducing and set retarding admixture (Type HWRRe)

An admixture that combines the functions of a high range water-reducing admixture with those of a retarding admixture.

Medium-range, water-reducing admixture (Type MWR)

An admixture that has a significant water-reducing function, sufficient to raise the slump of concrete to produce a highly plastic consistency, without changing the water/cement ratio.

Special purpose normal-setting admixture (Type SN)

An admixture used to provide some specific property to concrete without affecting the normal setting characteristics of that concrete.

Special purpose set retarding admixture (Type SRe)

An admixture used to provide some specific property to concrete but with a set-retarding characteristic.

Special purpose set-accelerating admixture (Type SAc)

An admixture used to provide some specific property to concrete but with a set-accelerating characteristic.

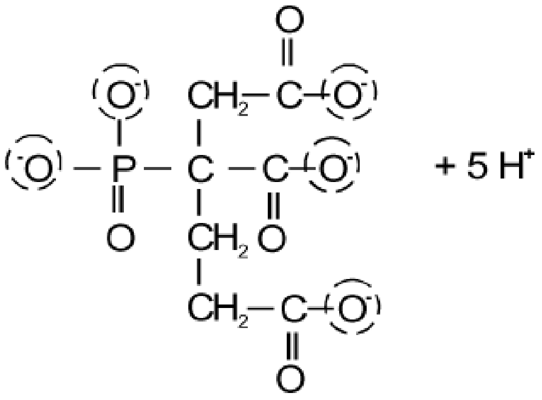
The admixtures of interests for this research were Water-reducing admixture (Type WR) and Special purpose set retarding admixture (Type SRe). The type SRe admixture also known as stabilizer or extended-retarding admixture or long – term retarder

2.6 Influence of a stabilizer or Long-Term Retarder (LTR) on the Hydration of Clinker and Cement

Contrary to the plasticizers, superplasticizers, and air entraining agents, where a wide range of knowledge has been gained concerning identification and mode of action in cement paste, mortar, and concrete, knowledge concerning long-term retarding admixtures is still inadequate.

Phosphonobutane- 1, 2, 4-tricarboxylic acid (PBTC)

PBTC is a hydroxycarboxylic acid with five acid sites, which can dissociate in an alkaline medium. Figure 2.19 shows the structure of PBTC in the deprotonated state. Above a pH value of approximately 12.7, five protons (H+) are fully dissociated. In this form, PBTC possesses five coordination sites, which are suitable for the complexation with metal ions. Studies by Bier (1993) revealed that in the neutral pH region (pH 7), calcium, aluminium, cadmium, and magnesium ions are only complexed to a maximum of 3%, and other metal ions, e.g., chromium, copper, iron, manganese, lead, and zinc, to over 85%. In an alkaline medium, the complexing ability of PBTC with calcium and aluminum ions increases with increasing pH value (Bier 1993).



empirical formula:	$C_7H_{11}O_9P$
molar mass:	270 g/mole
P-content:	11.5 %

Figure 2.19—PBTC—deprotonated (reproduced from Rickert and Thielen, 2004).

Influence of PBTC on the Hydration of Clinker and Cement

Skalny et al., (1980) reported that molecules with complex metals could be converted from the extended molecular shape into stable rings through the metal ion. Such chelating agents can retard the hydration of cement particularly strongly. Here, the retarder action increases with increasing number of free coordination sites. According to Skalny et al.(1980), a compound with a β hydroxycarboxylic group, which can form a stable 6-member ring with a metal ion are particularly good chelating agents and very effective retarders. PBTC can form similar ring structures by complexation with calcium ions. According to Kinney (1989), stabilizer based on PBTC slows the hydration of for an extended time. It's presumed that PBTC slows the formation of C-S-H and calcium hydroxide nuclei and as a result finer and more compact hydrates can form.

Bobrowski (1990, 1991and 1996) suggested that the stabilizing action of phosphoric acids is due to the binding of calcium ions in chelates. According to Paolini et al. (1998), Langenfeld et al. (1998) and Moeser et al. (1999) a PBTC- containing stabilizer retards the hydration of C_3A and C_3S very strongly. Instead of the initial hydration process, "spherical new formation" about 100 nm in size was observed on the surfaces of C_3A and C_3S after 20 min. These are thought to be chelate complexes. In experiments with C_3S, the formation of these complexes resulted in higher hydration heat rates in the initial minutes. In experiments with C_3A, the initial evolution of heat of hydration was decreased by PBTC.

In studies by Lipus et al. (2000) and Rickert (2004a), recycling aids based on PBTC retarded all further hydration reaction of Portland cement, except for the formation of small primary ettringite crystals. The new formation (chelate complexes) observed in Langfeld at al. (1998) were not observed on the surface of the cement particles.

In the literature, there are hardly any other references that address the mechanism of action of PBTC on the hydration of clinker and cement. The literature yields only a few and to some extent, contradictory findings concerning the influence of PBTC on the hydration of clinker phases, clinker, and cement are found. Also very often different experimental conditions and procedures hinder the ability to draw a conclusion regarding the retarding mechanism of PBTC.

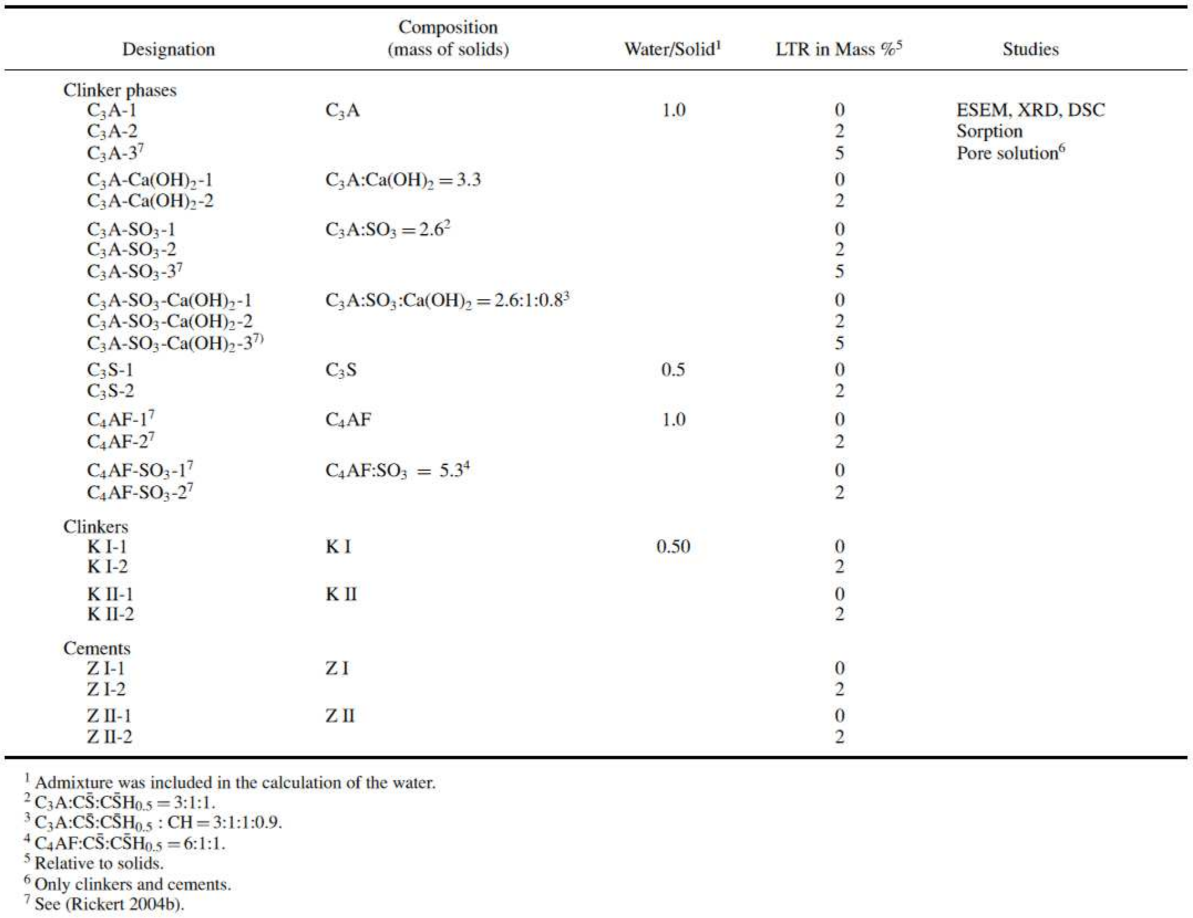
Aim and Extent of the Investigations

The aim of the Rickert and Thielen (2004) investigation is to extend the knowledge concerning the effects of the PBTC-based long term retarder on the hydration of clinker phases, clinker, and cement.

Firstly, the effect phases (C_3A, C_4AF, and C_3S) and on the hydration of mixture clinker phases, sulfate, and/or calcium hydroxide, as stated in Table 2.3, was studied chemically and mineralogically.

The retarding mechanism of long-term retarders associated with the reaction of C_3A or C_4AF fractions with dissolved sulfate to give ettringite was investigated by comparative studies between two industrial clinkers and on cement produced from them by the addition of sulfate. In this process, it was also necessary to examine whether the formation of primary ettringite is a necessary precondition for the further planned retardation of cement pastes by long term retarders, or whether long-term retarders can take over the regulation of the setting of clinker in place of sulfate carrier optimization.

Table 2.3 - Overview of experiments with clinker phases, clinkers, and cement. (reproduced from Joerg Rickert and Gerd Thielen 2004)



Designation	Composition (mass of solids)	Water/Solid[1]	LTR in Mass %[5]	Studies
Clinker phases				
C_3A-1	C_3A	1.0	0	ESEM, XRD, DSC
C_3A-2			2	Sorption
C_3A-3[7]			5	Pore solution[6]
C_3A-$Ca(OH)_2$-1	$C_3A:Ca(OH)_2 = 3.3$		0	
C_3A-$Ca(OH)_2$-2			2	
C_3A-SO_3-1	$C_3A:SO_3 = 2.6$[2]		0	
C_3A-SO_3-2			2	
C_3A-SO_3-3[7]			5	
C_3A-SO_3-$Ca(OH)_2$-1	$C_3A:SO_3:Ca(OH)_2 = 2.6:1:0.8$[3]		0	
C_3A-SO_3-$Ca(OH)_2$-2			2	
C_3A-SO_3-$Ca(OH)_2$-3[7)]			5	
C_3S-1	C_3S	0.5	0	
C_3S-2			2	
C_4AF-1[7]	C_4AF	1.0	0	
C_4AF-2[7]			2	
C_4AF-SO_3-1[7]	$C_4AF:SO_3 = 5.3$[4]		0	
C_4AF-SO_3-2[7]			2	
Clinkers				
K I-1	K I	0.50	0	
K I-2			2	
K II-1	K II		0	
K II-2			2	
Cements				
Z I-1	Z I		0	
Z I-2			2	
Z II-1	Z II		0	
Z II-2			2	

[1] Admixture was included in the calculation of the water.
[2] $C_3A:C\bar{S}:C\bar{S}H_{0.5} = 3:1:1$.
[3] $C_3A:C\bar{S}:C\bar{S}H_{0.5} : CH = 3:1:1:0.9$.
[4] $C_4AF:C\bar{S}:C\bar{S}H_{0.5} = 6:1:1$.
[5] Relative to solids.
[6] Only clinkers and cements.
[7] See (Rickert 2004b).

Mechanism of Action of the PBTC-Based LTR

The main mechanism of action of the LTR can be derived. By way of example, Figures 2.20 and 2.21 respectively show the mechanisms of action of the LTR on Portland cement clinker (KII-2) and Portland cement (Z II-2) schematically.

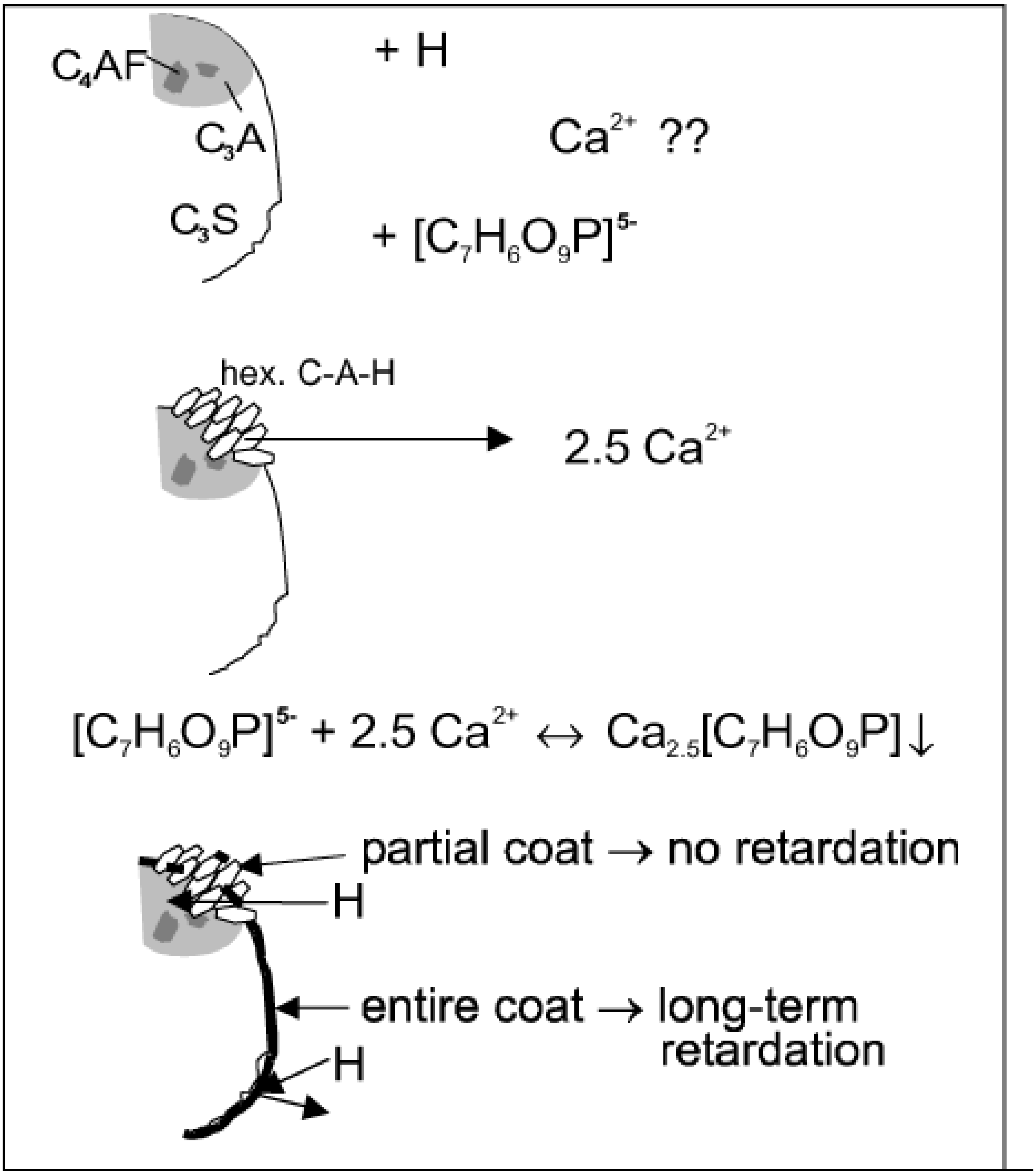


Figure 2.20 Effect of LTR on the hydration of Portland cement clinker without or with a non-optimized supply of CaSO4, (K II-2). (reproduced from Joerg Rickert and Gerd Thielen 2004)

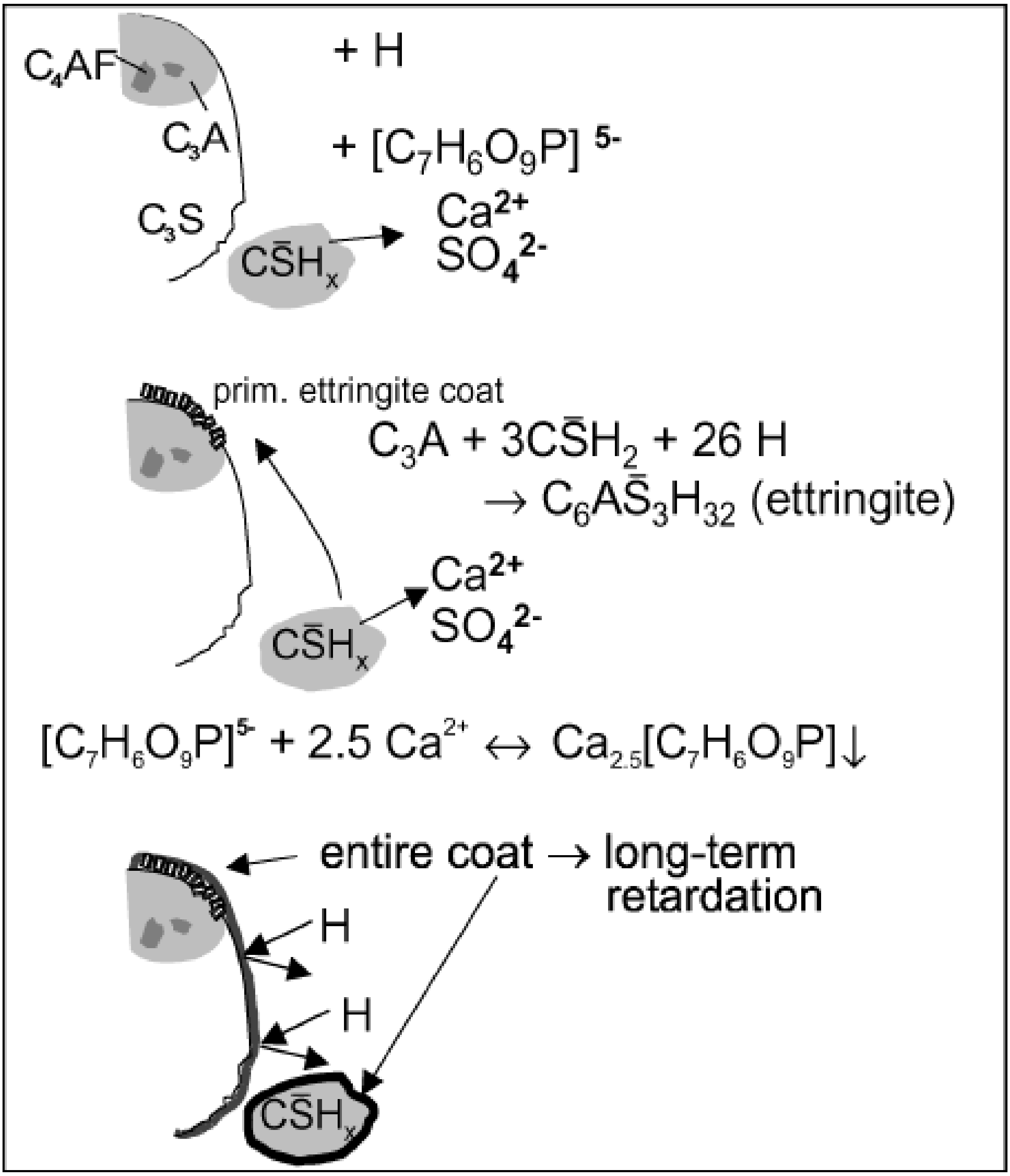


Figure 2.21 Effect of LTR on the hydration of Portland cement with an optimized supply of CaSO4, (Z II-2). (reproduced from Joerg Rickert and Gerd Thielen 2004)

In an alkaline medium, PBTC ($[C_7H_{11}O_9P]^{5-}$). For the immediate formation of sparingly soluble calcium phosphonate ($Ca_{2.5}[C_7H_6O_9P]$).2.5 moles of calcium are needed per mole of PBTC. If LTR is added to Portland cement clinkers without calcium sulfate carriers, Figure 20 shows that the calcium content in the pore solution is not sufficient to form sparingly soluble calcium phosphonate. Because of the calcium demand of PBTC, there is a short term accelerated hydration of reactive clinker phases, such as C_3A. This causes an increased formation of hexagonal C-A-H and results in marked stiffening of setting. PBTC binds the calcium ions released during this brief acceleration phase.

The sparingly soluble calcium phosphonate ($Ca_{2.5}[C_7H_6O_9P]$) thus formed coats the surface of the individual clinker particles differently. On the surfaces of the relatively unreactive clinker phases, such as C_3S and C_2S, which are still largely free from hydration products when the sparingly soluble compound is formed, essentially complete coating with calcium phosphonate can take place. As a result, the further accesses of water (H) or further ion exchange are markedly hindered, and hydration is retarded. Already hydrated surfaces, such as the C_3A, display a relatively large specific surface area, which cannot be completely covered with sparingly soluble calcium phosphonate. The access to water and ion exchange cannot be completely blocked. For this reason, compared to the less reactive clinker phases, the hydration of reactive calcium aluminates is only slightly retarded by calcium phosphonate formed from LTR.

Because of the sulfate carrier ($C\hat{S}Hx$) contained in the Portland cement (see Figure 21), the concentration of calcium and sulfate in the pore solution is much higher than in system containing the only clinker. A thin layer of primary ettringite can form on the surface of the calcium aluminate. Moreover, sufficient calcium ions are available for the immediate formation of sparingly soluble calcium phosphonate. The calcium phosphonate coats both the surfaces of the clinker particle and also those of the still undissolved sulfate carrier. As a result, further hydration is strongly blocked. The formation of primary ettringite and the coating of the surfaces with sparingly soluble calcium phosphonate constitute the precondition for planned prolongation of the workability by the long term retarder. This means that sulfate carrier optimization is not only the basis for the control of the setting of the cement but also a precondition for the desired mode of action of the admixture.

By systematic studies, the state of knowledge concerning the effect of a long-term retarder (LTR) based on 2-phosphonobutane-1, 2, 4-tricarboxylic acid (PBTC) on the hydration of clinker phases (C_3A, C_4AF, and C_3S), clinker and cement has been substantially extended.

The following conclusions were drawn from the research results:

- In the hydration pure C_3A and C_4AF, the retarder results in increased formation of hexagonal calcium aluminate hydrate(C-A-H). Apart from this the conversion of hexagonal C-A-H into cubic hydrates is strongly retarded. The conversion of C_3A is increased, and that of C_4AF decreased.
- The hydration of pure C_3S was completely blocked for up to 180 days.
- The retarder action is attributable to the formation of sparingly soluble calcium phosphonate ($Ca_{2.5}[C_7H_6O_9P]$ x H_2O). The formation of sparingly soluble calcium phosphonate requires 2.5 moles Ca^{2+} per mole of PBTC. If enough Ca^{2+} is available in the pore solution, sparingly soluble calcium phosphonate precipitates and forms a closed layer around the cement particles, which retards further hydration immediately. Conversely, a lack of Ca^{2+} causes short-term acceleration in hydration of the reactive clinker phase C_3A. Due to the formation of C-A-H the specific surface area increases. Therefore, the formation of a closed layer of calcium phosphonate is impeded, and the hydration of the calcium aluminates progresses.
- With Portland cement, owing to the content of calcium sulfate, sufficient quantities of dissolved calcium phosphonate. The formation of primary ettringite and the coating of the sulfate is absent or present in an insufficient amount, for example in the case of Portland cement clinkers, the calcium demand of the LTR active substances PBTC results in a short term acceleration of the hydration of reactive clinkers phases. e.g. C_3A.
- The direct formation of an ettringite layer on the cement particle and the simultaneous supply of calcium ions are not only important for controlling the setting of the cement but also for the desired mode of action of the long term retarder.

Prediction of stabilizer

In the study by Lobo et al. (1995) to predict the admixture dosage required to hold the concrete without setting; the admixture dosage was calibrated with the cement. A 0.07 m^3 batch of concrete was mix and split into 4 portions. Each portion was held, with mixing and retempering at regular intervals until the desired age of 8 min, 45 min, 90 min, and 180 min. At each age, the incremental dosage of the stabilizing admixture was mixed into the concrete batch and several set time samples, each containing different amount of admixture were obtained. Proctor penetrometer test was prformed to determine the setting time of concrete. This data provided dosage versus set time curves for concrete treated at different ages. The dosage versus setting time curves for concrete treated at 45 min and 180 min are plotted in Figure 2.22.

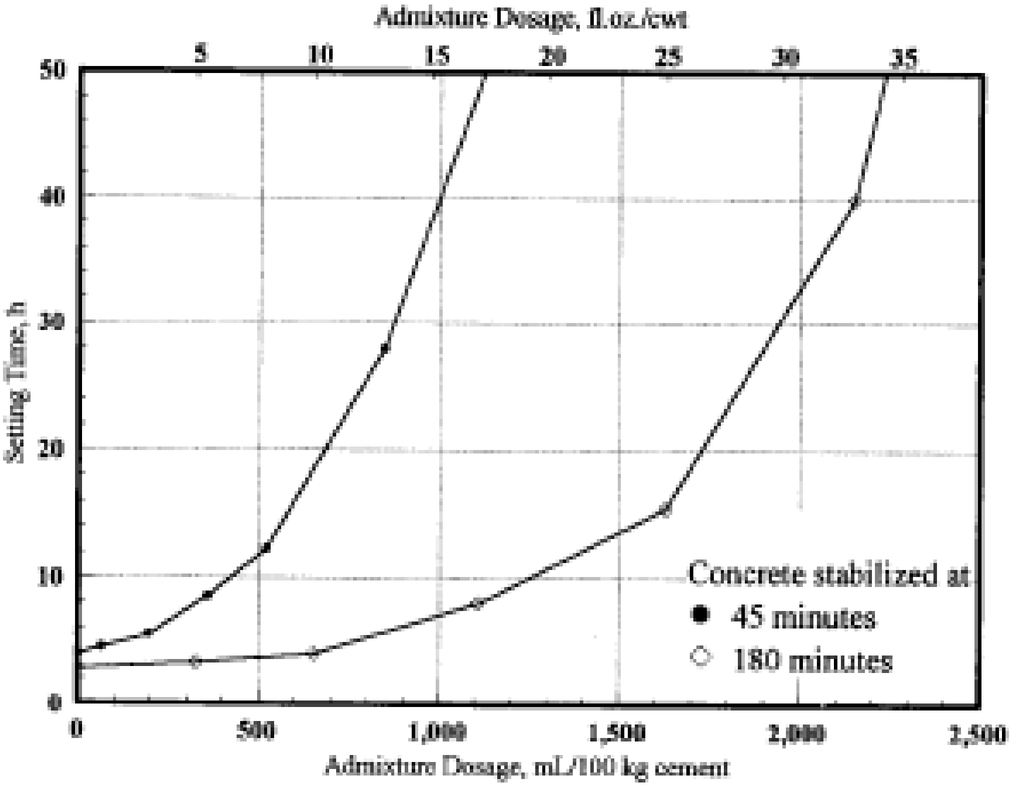


Figure 2.22 Dosage—set time curves for stabilized concrete. (reproduced from Colin Lobo, 1995)

This data was used to estimate the lower and higher stabilizer doses, based on the required holding time for the stabilized concrete. Figure 22 illustrates that for the same holding time, concrete that was 180 min old when treated required a much higher stabilizer dose than that for all concrete that was 45 min old. This set of curves is only valid for this set of material and concrete temperature of 21°C. While these curves are developed from 100 mm X 100 mm mortar sample, it should be recognized that the setting characteristics of a larger volume of concrete would be significantly different.

The limitation of the calibration of stabilizer dosage in this study was that only OPC cement was used, and no SCM modified cement e.g. blending of slag and fly ash with OPC was used. The process of establishing stabilizer dosage on cement mortar and determining the setting time with Proctor penetrometer would require a lot of effort and trial and error. The study does not consider the effect of water reducer or any other admixture added in the returned plastic concrete.

In the current study OPC cement, blended cement containing 35% OPC +65% Slag and 75% OPC+25% Fly Ash were considered.

Other advantages in the current study compared to the earlier study are as follows:

- The “Marsh cone method” and Coffee cup method” used to determine the dosage of stabilizer to hold the setting time of cement and cementitious grout was simple and less laborious.
- Considering the variation in setting time of cement and cementitious material, the effect of varied stabilizer dosages with constant water reducing admixture on the measured flowability of cement and cementitious grouts at 35 seconds was comparable to reference grouts.
- The data for Marsh cone (flow time) in seconds versus Holding time in minutes was plotted to generate curves to achieve 35 seconds flow time to determining the holding time of the cement and cementitious grouts.
- The data generated from Coffee cup method for temperature versus time was plotted, the temperatures difference shown on the hydration curves make the results relevant.
- All tests are done with grout samples.

In a combination of the Marsh cone test to determine the effect of stabilizer dosage on the flowability of cement and cementitious grouts, the effect of stabilizer dosage on the hydration of cement and cementitious grout was studied with Coffee cup method. The combination of both methods give a clear indication of minimum stabilizer dosage to be used for the required duration of concrete to be stabilized (24 hours and more) and a good prediction of required dose of stabilizer to hold the setting time of concrete without setting.

As discussed in earlier studies by Lobo et al. (1995) it should be recognized that the setting characteristics of a larger mass of concrete in the laboratory or truck mixer could be significantly different due to different in temperature history on the rate of heat build-up. Continued agitation of stabilized concrete in a truck mixer also modifies the dosage requirements. On safer side, it is advisable to use a stabilizer dose that is somewhat greater than measured on the model sample.

Since it was not feasible to study all of the variables due to the length of the experiment on different grades of concrete, the experiment was limited to the reference cement or cementitious grouts of 340 kg/m^3 at water-to-cement ratio of 0.55, and similar grout with water reducing admixture at a dose of 300 m/100kg of cement and cementitious material with varying stabilizer dosage. The set of data used to generate graphs and correlation were determined at the grouts temperature of 21°C. The stabilizer was added to the cement and cementitious grout after holding it for 60 minutes, considering the requirement of Australian standard AS1379 for placement of concrete, discharge of all the concrete in a batch shall be completed within 90 min from the commencement of mixing.

The overall advantages of the tests performed in phase 2 and 3 in comparison to determining the dosage of stabilizer for holding the stabilized concrete for required duration without setting are:

- The test is simple and less laborious. It reduces the lengthy testing procedures of trial and error on actual concrete.
- The test can be performed on the different type of cement and cementitious material at varying dosages of the stabilizer with or without the combination of any other admixtures with varying cement and cementitious grout at varying temperatures.
- The correlation of the data achieved from Marsh cone and Coffee e cup method gives a higher level of confidence to use the determined stabilizer dosage to stabilize the concrete for required duration.

Lobo et al., (2007) studied the effect of stabilizer dosage on plastic and mechanical properties of concrete by replacing 5% and 50% stabilized concrete with fresh OPC concrete. In the current study, the effect of stabilizer dosage on plastic and mechanical properties was studied by replacing 10%, 25%, 50% and 100% stabilized concretes produced by OPC and two blended types of cement containing 35% OPC and 65% Slag and 75% OPC and 25% Fly Ash. The earlier study considered two different stabilizer dosage levels for 45 and 180 minutes.

In the current study, holding time of 60 minutes was considered for the addition of a stabilizer to the concrete and stabilized dosage of 800 ml/100 kg of cement, and cementitious material was considered reduces the variability in the experiment. A fixed stabilizer addition dosage time and stabilizer dosage for all the series give a better comparison of data to study the effect of stabilizer dosage on the plastic and mechanical properties of concrete.

In the last phase of the study lower grade 32MPa stabilized concrete (OPC, 35% OPC +65% Slag and 75% OPC +25% Fly Ash) was upgraded to 40MPa. No study was found in the literature on plastic and mechanical properties on upgraded lower grade stabilized concrete to a higher grade of 40MPa concrete.

2.7 Summary

The literature reviewed on reuse of returned stabilized concrete provides very limited insight in earlier studies. Lobo et al., (1995) and Kinney (1989) investigated the effects of stabilizer for reusing returned plastic concrete. The limitations of those studies were that the study only used OPC cement, and there was no in-depth study to determine the safer dosage of stabilizer that would stabilize the concrete for required duration without affecting the plastic and chemical properties of concrete. The other authors, e.g. Rickert and Thielen (2004) conducted research on the chemistry of cement compounds (C_3A, C_3S, C_4AF) and the effects of stabilizer on the cement compounds. The limitations were that it was not applied to concrete. Reviewing the earlier works, it was commonly found that due to the length of experiment and limitations, most of the experimental study was carried out on OPC cement.

In the current study, a systematic approach was followed to understand the effect of stabilizer on OPC and two blended types of cement (35% OPC +65% Slag and 75% OPC +25% Fly Ash) grouts to predict a suitable stabilizer dosage to be used on actual concrete.

The predicted dosage was applied on concretes produced by OPC two blended types of cement (35% OPC +65% Slag and 75% OPC +25% Fly Ash) and the effect of stabilizer was also studied on different replacement levels of fresh concrete with stabilized concrete. The plastic and mechanical properties of above concretes also studied. In earlier studies, effect of stabilizer on a small range of replacement of fresh concrete by stabilized concrete was studied. Lastly, up gradation of lower grade stabilized concrete to upper-grade concrete was studied for the plastic and mechanical properties.

CHAPTER III

METHODOLOGY

3.1 Introduction

The chapter describes the process flow of the experiments to study the effect of stabilizer (long – term retarder) on cement and blended cement grouts and concrete. In addition to the normal process control factors that affects the uniform production of concrete, there are several additional processing factors that need to be considered when stabilized concrete is mixed with the fresh material to produce a blended concrete. Since it was not possible to study all of these factors, the first step in planning the experiment was to identify the most important processing factors. The following factors were chosen as variables in this study:

1. The stabilizer dose used to keep the treated concrete from setting for the desired period
2. The duration for which the stabilized concrete was held before addition of fresh material
3. Concrete addition time, and
4. The percent (by mass) of treated concrete in the blended batch.

3.2. Experimental Plan

The experiment was conducted in five phases:

Phase 1 assessed the variation in setting time of OPC; blended cement containing 35% OPC and 65% Slag; and blended cement containing 75% OPC and 25% Fly Ash

Phase 2 assessed the effect of stabilizer dosages on holding time (stabilized duration) of above three grouts using Marsh cone method.

Phase 3 assessed the effect of stabilizer dosage on temperature rise during hydration of above three grouts

Phase 4 evaluated the effect of stabilizer dosage on the plastic and mechanical properties of above three concrete containing 10%, 25% and 50% by Wt. of above-stabilized concrete blended with fresh concrete; and 100% stabilized concrete.

Phase 5 assessed the feasibility of upgrading of 32 MPa stabilized concrete to 40 MPa.

3.3 Constant Factors

The following factors were held constant during the experiment:

1. The content of cement or cementitious materials used in the concrete mixes was 340kg/m^3.

2. The water/cement ratio in all concrete mixes was 0.55.

3. To understand the effect of admixture and stabilizer on cement grout, cementitious grout and water content was similar to the concrete.

4. The mix proportions of all concrete batches were same in every trial.

5. Holding grout for various extended periods, a 35 second efflux time was used for Marsh cone method in accordance with ASTM C 939.

6. The age of concrete when the admixture was added—stabilizer addition time was 60 minutes.

7. The dosage of water reducer added to all grouts, fresh concrete, and control concrete mixes were 300ml/100kg of cement or cementitious materials.

8. Fresh concrete for all types of cement was replaced with 10%, 25% and 50% of stabilized concrete.

9. 32MPa stabilized concrete upgraded to 40MPa for all the types of cement and blended cement concrete was replaced with 25% of 32MPa stabilized concrete.

3.4 Variable Factors

The following factors were varied in the experiment:

1. Stabilizer dosages were variable for phase 2 and phase 3 of the experiment.

2. Three types of cement were used in all phases of the experiment.

a) Ordinary Portland cement (OPC cement).

b) Low heat cement containing 35% OPC and 65% Ground Granulated Blast Furnace Slag (GGBS).

c) Blended cement containing 75% OPC cement and 25% Fly Ash.

3.5 Response Variable

The response variables evaluated in this study were:

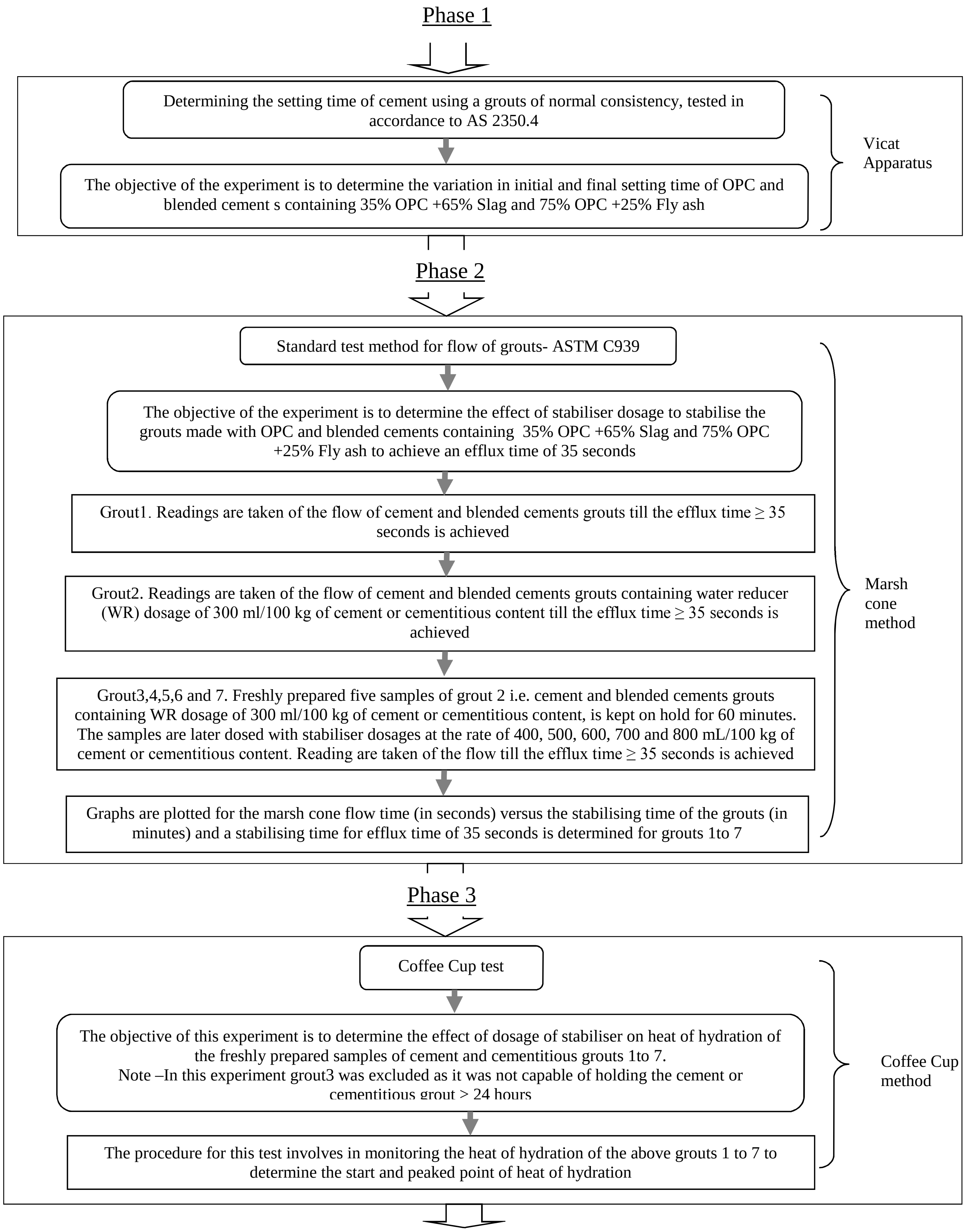
1. Setting time of three types of cement tested in accordance with AS 2350. 4.
2. Holding time required to achieve an efflux time (flow time) of 35 seconds for three cementitious grouts tested in accordance with ASTM C 939.
3. Temperature rises during hydration of three cementitious grouts using Coffee Cup method.
4. Concrete temperature tested in accordance with AS1012.1
5. Slump values of concrete tested in accordance with AS 1012.09-1999.
6. Initial and final setting times of concrete tested in accordance with AS 1012.18-1996.
7. Mass per unit volume of hardened concrete tested in accordance with AS1012.12.1
8. 7, 28, and 56 days compressive strength of concrete tested in accordance with AS 1012.09-1999.
9. Drying shrinkage of concrete tested in accordance to 1012.13.

3.6 Experimental Procedure

Figure 3.1 shows the process flowchart for all the phases of the experiment as follows:

Methodology, Process and Objective

Testing Method



Phase 1

Determining the setting time of cement using a grouts of normal consistency, tested in accordance to AS 2350.4

The objective of the experiment is to determine the variation in initial and final setting time of OPC and blended cement s containing 35% OPC +65% Slag and 75% OPC +25% Fly ash

Vicat Apparatus

Phase 2

Standard test method for flow of grouts- ASTM C939

The objective of the experiment is to determine the effect of stabiliser dosage to stabilise the grouts made with OPC and blended cements containing 35% OPC +65% Slag and 75% OPC +25% Fly ash to achieve an efflux time of 35 seconds

Grout1. Readings are taken of the flow of cement and blended cements grouts till the efflux time ≥ 35 seconds is achieved

Grout2. Readings are taken of the flow of cement and blended cements grouts containing water reducer (WR) dosage of 300 ml/100 kg of cement or cementitious content till the efflux time ≥ 35 seconds is achieved

Grout3,4,5,6 and 7. Freshly prepared five samples of grout 2 i.e. cement and blended cements grouts containing WR dosage of 300 ml/100 kg of cement or cementitious content, is kept on hold for 60 minutes. The samples are later dosed with stabiliser dosages at the rate of 400, 500, 600, 700 and 800 mL/100 kg of cement or cementitious content. Reading are taken of the flow till the efflux time ≥ 35 seconds is achieved

Graphs are plotted for the marsh cone flow time (in seconds) versus the stabilising time of the grouts (in minutes) and a stabilising time for efflux time of 35 seconds is determined for grouts 1to 7

Marsh cone method

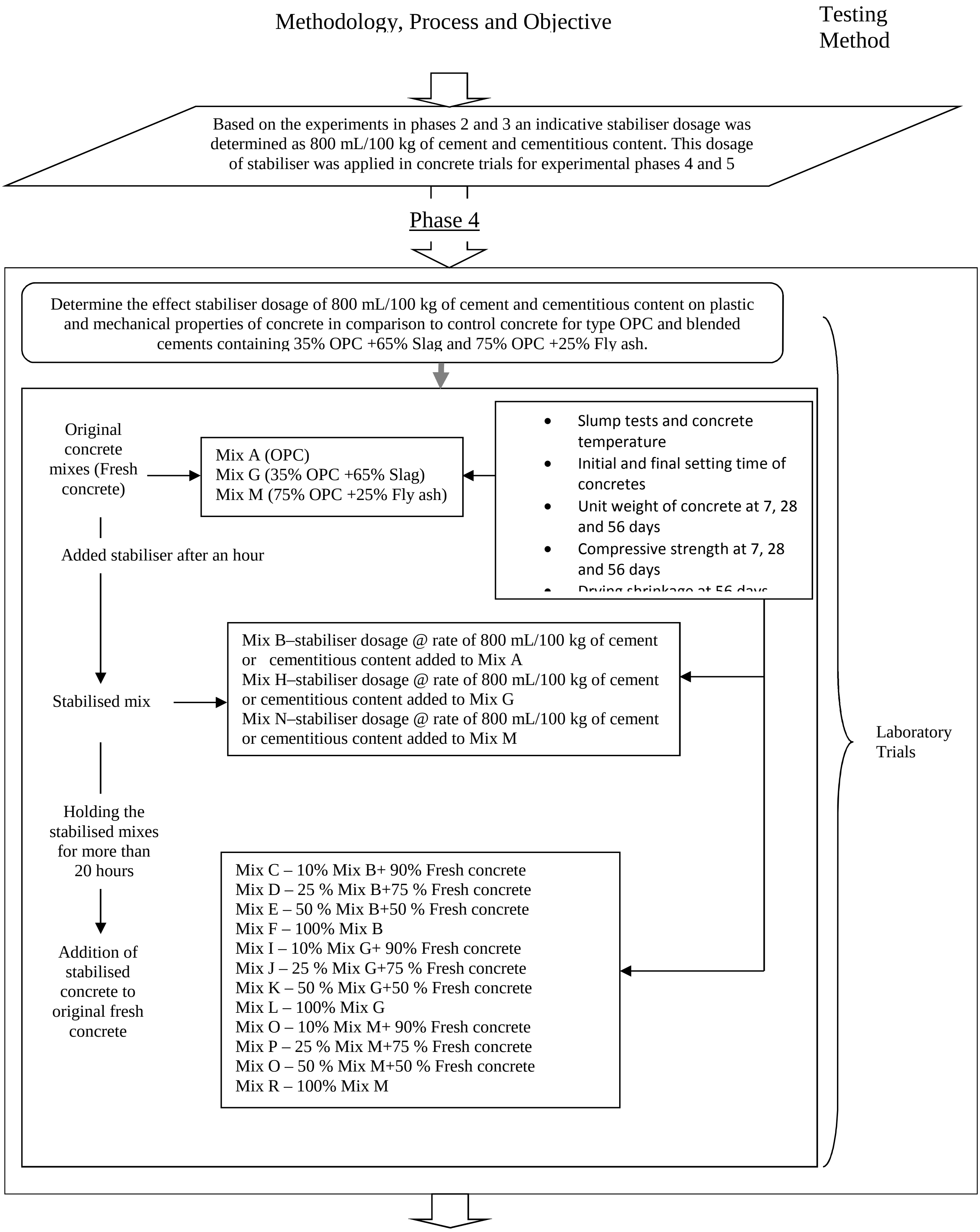
Phase 3

Coffee Cup test

The objective of this experiment is to determine the effect of dosage of stabiliser on heat of hydration of the freshly prepared samples of cement and cementitious grouts 1to 7.
Note –In this experiment grout3 was excluded as it was not capable of holding the cement or cementitious grout > 24 hours

The procedure for this test involves in monitoring the heat of hydration of the above grouts 1 to 7 to determine the start and peaked point of heat of hydration

Coffee Cup method


Methodology, Process and Objective
Testing Method
Based on the experiments in phases 2 and 3 an indicative stabiliser dosage was determined as 800 mL/100 kg of cement and cementitious content. This dosage of stabiliser was applied in concrete trials for experimental phases 4 and 5
Phase 4
Determine the effect stabiliser dosage of 800 mL/100 kg of cement and cementitious content on plastic and mechanical properties of concrete in comparison to control concrete for type OPC and blended cements containing 35% OPC +65% Slag and 75% OPC +25% Fly ash.
Original concrete mixes (Fresh concrete)
Mix A (OPC)
Mix G (35% OPC +65% Slag)
Mix M (75% OPC +25% Fly ash)
Slump tests and concrete temperature
Initial and final setting time of concretes
Unit weight of concrete at 7, 28 and 56 days
Compressive strength at 7, 28 and 56 days
Drying shrinkage at 56 days
Added stabiliser after an hour
Stabilised mix
Mix B–stabiliser dosage @ rate of 800 mL/100 kg of cement or cementitious content added to Mix A
Mix H–stabiliser dosage @ rate of 800 mL/100 kg of cement or cementitious content added to Mix G
Mix N–stabiliser dosage @ rate of 800 mL/100 kg of cement or cementitious content added to Mix M
Laboratory Trials
Holding the stabilised mixes for more than 20 hours
Addition of stabilised concrete to original fresh concrete
Mix C – 10% Mix B+ 90% Fresh concrete
Mix D – 25 % Mix B+75 % Fresh concrete
Mix E – 50 % Mix B+50 % Fresh concrete
Mix F – 100% Mix B
Mix I – 10% Mix G+ 90% Fresh concrete
Mix J – 25 % Mix G+75 % Fresh concrete
Mix K – 50 % Mix G+50 % Fresh concrete
Mix L – 100% Mix G
Mix O – 10% Mix M+ 90% Fresh concrete
Mix P – 25 % Mix M+75 % Fresh concrete
Mix O – 50 % Mix M+50 % Fresh concrete
Mix R – 100% Mix M

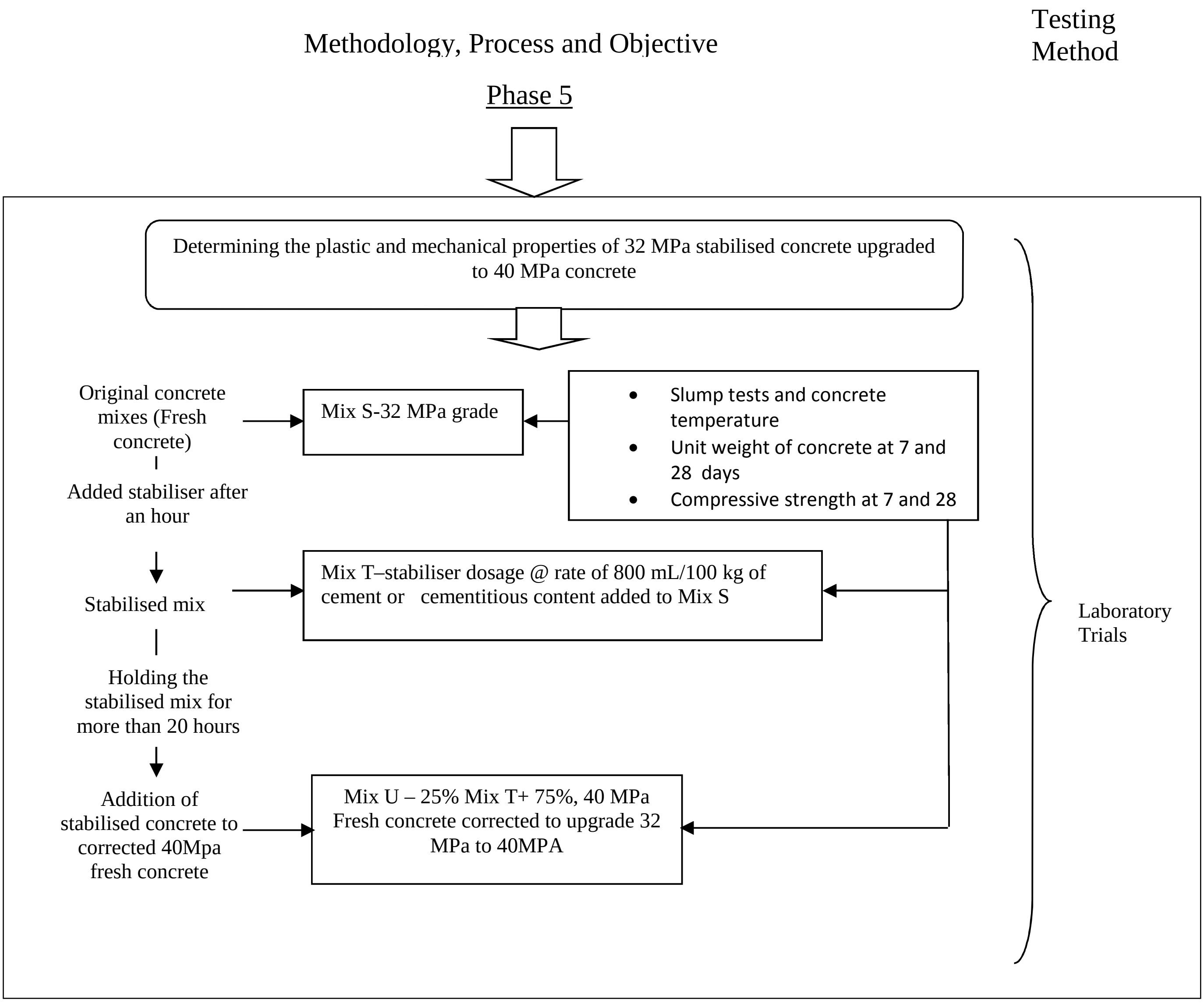


Figure 3.1 Experimental process flow chart.

3.7 Materials

Ordinary Portland cement (OPC)

Ordinary Portland cement is the hydraulic cement that is manufactured as a homogeneous product by grinding together Portland cement clinker and calcium sulfate. The OPC is used in all the phases of this study. This cement complies with the Australian Standard AS 3972 (2010).

Ground granulated iron blast-furnace Slag (Slag)

Ground granulated iron blast-furnace Slag is the by-product of Iron industry consisting essentially of silica, alumina and calcium oxides compounds. It complies with the Australian Standard - AS 3582.2.

Fly ash

Fly ash is the solid material extracted from the flue gasses of a boiler fired with pulverized coal. Fly ash complies with Australian Standard AS 3582.1. Table 3.1 shows the chemical constituents of the three cement and cementitious materials.

Table 3.1- General Chemical constituents of OPC and fly ash (FA) and GGBS cementitious materials

Chemical constituents	OPC (%)	FA Cementitious Material (%)	GGBS Cementitious Material (%)
SiO_2	20.1	51.80	40.00
$Al2O_3$	4.9	0.21	13.60
Fe_2O	2.3	13.20	1.40
CaO	63.3	1.61	39.20
MgO	2.2	1.17	5.60
SO_3	2.3	0.21	0.70

Coarse and Fine Aggregates

The coarse and fine aggregates used were natural granite and river sand, respectively, in accordance with Australian Standard AS 2758.1 – 2014. The aggregates were batched in the saturated surface dried (SSD) condition. The amount of added water was adjusted for the aggregate moisture content. The aggregates were sourced from a single source for all the trials. In some of the batches, of course, aggregate some traces of dolerite was seen, which had slightly affected the density of hard concrete in some batches.

Admixtures (Water reducer and Stabilizer)

The water reducer and stabilizer used in this study were from a single source, and both are commercially available. The water reducer used in this study was non-retarding, water reducing and strength enhancing admixture. The admixture does not contain any trace of chloride. The admixture is made up of two key ingredients; calcium lignosulfonate and triethanolamine

Calcium lignosulfonate is an anionic polymeric surfactant which primarily acts as a water reducer or wetting agent. It is found active at the interfaces of the water/air and water/particle surface and decreases the surface tension within the system. The result is an increased ability of the flow and spread of water across the surfaces of aggregates and thus reduces the need for water. Calcium lignosulfonate also works as a retarder which prolongs the hydration process of cement, ultimately increases the compressive strength (Griersona et al., 2005).

Triethanolamine is an organic chemical compound which serves two purposes within the admixture. Its primary purpose is as a pH balancer and aims to increase the pH of a mixture (although the pH of the concrete water will already is high), but it also helps to keep the lignosulfonate in its charged (active) form.

The stabilizer is a ready-to-use, liquid admixture for making more uniform and predictable high-performance concrete. Stabilizer retards the setting time by controlling the hydration of Portland cement and facilitates operations. It can be used to stabilize returned plastic concrete and concrete wash water to reduce waste.

Stabilizer specifically increases strength (compressive and flexural), provides resistance to damage due to freezing and thawing, reduces water content required for a given workability and retards setting time characteristics.

The water reducer and the stabilizer used in this study comply with Australian Standard AS1478.1-2000.

3.8 Phase 1– Determination of setting time

The objective of this phase is to determine the initial and final setting time of OPC and blended cement containing slag and fly ash using a paste of normal consistency. The results of this experiment are used to study and to assess the variation in setting time of above cement. The experiment is performed in accordance to Australian standard AS 2350.4 – 2006.

3.9 Phase 2- Effect of stabilizer on efflux time with increased stabilize time

In this phase, the effect of stabilizer dosage to achieve an efflux time of 35 seconds of OPC and blended cement grouts using Marsh cone method is evaluated. The advantages of this method are its simplicity and speed compared to more accurate methods, such as the viscometer. The Marsh cone method has been used previously to determine the optimum superplasticizer content (de Larrard, 1990; Aïtcin et al., 1994; Toralles-Carbonari et al., 1996; Gettu et al., 1997) and the cement-superplasticizer compatibility (Aïtcin and Baalbaki, 1994). The Marsh cone method has also been used to characterize the consistency and to study the variations in the fresh properties of cement grouts used in structural repair with regards to the ease of pumping and filling narrow spaces. The test is similar to that used for grouts in the ASTM C 939-87 standard and the French standard P18-358. The repeatability and reproducibility of the test have been verified by de Larrard et al. (1997) in 6 different laboratories.

The experiment was performed in accordance to ASTM C939. However, looking at the span of the experiment which prolonged to about 64 hours the experiment was modified to suit the conditions of the tests. This test method covers a procedure used both in the laboratory and in the field to determine the efflux time of a specified volume of fluid hydraulic cement and cementitious grout through a standardized flow cone. This test method is intended for use with grouts having an efflux time of 35 seconds or less.

The Flow Cone, with dimensions shown in Figure 3.2. It consists of a hollow metal cone with a small opening at the bottom. In this study, an opening diameter of 12.7 mm is chosen for the cement pastes.The discharge tube including the body (receiving container) is made of stainless steel. The capacity of the receiving container is about 2000 ml. A ring stand or another device is also used to hold the flow cone in a vertical and steady position. The inner side of the flow cone is moistened by filling the cone with water and one minute before introducing the grout sample the water is drained from the cone. Then the outlet of the discharge tube is closed using the stopper. The cone is then filled with grout until the grout surface rises to contact the point gauge; the stopwatch is then started simultaneously with the opening of the outlet. The stopwatch record the time requires emptying the cone until the light is visible through the discharge tube. The time indicated by the stopwatch is the time of efflux of the grout. If the light is not visible through the discharge tube, the use of the flow cone is not applicable for the grout of that consistency.

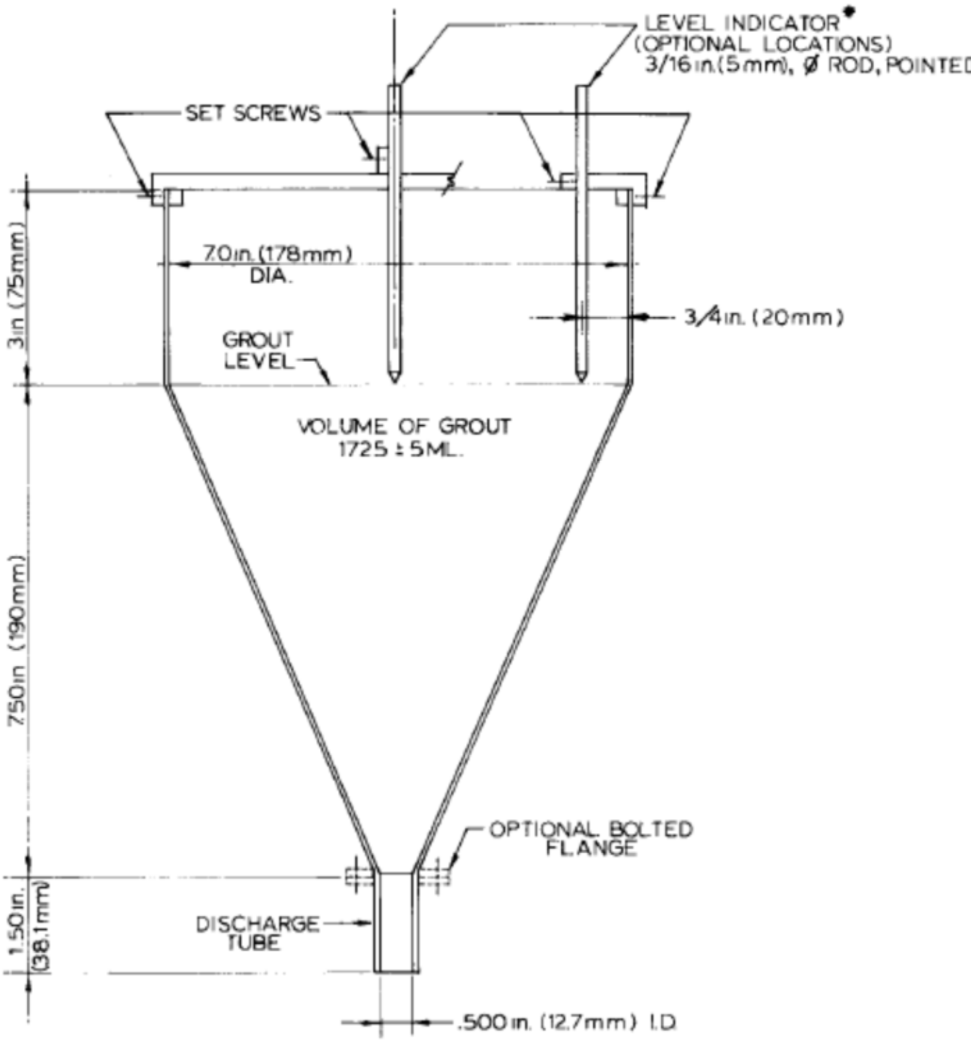


Figure 3.2 Cross Section of Flow Cone.

Mixing sequence of OPC or blended cement grouts

The grouts for all the tests were mixed in a 5-liter Hobart-type blender with two velocities, 120 rpm (high) and 60 rpm (low). The OPC; blended cement containing 35% OPC and 65% slag; and blended cement containing 75%OPC and 25% fly ash grout samples tested in this experiment is as follows:

1. Grout 1 – OPC; blended cement 35% OPC and 65% Slag; and blended cement 75% OPC and 25% fly ash cement grouts content of 340 kg/m^3 at water/binder ratio of 0.55.

2. Grout 2 – freshly prepared grouts same as above - Grout 1 plus WR @300 ml/100 kg of cement or cementitious material.

3. Grouts 3, 4, 5, 6 and 7 – freshly prepared five samples of Grout 2 were kept on hold for 60 minutes. These five samples were later dosed with stabilizer at the rate of 400, 500, 600, 700 and 800 ml/100 kg of cement or cementitious material.

For, all cement and blended cement grouts after addition of water and admixture to the grouts, in the case of grouts 1 and 2 the readings were taken at an interval of 15 – 20 minutes as the span of the experiment was 2 – 5 hours. For, all the cement and blended cement grouts after addition of stabilizer the readings for grouts 3 to 7 were taken at an interval of 1 – 4 hours as the span of the experiment was around 40 – 70 hours. After obtaining the results from the experiments, graphs were plotted for the Marsh cone flow time in seconds to the stabilizing time of grout in minutes and the stabilized time for efflux time of 35 seconds was determined from the graph for all the grouts.

3.10 Phase 3 - The effect of stabilizer on temperature rise during hydration

The objective of the experiment is to determine the effect of stabilizer dosage on the heat of hydration of OPC grout; blended cement grouts containing 35% OPC and 65% slag; and containing 75%OPC and 25% fly ash. The grouts samples in this phase were prepared following the same procedure as in Phase 1. In this experiment grout, 3 i.e. grout containing stabilizer at 400 ml/100 kg of cement or cementitious content was excluded based on the results in Phase 1 as it was found that this dosage was not capable of stabilizing the grout for more than 24 hours.

To determine the heat of hydration Coffee, Cup test method was used. Coffee cup method is an easy test to conduct with cement and blended cement grouts. Temperature sensors (thermocouple) and data logger are used to measure and record the sample temperature history. The thermocouples attached to data logger are immersed in the coffee cup containing grouts 1, 2, 4-7 (note grout 3 excluded in this experiment). The readings generated by the heat of hydration of the grouts are recorded. The temperature differences between the grout samples 4, 5, 6, 7 and the reference sample grouts 1 and 2 are analyzed. The effect of stabilizer on temperature rise during hydration (and therefore holding time) was assessed to establish a holding time vs. temperature profile by measuring the temperature of all three grouts samples over an extended period. Figure 3.3 shows the setup of Coffee Cup test method. The coffee cup is a good method to check the compatibility of material and it works well for cement, blended cement grouts, and admixtures. This method was used in the report by National Concrete Pavement Technology Centre, (Wang, 2006).

The results of the experimental phases 2 (Marsh cone method) and 3 (Coffee Cup method) are discussed in chapter 5. Stabilizer dosage of 800 ml/100 kg of cement or blended cement content was chosen for concrete trials in phases 4 and 5.

Figure 3.3 Coffee Cup test setup

3.11 Phase 4 – Effect of stabilizer on plastic and mechanical properties of concrete

The effect of stabilizer dosage of 800 ml/100 kg of cement or blended cement content on the plastic and mechanical properties of stabilized concrete was evaluated in this phase. The following trials are carried out to measure the plastic and mechanical properties of control concrete and stabilized concrete. Table 3.2 shows the mix proportion used for the trials of all the three types of cement and cementitious material.

Table 3.2 Mix proportions of concrete containing OPC and blended cement and for Phase 4.

Control Mix	Mix A	Mix G	Mix M
	OPC	35% OPC+65% Slag	75% OPC+25% Fly ash
Total Cementitious), kg/m^3	340	340	340
Cement (OPC), kg/m^3	340	119	255
Cementitious (65% Slag), kg/m^3	–	221	–
Cementitious (25% Fly ash), kg/m^3	–	–	85
Water to Binder Ratio	0.55	0.55	0.55
Aggregate 20 mm, kg/m^3	458	458	458
Aggregate14 mm, kg/m^3	313	313	313
Aggregate10 mm, kg/m^3	255	255	255
River sand, kg/m^3	781	800	791
Water, $litre/m^3$	187	187	187
Water Reducer (WR), ml/m^3	1020	1020	1020

The detailed procedure of casting and testing of plastic and mechanical properties in this phase is as follows:

1. Two replicate batches of concrete are made for each type of cement.
2. Control concrete batches of mixes A, G and M with water reducer at a dosage of 300 ml/100 kg of cement or blended cement content are prepared.
3. Similarly, replicate concrete batches of Mix B, H and N with water reducer at a dosage of 300 ml/100 kg of cement or blended cement content are prepared. However, this concrete batches after 60 minutes are dosed with stabilizer at 800 ml/100 kg of cement or blended cement content.

4. The slump of all the above batches of mixes A, G, M, B, H, and N after re-mixing at 60 minutes was measured. Concrete temperatures were also measured at the time of slump test.

5. The setting time and unit weight tests are performed on control concrete mixes of A, G, and M immediately after measuring the 60 minutes slump. Specimens are cast to measure the compressive strength and shrinkage at 7, 28 and 56 days.

6. The slump, setting time and unit weight tests are performed on mixes B, H and N after addition of a stabilizer.

7. The mixes B, H and N are left for 20 – 24 hours and this stabilized mixes are added to the fresh batch of concrete replacing the fresh concrete by 10% (Mixes C, I and O), 25% (Mixes D, G, and P) and 50% (Mixes E, K, and Q). After addition of the reworked stabilized concrete to the fresh concrete the initial slump and the slump after 60 minutes were also measured. Immediately after the 60 minutes slump test, the concrete samples were taken to measure the setting time and unit weight of concrete. Specimens were cast using the above concrete to measure the drying shrinkage and compressive strength at 7, 28 and 56 days.

8. For 100% stabilized concrete (Mix F =B, L =H and R =N) after 26 hours, concrete samples were taken to measure the setting time and unit weight of concrete. Specimens were also cast using the above concrete to measure the drying shrinkage and compressive strength at 7, 28 and 56 days.

The slump test, setting time of concrete, unit weight, compressive strength and drying shrinkage of above concrete are measured according to AS 1012 .3 .1 – 2014, AS 1012 .18 – 1996, AS 1012. 12.1 – 1998, AS 1012. 9 – 2014 and AS 1012. 13 – 1992, respectively.

3.12 Phase 5 – Plastic and mechanical properties of 32MPa stabilized concrete upgraded to 40MPa

In this phase, the feasibility of upgrading lower grade stabilized concrete to upper-grade concrete is evaluated. The mix proportion used for the trials and correction for all the three types of concrete are shown in Table 3.3.

Table 3.3 Mix proportion and correction of cement and cementitious materials for Phase 5.

	OPC Concrete			35% OPC+65% Slag Concrete			75% OPC+25% Fly ash Concrete		
	32MPa	40MPa	Correction	32MPa	40MPa	Correction	32MPa	40MPa	Correction
Total Cementitious	300	360	60	300	360	60	300	360	60
Cement (Type OPC), kg/m^3	300	360	60	105	126	21	–	–	–
Cementitious (65% Slag), kg/m^3	–	–	–	195	234	39	225	270	45
Cementitious (25% Fly ash), kg/m^3	–	–	–	–	–	–	85	90	15
Water to Binder Ratio	0.57	0.47	–	0.57	0.47	–	0.57	0.47	–
Aggregate 20 mm, kg/m^3	440	450	10	450	460	10	465	475	10
Aggregate14 mm, kg/m^3	320	320	–	320	320	–	325	320	-5
Aggregate10 mm, kg/m^3	300	300	–	300	300	–	255	250	-5
Coarse river sand, kg/m^3	195	195	–	180	225	45	247	275	28
Fine river sand, kg/m^3	625	595	-30	605	515	-90	575	535	-40
Water, litre/m^3	172	172	–	172	172	–	172	172	–
Water Reducer (WR), ml/m^3	900	1080	180	900	1080	180	900	1080	180

Procedure

1. Two replicate batches of 32MPa concrete for all types of cement and blended cement were prepared.

2. One of the batches was control concrete batch with water reducer dosage of 300 ml/100 kg of cement or blended cement content. The other batch stabilizer of 800 ml/100 kg of

cement or blended cement content was added after 60 minutes of mixing and the concrete was re-mixed.

3. For, both the batches the initial slumps and slump after 60 minutes were measured before addition of a stabilizer to the second batch.

4. In the case of control concrete batch after 60 minutes concrete samples were taken to measure the setting time and unit weight of concrete. Specimens were cast to measure the drying shrinkage and compressive strength at 7, 28 and 56 days.

5. Next day after 24 hours, the freshly mixed 40MPa grade concrete was replaced by 25% of stabilized 32MPa concrete. However, corrections for the cement content and aggregates were made to upgrade the stabilized 32MPa concrete to 40MPa. The correction value showed in Table 3.2 indicates the correction for meter cube of concrete. This correction when applied to 25% of 32MPa concrete replaced by 40MPa concrete the yield of the concrete increased between half to one percent within the expectable limit.

6. After mixing of 32MPa concrete to 40MPa concrete initial slumps were measured. After 60 minutes slumps were measured and concrete samples were taken to measure the setting time and unit weight of concrete. Specimens were cast to measure the drying shrinkage and compressive strength at 7, 28 and 56 days.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Introduction

In the previous chapter, the experimental method to achieve an appropriate stabilizer dosage was explored. One of the key points to stabilize the concrete for the required duration is the determination of an optimum dosage of the stabilizer. As explained in chapter 2, the stabilization of concrete is to control the setting time and hydration time of concrete. Cement hydration is a complex process and can be influenced by several factors, like the source of raw materials, different fuel for clinker burnings and different conditions of burning that influence the rate and amount of heat liberated from hydration of the cementitious materials. It was seen that there are several aspects of the behavior of cement that are not clearly understood and others that are difficult to evaluate while concrete is stabilized. Obviously, the most important influence of the stabilizer is in the fresh concrete where it provides workability for a longer period and modifies the setting times. Therefore, the principal objective of this chapter is to study the stabilizer effects through tests on the cement grouts and analyze the correlation between the behavior at this level and the response of the concrete when stabilized.

The results are studied initially for the setting time on the freshly mixed OPC and blended cement pastes i.e. blended cement containing 35% OPC and 65% slag and 75% OPC, and 25% fly ash paste without stabilizer. To determine the setting times of OPC and blended cement a total of twelve different OPC and blend cement samples were tested using Vicat apparatus. Later the effect of the stabilizer on the behavior of each type of OPC and blend cement grouts is studied for setting time to determine the optimal dosage of stabilizer using Marsh cone and “Coffee Cup” methods. Further, the determined dosage of the stabilizer is incorporated in OPC and blend cement concretes i.e. blended cement containing 35% OPC and 65% slag; 75% OPC and 25% fly ash. Next day the freshly produced concrete is replaced with 10%, 25%, 50% and 100% of above stabilized concretes and the effect on various properties, such as setting time of concrete, concrete temperature, workability, hardened density, compressive strength, and shrinkage are discussed in this chapter.

4.2 Setting time without stabilizer

4.2.1 OPC

The initial setting time of the OPC paste was between 90 and 135 minutes while the final setting time occurred between 145 and 205 minutes (see Figure 4.1). The standard deviation (SD) for the initial and final setting time was 19.5 and 19.7 with a coefficient of variation (COV) of 17.8 and 11.4, respectively.

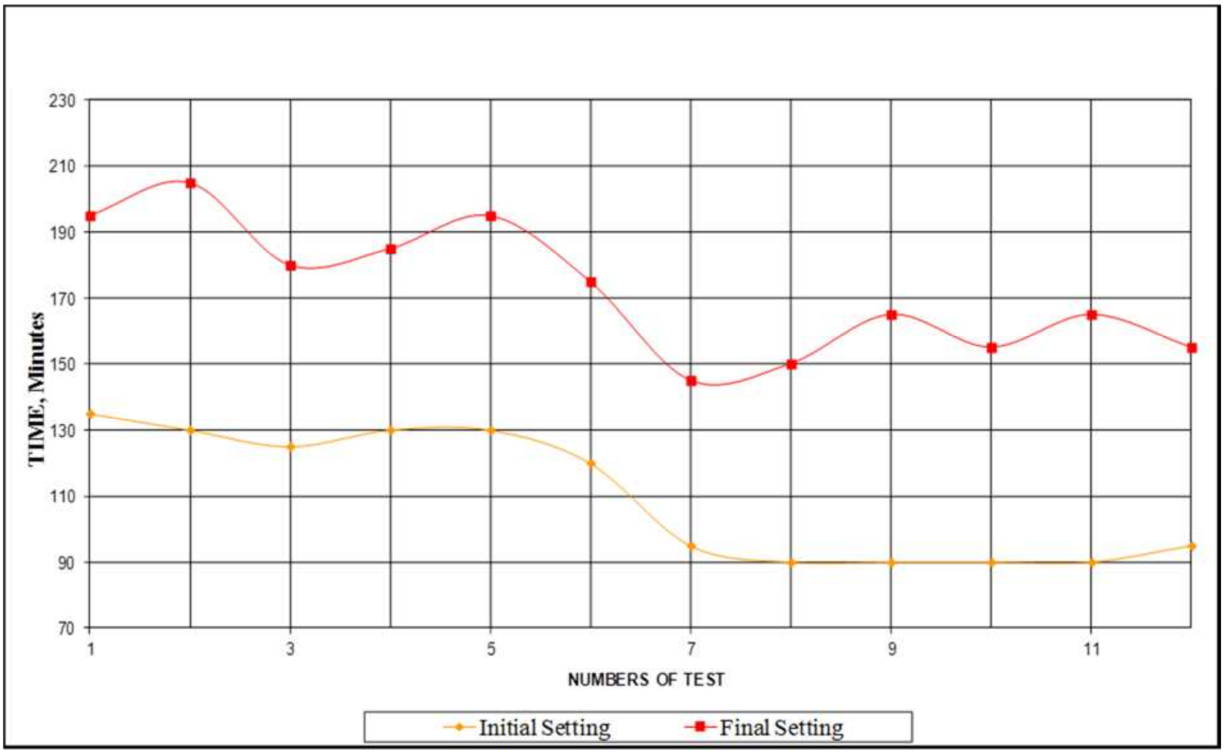


Figure 4.1 Initial and final setting time of OPC.

4.2.2 Blended cement containing 35% OPC and 65% slag

The initial setting time of blended cement paste containing 35% OPC and 65% slag was between 145 and 220 minutes while the final setting time was between 195 and 290 minutes (see Figure 4.2). The standard deviation (SD) for the initial and the final setting time was 28.1 and 29.1 with a coefficient of variation (COV) of 15.7 and 11.8, respectively.

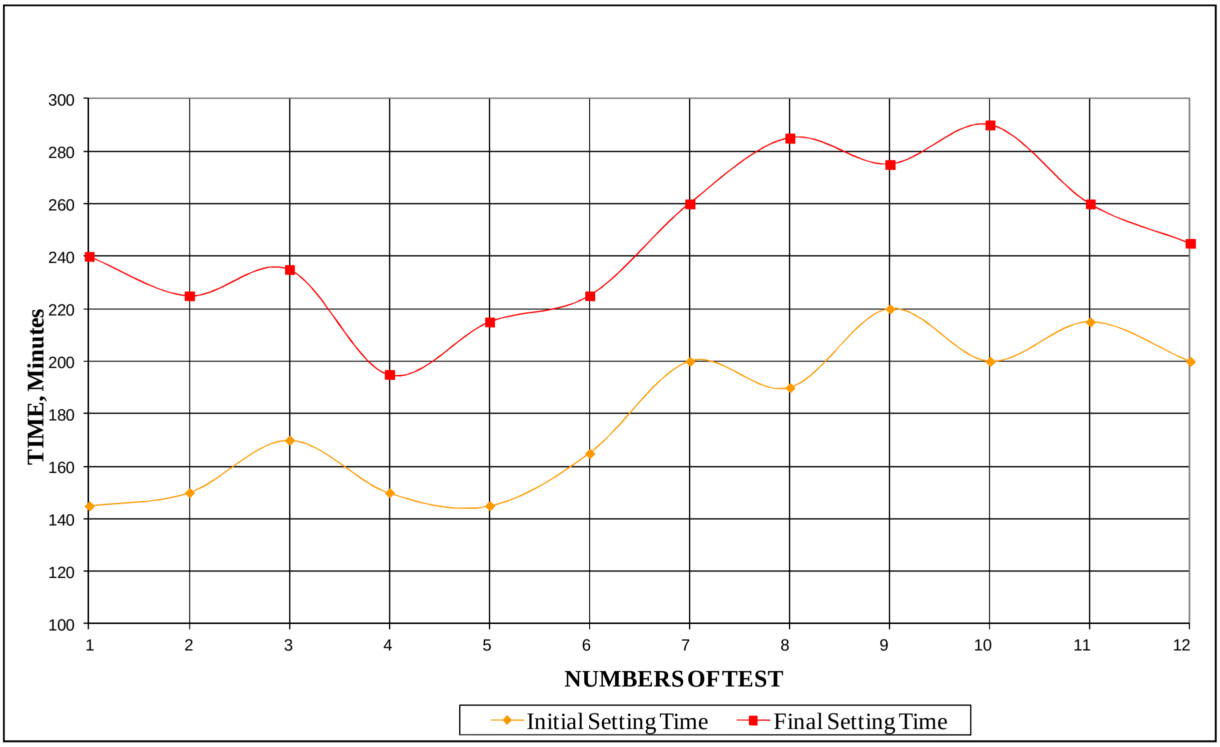


Figure 4.2 Initial and final setting time of 35% OPC and 65% slag.

4.2.3 Blended cement containing 75% OPC and 25% fly ash

The initial setting time of blended cement paste containing 75% OPC and 25% fly ash was between 120 and 130 minutes while the final setting time was between 160 and 200 minutes (see Figure 4.3). The standard deviation (SD) for the initial and the final setting time was 4 and 10.9 with a coefficient of variation (COV) of 3.2 and 6.0, respectively.

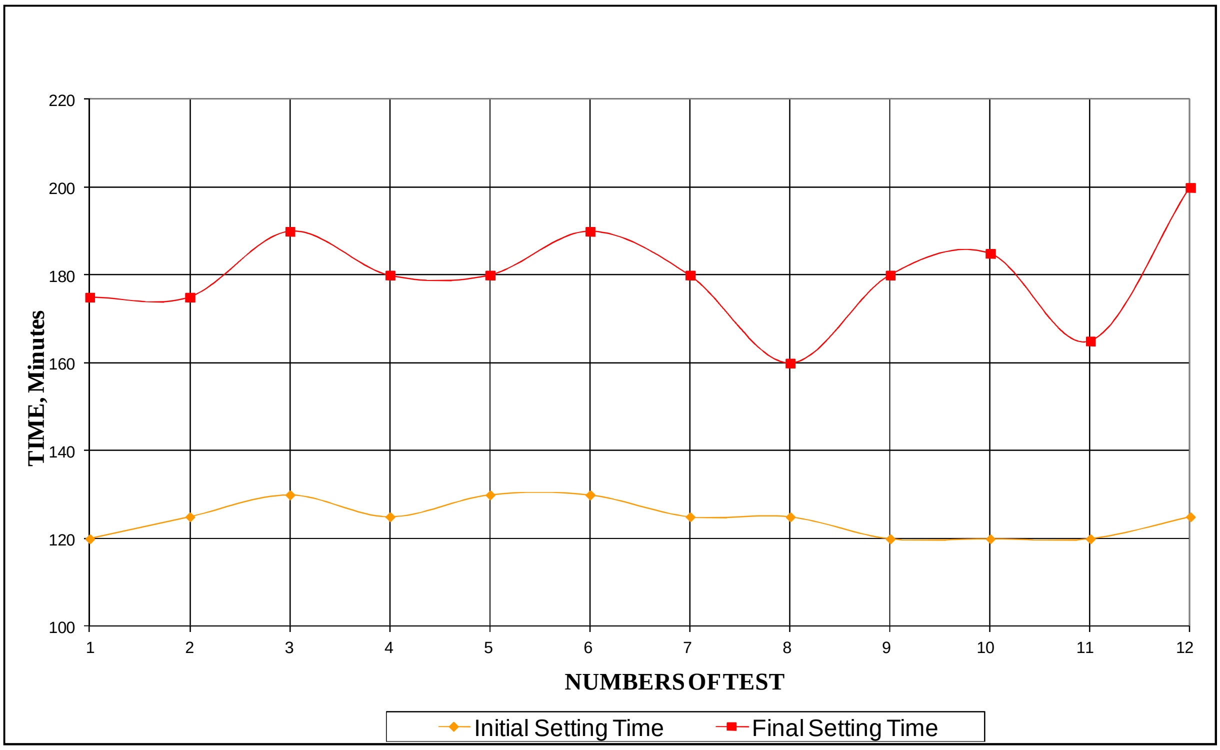


Figure 4.3 Initial and final setting time of blended cement 75% OPC and 25% fly ash.

4.2.4 Discussion on setting times without stabilizer

Variations in setting time of key cement and blended cement materials are significantly high. The above graph represents the variation of a sample data of cement extracted form a larger data for 50 numbers of samples to visually indicating the variation in cement. Even though all cement and blended cement materials comply with Australian Standard AS 3972, the coefficient of variations of most cement are quite high, and this could be due to change of supply of source of raw material, different fuel for clinker burnings and different conditions of burning.

The setting is the condition attained when cement paste lose its plasticity to an arbitrary degree, as defined in the various national standards and is normally measured by resistance to penetration or deformation. Initial setting refers to the first normal stiffening of the paste, while the final setting refers to the achievement of a significant rigidity or setting of Portland cement (Locher et al., 1976). Examination of Portland cement samples directly hydrated to initial and final setting time demonstrated that setting is associated with the loss of mobility of water from the cement paste. This loss in mobility of water is primarily due to the onset of C-S-H formation. Pozzolanic materials (slag and fly ash) being slow in reactivity enhance the setting time on mixing with cement; Davis (1937) concluded that fly ash cement mixes set more slowly than corresponding cement, but the setting time was within the usually specified limit. Costa and Massazza (1980) observed that the addition of fly ash prolongs the initial and final setting time. This effect decreases with increasing cement fineness, but very high fineness does not modify the setting time. The higher the carbon content in fly ash the more is the amount of water required for standard consistency and the higher is the setting time so are the findings have also shown an increasing setting time (initial and final) at all levels of replacement of cement by fly ash. Hence, it is seen with varying percentage replacement of cement, properties of fly ash and source of fly ash, affects the initial and final setting time.

Similarly, various studies have revealed that initial and final setting time prolongs as the percentage replacement of slag in OPC increases. The increasing setting time was correspondingly less for the cement with higher fineness. However, the effect of fineness was remarkable at high slag content. Vladimir and co-workers (1993) while working on the effect of the addition of slag on the OPC found that both initial and final setting time of the cement is prolonged on increasing the quantity of slag in the cement. However, fine grinding reduces the setting time but not below that of control cement. Hogen and Meusel (1981) found that setting time of cement containing slag is delayed at the rate of 10 to 20 minutes per 10% of slag addition as compared to that of control cement. The findings of Sharma (1999) revealed that as the amount of fly ash and slag in OPC increases the initial and final in setting time of the resulting cement also increases. The values of initial and final setting time for grounded fly ash and slag are slightly lower because of improvement in the reactivity of the material on grinding.

Reviewing the results obtained from the tests performed on OPC and blended cement pastes containing; 35% OPC and 65% slag; 75% OPC and 25% fly ash, it is seen that the OPC and blended cement have variation in setting time as an individual due to change of supply of source of raw material, different fuel for clinker burnings and different conditions of burning. The results also show the difference in setting time in comparison to OPC and blended cement (slag and fly ash). Blend of 35% OPC and 65% slag had the capability to prolong the initial and final setting time in comparison to OPC and blended cement containing 75% OPC, and 25% fly ash. The blending of 75% OPC and 25% fly ash the initial setting time was delayed around 15 minutes in comparison to OPC paste and the final setting time was delayed by 7 minutes of OPC paste. Similarly, the initial setting time for 35% OPC and 65% slag was delayed by around 44 minutes and final setting time was delay by 50 minutes in comparison to OPC paste. It can also be noted that the time lag between the initial and final setting time for OPC was around 63 minutes, blended cement 35% OPC and 65% slag was near about similar to OPC around 67 minutes. However, the time lag between initial and final setting time for blended cement 75% OPC and 25% fly ash was 55 minutes less than OPC and blended cement 35% OPC and 65% slag. The summary of initial and final setting time is shown in Appendix A, Table 1. Hence, as discussed by various authors, there will be variation in the initial and final setting time of cement and cement blends depending on their source of raw material, properties and methodology of manufacturing and processing cement and cement blend.

In a later phase, to understand the effect of stabilizer on OPC and blended cement, was based on studies by Massazza (1980) and Huynh (1996) who reported that the formation of finer ettringite over the cement particles when a superplasticizer is incorporated, which further prevents the access of water. Moreover, Meyer and Perenchio (1979) in their studies concluded that the finer morphology of the ettringite was due to the effect of the superplasticizer on the concentration of ions in the solution and, therefore, on the growth of crystals. Based on this principal stabilizer was used for the formation of finer ettringite over the cement particles, which further prevents the access of water to cement particles and prolong the setting time of cement paste. Further, to avoid the experimental difficulties associated with holding the concrete mixes for extended period (> 24 hours) with stabilizer, test results with Marsh cone and “ Coffee cup “ test calorimeter was studied to determine the optimal dosage of the stabilizer.

4.3 Results and its validation with Marsh cone

The fluidity of cement paste, and consequently, that of fresh concrete varies with time due to the hydration, setting process, adsorption of water by the cement and aggregate, and evaporation of water. This behavior has important consequences for the transport and placing under different climatic conditions. In stabilized grout, the change in the effectiveness of the chemical admixture is an additional factor to be considered.

The objective of this experiment is to determine the saturation dosage of stabilizer on OPC and blended cement grouts and later validate the dosage to hold the cement grouts from setting for an extended period (>24hrs).

4.3.1 Ordinary Portland cement

Figure 4.4 shows the times required to empty completely the marsh cone containing OPC grout hold for different holding periods to achieve a flow time of 35 seconds. The effect of water reducer on the same is also shown in this figure. It can be seen that the time required by OPC grout to achieve a flow of 35 seconds was 125 minutes (see Figure 4.4). Once the water reducer is added in the OPC grout, the time measured to achieve a flow of 35 seconds increased to 240 minutes (see Figure 4.4). Thus, the addition of water reducer retards the cement grout further than the normal cement grout.

The influence of stabilizer on OPC grout to hold or retard with increasing stabilizer dosages is shown in Figure 4.5. It can be seen that the ability to hold or retard the cement grout containing water reducer after addition of a stabilizer to an hour old grout is very high. The time of stabilized grout to achieve a flow time of 35 seconds increased with increase in stabilizer dosages. For 400ml, 500ml, 600ml, 700ml and 800ml of dosage for 100kg of cement the time achieved was 1010 minutes, 1240 minutes, 1920 minutes, 2000 minutes and 2320 minutes, respectively. It can be seen the ability of stabilizer to hold the cement grout more than 24 hours (1440 minutes). Figure 4.6 shows the ability of stabilizer to hold or retard the cement grout for an efflux time of 35 seconds, where the holding time increases with increase in stabilizer dosages compared to control OPC grout.

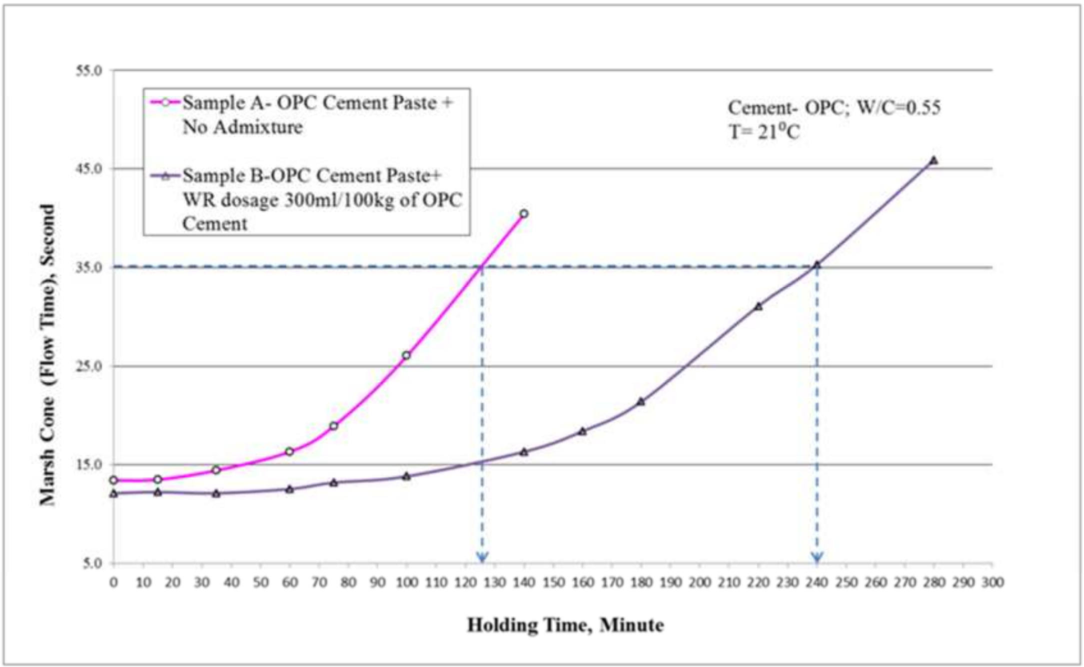


Figure 4.4 Holding time required achieving 35 seconds flow for OPC grout with and without water reducer.

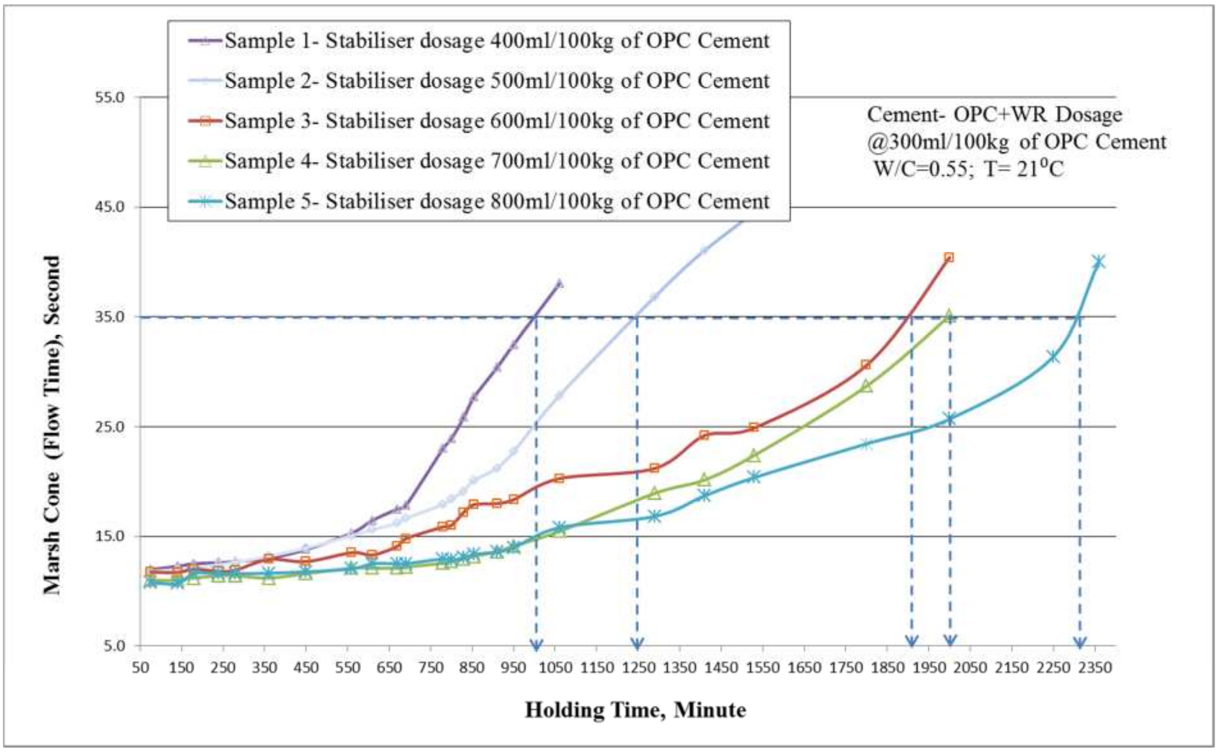


Figure 4.5 Holding time to achieve 35 seconds flow for OPC grouts with water-reducer and stabilizer.

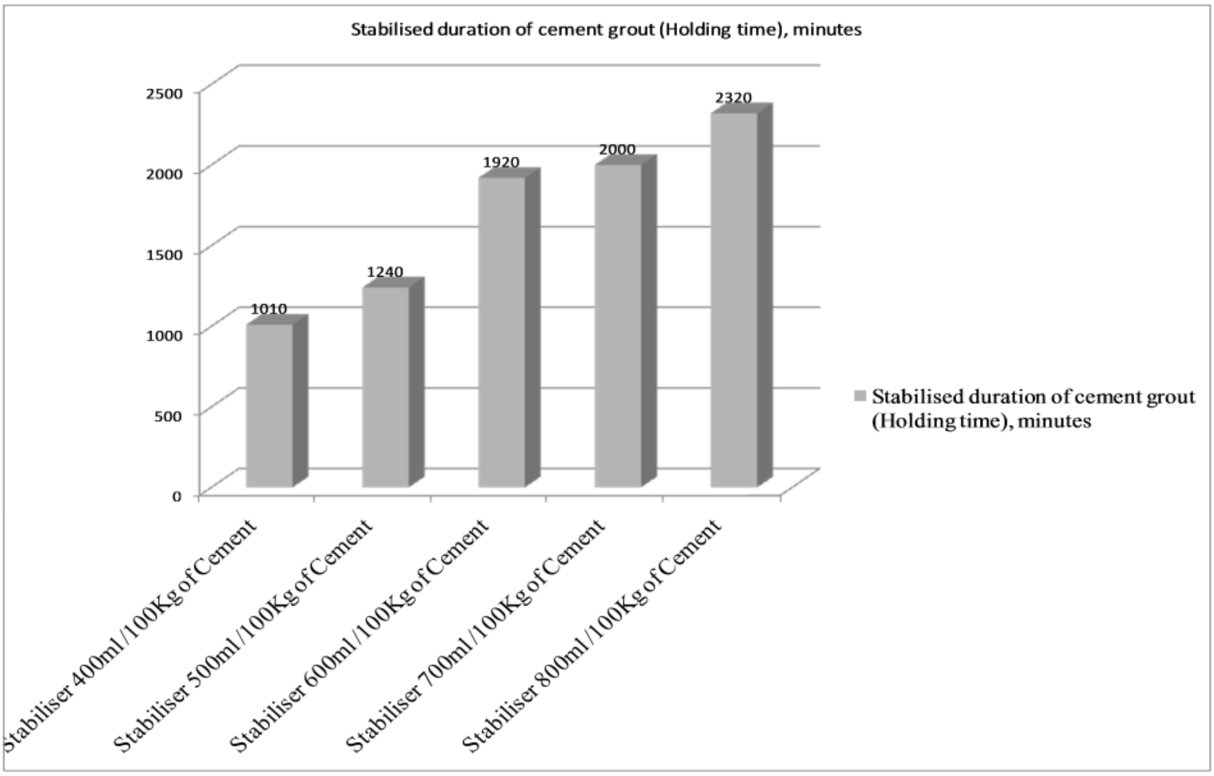


Figure 4.6 Effect of stabilizer to hold the OPC grout.

4.3.2 Blended cement containing 35% OPC and 65% slag

Figure 4.7 shows the time required to empty completely the marsh cone containing 35% OPC and 65% slag blended grout hold for different holding periods. The effect of water reducer on the same is also shown in this figure. It can be seen that the time required to empty the Marsh cone containing 35% OPC and 65% slag grout to achieve a flow of 35 seconds is 250 minutes (see Figure 4.7). Once the grout is incorporated with water reducer, the time measured to achieve a flow of 35 seconds is increased to 359 minutes (see Figure 4.7). Thus, the addition of water reducer retards the 35% OPC and 65% slag blended grout further than the normal OPC grout.

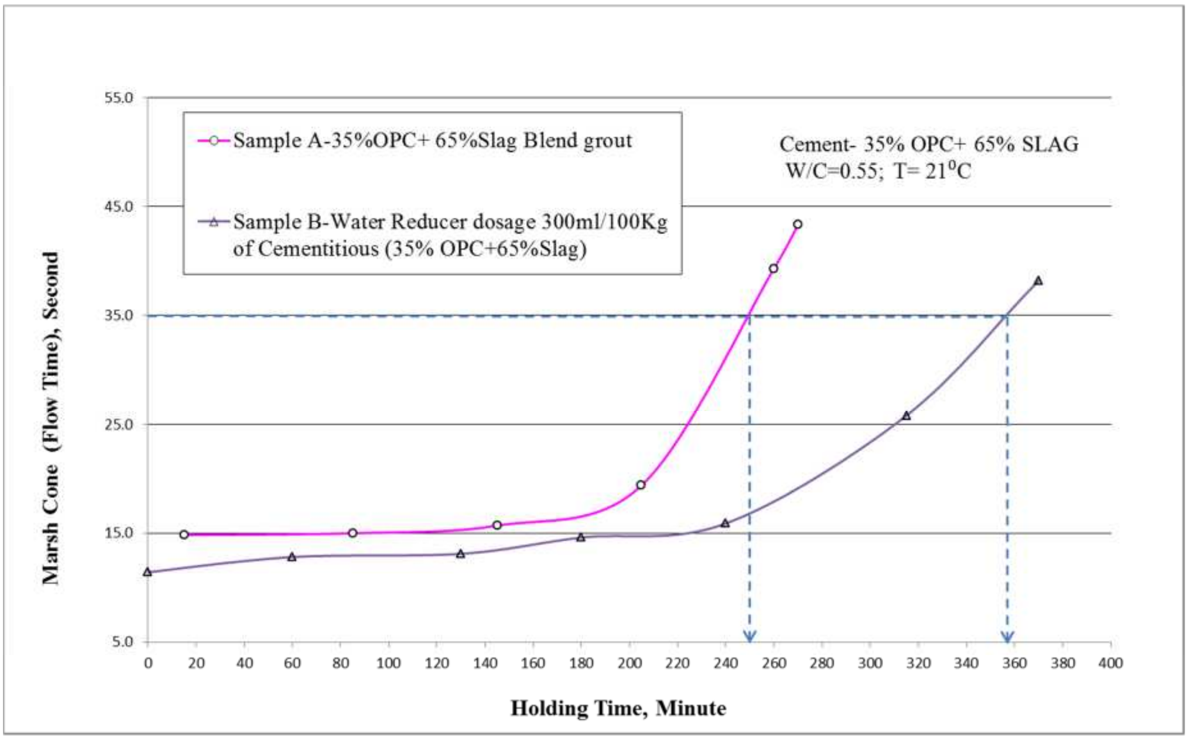


Figure 4.7 Holding time required achieving 35 seconds flow for 35%OPCand 65% slag grout with and without water-reducer.

The influence of different stabilizer dosages on the flow time of grout containing 35% OPC and 65% slag is shown in Figures 4.8 & 4.9. It can be seen that the time required by the stabilized grout to achieve a flow time of 35 seconds increased with increase in stabilizer dosages, i.e. for 400ml/100kg of cement blend the time was 1030 minutes, for 500ml/100kg of cement blend the time was 1860 minutes, for 600ml/100kg of cement blend the time was 2280 minutes, for 700ml/100kg of cement blend the time was 2610 minutes and with 800ml/100kg of cement blend the time was 3020 minutes. It can be seen that the ability of stabilizer to hold or retard the blended cement grout more than 24 hrs (1440 minutes) and its capability to increases the flow time with an increase in stabilizer dosages for a constant efflux time of 35 seconds.

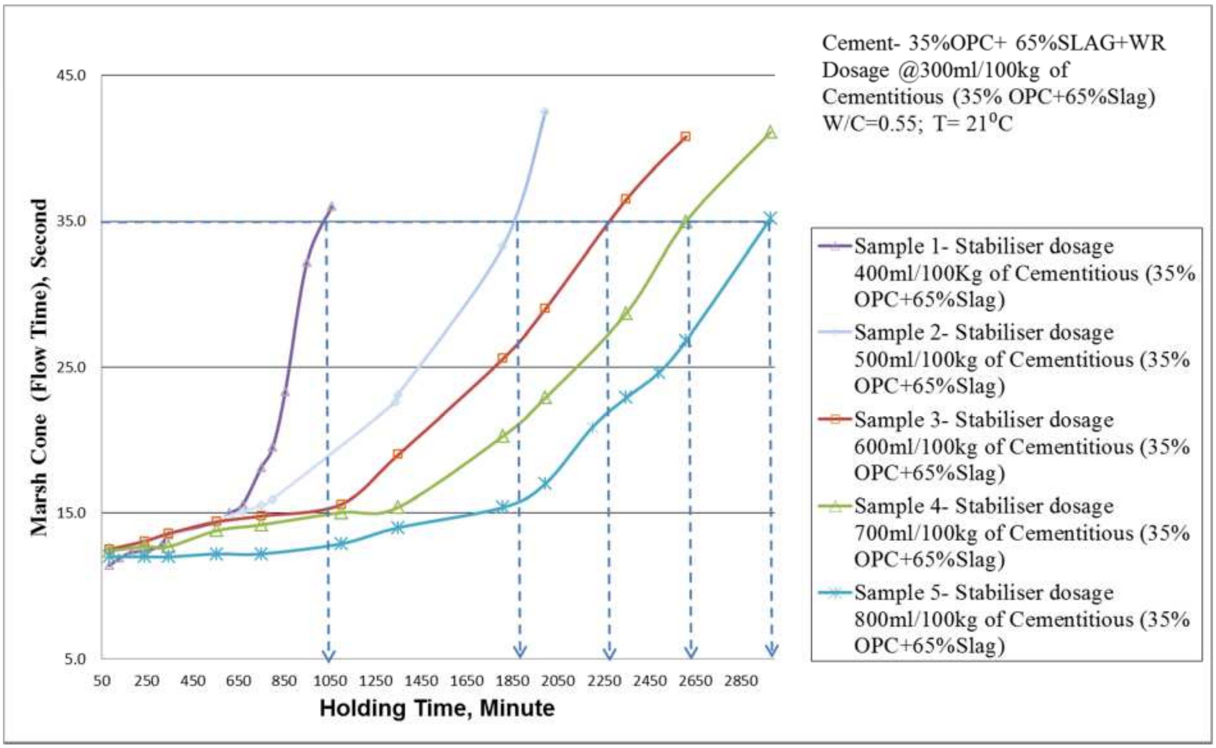


Figure 4.8 Holding time required to achieve 35 seconds flow for 35% OPC and 65% slag grout with water-reducer and stabilizer.

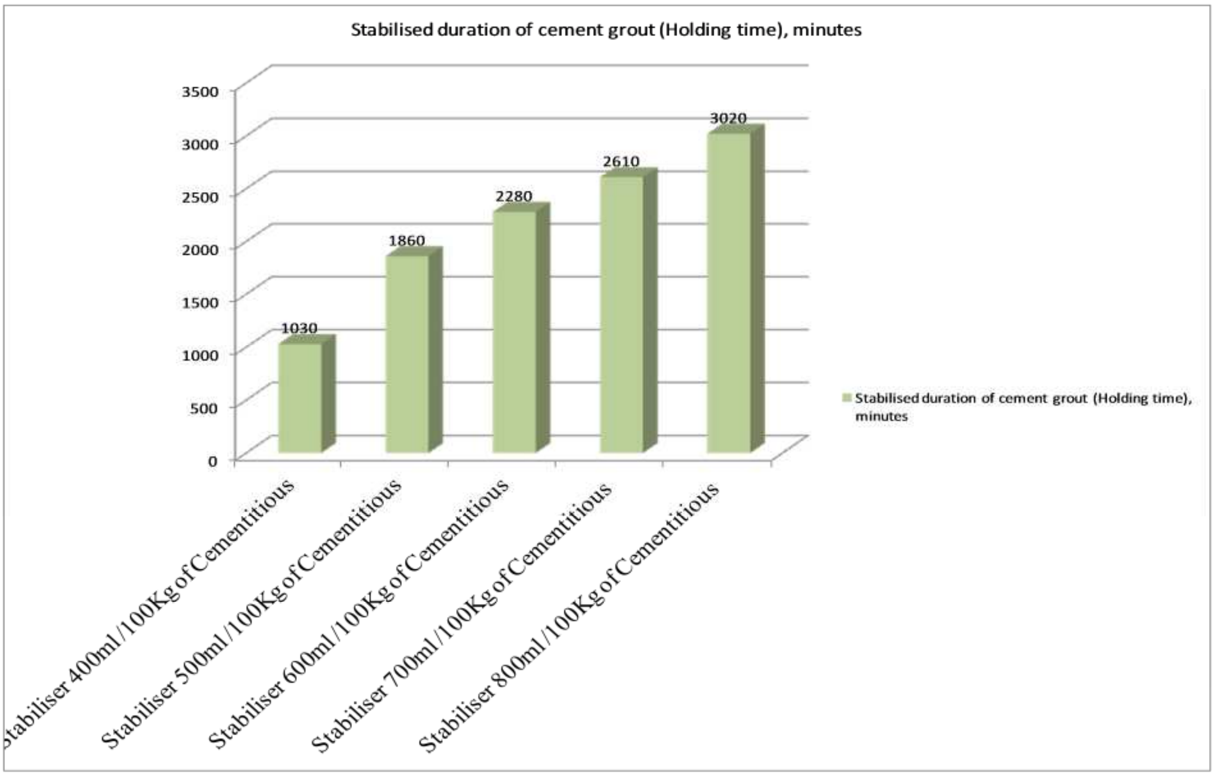


Figure 4.9 Effect of stabilizer to stabilize the 35% OPC and 65% slag grout.

4.3.3 Blended cement containing 75% OPC and 25%fly ash

Figure 4.10 shows the time required to empty completely the marsh cone containing 75% OPC and 25% fly ash blended grout hold for different holding periods. The effect of water reducer on the same is also shown in this figure. It can be seen that the time required to empty the Marsh cone containing 75% OPC and 25% fly ash grout to achieve a flow of 35 seconds is 265 minutes (see Figure 4.10). Once the grout is incorporated with water reducer, the time measured to achieve a flow of 35 seconds is increased to 402 minutes (see Figure 4.10) Thus, the addition of water reducer retards the 75% OPC and 25% fly ash blended grout further than the normal grout.

The influence of different stabilizer dosages on the flow time of grout containing 35% OPC and 65% slag is shown in Figures 4.11 & 4.12. It can be seen that the time required by the stabilized grout to achieve a flow time of 35 seconds increased with increase in stabilizer dosages, i.e. for 400ml/100kg of cement blend the time was 1200 minutes, for 500ml/100kg of cement blend the time was 2110 minutes, for 600ml/100kg of cement blend the time was 3210 minutes, for 700ml/100kg of cement blend the time was 3600 minutes and with 800ml/100kg of cement blend the time was 3870 minutes. It can be seen that the ability of stabilizer to hold or retard the blended cement grout more than 24 hrs (1440 minutes) and its capability to increases the flow time with an increase in stabilizer dosages for a constant efflux time of 35 seconds.

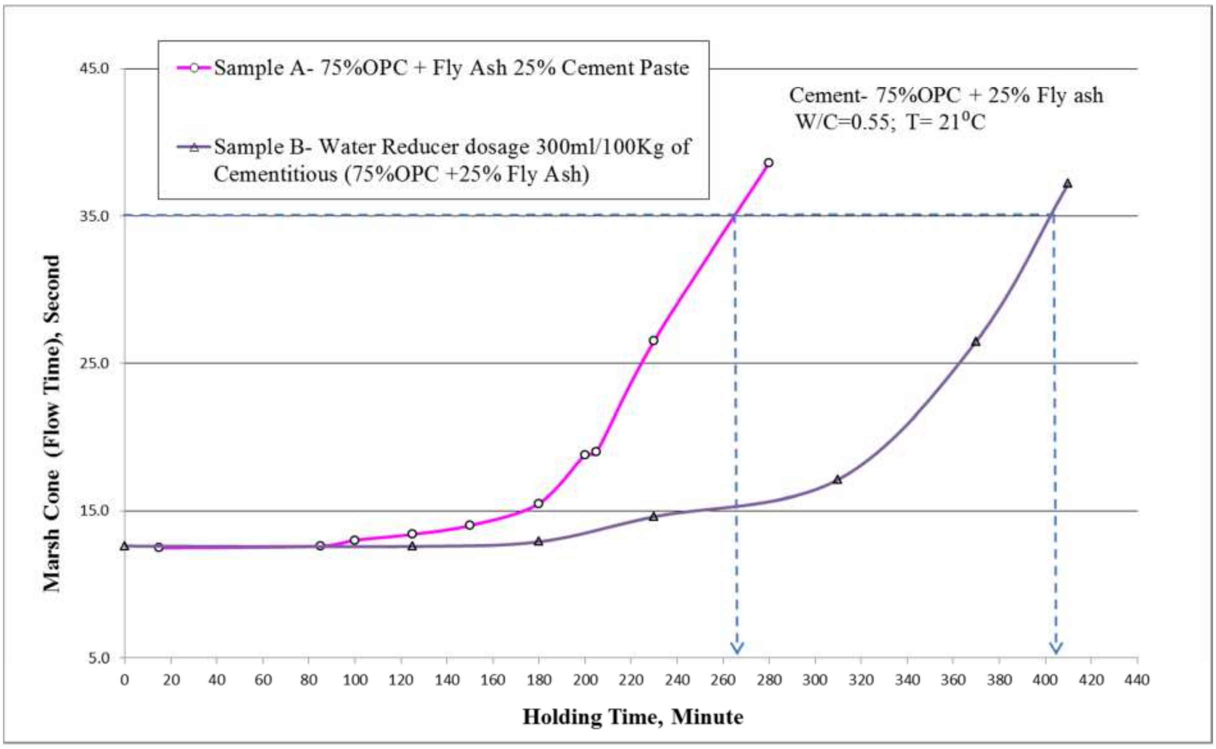


Figure 4.10 Holding time required to achieve 35 seconds flow for 75% OPC and 25% fly ash grout with and without water reducer.

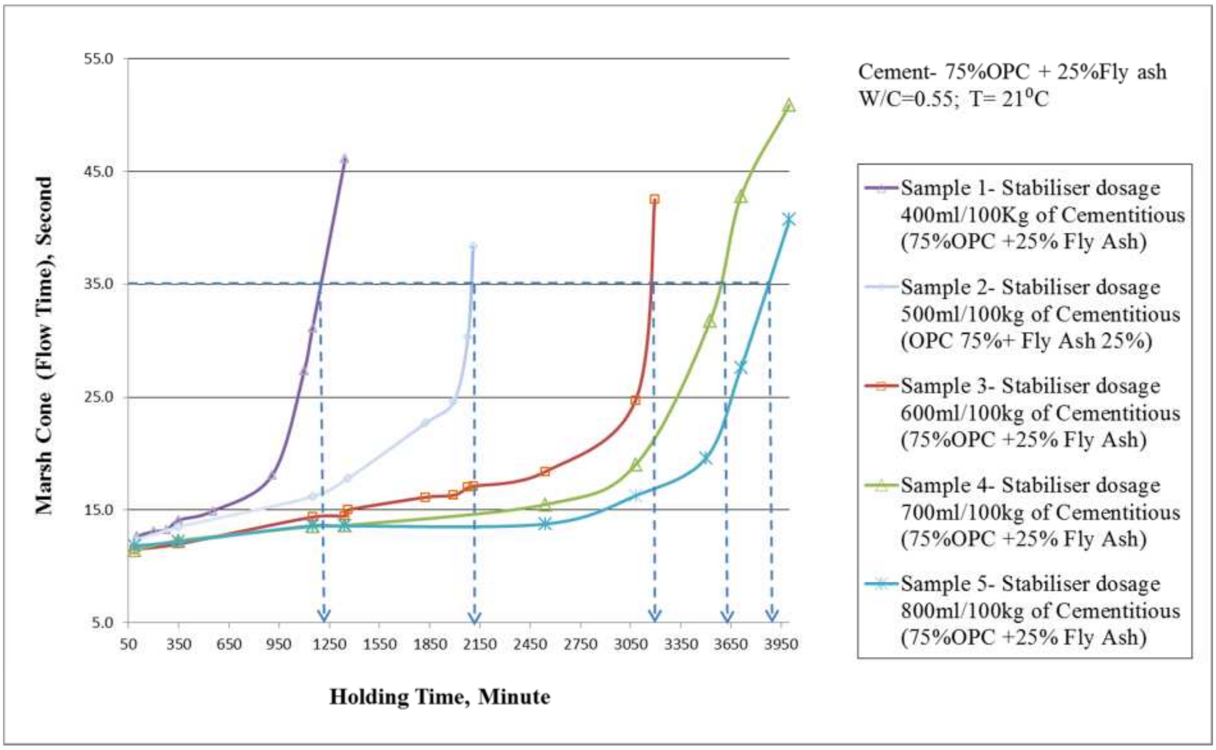


Figure 4.11 Holding time required to achieve 35 seconds flow for 75% OPC and 25% fly ash grout with water reducer and stabilizer.

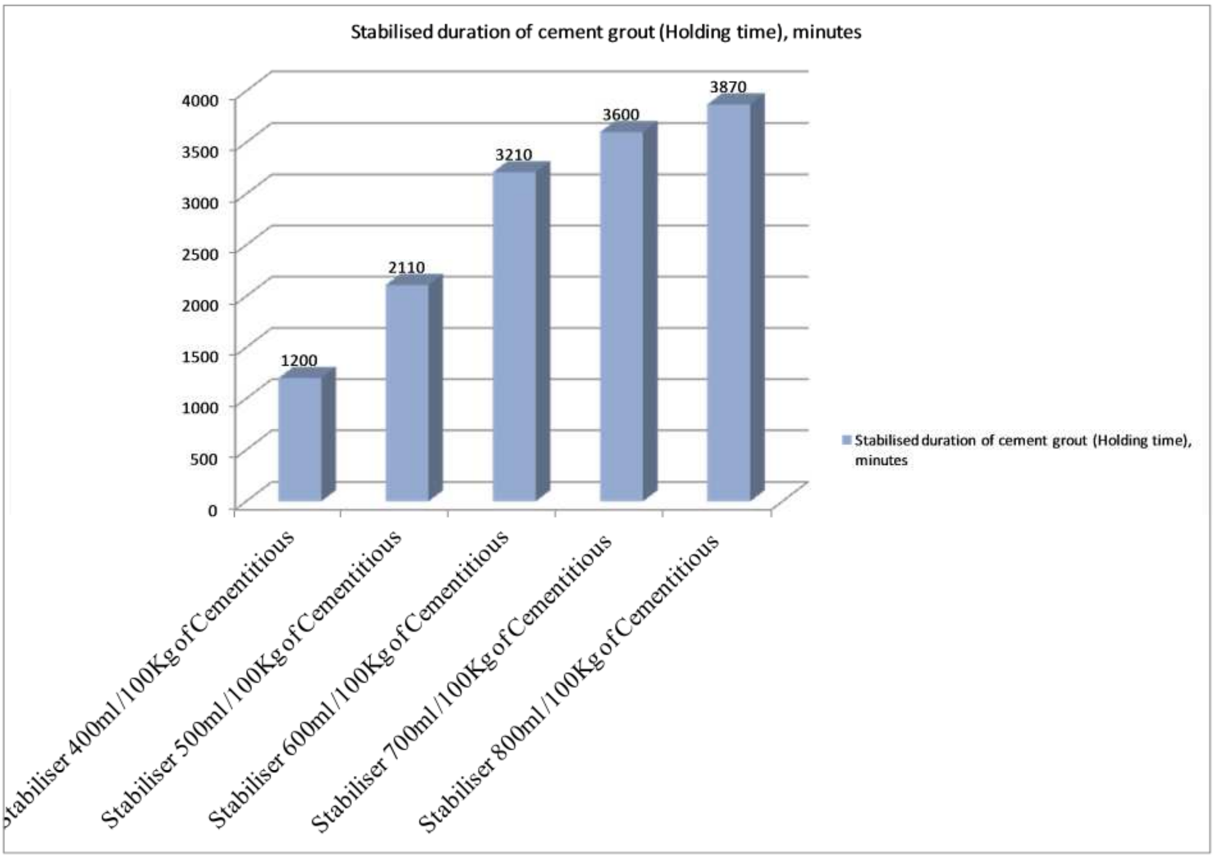


Figure 4.12 Effect of stabilizer to retard the 75% OPC and 25% fly ash grout.

4.3.4 Discussion on Marsh cone results

This method is used to evaluate and compare the loss in the fluidity of OPC and blended cement grouts with time due to different stabilizer dosages. The increase in fluidity with increasing stabilizer dosages is a consequence of the stabilizer's dispersing effect. The repulsive forces between the cement and cement blends particles prevent flocculation leading to the desired performance (Hu and De Larrard, 1996). Nevertheless, it is also noted that different blended cements like slag and fly ash affect this behaviour; for example, the fineness of cement, its C_3A and C_4AF content (Hanna et al., 1989: Paillere et al., 1990), the amount of sulphate (Nawa et al., 1989) and the nature of stabilizer. The results indicate that the retardation of blended cement is higher than the OPC. At the beginning of the hydration reaction in blended cement containing slag, the sulfate ions are utilized to slow the hydration of C_3A present in the clinker and to activate the hydration of the slag. According to De Jong (1977), the grains of slag are surrounded by an acid gel of hydrated silica and aluminates, deriving from the hydration of the slag with water; this prevents the water from penetrating and slows down their hydration. In the presence of sulfate ions, hydrates of a larger structure are formed and consequently, the hydration is not retarded.

Similarly, fly ash particles are usually of spherical shape, particularly as they are produced from burnt coal of high fineness. This property of fly ash gives the ability of mobility to the blended cement grout containing fly ash and increases the flowability of the grout. However, the degree of hydration after 1 day and later on is higher than in OPC. One can conclude that the fly ash slows the hydration rate of C_3S at very early age but later on it acts as an accelerator. The beginning of rapid C_3S hydration in OPC paste coincides with the time of maximum liquid phase saturation with $Ca(OH)_2$. In the presence of fly ash, the saturation of liquid phase with $Ca(OH)_2$ is slowed down and consequently the C_3S hydration is retarded. Fly ash and grounded granulated blast furnace slag is the mineral admixture commonly used in cement technology. These admixtures, apart from the modification of hydration process and consequently setting and physical properties, also affect the rheology of fresh cement paste.

Figure 4.13 shows the rate of increase of holding time (stabilized duration) with an increase in stabilizer dosage for efflux time of 35 seconds of all three cement grouts. The Linear increasing trend in the holding time with stabilizer dosages can be seen in all three cement grouts. However, the rate is slightly higher in the 35% OPC and 65% slag; and 75% OPC and 25% fly ash grouts than the OPC grout. The theory, (if correlated with the results obtained in the Marsh cone experiment) indicates that with the same dosage of stabilizer the effect is different to the blended cement grouts in comparison to OPC cement grout. The OPC losses the fluidity faster compared to blended cement containing granulated grounded slag and fly ash.

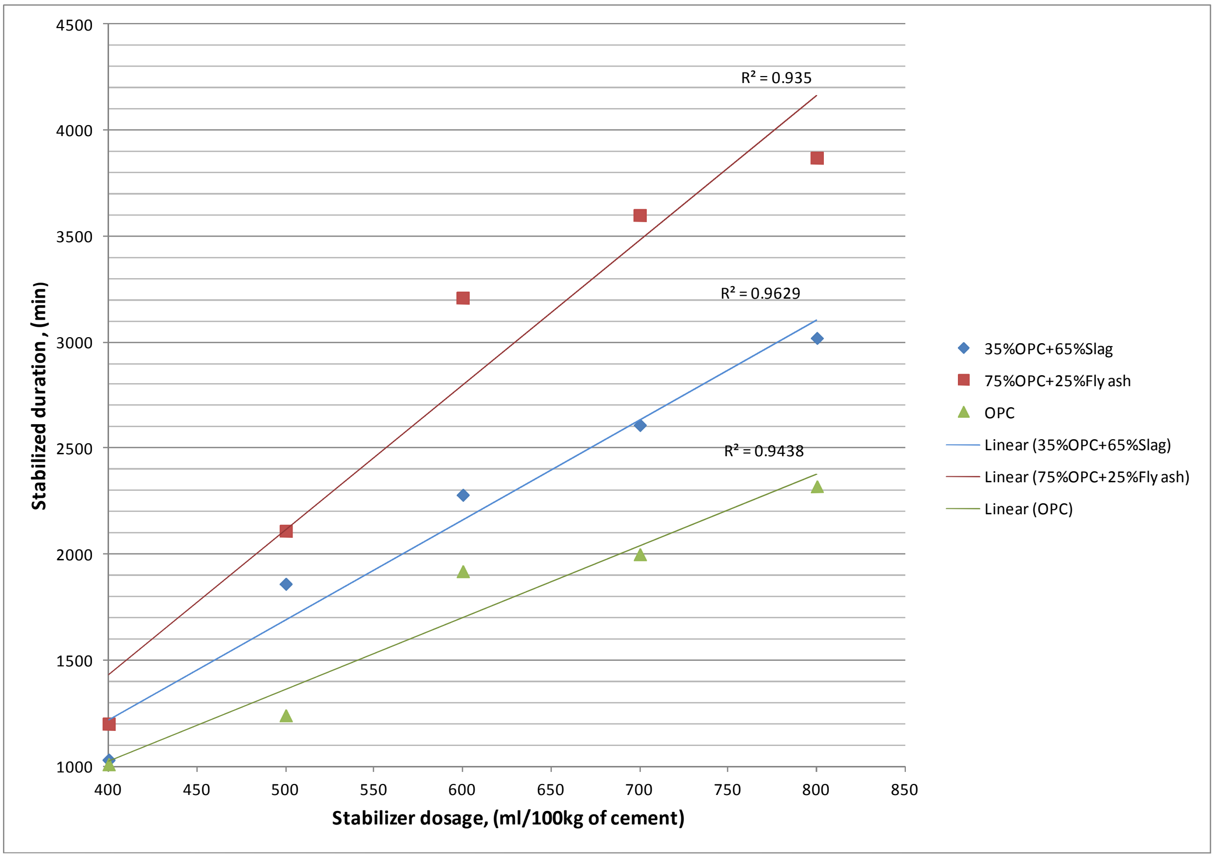


Figure 4.13 Relationship between holding times and stabilizer dosage of all three cement grouts for a particular efflux time of 35 seconds.

4.4 Results and its validation with Heat of Hydration- Coffee Cup Method

The monitoring of heat of hydration reflected the characteristics of OPC and blended cement and mix proportion of admixture as well as the changes in construction and environmental conditions. The hydration process also directly influences concrete workability, setting behavior, strength gain rates, and pore structure development. Therefore, proper information on the hydration process of concrete in the field can be used to control the concrete quality and/or to predict the concrete performance.

The hydration of OPC and blended cement in concrete mixture results in a number of exothermic chemical reactions which liberate heat. The hydration process can be monitored by measuring the total liberated heat (via temperature changes) over time.

Research has demonstrated that the rate and amount of heat liberated from hydration greatly depends on the chemical compositions and physical properties of the cement, blended cement, and chemical admixtures.

To study the behavior of hydration of OPC and blended cement grouts containing admixture and stabilizer, coffee cup method was used. The temperature differences between the grouts samples with those containing various stabilizer dosages were conducted and the curves generated due to heat generate was studied.

4.4.1 Effect of stabilizer on heat of hydration on ordinary Portland cement grout

The effect of stabilizer on the heat of hydration of OPC grout is shown in figure 4.14. It can be seen in sample “A” (grout without admixture and stabilizer) that the temperature rises as soon as the water is mixed with cement. Initially, the temperature increased gradually from 23.2°C and peaked to 54.9°C in 11:26 hours. With the addition of water-reducer to OPC grout (sample B) the temperature rise is initiated in 02:11hours at a temperature of 25.7°C and peaked to 59.5°C in 13:15 hours. It can be seen that when stabilizer dosage of 500ml/100kg of cement is added to sample B (sample 1) the rise in temperature initiates in 22:19 hours at a temperature of 21.1°C and peaked to 48.1°C in 34:41 hours. Further, when stabilizer dosages were increased to 600ml (sample 2), 700ml (sample 3) and 800ml (sample 4) dosage per 100kg of cement, the rise in temperature for sample 2 is initiated in 26:45 hours at a temperature of 20.3°C and peaked to 46.3°C in 45:23 hours, the rise in temperature for sample 3 is initiated in 28:05 hours at a temperature of 21.7°C and peaked to 44.1°C in 50:33 hours and the rise in temperature for sample 4 is initiated in 49:36 hours at a temperature of 20.6°C and peaked to 34.1°C in 76:25 hours, respectively. An individual graph with details for each OPC sample grout is shown in Appendix B.

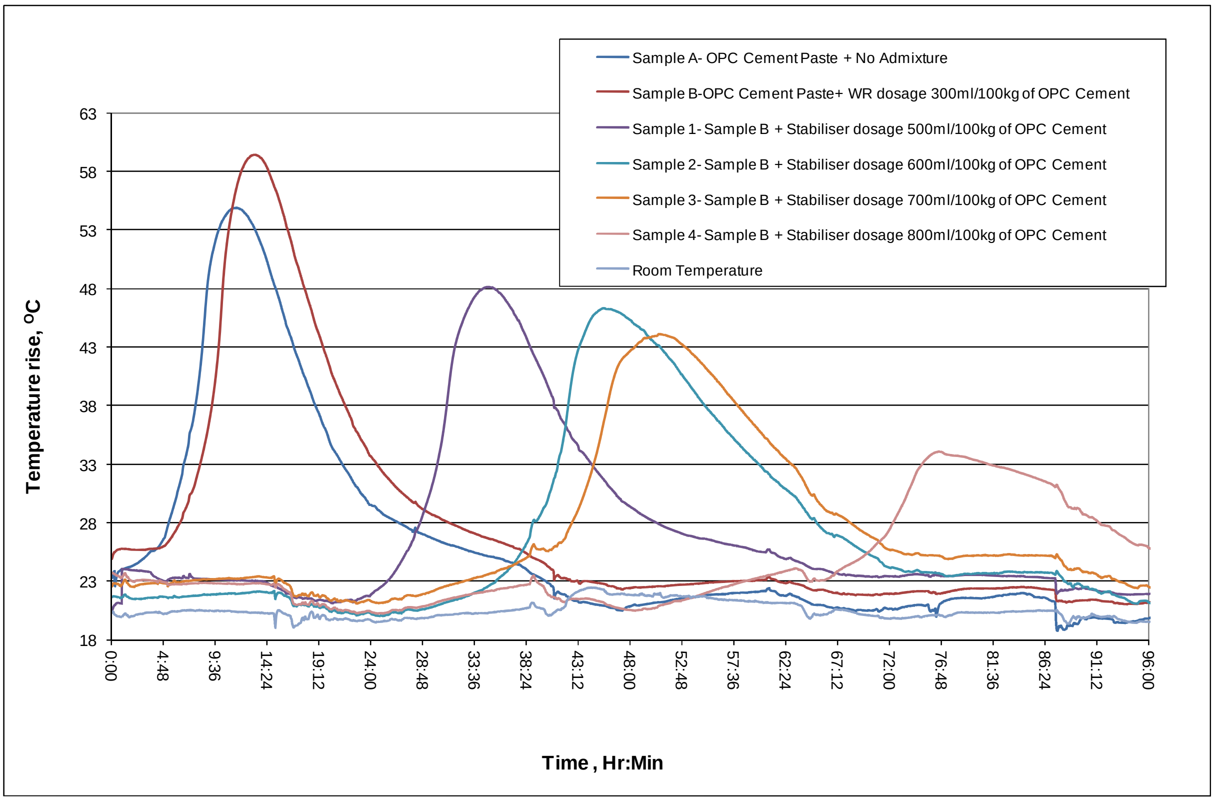


Figure 4.14 Effect of stabilizer on temperature rise during hydration of OPC grout.

The initial rise in temperature with water-reducing admixture (sample B) is not instant as that with OPC grout without admixture and the rise in temperature was delayed for 2:11hours. The addition of water-reducer not only delayed the initial rise in temperature but also delayed the time of peak temperature rise by 13:40 hours. The reason for this effect is discussed in earlier chapter 2 on the effect of water reducer on cement. It is also observed that the addition of stabilizer with increasing dosages increases the time required for initial temperature rise increase the time required to reach the peak temperature and also decreases the peak temperature.

4.4.2 Effect of stabilizer on heat of hydration on blended cement grout (35% OPC and 65% slag)

The effect of stabilizer on the heat of hydration on blended cement grout containing 35% OPC and 65% slag is shown in figure 4.15. It can be seen in sample "A" (grout without admixture and stabilizer) that the temperature rises as soon as the water is mixed with cement. Initially, the temperature increases gradually from 19.2°C and first peaked approximately at 31.2°C in 14:17 hours; and later peaked (second peak) at 34.6°C in 20:35 hours. With the addition of water-reducer to blended cement grout sample B, the temperature rise is initiated in 03:53hours at a temperature of 21.2°C and first peaked approximately at 32.9°C in 16:43 hours; and later second peak at 35.7°C in 22:47 hours. The effects of addition of stabilizer with its increasing dosages on the peak temperature and the time required to reach the peak temperature of blended cement grout are shown in the same figure 4.15. Samples 1, 2, 3 and 4 in figure 4.15 are designated as the blended cement grout containing stabilizer dosage of 500ml, 600ml, 700ml and 800ml dosage per 100kg of blended cement, respectively. It can be seen in sample 1 that the rise in temperature initiates in 18:44 hours at a temperature of 18.8°C and first peaked to 27.7°C in 33:33 hours; and later second peak at 28.4°C in 50:49 hours. In sample 2, the rise in temperature is initiated in 27:32 hours at a temperature of 20.9°C and first peaked to 29.6°C in 43:06 hours; and later second peaks at 29.8°C in 52:56 hours. In, sample 3 the rise in temperature is initiated in 39:07 hours at a temperature of 21.9°C and first peaked to 28.1°C in 51:46 hours; and later second peaks at 29.4°C in 59:26 hours. Similarly, sample 4 the rise in temperature is initiated in 41:15 hours at a temperature of 21.7°C and first peaked to 29.2°C in 57:53 hours; and later second peaks at 29.7°C in 64:09 hours. An individual graph with details for each stabilizer dosage in blended cement 35% OPC and 65% Slag grout is shown in Appendix B.

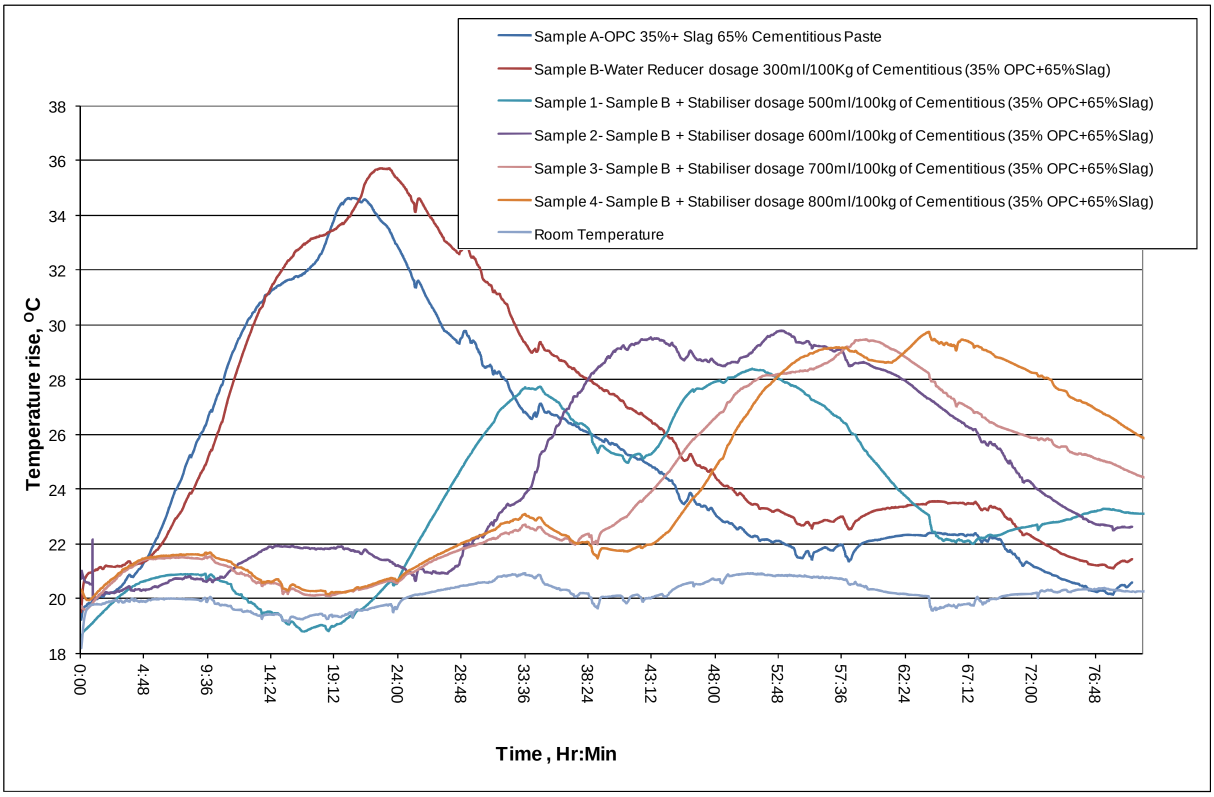


Figure 4.15 Effect of stabilizer on temperature rise during hydration of 35% OPC and 65% slag blend cement grout.

It can be seen that the initial rise in peak temperature of grout containing water-reducer (Sample B), is not instant compared to control grout and the rise in temperature initially is delayed by 3:53 hours. The addition of water-reducer delayed the initial rise in temperature but also delayed the time to reach peak temperatures. The water-reducer not only delayed the rise in temperature but increased the peak temperature than the control paste. The reason for this effect is discussed in chapter 2, that when water- reducer is used without changing the mix proportion, the heat of hydration and temperature rise for concrete at an early age may increase (Massazza et al., 1980). Similar to OPC grout, after addition of stabilizer with increasing dosages the time for the initial rise in temperature is increased and the peak temperature is decreased. By comparing the OPC grout and the blended cement grout containing 35% OPC and 65% slag, it can be seen that the delay in the initial rise of peak temperature is greater for blended cement grout. As discussed in Chapter 2, there are two peaks for blended cement containing 35% OPC and 65% slag- the first is caused by cement hydration and the second is due to slag reaction. The peaks are shown in details in Appendix B, figure 2g-l. In, the blended cement the slag content is high i.e. 65%, both the time and the maximum heat are reduced simultaneously; according to Escalante-Garcia and Sharp (1998) and Zhou et al. (2006), this reduction can be attributed to the effect of dilution on both OPC and slag reactions. This dilution may be explained by the increased water available for OPC hydration concerning the increased slag level, which accelerates the hydration of C_3S and C_3A in the OPC. Furthermore, the reaction is responsible for the reduced time to obtain the maximum rate of the heat of hydration compared to the OPC paste, particularly with an increased amount of slag addition (Escalante-Garcia and Sharp, 1998 and Zhou et al., 2006). In conjunction with this reduction in time, the hydration reaction of slag will be limited (due to a lack of Calcium hydroxide available), which contributes to the low heat of hydration (Domone and Sautsos, 1995). However, the later rate of slag hydration is accelerated with the progressive release of alkalis by slag; together with the Calcium hydroxide provided the OPC hydration (Neville, 1995).

4.4.3 Effect of Stabilizer on Heat of Hydration of blended cement grout containing 75% OPC and 25%fly ash

Figure 4.16 shows the effect of stabilizer on the heat of hydration of blended cement containing 75% OPC and 25% fly ash. It can be seen in sample “A” (grout without admixture and stabilizer) that the temperature rises as soon as the water is mixed with blended cement. Initially, the temperature increased gradually from 21.9°C and peaked to 51.6°C in 7:06

hours. With the addition of water-reducer to blended cement grout (Sample "B") the temperature rise is initiated in 02:13 hours at a temperature of 23.7°C and peaked to 49.4°C in 08:50 hours. The effects of addition of stabilizer and its increasing dosages on the peak temperature and the time required to reach that temperature of blended cement grout are also shown in the same figure 4.16. Samples 1, 2, 3 and 4 in figure 4.16 are designated as the blended cement grout containing stabilizer dosage of 500, 600, 700 and 800ml/100kg of blended cement, respectively. It can be seen that in sample 1 the rise in temperature initiates in 28:00 hours at a temperature of 21.6°C and peaked to 36.2°C in 36:09 hours. In sample 2, the rise in temperature is initiated in 33:32 hours at a temperature of 22.9°C and peaked to 34.7°C in 49:43 hours. In "sample 3" the rise in temperature is initiated in 48:02 hours at a temperature of 20.1°C and peaked to 34.5°C in 58:34hrs. Similarly, in "sample 4" the rise in temperature is initiated in 63.52 hours at a temperature of 21.1°C and peaked to 27.4°C in 87:08 hours. An individual graph with details for each grout sample of 75% OPC and 25% fly ash is shown in Appendix B.

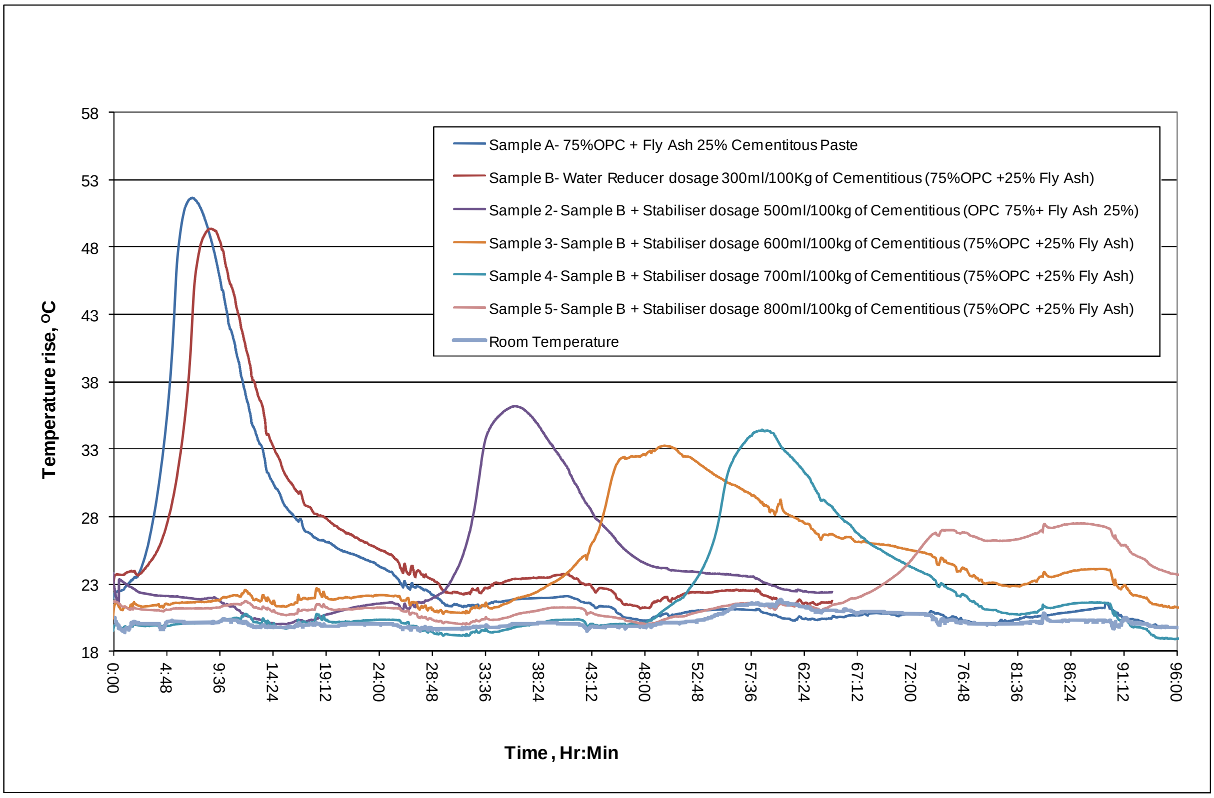


Figure 4.16 Effect of stabilizer on temperature rise during hydration of 75% OPC and 25% fly ash blend cement grout.

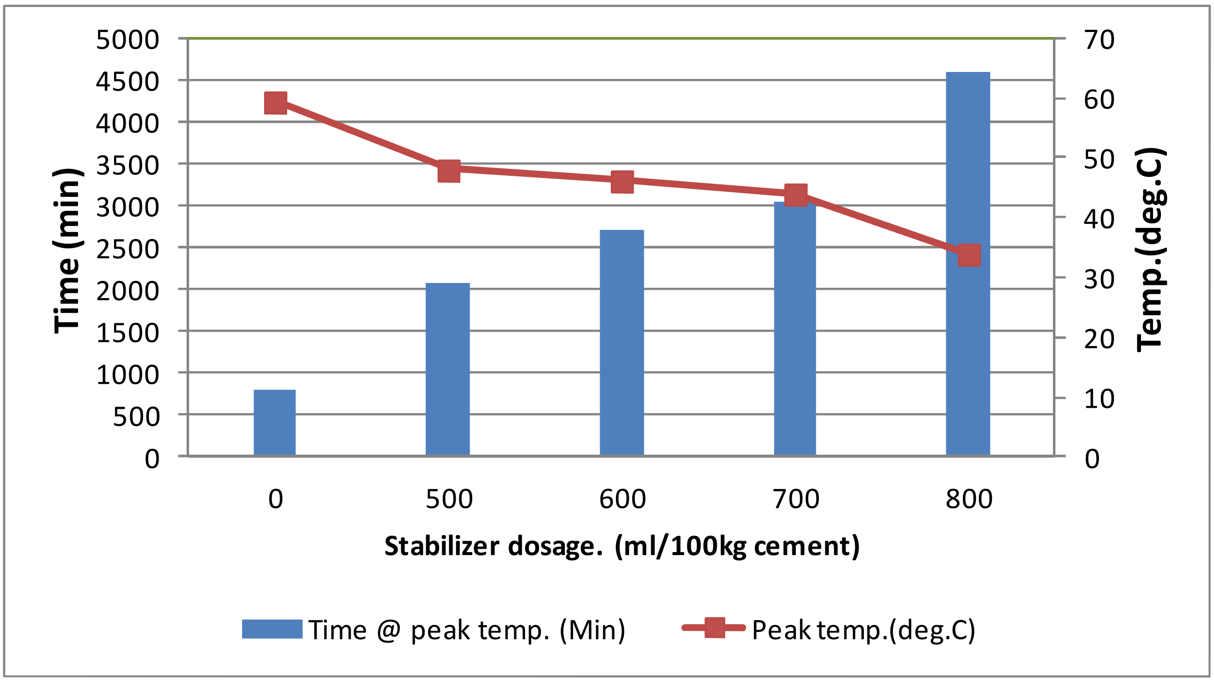
It can be seen that the initial rise in peak temperature of blended grout (75% OPC and 25 % fly ash) with water-reducer (Sample B) was not instant as that without admixture and the rise in temperature was delayed for 2:13 hrs. The effect of water-reducer not only delayed the initial rise in temperature but also delayed the time for peak temperature by 8:50 hrs.

In comparison to OPC with water reducing admixture, the delay in initial temperature rise was nearly same for blended cement 75% OPC and 25% fly ash. However, the time to reach the peak temperature was earlier in blended cement containing 75% OPC and 25% fly ash compared to OPC. On the other hand, the blended cement containing 35% OPC and 65% slag exhibited more delay in initial temperature rise and increased the time to reach the peak temperature compared to OPC and blended cement containing 75% OPC and 25% fly ash.

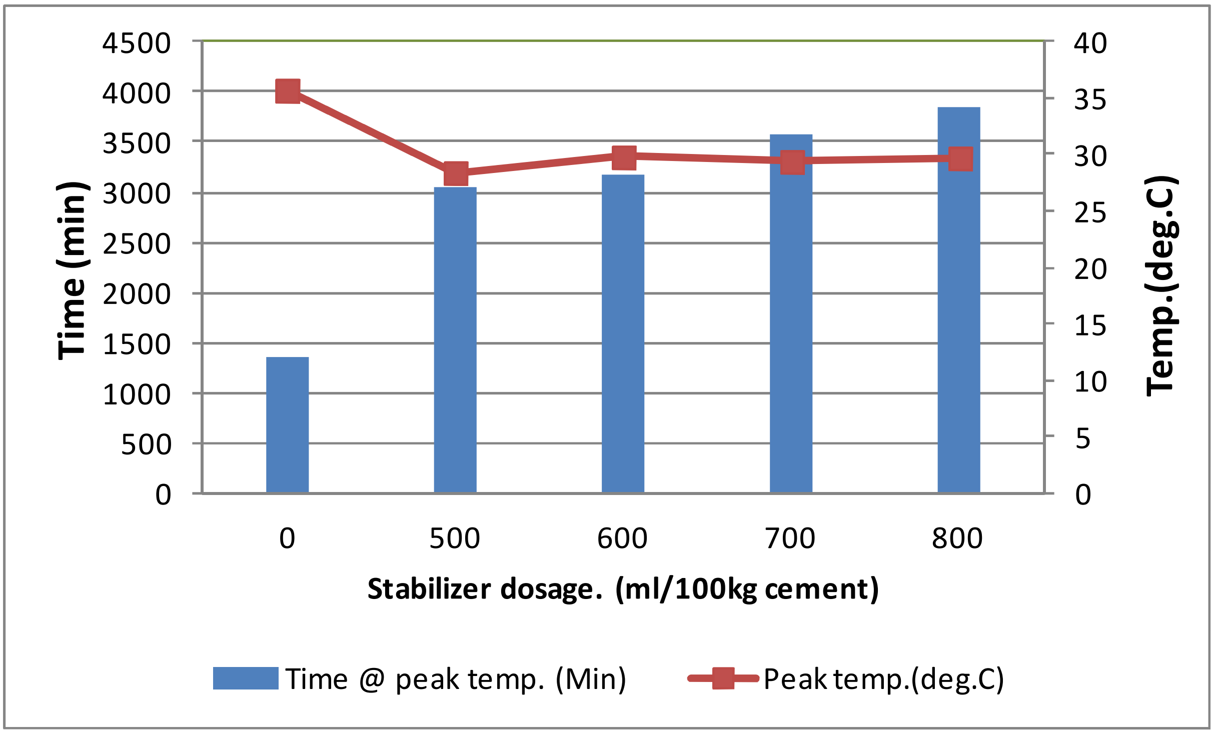
The results indicate that the time for a peak temperature of 75% OPC and 25% fly ash grout was earlier or nearly similar to that of OPC. Kurdowski and Thiel (1981) explained that as the hydration of cement with fly ash is a complex process because of the mutual interaction between the cement and fly ash particles. The hydration process can be considered on the basis of the particular reaction of cement component as well as on the liquid phase and hydration products composition. The liquid phase composition is the factor affecting the type and rate of hydration products. There are two opposite theories with the formation of C_3A hydration with OPC and fly ash blended cement (Uchikawa, 1986). One indicates the accelerating effect on C_3A hydration and the others retarding on C_3A hydration. In the presence of water reducer comparing to OPC the early peak time of 75% OPC and 25% fly ash blend in the presence of water, reducer indicates that fly ash worked as an accelerator on C_3A hydration.

4.4.4 Discussion on Coffee Cup Method

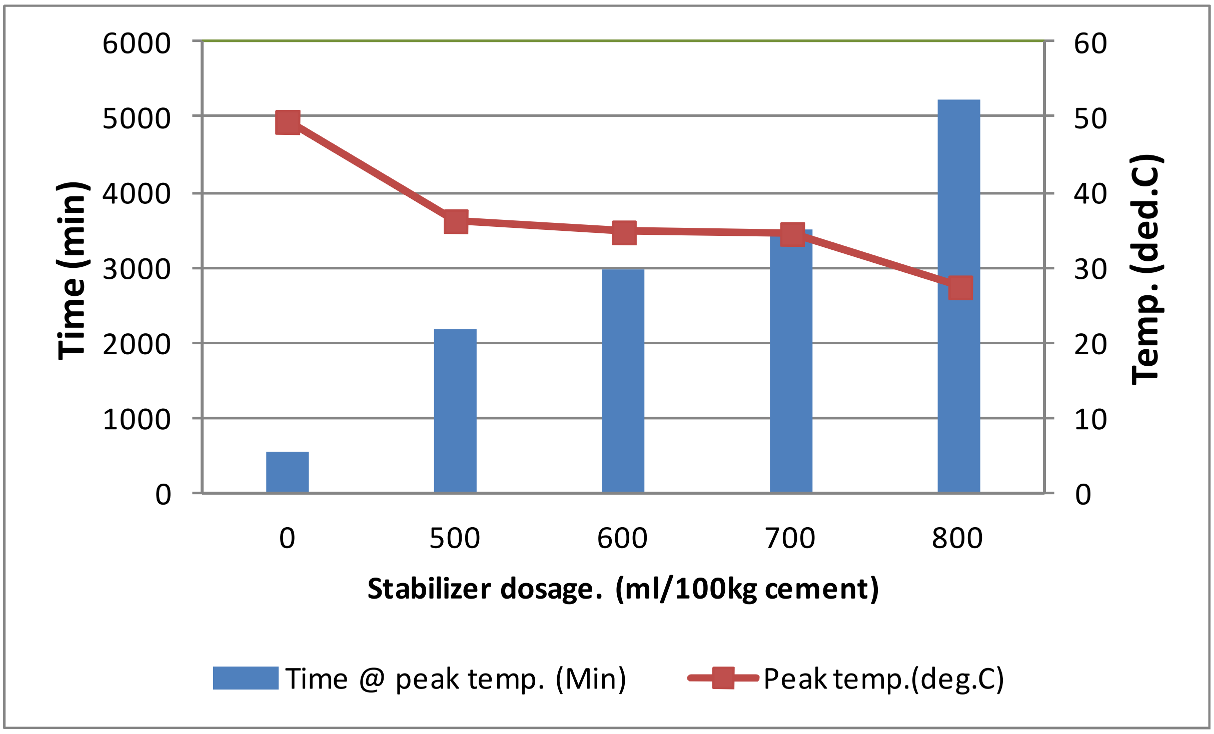
The effect of different stabilizer dosages on the heat of hydration of above cement pastes is shown in Figures 4.14 - 4.16. It can be seen in all three types of cement that the time required to reach the peak temperature during hydration increases with increase in stabilizer dosages, with most significant in 75% OPC and 25% fly ash cement. It is also observed (see Figure 4.17a) that the heat of hydration of OPC pastes decreases with increase in stabilizer dosages. However, the reduction of peak temperatures with an increase in stabilizer dosages in 35% OPC and 65% slag; and 75% OPC and 25%flyash cement grouts (see Figure 4.17b and 4.17c) is more than the OPC (see Figure 4.17a). No significant change in peak temperatures is observed in 35% OPC and 65% slag cement grout due to increasing in stabilizer dosages. This is due to significantly higher replacement of cement by slag at 65% slag. The longer time required by the 35% OPC and 65% slag; and 75% OPC and 25% fly ash cement grouts to reach the peak temperature and the reduction of peak temperature rise during hydration can be attributed to the replacement of cement by fly ash and slag in those cement blends. By comparing the chemical compositions of all three, it can be seen that the total SiO_2 and Al_2O_3 contents in 35% OPC and 65% slag; and 75% OPC and 25%flyash cement are about 50% and 100% higher than the OPC and the CaO content is about 24% lower than the OPC. Thus the OPC produced more heat and subsequently higher peak temperature during hydration than the blended cement when mixed with water, even by the addition of a stabilizer.



(a) OPC grouts.



(b) 35% OPC and 65% slag grouts.



(c) 75% OPC and 25% fly ash grouts.

Figure 4.17 Effects of stabilizer dosage on peak temperature and time required to reach that temperature during hydration of all three cement grouts.

4.5 Correlation between dosage of stabilizer with holding time and heat of hydration

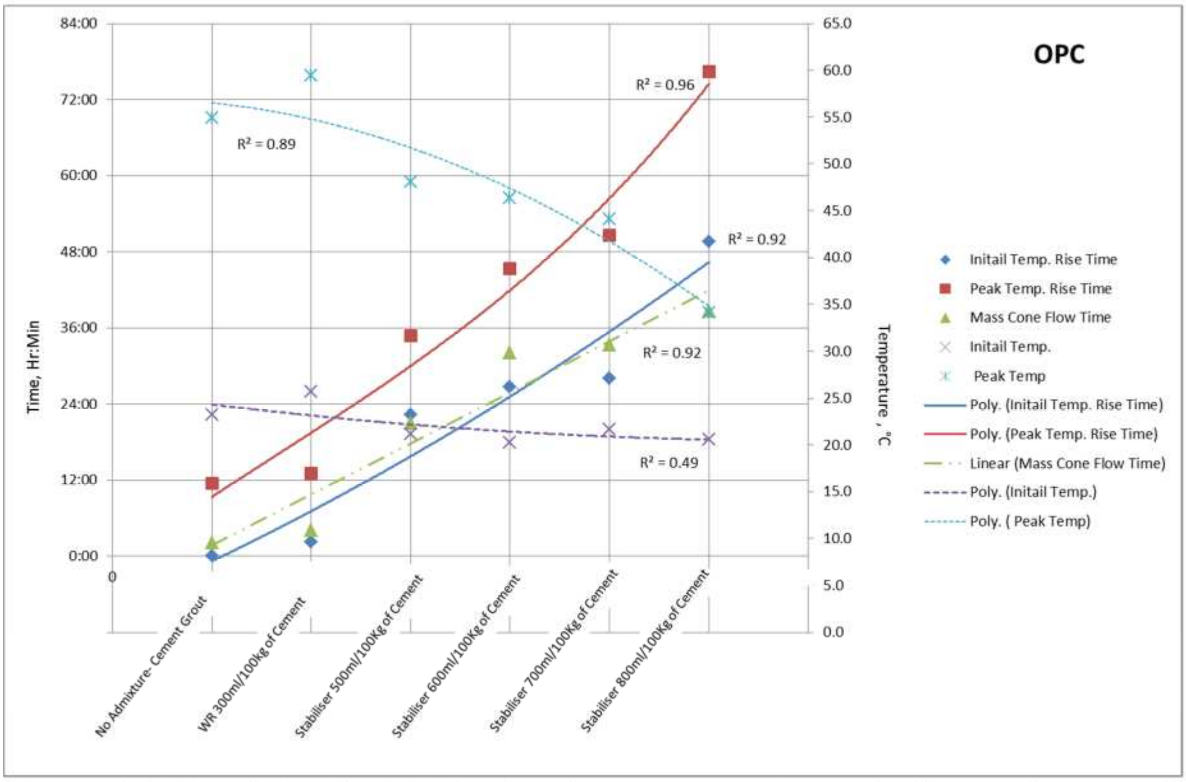


Figure 4.18 Correlation for initial and peak temperature rise results for Marsh cone and Coffee cup method OPC grout.

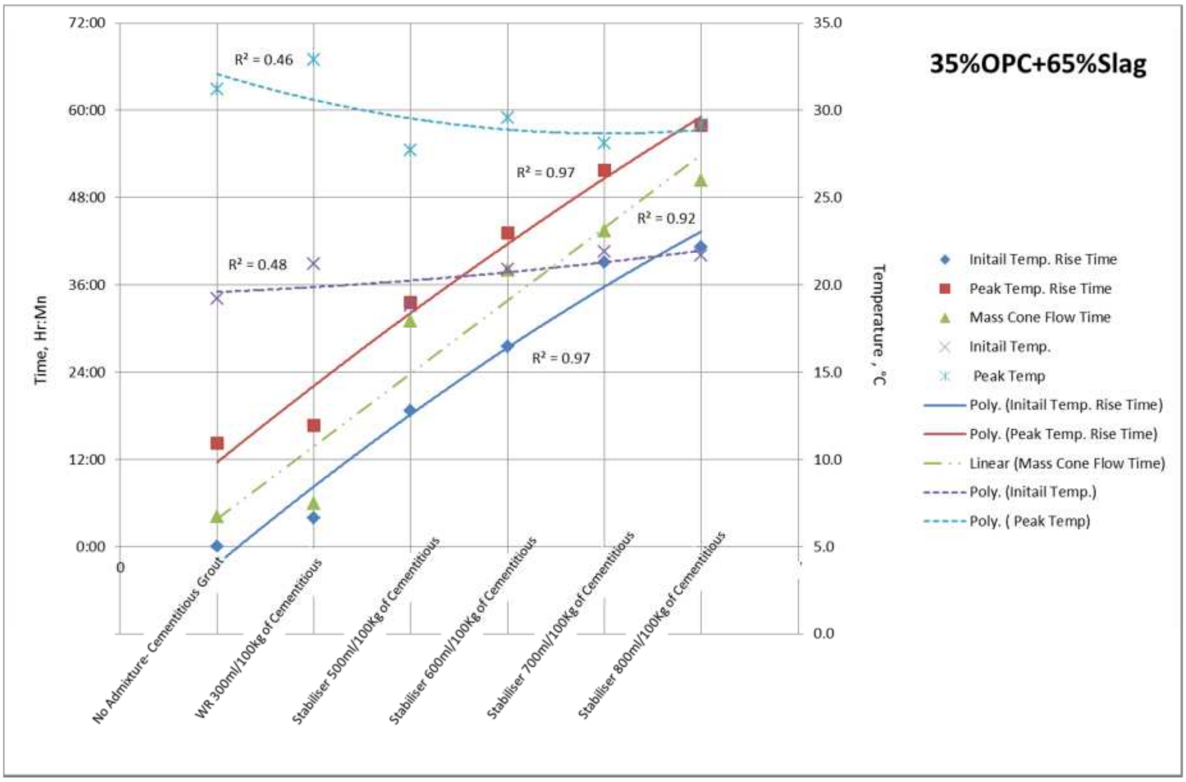


Figure 4.19 Correlation for initial and peak temperature rise results for Marsh cone and Coffee cup method 35% OPC and 65% slag cement grout.

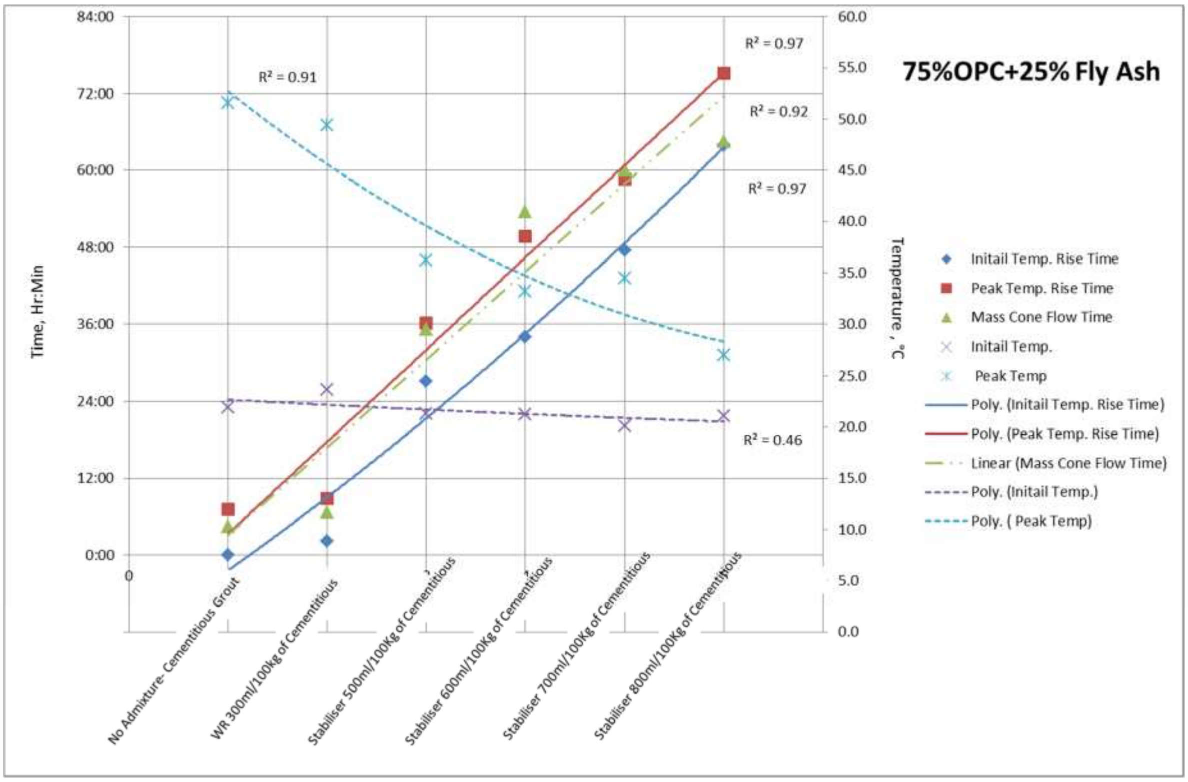


Figure 4.20 Correlation for initial and peak temperature rise results for Marsh cone and coffee cup method 75% OPC, and 25% fly ash cement grout

Figures 4.18- 4.20, show the correlation between the holding times; time to peak temperature rise and peak temperatures of OPC and two blended cement grouts. The results show that with an increase in stabilizer dosages the time to initial temperature rise of cement and blended cement grout increase. Similarly, the time to reach the peak temperature increases with increase in stabilizer dosages. However, with an increase in stabilizer dosages the peak temperature drops gradually indicating the slowing down of hydration process.

If the results of holding times in Marsh cone method are compared with the heat of hydration monitored in the Coffee cup method, an increasing trend of holding time of the OPC grout is observed similar to increase in time of initial temperature rise with an increase in stabilizer dosages. Similar relationships can also be observed in the case of two blended types of cement. As discussed earlier the accuracy and sensitivity of such simple tests are rarely reported. Still, the test results give a good prediction of concrete setting time. The aim of this study was to find a reasonable stabilizer dosage to stabilize the concrete and its reuse without affecting the key properties of the concrete. To get a better comparison between OPC and blended cement considering significant variations in the quality of the constituents of concrete e.g. variations in cement and cementitious material's compositions from different sources, any unforeseen chemical impurities in aggregates, etc. may affect the stabilizer's performance. Hence, for a safer option a slightly higher stabilizer dosage of 800ml/100kg of cement or cementitious materials compared to about 600-700ml/100kg of cement or cementitious materials of stabilizer dosage was considered to stabilize concrete for more than 24 hrs. However, this dosage is not an absolute value, but a conservative one and more importantly it will show the effect of stabilizer on the properties of various stabilized concretes made from above cement and blended cement.

4.6 Effect of stabilizer on workability of concretes

4.6.1 OPC concrete

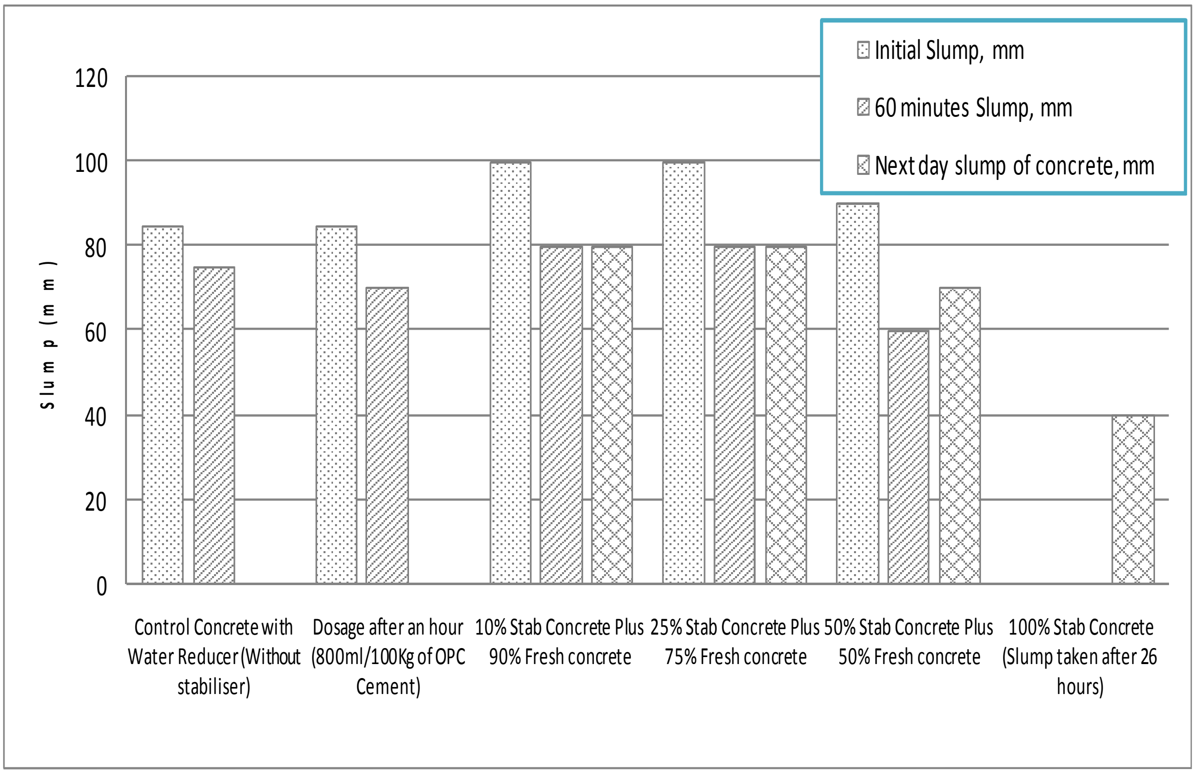


Figure 4.21 Slumps for OPC concrete.

Figure 4.21 shows the effect of stabilizer on a slump of OPC concrete. The initial slump of control OPC concrete was 85mm and after 60 minutes it dropped to 75mm. In the second batch of same concrete the initial slump was 85mm and after 60 minutes it dropped to 70mm. At this point i.e. after 60 minutes, at 70mm slump the stabilizer of 800ml/100kg of cement was added to the concrete. Results show that by stabilizing the concrete for more than 26 hours (i.e. in 100% stabilized) concrete the slump had dropped to 40mm from 70mm. Next day three batches of fresh concrete were prepared and the initial slump of these concretes before mixing with of stabilized concrete was 100mm, 100mm, and 90mm. After addition of stabilized concrete of 10%, 25% and 50% of the fresh concrete the measured slump was 80mm, 80mm, and 70mm, respectively. The measured slump after 60 minutes at the time of casting test cylinders for these blends of fresh and stabilized concretes of 10%, 25%, and 50% was 80mm, 80mm, and 60mm, respectively. The reduction of the final slump at 60 minutes of 50% blended concrete was about 14%. There was no reduction to the initial slump for 10% and 25% blended concrete at 60minutes.

It is evident that the 100% stabilized concrete had a large drop of slump i.e. 40% after 26 hours. However, for all blended concrete batches, the drop of a slump after addition of fresh concrete did not vary much after 60 minutes.

4.6.2 Blended cement (35% OPC and 65% slag) concrete

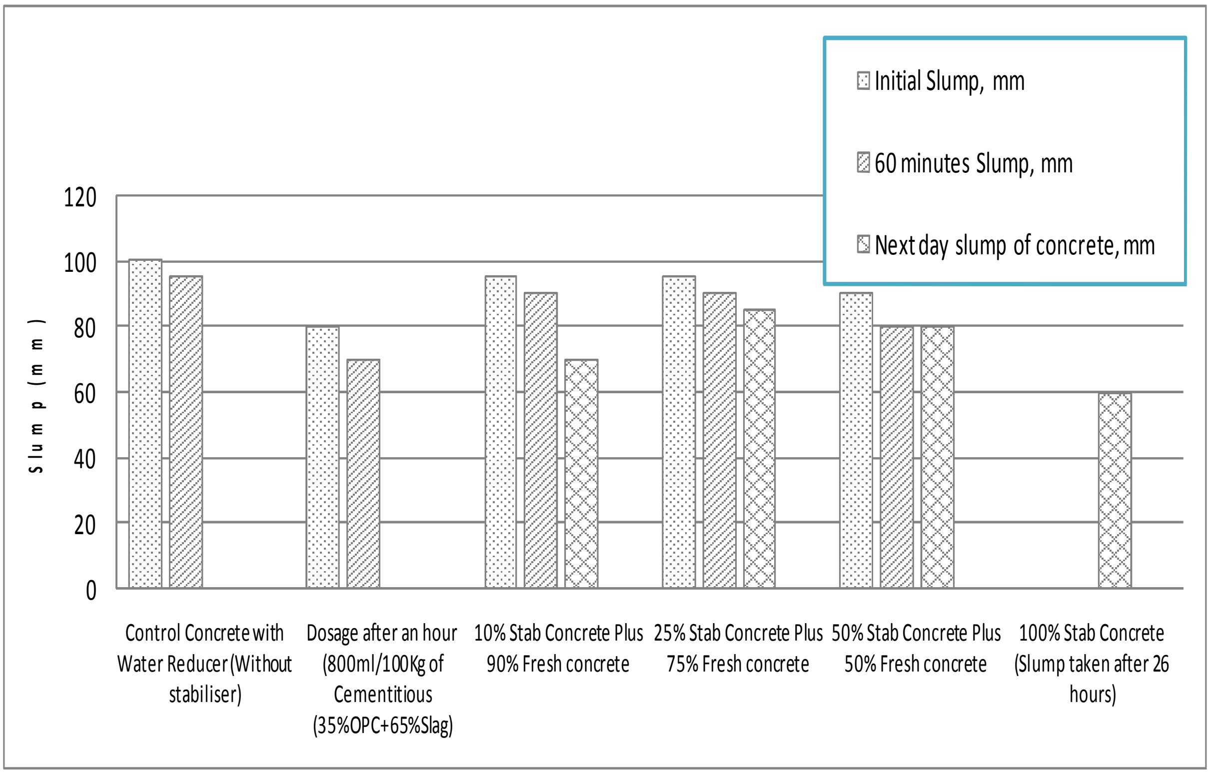


Figure 4.22 Slumps for 35% OPC and 65% slag cement concrete.

Figure 4.22 shows the effect of stabilizer on the slump of blended cement (35% OPC and 65% Slag) concrete. The control concrete’s initial slump was 100mm and after 60 minutes it dropped to 95mm. In the second batch of same concrete the initial slump was 80 mm and after 60 minutes it dropped to 70mm. It can also be seen that by stabilizing the concrete for more than 26 hours (i.e.100% stabilized concrete) the slump is dropped to 60mm from 70mm. Next day three batches of fresh concrete were prepared and the initial slump of these concretes before mixing with of stabilized concrete was 95mm, 95mm, and 90mm. After addition of stabilized concrete of 10%, 25% and 50% of the fresh concrete the measured slump was 90mm, 90mm, and 80mm, respectively. The measured slump after 60 minutes of the same concretes was 70mm, 85mm, and 80mm, respectively. The reduction of the final slump at 60 minutes for the blend concrete was about 20% for 10% blended concrete; about 5% for 25%. There was no reduction to the initial slump for 50% blended concrete at 60minutes.

The results shows that in case of blended cement concrete (35% OPC and 65% slag), with an increase in quantities of stabilized concrete in the fresh concrete the slump decreases for 10% and 25% blend concrete. It is also evident that the 100% stabilized concrete had a drop of slump value of about 14% after 26 hours. Interestingly the stabilized concrete containing 50% blend concrete exhibited the capability of holding the slump to the initial slump after 60 minutes.

4.6.3 Blended cement (75% OPC and 25% fly ash) concrete

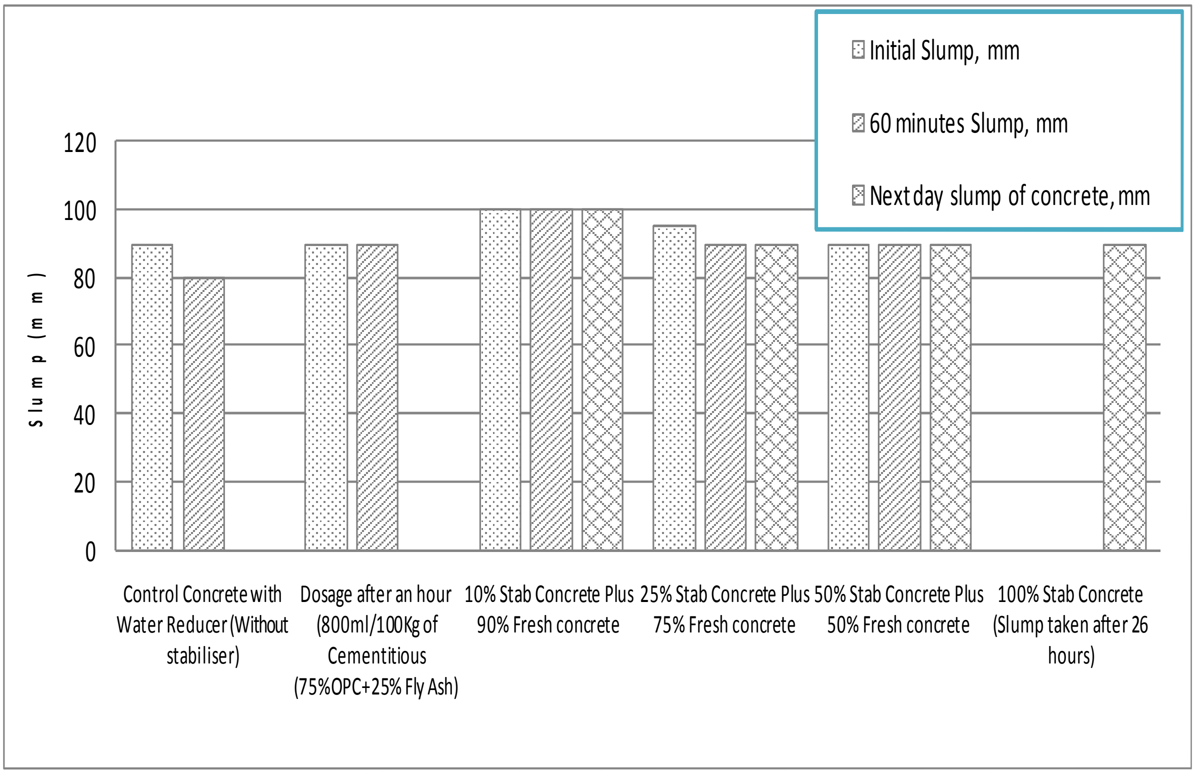


Figure 4.23 Slumps for 75% OPC and 25% fly ash cement concrete.

Figure 4.23 shows the effect of stabilizer on the slump of blended cement concrete containing 75% OPC and 25% fly ash. It can be seen that the control concretes initial slump was 90mm and after 60 minutes it dropped to 80mm. In the second batch of the same concrete the initial slump was 90 mm and after 60 minutes it was 90mm, i.e. there was no drop in the slump. The same concrete was used to stabilize for 26 hrs by adding stabilizer at the rate of 800ml/100kg of cementitious materials. It can be seen that by stabilizing the concrete for more than 26 hours (i.e. in100% stabilized concrete) the slump was unchanged. Next day three batches of fresh concrete were prepared and the initial slump of these concretes before mixing with of stabilized concrete was 100mm, 95mm, and 90mm. After addition of stabilized concrete of 10%, 25% and 50% of the fresh concrete the measured slump was 100mm, 90mm, and 90mm, respectively. The measured slump after 60 minutes was about 100mm, 90mm, and 90mm, respectively. There was no significant reduction of the final slump (at 60minutes) of blend concrete to the fresh concrete.

The results show that in the case of blended cement concrete containing 75% OPC and 25% fly ash no significant change in the slumps are observed due to the addition of increasing quantities of stabilized concretes. It is also evident that the slump in 100% stabilized concrete did not drop after 26 hours. In comparison to stabilized concrete of OPC and blended cement concrete containing 35% OPC and 65% slag, the blended cement concrete containing 75% OPC and 25% fly ash had a higher capability of holding the concrete slump for a longer period. It should also be noted that the total CaO content in both OPC and blended 35% OPC and 65% slag cement is higher than the blended 75% OPC and 25%flyash cement, and this influence the hydration reaction and subsequent setting times of those concretes.

By reviewing the above results, it can be seen that the stabilizer has a significant influence on the slump of concrete. The stabilizer had the capability of holding the slump for more than 24 hours and kept the concrete workable. However, it was noted that the drop in the slump was higher in concrete with OPC in comparison to blended cement containing 35% OPC and 65% slag, and 75% OPC and 25% fly ash.

4.7 Effect of stabilizer on setting time of concrete

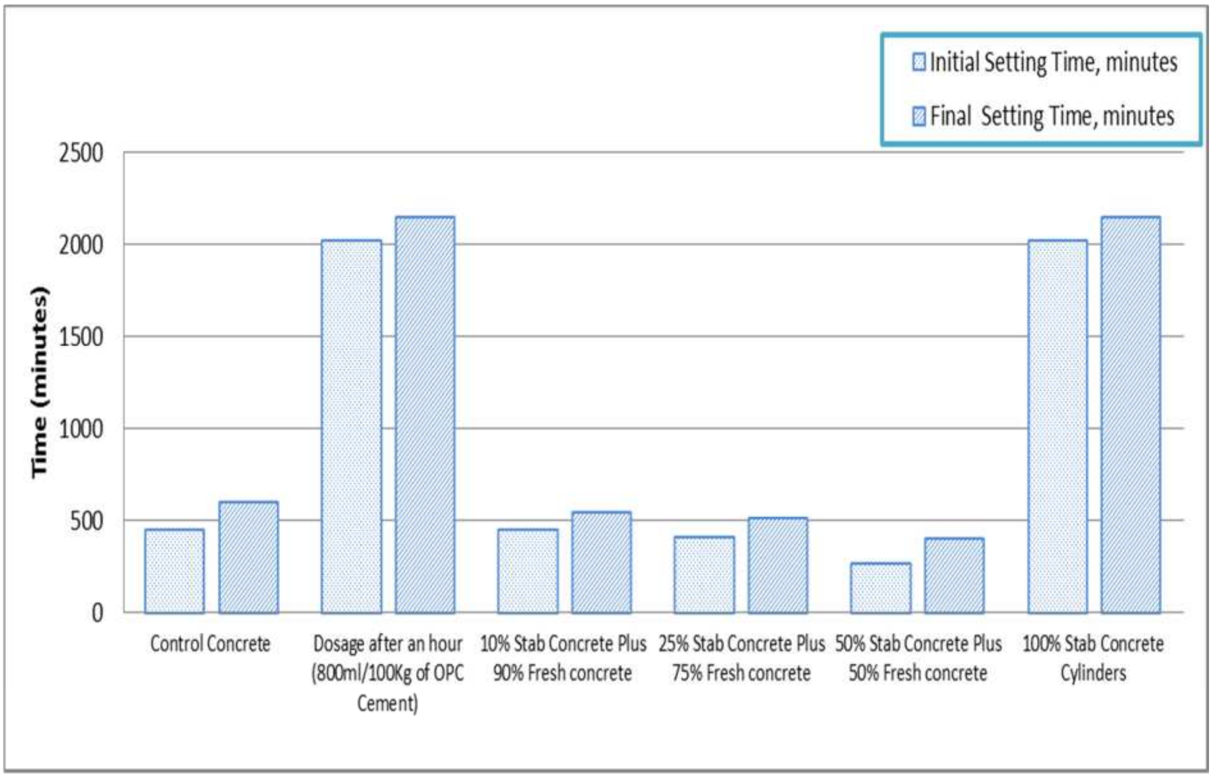


Figure 4.24 Setting time for OPC concrete.

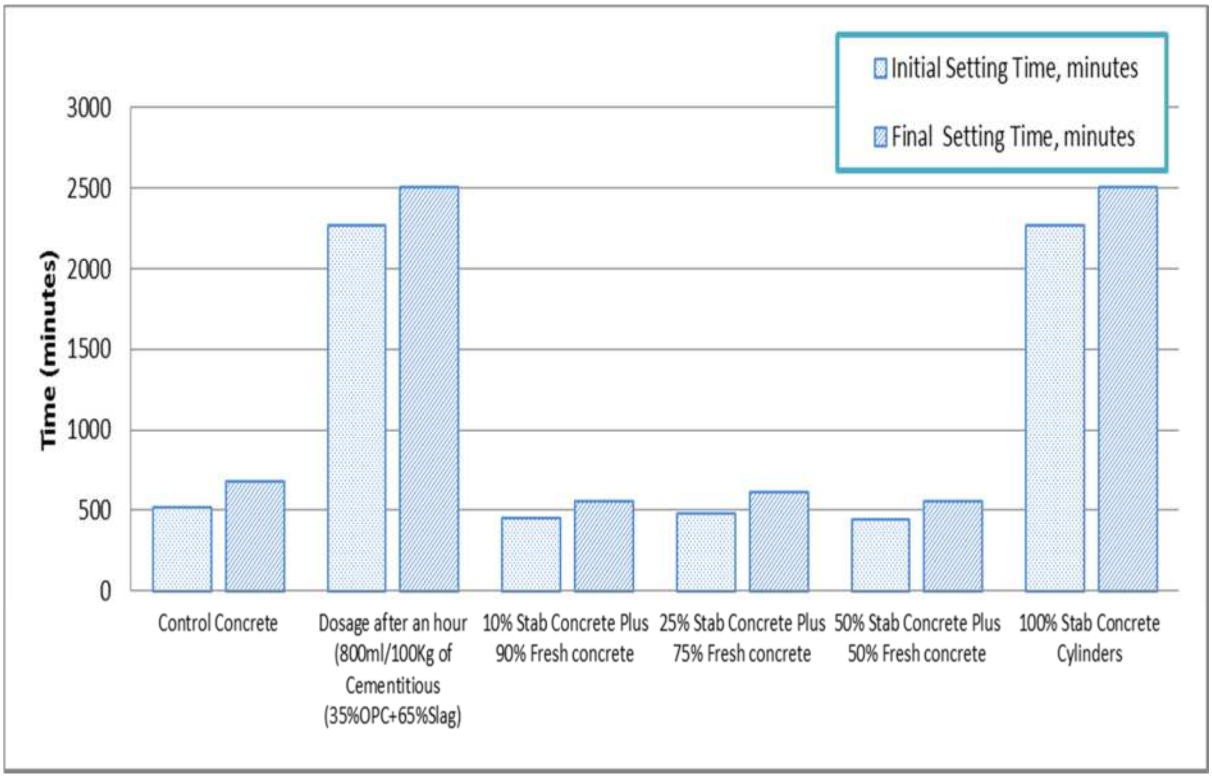


Figure 4.25 Setting time for 35% OPC and 65% slag concrete.

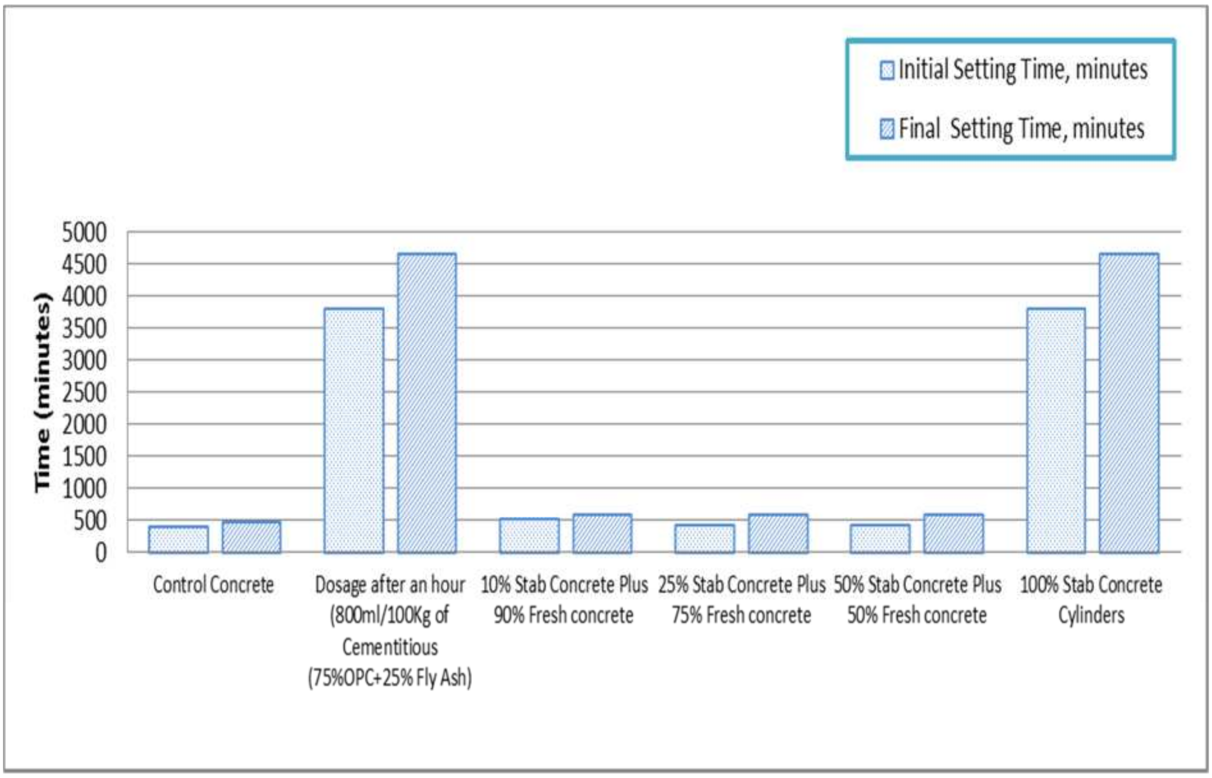


Figure 4.26 Setting time for 75% OPC and 25% fly ash concrete.

Figures 4.24- 4.26 show the effect of stabilizer on setting times of concretes containing all three types of cement and cement blends. It can be seen that both initial and final setting times are significantly increased due to the addition of stabilizer after 60 minutes in all three concretes. However, after 24 hours when different quantities of stabilized concrete i.e. 10%, 25% and 50% by weight of fresh concrete was mixed with freshly prepared concretes no significant differences in both initial and final setting times are observed compared to control concretes for all three cement types. However, in the case of 24 hrs, 100% stabilized concretes the setting times are much higher than those different replacement levels of stabilized concrete added to fresh concrete. Similar behaviors are also observed in the case of concretes containing slag and fly ash. In general, concrete containing fly ash shows longer setting times due to the addition of stabilizer than those of OPC concrete and concrete containing slag. When stabilized concrete is added to fresh concrete for all three types of cement, it appears that fresh concrete accelerates the setting time of the stabilized concrete. The stabilizer inhibits cement hydration for few hours up to several days depending on the dosage. However, after addition of the fresh concrete to stabilized concrete fresh concrete activates the hydration process of the concrete.

For, OPC concrete the initial setting time of 10% stabilized concrete and 25% stabilized concrete was similar to control concrete. However, the final setting time was slightly shorter for both concretes. Initially the stabilized concrete work as a retarder and later the fresh stabilized concrete work as an accelerator activating the concrete, making it to set early. The 50% stabilized concrete added to fresh concrete work as an accelerator at both instances, for final and initial setting time. This could be due to the effect of stabilizer weakening with the time.

In the case of blended cement concrete containing 35% OPC and 65% slag the initial and final setting time for all concretes replaced with stabilized concrete, the fresh concrete worked as an activator accelerating initiating the initial and final setting time of the blended concrete slightly earlier in comparison to control 35% OPC and 65% slag concrete.

The 75% OPC and 25% fly ash concrete had a reverse effect of retardation on final and initial setting time for all concretes replaced with stabilized concrete. The effect of the stabilizer with a combination of fly ash worked as a retarder increasing the initial and final setting time compared to control 75% OPC and 25% fly ash concrete.

The data of setting time of concrete shows that for all type of cements, the stabilizer has a good potential of prolonging the setting time of concrete and setting time can be accelerated with the addition of fresh concrete.

4.8 Effects of stabilizer on unit weight of hardening concretes

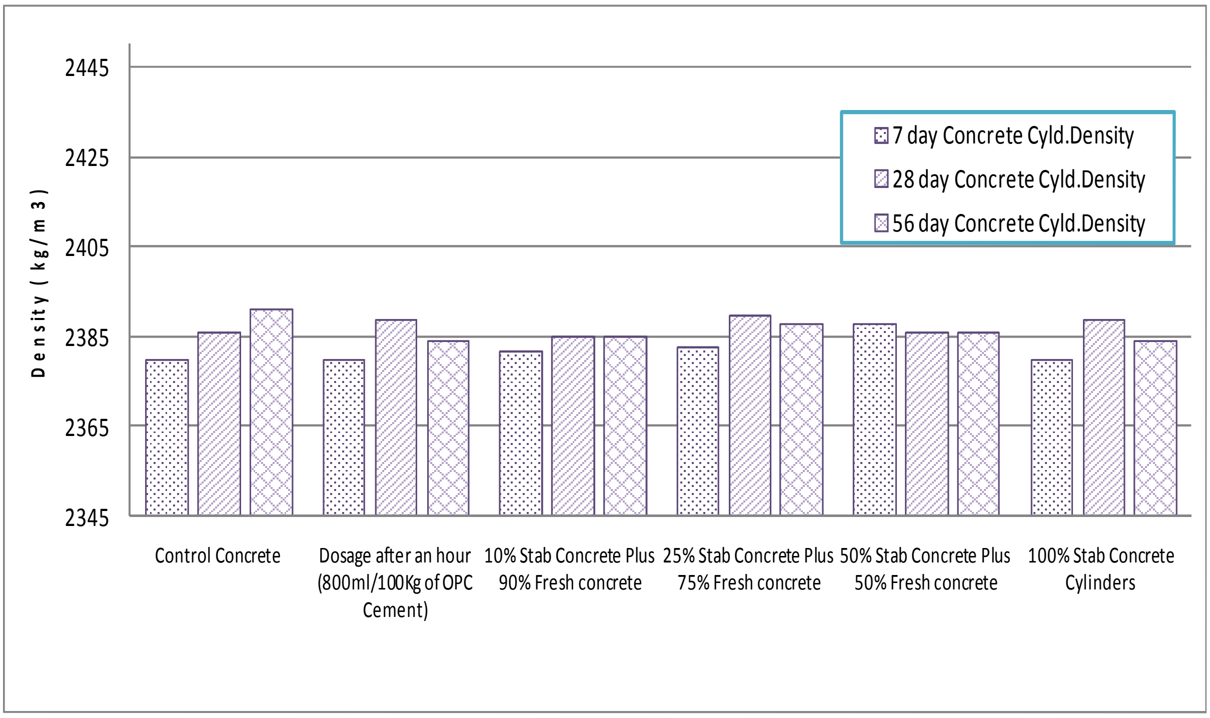


Figure 4.27 Unit weight for OPC concrete.

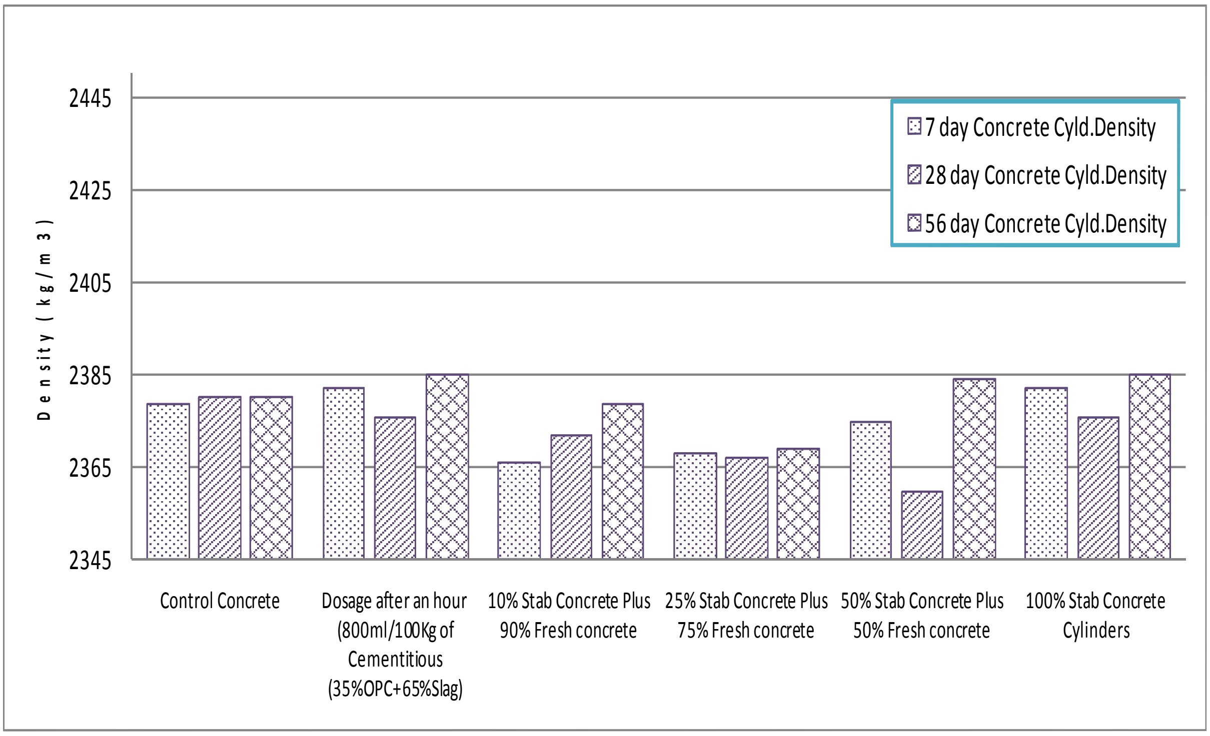


Figure 4.28 Unit weight for 35% OPC and 65% slag concrete.

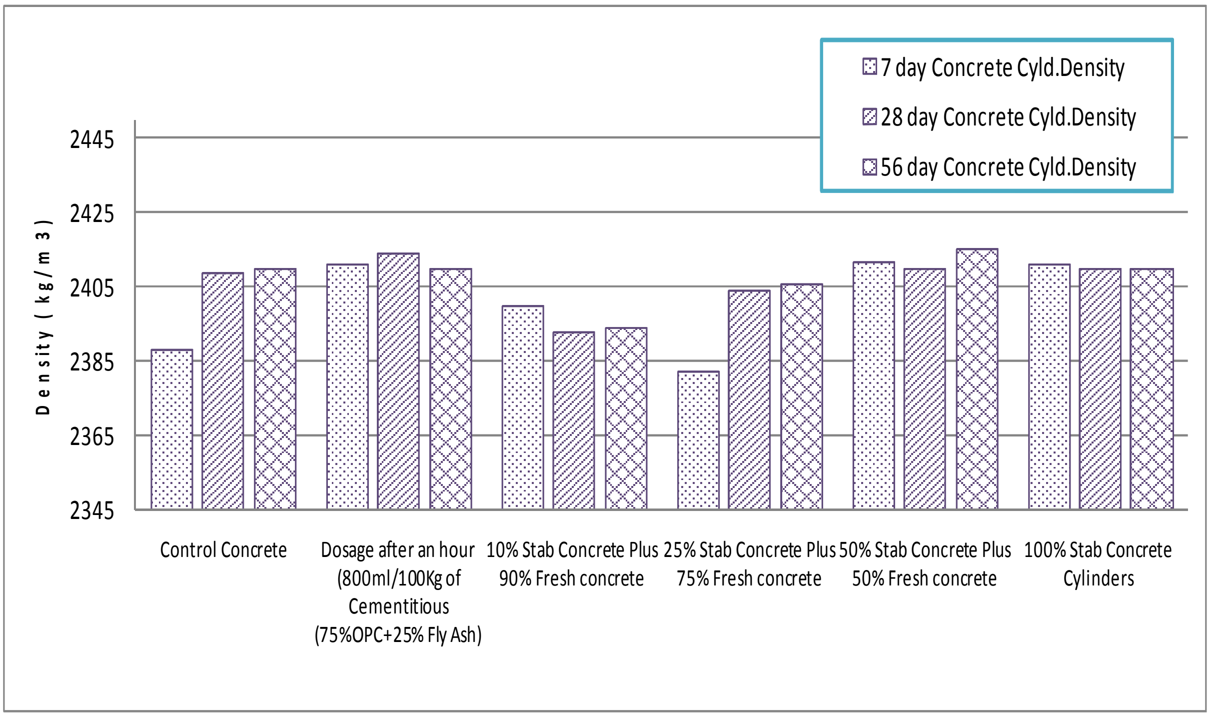


Figure 4.29 Unit weight for 75% OPC and 25% fly ash concrete.

Figures 4.27-4.29 illustrate the unit weight of concretes made with three types of cement. The average unit weight OPC concrete was around 2385kg/ m^3; for 35% OPC and 65% slag concrete the average unit weight was around 2375 kg/ m^3, and for 75% OPC and 25% fly ash, the average unit weight was around 2405 kg/ m^3 respectively. In comparison to OPC concrete, the average unit weight for slag was slightly lower whereas the average unit weight of fly ash was higher in compression to OPC concrete.

4.9 Effect of stabilizer on temperature of plastic concretes

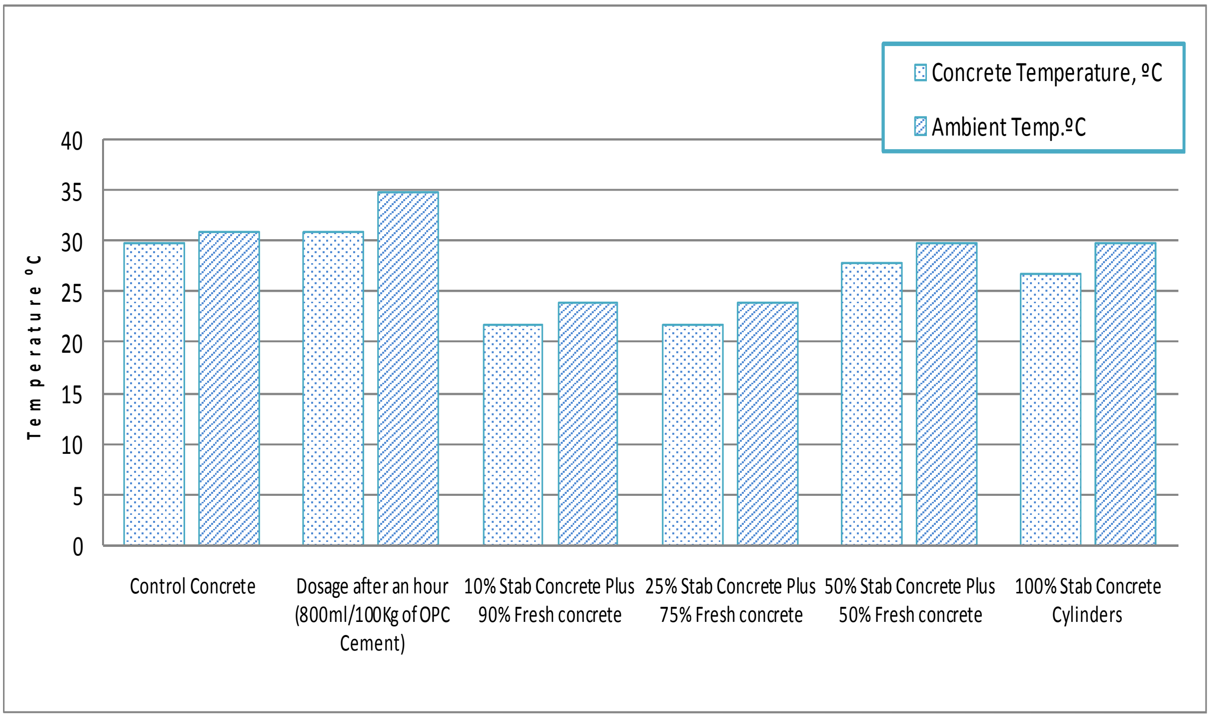


Figure 4.30 Concrete and ambient temperatures for OPC concrete

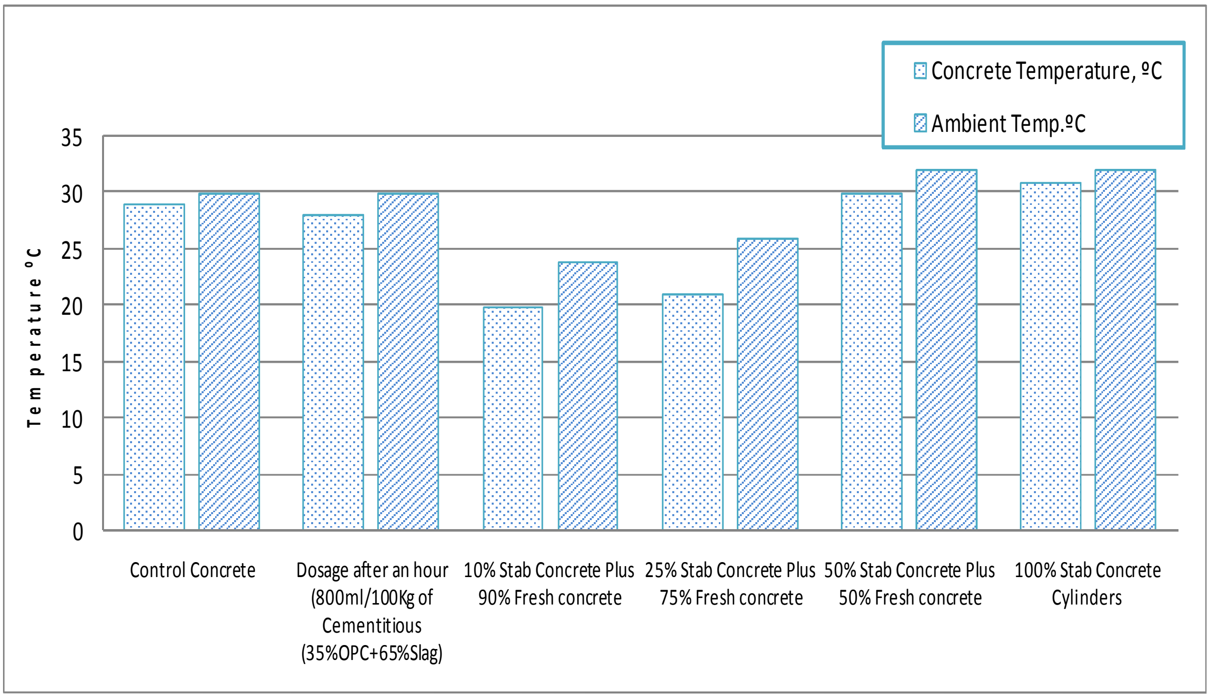


Figure 4.31 Concrete and ambient temperatures for 35% OPC and 65% slag concrete.

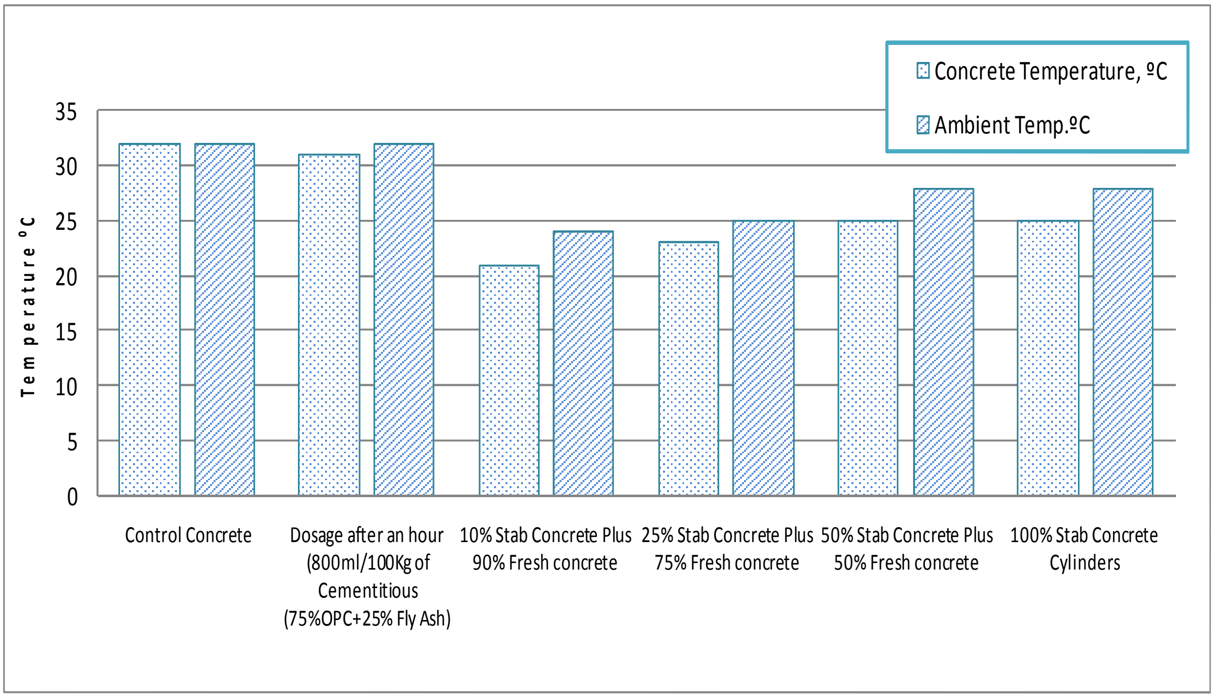


Figure 4.32 Concrete and ambient temperatures for 75% OPC and 25% fly ash concrete

Figures 4.30-4.31 show the temperature developed in all three types of concretes at their plastic stage. It can be seen that the measured concrete's temperature did not exceed the required upper limit of 35°C specified in the Australian Standard AS 1379 (2007). Typical values specified in ASTM C1064-86 are between 27°C and 35°C. Along with concrete temperature ambient temperature is also shown in the figures, to compare the developed temperature inside the concrete with that in ambient. It can be seen that the concrete temperatures developed in all three types of plastic concretes after addition of stabilizer and measured temperature after one hour are very similar to those of respective control concretes. However, when 24 hrs stabilized concretes of different quantities (e.g. 10%, 25%, and 50%) are mixed with freshly produced respective concretes, the concrete temperatures are lower than the respective control concretes and concrete temperature increases with increasing percentages of stabilized concretes, except the 100% stabilized concrete. It can also be seen that the concrete temperature is lower when the ambient temperature is lower and vice-versa. Nevertheless, the measured temperature of all stabilized concretes is lower than the respective control concrete, except in 50% and 100% stabilized slag concrete where the measured temperature is slightly higher than the control, and this is due to slightly higher ambient temperature.

4.10 Effect of stabilizer on compressive strength of concrete

To evaluate the use of stabilized concrete in a real application, the evaluation of the development of compressive strength with time is the most important mechanical properties of concrete needed to confirm as compressive strength changes during the life of the concrete structures. In these section three types of cement concrete the development of compressive strength after stabilizing for 24 hrs is studied.

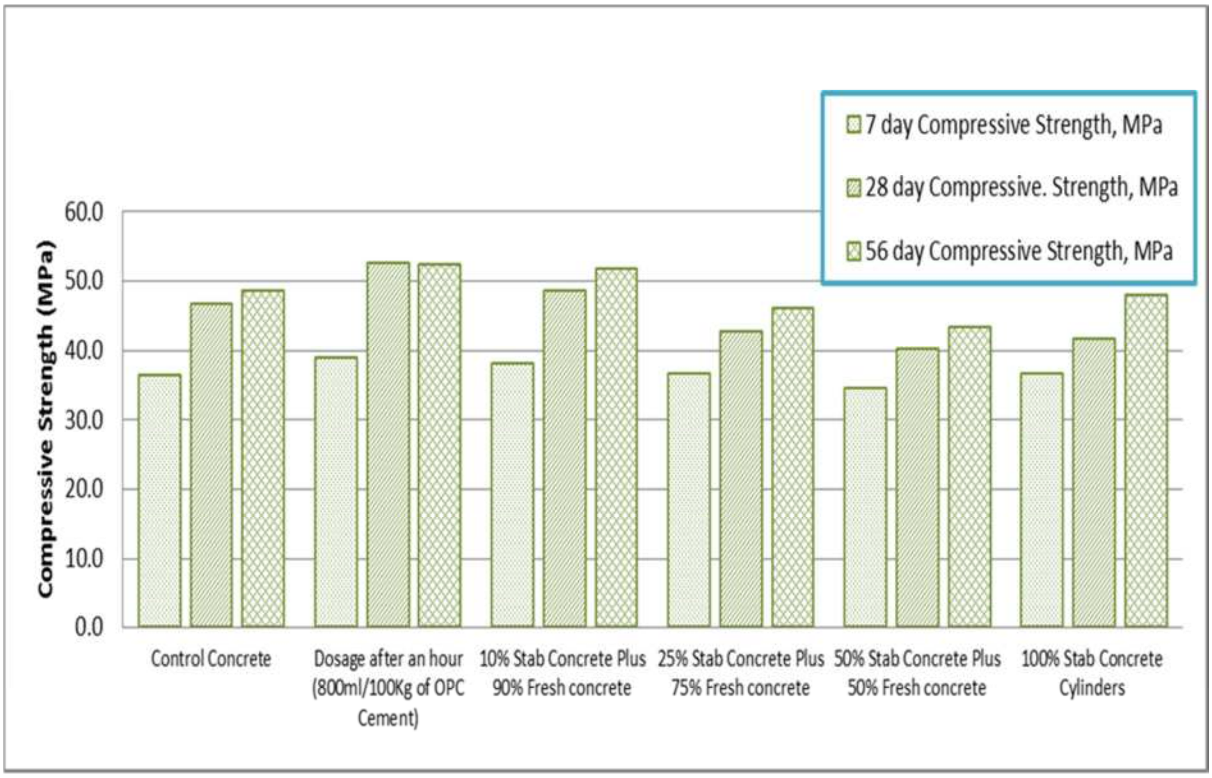


Figure 4.33 Effect of stabilizer on compressive strength of OPC concrete.

Figure 4.33 illustrates the effect of stabilizer on compressive strength of OPC concrete. It can be seen in the figure that the stabilized OPC concretes exhibited comparable compressive strengths to the control OPC concrete. It can also be seen that the OPC concretes containing 10%, 25%, and 100% stabilized OPC concretes retained about more than 90% of the compressive strength of control OPC concrete of all ages. In particular, the concrete containing 50% stabilized concrete exhibited less than 90% of the compressive strength of control at 28 and 56 days. It is also interesting to note that the concrete where the stabilizer was added after one hour of mixing and the concrete containing 10% stabilized concrete exhibited higher compressive strength than that of control of all ages. Since the total water content in stabilized mixture was the same as those used in the respective control mixtures, differences in compressive strength cannot be attributed to the difference in the water cement ratio. The differences in compressive strength may be attributed due to the increasing content of the stabilize concrete. It is also interesting to see that the 100% stabilized concrete exhibited slightly higher compressive strength of all ages than the concrete containing 50% stabilized concrete, and this can be attributed to the favorable modification of the cement hydration reaction and paste microstructure in comparison to 50% stabilized concrete. In general, all concretes containing different amounts of stabilized concretes and the concrete specimens cast after addition of stabilizer meet the acceptance requirement of 90% strength range by ASTM C 94 with the only exception of 50% stabilized concrete which slightly deviated from this criteria. The graph showing percentage growth in compressive strength is attached in Appendix B.

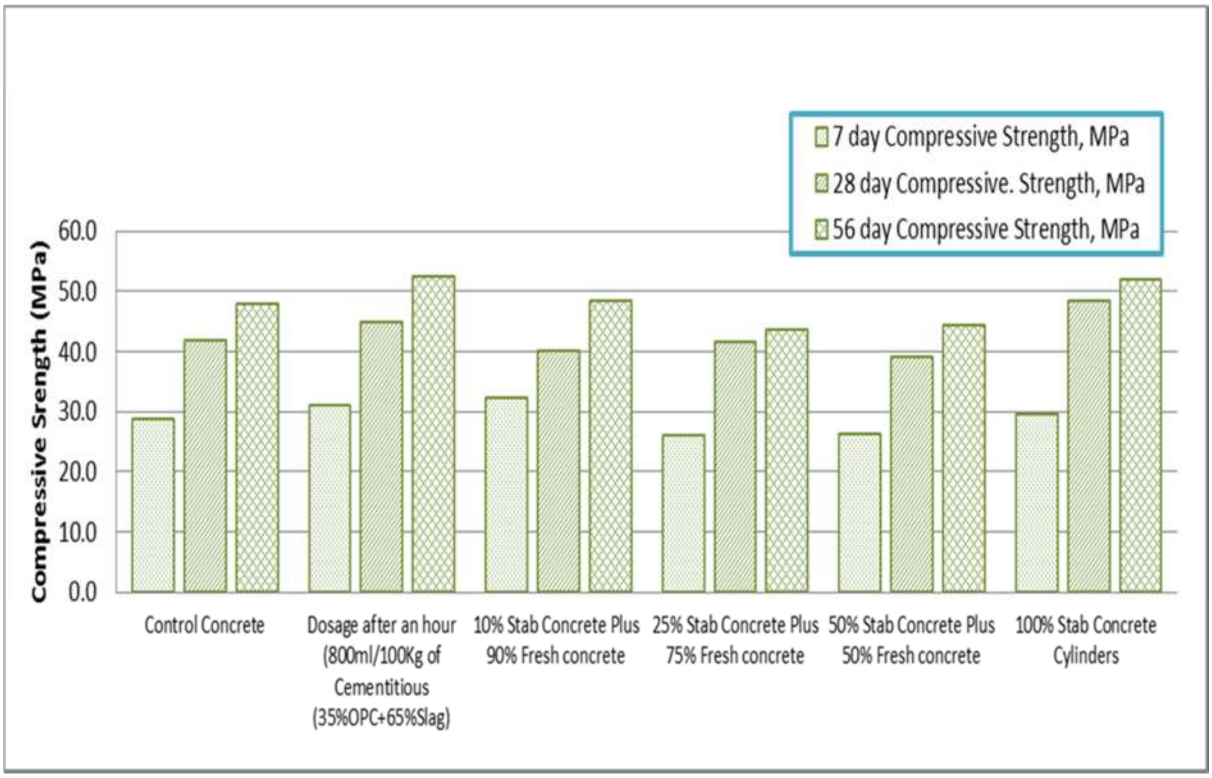


Figure 4.34 Effect of stabilizer on compressive strength for 35% OPC and 65% slag concrete.

Figure 4.34 illustrates the effect of stabilizer on compressive strength of 35% OPC and 65% slag concrete. It can be seen in the figure that the stabilized 35% OPC and 65% slag concretes exhibited comparable compressive strengths to the control 35% OPC and 65% slag concrete. It can also be seen that the 35% OPC and 65% slag concretes containing 10%, 25% and 100% stabilized concretes retained about more than 90% of the compressive strength of control concrete of all ages. It is also interesting to note that the concrete where the stabilizer was added after one hour of mixing exhibited higher compressive strength than that of control concrete at all ages. It is also interesting to see that the 100% stabilized concrete exhibited higher compressive strength of all ages than the control concrete, and this can be attributed to the favourable modification of the cement hydration reaction and paste microstructure in comparison to control concrete. In general, all concretes containing different amounts of stabilized concrete and the concrete specimens cast after addition of stabilizer meet the acceptance requirement of 90% strength range by ASTM C 94 criteria. The graph for percentage growth in compressive strength is attached in Appendix B.

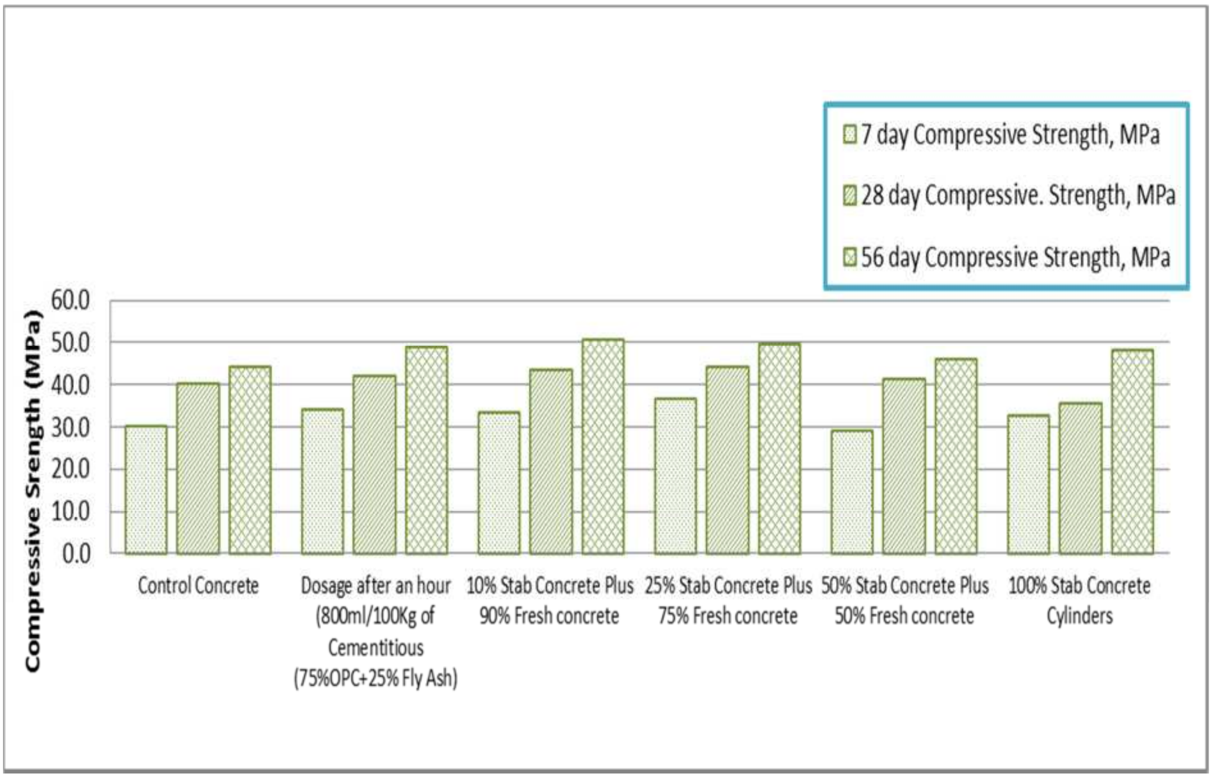


Figure 4.35 Effect of stabilizer on compressive strength for 75% OPC and 25% fly ash concrete.

Figure 4.35 illustrates the effect of stabilizer on compressive strength of 75% OPC and 25% fly ash concrete. It can be seen in the figure that the stabilized 75% OPC and 25% fly ash concretes exhibited comparable compressive strengths to the control 75% OPC and 25% fly ash concrete. It can also be seen that the 75% OPC and 25% fly ash concretes containing 10%, 25% and 50% stabilized concretes retained about more than 100% of the compressive strength of control concrete at 28 and 56 days. In particular, the concrete containing 100% stabilized concrete exhibited less than 90% of the compressive strength of control at 28days but the increase in strength at 56 days is above 100%. The lower than 90% at 28 days can be due to the retarding effect of both the fly ash and stabilizer in the concrete leading to latter compressive strength gain in the concrete. It is also interesting to note that the concrete where the stabilizer was added after one hour of mixing and the concrete containing 10% stabilized concrete and concrete containing 25% stabilized concrete exhibited higher compressive strength than that of control of all ages. Since the total water content in stabilized mixture was the same as those used in the respective control mixtures, differences in compressive strength cannot be attributed to the difference in the water cement ratio. The differences in compressive strength may be attributed due to the increasing content of the stabilize concrete. It is also interesting to see that the 25% stabilized concrete exhibited slightly higher compressive strength of all ages than the other concretes; this can be attributed to the favourable modification of the cement hydration reaction and paste microstructure in the concrete. In general, all concretes containing different amounts of stabilized concretes and the concrete specimens cast after addition of stabilizer meet the acceptance requirement of 90% strength range by ASTM C 94 with the only exception of 100% stabilized concrete which slightly deviated from this criteria. The graph for percentage growth in compressive strength is attached in Appendix B.

4.11 Effect of stabilizer on drying shrinkage of concrete

Similar to the compressive strength to evaluate the use of stabilized concrete in a real application, the evaluation of the development of shrinkage strains with time is the most important mechanical properties of concrete needed to be confirmed as both properties change during the life of the concrete structures. Drying shrinkage of 24 hrs stabilized concretes made with three types of cement is studied in this study.

The drying shrinkage of all three types of stabilized concretes is measured after different drying period up to 56 days and is shown in Figure 4.36 to 4.38. It can be seen a general trend of increasing drying shrinkage with an increase in drying periods of all three concretes with different amounts of stabilized concretes. The 35% OPC and 65% slag; and 75% OPC and 25% fly ash cement concretes showed slightly lower shrinkage than the ordinary concrete for all stabilized contents. When the amounts of stabilized concretes are increased, there is a slight increase in trend of drying shrinkage for all three types of cement concrete. Similar to compressive strength results, the blended concretes containing 10% and 25% stabilized concretes for all three types of cement shows similar shrinkage at all ages to control the mix of the respective cement. In accordance with AS

3972 (2010), the maximum shrinkage limit specified for a shrinkage limited cement is 750 microstrain, in all three type of concrete, the drying shrinkage is below 750 microstrains.

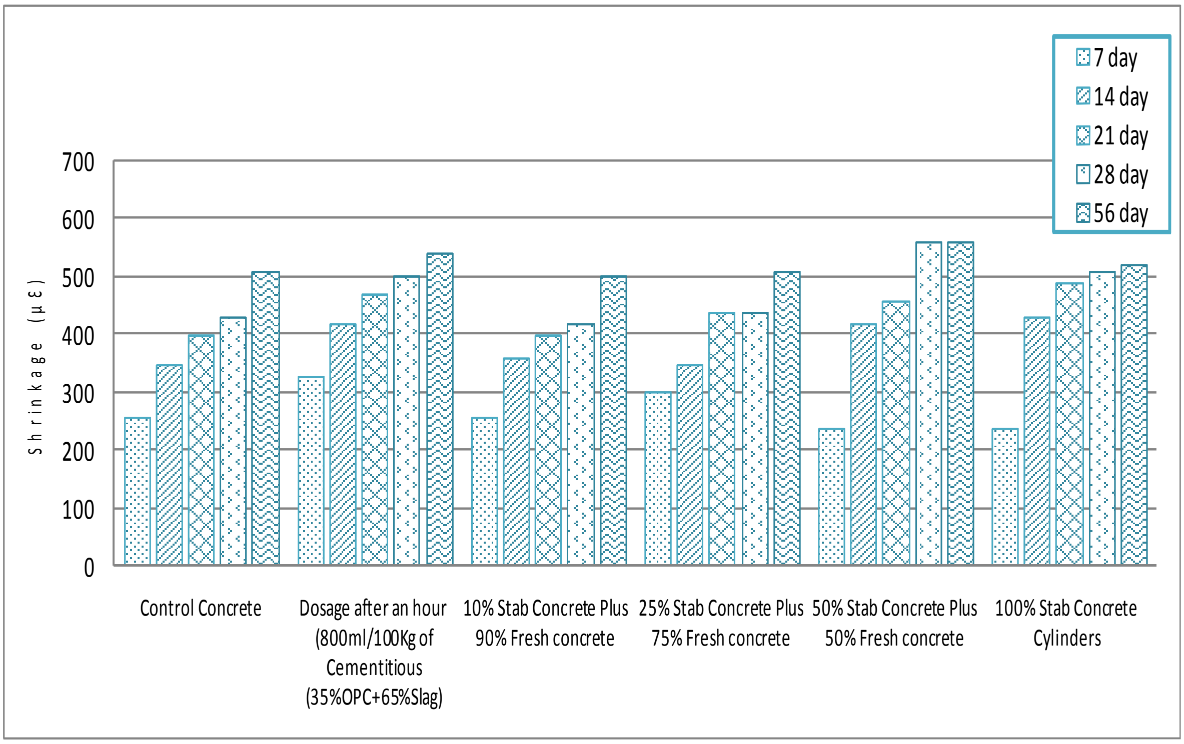


Figure 4.36 Effect of stabilizer on shrinkage for OPC concrete.

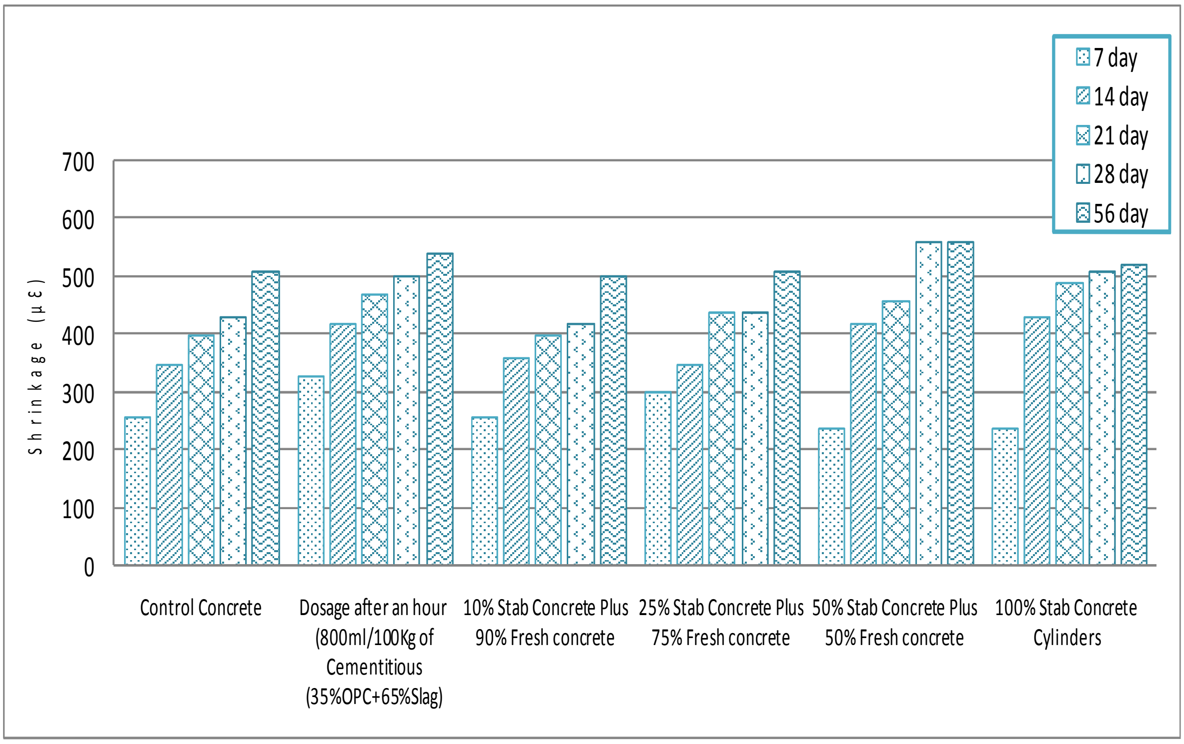


Figure 4.37 Effect of stabilizer on shrinkage for 35% OPC and 65% slag concrete.

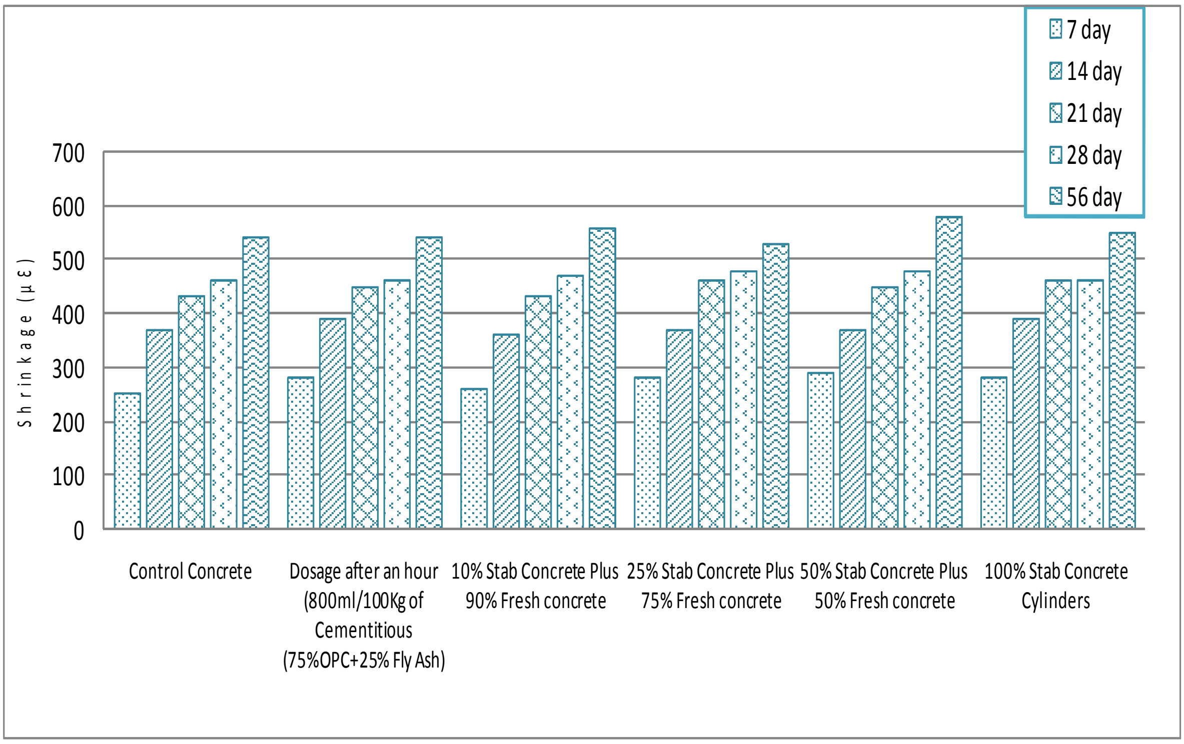


Figure 4.38 Effect of stabilizer on compressive strength for 75% OPC and 25% fly ash concrete.

4.12 Studies on upgrading 32MPa stabilized concrete to 40MPa

In the above sections, the feasibility of using stabilizer in stabilizing OPC concrete and other blended cement concretes containing slag and fly ash are evaluated in terms of measuring plastic and mechanical properties. The results show that the addition of stabilizer at 800ml/100kg of cementitious materials in concrete did not significantly affect the plastic and mechanical properties of 24 hrs stabilized concretes and meets the requirement for compressive strength in accordance with ASTM C 94.

The benefit of using stabilizer to stabilize the concretes for at least 24 hrs for subsequent re-use is further extended to upgrade the lower grade stabilized concrete to upper-grade concrete by adjusting the ingredients is discussed in this section. The mechanical properties of concrete were studied as discussed after stabilizing 32MPa grade concrete for 24 hours and later upgrading it to 40MPa grade of concrete. 25% of stabilized 32MPa concrete was used with 75% fresh 40MPa grade concrete mixes to study the mechanical properties of the concrete. Upgrading of concrete was achievable with proper determination of stabilizer dosage and proper calculation of raw material required to compensate the shortfall in 32MPa grade concrete to achieve the 40MPa grade concrete.

Figures 4.37 to 4.40 show the comparative properties of 32MPa grade concrete, and the upgraded 40MPa grade concretes made by all three types of cement.

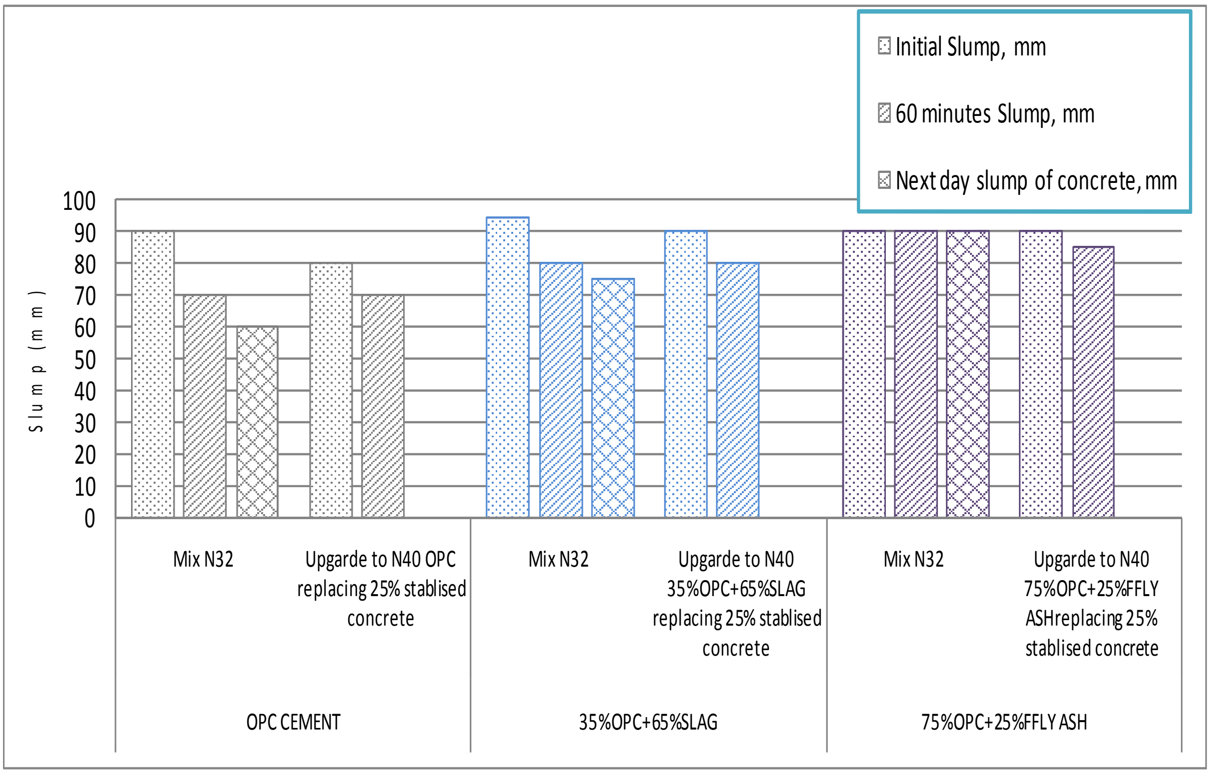


Figure 4.39 Slump of stabilized 32MPa concrete and upgraded 40MPa concrete for OPC, slag and fly ash.

Figure 4.39 illustrates the slumps of all three types of concrete with OPC and blended cement containing slag and fly ash of 32MPa grade and those upgraded to 40MPa. It can be seen that in 32MPa OPC concrete the initial slump was 90mm which dropped to 70mm after an hour and at this stage, the stabilizer at a rate of 800ml/100kg of cementitious materials was added to the concrete. The measured slump at next day after 24 hours of stabilized concrete was 60mm. The drop in a slump after addition of stabilizer was just 10mm; this indicates the capability of stabilizer to retard the concrete and hold the workability of the concrete after 24 hours. In the case of upgraded 32MPa concrete to 40MPa, the initially measured slump was 80mm and that after an hour was 70mm. The slump drop for upgraded 40MPa concrete after one hour was less (10mm) than the drop in stabilized 32MPa (20mm), indicating the effectiveness of stabilizer on the upgraded 40MPa concrete.

In the case of concrete containing 35% OPC and 65% Slag the initial slump was 95mm which dropped to 80mm after an hour, at this stage the stabilizer was added to the concrete. The measured slump next day after 24 hours of stabilized concrete was 75mm. The drop in a slump after addition of stabilizer was just 5mm which indicates the capability of stabilizer and slag to retard the concrete and hold the concrete for 24 hours. In the case of upgraded 40MPa concrete, the initial slump was 90mm, and it dropped to 80mm after an hour. The drop of a slump for 40MPa concrete after one hour was less (10mm) than the drop in 32MPa (15mm), indicating the effectiveness of stabilizer on the upgraded 40MPa concrete.

In the case of 40MPa upgraded concrete containing 75% OPC and 25% fly ash, the initial slump was similar to that of stabilized 32MPa concrete. However, a slight reduction in one-hour slump value from 90mm to 85mm is observed. In some cases, the drop of a slump of the stabilized concrete could have been due to the effect of ambient temperature and evaporation of water that may have taken place while holding the concrete in a closed container without mixing or disturbing the concrete for more than 24 hours. In all three types of concretes, it was noted that the slump dropped after upgrading the stabilized 32MPa concrete to 40MPa, and this shows that the freshly added ingredients e.g. cement and cementitious material, aggregate, water and normal water reducing admixture works as an activator and initiates the process of setting.

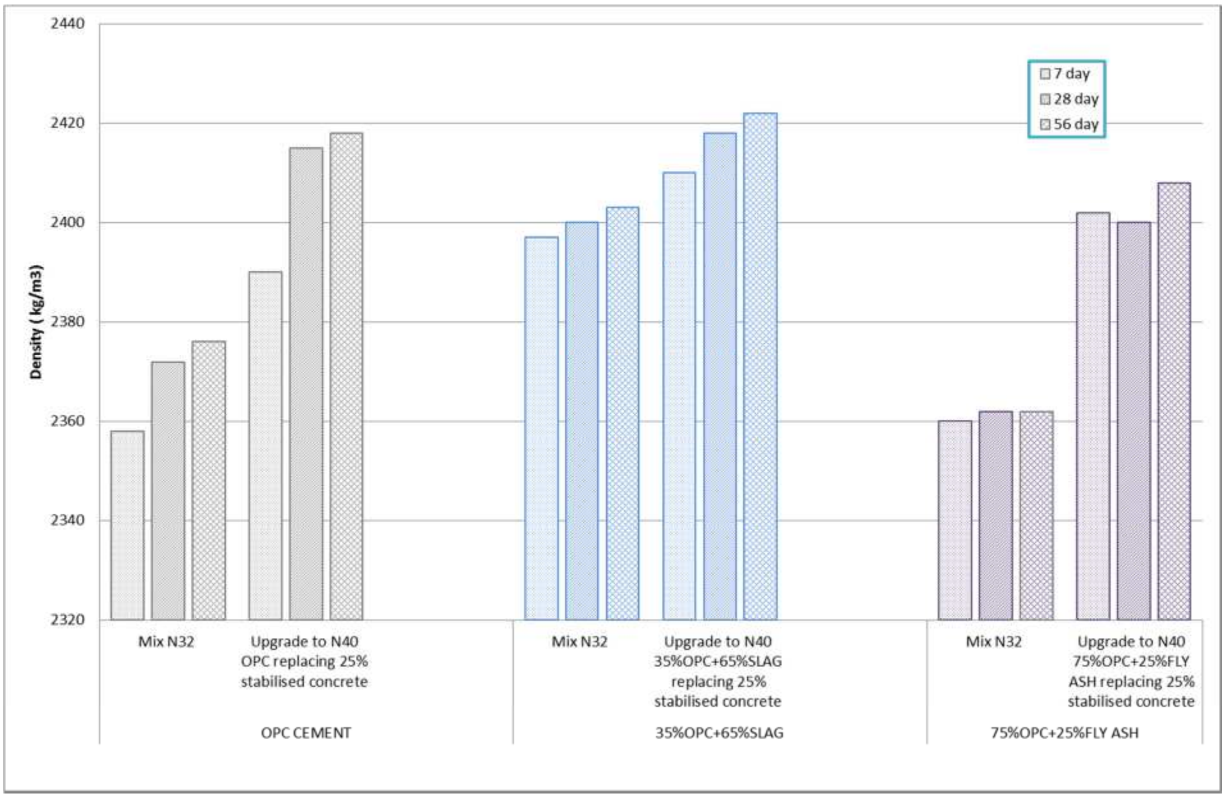


Figure 4.40 Unit weights of stabilized 32MPa concrete and upgraded 40MPa concrete for OPC, slag and fly ash.

Figure 4.40, illustrates the unit weight of 32MPa stabilized concretes and upgraded 40MPa concretes of all three types. It can be seen that there is an increase in unit weight of concrete due the addition of ingredients; cementitious content, coarse and fine aggregate, water and normal water reducing admixture for all type of concrete. The therotical value checked using the densities of the materials and assuming air content of 2% indicates the increase in density of concrete around 0.5% to 1% that is within the accepatable limit. Apart from this variation of unit weight, comparing the concrete with different types of binder the unit weight of concrete with slag was slightly higher than OPC concrete and concrete containing fly Ash. The lowest unit weight was for fly ash concrete. This variance is partially attributed due to the types of binders (slag and fly ash) used considering the density of the binders and the correction made to achieve the yield of concrete to 100 percent.

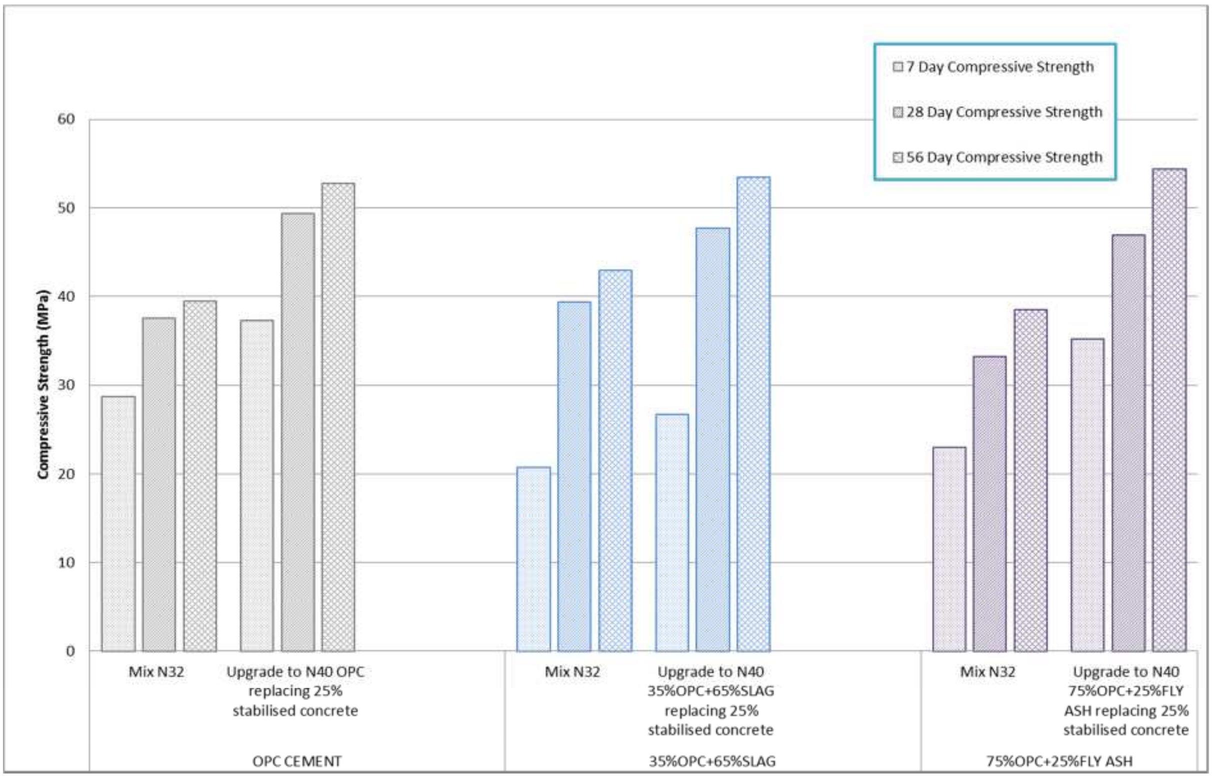


Figure 4.41 Compressive strength of stabilized 32MPa concrete and upgraded 40MPa concrete for OPC, slag and fly ash.

Figure 4.41 shows the compressive strength development of upgraded 40MPa concrete compared to stabilized 32MPa concrete of all three types of cement. It can be seen that upgraded all three types of concretes exceeded the target 28 days compressive strength of 40MPa. However, there was variation in the strength gain at 7, 28 and 56 days for different types of binders. For example, at 7days, the compressive strength achieved by slag and fly ash concrete was about 72% and 94 % of that of OPC concrete and at 28days those values were about 96% and 95% of that of OPC concrete. At 56 days that concrete overcome the deficiency in compressive strength and the strengths were about 101% and 103% of that of OPC concrete

The slightly lower compressive strength at 7 and 28 days can be attributed to the slow pozzolanic reaction of slag and fly ash in those concrete and increase in 56 days compressive strength of those concretes may be due to favorable modification of microstructure due to formation of additional calcium silicate hydrate gels during pozzolanic reaction on silicon dioxide and aluminium oxide of slag and fly ash with free lime ($Ca(OH)_2$) in those concretes.

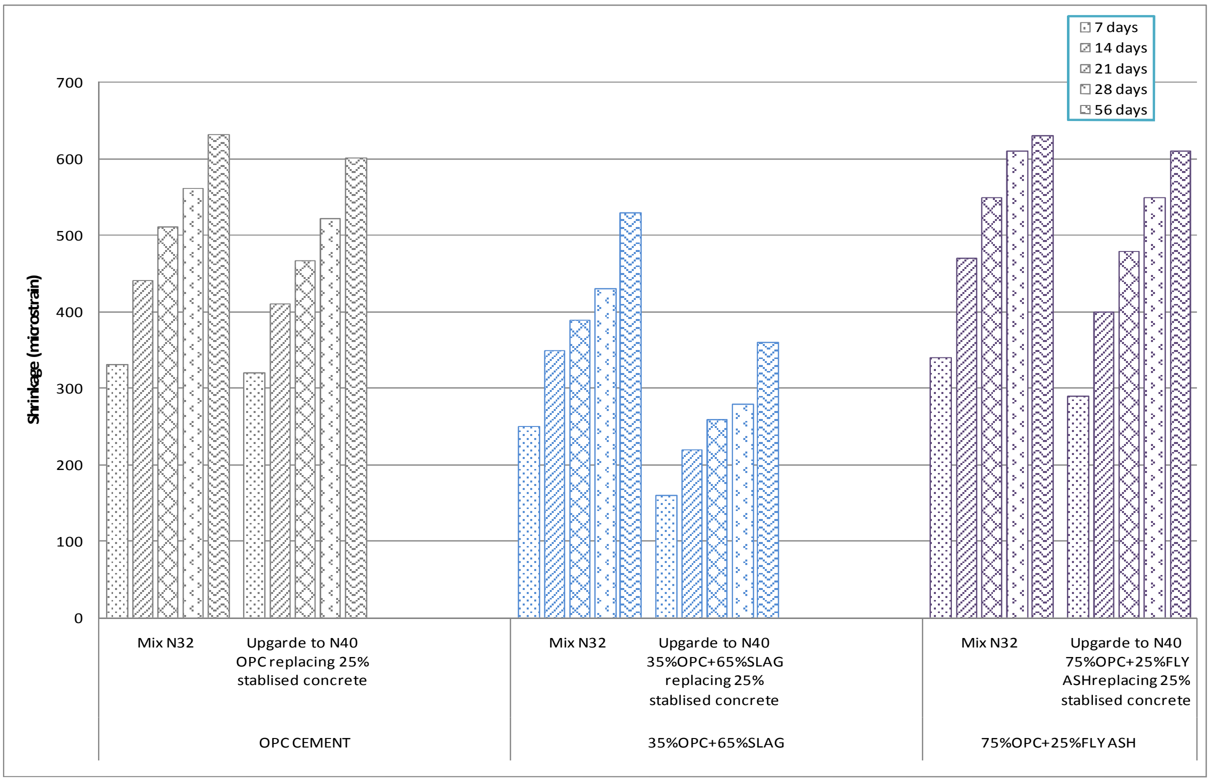


Figure 4.42 Drying shrinkages of stabilized 32MPa concrete and upgraded 40MPa concrete for OPC, slag and fly ash.

Figure 4.42 illustrates the drying shrinkage of stabilized 32MPa and upgraded 40MPa concretes of all three types. It can be seen that the drying shrinkage of upgraded stabilized concrete of all three types is lower than their respective stabilized concretes. By comparing the three concrete types, the slag concrete had the lowest shrinkage compared to the OPC and Fly Ash concretes.

CHAPTER V

CONCLUSIONS AND RECOMMENDATION

5.1 Introduction

The study was conducted to study the effect of stabilizer dosages on efflux time of OPC and blended cement containing 35%OPC and 65% slag, and 75%OPC and 25% fly ash grouts and temperature rise during hydration reaction of respective cement grouts. The effect of selected stabilizer dosage on plastic and mechanical properties of stabilized concretes along with upgrading 32MPa stabilized concrete to 40MPa concrete containing above three types of cement is also presented.

A systematic process was followed to reach and conclude the outcome of the experiment. As discussed in Chapter 3 proper process and methodology was followed to study the effect of stabilizer on a slump (workability), concrete temperature, setting time, unit weight, and compressive strength and drying shrinkage.

Based on the obtained experimental results the following conclusions are summarized:

1. For a particular efflux time and stabilizer dosage, the holding time of blended cement containing 35% OPC and 65% slag; and 75%OPC and 25%fly ash grouts is longer than the OPC cement grout. Among blended cement, the 75%OPC and 25%fly ash cement grout showed longest holding time. It is observed that the stabilizer has a strong capability of holding the setting time all three cement grouts. This property of stabilizer is beneficially used in this study to stabilize the concrete.

2. The time required to reach the peak temperature during hydration of all three cement pastes is increased with increase in stabilizer dosages. The blended 75%OPC and 25%fly ash cement grout showed about more than 40% longer time required to reach the peak temperature than the OPC and blended 35%OPC and 65%slag cement grouts. The rate of decrease of peak temperature with increasing stabilizer dosages is higher in OPC and blended 75%OPC and 25%fly ash cement than the blended 35%OPC and 65% slag

cement. This concludes that with the extended time of the peak temperature prolongs the hydration of the cement providing longer life for the reuse of concrete stabilized concrete.

3. The initial slump value of all three concretes is within the tolerance except it is higher when stabilizer dosage is added after an hour. The final slump of all three concretes containing different amounts of stabilized concretes is comparable to the control concrete without stabilizer indication the slumps can be maintained for a longer period.

4. The initial and final setting time of stabilized concretes of all three types of cement are increased by more than 5 times than those of control concrete, with about 11 and 6 times increase in blended cement concretes, respectively.

5. An increase in compressive strengths of all ages is observed in blended concretes containing 10% stabilized concretes for all three types of cement. 100% stabilized concretes of blended cement held for 24 hrs exhibited higher compressive strength at all ages than the control mix. At 7 days, the compressive strength of both blended cement stabilized concretes is lower than its OPC cement counterpart. However, they showed recovery at 28 and 56 days.

6. All three types of concretes showed almost the same drying shrinkage with no significant difference irrespective of the increase of stabilized concretes in the fresh concrete. Hence, conclude that the concrete can be stabilized and reused without effecting the harden properties of the concrete.

7. The 32MPa stabilized concrete for all three types of cement could be upgraded to 40MPa without affecting the concrete performance on workability, compressive strength and drying shrinkage.

8. Stabilization of plastic ordinary Portland cement concrete and concretes containing fly ash and slag using this particular stabilizer is a viable option to recycle and reuse of such plastic returned concrete without sacrificing plastic state and harden state mechanical properties of above concretes.

5.2 Summary

Understanding the variation of setting time in cement and blended cement using Vicat apparatus was beneficial to determine the effect of stabilizer dosages on the cement and blended cement grouts with Marsh cone and Coffee cup method to achieve a reasonable dosage of stabilizer which could be used without affecting the plastic and mechanical properties of concrete. The plastic and mechanical properties of stabilized concrete did not significantly vary in comparison to control concrete. Hence, the study indicates that addition of a stabilizer to return concrete within 60 minutes of addition of water will extend setting time enough to permit and incorporate to fresh concrete within certain limits without significantly affecting the plastic and mechanical properties of final concrete. The experiment showed the ability of the stabilizer to upgrade lower grade stabilized concrete higher grade, without affecting affect the plastic and mechanical properties of final concrete. Finally, the results of this research confirm the potential use of a stabilizer in recycling concrete in its plastic stage particularly without sacrificing plastic state and harden state mechanical properties of concrete of different types of cement. The reusing of concrete in the plastic state with stabilizer can produce excellent environmental benefits and mitigating the problem concrete industry encounters with the disposal of unused concrete.

5.3 Recommendations for further studies

From the results and conclusions drawn from the analysis, some recommendations for further works are included as follows:

1. The compressive strength results that have been found in this study should be validated by a wider testing scope such as tensile and flexural strength tests.

2. The experimental work is done on mechanical durability; properties of concrete focused the compressive strength and drying shrinkage. However, the durability properties tests such as alkali-silica reaction (ASR), sulfate resistance, water sorptivity, chloride permeability, chloride-induced corrosion, carbonation, etc. needed to validate the findings on this study based on experimental evidence. The long term testing should be further examined and validated.

3. A limited study being done on stabilized blended cement concrete, further more studies is necessary to carry out on different blends of cement from different resources to validate the effect of stabilizer particles in the performance of concrete.

4. From the outcome, the experimental results and the analysis, the challenge for further research on the use of stabilized concrete for building construction and its compatibility in environmental issues are still necessary.

5. The average stabilizer cost required to stabilize the concrete is approximately around 18% of the total ingredient cost used in the concrete. However, as the concrete is reused the recycling cost would be minimal. The cost related to the process requires further investigation and validation based on the raw material cost plus the operational cost to store the concrete in a plastic state and the overheads cost incurred to handle the process.

REFERENCES

- Aïtcin, P.C. and Baalbaki, M. (1993), Concrete admixtures. Key components of modern concrete: Concrete Technology. New trends, Industrial applications (Proc. Intl. Rilem Workshop, ConTech94, Barcelona, Spain), ed. A. Aguado, R. Gettu, and S.P.Shah, E & FN Spon, London, UK, PP.33-47.
- Al-Shamshi, A.M., Sabouni, A.R., and Bushlaibi, A.H. (1993) Influence of self-retarding superplasticizer and micro silica on setting time of pastes at various temperatures. Cement and concrete research, 23:592-598.
- AS1012.1 (2014), "Method 1: Methods of testing concrete –Sampling of concrete. Standards Australia.
- AS1012.3.1 (1998), "Method 3.1.: Determination of properties related to the consistency of concrete-Slump Test". Standard Australia.
- AS1012.9 (1999), "Method 9: Determination of the compressive strength of concrete specimen". Standard Australia.
- AS1012.12 (1998), "Method 12.1: Determination of mass per unit volume of hardened concrete- Rapid measuring method". Standards Australia.
- AS1212.13 (1992) "Determination of the Drying Shrinkage of concrete samples prepared in the field or in the laboratory'. Standard Australia.
- AS1012.18 (1996). "Method 18: Determination of setting time of fresh concrete, mortar, and grout by penetration resistance." Standards Australia.
- AS 1379 (2007), "Specification and supply of concrete- Standards Australia", Sydney NSW 2001.
- AS2350.4 (2006), "Methods of testing Portland, blended and masonry cement-Setting time"- Standards Australia.
- AS 2758.1 (2014), "Aggregates and rock for engineering purposes – Concrete aggregates", Standard Australia.
- AS3582.1 (1998), "Supplementary cementitious for use with Portland and blended cement- Fly ash". Standard Australia.
- AS3582.2 (2001), "Supplementary cementitious for use with Portland and blended cement- Slag- Ground granulated iron blast-furnace", Standard Australia.
- AS 3972 (2010), "General purpose and blended cement", Standards Australia.
- ASTM C 94,(2001), Standard specification for Ready-Mixed concrete, American Society for Testing and Materials
- ASTM C 186, (2002), Standard test method for heat of hydration of hydraulic cement, American Society for Testing and Materials
- ASTM C 403-05 (2005). Standard test method for time of setting of concrete mixtures by penetration resistance. American Society for Testing and Materials.
- ASTM C 451 (1989). Standard test method for early stiffening of hydraulic cement (Paste method). American Society for Testing and Materials.
- ASTM C 939 (2005). Standard test method for the flow of grout for preplaced-aggregate concrete (Flow cone method. American Society for Testing and Materials. Annual book of ASTM standards. V. 04.02 Construction. Philadelphia, USA.
- ASTM C 1064, (1993), Standard test method for temperature of freshly mixed Portland cement concrete, American Society for Testing and Materials

- Ballim,Y. (2004). A numerical model and associated calorimeter for predicting temperature profiles in mass concrete. Cement Concrete and Composites 26:695-703.
- Bascoka, A., Ozkul, M.H. and Artirma, S. (1998) Effect of Chemical Admixtures on Workability and Strength Properties of Prolonged Agitated Concrete. Cement and concrete research, 28:737-747.
- Ben Bassat,M.(1995). Water reducing/retarding admixtures. Application of Admixtures in Concrete. State -of-the -art report. RILEM TC 84 –AAC.Rilem Technical Committee.
- Bhaty, J.I., and Benfill, P.F.G. (1984) A viscometric method of monitoring the effect of retarding admixture on the setting of cement paste. Cement and concrete research, 14:64-72.
- Bier, A. W., (1993), Computer-Einsatz in der Analytischen Chemie Zur Untersuchung von Prototype- und Komplexbildungsgleichgewichten is Beispiel der Phosphonocarbonsauren. ¨ Heinrich-Heine-Universitat D ¨ Dusseldorf, Mathematisch- Naturwissenschaftliche Fakultat, Diss.
- Bobrowski, G. S., Guecia, G. C. J., Lupyan, D. A., and Kinney, F. D.,(1990), Methods and Composition for Reclaiming Concrete, the United States Patent 4,964,917.
- Bobrowski, G. S., Guecia, G. C. J., Lupyan, D. A., and Kinney, F. D., (1996), Wiederaufbereitung von Betonmischungen, German Patent DE 3727907.
- Bobrowski, G. S. and Ryan, R. J., (1991), Method for Stabilizing Concrete Residues, European Patent 0 324 501 B1. Bodamer, A., 1997, “H
- Breugel K. van, (1997), Simulation of Hydration and Formation of Structure in Hardening Cement-Based Materials, 2nd Edition.
- Byfors, J. 1980, Plain Concrete at Early Ages, CBI report FO 3:8, Swedish Cement and Concrete Research Institute, Stockholm, Sweden.
- G.L. Low, K.Y. Ng, W.L. Ng, C.T. Tam, R.B.W. Heng, Use of recycled cement-based slurry water for making concrete, Journal - The Institution of Engineers, Malaysia (Vol. 68, No.4, December 2007)
- Crow, R.D. and E.R. Dunstan, (1981) Properties of Fly Ash Concrete., Effect of Fly Ash Incorporation in Cement and Concrete, Proceedings of Symposium N. Materials Research Society, 214-224.
- Davis, R.E., Carlson, R.W., Kelly, J.W. and Davis, H.E.,(1937) “Properties of Cements and Concretes Containing Fly Ash,” Journal of the American Concrete Institute, Vol. 33, pages 577 to 611.
- De Larrard, F. (1990) ” A method for proportioning high-strength concrete mixtures”, Cement, Concrete and Aggregates, Vol12, No. 2 pp. 47-52.
- De Larrard, F .;Bosc,F; Catherine, C., And Deflorenne, F. (1997) “A method for Optimizing the binder/superplasticizer system in Hight-Performance Concrete mixture proportioning”, Fifth CANMET/ACI Intnl Conf. on Superplasticizers and Other International, Michigan USA, Supplementary papers, pp 37-55.
- De Schutter, G. and L. Taerwe. (1995) General hydration model for Portland cement and blast furnace slag cement. Cement and Concrete Research 25 (3): 593-604.
- Dias, W.P.S., Dewapriya, M.A.N., Edirisooriya, E.A.C.K. and Jayathuniga, C.G. (2010) Effects of large retarder dosages on concrete strength development. Journal of Institution of Engineers, Sri Lanka. 43(3):13-19.
- Domone, P.L., and M.N. Soutsos, (1995) Properties of high-strength concrete mixes containing PFA and ggbs. Magazine of Concrete Research, 47: 355-367.

- Environchem Services, “Ready Mix Concrete Industry Environmental Code Of Practice (1993) ”Update Report prepared for Environment, Canada, North Vancourver and B.C., 1993
- Escalante-Garcia, J. I., and J.H. Sharp (2000) The effect of temperature on the early hydration Portland cement and blended cement. Advances in Cement Reseach 12(3): 121-130.
- F.W.Locher, W. Richartz and S.Sprung (1977), Cembureau sSeminar on Reaction of Aluminates during the Setting of Cements, Technische Hogeschool Eindhoven, Netherlands 13th-14th April 1977
- Gettu, R.; Aguado, A,; Agullo, l; Toralles-Carbonari, B. And Roncero, J. (1997), “Characterization of cement pastes with silica fume and superplasticizer as components of high-performance concretes”, Proc, Mario Collepardi Symposium on Advances in Concrete Science and Technology(Fifth CANMET/ACI Intl. Conf. on Superplasticizer and Other Chemical Admixtures, Rome, Italy), ed. P.K. Mehta, CANMET/ACI, pp.331-344.
- Griersona, L. H., Knightb, J. C., & Maharaj, R. (2005). The role of calcium ions and lignosulphonate plasticizer in the hydration of cement. Cement and Concrete Research, Vol 35(Issue 4).
- Goetz H.W. (1967), “False set of cement as an influence by Hydroxylated-Carboxylic-Acid-Type Admixture”, Material Research & Standards, June, pp 246-249.
- Hanna, E.; Luke, K.; Perraton, D., and Ancin, P.C. (1989), "Rheological behavior of Portland cement in the presence of superplasticizer", Third Intl. Conf on superplasticizers and Other Chemical Admixtures in Concrete (SP-119, Ottawa, Canada), ed. by V.M. Malhotra, American Concrete Institute, Detroit, USA, pp. 171-188.
- Hogan, F.J. and J.W. Meusel (1981) “Evaluation of durability and strength development of a ground granulated blast furnace slag. Cement Concrete, and Aggregates”, CCAGDP 3(1): 40-52.
- Hu, C. and de Larrard, F.(1996), “The rheology of fresh high-performance concrete”, Cement and Concrete Research, Vol.18, No.5,pp.789-798.
- Hu, J., and Wang, K. (2007). “Effects of size and uncompacted voids of aggregate on mortar flowability.” Journal of Advanced Concrete Technology, 5, 75–85.
- Huynh, H.T.(1996) "La compatibilité ciment-superplastifiant dans les bétons à haute performance: Synthèse bibliographique". Bulletins des Laboratoires des Ponts et Chaussées, 1996, 206(Nov-Dec): p. 63-73.
- I.S. Vladimir B.E Zinovity and Nusina O Betrovna, (1993) Experimental study on improving hardening speed pf Portland phosphorous slag cement. The 3rd Beijing Int. Symp.Cem.Concr. Beijing, China, 548-553
- J.C.M. De Jong(1977), Silic. Ind., 42(1)5.
- Jolicoeur, C., and M.A. Simard (April-June 1998), Chemical admixture-cement interactions: Phenomenology and physico-chemical concepts. Cement & Concrete Composites 20 (2-3): 87-101.
- Joshi, R.C., and R.P. Lothia (1997) Fly ash in concrete, Gordon & Breach Science Publishers.
- Kinney F. D. (1998). “Reused of Returned Concrete by Hydration Control: Characterisation of New Concept, Superplasticiser, and other chemical Admixture in Concrete, ACI SP-119,” American Concrete Institute, Detroit MI, pp 19-40.
- Kishi T., and K, Maekawa (1994). Thermal and mechanical modeling of young concrete based on hydration process of multi-component cement minerals. In

thermal cracking in concrete at early ages, proceedings of RILEM ed. R. Springenschmid 11-18.

- Kruml F (1990). Setting process of concrete. Properties of fresh concrete. H.-J. Wierig HJ (Ed.). Chapman & Hall. pp. 10-16.
- Klieger, P, and J.F. Lamond (1994). The significance of tests and properties of concrete and concrete making materials. Philadelphia, PA: American Society for Testing and Materials.
- Kurdowski. W, Thiel. A (1981), Beijing Internal Symp on Cement and Concrete, p.115. Pergamon Press, Oxford.
- Langan B.W., Wen, and M.A. Ward, (2002). Effect of silica fumes and fly ash on the heat of hydration of Portland cement. Cement and Concrete Research 32(7): 1045-1051.
- Langenfeld, M. and Stark, J. (1998), “Der Einfluss von Verzogerern ¨ auf die fruhe Hydratation von Portlandzementklinker- ¨ phasen, dargestellt in einem ESEM-FEG”, Thesis, Vol. 44, No. 1, pp. 82–90.
- Lea, F.M. (1970). The Chemistry of cement and concrete, 3rd edition. London: Edward Arnold Publication Ltd.
- Lerch, W., F. W. Ashton, and R. H. Bogue. (1929). The sulfoaluminates of calcium. Journal of Research of National Bureau Standards 2:715-731.
- Lerch, W., R.H. Bogue. (1934). The heat of hydration of Portland cement pastes. Journal of Research of National Bureau Standards 12:645-664
- Lerch, W. (1946). The influence of gypsum on the hydration and properties of Portland cement pastes. Proceedings of American Society for Testing Materials 46:1252-1297.
- Lewandowski R. (1983). “Anforderungen des Transportbeton herstellers a Betonzusatzmittel,” Beton, Vol.33, No.8 pp 285-288.
- Lipus, K., Rickert, J., and Sylla, H. -M., (2000). ESEM-Untersuchungen zur Hydratation von Portlandzement unter Ein- fluß von verzogernden Zusatzmitteln ¨ , 14th ibausil, Weimar, Bauhaus-Universitat Weimar, pp. 301–313.
- Lobo. C, Gurthrie. W. F and Kacker. R, (1995) A Study on Reuse of Plastic Concrete Using Extended Set-Retarding Admixtures, Journal of Research of the national Institute of Standards and technology, Volume 100, Number 5, 575-589.
- Lobo. C, and Mullings. G,(2003) Recycled Water in Ready Mixed concrete, Concrete Infocus, Spring.
- Ma, W., D. Sample, R. Martin, and P.W. Brown (1994). Calorimetric study of cement blends containing fly ash, silica fume, and slag at elevated temperatures. Cement, Concrete, and Aggregates, CCAGPD 16 (2): 93-99.
- Massazza F. and U. Costa,(1980). Effect of superplasticizers on the C_3A hydration. Proceedings of Seventh International Symposium on Chemistry of Cement 4:529-534, Paris.
- Meininger R. (1964) “Disposal of Truck Mixer Wash Water and Unused Concrete”, Cement and concrete composites. Vol. 20: 129-136.., NRMCA Publication No. 116, National Ready Mixed Concrete Association, Silver Spring, MD, 1964
- Meyer L.M. and Perenchio W.F. (1979), “Theory of Concrete Slump Loss as Related to the Use of Chemical Admixtures”, Concrete International pp 36-43.
- Mindess, S. and J.F. Young (1981). Concrete. Englewood Cliffs, N. J.: Prentice-Hall, Inc.
- Moeser, B., Langenfeld, M., and Stark, J. (1999), Fruhe Hydration ¨ von Portland

cement under Zusatzmitteleinfluss dargestellt im ESEM-FEG. 37th DAfStb-Forschungskolloquium, Inst. f. Konstruktiven Ingenieurbau F. A.-Finger-Institut fur¨ Baustoffkunde, Weimar, pp. 123–134

- Nagataki S.(1995). Hardening accelerators. Application of Admixture in Concrete. State of the art Report. RILEM TC 84-AAC. Rilem Technical Committee.
- Nawa, T.; Eguchi, H., and Fukaya, Y. (1989), "Effect of alkali sulfate on the rheological behavior of cement paste containing a superplasticizer", Third Intl. Conf. on Superplasticizers and Other Chemical Admixtures in Concrete (SP-119, Ottawa, Canada), ed. by V.M. Malhotra, American Concrete Institute, Detroit, USA, pp. 405-424.
- Neville, A.M. (1995). Properties of concrete, Longman.
- Nielsen. C. V and Glavind. M, (2007) “Danish Experiences with a Decade of Green Concrete” Journal of advanced technology, Vol No.1, 3-12
- Nocuñ-Wczelik, W. (2001). Heat evolution in hydrated cementitious system admixtured with fly ash. Journal of Thermal Analysis and Calorimetry 65:613-619.
- Morabito, P. (1998). Methods to determine the heat of hydration of concrete. In Prevention of the Thermal Cracking in Concrete at Early Ages, ed.R. Springenschmid. London: E&FN Spon. 1-25
- Paillere, A.M.; Serrano, J.J., and Grimaldi, G. (1990), "Influence du dosage et du mode introduction des superplastifiants sur le maintien de la maniabilite optimale des Mons a hautes performances avec et sans fumees de silice", Bulletin des Laboratories des Ponts et Chaussees, Vol. 170, pp.37-45.
- P18-358 (1985) Admixtures for concrete, mortars, and grouts for prestressing ducts. Measurement of fluidity and water reduction. France Standard
- Paolini. M. and Khurana, R. (1998) Admixtures for recycling of waste concrete. Cement and concrete composites. Vol. 20: 221-229.
- Pinto RCA, Hover KC (1999). Application of maturity approaches to setting times. ACI Mat. J., 96(6): 686-691.
- Portland cement Association, Portland Cement (1997) Concrete and Heat of Hydration. Concrete Technology Today 18(2): 1-4.
- Previte. R.W. (1971) Some insights on the mechanisms of saccharose set retardation of Portland cement. Cement and concrete research, 1:301-316.
- Ramchadran V.S., and Mailvaganam N.P. (1992), “New Development in Chemical Admixtures”, Advances in Concrete Technology, CANMET, 1992-P 879.
- Rixom, M.R.; Mailvaganam, N.P. (1986) Chemical Admixtures for Concrete. 2nd ed.; E.&F.N.: New York, pp XVI, 153-156.
- Reinhardt HW, Grosse CU (2004). Continuous monitoring of setting and hardening of mortar and concrete. Const. Build. Mat. J., 18(3): 145- 154.
- Richartz W. (1983), “Einfluss von Zusatxen auf das Erstarrungsverhalten von Zement”, Beton Vol. 33, No.11 pp 425-429 and No 12 pp 465-471
- Rickert J. and Thielen G (2004), “Influence of Long-term Retarder on the Hydration of Clinker and Cement”, fib Symposium, 26-28 April 2004, Avignon p.144-145
- Rickert J. (2004), “Influence of Retarders on the Hydration of Clinker and Cement”, Concrete Technology Reports 2001-2003, Verlag Bau+technik Duesseldorf.
- RILEM 42-CEA (1981). Properties of set concrete at early ages: State of the art reports. Materials and Structures 14(84):399-450
- R.L.Sharma and S.P.Pandey, (1999) The effect of mineral additions on the performance of OPC paste and mortar. Cem.Concr.Res.

- Scanlon, J. M. (1994). “Factors influencing concrete workability.” P. Klieger, and J. F. Lamond, ed., Significance of tests properties of concrete and concrete making. American Society for testing and materials.
- Schindler A.K. (2003). Influence of Supplementary cementing materials on the heat of hydration of concrete. Advances in Cement and Concrete IX Conference. Copper Mountain, CO.17-26.
- Seiler K, (1969). Die Wurjybgsweise von Erstarrungsverzogerern unter besonderer Berticksichtigung silicofluorhaltiger Verbindungen RWTH Aachen, Dissertation.
- Senbetta. E, and Bury. M.A. (1992). Controlled Cement Hydration: Its Effect on Durability of Concrete, G. M. Idorn International Symposium on Durability of Concrete, ACI SP-131, American Concrete Institute, Detroit, MI p. 17
- Skalny, J. and Young, J. F. (1980). Mechanisms of Portland Cement Hydration; Proceedings, 7th International Symposium Chemical of Cement, Paris, 1980, S. II 1, pp. 3– 45.
- Soroka, I., and Ravina, D. (1998). Hot weather concreting with admixtures.
- Toralles-Carbonari, B. (1996), Ph.D. Thesis, “Estudio parametrico de variables y components ralativos a la dosification y produccion de hormigones de altas prestaciones”, Universitat Plitecnica de Catalunya, Barcelona Spain
- United States Geological Survey (USGS), Minerals Information, Minerals Yearbooks and Mineral Commodity Summaries for cement at http://minerals.usgs.gov/minerals/pubs/commodity/cement/mcs-2016-cemen.pdf
- Uchikawa H. (1986). Effect of blending component on hydration and structure formation. 8th International Congress on the Chemistry of Cement. Rio de Janeiro 249-280.
- UNEP DTIE IETC; Sustainable Building Construction, Osaka 538-0036, Japan. This document can also be downloaded from the web at: www.unep.or.jp/ietc/kms/data/2842.pdf
- Wang K., Z. Ge, Jim Grove, J. Mauricio Ruiz, Rob Rasmussen, Developing a Simple and Rapid Test for Monitoring the Heat Evolution of Concrete Mixtures for Both Laboratory and Field Applications; January 2006
- Wadsö, L. (2004). Un-thermostated multichannel heat conduction calorimeter. Cement, Concrete, and Aggregates 26 (December) (2): 1-7.
- Xiong, X. and K. van Breugel. (2001). Isothermal calorimetry study of blended cement and its application in numerical simulations. HERON 46 (3): 151-159.
- Zhou, J. (2006). Microstructure and permeability of Portland cement blended with blast furnace slag, fly ash and limestone powder. Master Thesis, Geosciences of Delf University of Technology.

APPENDIX A

Summary of results- Setting time of cement; and Plastic and mechanical properties of concrete

A4.2: Setting time of cement and blended cement

	Initial, (Minutes)	**Final, (Minutes)**
OPC	110	173
35% OPC and 65% Slag	179	246
75% OPC and 25% Fly Ash	125	180

A4.6: Workability results

	Control Concrete (Without stabilizer dosage)	Stabilizer dosage after one hour	**10%** Stab Concrete + 90% Fresh concrete	**25%** Stab Concrete + 75% Fresh concrete	**50%** Stab Concrete + 50% Fresh concrete	**100%** Stab Concrete
OPC Concrete						
Initial Slump, mm	85	85	100	100	90	-
60 minutes Slump, mm	75	70	80	80	70	-
Next day slump of Stabilized concrete, mm	-	-	80	80	60	40
Concrete containing 35% OPC and 65% Slag						
Initial Slump, mm	100	80	95	95	90	-
60 minutes Slump, mm	95	70	90	90	80	-
Next day slump of Stabilized concrete, mm	-	-	70	85	80	60
Concrete containing 75% OPC and 25% fly ash						
Initial Slump, mm	90	90	100	95	90	-
60 minutes Slump, mm	80	90	100	90	90	-
Next day slump of Stabilized concrete, mm	-	-	100	90	90	90

A4.7: Initial and final setting time of concrete

	Control Concrete (Without stabilizer dosage)	Stabilizer dosage after one hour	**10%** Stab Concrete + 90% Fresh concrete	**25%** Stab Concrete + 75% Fresh concrete	**50%** Stab Concrete + 50% Fresh concrete	**100%** Stab Concrete
OPC Concrete						
Initial Setting Time, min	450	2020	445	410	262	2020
Final Setting Time, min	600	2140	545	510	402	2140
Concrete containing 35% OPC and 65% Slag						
Initial Setting Time, min	518	2270	452	480	439	2270
Final Setting Time, min	680	2510	560	612	555	2510
Concrete containing 75% OPC and 25% fly ash						
Initial Setting Time, min	398	3800	506	425	425	3800
Final Setting Time, min	465	4650	573	570	570	4650

A4.9: Concrete and Ambient temperature

	Control Concrete (Without stabilizer dosage)	Stabilizer dosage after one hour	**10%** Stab Concrete + 90% Fresh concrete	**25%** Stab Concrete + 75% Fresh concrete	**50%** Stab Concrete + 50% Fresh concrete	**100%** Stab Concrete
OPC Concrete						
Concrete Temp, ºC	30	31	22	22	28	27
Ambient Temp, ºC	31	35	24	24	30	30
Concrete containing 35% OPC and 65% Slag						
Concrete Temp, ºC	29	28	20	21	30	31
Ambient Temp, ºC	30	30	24	26	32	32
Concrete containing 75% OPC and 25% fly ash						
Concrete Temp, ºC	32	31	21	23	25	25
Ambient Temp, ºC	32	32	24	25	28	28

A4.8: Concrete mass per unit weight

	Control Concrete (Without stabilizer dosage)	Stabilizer dosage after one hour	**10%** Stab Concrete + 90% Fresh concrete	**25%** Stab Concrete + 75% Fresh concrete	**50%** Stab Concrete + 50% Fresh concrete	**100%** Stab Concrete
OPC Concrete						
7 day, kg/m^3	2380	2380	2382	2383	2388	2380
28 day, kg/m^3	2386	2389	2385	2390	2386	2389
56 day, kg/m^3	2391	2384	2385	2388	2386	2384
Concrete containing 35% OPC and 65% Slag						
7 day, kg/m^3	2379	2382	2366	2368	2375	2382
28 day, kg/m^3	2380	2376	2372	2367	2360	2376
56 day, kg/m^3	2380	2385	2379	2369	2384	2385
Concrete containing 75% OPC and 25% fly ash						
7 day, kg/m^3	2388	2411	2400	2382	2412	2411
28 day, kg/m^3	2409	2414	2393	2404	2410	2410
56 day, kg/m^3	2410	2410	2394	2406	2415	2410

A4.10: Compressive strength

	Control Concrete (Without stabilizer dosage),	Stabilizer dosage after one hour,	**10%** Stab Concrete + 90% Fresh concrete,	**25%** Stab Concrete + 75% Fresh concrete	**50%** Stab Concrete + 50% Fresh concrete	**100%** Stab Concrete
OPC Concrete						
7 day , MPa	36.2	38.8	38.0	36.5	34.3	36.4
28 day , MPa	46.5	52.5	48.5	42.5	40.0	41.5
56 day	48.5	52.3	51.5	46.0	43.2	47.8
Concrete containing 35% OPC and 65% Slag						
7 day , MPa	28.7	31.1	32.2	26.0	26.3	29.5
28 day, MPa	41.8	45.0	40.0	41.5	39.0	48.5
56 day, MPa	48.0	52.5	48.5	43.5	44.3	52.0
Concrete containing 75% OPC and 25% fly ash						
7 day, MPa	30.3	34.1	33.5	36.5	29.0	32.7
28 day , MPa	40.3	42.0	43.5	44.3	41.2	35.5
56 day, MPa	44.0	49.0	50.5	49.5	46.1	48.0

A4.11: Drying Shrinkage

	Control Concrete (Without stabilizer dosage)	Stabilizer dosage after one hour	**10%** Stab Concrete + 90% Fresh concrete	**25%** Stab Concrete + 75% Fresh concrete	**50%** Stab Concrete + 50% Fresh concrete	**100%** Stab Concrete
OPC Concrete						
7 day, με	36.2	38.8	38.0	36.5	34.3	36.4
14 day, με						
21 day, με						
28 day, με	46.5	52.5	48.5	42.5	40.0	41.5
56 day, με	48.5	52.3	51.5	46.0	43.2	47.8
Concrete containing 35% OPC and 65% Slag						
7 day, με	28.7	31.1	32.2	26.0	26.3	29.5
14 day, με	41.8	45.0	40.0	41.5	39.0	48.5
21 day, με						
28 day, με						
56 day, με	48.0	52.5	48.5	43.5	44.3	52.0
Concrete containing 75% OPC and 25% fly ash						
7 day, με	30.3	34.1	33.5	36.5	29.0	32.7
14 day, με	40.3	42.0	43.5	44.3	41.2	35.5
21 day, με						
28 day, με						
56 day, με	44.0	49.0	50.5	49.5	46.1	48.0

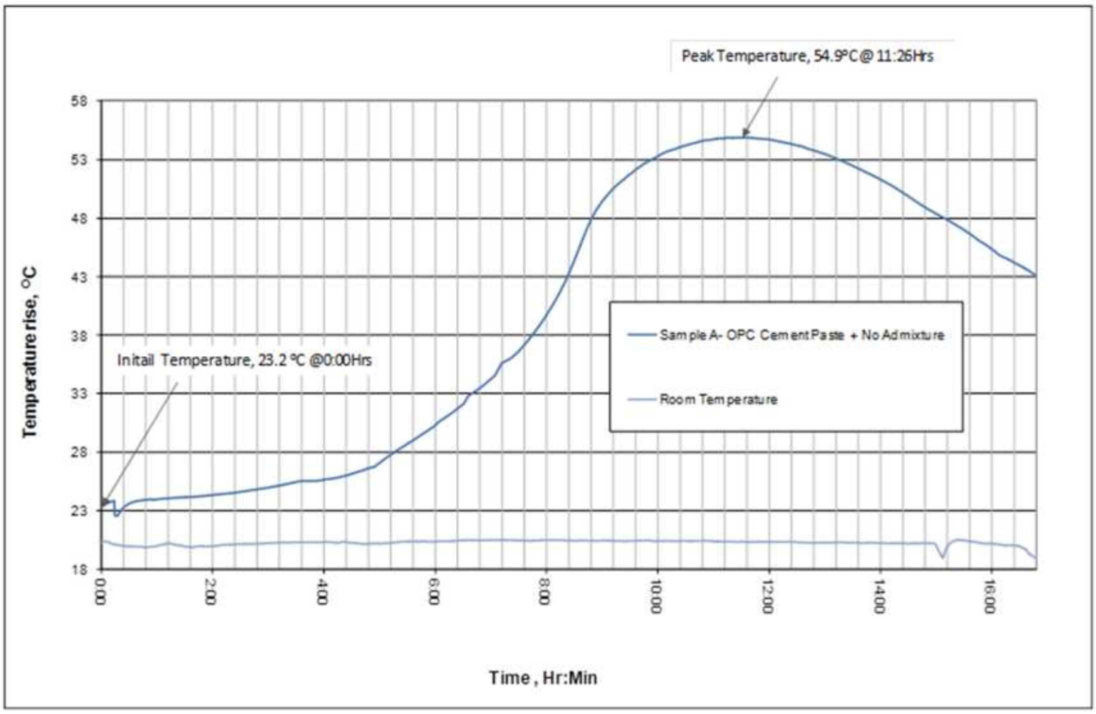
A4.12: Plastic and mechanical properties of upgrade 32MPa concrete to 40MPa

	OPC CEMENT		**35%OPC+65%SLAG**		**75%OPC+25%FLY ASH**	
	Mix N32	Upgraded 32MPa to 40MPa replacing 25% 32MPa stabilized concrete	Mix N32	Upgraded 32MPa to 40MPa replacing 25% 32MPa stabilized concrete	Mix N32	Upgraded 32MPa to 40MPa replacing 25% 32MPa stabilized concrete
Concrete Temperature						
Concrete Temp, ºC	28	27	26	25	28	26
Ambient Temp, ºC	30	32	31	32	31	32
Workability results						
Initial Slump, mm	90	80	95	90	90	90
60 minutes Slump, mm	70	70	80	80	90	85
Next day slump of concrete, mm	60	-	75	-	90	--
Mass per unit weight						
7 day, kg/m^3	2358	2390	2397	2410	2360	2402
28 day, kg/m^3	2372	2415	2400	2418	2362	2400
56 day, kg/m^3	2376	2418	2403	2422	2362	2408
Compressive strength						
7 day, MPa	28.7	37.3	20.7	26.7	23.0	35.2
28 day, MPa	37.5	49.3	39.4	47.7	33.2	46.9
56 day, MPa	39.4	52.7	42.9	53.4	38.5	54.4
Drying shrinkage						
7 days, με	330	320	250	160	340	290
14 days, με	440	410	350	220	470	400
21 days, με	510	465	390	260	550	480
28 days, με	560	520	430	280	610	550
56 days, με	630	600	530	360	630	610

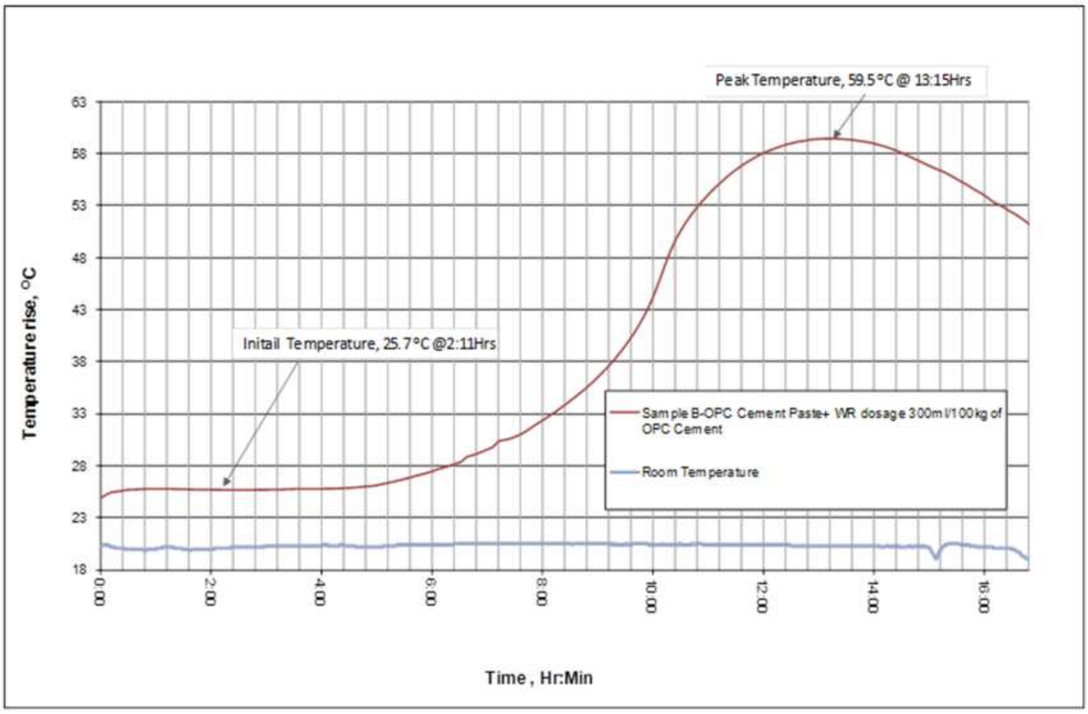
APPENDIX B

Effect of stabilizer dosage on heat of hydration of OPC and blended cement and Percentage compressive strength growth

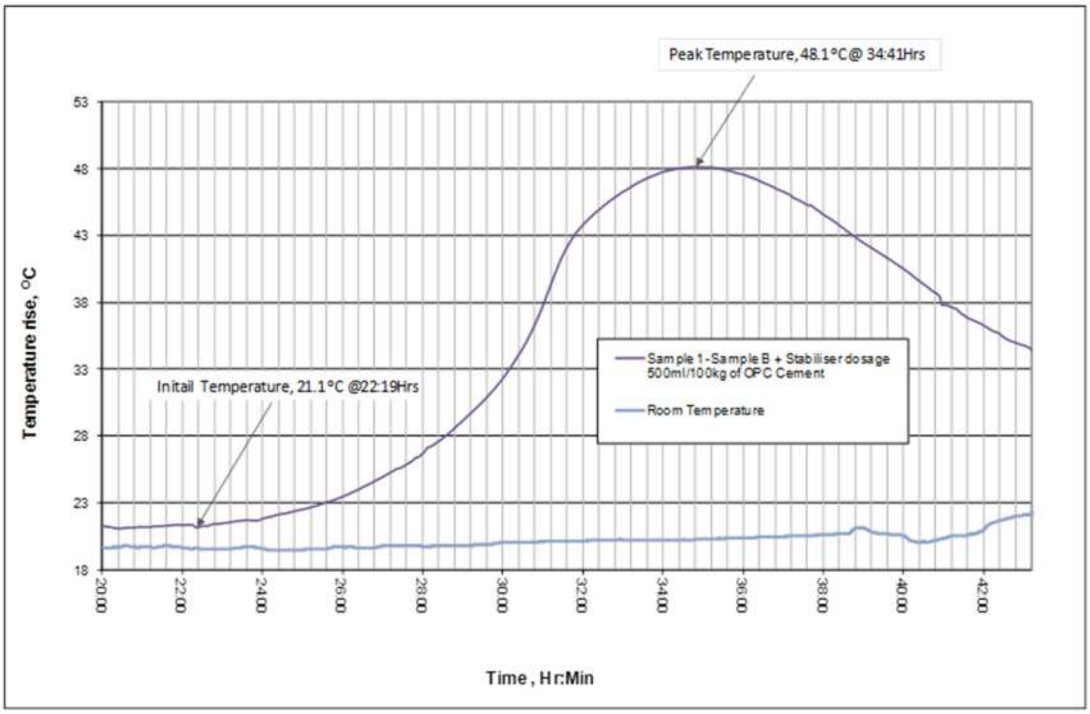
B 4.4.1: Effect of stabilizer dosage on the heat of hydration of OPC grouts.



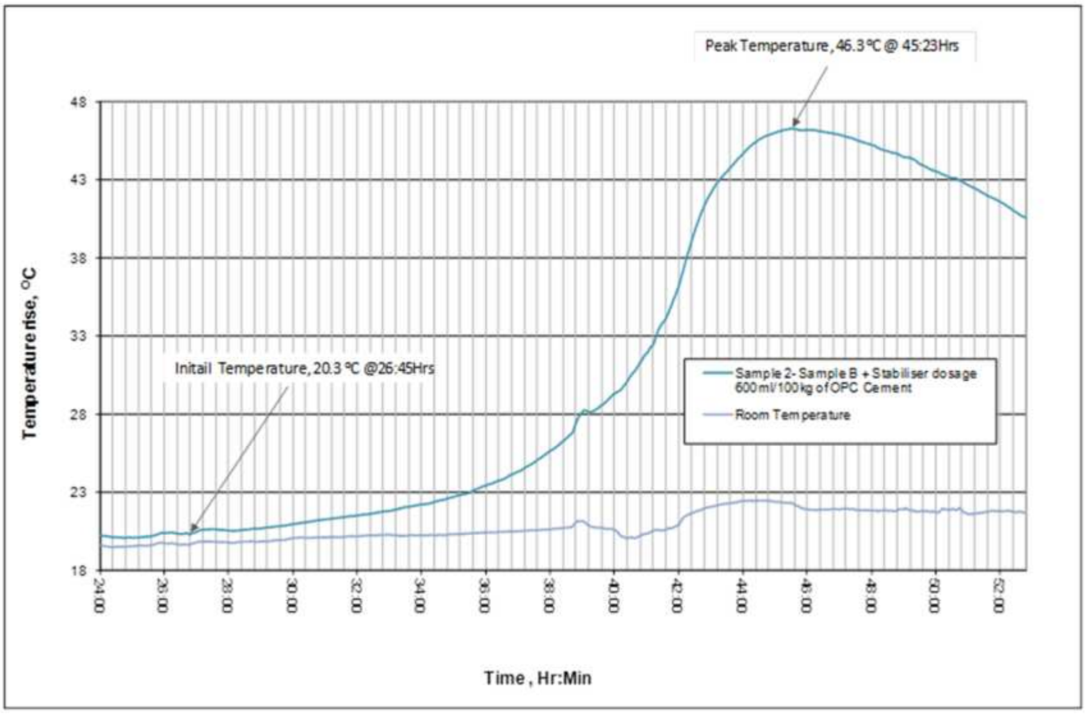
(a) OPC grout without admixtures.



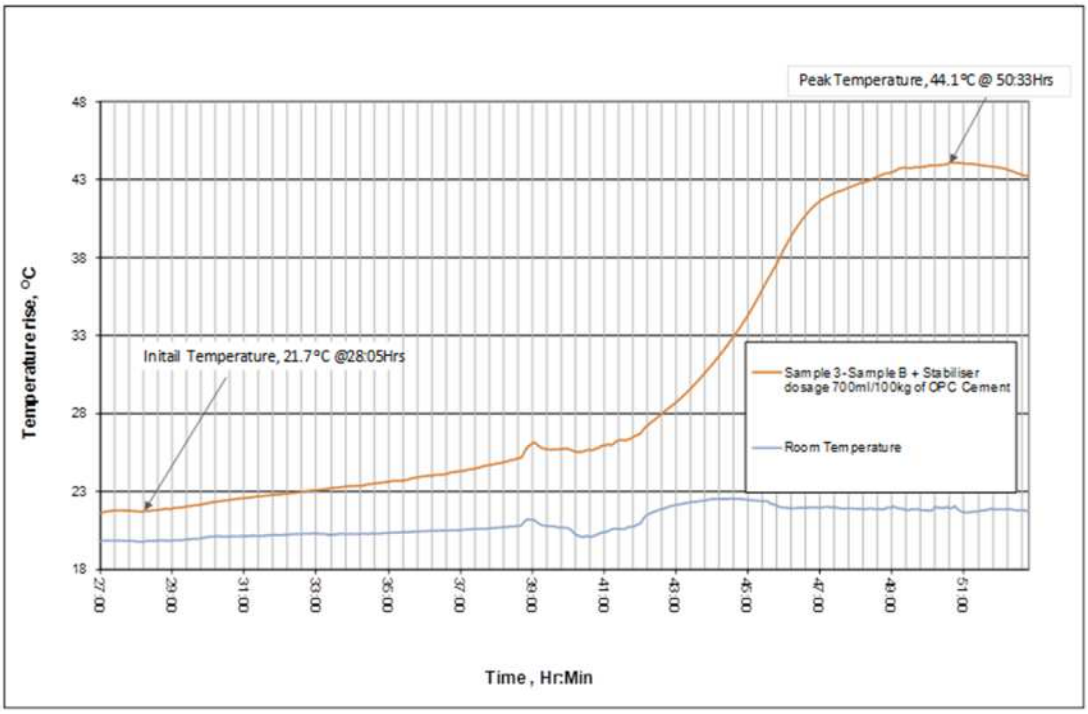
(b) OPC grout and water reducer dosage at 300ml/100kg of cement (Sample B).



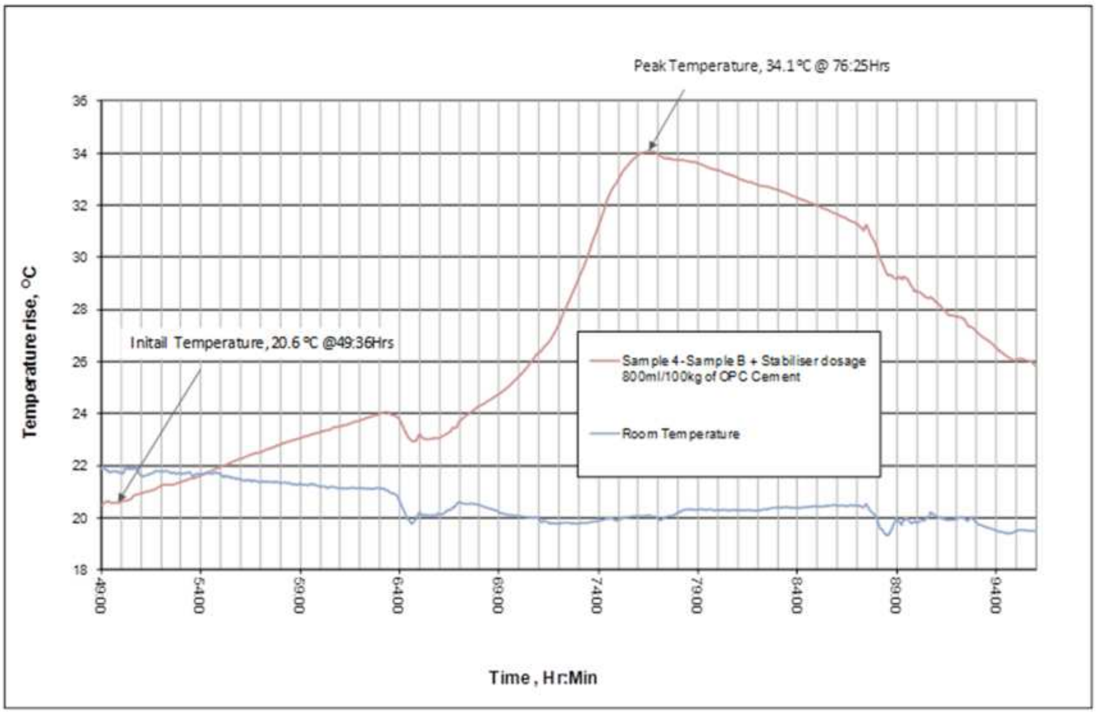
(c) Sample B and stabilizer dosage at 500ml/100kg of cement.



(d) Sample B and stabilizer dosage at 600ml/100kg of cement.

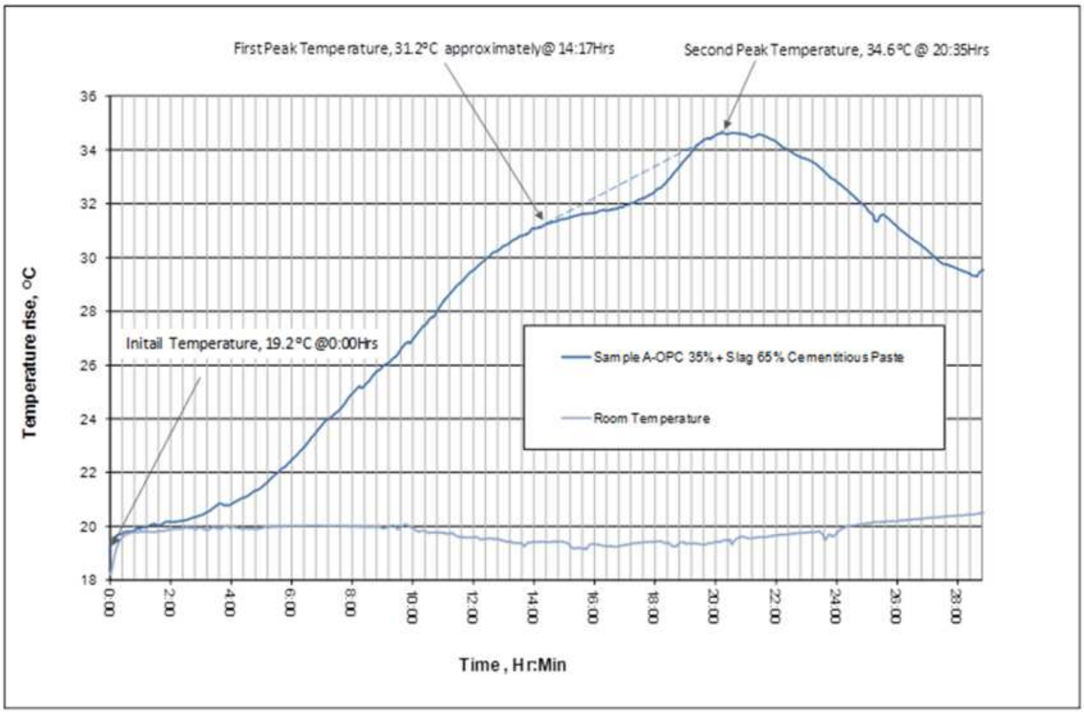


(e) Sample B and stabilizer dosage at 700ml/100kg of cement.

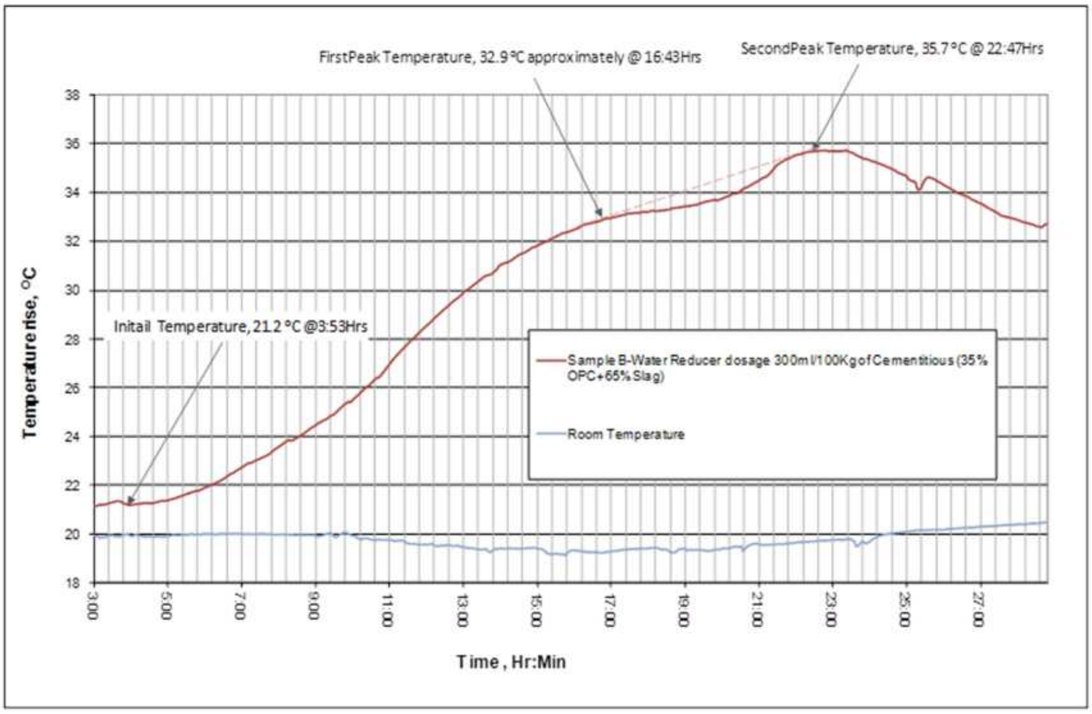


(f) Sample B and Stabilizer dosage at 800ml/100kg of cement.

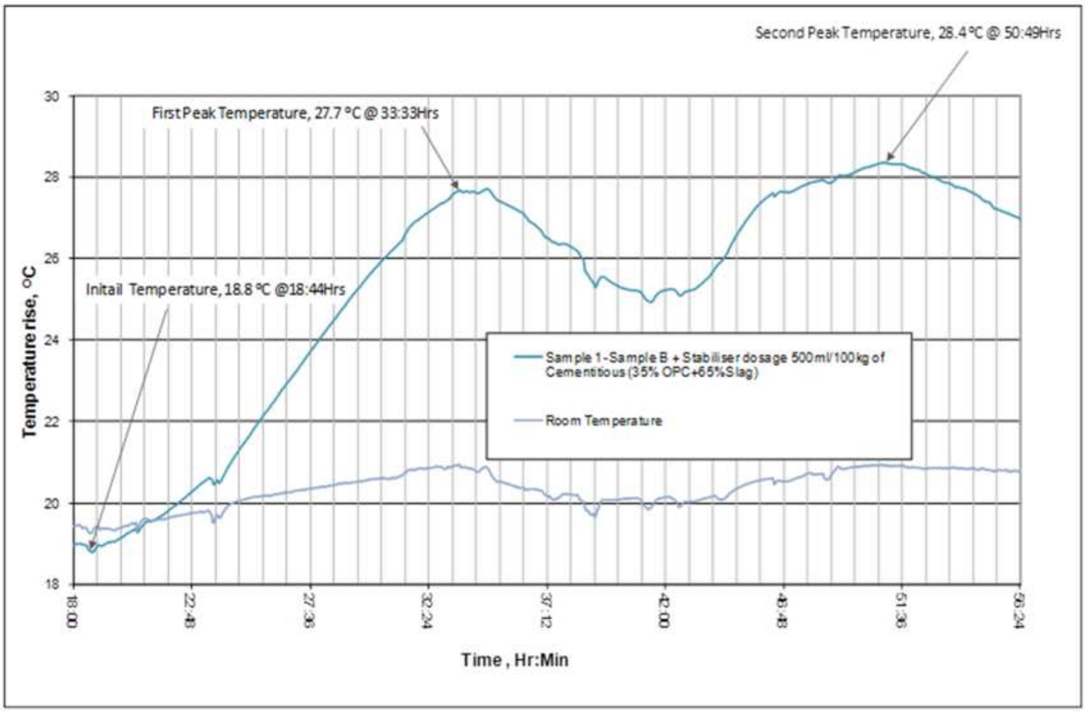
A4.4.2 Effect of stabilizer dosage on the heat of hydration of 35%OPC and 65%slag grout.



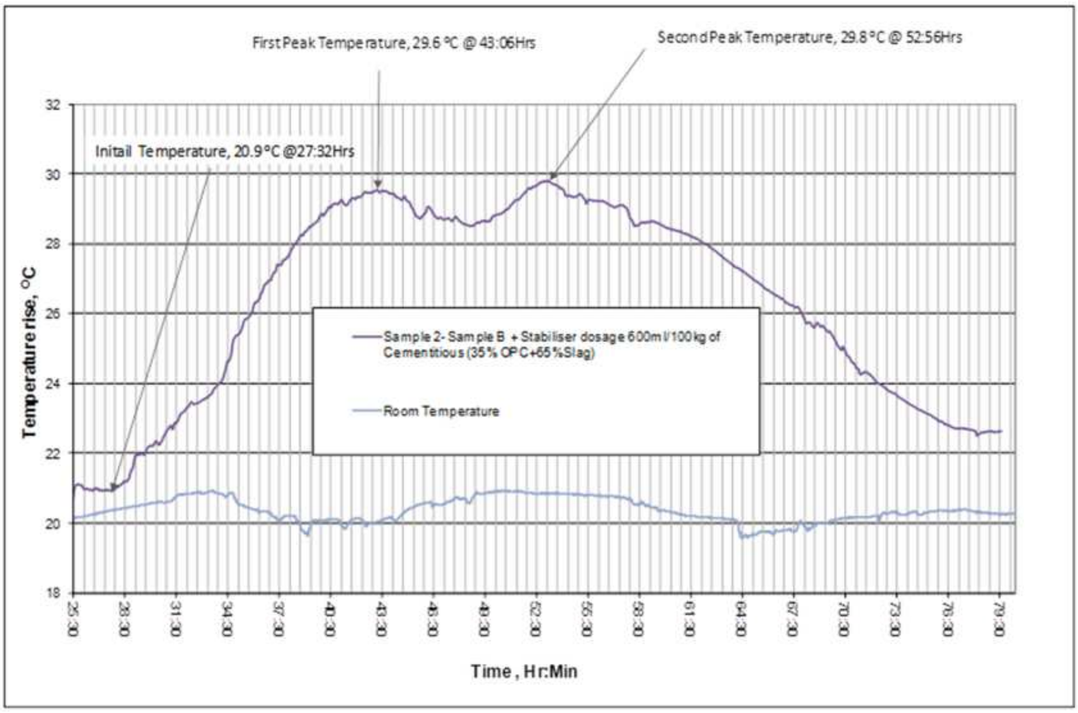
(g) 35%OPC and 65%slag grout without admixtures



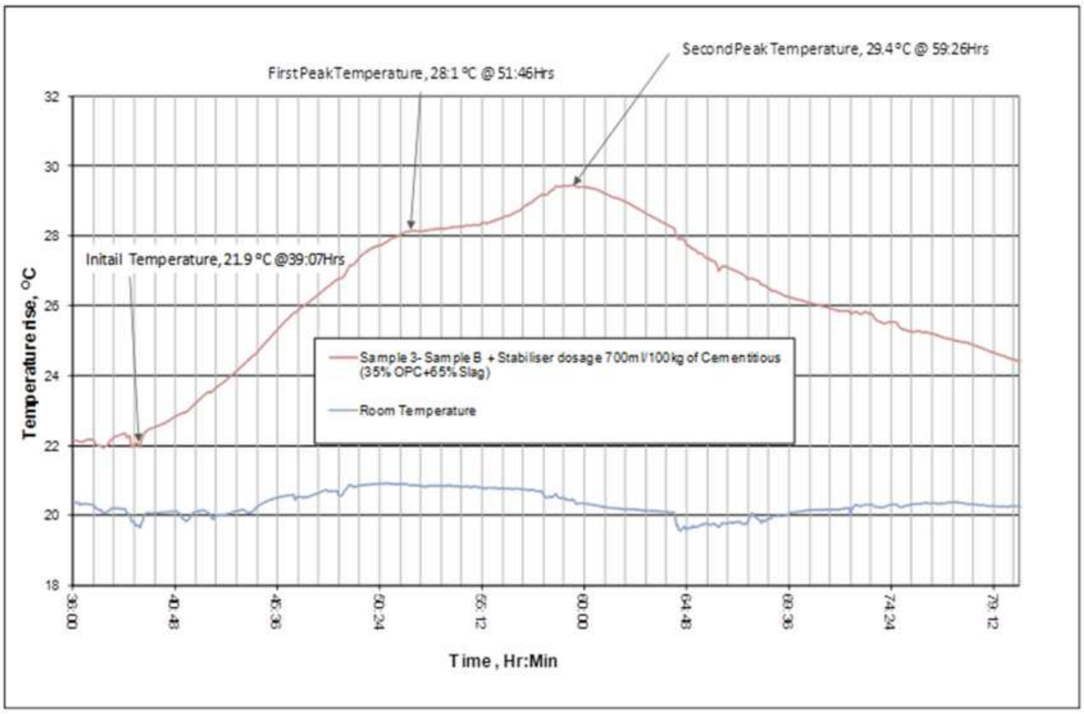
(h) 35%OPC and 65%slag grout and water reducer dosage at 300ml/100kg of cementitious (Sample B)



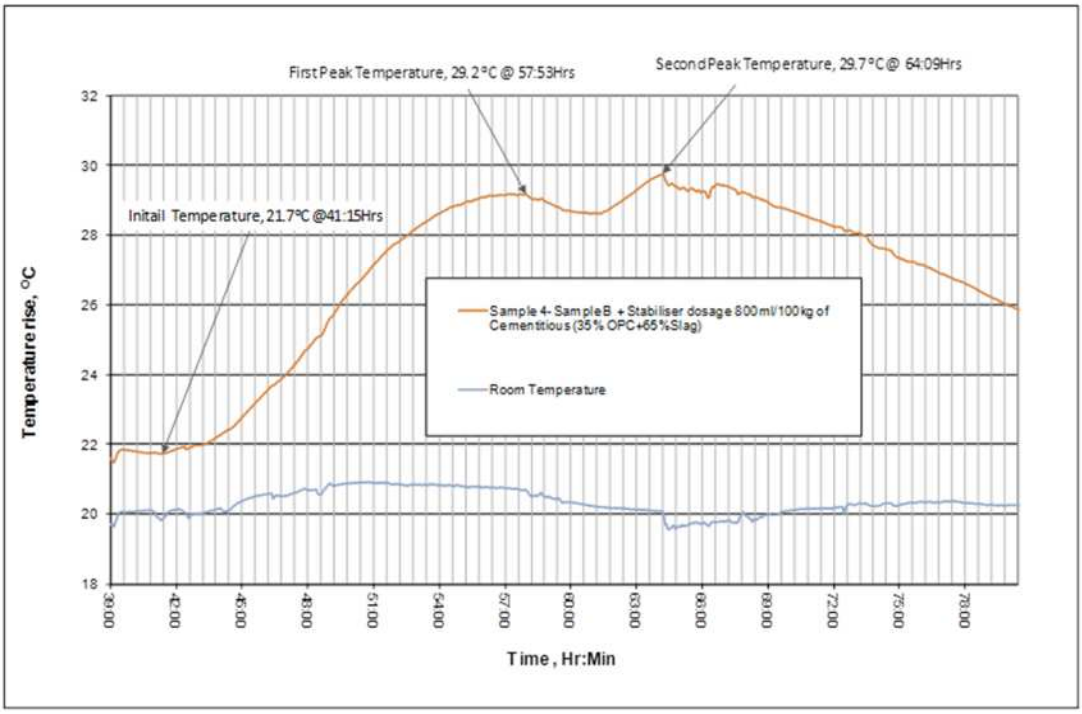
(i) Sample B and stabilizer dosage at 500ml/100kg of cementitious



(j) Sample B and stabilizer dosage at 600ml/100kg of cementitious

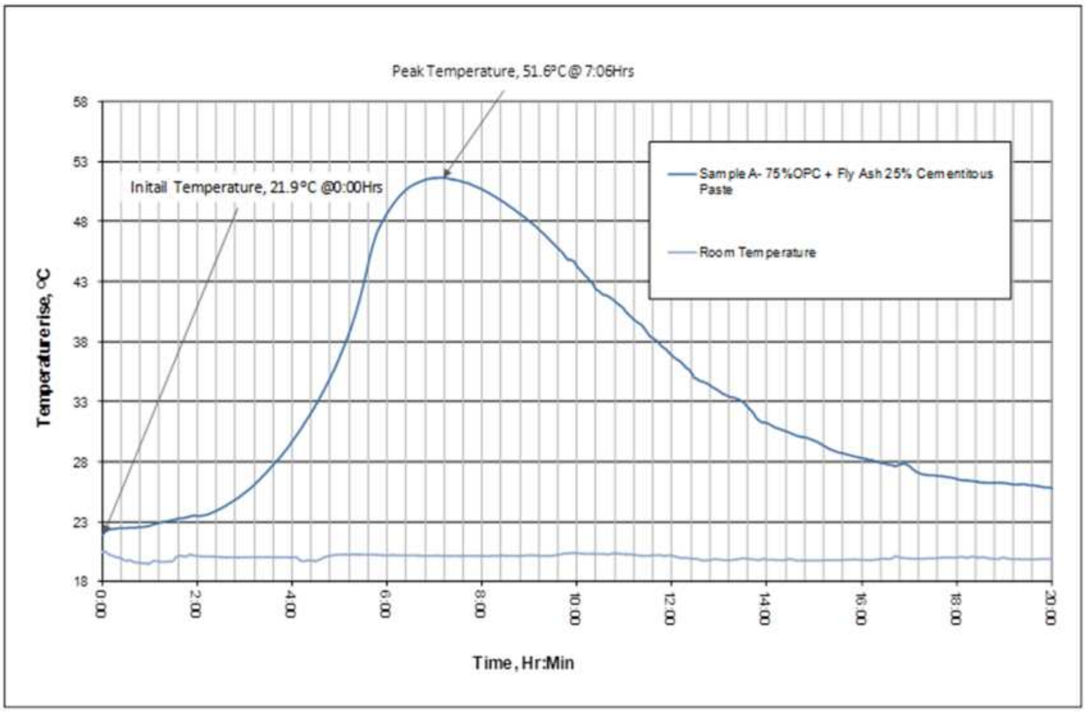


(k) Sample B and stabilizer dosage at 700ml/100kg of cementitious

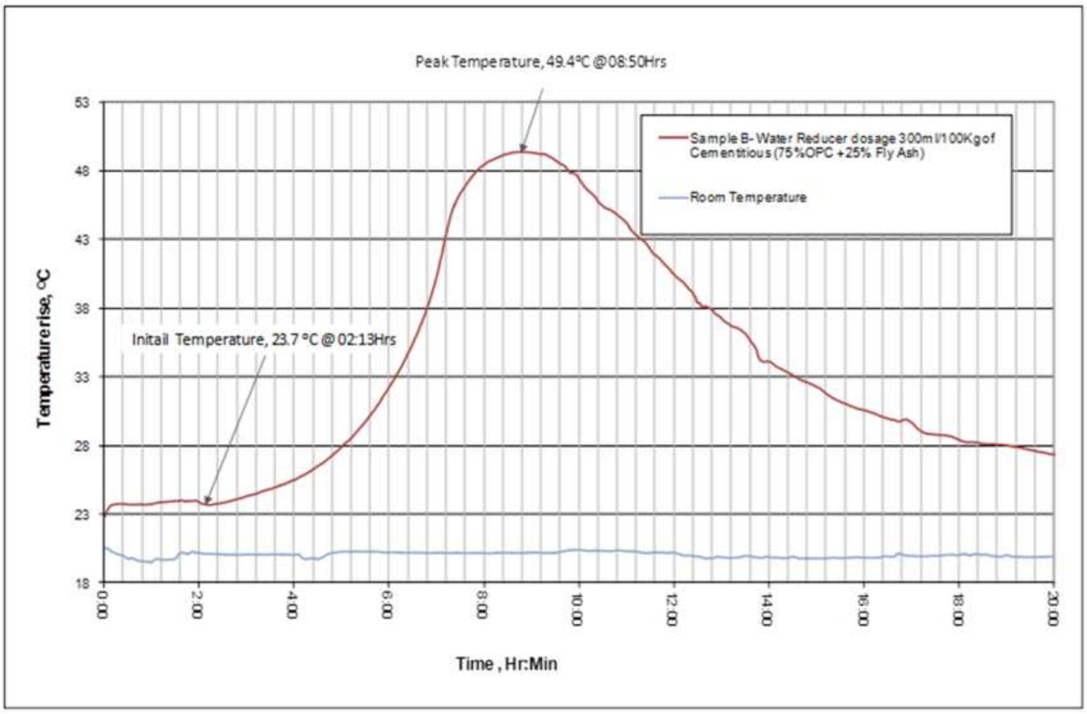


(l) Sample B and stabilizer dosage at 800ml/100kg of cementitious

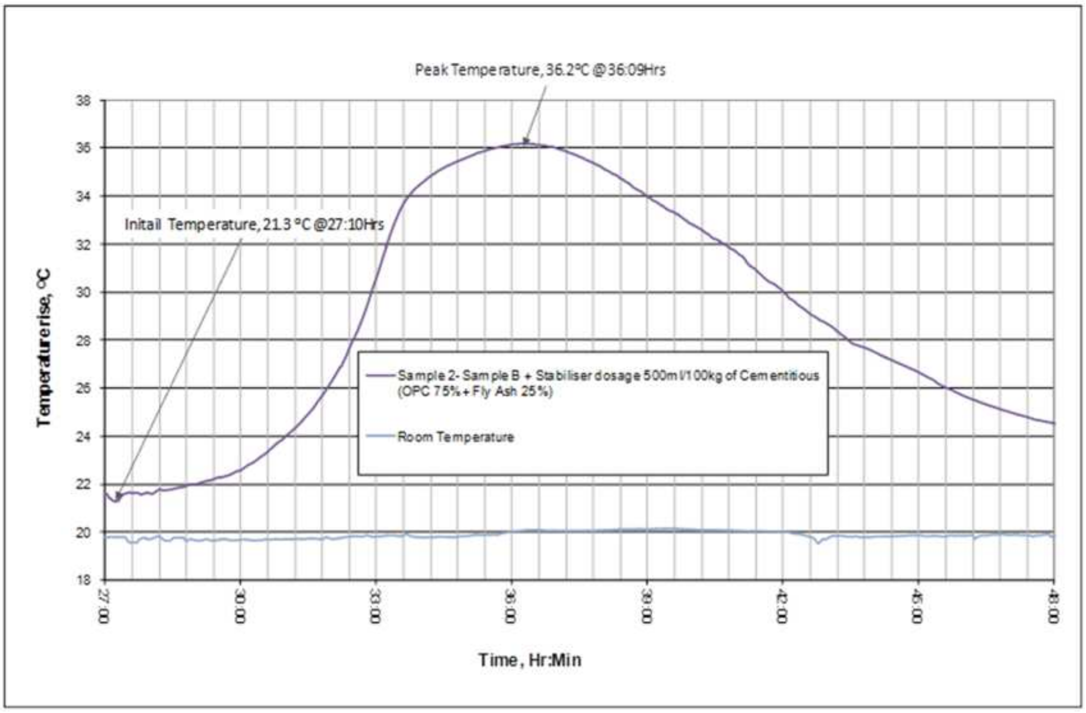
Figure 4.4.3 Effect of stabilizer dosage on heat of hydration of 75%OPC and 25%fly ash grout



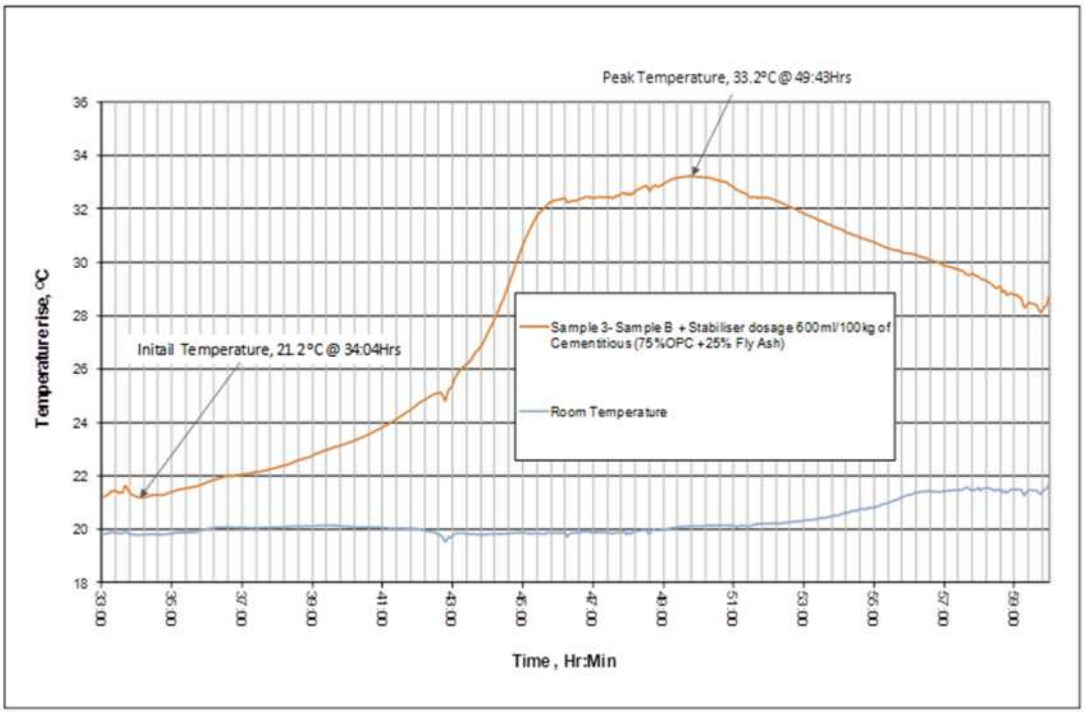
(m) 75%OPC and 25%Fly ash grout without admixtures



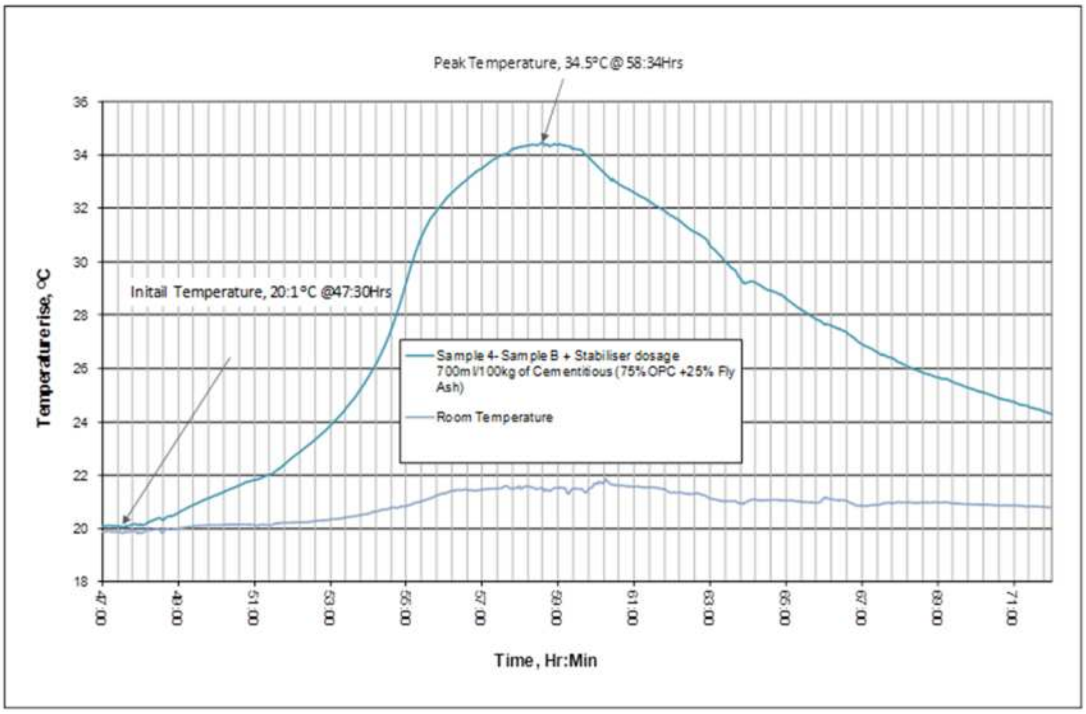
(n) 75%OPC and 25%Fly ash grout and water reducer dosage at 300ml/100kg of cementitious (Sample B)



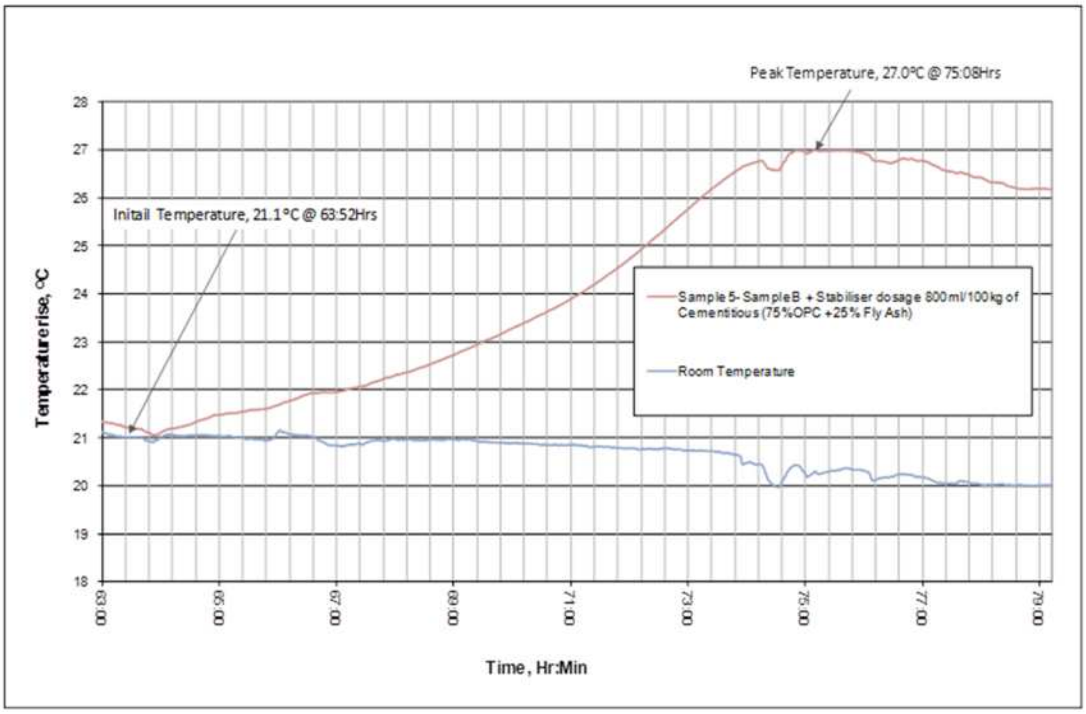
(o) Sample B and stabilizer dosage at 500ml/100kg of cementitious



(p) Sample B and stabilizer dosage at 600ml/100kg of cementitious

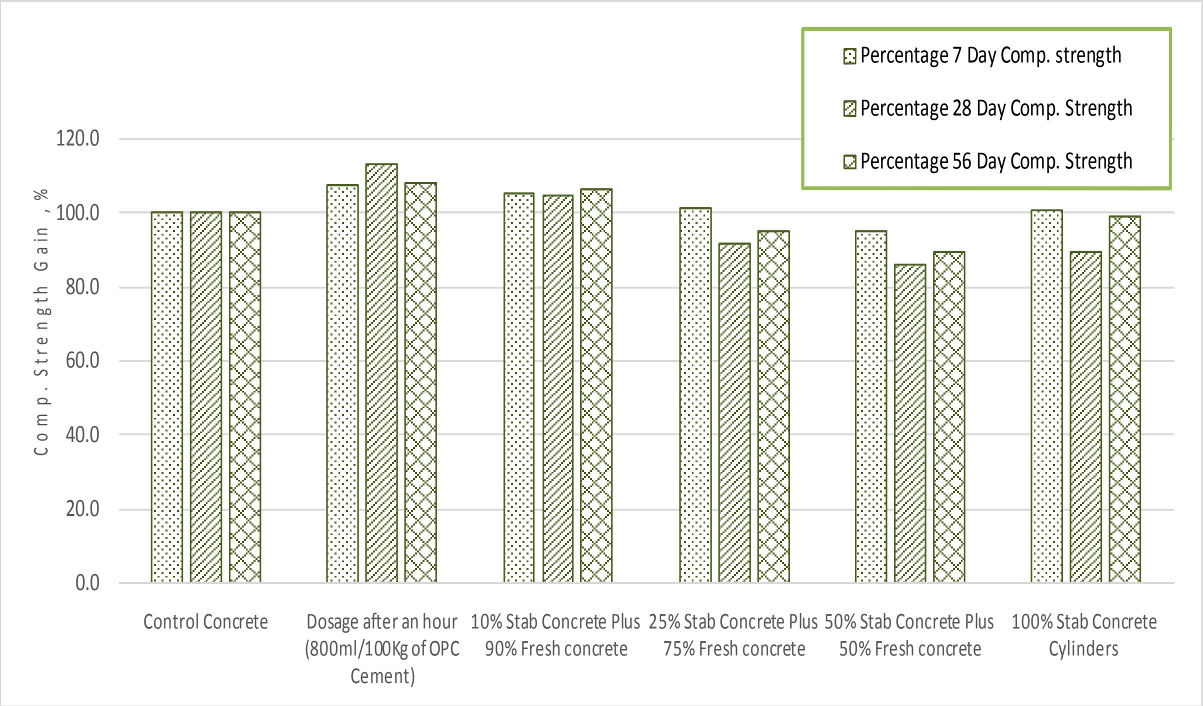


(q) Sample B and stabilizer dosage at 700ml/100kg of cementitious

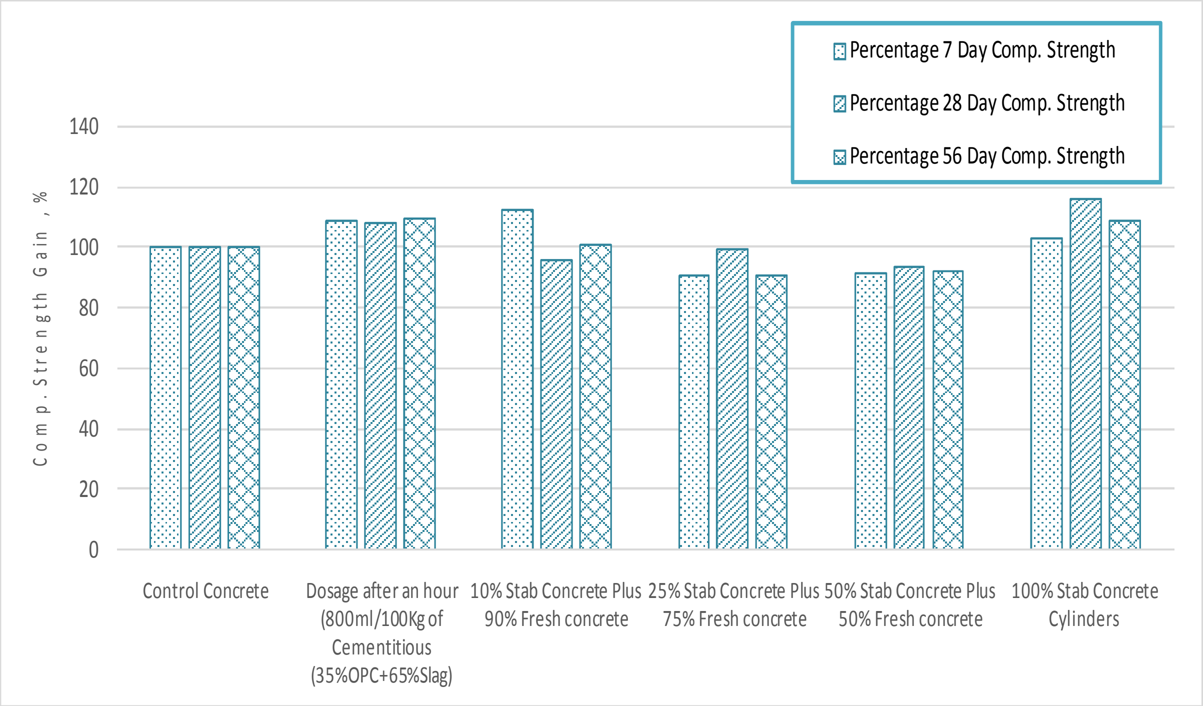


(r) Sample B and stabilizer dosage at 800ml/100kg of cementitious.

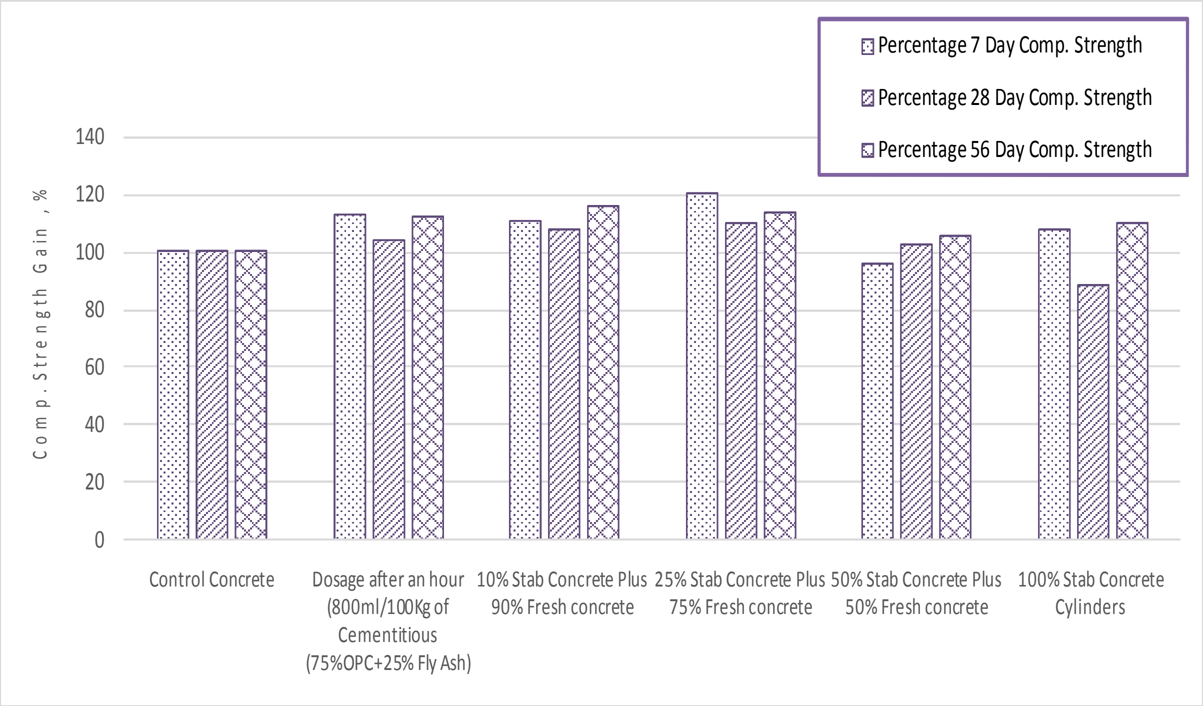
B 4.10.1: Compressive strength gain in percentage comparing to control concrete.



(a) OPC concrete.



(b) 35%OPC and 65% slag concrete.



(c) 75%OPC and 25% fly ash concrete.