UTILIZATION OF FLY ASH FROM FLUIDIZED BED COMBUSTION OF A TURKISH LIGNITE IN PRODUCTION OF BLENDED CEMENTS

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A BSTRACT

UTILIZATION OF FLY ASH FROM FLUIDIZED BED COMBUSTION OF A TURKISH LIGNITE IN PRODUCTION OF BLENDED CEMENTS

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Fly ashes generated from fluidized bed combustion of low calorific value, high ash content Turkish lignites are characterized by high content of acidic oxides, such as SiO_2, Al_2O_3 and Fe_2O_3, varying in the range 50-70%. However, there exists no study for the investigation of the possibility of using these ashes as concrete admixture.

Therefore, in this study, characterization of fly ashes from fluidized bed combustion of a Turkish lignite and evaluation of these fly ashes as a substitute for Portland cement in production of pastes and mortars were carried out. The samples were subjected to chemical, physical, mineralogical and morphological analyses. Results of chemical and physical analyses of three fly ash samples show that they satisfy the requirements of EN 197-1, EN 450 and ASTM C 618, except for CaO and SO_3, owing to high content of acidic oxides of these ashes contrary to majority of FBC fly ashes reported in the literature. In addition to characterization studies, water requirement, compressive strength, setting time and soundness tests were also performed for 10%, 20% and 30% fly ash-cement blends and the reference cement. Results of these tests reveal that the blends meet compressive strength, setting time and soundness requirements of ASTM C 595 without any pre-hydration treatment, and that fly ashes from fluidized bed combustion of Turkish lignites have significant potential for utilization as an admixture in manufacture of blended cements.

Keywords: fly ash, ash utilization, fluidized bed combustion, blended cement and lignite.

ÖZ

BİR TÜRK LİNYİTİNİN AKIŞKAN YATAKTA YANMASIYLA ÜRETİLEN UÇUCU KÜLÜN KATKILI ÇİMENTO ÜRETİMİNDE KULLANIMI

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Kalorifik değeri düşük, külce zengin Türk linyitlerinin akışkan yataklı kazanlarda yakılması sonucu oluşan uçucu küllerin zengin asidik oksit içeriğine sahip oldukları bilinmektedir. Ancak, bu küllerin çimento ve beton katkısı olarak kullanılması üzerine herhangi bir çalışma bulunmamaktadır.

Bu nedenle önerilen çalışmanın amacı, bir Türk linyitinin akışkan yatakta yakılması sonucu oluşan uçucu küllerin özelliklerinin belirlenmesi ve bu küllerin çimento harcı ve pastası yapımında çimentoya katkı olarak kullanımına yönelik potansiyelinin değerlendirilmesidir. Uçucu kül numuneleri, kimyasal, fiziksel, mineralojik ve morfolojik özellikleri açısından incelenmiştir. Fiziksel ve kimyasal testlerin sonuçları, özellikleri incelenen uçucu küllerin, literatürde yer alan çoğu

uçucu küle göre yüksek asidik oksit içeriği sayesinde EN 197-1, EN 450 and ASTM C 618 standartlarının, CaO ve SO_3 içeriği dışındaki koşullarını sağladığını göstermiştir. Bu çalışmaların yanı sıra, Portland çimentosunun %10, 20 ve 30 oranında uçucu kül ile ikame edilmesi ile hazırlanan pasta ve harçların su ihtiyacı, basınç dayanımı, priz süreleri ve hacim genleşmeleri de incelenmiştir. Bu testlerin sonuçları da uçucu kül-çimento karışımlarının ASTM C 595 standardının basınç dayanımı, priz süreleri ve hacim sabitliği koşullarını, herhangi bir ön hidratasyona gereksinim duyulmaksızın sağladığını; bu nedenle Türk linyitlerinin akışkan yatakta yakılmasıyla üretilen uçucu küllerin, katkılı çimento üretiminde değerlendirilmesine yönelik önemli potansiyele sahip olduğunu göstermiştir.

Anahtar sözcükler: uçucu kül, uçucu kül değerlendirilmesi, akışkan yatakta yakma, katkılı çimento ve linyit.

to *My Father*

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ABBREVIATIONS

FBC : Fluidized Bed Combustion

FC : Fixed Carbon

LHV : Lower Heating Value

LOI : Loss on Ignition

PCC : Pulverized Coal Combustion

SAI : Strength Activity Index

SEM : Scanning Electron Microscope

VM : Volatile Matter

XRD : X-Ray Diffraction

CHAPTER 1

INTRODUCTION

Increasing demand of energy has resulted in worldwide consumption of approximately 2.2 billion tons of coal for electricity generation in 2001. In Turkey, 54.7 million tons of coal was consumed in thermal power plants in the same period [1-3]. Consumption of coal for electricity generation leads to production of fly ash in gigascale quantities. The global production of fly ash is estimated to be 600 million tons per year [4]. In Turkey, 13 million tons of fly ash is annually produced due to utilization of vast lignite reserves for power generation [3,4].

Conventionally, fly ashes generated from combustion of pulverized coal is utilized as cement and concrete admixture, structural fill, cover material, in waste solidification and stabilization, roadway and pavement applications, lightweight aggregate manufacture and underground void filling [5]. In many industrialized countries, high amounts of fly ashes are utilized in above mentioned areas. Table 1.1 displays ratio of fly ash utilized in some industrialized countries [3].

Approximately 50% of fly ashes utilized are used as cement or concrete admixture owing to improved physical properties of fly ash incorporated cements or concrete. Previous studies have shown that utilization of fly ash as cement or concrete admixture results in improved compressive strength and durability characteristics [24-56]. These studies have revealed that compressive strength of cement mortars or concrete is improved by incorporation of fine fractions of fly ash. It has been further verified that utilization of fly ash as cement or concrete admixture also provides improved durability characteristics, such as sulfate resistance and reduced alkali-aggregate reactivity.

Table 1.1: Percent ratio of fly ash utilized in industrialized countries [3]

Country	% Fly Ash Utilized
Netherlands	100
Germany	95
Belgium	95
United Kingdom	50
China	40
USA	32

Utilization potential of conventional fly ashes has led to international standards for classification and specifications of fly ashes to be used as cement or concrete admixture. EN 197-1 defines classification and specifications of fly ashes generated from combustion of pulverized coal, to be utilized in production of blended Portland cements [6]. Similar requirements are included in EN 450, which defines specifications of fly ashes to be incorporated in concrete [7]. In ASTM C 618, classification and specifications of fly ashes are defined depending on the rank of coal burnt [8]. There exists, however, no international standard for use of fly ash from fluidized bed combustion in blended Portland cement or concrete production.

Steady increase in the applications of FBC technology in both number and capacity over the past decade has led to the investigation of the possibilities for utilization of FBC fly ashes. Studies on characterization of these fly ashes have shown that they contain high amounts of calcined limestone and desulfurization products, such as

$CaSO_4$, free CaO and $CaCO_3$, compared to fly ashes generated from pulverized coal combustion [60,61]. Studies on utilization possibilities of FBC fly ashes, on the other hand, point out that pre-hydration of these ashes is required in order to prevent deleterious expansion due to high free CaO content [64,65]. However, it should be borne in mind that all these studies were carried out on fly ashes generated from combustion of higher grade coals with relatively low ash content.

Fly ashes generated from fluidized bed combustion of low calorific value, high ash content Turkish lignites, on the other hand, are characterized by high acidic oxide contents varying in the range 50-70%. However, there exists no study for the investigation of the possibility of using these ashes as cement or concrete admixture.

Therefore, in this study,

- characterization of fly ashes generated from fluidized bed combustion of Turkish lignites
- evaluation of these fly ashes for partial Portland cement replacement in production of pastes and mortars

were carried out.

CHAPTER 2

STRUCTURE AND HYDRATION OF PORTLAND CEMENT

2.1 Structure of Portland Cement

Portland cement is a hydraulic binder produced by grinding cement clinker, which is a mixture of hydraulic calcium silicates, with minor amounts of gypsum [9]. Characteristics of Portland cement are primarily influenced by the relative amounts of metal oxides present in the clinker. Table 2.1 shows an approximate oxide composition of a typical cement clinker. The oxides constituting cement and cement clinker are prefereably denoted by the abbreviations listed in Table 2.2.

Microscopic examination of cement clinker indicates that its components are not found in their simple oxide forms but found in forms of composites, such as calcium silicates and calcium aluminates. Names and abbreviations of clinker components are shown in Table 2.3.

Table 2.1: Approximate composition of a typical cement clinker [10]

Component	Weight %
SiO_2	19-21
Al_2O_3	4-7
Fe_2O_3	2-4
CaO	63-66
MgO	0.5-2
SO_3	2-3
CO_2	0-1
Na_2O	0-1
K_2O	0-1
TiO_2	0-0.5
P_2O_5	0-0.2
Mn_2O_3	0-0.2

Table 2.2: Abbreviations of major oxides in cement and cement clinker [11]

Component	Abbreviation
SiO_2	S
Al_2O_3	A
Fe_2O_3	F
CaO	C
MgO	M
SO_3	$\overline{S}$
Na_2O	N
K_2O	K
H_2O	H

Table 2.3: Names and abbreviations of major clinker components

Component	Name	Abbreviation
$3CaO.SiO_2$	Tricalcium silicate	C_3S
$2CaO.SiO_2$	Dicalcium silicate	CB_2S
$3CaO.Al_2O_3$	Tricalcium aluminate	C_3A
$4CaO.Al_2O_3 .Fe_2O_3$	Tetracalcium aluminoferrite	C_4AF

The relative amounts of major clinker components are controlled by relative amounts of oxides present in the clinker and can be estimated by a set of equations proposed by Bogue [10,12]. Table 2.4 displays approximate relative amounts of major clinker components.

Table 2.4: Relative amounts of major clinker components [11]

Component	Weight %
C_3S	50
C_2S	25
C_3A	12
C_4AF	8

It is worth noting that the composites constituting clinker are rarely in their pure states, since Ca atoms might be replaced by other metal atoms. Consequently, the mineral name alite is preferably used to denote C_3S to indicate that it is actually in impure state. It should also be stressed that C_2S can be found in several distinct phases, among which only β-C_2S has cementitious property. Therefore the name belite is used to denote impure β-C_2S phase in cement clinker [11].

2.2 Hydration of Portland Cement

Hydration of Portland cement components occur in the water-cement paste. In other words, constituents of cement are converted to hydrated compounds which eventually deposit and form a hardened structure. Due to complexity of hydration process, it is beneficial to examine the hydration of individual cement components and that of cement mix separately.

2.2.1 Hydration of Clinker Components

C_3S is the most important clinker component, as it dominantly controls the strength development and setting process of cement paste. Hydration of C_3S results in formation of an amorphous calcium silicate hydrate phase, denoted by C-S-H, and $Ca(OH)_2$ according to the following reaction [10]:

$$3CaO.SiO_2 + (3+m-n)H_2O \rightarrow nCaO.SiO_2.mH_2O + (3-n)Ca(OH)_2$$

Due to their limited solubility, the C-S-H phases precipitate and fill the space initially occupied by water, leading to a decrease in the porosity, setting and ultimately attaining strength [11]. The Ca/Si ratio of the resultant C-S-H phase generally falls in the range 1.4-2.0 [10].

Even though its hydration is significantly slower, hydration mechanism of β-C_2S (belite) has been found to be close to that of C_3S [10]. However it is also claimed that hydration of β-C_2S yields several distinct C-S-H phases with Ca/Si ratios ranging from 1.1 to 1.6 [10,12].

Experience derived from past studies on hydration of C_3A indicates that it is beneficial to examine hydration of C_3A both in absence of $CaSO_4$ and in presence of $CaSO_4$. In absence of $CaSO_4$, hydration of C_3A results in formation of a calcium alumino hydrate phase, C_3AH_6, in a violent pattern, through a reaction mechanism strongly influenced by temperature and presence of $Ca(OH)_2$. The rapid hydration of C_3A causes a sudden hardening of the cement paste, which is termed as *flash set*. Flash set is avoided by grinding cement clinker with gypsum ($CaSO_4.2H_2O$), which changes the hydration mechanism of C_3A. An insoluble calcium sulfoaluminate, also known as ettringite, is generated from the reaction between C_3A and gypsum according to the following reaction [10]:

$$C_3A + 3C\overline{S}H_2 + 26H \rightarrow C_6A\overline{S}_3H_{32} \text{ (ettringite)}$$

However, ettringite is eventually consumed and monosulfate and tetracalcium aluminate hydrates are formed [11-13]. It should be borne in mind that formation of ettringite results in volumetric expansion in structures; therefore C_3A content of cements to be utilized in sulfatic environments are preferably limited.

Hydration of C_4AF phases is known to be similar to that of C_3A, but the reaction rates are different. Hydration of C_4AF in presence of gypsum and $Ca(OH)_2$ results in formation of iron analogs of ettringite, such as monosulfate and calcium alumino hydrates. Calcium alumino silicates and calcium ferro silicates, also known as *hydrogarnets*, are also eventually produced [11].

Interaction between basic clinker components during their hydration is also worth considering. Majority of the studies carried out on β-C_2S-C_3S system have shown that the hydration products of one phase are not significantly influenced by the presence of the other. Consequently the C-S-H phases generated by the hydration of C_3S and β-C_2S mixtures were found to be similar to products of their individual hydration [10].

Studies carried out on interactions between C_3S and C_3A or C_4AF contradictorily point out that the rate of hydration might be either retarded or accelerated. Besides, it is well known that hydration of C_3S in presence of C_3A produces C_4AH_x, C-S-H and $Ca(OH)_2$. Hydration of C_4AF and $Ca(OH)_2$ in presence of C_3S, on the other hand, results in generation of hydrogarnet phases like C_6AFSH [10].

2.2.2 Hydration of Portland Cement

Hydration of Portland cement is a group of reactions among clinker components, gypsum and water, which take place at different rates and influence the hydration of one another. It is known that hydration of Portland cement proceeds in several stages.

In the first few minutes of contact with water, which is termed as *pre-induction period*, rapid hydration of clinker components is observed. During this period, Ca^{2+}, SO_4^{2-} and OH^- concentrations in the liquid phase increase; C-S-H phases develop and surround the cement particles. Ettringite is also produced due to rapid hydration of C_3A. Hydration of C_4AF yields phases analogue to ettringite. After the pre-induction period, the rate of hydration is significantly reduced due to deposition of hydration products on the surface of unreacted cement particles and hydration proceeds very slowly for a few hours. This period is called the *induction* or *dormant period*. After the termination of the dormant period, which has been the subject of many theories in the open literature, hydration begins to accelerate again. In the *acceleration period*, the hydration accelerates again particularly associated with hydration of C_3S. During this stage, C-S-H phases are developed. At the end of approximately 12 hours after the contact of cement with water, hydration begins to slow down gradually, but C-S-H phases continue to develop due to hydration of β-C_2S and C_3S (*post-induction period*). At sufficiently high water/cement ratios, hydration of cement continues until all the cement is hydrated. However, at low water/cement ratios, unreacted cement remains, even after long periods of time [10,11].

CHAPTER 3

CHARACTERISTICS AND UTILIZATION OF FLY ASHES

3.1 Characteristics and Utilization of Fly Ashes

The characteristics of fly ashes depend on a variety of factors, such as the type of coal used or the technology employed for combustion. A vast number of studies have been carried out on characterization of conventional fly ashes, in order to discover their possible environmental impacts and potential of utilization.

Studies carried out on chemical compositions of fly ashes reveal that they are predominantly composed of acidic oxides, such as SiO_2, Al_2O_3, Fe_2O_3, and CaO. It was also found that they contain SO_3, MgO, Na_2O, K_2O, TiO_2 and some other trace elements. Past studies on characterization of fly ashes from pulverized coal combustion point out that compositions of fly ashes primarily depend on the characteristics of the coal burnt. Studies of Bayat [14] and Enders [15] reveal that fly ashes generated from combustion of lignites were predominantly composed of acidic oxides, however they might contain up to 25% CaO. Similar studies carried out on fly ashes generated from combustion of higher grade coals, on the other hand, indicate that these fly ashes contain nearly 90% SiO_2, Al_2O_3 and Fe_2O_3; and their CaO contents are hardly above 10% [16-18]. The findings of above mentioned studies were recently confirmed by Moreno *et al.* [19], by comparing physico-chemical characteristics of European fly ashes.

Mineralogical examinations of fly ashes reveal that low-calcium fly ashes have simple mineralogical compositions dominated by amorphous phases. X-ray diffraction (XRD) studies performed by Lee *et al.* [17] indicate that these fly ashes primarily contain quartz, mullite, hematite and amorphous phase. Char and kaolinite have also been identified in the XRD studies [18]. Foner *et al.* have finally shown that trace amounts of lime, calcite, anhydrite and graphite could be also detected in low-calcium fly ash samples [16]. The research carried out on high-calcium fly ashes have contrarily revealed that these fly ashes have more complex mineral assemblages. A large variety of minerals, such as marcasite, anorthite, gehlenite, free lime, gypsum, bassanite, ferrite spinel, melilite, merwinite, brown millerite and sodalite were found to exist in fly ashes from combustion of lignites [14,15].

In scanning electron microscope (SEM) studies, morphological structures of fly ashes from pulverized coal combustion have been found to be in form of glassy spheres, cenospheres and pleurospheres, due to high operating temperatures (around 1200-1500ºC) of pulverized coal combustors [15]. Irregularities observed in high-calcium fly ashes have been attributed to presence of crystalline phases and incomplete melting of ash components for homogenization [14].

Conventionally, fly ashes generated from combustion of pulverized coal is utilized as cement and concrete admixture, structural fill, cover material, in waste solidification and stabilization, roadway and pavement applications, lightweight aggregate manufacture and undergroung void filling [5]. Approximately 50% of fly ashes utilized is used as cement or concrete admixture owing to improved physical properties of fly ash incorporated cements or concrete.

3.2 Effects of Fly Ash on Cement or Concrete Properties

3.2.1 Effects of Fly Ash on Hydration of Portland Cement

Investigation of the effects of fly ashes on the hydration of Portland cement has been given particular attention in order to understand the mechanism through which fly ashes influence cement or concrete properties. The related studies carried out so far indicate that fly ashes behave as inert and have almost no influence on cement hydration during the first few weeks, due to slow rate of pozzolanic reactions [20,21]. In some similar studies, this inert period was claimed to be as long as 90 days [22,23]. During the process of hydration, $Ca(OH)_2$ concentration in fly ash containing cement pastes were found to decline with time due to reactions of $Ca(OH)_2$ with SiO_2 and Al_2O_3 in fly ash, whereas it was stable in pure cement pastes. However, it was also found that the $Ca(OH)_2$ concentration is stable in fly ash cement pastes after 360 days. Besides the pozzolanic nature of fly ashes, the study of Marsh and Day [20] points out that high-calcium fly ashes directly react with water at early ages and form hydrates similar to those produced from cement hydration.

Hydration rate of C_3S is known to be accelerated by fly ash incorporation. Past studies indicate that fly ash particles provide additional surface area for deposition of hydration products, therefore the hydrate layers on the cement particles get thin and hydration is accelerated [11,23]. As well as C_3S, hydration of C_3A is also influenced by fly ashes. Formation of ettringite was observed to occur in a few days. Similarly, conversion of ettringite to monosulfate is also accelerated. The acceleration in conversion of ettringite to monosulfate is attributed to dilution effects of fly ashes with low SO_3 content [22]. However, fly ashes with high content of SO_3 enhance production of ettringite.

The rate of pozzolanic reactions and the effects of fly ashes on hydration of cement pastes are strongly influenced by temperature, since rates of pozzolanic reactions highly depend on temperature.

It is worth noting that although the hydration of cement constituents are influenced and the porosity of the cement paste is reduced by the presence of fly ash, the primary hydration products were known to be quite similar to those of pure cement [20,22,23].

3.2.2 Effects of Fly Ash on Physical Properties of Cement and Concrete

Extensive scientific research has been carried out on effects of fly ash utilization on physical properties of cement and concrete. These studies reveal that utilization of fly ash generally results in reduced water requirement, improved compressive strength at later ages, extended setting times and improved durability.

In past studies, the contribution of fly ash to the strength development of mortars or concrete at early ages was found to be quite limited. However, the strength of concrete is improved with fly ash incorporation, generally starting from 28 days, depending on a variety of factors such as fly ash fineness or percent of cement replaced by fly ash [30,32,33,36,38,41,42,45,47,52]. The studies carried out with different size fractions of fly ashes point out that incorporation of ground or fine fractions of fly ash resulted in improved compressive strength [33,39,41,58,59]. However, the improvement in compressive strength is strongly influenced by the ratio of cement replaced by fly ash. Lam *et al.* [32] and Kula *et al.* [42] found that replacing cement with fly ash results in improved strength up to 20%, but leads to a decline in strength beyond this ratio. In contrast to these findings, Oner *et al.* proposed that the compressive strength could be improved by replacing up to 40% of cement with fly ash [54].

Although there are some contradictory findings, fly ashes proved to achieve considerable reduction in water requirement of pastes, mortars and concrete. The reduction in water requirement is related to the grain morphology and glass phase activity of fly ashes. Sun *et al.* [57] claimed that the spherical low-calcium fly ashes increase the fluidity of cement pastes since their particles have a lubricating effect between cement particles, lower tendency to absorb water, and lower density compared to Portland cement. However, water reducing effect of high-calcium fly ashes were found to be limited due to the irregularities in the fly ash morphology. The study of Bouzoubaâ *et al.* [39], on the other hand, shows that incorporation of ground fly ash in cement increases the water requirement, due to increased surface area.

The studies carried out on effects of fly ash on setting times of cement and concrete uniformly revealed that incorporation of fly ashes results in extended setting times due to reduced cement quantity and super plasticizing effect of fly ash [37]. In almost all of these studies setting times of pastes prepared by Portland cement-fly ash blends were reported to be within the limits set out by the standards [30,37,42,53]. The study of Liu *et al.* [40] also reveals that incorporation of fine fractions of fly ash, with a Blaine surface area of 740 m^2/kg, in cement blends marginally extends the setting times.

It is well known that the volume stability of pastes containing fly ash primarily depends on fly ash composition. The findings of past studies indicate that fly ashes with high content of CaO exhibit poor volume stability due to hydration of free CaO [13,30]. Low-calcium fly ashes, on the other hand, were not found to have any negative effects on the volume stability owing to their low free CaO content [42].

One of the most important advantages of the use of fly ash as cement or concrete admixture is the improvement in durability characteristics. The studies carried out by Al-Dulaijan *et al.* [49] and Chindaprasirt *et al.* [51] showed that the mortars prepared by incorporation of fly ash achieved the best sulfate resistance among all mineral admixtures, when exposed to varying concentrations of Na_2SO_4. In the study of Monteiro and Curtis [50], fly ash also proved to improve the sulfate resistance of cements with low C_3A content, which inherently have sulfate resisting property. In the recent study of Nehdi and Hayek [55], fly ash containing pastes and mortars improved durability in sulfate solutions.

Fly ashes are also known to increase the resistance of cement and concrete against alkali silica and alkali aggregate reactions, provided that their Na_2O and KB_2O contents are below 1.5%, as given in international standards [8,29]. It was also shown that fly ashes with relatively higher contents of alkali oxides (2-3%) can also improve the resistance against alkali-silica reactions, except for fly ashes with very high alkali oxide contents (around 8%) [44].

As well as their resistance against sulfate attack and alkali-silica reactions, fly ash bearing structures were found to have lower depths of chloride ion penetration, which causes corrosion in steel reinforcement in concrete [24,25,28,38,39]. It was also shown that fly ash containing structures have improved strength under wet-dry conditions and have reduced shrinkage upon drying [41,51].

Besides their advantages, fly ashes also have negative effects on durability properties. Past studies claim that utilization of fly ash as cement and concrete admixture reduces abrasion-erosion resistance [36,56] and durability in freeze-thaw environments [52].

Table 3.1 summarizes the open literature regarding the efects of fly ash utilization on physical properties of cement and concrete. Nomenclature for Table 3.1 is provided in Table 3.2.

Table 3.1: Summary of literature on effects of fly ash on cement or concrete properties

Author	**Year**	**Type of Specimen**	**Ratio of Fly Ash Substitution (%)**	**Fresh State Properties**	**Hardended State Properties**	**Durability**
Thomas [24]	1991	2	15-50			Improved CP
Thomas & Matthews [25]	1993	3				Improved CP Increased DC Improved AS
Cerkanowicz *et al.* [26]	1993	1 & 2	25		Improved CS with FAF	
Saravanos & Nasser [27]	1993	2	20-60	Reduced WR	Reduced CS	
Mangat & Molloy [28]	1995	2	22			Improved CP
Shayan *et al.* [29]	1996	1	25			Improved AA
Zhang *et al.* [30]	1997	1 & 2	50-60	Extended ST	Improved CSL Poor VS	
Monteiro *et al.* [31]	1997	1	15-30			Improved AA

Table 3.1: Summary of literature on effects of fly ash on cement or concrete properties (Continued)

Author	**Year**	**Type of Specimen**	**Ratio of Fly Ash Substitution (%)**	**Fresh State Properties**	**Hardended State Properties**	**Durability**
Lam *et al.* [32]	1998	2	15-55		Improved CSL at low FA %	
Tan & Pu [33]	1998	2	20		Improved CSL with FAG	
Blezynski & Thomas [34]	1998	2	25-40			Improved AS
Lane & Özyıldırım [35]	1999	2	15-35		Reduced CS	Improved AS
Malhotra *et al.* [36]	2000	2	20	Reduced WR	Improved CSL	Reduced AE
Brooks *et al.* [37]	2000	2	10-30	Extended ST		
Hassan *et al.* [38]	2000	2	30	Reduced WR	Improved CSL	Improved CP
Bouzoubaâ [39]	2000	2	40-55	Increased WR and reduced AE with FAG	Improved CS with FAG	Improved CP

Table 3.1: Summary of literature on effects of fly ash on cement or concrete properties (Continued)

Author	**Year**	**Type of Specimen**	**Ratio of Fly Ash Substitution (%)**	**Fresh State Properties**	**Hardended State Properties**	**Durability**
Jiang & Malhotra [40]	2000	2	55	Reduced WR	Reduced CS	
Liu *et al.* [41]	2000	2	35-60	Reduced WR	Improved CSL	Reduced DS
Kula *et al.* [42]	2001	1	5-25	Increased WR Extended ST	Improved CSL up to 20% FA	
Roy *et al.* [43]	2001	1	7.5-30		Reduced CS at high FA	Improved CA
Duchesne & Bérubé [44]	2001	1	20-40			Improved AS
Memon *et al.* [45]	2002	2	30-70		Improved CSL	Reduced SW
Shetata & Thomas [46]	2002	1 & 2	15-60			Improved AS
Demirboğa [47]	2003	1	10-30		Improved CSL	
Siddique [48]	2003	2	40-50	Unaffected WR	Reduced CS	Reduced AE

Table 3.1: Summary of literature on effects of fly ash on cement or concrete properties (Continued)

Author	**Year**	**Type of Specimen**	**Ratio of Fly Ash Substitution (%)**	**Fresh State Properties**	**Hardended State Properties**	**Durability**
Al-Dulaijan *et al.* [49]	2003	1	20%			Improved SR
Monteiro & Curtis [50]	2003	2	25-45			Improved SR
Chindaprasirt *et al.* [51]	2004	1	40	Reduced WR	Improved CS	Reduced DS Improved SR
Toutanji *et al.* [52]	2004	2	20-30		Improved CSL	Reduced FT Improved WD
Chindaprasirt *et al.* [53]	2005	1	20-40	Extended ST Reduced WR	Reduced CS	
Öner *et al.* [54]	2005	2	15-58	Unaffected WR	Highest CS at 40% FA	
Nehdi & Hayek [55]	2005	1	25			Improved SR
Yen *et al.* [56]	2005	1 & 2	15-20			Reduced AE

Table 3.2: Nomenclature for Table 3.1

Types of Specimen	
1	Paste and/or mortar
2	Concrete
3	Existing concrete structures built by utilizing fly ash
Fresh State Properties	
AC	Air content
ST	Setting times
UW	Unit weight
WR	Water requirement
Hardened State Properties	
CS	Compressive strength
CSL	Compressive strength at ages 28 days or later
FA	Substitution of fly ash
FAF	Substitution of fine fractions of fly ash
FAG	Substitution of ground fly ash
VS	Volume stability or soundness
Durability Properties	
AA	Resistance against alkali-aggregate reactions
AE	Resistance against abrasion-erosion
AS	Resistance against alkali-silica reactions
CA	Resistance against chemical attack
CP	Resistance against chloride-ion penetration
DC	Depth of Carbonation
DS	Drying shrinkage
FT	Freeze-thaw resistance
SR	Sulfate resistance
SW	Sea water deterioration
WD	Strength under wet-dry conditions

3.3 Standards for Use of Fly Ash in Cement and Concrete

There are international standards for classification and specifications of fly ashes to be used as cement or concrete admixture. EN 197-1 defines classification and specifications of fly ashes generated from combustion of pulverized coal, to be utilized in production of blended Portland cements [6]. Similar requirements are included in EN 450, which defines specifications of fly ashes to be incorporated in concrete [7]. Chemical and physical requirements imposed by the European standards are given in Table 3.3.

In ASTM C 618, classification and specifications of fly ashes are defined depending on the rank of coal burnt [8]. Chemical and physical requirements included in ASTM C 618 are given in Table 3.4.

Table 3.3: Fly ash specifications according to European standards

	EN 197-1 Limit	EN 450 Limit
LOI, max. %	5.0	5.0
SO_3, max. %	-	3.0
Free CaO, max. %	1.0	1.0
Reactive SiO_2, min. %	25.0	25.0
Cl^-, max. %	0.1	0.1
Fineness, max. %	-	40
SAI at 28 days, min. %	-	75.0
SAI at 90 days, min. %	-	85.0
Soundness, max. mm	-	10

Table 3.4: Fly ash specifications according to ASTM C 618

	ASTM C 618 Limits	
	Class F	Class C
Moisture, max. %	3.0	3.0
LOI, max. %	6.0	12.0
SO_3, max. %	5.0	5.0
SiO_2+Al_2O_3+Fe_2O_3, min. %	70.0	50.0
Equivalent Na_2O*, max. %	1.5	1.5
Fineness, max. %	34	34
Water Requirement, max. %	105	105
SAI at 7 days, min. %	75	75
SAI at 28 days, min. %	75	75
Soundness, max. %	0.8	0.8

* Equivalent Na_2O = % Na_2O + 0.653 × % KB_2O

CHAPTER 4

CHARACTERISTICS AND UTILIZATION OF FBC FLY ASHES

4.1 Characteristics of FBC Fly Ashes

Steady increase in the applications of FBC technology in both number and capacity over the past decade has led to the investigation of the characteristics of FBC fly ashes in order to predict their possible environmental impacts and discover their potential of utilization. Studies on characterization of FBC fly ashes indicate that they significantly differ from PCC fly ashes due to major differences between FBC and PCC technologies.

Fly ashes from fluidized bed combustion were found to be predominantly composed of calcined limestone and desulfurization products due to continuous limestone injection for SO_2 capture during combustion. The study of Lecuyer *et al.* [60], carried out for characterization of fly ash samples from fluidized bed combustion of a lignite containing 15% CaO, has shown that these fly ashes were composed of 33-52% CaO due to high CaO content of the lignite and 16-26% SO_3 due to auto desulfurization. High inherent Ca/S ratio of the lignite (2.5-3) has been found to result in 10-15% free CaO in fly ashes. Similar results have been obtained by

Anthony *et al.* [61], who examined the characteristics of fly ashes from an industrial scale FBC boiler (36-43% CaO, 16-19% SO_3 and 10-16% free CaO). These studies indicated that acidic oxide content of FBC fly ashes are lower (20-35% SiO_2+Al_2O_3+Fe_2O_3) compared to PCC fly ashes. On the other hand, Lecuyer *et al.* (1996) have shown that FBC fly ashes might have appreciable content of acidic oxides when the Ca/S ratio is relatively low (2.3) [62].

XRD studies on FBC fly ashes have shown that they have complex mineralogical structures similar to those of high-calcium PCC fly ashes, and might contain minerals such as quartz, mullite, haematite, anhydrite, free CaO, portlandite, calcite, illite [60,62,63].

Unlike PC fly ashes, morphological structures of FBC fly ashes were found to be in quite irregular geometry. The irregular microstructure of FBC fly ashes has been attributed to lower operating temperature of FBC (around 850ºC), which restricts the melting and sintering of ash components to form glassy phases in form of microspheres [62].

4.2 Utilization of FBC Fly Ash as Cement or Concrete Admixture

There is a limited amount of scientific research regarding the utilization of FBC fly ashes as cement or concrete admixture. These studies have revealed that incorporation of FBC fly ashes in cement or concrete results in either improved or decreased compressive strength, similar to conventional PCC fly ashes. In the study of Behr-Andres and Hutzler [63], compressive strength of concrete samples prepared by replacing 20-55% of cement with fly ash were found to be reduced with increasing ratio of cement replaced with fly ash. The decrease in compressive strength was attributed to hydration of anhydrite in the fly ash. It was also found that the air entrainment and unit weight of the samples were reduced due to rapid hydration of fly ash and filling voids in the cement and the aggregates. In this study, the water requirement of the concrete samples were not influenced by utilization of fly ash.

Cement pastes prepared by incorporation of FBC fly ashes were found to show poor volume stability, due to their high free CaO content. Hydration treatments have been employed in order to convert free CaO in FBC fly ashes to $Ca(OH)_2$ and avoid deleterious expansion due to hydration of free CaO. Blondin and Anthony [64] have studied the perfromance of FBC fly ash as concrete admixture by employing a prehydration treatment for FBC fly ash which converts free CaO to $Ca(OH)_2$. Compressive strength of the specimens prepared by replacing 15% of cement with fly ash were found to be improved particularly at later ages. However, the strength was reduced for 30% substitution. The volume stability of the pastes prepared by fly ash substitution was poor and deleterious expansions were observed.

As well as their utilization as partial cement replacement, FBC fly ashes were also examined in order to determine their potential use in production of non-cement concrete. Burwell *et al.* [65] have studied mechanical properties of non-cement concrete samples containing both FBC and PCC fly ashes. The blends prepared with PCC and hydrated FBC fly ashes were found to have lower compressive strength and extended setting times compared to Portland cements. In this study, it was verified that FBC fly ashes contribute to the early strength development owing to the presence of calcined clays. PCC fly ashes, on the other hand, had almost no contribution to early strength development, but contributed to long term strength due to their pozzolanic properties.

Besides these limited number of studies, there are still questionable points about utilization potential of FBC fly ashes as cement or concrete admixture, particularly due to their high free CaO content. It should also be borne in mind that above mentioned studies related to utilization of FBC fly ashes were carried out with fly ashes generated from combustion of high grade coals, such as high-sulfur bituminous or low-sulfur bituminous coals containing less than 2% sulfur and 12% ash. However, fly ashes generated from fluidized bed combustion of lignites potentially have higher content of acidic oxides, therefore their potential utilization in cement or concrete is worth investigating.

CHAPTER 5

EXPERIMENTAL STUDY

In this study, chemical, mineralogical, morphological and physical properties of three fly ash samples from fluidized bed combustion of a typical Turkish lignite, and physical properties of Portland cement-fly ash blends were determined. Chemical and physical characterization of fly ash samples were performed strictly according to the standards referred in EN 450, EN 197-1 and ASTM C 618 [6-8]. Physical properties of Portland cement-fly ash blends were determined according to the standards referred in ASTM C 595 [66].

5.1 Fly Ash Samples and Reference Cement

The three fly ash samples examined in this study were generated from fluidized bed combustion of a typical Turkish lignite. Characteristics of lignite, its ash and limestone utilized are given in Tables 5.1, 5.2 and 5.3, respectively.

The reference cement used in determination of physical properties of fly ashes and fly ash-cement blends was CEM I 42.5 type Portland cement.

Table 5.1: Characteristics of the lignite

Proximate Analysis		Ultimate Analysis	
Moisture, %	21.08	C, %	38.88
Ash, %	23.84	H, %	1.93
VM, %	28,61	N, %	1.05
Fixed C, %	26.46	O, %	10.67
S_{comb}, %	2.55		
LHV, MJ/kg	14.79		

Table 5.2: Analysis of the coal ash

SiO_2, %	55.60
Fe_2O_3, %	9.22
Al_2O_3, %	23.07
CaO, %	4.06
SO_3, %	3.75
MgO, %	1.93
Na_2O, %	0.64
K_2O, %	0.44
P_2O_5, %	0.17
TiO_2, %	0.96

Table 5.3: Analysis of the limestone

Moisture, %	0.12
$CaCO_3$, %	92.54
$MgCO_3$, %	4.98
SiO_2, %	1.03
Na_2O, %	0.28
K_2O, %	0.06
Al_2O_3, %	0.09
Fe_2O_3, %	0.15

5.2 Chemical Analyses of Fly Ashes

Chemical analyses of fly ash samples were performed strictly according to the standards referred in EN 450 and ASTM C 618. Referenced test methods for the chemical analyses according to European and ASTM standards are shown in Tables 5.4 and 5.5, respectively. The test methods are only briefly described in Appendix A, since their details are already given in the referenced standards.

Table 5.4: European standards for chemical analyses of fly ashes [67-69]

Fly Ash Component	Reference Standard
Loss on Ignition	EN 196-2
SO_3	EN 196-2
Total CaO	EN 196-2
Reactive SiO_2	EN 196-2
Free CaO	EN 451-1
Cl^-	EN 196-21

Table 5.5: ASTM standards for chemical analyses of fly ashes [70,71]

Fly Ash Component	Reference Standard
Loss on Ignition	ASTM C 311
Moisture	ASTM C 311
SiO_2, %	ASTM C 114
Fe_2O_3, %	ASTM C 114
Al_2O_3, %	ASTM C 114
CaO, %	ASTM C 114
SO_3, %	ASTM C 114
Na_2O, %	ASTM C 114
K_2O, %	ASTM C 114

5.3 Determination of Physical Properties of Fly Ashes

Physical properties of fly ash samples were also investigated according to the standards referred in EN 450 and ASTM C 618. Referenced standards according to European and ASTM standards are given in Tables 5.6 and 5.7, respectively. The standard test methods are briefly outlined in Appendix B.

Table 5.6: European test standards for physical properties of fly ashes [72-74]

Physical Property	Reference Standard
Fineness	EN 451-2
Soundness	EN 196-3
Strength Activity Index	EN 196-1

Table 5.7: ASTM test standards for physical properties of fly ashes [75-77]

Physical Property	Reference Standard
Fineness	ASTM C 430
Soundness	ASTM C 151
Water Requirement	ASTM C 109
Strength Activity Index	ASTM C 109

5.4 Determination of Mineralogical and Morphological Properties

Mineralogical characterization of fly ashes was carried out by using X-Ray Diffraction (XRD). Additionally, Scanning Electron Microscope (SEM) was used for the investgation of morphological structures of the fly ash samples.

5.5 Physical Properties of Portland Cement-Fly Ash Blends

After the characterization of fly ash samples, physical properties of Portland cement pastes and mortars prepared by incorporating 10%, 20% and 30% fly ash 2 and 3 were determined. Physical tests of the fly ash-cement blends were performed according to the standards referred in ASTM C 595, which defines specifications for blended cements containing up to 40% mineral admixtures [66]. Standards for determination of physical properties of fly ash-cement blends referred in ASTM C 595 are given in Table 5.8. The standard test procedures are briefly explained in Appendix C.

Table 5.8: Test standards for determination of properties referred in ASTM C 595 [76-79]

Physical Property	Reference Standard
Consistency of Mortar	ASTM C 109
Compressive Strength	ASTM C 109
Consistency of Paste	ASTM C 187
Setting Times	ASTM C 191
Soundness	ASTM C 151

CHAPTER 6

RESULTS AND DISCUSSION

6.1 Chemical Analyses

Chemical analyses of fly ash samples were carried out and the results are compared with the requirements of EN 450 and EN 197-1 in Table 6.1. As can be seen from the table, fly ashes can meet the European standards except free CaO and SO_3. The fly ashes contain appreciable amounts of CaO and SO_3. CaO content of fly ashes 2 and 3 were higher due to higher Ca/S ratio. However, CaO and SO_3 contents of these fly ashes were found to be lower than those of fly ashes reported in the literature [60,61].

Table 6.1: Chemical compositions of fly ashes vs. EN 450 specifications

	Fly Ash 1	Fly Ash 2	Fly Ash 3	EN 450
LOI, %	1.54	5.27	3.95	max. 5.0
SO_3, %	4.14	9.23	10.81	max. 3.0
Free CaO, %	2.16	1.35	8.78	max. 1.0
Total CaO, %	9.34	13.54	24.23	-
Reactive SiO_2, %	52.61	39.25	29.87	min. 25.0
Cl^-	0.0057	0.0284	0.0269	max. 0.1

With respect to conformity to ASTM standards, fly ash samples satisfy the requirements of ASTM C 618, apart from SO_3 and equivalent Na_2O contents (Table 6.2). It is worth noting that fly ashes 1 and 2 have higher acidic oxide content contrary to the majority of FBC fly ashes previously studied [60,61]. However, acidic oxide content required by Class C fly ashes was not found to be satisfied by fly ash 3, due to higher Ca/S ratio.

Table 6.2: Chemical compositions of fly ashes vs. ASTM C 618 specifications

	Fly Ash 1	Fly Ash 2	Fly Ash 3	ASTM C 618
Moisture, %	0.14	0.15	0.09	max. 3.0
LOI, %	1.30	3.31	4.46	max. 12.0
SO_3, %	4.20	9.02	10.03	max. 5.0
SiO_2, %	51.40	32.37	22.28	-
Al_2O_3, %	16.11	11.92	14.37	-
Fe_2O_3, %	8.96	10.19	7.80	-
SiO_2+Al_2O_3+Fe_2O_3, %	76.47	67.39	44.45	min. 50.0
CaO, %	15.78	13.40	23.14	-
Na_2O, %	1.67	1.14	1.14	-
K_2O, %	0.10	0.08	0.24	-
Equivalent Na_2O, %	1.73	0.95	2.36	max. 1.5

6.2 Physical Properties

Table 6.3 shows comparison between physical properties of fly ash samples and corresponding European standard specifications. All fly ash samples were found to exhibit very low Le Chatelier expansions, satisfying the soundness requirement.

Fineness and 28-days strength activity index (SAI) requirements of EN 450 were satisfied by fly ashes 2 and 3. However, SAI requirement at 90 days was not met by any samples.

Table 6.3: Physical properties of fly ashes vs. EN 450 specifications

	Fly Ash 1	Fly Ash 2	Fly Ash 3	EN 450
Fineness, % retained	41	29	40	max 40
Soundness, mm	1	0	0	max 10
SAI at 28 days, %	68.4	77.7	79.3	min 75
SAI at 90 days, %	62.9	76.9	76.5	min 85

Comparison between physical properties of fly ash samples and ASTM C 618 specifications are shown in Table 6.4. Fly Ash 1 could not be physically tested according to ASTM standards since limited amount of sample was obtained during the test run. As can be seen from the table, fly ashes 2 and 3 were found to satisfy the requirements for soundness and SAI at 28 days. However, 7-days SAI of fly ash 2 and finenesses of fly ashes 1 and 3 did not satisfy the ASTM requirements. Water requirements of both samples were also not in compliance with the standard.

Table 6.4: Physical properties of fly ashes vs. ASTM C 618 specifications

	Fly Ash 1	Fly Ash 2	Fly Ash 3	ASTM C 618
Fineness, % retained	41	29	40	max 34
Soundness, %	-	0.11	0.16	max 0.8
Water Requirement, % of control	-	117	114	max 105
SAI at 7 days, %	-	71.9	83.9	min 75
SAI at 28 days, %	-	97.6	79.9	min 75

6.3 Mineralogical and Morphological Properties

Mineralogical analyses performed by XRD indicated that the samples had a complex mineral assemblage, similar to other FBC fly ashes reported in the literature, and were composed of minerals given in Table 6.5 [60,61]. Contrary to fly ash 1, fly ashes 2 and 3 were found to contain calcite.

Table 6.5: Mineralogical compositions of fly ash samples

Fly Ash 1	Fly Ash 2	Fly Ash 3
Quartz	Quartz	Quartz
Anhydrite	Anhydrite	Anhydrite
Free lime	Free lime	Free lime
Silicon oxide	Silicon oxide	Gehlenite
Hematite	Hematite	Hematite
Feldspar	Feldspar	Feldspar
	Calcite	Calcite

Examination of scanning electron micrographs of fly ashes 1 and 2, as shown in Figures 6.1 and 6.2 respectively, reveal that fly ash samples under consideration have quite irregular microstructure like all other FBC fly ashes reported in the literature, due to lower operating temperature of FBC (around 850ºC) [60,61]. Investigation of fly ash 3 by SEM was not found necessary as it was also generated under similar operating temperature typical of FBC.

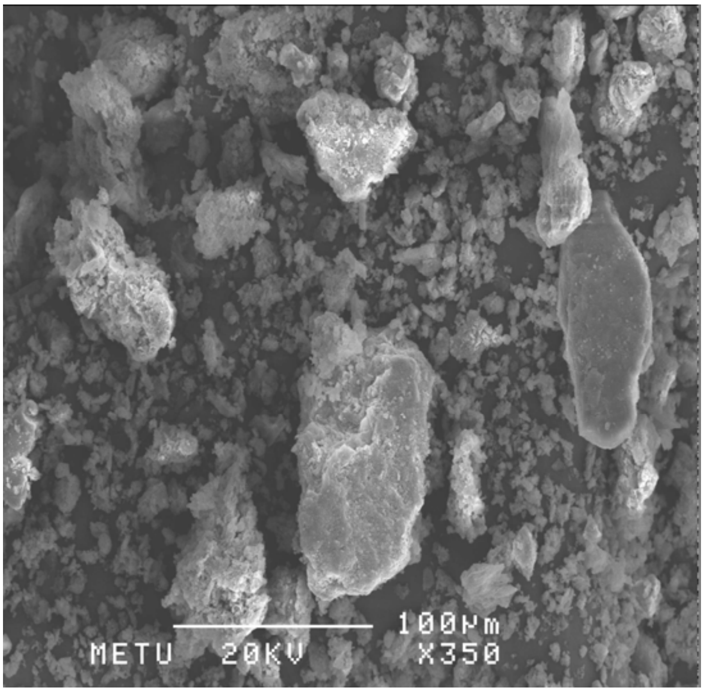

Figure 6.1: Scanning electron micrograph of fly ash 1

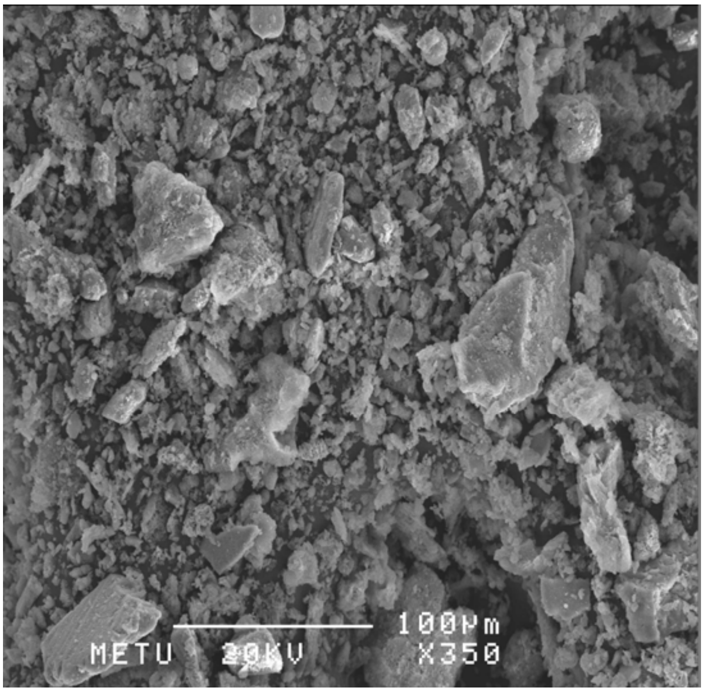

Figure 6.2: Scanning electron micrograph of fly ash 2

6.4 Physical Properties of Portland Cement-Fly Ash Blends

6.4.1 Consistency of Mortars

Flow table tests performed according to ASTM C 109 indicated that the water-to-cement (w/c) ratios of Portland cement-fly ash blends increased with increasing fly ash content. The increase in water requirement can be attributed to irregular morphology of the fly ash samples as stated by Sun *et al.* [57]. Variation of w/c ratio of the mortars with respect to fly ash content is illustrated in Figure 6.3. Compositions of mortars to be tested for compressive strength are shown in Table 6.6.

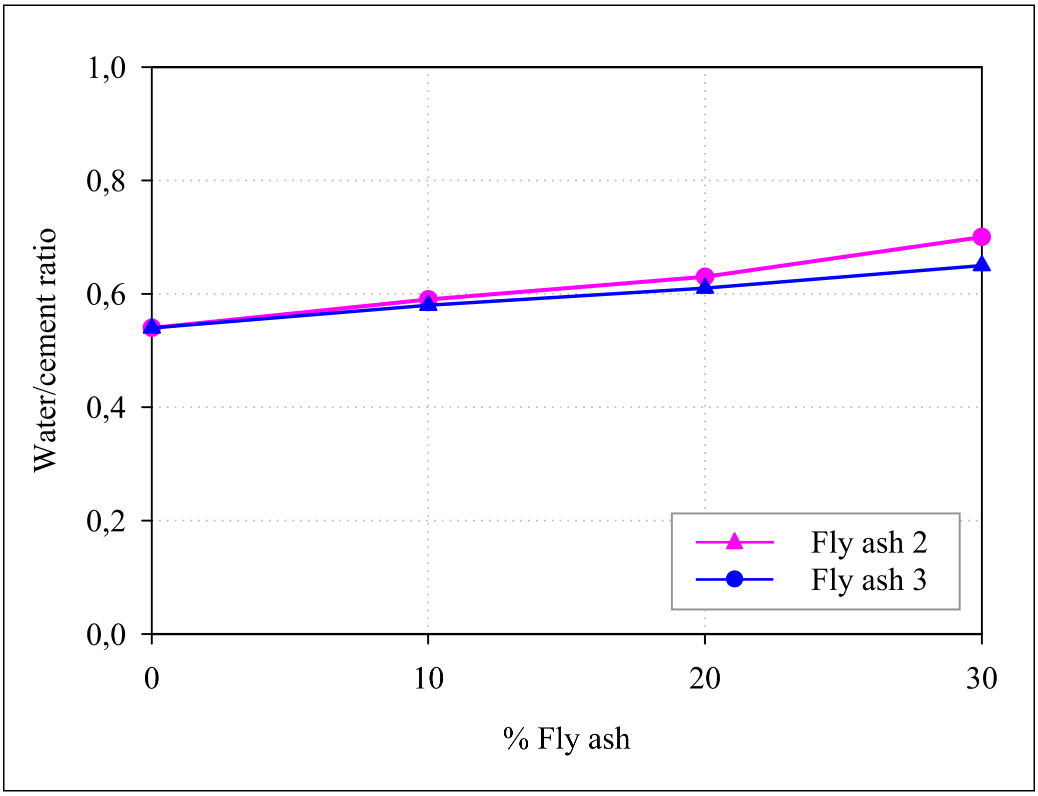

Figure 6.3: Variation of w/c ratio with respect to fly ash content

Table 6.6: Compositions of mortars prepared by Portland cement-fly ash blends

	Fly Ash 2				Fly Ash 3			
	0%	10%	20%	30%	0%	10%	20%	30%
Cement, g	500	450	400	350	500	450	400	350
Fly ash, g	0	50	100	150	0	50	100	150
Water, g	242	265	283	315	242	259	275	291
Sand, g	1375	1375	1375	1375	1375	1375	1375	1375

6.4.2 Compressive Strength of Mortars

Figure 6.4 and 6.5 show variation of compressive strength with fly ash content for both samples, at 7 and 28 days respectively, and the limits dictated by ASTM C 595. As can be seen from the figure, both samples satisfy the ASTM requirement. The decrease in 7 days compressive strength is consistent with the findings of past studies, which indicate that fly ashes do not contribute to strength development at early ages.

As can be seen from Figure 6.5, fly ash 2 attains satisfactory strength similar to almost all fly ashes reported in the literature. However, incorporation of fly ash 3 led to decrease in 28-days compressive strength. The difference between strength contribution of fly ashes 2 and 3 originates from coarser particle size of fly ash 3 and hydration of higher content of anhydrite.

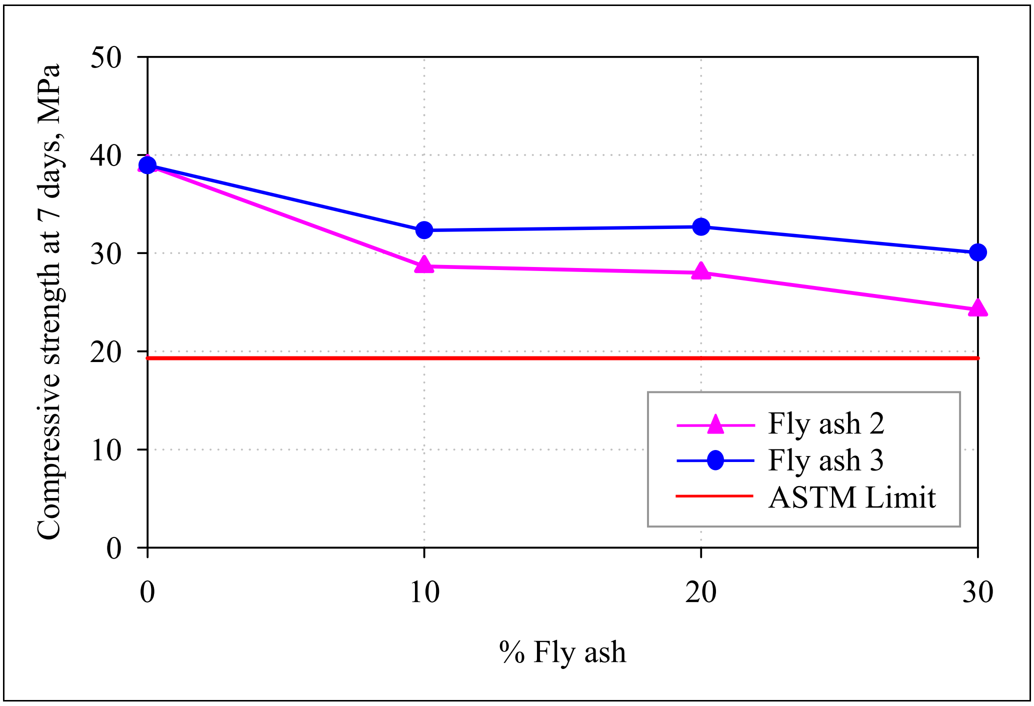

Figure 6.4: Variation of 7 days compressive strength with respect to fly ash content

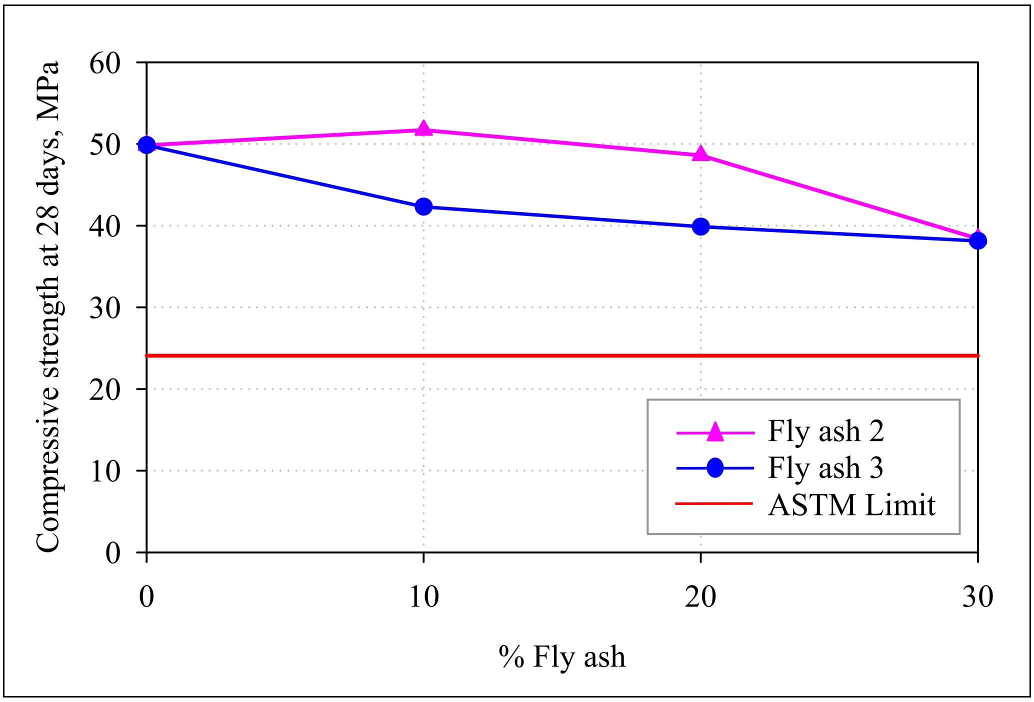

Figure 6.5: Variation of 28 days compressive strength with respect to fly ash content

6.4.3 Consistency of Pastes

Consistency tests performed according to ASTM C 187 indicated that the water requirement of Portland cement-fly ash blends for 10±1 mm penetration of Vicat plunger increased with increasing fly ash content. Compositions of mortars to be tested for setting times and soundness are shown in Table 6.7.

Table 6.7: Compositions of pastes prepared by Portland cement-fly ash blends

	Fly Ash 2				Fly Ash 3			
	0%	10%	20%	30%	0%	10%	20%	30%
Cement, g	650	585	520	455	650	585	520	455
Fly ash, g	0	65	130	195	0	65	130	195
Water, g	175	216	243	295	175	195	226	249

6.4.4 Setting Times of Pastes

Variations of setting times determined according to ASTM C 191 are displayed in Figure 6.6. It can be noted that both setting times are extended with increasing fly ash content and remain within the limits set by the standard. Slight increase in setting times with increasing fly ash content is similar to findings of the past research on utilization of conventional fly ashes as cement admixture [30,37,42,53]. The extensions in setting times resulted from reduced cement quantitity, even though the fly ash samples did not have any super plasticizing effect on pastes and mortars.

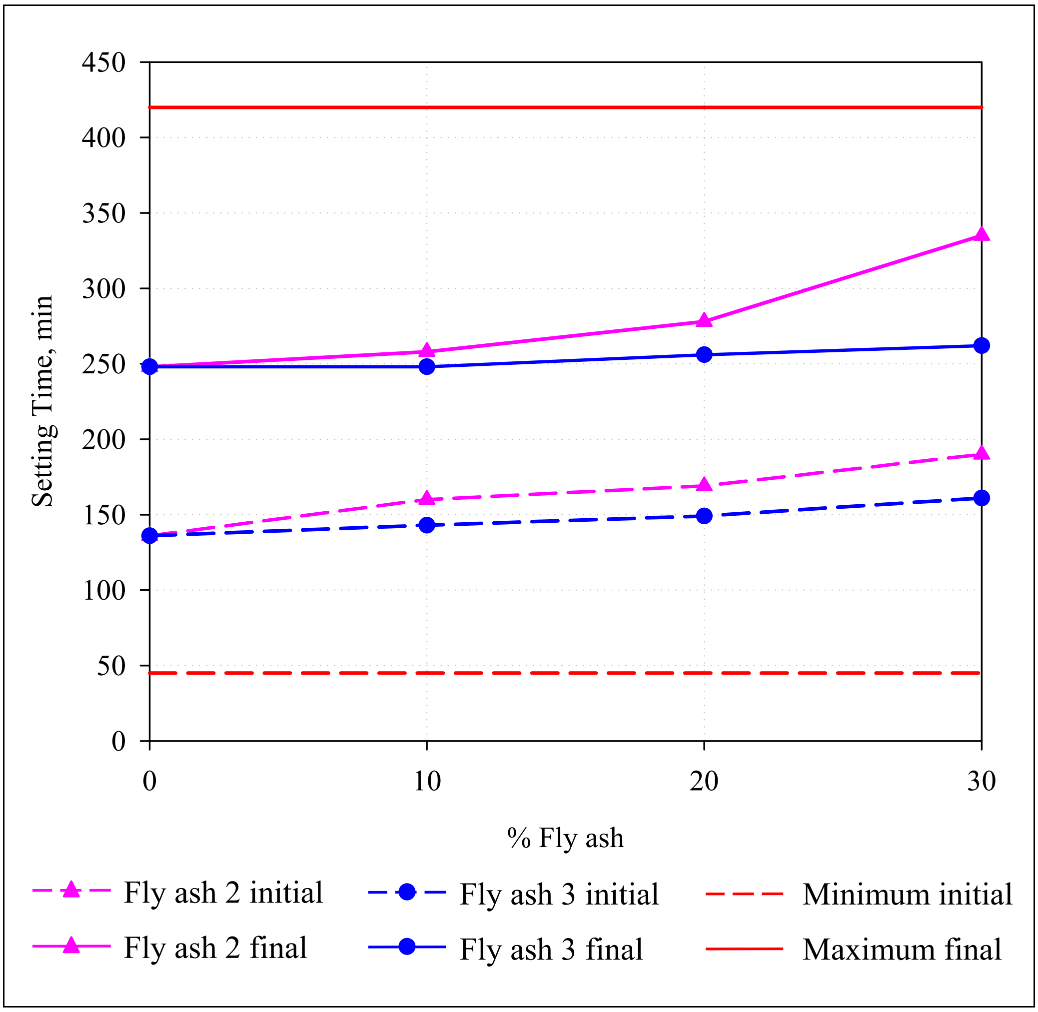

Figure 6.6: Variation of setting times with respect to fly ash content

6.4.5 Autoclave Expansion of Pastes

Inspection of autoclave expansions of Portland cement-fly ash blends and control paste determined according to ASTM C 151 and shown in Table 6.8 pointed out that expansions of the blends are higher than that of the control paste. It can also be seen that expansion of the blend of fly ash 3 increases with the fly ash content due to higher free CaO content of this sample. It is worth noting that, despite the increase in autoclave expansion, the samples under study are in compliance with ASTM C 595 without any prehydration requirement.

Table 6.8: Autoclave expansion of fly ash-cement blends

	Fly Ash 2	Fly Ash 3	ASTM C 595
Control Paste	0.0206	0.0206	0.5
10% Fly Ash	0.1176	0.1411	0.5
20% Fly Ash	0.1078	0.1611	0.5
30% Fly Ash	0.0725	0.2362	0.5

CHAPTER 7

CONCLUSIONS

In this thesis study, characterization of fly ashes generated from fluidized bed combustion of a Turkish lignite and evaluation of these fly ashes as partial Portland cement replacement in production of pastes and mortars were carried out. The samples were subjected to chemical, physical, mineralogical and morphological analyses. In addition to characterization studies, water requirement, compressive strength, setting time and soundness tests were also performed for 10%, 20% and 30% fly ash-cement blends and the reference cement. The following conclusions were reached under the observations of this study:

- The fly ash samples from fluidized bed combustion of a typical Turkish lignite have higher acidic oxide content compared to majority of the FBC fly ashes reported previously. However, acidic oxide content of fly ashes decreases with increasing Ca/S ratio.
- Fly ashes conform to physical requirements of EN 450 except 90-days strength activity index.
- Fly ashes are in compliance with physical requirements of ASTM C 618 for soundness and 28-days strength activity index.

- 10%, 20% and 30% fly ash-cement blends meet compressive strength, setting time and soundness requirements of ASTM C 595 without any pre-hydration treatment.
- Fly ashes generated from fluidized bed combustion of Turkish lignites have significant potential for utilization as an admixture in manufacture of blended cements.

7.1 Recommendations for Future Work

Based on the experience of this study, following recommendations for further improvement of the investigation of the possibilities for utilization of FBC fly ashes are proposed:

- Long-term durability characteristics of pastes, mortars or concrete structures prepared by Portland cement-FBC fly ash blends need to be investigated, particularly in order to examine the effects of relatively higher SO_3 content of FBC fly ashes on durability.

- Possibilities for utilization of FBC fly ashes as a raw material for production of Portland cement is worth investigating, especially owing to high CaO content of these ashes.

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APPENDIX A

TEST METHODS FOR CHEMICAL ANALYSES OF FLY ASHES

Table A.1: Brief description of analysis methods referred in EN 450

Component	Description of the Test Method
Loss on Ignition	1±0.05 g sample was kept in the furnace at 975±25ºC for 1 hour
SO_3	Sulfate ions, which are released when 1±0.05 g sample is dissolved in HCl solution, are precipitated with $BaCl_2$ at a pH of 1-1.5
Free CaO	Mixture of sample, butanoic acid, 3-oxy-ethyl ester and butane-2-ol was boiled for one hour and the hot mixture was filtrated. The filtrate was washed with proppane-2-ol and the elutriate is titrated with HCl. The content of free CaO is calculated from the mass of acid consumed.
Cl^-	Cl^- ions, released when 5±0.05 g sample is degraded in HNO_3 solution, are precipiteted with $AgNO_3$ solution
Total CaO	After the determination of SiO_2 and Al_2O_3, calcium was precipitated as oxalate and the oxalate was redissolved and titrated with $KMnO_4$.
Reactive SiO_2	Reactive SiO_2 was determined by subtracting insoluble residue in HCl and KOH from total SiO_2.

Table A.2: Brief description of analysis methods referred in ASTM C 618

Component	Description of the Test Method
Moisture	As received sample was dried to constant weight in an oven at 105 ºC
Loss on Ignition	1 g of sample was ignited to a constant weight at 750±25ºC
SO_3	Sulfate was precipitated from an acid solution of the sample, with $BaCl_2$
SiO_2	The method is based on Na_2CO_3 fusion followed by evaporation of HCl solution of the fusion product to convert SiO_2 to insoluble form
Al_2O_3	Aluminum was precipitated from the the filtrate after SiO_2 removal, by means of ammonium hydroxide
Fe_2O_3	Fe_2O_3 was determined by reducing the iron to the ferrous state with $SnCl_2$ and titrating with $K_2Cr_2O_7$
CaO	After the determination of SiO_2 and Al_2O_3, calcium was precipitated as oxalate and the oxalate was redissolved and titrated with $KMnO_4$.
Na_2O	Water is added to 25.0 g of sample and the mixture was filtrated. Concentrated HCl and $CaCl_2$ were added to the filtrate and the mixture was diluted. Final mixture was analyzed either by flame photometry or atomic absorption
K_2O	Water was added to 25.0 g of sample and the mixture was filtrated. Concentrated HCl and $CaCl_2$ were added to the filtrate and the mixture was diluted. Final mixture was analyzed either by flame photometry or atomic absorption

APPENDIX B

TEST METHODS FOR PHYSICAL PROPERTIES OF FLY ASHES

Table B.1: Brief description of physical test methods referred in EN 450

Physical Property	Description of the Test Method
Fineness	1.0 g of fly ash was dried at 110 ºC, for 24 hours. The dried sample was wet sieved on a 45µ (No.325) sieve and the fineness was expressed as the percent mass retained above the sieve.
Strength Activity Index	The prismatic test specimens 40 mm×40 mm×160 mm in size were cast from batches of mortar prepared by mixing • 450 g cement, 1350 g standard sand and 225 g water (control mortar) • 337.5 g cement, 112.5 g fly ash, 1350 g standard sand and 225 g water. The specimens were kept in water at 20ºC until the time of testing and their compressive strengths were determined by applying load at a rate of 2400 N/s, at 28 and 90 days. The strength activity index was finally expressed as the percent ratio of the compressive strength of the mortar prepared by replacing 25% of cement with fly ash to the compressive strength of the mortar prepared with control cement.

Table B.1: Brief description of physical test methods referred in EN 450 (Continued)

Physical Property	Description of the Test Method
Soundness	Le Chatelier mould was filled with the paste prepared by substituting 50% of cement with fly ash. The mould was kept at 20ºC and 98% relative humidity for initial 24 hours. After the initial measurement was taken at the end of 24 hours, the water bath was heated gradually for 30 minutes and maintained at the boiling point for 3 hours. Final measurement is taken after the water bath is cooled down to 20ºC. The difference between the initial and final measurements are reported as the Le Chatelier expansion in milimeters.

Table B.2: Brief description of physical test methods referred in ASTM C 618

Physical Property	Description of the Test Method
Fineness	1.0 g of fly ash was dried at 110 ºC, for 24 hours. The dried sample was wet sieved on a 45µ (No.325) sieve and the fineness was expressed as the percent mass retained above the sieve.
Water Requirement	Water requirement of the mortar prepared by substituting 20% of cement with fly ash to achieve the same flow as the mortar prepared by the control cement was determined by using the flow-table. The control is composed of 500 g Portland cement, 1375 g standard sand and 242 g water.
Strength Activity Index	The 50 mm cubic specimens were cast from batches of mortar prepared by mixing • 500 g cement, 1375 g standard sand and 242 ml water • 400 g cement, 100 g fly ash, 1375 g standard sand and sufficient water determined by using the flow table. The specimens were kept in water at 20ºC until the time of testing. Compressive strengths of mortars were determined by applying a load of 300 N/s, at 7 and 28 days. The strength activity index was finally expressed as the percent ratio of the compressive strength of the mortar prepared by replacing 20% of cement with fly ash to the compressive strength of the mortar prepared with control cement.

Table B.2: Brief description of physical test methods referred in ASTM C 595 (Continued)

Physical Property	Description of the Test Method
Soundness	25-cm rods of 1-in cross-section made from the paste prepared by substituting 20% of cement with fly ash were exposed to saturated steam in the Autoclave apparatus, which consists of a pressurized vessel. The pressure of the autoclave, which initially contains 1.7 liter of water, was increased to 2 MPa in 45 minutes and maintained at 2 MPa for 3 hours. At the end of 3 hours, the heat supply was shut down and the autoclave was cooled at a rate that the pressure was below 10 psi in 1.5 hours. The autoclave was opened after the pressure was below 10 psi and the specimens were taken into the water bath at 90ºC. After the temperature of the water bath was lowered to 23 ºC in 15 minutes, the specimens were wiped dry and length comparator readings were obtained for each specimen. Percent differences in initial and final lengths of the specimens were reported as "soundness" data.

APPENDIX C

TEST METHODS FOR PHYSICAL PROPERTIES OF FLY ASH-CEMENT BLENDS

Table C.1: Brief description of physical test methods referred in ASTM C 595

Physical Property	Description of the Test Method
Normal Consistency of Mortar	The water requirement of mortars to achieve the same flow as the mortar prepared by the control cement was determined by using the flow-table. The control mortar is composed of 500 g Portland cement, 1375 g standard sand and 242 g water.
Compressive Strength	Six 5-mm cube specimens were prepared form a batch of mortar, three specimens for testing at 7 days and the remaining three for testing at 28 days. The specimens were demoulded 24 hours after moulding and kept in water until the time of testing. After 7 and 28 days, compressive strength of the specimens were determined by applying load at a rate of 300 N/s, until the maximum load is attained.
Normal Consistency of Paste	The water requirement of the pastes for 10±1 mm penetration of the Vicat plunger was determined.
Setting Times	The Vicat ring is first filled with the paste and left without being disturbed for 30 minutes. For the initial setting time, the time elapsed for the penetration of the 1-mm Vicat needle not more than 25 mm was determined. The final setting time was when the Vicat neede did not visibly sink into the paste.

Table C.2: Brief description of physical test methods referred in ASTM C 595 (Continued)

Physical Property	Description of the Test Method
Soundness	25-cm rods of 1-in cross-section prepared from the Portland cement-fly ash blends were exposed to saturated steam in the Autoclave apparatus. The pressure of the autoclave, which initially contains 1.7 liter of water, was increased to 2 MPa in 45 minutes and maintained at this pressure for three hours. At the end of 3 hours, the heat supply was shut down and the autoclave was cooled at a rate that the pressure was below 10 psi in 1.5 hours. The autoclave was opened after the pressure was below 10 psi and the specimens were taken into the water bath at 90ºC. After the temperature of the water bath was lowered to 23 ºC in 15 minutes, the specimens were wiped dry and length comparator readings were obtained for each specimen.

APPENDIX D

XRD PATTERNS OF FLY ASH SAMPLES

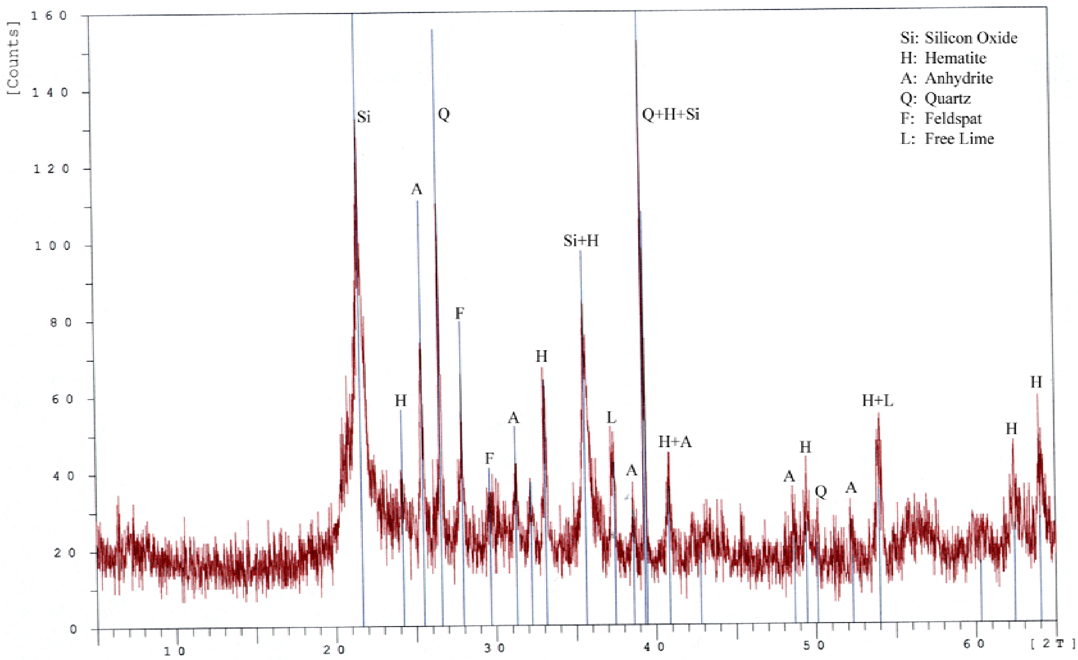

Figure D.1: XRD pattern of fly ash 1

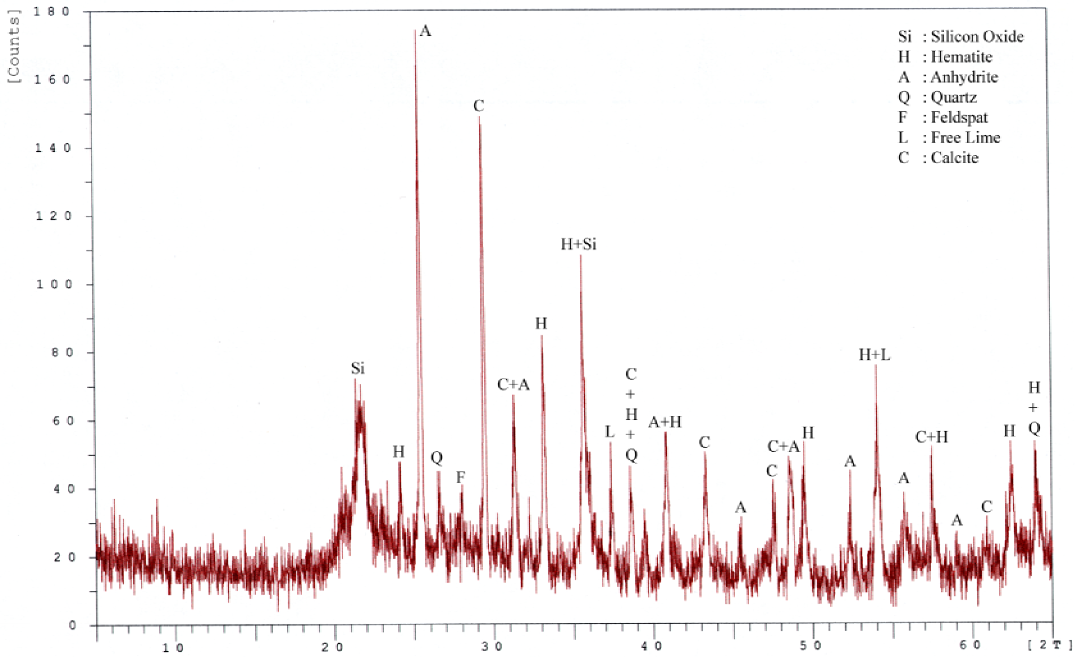

Figure D.2: XRD pattern of fly ash 2

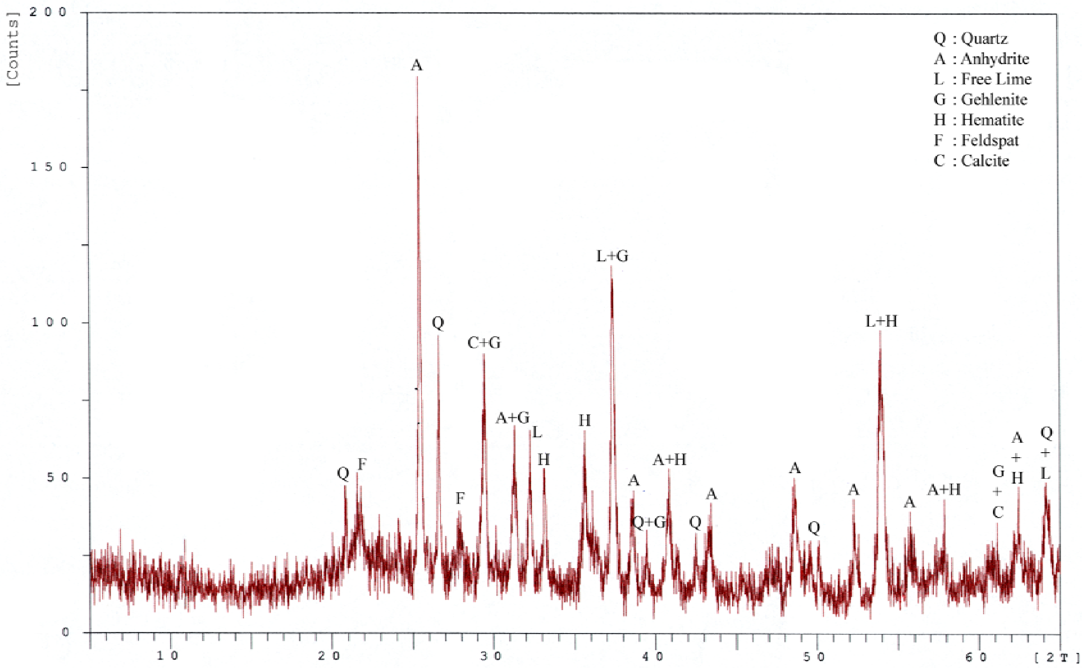

Figure D.3: XRD pattern of fly ash 3