EARLY HEAT EVOLUTION OF DIFFERENT – SIZED PORTLAND CEMENTS INCORPORATING GROUND GRANULATED BLAST FURNACE SLAG

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ABSTRACT

EARLY HEAT EVOLUTION OF DIFFERENT – SIZED PORTLAND CEMENTS INCORPORATING GROUND GRANULATED BLAST FURNACE SLAG

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Heat of hydration and rate of heat evolution are two important characteristics of portland cement hydration, significant for various concrete applications such as mass, hot-weather, and cold-weather concreting. The heat of hydration and rate of heat liberation of cement pastes, and concrete made with it, depend heavily on the chemical composition, fineness, and mineral admixture content of the cement used. This thesis investigates the influence of compound composition and GGBFS incorporation in different-sized portland cements on early heat of hydration and rate of heat liberation. Several portland cements are produced by intergrinding clinker, gypsum and GGBFS in different proportions. The cements are sieved into different particle size interval. Particle size distribution of each sample formed after sieving is measured with the laser diffraction method. Heat of hydration of samples is measured with an isothermal conduction calorimeter. Moreover, compound composition of each sample is calculated using the results of chemical analysis and quantitative determination of constituents. The result of each analysis is used to generate a correlation between fineness, GGBFS incorporation, chemical composition and heat of hydration.

It is found in this study that early heat of hydration and rate of heat evolution decrease as the content of GGBFS is increased. Moreover, the heat peak that occurs due to renewed ettringite formation occurs earlier as the content of gypsum decreases, alkalis and the content of GGBFS increases. Finally, GGBFS content decreases and C₂S content increases in the finer portions of the cements.

Keywords: Heat of hydration, portland cement, slag, isothermal calorimetry, particle size distribution

ÖΖ

FARKLI İNCELİKLERDEKİ, ÖĞÜTÜLMÜŞ YÜKSEK FIRIN CÜRUFLU PORTLAND ÇİMENTOSUNUN ERKEN YAŞTAKİ HİDRATASYON ISISI OLUŞUMU

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Çimentonun hidratasyon ısısı ve ısının oluşum hızı sıcak ve soğuk hava ile kütle beton dökümlerinde rol oynayan iki önemli faktördür. Çimento pastalarının ve bu çimento pastaları ile imal edilen betonun hidratasyon ısısı ve ısının oluşum hızı, kullanılan çimentonun kimyasal kompozisyonuna, inceliğine ve içerdiği mineral katkı miktarına önemli ölçüde bağlıdır. Bu tezdefarklı tane büyüklüğündeki Portland çimentolarının erken yaştaki hidratasyon ısılarında ve ısı oluşum hızlarında cürufun ve çimentonun içindeki bileşiklerin etkisi incelenmiştir. Klinkerin alçı ve öğütülmüş yüksek fırın cürufu ile farklı oranlarda beraber öğütülmesi ile farklı çimento tipleri oluşturulmuştur. Bu çimentolar farklı boy aralıklarına elenmişlerdir. Eleme işleminin ardından ortaya çıkan numunelerin tane dağılımı, lazer kırılımlı tane dağılımı analizi ile ölçülmüştür. Numunelerin hidratasyon ısısı izotermal kalorimetre ile ölçülmüştür. Ayrıca bütün numunelerdeki bileşik oranları, kimyasal analizlerin sonuçları ile toplam katkı miktarlarının kullanılmasıyla hesaplanmıştır. Analiz sonuçları numunelerin hidratasyon ısıları ile incelikleri ve cüruf oranları arasında bir bağlantı oluşturmak amacıyla kullanılmıştır.

Bu çalışmada çimentodaki cüruf oranının artmasının erken yaştaki hidratasyon ısısının azalmasına ve ısı oluşum hızının yavaşlamasına neden olduğu görülmüştür. Ayrıca gecikmiş etrenjit oluşumunun alçıtaşı miktarının azalması, granüle yüksek firin cürufu ve alkali miktarının artmasıyla hızlandığı görülmüştür. Son olarak katkılı çimentolardaki incelik arttıkça C₂S miktarının arttığı ve cüruf miktarının azaldığı görülmüştür.

Anahtar Kelimeler: Hidratasyon 1s1s1, çimento, cüruf, tane boyu dağılımı, izotermal kalorimetri

To My Parents,

Lale and Erdoğan Çetin

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LIST OF ABBREVIATIONS

- ACI: American Concrete Institute.
- ASTM: American Society for Testing and Materials.
- EN: European Norms
- CEN: European Committee for Standardization
- TS: Turkish Standards.
- GGBFS: Ground Granulated Blast Furnace Slag

CHAPTER 1

INTRODUCTION

1.1 General

While choosing the materials to be used for any kind of construction, the relative economy of available materials and properties of the materials are often compared. Concrete is the most common construction material in Turkey and all around the world because concrete is a water resistant, durable, economical material with a convincing compressive strength and it can be formed into any shape. According to the statistics published by Turkish Ready Mixed Concrete Association, more than 93 million m³ of concrete was produced in 2012 in Turkey [THBB, 2013].

Concrete is generally composed of cement, aggregate, water, mineral admixtures and chemical admixtures. When water is mixed with the cement in concrete, an exothermic reaction called hydration takes place between the cement compounds and water. Heat that is generated during the hydration is called heat of hydration. Concrete gains rigidity when sufficient amount of hydration products are formed. During the hydration, temperature of the concrete body increases, particularly in mass concrete applications such as dam construction. Concrete expands with the increasing temperature because it doesn't transfer the heat of hydration to its surroundings fast enough. As the concrete cools after hardening, contraction occurs. Since concrete has relatively low tensile strength, heat changes which occur on the body may result in unwanted cracks because of differential contraction movements. For applications like cold-weather concreting, relatively high heat of hydration can be beneficial [Erdoğan, 2005]. Consequently, heat of hydration and rate of hydration are important characteristics of concrete in many applications.

There are many factors that can affect the heat of hydration and rate of heat of hydration of cement such as compound composition and fineness of cement, ambient temperature, and amount of water in the mixture. Adiabatic, semi-adiabatic, isothermal conduction and solution calorimetry are four different methods used to measure the heat of hydration of cement. As described in EN 196-9 hile measuring the heat of hydration of cement by adiabatic calorimetry method by following the temperature rise in the sample, the heat that is generated during the hydration is not transferred from the adiabatic calorimeter to the environment. While measuring the heat of hydration of cement with the semi-adiabatic calorimetry method both the heat transferred from the calorimeter and the heat that caused an increase in the temperature of inside the calorimeter are calculated and added together. While measuring the heat of hydration of cement by isothermal conduction calorimetry method, the ambient temperature and the temperature of the cement paste stays the same and heat that is produced during the hydration process is transferred to the sensors that measure the instantaneous temperature changes of the sample. While measuring the heat of hydration of cement with the solution calorimetry method, the potential energy difference between dry cement particles and the partially or fully hydrated cement is measured by dissolving it in an acidic solution. Measurement of heat of hydration method by semi adiabatic calorimetry is described in EN 196-9. Measurement of heat of hydration using solution calorimetry is described in ASTM C 186 and EN 196-8. Isothermal conduction calorimetry method is explained in ASTM C 1702.

In blended cement production, mineral admixtures can either be separately ground and added to clinker or can be interground with the clinker. Furthermore they can also be added to concrete to increase durability. Mineral admixtures support environmental sustainability, provide economy and increase durability. Mineral admixtures are divided into two as natural pozzolans and artificial pozzolans. Fly ash is an artificial pozzolan that is obtained in power plants which produces electricity by burning coal. GGBFS is another mineral admixture which is a byproduct of the metal industry. Mineral admixtures like volcanic ash, pumicite are natural pozzolans.

1.2 **Objective and Scope**

In this study, the influence of particle size distribution, chemical composition, and GGBFS content of cement on early heat of hydration and rate of heat liberation was investigated. Moreover, grindability of GGBFS, gypsum and clinker compounds were investigated. For that purpose, several cements containing different amounts of GGBFS were produced by intergrinding clinker, GGBFS and gypsum and sieved into different sizes. Then, chemical compositions of the sieved cement samples were determined, and their heat of hydration and rate of heat liberation were measured with isothermal conduction calorimetry.

There are six chapters in this thesis. An introduction of the topic is given in the first chapter. The second chapter presents a theoretical background, with a survey of the literature on the heat of hydration of cement, its early heat evolution behavior, the influence of slag, the meanings of features on heat evolution vs. time graphs, some factors affecting heat of hydration, methods for measuring heat of hydration and importance of the subject. Moreover, literature review on grindability of clinker compounds, gypsum and GGBFS is presented in this chapter. Chapter three describes the experimental methods used in this specific study. Results of the experiments are discussed in the fourth chapter. The conclusions of the study and recommendations for the future studies are given in the fifth chapter.

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Hydration and Heat Evolution of Cement Compounds

Portland cement is a material produced by intergrinding clinker, in turn produced by burning calcareous and clayey materials, with gypsum. Cement is a hydraulic binder and cement hydration is the reaction of cement with water. Cement contains compounds which react with water. The rate of reaction and heat produced as a result of the reaction of each compound are different. Furthermore, the products that are formed as a result of hydration of each compound are different [Mehta and Monteiro, 2006].

Heat of hydration is the heat released as a result of the exothermic reactions that occur when cement compounds react with water. J/g and cal/g are typical units generally used to express the heat of hydration of cement.

There are four major compounds of clinker which affects the rate of heat of hydration and the total heat of hydration of the portland cement. These compounds are formed through the combination of oxides present in the cement-making raw materials, in the rotary kiln. The oxides in cement are abbreviated with single letters as shown in Table 2.1. The abbreviation of major cement compounds are also given in Table 2.1 [Erdoğan, 2005].

Table 2.1 Oxides	and cor	npounds	of	cement
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Oxides			Compounds		
Name	Chemical Formula	Abbreviation	Name	Chemical Formula	Abbreviation
Lime	CaO	С	Tricalcium Silicate	3CaO.SiO ₂	C_3S
Silica	SiO ₂	S	Dicalcium Silicate	2CaO.SiO ₂	C_2S
Alumina	Al ₂ O ₃	А	Tricalcium Aluminate	3CaO.Al ₂ O ₃	C ₃ A
Iron	Fe ₂ O ₃	F	Tetracalcium alumino ferrite	3CaO.Al ₂ O ₃ .Fe ₂ O ₃	C ₄ AF
Water	H ₂ 0	Н	Gypsum Rock	CaSO ₄ .2H ₂ O	$C\bar{S}H_2$
Magnesia	MgO	М			
Sulfuric anhydride	SO ₃	\bar{S}			
Soda	Na ₂ O	Ν			
Potassa	K ₂ O	K			

The four major compounds that affect the rate and total heat of hydration of cement are C_3S , C_2S , C_3A and C_4AF . C_3S and C_2S are the silicates which comprise about 75 % of cement by mass. C_3A and C_4AF are the aluminates which make up the remainder of the mass, along with impurities and gypsum rock. As such, the four main compounds of cement account for less than 100 % of the mass of cement [Mindess et al., 2003].

The major oxides of cement can be measured with different methods of chemical analysis such as the wet chemical analysis, by using an inductively coupled plasma and x-ray diffraction methods. The contents of major compounds of cement can be calculated approximately using Bogue's Equations given below [Erdoğan, 2005].

$$\begin{split} C_3S~(\%) &= 4.071(CaO) - 7.600(SiO_2) - 6.718(Al_2O_3) - 1.430(Fe_2O_3) - 2.852(SO_3) \\ C_2S~(\%) &= 2.867(SiO_2) - 0.7544(C_3S) \\ C_3A~(\%) &= 2.650(Al_2O_3) - 1.692(Fe_2O_3) \\ C_4AF~(\%) &= 3.043(Fe_2O_3) \end{split}$$

2.2 Hydration of Portland Cement

Cement hydration starts with the dissolution of cement compounds such as the calcium silicates. When the saturation limits for some of the products are reached nucleation by budding a solid phase starts. This process is called through solution mechanism because cements compounds are dissolved in the solution. Through solution mechanism is dominant in the early stages of cement hydration. As time goes by, the volume of hydration products increases and the amount of water in the mix decreases. Finally, the ionic mobility of the mix is limited. At this stage, called topochemical or solid-state, hydration continues on the surface of the cement and the dissolution of the cement particles into the solution stops [Mehta and Monteiro, 2006].

The hydration of portland cement occurs with the chemical reactions between clinker compounds, calcium sulfate, and water. While some of the reactions happen at the same time, some of them happen consecutively. In fact, the rates of these various reactions differ from each other. Also, some of these reactions affect each other [Odler, 2004]. To better understand the hydration characteristics of cement, each compound of portland cement clinker must be examined separately.

2.2.1 Hydration of Calcium Silicates

The products of C_3S and C_2S hydration are the same. The reactions of these compounds are given below [Erdoğan, 2005].

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$$
$$2C_2S + 6H \rightarrow C_3S_2H_3 + CH$$

The structure of both calcium silicate hydrates ($C_3S_2H_3$), which is a rigid gel with amorphous structure produced by C_3S and C_2S are similar. However, the C/S ratios of calcium silicate hydrates produced by C_3S differ from the ones produced by C_2S , despite being shown as identical in the simplified formula above. In fact, the C/S ratio of calcium silicate hydrates differs depending on many factors such as water/cement ratio, temperature and the age, or the time after the beginning of hydration. As a conclusion, since the chemical composition of calcium silicate hydrates vary, they are generally shown as C-S-H. On the other hand, differences in the chemical composition of C-S-H don't have much influence on its physical properties [Mehta and Monteiro, 2006].

Hydration of C_3S starts with a high rate of dissolution. Solution becomes oversaturated and precipitation of C-S-H forms starts around the surface before the dissolved ions are separated homogenously in the solution. This period is called the pre-induction period and it lasts for few minutes. In this period, increase in the degree of reaction is greater than the other periods of the hydration [Odler, 2004].

A new period called the dormant or induction period starts when the rate of reaction and rate of heat of hydration decreases following the pre-induction period. This new period lasts for a few hours. There are some theories about the hydration kinetics of C_3S in the dormant period. According to one theory, an unstable C-S-H layer with a 1 nm average thickness is formed around the C_3S surface during the pre-induction period which blocks the dissolution of C_3S [Taylor, 1997]. Hydration rate decreases during the induction period since the rate of dissolution of C_3S is decreased. When C-S-H with stable characteristics starts to nucleate from the solution at the beginning of the induction period, the unstable C-S-H layer starts to dissolve. The dissolution of the protective layer gradually removes the block on unhydrated C_3S and rate of nucleation of C-S-H rises at the end of the induction period [Taylor, 1997].

After the induction period, a nucleation controlled period called acceleration or post induction starts. Nucleation of stable or a second stage C-S-H causes a high rate of reaction and increase in rate of heat of hydration evolution. The rate of the reaction in this period is the highest after the pre-induction period. As the amount of materials that are reacting decreases and the process becomes more diffusion controlled, the rate of reaction decreases and the decrease in the reaction continues until all the C_3S is consumed [Odler, 2004]. The hydration mechanism of C_2S and C_3S are similar. However, C_2S hydrates slower than C_3S [Odler, 2004].

2.2.2 Hydration of Aluminates

Calcium aluminates react differently with water in the environment containing calcium hydroxide and calcium sulfate. Calcium sulfate exists in unreacted cement, added to prevent rapid reaction of calcium aluminates with water resulting in flash set. Calcium hydroxide is a product of the reactions of calcium silicates. So, the behavior of the calcium aluminates must be examined with considering an environment containing calcium hydroxide and calcium sulfate [Mehta and Monteiro, 2006]. Reactions that result with the formation of ettringite and monosulfate are given below [Mehta and Monteiro, 2006]. When the amount of sulfate is sufficient, ettringite is produced firstly with a rapid reaction of C_3A . If SO_4^{-2} ions in the solution are not sufficient, monosulfate is produced [Odler, 2004].

Ettringite:

$$[AlO_4]^- + 3 [SO_4]^{2-} + [Ca]^{2+} + H \rightarrow C_6 A \bar{S}_3 H_{32}$$

Monosulfate:

$$[AlO_4]^- + [SO_4]^{2-} + 4 [Ca]^{2+} + H \rightarrow C_4 A \bar{S} H_{18}$$

The reaction rate decreases after the formation of ettringite on the surfaces of particles. A dormant period starts and it lasts until an increase in rate of reaction for the second time. The length of the dormant period is related with the amount of calcium sulfate in the reaction. Formation of ettringite from sulfate ions and C_3A is controlled by the dissolution of the C_3A [Bullard et al., 2011]. Many factors including amount of gypsum and alkalies affect the duration of the dormant period of C_3A hydration. In fact, it has been reported that an increase in alkali content increases the rate of reaction of C_3A with gypsum [Lerch, 1946]. During the second rise of reaction that results with the formation of monosulfate from ettringite is as follows [Mehta and Monteiro, 2006]:

$$C_6AS_3H_{32} + 2C_3A + 22H \rightarrow 3C_4A\bar{S}H_{18}$$

Furthermore, C_4AH_{19} and C_4ASH_{12} are formed as the hydration products of C_3A when the calcium sulfate is finished [Odler, 2004]. Products formed as a result of the reactions of C_4AF are thought to be similar with the products of C_3A . The main difference between the reactions of the two compounds is that C_4AF reacts slower than C_3A . As the amount of alumina in the structure of C_4AF increases, the reactivity of the C_4AF increases [Mehta and Monteiro, 2006].

2.3 **Periods of Heat Evolution in Portland Cement**

The heat evolution of a portland cement is typically evaluated in six different periods presented in Figure 2.1 Periods of heat evolution are explained below.

Pre-InductionPeriod (1, 2): Dissolution of alkali sulfates is responsible for the endothermic peak (1) that is observed in some types of cements. A few minutes after mixing

water with cement fast reactions of C_3S and C_3A causes a rise in the heat flow diagram. It is also thought that gypsum hydration has an influence on the second peak that is observed.

Dormant Period (3): A period called dormant or induction period where the rate of heat evolution decreases follows the pre-induction period. The main reasons for the slowing down of the heat evolution is the decrease in the reaction rate of C_3S because of the first stage C-S-H blocking the dissolution of unhydrated C_3S in the cement.

Acceleration Period (4): The formation of second stage C-S-H by nucleation and removal of the first stage C-S-H blocking the unhydrated C_3S causes a rise in the heat evolution curve. Acceleration period continues until the second exothermic peak.

Post Acceleration Period (5, 6): After the second exothermic peak, reactions slow down because the reactions become diffusion controlled. At later ages the reactions become topochemical and a gradual decrease in the rate of heat evolution is observed. Shoulder peaks (5, 6) can be observed in some cement types after the second exothermic reaction. This shoulder represents renewed ettringite formation. When the amount of solid sulfate coming from gypsum is exhausted, adsorbed sulfate in C-S-H structure starts to react with the dissolved C_3A . As a result, ettringite is formed [Odler, 1980]. Second shoulder is observed when the monosulfate is formed because of lack of calcium sulfate.



Figure 2.1 Rate of heat evolution curve of a typical portland cement [Odler, 2004].

2.4 Some Factors Influencing Heat of Hydration

Heat of hydration of cement is affected by many factors. The factors related to this particular are summarized in this section.

Particle size distribution is an important factor influencing heat of hydration. As the fineness of cement increases, the total surface area of the cement particles increases. As the surface area increases, the area of cement that is in contact with water increases. As a result, higher fineness causes a higher rate of reaction, and higher rate of heat liberation [Kosmatka, 1997].

Water-to-cement ratio also influences rate of heat of hydration and the rate of increase of the degree of hydration. It is calculated that water to cement ratio must at least be 0.42 for completion of the hydration of cement particles [Mindess et al., 2003]. As the content of water added to a mixture increase, while the content of cement is kept constant, the amount of space for dissolution of compounds increases. To sum up, rate of hydration is increased when the water-to-cement ratio is increased. For an ordinary portland cement, an 11 % increase in heat of hydration was observed when the water-to-cement ratio was increased from 0.4 to 0.6 [Kosmatka, 1997].

Effect of chemical composition is substantial for both heat of hydration and rate of heat liberation of cement. It is hard to comment on hydration characteristics of portland cement by solely looking at its oxide composition. For a better understanding of portland cement hydration compound composition must be measured or estimated.

The most reactive compound in portland cement is C_3A . It reacts immediately after water is mixed with cement. Furthermore, heat released from the hydration of C_3A is the greatest all the major compounds of cement as shown in Table 2.2. Rapid reaction of C_3A is controlled by the use of gypsum in the mix [Mehta and Monteiro, 2006].

	Heat of hydration at the given age (cal/g)						
Compound	3 days 90 days 13 years						
C₃S	58	104	122				
C ₂ S	12	42	59				
C ₃ A	212	311	324				
C ₄ AF	69	98	102				

Table 2.2 Heat of hydration of portland cement compounds [Mehta and Monteiro, 2006].

Rate of reaction of C_3S is higher than that of C_2S and the heat released from the hydration of C_3S is greater compares to heat from C_2S . Information about the heat of hydration of compounds is given in Figure 2.2 and Table 2.2 [Mehta and Monteiro, 2006].



Figure 2.2 Effect of cement composition on heat of hydration [Mehta and Monteiro, 2006].

2.5 Effect of GGBFS on Cement Hydration

GGBFS is a supplementary cementitious and pozzolanic material that can be added to cement or concrete in different proportions to improve their properties. GBFS is a byproduct of pig iron production facilities. GBFS can be used as a cementitious and pozzolanic material when it is cooled rapidly after it is taken from the furnace [Ramachandran, 1995].

GGBFS can be a cementitious material. However, it does not react as soon as it is mixed with the water. Compounds such as alkalis and sulfates are needed in the reaction with water to activate the GGBFS. It reacts after the needed activators are released as a part of hydration process. Pozzolanic property is the ability to react with lime that is produced during cement hydration to produce C-S-H at the end. The simplified formulas of pozzolanic reactions are given as follows [Mindess et al., 2003]:

$$S + CH + H \rightarrow C - S - H$$

 $A + CH + H \rightarrow C - A - H$

Use of GGBFS in cement decreases the heat of hydration [Bougara et al., 2009]. Rate of pozzolanic reaction is lower than the rate of cement compound hydration. In fact, its rate can be accepted to be similar to that of C_2S hydration [Mindess et al., 2003].

It is also known that alumina in the GGBFS reacts with the gypsum during the early ages of hydration [Regouro, 1980]. So, incorporating GGBFS may cause early exhaustion of gypsum.

2.6 Significance of Heat of Hydration

Heat of hydration and rate of heat of hydration are important characteristics for applications such as mass concreting, hot weather concreting, and cold weather concreting. Cement properties affecting the heat of hydration should be known to solve temperature-related problems in these applications. Rate of heat liberation graphs provide hints for a better understanding of hydration process of Portland cement.

Structures such as dams, deep beams, large columns, piers and locks where a large amount of concrete is poured are referred to as mass concrete applications. Extra effort must be made to deal with the rate of heat evolution and the volume change that subsequently occurs [Mehta and Monteiro, 2006]. Very large amounts of concrete are poured for mass concrete applications and the rate of heat dissipated from the chemical reactions between the water and cement increases. Since concrete is a rather effective heat insulator, the heat produced during hydration is not released from the concrete body immediately. At the end, increasing temperature causes expansions in the mass concrete. As time passes the concrete body cools down and contraction begins. The tensile stress caused by these restrained contractions can be greater than the tensile strength of the concrete at that time. In this situation cracks are formed in the structure. It is important to know the cement properties which cause high heat of hydration in such cases.

Generally it is accepted that pouring concrete between 5 °C and about 30 and 32 °C is normal [Erdoğan, 2010]. When the concrete is poured in hot weather, conventional concrete will tend to set and harden earlier than expected. Mass concreting on hot weather is also critical because the rate of hydration tends to increase with relatively high surrounding temperatures. Types of cement which will provide sufficient strength when hydrated and with a low heat of hydration must be known. In fact, hydration characteristics of the cement must be understood.

When concreting takes place at temperatures lower than +5 °C, the rate of reactions between cement and water is lowered significantly. As a result, concrete sets and hardens later than expected. Also, strength of the concrete does not reach the desired levels when expected and molds can't be removed on time. Water which does not react because of the slow hydration may freeze and occupy a big space in the mixture. The volume left over from the ice after hydration stays as a pore and decreases the strength of the concrete [Erdoğan, 2010]. Keeping the temperature of fresh concrete high in cold weather applications is a straight forward solution to speed up the hydration. Consequently, knowing the hydration characteristics of cement to have high initial rate of hydration is important.

Compound composition of cement is a factor influencing the heat of hydration and rate of heat liberation of portland cement [Mehta and Monteiro, 2006]. Since heat is produced from the reactions between water and cement compounds, monitoring hydration process is possible by investigating the rate of heat liberation curves. For applications where heat of hydration and rate of heat liberation is of importance, understanding the hydration process to utilize specific types of cements with predetermined compound compositions is crucial.

2.7 Heat Measurement Methods

2.7.1 Heat of Solution

A detailed explanation of measurement of hydration heat using the heat of solution method is given in ASTM C 186 and EN TS 196-8. The experiment is done for a specific period either 7 or 28 days. The total heat of hydration of cement during this specific period is measured. Unhydrated samples of cement and cement samples hydrated for the chosen time period are dissolved in a mixture containing nitric and hydrofluoric acids. Heat released during the dissolution is measured and heat of hydration calculated by subtracting the heat released during the dissolution process of the hydrated cement from heat released during the dissolution of the unhydrated cement.

According to the heat of solution method, dissolution of hydrated and unhydrated cement particles reveals their potential energy. The potential energy difference between unhydrated and hydrated cement is the heat of hydration of the hydrated cement [Poole, 2007]. The advantage of this method is that utilization of laboratory equipment for this method is easier than the other methods. On the other hand, this method does not let the user to observe rate of heat evolution. It only gives the total heat of hydration for a chosen period.

2.7.2 Semi-adiabatic Calorimetry

Heat of hydration and rate of heat liberation of cement can be observed using the semiadiabatic method described in EN 196-9. In this method, a cement sample is mixed with a specific amount of graded sand and water. After mixing, the mortar is placed into a cylindrical container which is immediately placed into the semi-adiabatic calorimeter. The calorimeter keeps some of the heat that is produced during the hydration inside and the rest of the heat is released from the calorimeter. Heat inside the calorimeter is measured by observing the temperature changes with a temperature probe. The total heat of hydration is calculated by adding the calculated heat kept inside of the calorimeter to heat that was leaked from the calorimeter.

2.7.3 Adiabatic Calorimetry

When the volume of concrete placed without the joints is large, heat that is formed at the core of the concrete does not pass to the environment. It is known that when the ambient temperature ascends, rate of heat liberation and rate of hydration ascends. When the heat formed during the hydration stays in the body of high volume concrete structure, rate of heat liberation increases. Adiabatic calorimetry method is applied to model the heat of hydration of the large volume concrete bodies. In this method temperature differences of the center of the concrete specimen is measured and recorded. Heat of hydration can be measured if the heat capacity of the specimen is known [Poole, 2007].

2.7.4 Isothermal Conduction Calorimetry

Heat of hydration and rate of heat liberation of cement can be observed using isothermal calorimetry method which is described in ASTM C 1702. In this method, the ambient temperature of the mixture containing cement and water are kept constant by the use of a heat sink in touch with the cement sample. The heat which is produced by the sample is measured immediately after formation and the heat sink adsorbs the heat produced by the sample. In fact, the heat created by the sample produces a voltage signal which is proportional with heat liberation and this signal is measured by heat flow sensors.

Also, there are two different samples in the isothermal conduction calorimeter; one of them is the sample that is prepared for heat measurement and the other one is an inert sample. While measuring the heat of hydration, signals coming from the inert sample are subtracted from the signals coming from the active sample. This subtraction helps provide stability. The configuration of the isothermal conduction calorimetry is given in Figure 2.3 Rate of heat

evolution is measured and related graphs are produced with this method. Furthermore, the graph of total heat of hydration can be drawn by integrating the heat flow graph.

Heat flow is measured with a high sensitivity in the isothermal conduction calorimetry method. So, this method is applicable for measuring heat of hydration of cements with admixtures [Poole, 2007].



Figure 2.3 Cutaway view twin configuration [TAM Air Calorimeter Operator's Manual, 2007]

2.8 Ease of Grinding of Clinker Compounds, Gypsum and GGBFS

Compounds of cement don't have identical grindabilities. After intergrinding the cement with gypsum it is observed that gypsum is ground to the finer fractions. In fact, gypsum contributes 15 % of the total surface area of the cement [Taylor, 1997]. It is also observed that C_3S content increases while C_2S content decreases, as the particle size of the cement increases. Aluminates and ferrite phases are distributed evenly on different particle size fractions [Taylor, 1997]. Moreover, clinker is easier to grind than GGBFS [Öner, 2000].

2.9 Measuring the Particle Size Distribution of Cement

Different particle size distribution measurement methods give different results since there is more than one true way of measuring the particle size distribution of particles. Compared to sieve analysis, the result of laser diffraction analysis can be different because of the differences between measurement methods. In laser diffraction analysis the volume of equivalent spheres of particles in different size ranges are calculated. When samples which are sieved from a certain sieve size are measured using laser diffraction method, particles having larger diameter than the sieve opening can be observed. To illustrate, a particle having relatively small width and thickness but a large length can pass from the sieves having opening sides larger than the thickness and width of the particle. When the same particle having relatively small width and thickness but a large length is transformed to an equivalent sphere, the diameter of the sphere can be larger than the opening of the specified sieve size.

CHAPTER 3

EXPERIMENTAL METHODS AND PROCEDURE

3.1 General

Influence of GGBFS addition on the rate of heat liberation and heat of hydration of cement having different particle size distributions is investigated in this study. Clinker, GGBFS and gypsum were interground in R&D Institute of Turkish Cement Manufacturers Association (TCMA) in a ball mill with the balls conforming to TS 7700. Three groups having different amounts of clinker, GGBFS, and gypsum were prepared. Furthermore, a control group containing clinker and gypsum was prepared. All 4 groups were interground to specific surface area $3770 \pm 50 \text{ cm}^2/\text{g}$. Then, each group of cement was sieved into 4 different particle size subgroups which have sizes from 0 to 10, 10 to 30, 30 to 50 and over 50 micrometers. The sieving was performed in the Materials of Construction Laboratory of Middle East Technical University by using a sonic sifter. Consequently, 20 samples were produced with the designation given in Table 3.1.

Table 3.1 Designation of samples

Sine Course	GGBFS Content (%)				
Size Group	0	6	20	35	
Before Sieving	UC	US6	US20	US35	
0 to 10 µm	0C	0S6	0S20	0835	
10 to 30 µm	10C	10S6	10S20	10S35	
30 to 50 µm	30C	30S6	30S20	30S35	
>50 μm	50C	50S6	50S20	50S35	

C and S are used in Table 3.1 to represent the control and GGBFS incorporating cement, respectively. The numbers before C or S represents the particle size distribution group. The numbers following C or S represent the content of GGBFS introduced into the unsieved samples. Finally, capital U stands for the unsieved samples.

Percentages of constituents of each group before grinding is given in Table 3.2. Chemical analyses of the cement samples, clinker, GGBFS and gypsum were done in the R&D Institute of TCMA and the results are given in Tables 3.3 to 3.7 Compound composition of the samples produced after sieving are also calculated using a method for quantitative determination of the constituents described in TSE CEN/TR 196-4 and the results of the chemical analysis of clinker, GGBFS and gypsum. The calculations are shown in Appendix A and the results of the calculations are given in Tables 3.4 to 3.7 with the compound compositions of unsieved samples of each group that are calculated using Bogue's Equations. Moreover, rate of heat liberation and heat of hydration of each sample were measured in Materials of Construction Laboratory of Middle East Technical University using isothermal conduction calorimetry.

Table 3.2 Percentages of constituents of each group before grinding

	Group 1 (%)	Group 2 (%)	Group 3 (%)	Group 4 (%)
Clinker	95	89.3	76.8	62.4
GGBFS	-	6	20	35
Gypsum	5	4.7	3.2	2.6

Table 3.3 Oxide compositions of clinker, gypsum and GGBFS

		Clinker	Gypsum	GGBFS
SiO ₂	(%)	20.49	1.85	40.94
Al ₂ O ₃	(%)	4.49	0.05	13.54
Fe ₂ O ₃	(%)	4.29	0.19	0.95
CaO	(%)	66.41	32.40	32.64
MgO	(%)	0.97	0.21	7.38
SO3	(%)	0.77	44.47	2.19
Na ₂ O	(%)	0.21	< 0.01	0.24
K ₂ O	(%)	0.80	0.07	1.23
Na ₂ O Equivalent	(%)	0.74	0.05	1.05
LOI	(%)	1.10	20.89	< 0.01

С							
		0-10 μm	10-30 µm	30-50 μm	>50 μm	Unsieved	
SiO ₂	(%)	18.25	20.26	20.22	20.42	20.23	
Al ₂ O ₃	(%)	4.15	4.10	4.52	4.62	4.51	
Fe ₂ O ₃	(%)	4.30	4.32	4.61	4.71	4.15	
CaO	(%)	60.10	64.41	63.89	64.59	64.07	
Free CaO	(%)	3.14	1.95	1.85	1.99	2.23	
MgO	(%)	1.07	1.10	1.10	1.03	0.98	
SO ₃	(%)	4.88	1.89	1.46	1.78	2.37	
Na ₂ O	(%)	0.20	0.20	0.21	0.21	0.20	
K ₂ O	(%)	0.74	0.75	0.78	0.78	0.76	
Na2O Equivalent	(%)	0.68	0.69	0.72	0.72	0.70	
LOI	(%)	4.33	1.90	1.61	1.93	2.61	
C ₃ S	(%)	56.6	63.3	66.6	65.6	62.3	
C_2S	(%)	11.8	7.6	7.3	7.8	8.7	
C ₃ A	(%)	4.3	4.4	4.5	4.5	4.4	
C ₄ AF	(%)	12.1	12.3	12.8	12.7	12.4	

Table 3.4 Oxide and compound compositions of the control group cement samples

Table 3.5 Oxide and compound compositions of sieved subgroups of S6

	\$6											
		0-10 μm	10-30 µm	30-50 μm	>50 μm	Unsieved						
SiO ₂	(%)	19.50	21.45	22.07	22.14	21.53						
Al ₂ O ₃	(%)	4.57	4.54	5.06	5.11	5.01						
Fe ₂ O ₃	(%)	4.36	4.21	4.24	4.45	4.01						
CaO	(%)	59.25	62.91	62.48	61.85	62.56						
Free CaO	(%)	2.95	1.83	1.74	1.87	2.10						
MgO	(%)	1.36	1.48	1.18	1.73	1.11						
SO ₃	(%)	4.35	1.93	1.35	1.68	2.37						
Na ₂ O	(%)	0.19	0.20	0.21	0.21	0.20						
K ₂ O	(%)	0.74	0.77	0.81	0.81	0.78						
Na ₂ O Equivalent	(%)	0.68	0.71	0.74	0.74	0.72						
LOI	(%)	4.52	1.91	0.63	1.77	2.16						
C₃S	(%)	54.5	60.2	62.0	60.3	58.9						
C ₂ S	(%)	11.1	7.2	6.8	7.3	8.2						
C ₃ A	(%)	4.1	4.1	4.2	4.2	4.1						
C₄AF	(%)	11.6	11.7	11.9	11.7	11.7						

	<u>S20</u>										
		0-10 μm	10-30 µm	30-50 µm	>50 µm	Unsieved					
SiO ₂	(%)	22.32	24.27	25.11	26.02	24.47					
Al ₂ O ₃	(%)	5.75	5.95	7.02	7.39	6.51					
Fe ₂ O ₃	(%)	4.16	3.83	3.55	3.77	3.71					
CaO	(%)	56.79	59.93	57.33	55.82	58.18					
Free CaO	(%)	2.51	1.56	1.48	1.59	1.78					
MgO	(%)	2.15	2.44	2.42	2.98	1.92					
SO ₃	(%)	3.37	1.28	0.88	0.98	1.80					
Na ₂ O	(%)	0.20	0.21	0.22	0.22	0.21					
K ₂ O	(%)	0.81	0.86	0.89	0.89	0.85					
Na₂O Equivalent	(%)	0.74	0.78	0.80	0.80	0.77					
LOI	(%)	3.44	1.24	1.54	1.11	1.89					
C₃S	(%)	52.4	54.1	51.7	50.0	53.1					
C ₂ S	(%)	9.5	6.1	5.7	6.1	6.9					
C ₃ A	(%)	3.8	3.7	3.5	3.5	3.7					
C ₄ AF	(%)	10.9	10.4	9.9	9.7	10.4					

Table 3.6 Oxide and compound compositions of sieved subgroups of S20

Table 3.7 Oxide and compound compositions of sieved subgroups of S35 $\,$

	\$35										
		0-10 μm	10-30 µm	30-50 μm	>50 μm	Unsieved					
SiO ₂	(%)	24.03	26.94	28.13	30.46	27.59					
Al ₂ O ₃	(%)	7.03	7.81	8.04	9.57	7.94					
Fe ₂ O ₃	(%)	3.70	3.26	3.04	3.04	2.97					
CaO	(%)	53.92	53.58	51.75	48.99	53.58					
Free CaO	(%)	2.04	1.27	1.20	1.29	1.45					
MgO	(%)	2.85	3.38	3.25	4.47	3.02					
SO ₃	(%)	2.80	0.96	0.51	0.62	1.48					
Na ₂ O	(%)	0.21	0.22	0.22	0.22	0.22					
K ₂ O	(%)	0.86	0.92	0.96	0.96	0.91					
Na₂O Equivalent	(%)	0.78	0.83	0.85	0.85	0.81					
LOI	(%)	3.01	0.93	0.95	0.32	1.45					
C₃S	(%)	46.9	45.9	40.9	34.3	50.1					
C₂S	(%)	7.8	5.0	4.6	4.8	1.2					
СзА	(%)	3.4	3.1	2.8	2.4	3.1					
C ₄ AF	(%)	9.6	8.8	7.9	6.8	8.7					

GGBFS, gypsum and clinker contents of the samples produced after sieving are measured using TSE CEN/TR 196-4 and the results are given in Table 3.8.

			0-10) µm			10-3	0 µm			
		С	S6	S20	S35	С	S6	S20	S35		
Gypsum	(%)	7.8	7.0	5.4	4.5	6.0	3.1	2.1	1.5		
GGBFS	(%)	0.0	2.5	11.7	22.5	0.0	4.7	18.2	31.2		
Clinker	(%)	92.2	88.3	83.0	73.1	94.0	89.2	79.7	67.2		
			30-5	0 μm			> 50) μm	3.20 3.00 2.1 1.5 18.2 31.2 79.7 67.2 μm S20 S35 1.6 1.0 24.0 43.8		
		С	S6	S20	S35	С	S6	S20	S35		
Gypsum	(%)	2.3	2.2	1.4	0.8	2.8	2.6	1.6	1.0		
GGBFS	(%)	0.0	6.8	22.6	38.9	0.0	7.9	24.0	43.8		
Clinker	(0/.)	077	01.1	76.0	60.3	07.2	80.5	74.4	52.1		

Table 3.8 Constituent percentages of the cements

3.2 **Procedure**

3.2.1 Sieving the Cement Groups

16 samples in particle size intervals between 0 and 10 μ m, 10-30 μ m, 30-50 μ m, > 50 μ m were produced from 4 cement groups using the sonic sifter separator shown in Figure 3.1 While the column built in sonic sifter vibrates in an intensity chosen by the user, a vertical mechanical pulse which changes the orientation of the particles and prevents agglomeration is applied to the sieves. While producing the samples, a horizontal pulse accessory shown in Figure 3.1 was also used to prevent agglomeration of fine particles.

Cement cannot be sieved in very fine particle size intervals with a liquid like water since it hardens when it is mixed with the water. The sonic sifter provides a way to sieve the cement groups using a dry method. Since the sieves shown in Figure 3.2 are very fragile, 3 grams of samples are added in each sieving period. As the cement gets finer, the amount of time needed to get the products increases. To get an average 0.6 g of sample having particle size between 0 and 10 μ m, 3 g of cement is sieved around 60 to 70 minutes. A minimum of 13 g of cement was produced for each sample to be used for chemical analysis, heat of hydration measurements, and particle size distribution analyses.

It was also observed that efficiency of the separator increases when the sieves are washed periodically. Moreover, it is not efficient to sieve the cement through more than two sieves at once with sonic sifter.



Figure 3.1 Sonic sifter and horizontal pulse accessory



Figure 3.2 Sieve used in sonic sifter

3.2.2 Measuring the Particle Size Distribution of the Samples

Particle size distribution of all 20 samples was measured using laser diffraction analysis with the Malvern Mastersizer 2000 shown in Figure 3.3. In Mastersizer 2000, a laser light is sent through a cloud of particles which scatter the light. The scattered light is measured using the detectors at various angles behind the particles. The angle of scattered light gets smaller as the size of the particles gets bigger. Moreover, particles are accepted as spheres with volumes equivalent to those of the real particles in this method.



Figure 3.3 Malvern Mastersizer 2000

3.2.3 Measurement of Rate of Heat Liberation and Heat of Hydration

Rate of heat liberation and heat of hydration of all 20 samples were measured with isothermal conduction calorimeter shown in Figure 3.4 For each measurement, 3.5 g of powder sample was mixed with 1.4 g of deionized water. In fact, water-to-cementitious material ratio was chosen as 0.4. However, it was observed for samples in particle size interval 0-10 μ m that water used for the measurement was not adequate to hydrate all of the cement. So, for the samples having particles between 0 and 10 μ m, 2 g of water was used in the mix. Moreover, channel temperature was chosen to be 23 °C during the measurements of all samples.



Figure 3.4 Isothermal conduction calorimeter

For the measurement of the rate of heat liberation and heat of hydration, the following steps were applied. First, cement sample is weighed and placed into the 20 ml disposable glass ampoule. Second, a syringe shown in Figure 3.5 with two tubes for water and a mechanical device for mixing the sample, when the water is added is used. The syringe is installed to the ampoule and placed into the channel.



Figure 3.5 Syringe used in isothermal calorimeter

Since the heat flow sensors are highly sensitive, heat flow graph that is observed on the screen of computer becomes unstable because of the heat exchange when the channel is exposed to the ambient conditions during the placement of the sample. In order to observe the rate of heat of hydration of the sample correctly at early ages, water in the syringe was added to the sample only after the heat flow in the channel was stabilized. Finally, the measurement of heat was stopped more than 48 hours after the start of the reaction upon addition of the mixing water.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 General

Results of the conduction calorimetry analysis of each sample with varying content of GGBFS are presented in this chapter. To understand the heat of hydration and heat liberation behavior of the samples, results of the chemical analysis and particle size distributions of the samples are examined. Moreover, the ease of grinding of each cement compound, GGBFS and gypsum is presented.

4.2 **48-h Heat of Hydration of the Samples**

The 48-h heat of hydration values obtained for each cement sample from isothermal conduction calorimetry are given in Table 4.1 Moreover, the heat of hydration evolution for the cement groups is given in Figures 4.1, 4.2.

Designation	0-10 µm	10-30 µm	30-50 μm	>50 µm	Unsieved
C0	337.1	200.2	126.6	129.1	224.4
S6	327.4	200.8	118.1	120.7	213.4
S20	310.0	160.2	87.1	73.9	186.3
S 35	265 1	128.0	55.5	55.7	154.4

Table 4.1 Total heat of hydration values of 20 cement samples (J/g)





Figure 4.1 Total heat of hydration graphs of (a) control group, (b) cement group containing 6 % GGBFS, (c) 20 % GGBFS, (d) 35 % GGBFS respectively





Figure 4.2 Total heat of hydration graphs of cement groups in particle size interval (a) 0-10 μ m, (b) 10-30 μ m, (c) 30-50 μ m, (d) >50 μ m and (e) that are not sieved

4.3 Effect of GGBFS Content and Particle Size Distribution on Early Heat of Hydration

The effect of GGBFS content and sieving particles to separate size intervals on the early heat of hydration of cement samples can be explained as follows:

1- As the particle size of the cement samples containing equal GGBFS contents increases, the 48-h heat of hydration of the cement samples decreases. However, 48-h heat of hydration of 30C, 30S6 and 30S35 are smaller than 50C, 50S6 and 50S35 respectively. Moreover, early heat of hydration values of 30S20 and 50S20 are close to each other. It can be seen in Figure 4.3 and Table 4.2 that actual particle size distribution of cement samples retained on the 50 μ m sieve contain slightly more fines below 15 μ m than the 30-50 μ m.





Figure 4.3 Particle size distribution of (a) control group cements, (b) cement samples containing 6 % GGBFS, (c) 20 % GGBFS, (d) 35 % GGBFS

Table 4.2 Differences in the con	ntent of materials	s below 15	µm bet	ween the	cement	samples
>50 and in particle size interval	30-50 μm					

		([>50 µm] – [30-50 µm]) (%)
	C0	7.7
<15 um	S6	8.5
<15 μm	S20	5.9
	S35	3.7

2- As the content of added GGBFS increases, the 48-h heats of hydration of the cement samples decrease for samples sieved into identical size intervals except for 10C and 10S6. When the particle size distributions of 10C and 10S6 are examined, it is observed that content of particles of 10C finer than 10 μ m is lower than that of 10S6 by 1.7 %.

4.4 Effect of GGBFS Content and Fineness on the Rate of Heat Liberation

4.4.1 Effect of GGBFS Content and Fineness on the Dormant Period

It is observed in Figure 4.4 that the start of the dormant period is delayed with increasing content of GGBFS or with decreasing content of clinker. On the other hand, a relation between time needed to get to dormant period and fineness of the cement is not detected as shown in Table 4.3. Also, the amount of clinker in the larger size groups is less than in the smaller size groups, due to differences in grindability (Table 3.8).







Figure 4.4 Dormant periods of cement samples in particle size (a) 0-10 μ m, (b) 10-30 μ m, (c) 30-50 μ m, (d) >50 μ m, and (e) unsieved cements

Table 4.3 Minima of Rate of Heat Hydration Time Curves of the cements

	Duration untill heat rate minima is obtained (min)								
Cement	0-10 (μm) 30-50 (μm) 30-50 (μm) >50 (μm) 1								
Control	92	110	90	109	92				

4.5 Effect of Constituents, Chemical Composition and Fineness on the Acceleration and Deceleration Periods

4.5.1 Effect of GGBFS Content and Fineness on the Acceleration Period

It is observed in Figure 4.5 that rate of heat liberation in the acceleration period increases as the fineness of cement increases. However, the rate of heat evolution of cements in particle size interval $30-50 \ \mu\text{m}$ and $> 50 \ \mu\text{m}$ observed in the acceleration period are found to be close to each other. It is found using particle analysis that there are more fines below 15 $\ \mu\text{m}$ in cements sieved over 50 $\ \mu\text{m}$ than cements in particle size interval 30-50 $\ \mu\text{m}$ (see Figure 4.1 and Table 4.2). It is observed at Figure 4.6 that rate of heat liberation during at the acceleration period decreases as GGBFS content increases.

4.5.2 Effect of Constituents, Chemical Composition and Fineness on the Deceleration Period

It is shown in Figures 4.5 and 4.6 that the rates of heat liberation of the cements are similar in the deceleration periods. Eventually, all curves achieve similar slope regardless of their GGBFS contents and finenesses. However, the formation of a shoulder after the second exothermic peak is observed in the control group cements and cements containing 6 % GGBFS in contrast to the cements containing 20 % or 35 % GGBFS. Moreover, exothermic peaks of cements containing 20 % and 35 % GGBFS are unexpectedly high compared to the ones of the control group cements and cements containing 6 % GGBFS. Height differences of the second exothermic peaks are clearer in Figure 4.6 (a), and in Figure 4.6 (e) which present comparisons of the 0-10 µm cements and the unsieved cements, respectively. It is known that an increase in alkali content of cement increases the reaction rate of C_3A with gypsum [Lerch, 1946]. Also, it is given in Table 4.4 that the alkali contents of the cements increases with increasing content of added GGBFS. It is known that the shoulder is formed after the main exothermic peak due to renewed ettringite formation which occurs when gypsum in the solution is exhausted. It is observed in Table 4.5 and in Figures 4.5 and 4.6 that as the ratio of gypsum to C_3A gets smaller the shoulder that is seen after main exothermic peak disappears and the main exothermic peaks of the cements that don't exhibit the shoulder are unexpectedly high. Moreover, it is known that alumina coming from the GGBFS reacts with gypsum [Regouro, 1980]. So, incorporating 20 % or 35 % of GGBFS may cause early exhaustion of the gypsum and earlier renewed ettringite formation.





Figure 4.5 Rate of Heat of Hydration vs. Time graphs of cements, (a) control group, (b) cement with 6 % GGBFS, (c) cement with 20 % GGBFS, (d) cement with 35 % GGBFS

Table 4.4 Alkali	content of	cements in	particle size	intervals 0-10), 10-30,	30-50, >50	μm and
unsieved cement							

	0	- 10 µ	ım (%)	1	0-30 µ	ım (%)	30-50 µm (%)				
	Na ₂ O	K ₂ O	Na2O Equivalent	Na ₂ O	K ₂ O	Na2O Equivalent	Na ₂ O	K ₂ O	Na2O Equivalent		
С	0.20	0.74	0.68	0.20	0.75	0.69	0.21	0.78	0.72		
S6	0.19	0.74	0.68	0.20	0.77	0.71	0.21	0.81	0.74		
S20	0.20	0.81	0.74	0.21	0.86	0.78	0.22	0.89	0.81		
S35	0.21	0.86	0.78	0.22	0.92	0.83	0.22	0.96	0.85		
	:	>50 µı	m (%)	U	nsiev	ed (%)					
	Na ₂ O K ₂ O Na ₂ O Equivalent		Na ₂ O	K ₂ O	Na2O Equivalent						
С	0.21	0.78	0.72	0.20	0.76	0.70					
S6	0.21	0.81	0.74	0.20	0.78	0.72					
S20	0.22	0.89	0.80	0.21	0.85	0.77					
S35	0.22	0.96	0.85	0.22	0.91	0.81					

		0- 10 (μm)				10-30 (µm)				
	С	S6	S20	S35	С	S6	S20	S35		
Gypsum/C ₃ A	1.83	1.70	1.40	1.32	0.69	0.75	0.56	0.49		
		30-50 (μm)				>50	>50 (µm)			
	С	S6	S20	S35	С	S6	S20	S35		
Gypsum/C ₃ A	0.52	0.51	0.40	0.29	0.63	0.62	0.45	0.41		
		Unsi	eved							
	C	S 6	S20	S35						
Gypsum/C ₃ A	1.09	1.05	0.88	0.81						





Figure 4.6 Rate of Heat of Hydration vs. Time graphs of cements, in particle size intervals (a) 0-10 μ m, (b) 10-30 μ m, (c) 30-50 μ m, (d) >50 μ m, and (e) unsieved cement

4.6 Ease of Grinding of Clinker Compounds, Gypsum and GGBFS

Compound composition of the control group cements are, given in Table 4.6. These values were calculated using constituent percentages of the control group (given in Table 3.8) and the compound compositions of the control group cements (given in Table 3.4) Calculation of compound composition of clinker is given in Appendix B. It is observed that C_3A and C_4AF are distributed homogeneously in all size groups. On the other hand, it is hard to make any observation about the grindability of C_3S and C_2S with the results given in Table 4.6 because the values are very close to each other.

Table 4.6 Compound composition of control group cements as if they have equal amounts of clinker

	Clinker (%)			
	0-10 µm	10-30 μm	30-50 μm	> 50 µm
C ₃ S	61.4	67.3	68.2	67.5
C ₂ S	12.9	8.1	7.4	8.0
C ₃ A	4.6	4.6	4.6	4.6
C ₄ AF	13.1	13.1	13.1	13.1

It is observed in Figure 4.7 that clinker content increases and gypsum content decreases when the particles of the control group cements get coarser. Moreover, it is seen that the GGBFS content of cements of each group containing 6 %, 20 %, 35 % GGBSF increases as the particle size intervals get coarser. It shows that ease of grinding of Gypsum > Cement > GGBSF.



Figure 4.7 Distribution of (a) clinker content, (b) gypsum content, (c) GGBSF content of cements at different particle size intervals

CHAPTER 5

CONCLUSIONS

5.1 General

In this thesis, the influence of slag content interground with clinker and gypsum, and the influence of cement fineness, on the 48-h heat of hydration and rate of heat evolution of blended cements were, investigated. Isothermal conduction calorimetry was used to measure the heat of hydration and rate of heat of evolution of the cement samples.

First, groups containing 6 %, 20 %, and 35 % of GGBFS were produced. Second, each group was sieved to subgroups in particle size intervals 0-10, 10-30, 30-50 and >50 μ m. Particle size distribution and percentages of constituents in each group and subgroup were measured with laser diffraction analysis and according to TSE CEN/TR 196-4, respectively. Third, results of the laser diffraction and quantitative determination of constituents analyses were used to interpret the differences in rate of heat of hydration and 48-h heats of hydration of each group and subgroup. Finally, the compound composition of each group and subgroup was calculated and results were used to assess the ease of grinding of each of the cement compounds.

Important findings of this study are as follows:

1. Rate of heat of hydration and 48 h heat of hydration of the cements increase as the content of the finer portions in the cement increases.

2. Rate of heat of hydration and 48-h heat of hydration of the cements decrease as the amount of added GGBFS increase. Furthermore, the dormant period lasts longer as the content of added GGBFS increases.

3. As the content of the alkalis increases, the gypsum-to- C_3A ratio decreases and GGBFS content increases in the cement, renewed ettringite formation occurs earlier.

4. The content of gypsum is more in finer portions of control group cement samples. It is also found content of GGBFS is less in finer portions of the blended cement samples. Comparison of grindability of gypsum, clinker and GGBFS is given as follows:

Gypsum > Clinker > GGBFS

5.2 **Recommendations for Future Studies**

Following studies are recommended:

1. The same study can be conducted using mineral admixtures other than GGBFS to understand individual behaviors of different mineral admixtures.

2. The same study can be conducted using separately-ground cements to compare the rate of heat of hydration and heat of hydration of separately ground and interground cements.

3. Modeling of the heat of hydration behavior of cements incorporating GGBFS can be attempted using the data gathered in this study.

4. A study investigating the rate of heat evolution and amount of heat of hydration including incorporation of various amounts of gypsum and GGBFS to cement with a known amount of C_3A is recommended to understand C_3A hydration better.

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APPENDIX A

CALCULATING COMPOUND COMPOSITION OF CEMENTS CONTAINING GGBFS

Compound composition of the cement samples containing GGBFS were calculated using the results of the quantitative determination of constituents by TSE CEN/TR 196-4, and chemical analyses of clinker, gypsum and GGBFS. Also Bogue's equations were used to calculate the compound composition of the cement samples. Part of the calculation of compound composition of cement containing 6 % GGBFS and in particle size interval 0-10 μ m is given below as an illustration.

To find the compound composition of the cement sample containing GGBFS, content of oxides coming from the clinker and gypsum must be calculated. This calculation made for finding the CaO content coming from the clinker is given below:

 $\frac{C \times C_C + G \times G_C}{100} = T_c$

$$\frac{88.26 \times 66.41 + 6.96 \times 32.40}{100} = 60.60\%$$

Where,

C is the content of the clinker in the cement sample (%),

G is the content of gypsum in the cement sample (%),

 C_C is the content of CaO in the clinker (%),

G_C is the content of CaO in the gypsum (%),

T_c is the content of CaO that is used in the Bogue's formula for the cement samples (%).

Contents of other oxides were calculated as above and used in the Bogue's equations which are the last step of calculating compound composition of each sample containing slag.

APPENDIX B

CALCULATING COMPOUND COMPOSITION OF CONTROL GROUP CEMENTS WITH EQUAL AMOUNTS OF CLINKER

Compound composition of control group cements, as if they have equal amounts of clinkers, was calculated using the results of the quantitative determination of constituents by TSE CEN/TR 196-4 and compound composition of control group cements found using Boque's equations. Calculation of C_3S content of a cement sample of control group in size interval 10-30 µm is presented below:

$$\frac{C_C \times 100}{C} = T_C$$

$$\frac{63.3 \times 100}{94.0} = 67.34 \%$$

Where,

C is the content of clinker in the cement sample (%),

 C_C is the content of C_3A in the cement sample (%).