EARLY HEAT EVOLUTION IN NATURAL POZZOLAN-INCORPORATED CEMENT HYDRATION

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ABSTRACT

EARLY HEAT EVOLUTION IN NATURAL POZZOLAN-INCORPORATED CEMENT HYDRATION

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Portland cement hydration is an exothermic process. The heat evolved during the hydration process is especially important in mass concrete, and hot and cold weather concreting. Heat of hydration is affected by several factors like chemical composition of cement, fineness of cement and ambient temperature. The major aim of this thesis is to investigate the effect of cement composition and fineness, amount and composition of the fine portion (<45 μm) of natural pozzolan-incorporated cement on hydration heat.

For this purpose, a portland cement and pozzolan-incorporated blended cements containing different amounts of natural pozzolan (trass) were used. The heat of hydration was measured using isothermal calorimetry. The values of heat of hydration for mixtures with different finenesses containing different amounts of added pozzolan were determined. The results obtained were used to find a correlation between the fineness, composition of cement and heat of hydration.

According to this study, pozzolan incorporation in small amounts accelerates hydration. A similar effect was obtained for higher pozzolan amounts. Finer cements react faster and result in higher amounts of early heat evolved compared to coarser cements. In addition, it was found that the sum of the heat of hydration values of fine and coarse portion of cements was less than the total heat of hydration of blended cements. Moreover, a satisfactory correlation could not be established between results of isothermal calorimetry, and adiabatic calorimetry, setting time, and strength.

Keywords: Heat of hydration, pozzolan, isothermal calorimetry, fineness.

ÖZ

DOĞAL PUZOLAN İÇERİKLİ ÇİMENTO HİDRATASYONUNDA ERKEN ISI OLUŞUMU

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Çimentonun hidratasyonu ekzotermik bir olaydır. Hidratasyon sırasında açığa çıkan ısı özellikle kütle betonu yapımında ve sıcak ve soğuk havalarda beton dökümünde önemlidir. Hidratasyon ısısı, çimentonun kimyasal kompozisyonu, inceliği ve ortam sıcaklığı gibi faktörlerden etkilenir. Bu tez çalışmasının ana amacı çimento kompozisyonunun ve inceliğinin, doğal puzolan içeren çimentonun ince kısmının miktarının ve kompozisyonunun hidratasyon ısısına etkisinin araştırılmasıdır.

Bu maksatla, bir portland çimentosu ve değişik miktarlarda doğal puzolan içeren katkılı çimentolar kullanılmıştır. Hidratasyon ısısı izotermal kalorimetre ile ölçülmüştür. Farklı inceliklerde ve farklı miktarlarda puzolan içeren karışımların hidratasyon ısıları ölçülmüştür. Elde edilen sonuçlar çimento inceliği ve kompozisyonuyla hidratasyon ısısı arasındaki ilişkilerin belirlenmesinde kullanılmıştır.

Bu çalışmaya göre, küçük miktarlardaki puzolan içeriği hidratasyonu hızlandırır. Benzer etki daha yüksek puzolan içeren çimentolarda da görülmüştür. İnceliği fazla olan çimentolar daha kalın taneli çimentolara göre daha hızlı reaksiyona girer ve daha yüksek erken hidratasyon ısısı açığa çıkarır. Ayrıca, katkılı çimentolarda, çimentonun ince kısmının ve kalın kısmının hidratasyon ısıları toplamı, çimentonun hidratasyon ısısından daha azdır. Buna ek olarak, izotermal kalorimetre test sonuçları ve adiabatik yöntem test sonuçları, priz süreleri ve dayanım değerleri ile arasındaki ilişki, tatmin edici değildir.

Anahtar kelimeler: Hidratasyon ısısı, puzolan, izotermal kalorimetre, incelik

To my parents,

Sadiye and Adil Över

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LIST OF ABBREVIATIONS

ACI: American Concrete Institute.

ASTM: American Society for Testing Materials.

EN: European Norms.

TS: Turkish Standards.

GGBFS: Ground Granulated Blast Furnace Slag

CHAPTER 1

INTRODUCTION

1.1. General

Concrete is the most commonly used construction material all over the world with an estimated annual consumption of 7.9 billion m^3 [U.S. Geological Survey, 2009]. It is used in the construction of buildings, dams, tunnels, roads and many other structures. Since it is used in such a high volume, its quality and durability obviously are highly important for both manufacturers and consumers.

Conventional concrete is formed of cement, water and aggregate. Generally speaking, cement plays the most important role in affecting most of the properties of concrete. When cement is mixed with water, a series of chemical reactions occur. These reactions are called hydration, and for cement this hydration is an exothermic process. The compounds of cement, being produced at very high temperatures, are in a state of high energy. Upon reacting with water they form more stable hydration products with lower energy, while the rest of the energy stored in the clinker compounds is released as heat. This heat, called the heat of hydration of cement, is important for many aspects of concrete use such as mass concreting, hot and cold weather concreting and for determining the degree of hydration.

Cements are composed of different constituents and different compounds of varying proportions. Therefore, the hydration process is complex. It is affected by the phase composition, presence of foreign ions in the individual components, fineness, water content, ambient temperature and presence of admixtures and additives [Mehta and Monteiro, 2006].

Heat of hydration of cements can be determined by several methods. One of these methods is the heat of solution, which is described in ASTM C 186 and TS EN 196-8. The principle of this method is to measure the heat of solution of unhydrated and hydrated cements by dissolving them in a mixture of nitric acid and hydrofluoric acid. Another method is the adiabatic or the semi-adiabatic method that is described in TS EN 196-9. In this method a freshly made mortar is introduced into a calorimeter to determine the heat emission due to temperature rise. In addition to the previous two methods, the isothermal conduction calorimetry method is commonly used. As stated in ASTM C1702-09, the principle of isothermal conduction is to keep the specimen and the environment at a constant temperature to monitor the heat flow from the specimen by comparing it with the one of a reference material; hence the heat of hydration of the cement is measured directly.

Pozzolans are mineral admixtures commonly used in cement and concrete due to their ecological, economical and technical advantages. Pozzolans are broadly classified in two groups as natural pozzolans and artificial pozzolans. Natural pozzolans are widely used in the cement industry. Some types of natural pozzolans are volcanic tuffs, volcanic glasses, calcined clay or shale and diatomaceous earth. Artificial pozzolans are generally industrial by-products such as, fly ash, granulated blast furnace slag, silica fume and rice husk ash.

1.2. Objective and scope

The objective of this study is to investigate the effect of using trass (a natural pozzolan commonly being used in blended cements) and the fineness of trass-incorporated cements on the heat of hydration. Isothermal conduction calorimetry method was used to measure the heat of hydration, and the results were compared with those obtained using adiabatic method.

This thesis is composed of five chapters. Chapter 1 contains introductory information. In Chapter 2, a theoretical background and a literature review presenting information about the mechanism of hydration, heat of hydration, pozzolan use in cement mixtures, pozzolanic reaction and its effect on heat of hydration, benefits of using pozzolan in cement, and the different methods of measuring heat of hydration are given. Chapter 3 contains the details of the experimental procedure to determine the heat of hydration by isothermal conduction calorimetry and information on different cement samples used in this study. Chapter 4 gives the experimental results and their interpretations and discussions. Finally, the outcomes of the experimental study are summarized and conclusions and recommendations for future research are given in Chapter 5.

CHAPTER 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 General Information about Portland and Blended Cements

Portland cement is defined as “hydraulic cement produced by pulverizing Portland cement clinker and usually containing calcium sulfate” [ASTM C219]. Portland cement clinker is a product of burning a raw mix containing appropriate amounts of CaO, SiO_2, Al_2O_3, Fe_2O_3 (plus other oxides of much smaller amounts) to temperatures of partial melt formation. $CaCO_3$ in the raw mix reveals CaO upon dissociation at about 900°C and this CaO reacts with SiO_2, Al_2O_3 and Fe_2O_3 coming mostly from the clayey component of the raw mix to yield the clinker minerals [Mehta and Monteiro, 2006].

The four major clinker minerals are tricalcium silicate, dicalcium silicate, tricalcium aluminate and the ferrite phase. The oxides and the compounds present in a clinker or a Portland cement are given in Table 2.1. Instead of the conventional chemistry formulas, a special abbreviation method, which is more practical, is commonly used in cement chemistry. These abbreviations of the oxides and compounds are also given in Table 2.1. [Erdoğan, 2007].

Table 2.1. Oxides and Compounds in Clinker or Portland Cement

Oxide	**Name Of Oxide**	**Cement Chemistry Abbreviation**	**Compound**	**Name**	**Cement Chemistry Abbreviation**
CaO	Lime	C	Ca_3SiO_5	Tricalcium silicate	C_3S
SiO_2	Silica	S	Ca_2SiO_4	Dicalcium silicate	C_3S
Al_2O_3	Alumina	A	$Ca_3Al_2O_6$	Tricalcium aluminate	C_3A
Fe_2O_3	Iron oxide	F	$Ca_4Al_2Fe_2O_{10}$	Tetra calcium alumino ferrite	C_4AF
MgO	Magnesium oxide	M	$CaSO_4·2H_2O$	Gypsum	$\mathrm{CSH_2}$
SO_3	Sulphur trioxide	S			
Na_2O	Soda	N			
K_2O	Potassa	K			

Tricalcium silicate (C_3S) is an essential constituent of all Portland cements. Its crystalline lattice contains Ca^{2+} (calcium cations) and SiO_4^{4-} and O^{2-} (silicate and oxygen anions) in a ratio of 3:1:1. In commercial clinkers and Portland cements, small amounts of aluminum, magnesium, sodium, potassium or iron ions may replace calcium ions at certain lattice points. The presence of these foreign ions results in an impure C_3S which resembles a naturally occurring mineral, “Alite”. Therefore, the term alite is more commonly used in cement jargon instead of tricalcium silicate [Domone and Illston, 2010].

Dicalcium silicate (C_2S) is the other calcium silicate present in the clinkers and Portland cements. The crystal structure of C_2S is formed of Ca^{2+} and SiO_4^{4-}. There are five different polymorphic forms of C_2S. Among them, β-C_2S, which is also named “Belite” in cement chemistry, is the only cementitious form [Mindess et al., 2003].

Tricalcium aluminate (C_3A) is the fundamental alumina-bearing compound in Portland cement. Calcium aluminoferrite which is generally abbreviated as C_4AF is actually a solid solution of a series of alumina- and ferrite-bearing compounds whose compositions vary between $C_2(A_{0.7},F_{0.3})$ and $C_2(A_{0.3},F_{0.7})$. C_4AF is the approximate formula for the solid solution. Ferrite solid solution (Fess) is another common name for this compound [Odler, 2004].

The four major compounds constitute more than 90% of the Portland cement. Besides them, there is gypsum, free lime, magnesia, alkali oxides, etc. in much smaller amounts, and usually their amounts are restricted in the standards due to their possible deleterious effects on the durability of cementitious systems. Gypsum is added to clinker in limited amounts and interground. It controls the setting of cement.

Inorganic binders that contain latent hydraulic materials, pozzolans, or non-reactive mineral constituents together with Portland cement are called “composite” or “blended” cements [Mehta and Monteiro, 2006].

Latent hydraulic materials such as Ground Granulated Blast Furnace Slag (GGBFS) are able to react with water. However, a suitable activator such as alkali hydroxides is usually necessary. Non-reactive constituents like limestone powder do not react chemically to any significant extent during the hydration process. However, they may alter the rheology and/or various properties of cementitious systems by physico-chemical means.

Pozzolans are defined as amorphous siliceous or siliceous and aluminous materials that have little or no binding value by themselves. However, in pulverized form and in the presence of moisture, they react with calcium hydroxide to yield phases possessing cementitious value.

Due to economical, environmental and technical reasons, it is a common practice to use different mineral admixtures belonging to one of the groups stated above in the production of blended cements. The types of blended cements and their relative constituent proportions, as described in TS-EN 197-1, are given in Table 2.2.

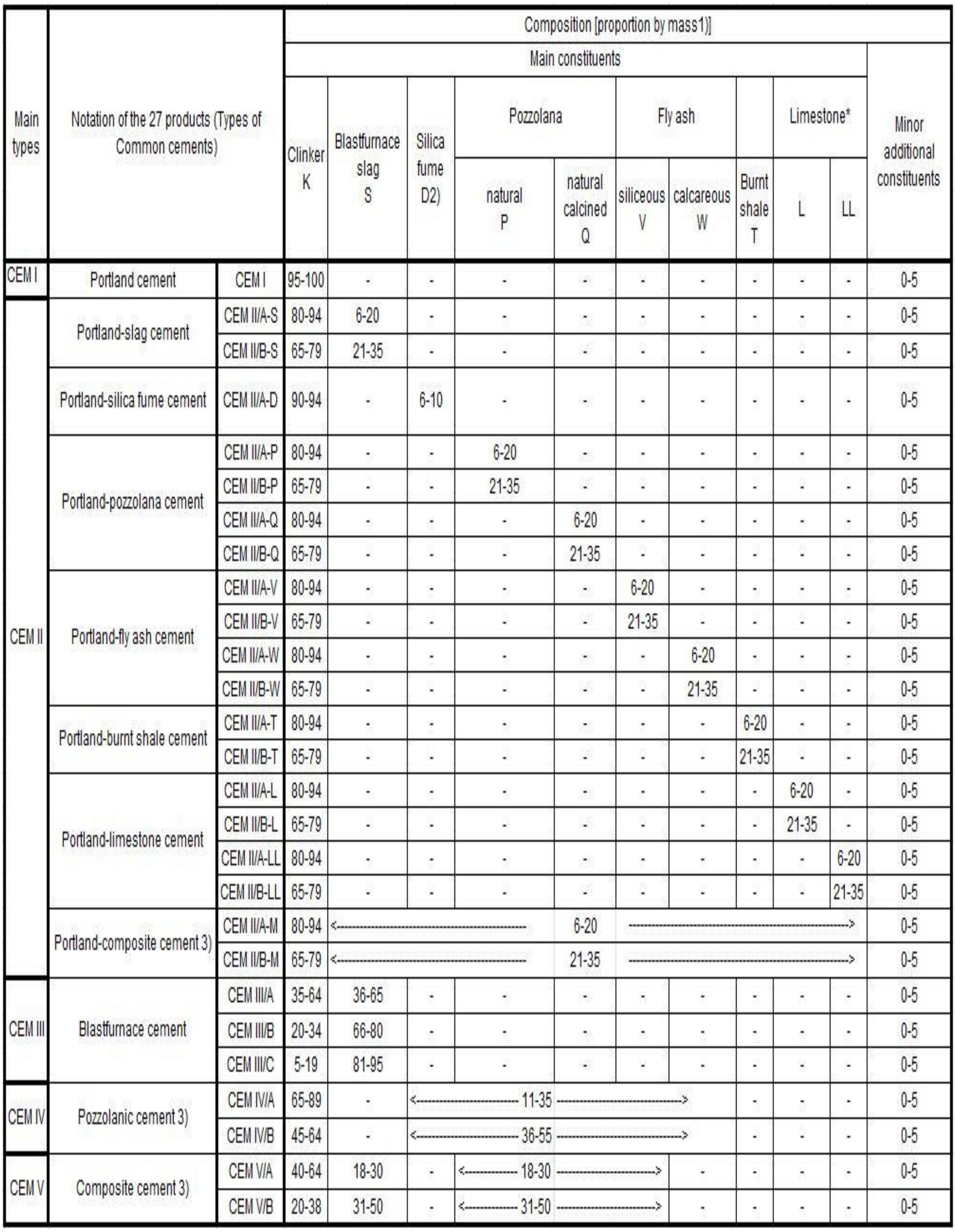
The interaction of the mineral admixtures with the clinker both during the production and hydration processes may result in important changes in the characteristics of the cements.

2.1. Hydration of Portland Cements

The hydration of cement is a complex process. It involves not only the reactions of the individual constituents with water but also the interactions between them. Hydration of cement consists of a series of simultaneous and successive reactions. It is affected by many factors, especially

- The composition of the cement;
- Fineness of the cement, its particle size distribution and specific surface area;
- Water-cement ratio used;
- Curing temperature;
- Presence of admixtures and additives [Odler, 2004].

Table 2.2. Blended Cements [TS EN 197-1, 2000]



Main types	Notation of the 27 products (Types of Common cements)		Composition [proportion by mass1)]										
			Main constituents										Minor additional constituents
			Clinker K	Blastfurnace slag S	Silica fume D2)	Pozzolana		Fly ash			Limestone*		
						natural P	natural calcined Q	siliceous V	calcareous W	Burnt shale T	L	LL	
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21-35	-	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-burnt shale cement	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	-	0-5
	Portland-limestone cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	21-35	0-5
	Portland-composite cement 3)	CEM II/A-M	80-94	<------ 6-20 ------>									0-5
		CEM II/B-M	65-79	<------ 21-35 ------>									0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement 3)	CEM IV/A	65-89	-	<------ 11-35 ------>					-	-	-	0-5
		CEM IV/B	45-64	-	<------ 36-55 ------>					-	-	-	0-5
CEM V	Composite cement 3)	CEM V/A	40-64	18-30	-	<------ 18-30 ------>			-	-	-	-	0-5
		CEM V/B	20-38	31-50	-	<------ 31-50 ------>			-	-	-	-	0-5

1) The values in the table refer to the sum of the main and minor additional constituents. 2) The proportion of silica fume is limited to 10%. 3) In Portland-composite cements CEM II/A-M and CEM II/B-M, in Pozzolanic cements CEM IV/A and CEM IV/B and in Composite cements CEM V/A and CEM V/B the main constituents besides clinker shall be declared by designation of the cement.* L : total organic carbon (TOC) shall not exceed 0.5% by mass; LL: TOC shall not exceed 0.20% by mass.

In cement chemistry if the starting material becomes dissolved first, the hydration reaction may be called topochemical as long as the reaction products precipitate only within the space that became available by the dissolution process or in its immediate neighborhood. Some examples of topochemical processes are the formation of C-S-H gel upon the hydration of C_3S and the conversion of periclase [MgO] to brucite [$Mg(OH)_2$], which takes place in the hydration of cements with a high MgO content. In an opposite way, when the reaction product precipitates randomly from the liquid phase after sufficient amounts of the starting material became dissolved and a sufficiently high degree of oversaturation was attained, the process is commonly called through-solution reaction [Mehta and Monteiro, 2006].

In the hydration of cement, at early ages the through-solution mechanism looks like the dominant one, while the topochemical reaction plays the greater part at later ages when the ionic mobility in the solution becomes restricted. The occurrence of these two types of reaction processes in cement hydration is because that portland cement is comprised of several compounds, where these compounds do not hydrate at the same rate [Skalny et al., 2002]. It is more appropriate to discuss the hydration of individual Portland cement compounds first.

2.1.1. Hydration of Calcium Silicates

The hydrations of the two calcium silicates are chemically similar. Upon full hydration both C_3S and C_2S result in $C_3S_2H_3$ and CH as given below:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$$
$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH$$

During the course of hydration the composition of the C-S-H gel varies over a wide range; lime-silica molar ratio may change between 1.5 and 2. There are two major differences between the hydration of C_3S and C_2S: First, the rate of hydration of C_2S is lower than that of C_3S, and second, C_2S results in much less CH than does C_3S [Mindess et al., 2003].

A typical curve describing the progress of C_3S hydration is given in Figure 2.1. Upon mixing cement with water, an intense but short lived hydration occurs. The stage is called pre-induction period. This takes a few minutes with a rate of hydration about 5/day (A-B), where the rate of hydration is defined as $d\alpha \quad dt$, where α is the degree of hydration and t is the time. In other words, this ratio is the slope of the curve on Figure 2.1. of the desired period. Pre-induction period is followed by a dormant period (B-C), where the rate of hydration is about 0.02/day, and it lasts a few hours. After the dormant period, the rate of hydration increases to about 1/day and reaches a maximum within 5-10 h, (C-D).

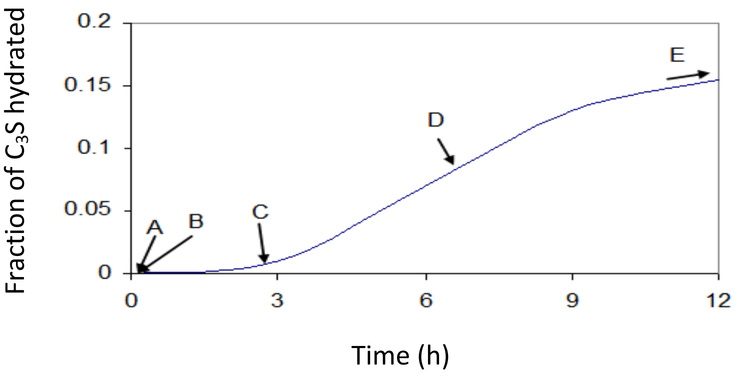


Figure 2.1. Kinetics of C_3S hydration (A-B: pre-induction period; B-C: dormant period; C-D: acceleration stage; D-E: deceleration stage).

This last stage is called the acceleration stage. Within this period, the process follows the Avrami Equation:

$$-ln\ 1-\alpha^{\frac{1}{3}} = k_N t \qquad \text{Equation 2.1.}$$

where α is the degree of hydration, t is the time and k_N is a constant for nucleation rate controlled process. CH concentration in the liquid phase reaches the maximum in this stage and begins to decline by CH precipitation. In the last stage which is called as deceleration stage (D-E) the reaction slows down and finally stops. The process follows the Jander Equation within this stage:

$$1-\quad 1-\alpha^{\frac{1}{3}}\ {}^{2} = k_D t \qquad \text{Equation 2.2.}$$

where α is the degree of hydration, t is the time and k_D is a constant for diffusion rate controlled process [Odler, 2004].

2.1.2. Hydration of Aluminates

C_3A reacts with water with a high reaction rate producing hydrates such as C_3AH_6, C_4AH_{19}, and C_2AH_8 and releasing high amount of heat of hydration. The rapid reaction of C_3A is slowed down by adding gypsum to clinker. Calcium aluminate trisulfate hydrate or calcium aluminate monosulfate hydrate may be produced depending on the concentration of aluminate and sulfate ions in the solution. If the solution is saturated with calcium and hydroxyl ions, the obtained product is ettringite which crystallizes as short prismatic needles. The monosulfate crystallizes as thin hexagonal plates [Mehta and Monteiro, 2006].

The reactions that represent the productions of ettringite and monosulfate are [Mehta and Monteiro, 2006]:

Ettringite:

$$[AlO_4]^- + 3\,[SO_4]^{2-} + 6\,[Ca]^{2+} + \text{aq.} \rightarrow C_6A\mathit{S}_3H_{32}$$

Monosulfate form:

$$[AlO_4]^- + [SO_4]^{2-} + 4\,[Ca]^{2+} + \text{aq.} \rightarrow C_4A\mathit{S}H_{18}$$

Ettringite causes stiffening and early strength development. In cements containing more than 5 percent of C_3A, when the sulfate is depleted, the aluminate compounds start to react with ettringite and the ettringite converts into monosulphate phase.

The reaction is;

$$C_6A\mathit{S}_3H_{32} + 2C_3A + 22H \rightarrow 3C_4A\mathit{S}H_{18}$$

This reaction between ettringite and C_3A is undesirable because at later ages, in the presence of sulfate, monosulfate can convert into ettringite again which causes cracks [Taylor et al., 2001]. As a result, the amounts of both gypsum and C_3A are important, and they should be in appropriate amounts otherwise some undesirable incidents like quick set, flash set, false set, expansion at later ages may occur [Mehta and Monteiro, 2006].

2.2. Heat of Hydration

2.2.1. Definition

The heat liberated during the hydration of cement, which is a result of the exothermic chemical reaction between cement and water is called the heat of hydration. Since the cement compounds which are formed at very high temperatures in the rotary kiln are in a state of high energy, upon hydration they react with water to form hydration products of higher stability and less energy. The excess energy is dissipated as heat. The heat generated upon hydration raises the temperature of concrete [Odler, 2004].

2.2.2. Heat Evolution during Hydration Stages

In portland cement, C_3S and C_3A have the greatest reactivity, resulting in much higher heat liberation values than both C_2S and C_4AF. It is also known that gypsum decreases the early rate of hydration of C_3A and it has a retarding effect on the hydration reaction of C_4AF. Calcium silicate compounds have the greatest effect on strength development in portland cement. A graphical explanation of the degree of hydration vs. time values is shown in Figure 2.2. [Mindess et al., 2003].

Since the chemical reactions are exothermic there is heat liberation during the hydration process. The amount of heat that is liberated and the rate of heat evolution are very important. In addition to that, the amount and the rate of heat loss from the concrete to the surroundings should be considered [Mindess et al., 2003].

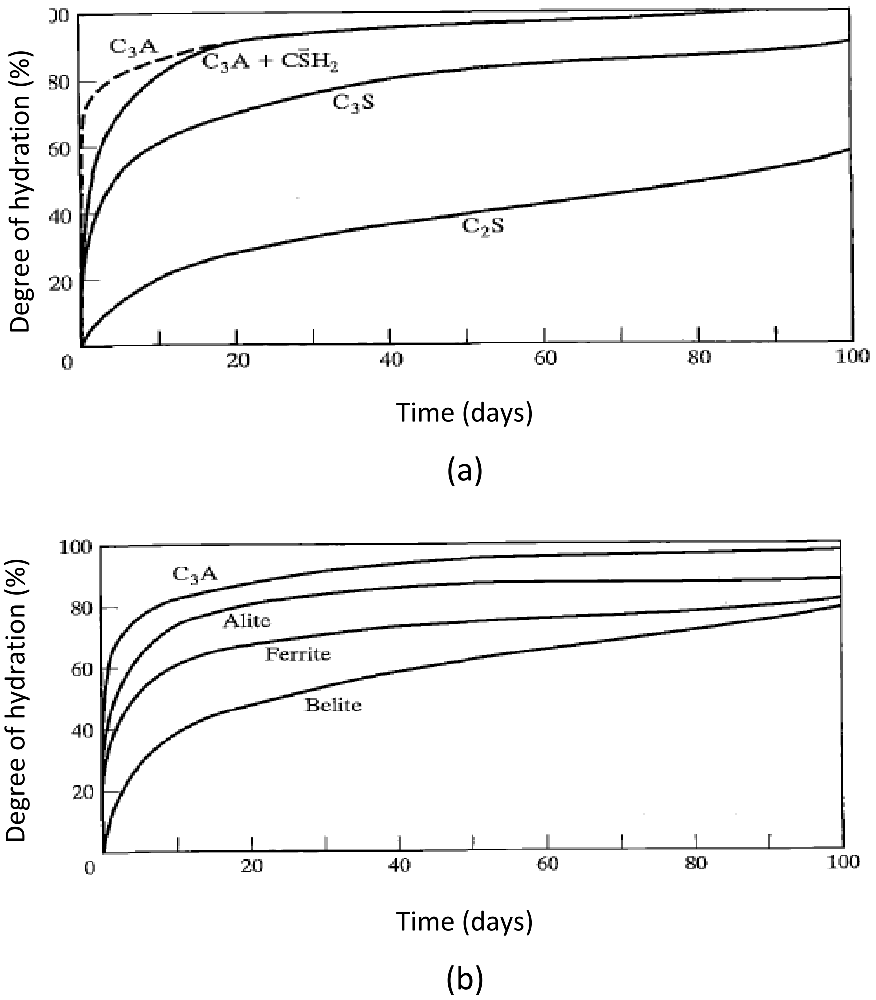


Figure 2.2 Rate of hydration of the cement compounds (a) in pastes of pure compounds (b) in a Type I cement paste [Mindess et al., 2003].

Hydration reactions occur through six stages (periods), as shown in Figure 2.3., where each stage has its own reaction rate, and in all the stages the strength formation is different [Mehta and Monteiro, 2005; Odler, 2004; Domone and Illston, 2010; Kosmatka et al., 2003].

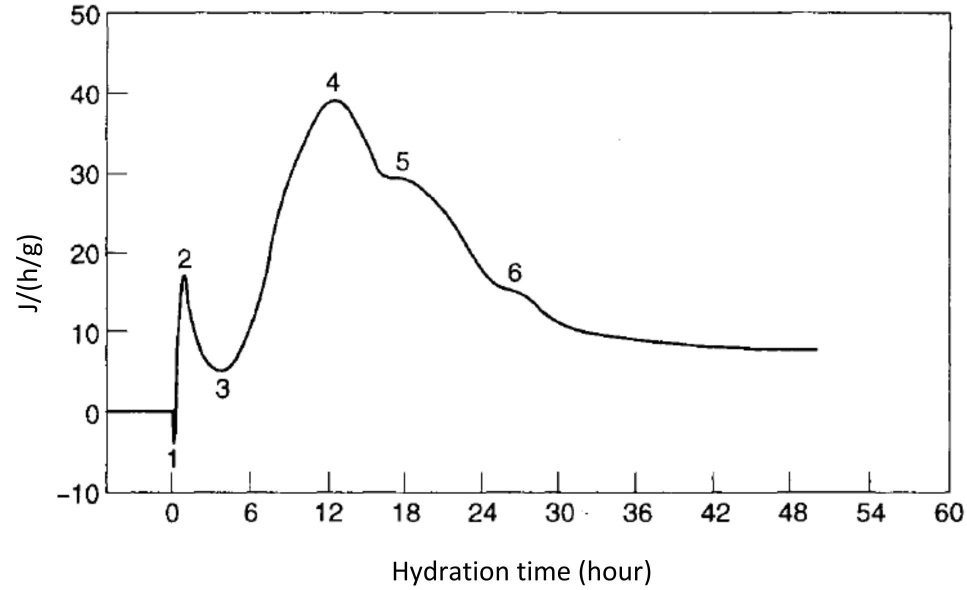


Figure 2.3. Typical heat evolution curve of a portland cement [Odler, 2004].

1. **Pre-Induction Period:** The first stage of hydration is called the pre-induction period or the period of rapid evolution of heat. This period consists of the first minutes of hydration. In this period C_3S reacts with water and the hydration reactions begin. The immediate endothermic peak **(1)** is observed only in cements that contain potassium sulfate, therefore it is seldom seen. Immediately after mixing with water K_2SO_4 dissolves and results in the endothermic peak.

2. **Period Of Rapid Heat Evolution:** Within few minutes, very rapid hydration of C_3S (and C_3A) results in intense heat liberation. The hydration of gypsum may also contribute to this peak, peak (2).

3. **Dormant Period:** The dormant period exhibits a distinct minimum peak marked by (3). In this stage the chemical reactions of C_3S occur slower than

the previous period, and with the help of sulfate the ettringite formation begins as a fundamental product of tricalcium aluminate (C_3A) reactions.

4. **Acceleration Period:** Acceleration period is the period during which initial formation of hydration products occur. After the dormant period, when the concentrations of calcium and hydroxide reach a critical value in the pore solution, the hydration products (C-S-H and CH) start to precipitate from the solution and the reaction proceeds rapidly [Mindess et al., 2003]. In the acceleration stage, the reaction rate and heat evolution reach their maximum values and the stage is completed with the final set of the paste. Peak (4) occur due to the formation of C-S-H and CH upon the hydration of C_3S. After that, the heat release is slowed down.

5. **Period of Slowing Down:** This period is the stage in which the reaction rate decreases and the hydration continues slowly [Dweck et al., 2003]. In most but not all cements a shoulder or a peak may be observed in the descending portion (5) due to AF_t formation.

6. **The Steady State Period:** Finally, a second shoulder may be observed in some cements upon AF_t-AF_m conversion. The steady state period is reached then, Peak (6). In this stage, the diffusion controlled reactions continue slowly [Dweck et al., 2003].

2.2.3. Effects of Heat of Hydration on Concrete Properties (Cementitious System)

Temperature changes within the structure are not significant in normal concrete constructions under ordinary ambient temperatures. However, they are very important in massive structures, such as dams, mat foundations or any element that has a thickness over approximately a meter, where the heat cannot be readily released. Besides, particularly during hot and cold weather concreting, or for concretes containing high amounts of cement, heat evolution during hydration may be of critical importance.

The temperature of mixtures with high cement content can reach 55°C. While the concrete is hardening, these temperature rises result in expansion. If the temperature rise is very high and the concrete cools rapidly, a temperature difference occurs between the interior and exterior parts of the concrete. In concrete, the expansion starts from inside but because of cooling the structure restrains the expansion resulting in thermal cracks. As a result, the maximum temperature difference between the inner and outer part of concrete should not exceed 20°C to avoid crack development. Insulation has a very important role in controlling temperature changes on massive elements [Kosmatka et al., 2003]. Heat of hydration has a positive effect on cold weather concreting by protecting the concrete from freezing. To benefit from the heat of hydration, insulation is added to formwork to trap the heat in the concrete which helps the concrete to achieve the desired strength [Kosmatka, 1997].

2.2.4. Factors Affecting Heat of Hydration and Methods Used to Reduce It

For ordinary portland cements, about one half of the total heat is released in the first three days, about three-quarters released in the first seven days and nearly 90 percent in 6 months. Heat of hydration is affected by the chemical composition of cement and is approximately equal to the sum of the heats of hydration of the individual compounds. Heat of hydration values of a typical portland cement compounds up to different ages are shown in Table 2.3.

Cements that contain higher values of tricalcium silicate and tricalcium aluminate, such as Type III cements (ASTM C 186), have higher rates of heat liberation. Tricalcium silicate and tricalcium aluminate chemically produce more heat, and at a faster rate, than dicalcium silicate or other cement compounds. To reduce the rate of heat of hydration, a ‘low-heat’ cement with lower C_3S and higher C_2S contents may be used. Higher fineness provides a greater surface area to be wetted, resulting in speeding up the reaction between cement and water. This causes an increase in the rate of heat generation at early ages, but may not influence the total amount of heat over several weeks.

The cement content, water-cement ratio, placing and curing temperature, the presence of mineral and chemical admixtures, and the dimensions of the structural element are the other factors that influence heat development in concrete. In general, higher cement contents result in more heat development [Odler, 2004].

Table 2.3. Heat of Hydration of Portland Cement Compounds [Mehta and Monteiro, 2006].

	Heats of hydration evolved up to the given age (cal/g)		
Compound	**3 days**	**90 Days**	**13 years**
C_3S	58	104	122
C_2S	12	42	59
C_3A	212	311	324
C_4AF	69	98	102

In massive structures, the heat of hydration factor is extremely important, and there are several methods used to reduce it. For example, it is a common method to precool mass concrete before placement. To reduce the concrete placing temperature, finely chipped ice can be used instead of mixing water, and also using damp aggregate will be efficient in hot weather conditions. When ice is intended to be used instead of water, it's better to reduce the water content of fine aggregate to a maximum ratio of 5 percent. Aggregates can be cooled by drying up by air suction, being subjected to cold water spraying and by using cold air circulation.

Concrete in massive structures tend to crack, so it is very important to protect concrete from higher ambient temperature difference to reduce the risk of thermal crack development. Another method that can be used to reduce the effect of the heat of hydration is to place the concrete at night, but if it is not possible fog spraying may be helpful. During the curing period some practices like the use of steel forms, shading and water curing can be used. In restrained zones near foundations a special method called pipe cooling can be used to control the temperature development in concrete [ACI 207.1R, 1996].

2.3. Cement Replacement Materials

Commonly, finely ground solid materials, known as supplementary cementing materials, are added to cement for different purposes. The additives are mainly considered in three groups named pozzolanic materials, latent hydraulic materials and non-reactive materials. Pozzolanic materials and latent hydraulic materials are used to produce additional reaction products of cementitious value in concrete mixtures. They take place in the chemical reactions with or upon the hydration of portland cement to generate pastes of different characteristics. Examples of non-reactive materials are limestone, hydrated lime, etc. Although these materials are classified as nonreactive; sometimes they can react with cement under appropriate conditions. These fine materials are used to improve workability and they are also known as ‘’workability aids’’ [Kosmatka et al., 2003]. Pozzolanic materials are grouped into two catagories as natural pozzolans and artificial pozzolans (by-product materials) as presented in Table 2.4.

2.3.1. Natural Pozzolans

Natural pozzolan is a raw or calcined natural material (such as volcanic ash), which has a little or no cementitious value by itself but in finely divided form and in the presence of moisture, has a chemical reaction with calcium hydroxide to form compounds which have hydraulic and cementitious properties. Pozzolan contains high amounts of silica and alumina and small amounts of iron oxide, magnesium oxide and calcium oxide. There are different usages of natural pozzolan like producing portland-pozzolan cements, usage as admixtures in concrete and directly usage by combining lime, natural pozzolan and water together [Erdoğan, 2007].

Natural pozzolans come from volcanic rocks or minerals. They are mainly classified as volcanic glasses, volcanic tuffs, calcined clay or shales and diatomaceous earth, based on their principle constituent [Mehta and Monteiro, 2006].

Table 2.4. Common Pozzolanic Materials [Mindess et al., 2003]

Category	Typical Minerals	Active Components
Natural Materials	Unaltered volcanic ash Weathered volcanic ash (tuff, trass, etc.) Pumice Diatomaceous earth Opaline cherts and shales	Aluminosilicate glass Aluminosilicate glass; zeolites Aluminosilicate glass Amorphous hydrated silica Hydrated silica gel
By-product materials	Fly ash - Class F -Class C Silica Fume Rice husk ash Calcined clays	Aluminosilicate glass Calcium aluminosilicate glass Amorphous silica Amorphous alumino-silicate (metakaolin)

2.3.1.a. Volcanic Glasses:

Volcanic glasses mainly take their lime-reactivity characteristic from the unmodified aluminosilicate glass. Volcanic glasses have a porous surface which provides high surface area and reactivity. Some wellknown examples of volcanic glasses are Santorini Earth of Greece, Bacoli Pozzolan of Italy, and Shirasu Pozzolan of Japan. Volcanic glasses also have small amounts of noncrystalline minerals such as quartz, feldspar and mica in their glassy matrix [Mehta and Monteiro, 2006].

2.3.1.b. Volcanic Tuffs:

Volcanic glasses are modified under hydrothermal conditions and produce zeolite minerals called volcanic tuffs. Volcanic tuffs react with lime and gain cementitious properties after grinding to fine particle sizes. They can reach compressive strength values from 10 to 30 MPa. The roman pozzolan in Italy and the trass of Rheinland and Bavaria (Germany) are some examples of volcanic tuffs [Mehta and Monteiro, 2006].

2.3.1.c. Calcined Clays or Shales:

Clays and shales are the minerals that have no reaction with lime unless they undergo thermal treatment. They are calcined at high temperatures of 600° to 900°C, in oil-, gas-, or coal-fired rotary kilns after which they become amorphous, which is a requirement for showing pozzolanic properties. Clays and shales that contain large amounts of quartz and feldspar are not very suitable to be used as pozzolan in concrete [Mehta and Monteiro, 2006].

2.3.1.d. Diatomaceous Earth:

Diatomite is a siliceous sedimentary rock that consists of fossilized remains of diatoms from a type of hard-shelled algae [Fields et al., 2002]. It actively reacts with lime but has a porous structure, in other words, it has a high water requirement which is undesirable for the strength and durability of concrete. Diatomite generally contains large amounts of clay and needs thermal process to show pozzolanic properties. There are deposits of diatomaceous earth in California, Algeria, Canada, Germany and Denmark [Mehta and Monteiro, 2006].

2.3.2. Artificial Pozzolans

Artificial pozzolans are generally industrial by-product materials. Some examples are fly ash, silica fume, ground granulated blast furnace slag and rice husk ash [Erdoğan, 2009]. They are finely divided particles, so they reduce the size and volume of the voids and improve the workabilitiy of fresh concrete mixture. Blast furnace slag and fly ash have very fine particles and they have glassy textures that allow a reduction of water for a required consistency. Not to mention the improvement in durability that can be obtained when these by-products are used properly in concrete mixtures [Wesche, 1991].

2.3.3. Pozzolanic Reaction

One of the final products of portland cement hydration reactions is calcium hydroxide, which reacts slowly with pozzolan in the presence of water and forms C-S-H gels. A comparison between portland cement and portland-pozzolan cement with respect to the main C-S-H forming reaction is shown in the below formula [Mehta and Monteiro, 2006]. Calcium hydroxide that comes from portland cement reacation is not a desirable product in concrete (it is one of the factors that helps the occurrence of alkali silica reaction for example), thus when the pozzolanic reaction uses calcium hydroxide this use is beneficial from the durability point of view [Taylor, 1997].

Portland cement:

$$C_3S + H \xrightarrow{\text{fast}} C\text{-}S\text{-}H + CH$$

Pozzolanic reaction (Portland-pozzolan cement) :

$$\text{Pozzolan} + CH + H \xrightarrow{\text{slow}} C\text{-}S\text{-}H + CH$$

The pozzolanic reaction is lime-consuming and has an important role on the durability of the hydrated paste in acidic environments. The reaction is slow; therefore the rate of heat liberation will be low. Figure 2.4 shows the effect of increasing the amount of pozzolan on the heat of hydration of portland-pozzolan cements.

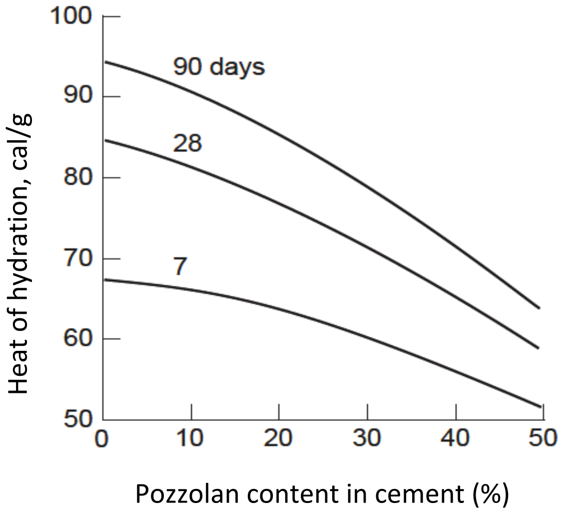


Figure 2.4. Effect of substituting an Italian natural pozzolan on the heat of hydration of Portland cement [Mehta and Monteiro, 2006]

Generally, increasing the amount of pozzolan in the cement increases the strength development on the long term. This is because of the increase in C-S-H and other hydration products at the expense of calcium hydroxide and the pore refinement which depends on the pozzolanic reaction [Massazza, 1993].

In addition to that, the type of pozzolan plays a significant role on the ultimate strength. Strength development of different 20 % pozzolan cement mixes under equal curing and temperature conditions are shown in Figure 2.5.

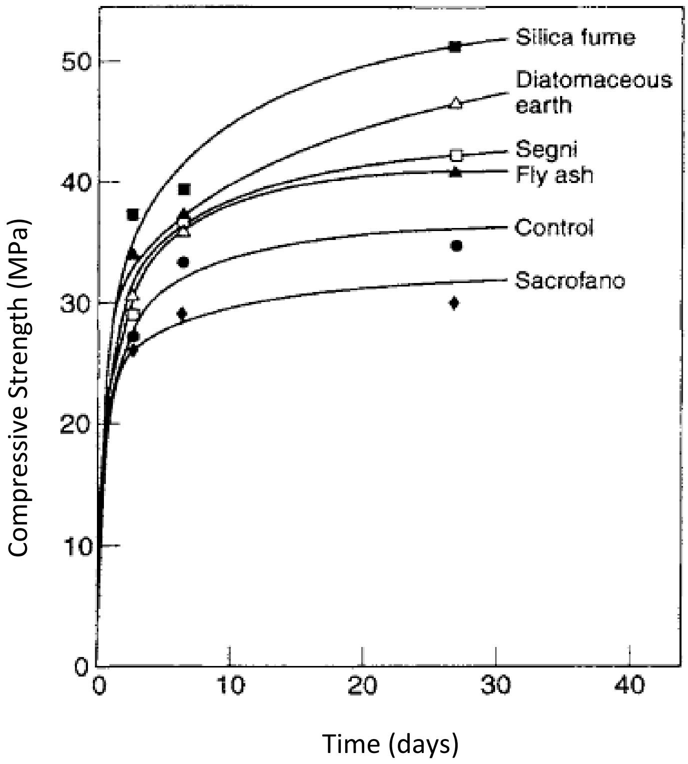


Figure 2.5. Strength development of different 20 percent pozzolan cement mixes under equal curing and temperature conditions [Massazza, 2004]

2.3.4. Pozzolanic Activity

The principle of pozzolanic reactivity can be defined as the maximum amount of $Ca(OH)_2$ that can form a chemical bond with the pozzolan, and the speed of this reaction. These two factors are related to the properties of the pozzolan and the amount and the quality of the reactive phases that this pozzolan has. The amount of $Ca(OH)_2$ which is bonded to the pozzolan is associated with the amount of SiO_2 in the reactive phases of pozzolan. The short-term activity of a pozzolan is related to its specific surface area, and the long-term activity of a pozzolan is related to the chemical and mineralogical compositions of this pozzolan [Erdoğdu et al., 2009].

2.3.5. The Advantages of Using Pozzolan

Pozzolanic materials are used as an additive to the clinker due to their cementitious properties. Cement mortar properties like setting time, strength, workability and soundness will change for different mixture proportions. Generally, pozzolan addition decreases the early strength and soundness, creates a delay on setting and improves the workability of the cement paste [Yetgin and Çavdar, 2006]. The use of pozzolan has some ecological advantages. It decreases the consumption of clinker resulting in less emission of dust and harmful gasses, less energy consumption and less exploitation of clinker's raw materials.

2.4. Methods Used to Measure the Heat of Hydration

2.4.1. Heat of Solution Method

The heat of solution method is described in ASTM C 186 and TS EN 196-8. The principle of this method is to dissolve the unhydrated and hydrated cements in a mixture of nitric acid and hydrofluoric acid. The heat of hydration is calculated by subtracting the heat of solution of hydrated cement from that of unhydrated cement.

This testing method is appropriate for determining the heat of hydration of cement pastes that have gained enough rigidity to be ground so that the cement paste particles are fine enough to be dissolved in acid solution. This means that heat of solution method is an appropriate method for hardened cement pastes. However, with this method it is not possible to observe the heat of hydration of cement at early ages. Also it is not possible to monitor the stages of hydration process.

2.4.2. Adiabatic or Semi-adiabatic Method

The principle of semi-adiabatic method is to introduce a freshly made mortar sample into a calorimeter to determine the heat emission due to temperature rise. For a determined period of time, the sum of the heat lost into the atmosphere and the heat stored in the calorimeter equals to the heat of hydration.

The temperature development of the mortar is compared to the temperature of a reference sample in the reference calorimeter. This method can be applied on cement paste and as well as concrete specimens. In addition, by using the adiabatic method, the heat of hydration measurements can start just after mixing and placing, hence, there is no need to wait until the material hardens like in the heat of solution method [TS EN 196-9, 2011; Morabito, 1997].

2.4.3. Isothermal Conduction Calorimetry Method

As stated in ASTM C1702-09, the method of isothermal conduction keeps the specimen and the environment at a constant temperature to monitor the heat flow from the specimen by comparing it with heat flow of the reference material, hence the heat of hydration of the cement is measured directly. As the heat conducts away from the sample, the calorimeter measures the heat produced in the sample at that time. This implies that a constant temperature should be maintained during the test, and in addition to that the increment in temperature should be trivial.

In this method, an appropriate reference sample is prepared and put in the “reference sink” of the calorimeter. Also a small amount of cement is mixed with water and the prepared paste is put in the ‘‘sample sink’’ of the calorimeter. The thermal power from the sample is measured in short time intervals. This method is not appropriate for measurements longer than 7 days, because problems with precision and bias are expected to develop at later ages [Poole, 2007].

The calorimetric channel is constructed in twin configuration with one side for the sample and the other side for a reference as shown in Figure 2.6. Within the calorimetric channel, there are two Seebeck heat flow sensors, one under the sample and one under the reference. The main route for heat exchange between the sample and its surrounding is through the heat flow sensor. The flow of heat, caused by the temperature gradient across the sensor, creates a voltage signal proportional to the heat flow. The twin configuration of sample and reference within a channel allows the heat flow from the active sample to be compared directly with the heat flow from the inert reference. The voltage difference is a quantitative expression of the overall rate of heat production in the sample. This twin measuring principle enhances the heat flow stability and reduces noise within the system.

In this method, heat flow, which means the rate of hydration heat generation with respect to time is measured and monitored. By taking the integral of the measured heat flow the heat of hydration value is calculated. This process is explained in Figure 2.7.

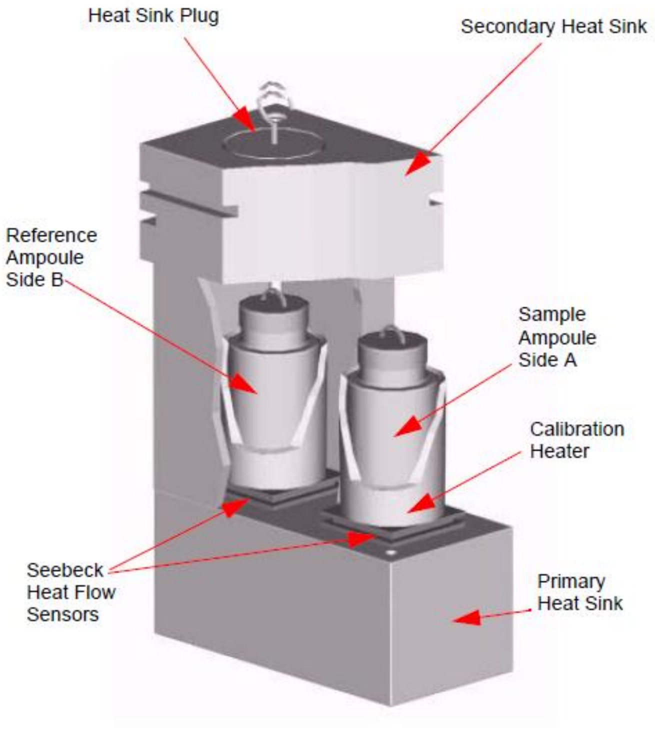
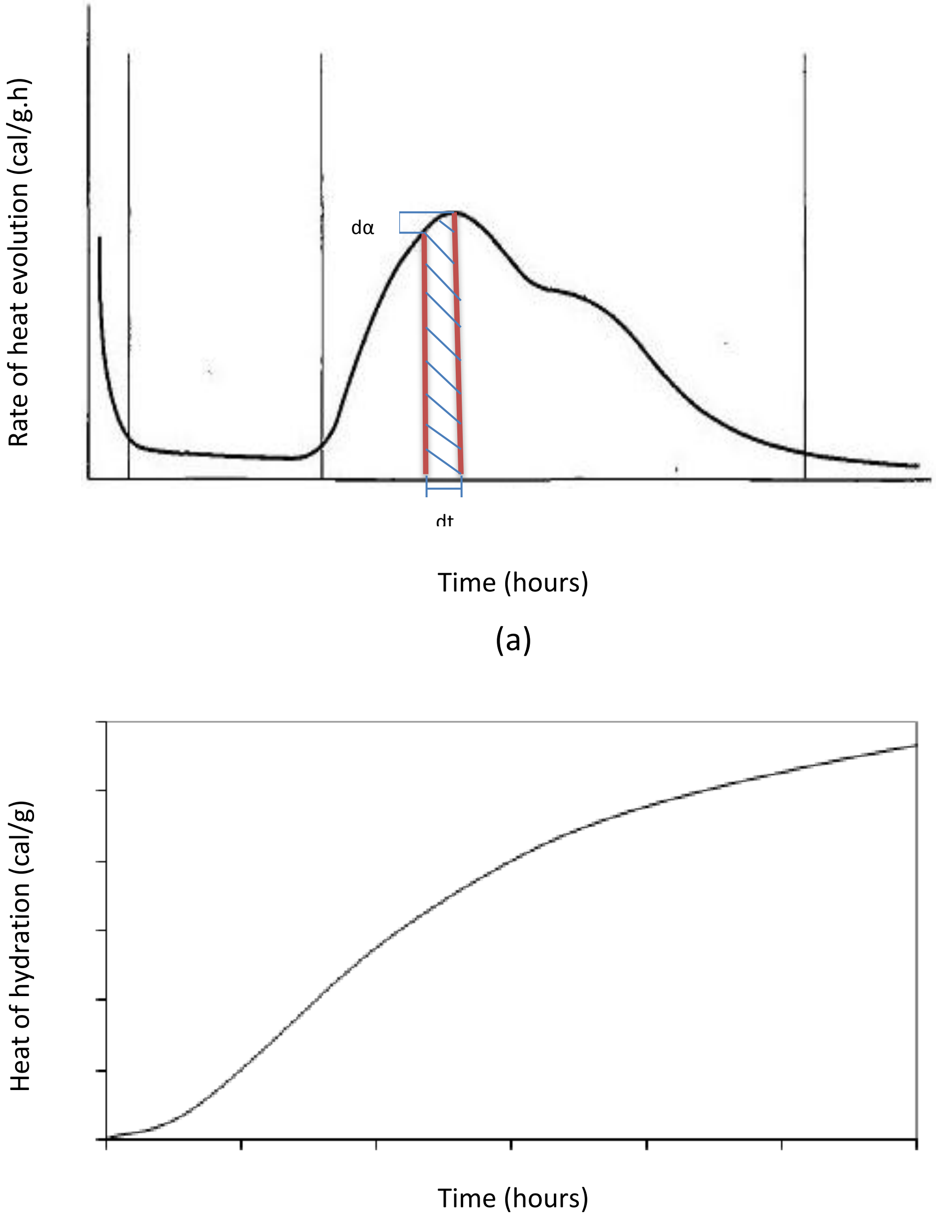


Figure 2.6. Cutaway view twin configuration for one of the eight calorimetric channels [TAM Air Calorimeter Operator’s manual, 2007]



(a)

(b)

Figure 2.7. (a) Rate of heat evolution vs. time graph [Mindess et al., 2003]. (b) Heat flow vs. time graph which is obtained by the integration of rate of heat evolution vs. time graph.

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. General

This study was intended to determine the effects of pozzolan on the rate and the amount of heat evolution within early hydration period. The results were compared with the ones from previous works. Isothermal conduction calorimetry method was used in the experimental work.

All the tests were performed in Middle East Technical University Materials of Construction Laboratory. The materials used in this study were obtained from a previous work performed by Tokyay et. al, 2010 at Turkish Cement Manufacturers Association (T.C.M.A). A total of 36 samples were tested under three different fineness groups of approximately 3000, 5000, and 6000 cm^2/g (Blaine). Besides the Portland cements for control purposes, 3 groups of pozzolan incorporated specimens, with cement replacement ratios of 6, 20 and 35% by mass, were prepared. The sample designation is given in Table 3.1. The chemical compositions of the clinker, gypsum and trass used to produce the cements used in this study along with the chemical composition of the cement mixes are all presented in Tables 3.2. to 3.6. Moreover, the particle size distributions of the cements are presented in Figures 3.1 to 3.4.

In Table 3.1., in the mixes that start with C, the capital letter C stands for control cement. For the mixes that start with one of these numbers (6, 20 and 35) followed by capital P letter, the number here refer to the pozzolan ratio and the letter P indicates that the content is pozzolan. Then, the Number after letter C or P refers to the blaine value of the mix. The small letter found on the end of mix ID refers to the fineness of the mix where: “f” means fine (<45 µm), “c” means coarse (>45 µm) and “o” indexes that it is the original mix.

Table 3.1. Cements Used in the Tests

Pozzolan Content (%)		0	6	20	35
3000 cm^2/g Blaine	<45 µm	C3000 f	6P3000 f	20P3000 f	35P3000 f
	Normal	C3000 o	6P3000 o	20P3000 o	35P3000 o
	>45 µm	C3000 c	6P3000 c	20P3000 c	35P3000 c
5000 cm^2/g Blaine	<45 µm	C3000 f	6P5000 f	20P5000 f	35P5000 f
	Normal	C3000 o	6P5000 o	20P5000 o	35P5000 o
	>45 µm	C3000 c	6P5000 c	20P5000 c	35P5000 c
6000 cm^2/g Blaine	<45 µm	C6000 f	6P6000 f	20P6000 f	35P6000 f
	Normal	C6000 o	6P6000 o	20P6000 o	35P6000 o
	>45 µm	C6000 c	6P6000 c	20P6000 c	35P6000 c

Table 3.2. Chemical Composition of the Clinker, Trass and Gypsum

		Clinker	Gypsum	Control Cement	Trass
LOI	(%)	1.02	21.54	2.59	3.49
SiO_2	(%)	20.43	2.26	19.65	62.59
Al_2O_3	(%)	5.73	0.08	5.48	15.56
Fe_2O_3	(%)	3.25	0.28	3.08	3.86
CaO	(%)	65.50	32.16	63.25	6.79
MgO	(%)	2.67	0.68	2.58	1.77
SO_3	(%)	0.42	42.68	2.43	0.05
Na_2O	(%)	0.37	0.34	0.35	3.35
K_2O	(%)	0.58	0.12	0.57	1.62
Cl^-	(%)	0.0098	0.00	0.0118	0.00
Na_2O Equivalent	(%)	0.75	0.42	0.73	4.42

Table 3.3. Chemical Compositions and Physical Properties of Control Cements

		C3000			**C5000**			**C6000**		
		Normal	**<45**	**>45**	**Normal**	**<45**	**>45**	**Normal**	**<45**	**>45**
LOI	(%)	2.59	3.01	1.51	2.59	2.70	1.75	2.59	2.60	2.23
SiO_2	(%)	19.65	19.30	20.18	19.65	19.44	20.08	19.65	19.49	20.01
Al_2O_3	(%)	5.48	5.27	5.90	5.48	5.38	5.86	5.48	5.45	5.74
Fe_2O_3	(%)	3.08	2.94	3.25	3.08	3.01	3.25	3.08	2.93	3.24
CaO	(%)	63.25	62.96	63.79	63.25	63.22	63.44	63.25	63.37	62.95
MgO	(%)	2.58	2.49	2.69	2.58	2.51	2.74	2.58	2.57	2.65
SO_3	(%)	2.43	3.13	1.74	2.43	2.77	1.81	2.43	2.64	2.18
Na_2O	(%)	0.35	0.31	0.36	0.35	0.32	0.39	0.35	0.34	0.35
K_2O	(%)	0.57	0.60	0.53	0.57	0.59	0.55	0.57	0.57	0.60
Cl^-	(%)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na_2O Equivalent	(%)	0.73	0.70	0.71	0.73	0.71	0.75	0.73	0.72	0.74
C_3S	(%)	59.96	61.05	57.03	59.96	61.23	56.43	59.96	61.48	54.74
C_2S	(%)	11.12	9.29	14.85	11.12	9.55	15.01	11.12	9.51	16.09
C_3A	(%)	9.31	8.99	10.14	9.31	9.17	10.03	9.31	9.49	9.73
C_4AF	(%)	9.37	8.95	9.89	9.37	9.16	9.89	9.37	8.92	9.86
Blaine fineness	(cm^2/g)	3000	-	-	5010	-	-	6000	-	-
Density	(g/cm^3)	3.15	-	-	3.15	-	-	3.15	-	-

Table 3.4. The Chemical Composition and Physical Properties of the Cements Containing 6% Pozzolan

		6P3000			6P5000			6P6000		
		Normal	<45	>45	Normal	<45	>45	Normal	<45	>45
LOI	(%)	2.40	3.12	1.32	2.40	2.83	1.78	2.40	2.53	2.82
SiO_2	(%)	21.81	21.96	21.80	21.81	21.81	21.74	21.81	21.77	21.68
Al_2O_3	(%)	6.09	5.90	6.34	6.09	6.08	6.15	6.09	6.09	6.10
Fe_2O_3	(%)	3.26	3.13	3.36	3.26	3.22	3.34	3.26	3.26	3.34
CaO	(%)	60.12	59.04	61.88	60.12	59.62	61.37	60.12	60.11	60.10
MgO	(%)	2.55	2.44	2.65	2.55	2.46	2.57	2.55	2.54	2.55
SO_3	(%)	2.59	3.20	1.58	2.59	2.79	1.88	2.59	2.53	2.28
Na_2O	(%)	0.52	0.54	0.49	0.52	0.52	0.47	0.52	0.53	0.51
K_2O	(%)	0.65	0.67	0.58	0.65	0.66	0.58	0.65	0.65	0.60
Cl^-	(%)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na_2O Equivalent	(%)	0.95	0.98	0.87	0.95	0.95	0.85	0.95	0.94	0.86
Blaine fineness	(cm^2/g)	2930	-	-	4930	-	-	5950	-	-
Density	(g/cm^3)	3.01	-	-	3.01	-	-	3.01	-	-

Table 3.5. The Chemical Composition and Physical Properties of the Cements Containing 20% Pozzolan

		20P3000			20P5000			20P6000		
		Normal	<45	>45	Normal	<45	>45	Normal	<45	>45
LOI	(%)	2.64	3.27	1.43	2.64	3.03	1.79	2.64	2.88	1.93
SiO_2	(%)	27.23	28.00	26.27	27.23	27.85	25.93	27.23	27.51	25.88
Al_2O_3	(%)	7.55	7.50	7.61	7.55	7.52	7.41	7.55	7.56	7.33
Fe_2O_3	(%)	3.59	3.62	3.55	3.59	3.59	3.61	3.59	3.56	3.64
CaO	(%)	52.53	50.80	55.05	52.53	50.95	55.23	52.53	51.63	55.33
MgO	(%)	2.50	2.43	2.62	2.50	2.46	2.63	2.50	2.50	2.65
SO_3	(%)	2.15	2.40	1.40	2.15	2.36	1.56	2.15	2.32	1.75
Na_2O	(%)	0.90	0.94	0.86	0.90	0.90	0.86	0.90	0.90	0.80
K_2O	(%)	0.80	0.83	0.74	0.80	0.82	0.71	0.80	0.81	0.72
Cl^-	(%)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na_2O Equivalent	(%)	1.43	1.49	1.35	1.43	1.44	1.33	1.43	1.43	1.27
Blaine fineness	(cm^2/g)	2950	-	-	4980	-	-	6010	-	-
Density	(g/cm^3)	2.96	-	-	2.96	-	-	2.96	-	-

Table 3.6. The Chemical Composition and Physical Properties of the Cements Containing 35% Pozzolan

		35P3000			35P5000			35P6000		
		Normal	**<45**	**>45**	**Normal**	**<45**	**>45**	**Normal**	**<45**	**>45**
LOI	(%)	2.83	3.89	2.17	2.83	3.28	2.08	2.83	3.20	2.00
SiO_2	(%)	33.85	35.77	32.88	33.85	34.78	32.30	33.85	34.61	32.01
Al_2O_3	(%)	8.99	9.25	8.87	8.99	9.18	8.65	8.99	9.16	8.57
Fe_2O_3	(%)	3.63	3.76	3.44	3.63	3.70	3.48	3.63	3.67	3.52
CaO	(%)	44.20	40.05	45.94	44.20	42.09	46.91	44.20	42.59	47.63
MgO	(%)	2.41	2.27	2.44	2.41	2.31	2.55	2.41	2.37	2.61
SO_3	(%)	1.80	2.65	1.74	1.80	2.38	1.66	1.80	2.11	1.42
Na_2O	(%)	1.35	1.38	1.28	1.35	1.36	1.28	1.35	1.32	1.27
K_2O	(%)	0.93	0.97	0.91	0.93	0.95	0.86	0.93	0.97	0.86
Cl^-	(%)	0.0076	0.0082	0.0069	0.0076	0.008	0.0077	0.0076	0.0077	0.0084
Na_2O Equivalent	(%)	1.97	2.02	1.88	1.97	1.99	1.85	1.97	1.96	1.84
Blaine fineness	(cm^2/g)	3020	-	-	5070	-	-	5980	-	-
Density	(g/cm3)	2.89	-	-	2.89	-	-	2.89	-	-

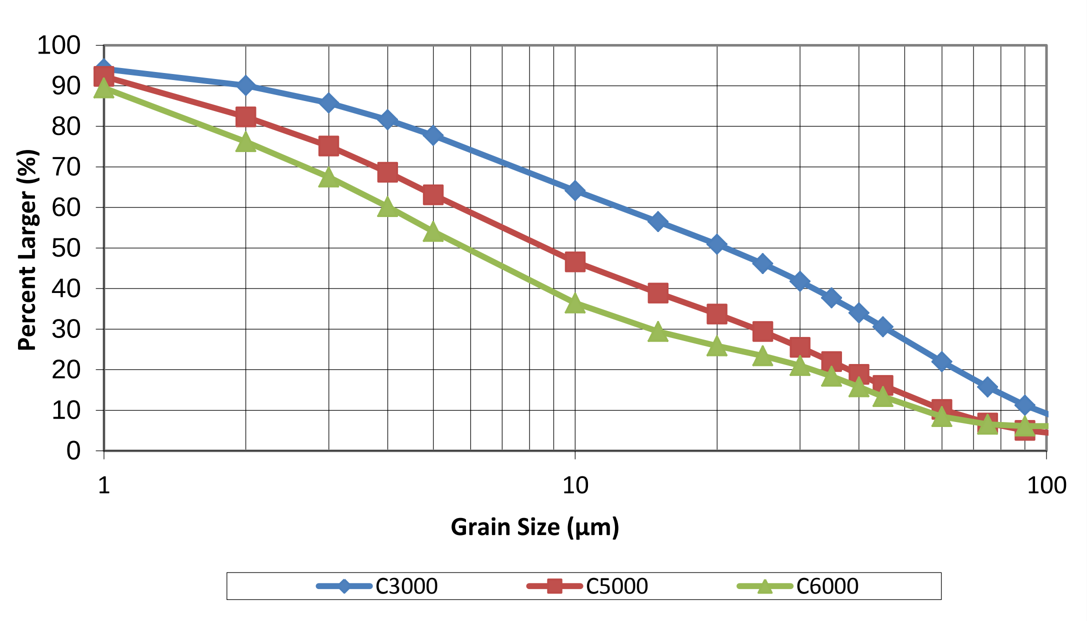


Figure 3.1. Particle Size Distributions of Control Cements

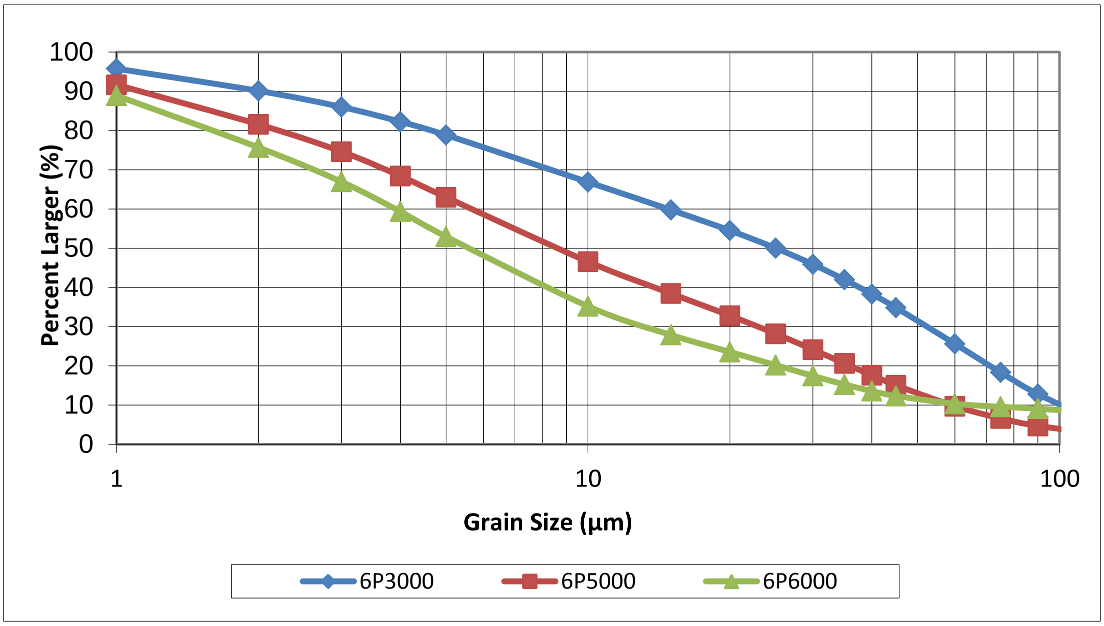


Figure 3.2. Particle Size Distributions of the Cements Containing 6% Pozzolan

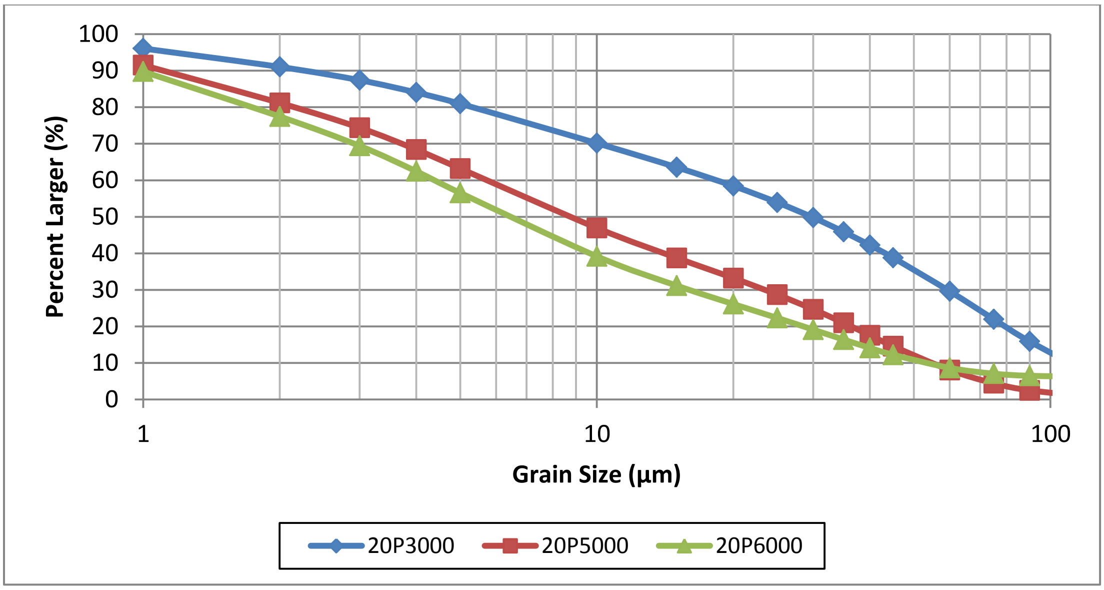


Figure 3.3. Particle Size Distributions of the Cements Containing 20% Pozzolan

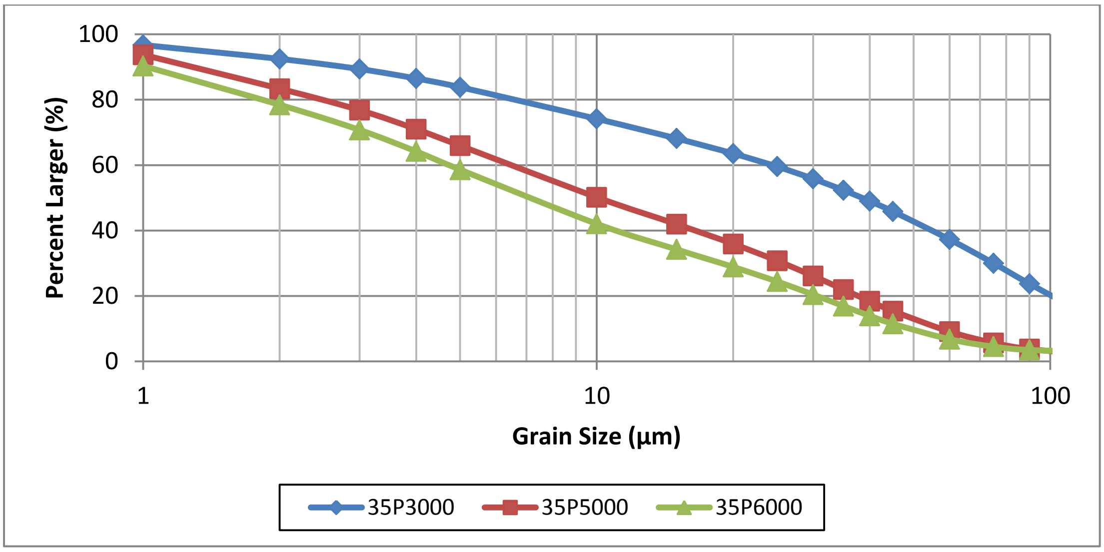


Figure 3.4. Particle Size Distributions of the Cements Containing 35% Pozzolan

3.2. Sample Preparation and Experimental Procedure

The isothermal calorimeter device used in this study, Figure 3.5., performs eight measurements at the same time with two channels for each measurement. The first channel is for reference sample and the second one is for the test sample. 20 ml disposable glass ampoules were used in this experiment for both reference and testing samples.

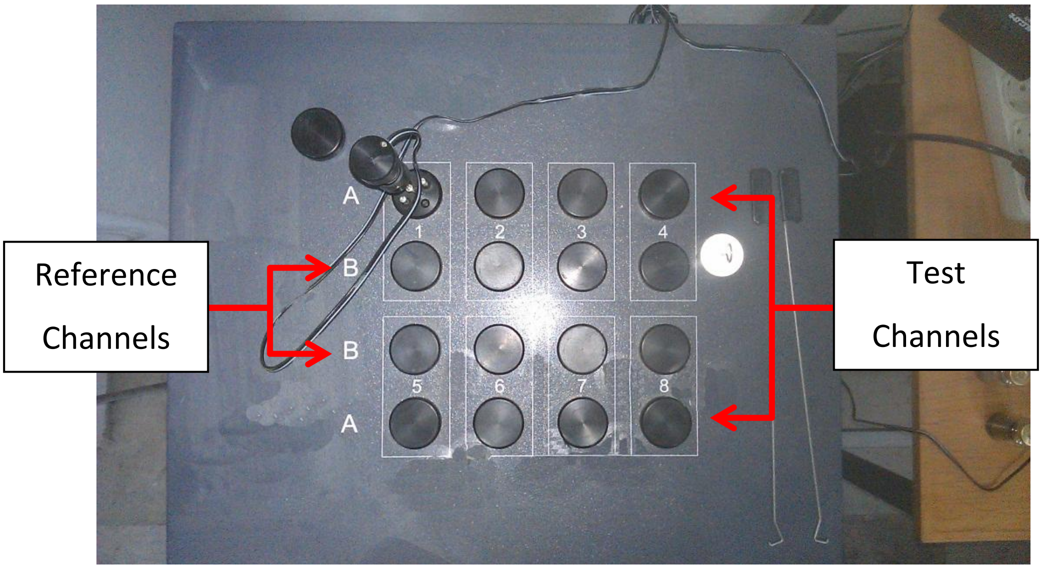


Figure 3.5. Isothermal calorimeter device (top view)

10.065 g of reference cement samples are weighed and put in disposable glass ampoules to be placed into calorimeter’s reference channels. The process of choosing a reference material and calculating its weight is explained APPENDIX A. These samples are prepared from randomly selected cement for all eight channels of the calorimeter and they are used with all the testing samples during the testing procedure. The reference sample was placed into the calorimeter’s reference channel prior to the test to balance the temperature between the reference sample and the environment.

To perform the test, an ampoule experiment type was started on the computer, the detailed data of the test sample were entered into the software and the instructions on computer screen were followed. 7.5 g of one of the cement sample from Table 3.1. is weighed and mixed carefully with 3 g of water. After that, 5 g of the mortar was put in the glass ampoule without letting the mortar touch the walls or the neck of the ampoule. The test sample was placed into calorimeter’s test sample sink immediately. The test is performed for all the 36 cement samples, and each sample was tested at least for 48 hours. The heat flow data were recorded by the software in short intervals and exported to MS Excel. Heat flow data was integrated with respect to time and heat of hydration value was obtained.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. General

In this section the data gathered from the experimental study conducted on cements with different pozzolan ratios and fineness are presented. The results are discussed and compared with the results of the previous studies published in the literature.

4.2. 24-h Heat of Hydration of Cements as Determined by Isothermal Calorimetry

The values of heat of hydration for each sample according to pozzolan amount and particle size distribution are presented in Table 4.1.

Table 4.1. The Heat of Hydration Values of Cement Samples (J/g)

Mixture Name	Sample Name	<45 µm	Normal	>45 µm
Control cements	C3000	168.21	106.45	47.60
	C5000	167.26	165.91	78.28
	C6000	187.28	168.15	84.98
6 % pozzolan cements	6P3000	177.79	130.96	50.36
	6P5000	201.28	173.58	115.72
	6P6000	187.46	176.37	109.09
20 % pozzolan cements	20P3000	144.44	100.83	34.51
	20P5000	164.65	145.06	78.01
	20P6000	169.81	154.38	95.33
35 % pozzolan cements	35P3000	117.24	68.73	43.85
	35P5000	136.11	119.36	71.08
	35P6000	149.29	132.86	85.90

4.3. Effect of Pozzolan Incorporation and Fineness on Early Heat Evolution

24 hour heat of hydration values of the cement which were measured by isothermal calorimetry method, are shown in Figure 4.1.

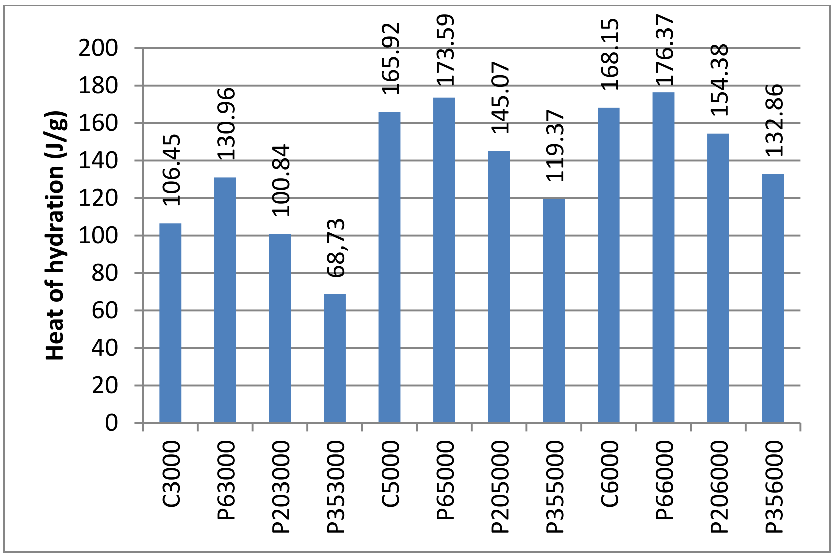


Figure 4.1. 24 hour heat of hydration values of the cements studied

When 3000 cm^2/g Blaine fineness is taken as the basis, the important features of Figure 4.1 can be stated as follows:

a) Amounts of interground pozzolan up to about 20% results in 24 hour heat evolution higher than or at least as same as that of control in coarser cements. The noticeable reductions in early heat evolution can be experienced at pozzolan contents greater than 20%.

b) All pozzolan incorporated cements finer than 3000 cm^2/g Blaine fineness investigated in this research had higher early heat of hydration values than the 3000 cm^2/g control cement.

On Figure 4.2, it can be seen that the effect of pozzolan content on heat evolution at early ages varies within a wider range for coarser cements. As indicated in the same figure, 5.71% pozzolan (6P cements) incorporation results in higher heat of hydration than the control cements for all the three finenesses of cements investigated. The pozzolan ratio previously mentioned represents the actual ratio of 6% pozzolan cements. This ratio can be calculated for cement with 94% clinker and 6% pozzolan with an addition of 5% percent gypsum by dividing the ratio of pozzolan to the total ratios of cement ingredients, which is 6/(94+6+5) = 6/105 = 5.71%.

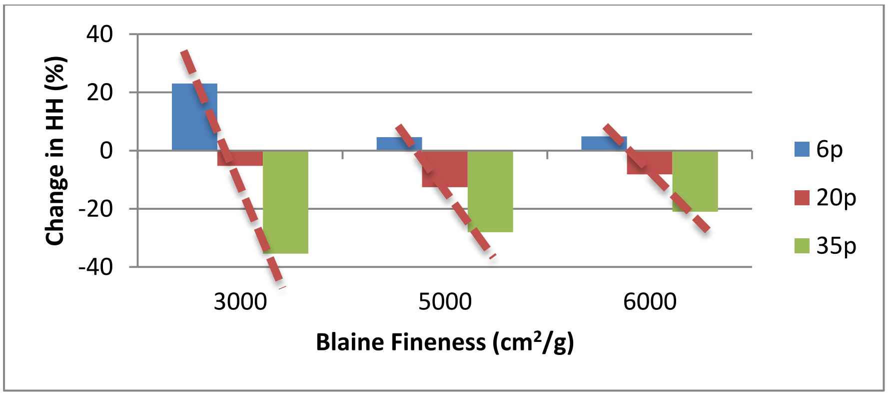


Figure 4.2. Effect of pozzolan content and cement fineness on the relative change in 24 hour heat of hydration in comparison to control cements.

The increase shown in Figure 4.2 was 23.02% in 3000 cm^2/g Blaine cements and 4.62 and 4.89% for 5000 cm^2/g and 6000 cm^2/g Blaine cements, respectively. The other extreme was 33.65% pozzolan incorporation (35P cements). The reductions in heat of hydration with respect to those of control cements were 35.43%, 28.06% and 20.99% for 3000, 5000, and 6000 cm^2/g Blaine cements. The ranges of change of 24-h heat evolution for these cements were 58.45%, 32.68%, and 25.88%, respectively. The 24-h heat evolution curves of the cements investigated in this research are given in Figure 4.3.

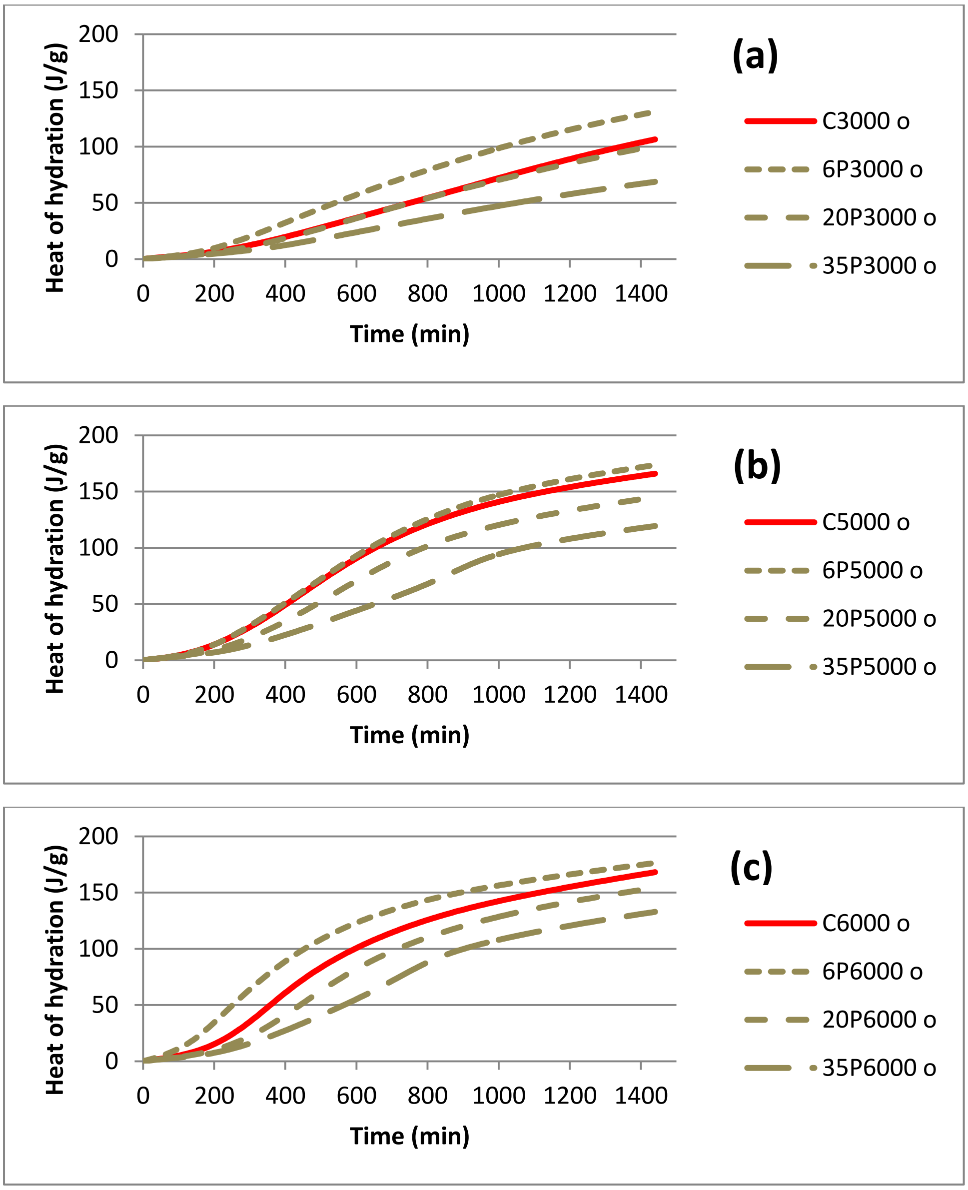


Figure 4.3. Early heat of hydration of (a) 3000 cm^2/g Blaine (b) 5000 cm^2/g Blaine 6000 cm^2/g Blaine fineness cements.

The comparisons in Figure 4.3. reveal that, besides the obvious heat evolution increasing effect of higher cement fineness, there occurs a change in the rate of heat evolution within 6 to 13 hours of hydration in the finer cements. This change indicates an acceleration of the hydration reactions after the dormant period. The accelerating effect of pozzolan addition to portland cements were known as early as 1950s [Davis, 1950].

The inflection point on the heat of hydration curves varies both with the fineness of cement and the amount of pozzolan incorporated. The slowing down of the rate of heat evolution generally corresponds to the C_3S hydration peak (Peak 4 on Figure 2.3.) of the rate of heat evolution-time curve. The following discussions are based on these curves, and comparisons are made within each cement fineness value investigated and for each pozzolan content.

4.4. Effect of Pozzolan Content and Fineness on the Rate of Early Heat Evolution

4.4.1. Effect of Pozzolan Content on the Dormant Period

The dormant period is shortened for small amounts of pozzolan incorporation at all Blaine fineness values used in this research as shown in Figure 4.4. While the increased fineness of the cements result in shorter dormant periods, increased amount of pozzolan beyond about 10% lengthens the dormant period. The minima of the rate of heat evolution-time data (peak 3 in Figure 2.3.) are given in Table 4.2.

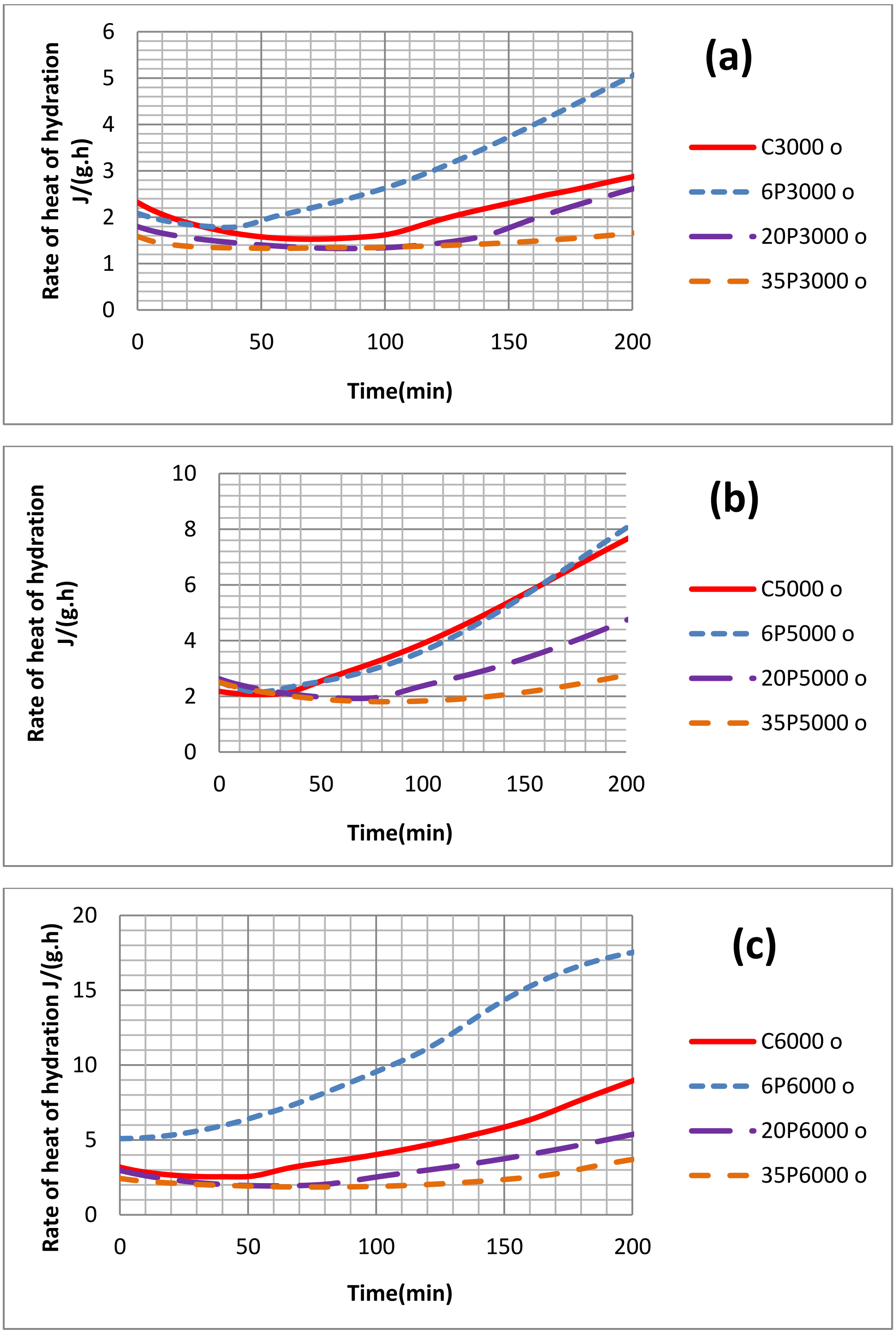


Figure 4.4. Dormant periods of pozzolan incorporated cements in comparison with their control cements. (a) 3000 cm^2/g Blaine (b) 5000 cm^2/g Blaine (c) 6000 cm^2/g Blaine fineness

Table 4.2. The Minima of Rate of Heat Evolution-Time Curves

Cement	**Time to reach the minima for different Blaine fineness of cements (min)**		
	3000 (cm2/g)	**5000 (cm2/g)**	**6000 (cm2/g)**
Control	70	20	42
6P	35	20	15
20P	85	67	60
35P	56	82	77

4.4.2 Effect of Pozzolan Content on the Acceleration Period

The accelerating effect of both increased fineness and small amount of pozzolan incorporation can be observed from the slopes of the acceleration periods of rate of heat evolution-time curves upto the C_3S peak of the cements given in Figure 4.5. Slope calculation of the linear portion of the acceleration period reveals that increased fineness of the cement results in higher rate of acceleration. Small amount (6%) of pozzolan incorporation increases the rate of acceleration for all cement finenesses investigated in this research. For 3000 cm^2/g Blaine cements, even 20% pozzolan resulted in higher acceleration rate than its control. On the other hand, 20% pozzolan caused slower rates of acceleration than the control cements in 5000 and 6000 cm^2/g Blaine cements and 35% pozzolan incorporation caused slower rate of acceleration for all cements. This slowing down effect is more pronounced in finer cements. A comparison of the relative rates of acceleration of the cements studied is given in Figure 4.6.

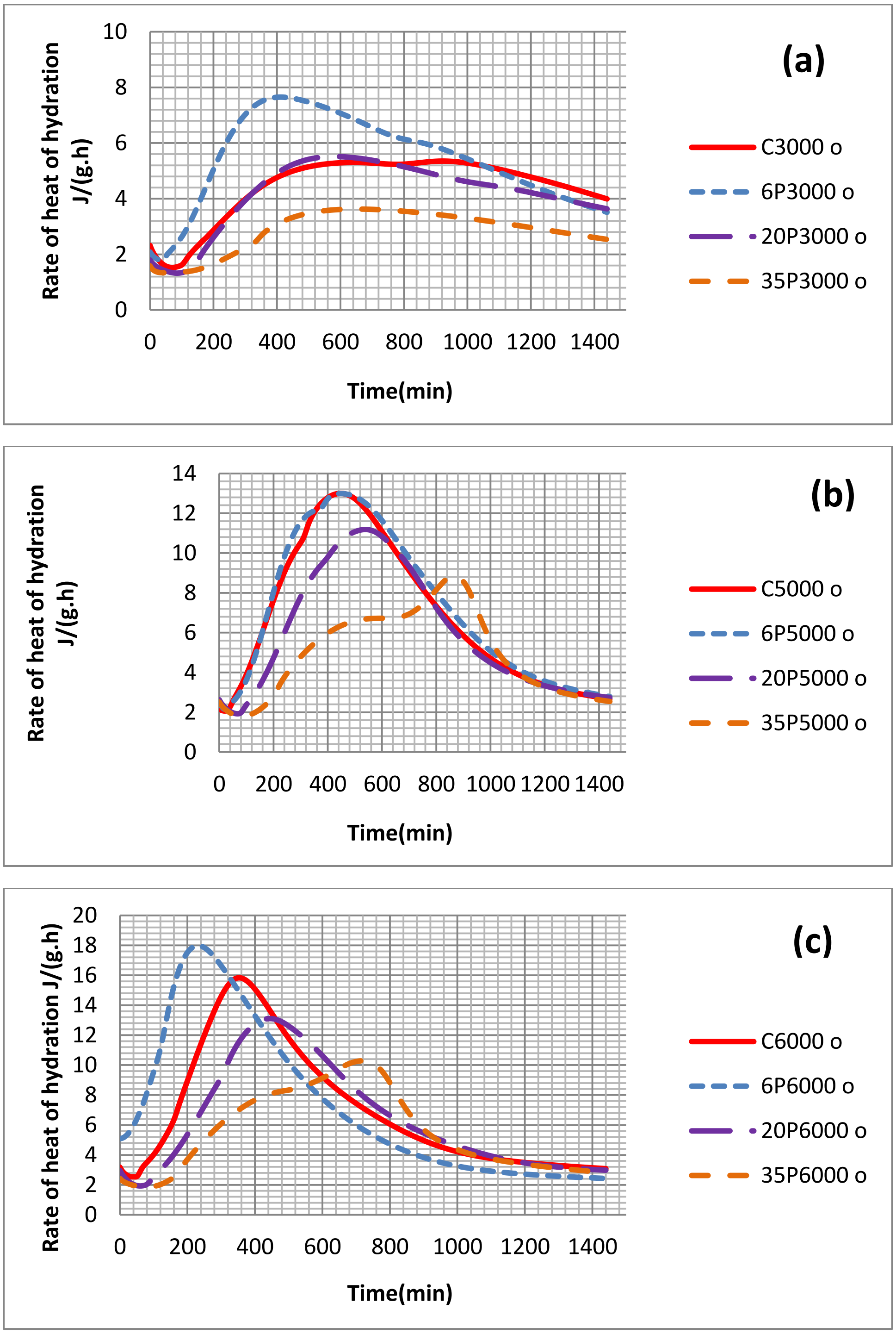


Figure 4.5. Rate of heat evolution-time curves of the pozzolan incorporated cements in comparison with their control cements. (a) 3000 cm^2/g Blaine, (b) 5000 cm^2/g Blaine and (c) 6000 cm^2/g Blaine.

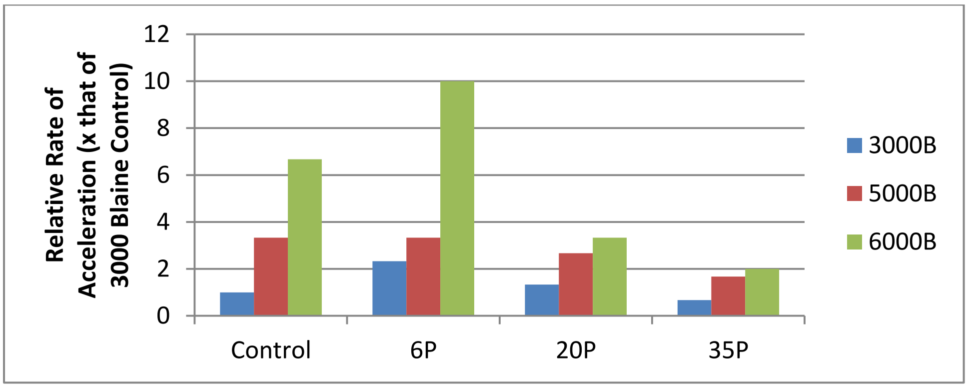


Figure 4.6. Relative rates of acceleration of the cements with respect to 3000 cm^2/g Blaine control cement.

The presence of pozzolan causes some changes in hydration reactions of portland cement. Consequently, these changes can affect the engineering properties of cement. Since the two important parameters causing the changes in the hydration mechanism are the fineness of the cement and the amount of pozzolan incorporation, in order to see the effect of particle fineness and the amount of fine particles on the rate of heat evolution, portions of the cements finer and coarser than 45 µm were treated separately. For the interpretation of the curves, the amounts of portland cement and pozzolan portions of the cements were calculated by making use of their chemical compositions and the results are given in Table 4.3. An example of the calculations is provided in APPENDIX B. It is obvious from the table that the natural pozzolan which is a softer material than the clinker is ground finer and therefore higher amount of pozzolan appears in finer (<45 µm) portion of the cements (except for 35P 3000) which contain 5.71, 19.23 and 33.65% for 6P, 20P and 35P cements, respectively.

Table 4.3. Portland Cement and Pozzolan Contents Smaller and Larger than 45 µm.

Amount of (%)	Control Cement			6P Cement			20P Cement			35P Cement		
	3000 cm^2/g	5000 cm^2/g	6000 cm^2/g	3000 cm^2/g	5000 cm^2/g	6000 cm^2/g	3000 cm^2/g	5000 cm^2/g	6000 cm^2/g	3000 cm^2/g	5000 cm^2/g	6000 cm^2/g
< 45µm material	58.17	64.92	69.67	54.29	74.33	74.33	57.48	65.34	79.14	31.18	58.91	69.23
< 45 µm Pozzolan	-	-	-	3.19	3.95	3.71	11.57	12.92	14.93	12.01	21.09	24.41
< 45 µm P. cement	58.17	64.92	69.67	51.10	70.38	70.62	45.92	52.42	64.21	19.17	37.82	44.82
> 45µm material	41.83	35.08	30.33	45.71	25.67	25.67	42.52	34.66	20.86	68.82	41.09	30.77
> 45 µm Pozzolan	-	-	-	2.52	1.76	2.00	7.66	6.31	4.30	21.64	12.56	9.24
> 45 µm P. cement	41.83	35.08	30.33	43.19	23.91	23.67	34.86	28.35	16.56	47.18	28.53	21.53

In general, it would seem that, in the course of the first 24 hours, natural pozzolans accelerate the hydration of C_3S. The acceleration of the early hydration of C_3S caused by pozzolans has been ascribed to the fineness of pozzolan particles which offer a greater surface for the precipitation of C-S-H from the pore solution. In other words, acceleration is not due to the pozzolanic reaction which may be observed, at the very best, after several days [Massazza, 2004].

In order to see the relative effects of the coarse and fine portions of the cements on total heat of hydration within the first 24 hours, the heat of hydration ratios (HH ratio) of the fine portion and coarse portion to original cement were calculated and plotted against time of hydration (Figure 4.7). When the original cement is coarser (3000 cm^2/g in this investigation), the relative contribution of the finer portion is higher, as shown in Figure 4.7.a. Furthermore, this effect becomes more pronounced as the amount of pozzolan in the cement increases. As the original cement gets finer, the relative contribution of the finer portion reduces, as shown in Figures 4.7.b and 4.7.c.

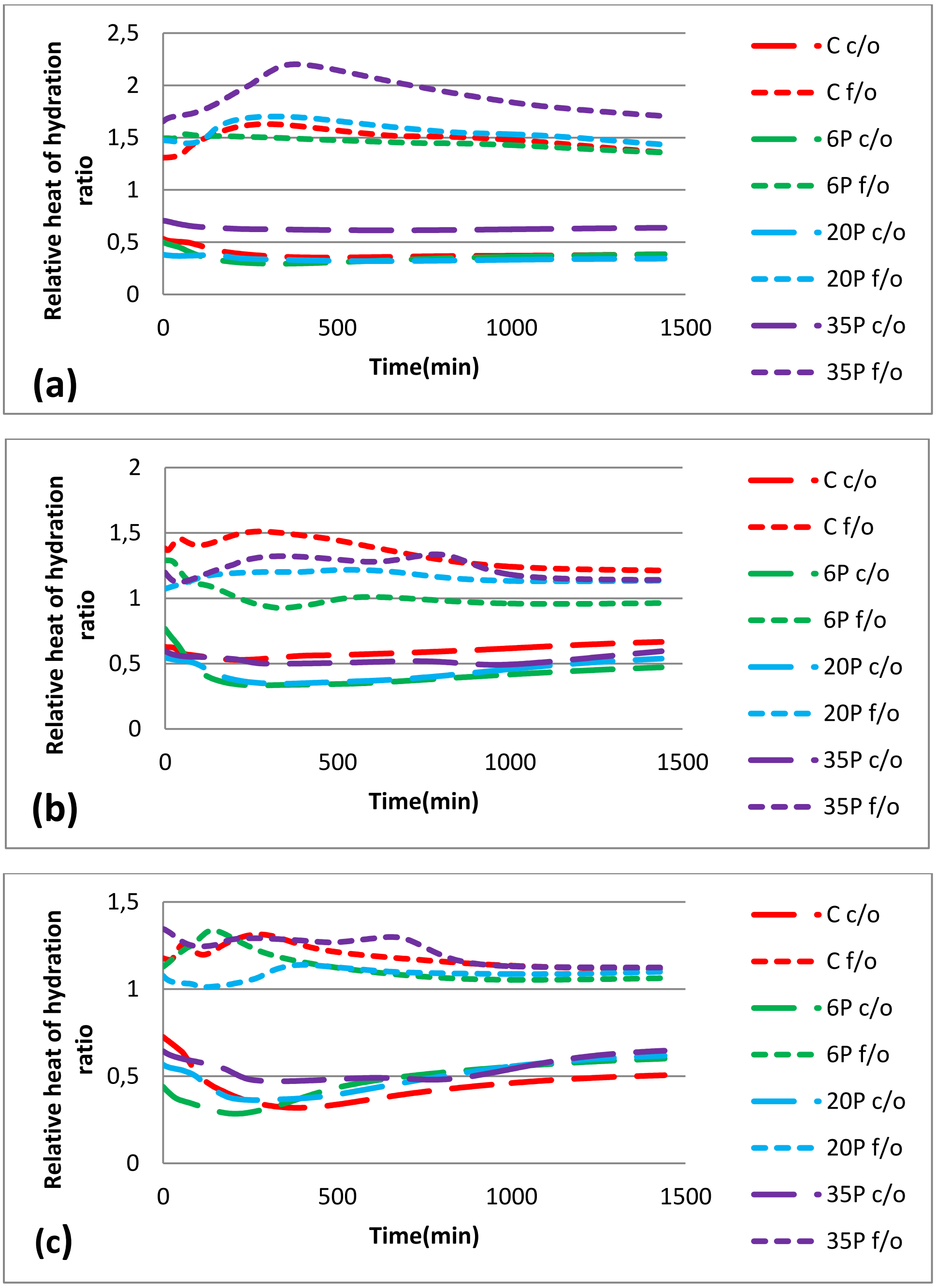


Figure 4.7. Heat of hydration ratio of the coarse and fine portions of 6000 cm^2/g cements with respect to their originals. (a) 3000 cm^2/g Blaine, (b) 5000 cm^2/g Blaine, (c) 6000 cm^2/g Blaine

4.4.3. Effect of Pozzolan Content on the Deceleration Period:

The comparison of Figure 4.5 with the general rate of heat evolution-time curve of portland cements shows that the rate of deceleration does not change significantly with pozzolan incorporation. However, one peculiarity of this period that should be noted is related to the shoulder or the peak that results from renewed AF_t formation. Small amount of pozzolan (6%) results in the earlier formation of this shoulder in coarser (3000 cm^2/g) cements. This effect is consistent with the results of other similar investigations in that pozzolans result in the acceleration of trisulfate formation [Odler, 2004].

As the amount of pozzolan incorporation increased, the shoulder is observed later. This shoulder or small peak is suppressed in finer 6P and 20P cements (5000 and 6000 cm^2/g) as well as their controls. However, for finer 35P cements the peak becomes extraordinarily high as shown in Figures 4.8 to 4.11. In fact, this may be the delayed C_3S hydration peak due to excessive amount of pozzolan present in the cement rather than an AF_t peak, or a combination of both. Another possible reason would be the amount of gypsum being more than that it is necessary. Gypsum content is so adjusted in cements that C_3A forms ettringite while the cement paste is till plastic. The amount of gypsum was kept constant as 4% in this investigation for 20P and 35P cements. This amount may be a little high for 35P cements. Therefore, the excess gypsum may have been resulted in conversion of monosulfate phase into ettringite. This conversion may be responsible for the accentuated second peak in the rate of heat evolution curve.

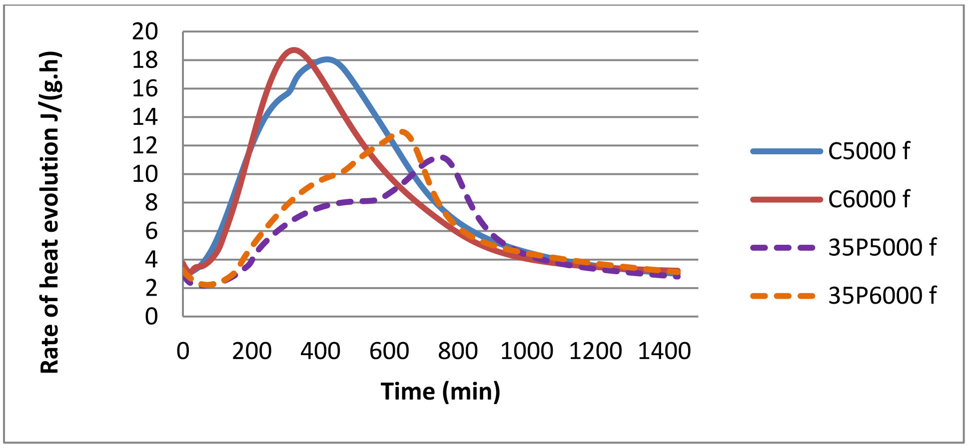


Figure 4.8. Extraordinarily high second peak in finer (<45µm) 35P cements

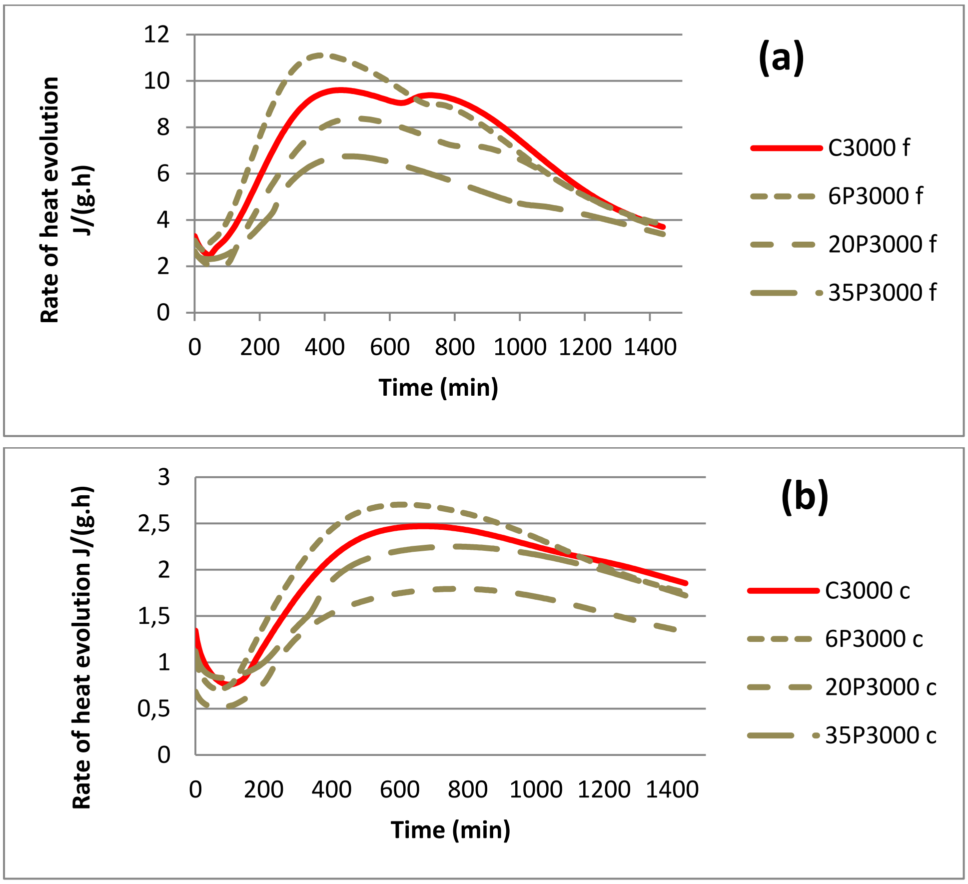


Figure 4.9. Rate of heat evolution-time curves of (a) <45µm portion of 3000 cm^2/g cements. (b) >45µm portion of 3000 cm^2/g cements.

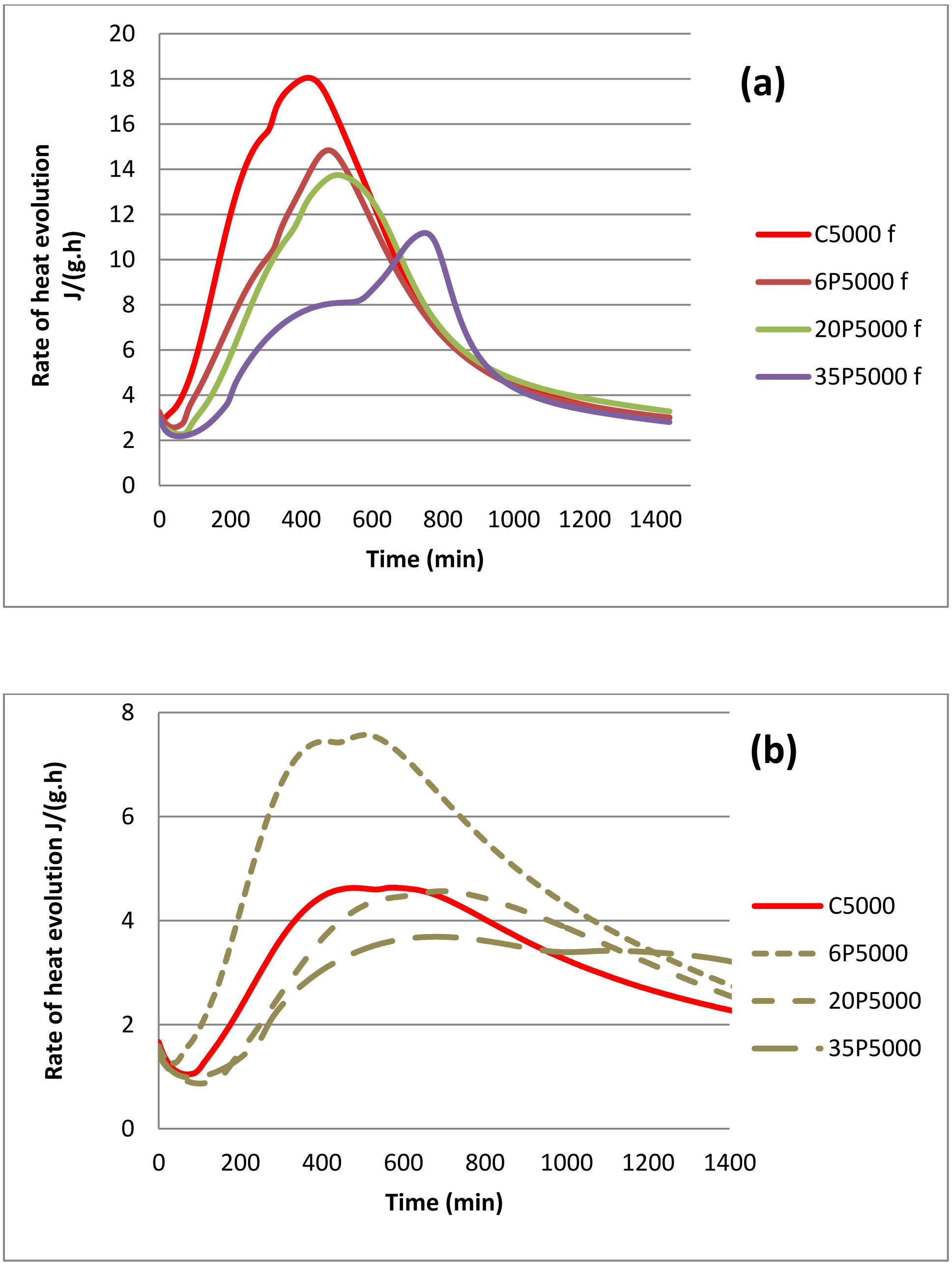
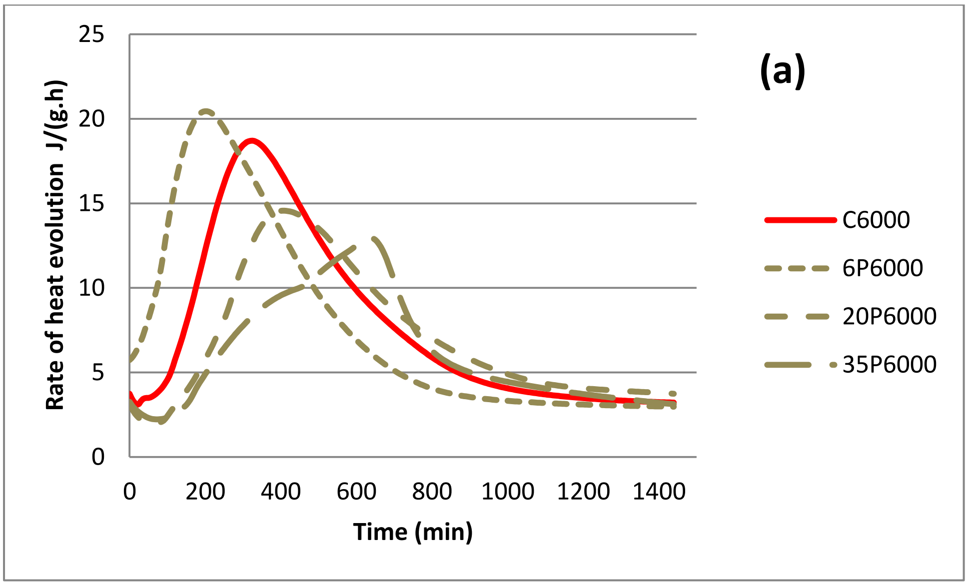


Figure 4.10. Rate of heat evolution-time curves of (a) <45µm portion of 5000 cm^2/g cements. (b) >45µm portion of 5000 cm^2/g cements.



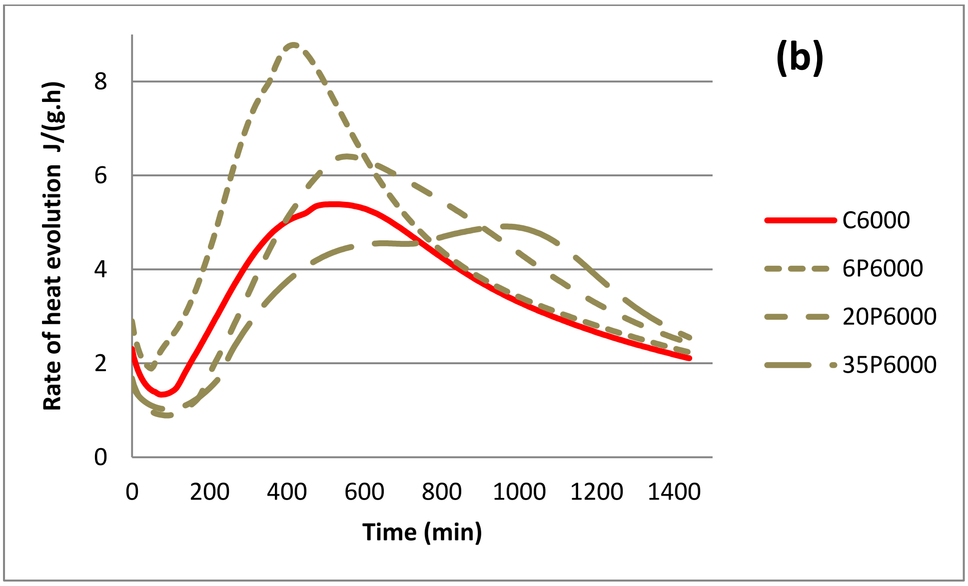


Figure 4.11. Rate of heat evolution-time curves of (a) <45µm portion of 6000 cm^2/g cements (b) >45µm portion of 6000 cm^2/g cements.

4.5. Estimating the Contribution of Pozzolan Incorporation on Early Heat Evolution

To determine the effect of the natural pozzolan on the early heat of hydration, the following comparisons were made with the assumptions that: (1) the total heat evolved at any time is the weighted average of the heat of hydration values of the coarse (> 45µm) and fine (< 45µm) portions of the cement measured seperately, and (2) no pozzolan reaction occurs at very early stages of hydration. Thus, after determining the amounts of portland cement in the coarse and fine portions the heat evolution at any time within the first 24 hours of hydration was calculated as:

$$HH_t = HH_{ct} \cdot C + HH_{ft} \cdot F$$

where, HH_t: calculated heat of hydration value at time, t

HH_{ct}: measured heat of hydration of the coarse portion of cement at time, t

HH_{ft}: measured heat of hydration of the fine portion of cement at time, t

C: fraction of the coarse portland cement portion

F: fraction of the fine portland cement portion

Then the measured and calculated values of heat of hydration, within the first 24 hours of hydration, were plotted. The ratio of measured heat of hydration values over the calculated ones are presented in Figures 4.12–4.14, where each figure contains the ratios for control cement and cements with pozzolan additions of one fineness group. The line of equality drawn in each of these figures represents the case where measured and calculated values are totally equlas. These figures clearly show that the first assumption is reasonable, since the lines of original cements are very close to the line of equalities. On the other hand, it is a well known fact that unless the pozzolan is in extremely finely divided form like silica fume, no chemical reaction occurs between the lime produced upon portland cement hydration and the pozzolan in the early stages of hydration. Therefore, the rest of the lines in Figures 4.12–4.14 were expected to be also close to the line of equality. However, as can be seen in these figures, there occurs a significant difference between the measured and calculated heat of hydration values, as the lines of pozzolan incorporated cements become distant from the equality line with the increase of pozzolan ratio. In other words, the values of calculated heat of hydration for pozzolan incorporated cements are smaller than the measured ones. This finding indicates that pozzolan incorporation results in an increasing effect on heat evolution at early hydration stages. The relative increase is proportional with the amount of pozzolan used as given in Table 4.4.

Since the pozzolan is not reactive at such an early age, this positive effect is attributed to its accelerating effect on portland cement hydration. In two investigations on the effects of fly ash on hydration, similar comments were made: It was found that after 28 days of hydration, four cements containing 25% fly ash resulted in 3-9% more Alite (C_3S) hydration than the portland cement alone. The accelerating effect was found to be dependent on the type of the fly ash and increases by increasing the amount replacing the portland cement [Massazza, 2004]. A similar accelerating effect was observed in the blended cements investigated in this research as shown in the plots of rate of heat evolution with time in Figures 4.15-4.17. In these figures, the calculated curves were obtained from the test results and the calculated curves were obtained by:

$$RHH_t = RHH_{ct} \cdot C + RHH_{ft} \cdot F$$

where, RHH_t: calculated rate of heat of hydration value at time, t

RHH_{ct}: measured rate of heat of hydration of the coarse portion of cement at time, t

RHH_{ft}: measured rate of heat of hydration of the fine portion of cement at time, t

C: fraction of the coarse portland cement portion

F: fraction of the fine portland cement portion

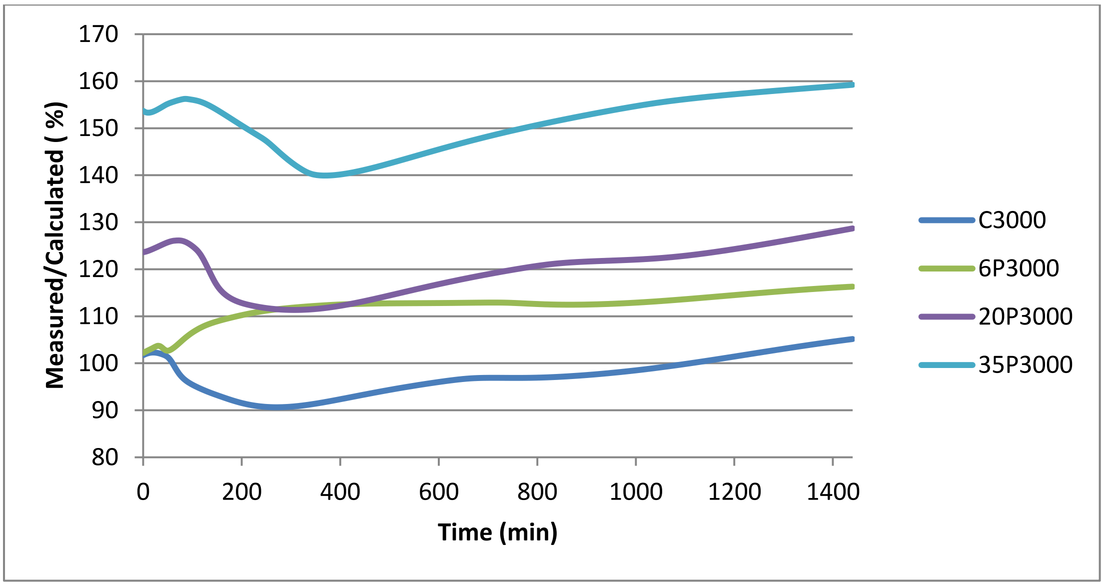


Figure 4.12. Measured Heat Of Hydration/Calculated Heat of Hydration vs. Time Graph for 3000 Blaine cements

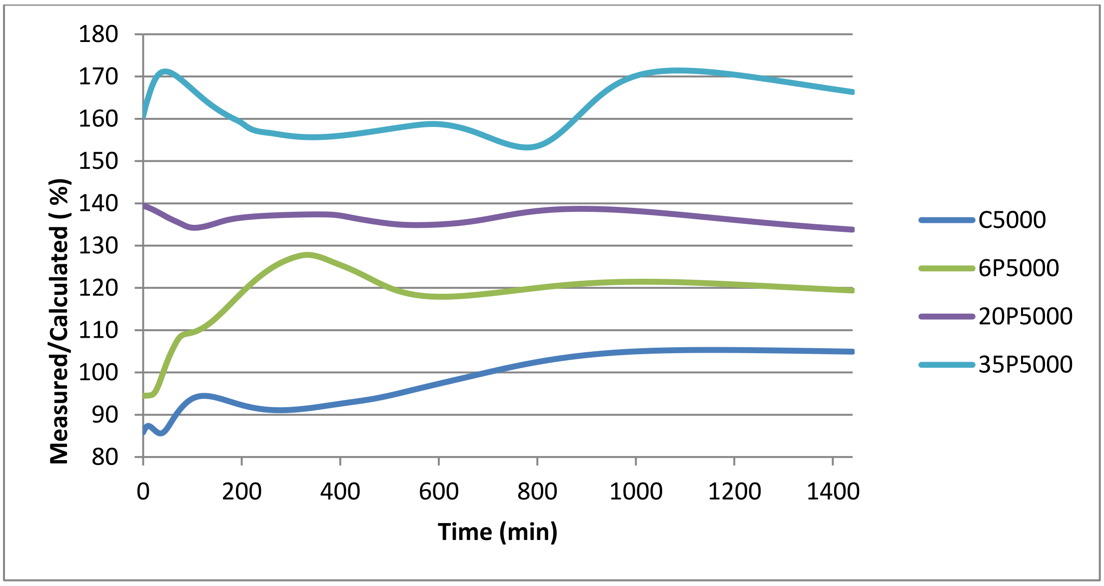


Figure 4.13. Measured Heat Of Hydration/Calculated Heat of Hydration vs. Time Graph for 5000 Blaine cements

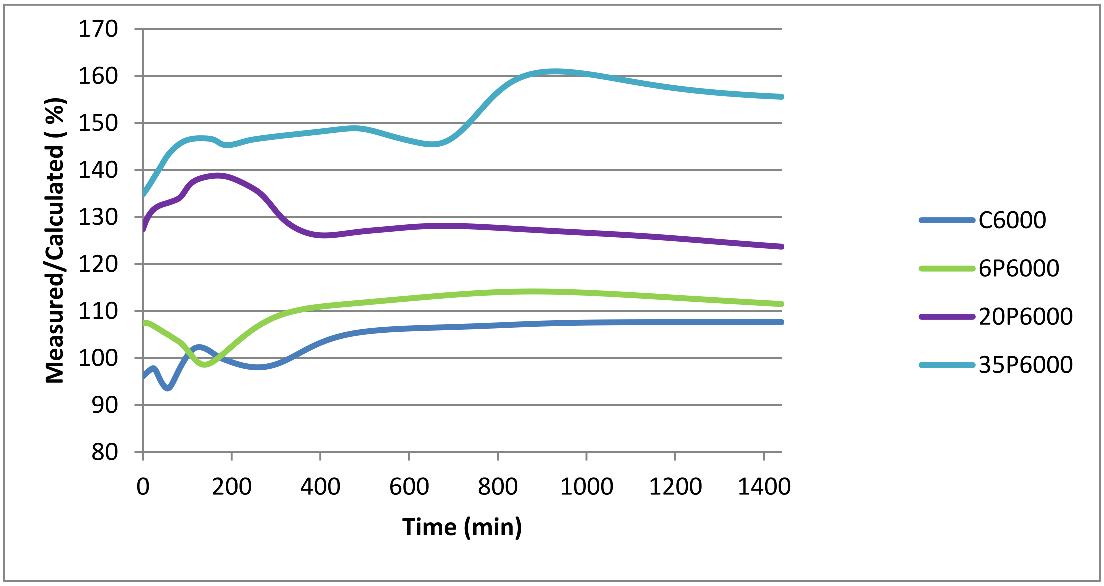


Figure 4.14. Measured Heat Of Hydration/Calculated Heat of Hydration vs. Time Graph for 6000 Blaine cements

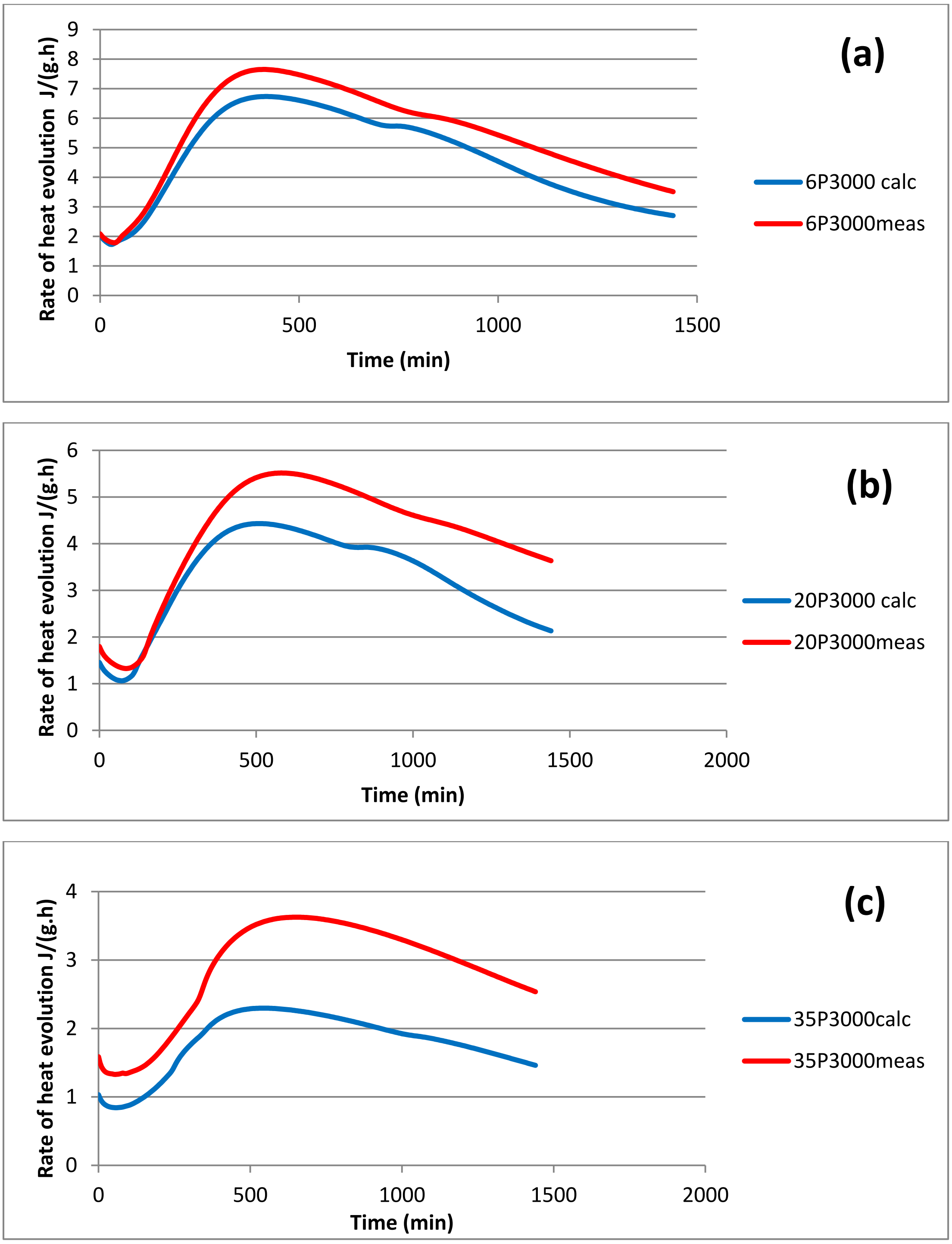


Figure 4.15. Rate of heat evolution of 3000 cm^2/g Blaine fineness blended cements (a) 6P, (b) 20P, and (c) 35P.

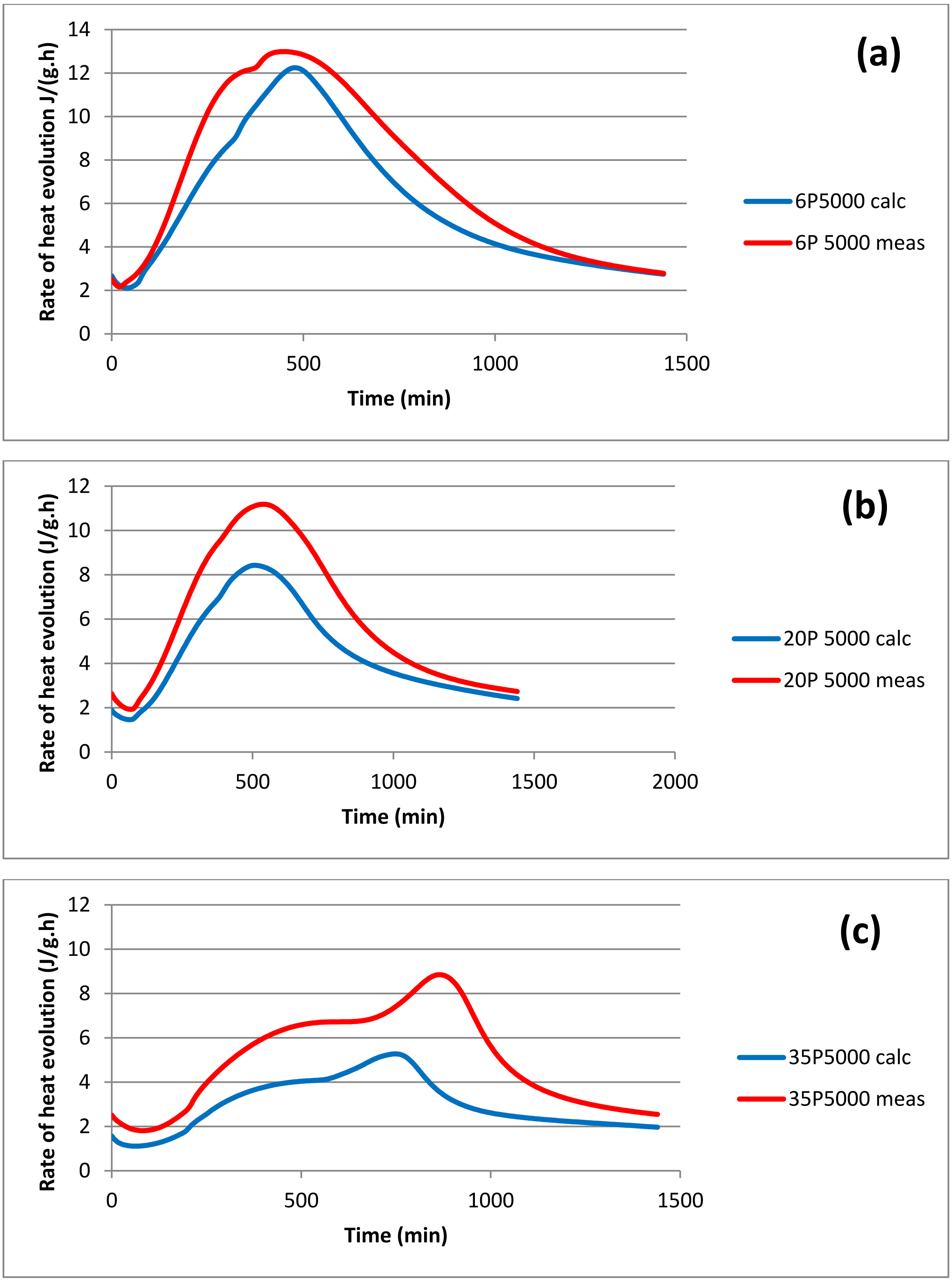


Figure 4.16. Rate of heat evolution of 5000 cm^2/g Blaine fineness blended cements (a) 6P, (b) 20P, and (c) 35P.

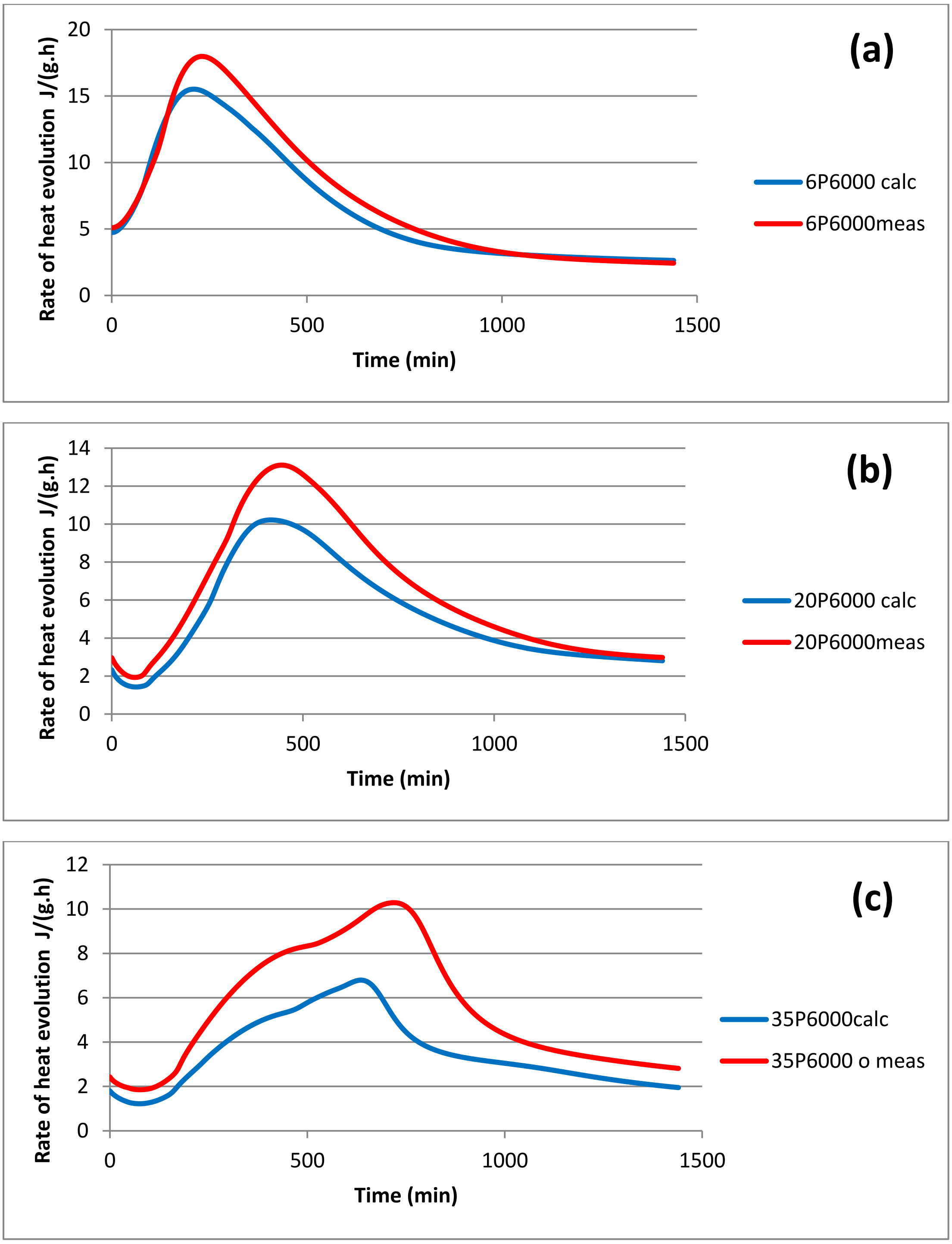


Figure 4.17. Rate of heat evolution of 6000 cm^2/g Blaine fineness blended cements (a) 6P, (b) 20P, and (c) 35P.

Table 4.4. Relative Increase in the Heat of Hydration of Blended Cements due to Pozzolan Incorporation at Different Fineness Values.

Amount of Pozzolan (%)	Relative increasing effect on 24h Heat of Hydration (%) for different Cement Finenesses		
	3000 (cm^2/g)	5000 (cm^2/g)	6000 (cm^2/g)
5.71	14.02	16.24	10.30
19.23	22.89	25.26	19.15
33.65	37.20	39.88	35.72

It is necessary to note that the positive effects of pozzolan as given in Table 4.4 and Figures 4.12-4.17 are relative. Although it is true for 6P blended cements, they do not necessarily mean that pozzolan incorporation increases the heat evolution as compared to the control cement. In other words, if only the dilution effect of pozzolan due to the reduction in cement content by replacement were effective, then 6P, 20P and 35P cements would evolve 5.71, 19.23 and 33.65% less heat than their respective control cements. For example, for "6P3000 o" cement, the measured heat of hydration was 131 J/g, while the expected value is calculated using the heat of hydration of "C3000 o" multiplied by the retained cement amount after a replacement of 5.71% of pozzolan, which is equal to: 106.45 x (100-5.71)/100 = 100.37 J/g

However, except for "35P3000 o", all blended cements resulted in higher 24h heat of hydration values than those expected by the above-mentioned assumption. The differences given in Table 4.5 show the positive effect of pozzolan on hydration.

Table 4.5. Differences of 24-h Measured and Calculated (by Simple Dilution Consideration) Heat of Hydration Values .

Cement	Cement Fineness, Blaine (cm^2/g)								
	3000			5000			6000		
	HH (J/g)		% Diff.	HH (J/g)		% Diff.	HH (J/g)		% Diff.
	Calc.	Meas.		Calc.	Meas.		Calc.	Meas.	
6P	100,37	131.0	30.5	156.4	173.6	11.0	158.6	176.4	11.2
20P	85.96	100.8	17.3	134.0	145.1	8.3	135.8	154.4	13.7
35P	70.63	68.7	-2.7	110.1	119.4	8.4	111.8	132.9	18.8

Thus, it can be stated that pozzolan incorporation into portland cement by intergrinding does not result in one-to-one reduction in heat evolution. For all levels of cement replacement by natural pozzolan investigated in this research, there is a positive effect of pozzolan in increasing the heat of hydration more than what it is expected. Therefore, when portland cement and clinker are interground to obtain blended cements, no matter what the amount of pozzolan is, it has an accelerating effect on the hydration of portland cement portion of the cement at early stages of hydration. This positive effect is thought to be suppressed in high pozzolan content cements due to the dilution effect.

4.6. Comparison of 24-h Isothermal Calorimetry Heat Values with Adiabatic Heat Values at 2 Days, 7 Days and 28 Days

In this work, heat of hydration values from both isothermal calorimetry and adiabatic methods were obtained and showed in Table 4.6. These values are compared as shown in Figure 4.18. Generally, when the heat of hydration value measured with adiabatic method increased the value obtained from isothermal colorimetry method also increased but a strong correlation between the two methods could not have been found.

Table 4.6. Heat values of Isothermal method at 24 Hours, and Adiabatic method at 2, 7 and 28 days (the values of heat of hydration measured by adiabatic method were obtained from [Tokyay et al., 2010])

Sample Name	**Isothermal 24 hour heat value (J/g)**	**Adiabatic 2, 7 and 28 Days value (J/g)**		
		2 Days	**7 Days**	**28 Days**
C3000 o	106.45	248.6	305.2	352.0
6P3000 o	130.96	227.7	256.2	321.9
20P3000 o	100.84	178.7	231.9	302.2
35P3000 o	68.73	148.2	201.8	258.3
C5000 o	165.92	275.4	319.4	365.0
6P5000 o	173.59	261.6	300.1	357.9
20P5000 o	145.07	220.2	285.1	333.2
35P5000 o	119.37	184.2	257.4	296.8
C6000 o	168.15	296.0	339.9	373.8
6P6000 o	176.37	268.7	351.6	388.9
20P6000 o	154.38	239.0	300.1	342.8
35P6000 o	132.86	198.4	266.6	310.2

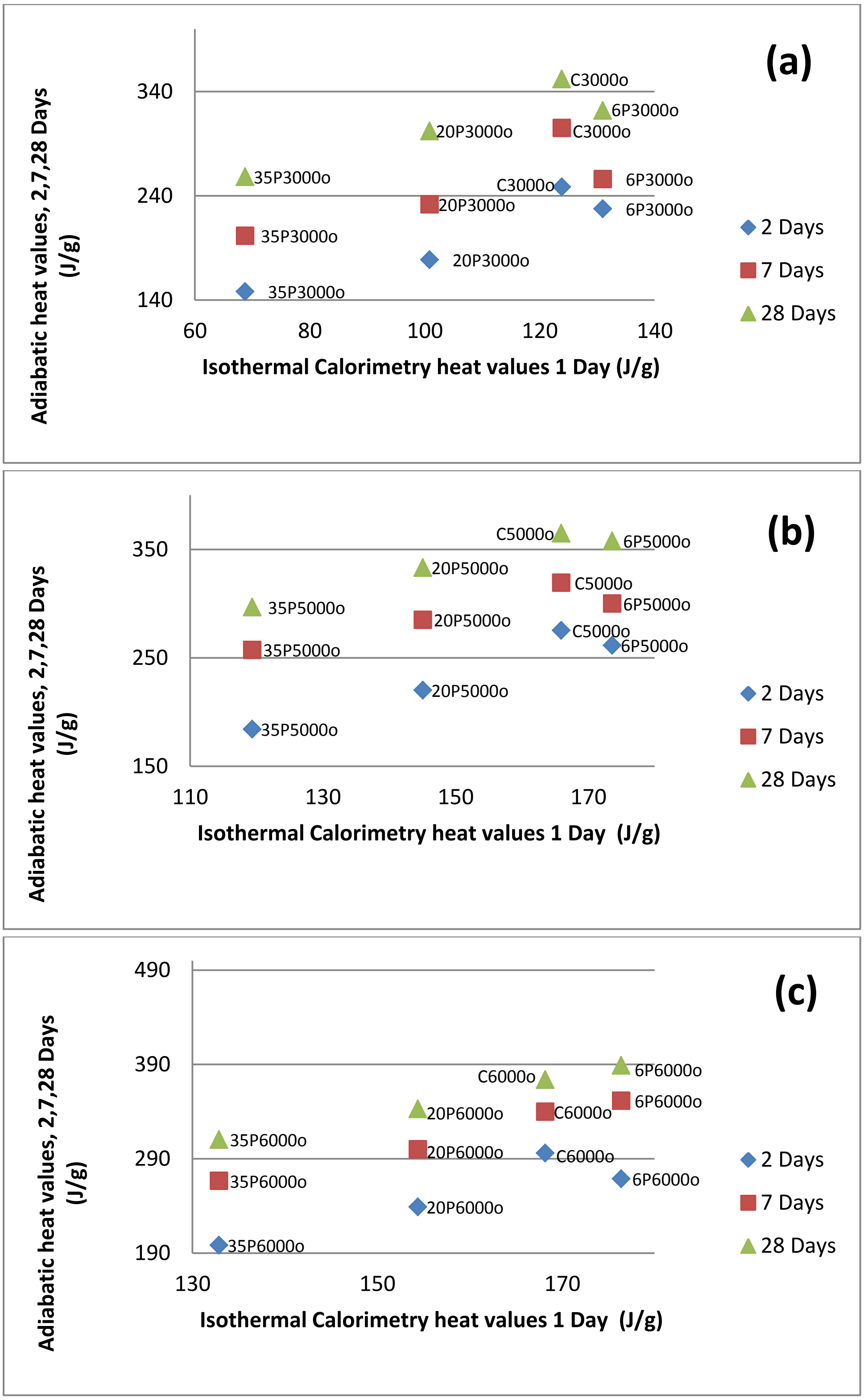


Figure 4.18. Isothermal heat of hydration values vs. adiabatic heat values (a) 3000 cm2/g, (b) 5000 cm^2/g and (c) 6000 cm^2/g Blaine fineness.

4.7. Relation between the 24 Hour Isothermal Calorimetry Heat Values and the Strength Values at 2 Days, 7 Days and 28 Days

The strength values obtained according to both ASTM C 109 and TS EN 196-1 methods. In TS EN Standards the amount of water is constant for any mixture. However, ASTM C 109 distinguishes between Ordinary Portland Cement and other types of cement where for OPC the amount of water is given, while for the rest types the amount of water is determined upon flow table test as they should produce a flow of 110 ±5 mm.

The relation between the 24 hour isothermal calorimetry heat values and the strength values of 2 days, 7 days and 28 days (ASTM C 109) are given in Table 4.7., and the charts related to these values are presented in Figure 4.19.

It was observed that, the results of the isothermal calorimetry heat values compared with the ASTM C 109 strength values are contradictory for 3000 cm^2/g, 5000 cm^2/g and 6000 cm^2/g Blaine fineness.

Table 4.7. 24 hour isothermal calorimetry heat values and the strength values at 2 days, 7 days and 28 days (ASTM C 109)

Sample Name	**Isothermal 24 hour heat value (J/g)**	**Strength (MPa) (ASTM C 109)**		
		2 Days	**7 Days**	**28 Days**
C3000 o	106.45	12.8	23.0	34.4
6P3000 o	130.96	10.4	19.0	29.4
20P3000 o	100.84	6.5	13.3	22.5
35P3000 o	68.73	3.1	6.7	12.1
C5000 o	165.92	14.7	24.8	32.4
6P5000 o	173.59	17.3	28.9	38.5
20P5000 o	145.07	11.4	23.0	34.8
35P5000 o	119.37	7.4	15.0	24.3
C6000 o	168.15	16.3	26.5	34.1
6P6000 o	176.37	15.3	26.8	36.5
20P6000 o	154.38	14.5	25.7	37.1
35P6000 o	132.86	9.2	16.7	26.3

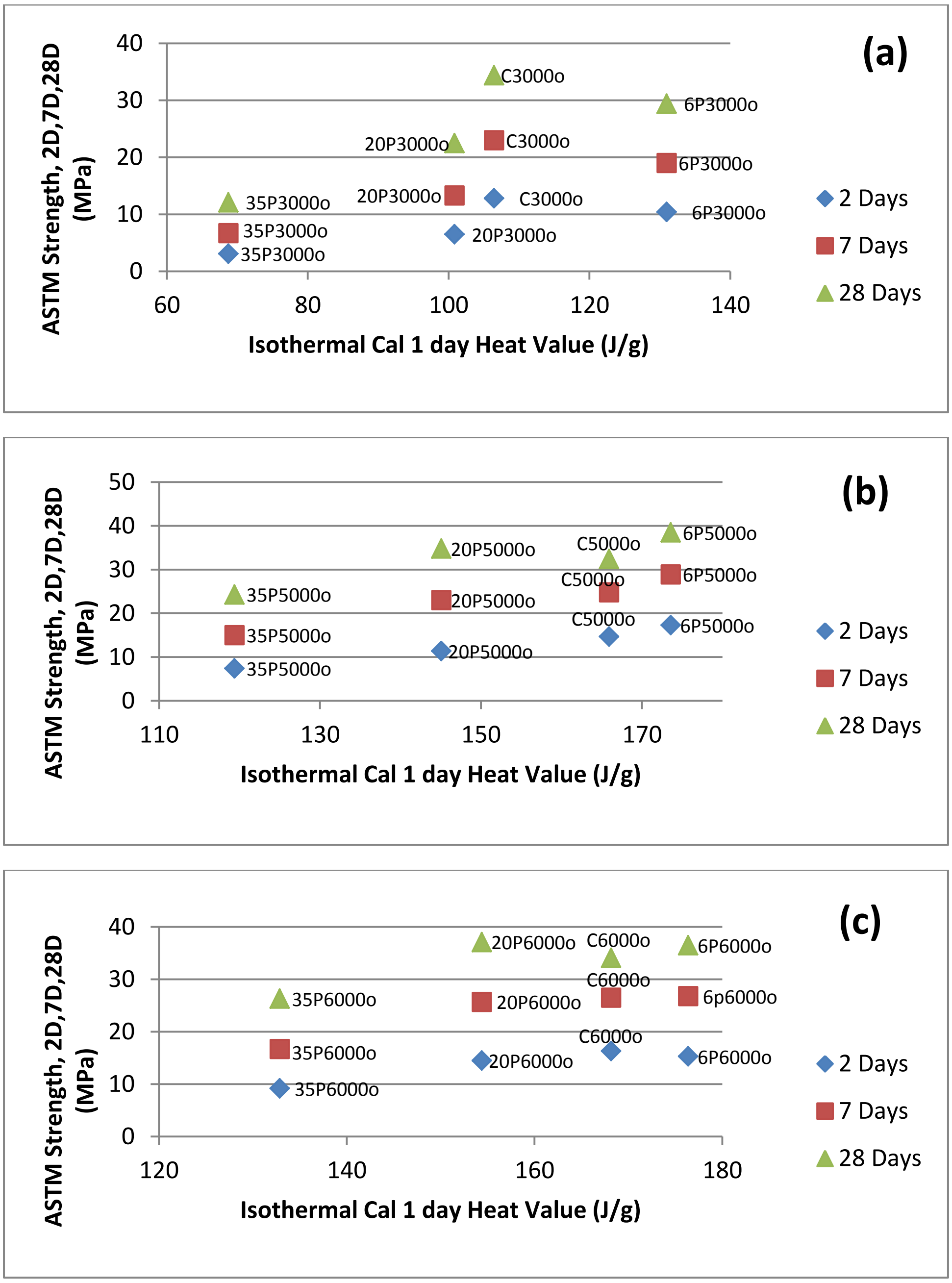


Figure 4.19. Isothermal 24 hour heat values vs. ASTM strength (a) 3000 cm^2/g Blaine, (b) 5000 cm^2/g Blaine (c) 6000 cm^2/g Blaine fineness.

The relation between the 24 hour isothermal calorimetry heat values and the strength values of 2 days, 7 days and 28 days (TS EN 196-1) are given in Table 4.8., and the related charts are presented in Figure 4.20. Generally, strength values increased with the increase on heat of hydration value measured with isothermal calorimetry method.

Table 4.8. 24 hour isothermal calorimetry heat values and the strength values of 2 days, 7 days and 28 days (TS EN 196-1)

Sample Name	**Isothermal 24 hour heat value (J/g)**	**Strength (MPa) (TS EN 196-1)**		
		2 Days	**7 Days**	**28 Days**
C3000 o	106.45	13.0	23.0	33.5
6P3000 o	130.96	14.5	24.9	36.6
20P3000 o	100.84	10.1	18.4	28.3
35P3000 o	68.73	5.1	9.6	17.6
C5000 o	165.92	23.8	35.7	43.8
6P5000 o	173.59	25.6	38.5	48.5
20P5000 o	145.07	18.8	32.9	45.2
35P5000 o	119.37	14.0	24.1	36.7
C6000 o	168.15	29.9	42.9	50.8
6P6000 o	176.37	31.3	44.3	54.7
20P6000 o	154.38	24.2	37.3	50.0
35P6000 o	132.86	17.2	27.5	39.2

For all 3000 cm^2/g , 5000 cm^2/g and 6000 cm^2/g Blaine finess, 6% pozzolan-incorporated cement has the both the highest heat of hydration value and strength value. According to Figure 4.20, pozzolan addition in low amounts increases both the heat of hydration and the strength but there is no strong correlation between them.

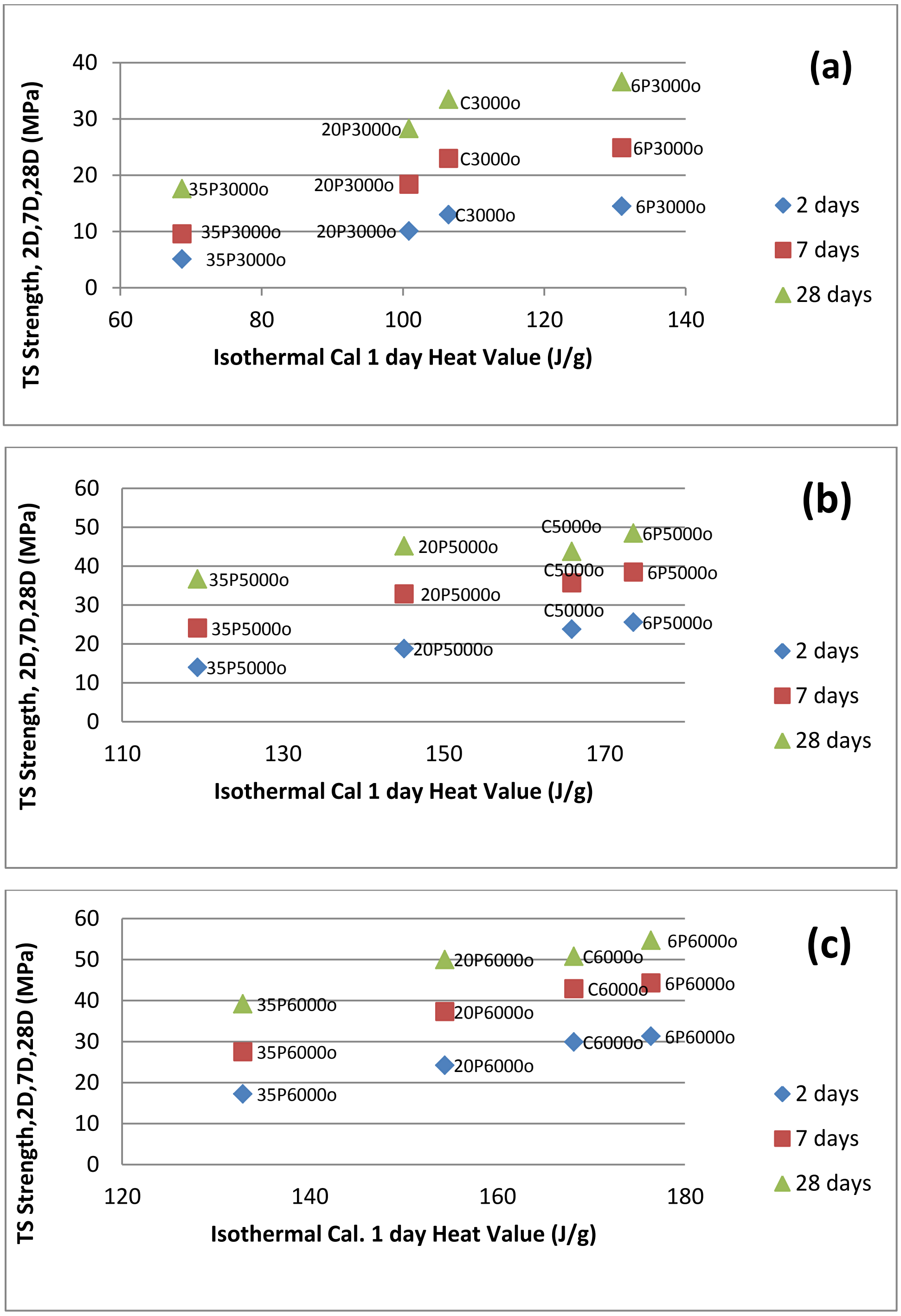


Figure 4.20. Isothermal 24 hour heat values vs. TS strength, (a) 3000 cm^2/g Blaine, (b) 5000 cm^2/g Blaine (c) 6000 cm^2/g Blaine fineness.

4.8. Relation between Pozzolan Content in the Samples and Setting Time

Generally, pozzolan addition retards setting but for cements containing low amount of pozzolan, reaction rate is increased and setting occurs faster than the control cement. However, the test results for 5000 Blaine cements show a decrease in the reaction rate for a small amount addition (6% pozzolan addition) represented by the increase of the setting time.

The initial setting time and final setting time data are shown in Table 4.9. The relation between pozzolan content in the samples and the setting times for (a) 3000 cm^2/g Blaine, (b) 5000 cm^2/g Blaine (c) 6000 cm^2/g Blaine fineness are presented in Figure 4.21.

Table 4.9. Initial and Final Setting Time Data

Sample Name	**Initial Setting Time (min)**	**Final Setting Time (min)**
C3000 o	160	205
6P3000 o	140	200
20P3000 o	160	250
35P3000 o	225	305
C5000 o	65	100
6P5000 o	80	115
20P5000 o	155	230
35P5000 o	175	260
C6000 o	40	70
6P6000 o	45	65
20P6000 o	115	170
35P6000 o	145	185

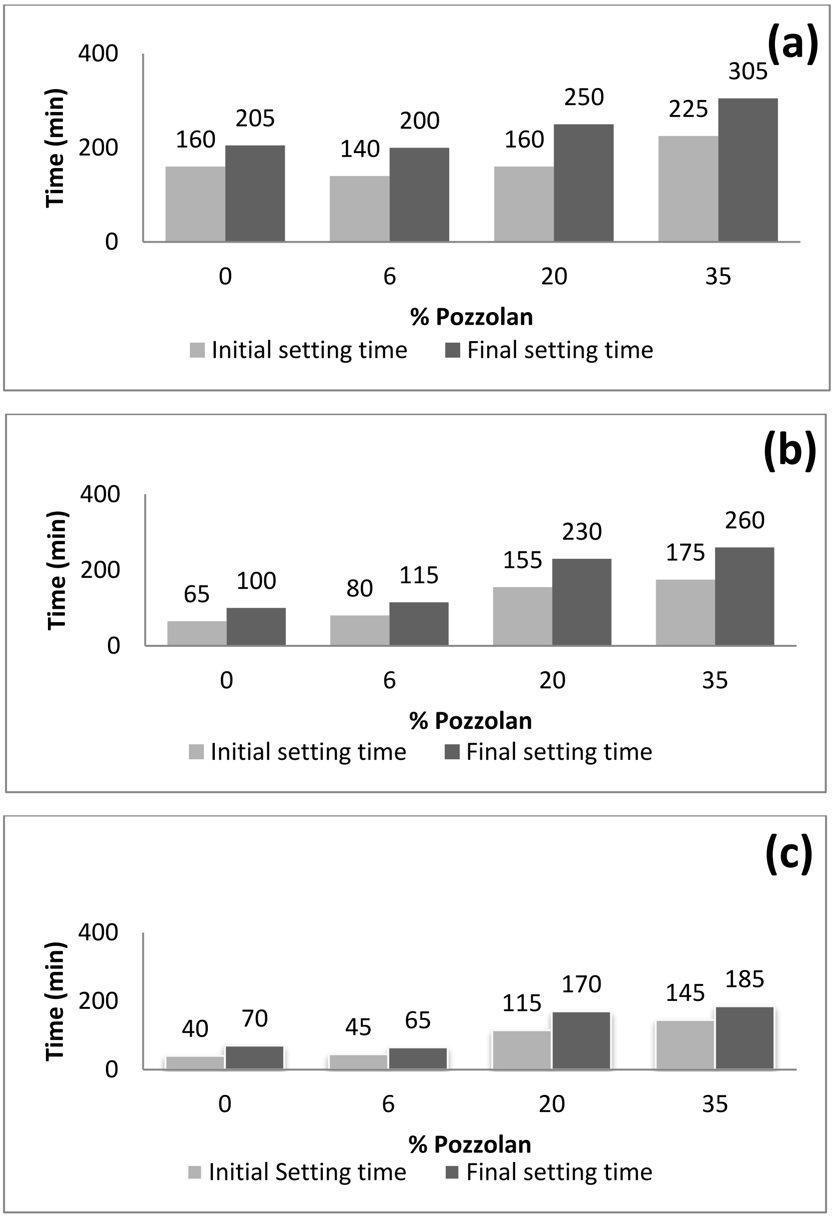


Figure 4.21. The relation between pozzolan content in the samples and the setting times. (a) 3000 cm^2/g Blaine, (b) 5000 cm^2/g Blaine (c) 6000 cm^2/g Blaine fineness.

According to Figure 4.21., both initial setting time and final setting time were decreased by the increment in fineness. For each fineness group, 35% pozzolan incorporated cements set later than the others.

4.9. Relation between Isothermal Calorimetry Heat Values of the Samples and Setting Time

The setting time indicates that a critical degree of hydration is reached because it tries to measure in an indirect way how solid the mix is through time. Moreover, when a cement sample has a high value of heat of hydration, this shows that the hydration reactions occur faster in it, hence the products of the reaction will come out earlier. For that reason, it was expected that a cement with a higher heat of hydration value will have a lower setting time. This can be seen clearly in Figure 4.22 for both initial and final setting times, except for the 6% pozzolan incorporation of 5000 and 6000 Blaine cements.

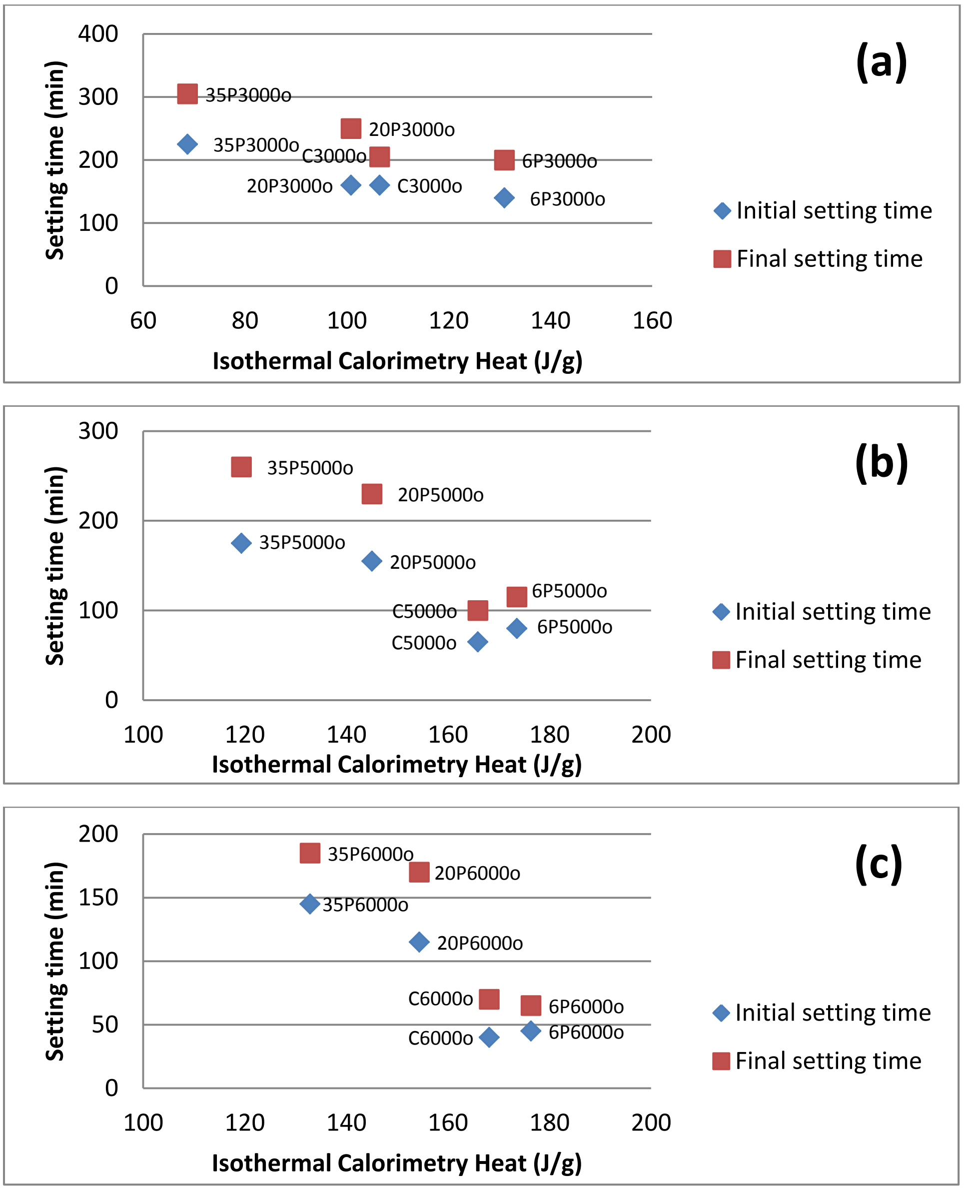


Figure 4.22. The relation between isothermal calorimetry heat values of the samples and the setting times. (a) 3000 cm^2/g Blaine, (b) 5000 cm^2/g Blaine (c) 6000 cm^2/g Blaine fineness.

CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1. General

In this work, the effects of interground natural pozzolan on the early hydration of blended cements were investigated by measuring the heat evolution and its rate within the first twenty four hours of hydration by isothermal calorimetry.

The behavior of 6, 20, and 35% pozzolan-incorporated cements was compared with control portland cements. As fineness is another important parameter affecting the hydration, cements with three different fineness values were comparatively studied. Furthermore, the effects of the coarse (>45µm) and fine (<45µm) portions of the cements were separately determined and analyzed to find out their relative effects on heat evolution.

The results obtained from the experimental study had led to the following conclusions:

1. Intergrinding of pozzolan and clinker results in finer pozzolan and coarser portland cement portions in blended cements since pozzolan is a softer material than clinker.
2. Finer cements result in more rapid hydration and higher amount of early heat evolution than coarser cements.

3. Pozzolan incorporation accelerates the hydration. This is a well-known fact for small amounts of pozzolan and it is attributed to the nucleus effect of fine pozzolan particles. It was determined in this investigation that a similar effect is true for higher levels of pozzolan incorporation also. However, this accelerating effect is suppressed by the slowing down effect due to the reduction of the portland cement portion by high pozzolan content.
4. Individual effects of coarse and fine portions of portland cements on heat of hydration are additive. However, this is not true for blended cements. Considering that in the early hydration period no pozzolanic reaction occurs, it was determined that the total heat evolution of the blended cements was greater than the sum of the heat of hydration values of fine and coarse portions. The difference gets larger as the amount of pozzolan increases.
5. Presence of pozzolan results in offering a larger surface for C-S-H hydration and thus accelerates the early hydration of C_3S. This effect is more pronounced in coarser blended cements in which the pozzolan portion is comparatively much finer than the portland cement portion.
6. Pozzolan incorporation by intergrinding does not result in one-to-one reduction in heat evolution.
7. The attempts for correlating isothermal calorimetry test results with those of adiabatic calorimetry, setting time and strength were not successful.

5.2. Recommendations for Further Studies

Based on the findings of this research, the followings are recommended for future research:

1. Similar studies with,
    a. gypsum contents of the cements adjusted according to the C_3A contents of the cements
    b. separately ground cements

    can be carried out to get a more comprehensive view of the effects of pozzolan incorporation on early heat heat evolution.
2. The effects of different size proportions can be studied to see their relative influences on hydration behavior and interactions between pozzolan and clinker phases during hydration.
3. Other mineral admixtures such as blast furnace slag, limestone powder, fly ash, silica fume, etc. can be similarly studied.

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APPENDIX A

CHOOSING A REFERENCE, AND CALCULATING THE WEIGHT OF THE REFERENCE SAMPLE

Through the isothermal calorimetry experiment, the desired water/cement ratio was kept constant at 0.4 to prevent bleeding, settling of cement grains within the sample ampoule. It was decided to prepare a 5 g paste for each test. The mortar contained 3.571 g cement and 1.429 g water to satisfy the desired water/cement ratio. To perform the mixing process easily, 7.5 g cement and 3 g water were weighed and mixed but 5 g of the paste mix were used in the experiments.

It is recommended that the test sample and the reference sample both have approximately identical heat capacity. The reference sample was decided to be a cement and according to specific heat values of cement and water, which are C_p (cement)= 0,9196 J/g.K and C_p (water)=4,18 J/g.K, the weight of the reference sample is calculated according to the following equation;

$$(C_p(\text{water}) \times W_{\text{water}}) + (C_p(\text{cement}) \times W_{\text{cement}}) = (C_p(\text{cement}) \times W_{\text{reference}})$$

$$W_{\text{reference}} = \frac{4.18 \times 1.429 + 0.9196 \times 3.571}{0.9106}$$

$$W_{\text{reference}} = 10.065 \text{ g}$$

APPENDIX B

AN EXAMPLE FOR CALCULATING THE AMOUNTS OF PORTLAND CEMENT AND POZZOLAN PORTIONS OF THE CEMENTS

STEP 1

First the fraction of trass found in the cement is calculated by using the ratios of CaO and SiO_2 composition of clinker and trass from Table 3.2.;

$K*C_k + T*C_t = C_{target}$

$K*S_k + T*S_t = S_{target}$

where: K: The ratio of clinker found in the cement

T: The ratio of trass found in the cement

C_k : The ratio of CaO in the clinker

S_k : The ratio of SiO_2 in the clinker

C_t : The ratio of CaO in the trass

S_t : The ratio of SiO_2 in the trass

C_{target} : The ratio of CaO in the cement mix, taken from Tables 3.3. – 3.6.

S_{target} : The ratio of SiO_2 in the cement mix, taken from Tables 3.3. – 3.6.

For example, the calculation for ″6P3000 f” cement follows:

$(65.5*K) + (6.79*T) = 59.04$

$(20.43*K) + (62.59*T) = 21.96$

By solving these equations simultaneously, T is obtained as 5.86%.

STEP 2

The ratio of each of fine and coarse portions in the cement mix is calculated by solving the equations written below.

$F*F_C + C*C_C = O_C$

$F*F_S + C*C_S = O_S$

where: F: is the ratio of the finer portion

F_C: is the ratio of CaO in the finer portion

C: is the ratio of the coarser portion

C_C: is the ratio of CaO in the coarser portion

O_C: is the ratio of CaO in the original portion

F_S: is the ratio of SiO_2 in the finer portion

C_S: is the ratio of SiO_2 in the coarser portion

O_S: is the ratio of SiO_2 in the original portion

All the values in this step are obtained from Tables 3.3. – 3.6.

For example, to continue the calculations for “6P3000 f” cement:

(59.04*F) + (61.88*C) = 60.12
(21.96*F) + (21.8*C) = 21.81

By solving these equations simultaneously, F and C are obtained as 54.29% and 45.36% respectively.

STEP 3

In Table 4.3., for 6P3000 cement:

< 45µm material = F = 54.29%

< 45µm pozzolan = F*T = 54.29% * 5.86% = 3.18%

< 45µm P. Cement = F(1-T) = 54.29% * (100%-5.86%) = 51.11%