EFFECT OF COMBINING DIFFERENT CEMENT CLINKERS AND SLAG WITH CONTROLLED FINENESSES ON MORTAR STRENGTH AND HEAT OF HYDRATION

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ABSTRACT

EFFECT OF COMBINING DIFFERENT CEMENT CLINKERS AND SLAG WITH CONTROLLED FINENESSES ON MORTAR STRENGTH AND HEAT OF HYDRATION

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Portland cement production is an energy consuming activity. Increasing efficiency in concrete production is one of the ways of reducing energy consumption. To improve the efficiency of the properties of both materials and concrete system, reduction of undesired effects (loss of strength, decrease in lifetime, etc.) is important. The main purpose of this study is to combine different Portland cement clinkers and blast furnace slag with different fineness to obtain a cement with a controlled grading, in order to investigate their effects on properties of concrete.

For this purpose three different Portland cements, and a blast furnace slag, each ground to three finenesses, are used. Strength and hydration heat development of these combinations are measured. Isothermal calorimetry is used to measure heat of hydration. Results obtained are used to determine relationships between controlled gradation, strength, fineness and composition of the cements.

According to this study, the individual strength of clinkers is the main factor affecting strength development mixtures containing fine blast furnace slag and mixtures containing clinkers only. Meanwhile, activation of blast furnace slag is the main factor affecting strength development for mixtures containing medium blast furnace slag.

Keywords: Portland cement, blast furnace slag, heat of hydration, controlled gradation, fineness.

ÖZ

FARKLI ÇİMENTO KLİNKERLERİNİN VE CURÜFUN ÇEŞİTLİ İNCELİKLERDEKİ KARIŞIMLARININ HARÇ DAYANIMI VE HİDRATASYON ISISINA ETKİLERİ

Çelikkol Koçak, Tümay
Yüksek lisans, İnşaat Mühendisliği Bölümü
Tez Yöneticisi:. Doç. Dr. Sinan T. Erdoğan

Eylül 2013, 54 sayfa

Portland çimentosu üretimi enerji tüketimi yüksek bir ativitedir. Beton üretimindeki verimi arttırmak Portland Çimentosu tüketimini azaltmanın yollarından biridir. Verimi arttırmak için malzeme ve sistem özelliklerinin iyileştirilmesi ve negatif etkilerin (dayanım kaybı, yaşam süresinde kısalma, vb) cürufu, farklı inceliklerde ve kombinasyonlarda karıştırılarak beton üzerindeki etkilerinin araştırılmasıdır.

Bu amaçla 3 farklı Portland çimentosu, yüksek fırın cürufu farklı incelik kombinasyonlarıyla kullanılmıştır. Bu kombinasyonların dayanım ve hidratasyon ısıları ölçülmüştür. Hidratasyon ısılarını ölçmek için izotermal kalorimetre yöntemi kullanılmıştır. Elde edilen sonuçlar kontrollü gradasyon, dayanım, çimento inceliği ve kompozisyonu arasındaki ilişkilerin belirlenmesinde kullanılmıştır.

Bu çalışmaya göre cüruf içermeyen ve ince cüruf içeren karışımlarda dayanım değerini etkileyen ana faktör çimentonun bireysel dayanımı iken orta incelikte cüruf içeren karışımlarda dayanım değerini etkileyen ana faktör cürufun aktivasyon oranıdır. Cüruf kullanılarak erken ısı salınımı azaltılmış, hidratasyon ürün miktarı arttırılmıştır.

Anahtar Kelimeler: Portland çimentosu, yüksek fırın cürufu, hidratasyon ısısı, kontrollü gradasyon, incelik.

To my parents,
Tülay and Hilmi Çelikkol

To my co-adventurer,
Deniz Koçak

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INTRODUCTION

1.1. General

Concrete is a widely used construction material all over the world. As the population increases concrete consumption increases to meet the different needs of modern cities. The increase in population forces the construction industry to achieve more economical solutions to problems of limited space and resource consumption. Unfortunately, physical and mechanical properties of such a desirable material limits creativity of architects and engineers as designers and builders. To answer the different needs and desires, some properties of concrete are required to be improved (Aïtcin and Mindess 2011).

Concrete-making materials determine properties of concretes. Hence, their qualities directly affect the quality of the concrete. Cement is the key material that binds all materials in concrete. Cements in the commercial market are standardized but it is difficult to achieve high strength, high durability, and economy all at the same time. To achieve better solutions and high performance, it is quite important to understand properties of existing materials and their behavior, in different cases and combinations. Turkey is one of top cement-producing countries in the world. Different types of clinkers and slags are produced in different regions of Turkey. In such a productive market, it is beneficial to study different clinkers and mineral additives in order to make improvements.

1.2. Object and scope

The purpose of this study is to investigate behaviors of different clinkers in different combinations in order to improve the efficiency with which the materials are used. In this study, the effect on strength and heat of hydration of different combinations of clinkers and blast furnace slag with different finenesses, is investigated. To observe behavior, strength and heat of hydration properties are examined in detail. To conduct experiments clinkers and Blast Furnace Slag (BFS) are ground to three different finenesses and mixed in pre-determined proportions. Gypsum is used to prevent flash setting in different amounts according to structure of the mixture. Mixtures are tested for strength and heat of hydration. Chemical analyses are performed to understand and compare behavior accordingly.

CHAPTER 2

LITERATURE SURVEY

2.1. General

In terms of concrete production and consumption, Turkey is one of the leading countries in Europe. As an indicator of concrete consumption, in 2012 93,050,000 m^3 ready-mixed concrete was produced in Turkey (TRMCA 2013). Turkey also ranks fairly high in the world. The same situation is valid for cement production and consumption. Due to the difficulty in protecting and improving such an important sector simultaneously, scientific support is important. This research is inspired from studies conducted on fineness of concrete-making materials and the effect of their particle size distributions on properties. To make useful comparisons, the study focused on three basic properties of concrete; strength, heat of hydration and chemical composition. Experimental procedures are planned according to these indicators (Ekincioglu et al. 2013, Ulubeyli 2013).

To briefly summarize; concrete is a composite construction material and its basic components are cement, water, and aggregates. Working principle of concrete is based on binding property of cement. Cement is a hydraulic binder which means cement gains binding property when exposed to water and is not soluble under water. When cement is mixed with water, cement paste is obtained. The paste covers aggregate surfaces. After addition of aggregates and adequate mixing, fresh concrete is obtained. Fresh concrete is given form by molding, it sets, and hardens into the desired shape (Erdoğan 2007). Hence concrete is composed of at least three components (number can be increased by additives and other cement replacement materials), its behavior as a single material is dominated by compatibility of these components. As the bond between components gets stronger, its strength increases, and its durability improves. Research in this area aims to understand this mechanism for many reasons. Some examples are increasing quality, decreasing material consumption, decreasing carbon footprint, etc. To present basis of the experimental work in this study, a theoretical background is provided in this chapter.

2.2. Information about Portland Cement and Blast Furnace Slag

An internationally accepted definition of Portland cement, given by ASTM 219 is “a hydraulic cement produced by pulverizing clinker, consisting essentially of crystalline hydraulic calcium silicates, and usually containing one or more of the following: water, calcium sulfate, up to 5 % limestone, and processing additions”. As mentioned in this definition, Portland cement is produced by intergrinding Portland cement clinker and gypsum. Portland cement clinker is produced by burning raw materials consisting of calcareous and clayey materials in a rotary kiln at around 1450 ºC. The percentage of gypsum is between 3 % - 6 % of the total product. A typical ASTM Type I Portland cement contains CaO, SiO_2, Al_2O_3, Fe_2O_3, SO_3, MgO, Na_2O, K_2O, Free CaO, and Cl^-, and some unreacted starting materials like carbon, free silica etc. The chemical composition of an ASTM Type I cement is given in Table 2.1 (Erdoğan 2007).

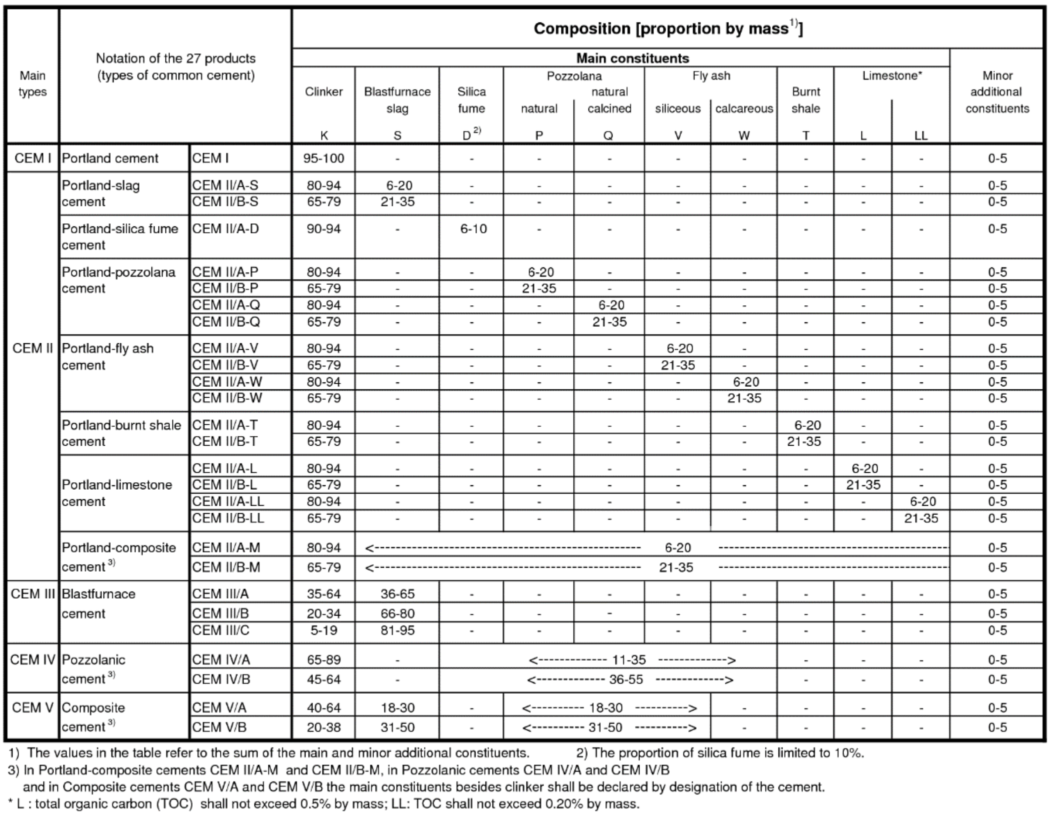
CaO, SiO_2, Al_2O_3, Fe_2O_3 form the main constituents of the strength-providing compounds, called Dicalcium silicate ($2CaO \cdot SiO_2$); Tricalcium silicate ($3CaO \cdot SiO_2$); Tricalcium aluminate ($3CaO \cdot Al_2O_3$); Tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) (Mehta and Monteiro 2005). The properties and hydration process of these constituents are explained in Chapter 2.2.

Table 2.1. Typical chemical composition of an ASTM Type I cement.

Oxides and Other Ingredients	Mass Percentage (%)
CaO	63.6
SiO_2	20.7
Al_2O_3	6.0
Fe_2O_3	2.4
SO_3	2.1
MgO	2.6
Na_2O	0.1
K_2O	0.9
Insoluble Residue	0.2
Loss on Ignition	1.4
Free CaO	1.4
Cl^-	0.1 (maximum)

Cement production in Turkey started in 1911 by establishment of the Darıca Cement Factory, in İstanbul. Production capacity of this factory was 20,000 tons per year. In 102 years, cement industry developed rapidly. The current number of cement factories in Turkey is 48, with a cement production capacity of approximately 109.million tons. In 2012, roughly 63 million tons of cement and 54 million tons of clinker were produced in Turkey. The total cement production in 2013 was about 28 million tons, as of May (TCMA 2013). According to a report prepared by US Geological Survey, Turkey ranks among the top five cement-producing countries in the world. The cement produced is exported as well as used for local consumption (USGS 2011).

In Turkey, the standard used for cement classification and production is TS EN 197-1. EN 197-1, the European standard for cement classification is directly adopted into Turkish standards without any modification and labeled as TS EN 197-1. EN 197-1 divides cements into 5 main groups and 27 cement types. The main groups are CEM I Portland Cement, CEM II Portland - composite Cement, CEM III - Blastfurnace Cement, CEM IV Pozzolanic Cement, and CEM V Composite Cement. All possible cement types according to EN 197-1 are given in Figure 2.1.



Main types	Notation of the 27 products (types of common cement)		Composition [proportion by mass[1]]										
			Main constituents										Minor additional constituents
			Clinker	Blastfurnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone*		
						natural	natural calcined	siliceous	calcareous				
			K	S	D[2]	P	Q	V	W	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.

Figure 2.1. Cement classification according to EN 197-1

In addition to cement, blast furnace slag was also used as a cement replacement material in this study. The definition of blast-furnace slag according to ASTM C 989 is; the nonmetallic product, consisting essentially of silicates and aluminosilicates of calcium and other bases that is developed in a molten condition simultaneously with iron in a blast furnace. Blast furnace slag is thus a by-product of the steel industry. Blast furnace slag is obtained by separating chemical compounds and elements from impure iron ore at high temperatures (around 1600 ºC) in a blast furnace. Due to density difference, the melted iron is separated at high temperatures and remaining mix is the chemical composition of blast furnace slag. If the melted residue is cooled rapidly, blast furnace slag gains an amorphous structure. Blast furnace slag contains different amounts of CaO, SiO_2, Al_2O_3, MgO, S, minor compounds (Erdoğan 2007). Sample chemical compositions of various blast furnace slags and other types of slag are given in Table 2.2 (Tokyay and Erdoğdu 2009).

Due to the fact that blast furnace slag is a by-product of the steel industry. data related to yearly production amounts is not available for Turkey. Studies show that for an ore including 60 % to 66 % iron, about 0.25 to 0.30 metric tons of blast furnace slag can be obtained per ton of the ore. As the iron content of the ore decreases, slag production increases up to 1.0 to 1.2 tons of slag per metric ton of crude iron. During steel production about 10 % to 15 % of the mass of the processed material is obtained as blast furnace slag (USGS 2003). The yearly steel production in Turkey from 2005 to 2012 is presented, in million tons, in Table 2.3 (Industry General Directorate 2013). By rough estimation it can be said that the blast furnace slag production for 2012 is about 3.58 million tons to 5.37 million tons.

Table 2.2 Examples related to chemical composition of Blast Furnace Slag (Tokyay and Erdoğdu 2009)

Compound (%)	Iron slags					Other slags			
	Blast furnace slag				Linz Doawits Slag	Lead-Zinc slag (England)	Nickel slag (Canada)	Copper slag (South	Phosphor slag (USA)
	1 (France)	2 (Japan)	3 (Turkey	4 (Turkey)					
SiO2	35	31	40.2	38.6	13	18	29	34	41
CaO	43	37	34.5	31.7	47	20	4	9	44
MgO	8	8	9.4	9.3	1	1	2	4	1
AI2O3	12	16	11	15.2	1	6	1	6	9
Fe2O3	0.4	0.7	0.8	0.8	31	38	53	44	1

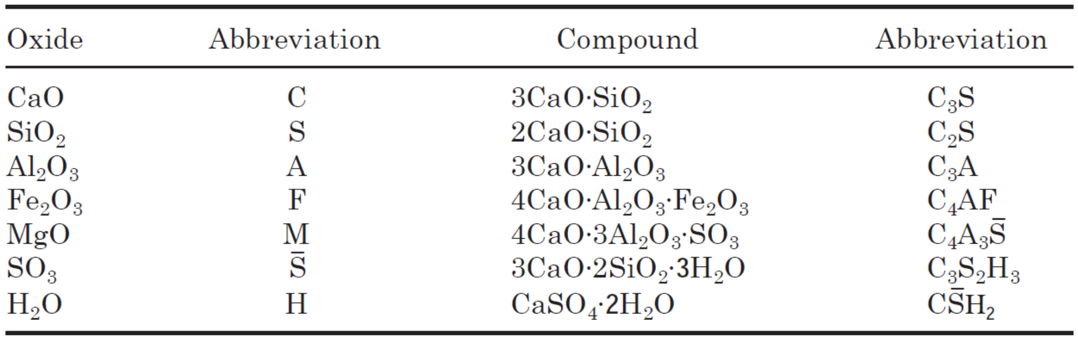
Table 2.3. Yearly steel production in Turkey million tons (Industry General Directorate 2013)

2005	2007	2008	2009	2010	2011	2012
20.9	25.8	26.8	25.3	30.0	34.1	35.8

2.3. Hydration Mechanism

2.3.1.Cement

When Portland cement is exposed to water cement paste is formed and chemical reactions start. These chemical reactions are called hydration reactions. Hydration reactions are exothermic and the heat liberated as a result of these reactions is called the heat of hydration. Resulting products are called hydration products and those products provide binding property to the cement paste. Quality of binding and proceeding formations are shaped by physical and chemical properties of cement and environmental conditions. As mentioned in Section 2.1 the four major clinker minerals are tricalcium silicate, dicalcium silicate, tricalcium aluminate and the ferrite phase. For practical purposes abbreviations are used instead of conventional chemistry formulas in cement chemistry (Mehta and Monteiro 2005). Abbreviations used to express oxides and compounds of cement are given in Figure 2.2.



Oxide	Abbreviation	Compound	Abbreviation
CaO	C	$3CaO{\cdot}SiO_2$	C_3S
SiO_2	S	$2CaO{\cdot}SiO_2$	C_2S
Al_2O_3	A	$3CaO{\cdot}Al_2O_3$	C_3A
Fe_2O_3	F	$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	C_4AF
MgO	M	$4CaO{\cdot}3Al_2O_3{\cdot}SO_3$	$C_4A_3\bar{S}$
SO_3	$\bar{S}$	$3CaO{\cdot}2SiO_2{\cdot}3H_2O$	$C_3S_2H_3$
H_2O	H	$CaSO_4{\cdot}2H_2O$	$C\bar{S}H_2$

Figure 2.2. Abbreviations used to express oxides and compounds of cement (Mehta and Monteiro 2005)

Hydration mechanisms of the four major compounds of Portland cement vary according to environmental conditions, rate of the reactions and chemical composition. Although C_3S, C_2S, C_3A and C_4AF are commonly used formulas to represent major compounds of Portland cement real compounds can be different in terms of chemical composition. Compounds can contain different elements due to impurities present prior to the production phase (Hewlett 2003). The hydration reactions that the main clinker compounds are given as follows;

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

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH$$

$$2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8$$

$$C_3A + CSH_2 + 10H \rightarrow C_4ASH_{12}$$

$$C_3A + CSH_2 + 26H \rightarrow C_6AS_3H_{32}$$

$$C_4AF + 2CH + 14H \rightarrow C_4(A,F)H_{13} + (A,F)H_3$$

2.3.2.Blast Furnace Slag and cement

When slag is present in the cementitious system, the hydration process becomes a little complex and much slower than with only Portland cement. When added to water only, the hydration reaction of slag is very slow due to the latent hydraulic property of slag. By blending the slag with cement the slag hydration reaction is accelerated. This is because the slag needs first to be activated by alkalis and sulfates that come from the hydration process of the cement itself. Since the slag reaction waits for the product of cement reaction, the rate of strength development is low comparing to Ordinary Portland Cement (OPC). However, at the end, the main hydration products formed from the slag reaction are similar to the ones of OPC, which are CSH gel, C_3AH_6 and Aft. The hydration reaction can be divided into two stages. At early hydration, the predominant reaction is with alkali hydroxides, and after that, the reaction with calcium hydroxide is the one that gives the final hydration products such as calcium silicate-hydrates (Barnes and Bensted 2002, Siddique and Khan 2011).

2.4. Factors contributing to heat of hydration

Since the heat of hydration is evolved because of the reaction between the cement particles and water, every parameter (e.g. size, shape, number, morphology) of the cement can affect this heat evolution. Moreover, the amount of water, ambient conditions, and the availability of admixtures that can be involved into the hydration reaction might all affect the heat of hydration process. Below, some of the major factors that influence the heat of hydration evolution are briefly explained.

2.4.1. Fineness

Since the chemical composition of the same cement does not change when the fineness is changed, it is expected that the end results of the hydration reactions between the cement constituents and the water will be same for all the fineness, provided that the reactions go to completion. This implies that no matter what size it is, the same amount of C_3S will release the same amount of heat at the end of the complete hydration process. However, in reality, when water comes in contact with a C_3S particle the hydration reaction starts from the outer layer going to the center of the particle. For this reason, if there is not a sufficient amount of water, or the size of the particle is relatively large, the inner part of C_3S particle will remain unreacted. In other words, the finer the cement particles are, the higher the possibility of these particles to go into full hydration reactions, which will lead to a higher total amount and rate of heat of hydration (Taylor 1997, Mehta and Monteiro 2005).

2.4.2.Chemistry of cement

The effect of chemical composition of the cement on the heat of hydration can be best understood when the hydration of each cement compound is examined separately. In Table 2.4, the total heats of hydration coming from the main cement compound are presented, while in Figure 2.3 the rates of hydration of some of these compounds are shown, (Mindess, Young et al. 2003). For example, it can be clearly seen that the highest contribution to the heat of hydration at both early and late ages comes from the compound C_3A. Moreover, for the same compound, the heat released and its rate are related to many factors like the rate of cooling the clinker, the amount of impurities found in that compound, and the amount of other compounds. For that, cements with similar chemical compositions can have different heat of hydrations.

Table 2.4. Heats of Hydration of the Cement Compounds (Mindess, Young et al. 2003)

Reaction	ΔH (J/g) for Complete Hydration[a]			
	Pure Compounds		Clinker [b,d]	Cement [c,d]
	Calculated	Measured	Measured	Measured
$C_3S \rightarrow$ C-S-H + CH	~380	520	570	490
$C_2S \rightarrow$ C-S-H + CH	~170	260	260	225
$C_3A \rightarrow C_4AH_{13} + C_3AH_8$	~1160	-	-	-
$\rightarrow C_3AH_6$	900	880	840	-
→ ettringite	1670	1670	-	-
→ monosulfoaluminate	1150	1140	1170	-
$C_4AF \rightarrow C_3(A,F)H_6$	420	420	335	-
→ monosulfoaluminate	-	-	-	380
→ ettringite	730	-	-	-

a These values should be negative since they refer to exothermic reactions, but they are customarily written without the negative sign.

b One-year-old pastes of ground clinker (no added gypsum).

c One-year-old pastes assumed to be completely hydrated.

d lndividual contributions determined by multiple linear regression analysis.

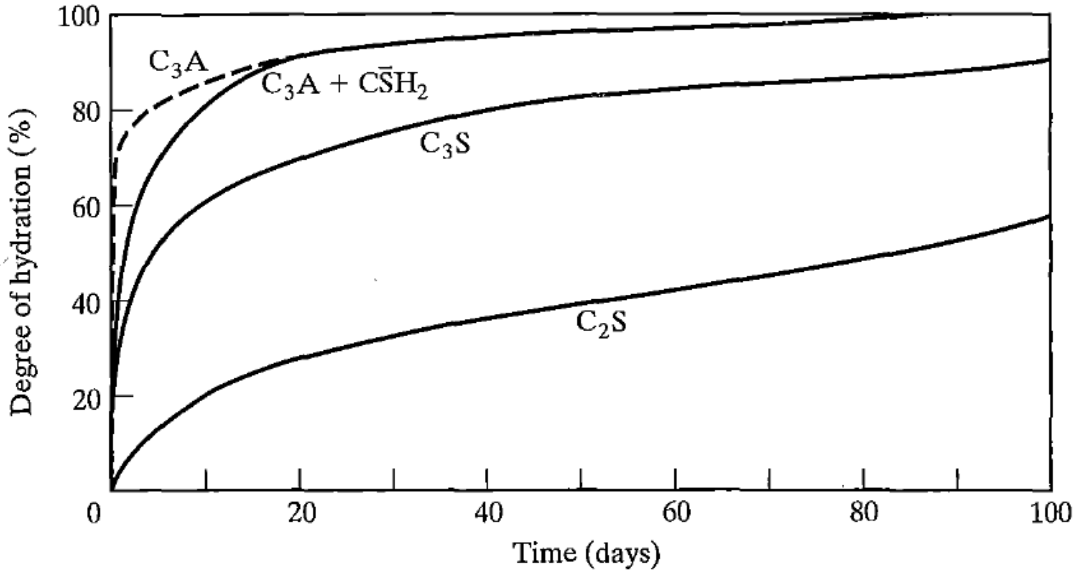


Figure 2.3. Rate of hydration of the cement compounds in pastes of the pure compounds (Mindess, Young et al. 2003)

2.4.3.Admixtures

Depending on weather conditions or work requirements set accelerating or set-retarding admixtures are used. Since the hydration process is affected by these admixtures, the heat of hydration will also be changed. The through solution reaction between cement compounds and water first starts with the ionizing of the anhydrous compounds, which forms the first hydration products. After that, these products crystallize out leading to the stiffening, setting and hardening of the cement paste. For this reason, some admixtures can be used to interfere with the rate of either cement compound ionization or hydration products crystallization (Mehta and Monteiro 2005). These admixtures are divided into two categories, organic and inorganic. As an accelerator, calcium chloride is the most widely used product. It provides accelerating effect by speeding the hydration of C_3S compound. As for the retarding action, sugar acids for example adsorbs on Ca+ ions on the hydrating C_2S surface and poison the C-S-H nucleating sites. However, according to the precipitation theory, the concentration of Ca, Al, and Fe is increased by the addition of mono or polysaccharides, where a coating is formed around the cement grains when the sugar combines with them forming insoluble metal organic, which retard the hydration. (Ramachandran 1996).

2.4.4.Mineral additions

Using cement replacement materials has a significant effect on the heat of hydration. Having the ability to show cementitious properties when reacting with cement hydration products, these additions need only an efficient size reduction in the general case. The reduction process can be intergrinding (along with cement) or separate grinding. Althoughintergrinding can give a homogenous product easily by feeding the mineral addition to same mill with the cement, the different grindabilities of the minerals and the clinker compounds will make it harder to control the particle size distribution of the output product. This means that the clinker portion might be overground if an easily grindable mineral is used, and vice versa. On the other hand, the second method, separate grinding, will give better control on the particle size distribution of all the compounds of the blended cement, which means better control over some of the cement properties. However, this method needs extra costs for running the second grinding plant (Öner, Erdoğdu et al. 2003, Geven 2009).

2.4.5. Other factors

The gypsum content, water-to-cement ratio, concrete pouring location and temperature, curing process, and the dimension of the structure can all influence the release of hydration heat.

2.5. Measuring the heat of hydration

To measure the heat of hydration there are three common methods, which are listed below.

2.5.1. Heat of Solution Method:

This method uses a mixture of nitric acid and hydrofluoric acid. To dissolve the unhydrated and hydrated cements, then by subtracting the heat of solution of the hydrated cement from that of unhydrated cement the heat of hydration is calculated (ASTM C 186 and TS EN 196-8).

- Advantages: The heat of hydration of hardened cement paste can be determined by this method. It can be used for later ages.
- Disadvantages: Early ages determinations of heat of hydration cannot be done with this method. In addition to that, this method is not suitable for monitoring the heat of hydration process.

2.5.2. Adiabatic or Semi-adiabatic Method

This method uses a calorimeter to measure the heat emission coming from freshly mixed mortar sample during a specific period. The heat of hydration in this method is determined as the sum of the heat lost into the atmosphere and the heat stored in the calorimeter. A reference sample is used for temperature comparison (TS EN 196-9, 2011; RILEM TC119-TCE1, 1997).

- Advantages: This method is suitable for both cement paste and concrete samples. Measurements can be performed at the beginning of the hydration process right after the mixing process and placing processes are done.
- Disadvantages: The true adiabatic heat development has to be calculated from the test results, and losses associated with the test have to be accounted for.

2.5.3. Isothermal Conduction Calorimetry Method

This method tries to determine the heat of hydration directly from a cement paste sample. A constant temperature is maintained over the sample and container that hold it, measuring the heat flow from the specimen. By comparing this heat flow with that of a reference material the heat of hydration is determined (ASTM C1702-09).

- Advantages: Monitoring process can start from the very first moment of mixing.
- Disadvantages: This test is not effective after 7 days.

2.6. The importance of particle size distribution of cement

In the continuous search to improve the performance of concrete developing a better cement might be considered as the best solution. One way to do this, without changing the cement making process, is to choose the best parts of a cement, or in other words choose what particles would take place in the final product. This can be done by controlling the particle size distribution of the cement. Full control is not possible for sure, at least not with today's technology, but increasing the number of specific compounds is achievable by altering the particle size distribution. For example, in a study performed by Zhang et al. (2011), a new blended cement with gap-graded particle size distribution was introduced. In that study, they use an air separator to divide the clinker and the cement replacement material (CRM) into three categories according to the size. These categories are Coarse (>32 µm), Medium (8–32 µm) and Fine (<8 µm), with a mean size of 45, 16, and 6 µm respectively. New mix combinations were prepared by taking 39 % of the Coarse (CRM), 25% of the Medium (clinker), and 36% of Fine (CRM) categories. The combinations are different from each other according to the type of CRM used in Coarse and Fine categories. The study revealed that by using a high activity SCM in Coarse, cement clinker in Medium, and a low activity SCM in Fine categories, a high-performance blended cement was produced. This new product had a low water requirement, a high packing density, a homogeneous, dense microstructure, and low heat of hydration at the first 20 hours. In addition to that, early and late strength values are close to those of the control cement (Zhang, Yu et al. 2011).

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1. General

This chapter introduces the materials used in the study and some of their relevant properties.

3.2. Materials

In this thesis three different clinkers obtained from different factories in Turkey, one type of blast furnace slag, and one type of gypsum were used as test materials. “Clinker A” refers to the clinker obtained from Akçansa Çanakkale Cement Factory, “Clinker B” refers to the clinker obtained from Sanko Bartın Cement Factory, “Clinker S” refers to the clinker obtained from Akçansa Samsun Ladik Cement Factory, “Slag” refers to blast furnace slag obtained from Akçansa Gebze Cement Factory, “Gypsum” refers to gypsum obtained from Ankara Bala Gypsum quarry.

The clinkers used in the experiments were produced in different kilns and have different chemical compositions. Blended clinkers were made by combining different ratios of clinkers A, B, and S. The aim of using these new blends was to observe the interaction between materials with different hydration rates in these new mixes and the effect of this combination on the properties of the final product. The materials were kept under the same environmental conditions according to relevant standards, in a dry place away from sunlight.

3.2.1 Clinkers

All the clinkers were classified as CEM I 42.5 according to EN 197-1. Chemical analyses were performed at the Central Laboratory at Middle East Technical University. Chemical composition of the materials used are given in Table 3.1

3.2.2 Blast Furnace Slag

Blast furnace slag was obtained from Akçansa Gebze Cement Factory. Its chemical composition is given in section 3.5.

3.2.3 Gypsum

Blast furnace slag was obtained from Ankara Bala Gypsum quarry Its chemical composition is given in section 3.5.

Table 3.1 Chemical compositions of the used materials.

Sample/Oxide (%)	Clinker A	Clinker B	Clinker S	Blast Furnace Slag	Gypsum
CaO	66.12	66.81	67.65	36.69	44.06
SiO_2	19.08	19.36	19.71	36.42	1.04
Al_2O_3	4.27	4.72	4.86	10.34	0.21
Fe_2O_3	3.58	3.92	3.52	1.54	0.12
MgO	3.41	1.63	1.46	6.11	0.35
SO_3	1.82	1.33	1.16	1.14	55.35
K_2O	1.25	1.33	0.91	1.75	0.07
TiO_2	0.29	0.64	0.52	1.48	-
Na_2O	0.18	0.25	0.22	0.32	-
BaO	-	-	-	1.75	-
MnO	-	-	-	2.3	-
SrO	-	-	-	-	0.81

3.3. Preliminary Works

3.3.1 Grinding

In order to reduce the size of the materials to achieve the desired fineness, it was decided to prepare fineness vs. grinding time graphs for each material. This way it was aimed to prevent material and energy waste. The apparatus used for this application is the grinding mill available at Materials of Construction Laboratory at the Department of Civil Engineering of Middle East Technical University.

To obtain data for fineness versus grinding time first the optimal mass of material for grinding was determined for the mill based on the ball size and distribution (charge). It was decided that 4.5 kg material can be effectively ground. Each material (three types of clinkers, blast furnace slag and gypsum) was ground separately for 10 h. This material was later used as very fine materials.

Preparatory works were done according to the outline given below.

- Clinkers, gypsum and blast furnace slag were transferred from packages to containers for weight measurement.
- Optimal weight for the mill which is used for grinding was computed according to the mill charge. Part of material samples were separated according to this amount (4.5 kg).
- Each material was ground for ten hours. Samples were taken at 30 min, 1 h, 2 h, 3 h, 5 h, 7 h, 8.5 h, 10 h for each material.
- Densities of the materials were measured for the Blaine fineness test.
- Blaine test was performed for every sample.

- Fineness versus Grinding Time graphs was drawn according to test results.
- Remaining materials were ground up to the desired fineness according to the Fineness versus Grinding Time graphs.
- Fineness measurements were done by air permeability tests according to ASTM C 204 to obtain exact fineness values. Same procedure is repeated until the desired fineness range is obtained.
- Using the data obtained from the previous steps, for each material three fineness groups were prepared, 2000, 4000 and 6000 Blaine.
- Different combinations of the different clinker and slag form various fineness were prepared.
- Using these combinations, compressive strength tests and heat of hydration measurements were conducted.

3.3.2 Density Measurements

The densities of the materials need to be known to perform the Blaine fineness test. To determine density, tests were performed according to ASTM C 188. Residual materials which are ground for 10 hours were used in this test. Test results are given in Table 3.2.

Table 3.2 Density Values of Used Materials

Material	Density (g/cm³)
Clinker A	3.24
Clinker B	2.98
Clinker S	3.23
Slag	3.00
Gypsum	2.21

3.3.3 Fineness Measurements

To determine fineness, an air permeability test was applied according to ASTM C 204. The parameters used for the particular apparatus are given in Table 3.3. $\mathbf{t_0}$ is the air permeability test result of the reference material in seconds, $\boldsymbol{\rho_0}$ is the amount of reference material in grams, and $\mathbf{S_0}$ is the measured fineness value of the reference material in cm²/g. Fineness of the test specimen is computed using these parameters. Material amounts are computed using the density values given in Table 3.2. Amount of used material in the air permeability test for Clinker A is 2.79 grams, for Clinker B is 2.56 grams, for Clinker S is 2.78 grams, for slag is 2.57 grams and for Gypsum is 1.90 grams. Results are given in Figure 3.1.

Table 3.3 Parameters of the Air Permeability Apparatus Used.

$\mathbf{t_0}$	83.0	s
$\boldsymbol{\rho_0}$	3.15	g

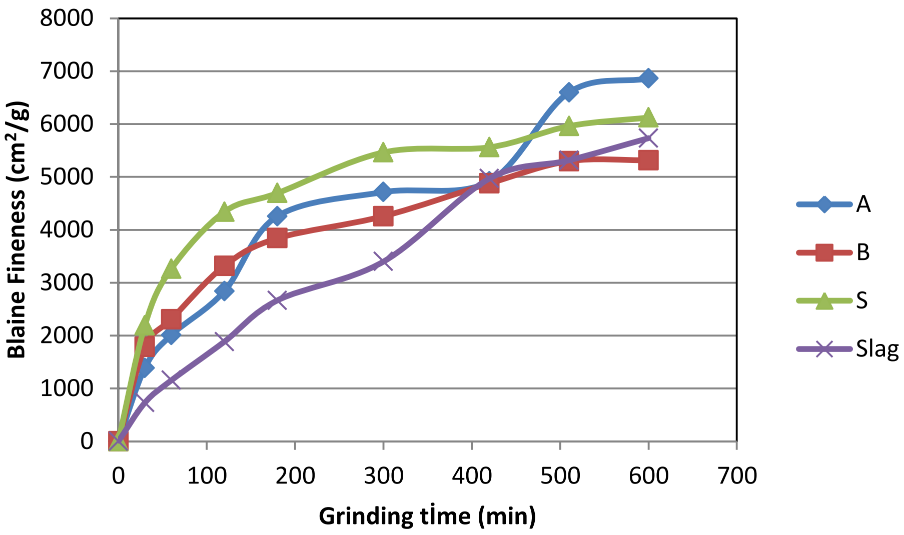


Figure 3.1 Fineness versus Grinding Time graphs for Clinker A, Clinker B, Clinker S, and Slag.

Gypsum is not given in Figure 3.1 because it was used at the same fineness in all mixtures. The data in Figure 3.1 were used to determine the length of time to grind the remaining materials to achieve the desired finenesses. The ground materials were tested for fineness to check the accuracy of the operation. This process was repeated until the desired range is provided. Slight variations were observed from the curves given in Figure 3.1. The main reason for this is probably that the materials with high fineness flocculate and gave misleading results in fineness measurement tests.

shows the finenesses of the materials eventually used in preparing the paste and mortar mixtures.

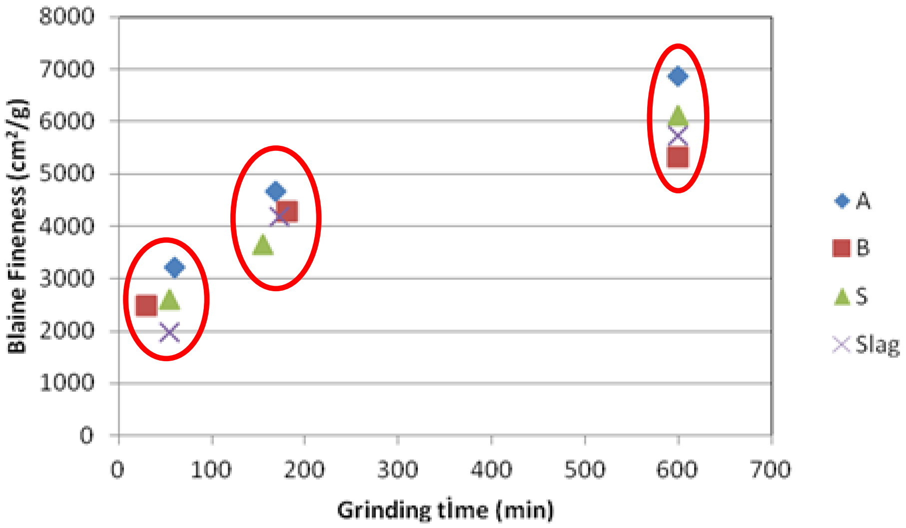


Figure 3.2 Fineness values of materials to be used in mixtures.

3.4. Mixture Preparation

In conformance with ASTM C 109 and ASTM C 1702 strength determination and heat of hydration determination tests were performed. Two different test specimens are needed to perform these tests. Mixture preparation for strength determination test specimens is explained in Section 3.4.1, and mixture preparation for heat of hydration determination test specimens is explained in Section 3.4.2.

3.4.1.Mixtures for Strength Tests

To obtain controlled mixtures according to fineness and observe their effects on the properties of hydration products, mixture proportions were designed accordingly. As explained in previous sections all clinkers and blast furnace slag were ground to three different fineness values. The clinkers and the blast furnace slag were separated into three groups; coarse, medium, and fine, according to fineness values. The fineness percentage combination pattern used in the mixtures was meant to obtain a controlled grading of the particles with a balanced fineness value around 3850 cm²/g, and also to observe heat liberation in detail. According to this combination pattern 35 % fine, 25 % medium, and 40 % coarse material with a total mass of 500 g was used. The amount of gypsum used was 5 % of the mass of the clinker, and 1375 grams of standard sand was used in each mixture. 242 g of water was used for the mixtures without any cementitious material except clinker, and the amount of water used for mixtures containing blast furnace slag was determined as the amount necessary to provide 110 mm flow value in the flow table test according to ASTM C 230. Mixture proportions are given in Table 3.4 to Table 3.6

.

Table 3.4 Proportion of materials used in the clinker blended mixtures

Mixture / Materials (g)	ABS	SAB	BSA	ASB	SBA	BAS
Clinker A Coarse	-	-	200	-	200	-
Clinker A Medium	-	125	-	-	-	125
Clinker A Fine	175	-	-	175	-	-
Clinker B Coarse	-	200	-	200	-	-
Clinker B Medium	125	-	-	-	125	-
Clinker B Fine	-	-	175	-	-	175
Clinker S Coarse	200	-	-	-	-	200
Clinker S Medium	-	-	125	125	-	-
Clinker S Fine	-	175	-	-	175	-
Slag Coarse	-	-	-	-	-	-
Slag Medium	-	-	-	-	-	-
Slag Fine	-	-	-	-	-	-
Gypsum	25	25	25	25	25	25
Water	242	242	242	242	242	242
Sand	1375	1375	1375	1375	1375	1375

A coding system is used to identify the prepared mixtures. Since the percentages of finely-, medium-, and coarse-ground materials do not change, the blended mixtures are named using abbreviations of clinker types in a descending order in terms of Blaine fineness. For example, mixture "ABS" is the mixture which contains 35 % fine clinker A (with 6862 cm²/g Blaine) , 25 % medium clinker B (with 4285 cm²/g Blaine), and 40 % coarse clinker S (with 2598 cm²/g Blaine), of the total cementitious content.

Table 3.5 Proportions of mixtures containing slag as their medium-sized component.

Mixture / Materials (g)	ACB	SCA	BCS	ACS	SCB	BCA
Clinker A Coarse	-	200	-	-	-	200
Clinker A Medium	-	-	-	-	-	-
Clinker A Fine	175	-	-	175	-	-
Clinker B Coarse	200	-	-	-	200	-
Clinker B Medium	-	-	-	-	-	-
Clinker B Fine	-	-	175	-	-	175
Clinker S Coarse	-	-	200	200	-	-
Clinker S Medium	-	-	-	-	-	-
Clinker S Fine	-	175	-	-	175	-
Slag Coarse	-	-	-	-	-	-
Slag Medium	125	125	125	125	125	125
Slag Fine	-	-	-	-	-	-
Gypsum	18.75	18.75	18.75	18.75	18.75	18.75
Water	258.0	260.0	280.3	260.3	264.5	280.0
Sand	1375	1375	1375	1375	1375	1375

The material amounts given in Table 3.4 to Table 3.6 were weighed, and after that each mortar was mixed in compliance with ASTM C 109. Mixtures are poured into 50 mm cubes, and cured in compliance with ASTM C 109.

3.4.2.Mixtures for Heat of Hydration Tests

In order to study the hydration behavior of the mixtures smaller paste samples of these mixtures were prepared. The dry weights of the samples were 1 % of the weight of the original mixtures without sand. The water-to-cement ratio was changed to 0.4 to prevent bleeding. The size of the samples was chosen to fit into 20 ml volume (the capacity of the ampoules used in the isothermal calorimeter, Figure 3.3).

Table 3.6 Proportions of mixtures using only a single clinker.

Mixture / Materials (g)	AAA	BBB	SSS	CAA	CBB	CSS	ACA	BCB	SCS
Clinker A Coarse	200	-	-	200	-	-	200	-	-
Clinker A Medium	125	-	-	125	-	-	-	-	-
Clinker A Fine	175	-	-	-	-	-	175	-	-
Clinker B Coarse	-	200	-	-	200	-	-	200	-
Clinker B Medium	-	125	-	-	125	-	-	-	-
Clinker B Fine	-	175	-	-	-	-	-	175	-
Clinker S Coarse	-	-	200	-	-	200	-	-	200
Clinker S Medium	-	-	125	-	-	125	-	-	-
Clinker S Fine	-	-	175	-	-	-	-	-	175
Slag Coarse	-	-	-	-	-	-	-	-	-
Slag Medium	-	-	-	-	-	-	125	125	125
Slag Fine	-	-	-	175	175	175	-	-	-
Gypsum	25	25	25	16.25	16.25	16.25	18.75	18.75	18.75
Water	258.0	258.0	258.0	259.4	260.0	256.9	256.9	256.9	256.9
Sand	1375	1375	1375	1375	1375	1375	1375	1375	1375

3.4.3.Materials for Chemical and Particle Size Distribution Analyses

Samples of ~200 g were taken from the different fineness fractions of all materials used in preparing the mixtures.

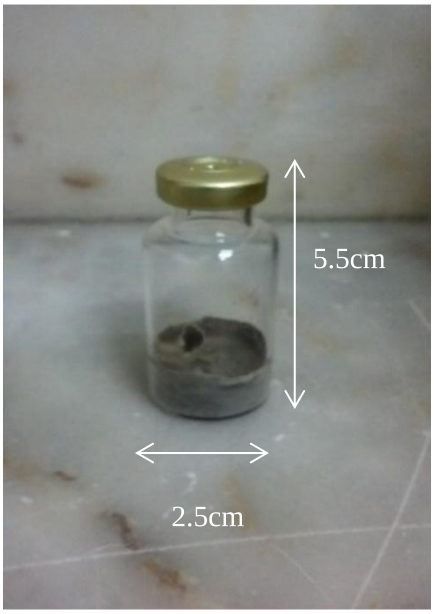


Figure 3.3. A sample after testing with the Tam Air Isothermal Calorimeter.

3.5. Mixture Testing

3.5.1.Compressive Strength Tests

Cured cube specimens were removed from water on the day of testing and prepared for compressive strength tests. The tests were applied in compliance with ASTM C 109 on the specimens cured for 1 d, 3 d, 7 d, and 28 d. The results are given in Chapter 4.

3.5.2.Heat of Hydration Tests

The isothermal calorimeter used has 8 measurement channels. Each consists of one reference sample slot and one tests sample slot. The working principle of this equipment is based on keeping the temperature stable at a fixed value. The reference sample is left in the channel at a stable temperature of 23 ºC. When the test sample is placed in the twin channel, the stability is disturbed, and the device uses energy to restabilize the temperature. This energy is recorded as the rate of heat of hydration. Cumulative heat is also calculated in joules.

In practice placing test samples is quite important to obtain reliable results. Since very early heat of hydration rates are not in the scope of this study, test specimens were not mixed inside the equipment. The dry materials were weighed, placed inside the ampoule, and then water was added. Mixing outside the ampoule was not preferred due to difficulties in placing the pastes into the ampoules. After addition of water the materials were mixed inside the ampoule by a water drop shaped metal wire. The same procedure and same mixing time was used for all samples. After mixing, the ampoule was capped and placed into the channel. The experiment was continued for 48 hours and the data recorded. The results are given in Chapter 4.

3.6. Materials Testing

The particle size distributions (PSDs) of the mixtures were determined using the PSDs of the materials used in the blend and their combination percentages. Particle size distributions of the mixtures are given in Figure 3.4 to Figure 3.30.

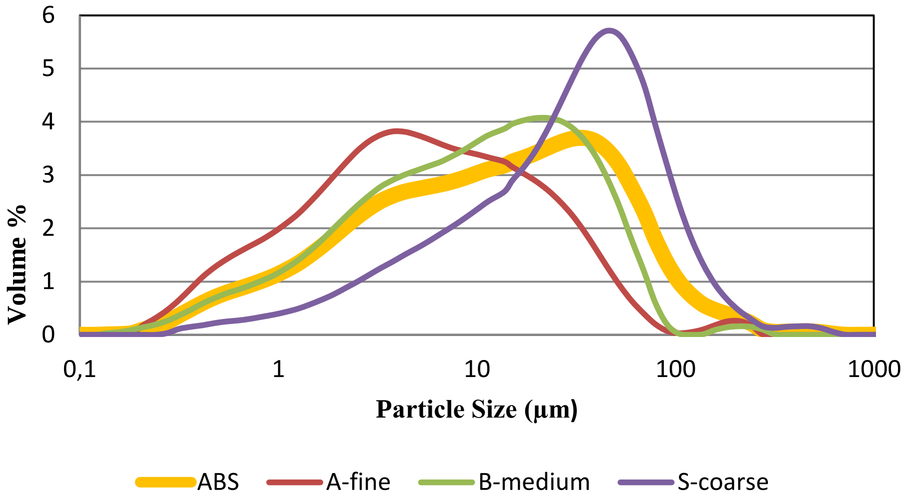


Figure 3.4. Particle Size Distribution of Mixture ABS

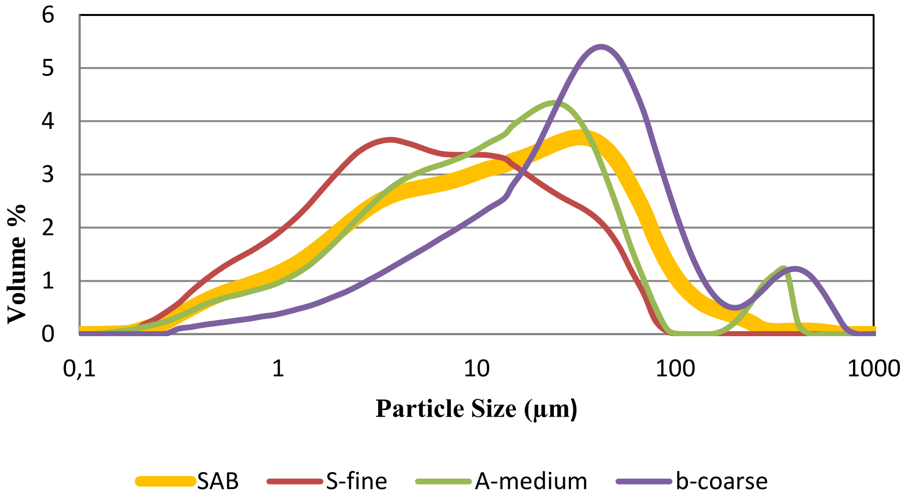


Figure 3.5. Particle Size Distribution of Mixture SAB

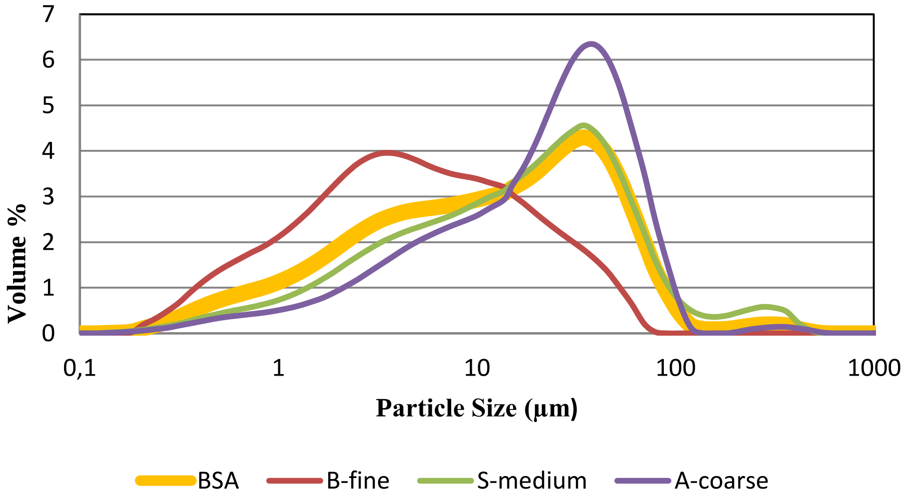


Figure 3.6. Particle Size Distribution of Mixture BSA

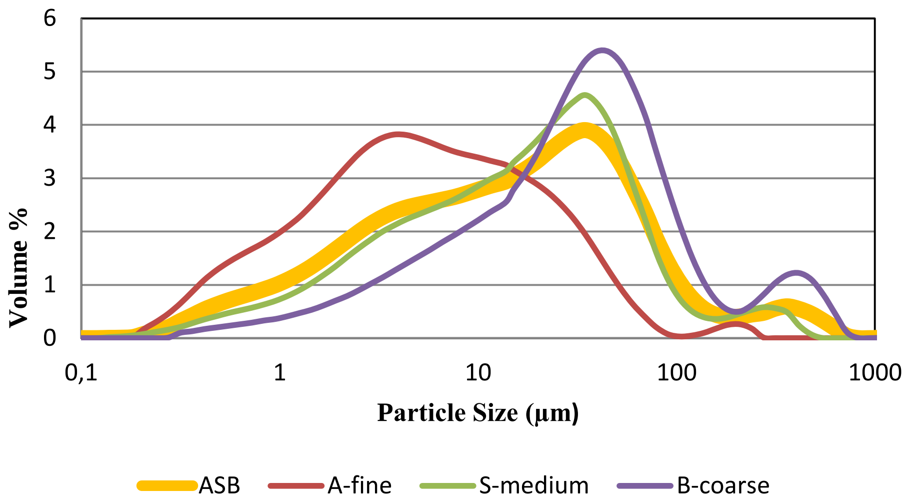


Figure 3.7. Particle Size Distribution of Mixture ASB

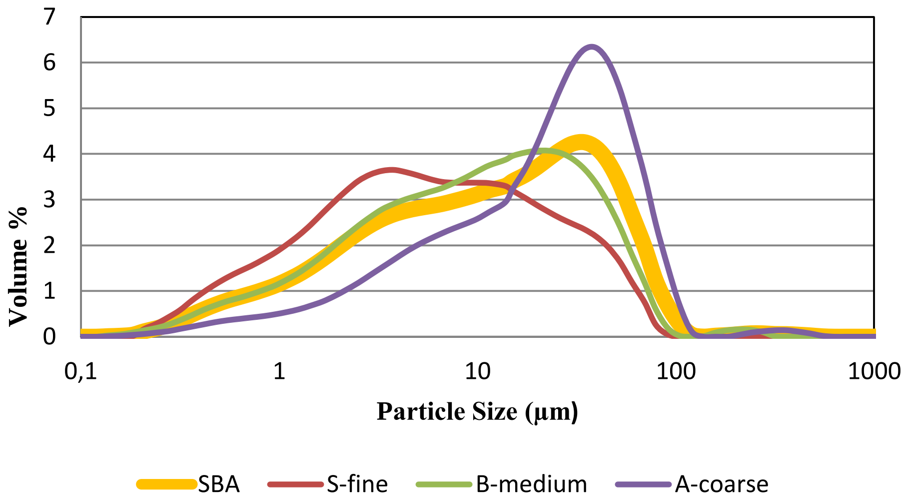


Figure 3.8. Particle Size Distribution of Mixture SBA

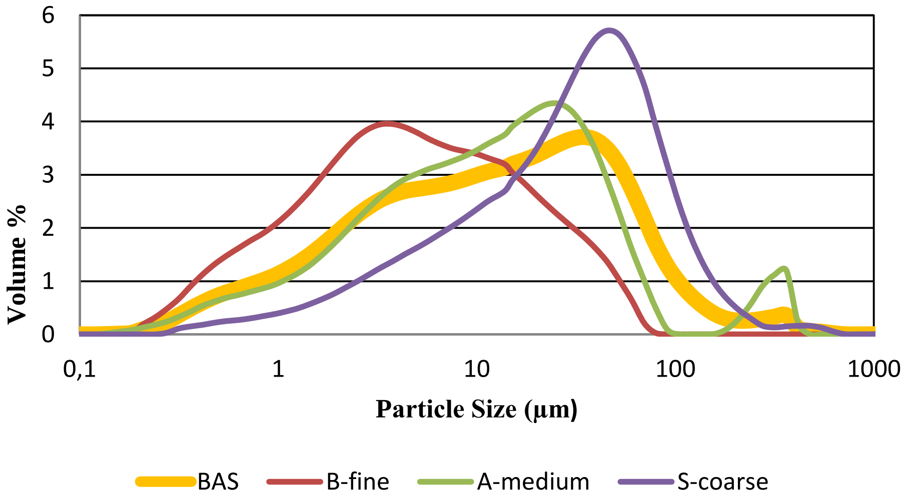


Figure 3.9. Particle Size Distribution of Mixture BAS

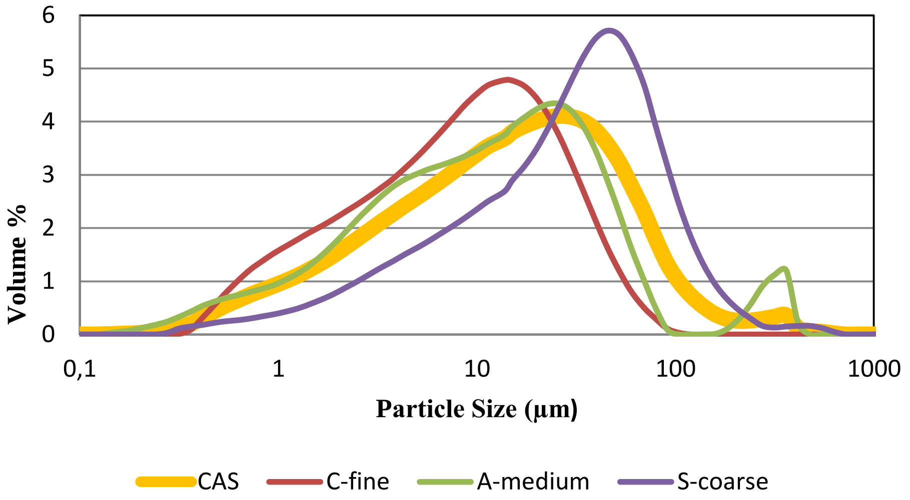


Figure 3.10. Particle Size Distribution of Mixture CAS

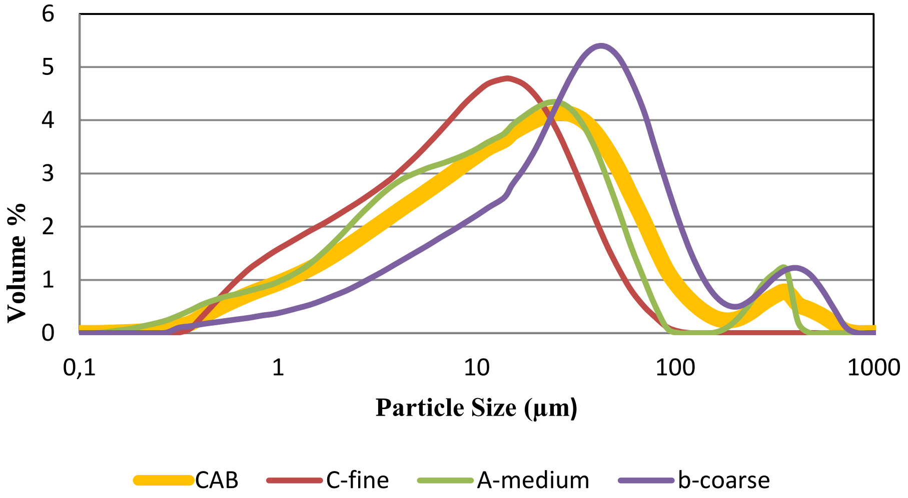


Figure 3.11. Particle Size Distribution of Mixture CAB

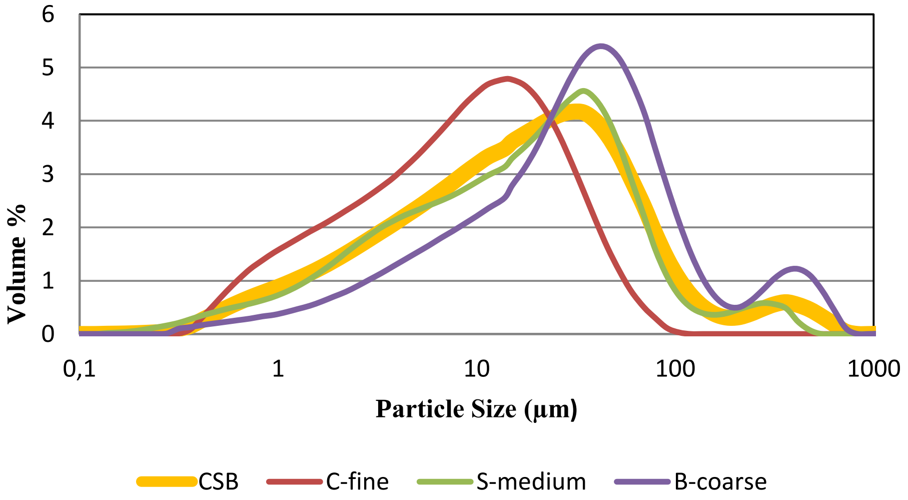


Figure 3.12. Particle Size Distribution of Mixture CSB

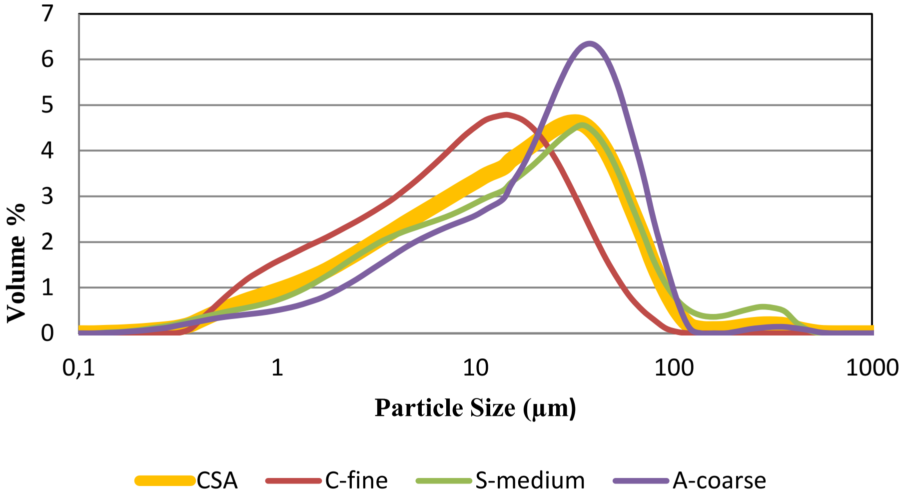


Figure 3.13. Particle Size Distribution of Mixture CSA

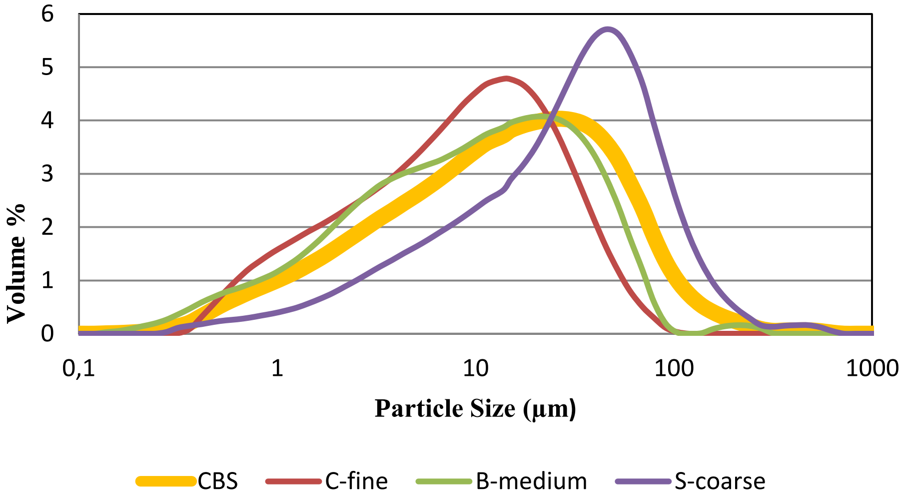


Figure 3.14. Particle Size Distribution of Mixture CBS

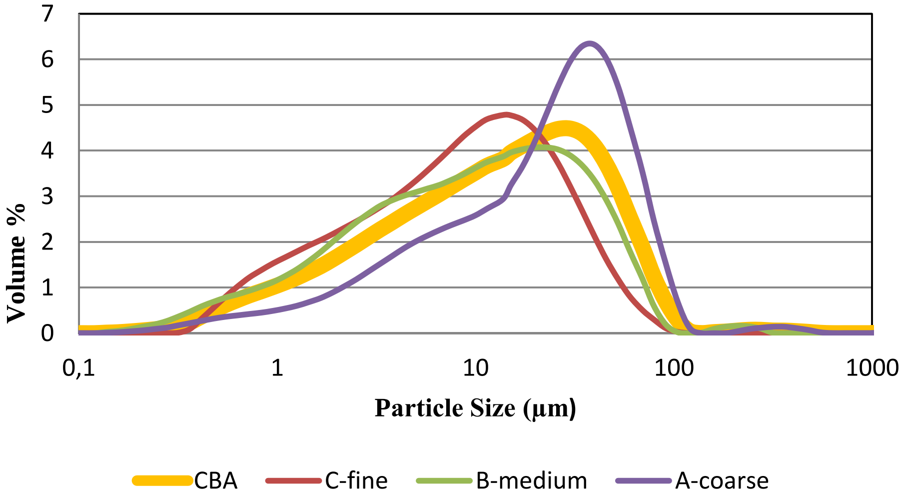


Figure 3.15. Particle Size Distribution of Mixture CBA

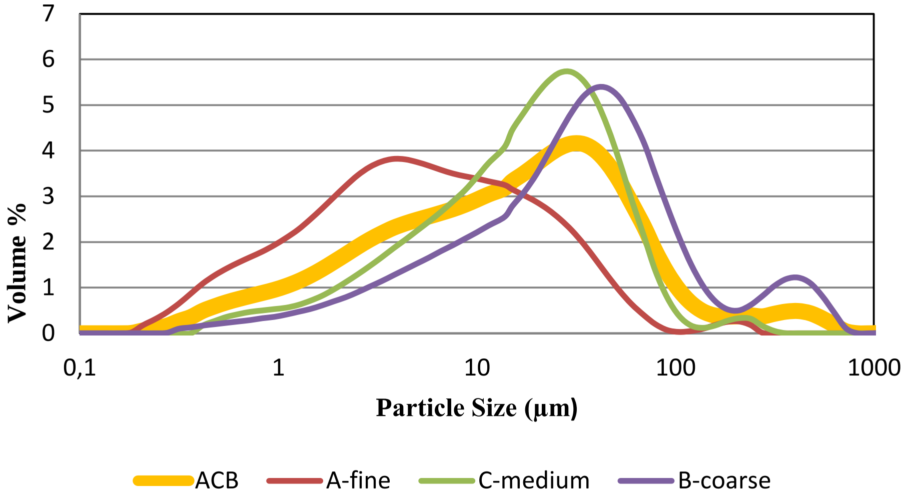


Figure 3.16. Particle Size Distribution of Mixture ACB

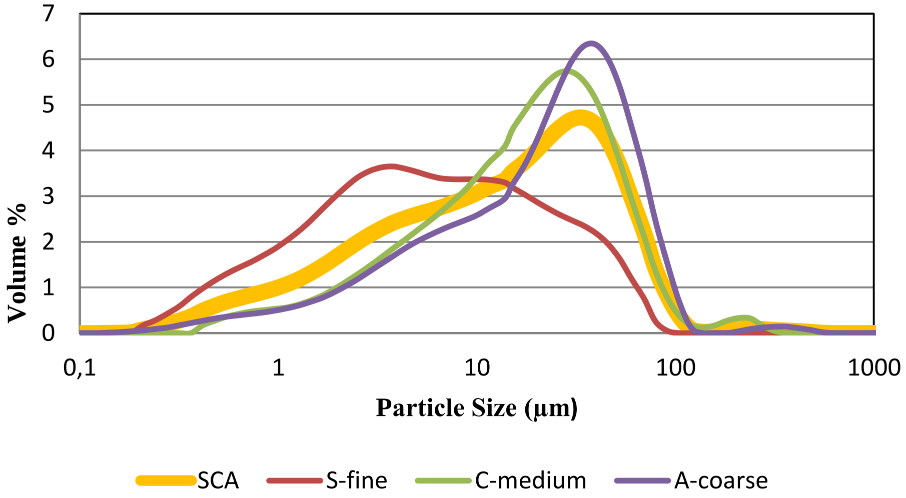


Figure 3.17. Particle Size Distribution of Mixture SCA

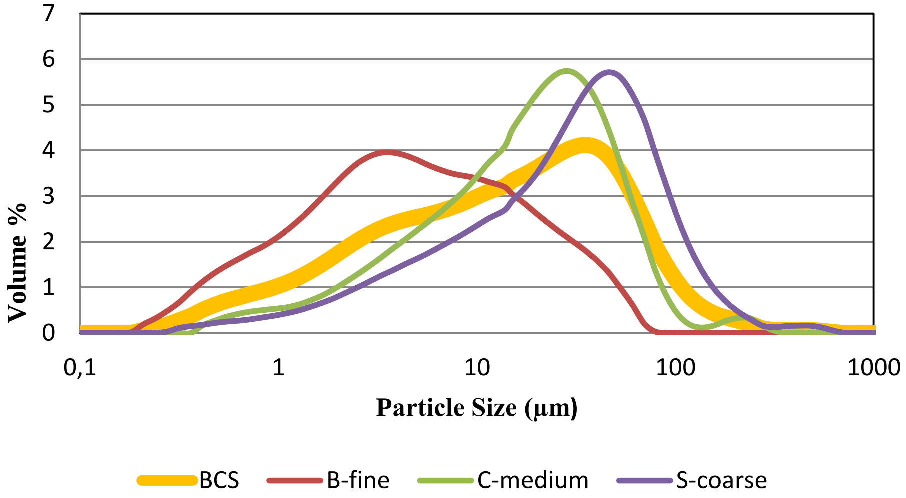


Figure 3.18. Particle Size Distribution of Mixture BCS

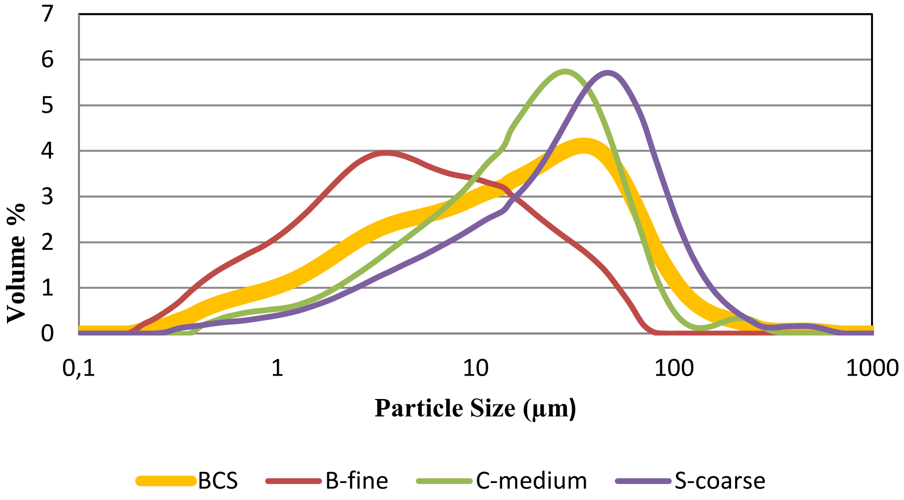


Figure 3.19. Particle Size Distribution of Mixture ACS

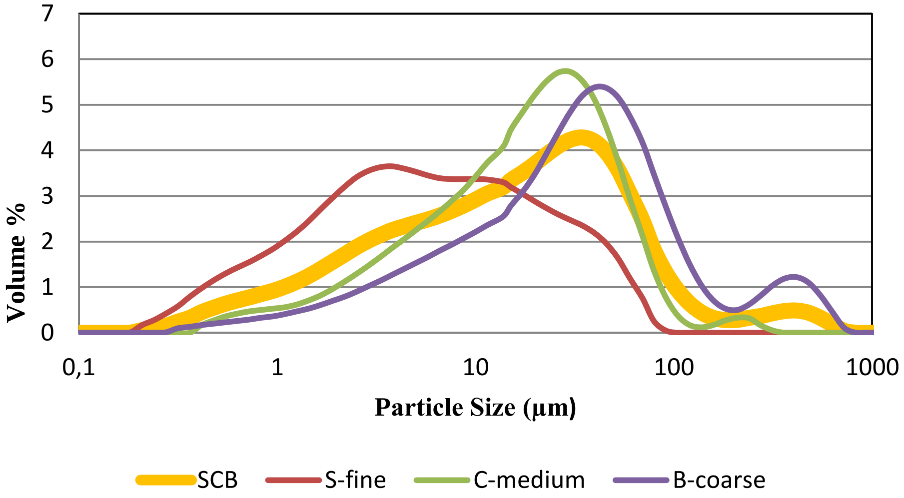


Figure 3.20. Particle Size Distribution of Mixture SCB

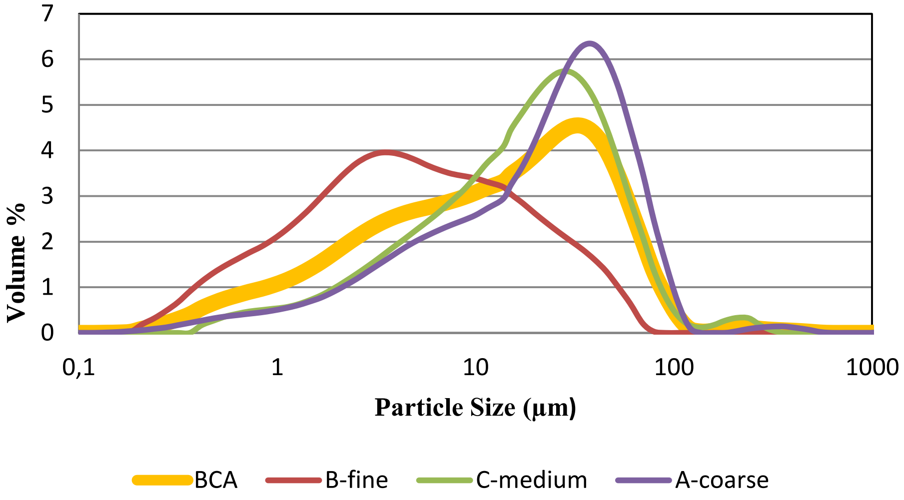


Figure 3.21. Particle Size Distribution of Mixture BCA

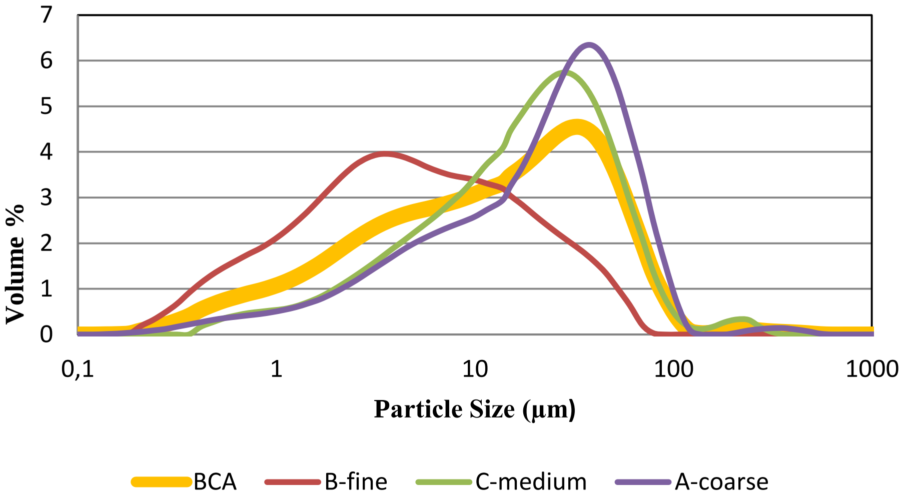


Figure 3.22. Particle Size Distribution of Mixture AAA

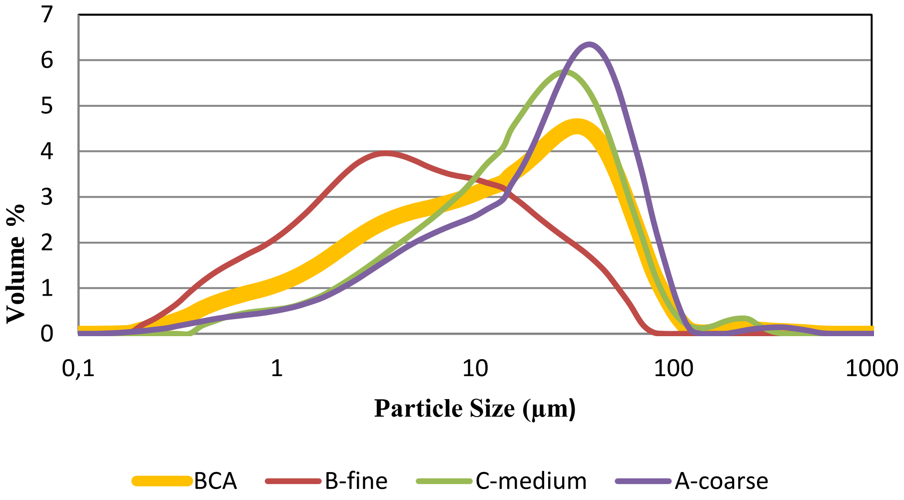


Figure 3.23. Particle Size Distribution of Mixture BBB

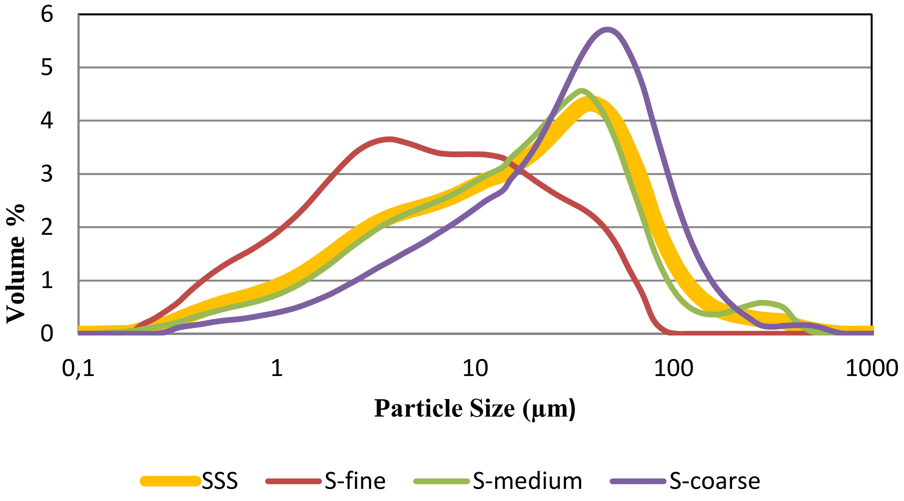


Figure 3.24. Particle Size Distribution of Mixture SSS

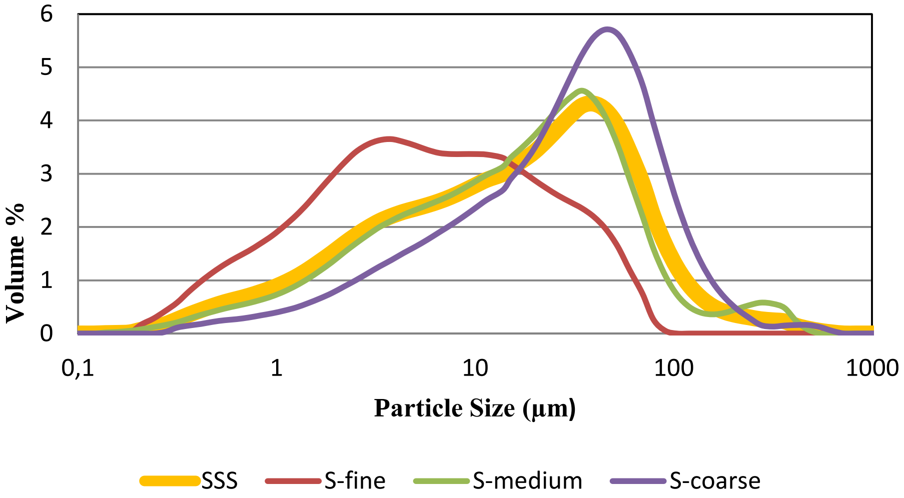


Figure 3.25. Particle Size Distribution of Mixture CAA

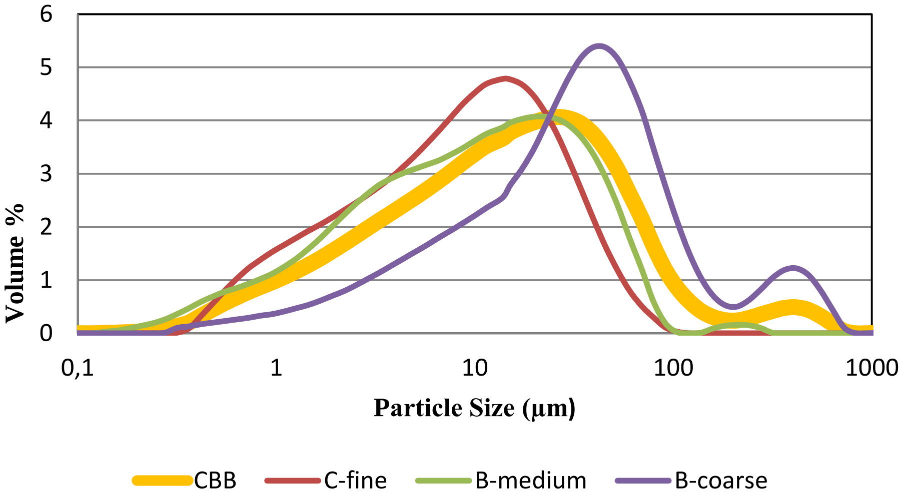


Figure 3.26. Particle Size Distribution of Mixture CBB

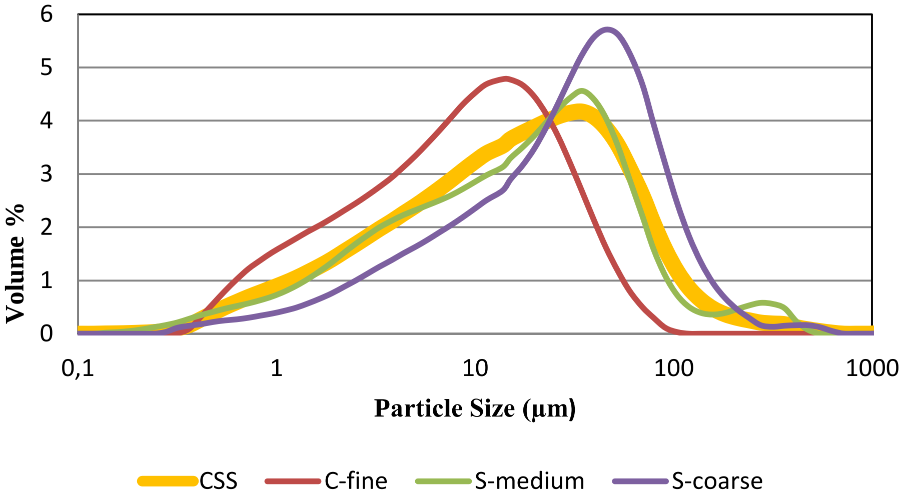


Figure 3.27. Particle Size Distribution of Mixture CSS

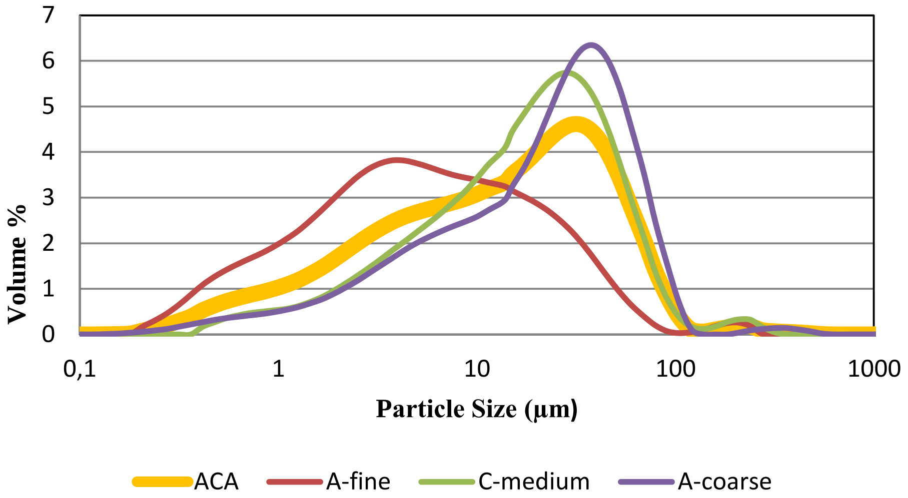


Figure 3.28. Particle Size Distribution of Mixture ACA

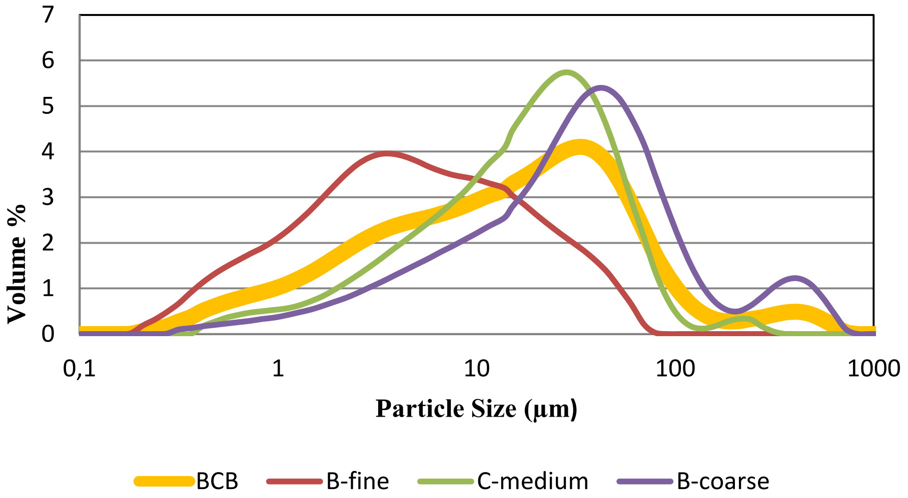


Figure 3.29. Particle Size Distribution of Mixture BCB

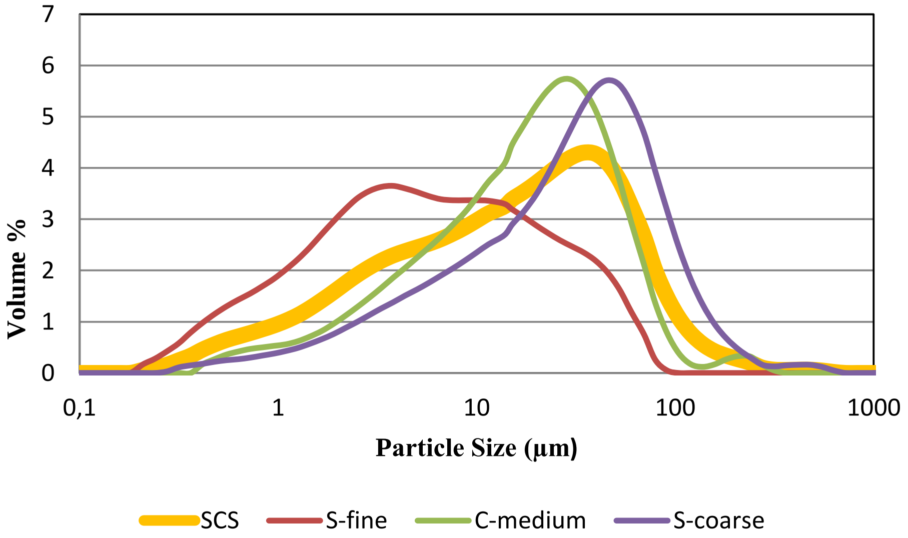


Figure 3.30. Particle Size Distribution of Mixture SCS

CHAPTER 4

RESULTS AND DISCUSSION

4.1. General

The results obtained from the experimental study are presented and discussed in this chapter.

4.2. Results of Compressive Strength Tests

The 1-, 3-, 7-, and 28-day strengths of mixtures are presented in Figure 4.1. The 1-, 3-, 7-, and 28day strength of mixtures in table form are presented in Table A.1 in Appendix A.

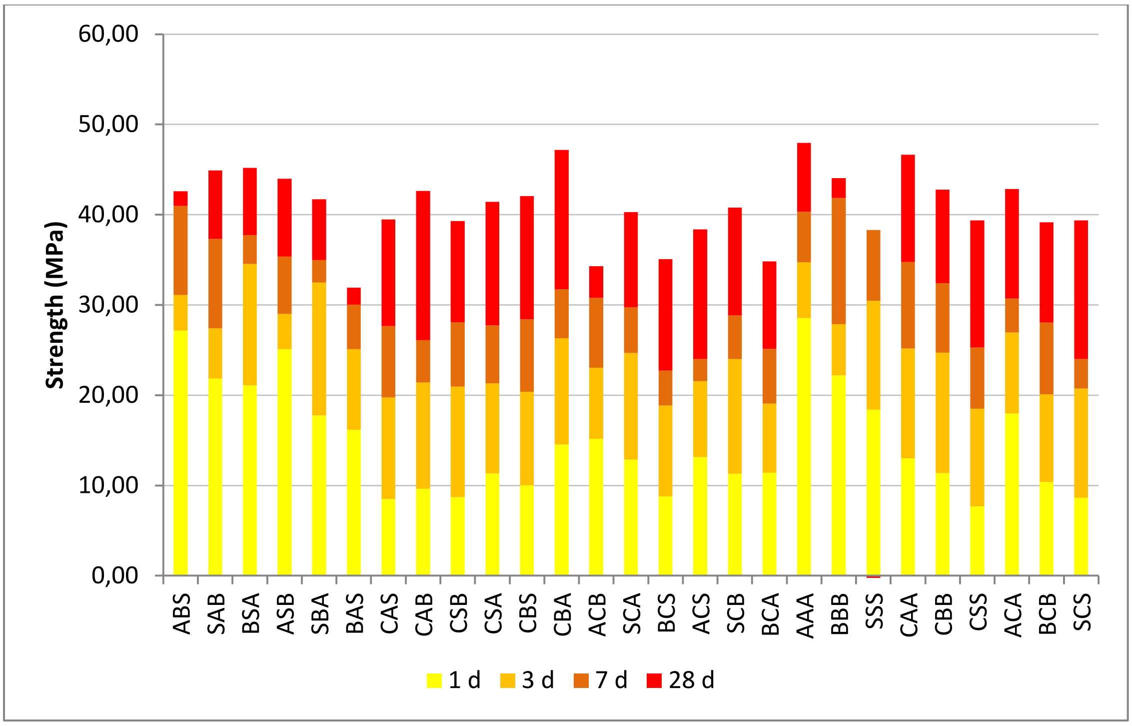


Figure 4.1. 1, 3, 7 and 28 day strength development of mixtures

4.3. Results of Heat of Hydration Tests

The 48-h heats of hydration for the mixtures are presented in Figure 4.2. The heat of hydration results in descending order are presented in Figure A.2 in the Appendix A.

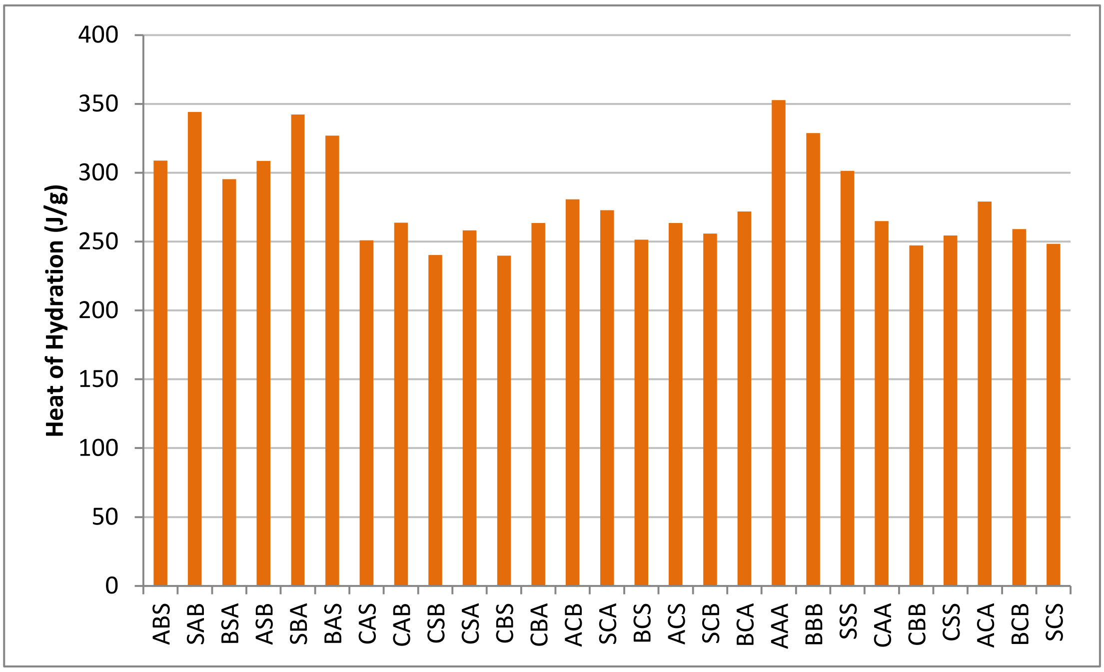


Figure 4.2. 48-h heast of hydration of the mixtures

When the mixtures are listed in ascending order according to their 28-day strengths, it is observed that mixture AAA reached the highest value. Mixture AAA contains only clinker A as binding agent, it does not contain any blast furnace slag. Mixture CBA which reached the second highest strength contains fine blast furnace slag, medium Clinker B and coarse Clinker A with 35 %, 25 %, 40 % percentages respectively as its binding agents. This result shows that amount of strength in Mixture CBA with fine blast furnace slag instead of using fine clinker is very close to AAA. Mixture CAA which reached the third highest strength contains very fine blast furnace slag, medium Clinker A and coarse Clinker A. Comparison between material contents of Mixture CBA and Mixture CAA reveals that medium fine Clinker B used in Mixture CBA instead of medium fine clinker A in mixture 22 increased the amount of hydration products and eventually increased strength.

Observation of the first seven mixtures with highest 28-day strength shows that strength contribution of fine slag is very close to that of fine clinker. In terms of 28-day strengths mixtures reached medium high values compared to others are CAS, CSS, and SCS. All three of these mixtures contain blast furnace slag and Clinker S. This result shows that Clinker S is not compatible with blast furnace slag in terms of hydration activation.

Mixtures with the lowest 28-day strengths are mixtures BCA, ACB and BAS. Ingredients of this three mixtures are given as follows, Mixture BCA contains fine clinker B, medium slag and coarse Clinker A, mixture ACB contains fine clinker A, medium fine blast furnace slag and coarse Clinker B and mixture BAS contains fine clinker B, medium fine Clinker A and coarse Clinker S. The 28-day test result of mixture BAS is interesting because it is expected to show a lower 28-day strength than a mixture containing blast furnace slag than a mixture containing clinker only as a binding agent.

Nine of the twenty seven mixtures did not contain blast furnace slag. Those mixtures are; ABS, SAB, BSA, ASB, SBA, BAS, AAA, BBB, and SSS. AAA, BBB and SSS can be considered as the control mixtures. The strength development of AAA, BBB, and SSS are presented in Figure 4.3 and those of ABS, SAB, BSA, ASB, SBA, and BAS are presented in Figure 4.4. It is possible to see the relationship between different clinkers in terms of compatibility by comparing their individual behaviors. Since these six mixtures contain the same materials with different fineness combinations, the compatibility of materials can be related to fineness.

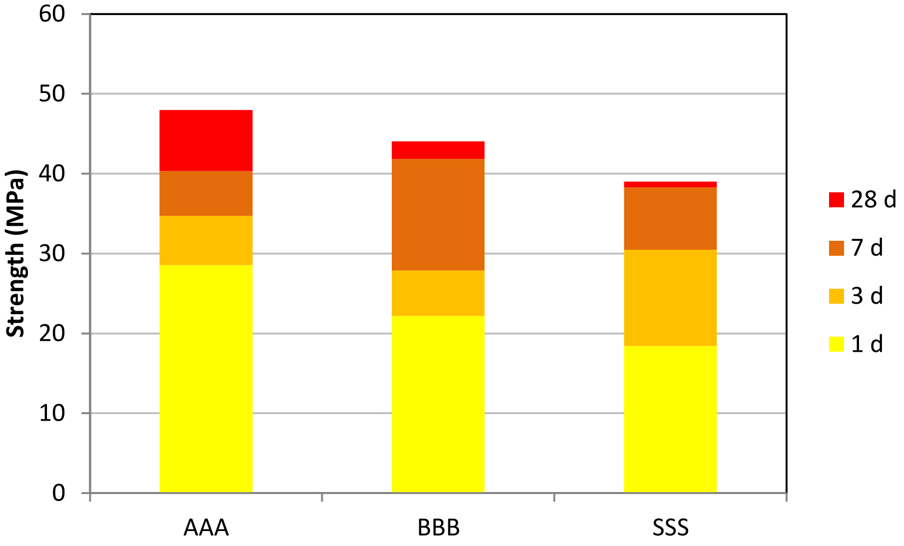


Figure 4.3 Strength development of AAA, BBB and SSS

Figure 4.3 shows that mixture AAA has the highest early strength and the highest 28 day strength. Clinker B and Clinker S have lower strength values in descending order. As explained in Chapter 2 as fineness increases, early and 28 day strengths of a mixture generally increases due to the increment in the surface area of the particles. In these circumstances mixtures containing fine clinker A are expected to have high early and 28 day strengths and mixtures containing coarse clinker S are expected to have low early and 28 day strengths. Mixtures ABS and ASB supports this expectation in terms of early strength. Unlike it was expected in terms of 28-day strength BSA reached the highest. This result can be related to low strength effect of clinkers B and S being neutralized by increasing fineness.

In terms of strength contribution and compatibility BSA and BAS show remarkable differences. This difference relies upon change in fineness of clinkers A and S. Strength is increased 42 % by using medium fine clinker S and coarse clinker A in place of medium fine clinker A and coarse clinker S. Similar behavior is observed in clinker when ABS versus ASB and SAB versus SBA are compared, but greatest difference is observed in BSA and BAS couple among others. This result can be related individual strength of clinkers because the highest individual strength difference is observed between clinker A and clinker S. Fineness differences in fineness classes are also increasing amount of difference. For example; although both are considered as medium fine, fineness of medium fine clinker A is 4675 cm^2/g and fineness of medium fine clinker S is 3644 cm^2/g. Cumulative heat evolution of pastes BAS and BSA are presented in Figure 4.5.

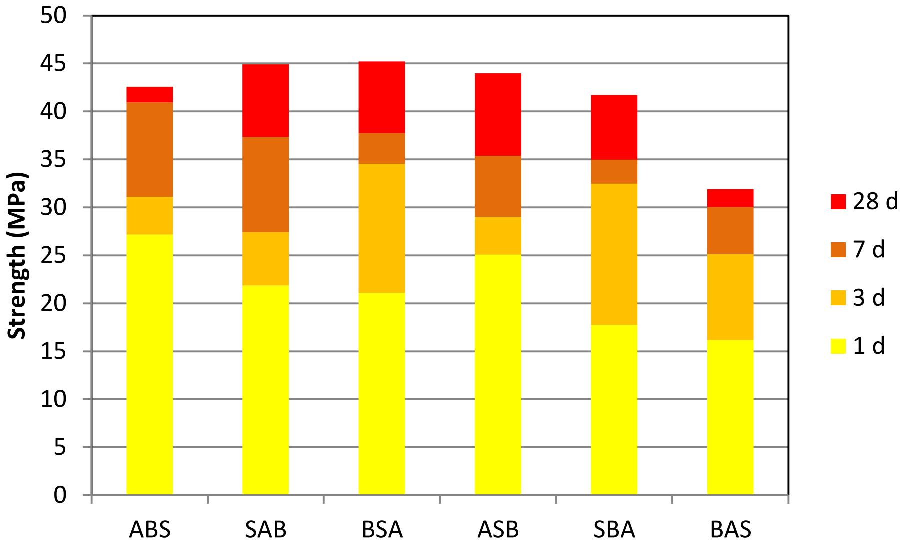


Figure 4.4 Strength development of ABS ,SAB, BSA, ASB, SBA and BAS

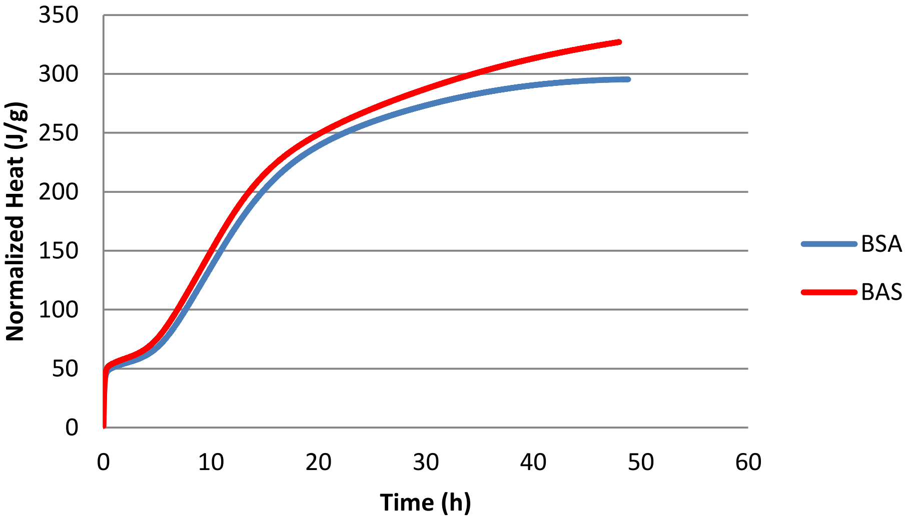


Figure 4.5. Cumulative heat evolution of pastes BAS and BSA

As it can clearly be seen in Figure 4.5 pastes release heat demonstrating the same line up to 10 h and rate of heat evolution increases after 10 h in paste BAS. This result demonstrates possibility of two conclusions. One of those conclusions is that more hydration reactions had taken place and eventually more hydration products are formed in paste BSA. The other conclusion is that compounds which release more heat were hydrated in paste BSA. The strength difference supports both of those results.

First peak in rate of heat evolution versus time curves of pastes BAS and BSA is presented in Figure 4.6. It is observed in this figure that the rate of heat evolution of paste BSA is 11 % greater than the rate of heat evolution of paste BAS between 5 h and 10 h. Reverse is valid for the time domain between 15 h to 20 h. The rate is stabilized for both of the pastes after 25 h. Difference in cumulative heat evolution is increased after 30 h. This result demonstrates that compounds which release more heat were hydrated after 20 h in paste BAS. Heat evolution of pastes ABS and ASB are presented in Figure 4.7 and first peak in rate of heat evolution versus time curves of pastes ABS and ASB are presented in Figure 4.8.

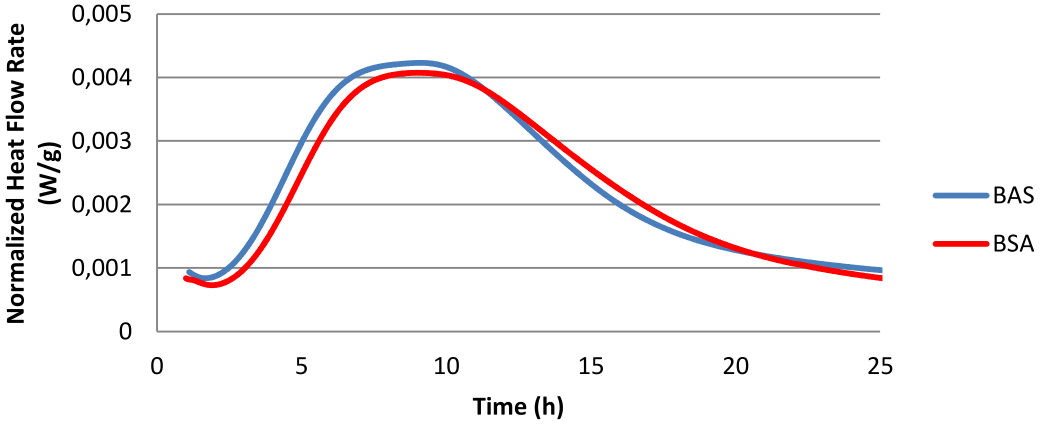


Figure 4.6. First peak in rate of heat evolution versus time curves of pastes BAS and BSA

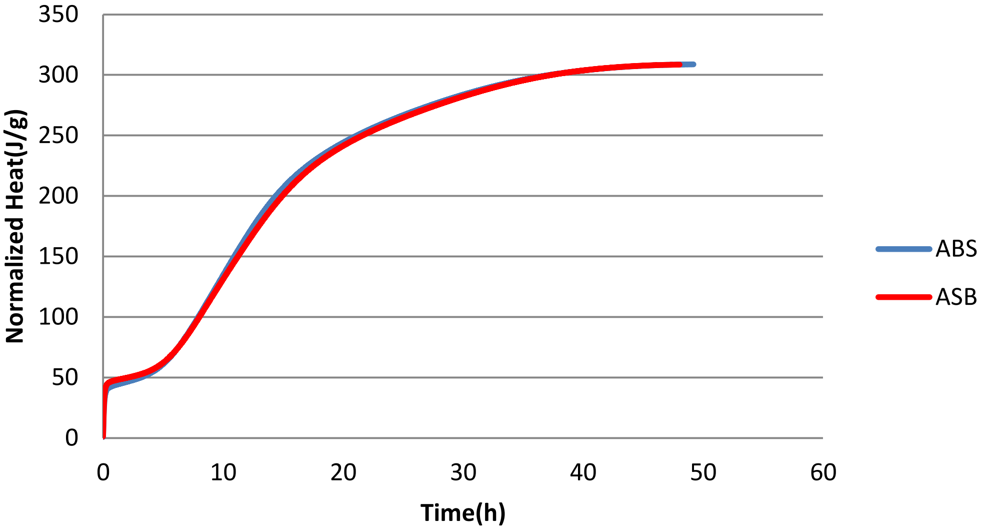


Figure 4.7. Heat evolution of pastes ABS and ASB

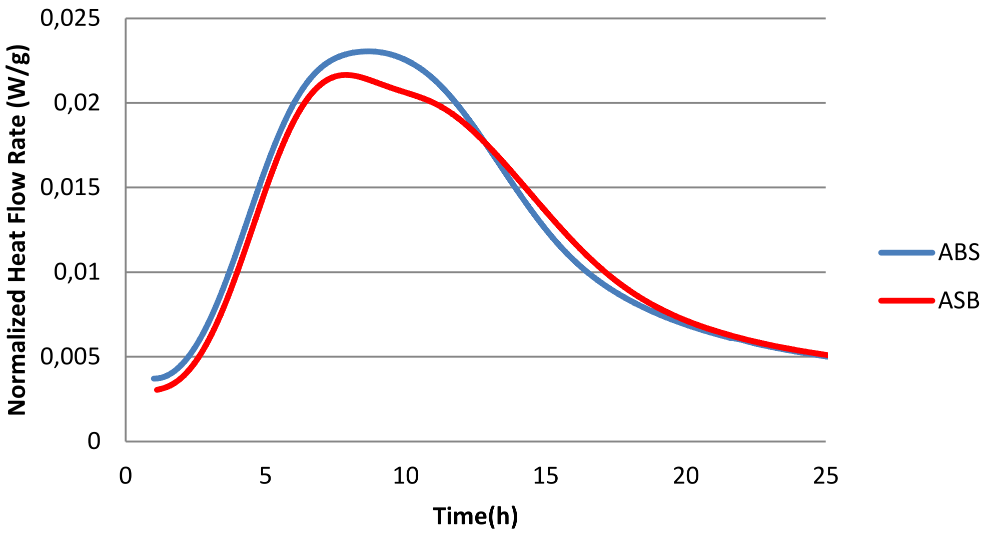


Figure 4.8. First peak in rate of heat evolution versus time curves of pastes ABS and ASB

Pastes ABS and ASB show similar behavior in terms of heat evolution. This is an expected result because 28 day strengths are close to each other. Similarity in chemical composition supports this conclusion. Rate of heat evolution of paste ABS is greater than ASB between 10h and 15h. Although calculated average fineness of two pastes are closer ASB is expected to include more coarse particles than ABS according to particle size distribution graphs. Difference in heat evaluation rate can be related to this difference.

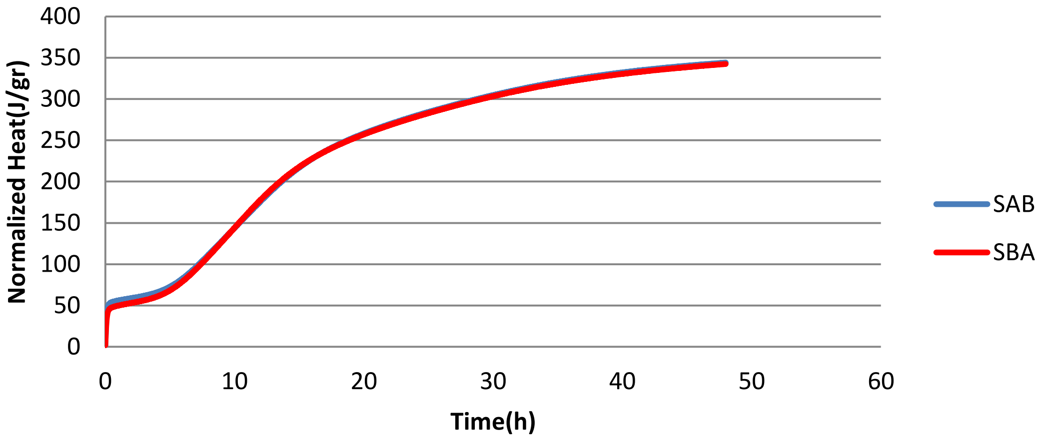


Figure 4.9. Heat evolution of pastes SAB and SBA

Heat evolution of pastes SAB and SBA are presented in Figure 4.9. Pastes show similar behavior in terms of heat evolution. This is an expected result because 28 day strengths are close to each other. Based on its chemical composition, it is expected that clinker B can contain more C_3A and C_4AF. Since paste SAB contains more clinker B compared to paste SBA according to fineness percentage combination, slight excess observed in early heat evolution in paste SBA can be related to this fact.

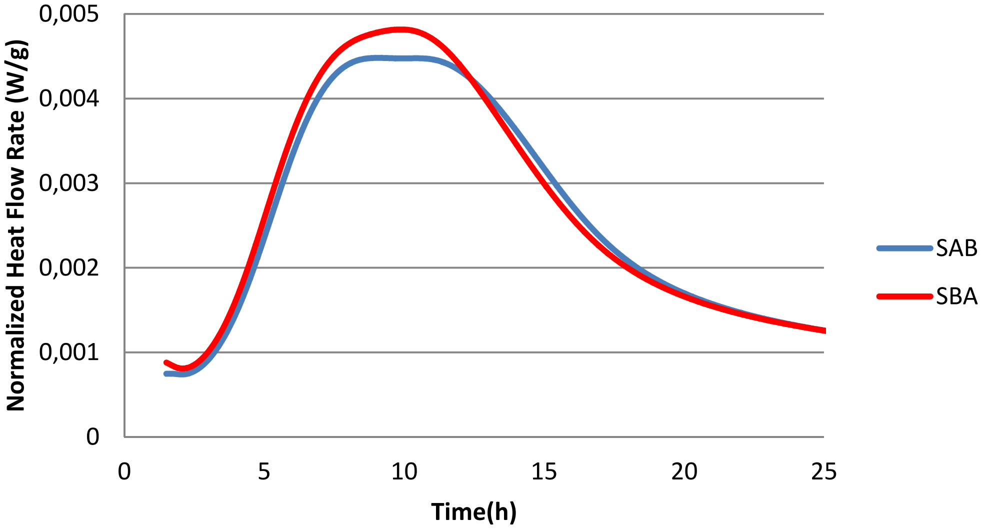


Figure 4.10. First peak in rate of heat evolution versus time curves of pastes SAB and SBA

Blast furnace slag is used in 18 of the 27 mixtures. Six of them can be considered as control groups containing one type of clinker and blast furnace slag. Those mixtures are CAA, CBB, CSS, ACA, BCB and SCS. Strength development of these mixtures is presented in Figure 4.11.

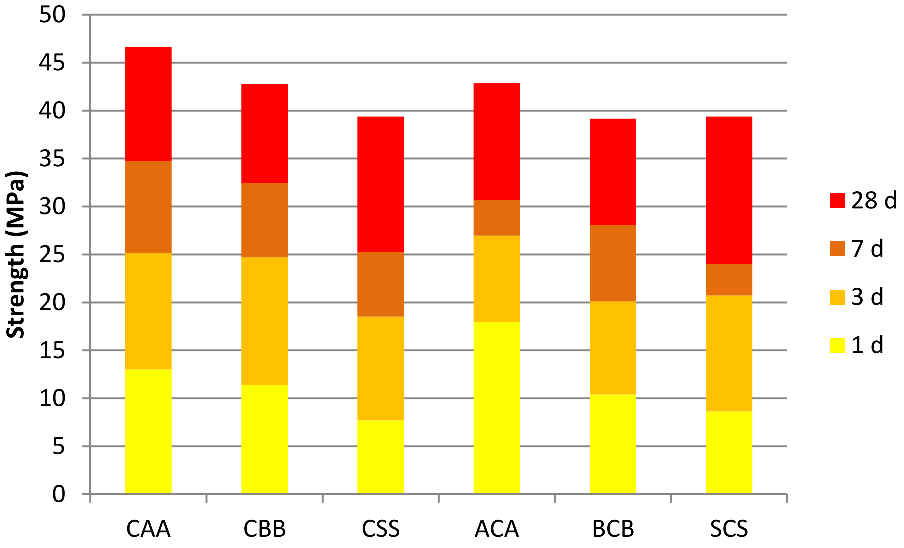


Figure 4.11. Strength development of CAA, CBB, CSS, ACA, BCB and SCS

The control mixtures containing blast furnace slag demonstrated similar strength development as control group of clinkers, except the control group containing medium slag. For clinker controls, Clinker A reached the highest-28 day strength, clinker B came second and clinker S third. For fine slag containing Control group the same pattern was observed as CAA reached the highest 28 day strength CBB ranked second and CSS third. The medium slag containing control group ACA reached the highest 28 day strength but SCS had the second highest 28 day strength and BCB the third. This result can be related to effective usage of blast furnace slag because as it is expected according to hydration principle of pozzolans explained in Chapter 2, mixture SCS gained 39 % of its total strength between 7 and 28 days.

Strength development of CAS, CAB, CSB, CSA, CBS and CBA are presented in Figure 4.12. Mixture containing fine slag demonstrated low early strength as expected due to low cement content. 28 day strengths are fairly high compared to 28 day strength of the individual clinkers. Activation of blast furnace slag can be observed at the strength gain percentage between 7 and 28 days compared to total strength.

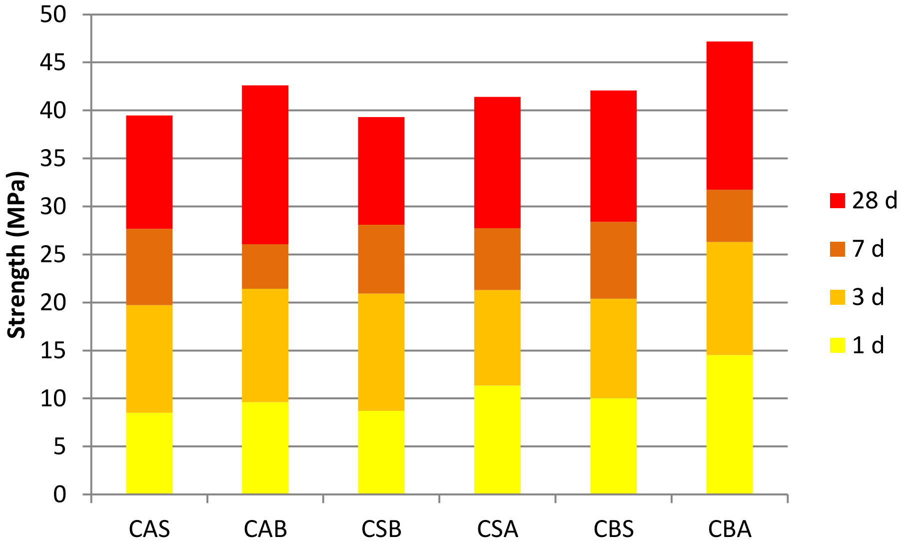


Figure 4.12. Strength development of CAS, CAB, CSB, CSA, CBS and CBA

When results given in Figure 4.9 are examined in terms of compatibility and strength contribution it is seen that same pattern given in Figure 4.4 is repeated. For example when two mixtures with one material difference like CAS and CAB are compared CAS reached higher 28 day strength than CAB as expected because clinker B reached higher strength than clinker S individually. This means that 28 day strength of clinker dominates the 28 day strength behavior in mixtures containing fine blast furnace slag.

Heat evolution of pastes CAS and CSA are presented in Figure 4.13. Results are very close to each other. This situation demonstrates that despite the change in fineness behavior of materials did not change. Close 28 day strength results support this argument. Different slope is observed between 20h and 48h compared to heat of hydration graph of cement pastes as expected due to activation of blast furnace slag. Remarkable difference observed is the second peak in rate of heat evolution of CAS. This second peak demonstrates that more slag is activated in paste CAS that CSA. Higher 28 day strength and lower total heat evolution of CSA support this conclusion.

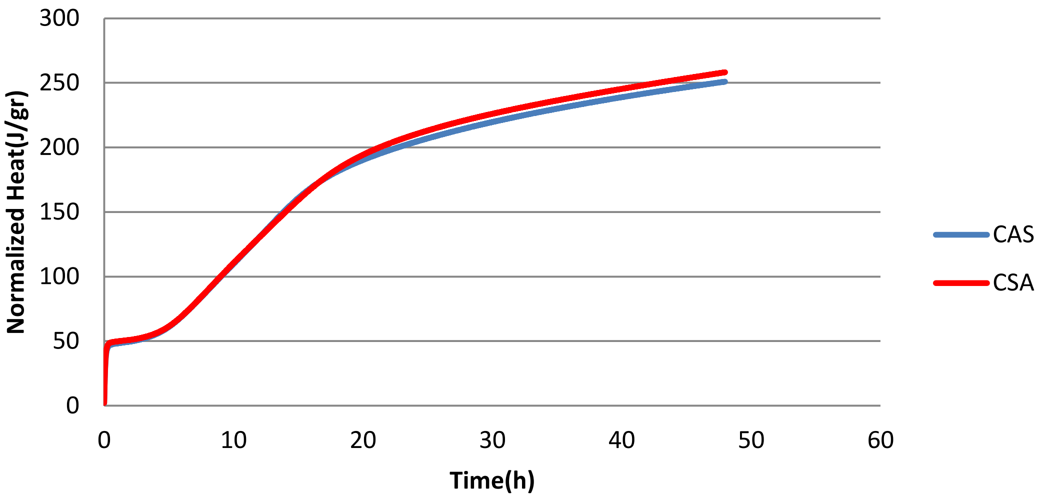


Figure 4.13. Heat evolution of pastes CAS and CSA

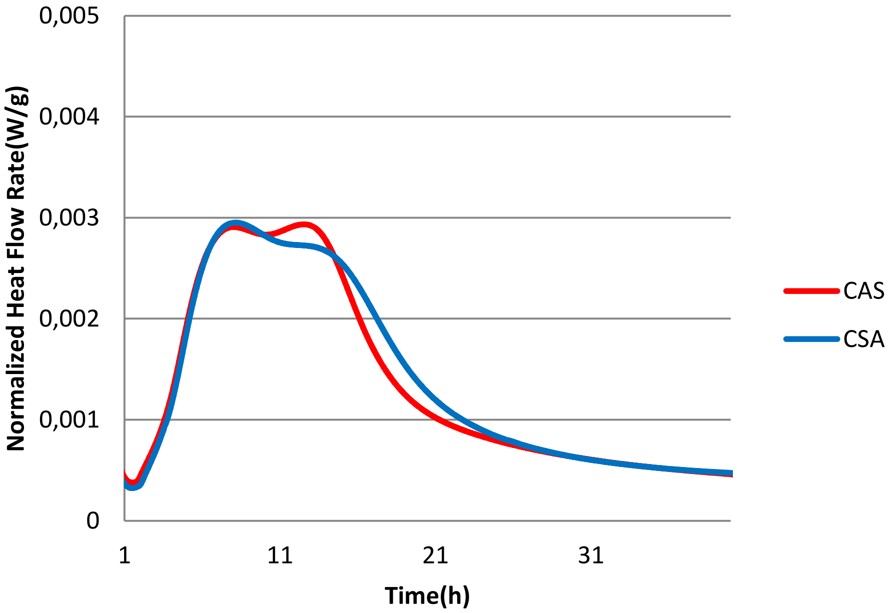


Figure 4.14. First peak in rate of heat evolution versus time curves of pastes CAS and CSA

Heat evolution of pastes CAB and CBA are presented in Figure 4.15. First peak in rate of heat evolution versus time curves of pastes CSB and CBS are presented in Figure 4.16. Except slightly excess early strength, heat evolution curve of pastes are very close to each other. This situation demonstrates that despite the change in fineness behavior of materials did not change. Close 28-day strength results support this argument. Different slope is observed between 20 h and 48 h compared to heat of hydration graph of cement pastes as expected due to activation of blast furnace slag. Remarkable difference observed is the second peak in rate of heat evolution of CAS. This second peak demonstrates that more slag is activated in paste CAS that CSA. Higher 28-day strength and lower total heat evolution of CSA support this conclusion. Early heat evolution of paste CBS is more than paste CSB.

This is an unexpected result since CBS contains more C_3A and C_4AF compounds according to fineness percentage combination.

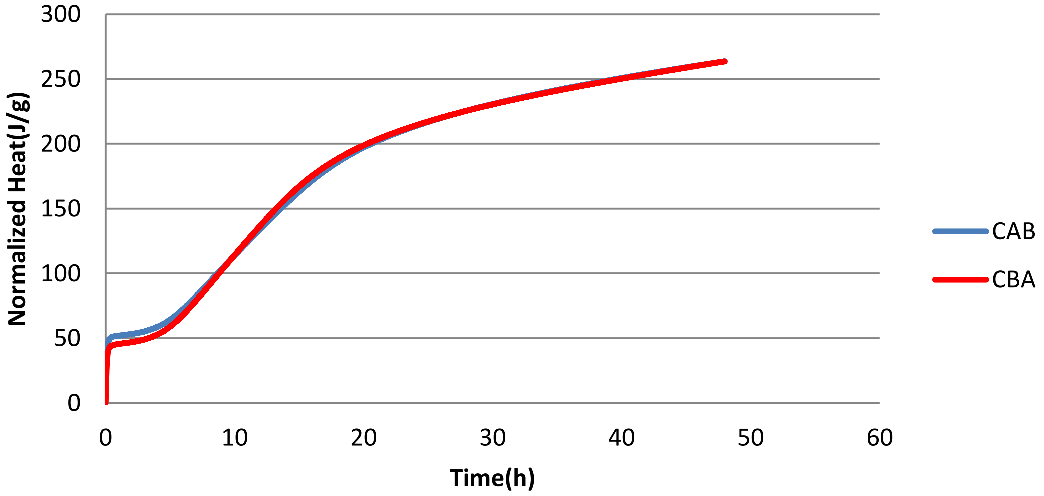


Figure 4.15. Heat evolution of pastes CAB and CBA

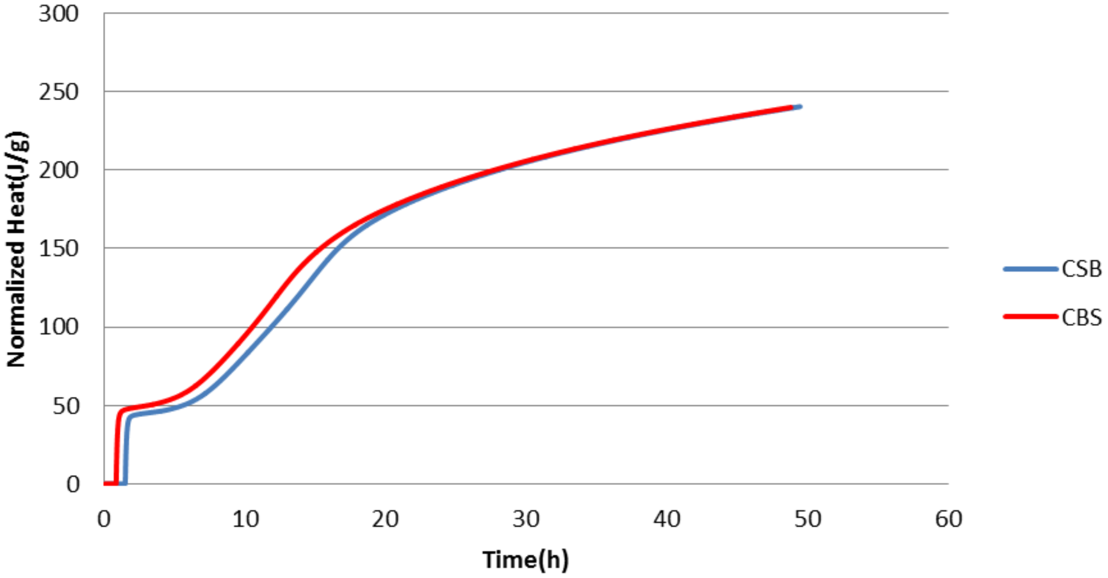


Figure 4.16. First peak in rate of heat evolution versus time curves of pastes CSB and CBS

Strength development of ACB, SCA, BCS, ACS, SCB and BCA are given in Figure 4.17. When this figure. is examined most notable difference is the lowest 28 day strength of ACB and low strength gaining rate of ACB between 7 and 28 days compared to mixtures in the same group. This result indicates that blast furnace slag in medium fineness is not effectively activated in mixture combination of ACB. In terms of 28 day strength mixtures SCB and SCA reached highest values but highest strength contribution of blast furnace slag is observed in ACS because highest strength gaining rate between 7 and 28 days is observed in this mixture.

When results given in Figure 4.16 are examined in terms of compatibility and strength contribution it is seen that behavior is different than the group of mixtures containing fine blast furnace slag. For example when two mixtures with one type of material difference like ACB and ACS are compared ACS reached higher 28 day strength than ACB which is an unexpected result because clinker B reached higher strength than clinker S individually. This means that behavior in mixtures containing fine blast furnace slag is dominated by cooperation of materials more than individual strength of clinkers.

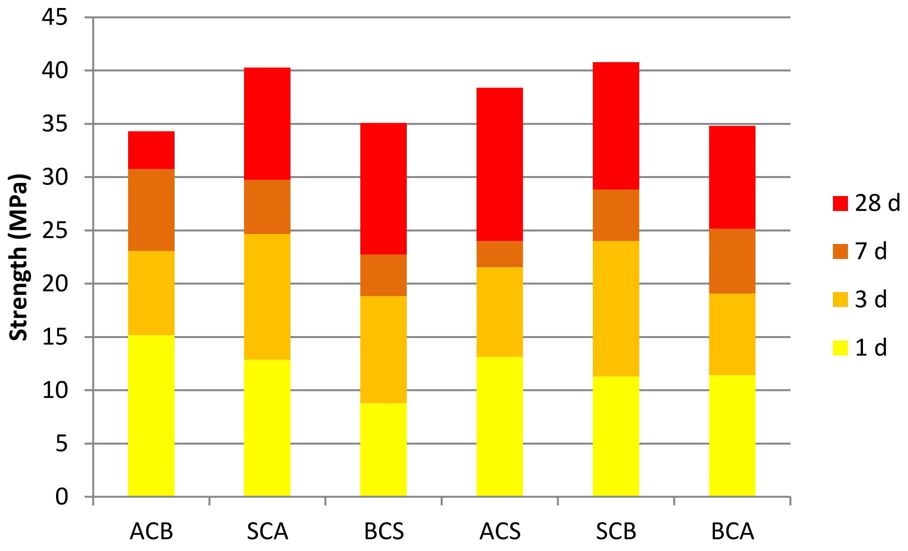


Figure 4.17. Strength development of ACB, SCA, BCS, ACS, SCB and BCA

To observe performance of slag, mixtures containing fine slag and medium slag are compared. Strength development of CAS and ACS are given in 4.18. When 1d strength development is considered it is seen that CAS has a lower early strength. This result is expected since cement content of ACS is higher than CAS. On the contrary 28d strength of CAS is slightly higher than ACS. This result shows that although ACS contains more cement, more hydration products and more strength contribution is obtained in CAS as a result of slag activation.

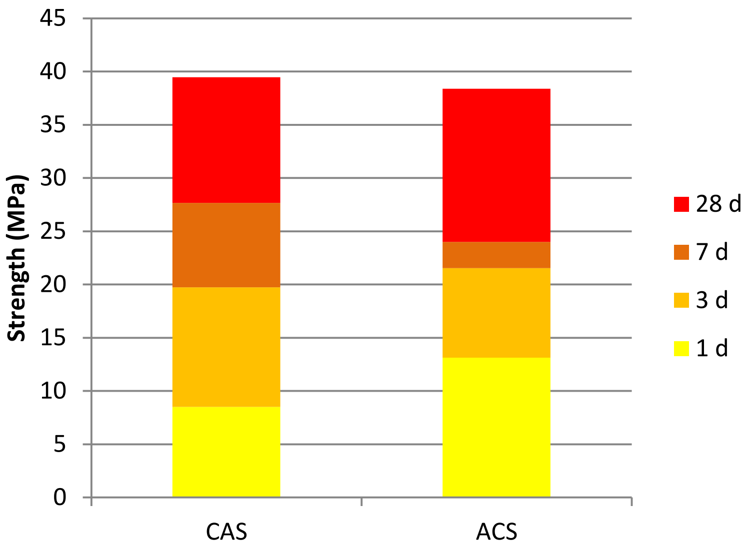


Figure 4.18. Strength development of CAS and ACS

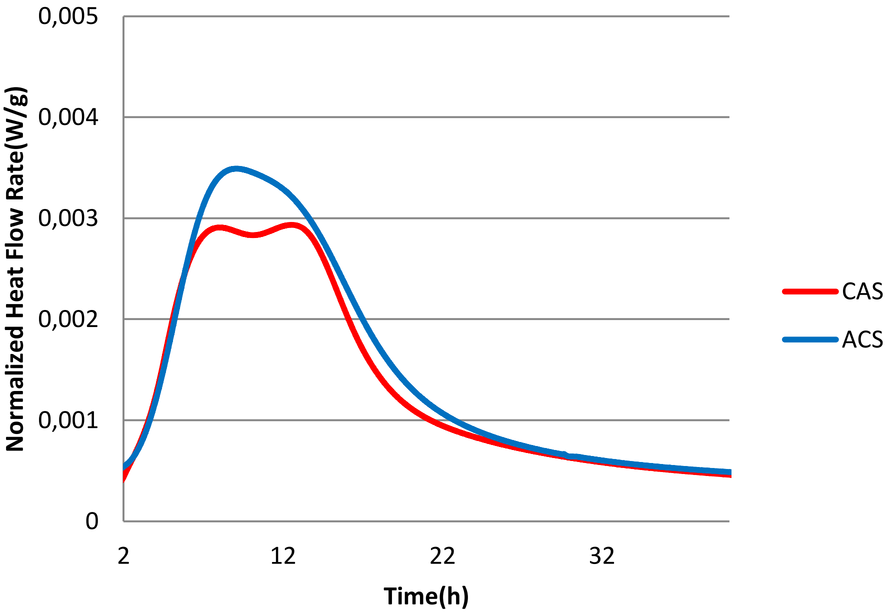


Figure 4.19. First peak in rate of heat evolution versus time curves of pastes CAS and ACS

First peak in rate of heat evolution versus time curves of pastes CAS and ACS are presented in Figure 4.19. Although liberated heat is low compared to control mixtures containing cement only, ACS has a rate of heat evolution curve similar to cement mixtures. This result demonstrates that cement content dominates the hydration behavior. On the contrary a second peak is observed in rate of heat evolution curve of CAS. This result demonstrates that in case of CAS slag dominates the hydration behavior. As it is given in Figure.4.2 amount of liberated heat of CAS is lower than ACS and supports the difference in hydration behavior of two pastes. Since particle size distribution curves of two mixtures are close to each other difference is not related to particle size distribution.

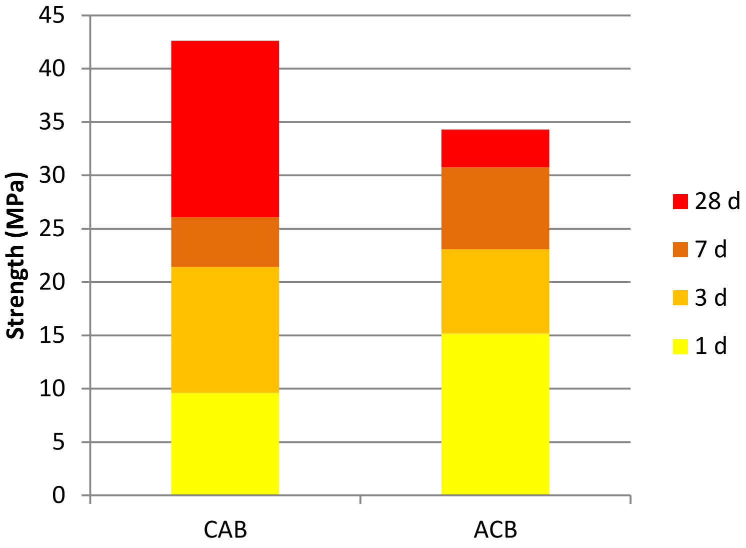


Figure 4.20. Strength development of CAB and ACB

Strength development of CAB and ACB are given in Figure 4.20. Although 1 d strength of ACB is higher than CAB, 28 d strength of CAB is remarkably higher. In addition strength development of CAB is the highest between 7 and 28 th days. Despite the 28 d strength difference, as it is given in Figure.4.2 amount of liberated heat of CAB is lower than ACB . This result shows that slag hydration is remarkably high in CAB.

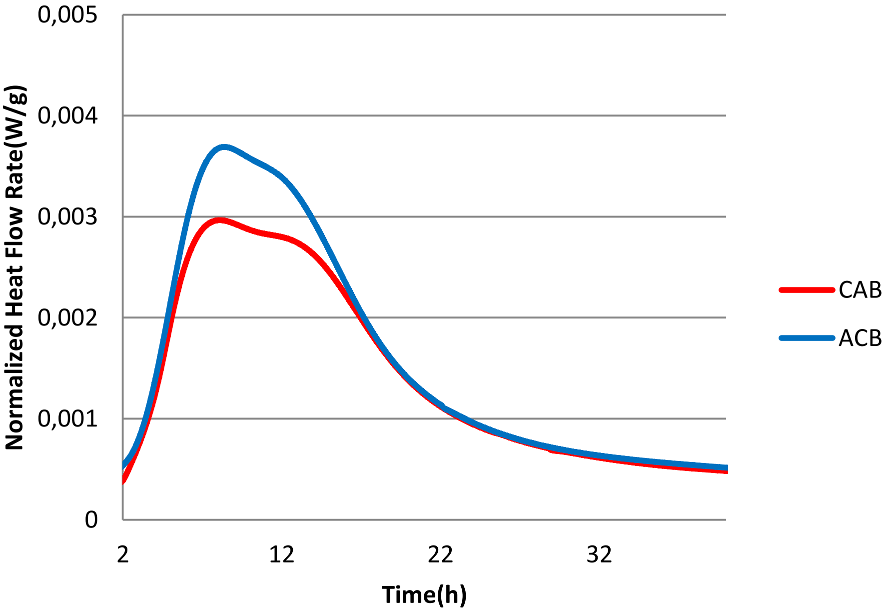


Figure 4.21. First peak in rate of heat evolution versus time curves of pastes CAB and ACB

First peak in rate of heat evolution versus time curves of pastes CAB and ACB are presented in Figure 4.21. Both of the rate of heat evolution curves of CAB and ACB show a tendency to a second peak but a definite second peak is not observed. Observation of second peak at CAB curve is expected since strength development graph show definite slag hydration. On the contrary second peak tendency is not expected at ACB curve because of low strength despite contribution of slag. This result shows that in terms of strength development controlled gradation of ACB is not suitable since with same materials and different gradation combination high strength is obtained in CAB.

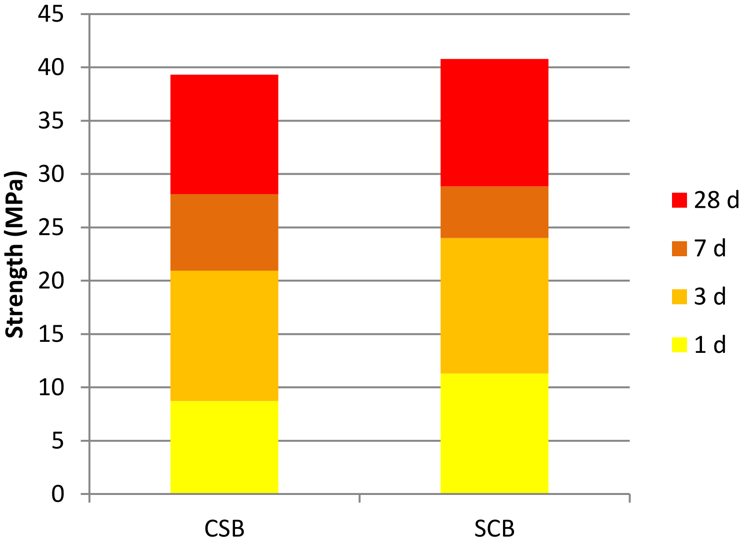


Figure 4.22. Strength development of CSB and SCB

Strength development of CSB and SCB are given in Figure 4.22. Strength development behavior of CSB and SCB are close to each other. Strength development between 7th and 28th days is also close to each other which is an indicator of slag hydration. Thus higher 28 d strength of SCB can be related to higher cement content compared to CSB.

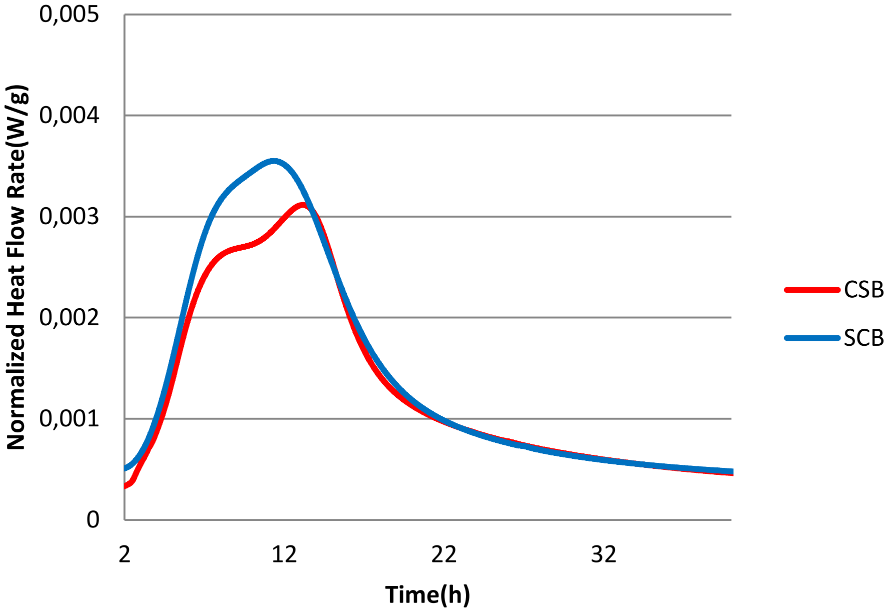


Figure 4.23. First peak in rate of heat evolution versus time curves of pastes CSB and SCB

First peak in rate of heat evolution versus time curves of pastes CSB and SCB are presented in Figure 4.23. A definite and a higher second peak is observed in CSB. This result shows that controlled gradation is effective in terms of slag activation in CSB. SCB has a rate of heat evolution curve similar to cement mixtures. This result demonstrates that cement content dominates the hydration behavior.

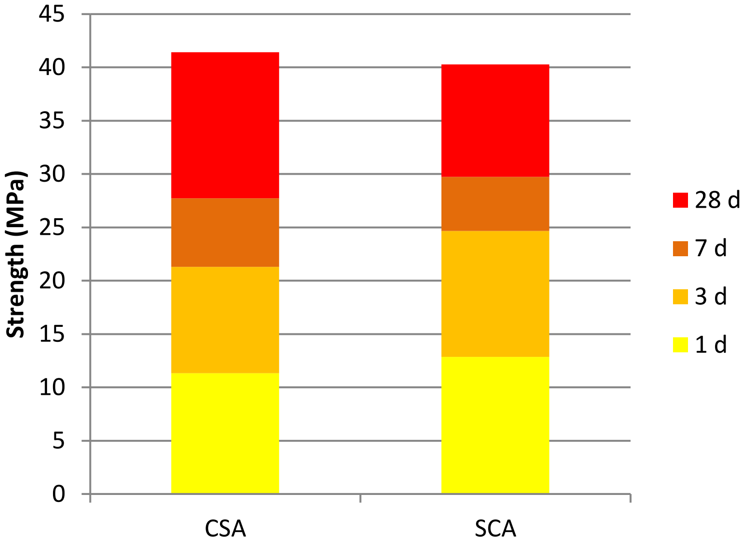


Figure 4.24. Strength development of CSA and SCA

Strength development of CSB and SCB are given in Figure 4.24. Strength development behavior of CSA and SCA are close to each other. CSA has a higher strength development between 7th and 28th days. Slightly higher 28 d strength of CSA can be related to hydration of slag. Compared to CSA low strength and high heat liberation is observed in SCA.

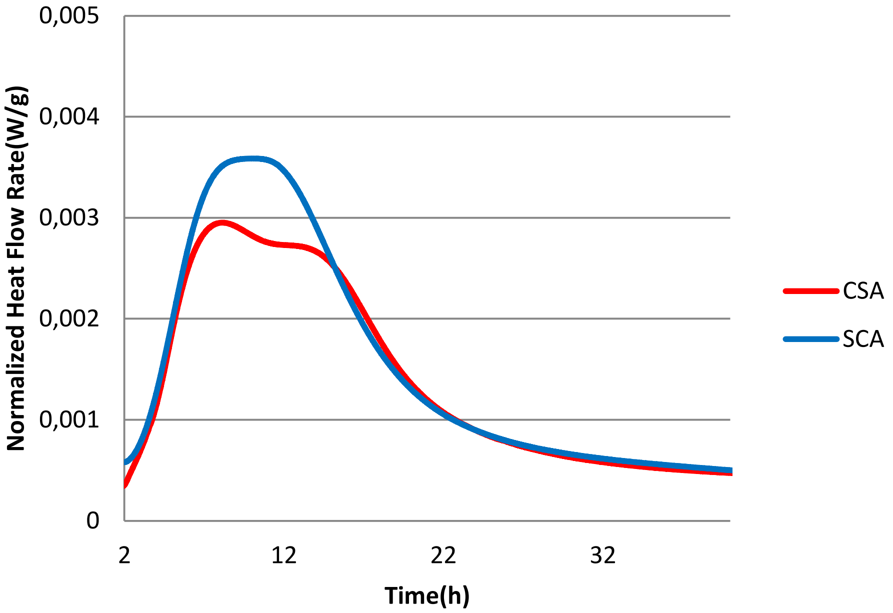


Figure 4.25. First peak in rate of heat evolution versus time curves of pastes CSA and SCA.

First peak in rate of heat evolution versus time curves of pastes CSA and SCA are presented in Figure 4.25. Effect of slag hydration is not observed in CSA rate of heat evolution curve, since only one peak is seen with a typical curve similar to mixtures containing cement only. A second peak is observed rate of heat evolution curve of SCA. Slag hydration taken place but not very effective since second peak is lower than first one. In terms of slag activation this result is positive cause because effect of slag hydration is observed despite the fact that slag content is low and coarser compared to CSA.

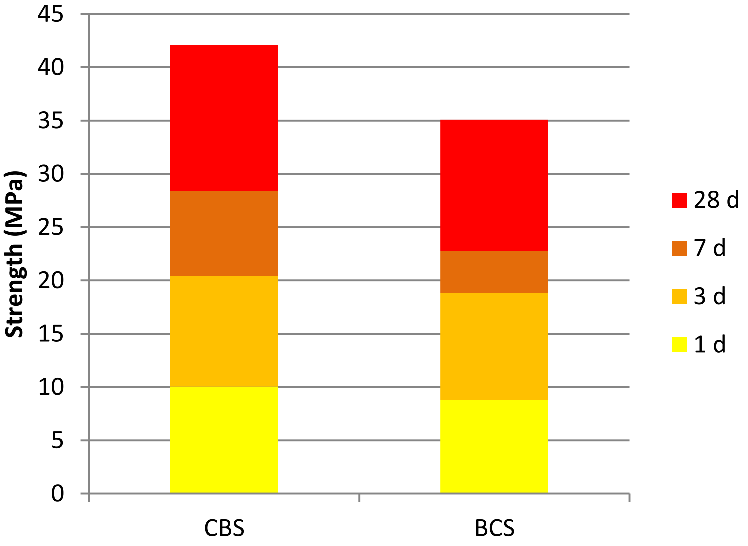


Figure 4.26. Strength development of CSB and BCS

Strength development of CSB and SCB are given in Figure 4.26. Although 1 d strength is close to each other strength development of CBS in latter stages is the main reason of the 28 d strength difference. This result shows that slag activation of CBS is more than BCS.

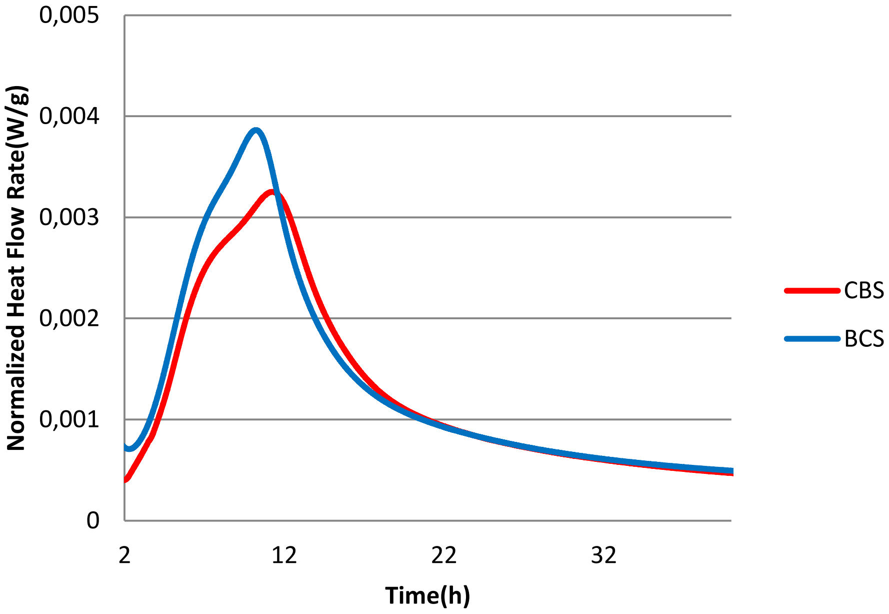


Figure 4.27. First peak in rate of heat evolution versus time curves of pastes CBS and SCB.

First peak in rate of heat evolution versus time curves of pastes CBS and SCB are presented in Figure 4.27. Definite and higher second peaks are observed in both of the rate of heat evolution curves of the pastes. Although a sharper and higher second peak of BCS shows that slag is hydrated, 28 d strength is low and heat liberation is high compared to CBS.

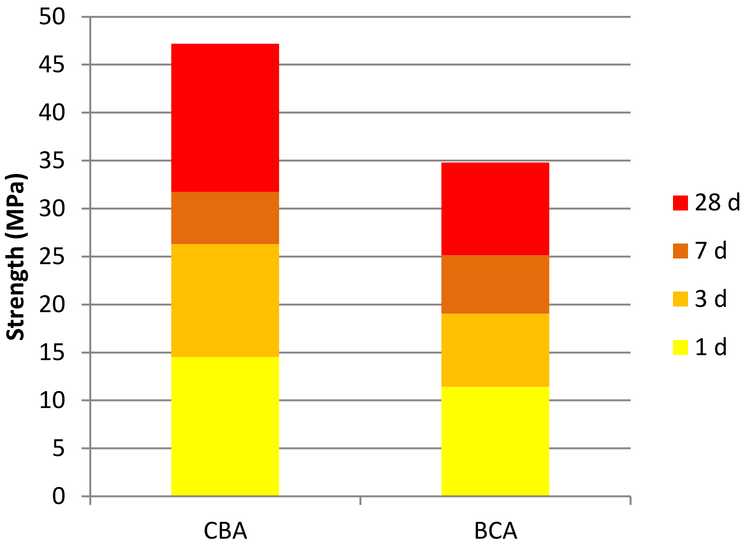


Figure 4.28. Strength development of CBA and BCA

Strength development of CBA and BCA are given in Figure 4.28. 28 d strength of CBA is 35% higher than 28 d strength of BCA. Except the period between 3 rd and 7 th days strength development of CBA is faster than BCA.

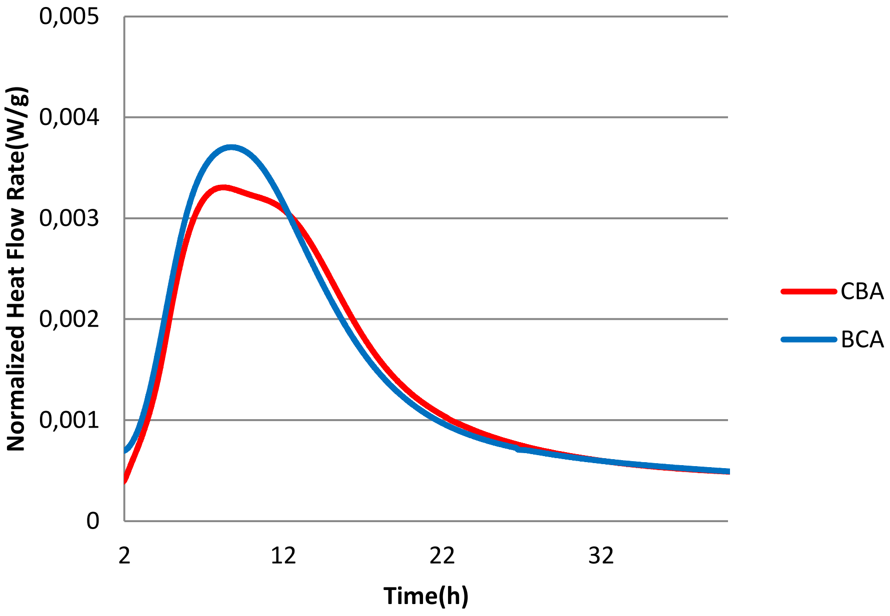


Figure 4.29. First peak in rate of heat evolution versus time curves of pastes CBA and BCA.

First peak in rate of heat evolution versus time curves of pastes CBS and SCB are presented in Figure 4.27. Effect of slag hydration is not observed in rate of heat evolution curve of BCA since a second peak is not observed. For CBA a second peak is observed but it is lower than the first peak which means that hydration rate of cement is higher than slag hydration.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. General

In this study, the effects of controlled gradation of cement and blast furnace slag on strength and heat of hydration development were investigated by measuring 1-d, 3-d, 7-d, and 28-d strengths and 48-h heat of hydration.

The behavior of mixtures containing different types of clinkers, prepared to obtain a controlled overall gradation, was compared with those in the control group of mixtures containing only one type of clinker. In addition behavior of clinkers with different fineness were investigated in terms of compatibility. The following conclusions were drawn:

- Using fineness versus grinding time tables to obtain materials with desired, specific finenesses does not give successful results since widely varying results were obtained from air permeability test.
- Increase in fineness results in more rapid hydration and higher early strength for Portland cements but this is not valid for blast furnace slag-containing mixtures. Blast furnace slag can activate more efficiently in coarser particles depending on its compatibility with the cement.
- The individual strength developments of clinkers dominate the 28-day strength of mixtures containing only clinkers.
- When blast furnace slag is efficiently activated it is possible to obtain high strength with low heat of hydration.
- Controlled gradation is not very successful in terms of strength development in mixtures not containing blast furnace cement but with the right combination, it can be very effective in mixtures containing blast furnace slag.

5.2. Recommendations for Further Studies

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

- Similar studies can be carried out with clinkers having more widely varying chemical compositions.
- Other mineral admixtures such as limestone powder, fly ash, silica fume, etc. can be studied.

Similar studies can be carried out with different fineness percentage combinations and comparisons between those studies may lead to more successful combinations for usage of mineral admixtures.

REFERENCES

Aïtcin, P.-C. and S. Mindess (2011). Sustainability of Concrete (Modern Concrete Technology), Spon Press, London.

Barnes, P. and J. Bensted (2002). Structure and Performance of Cements, Taylor & Francis.

Ekincioglu, O., A. P. Gurgun, Y. Engin, M. Tarhan and S. Kumbaracibasi (2013). "Approaches for sustainable cement production – A case study from Turkey." Energy and Buildings **66**(0): 136-142.

Erdoğan, T. Y. (2007). Beton Ankara, Turkey, Metu Press Publishing Company.

Geven, Ç. (2009). Investigation of the properties of portland slag cement produced by separate grinding and intergrinding methods M.Sc Thesis, METU.

Hayes, D. (2007). Global Slag Magazine. Turkish slag cement industry seeks new markets. Surrey, UK, PRo Publications International Ltd**:** 30-32.

Hewlett, P. (2003). Lea's chemistry of cement and concrete, Butterworth-Heinemann.

Industry General Directorate (2013). Demir çelik sektörü raporu. Sektörel Raporlar ve Analizler Serisi. M. o. S. Republic of Turkey, Industry and Technology Internet.

Mehta, P. and P. J. M. Monteiro (2005). Concrete : Microstructure, Properties, and Materials, Mcgraw-hill.

Mindess, S., J. F. Young and D. Darwin (2003). Concrete, Prentice Hall PTR.

Naik, T. (2008). "Sustainability of Concrete Construction." Practice Periodical on Structural Design and Construction **13**(2): 98-103.

Öner, M., K. Erdoğdu and A. Günlü (2003). "Effect of components fineness on strength of blast furnace slag cement." Cement and Concrete Research **33**(4): 463-469.

Ramachandran, V. S. (1996). Concrete admixtures handbook: properties, science and technology, Access Online via Elsevier.

Siddique, R. and M. I. Khan (2011). Supplementary cementing materials, Springer.

Taylor, H. F. (1997). Cement chemistry, Thomas Telford.

TCMA. (2013). "Monthly Data." Retrieved 15/08/2013, 2013.

Tokyay, M. and K. Erdoğdu (2009). Curüflar ve Curüflu Çimentolar. Ankara, Turkey, Turkish Cement Manufacturers Association.

TRMCA. (2013). "STATISTICS." Retrieved 25 August, 2013, from http://www.thbb.org/Content.aspx?ID=12.

Ulubeyli, S. (2013). "Drivers of environmental performance of cement plants." Industrial Management & Data Systems **113**(8): 8-8.

USGS (2003). SLAG—IRON AND STEEL. U.S. GEOLOGICAL SURVEY MINERALS YEARBOOK—. U. G. Survey. Internet.

USGS (2011). Report on USGS Mineral Program Cement. Mineral Commodity Summaries. U. G. Survey. Internet.

Zhang, T., Q. Yu, J. Wei and P. Zhang (2011). "A new gap-graded particle size distribution and resulting consequences on properties of blended cement." Cement and Concrete Composites **33**(5): 543-550.

APPENDIX A

COMPRESSIVE STRENGTH AND HEAT OF HYDRATION RESULTS

Table A.1 Compressive strength and 48-h heat of hydration results

Mixture ID	**Strength (MPa)**				**48-h Heat of Hydration (J/g)**
	1 Day	**3 Days**	**7Days**	**28 Days**	
ABS	27.2	31.1	41.0	42.6	308.7
SAB	21.8	27.4	37.3	44.9	344.1
BSA	21.1	34.6	37.8	45.2	295.4
ASB	25.1	29.0	35.4	44.0	308.5
SBA	17.8	32.5	35.0	41.7	342.4
BAS	16.2	25.1	30.0	31.9	327.0
CAS	8.5	19.7	27.7	39.5	250.9
CAB	9.6	21.4	26.1	42.6	263.7
CSB	8.7	20.9	28.1	39.3	240.2
CSA	11.3	21.3	27.7	41.4	258.2
CBS	10.0	20.4	28.4	42.1	239.8
CBA	14.5	26.3	31.7	47.2	263.6
ACB	15.2	23.1	30.8	34.3	280.7
SCA	12.8	24.7	29.7	40.3	272.7
BCS	8.8	18.8	22.7	35.1	251.5
ACS	13.1	21.6	24.0	38.4	263.6
SCB	11.3	24.0	28.8	40.8	255.8
BCA	11.4	19.1	25.1	34.8	271.9
AAA	28.6	34.7	40.3	48.0	352.6
BBB	22.2	27.9	41.9	44.1	328.8
SSS	18.4	30.5	38.3	37.8	301.4
CAA	13.0	25.2	34.7	46.7	264.8
CBB	11.4	24.7	32.4	42.8	247.2
CSS	7.7	18.5	25.3	39.4	254.5
ACA	18.0	27.0	30.7	42.9	279.1
BCB	10.4	20.1	28.1	39.2	259.1
SCS	8.6	20.7	24.0	39.4	248.4

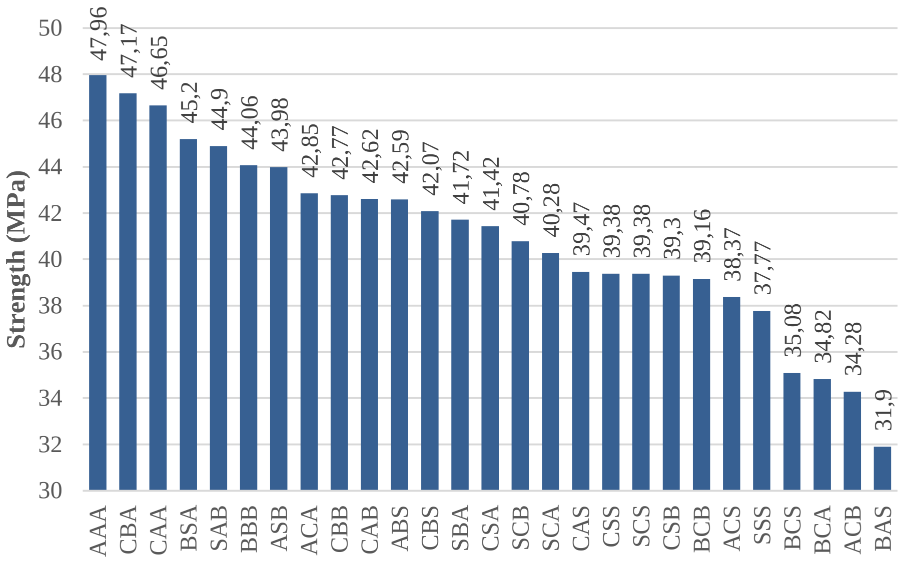


Figure A.1 28-day strength results in descending order

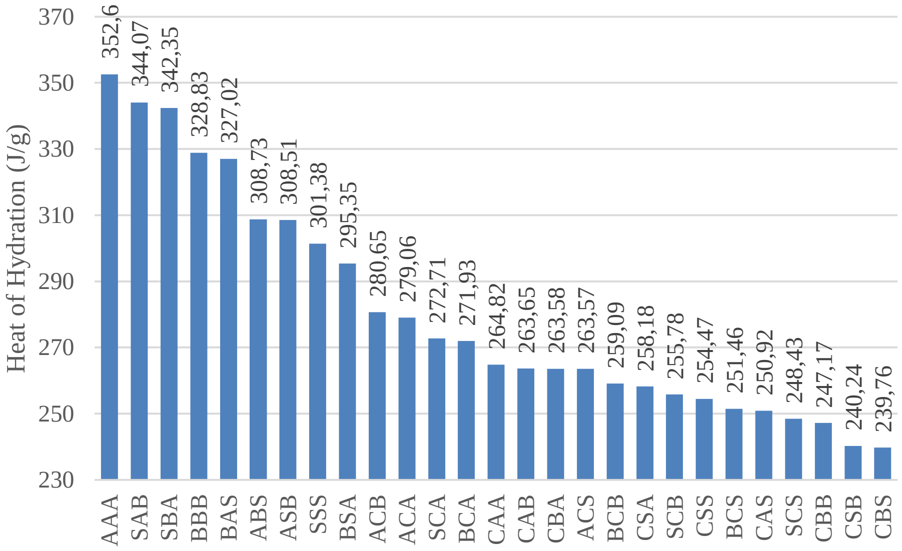


Figure A.2 48 h heat of hydration at results in descending order