

A STUDY ON BLENDED BOTTOM ASH CEMENTS

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## **ABSTRACT**

### **A STUDY ON BLENDED BOTTOM ASH CEMENTS**

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Cement production which is one of the most energy intensive industries plays a significant role in emitting the greenhouse gases. Blended cement production by supplementary cementitious materials such as fly ash, ground granulated blast furnace slag and natural pozzolan is one of the smart approaches to decrease energy and ecology related concerns about the production.

Fly ash has been used as a substance to produce blended cements for years, but bottom ash, its coarser counterpart, has not been utilized due to its lower pozzolanic properties. This thesis study aims to evaluate the laboratory performance of blended cements, which are produced both by fly ash and bottom ash.

Fly ash and bottom ash obtained from Seyitömer Power Plant were used to produce blended cements in 10, 20, 30 and 40% by mass as clinker replacement materials. One ordinary portland cement and eight blended cements were produced in the laboratory. Portland cement was ground 120 min to have a Blaine value of  $3500\pm 100$

cm<sup>2</sup>/g. This duration was kept constant in the production of bottom ash cements. Fly ash cements were produced by blending of laboratory produced portland cement and fly ash. Then, 2, 7, 28 and 90 day compressive strengths, normal consistencies, soundness and time of settings of cements were determined.

It was found that blended fly ash and bottom ash cements gave comparable strength results at 28 day curing age for 10% and 20% replacement. Properties of blended cements were observed to meet the requirements specified by Turkish and American standards.

Keywords: Blended Cement, Fly Ash, Bottom Ash, Compressive Strength

## ÖZ

### TABAN KÜLÜ KATKILI ÇİMENTOLARA YÖNELİK BİR ÇALIŞMA

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Enerji sarfiyatı yüksek imalat sürecine sahip endüstrilerden biri olan çimento üretimi, salınan sera gazları hususunda ciddi bir orana sahiptir. Uçucu kül, öğütülmüş fırın cürufu ve doğal puzolan gibi çimento yerine kullanılabilir maddelerin yardımıyla gerçekleştirilen katkılı çimento üretimi, enerji sarfiyatını ve ekolojik olumsuzlukları indirmek amacıyla uygulanabilecek yöntemlerden biridir.

Uçucu külün katkılı çimento üretiminde yıllardır kullanılmasına rağmen, uçucu külün daha büyük tane boyutlu emsali olarak tanımlanabilecek taban külü, düşük puzolanik özellikleri sebebiyle kullanılmamaktadır. Bu tez, uçucu kül ve taban külü kullanılarak üretilmiş katkılı çimentoların laboratuvar ortamındaki performanslarının değerlendirilmesini amaçlamaktadır.

Seyitömer Termik Santralinden tedarik edilen uçucu kül ve taban külü, klinker muadili olarak kütlece %10, 20, 30 ve 40 oranlarında kullanılmıştır. Laboratuvar ortamında bir portland çimentosu ve sekiz katkılı çimento örneği hazırlanmıştır.

Portland çimentosu  $3500\pm 100$  cm<sup>2</sup>/g Blaine deęerine sahip olacak şekilde 120 dk öğütölmüştür. Bu öğütme süresi, taban külü katkılı çimento üretiminde de aynen uygulanmıştır. Uçucu külü katkılı çimento, laboratuvar ortamında hazırlanmış çimento ile uçucu külü harmanlanması ile hazırlanmıştır. Daha sonra, çimentoların 2, 7, 28 ve 90 günlük mukavemetleri, normal kıvamları, hacim sabitlilięi ve priz süreleri belirlenmiştir.

%10 ve %20 oranlarında uçucu külü ve taban külü kullanılan katkılı çimentolar, 28 gün kütleme süresi sonunda kıyaslanabilir sonuçlar vermişlerdir. Hazırlanan tüm katkılı çimentoların, Türk ve Amerikan standartları tarafından belirlenen özellikleri karşıladığı tespit edilmiştir.

Anahtar Kelimeler: Katkılı Çimento, Uçucu Külü, Taban Külü, Basınç Dayanımı

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## TABLE OF CONTENTS

ABSTRACT .....	iv
ÖZ .....	vi
ACKNOWLEDGMENTS .....	viii
TABLE OF CONTENTS .....	ix
LIST OF TABLES .....	xi
LIST OF FIGURES .....	xii
LIST OF ABBREVIATIONS .....	xiii
CHAPTERS	
1. INTRODUCTION.....	1
1.1 General .....	1
1.2 Objective and Scope .....	2
2. LITERATURE SURVEY .....	4
2.1 Portland Cement .....	4
2.2 Blended Cements.....	4
2.3 Types of Portland and Blended Cement.....	5
2.4 Mineral Admixtures.....	7
2.5 Fly Ash .....	8
2.5.1 Definition and Classification of Fly Ash.....	8
2.5.2 Physical Properties of Fly Ash .....	9
2.5.3 Chemical Composition of Fly Ash .....	10
2.5.4 Use of Fly Ash in the Cement Industry .....	11
2.5.4.1 Effects of Fly Ash on Cement or Concrete Properties.....	11
2.5.4.2 Effects of Fly Ash on Fresh Cement or Concrete .....	12
2.5.4.3 Effects of Fly Ash on Hardened Cement or Concrete.....	13
2.6 Bottom Ash.....	16
2.6.1 Definition and Classification of Bottom Ash .....	16
2.6.2 Physical Properties of Bottom Ash.....	17
2.6.3 Chemical Composition of Bottom Ash.....	17

2.6.4 Use of Bottom Ash in the Cement Industry.....	18
2.6.4.1 Effects of Ground Bottom Ash on Mortar and Concrete Properties....	19
3. EXPERIMENTAL STUDY.....	24
3.1 Experimental Program.....	24
3.2 Materials.....	26
3.3 Production of Blended Cements.....	27
3.4 Tests Conducted on Materials.....	29
3.5 Tests Conducted on Cement Pastes and Cement Mortars.....	30
3.5.1 Tests on Cement Paste.....	31
3.5.2 Test Performed on Cement Mortar.....	32
3.6 Curing Conditions.....	32
4. RESULTS AND DISCUSSIONS.....	33
4.1 Material Properties.....	33
4.1.1 Portland Cement Clinker and Gypsum.....	33
4.1.2 Coal Ashes.....	33
4.2 Blended Cements.....	36
4.3 Physical and Mechanical Properties of Cements.....	37
4.3.1 Fineness and Specific Gravity.....	37
4.3.2 Normal Consistency.....	40
4.3.3 Setting Times.....	41
4.3.4 Volume Expansion (Soundness).....	42
4.3.5 Compressive Strength.....	43
4.4 Statistical Analysis of Compressive Strength of Cements.....	46
5. CONCLUSIONS AND RECOMMENDATIONS.....	52
REFERENCES.....	54
APPENDIX A PARTICLE SIZE DISTRIBUTIONS.....	60

## LIST OF TABLES

### TABLES

Table 3.1 Cement Labels in the Study .....	25
Table 3.2 The Description of the Abbreviations Used for the Cement Labels .....	26
Table 3.3 Size Distribution of the Grinding Media.....	28
Table 3.4 Raw Material Proportions Used in Producing Cements .....	28
Table 3.5 Tests Performed on Materials .....	29
Table 3.6 Tests Performed on Cement Pastes and Mortars .....	31
Table 4.1 Oxide Composition of the Portland Cement Clinker.....	33
Table 4.2 Some Chemical and Physical Properties of Coal Ashes .....	34
Table 4.3 Variation of Blaine Fineness and Specific Gravity of Portland Cement with Grinding Time.....	37
Table 4.4 Specific Gravity and Blaine Fineness Results of Cements .....	38
Table 4.5 Normal Consistency Results of Pastes.....	40
Table 4.6 Setting Times of Cements .....	41
Table 4.7 Le Chatelier Expansion Values of Cements .....	42
Table 4.8 Compressive Strength Results of Cements .....	43
Table 4.9 Statistical Analysis of Compressive Strength of Blended Cements on 2 <sup>nd</sup> Day .....	47
Table 4.10 Statistical Analysis of Compressive Strength of Blended Cements on 7 <sup>th</sup> Day .....	49
Table 4.11 Statistical Analysis of Compressive Strength of Blended Cements on 28 <sup>th</sup> Day .....	50
Table 4.12 Statistical Analysis of Compressive Strength of Blended Cements on 90 <sup>th</sup> Day .....	51
Table A.1 Particle Size Distribution for Fly Ash, Ordinary Portland Cement and Blended Cements .....	60

## LIST OF FIGURES

### FIGURES

Figure 4.1 General Morphology of Fly Ash .....	35
Figure 4.2 Microstructure of Fly Ash .....	35
Figure 4.3 Particle Size Distribution of Fly Ash.....	36
Figure 4.4 Particle Size Distributions of Blended Fly Ash Cements.....	39
Figure 4.5 Particle Size Distributions of Blended Bottom Ash Cements .....	39
Figure 4.6 Strengths of Blended Fly Ash Cements as Percentage of that of OPC ....	45
Figure 4.7 Strengths of Blended Bottom Ash Cements as Percentage of that of OPC .....	45
Figure 4.8 Compressive Strengths of Blended Cements at 2 <sup>nd</sup> Day as Percentage of Strength of OPC at 28 <sup>th</sup> Day .....	47
Figure 4.9 Compressive Strengths of Blended Cements at 7 <sup>th</sup> Day as Percentage of Strength of OPC at 28 <sup>th</sup> Day .....	48
Figure 4.10 Compressive Strengths of Blended Cements at 28 <sup>th</sup> Day as Percentage of Strength of OPC at 28 <sup>th</sup> Day .....	49
Figure 4.11 Compressive Strengths of Blended Cements at 90 <sup>th</sup> Day as Percentage of Strength of OPC at 28 <sup>th</sup> Day .....	51

## **LIST OF ABBREVIATIONS**

<b>ASTM</b>	:	American Society for Testing and Materials
<b>BA</b>	:	Blended Bottom Ash Cement
<b>CA</b>	:	Calcium Hydroxide
<b>CSH</b>	:	Calcium Silicate Hydrate
<b>FA</b>	:	Blended Fly Ash Cement
<b>PC</b>	:	Portland Cement
<b>OPC</b>	:	Ordinary Portland Cement
<b>TCMA</b>	:	Turkish Cement Manufacturers' Association
<b>TS EN</b>	:	Turkish Standard Harmonized to European Norms

# CHAPTER 1

## INTRODUCTION

### 1.1 General

Cement production is an energy intensive industry. There are also environmental concerns like greenhouse gas emissions, fuel consumptions and mining activities related with extracting raw materials. It is reported that one ton of cement production approximately gives one ton of CO<sub>2</sub> emission and minor amounts of other greenhouse gases such as NO<sub>x</sub> and CH<sub>4</sub> into the atmosphere (Bouzoubaa et al., 1998). Nearly half of the CO<sub>2</sub> emissions derived from the production stem from calcination of the limestone and other half stems from burning of fossil fuels (Bouzoubaa et al., 1998). Furthermore, the Earth has limited amounts of natural resources. Therefore, the use of by products from thermal power generation and metallurgical operations as clinker substitute generally in amount of 20% to 60% by mass might result in energy savings (Malhotra and Mehta, 1996).

Cement replacement materials include by-products of other industries such as fly ash from power plants and granulated blast furnace slag from iron and steel factories or natural materials such as volcanic tuffs and diatomaceous earths. Those materials are known as mineral admixtures which have pozzolanic, hydraulic or both pozzolanic and hydraulic properties (Erdoğan, 1997). The incorporation of these materials increases the performance of fresh and hardened concrete (Detwiler et al., 1996). The utilization of waste materials as both cement additive and fillers in concrete have increased remarkably in recent years (Erdoğan et al., 1999) due to economical, ecological and engineering benefits of the usage (Plessis et al., 2007).

Among these additives, fly ash has been utilized since 1930's as

cement replacement material and mineral additive in concrete whereas bottom ash and boiler slag are utilized as a replacement material for sand or as a construction fill rather than pozzolanic properties due to insufficient pozzolanic properties and high unburned carbon content. This thesis study deals with the usage of bottom ash as mineral admixture in blended cement production.

In short, uprising environmental awareness, increasing cost associated with cement production and problems with more space to build new landfills and ash ponds for coal combustion by products and wishes for the protection of the natural resources from being exhausted, environmentally sound and profitable solutions should be put into action.

## **1.2 Objective and Scope**

The main goal of this thesis is to evaluate the performance of bottom ash when used as a partial replacement of clinker in blended cement production. For this purpose, bottom ash and fly ash were obtained from the same power plant, named Seyitömer. Then blended cements were produced by 10, 20, 30 and 40% clinker replacement by mass. Performance of bottom ash was compared with that of fly ash in terms of fresh and hardened properties of cement pastes and mortars.

This thesis consists of six chapters:

Chapter 2 describes portland cement and blended cements with their types. This chapter also gives information about mineral admixtures, fly ash and bottom ash and their effects on cementitious systems.

Chapter 3 presents experimental program applied through the study, the description of the materials used, production of the cements and tests conducted on the materials.

Chapter 4 presents the performance of blended fly ash and bottom ash cement such

as that of normal consistency, setting time, soundness, compressive strength and statistical analysis of average compressive strength of blended fly ash and blended bottom ash cements.

Chapter 5 presents the conclusion of the evaluation of performance of cements and provides recommendations for future studies.



## **CHAPTER 2**

### **LITERATURE SURVEY**

#### **2.1 Portland Cement**

Cement is an adhesive substance with the ability of bonding fragments into a compact whole (Hawlett, 2004). For construction purposes, the cements of interest in making of concrete have the ability of setting and hardening under water by virtue of a chemical reaction with it (Neville, 2000). Chemical composition of these cements change in a wide range, but most preferable concrete today is produced from portland cements (Mindness and Young, 1981).

Portland cement is a hydraulic binder which retains strength and stability by time and has the ability of bonding of other materials together, is produced from ground portland cement clinker and calcium sulfate. The term hydraulic cement refers to a powdery material that produces a durable and water insoluble product after reacting with water (Popovics, 1992). Portland cement clinker is made from a mixture of raw materials consisting lime, silica and small amounts of alumina and iron which are treated in hot temperature. Since Joseph Aspdin first produced portland cement in 1824, the production process enhances; but, the term of portland cement is used for all the cements manufactured by the burning of calcareous and clayed materials (Erdoğan, 2005).

#### **2.2 Blended Cements**

Blended cements are hydraulic binders consisting essentially of an intimate and uniform blend of at least two inorganic constituents including portland cement clinker. They are used in the same manner as portland cements (Nawy, 1997) or

are designed for an specific purpose and may improve some mechanical or physical properties of the ordinary portland cement.

A number of latently hydraulic, pozzolanic or inert fillers can be used as additions to blended cements or as mineral admixtures in concrete, with granulated blast furnace slag and fly ash leading the way (Mullick, 1997).

Blended cements are made either by intergrinding portland cement clinker and the supplementary cementitious materials such as natural pozzolan, fly ash, slag, etc. by blending portland cement and finely divided replacement materials, or a combination of intergrinding and blending (Popovics, 1992).

### **2.3 Types of Portland and Blended Cement**

The demands of the construction industry for various applications lead to different kinds of portland cements to meet different physical and chemical requirements. ASTM and Turkish standards describe the different types of cements and their required properties.

The European and Turkish standard TS EN 197-1, Compositions and Conformity Criteria for Common Cements covers five main types of cements:

- CEM I (Portland cement) is produced by intergrinding the portland cement clinker and calcium sulfate and also at most 0-5% mineral additives together.
- CEM II (Portland-composite cement) includes 6-35% supplementary material and portland cement. Cement is labeled as either Portland slag cement or Portland Pozzolan cement depending on the additive type.
- CEM III (Blastfurnace cement) contains portland cement and up to 95% of granulated blast furnace slag.
- CEM IV (Pozzolanic cement) contains 11-55% of pozzolans and fly ash as additives. Granulated blast furnace slag and limestone is not added as

supplementary materials into this kind of cement type.

- CEM V (Portland composite cement) includes portland cement and up to 50% of blastfurnace slag or fly ash and pozzolana.

In the above list, CEM II through V designates blended cements.

According to TS EN 197-1, CEM cements consist of at least 50% of total reactive CaO and reactive SiO<sub>2</sub> by mass. It may consist of portland cement clinker, calcium sulfate and different types of mineral admixtures.

On the other hand, American standards differentiate portland cement and blended cements, and provide two different standards. American Standard ASTM C 150, Standard Specification for Portland Cement covers five types of portland cements:

- Type I is used for general purposes that the use of the special cements are not required.
- Type II portland cement is preferred when moderate sulfate resistance is needed.
- Type III is used to meet high early strength requirement.
- Type IV provides low heat of hydration.
- Type V is used in applications that severe sulfate resistance is required.

ASTM C 595, Standard Specifications for Blended Portland Cements specifies following types of blended cements: Blended hydraulic cements to use in general concrete applications, Type IS portland-blast furnace slag and Type IP portland-pozzolan cement.

Type IS is an intimate and uniform blend of portland cement and fine granulated blast furnace slag in which slag constituent is up to 95% of the weight of portland blast-furnace slag cement.

Type IP is an intimate and uniform blend of portland or portland blast-furnace slag cement and fine pozzolan in which the pozzolan constituent is up to 40% of the weight of the portland pozzolan cement.

According to ASTM C 595, these blended cements may also come in the form of carrying features such as air-entraining, moderate sulfate resistant, or with moderate or low heat of hydration.

All portland and blended cements are hydraulic cements. In addition the standards mentioned above, ASTM C 1157, Performance Specification for Hydraulic Cements pertains to hydraulic cements including portland cement, modified portland cement and blended portland cement. ASTM C 1157 covers six types of hydraulic cements given as follows:

Type GU General use

Type HE High early strength

Type MS Moderate sulfate resistance

TYPE HS High sulfate resistance

Type MH Moderate heat of hydration

Type LH Low heat of hydration

## **2.4 Mineral Admixtures**

Mineral admixtures are added to concrete in finely divided form either before or during mixing (Erdoğan, 1997). They may change various properties of fresh and hardened concrete. The properties of concrete are affected by physical and chemical properties of the admixtures and also the amount of it used in concrete. Mineral admixtures can be examined in four broad parts as follows (Erdoğan, 1997):

- By-product or waste materials such as fly ashes or slags
- Natural materials derived from volcanic rocks and minerals and diatomaceous earths

- Calcined natural materials such as calcined shales and clays
- Cementitious materials such as natural cements and hydraulic limes

Mineral admixtures have pozzolanic, cementitious and also both pozzolanic and cementitious properties. Most of the mineral admixtures today are pozzolanic materials.

A pozzolan is defined as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementing property but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (Mehta and Monterio, 2006).

Volcanic ashes, trasses, volcanic glasses, pumicities, calcined clays, diatomaceous earths, fly ashes, silica fumes and rice husk ashes are the commonly known materials that carry pozzolanic properties.

## **2.5 Fly Ash**

### **2.5.1 Definition and Classification of Fly Ash**

Fly ash is the fine solid residue generated from combustion of ground or powdered coal to produce electricity, which can be easily transported by flue gases and collected with the help of electro filters or cyclones. During coal combustion, carbon particles are burned, volatile matter evaporates and most of the remainder mineral part disintegrates (Ramachandran, 1995). The disintegrated particles turning out to molten state due to high burning temperature of coal, and later solidifies are mostly spherical particles called fly ash.

Most of the fly ash from the precipitators and bottom ash (coarser and denser particles that can not be collected from the exhaust gases) from the boilers are mixed

together and sent into the ash ponds in the form of slurry (Cheriat et al., 1999) or dumped to landfills (Kumar et al, 2004).

Fly ash has pozzolanic properties (American Concrete Institute [ACI], 1990). Therefore, it is a good cement replacement material to attain economic, environmental and technical benefits.

American standard ASTM C 618 specifies two types of fly ash considering the type of coal burned. First type, Class F fly ash is generally produced from burning anthracite or bituminous coal. Second type, Class C fly ash is produced from lignite or sub-bituminous coal. Class F fly ash include more than 70% of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ . Besides, the diagnosis of this type of ash is done by low CaO property which does not pass 10%. Class F type fly ash only possesses pozzolanic property. Class C fly ash contains more than total 50% of  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  and more than 10% of CaO. Class C type fly ash has self binding property in addition to pozzolanic property.

In TS EN 197-1, fly ashes are classified as siliceous (V) and calcareous (W) fly ashes. V type fly ash is a kind of ash in which reactive lime content should be less than 10% and reactive silica content should be more than 25%. V class fly ash has pozzolanic property. W class fly ash comprises more than 10% of reactive CaO and more than 25% of reactive  $\text{SiO}_2$ . This type of fly ash possesses self binding and pozzolanic properties.

### **2.5.2 Physical Properties of Fly Ash**

Physical properties of fly ash like the shape, particle-size distribution, and density have great importance on the properties of freshly mixed, unhardened concrete and strength development of hardened concrete (ACI, 1990).

The properties of particle size and shape of fly ashes are designated from the origin and uniformity of coal, the grade of pulverization, the combustion conditions

(temperature and oxygen levels), uniformity of combustion, the type of collection system used and the cooling rate (ACI, 1990; Ramachandran, 1995).

Fly ash particles range in size from 0.5  $\mu\text{m}$  to over 100  $\mu\text{m}$  in diameter. Fly ash particles mostly consists of glassy spherical solid and hollow forms which are either completely empty (cenospheres ) or spheres involving conglomeration of smaller particles existing in the bigger spheres (plerospheres) (Türker et al., 2007).

Specific gravity of fly ash shows great difference from average of 1.9 to 3.02. Wesche (1991) states that the maximum specific gravity value for fly ashes corresponds to the maximum  $\text{Fe}_2\text{O}_3$  content. Likewise, high carbon content reduces the specific gravity due to its porous structure.

### **2.5.3 Chemical Composition of Fly Ash**

Chemical properties of fly ashes depend on several factors including origin and geology of coal used, combustion process and techniques applying handling of coal (coal preparation, dust collection, desulfurization etc.) (Türker et al., 2007).

Fly ashes consist mostly of oxides including silicon dioxide ( $\text{SiO}_2$ ), aluminium oxide ( $\text{Al}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ). Besides, Class C fly ashes can include considerable amounts of calcium oxide ( $\text{CaO}$ ). Fly ash particles show a generally highly heterogeneous formation which consists of a combination of glassy particles and different crystalline phases such as quartz, mullite, and various iron oxides (ACI, 1990; Kumar and Theerthan, 2008).

Minor elements arised from the coal ash source encompass titanium, iron, magnesium, phosphorus, sulfur, oxygen, potasium, sodium, carbon and others as traces (ACI, 1990).

Loss on ignition rate derived from unburned carbon content, combined water and

carbon dioxide are at least 2% or more for Class F fly ashes and drop up to 1% for Class C fly ashes; (Görhan et al., 2009) indeed loss on ignition rate is mostly considered to equal unburned carbon content due to the trace existence of other constituents (Külaots et al., 2004).

#### **2.5.4 Use of Fly Ash in the Cement Industry**

First appearance of fly ash in concrete goes back to 1930's to reduce the heat of hydration in mass concrete. Since then fly ash has been utilized to improve durability of concrete. Fly ash can be used either as an additive in blended cement or an admixture in concrete. It can also be used as a raw material alternative to clay, shale etc. of portland cement clinker (low quality fly ash) and a fuel in the kiln (high-carbon fly ash) in cement industry (ACI, 1990; Wesche 1991).

Portland fly ash cement is a homogeneous mixture of portland cement clinker, fly ash and gypsum. In general, the fly ash content is 30% (Wesche, 1991). According to EN 197-1 portland fly ash cement may consist of up to 35% of fly ash by mass of the cementitious material.

There are also applications where fly ash is used as a replacement of lightweight aggregate.

##### **2.5.4.1 Effects of Fly Ash on Cement or Concrete Properties**

Fly ashes incorporating cementitious systems are generally known as their low heat of hydration natures. Besides, it is used in concrete for reasons including economics, improvements in workability, and contribution to durability and strength in hardened concrete (ACI, 1990). Since there are a great deal of investigations about fly ash incorporating cementitious systems, only general information will be given about the subject.



#### **2.5.4.2 Effects of Fly Ash on Fresh Cement or Concrete**

**Setting Time** - There is a general agreement that the use of fly ash as a partial replacement of cement increases both initial and final setting time of the concrete. Characteristics of fly ash and the amount used have influence on time of setting of fly ash cement. All Class F fly ashes generally increase the time of setting as most Class C fly ashes do. However, some Class C fly ashes containing high amounts of calcium oxide may have no significant effect to retard the setting time of concrete (Erdoğan, 1997).

**Water Requirement** - It is known that the use of fly ash reduces the water requirements at equal consistencies and increases the fluidity of cementitious systems. The effect of fly ash on the water requirement of the concrete mixture depends on the fineness of the fly ash particles and shape of the particles. The spherical particle shape provides lower internal friction and lowers the amounts of water (Erdoğan, 1997).

**Heat of Hydration** - Fly ash usage can reduce the rate and amount of heat evolution. Hydration processes of fly ash incorporating cementitious systems are much slower than the hydration of cement itself. This results in slower heat generation. Fly ash helps to reduce heat generation by as much as 15 to 35% as compared to cement at early days (Headwaters, 2005).

**Air-Entrainment** - Fly ash may influence the air content and the stability of entrained air voids (ACI, 1990). The reason that fly ash has such a critical role regarding air entrainment is related to unburned residual carbon. Fly ash carbon aims to interact with the surfactants used as air-entraining admixtures (Hill and Folliard, 2006). If constant air content is required, admixture dosage can be increased depending on the carbon content, loss on ignition, fineness and other organic material (ACI, 1990). The amount of increase depends on the type of fly ash used. A fly ash with a low loss on ignition (low carbon content) results in lower increase in

the amount of air-entraining admixtures than fly ash with a high loss on ignition (Erdoğan, 1997).

**Workability** - Workability of concrete mix containing fly ash is enhanced due to the fine particle size and spherical shape of fly ash particles (Ramachandran, 1995). When fly ash is added to concrete, paste volume increases. Increase in paste volume produces a concrete with improved plasticity and better cohesiveness (Halstead, 1986). Furthermore, when paste volume is increased, both the workability and pumpability of a concrete mixture are enhanced by decreasing the friction between aggregate particles (Malhotra, 1989). The effect of addition fly ash as aggregate supplement in workability and pumpability is significant when sand content decreased and coarse aggregate content increased.

**Bleeding** - The use of fly ash in concrete reduces the bleeding by hindering the channels of bleed-water flow and increasing the ratio of surface area of solids to the volume of water with the use of very fine ash particles (Erdoğan, 1997; Malhotra, 1989).

**Finishability** - Because setting time of concretes containing fly ash is usually longer, such concretes should be finished at a later time to prevent sealing the bleed water under the top surface creating a plane of weakness (Erdoğan, 1997).

#### **2.5.4.3 Effects of Fly Ash on Hardened Cement or Concrete**

**Strength** - The use of fly ash as cement replacement material is generally resulted in low early compressive strength. The early strength reductions can be coped with a low w/c ratio and with the use of a water reducing admixture (Mindness and Young, 1981). However, at later ages concretes with fly ash usually develop higher compressive strengths than concretes without fly ash.

**Permeability** - Fly ash concrete has lower permeability than that of a concrete made with plain cement. Permeability of concrete depends upon the proportion of CSH to  $\text{Ca(OH)}_2$  in the cement paste.  $\text{Ca(OH)}_2$  (calcium hydroxide) is a water soluble substance and can leave voids for the ingress of water after leaching out of hardened concrete (ACI, 1990). When the proportion of CSH to  $\text{Ca(OH)}_2$  is higher, the permeability of the concrete will be lower. Since fly ash concrete is used  $\text{Ca(OH)}_2$  which is liberated by the hydration reactions of cement to form new CSH, permeability of the concrete decreases.

**Sulfate resistance** - Fly ash also improves the sulfate resistance of concrete. Fly ash in concrete reduces sulfate attack by reacting with calcium hydroxides to form new calcium silicate hydrates. Additional calcium silicate hydrates fills the capillary pores in the cement paste reducing permeability of concrete. Since sulfate attack occurs when water containing sulfates and tricalcium aluminate or calcium hydroxide in cement comes in contact producing calcium sulfoaluminate hydrates which can expand excessively and thus forms cracks on the concrete. When fly ash is used in concrete, the amount of tricalcium aluminate will be reduced and thus the potential of this type of expansion is also reduced (Headwaters, 2005).

**Alkali-Silica Reactivity** - Aggregates containing certain forms of silicate react with high soluble alkalis in concrete to form a reaction product that expands in the presence of moisture and results in deleterious cracking of concrete (Obla, 2005). The reaction between the siliceous glass in fly ash and the alkali hydroxides in the portland cement paste consumes alkalis, which reduces their availability for expansion reactions with reactive silica aggregates. When the amount of fly ash in concrete is properly adjusted, detrimental effects of alkali silica reaction can be eliminated (ACI, 1990). Often the amount of fly ash necessary to prevent damage due to alkali-aggregate reaction is more than the optimum amount necessary for improvement of workability and strength properties of concrete (Erdoğan, 1997; ACI, 1990).

**Resistance to Freezing and Thawing** - The addition of fly ash does not affect the frost resistance of concrete significantly if the strength and air content are maintained constant (Ramachandran, 1995). Besides, proper amount of entrained air and air void distribution should be adjusted. When high amount of carbon containing fly ash is used (carbon content >6%), the dosage of air entraining admixtures (air entraining admixtures are introduced to improve freeze-thaw resistance of concrete) are increased to gain equal resistance like concrete without fly ash (ACI, 1990).

**Drying Shrinkage** - Drying shrinkage of concrete is mostly influenced by the fractional volume of the paste, the water and cement content, the cement type, and the type of aggregate (ACI, 1990; Erdoğan, 1997; Malhotra, 1989). Since water content is one of the factors of drying shrinkage and the usage of fly ash in concrete generally reduces the water requirement of the paste, drying shrinkage may be reduced or retain in same level as the concrete without fly ash. Yet, fly ash incorporation in concrete may increase paste volume. In that case, drying shrinkage may also be increased slightly if the water content remains constant (ACI, 1990). It has been reported that the addition of fly ash up to 25% does not significantly affect the drying shrinkage of the concrete (Malhotra, 1989).

**Bond of Concrete to Steel and to old Concrete** - The bond of concrete to steel aims to be affected by the surface area of steel in contact with the concrete, the depth of reinforcement, and the density of the concrete. The bleeding water accumulates at the lower interfaces of the reinforcing bars decreasing adhesion between the concrete and steel. The incorporation of fly ash in concrete increases the paste volume and decreases bleeding (ACI, 1990). Since fly ash reduces the bleeding of concrete, the bond of the concrete to steel may enhance.

**Corrosion of Reinforcing Steel in Concrete** - Corrosion indicators of reinforcing steel in concrete are by pH, electrical resistivity, soluble chloride content, and soluble sulfate content (Hosin, 2006). High amount of unburned carbon content of the fly ash can also worsen the corrosion of reinforcing steel. Corrosion of steel is an

electrochemical process. Unburned carbon content increases the electrical conductivity of the concrete. Yet, fly ash concrete with up to 6% unburned carbon content does not show any difference in reinforcing steel corrosion than concrete without fly ash (Ha et al., 2005). Likewise, sulfur compounds in fly ash are usually within the limits determined by the specifications and they are not materially different in the concrete whether fly ash is used or not (Erdoğan, 1997). Although the  $\text{Ca(OH)}_2$  which contributes to the alkalinity of concrete is utilized by the pozzolanic reaction of fly ash, similar pH degree to that in concrete without fly ash remains to provide a passive film protection (ACI, 1990).

## **2.6 Bottom Ash**

### **2.6.1 Definition and Classification of Bottom Ash**

Bottom ash, the solid residue from electric power generation process, represents the coarser size fraction which falls to the bottom of the combustion boiler. The combustion technologies and furnace type determines the characteristics of the material generated.

In dry pulverized bottom furnaces, ashes are collected as dry solids before complete melting occurs. These solid particles are collected in a collection hopper and removed by high- pressure water jets and conveyed to a disposal pond or a decant basin for dewatering, crushing, and stockpiling for disposal or use (Hecht and Duvall, 1975). This type of bottom ash is known as dry bottom ash. Material is dark gray in color and has porous, granular sand like appearance. On the other hand, the coarser ash obtained from wet boilers is called as boiler slag. During coal combustion, bottom ash is kept in molten state and tapped off as liquid. Molten material flows into the hopper where quenching water is held. When the molten slag comes in contact with water, it starts to crystallize and then forms pellets. Boiler slag consists of hard, black, angular and having glassy-like appearance materials (Coal Bottom Ash/Boiler Slag, 2009).

### **2.6.2 Physical Properties of Bottom Ash**

Like fly ash, physical properties of bottom ash depend on the coal type, preparation before combustion and temperature of combustion. Bottom ash displays physical properties similar to the that of natural sands (Kumar et al., 2004). Bottom ash has a high porous surface, large particle size, angular shape and glassy texture. Bottom ash particles range in size from a fine gravel to a fine sand (Kumar et al., 2004). The ash is usually a well-graded material; yet, the particle size distribution of ash samples obtained from the same power at different times can display variations (Kumar et al., 2004). Bottom ash particles tend to range in size between 50.8 mm and 0.075 mm (Churchill and Amirkhanian, 1999).

### **2.6.3 Chemical Composition of Bottom Ash**

Chemically, coal bottom ash has similar properties to fly ash and composition of bottom ash particles is controlled by the source of coal. Three predominant oxides are silicon dioxide ( $\text{SiO}_2$ ), aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and ferric oxide ( $\text{Fe}_2\text{O}_3$ ). Calcium oxide ( $\text{CaO}$ ), magnesium oxide ( $\text{MgO}$ ), sodium oxide ( $\text{Na}_2\text{O}_3$ ), potassium oxide ( $\text{K}_2\text{O}$ ), sulfur trioxide ( $\text{SO}_3$ ) and other minor oxides such as  $\text{P}_2\text{O}_5$ ,  $\text{TO}_2$  also occurs in lower amounts. Bottom ash which originally comes from lignite or sub-bituminous coals has a higher percentage of calcium than that of derived from anthracite or bituminous coals. There can also be some percentage of carbon particulate resulting from incomplete combustion.

Bottom ash and boiler slag could exhibit corrosive properties due to salt content and low pH. The potential for corrosion of metal components that would come in contact with boiler slag could be a concern and should be tested when bottom ash or boiler slag is used in embankment, backfill, subbase, or in a base course (Ke and Lowell, 1992). Information pertinent to this issue can be found in ACAA Technical Bulletin TB 51 Underground Corrosion of Metals in Bottom Ash Backfills. Testing to indicate potential corrosivity of boiler slag (or bottom ash) should evaluate pH,

electrical resistivity and soluble chlorides and sulfates (Ke and Lowell, 1992).

Materials are judged to be noncorrosive if the pH exceeds 5.5, the electrical resistivity is greater than 1,500 ohm-centimeters, the soluble chloride content is less than 200 parts per million (ppm), or the soluble sulfate content is less than 1,000 parts per million (ppm) (Ke and Lowell, 1992).

#### **2.6.4 Use of Bottom Ash in the Cement Industry**

Although the utilization of bottom ash either as a cement replacement material or a concrete mineral additive is not practiced due to high unburned carbon content as well as large particles size and a high porous surface, it possess pozzolanic properties. When it is ground, the pozzolanic properties will be enhanced. There are not any practical or industrial usages of bottom ash as a cement additive. Likewise there are not any standard that explains its usage in cement works. Nevertheless, TS EN 450 and ASTM 618 can be used as guides since chemical properties and mechanical properties are similar to that of fly ash.

The previous studies conducted showed that bottom ash could be a natural sand replacement material in concrete (Bai et al., 2005). Combustion process in power plants makes them a convenient alternative to lightweight aggregate with their well graded nature. One of the pioneering research about use of bottom ash as fine aggregate replacement material was done by Ghafoori and Bucholc (1997). They use a lignite based bottom ash from a power plant in Indiana as a fine aggregate in production of structural normal weight concretes. They observed that porous surface and angular shape of bottom ash particles increased quantity of mixing water causing the concrete mixture with bottom ash and combined bottom ash and natural sand mixture showed higher degree of bleeding than the reference concrete. Higher water requirement of bottom ash was also resulted in lower compressive strengths of concretes with bottom ash and combined bottom ash and natural sand mix. Yet, at later ages, the compressive strength of the bottom ash incorporated specimens

reached to similar values to the reference samples. Bottom ash incorporation systems had a lower modulus of elasticity than the reference sample. Concrete containing bottom ash as fine aggregate showed similar resistance to sulfate environment. Also, their resistances to abrasion were as 40% worse as the reference concrete whereas the resistance of concrete containing both natural sand and bottom ash was about 13% better than the reference concrete.

Detrimental effects of porous structure of bottom ash particles on permeation process beyond 30% replacement of natural sand was reported by Bai et al. (2005). Kohno et al. (1986) also indicated the improving effects of porous structure on shrinkage of concrete due to its internal curing effect through slow release of moisture from the saturated porous particle.

#### **2.6.4.1 Effects of Ground Bottom Ash on Mortar and Concrete Properties**

There are very limited amounts of studies about the usage of bottom ash as cement replacement or as concrete admixtures. Hopkins and Oates. (1998) stated that if particle size distribution of bottom ash is reduced under 45 $\mu$ m, the cementitious properties will enhance. Lower limit of the particle size after reduction might not be less than 1-2 $\mu$ m due to higher grinding costs.

**Strength Activity of Bottom Ash** - The strength activity index is the ratio of average compressive strength of test-mixture mortar cube or bar to the average compressive strength of control-mixture mortar cube or bar. ASTM C 311 describes strength activity test as “the test for strength activity index is used to determine whether fly ash or natural pozzolan results in an acceptable level of strength development when used with hydraulic cement in concrete”. Strength activities of pozzolans are determined according to the European standard EN 450 and American standard ASTM C 311.

Cherief et al. (1999) studied the strength activity index of a Brazilian bottom ash and



portland cement mixture mortar bars prepared according to EN 450. Results indicated that bottom ash was convenient for use in concrete. Strength activity index of bottom ash reached to 0.88 at 28 days and 0.97 at 90 days which were higher than those specified by the EN 450.

**Water Requirement** - Jaturapitakkul and Cheerarot (2003) stated that original bottom ash mortars needed more water than that of original cement mortar due to porous and rounded nature of particles. The water requirement increased when replacement rate increased while the water requirements of ground bottom ash mortars were less than those of the original cement and original bottom ash mortars.

**Workability** - Jaturapitakkul and Cheerarot (2003) investigated the normal consistency of bottom ash incorporating mortars. They concluded that ground bottom ash did not enhance the normal consistency dramatically. A slight improvement was seen in normal consistency up to 20 % ground bottom ash replacement of cement amount. Yet, normal bottom ash containing mortars showed a decrease in normal consistency.

Kohno and Komatsu (1986) showed that flows of mortars containing 5 to 15% ground bottom ash as a percentage substitution were lower than that of reference mortar. On the other hand, the flow values of mortars containing 5 to 15% ground bottom ash as a percentage addition were observed to somewhat higher than that of concrete without ground bottom ash. They also indicated that the water content of the ground bottom ash concrete decreased slightly to have the same slump (10 cm) for each fresh concrete.

**Setting time** - When bottom ash is used in cementitious systems as a substitution material of portland cement; due to diminution in the amount of  $C_3S$ , setting times of the mortars or concretes increase.

Jaturapitakkul and Cheerarot (2003) revealed that the initial setting times of original

and ground bottom ash cement paste retarded about 9-23 min compared to cement paste. Final setting times of original bottom ash cement pastes lasted 15-30 min longer than that of the cement paste.

**Strength and Strength Gain** - Substitution of bottom ash in cement and concrete either decreased or increased the compressive strength of the samples. Kurama and Kaya (2008) indicated that the compressive and flexural strengths of representative concrete specimens prepared by incorporation of bottom ash in place of portland cement were increased with replacement up to 10%. Higher substitution rates were observed to give lower strength values. This situation was more significant for the lower curing times (7 and 28 days). In the investigation, the decrease in compressive and flexural strength was attributed to the different phase distributions and higher unburned carbon contents of coal bottom ash.

Investigation conducted by Jaturapitakkul and Cheerarot (2003) concluded that compressive strengths of mortar specimens with a replacement ratio of 10, 20 and 30% ground bottom ash by weight of cementitious material were observed to give higher strength values than that of portland cement after 28 days. Yet, the compressive strengths of original bottom ash mortars with same replacement ratios were found to be lower than the minimum value stated by EN 197-1. They related this situation to smaller surface area of large particle size of original bottom ash to react with lime. Jaturapitakkul and Cheerarot (2003) have also studied concrete samples incorporating 20% of ground bottom ash replacement which was designed to reach 25, 35 and 45 MPa at the age of 28 days. Concretes including bottom ash substitution designed to reach same strength to its ordinary portland cement equivalent in which both of them had same w/c. They have found that mixture with higher cement content had higher development rate of compressive strength. The strength of bottom ash concrete designed as 45 MPa got close to that of its portland cement counterparts as early as 14 days. Other bottom ash incorporating concretes showed enhanced progress in compressive strength values as ordinary portland cement at the age of 28 days or later. Finally, they stated that higher cement content

led to higher hydration reaction and gave more  $\text{Ca(OH)}_2$ , which was needed for pozzolanic reactions.

Researches conducted by Kohno and Komatsu (1986) on mortar and concrete specimens showed that ground bottom ash is a good mineral admixture up to 15% replacement amount since comparable strength values were obtained. Yet, when percentage of ground bottom ash substitution was increased, strength values decreased. The strength of the mortar with bottom ash and without bottom ash became nearly the same at 91 days. Kohno and Komatsu (1986) also studied the ground bottom ash concrete which ground bottom ash used as a substitute of 5 and 10% of the initial cement amount. The concrete specimens were cured in three different ways. The strengths of concretes were slightly lower than concrete with ordinary portland cement at the end of the 28 days for standard curing, but, strength development of ground bottom ash concretes were higher than that of reference concrete from 28 to 91 days. In case of steam curing, ground bottom ash concretes have higher 7 and 28 day strength values than the reference concrete. The strengths of concretes were higher than that of reference concrete when autoclave curing was applied for 3 day treatment. The 3 days strength of the specimens were almost 80% of the 28 days strength values of standard curing specimens since autoclave curing speeds up the hydration. The tensile strength of ground bottom ash concretes also showed higher results for all ages.

The improvement in strength was also observed by the research conducted by Hopkins and Oates et al. (1998). Cementitious composition consisted of approximately 80% by weight of cement and 20% by weight of the pozzolanic material which contained fly ash, silica fume and ground bottom ash mixture. When pozzolanic material was comprised of ground bottom ash and silica fume mixture, it included approximately 80% by weight of ground bottom ash and 20% by weight of silica fume. Cementitious material was designed to constitute  $380 \text{ kg/m}^3$  of the concrete samples. The concretes were prepared with a fixed water cementitious ratio of 0.45. They found that replacement with ground bottom ash and dry silica fume

mixture resulted in highest 28 day strength. Similarly, concrete which was comprised of portland cement and ground bottom ash also showed a good performance with a 9% increase over control at 28 days whereas fly ash replacement showed a decrease of about 9% over control. Later, they conducted the same procedure with other cement types (Bath T-10 and St.Constant T-10). Replacing cement with bottom ash and fly ash decreased 28 day compressive strength compared to the control. Yet, blends of bottom ash and either dry or wet silica fume showed a slight increase in 28 days compressive strengths. They contribute that to a remarkable increase in slump of bottom ash mixture. They stated that when high slump would be lowered by reducing water content, the compressive strength of bottom ash blend would increase.

**Drying Shrinkage** - Kohno and Komatsu (1986) indicated that drying shrinkage of concretes containing ground bottom ash were about 6 % higher than that of concrete without them when ground bottom ash was used as 5 to 10% substitution.

**Water Permeability** - It was reported that the coefficient of water permeability of ground bottom ash concrete were lower than that of concrete without ground bottom ash by Kohno and Komatsu (1986).

## CHAPTER 3

### EXPERIMENTAL STUDY

#### 3.1 Experimental Program

Experimental study deals with producing eight different blended cements and an ordinary portland cement. The labels and descriptions of the cements are given in Table 3.1. To produce blended cements, 10, 20, 30 and 40% clinker replacement by weight was done with fly ash and bottom ash. Blended bottom ash cements were produced by intergrinding clinker and other materials in a ball mill in the construction materials laboratory. On the other hand, blended fly ash cements were produced by blending portland cement and fly ash since fly ash is fine enough to be used directly.

The experimental study of this thesis is composed of four parts.

- i) Determination of general physical and chemical properties of the materials used in the study.
- ii) Determination of various properties of laboratory produced portland cement such as density, fineness, normal consistency, time of setting, soundness and compressive strengths in accordance with ASTM C 188, ASTM C 204, ASTM C 187, ASTM C 191, TS EN 196-3 and ASTM C 109, respectively.
- iii) Determination of effects of interground portland cement clinker, gypsum and bottom ash with different percentages on the various properties of blended cements such as density, fineness, normal consistency, time of setting, soundness and normal consistency in accordance with ASTM C

188, ASTM C 204, ASTM C 187, ASTM C 191 , TS EN 196-3 and ASTM C 109, respectively.

- iv) Determination of effects of fly ash addition with different percentages to the laboratory produced blended cements on the various properties of blended cements such as density, fineness, normal consistency, time of setting and compressive strengths in accordance with ASTM C 188, ASTM C 204, ASTM C 187, ASTM C 191 , TS EN 196-3 and ASTM C 109, respectively.

Chemical properties of coal ashes, particle size distributions of the materials and SEM view of fly ash were done in TCMA in Ankara. Chemical properties of the clinker were conducted in Bolu Cement Factory.

Cements produced in this study are given in Table 3.1 along with their descriptions.

Table 3.1 Cement Labels in the Study

<b>Cement Label</b>	<b>Description</b>
PC	Ordinary portland cement with Blaine fineness of 3480 cm <sup>2</sup> /g
FA10	Blended cement including 10% of fly ash by mass as a replacement of clinker with Blaine fineness of 3230 cm <sup>2</sup> /g
FA20	Blended cement including 20% of fly ash by mass as a replacement of clinker with Blaine fineness of 3320 cm <sup>2</sup> /g
FA30	Blended cement including 30% of fly ash by mass as a replacement of clinker with Blaine fineness of 3400 cm <sup>2</sup> /g
FA40	Blended cement including 40% of fly ash by mass as a replacement of clinker with Blaine fineness of 3450 cm <sup>2</sup> /g
BA10	Blended cement including 10% of bottom ash by mass as a replacement of clinker with Blaine fineness of 4200 cm <sup>2</sup> /g
BA20	Blended cement including 20% of bottom ash by mass as a replacement of clinker with Blaine fineness of 4570 cm <sup>2</sup> /g
BA30	Blended cement including 30% of bottom ash by mass as a replacement of clinker with Blaine fineness of 5160 cm <sup>2</sup> /g
BA40	Blended cement including 40% of bottom ash by mass as a replacement of clinker with Blaine fineness of 5150 cm <sup>2</sup> /g

The descriptions of the abbreviations used to describe cements were shown in Table 3.2.

Table 3.2 The Description of the Abbreviations Used for the Cement Labels

<b>Cement Label</b>
PC – Portland cement
FA – Blended fly ash cement
BA – Blended bottom ash cement
<b>First number following the source indicated</b>
Percent of pozzolanic material by weight of portland cement clinker

### 3.2 Materials

The materials used in this study comprised of one type of ordinary portland cement clinker, one type of gypsum, one type of fly ash and one type of bottom ash. To determine raw material properties, chemical analysis (according to TS EN 197-1), physical analysis such as fineness by Blaine air permeability (according to ASTM C 204) and density (according to ASTM C 188) were conducted. In addition, particle size distribution by laser diffraction method and microstructural analysis by SEM technique of fly ash were also determined.

Portland cement clinker and gypsum were obtained from Bursa Cement Factory. Fly ash and bottom ash were obtained from Seyitömer Power Plant.

Standard sand relevant to TS EN 196-1 was used in the preparation of all cement mortars.

Tap water was used for the production of cement mortar and pastes and for the curing of specimens.

### 3.3 Production of Blended Cements

To produce cements, clinker, fly ash and bottom ash were first dried at 100°C for 48 hours. Gypsum was dried at 60°C for 24 hours to prevent unhydration. Later, portland cement clinker and gypsum were crushed to size of 5-10 mm in the laboratory type jaw crusher to reduce particle size before grinding. Fly ash and bottom ash were not crushed since they were fine enough to use directly in cement or to feed directly to the ball mill. Last stage in production process was the grinding of the materials in laboratory type ball mill.

Ordinary portland cement was produced by intergrinding of portland cement clinker and gypsum to a fineness of  $3500 \pm 100 \text{ cm}^2/\text{g}$ . Blended bottom ash cements were produced with a ratio of 10, 20, 30 and 40% clinker replacement by intergrinding of portland cement clinker, bottom ash and gypsum. However, fly ash was fine enough to be used in blended cement directly with a Blaine value of  $3850 \text{ cm}^2/\text{g}$  so it was also used with 10, 20, 30 and 40% replacement ratio. Fly ash and portland cement were mixed in smaller amounts to gain a homogenous mixture. Blended fly ash cements were prepared in 1000 g batches. Gypsum ratio was kept constant for all laboratory produced cements (3.5 % by mass).

Before grinding, portland cement clinker was crushed in the jaw crusher to maximum size of the materials to be finer than 1 cm to prevent very big particles left after grinding. Grinding was carried out with a laboratory type ball mill of 460 mm in length and 400 mm in diameter whose rotational speed was 30 revolutions per minute. Grinding media had a size distribution with a combination of spherical and cylpebs elements. Approximately 36% of the total volume of the ball mill was filled by the grinding media. Size of the grinding media was 30 to 70 mm for spheres, and 10 to 30 mm for cylpebs. Size distribution of the grinding media during production of all cements is given in Table 3.3.



Table 3.3 Size Distribution of the Grinding Media

Grinding Media	Dimensions	Weight (kg)
Spherical Balls (diameter)	30	21.76
	40	13.40
	50	12.00
	55	11.74
	60	10.00
	65	8.05
	70	7.05
Cylpebs (diameter x length)	10 x 10	14.00
	20 x 20	
	30 x 30	
<b>Total</b>		98.00

Ball mill feed was 8500 g and kept constant through all grinding processes and grinding processes lasted 120 min. Raw material proportions used in grinding is given in Table 3.4.

Table 3.4 Raw Material Proportions Used in Producing Cements

	Amount (%)			
	Clinker	BA	FA	Gypsum
PC	100	-	-	3.5
FA10	90	-	10	3.5
FA20	80	-	20	3.5
FA30	70	-	30	3.5
FA40	60	-	40	3.5
BA10	90	10	-	3.5
BA20	80	20	-	3.5
BA30	70	30	-	3.5
BA40	60	40	-	3.5

At the end of the grinding operation, a representative sample was taken from the cement and specific gravity according to ASTM C 188 and Blaine fineness according to ASTM C 204 were calculated. Particle size distributions of the cements were determined by laser diffraction method. Particle size distribution is an important factor affecting the behavior of cementitious systems. A reduction in median size

usually increases hydration rate and the properties depending on high hydration rates such as high early strength. Thus, fineness of the portland cement has increased over time (Bentz et al., 1999). A particle size distribution gives an idea about the efficiency of grinding and optimum size of the feed to a process to increase efficiency (Gupta and Yan, 2006). A particle size distribution of the material is generally tabulated as a cumulative curve.

Particle size distributions of the cements are given in Chapter 4.

### 3.4 Tests Conducted on Materials

Tests performed on materials are given in Table 3.5.

Table 3.5 Tests Performed on Materials

Tests Performed on Materials	Related Standard
Chemical Analysis	TS EN 450-1, TS EN 451-1, TS EN 197-1, TS EN 196-2
Specific Gravity	ASTM C 188
Fineness of the Materials	ASTM C 204
Particle Size Distribution	-
SEM	-

**Chemical Analysis** – Chemical analysis of clinker was conducted by Bolu Cement Factory, chemical analyses of fly ash and bottom ash were done in TCMA according to related standards mentioned in Table 3.5

**Specific Gravity** - Le Chatelier flask was used to measure specific gravities of the materials (According to ASTM C 188). Specific gravity technique employs Archimedes principle of liquid displacement. Flask was filled to the level between 0 and 1 cm<sup>3</sup> with a liquid that do not react with materials. Then, flask was placed in

water tank that can stabilize the temperature during the experiment. Level of the liquid in the flask was measured after waiting an appropriate time, then; material (64 g for portland cement and 50 g for pozzolans) was introduced to the flask. New level of the liquid was measured after holding the flask in water tank for sufficient time of period. Density was found by dividing mass to volume of the material. Since specific gravity is the relative density with respect to water, it was approved to use this technique to measure specific gravity.

**Fineness** - Blaine apparatus was used to measure fineness of the materials. Blaine air permeability method works on the principle of determining the rate of air flow through a prepared sample of definite density. The rate of air flow is influenced by the number and size of pores in a sample that is a function of the size of the particles and their distributions (Erdoğan, 2005).

**Particle Size Distribution** – Particle size distribution is another method to determine the fineness of the material. Particle size distributions of fly ash and laboratory produced cements were observed by means of laser granulometry technique in TCMA laboratory. The method relies on the principle that each particle passing through the spout between the laser beam and the lens scatters light at an angle that is directly related to its size. Large particles scatter light at low angles whereas small particles scatter at high angles (Kippax, 2010).

**SEM** - Scanning electron microscope image of fly ash gives an idea about its morphology and microstructure and was determined in TCMA laboratory.

### **3.5 Tests Conducted on Cement Pastes and Cement Mortars**

Tests performed on cement pastes and mortars and relevant standards are given in Table 3.6.

Table 3.6 Tests Performed on Cement Pastes and Mortars

<b>Tests Performed on Cement Paste</b>	<b>Related Standard</b>
Normal Consistency	ASTM C 187
Setting Time	ASTM C 191
La Chatelier	TS EN 196-3
<b>Tests Performed on Cement Mortar</b>	
Flow	ASTM C 109
Compressive Strength	ASTM C 109

### 3.5.1 Tests on Cement Paste

**Normal Consistency** - Normal consistency of the cement is measured by Vicat apparatus. According to ASTM C 187, 650 g of cement and water was mixed with a laboratory mixer. Prepared cement paste is placed in the mold. Plunger end of the apparatus is introduced the top surface of the cement paste. Then, plunger is released. When the plunger penetrates the paste to a point where it is  $10 \pm 1$  cm below the original surface in 30 min, the paste is considered to obtain normal consistency. Trial pastes with varying percentages of water are made to get normal consistency. When the correct water content of the paste is determined, setting time and soundness of the cement paste are also determined.

**Setting Time** - A paste that is mixed according to normal consistency is molded and placed in a moist cabinet where it starts setting. Initial and final setting time of the paste is determined by the penetration of 1 mm diameter needle of Vicat apparatus. Initial setting is the time elapsed between first contact of the cement with water and the time when the 25 mm penetration of the needle into the cement. Final setting is the time elapsed between first contact of the cement with water and the time when needle no longer leave a visible circular pattern in the paste surface.

**Soundness** - Le Chatelier Test can be conducted to determine the soundness of the cement. The test is done according to Turkish standard TS EN 196-3.

Soundness test measures the volume stability of cement paste after setting. Cement paste prepared according to Turkish Standard TS EN 196-3 is placed into Le Chatelier apparatus. Both surfaces of the cylinder are covered with glass plates. Then, whole assembly is submerged to the water at  $20\pm 2^{\circ}\text{C}$  for 24 hours. The distance between indicator points of apparatus is measured. The apparatus is then submerged to the water. It is brought to boiling point within  $30\pm 5$  minutes and kept at this point for 3 hours. It is removed from the water and the distance between the indicator points is measured again. The increase between the two measurements gives the expansion of the cement paste.

### **3.5.2 Test Performed on Cement Mortar**

**Compressive Strength and Flow** - According to ASTM C 109, the mortar with water/cement ratio of 0.485 for portland cement (consisting of 1 part cement and 2.75 parts standard sand) is prepared in a laboratory mixer. For other cements, the ratio of cement and standard sand do not change; but, water content is adjusted to obtain a flow of  $110 \pm 5$  in 25 drops of the flow table. After mixing, mortars are molded in 5 cm cube molds where they stay for one day. After mortars are unmolded, they are immersed in lime saturated water until the day strength test will be conducted.

### **3.6 Curing Conditions**

Molded test specimens were placed in the moist room for 24 hours. After removing the specimens from molds, the specimens were immersed in lime saturated water at  $23\pm 2^{\circ}\text{C}$  in the moist room. The specimens were taken out of water before testing and their surface was wiped to a dry state condition.

## CHAPTER 4

### RESULTS AND DISCUSSIONS

#### 4.1 Material Properties

##### 4.1.1 Portland Cement Clinker and Gypsum

The oxide composition as determined by chemical analysis of the clinker is given in Table 4.1.

Table 4.1 Oxide Composition of the Portland Cement Clinker

Oxides	Weight Percentage
SiO <sub>2</sub>	21.36
Al <sub>2</sub> O <sub>3</sub>	6.19
Fe <sub>2</sub> O <sub>3</sub>	4.04
CaO	65.40
MgO	1.39
SO <sub>3</sub>	0.55
Na <sub>2</sub> O	0.24
K <sub>2</sub> O	0.46

##### 4.1.2 Coal Ashes

Fly ash and bottom ash were taken from the same unit at Seyitömer Power Plant on the same day. Chemical properties of ashes were determined and are given in Table 4.2 along with their specific gravity and Blaine fineness value. Coal ashes are checked for the conformity to the requirements of current American Standard ASTM C 618 and the results are added to Table 4.2. Chemical analysis revealed that both

coal ashes contain more than 70% of  $\text{SiO}_2+\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3$ . Fly ash has more than 10% of CaO. According to ASTM C 618, it meets both Class F and Class C fly ash classifications. Loss on ignition of the bottom ash is higher than the allowable limit. Loss on ignition value is considered as a determinant for unburned carbon degree of fly ash and bottom ash (Külaots et. al., 2002). Unburned carbon is an inert material which gives no contribution the strength of the cement. It affects the color of the concrete which makes it unsuitable for some applications. It also increases the water requirement of fresh cementitious systems due to high porosity of the particles and leads to mixture segregation (Freeman et al., 1996).

Table 4.2 Some Chemical and Physical Properties of Coal Ashes

Properties	Fly Ash	Bottom Ash	ASTM C 618
<b>Chemical Properties</b>			
Loss on Ignition (%)	2.47	8.22	Max 6.0
$\text{SiO}_2$ (%)	51.43	53.38	
$\text{Al}_2\text{O}_3$ (%)	14.98	14.54	
$\text{Fe}_2\text{O}_3$ (%)	11.19	8.39	
$\text{SiO}_2+\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3$ (%)	77.60	76.14	>50.0 for Type C >70.0 for Type F
CaO (%)	10.25	6.80	>10 for Type C < 10 for Type F
MgO (%)	4.58	4.37	
$\text{SO}_3$ (%)	1.74	0.78	Max 5.0
$\text{Na}_2\text{O}$ (%)	0.71	0.64	
$\text{K}_2\text{O}$ (%)	1.31	1.31	
Free CaO (%)	0.43	0.03	
Reactive $\text{SiO}_2$ (%)	44.31	44.56	
Reactive CaO (%)	8.38	5.27	
<b>Physical Properties</b>			
Specific Gravity	1.88	2.17	
Blaine Fineness ( $\text{cm}^2/\text{g}$ )	3850	-	

A representative fly ash sample was coated with gold to investigate microstructural properties by scanning electron microscopy (SEM). Results are given in Figures 4.1 and 4.2.

According to SEM analysis, fly ash particles which consist of partly spherical particles generally range in size between 1 and 30 micrometer. Besides, fly ash was observed to have angular particles as small as 70 micrometer in size (such as clay traces and feldspar).

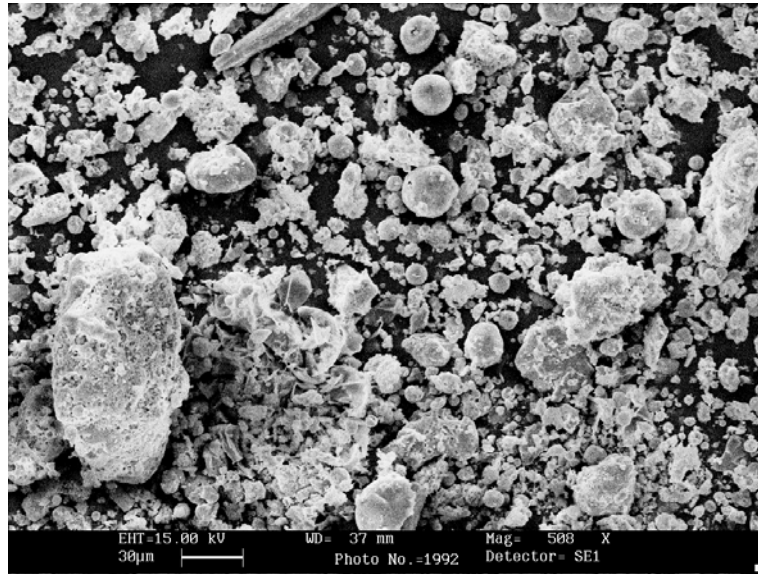


Figure 4.1 General Morphology of Fly Ash

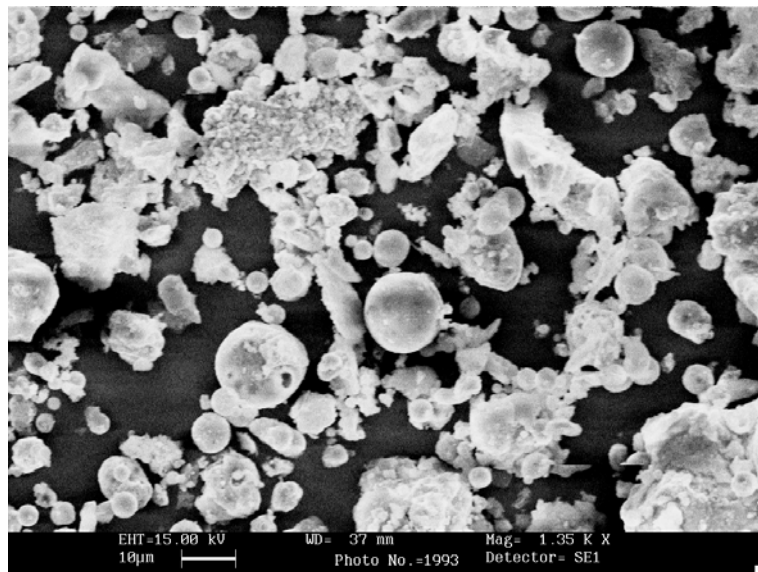


Figure 4.2 Microstructure of Fly Ash



Fineness of fly ash was also determined. The result of the particle size distribution of the fly ash presented on a graph shown in Figure 4.3.

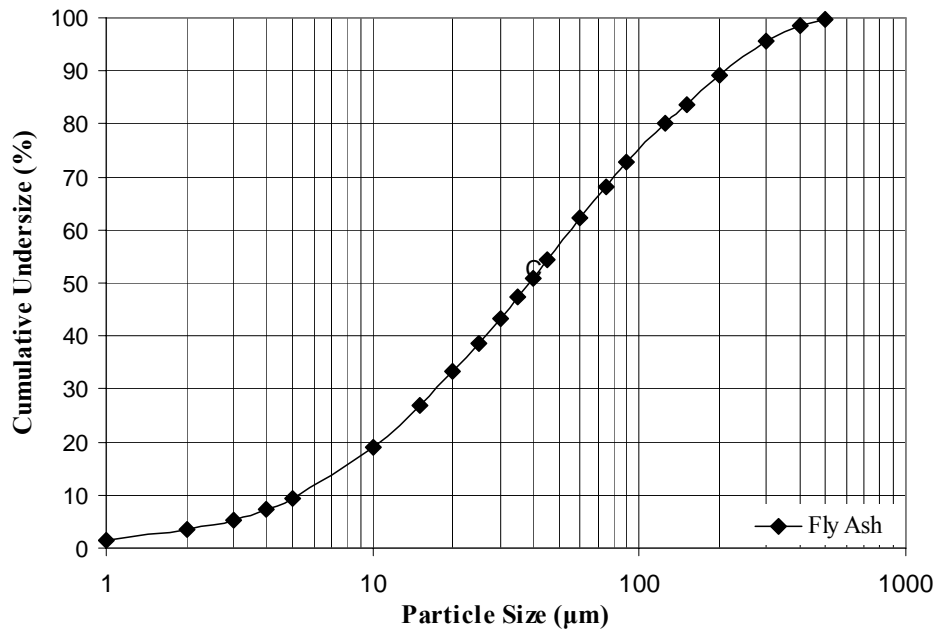


Figure 4.3 Particle Size Distribution of Fly Ash

## 4.2 Blended Cements

A reference portland cement and eight blended cements were produced by grinding of clinker and gypsum obtained by the same supplier. Fly ash and bottom ash were used as clinker replacement material at levels of 10, 20, 30 and 40% by mass of the cementitious body. Portland cement is produced by intergrinding of portland cement clinker and gypsum in proportions of 100/3.5, respectively. Blended fly ash cement was produced by blending of portland cement and fly ash since Blaine fineness of fly ash was determined as  $3850 \text{ cm}^2/\text{g}$ . Blended bottom ash cements were produced by intergrinding portland cement clinker, gypsum and bottom ash.

The Blaine fineness of laboratory scale portland cement was determined to be around

3500 ±100 cm<sup>2</sup>/g. 8500 g batches consisting of portland cement clinker and gypsum were ground for 120 minutes to reach a Blaine fineness of 3500±100 cm<sup>2</sup>/g. The laboratory type ball mill was stopped for predetermined periods and samples were taken to determine the specific gravity and Blaine fineness of the ordinary portland cement. The variation in specific gravity and Blaine fineness of portland cement with time is given in Table 4.3.

Table 4.3 Variation of Blaine Fineness and Specific Gravity of Portland Cement with Grinding Time

<b>Time (min)</b>	<b>Specific Gravity</b>	<b>Blaine Fineness(cm<sup>2</sup>/g)</b>
60	3.11	2300
75	3.12	3230
90	3.13	3370
105	3.13	3390
120	3.13	3480

As seen from the table above, specific gravity of portland cement clinker has a tendency of increasing slightly with time due to the reduction of grain porosity.

Targeted Blaine fineness was reached at 120 min. This duration was also kept constant to produce blended bottom ash cements.

### **4.3 Physical and Mechanical Properties of Cements**

#### **4.3.1 Fineness and Specific Gravity**

Blaine fineness and specific gravity results of the cements produced in the laboratory are presented in Table 4.4.

Table 4.4 Specific Gravity and Blaine Fineness Results of Cements

<b>Cement Label</b>	<b>Specific Gravity</b>	<b>Blaine Fineness (cm<sup>2</sup>/g)</b>
PC	3.14	3480
FA10	2.94	3230
FA20	2.75	3320
FA30	2.61	3400
FA40	2.52	3450
BA10	3.06	4200
BA20	2.94	4570
BA30	2.85	5160
BA40	2.80	5150

Blaine finenesses of blended bottom ash cements were higher than that of ordinary portland cements; although grinding durations were kept constant for the production of all cements. Additionally, Blaine fineness of blended bottom ash cements increased with increasing replacement degree of portland cement by mass. It is obvious that grinding of cement with bottom ash was easier than that of portland cement due to soft and porous particles of bottom ash.

Results of particle size distributions of the cements are given in detailed in Appendix A. The cumulative distribution plots are presented in Figure 4.4 for blended fly ash cements and in Figure 4.5 for blended bottom ash cements. As seen from the plots, blended fly ash cements are coarser than ordinary portland cement, and blended bottom ash cements are finer than ordinary portland cement.

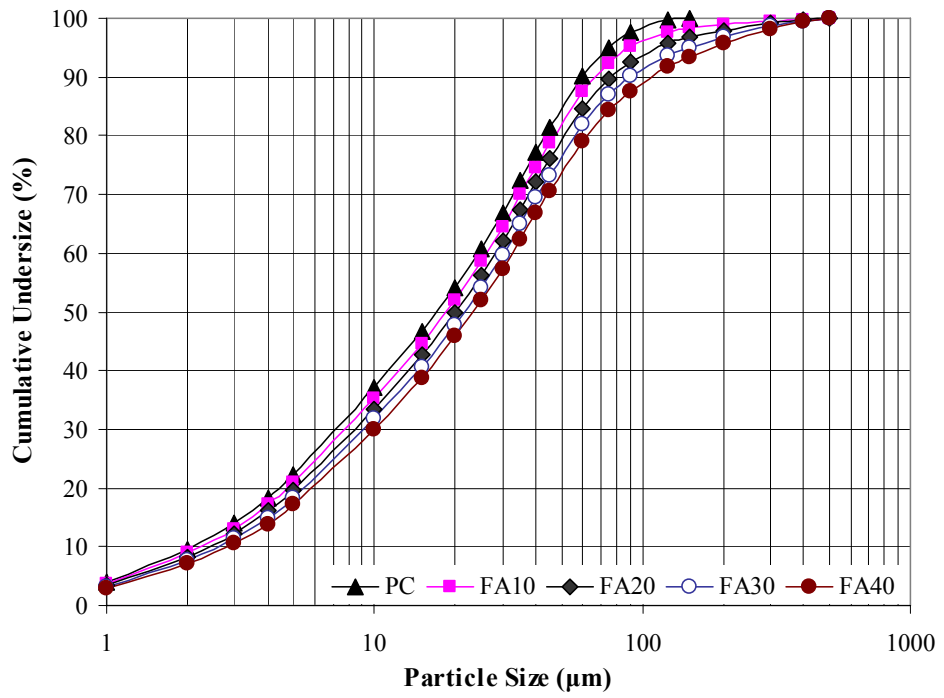


Figure 4.4 Particle Size Distributions of Blended Fly Ash Cements

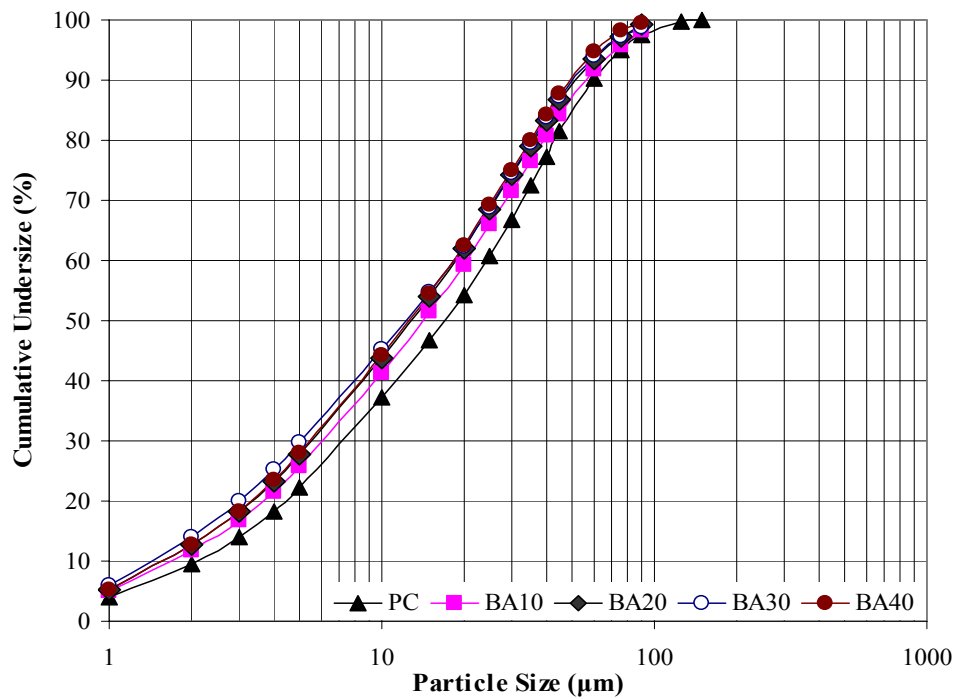


Figure 4.5 Particle Size Distributions of Blended Bottom Ash Cements

### 4.3.2 Normal Consistency

Normal consistencies of cement pastes were investigated according to ASTM C 187. The results of the normal consistency test are given in Table 4.5.

Considering the results given in Table 4.5, it can be concluded that water requirement to produce normal consistency of ordinary portland cement is less than that of blended cements. Normally, fly ash is known to reduce the water amount to reach normal consistency due to sphere particles shape and smooth particles surface. Sphere particles decrease the friction between particles and enhance the workability. In the study, consistency was higher for blended cements. This was probably due to porous and rough particle morphology of coal ash particles. It was also observed that blended cements required higher water volume for normal consistency with an increase in mineral admixture amount from 10 to 40% by weight. Higher porosity levels in higher replacement ratios can be the most important reason of it. Also, coal ashes were found to have unburned carbon content as expected. High unburned carbon particles can also increase the water requirement for normal consistency. The normal consistency of blended fly ash and blended bottom ash pastes were very similar to each other ranging from 27 and 34%.

Table 4.5 Normal Consistency Results of Pastes

Cement Label	Required Amount of Water for Normal Consistency	
	(g)	(%)
PC	149.5	23.0
FA10	176.8	27.3
FA20	185.3	28.0
FA30	188.5	30.6
FA40	221.0	33.9
BA10	177.5	27.2
BA20	182.0	28.5
BA30	198.9	29.0
BA40	220.4	34.0

### 4.3.3 Setting Times

Setting time tests on portland cement paste and blended cements with replacement rate of 10, 20, 30 and 40% by weight of cementitious material were conducted according to ASTM C 191. The results of the initial and final setting time are presented in Table 4.6 with the limit values given in ASTM C 595.

As expected, initial and final time of setting of ordinary portland cement was shorter than that of blended cements. When coal ash contents rose from 10 to 40% by weight of cementitious materials, initial and final setting times usually tended to increase. Fly ash and bottom ash retarded the initial and final setting times due to the reduced amount of ordinary portland cement clinker and higher amount of water.

Blended fly ashes with up to 20% replacement ratio only had 30 minutes longer initial setting times than that of ordinary portland cement. Also, blended bottom ash cements had shorter initial setting and higher final setting times than blended fly ashes have.

Table 4.6 Setting Times of Cements

<b>Cement Label</b>	<b>Initial Setting Time (min)</b>	<b>Final Setting Time (min)</b>	<b>ASTM C 595</b>
PC	135	205	> 45 min < 420 min
FA10	165	255	
FA20	165	240	
FA30	195	310	
FA40	195	330	
BA10	175	255	
BA20	180	255	
BA30	195	285	
BA40	205	280	

#### 4.3.4 Volume Expansion (Soundness)

Le Chatelier soundness of the ordinary portland cement paste and blended cement pastes were determined according to TS EN 196-3 and results were presented in Table 4.7.

Volume stability of blended cements were better than that of portland cement due to the lower CaO content of the blended cements. There was a tendency for volume expansion to decrease when clinker replacement ratio was increased. All blended cements had less than 1mm expansion except BA10.

Volume expansion of cement results from the reactions of free lime, magnesia and calcium sulphate. Le Chatelier soundness test only takes into account CaO. Mechanism occurs when free lime intercrystallized with other compounds and hydrates slowly after cement hardens. Hydration product has larger volume than that of free lime and finally gives rise to cracks in the concrete (Neville and Brooks, 2007). Thus, blended cements give advantageous volume expansion results due to lower free lime value in cement paste.

Table 4.7 Le Chatelier Expansion Values of Cements

Cement Label	Expansion (mm)	TS EN 196-3
PC	3	≤ 10 mm
FA10	1	
FA20	0	
FA30	1	
FA40	0	
BA10	2	
BA20	1	
BA30	0	
BA40	0	

### 4.3.5 Compressive Strength

Compressive strength of mortars were determined at 2, 7, 28, 90 days according to ASTM C 109. Blended cement mortars were prepared with a flow of 110±5. Compressive strength results of the mortars together with their w/c ratio are given in Table 4.8. Compressive strength of the samples were determined by taking average of six 50x50 mm cube shaped specimens.

Table 4.8 Compressive Strength Results of Cements

Cement Label	W/C	Flow (mm)	Mean Compressive Strength (MPa)				Coefficient of Variation (%)			
			2 Days	7 Days	28 Days	90 Days	2 Days	7 Days	28 Days	90 Days
PC	0.48	91	21.0	35.8	42.8	*	5.5	6.6	9.9	6.4
FA10	0.54	105	14.9	30.6	42.3	46.2	4.0	9.0	8.8	5.9
FA20	0.57	110	9.9	25.2	38.8	46.3	3.6	4.5	6.2	7.3
FA30	0.59	115	9.2	18.9	34.5	39.3	2.9	4.5	4.9	6.9
FA40	0.61	105	6.0	15.0	26.3	36.1	3.6	9.4	6.7	5.5
BA10	0.54	105	16.6	31.4	40.4	43.3	6.4	5.9	6.9	7.7
BA20	0.57	105	14.5	29.3	36.4	44.6	5.8	2.7	9.0	9.0
BA30	0.58	105	10.6	23.9	36.2	40.8	5.3	9.6	8.1	8.9
BA40	0.60	105	7.1	15.4	26.9	35.2	2.5	4.6	8.9	8.9

\* Due to technical problems the strength at this age could not be determined

As seen in Table 4.8, mortars having higher replacement ratio need more water amount to give the same flow. This situation can be related to porous structure, high unburned carbon of coal ashes and rough surface of the coal ashes. Kanazu et al. (1998) observed that unburned carbon amount up to 1.5% did not change flow value of mortars; yet, above this amount flow value of mortars decreased when the amount of unburned carbon of fly ashes increased (Lee et al., 2003), since water retention of samples increased due to higher unburned carbon content.

The compressive strength of blended cements were observed to decrease with an



increase in mineral admixtures addition from 10 to 40% as expected. Higher water requirements of the blended cements and dilution of portland cement compounds gave lower compressive strengths. Specially, early compressive strength decreased with high replacement ratios of coal ashes.

The compressive strength of blended bottom ash cements with replacement ratio of 10, 20, 30 and 40% of bottom ash were higher than that of blended fly ash cements at 2 and 7 days of curing age. This difference can be attributed to fineness of blended bottom ash cement. High surface areas of blended bottom ash cements surely give high reaction rates at early ages. Yet, specific surface area is generally accepted as it doesn't affect the ultimate strength after hydration completes (Hawlett, 2004).

Compressive strength of blended cements is also expressed as percentage rate of that of ordinary portland cement at same curing age as shown in Figures 4.6 and 4.7.

According to Figure 4.6 and 4.7, for 10% replacement, blended cements have the highest compressive strength values. For 2 and 7 days, blended fly ash cements with 10% replacement have approximately 70 and 85% of compressive strength of that of reference sample, respectively. On the other hand, blended bottom ash cements with same replacement have approximately 80 and 87% of compressive strength of that of reference sample for same age. At 28 day, blended fly and bottom ash cements with 10% replacement show comparable compressive strength values to that of reference sample.

For 20% fly ash replacement, the percentages of compressive strength of blended fly ash cements with respect to that of portland cement are 47, 70, and 90 for 2, 7, and 28 day curing time, respectively. For blended bottom ash cements, percentages are 69, 82, and 85 for 2, 7, and 28 day curing time, respectively.

FA 30, FA 40, BA 30 and BA 40 have similar compressive strength at the same curing ages.

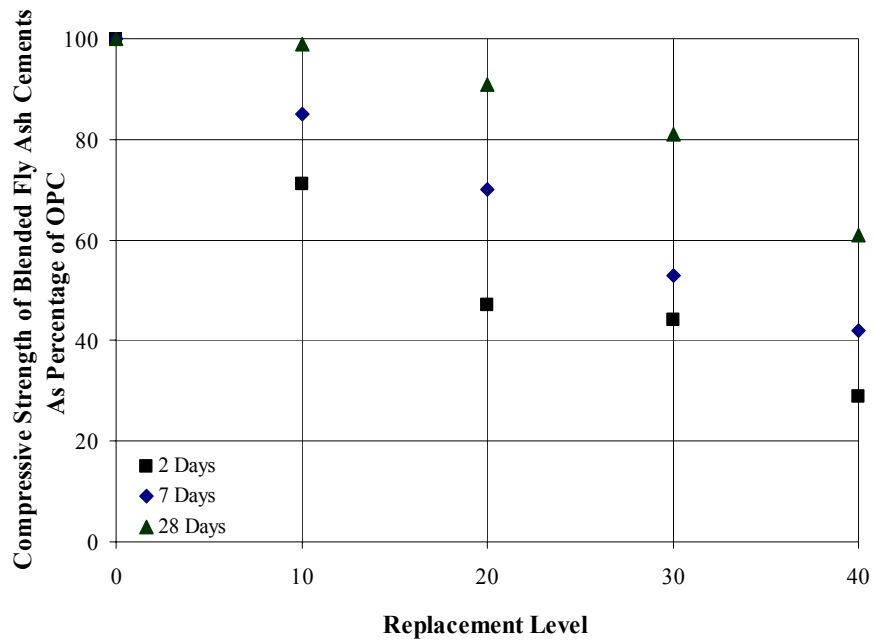


Figure 4.6 Strengths of Blended Fly Ash Cements as Percentage of that of OPC

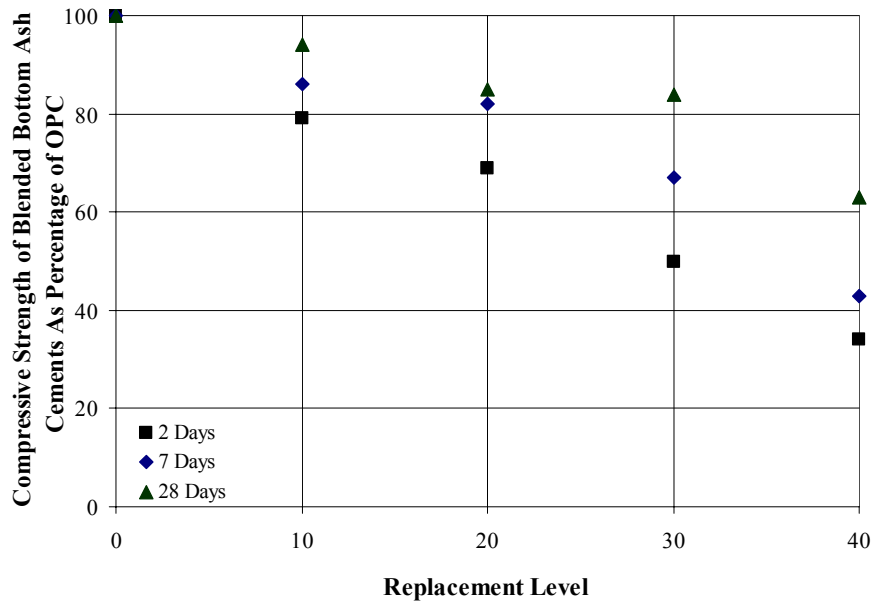


Figure 4.7 Strengths of Blended Bottom Ash Cements as Percentage of that of OPC

#### 4.4 Statistical Analysis of Compressive Strength of Cements

Even though, the fineness of blended fly ash cement and blended bottom ash cement were not same, since they were obtained from the same power plant a comparison of the performance of blended cements prepared with fly ash and bottom ash, blended cements with same replacement ratios by mass were evaluated with respect to 28 day compressive strength of portland cement. That is, mean compressive strengths of blended cements of the same age are expressed as percentage of 28 day compressive strength of portland cement. The results are presented in Figures 4.8 through 4.11. This comparison is verified with statistical analysis. T-test is applied to compare the mean value of compressive strengths. Main subject is to decide whether the mean value of blended fly ash cements and blended bottom ash cements for same replacement ratios at same ages is equal or not. Therefore, the null and alternative hypotheses are:

**H<sub>0</sub>:** the average strength value of blended fly ash cement and blended bottom ash cement for a given age are not different from each other.

**H<sub>1</sub>:** the average strength value of blended fly ash cement and blended bottom ash cements are different from each other.

T test two sample assuming unequal variances was conducted on Microsoft Excel software. The average compressive strengths of two samples were checked at a 95% confidence level. For each sample, six cube specimens were evaluated. If the probability function (P) of the T-test is found to be less than 0.05, the null hypothesis is rejected. In other words, the averages of strength values of two samples are proven as different from each other.

For example, at 2 days, the comparison of fly ash and bottom ash cements are presented in Figure 4.8. Bottom ash cements gave relatively higher results when compared to fly ash cements. When the statistical comparison was performed as presented in Table 4.9, it can be seen that the null hypothesis is incorrect for 2 day

compressive strength, i.e., the mean compressive strengths of blended fly ash cement and blended bottom ash cement are different from each other statistically. There is an important difference between average compressive strength of the blended fly ash cements and blended bottom ash cements.

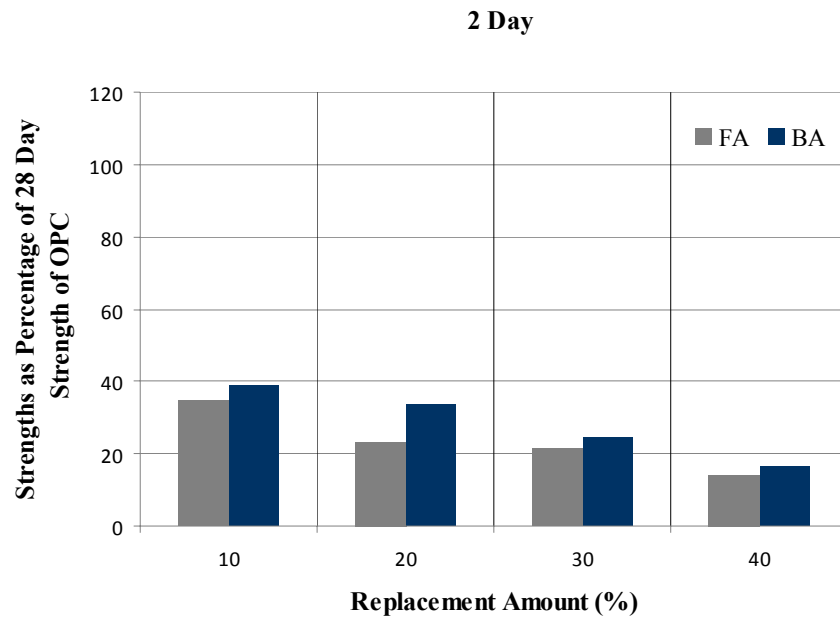


Figure 4.8 Compressive Strengths of Blended Cements at 2<sup>nd</sup> Day as Percentage of Strength of OPC at 28<sup>th</sup> Day

Table 4.9 Statistical Analysis of Compressive Strength of Blended Cements on 2<sup>nd</sup> Day

Compared Cement Type	Days	P	Ho	Conclusion
FA 10 vs BA10	2	0.01	Reject	Statistically different
FA 20 vs BA 20	2	0.00	Reject	Statistically different
FA 30 vs BA 30	2	0.00	Reject	Statistically different
FA 40 vs BA 40	2	0.00	Reject	Statistically different

The comparison between 7 day compressive strength of blended fly ash cement and blended bottom ash cement are presented in Figure 4.9. 10 and 40% replacement ratios by mass were observed to give similar compressive strength values. For other

replacement ratios, there was a significant difference. Also, mean compressive strength of the cements were evaluated statistically. Statistical analyses of the blended cements are given in Table 4.10, the null hypothesis can be accepted for comparison between blended fly ash cement and blended bottom ash cement with 10 and 40% replacement by mass. It can be concluded that the mean compressive strength of blended cements with 10 and 40% replacement ratios are statistically equal.

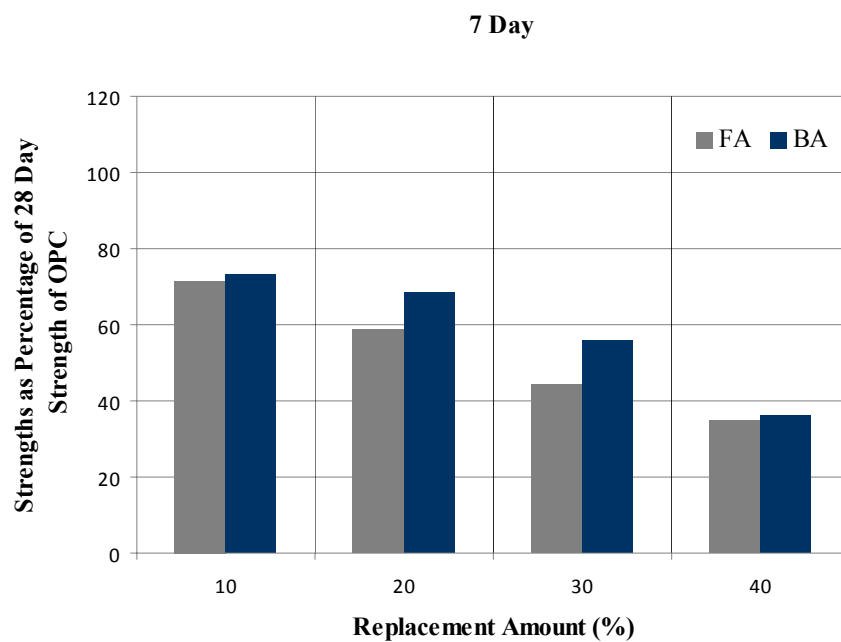


Figure 4.9 Compressive Strengths of Blended Cements at 7<sup>th</sup> Day as Percentage of Strength of OPC at 28<sup>th</sup> Day

Table 4.10 Statistical Analysis of Compressive Strength of Blended Cements on 7<sup>th</sup> Day

Compared Cement Type	Days	P	Ho	Conclusion
FA 10 vs BA 10	7	0.58	Fail to reject	Statistically the same
FA 20 vs BA 20	7	0.00	Reject	Statistically different
FA 30 vs BA 30	7	0.00	Reject	Statistically different
FA 40 vs BA 40	7	0.61	Fail to reject	Statistically the same

The comparisons of 28 day strength of blended cements are given in Figure 4.10. For 40% replacement, blended fly ash and blended bottom ash cements showed similar results. For other replacement ratios, results were also comparable, but difference became wider. When comparisons were evaluated statistically as presented in Table 4.11, it is seen that the null hypothesis of all specimens are correct, that is, mean compressive strength of all blended cements for same replacement ratios are equal to each other.

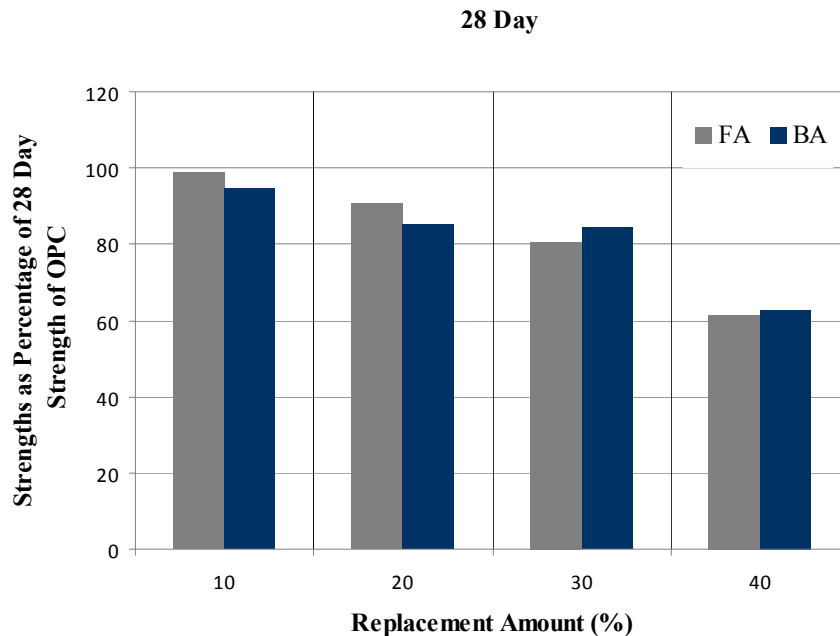


Figure 4.10 Compressive Strengths of Blended Cements at 28<sup>th</sup> Day as Percentage of Strength of OPC at 28<sup>th</sup> Day

Table 4.11 Statistical Analysis of Compressive Strength of Blended Cements on 28<sup>th</sup>  
Day

Compared Cement Type	Days	P	Ho	Conclusion
FA 10 vs BA10	28	0.40	Fail to reject	Statistically the same
FA 20 vs BA 20	28	0.20	Fail to reject	Statistically the same
FA 30 vs BA 30	28	0.30	Fail to reject	Statistically the same
FA 40 vs BA 40	28	0.63	Fail to reject	Statistically the same

For 90 day, the comparison of strengths of blended fly ash and bottom ash cements are given in Figure 4.11. Blended fly ash cements with 10, 20 and 30% replacement ratios gave higher results; yet, this phenomenon does not mean that mean compressive strength of blended cements are different from each other. Specially, strength values were close to each other for 40% replacement by mass. Statistical analyses were also done to compare mean strength values. Results given in Table 4.12, revealed that all of the null hypotheses are correct, that is, the mean compressive strengths of blended fly ash cements and blended bottom ash cements are equal to each other statistically.

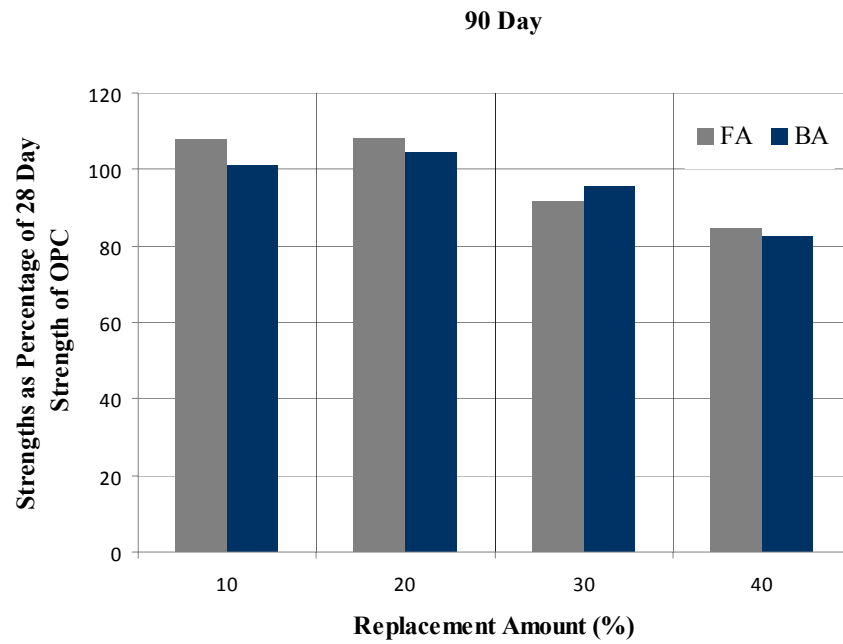


Figure 4.11 Compressive Strengths of Blended Cements at 90<sup>th</sup> Day as Percentage of Strength of OPC at 28<sup>th</sup> Day

Table 4.12 Statistical Analysis of Compressive Strength of Blended Cements on 90<sup>th</sup> Day

Compared Cement Type	Days	P	Ho	Conclusion
FA 10 vs BA 10	90	0.16	Fail to reject	Statistically the same
FA 20 vs BA 20	90	0.40	Fail to reject	Statistically the same
FA 30 vs BA 30	90	0.31	Fail to reject	Statistically the same
FA 40 vs BA 40	90	0.90	Fail to reject	Statistically the same



## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are derived according to the thesis study:

1. The grinding of blended bottom ash cements was easier than that of portland cement due to soft and porous particle properties of bottom ash.
2. Water requirements of the blended cements were much higher than that of control sample. The amount of water to obtain normal consistency increased by increasing the clinker replacement ratio. This phenomenon can be attributed to high amount of unburned carbon and the porous and rough particles of coal ashes. The normal consistencies of blended fly ash and blended bottom ash cements are nearly equal each other when blended cements with same substitution rates are evaluated.
3. Initial and final setting times of the blended cements prolonged by an increase in replacement amount due to higher water content of the pastes and the dilution of cement clinker.
4. Le Chatelier soundness test results of the blended cements were lower than that of reference sample due to the dilution of portland cement clinker.
5. Early compressive strength of blended cements were lower than that of portland cement. Furthermore, the reductions in compressive strength values became more significant with an increase in mineral admixture amount. The strength of blended cements gave similar results at 28 day curing age for 10% and 20% replacement by mass.

As a result of the experimental work, following recommendations are suggested for future studies:

Blaine fineness of the cements can be kept constant; thus, effect of the specific surface area on properties such as early strength, water requirement, the initial and final setting time of the cements are eliminated. In this study, fresh and hardened properties of blended cements were evaluated and the durability characteristics of the cements were not studied. Durability characteristics of the blended bottom ash cement can also be determined.

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## APPENDIX A

### PARTICLE SIZE DISTRIBUTIONS

Table A.1 Particle Size Distribution for Fly Ash, Ordinary Portland Cement and Blended Cements

Size (µm)	Volume over (%)									
	Fly Ash	OPC	FA10	FA20	FA30	FA40	BA10	BA20	BA30	BA40
1	98.60	95.98	96.24	96.50	96.77	97.03	95.10	94.66	94.07	94.68
2	96.47	90.50	91.10	91.69	92.29	92.89	88.31	87.23	85.98	87.27
3	94.66	86.07	86.93	87.79	88.65	89.51	83.24	81.77	80.11	81.66
4	92.73	81.71	82.81	83.91	85.02	86.12	78.57	76.82	74.85	76.51
5	90.73	77.64	78.95	80.26	81.57	82.88	74.32	72.36	70.21	71.88
10	81.09	62.80	64.63	66.46	68.29	70.12	58.79	56.30	54.66	55.69
15	73.19	53.36	55.34	57.33	59.31	61.29	48.59	45.94	45.25	45.43
20	66.79	45.86	47.95	50.05	52.14	54.23	40.69	37.99	37.83	37.44
25	61.41	39.21	41.43	43.65	45.87	48.09	34.10	31.40	31.37	30.72
30	56.75	33.15	35.51	37.87	40.23	42.59	28.40	25.72	25.58	24.88
35	52.64	27.60	30.10	32.61	35.11	37.62	23.48	20.88	20.54	19.89
40	48.98	22.73	25.36	27.98	30.61	33.23	19.29	16.79	16.31	15.69
45	45.7	18.58	21.29	24.00	26.72	29.43	15.77	13.37	12.84	12.19
60	37.72	9.75	12.55	15.34	18.14	20.94	8.36	6.38	6.10	5.21
75	31.82	4.92	7.61	10.30	12.99	15.68	4.19	2.66	2.83	1.85
90	27.3	2.40	4.89	7.38	9.87	12.36	1.83	0.76	1.21	0.44
125	19.98	0.35	2.31	4.28	6.24	8.21	-	-	-	-
150	16.30	0.03	1.66	3.28	4.91	6.54	-	-	-	-
200	10.87	-	1.09	2.17	3.26	4.35	-	-	-	-
300	4.52	-	0.45	0.90	1.36	1.81	-	-	-	-
400	1.59	-	0.16	0.32	0.48	0.64	-	-	-	-
500	0.28	-	0.03	0.06	0.08	0.11	-	-	-	-