CHARACTERIZATION OF FLY ASHES FROM THERMAL POWER PLANTS IN TURKEY

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ABSTRACT

CHARACTERIZATION OF FLY ASHES FROM THERMAL POWER PLANTS IN TURKEY

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Fly ash (FA) - a mainly amorphous, aluminosilicate fine powder- is the major by- product of coal-fired thermal power plants (TPP). FA is generated during the combustion of pulverized coal and collected in mechanical or electrostatic separators. FA is a widely used material in cement and concrete industry. According to the TPP technology, the characteristics of the burned coal and the operation conditions of the TPP; the characteristics of the FAs may vary considerably. The scope of this thesis is limited to chemical, physical, mineralogical (by XRD) and morphological (by SEM) analyses performed on 7 different FA samples collected from various TPPs. The FAs were classified according to TS EN 197-1 and the potentials of the FAs to be used in concrete industry was evaluated according to TS EN 450-1. In order to investigate the engineering performance of portland cement - fly ash binary systems, the strength development (up to 180 days) and heat of hydration (up to 7 days) were followed. Obtained results allow a better informed utilization of Turkish fly ashes in cement and concrete industry and provide a solid foundation for the characterization of other FAs produced in Turkey.

Keywords: Fly Ash, coal, portland cement, thermal power plant, TS EN 197-1, TS EN 450-1, ASTM C 618, strength, heat of hydration

ÖZ

TÜRKİYE TERMİK SANTRALLERİNDEN ELDE EDİLEN UÇUCU KÜLLERİN KARAKTERİZASYONU

Tangüler, Meltem
Yüksek Lisans, İnşaat Mühendisliği Bölümü
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Amorf, alüminosilikat ve ince toz halinde olan uçucu kül, kömürle çalışan termik santrallerin temel yan ürünüdür. Uçucu kül pulverize kömürün yanması esnasında üretilir ve mekanik veya elektrostatik ayırıcılarda tutulur. Uçucu kül çimento ve beton sanayinde yaygın olarak kullanılan bir malzemedir. Termik santrelde kullanılan teknolojiye, yakılan kömürün özelliklerine ve santralin işletim koşullarına göre, uçucu küllerin özellikleri oldukça değişiklik gösterebilmektedir. Bu tezin kapsamı çeşitli termik santrallerden alınan 7 farklı uçucu kül numunesi üzerinde yapılan kimyasal, fiziksel, mineralojik (XRD ile) ve morfolojik (SEM ile) analizlerle sınırlandırılmıştır. Uçucu küller TS EN 197-1 standartına göre sınıflandırılmış ve bu uçucu küllerin beton sanayi içerisinde kullanım potansiyelleri TS EN 450-1 standartına göre değerlendirilmiştir. Portland çimentosu - uçucu kül ikili sistemlerinin mühendislik performanslarını değerlendirmek için dayanım (180 güne kadar) ve hidratasyon ısısı (7 güne kadar) parametreleri takip edilmiştir. Elde edilen sonuçlar Türkiye uçucu küllerinin çimento ve beton sanayinde daha bilinçli kullanılmasını teşvik etmekte ve Türkiye'de üretilen diğer uçucu küllerin karakterizasyonu için bir temel niteliği göstermektedir.

Anahtar Kelimeler: Uçucu Kül, kömür, portland çimentosu, termik santral, TS EN 197-1, TS EN 450-1, ASTM C 618, dayanım, hidratasyon ısısı

To My Family

To My Love

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LIST OF ABBREVIATIONS

TS:	Turkish Standards.
EN:	European Norms.
ASTM:	American Society for Testing and Materials.
TCMA:	Turkish Cement Manufacturers’ Association.
PSD:	Particle size distribution.
TPP:	Thermal power plant.
FA:	Fly ash.
PC:	Portland cement.
CFA:	Fly ash taken from Çatalağzı Thermal Power Plant, B-1 unit.
T3FA:	Fly ash taken from Tunçbilek Thermal Power Plant, 3rd unit.
T5FA:	Fly ash taken from Tunçbilek Thermal Power Plant, 5rd unit.
AEFA:	Fly ash taken from Afşin Elbistan Thermal Power Plant, B unit.
KFA:	Fly ash taken from Kemerköy Thermal Power Plant, 2nd unit.
IFA:	Fly ash taken from İçdaş Thermal Power Plant.
YFA:	Fly ash taken from Yeniköy Thermal Power Plant, 1st unit.

CHAPTER 1

INTRODUCTION

1.1 General

Concrete is the most widely used construction material on earth. The annual production amount is estimated as more than 25 billion tons (Celik et al., 2014b; WBCSD, 2009). With this huge amount of production big amounts of portland cement (PC), water and aggregate are consumed leading to not only depletion of natural resources but also considerable amount of CO_2 generation, which is a major contributor to the global warming. Emissions due to PC manufacturing is responsible for ~5-8% of the global atmospheric emissions (Gürsel and Meral, 2012; Lloyd et al., 2009; Mehta, 2001). In addition, PC production needs substantial amount of energy through its different manufacturing steps. The environmental impacts caused by cement and concrete industry has been reduced by alternative methods. One of the most common methods is PC replacement of supplementary cementitious materials (SCMs) such as pozzolans, fly ash, silica fume and blast furnace slag. In this way, both the energy and raw material requirements and CO_2 emissions due to PC production are reduced (Mehta, 2002, 2001).

Among the SCMs used in this field fly ash (FA), the main by-product of coal-fired thermal power plants (TPP), seems to have the lead in the terms of usage due to its wide range availability and low cost. Furthermore, the appropriate usage of FAs in PC based systems generally leads to many technical advantages as durable concrete with enhanced strength and lower heat of hydration (Tangüler et al., 2014). Not to mention that the resulting cementitious systems have a lower carbon footprint (Celik et al., 2014a; Mehta and Monteiro, 2006; Tangüler et al., 2015, 2014).

In parallel to the world’s energy demand, the coal consumption has significantly increased and so FA production has also increased. However, this increment in the FA production requires large storage area for the FA besides disposal cost. Moreover, since FA contains different level of toxic elements, disposal of FAs arouses significant environmental concerns (Yao et al., 2013). Considering the environmental impact of both PC and FA, the use of FA in PC based system results in a sustainable production. However; not all the FAs are appropriate to be used in concrete. For that, the standards define some requirements which should be satisfied by FAs to be used in cement and concrete.

1.2 Objective and Scope

This thesis is a part of an ongoing project on detailed characterization of Turkish FAs in order to encourage their utilization in construction industry. The project is carried out in collaboration between METU and Turkish Cement Manufacturers’ Association (TCMA). Similar projects have been conducted prior to this study at 1998 by METU and TCMA (Tokyay and Erdoğdu, 1998) and at 2003 by TCMA only (Türker et al., 2003).

Within the scope of this project, 20 FA samples were collected from 10 coal-fired thermal power plants located at different regions of Turkey. The major goal of the project is to characterize the FAs in terms of their chemical (major oxide composition, heavy metal concentration), physical, morphological, mineralogical and radiological properties and investigate the performance of FA utilization in PC based system in terms of strength development and heat evolution. The project also aims to conduct life cycle assessment analysis, durability evaluation and acoustical tests on PC-FA systems. As an extra step, the alkali activation potential of the FAs will also be investigated.

The scope of this thesis is limited to FA samples gathered from Çatalağzı, Tunçbilek Unit 3 and 5, Afşin Elbistan, Kemerköy, Yeniköy and İçdaş Thermal Power Plants (TPP). The results of this study provides a basis for the investigation of the residual FAs. First, the selected FAs were classified according to TS EN 197-1 and then evaluated according to TS EN 450-1. Beside the basic chemical and physical tests, heavy metal concentration, mineralogical and morphological properties of the ashes were also investigated. Strength development and heat evaluation of the PC-FA systems were chosen as the investigated performance indicators.

The second chapter of this study gives a brief introduction to the FA production at TPPs and presents the current situation of FA production in Turkey. Then, the common chemical, physical and mineralogical properties of FAs are listed. Finally, the Turkish and ASTM standards for FAs are presented.

In the third chapter, the experimental methods used in this study are explained. The tests performed on cement and FA samples are divided on three main categories: (i) tests conducted on the raw materials, (ii) tests conducted on pastes and (iii) tests conducted on mortars.

The fourth chapter documents the chemical and physical analysis results and then classifies the FAs according TS EN 197-1. The conformity of the FAs to the TS EN 450-1 is also checked and listed. Within this chapter, the results of the mineralogical and morphological analysis of FAs are also presented. Obtained results on performance tests (heat of hydration tests on PC-FA pastes, and flexural and compressive strength tests on PC-FA mortars) were presented and discussed.

In the final chapter, chapter five, a summary of the results along with the conclusions of this study are provided. The ongoing tasks are listed and some recommendations for the future work are given.

CHAPTER 2

LITERATURE REVIEW

2.1 What is Fly Ash (FA)?

Fly ash is one of the by-products obtained from the combustion of pulverized coal to generate electric power in coal-fired thermal power plants (TPP). Coal is composed of two parts which are combustible organic matters and inorganic mineral matters. When pulverized coal is combusted the organic constituents in the coal (carbon and other combustible matters) are burned out. However, the inorganic mineral matters composed of impurities such as clay, shale, quartz, and feldspar remain suspended in the flue gases. Some of the suspended non-combustible mineral matters agglomerate and form coarser particles. These particles fall to the bottom of the boiler and to be collected as bottom ash. The remaining part is composed of fine mineral matters in the flue gases that are mostly melted. These particles are carried off through flue gases to a lower temperature zone to cool down. Cooled and solidified particles constitute glassy amorphous ash particles. By using electrostatic precipitators, mechanical separators or bag houses ash particles are separated from the flue gases and collected as fly ash in a silo (Benscheidt et al., 2010; Joshi and Lohtia, 1997; Ramachandran, 1996). The production scheme of fly ash is presented in Figure 2.1.

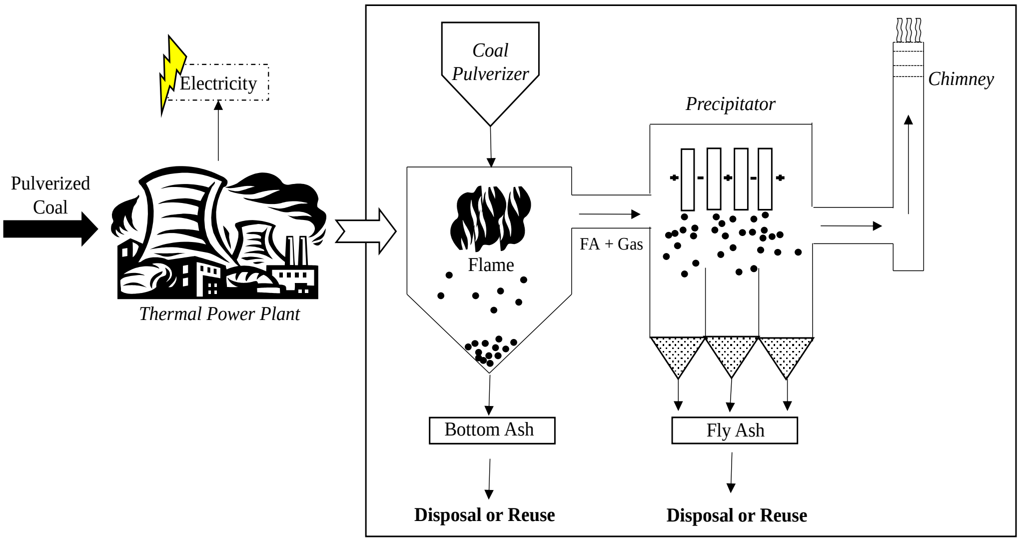

Figure 2.1 Fly ash production process in coal-fired thermal power plants (Adapted from (U.S. FHWA, 2012a))

The worldwide energy requirement increases day by day and this situation causes increment of the coal consumption leading to growing fly ash production. It is estimated that about 750 million tons of fly ash is produced in the world annually and nearly 25% of it finds various utilization areas such as cement and concrete sector, agriculture, ceramics and glass, soil stabilization, mining applications and structural fills. Unutilized capacity is almost 3 times of recycled fly ash amount. FAs mostly have a different level of heavy metal concentration like cadmiyum, vanadium, chromium, arsenic, lead, zinc, nickel leading to serious environmental concerns. Huge amount of unutilized fly ash waste is dumped into either landfill area or the ocean. This is a problematic situation from both ecologic and economic aspects since fly ash may cause environmental damages such as contamination of soils, water reservoirs, oceans, air pollution, and even allergies in the human body, and also it requires a cost for the storage area and transportation (Blissett and Rowson, 2012; Yao et al., 2013).

2.2 Fly ash in Turkey

In Turkey, maximum contribution to energy production comes from mainly 3 sources: hydroelectric power plants, natural gas power plants and coal-fired thermal power plants. The contribution of electricity source for Turkey in 2014 is shown in Figure 2.2 (TEİAŞ, 2014). As seen from this figure coal-fired thermal power plants have a big importance to meet over the fifth of Turkey's energy demand. There are coal-fired thermal power plants all over in Turkey. A map of these TPPs is shown in Figure 2.3. The list of these TPPs are presented in Table 2.1.

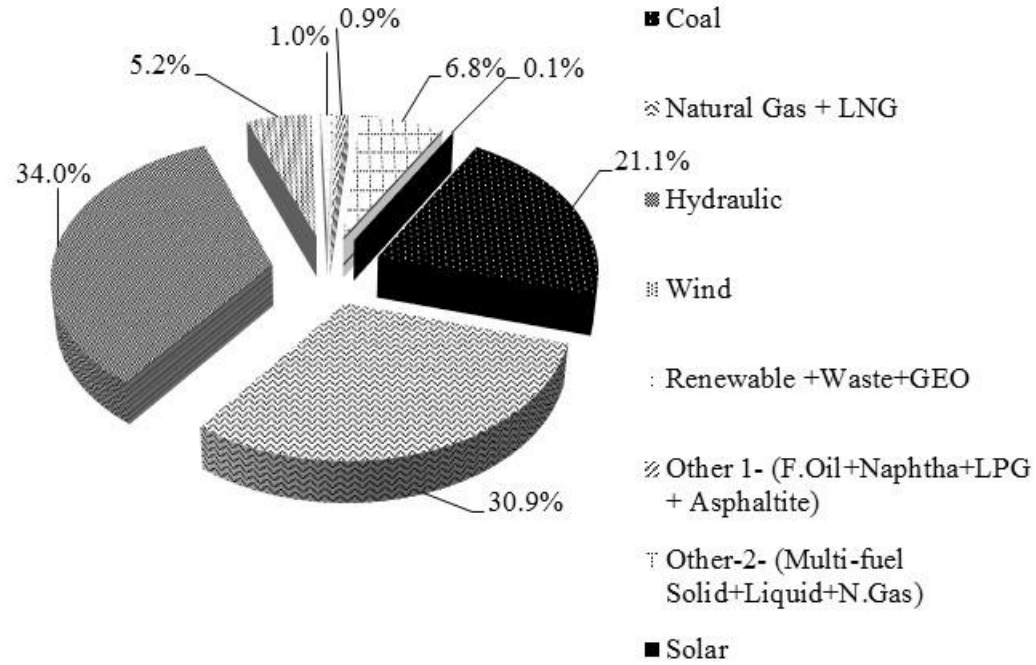

Figure 2.2 Contribution of electricity source of Turkey (TEİAŞ, 2014).

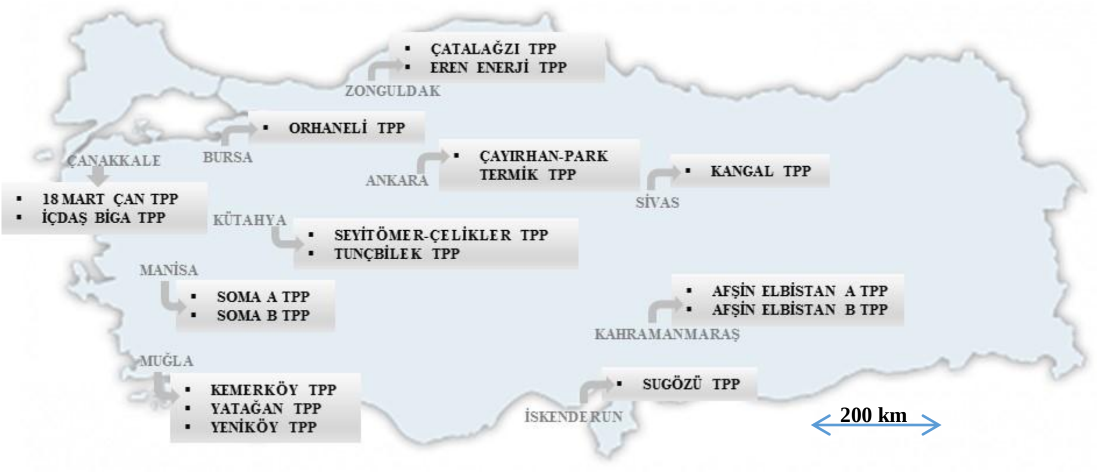

Figure 2.3 Map of major coal-fired thermal power plants in Turkey.

Table 2.1 Major coal-fired thermal power plant in Turkey (Global energy observatory website, 2015).

Coal-Fired Power Plants	**Unit**	**Installed Power (MW)**	**Coal Type**	**SOx control device**	**First Unit**	**Last Unit**
18 Mart Çan	2	320	Lignite	-	2004	2004
Afşin Elbistan-A	4	1355	Lignite	-	1984	1987
Afşin Elbistan-B	4	1440	Lignite	FGD	2006	2006
Çatalağzı	2	300	Anthracite	-	1948	1991
Çayırhan-Park Termik	4	620	Lignite	FGD	1987	2000
İçdaş Biga	3	405	Imported Coal	FGD	2005	2009
Kangal	3	457	Lignite	FGD	1987	2000
Kemerköy	3	630	Lignite	FGD	1995	1995
Orhaneli	1	210	Lignite	FGD	1992	1992
Seyitömer-Çelikler	4	600	Lignite	-	1973	1989
Soma A/B	2+6	44+990	Lignite	-	1957	1991
Sugözü	2	1320	Imported Bituminous Coal	FGD	2003	2003
Tunçbilek	3	365	Lignite	-	1956	1979
Yatağan	3	630	Lignite	FGD	1983	1985
Yeniköy	2	420	Lignite	FGD	1986	1987
Zetes	3	1390	Imported Coal	-	2010	2010

As it is seen from the Table 2.1, the primary fuel used in coal fired TPPs in Turkey is lignite coal. When the lignite coal is combusted, the ash produced is varied in the range between 17 and 46 % by weight depending on coal type and TPP’s technology (EÜAŞ, 2011). According to statistics reports, total mineral waste amount produced in TPPs (bottom ash, fly ash, slag, gypsum) was about 25.5 million tons in 2008. While approximately 80% of these wastes was disposed and about 16% was used in mines, only 3% was recycled (Turkish Statistical Institute, 2008). Assuming that 80% of the mineral waste is fly ash, the fly ash production could be predicted to be about 20 million tonnes annualy (Tangüler et al., 2014). The very high disposed portion dumped into ash disposal place or ash leads to important economic and environmental problems. For example, as shown in the table above, some facilities have flue gas desulfurization (FGD) technology, to get rid of the sulfur dioxide (SO_2) emission in order to solve one of these problems.

2.3 Classification of Fly Ashes

There are different classifications for fly ashes in Europe and USA. In Turkey, the European standard is used to classify fly ash. The standard used in USA, ASTM C 618: Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, defines fly ash as “the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gasses” and classifies fly ashes into two categories: Class F and Class C. Class F fly ash is normally obtained as a result of combustion of anthracite or bituminous coal. However, it may be also obtained from subbituminous coal or lignite. In this class the total content of silica, alumina and iron oxide is more than 70%. Class C fly ash is normally obtained as a result of combustion of lignite or subbituminous coal. But, it may be also obtained from anthracite or bituminous coal. The total content of silica, alumina and iron oxide in this class is more than 50%. The main difference is that Class F fly ash shows only pozzolanic properties whereas Class C fly ash shows both pozzolanic and some cementitious properties. In addition to that, the total content of calcium oxide is higher in Class C fly ash than it in Class F fly ash.

The standard used in Turkey, TS EN 197-1: Cement - Part 1: Composition, specifications and conformity criteria for common cements, divides fly ashes into two categories: Siliceous fly ashes (V) and Calcareous fly ashes (W). For siliceous fly ashes reactive silica and alumina are essential compounds. For calcareous fly ashes reactive calcium oxide is also an essential compound. For siliceous fly ash the minimum reactive silica content and the maximum reactive CaO content are 25% and 10%, respectively. On the other hand, for calcareous fly ash the minimum reactive CaO is 10%.

Also, fly ashes may be divided into subgroups according to CaO and SO_3 contents (Tokyay and Erdoğdu, 1998):

a) Silicoaluminous fly ashes: Those that are produced from anthracite coal and some bituminous coals. Main structure commonly consists of SiO_2 and Al_2O_3.
b) Sulfocalcic fly ashes: Those that are generally produced from lignite coal. This type of fly ashes has more SO_3 and CaO compared to other fly ashes.
c) Silicocalcic fly ashes: Those that are generally produced from lignite coal like sulfocalcic fly ashes. Content of SiO_2 and CaO of this type of fly ashes are high.

2.4 Characteristics of Fly Ashes

2.4.1 Chemical and Mineralogical Composition

Coal is the main parameter which effects the chemical composition of fly ash. Factors such as coal type (e.g. anthracite, bituminous, subbituminous or lignite), coal handling, storage techniques and burning system determine the chemical characteristics of fly ashes. According to burned coal type, the chemical composition ranges of the fly ashes are presented in Table 2.2 (Ahmaruzzaman, 2009).

The four main components which are silica (SiO_2), alumina (Al_2O_3), calcium oxide (CaO) and iron oxide (Fe_2O_3) constitute the chemical composition of fly ash. Also, sulfur oxide (SO_3), magnesium oxide (MgO), sodium oxide (Na_2O) and potassium oxide (K_2O) are found in fly ash. Besides, oxides of titanium (TiO_2), phosphorus (P_2O_5), chromium (Cr_2O_3) and organic composites may be exist in fly ash as minor constituents (ACI, 2003).

The chemical and mineral phase compositions of fly ash depend on the minerals that exist in the coal (Benscheidt et al., 2010). Clay minerals (e.g. kaolinite, illite, smectite) and quartz found in the coal are the main sources of the silica content in fly ash. The alumina content in fly ash comes from clay minerals and sometimes from organic constituents of the coal. The minerals containing iron in the coal are responsible for iron oxide in the fly ash. Calcium oxide content in fly ash arises from $CaCO_3$ and $CaSO_4$ in the coal. Organic constituents, smectite, ferromagnesian minerals and dolomite in the coal lead to magnesium oxide content in fly ash. The SO_3 content in fly ash is derived from pyrite (FeS_2) and gypsum ($CaSO_4.H_2O$) in the coal. Minerals containing sodium and potassium in the coal result in the alkali contents ($Na_2O + K_2O$) in fly ash. The carbon content in fly ash is due to incomplete coal combustion, combined water or carbon dioxide (ACI, 2003).

Fly ashes are composed of both glassy phase and crystalline phases. Table 2.3 shows the common crystalline phases found in fly ashes according to the type of fly ash. In addition, the crystalline phases which are cristobalite (SiO_2), calcite ($CaCO_3$), portlandite ($Ca(OH)_2$), dicalcium silicate (Ca_2SiO_4), tetracalcium aluminoferrite ($Ca_4(Al,Fe)_4O_{10}$) and maghemite (Fe_2O_3) may be rarely existed in fly ash (Smith, 1999).

Table 2.2 The range of chemical composition of fly ash according to coal type (Ahmaruzzaman, 2009).

Oxide (wt.%)	Bituminous	Subbituminous	Lignite
SiO_2	20–60	40–60	15–45
Al_2O_3	5–35	20–30	10–25
Fe_2O_3	10–40	4–10	4–15
CaO	1–12	5–30	15–40
MgO	0–5	1–6	3–10
SO_3	0–4	0–2	0–10
Na_2O	0–4	0–2	0–6
K_2O	0–3	0–4	0–4
LOI	0–15	0–3	0–5

Table 2.3 Common mineral phases of fly ash (Smith, 1999).

Mineral name	**Chemical formula**
Common phases for Class F and C fly ash	
Quartz	SiO_2
Mullite	$Al_6Si_2O_{13}$
Magnetite	Fe_3O_4
Hematite	Fe_2O_3
Additional phases for Class C fly ash	
Anhydrite	$CaSO_4$
Lime	CaO
Periclase	MgO
Tricalcium aluminate	$Ca_3Al_2O_6$
Melilite (akermanite-gehlenite)	$Ca_2Mg_{0.5}AlSi_{1.5}O_7$
Merwinite	$Ca_3Mg(SiO_4)_2$
Ferrite spinel (instead of magnetite)	$(Fe,Mg)(Fe,Al)_2O_4$

2.4.2 Physical Properties

Coal source, coal uniformity, the degree of coal pulverization, the temperature and uniformity of coal combustion, and the type of dust collection method used (electrostatic precipitators, mechanical separators or bag houses) influence the characteristic of shape and particle size of fly ash (ACI, 2003).

There are some disagreements among researchers over the determination of the fineness of fly ashes. Some researchers agree that the determination of the fineness in terms of specific surface (Blaine method) is a reliable technique, whereas some researchers think that this method is reliable for only portland cement. Investigations show that the specific surface area of fly ashes vary between 1800-5000 cm^2/g. On the other hand, the most practical method to measure the fineness of fly ash is the determination of the retained material on the 45 μm (ASTM No. 325) sieve. Other than these, there are different methods such as laser diffraction particle size analysis, hydrometer analysis, nitrogen adsorption and x-rays sedimentation (Tokyay & Erdoğdu, 1998)

Microscopic examinations show that fly ashes are composed of small glassy spherical, irregular or angular particles within the range of 0.2 μm - 200 μm. Some spherical particles are hollow and they are known as cenosphere. Also, fly ashes may comprise a set of many small spheres in a large sphere known as pherospheres (Bosbach and Enders, 1998; Siddique, 2007; Wesche, 2004).

Fly ashes have specific gravity ranging from 1.9 to 2.8. Color of fly ashes may show difference, but generally they have gray or tan color (Kosmatka et al., 2002).

2.5 Reutilization Potential of Fly Ash in Cement and Concrete Industry

Fly ash is one of the most commonly used SCMs. The strength development of PC-FA based systems is generally slower than that of only PC based systems especially at early-ages. The reaction between FA and calcium hydroxide (CH) which is the PC hydration product is slow. As a result of the reaction between

FA and CH, calcium-silicate-hydrate (C-S-H) comes out which lead to enhanced mechanical properties. In addition, durability advantages are gained due to CH depletion by FA (Malhotra and Ramezanianpour, 1994; Mehta and Monteiro, 2006; Wesche, 2004).

In the terms of fresh properties, fly ash can have a big influence on the workability, water requirement, air-entrainment, setting time, heat of hydration and bleeding of concrete. On the other hand, the strength development, alkali silica reactivity, sulfate resistance, freezing and thawing resistance, permeability and drying shrinkage can all be affected in a good way by the use of fly ash (Erdoğan, 1997; Siddique, 2007). When environmental considerations are taken into account, it is known that the need of excessive amount of raw material and the energy consumed to produce PC besides the CO_2 emissions, all of these are disadvantages of the cement production. With the PC replacement with FA energy and cost saving are provided. The need for raw materials is reduced and the CO_2 emissions is decreased (Gürsel and Meral, 2012).

2.5.1 Requirements

In Turkey, there are some requirements which should be satisfied by fly ashes to be used in cement and concrete according to TS EN 197-1, Cement - Part 1: Composition, specifications and conformity criteria for common cements and TS EN 450-1, Fly ash for concrete - Part 1: Definition, specifications and conformity criteria. The previous standard related to fly ash, TS 639: Fly ash-Used in cement, was cancelled in 2011. The chemical requirements for fly ashes given in TS EN 450-1 and TS EN 197-1 are summarized in Table 2.4. For the comparison, the requirements of TS 639 and ASTM C 618 are also given in the table below.

Table 2.4 Chemical requirements for FAs.

Weight (%)	**TS 639****	**TS EN 450-1**	**TS EN 197-1**		**ASTM C 618**	
			V	**W**	**F**	**C**
SiO_2+ Al_2O_3+ Fe_2O_3	≥ 70	≥ 70			≥ 70	≥ 50
CaO						
MgO	≤ 5	≤ 4				
SO_3	≤ 5	≤ 3			≤ 5	≤ 5
Na_2O eq**		≤ 5				
P_2O_5		≤ 5				
L.O.I.	≤ 10	Category A ≤ 5 Category B ≤ 7 Category C ≤ 9	a) 0 ≤...≤ 5 b) 2 ≤...≤ 7 c) 4 ≤...≤ 9		≤ 6	≤ 6
Cl^-		≤ 0.10				
S. P_2O_5		≤ 100 (mg/kg)				
Free CaO		≤ 1.5(1)	≤ 1 (2)			
Reac. CaO		≤ 10	< 10	≥ 10 (3)		
Reac. SiO_2		≥ 25	≥ 25	≥ 25 (4)		

* Na_2O eq.= $Na_2O + 0.658\ K_2O$ ** withdrawn standard (in 2011)
(1)(if Free CaO >1.5; soundness ≤ 10 mm) ; (2)(if 1< Free CaO <2.5; soundness ≤ 10 mm)
(3)(if Reac. CaO >15.00; σ_{28} ≥10 MPa); (4)(10<Reac.CaO<15)

According to TS EN 197-1, reactive calcium oxide is defined as the portion of CaO that can constitute calcium silicate hydrates or calcium aluminate hydrates. This portion is calculated by reducing the portion corresponding to calcium carbonate ($CaCO_3$) and calcium sulfate ($CaSO_4$) from the total CaO content. According to TS EN 197-1, reactive silicon dioxide is defined as the soluble portion of SiO_2 after treatment with hydrochloric acid and potassium hydroxide solution, and calculated by reducing the insoluble fraction in the solution from the total amount of SiO_2. The main physical requirements for fly ashes given in TS EN 450-1 and ASTM C 618 are summarized in Table 2.5.

Table 2.5 Main physical requirements for FAs.

Property	**TS EN 450-1**	**ASTM C 618**
Retain on 45 µm sieve	Category N : ≤ 40% Category S: ≤ 12%	≤ 34%
Soundness	≤ 10 mm (Le chatelier expansion)	≤ 0.8% (Autoclave expansion)
Water requirement	Category N: - Category S: ≤ 95%	≤ 105%
Activity index, 28 days	≥ 75% (for 25% replacement)	≥ 75% (for 20% replacement)
Activity index, 90 days	≥ 85% (for 25% replacement)	≥ 75% (for 20% replacement)
Density	Declared value ± 200 g/cm^3	Declared value ± 5%
Initial setting time	≤ twice the initial setting time of cement alone	-

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 General

This thesis is a part of an ongoing project on detailed characterization of Turkish FAs in order to encourage their utilization in construction industry with the collaboration of METU and TCMA. Within the scope of this thesis chemical, physical, mineralogical and morphological analyses were done on 7 different fly ash samples. Fly ashes were classified according to TS EN 197-1 and then evaluated according to TS EN 450-1. For the chemical characterization the results were compared to the requirements of ASTM C 618. In addition to those, heat liberation of 75%PC-25%FA pastes were measured throughout 7 days. Flexural and compressive strength tests on 75%PC-25%FA mortars were performed at the ages of 2, 7, 28, 90 and 180 days. Finally, hydration of the binary PC-FA pastes corresponding to the PC-FA mortar were followed by XRD analysis at the ages of 2, 7, 28 and 90 days.

3.1.1 Fly Ashes

The scope of this thesis is limited to fly ash samples gathered from Çatalağzı, Tunçbilek Unit 3 and 5, Afşin Elbistan, Kemerköy, Yeniköy, İçdaş Thermal Power Plants (TPP) located in different regions of Turkey. The fly ash samples taken from each of TPP were collected from electrostatic precipitator for five consecutive days. The reason for that is to check whether the fly ashes show consistent properties through the different days or not. For each TPP, a fly ash mix was also prepared by weighing equal amounts of ash from each of consecutive sampling day and then mixing them thoroughly with a shovel. Thus, a total of 6 fly ash samples was obtained for every TPP.

Figure 3.1 Fly ash samples.

3.1.2 Cement

CEM I 42.5 R type of portland cement was used in all binary PC-FA pastes and mortars. The density of the cement is 3.11 g/cm^3. Its Blaine fineness is 3700 cm^2/g. According to TS EN 196-3, the initial setting time of the cement paste was determined as 185 minutes and the soundness of the cement paste in terms of measured expansion according to Le Chatelier process was found to be 1.00 mm. According to ASTM C 230, the flow diameter is 175 mm. The major oxide composition of the cement is shown in Table 3.1.The x-ray diffraction pattern of cement is given in Figure 3.2.

Table 3.1 Major oxide composition of cement.

Weight %	
SiO_2	19.15
Al_2O_3	5.16
Fe_2O_3	3.56
CaO	63.26
MgO	1.28
SO_3	2.77
Na_2O	0.30
K_2O	0.37
L.O.I.	3.83

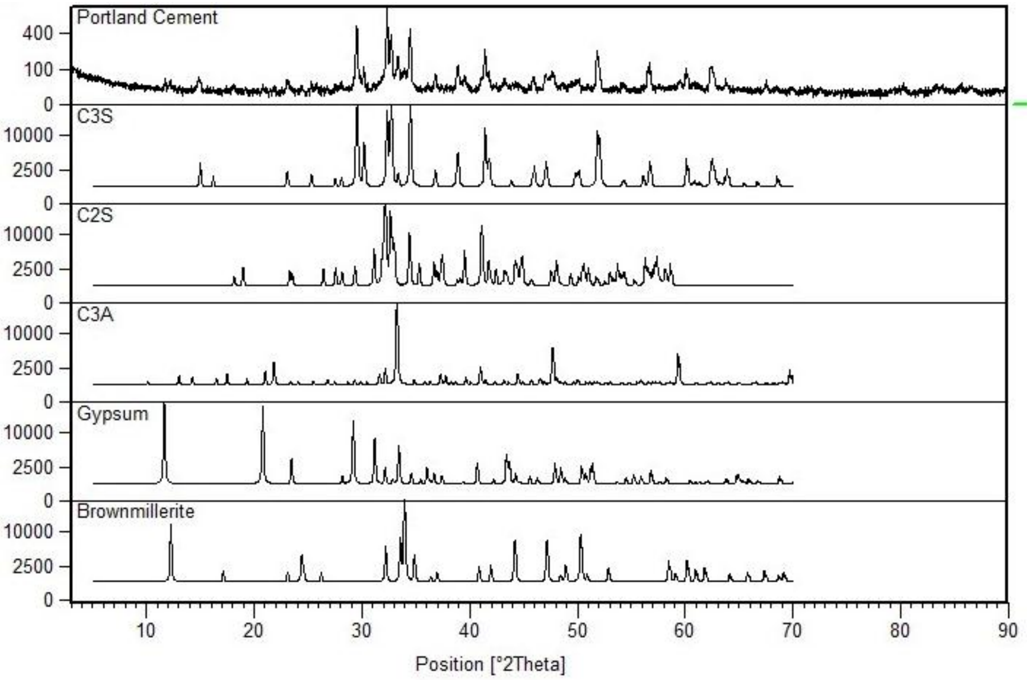

Figure 3.2 X-ray diffraction pattern of cement.

3.2 Analyses Performed

The performed analyses were grouped into three sections: (i) test on fly ash samples, (ii) tests on PC-FA pastes and (iii) tests on PC-FA mortars. In the preparation of the PC-FA pastes and mortars, only the 5-day mix fly ash samples were used.

3.2.1 Analyses Performed on Fly Ashes

3.2.1.1 Chemical Analysis

In order to identify the chemical composition of fly ashes, an inductively coupled plasma optical emission spectroscopy device, Spectro Genesis ICP-OES located at TCMA was used. This device uses the intensity of light emitted from plasma at a particular wavelength to determine the quantity of an element in a sample. This method show smaller residuals for lower levels of contamination (Pyle et al., 1995).

The oxide composition of the fly ashes taken from each TPP for 5 consecutive days were measured separately. For each oxide, the mean, the standard deviation (SD) and the coefficient of variation (CV) of the five results were calculated in order to see the variation of the chemical composition of the fly ashes through the sampling days. SD is a measure of how close the data are to the mean. If SD is close to zero, this means that the results are very close to the mean. Interpreting SD should be done in the context of the mean of the data. Hence, CV, the ratio of SD to the mean is also calculated. CV shows the percent variability of the data according to the mean in a distribution. The smaller the CV value the more uniform the data are. Thus, it can be inferred whether the fly ash production in each TPP is conducted at stable conditions or not. In other words, this will show whether the fly ash is uniform or not. The chemical analysis was also done on the 5-day mix samples, and their oxide compositions were compared with the mean of the 5 fly ash samples.

Along with the results obtained from ICP-OES, Cl- content according to TS EN 192-2 and soluble P_2O_5 according to TS EN 450-1 were determined for the 5 fly ash samples taken from each TPP at TCMA. Due to the large number of the samples some tests were performed only on the mix samples. These tests are the determination of free CaO (TS EN 451-1), the reactive CaO (TS EN 197-1), and the reactive SiO_2 (TS EN 197-1) contents. The results of the chemical analyses are compared with the lower and the upper limits in TS EN 197-1, TS EN 450-1 and ASTM C 618 standards.

The heavy metal concentrations in the fly ashes (only for the mix samples) were also determined with an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at TCMA.

3.2.1.2 Mineralogical and Morphological Analyses

In order to identify the crystal structure of the fly ashes, X-Ray Diffraction analyses (XRD) were conducted. For these analyses Rigaku Ultima-IV X-Ray Diffractometer equipment taken place in METU Central Laboratory was used. Samples were scanned using Cu radiation (40 kV/30 mA) in the range of 3 and 90 2Θ at a scan rate of 1°/min. X'Pert HighScore software was used to identify the crystalline phases of the fly ashes (PANalytical B.V., 2003). The morphological structures of the fly ashes were determined by LEO 435 VP Scanning Electron Microscope (SEM) at TCMA. Both XRD and SEM analyses were conducted only on the mix samples of the fly ashes for each TPP.

3.2.1.3 Physical Analyses

Density and percentages of mass retained on 45μm sieve as a fineness index (according to TS EN 451-2) were determined for the mix samples. Besides, fineness in term of specific surface area (Blaine method) was determined according to ASTM C 204.

The particle size distributions (PSD) of the fly ashes were determined as relative volume of particles in size bands using Malvern Mastersizer 2000 laser diffraction equipment at TCMA. PSD measurements were conducted for the 6 samples (fly ashes obtained from 5 consecutive days and the mix) obtained from each TPP. The obtained PSD parameters are D_{10}, D_{50}, D_{90} and D[4,3]. The definitions of these terms are found below:

D_{10}: The size of particles which 10% of the sample are below.

D_{50}: The size in microns at which 50% of the sample is smaller and 50% is larger. This value is also known as the Mass Median Diameter (MMD).

D_{90}: The size of particles which 90% of the sample are below.

D[4,3]: The volume mean diameter.

3.2.2 Tests Performed on Fly Ash-Portland Cement Pastes

3.2.2.1 Initial Setting Time and Soundness Tests

Initial setting time and soundness tests were done on the 5-days mix samples according to TS EN 196-3. TS EN 450-1 indicates that the PC replacement ratio with FA is 25% by mass for setting time test. On the other hand, this replacement ratio is 30% by mass for the soundness of the pastes in terms of the measured expansion according to Le Chatelier process.

3.2.2.2 Heat of Hydration

Hydration of portland cement is an exothermic reaction. In other words, as a result of the hydration process an energy in the form of heat is released (Mehta and Monteiro, 2006). Heat liberation can be measured with isothermal calorimetry (Langan et al., 2002; Pane and Hansen, 2005).

In this study, the heat of hydration released from paste specimens was determined using TAM air (Thermometric AB, Sweden) isothermal calorimeter, an 8-channel isothermal micro-calorimeter. Each channel consists of inner two channels which are for the sample and for the reference. Paste specimen was made from a mix of cement (4 grams) and water (2 grams). 25 % portland cement was replaced with fly ash, and pastes, a mix of cement (3 grams), fly ash (1 gram) and water (2 grams), were prepared. Each paste was rapidly stirred by hand using a metal rod into a 20-mL disposable glass ampoule. Powdered cement was chosen as reference material. Reference ampoules which have the same specific heat of the paste were also prepared. The calculation of the weight of the reference sample is shown in Appendix A. After both ampoules were placed into the channels of calorimeter, the heat liberation of each paste was measured at 23 °C throughout 7 days. The measured heat data were normalized by the weight of solid (PC+FA).

3.2.2.3 X-Ray Diffraction Analyses

First, a control paste with 100% PC was prepared with a water/cement ratio of 0.5. Then, for all fly ashes 75% PC-25% FC pastes were prepared with a water/binder ratio of 0.5. All pastes were cured in ambient conditions in their closed molds until test day. At the age of 2, 7, 28 and 90 days the pastes were pulverized and analyzed with Rigaku Ultima-IV X-Ray Diffractometer located at METU Central Laboratory.

3.2.3 Tests Performed on Fly Ash-Portland Cement Mortars

3.2.3.1 Flexural and Compressive Strength

In order to investigate the influence of substitution of portland cement with different fly ashes on flexural and compressive strength, 4x4x16 cm prismatic mortar specimens were casted according to TS EN 196-1. Before the mortars are casted, flow table test was done according to ASTM C 230. Standard sand as fine aggregate and tap water as water were used when the mortars were prepared. The PC replacement ratio was kept at 25 weight %. Casted mortar samples were cured in a moist room with a constant temperature for 24 hours. At the end of the 24 hours, the samples were removed from the molds and immersed in tap water under standard curing conditions until the test day. Flexural and compressive strength tests on the samples were conducted at the age of 2, 7, 28, 90 and 180 days.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Fly Ash Taken from Çatalağzı Thermal Power Plant (CFA)

Fly ash samples were supplied from Çatalağzı Thermal Power Plant B-1 unit in July, 2013 for five consecutive days. Besides, a mix was prepared from the five samples as described in Chapter 3.

4.1.1 Chemical Analysis Results

The chemical analyses of the five fly ash samples were conducted separately. The results of CFA for five days and the average of the results along with the standard deviation (SD) and the coefficient of variation (CV) are all shown in Table 4.1**.** The results of free CaO, reactive CaO and reactive SiO_2 obtained from the mix are also given in Table 4.1.

In terms of chemical composition it is seen that the component percentages of fly ashes taken from the five consecutive days are very close to each other and the standard deviation values are small. From that it can be concluded that Çatalağzı TPP has a uniform production. The evaluation of the average results according to the limiting values of the standards is given in Table 4.2. According to TS EN 197-1, CFA is a siliceous fly ash (V) due to the fact that its reactive CaO content (0.97%) is less than 10%. When CFA is evaluated in accordance with ASTM C 618, it can be said that since the total amount of SiO_2, Al_2O, Fe_2O_3 is more than 70% and the total calcium content is very low (1.70%) CFA is considered as Class F (low-calcium fly ash).

Table 4.1 Chemical analysis results of CFA.

Weight (%)	**Samples**					**Ave.**	**SD**	**CV (%)**	**Mix**
	1	**2**	**3**	**4**	**5**				
ICP									
SiO_2	55.78	56.72	54.74	56.70	56.71	56.13	0.88	1.56	-
Al_2O_3	24.76	25.48	24.74	24.98	25.08	25.01	0.30	1.20	-
Fe_2O_3	6.10	5.52	6.04	6.10	5.68	5.89	0.27	4.59	-
CaO	2.10	1.42	1.88	1.94	1.18	1.70	0.39	22.70	-
MgO	2.14	2.28	2.14	2.14	2.18	2.18	0.06	2.79	-
SO_3	0.10	0.08	0.06	0.07	0.10	0.08	0.02	21.82	-
Na_2O	0.50	0.36	0.48	0.46	0.27	0.41	0.10	23.39	-
K_2O	3.70	3.80	4.02	3.86	4.00	3.88	0.14	3.49	-
TiO_2	1.12	1.10	1.14	1.14	1.12	1.12	0.02	1.47	-
P_2O_5	0.14	0.10	0.12	0.12	0.10	0.12	0.02	14.61	-
Cr_2O_3	0.02	0.02	0.02	0.02	0.02	0.02	0.0011	5.27	-
Mn_2O_3	0.14	0.12	0.14	0.14	0.12	0.13	0.01	8.30	-
Other									
L.O.I.	2.45	2.76	3.55	2.16	2.08	2.60	0.59	22.87	-
Cl^-	0.0053	0.0007	0.0043	0.0050	0.0028	0.0036	0.0019	52.39	-
S. P_2O_5 (mg/kg)	6.60	10.32	7.04	5.67	8.56	7.64	1.83	23.92	-
Free CaO	-	-	-	-	-	-	-	-	0.03
Reac. CaO	-	-	-	-	-	-	-	-	0.97
Reac. SiO_2	-	-	-	-	-	-	-	-	42.31

Table 4.2 The evaluation of chemical analysis results of CFA according to the standards.

Weight	(%)	TS EN 450-1	TS EN 197-1		ASTM C 618	
			V	W	F	C
SiO_2	56.13					
Al_2O_3	25.01					
Fe_2O_3	5.89					
S+A+F	87.03	≥ 70			≥ 70	≥ 50
CaO	1.70					
MgO	2.18	≤ 4				
SO_3	0.08	≤ 3			≤ 5	≤ 5
Na_2O	0.41					
K_2O	3.88					
Na_2O eq*	2.96	≤ 5				
P_2O_5	0.12	≤ 5				
L.O.I.	2.60	Category A ≤ 5 Category B ≤ 7 Category C ≤ 9	a) $0 \leq ... \leq 5$ b) $2 \leq ... \leq 7$ c) $4 \leq ... \leq 9$		≤ 6	≤ 6
Cl^-	0.0036	≤ 0.10				
S. P_2O_5	7.64	≤ 100 (mg/kg)				
Free CaO	0.03	≤ 1.5(1)	≤ 1 (2)			
Reac. CaO	0.97	≤ 10	< 10	≥ 10 (3)		
Reac. SiO_2	42.31	≥ 25	≥ 25	≥ 25 (4)		

* Na_2O eq.= $Na_2O + 0.658\ K_2O$
(1)(if Free CaO >1.5; soundness ≤ 10 mm) ; (2)(if 1< Free CaO <2.5; soundness ≤ 10 mm)
(3)(if Reac. CaO >15.00; $\sigma_{28} \geq 10$ MPa); (4)(10<Reac.CaO<15)

All requirements (total amount of SiO_2, Al_2O, Fe_2O_3, content of MgO, sulphate, alkalis (Na_2O, K_2O), chloride, phosphate and soluble phosphate, free CaO, reactive CaO and reactive SiO_2) given in TS EN 450-1 are satisfied by CFA. Also, according to TS EN 450-1 the value of the loss on ignition means that the category of CFA is A.

As a result, it can be said that considering its chemical composition CFA is a proper fly ash based on the requirements of TS EN 197-1, TS EN 450-1 and ASTM C 618standards.

In addition to the evaluation above, heavy metals analysis was done for CFA mix sample, and the concentrations of the heavy metals are given in Table 4.3.

Table 4.3 Heavy metal concentration of CFA.

Element	**Symbol**	**Concentration (mg/kg)**
Beryllium	Be	6.85
Vanadium	V	225
Chromium	Cr	150
Manganese	Mn	546
Cobalt	Co	33.60
Nickel	Ni	78.60
Copper	Cu	114
Zinc	Zn	108
Arsenic	As	25.20
Selenium	Se	4.38
Silver	Ag	<0.88
Cadmium	Cd	0.35
Antimony	Sb	6.71
Barium	Ba	1053
Mercury	Hg	1.48
Thallium	Tl	4.87
Lead	Pb	114

4.1.2 Mineralogical and Morphological Analysis Results

CFA mix sample, the mix of the five samples, was used for these analyses. The x-ray diffraction pattern of CFA is given in Figure 4.1. Quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), hematite (Fe_2O_3) and titanomagnetite ($Fe_{3-x}Ti_xO_{4:}$ $Fe_{2.75}Ti_{0.25}O_4$) were identified as the major crystal phases.

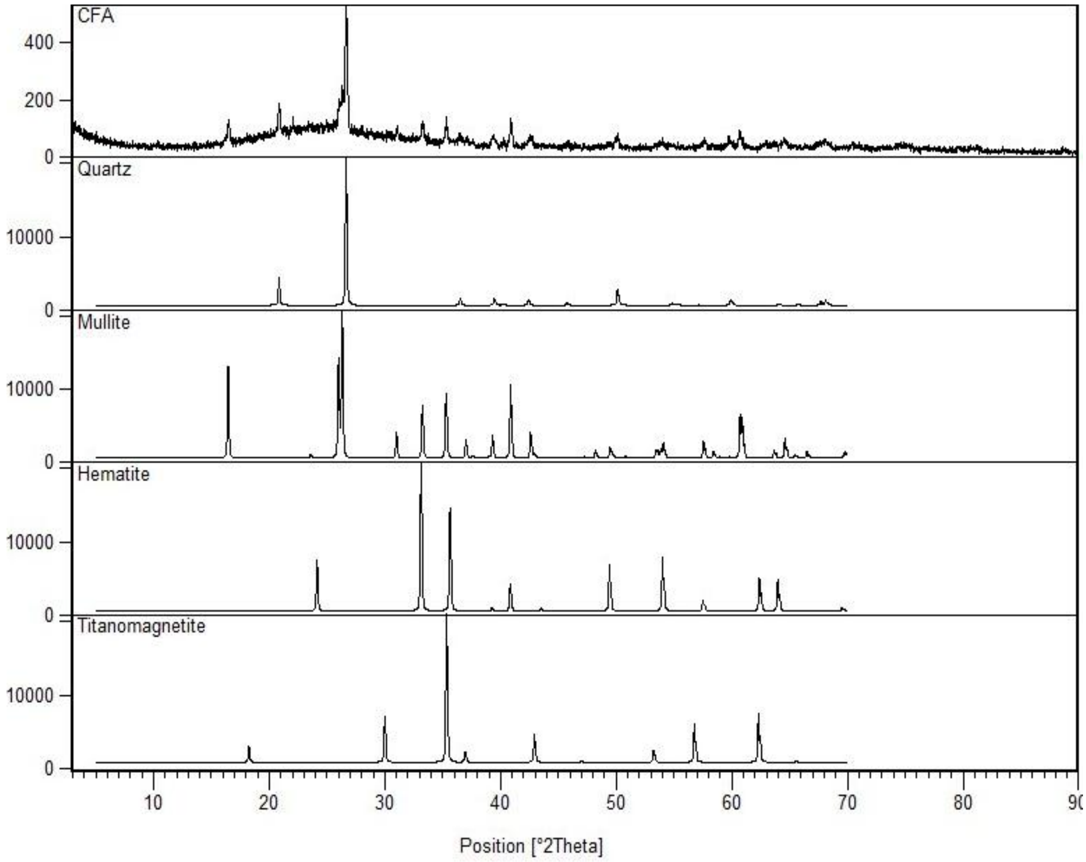

Figure 4.1 X-ray diffraction pattern of CFA.

As it can be seen from the scanning electron microscopy (SEM) image of CFA (Figure 4.2), this fly ash is composed of spherical and angular particles with a diameter between 1 µm to 120 µm. The small particles with a diameter of 5 µm to 15 µm are totally in spherical shape.

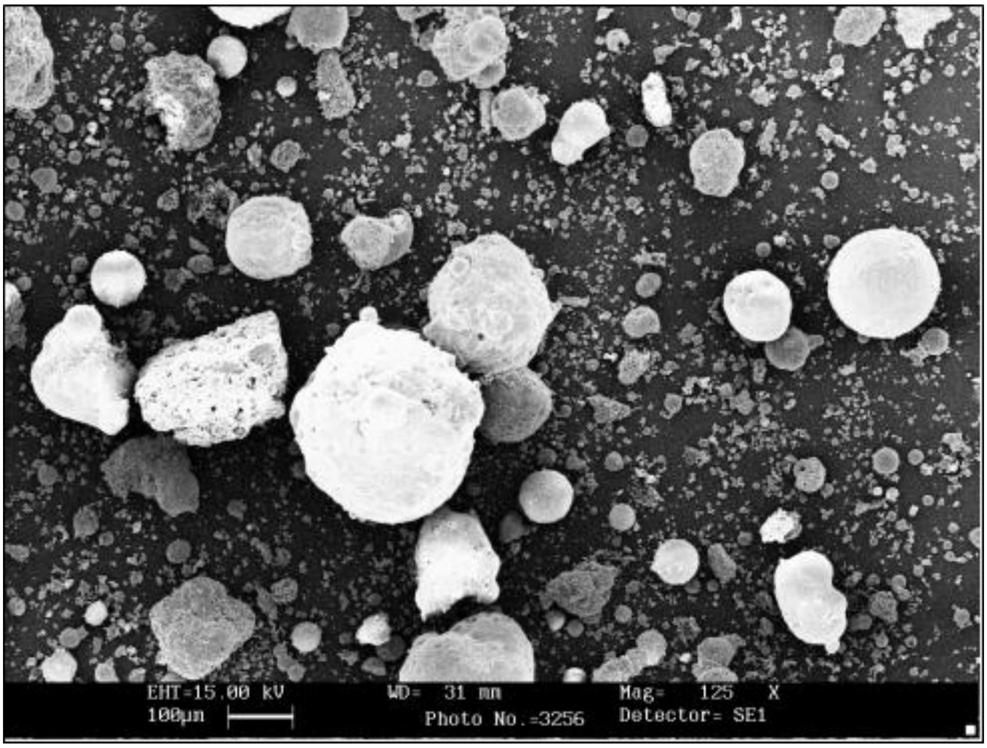

Figure 4.2 Scanning electron microscopy (SEM) image of CFA (125 x).

4.1.3 Physical Analysis Results

For the determination of physical properties of CFA the mix sample was used in the experiments. The results of the physical tests performed and the evaluation of these results in accordance with the physical requirements of TS EN 450-1 are presented in Table 4.4. In addition to this, according to ASTM C 204 the Blaine fineness value is 2889 cm^2/g. According to ASTM C 230, the flow diameter is 175 mm.

Also, the particle size distribution of CFA samples, the five samples and the mix sample, was determined by laser diffraction particle size analyzer separately. The curves of the particle size distribution belonging to the six samples are shown in Figure 4.3. The volume over percentages corresponding to 90 μm, 45 μm, 32 μm and D_{10}, D_{50}, D_{90} and D[4,3] diameters are presented in Table 4.5 for the six samples. As seen from Figure 4.3, there is a difference in the particle size distribution through the days of the production. However, the mix sample seems to be in the middle of these distributions.

Table 4.4 The physical properties of CFA.

Property	**Unit**	**CFA**	**TS EN 450-1**	**Satisfying Condition**
Density	g/cm^3	1.99	-	N.A
Standard consistency	%	28.20	-	N.A
Initial setting time	min	210	≤ twice the initial setting time of cement alone	S
Fineness (Retain on 45 µm sieve)	%	52.10	Category N ≤ 40 Category S ≤ 12	N
Soundness	mm	0	≤ 10	S
Activity index, 28 days	%	74.7	≥ 75	S
Activity index, 90 days	%	82.2	≥ 85	N

* N.A: Not applicable S: Satisfying N: Not satisfying

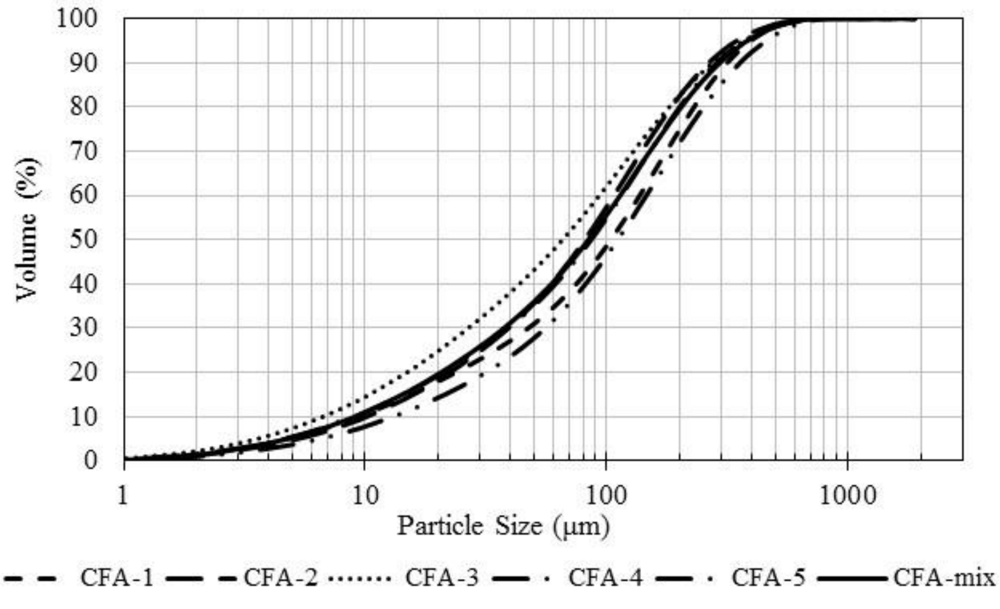

Figure 4.3 Particle size distribution of CFA samples.

Table 4.5 Percentages of particles and diameters of CFA.

CAF	90 µm	45 µm	32 µm	D_{10}	D_{50}	D_{90}	D[4,3]
	(%)			(µm)			
1	54.9	71	76.2	9.6	104.6	316.9	137.5
2	46.6	67	74.1	10.3	81.6	265.6	114.7
3	41.2	59.4	66.7	6.8	66.1	276.9	109.7
4	48.8	67.4	73.7	9.1	86.8	287.1	123.2
5	57.3	74.5	80.0	13.3	111.7	358.5	154.2
Mix	47.9	66.4	73.0	9.1	84.2	294.3	123.0

4.2 Fly ashes Taken from Tunçbilek Thermal Power Plant (T3FA, T5FA)

Fly ash samples were supplied from Tunçbilek Thermal Power Plant 3rd unit (T3FA) in July, and 5th unit (T5FA) in August 2013 for five consecutive days. In addition to that, for each unit a mix was prepared from the five samples as described in Chapter 3.

4.2.1 Chemical Analysis Results

Chemical analyses were done for all fly ash samples including the mixes. The results and the evaluation of conformity of the average of the results to the requirements of TS EN 450-1, TS EN 197-1 and ASTM C 618 are presented respectively in Table 4.6 and Table 4.7 for T3FA, in Table 4.8 and Table 4.9 for T5FA.

The oxide percentages of fly ashes taken from five consecutive days are very close to each other, and the standard deviation values are small. Moreover, the chemical analysis results of the mix are very close to the average the five fly ash samples. From that, it can be concluded that T3FA is uniform.

Table 4.6 Chemical analysis results of T3FA.

Weight (%)	**Samples**					**Ave.**	**SD**	**CV (%)**	**Mix**
	1	**2**	**3**	**4**	**5**				
ICP									
SiO_2	52.70	53.68	53.32	53.75	53.54	53.40	0.42	0.79	52.98
Al_2O_3	19.36	19.20	19.02	19.18	19.38	19.23	0.15	0.77	19.38
Fe_2O_3	13.56	13.98	13.54	13.44	13.70	13.64	0.21	1.54	13.38
CaO	1.26	1.30	1.32	1.24	1.24	1.27	0.04	2.86	1.30
MgO	3.80	3.46	3.46	3.48	3.36	3.51	0.17	4.77	3.92
SO_3	0.42	0.47	0.47	0.50	0.50	0.47	0.03	6.93	0.49
Na_2O	0.02	0.02	0.04	0.04	0.04	0.03	0.01	34.23	0.04
K_2O	1.32	1.28	1.26	1.34	1.30	1.30	0.03	2.43	1.36
TiO_2	1.08	1.10	1.08	1.12	1.12	1.10	0.02	1.82	1.08
P_2O_5	0.20	0.20	0.20	0.21	0.24	0.21	0.02	8.24	0.20
Cr_2O_3	0.26	0.26	0.26	0.26	0.26	0.26	0.00	0.00	0.26
Mn_2O_3	0.16	0.18	0.18	0.18	0.18	0.18	0.01	5.08	0.18
Others									
L.O.I.	4.95	4.81	5.49	5.37	5.19	5.16	0.28	5.48	4.93
Cl^-	0.0053	0.0018	0.0035	0.0053	0.0018	0.0035	0.0018	49.44	-
S. P_2O_5 (mg/kg)	5.93	4.35	5.25	7.68	9.52	6.55	2.06	31.50	-
Free CaO	0.010	0.020	0.020	0.020	0.020	0.018	0.0045	24.85	-
Reac. CaO	-	-	-	-	-	-	-	-	0.79
Reac. SiO_2	-	-	-	-	-	-	-	-	36.43

According to TS EN 197-1, T3FA is a siliceous fly ash (V) since its reactive CaO content (0.79%) is less than 10%, and according to ASTM C 618 it seems as Class F fly ash (low-calcium fly ash) owing to SiO_2+Al_2O+Fe_2O_3 content of greater than 70% and less amount of CaO.

Table 4.7 The evaluation of chemical analysis results of T3FA according to the standards.

Weight	**(%)**	**TS EN 450-1**	**TS EN 197-1**		**ASTM C 618**	
			V	**W**	**F**	**C**
SiO_2	53.40					
Al_2O_3	19.23					
Fe_2O_3	13.64					
S+A+F	86.27	≥ 70			≥ 70	≥ 50
CaO	1.27					
MgO	3.51	≤ 4				
SO_3	0.47	≤ 3			≤ 5	≤ 5
Na_2O	0.03					
K_2O	1.30					
Na_2O eq*	0.89	≤ 5				
P_2O_5	0.21	≤ 5				
L.O.I.	5.16	Category A ≤ 5 Category B ≤ 7 Category C ≤ 9	a) 0 ≤...≤ 5 b) 2 ≤...≤ 7 c) 4 ≤...≤ 9		≤ 6	≤ 6
Cl^-	0.0035	≤ 0.10				
S. P_2O_5	6.55	≤ 100 (mg/kg)				
Free CaO	0.018	≤ 1.5(1)	≤ 1 (2)			
Reac. CaO	0.79	≤ 10	< 10	≥ 10 (3)		
Reac. SiO_2	36.43	≥ 25	≥ 25	≥ 25 (4)		

* Na_2O eq.= Na_2O + 0.658 K_2O

(1)(if Free CaO >1.5; soundness ≤ 10 mm) ; (2)(if 1< Free CaO <2.5; soundness ≤ 10 mm)

(3)(if Reac. CaO >15.00; σ_{28} ≥10 MPa); (4)(10<Reac.CaO<15)

T3FA satisfies all the requirements in the three standards. But, with 3.51%, the MgO content is close the limit value (4%). The loss on ignition value of T3FA is 5.16%. In this case, according to TS EN 450-1 the category of loss on ignition of T3FA is B. However, since 5.16 is very close to the limit value of category A, (5%), and the loss on ignition value of the mix is 4.93, it can be accepted as category A.

As a result, it can be said that considering its chemical composition T3FA is a proper fly ash based on the requirements of TS EN 197-1, TS EN 450-1 and ASTM C 618 standards.

Table 4.8 Chemical analysis results of T5FA.

Weight (%)	**Samples**					**Ave.**	**SD**	**CV (%)**	**Mix**
	1	**2**	**3**	**4**	**5**				
ICP									
SiO_2	53.74	56.43	56.14	55.06	56.21	55.52	1.13	2.03	55.25
Al_2O_3	18.89	18.57	18.66	19.53	19.36	19.00	0.43	2.24	19.36
Fe_2O_3	10.46	11.73	11.70	11.69	11.38	11.39	0.54	4.74	11.61
CaO	2.86	2.76	2.72	2.83	2.65	2.76	0.08	3.05	2.80
MgO	5.29	5.76	5.85	5.85	5.87	5.72	0.25	4.30	5.79
SO_3	0.62	0.55	0.57	0.45	0.50	0.54	0.07	12.15	0.48
Na_2O	0.07	0.08	0.10	0.08	0.09	0.08	0.01	13.57	0.08
K_2O	1.75	1.90	1.95	1.89	1.90	1.88	0.08	4.01	1.85
TiO_2	0.79	0.81	0.82	0.77	0.79	0.80	0.02	2.45	0.79
P_2O_5	0.27	0.22	0.21	0.20	0.22	0.22	0.03	12.06	0.23
Cr_2O_3	0.13	0.17	0.19	0.18	0.18	0.17	0.02	13.80	0.17
Mn_2O_3	0.20	0.20	0.19	0.19	0.18	0.19	0.01	4.36	0.19
Others									
L.O.I.	4.59	0.85	1.07	0.86	0.64	1.60	1.68	104.70	1.23
Cl^-	0.0057	0.0028	0.0046	0.0035	0.0028	0.0039	0.0013	32.37	-
S. P_2O_5 (mg/kg)	4.28	5.70	3.83	3.60	3.53	4.19	0.89	21.36	-
Free CaO	-	-	-	-	-	-	-	-	0.02
Reac. CaO	-	-	-	-	-	-	-	-	2.34
Reac. SiO_2	-	-	-	-	-	-	-	-	42.28

The oxide percentages of T5FA for five consecutive days are very close to each other, and the standard deviation values are small. Furthermore, the chemical analysis results of the mix are very close the average of five fly ash samples. From that, it can be concluded that T5FA is uniform. However, the loss on ignition belonging to FA from the 1st day is about five times the loss on ignition values of other four samples. The reasons might be insufficient oxygen in furnace, too large particle size of coal or poor fuel for that day.

Table 4.9 The evaluation of chemical analysis results of T5FA according to the standards.

Weight	**(%)**	**TS EN 450-1**	**TS EN 197-1**		**ASTM C 618**	
			V	**W**	**F**	**C**
SiO_2	55.52					
Al_2O_3	19.00					
Fe_2O_3	11.39					
S+A+F	85.91	≥ 70			≥ 70	≥ 50
CaO	2.76					
MgO	5.72	≤ 4				
SO_3	0.54	≤ 3			≤ 5	≤ 5
Na_2O	0.08					
K_2O	1.88					
Na_2O eq*	1.32	≤ 5				
P_2O_5	0.22	≤ 5				
L.O.I.	1.60	Category A ≤ 5 Category B ≤ 7 Category C ≤ 9	a) 0 ≤...≤ 5 b) 2 ≤...≤ 7 c) 4 ≤...≤ 9		≤ 6	≤ 6
Cl^-	0.0039	≤ 0.10				
S. P_2O_5	4.19	≤ 100 (mg/kg)				
Free CaO	0.02	≤ 1.5(1)	≤ 1 (2)			
Reac. CaO	2.34	≤ 10	< 10	≥ 10 (3)		
Reac. SiO_2	42.28	≥ 25	≥ 25	≥ 25 (4)		

* Na_2O eq.= Na_2O + 0.658 K_2O
(1)(if Free CaO >1.5; soundness ≤ 10 mm) ; (2)(if 1< Free CaO <2.5; soundness ≤ 10 mm)
(3)(if Reac. CaO >15.00; σ_{28} ≥10 MPa); (4)(10<Reac.CaO<15)

Like T3FA, T5FA is also a siliceous fly ash (V) according to TS EN 197-1, and Class F fly ash according to ASTM C 618. Its loss on ignition category is A according to TS EN 450-1. Except the MgO content, all the requirements of the TS EN 197-1, TS EN 450-1 and ASTM C 618 are satisfied by T5FA.

In addition to the evaluation above, heavy metals analysis were done for T3FA and T5FA mix samples and the concentrations of the heavy metals are given in

Table 4.10. As seen, in terms of some heavy metal concentrations there are significant differences between the two units of the same TPP.

Table 4.10 Heavy metal concentration of T3FA and T5FA.

Element	**Symbol**	**Concentration (mg/kg)**	
		T3FA	**T5FA**
Beryllium	Be	11.23	4.83
Phosphorous	P	640.40	782.14
Vanadium	V	380.35	161.26
Chromium	Cr	1569.31	982.56
Manganese	Mn	727.26	1080.33
Cobalt	Co	152.86	100.67
Nickel	Ni	3201.18	1943.64
Copper	Cu	147.81	97.04
Zinc	Zn	116.00	103.17
Arsenic	As	106.98	53.72
Selenium	Se	4.01	2.97
Silver	Ag	1.35	0.19
Cadmium	Cd	0.43	0.36
Antimony	Sb	21.59	6.83
Barium	Ba	249.55	438.35
Mercury	Hg	0.56	3.48
Thallium	Tl	5.67	2.98
Lead	Pb	67.30	58.36

4.2.2 Mineralogical and Morphological Analysis Results

T3FA and T5FA mix samples were used for these analyses. The x-ray diffraction patterns of T3FA and T5FA are given in Figure 4.4 and Figure 4.5 respectively. As seen from the figures, mineral components like quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), hematite (Fe_2O_3) were found in both fly ash. In addition to that, in the mineralogical composition of T3FA magnetite (Fe_3O_4) and in T5FA magnesioferrite (Fe_2MgO_4) were identified.

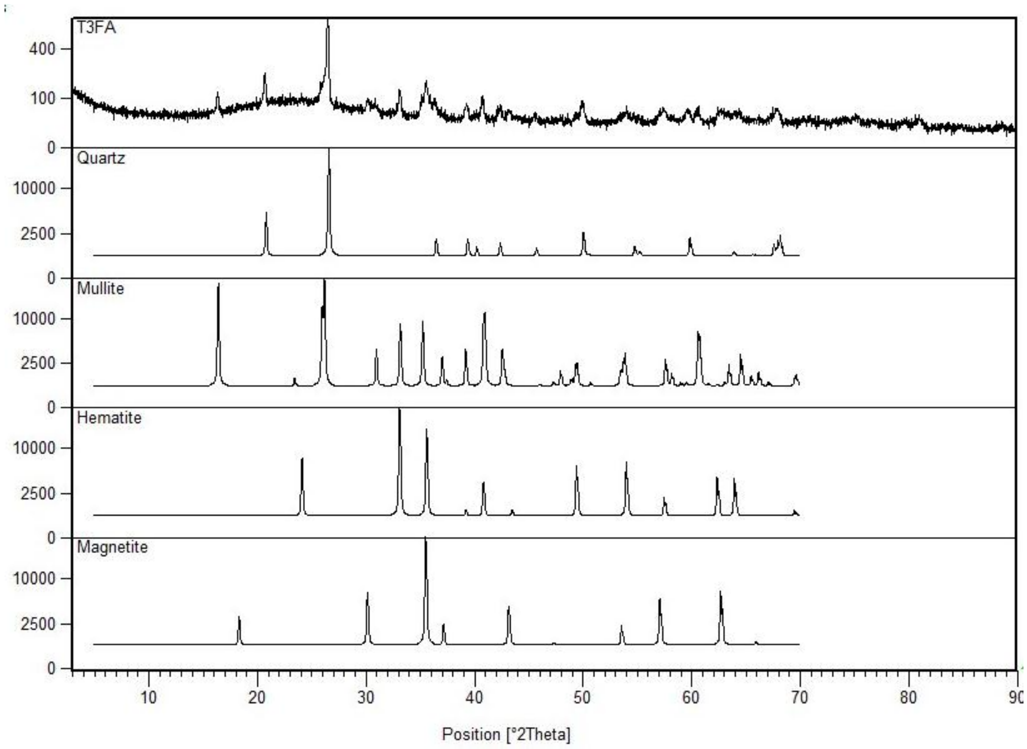

Figure 4.4 X-ray diffraction pattern of T3FA.

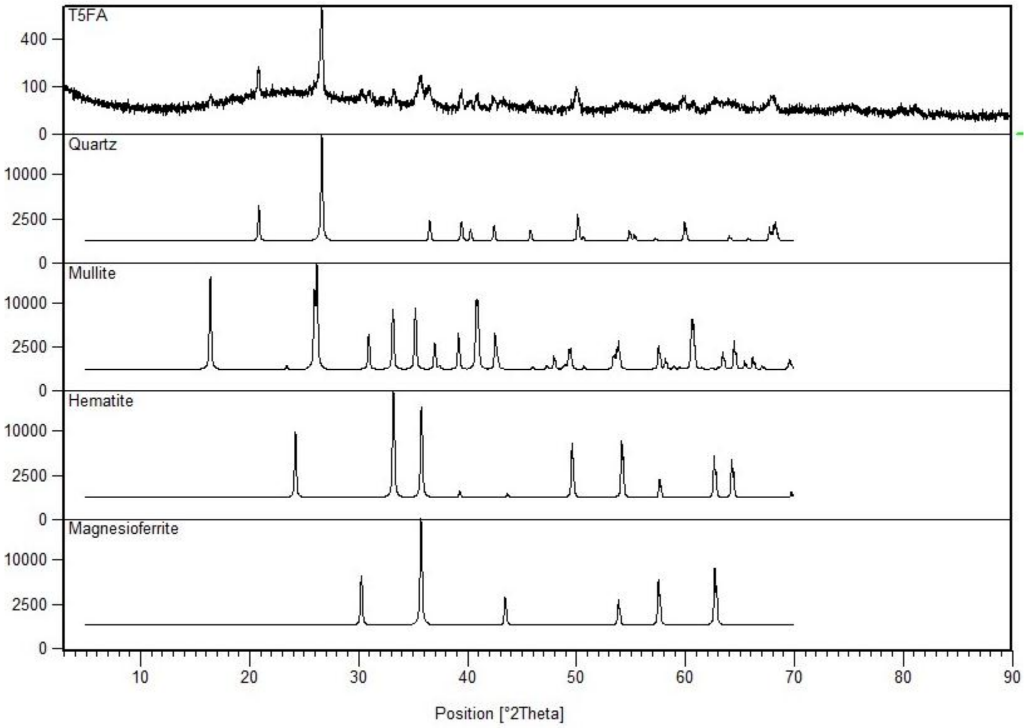

Figure 4.5 X-ray diffraction pattern of T5FA.

Figure 4.6 and Figure 4.7 contain the scanning electron microscopy (SEM) images of T3FA and T5FA, respectively. According to these images, T3FA is composed of spherical and angular particles with a diameter between 1 μm to 100 μm. The small particles with a diameter of 1 μm to 15 μm are totally in spherical shape. T5FA has coarser particles compared to T3FA. It has spherical and angular particles with a diameter between 1 μm to 150 μm. Especially small particles with a diameter of 1 μm to 25 μm are totally in spherical shape.

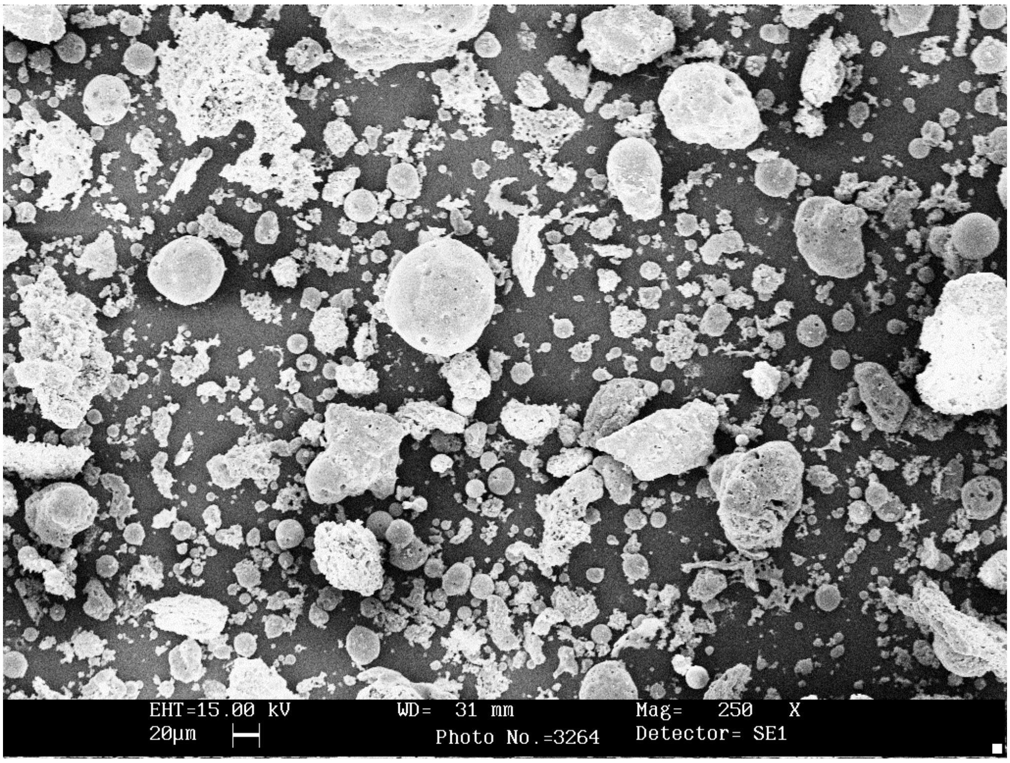

Figure 4.6 Scanning electron microscopy (SEM) image of T3FA (250 x).

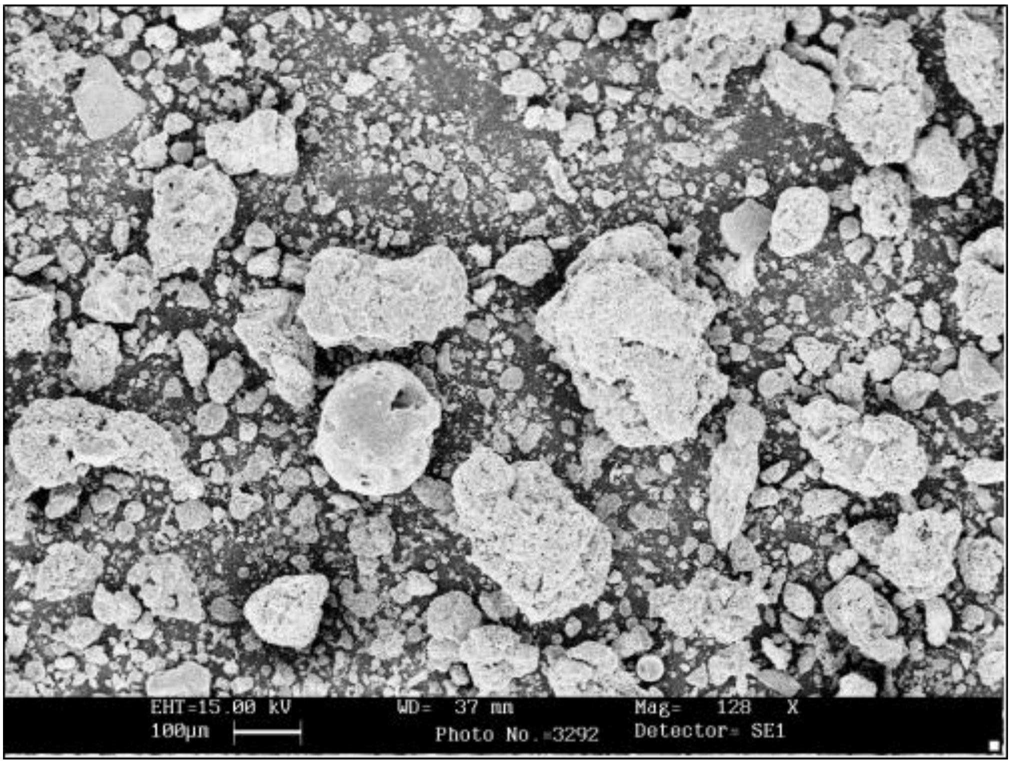

Figure 4.7 Scanning electron microscopy (SEM) image of T5FA (125 x).

4.2.3 Physical Analysis Results

For the determination of the physical properties of T3FA and T5FA the mix samples were used in the experiments. The results of the physical tests performed on both T3FA and T5FA, and the evaluation of these results in accordance with the physical requirements of TS EN 450-1 are shown in Table 4.11. In addition to this, according to ASTM C 204 the Blaine fineness values are 5214 and 2481 cm^2/g for T3FA and T5FA respectively. According to ASTM C 230, the flow diameters are 127 mm for T3FA and 133 mm for T5FA.

In addition, the particle size distribution curves for T3FA and T5FA samples, the five samples and the mix samples, determined by laser diffraction particle size analyzer are presented in Figure 4.8 for T3FA and in Figure 4.9 for T5FA.

Table 4.11 The physical properties of T3FA and T5FA.

Property	**Unit**	**T3FA**	**T5FA**	**Satisfying Condition**		
				TS EN 450-1	**T3FA**	**T5FA**
Density	g/cm^3	2.15	2.21	-	N.A	N.A
Standard consistency	%	34.60	29.40	-	N.A	N.A
Initial setting time	min	195	205	≤ twice the initial setting time of cement alone	S	S
Retain on 45 μm sieve	%	29.70	57.40	Category N ≤ 40 Category S ≤ 12	S	N
Soundness	mm	1	1	≤ 10	S	S
Activity index, 28 days	%	76.4	78.3	≥ 75	S	S
Activity index, 90 days	%	93.9	87.9	≥ 85	S	S

* N.A: Not applicable S: Satisfying N: Not satisfying

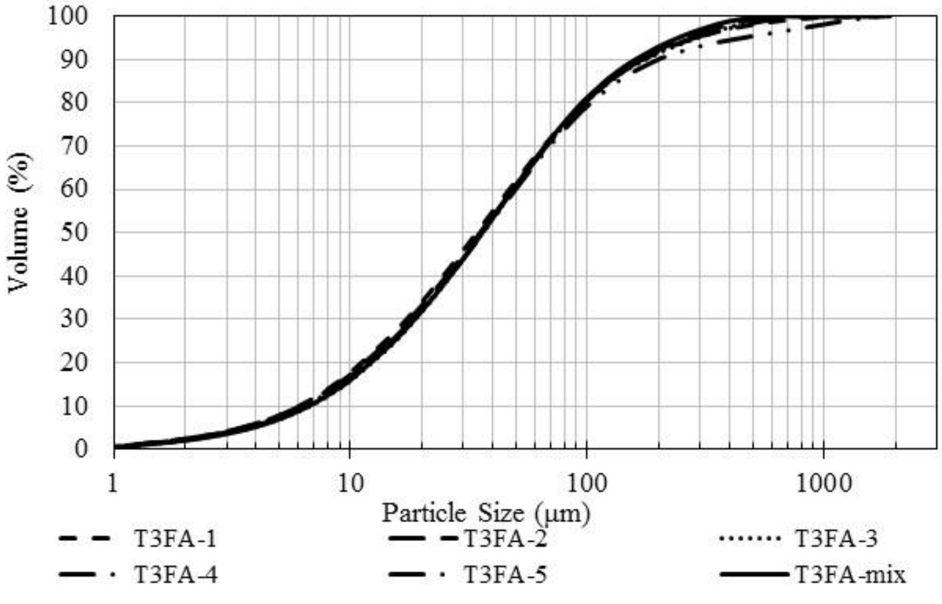

Figure 4.8 Particle size distribution of T3FA samples.

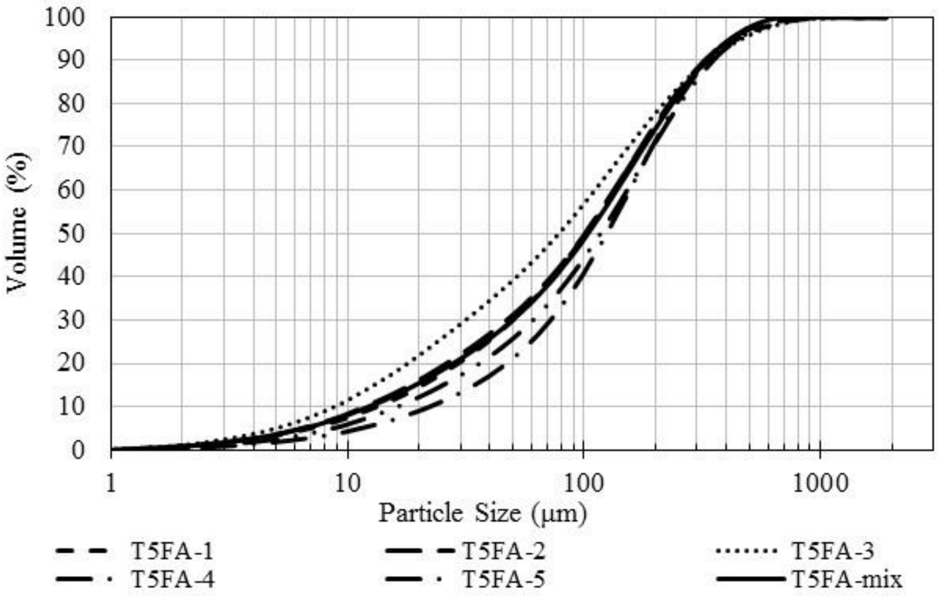

Figure 4.9 Particle size distribution of T5FA samples.

Also, the volume over percentages corresponding to 90 µm, 45 µm, 32 µm and D_{10}, D_{50}, D_{90} and D[4,3] diameters are presented in Table 4.12 for T3FA, and in Table 4.13 for T5FA samples. As seen from both 45 µm wet sieve results and laser particle size results T5FA has coarser particles compared to T3FA. The particle size distribution of the five samples and the mix sample for T3FA is almost the same while the particle size distribution of the five samples for T5FA shows some differences day by day. However, the mix sample seems to be in the middle of these distributions.

Table 4.12 Percentages of particles and diameters of T3FA.

T3FA	**90 µm**	**45 µm**	**32 µm**	**D_{10}**	**D_{50}**	**D_{90}**	**D[4,3]**
	(%)			**(µm)**			
1	21.8	41.5	52.2	6.1	34.3	172.9	75.8
2	22.2	42.5	53.2	6.2	35.5	168.8	68.5
3	22.2	42.9	54.1	6.8	36.3	176.3	71.8
4	22.1	42.6	53.5	6.4	35.7	171.1	72.8
5	23.3	43.4	54.1	6.5	36.5	202.1	103.7
Mix	21.3	42.6	53.9	6.7	36.0	159.4	65.1

Table 4.13 Percentages of particles and diameters of T5FA.

T5FA	90 µm	45 µm	32 µm	D_{10}	D_{50}	D_{90}	D[4,3]
	(%)			(µm)			
1	54.1	72.3	78.6	13.3	101.6	334.6	146.0
2	53.7	73.1	76.9	11.9	101.0	323.0	140.6
3	46.2	63.0	69.7	8.8	78.3	334.1	133.5
4	63.0	80.8	85.9	22.2	124.9	332.0	156.0
5	59.2	76.3	81.8	16.2	117.5	352.0	157.1
Mix	54.7	72.0	77.9	12.4	103.9	329.2	141.8

4.3 Fly ash Taken from Afşin Elbistan Thermal Power Plant (AEFA)

Fly ash samples were supplied from Afşin Elbistan Thermal Power Plant B unit in July, 2013 for five consecutive days. Besides, a mix was prepared from the five samples as described in Chapter 3.

4.3.1 Chemical Analysis Results

The chemical analyses of the five fly ash samples and the mix were performed separately. The results of the six AEFA samples with the standard deviation (SD) and the coefficient of variation (CV) values are all presented in Table 4.14.

When the oxide percentages of the five samples are examined, it can be inferred that Afşin Elbistan B TPP does not have a uniform production. However, the chemical analysis result of the mix is very close the average of five fly ash samples. The evaluation of conformity of the average results to the requirements of the standards is given in Table 4.15.

Table 4.14 Chemical analysis results of AEFA.

Weight (%)	Samples					Ave.	SD	CV (%)	Mix
	1	2	3	4	5				
ICP									
SiO_2	39.16	45.21	43.46	36.63	35.98	40.09	4.10	10.23	39.79
Al_2O_3	15.46	17.95	17.81	15.12	14.88	16.24	1.51	9.29	16.26
Fe_2O_3	6.81	7.98	8.08	6.63	6.57	7.21	0.75	10.41	7.11
CaO	23.46	15.58	17.01	24.67	25.47	21.24	4.60	21.64	21.13
MgO	2.25	2.37	2.38	2.17	2.15	2.26	0.11	4.77	2.26
SO_3	7.17	4.78	5.03	7.99	8.58	6.71	1.72	25.70	6.85
Na_2O	0.30	0.31	0.32	0.30	0.34	0.31	0.02	5.33	0.33
K_2O	1.30	1.48	1.44	1.24	1.18	1.33	0.13	9.68	1.40
TiO_2	0.75	0.85	0.83	0.72	0.70	0.77	0.07	8.66	0.75
P_2O_5	0.41	0.36	0.41	0.40	0.41	0.40	0.02	5.45	0.38
Cr_2O_3	0.04	0.05	0.04	0.04	0.04	0.04	0.0045	10.65	0.05
Mn_2O_3	0.04	0.05	0.04	0.05	0.05	0.05	0.01	11.91	0.04
Others									
L.O.I.	2.88	2.85	2.49	3.08	2.84	2.83	0.21	7.52	2.88
Cl^-	0.0050	0.0060	0.0053	0.0074	0.0067	0.0061	0.0010	16.26	-
S. P_2O_5 (mg/kg)	3.30	3.53	5.03	3.23	3.15	3.65	0.79	21.53	-
Free CaO	-	-	-	-	-	-	-	-	3.11
Reac. CaO	-	-	-	-	-	-	-	-	13.45
Reac. SiO_2	-	-	-	-	-	-	-	-	31.97

According to TS EN 197-1, AEFA is a calcareous fly ash (W) since it contains more than 10% reactive CaO. However, TS EN 197-1 states that if reactive CaO content of a FA is between 10% and 15%, its reactive SiO_2 should be greater than 25%. With 13.45%, reactive CaO content of AEFA remains in the range of 10% to 15%. Since SiO_2 content (31.97%) is greater than 25%, AEFA satisfies this requirement.

Table 4.15 The evaluation of chemical analysis results of AEFA according to the standards.

Weight	**(%)**	**TS EN 450-1**	**TS EN 197-1**		**ASTM C 618**	
			V	**W**	**F**	**C**
SiO_2	40.09					
Al_2O_3	16.24					
Fe_2O_3	7.21					
S+A+F	63.55	≥ 70			≥ 70	≥ 50
CaO	21.24					
MgO	2.26	≤ 4				
SO_3	6.71	≤ 3			≤ 5	≤ 5
Na_2O	0.31					
K_2O	1.33					
Na_2O eq*	1.19	≤ 5				
P_2O_5	0.40	≤ 5				
L.O.I.	2.83	Category A ≤ 5 Category B ≤ 7 Category C ≤ 9	a) 0 ≤...≤ 5 b) 2 ≤...≤ 7 c) 4 ≤...≤ 9		≤ 6	≤ 6
Cl^-	0.0061	≤ 0.10				
S. P_2O_5	3.65	≤ 100 (mg/kg)				
Free CaO	3.11	≤ 1.5(1)	≤ 1 (2)			
Reac. CaO	13.45	≤ 10	< 10	≥ 10 (3)		
Reac. SiO_2	31.97	≥ 25	≥ 25	≥ 25 (4)		

* Na_2O eq.= Na_2O + 0.658 K_2O
(1)(if Free CaO >1.5; soundness ≤ 10 mm) ; (2)(if 1< Free CaO <2.5; soundness ≤ 10 mm)
(3)(if Reac. CaO >15.00; σ_{28} ≥10 MPa); (4)(10<Reac.CaO<15)

In accordance with ASTM C 618, due to the content of SiO_2+Al_2O+Fe_2O_3 (63.55%) is less than 70% greater than 50% and the high amount of CaO, AEFA conforms to the category of Class C fly ash (high-calcium fly ash).

As it is seen from Table 4.15, the requirements related to the content of SiO_2+Al_2O+Fe_2O_3, free CaO, reactive CaO according to TS EN 450-1 and the SO_3 content requirement according to both TS EN 450-1 and ASTM C are not satisfied. The content of SiO_2+Al_2O+Fe_2O_3 remains below the limit value whereas the contents of SO_3, free CaO, and reactive CaO exceed the limit values. On the other hand, TS EN 450-1 indicates that if free CaO content is greater than

1.5%, soundness test should be done and the maximum value for the soundness should be 10 mm. For AEFA the soundness has determined as 1 mm. Thus, it can be said this requirement is met. Also, according to TS EN 450-1 the value of the loss on ignition means that the category of AEFA is A.

Except those mentioned above, the rest of the requirements are met for the three standards. As a consequence of these chemical analysis evaluations, it can be said that AEFA does not often fulfill the requirements of TS EN and ASTM standards related to fly ash.

In addition to the evaluation above, for AEFA mix sample the heavy metals analysis was done and the concentrations of the heavy metals are given in Table 4.16.

Table 4.16 Heavy metal concentration of AEFA.

Element	**Symbol**	**Concentration (mg/kg)**
Beryllium	Be	1.62
Phosphorous	P	1762.66
Vanadium	V	346.85
Chromium	Cr	308.74
Manganese	Mn	284.13
Cobalt	Co	23.70
Nickel	Ni	214.81
Copper	Cu	55.96
Zinc	Zn	115.23
Arsenic	As	39.41
Selenium	Se	8.33
Silver	Ag	<2.94
Cadmium	Cd	0.86
Antimony	Sb	2.06
Barium	Ba	300.56
Mercury	Hg	2.15
Thallium	Tl	1.31
Lead	Pb	24.26

4.3.2 Mineralogical and Morphological Analysis Results

AEFA mix sample was used for these analyses. The x-ray diffraction pattern of AEFA is given in Figure 4.10. Calcium oxide (CaO), anhydrite ($CaSO_4$), Quartz (SiO_2), hematite (Fe_2O_3) and calcite ($CaCO_3$) were identified as the major crystal phases.

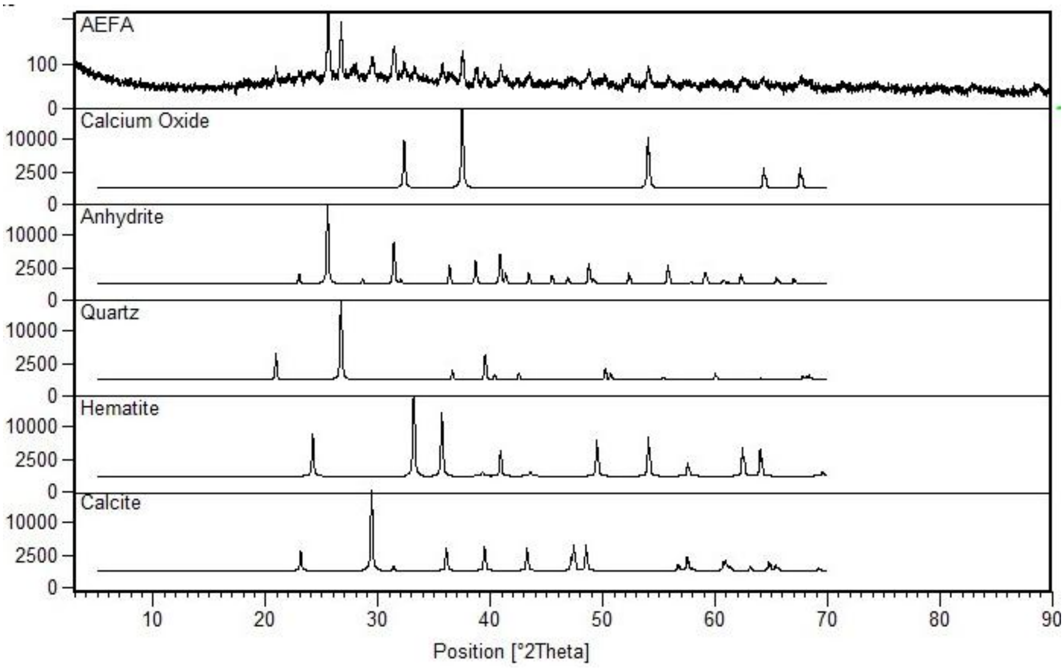

Figure 4.10 X-ray diffraction pattern of AEFA

According to the scanning electron microscopy (SEM) image of AEFA (Figure 4.11) this fly ash consists of spherical and angular particles with a diameter between 1 µm to 150 µm. Especially small particles with a diameter of 1 µm to 25 µm are totally in spherical shape.

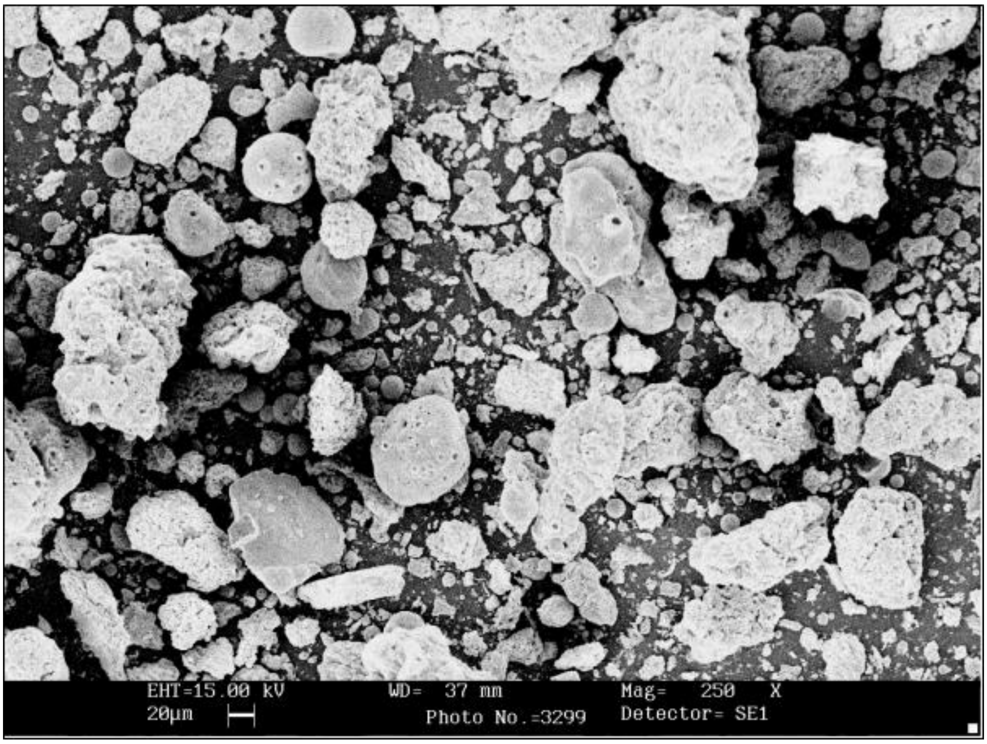

Figure 4.11 Scanning electron microscopy (SEM) image of AEFA (250 x).

4.3.3 Physical Analysis Results

The results of the physical tests performed on AEFA, and the evaluation of these results in accordance with the physical requirements of TS EN 450-1 are given in Table 4.17. In addition to this, according to ASTM C 204 the Blaine fineness value is 3367 cm^2/g. According to ASTM C 230, the flow diameter is 117 mm.

In addition, the particle size distribution curves of AEFA samples, the five samples and the mix sample were determined by laser diffraction particle size analyzer. The curves of particle size distribution belonging to the six samples are presented in Figure 4.12. Also, the volume over percentages corresponding to 90 µm, 45 µm, 32 µm and D_{10}, D_{50}, D_{90} and D[4,3] diameters are presented in Table 4.18. As seen from Figure 4.12, there is a difference in the particle size distribution through the production days. However, the mix sample seems to be in the middle of these distributions.

Table 4.17 Some physical properties of AEFA.

Property	**Unit**	**AEFA**	**TS EN 450-1**	**Satisfying Condition**
Density	g/cm^3	2.41	-	N.A
Standard consistency	%	33.20	-	N.A
Initial setting time	min	215	≤ twice the initial setting time of cement alone	S
Retain on 45 μm sieve	%	66.30	Category N ≤ 40 Category S ≤ 12	N
Soundness	mm	1	≤ 10	S
Activity index, 28 days	%	51.6	≥ 75	N
Activity index, 90 days	%	75.9	≥ 85	N

* N.A: Not applicable S: Satisfying N: Not satisfying

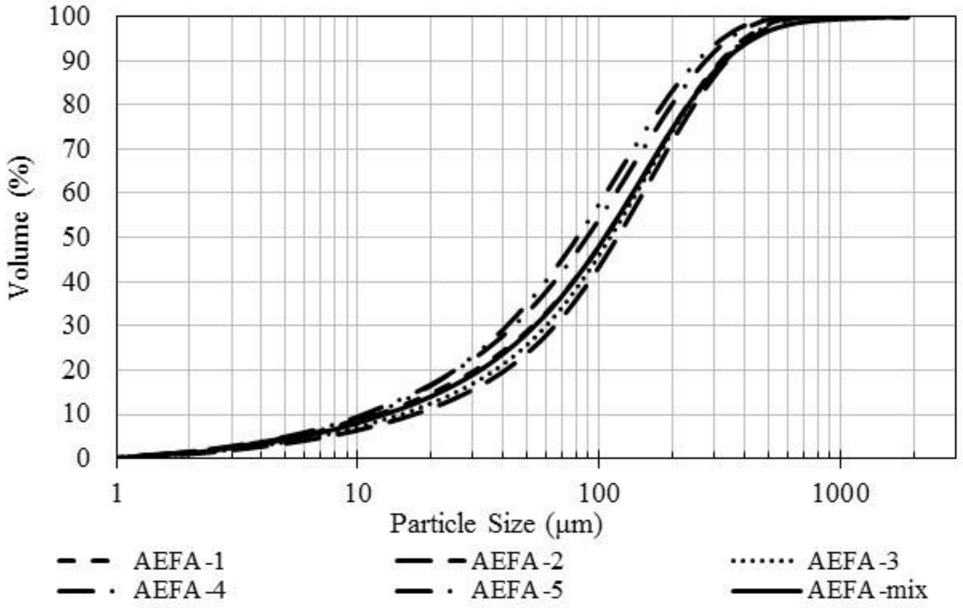

Figure 4.12 Particle size distribution of AEFA samples.

Table 4.18 Percentages of particles and diameters of AEFA.

T3FA	**90 µm**	**45 µm**	**32 µm**	**D_{10}**	**D_{50}**	**D_{90}**	**D[4,3]**
	(%)			**(µm)**			
1	55.6	73.5	79.4	12.3	105.9	319.6	140.1
2	60.4	78.4	83.7	17.3	119.0	339.1	153.4
3	57.8	76.6	82.2	15.2	111.2	326.0	145.2
4	49.6	69.7	76.5	10.7	89.0	275.9	119.9
5	46.3	68.0	75.7	11.5	81.3	255.2	111.1
Mix	55.4	74.0	80.0	13.0	105.1	330.0	150.3

4.4 Fly ash Taken from Kemerköy Thermal Power Plant (KFA)

Fly ash samples were supplied from Kemerköy Thermal Power Plant 2nd unit (KFA) in July, 2013 for five consecutive days. Besides, a mix was prepared from the five samples as described in Chapter 3.

4.4.1 Chemical Analysis Results

The chemical analyses were done for the five fly ash samples and the mix. The results of the six KFA samples with the standard deviation (SD) and the coefficient of variation (CV) values are shown in Table 4.19.

When the oxide percentages of the five samples are investigated, it is seen that the composition contents show differences especially for last two days compared to first three days. From that, it can be inferred that this Kemerköy TPP does not make the production in stable conditions. However, the chemical analysis result of the mix is very close the average the five fly ash samples. The evaluation of conformity of the average results to the requirements of the standards is given in Table 4.20.

Table 4.19 Chemical analysis results of KFA.

Weight (%)	Samples					Ave.	SD	CV (%)	Mix
	1	2	3	4	5				
ICP									
SiO_2	36.04	37.30	37.66	30.35	41.94	36.66	4.17	11.37	36.10
Al_2O_3	18.80	19.04	18.78	15.84	20.76	18.64	1.77	9.50	18.95
Fe_2O_3	8.06	8.04	8.22	8.18	7.30	7.96	0.38	4.73	7.92
CaO	26.28	25.12	24.76	34.10	20.74	26.20	4.89	18.65	26.30
MgO	2.02	2.42	2.22	2.00	2.21	2.17	0.17	7.90	2.28
SO_3	4.46	3.94	3.92	6.18	2.74	4.25	1.25	29.44	4.42
Na_2O	0.56	0.54	0.54	0.40	0.56	0.52	0.07	13.04	0.52
K_2O	2.10	1.96	1.98	1.54	2.06	1.93	0.22	11.63	1.92
TiO_2	0.76	0.78	0.76	0.62	0.86	0.76	0.09	11.44	0.78
P_2O_5	0.30	0.30	0.28	0.30	0.30	0.30	0.01	3.02	0.30
Cr_2O_3	0.04	0.02	0.04	0.02	0.04	0.03	0.01	34.23	0.04
Mn_2O_3	0.08	0.08	0.08	0.08	0.06	0.08	0.01	11.77	0.08
Others									
L.O.I.	0.36	0.41	0.47	0.37	0.41	0.40	0.04	10.73	0.37
Cl^-	0.0067	0.0025	0.0007	0.0103	0.0039	0.0035	0.0025	73.39	-
S. P_2O_5 (mg/kg)	2.93	3.00	4.43	3.23	3.08	3.33	0.62	18.68	-
Free CaO	-	-	-	-	-	-	-	-	3.46
Reac. CaO	-	-	-	-	-	-	-	-	23.05
Reac. SiO_2	-	-	-	-	-	-	-	-	29.29

According to TS EN 197-1, KFA is a calcareous fly ash (W) since it is composed of more than 10% reactive CaO (23.25%). In addition, for calcareous fly ash TS EN 197-1 states that if reactive CaO content of a FA is between 10% and 15%, its reactive SiO_2 should be greater than 25%. However, the reactive CaO content of KFA (23.45%) is more than 15%. Still, SiO_2 content (29.29%) is greater than 25%. Furthermore, since it's reactive CaO content is greater than 15% there is also an extra condition which states that the 28-days compressive strength of mortar sample prepared as described in TS EN 197-1 should be more than 10 MPa. The sample prepared by using only KFA instead of cement was casted but the compressive strength test has not been done yet. Thus, it is not known yet whether this requirement is met or not.

Table 4.20 The evaluation of chemical analysis results of KFA according to the standards.

Weight	**(%)**	**TS EN 450-1**	**TS EN 197-1**		**ASTM C 618**	
			V	**W**	**F**	**C**
SiO_2	36.66					
Al_2O_3	18.64					
Fe_2O_3	7.96					
S+A+F	63.26	≥ 70			≥ 70	≥ 50
CaO	26.20					
MgO	2.17	≤ 4				
SO_3	4.25	≤ 3			≤ 5	≤ 5
Na_2O	0.52					
K_2O	1.93					
Na_2O eq*	1.79	≤ 5				
P_2O_5	0.30	≤ 5				
L.O.I.	0.40	Category A ≤ 5 Category B ≤ 7 Category C ≤ 9	a) 0 ≤...≤ 5 b) 2 ≤...≤ 7 c) 4 ≤...≤ 9		≤ 6	≤ 6
Cl^-	0.0035	≤ 0.10				
S. P_2O_5	3.33	≤ 100 (mg/kg)				
Free CaO	3.46	≤ 1.5(1)	≤ 1 (2)			
Reac. CaO	23.05	≤ 10	< 10	≥ 10 (3)		
Reac. SiO_2	29.29	≥ 25	≥ 25	≥ 25 (4)		

* Na_2O eq.= Na_2O + 0.658 K_2O
(1)(if Free CaO >1.5; soundness ≤ 10 mm) ; (2)(if 1< Free CaO <2.5; soundness ≤ 10 mm)
(3)(if Reac. CaO >15.00; σ_{28} ≥10 MPa); (4)(10<Reac.CaO<15)

According to ASTM C 618, the fact that the content of SiO_2+Al_2O+Fe_2O_3 (63.26%) is less than 70% greater than 50%, and high amount of CaO, means that KFA conforms to the category of Class C fly ash (high-calcium fly ash). L.O.I and SO_3 content requirements of ASTM C 618 are satisfied by KFA.

As it seen from Table 4.20, the requirements of TS EN 450-1 which are more than 70% of SiO_2+Al_2O+Fe_2O_3, less than 3% of SO_3, less than 1.5% of free CaO and less than 10% reactive CaO content are not satisfied. Due to the presence of more than 1.5% of free CaO, soundness test should be performed. As a result of the test, 1 mm soundness have obtained. Since 1 mm is less than limit value (10 mm) there is no problem for this requirement. The loss on ignition category is A.

Consequently, KFA satisfies the requirements of ASTM C 618 whereas it does not totally fulfill the requirements of TS EN 450-1 in terms of chemical composition.

In addition to the evaluation above, for KFA mix sample heavy metals analysis was done and the concentrations of the heavy metals are given in Table 4.21.

Table 4.21 Heavy metal concentration of KFA.

Element	**Symbol**	**Concentration (mg/kg)**
Beryllium	Be	3.05
Vanadium	V	175.42
Chromium	Cr	161.34
Manganese	Mn	312.89
Cobalt	Co	16.03
Nickel	Ni	101.89
Copper	Cu	45.98
Zinc	Zn	101.77
Arsenic	As	64.93
Selenium	Se	4.18
Silver	Ag	0.41
Cadmium	Cd	0.49
Antimony	Sb	8.53
Barium	Ba	279.16
Mercury	Hg	0.61
Thallium	Tl	1.15
Lead	Pb	28.84

4.4.2 Mineralogical and Morphological Analysis Results

KFA mix sample was used for these analyses. The x-ray diffraction pattern of KFA is given in Figure 4.13. Calcium oxide (CaO), Quartz (SiO_2), anhydrite ($CaSO_4$), hematite (Fe_2O_3), gehlenite ($Ca_2Al_2SiO_7$) and C_2S were identified as the major crystal phases.

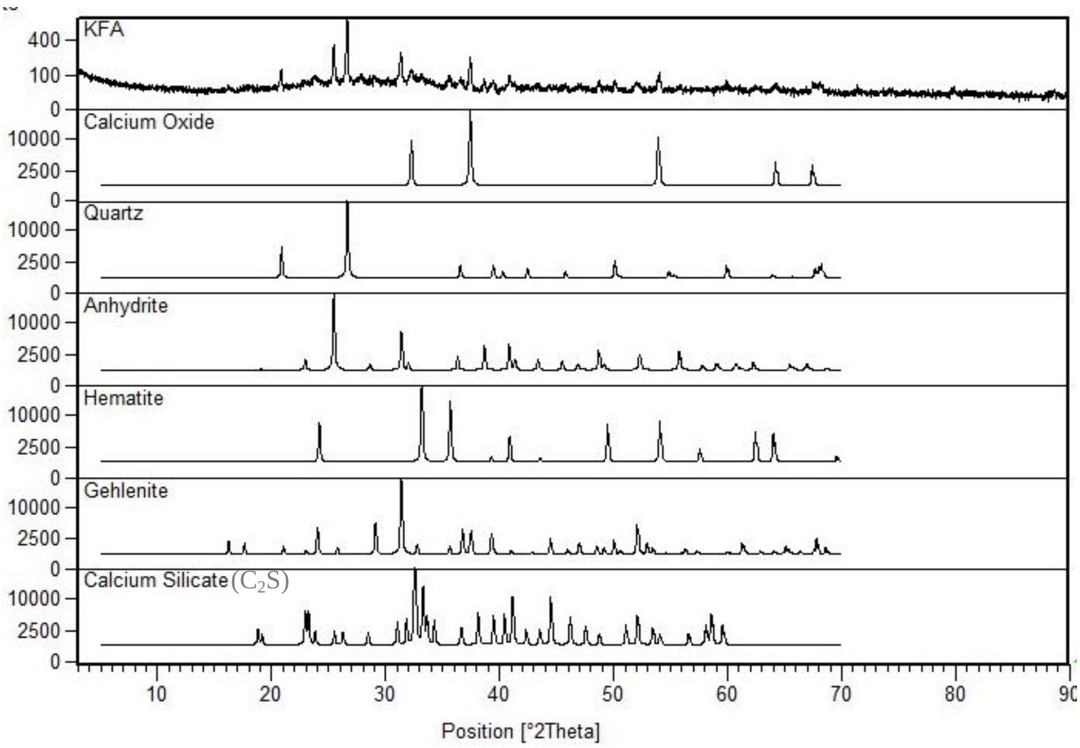

Figure 4.13 X-ray diffraction pattern of KFA.

According to the scanning electron microscopy (SEM) image of KFA (Figure 4.14), KFA is composed of spherical and angular particles with a diameter between 1 µm to 80 µm. The small particles with a diameter of 1 µm to 25 µm are totally in spherical shape.

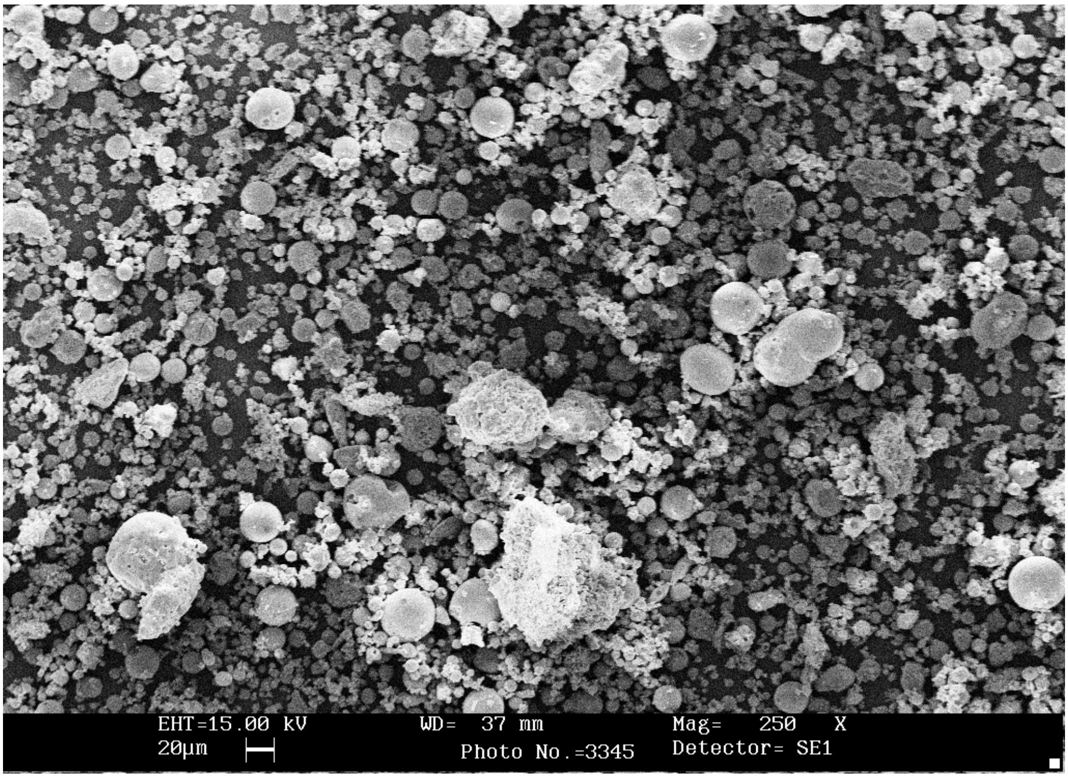

Figure 4.14 Scanning electron microscopy (SEM) image of KFA (250 x).

4.4.3 Physical Analysis Results

The results of the physical tests performed on KFA samples, and the evaluation of these results in accordance with the physical requirements of TS EN 450-1 are presented in Table 4.22. In addition to this, according to ASTM C 204 the Blaine fineness value is 2437 cm^2/g. According to ASTM C 230, the flow diameter is 175 mm.

Also, the particle size distribution of KFA samples, the five samples and the mix sample, was determined by laser diffraction particle size analyzer separately. The curves of particle size distribution belonging to the six samples are shown in Figure 4.15. The volume over percentages corresponding to 90 μm, 45 μm, 32 μm and D_{10}, D_{50}, D_{90} and D[4,3] diameters are presented in Table 4.23 for the six samples. As seen from Figure 4.15, the particle size of the first four samples is very close to each other. Only the 5th sample has coarser particles compared with the other samples.

Table 4.22 The physical properties of KFA

Property	**Unit**	**KFA**	**TS EN 450-1**	**Satisfying Condition**
Density	g/cm^3	2.50	-	N.A
Standard consistency	%	28.00	-	N.A
Initial setting time	min	190	≤ twice the initial setting time of cement alone	S
Retain on 45 μm sieve	%	34.8	Category N ≤ 40 Category S ≤ 12	N
Soundness	mm	1	≤ 10	S
Activity index, 28 days	%	89.4	≥ 75	S
Activity index, 90 days	%	98.4	≥ 85	S

* N.A: Not applicable S: Satisfying N: Not satisfying

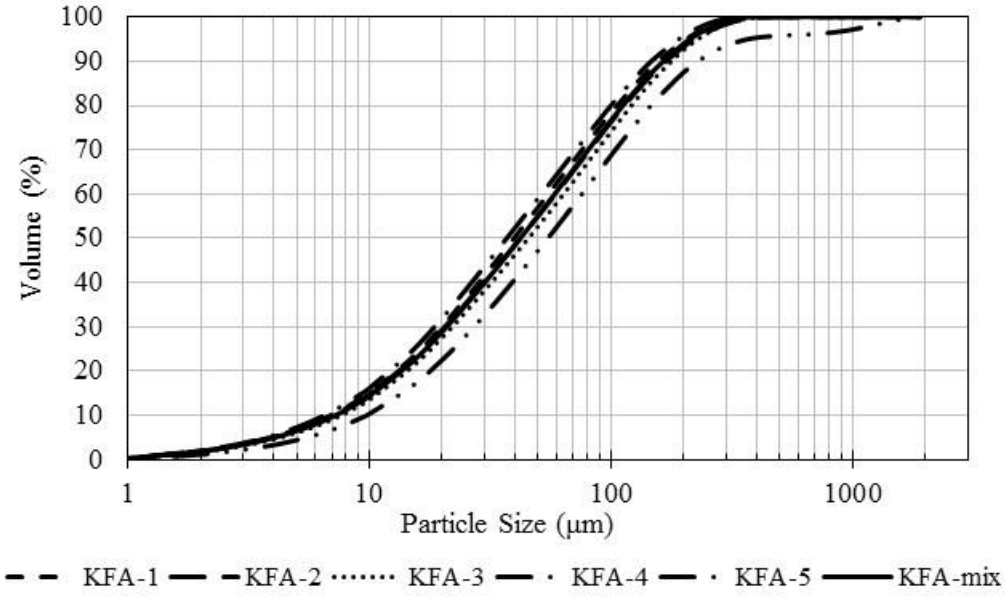

Figure 4.15 Particle size distribution of KFA samples.

Table 4.23 Percentages of particles and diameters of KFA.

KFA	90 µm	45 µm	32 µm	D_{10}	D_{50}	D_{90}	D[4,3]
	(%)			(µm)			
1	24.7	46.0	56.3	6.8	39.5	156.5	63.5
2	26.8	48.0	57.8	6.9	42.0	168.1	68.3
3	29.1	50.2	59.9	7.6	45.3	176.9	72.0
4	23.0	44.0	54.2	6.4	36.8	146.5	59.3
5	34.6	55.7	65.4	9.6	54.6	230.1	126.9
Mix	26.5	48.0	58.1	7.2	42.1	164.2	66.7

4.5 Fly ash Taken from İçdaş Thermal Power Plant (IFA)

Fly ash samples were supplied from İçdaş Thermal Power Plant in December, 2013 for five consecutive days. Besides, a mix was prepared from the five samples as described in Chapter 3.

4.5.1 Chemical Analysis Results

The chemical analyses were conducted for the five fly ash samples and the mix. The results of the six IFA samples with the standard deviation (SD) and the coefficient of variation (CV) values are shown in Table 4.24.

The oxide percentages of the fly ashes taken from five consecutive days are close to each other, and the standard deviation values are small. But, CaO content at the fifth day shows about 40% increment compared to the other four days. Additionally, the chemical analysis result of the mix is very close the average of the five fly ash samples. The evaluation of conformity of the average results to the requirements of the standards is given in Table 4.25.

Table 4.24 Chemical analysis results of IFA.

Weight (%)	**Samples**					**Ave.**	**SD**	**CV (%)**	**Mix**
	1	**2**	**3**	**4**	**5**				
ICP									
SiO_2	47.26	46.52	46.13	46.50	44.03	46.09	1.22	2.65	45.39
Al_2O_3	18.25	18.47	18.44	18.48	17.00	18.13	0.64	3.52	18.25
Fe_2O_3	10.35	10.27	10.36	10.07	9.66	10.14	0.29	2.89	10.15
CaO	13.07	13.04	13.37	12.92	18.11	14.10	2.25	15.93	14.20
MgO	4.52	4.51	4.50	4.53	4.18	4.45	0.15	3.38	4.48
SO_3	3.06	3.13	3.06	3.07	2.98	3.06	0.05	1.74	3.10
Na_2O	0.38	0.29	0.30	0.34	0.33	0.33	0.04	10.86	0.35
K_2O	1.69	1.66	1.66	1.73	1.38	1.62	0.14	8.58	1.65
TiO_2	0.58	0.56	0.59	0.58	0.52	0.57	0.03	4.93	0.57
P_2O_5	0.12	0.12	0.12	0.13	0.13	0.12	0.01	4.42	0.12
Cr_2O_3	0.10	0.10	0.09	0.10	0.08	0.09	0.01	9.52	0.09
Mn_2O_3	0.12	0.12	0.12	0.12	0.11	0.12	0.0045	3.79	0.12
Others									
L.O.I.	0.48	0.53	0.37	0.54	0.91	0.57	0.20	36.01	0.55
Cl^-	0.0021	0.0018	0.0088	0.0039	0.0014	0.0036	0.0031	85.01	-
S. P_2O_5 (mg/kg)	3.75	4.05	4.58	3.60	3.15	3.83	0.53	13.91	-
Free CaO	-	-	-	-	-	-	-	-	1.50
Reac. CaO	-	-	-	-	-	-	-	-	11.97
Reac. SiO_2	-	-	-	-	-	-	-	-	36.33

Due to the presence of more than 10% reactive CaO, IFA is a calcareous fly ash (W) in accordance with TS EN 197-1. Since the reactive CaO is in the range of 10% and 15%, the reactive SiO_2 should be greater than 25%. With the content of 36.33 % for reactive SiO_2 this requirement is satisfied. In accordance with ASTM C 618, the category of Class C fly ash (high-calcium fly ash) is more appropriate for IFA because of the high CaO content (14.10%).

Table 4.25 The evaluation of chemical analysis results of IFA according to the standards.

Weight	**(%)**	**TS EN 450-1**	**TS EN 197-1**		**ASTM C 618**	
			V	**W**	**F**	**C**
SiO_2	46.09					
Al_2O_3	18.13					
Fe_2O_3	10.14					
S+A+F	74.36	≥ 70			≥ 70	≥ 50
CaO	14.10					
MgO	4.45	≤ 4				
SO_3	3.06	≤ 3			≤ 5	≤ 5
Na_2O	0.33					
K_2O	1.62					
Na_2O eq*	1.40	≤ 5				
P_2O_5	0.12	≤ 5				
L.O.I.	0.57	Category A ≤ 5 Category B ≤ 7 Category C ≤ 9	a) 0 ≤...≤ 5 b) 2 ≤...≤ 7 c) 4 ≤...≤ 9		≤ 6	≤ 6
Cl^-	0.0036	≤ 0.10				
S. P_2O_5	3.83	≤ 100 (mg/kg)				
Free CaO	1.50	≤ 1.5$^{(1)}$	≤ 1 $^{(2)}$			
Reac. CaO	11.97	≤ 10	< 10	≥ 10 $^{(3)}$		
Reac. SiO_2	36.33	≥ 25	≥ 25	≥ 25 $^{(4)}$		

* Na_2O eq.= Na_2O + 0.658 K_2O

$^{(1)}$(if Free CaO >1.5; soundness ≤ 10 mm) ; $^{(2)}$(if 1< Free CaO <2.5; soundness ≤ 10 mm)

$^{(3)}$(if Reac. CaO >15.00; σ_{28} ≥10 MPa); $^{(4)}$(10<Reac.CaO<15)

According to TS EN 450-1, the MgO and SO_3 contents slightly exceed the limit values. The free CaO is 1.5% which is the limit value for that. Nevertheless, soundness test have been conducted and a 1 mm soundness have been obtained. The requirement of less than 10% reactive CaO is not met. For IFA the loss on ignition category is A. Except these, the other requirements are satisfied.

As a result, in terms of chemical composition IFA satisfies the requirements of ASTM C 618 and TS EN 197-1 whereas it does not totally meet the requirements of TS EN 450-1.

In addition to the evaluation above, for IFA mix sample heavy metals analysis was done and the concentrations of the heavy metals are given in Table 4.26.

Table 4.26 Heavy metal concentration of IFA.

Element	Symbol	Concentration (mg/kg)
Beryllium	Be	2.46
Vanadium	V	111.57
Chromium	Cr	352.44
Manganese	Mn	435.65
Cobalt	Co	34.41
Nickel	Ni	726.13
Copper	Cu	71.61
Zinc	Zn	101.47
Arsenic	As	207.69
Selenium	Se	1.95
Silver	Ag	10.93
Cadmium	Cd	0.75
Antimony	Sb	14.85
Barium	Ba	450.86
Mercury	Hg	0.73
Thallium	Tl	6.28
Lead	Pb	46.30

4.5.2 Mineralogical and Morphological Analysis Results

IFA mix sample was used for these analysis. The x-ray diffraction pattern of IFA is given in Figure 4.16. Quartz (SiO_2), calcium oxide (CaO), anhydrite ($CaSO_4$), hematite (Fe_2O_3), mullite ($Al_6Si_2O_{13}$) were identified as the major crystal phases.

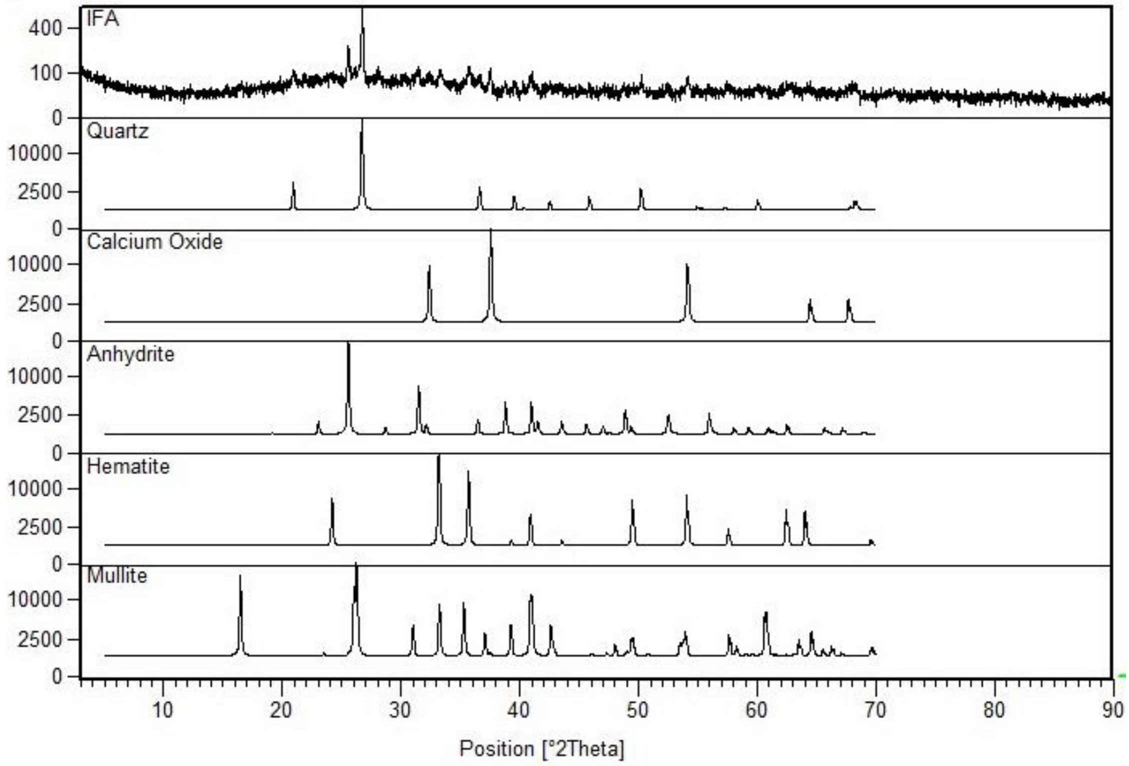

Figure 4.16 X-ray diffraction pattern of IFA.

According to the scanning electron microscopy (SEM) image of IFA (Figure 4.17), IFA consists of spherical and angular particles with a diameter between 1 μm to 50 μm. Especially small particles with a diameter of 1 μm to 25 μm are totally in spherical shape.

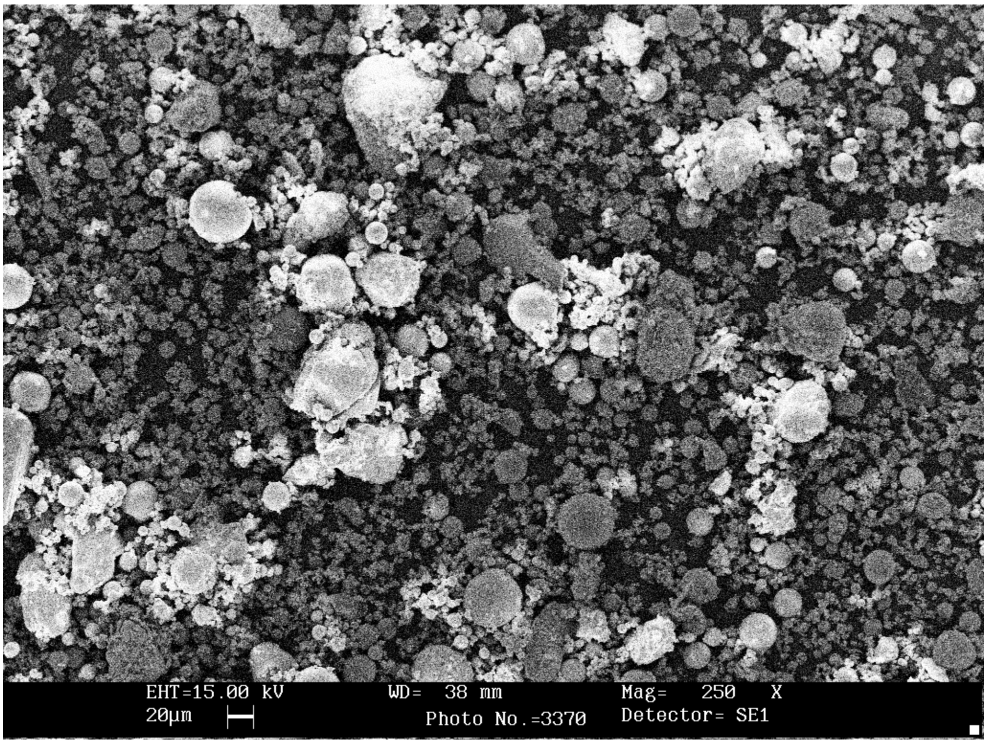

Figure 4.17 Scanning electron microscopy (SEM) image of IFA (250 x).

4.5.3 Physical Analysis Results

The results of the physical test performed on IFA, and the evaluation of the results in accordance with the physical requirements of TS EN 450-1 are given in Table 4.27. In addition to this, according to ASTM C 204 the Blaine fineness value is 3224 cm2/g. According to ASTM C 230, the flow diameter is 185 mm.

Also, the particle size distribution of IFA samples, the five samples and the mix sample, was determined by laser diffraction particle size analyzer separately. The curves of the particle size distribution belonging to the six samples are shown in Figure 4.18. The volume over percentages corresponding to 90 µm, 45 µm, 32 µm and D10, D50, D90 and D[4,3] diameters are presented in Table 4.28 for the six samples. As seen, the particle size of first four samples is almost the same. Only the fifth sample shows a very little difference.

Table 4.27 The physical properties of IFA.

Property	**Unit**	**IFA**	**TS EN 450-1**	**Satisfying Condition**
Density	g/cm^3	2.42	-	N.A
Standard consistency	%	29.40	-	N.A
Initial setting time	min	220	≤ twice the initial setting time of cement alone	S
Retain on 45 μm sieve	%	26.30	Category N ≤ 40 Category S ≤ 12	S
Soundness	mm	1	≤ 10	S
Activity index, 28 days	%	89.6	≥ 75	S
Activity index, 90 days	%	104.4	≥ 85	S

* N.A: Not applicable S: Satisfying N: Not satisfying

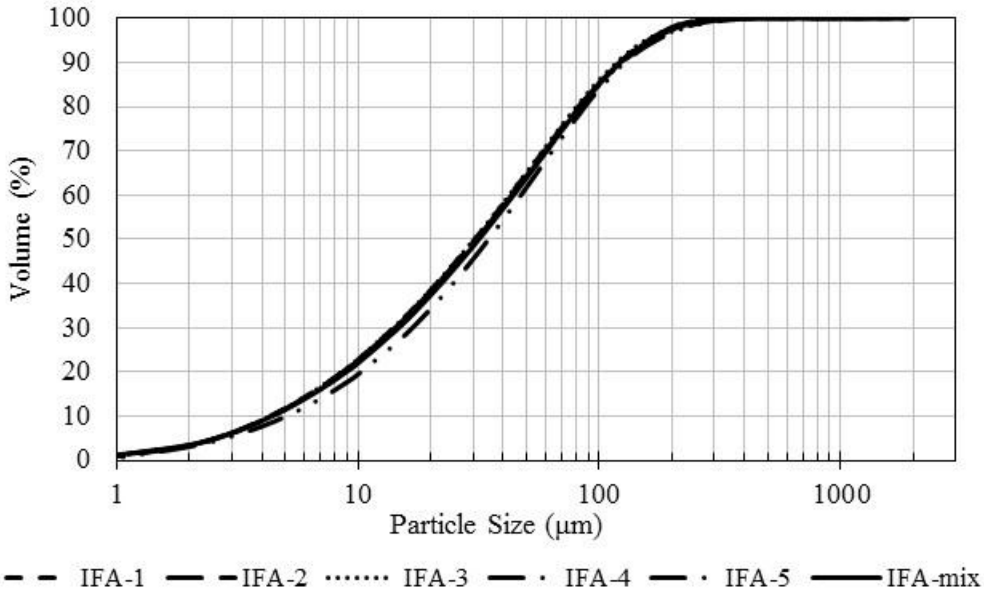

Figure 4.18 Particle size distribution of IFA samples.

Table 4.28 Percentages of particles and diameters of IFA.

IFA	**90 µm**	**45 µm**	**32 µm**	**D_{10}**	**D_{50}**	**D_{90}**	**D[4,3]**
	(%)			**(µm)**			
1	17.6	38.5	48.7	4.3	30.6	122.4	49.4
2	17.7	39.0	49.1	4.4	31.0	122.1	49.4
3	16.9	38.3	48.6	4.3	30.4	118.8	48.5
4	18.1	39.2	49.3	4.4	31.2	125.2	51.5
5	19.2	41.9	52.7	5.0	34.9	128.6	54.7
Mix	18.8	40.4	50.7	4.4	31.7	122.2	52.7

4.6 Fly ash Taken from Yeniköy Thermal Power Plant (YFA)

Fly ash samples were supplied from Yeniköy Thermal Power Plant 1st unit (YFA) in July, 2013 for five consecutive days. Besides, a mix was prepared from the five samples as described in Chapter 3.

4.6.1 Chemical Analysis Results

The chemical analyses were done for the five fly ash samples and the mix. The results of the six YFA samples are shown with the standard deviation (SD) and the coefficient of variation (CV) values in Table 4.29.

When the oxide percentages of the five samples are evaluated, it can be said that composition content shows slightly differences according to the days. However, the chemical analysis result of the mix is very close the average of the five fly ash samples. The evaluation of conformity of the average results to the requirements of the standards is given in Table 4.30.

Table 4.29 Chemical analysis results of YFA.

Weight (%)	**Samples**					**Ave.**	**SD**	**CV (%)**	**Mix**
	1	**2**	**3**	**4**	**5**				
ICP									
SiO_2	26.47	24.76	31.73	21.68	25.87	26.10	3.65	13.97	25.93
Al_2O_3	12.11	11.21	13.95	9.84	10.77	11.58	1.56	13.47	11.40
Fe_2O_3	5.26	4.87	5.11	4.47	4.57	4.86	0.34	6.97	4.85
CaO	39.93	42.78	33.91	45.42	40.98	40.60	4.28	10.55	40.52
MgO	2.02	1.95	1.87	1.87	1.95	1.93	0.06	3.28	1.93
SO_3	8.33	9.15	7.35	9.96	9.32	8.82	1.01	11.42	8.97
Na_2O	0.38	0.33	0.96	0.69	0.39	0.55	0.27	49.01	0.78
K_2O	1.31	1.21	1.50	1.12	1.24	1.28	0.14	11.17	1.40
TiO_2	0.52	0.49	0.62	0.42	0.48	0.51	0.07	14.50	0.51
P_2O_5	0.28	0.31	0.29	0.27	0.26	0.28	0.02	6.82	0.28
Cr_2O_3	0.04	0.03	0.04	0.03	0.03	0.03	0.01	16.11	0.03
Mn_2O_3	0.09	0.08	0.08	0.08	0.07	0.08	0.01	8.84	0.08
Others									
L.O.I.	2.39	2.42	2.06	3.44	3.18	2.70	0.58	21.63	2.53
Cl^-	0.0251	0.0223	0.0506	0.0180	0.0520	0.0336	0.0164	48.70	-
S. P_2O_5 (mg/kg)	4.80	4.88	4.65	5.25	4.88	4.89	0.22	4.52	-
Free CaO	-	-	-	-	-	-	-	-	9.59
Reac. CaO	-	-	-	-	-	-	-	-	31.71
Reac. SiO_2	-	-	-	-	-	-	-	-	20.84

According to TS EN 197-1, YFA is a calcareous fly ash (W) since it is composed of more than 10% reactive CaO (31.71%). Due to the presence of more than 15% reactive CaO, compressive strength test described in TS EN 197-1 should be done. The mortar prepared by using only YFA instead of cement was casted but the compressive strength test has not been done yet. Thus, it is not known yet whether this requirement is met or not.

Table 4.30 Evaluation of chemical analysis results of YFA according to the standards.

Weight	(%)	TS EN 450-1	TS EN 197-1		ASTM C 618	
			V	W	F	C
SiO_2	26.10					
Al_2O_3	11.58					
Fe_2O_3	4.86					
S+A+F	42.53	≥ 70			≥ 70	≥ 50
CaO	40.60					
MgO	1.93	≤ 4				
SO_3	8.82	≤ 3			≤ 5	≤ 5
Na_2O	0.55					
K_2O	1.28					
Na_2O eq*	1.39	≤ 5				
P_2O_5	0.28	≤ 5				
L.O.I.	2.70	Category A ≤ 5 Category B ≤ 7 Category C ≤ 9	a) $0 \leq ... \leq 5$ b) $2 \leq ... \leq 7$ c) $4 \leq ... \leq 9$		≤ 6	≤ 6
Cl^-	0.0336	≤ 0.10				
S. P_2O_5	4.89	≤ 100 (mg/kg)				
Free CaO	9.59	$\leq 1.5^{(1)}$	$\leq 1^{(2)}$			
Reac. CaO	31.71	≤ 10	< 10	$\geq 10^{(3)}$		
Reac. SiO_2	20.84	≥ 25	≥ 25	$\geq 25^{(4)}$		

* Na_2O eq.= $Na_2O + 0.658 K_2O$

$^{(1)}$(if Free CaO >1.5; soundness ≤ 10 mm) ; $^{(2)}$(if 1< Free CaO <2.5; soundness ≤ 10 mm)

$^{(3)}$(if Reac. CaO >15.00; $\sigma_{28} \geq 10$ MPa); $^{(4)}$(10<Reac.CaO<15)

In accordance with ASTM C 618, because of its very high CaO content (40.60%) YFA is more suitable to be classified as Class C fly ash (high-calcium fly ash). The requirements of the content of SiO_2+Al_2O+Fe_2O_3 to be a least 50% and SO_3 content to be maximum 5% are not met by YFA.

When it is evaluated according to TS EN 450-1, the amount of SiO_2+Al_2O+Fe_2O_3 is significantly under the limit. With the 8.82% SO_3 content the limit value, 3%, is exceeded. Free CaO content is over the limit. Thus, soundness test have been conducted and a 1 mm soundness have been obtained.

The requirements of less than 10% of reactive CaO and more than 25% of reactive SiO_2 are not satisfied. Except these, the rest of the requirements are met. For IFA the loss on ignition category is A.

As a result, it can be concluded that YFA does not totally fulfill the requirements of TS EN 197-1, TS EN 450-1 and ASTM C 618 in terms of chemical composition.

In addition, heavy metal analysis was performed for YFA and the concentrations of heavy metals of YFA are shown in Table 4.31.

Table 4.31 Heavy metal concentration of YFA.

Element	**Symbol**	**Concentration (mg/kg)**
Beryllium	Be	2.22
Vanadium	V	193.92
Chromium	Cr	188.73
Manganese	Mn	552.51
Cobalt	Co	11.96
Nickel	Ni	90.56
Copper	Cu	32.96
Zinc	Zn	72.79
Arsenic	As	45.35
Selenium	Se	10.70
Silver	Ag	13.17
Cadmium	Cd	0.97
Antimony	Sb	11.45
Barium	Ba	284.48
Mercury	Hg	0.33
Thallium	Tl	1.13
Lead	Pb	22.80

4.6.2 Mineralogical and Morphological Analysis Results

YFA mix sample was used for these analyses. The x-ray diffraction pattern of YFA is given in Figure 4.19. Calcium oxide (CaO), quartz (SiO_2), anhydrite ($CaSO_4$), hematite (Fe_2O_3), C_2S and mayenite ($Al_{14}Ca_{12}O_{33}$) were identified as the major crystal phases.

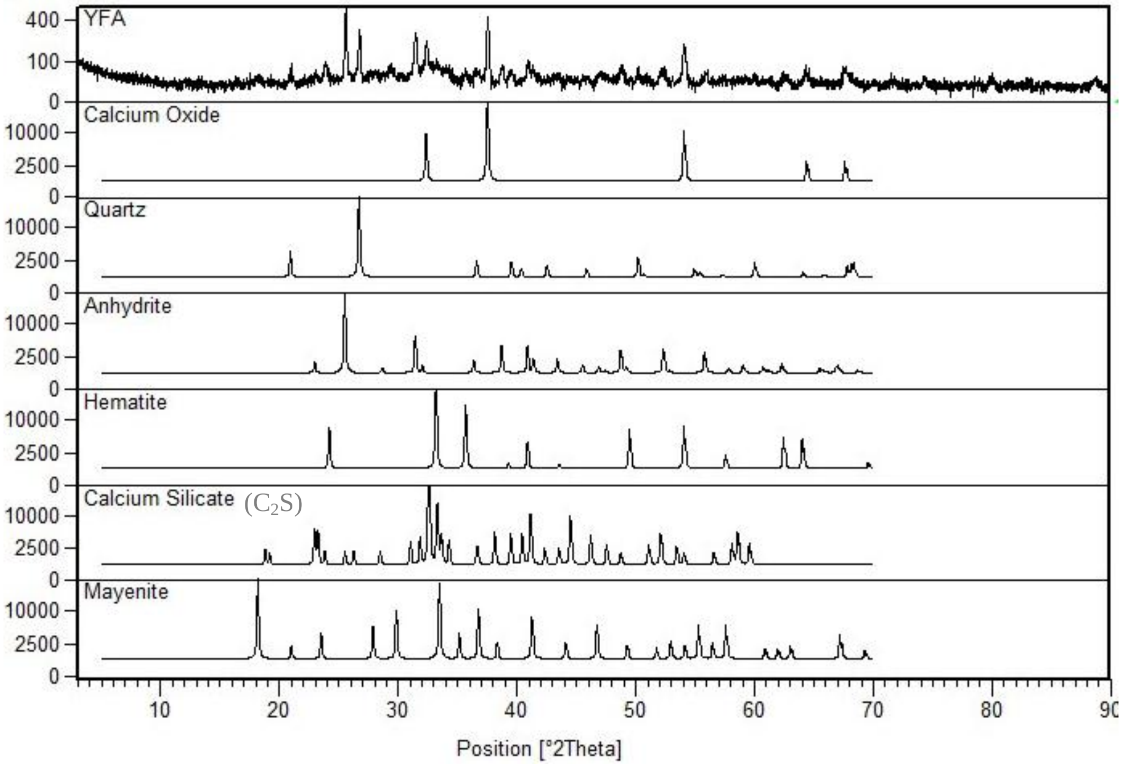

Figure 4.19 X-ray diffraction pattern of YFA.

According to the scanning electron microscopy (SEM) image of YFA (Figure 4.20), YFA consists of spherical and angular particles with a diameter between 1 μm to 80 μm. Especially small particles with a diameter of 1 μm to 25 μm are totally in spherical shape.

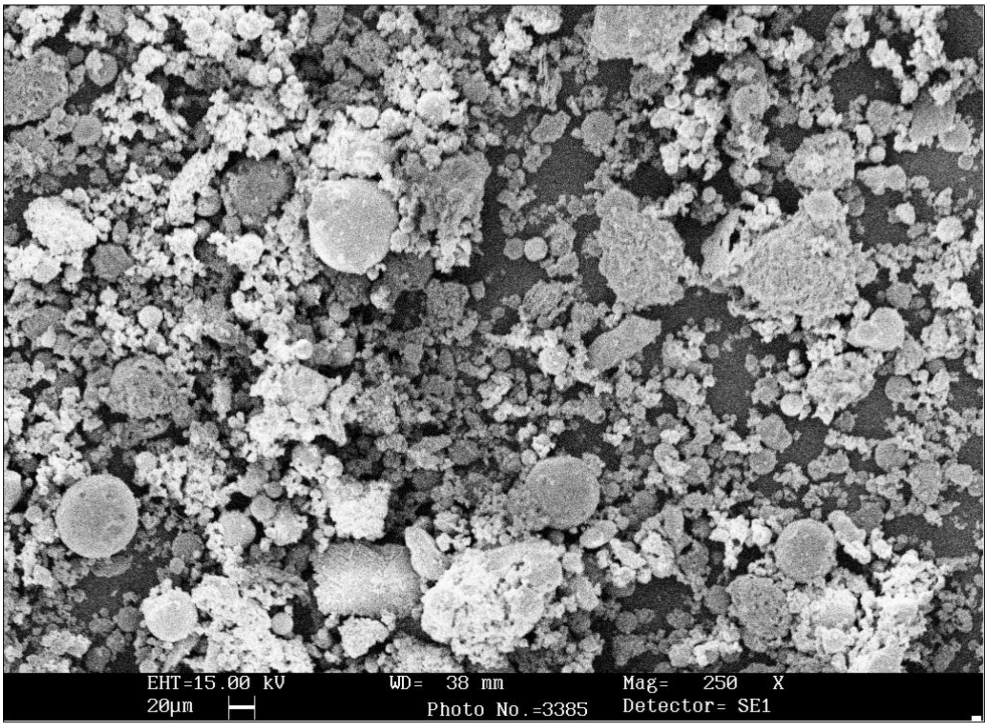

Figure 4.20 Scanning electron microscopy (SEM) image of YFA (250 x).

4.6.3 Physical Analysis Results

The results of the physical tests performed on YFA, and the evaluation of these results in accordance with the physical requirements of TS EN 450-1 are given in Table 4.32. In addition to this, according to ASTM C 204 the Blaine fineness value is 2224 cm^2/g. According to ASTM C 230, the flow diameter is 166 mm.

In addition, the particle size distribution curves for YFA samples, the five samples and the mix sample, were determined by laser diffraction particle size analyzer. The curves of particle size distribution belonging to the six samples are shown in Figure 4.21. Also, the volume over percentages corresponding to 90 μm, 45 μm, 32 μm and D_{10}, D_{50}, D_{90} and D[4,3] diameters are presented in Table 4.33. As seen from the Figure 4.21, the particle size distribution curves of the samples taken from the first, second and fifth days are very close to each other. On the other hand, it seems that the sample from the third day is a little coarser and the sample from the fourth day is a little finer compared to the other samples from Yeniköy TPP. However, the mix sample seems to be in the middle of these distributions.

Table 4.32 The physical properties of YFA.

Property	Unit	YFA	TS EN 450-1	Satisfying Condition
Density	g/cm^3	2.75	-	N.A
Standard consistency	%	29.40	-	N.A
Initial setting time	min	200	≤ twice the initial setting time of cement alone	S
Retain on 45 μm sieve	%	31.0	Category N ≤ 40 Category S ≤ 12	S
Soundness	mm	1	≤ 10	S
Activity index, 28 days	%	92.0	≥ 75	S
Activity index, 90 days	%	96.8	≥ 85	S

* N.A: Not applicable S: Satisfying N: Not satisfying

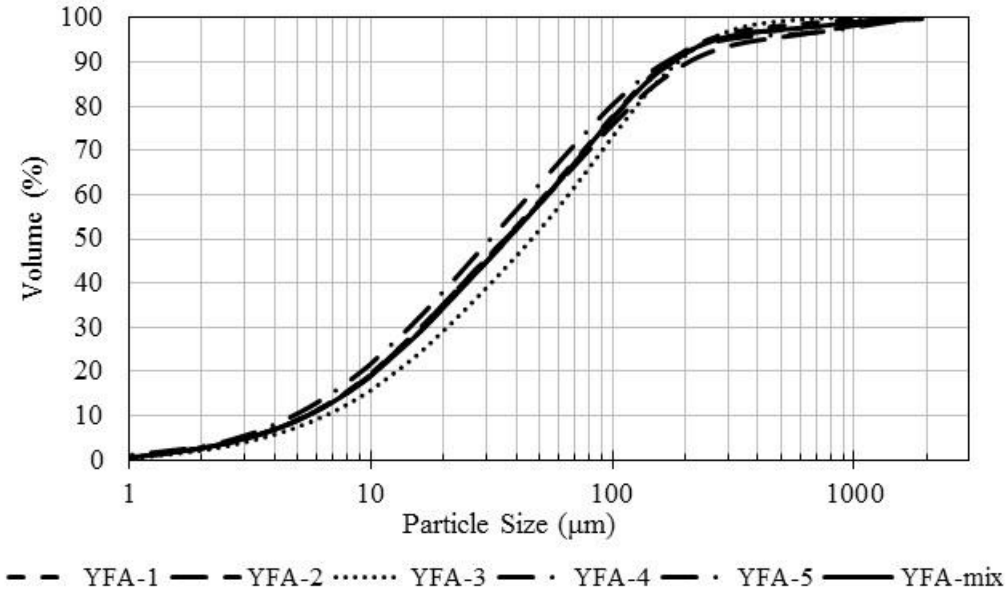

Figure 4.21 Particle size distribution of YFA samples.

Table 4.33 Percentages of particles and diameters of YFA.

IFA	**90 µm**	**45 µm**	**32 µm**	**D_{10}**	**D_{50}**	**D_{90}**	**D[4,3]**
	(%)			**(µm)**			
1	25.0	44.0	52.7	5.3	35.6	169.5	76.0
2	26.5	44.2	52.6	5.3	35.6	201.6	98.6
3	30.1	50.6	59.4	6.4	46.0	185.2	78.1
4	21.9	40.0	49.1	4.7	30.9	162.1	90.2
5	25.5	44.7	53.5	5.4	36.6	175.9	86.9
Mix	25.6	44.8	53.6	5.5	36.8	175.0	84.9

4.7 Summary of the Chemical Composition of the Fly Ashes

Considering the oxide composition of the fly ashes, CFA, T3FA and T5FA can be grouped as TS Class V (ASTM Class F), while AEFA, KFA, IFA and YFA are grouped as TS Class W (ASTM Class C). The major chemical compositions of PC and FAs are presented in Table 4.34.

Table 4.34 Major oxide composition of both PC and FAs.

	PC	**CFA**	**T3FA**	**T5FA**	**AEFA**	**KFA**	**IFA**	**YFA**
SiO_2	19.15	56.13	53.40	55.52	40.09	36.66	46.09	26.10
Al_2O_3	5.16	25.01	19.23	19.00	16.24	18.64	18.13	11.58
Fe_2O_3	3.56	5.89	13.64	11.39	7.21	7.96	10.14	4.86
S+A+F	27.87	87.03	86.27	85.91	63.54	63.26	74.36	42.54
CaO	63.26	1.70	1.27	2.76	21.24	26.20	14.10	40.60
MgO	1.28	2.18	3.51	5.72	2.26	2.17	4.45	1.93
SO_3	2.77	0.08	0.47	0.54	6.71	4.25	3.06	8.82
Na_2O	0.3	0.41	0.03	0.08	0.31	0.52	0.33	0.55
K_2O	0.37	3.88	1.30	1.88	1.33	1.93	1.62	1.28
Total	95.85	95.28	92.85	96.89	95.39	98.33	97.92	95.72
L.O.I	3.83	2.60	5.16	1.23	2.88	0.37	0.55	2.53
R.SiO_2	-	42.31	36.43	42.28	31.97	29.29	36.33	20.84
R.CaO	-	0.97	0.79	2.34	13.45	23.05	11.97	31.71
Free CaO	-	0.03	0.02	0.02	3.11	3.46	1.50	9.59

The fly ashes also contain some toxic elements in different ranges like vanadium, chromium, arsenic, lead (Sushil & Batra, 2006). The heavy metal concentrations for all the FAs are presented in Table 4.35.

Table 4.35 The heavy metal concentrations of the FAs.

mg/kg	CFA	T3FA	T5FA	AEFA	KFA	IFA	YFA	Limits*
Pb	113.7	67.3	58.4	24.3	28.8	46.3	22.8	300.0
Cd	0.4	0.4	0.4	0.9	0.5	0.8	1.0	3.0
Cr	150.0	1569.3	982.6	308.7	161.3	352.4	188.7	100.0
Cu	114.0	147.8	97.0	56.0	46.0	71.6	33.0	140.0
Ni	78.6	3201.2	1943.6	214.8	101.9	726.1	90.6	75.0
Zn	108.1	116.0	103.2	115.2	101.8	101.5	72.8	300.0
Hg	1.5	0.6	3.5	2.2	0.6	0.7	0.3	1.5
Be	6.8	11.2	4.8	1.6	3.0	2.5	2.2	-
P	-	640.4	782.1	1762.7	-	-	-	-
V	225.0	380.3	161.3	346.8	175.4	111.6	193.9	-
Mn	546.0	727.3	1080.3	284.1	312.9	435.6	552.5	-
Co	33.6	152.9	100.7	23.7	16.0	34.4	12.0	-
As	25.2	107.0	53.7	39.4	64.9	207.7	45.3	-
Se	4.4	4.0	3.0	8.3	4.2	1.9	10.7	-
Ag	<0.88	1.4	0.2	<2.94	0.4	10.9	13.2	-
Sb	6.7	21.6	6.8	2.1	8.5	14.8	11.4	-
Ba	1053.2	249.6	438.3	300.6	279.2	450.9	284.5	-
Tl	4.9	5.7	3.0	1.3	1.1	6.3	1.1	-

*****(Regulation on Control of Soil Pollution, 2005)

As seen from the Table 4.35, various amounts of toxic elements were detected in the fly ashes. For some elements, the concentration values were compared to the heavy metal limit values in soil given by the "Regulation on Control of Soil Pollution" for Turkey. It can be generally said that T3FA and T5FA are heavy metal rich ashes compared to the other fly ashes. All the fly ashes satisfied the limit values for lead, cadmium and zinc content; however, they exceeded the chromium and nickel limits. Most of the fly ashes produced are disposed in various ways. During the collecting process of the fly ash, a wet collection with a proper disposing method will reduce the dust emission in the air and can allow an easy rehabilitation method to the fly ash pond. However this method will not prevent the leaching of the heavy metals to the soil and the surrounding water reservoirs. This makes the usage of a dry collection method and after that the usage of the fly ashes in the cement and concrete production a perfect way to dispose this waste (Sushil and Batra, 2006). In the next phase of this study, obtained results will be compared to the heavy metal levels obtained for fly ashes from other countries.

4.8 Summary of the Physical Properties of the Fly Ashes

According to the particle size analysis performed by the laser diffraction method, the fly ashes can be sorted from coarser to finer as AEFA, T5FA, CFA, KFA, YFA, T3FA, and IFA (Figure 4.22). Although the values of 45 μm taken from laser diffraction and from the wet sieve analysis are not equal, the results of the two tests were parallel to each other.

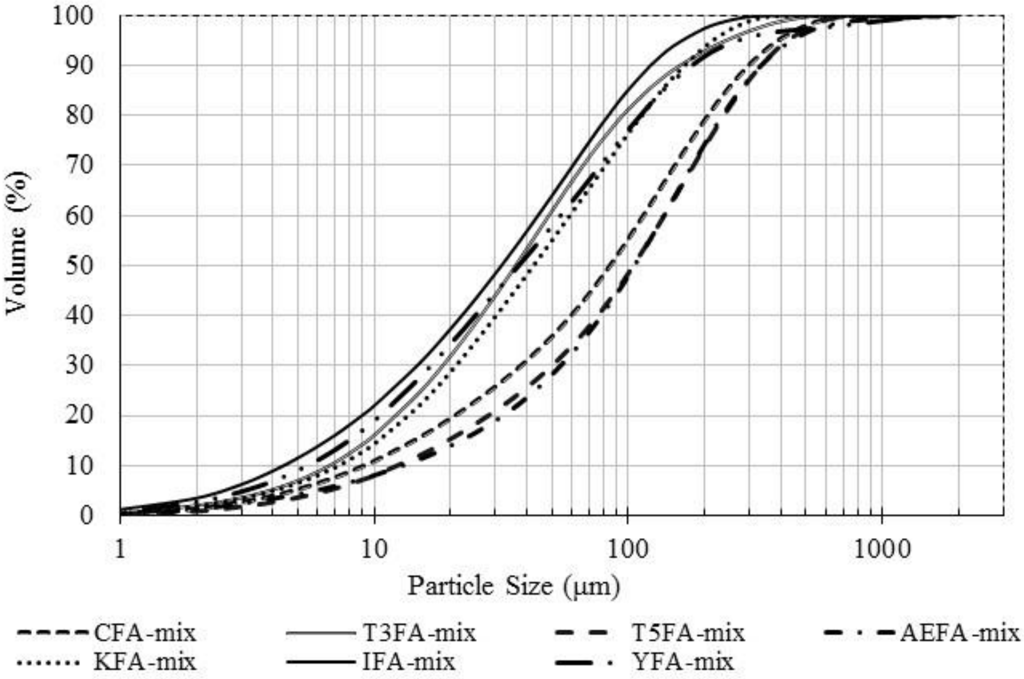

Figure 4.22 Comparison of particle size distribution of FAs.

When the obtained PSD parameters D_{10}, D_{50}, D_{90} and D[4,3] of FAs were compared (Figure 4.23), it can be seen that the AEFA and T5FA resulted in highest values and they were close to each other. CFA had lower parameters than that of AEFA and T5FA. Obtained parameters for KFA, YFA and T3FA were much lower and close to each other. Finally, IFA had the lowest parameters. The physical properties of the FAs were compared in Table 4.36.

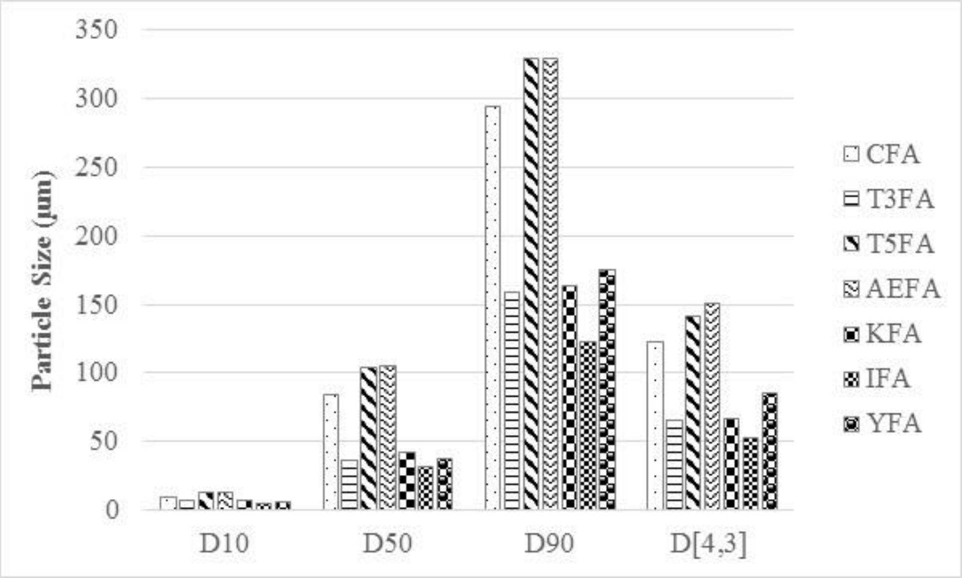

Figure 4.23 Comparison of parameters of D_{10}, D_{50}, D_{90}, D[4,3] of fly ashes.

Table 4.36 Comparison of the physical properties of PC and fly ashes.

Sample	Density (g/cm^3)	Standard consistency (%)	Initial setting time (min)	Retained on 45 µm (%)	Soundness (mm)	Flow %	Blaine (cm^2/gr)
PC	3.11	29.00	185	-	1	100	3717
CFA	1.99	28.20	210	52.10	0	86	2889
T3FA	2.15	34.60	195	29.70	1	73	5214
T5FA	2.21	29.40	205	57.40	1	76	2481
AEFA	2.41	33.20	215	66.30	1	67	3367
KFA	2.50	28.00	190	34.80	1	100	2437
IFA	2.42	29.40	220	26.30	1	106	3224
YFA	2.75	29.40	200	31.00	1	95	2224

Density of Class V FAs were lower than Class W FAs. Amongst the Class V FAs, T3FA resulted in highest water requirement for standard consistency. This might be attributed to T3FA being finer than the T5FA and CFA. The water requirements for standard consistency of Class W FAs cannot be generalized.

The initial setting time of portland cement was 185 minutes. As seen from Table 4.36, 25% FA substitution delayed the initial setting within the range of 5 to 35 minutes. In terms of soundness, even if Class W fly ashes have more amount of free CaO compared to Class V fly ashes, all FAs except CFA showed same expansion according to Le Chatelier process.

It is expected to have an inverse relationship between the Blaine and flow results. When Class V FAs are examined, T3FA has resulted in lowest flow with highest Blaine. T5FA and CFA have similar Blaine values, but CFA has more smooth particles when compared to T5FA. Hence, CFA resulted in higher flow. A generalization for Class W FAs has not been reached. Not all of the 45 μm and PSD test results are consistent with the Blaine results. The main reason for this might be that Blaine test does not give the absolute fineness value and the dependence on many test factors.

4.9 Performance Criteria

4.9.1 Heat of Hydration Analysis Results of Pastes

In the presence of calcium sulfate, when cement and water are mixed an initial peak occurs within minutes due to the rapid hydration of about 5-25% of C_3A and formation of the initial ettringite, and also hydration of about 2-10% of C_3S. Because the vial is placed in isothermal calorimeter after cement and water are mixed in the vial outside, the initial peak is missing (Bentz et al., 2010; Odler, 2014; U.S. FHWA, 2012b). There may be also a small contribution to the first peak from the hydration of calcium sulfate hemihydrate to the dihydrate. After a few hours, a second peak is seen, which is resulted from the hydration of C_3S. The rate of C_3S hydration, as followed from that of heat evolution passes through an initial maximum, decreases to a minimum (induction period), then passes through a second maximum and gradually declines as seen in Figure 4.24 (Bullard et al., 2011; Taylor, 1997). The hydration reaction of C_3S is generally explained in five periods of reaction: (1) the initial reaction, (2) the induction period, (3) the acceleratory period, in which the main reaction first begins to occur rapidly, (4) the deceleration period and (5) a period of slow, continued reaction (Bullard et al., 2011; Taylor, 1997).

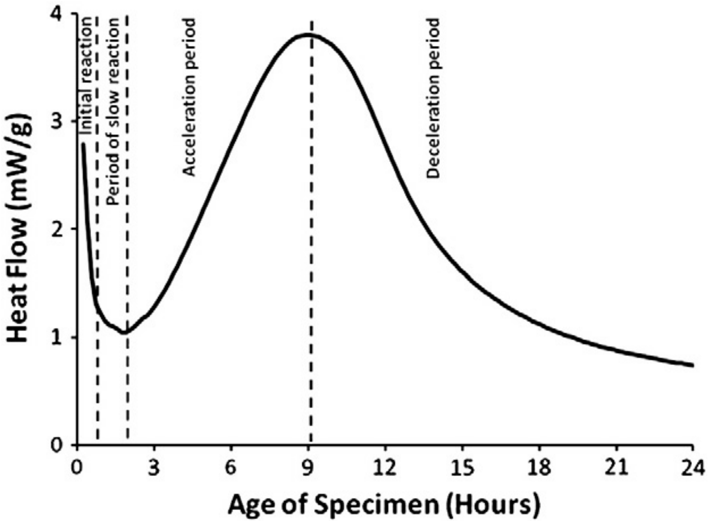

Figure 4.24 Isothermal calorimetric measurement relating the rate of heat liberation to time for an Alite paste (Bullard et al., 2011).

The third peak is related to secondary ettringite formation (Bullard et al., 2011). The fourth peak is attributed to the formation of AFm phase and conversion of ettringite to monosulfate (Odler, 2014). The peaks are summarized in Figure 4.25. The figure also shows typical shoulder peak where a secondary formation of ettringite occurs and subsequent broad peak corresponding to the formation of AFm phase (Bullard et al., 2011).

As stated previously, CFA, T3FA and T5FA can be grouped as Class V and AEFA, KFA, IFA and YFA can be grouped as Class W fly ashes. The heat evolution curves are shown in Figure 4.26 and Figure 4.27 for the pastes prepared with 100% PC (control sample) and 75% PC+25% Class V FA. Figure 4.28 and Figure 4.29 show the heat evolution curves of the pastes which contain 100% PC (control sample) and 75% PC+25% Class W FA. The pastes are labeled with the fly ash used. As seen from the Figures Figure 4.26 toFigure 4.29 there was a peak retardation on the heat flow of pastes containing FAs. PC-Class V FA blends had similar heat flow. On the other hand, PC-Class W FA blends showed diffrences. However, the pattern of KFA and IFA look similar in terms of the peak shapes of the control sample. Besides, the heat patterns of YFA and AEFA are similar in terms of the peak shapes but not like the contol sample.

Main peaks are represented by one Gaussian peak, in a rough estimate, then by using multi-peak fitting function of Igor Pro software (WaveMetrics, 2014) the location of peaks on the heat evolutions curve can be estimated for the PC-FA pastes (see Table 4.37). A fifth peak is also added to represent the continuous hydration reactions and residual shoulders of the reactions.

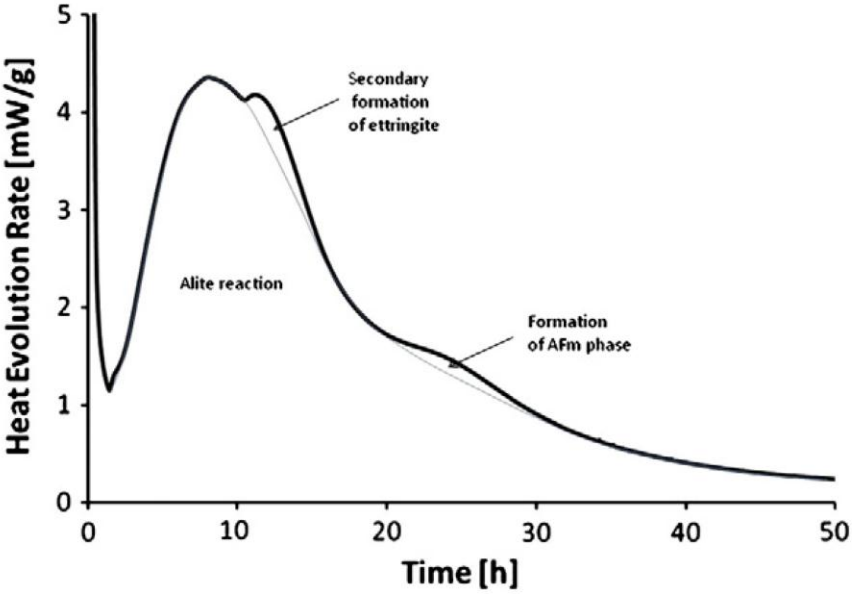

Figure 4.25 Calorimetry curve of modern portland cement (Bullard et al., 2011).

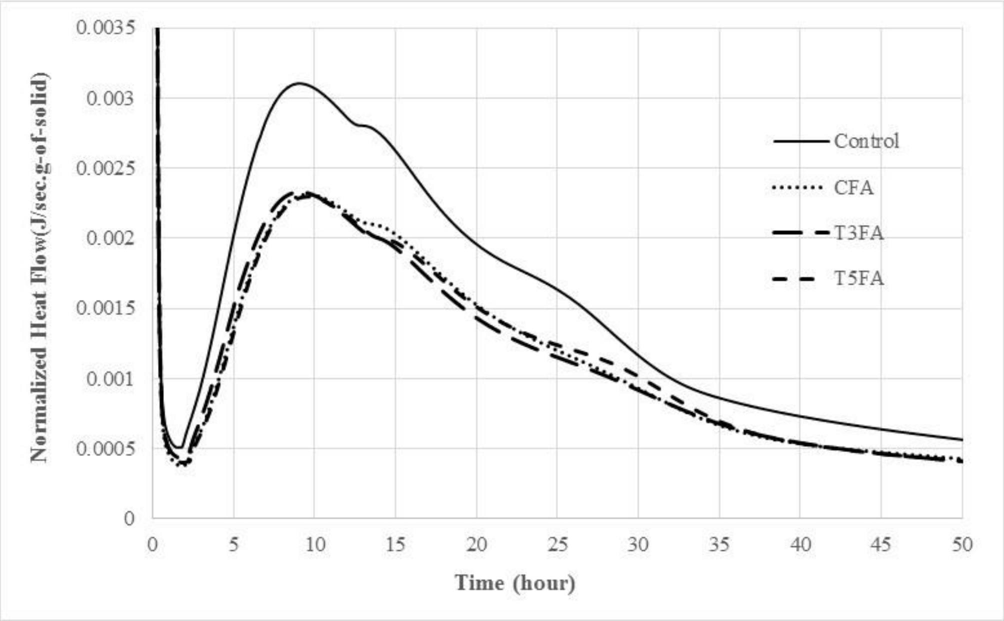

Figure 4.26 Heat flow of pastes with Class V fly ash throughout 2 days.

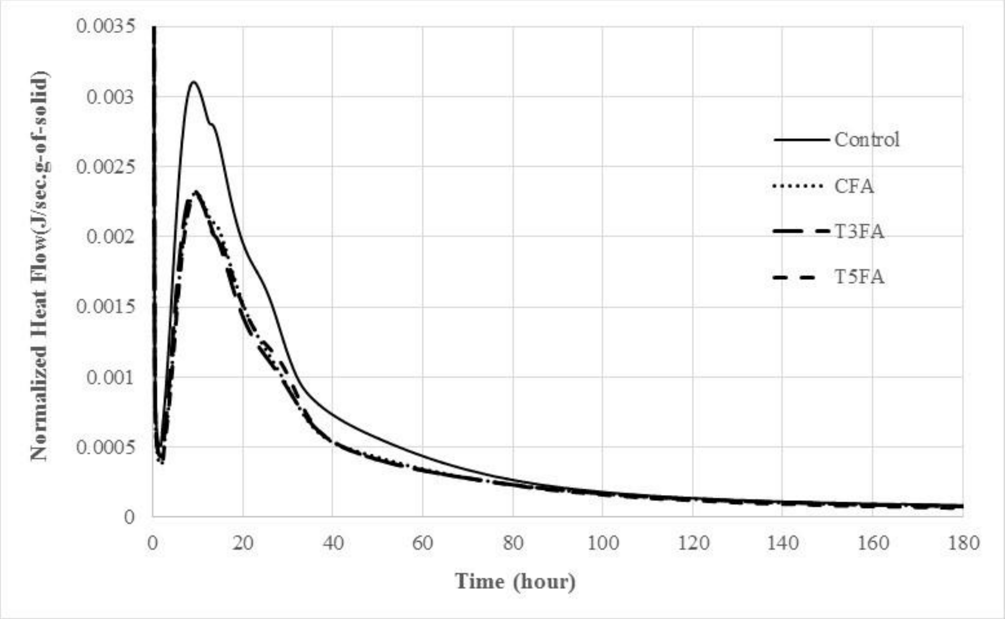

Figure 4.27 Heat flow of pastes with Class V fly ash throughout 7 days.

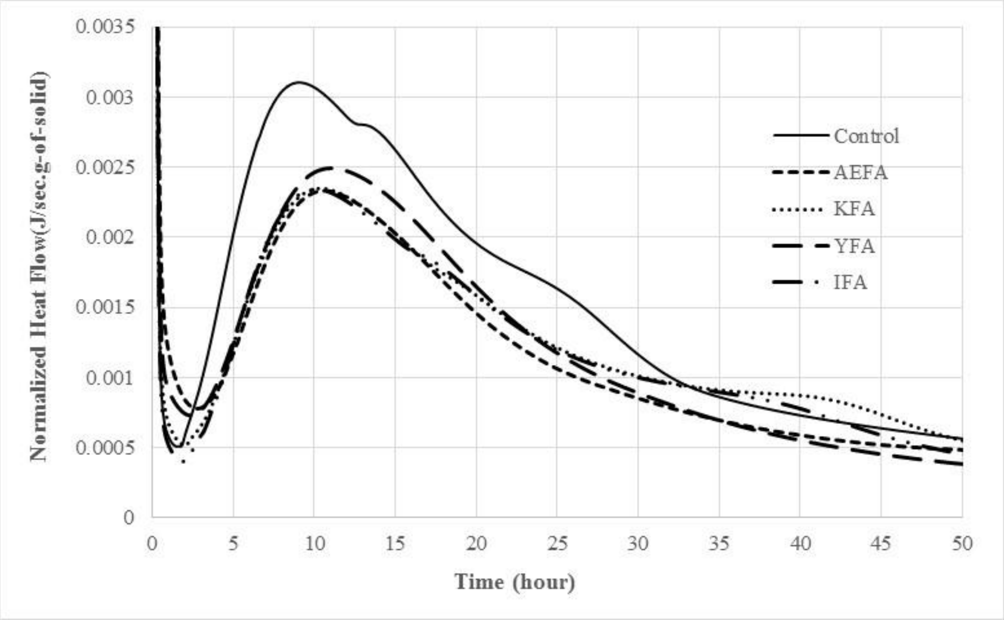

Figure 4.28 Heat flow of pastes with Class W fly ash throughout 2 days.

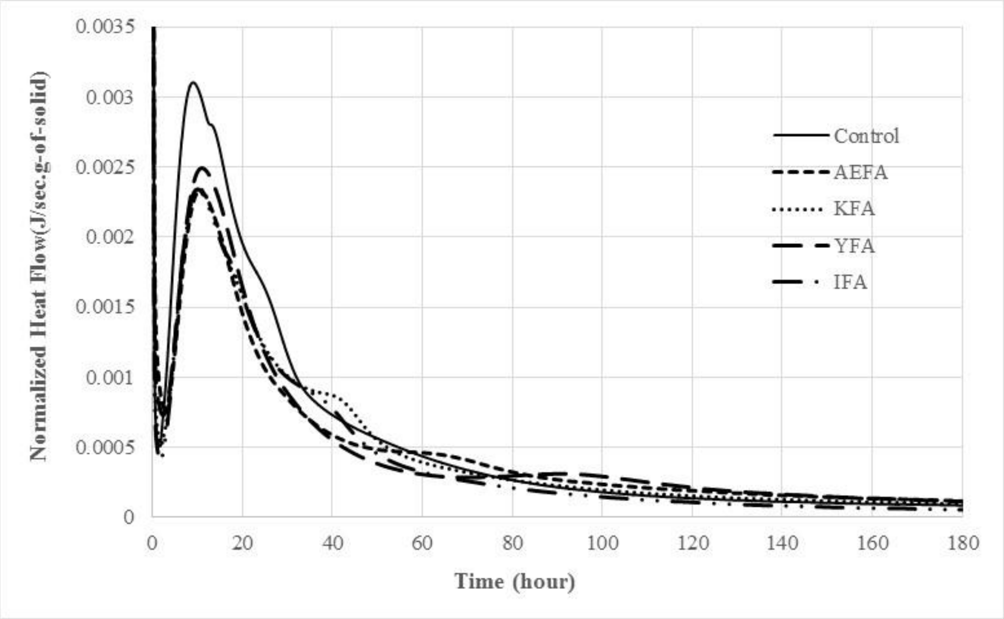

Figure 4.29 Heat flow of pastes with Class W fly ash throughout 7 days.

Table 4.37 Fitting results for the heat of hydration curves: Peak locations (h).

Peak location (h)	Peak 2	Peak 3	Peak 4	Peak 5
Control	7.03	12.12	20.72	36.46
CFA	7.46	12.76	21.56	39.33
T5FA	7.59	13.32	22.29	42.23
T3FA	7.33	12.66	22.12	41.71
AEFA	8.68	13.08	18.34	52.85
KFA	7.24	10.96	16.90	30.69
YFA	9.02	14.26	22.74	83.74
IFA	7.07	11.01	15.22	28.53

Examples to multifitting are given in Figure 4.30 for the heat flow curves of the control, T3FA and YFA samples. In each figure, the top curve represents the residual plot after the fitting, which decides how good the fitting is. The curves in the middle of the figure represents the original data (red) and the fit (blue). The curve at the bottom represents the individual traces of the peaks found. Here the peaks numbered 0, 1, 2 and 3 represents Peak 2, 3, 4 and 5 respectively.

In Figure 4.31 the fitted heat flow peak locations that correspond to each fly ash are compared to the peak locations of the control sample. From this figure, it can be seen that TS Class V fly ashes have small retardation effect on the peak times due to the dilution effect. Generally, during the first few hours of hydration fly ashes stay inert (U.S. FHWA, 2012b). The behavior of TS Class W samples are more complex. The IFA and KFA resulted accelerated peak formations; whereas YFA have retarded the peaks significantly. The AEFA retarded the first two peaks, while accelerating the third peak. This variation in the behavior of the Class W fly ashes should be analyzed in more detail considering the physical, chemical and mineralogical characteristics of the fly ashes. However, when Class W fly ashes are evaluated between each other it was seen that as the SO_3 content increase, the retardation on the peak times increased linearly, as it is seen in Figure 4.32.

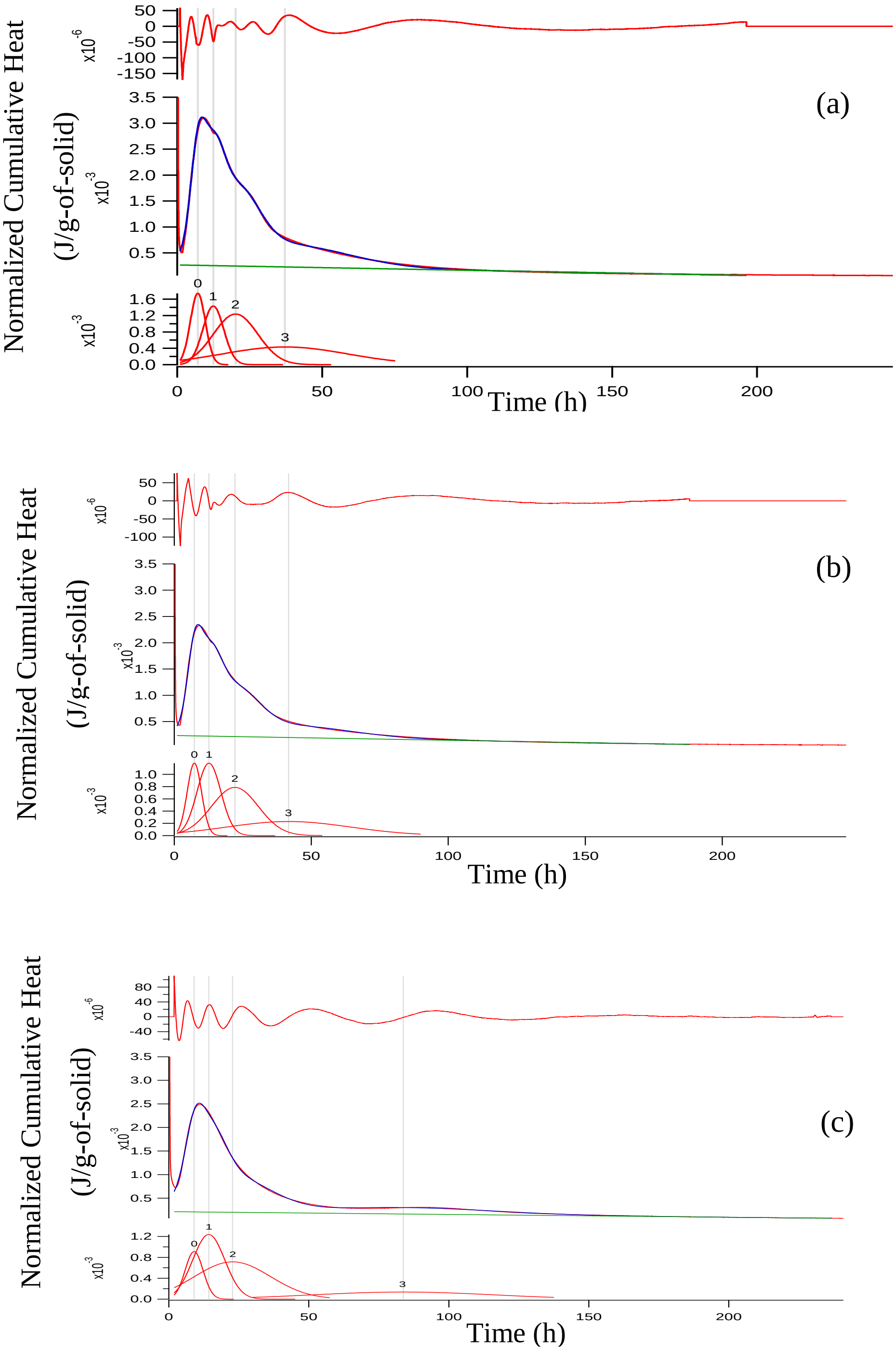

Figure 4.30 Examples for multipeak fitting: (a) control sample, (b) T3FA, (c) YFA.

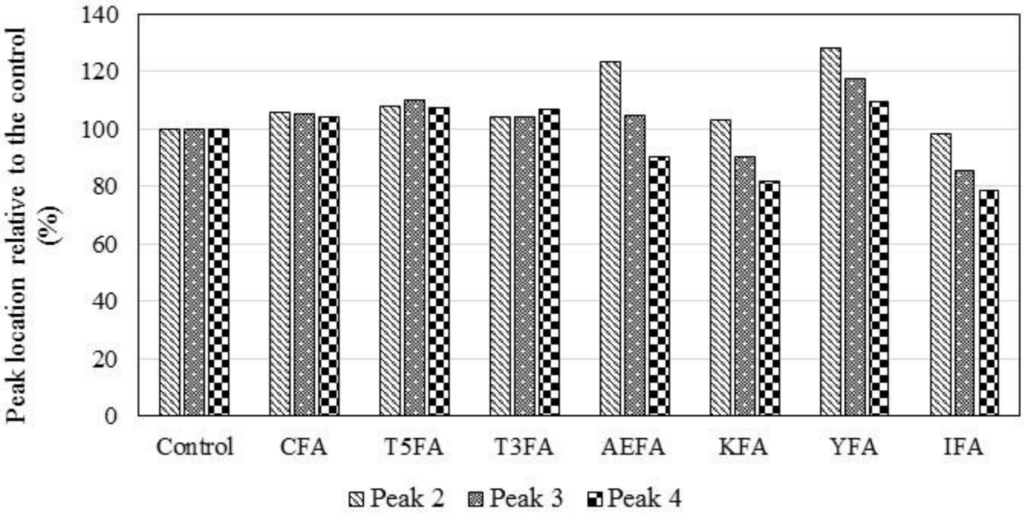

Figure 4.31 Comparison of fitted heat flow peak locations (h) relative to the control sample.

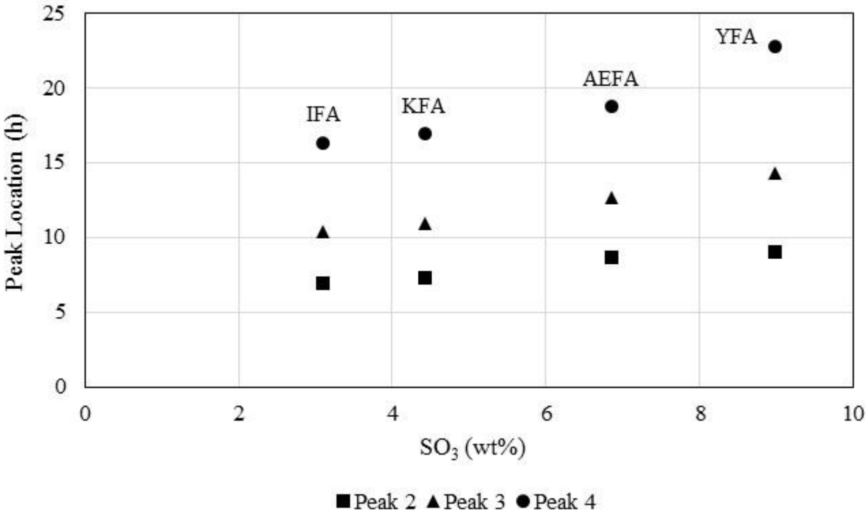

Figure 4.32 Relation between SO_3 content and peak location (h) for Class W fly ashes.

The use of Gaussian function to represent the hydration peaks was an approximation. For a more accurate fit more realistic heat evolution profiles obtained by analyzing the profiles of C_3S and C_3A in the presence of a calcium sulfate source, or by utilizing a theoretical model that represents those reactions should be used.

The cumulative heat plots of all pastes throughout the first 7-days is shown Figure 4.33. As seen, at the end of 7-days period cumulative heat was decreased for pastes containing FA due to the dilution effect, no matter what type of fly ash is used (Mostafa and Brown, 2005). Class W fly ashes had higher cumulative heat compared to Class V fly ashes at the end of the 7-days due to their both pozzolanic and cementititous properties (Mehta and Monteiro, 2006).

In Figure 4.34, the cumulative heat values for the pastes at the 24, 48 and 168 hours (1, 2 and 7 days) are presented. It is clear that all the fly ashes reduces the cumulative heat. However, while Class V fly ashes reduced the heat in a steady and consistent way in accordance with the PC replacement level, Class W fly ashes did not show a consistent behavior. Collected data will be analyzed in more detail in further studies.

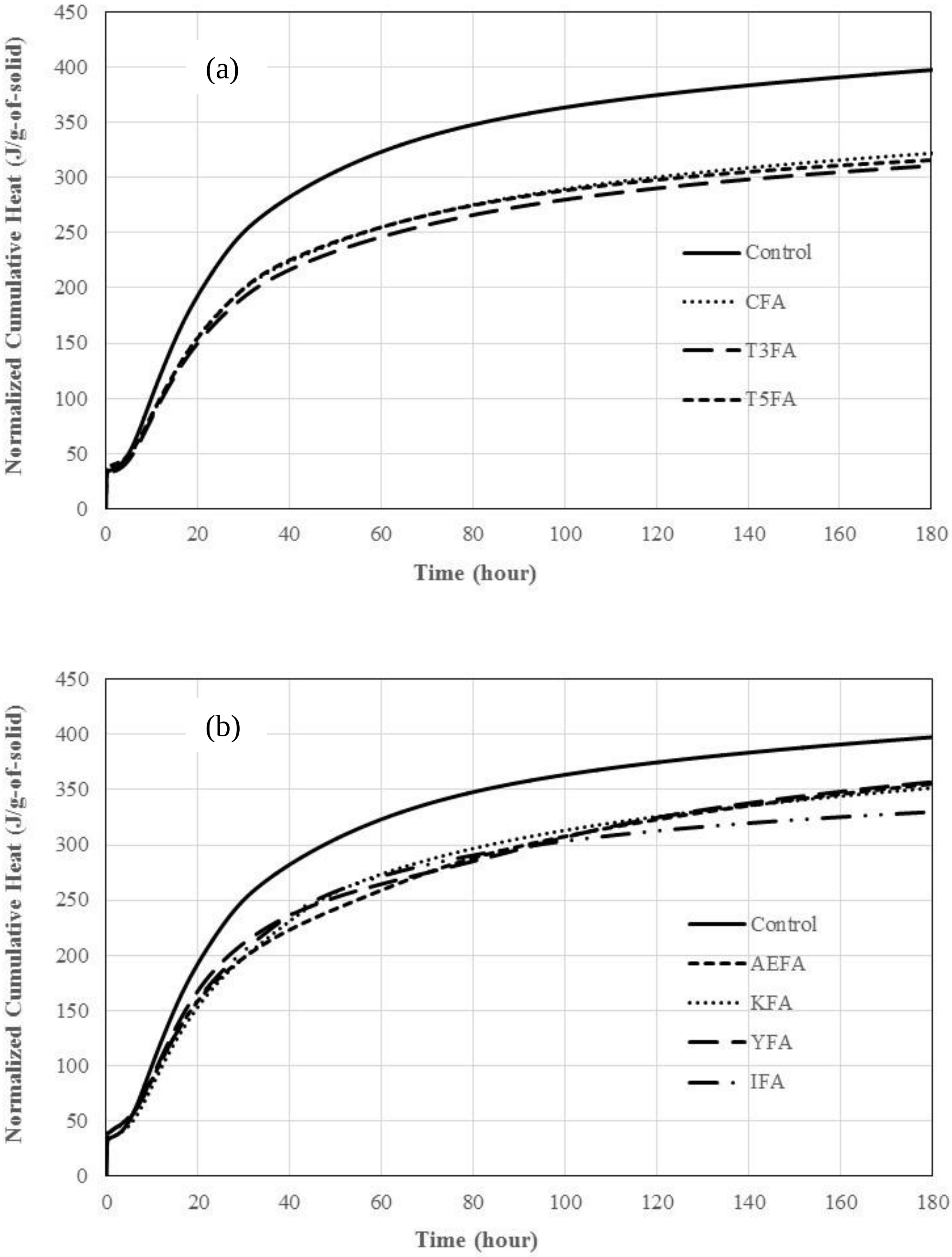

Figure 4.33 Cumulative heat pastes with FAs throughout 7 days (a) Class V, (b) Class W.

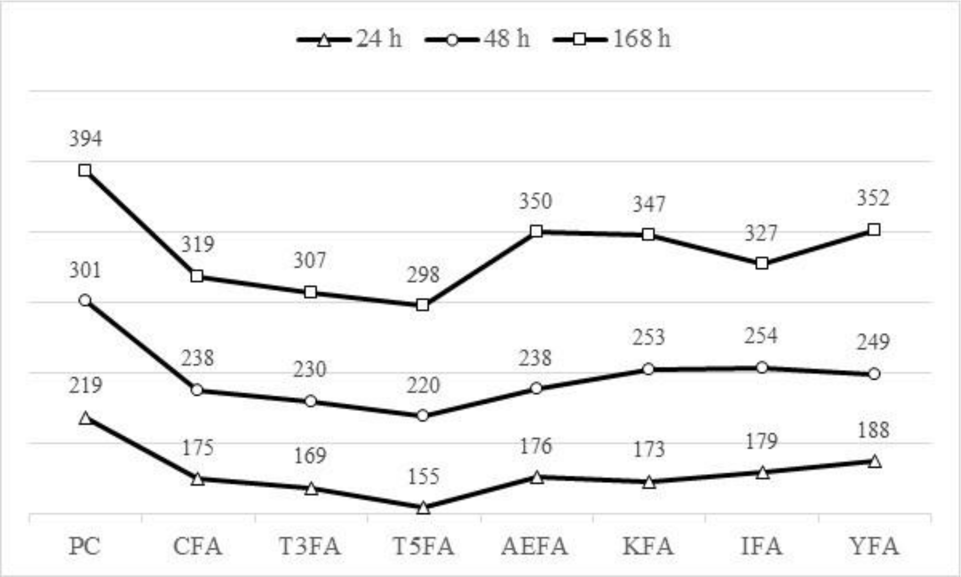

Figure 4.34 The cumulative heat values for the pastes (J/g-of-solid).

4.9.2 X-Ray Diffraction Analysis Results of Pastes

In order to follow the hydration of the binary PC-FA pastes the XRD analysis at the ages of 2, 7, 28 and 90 days were conducted. The focus was formation and depletion of portlandite ($Ca(OH)_2$) during the hydration reactions. The abbreviation of portlandite is CH. In the figures, CH is presented as C, ettringite as E, alite (C_3S) as A, belite (C_2S) as B, quartz as Q, calcium oxide as CaO and anhydrite as An.

Figure 4.35 shows that the XRD patterns of hydrated PC paste at the different ages. As seen from the figure, as a result of hydration of alite and belite, CH was formed. In this study, only a visual comparison of the peaks were conducted. In order to precisely quantify the phases Rietveld analysis needs to be conducted.

X-ray diffraction patterns of all pastes with FA are presented below showing gradual increase in CH over time owing to continued hydration reactions of C_3S and C_2S.

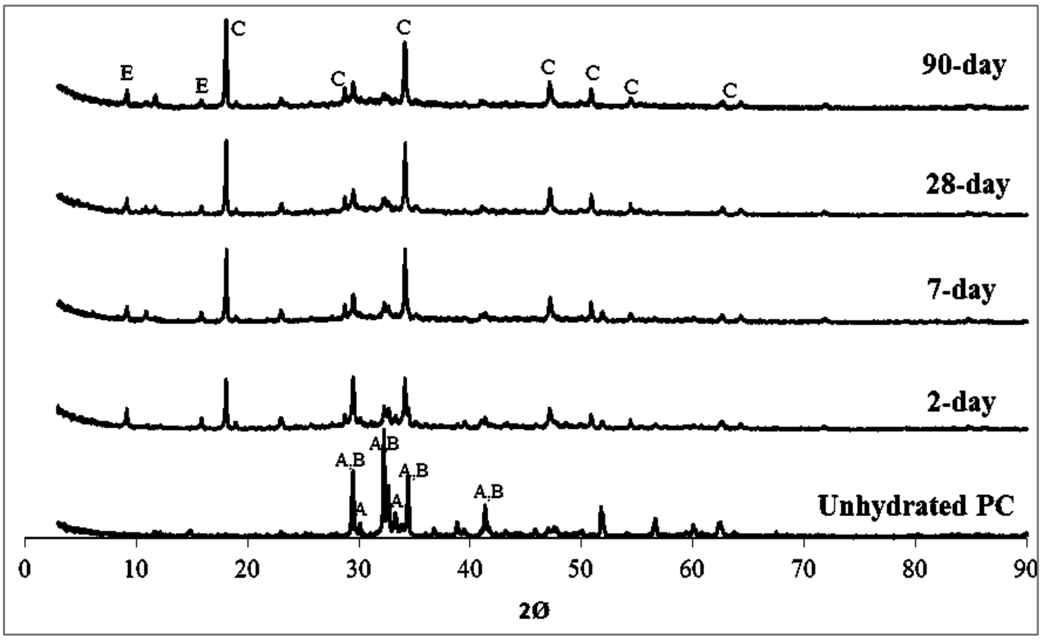

Figure 4.35 XRD patterns of hydrated PC paste at the different days.

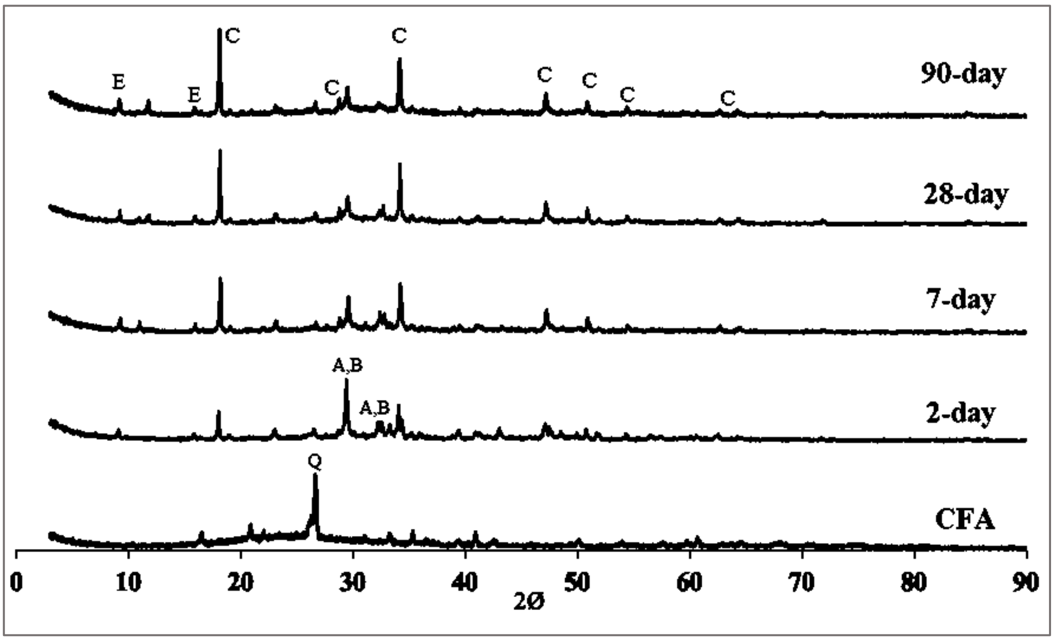

Figure 4.36 XRD patterns of hydrated 75%PC-25%CFA paste at the different days.

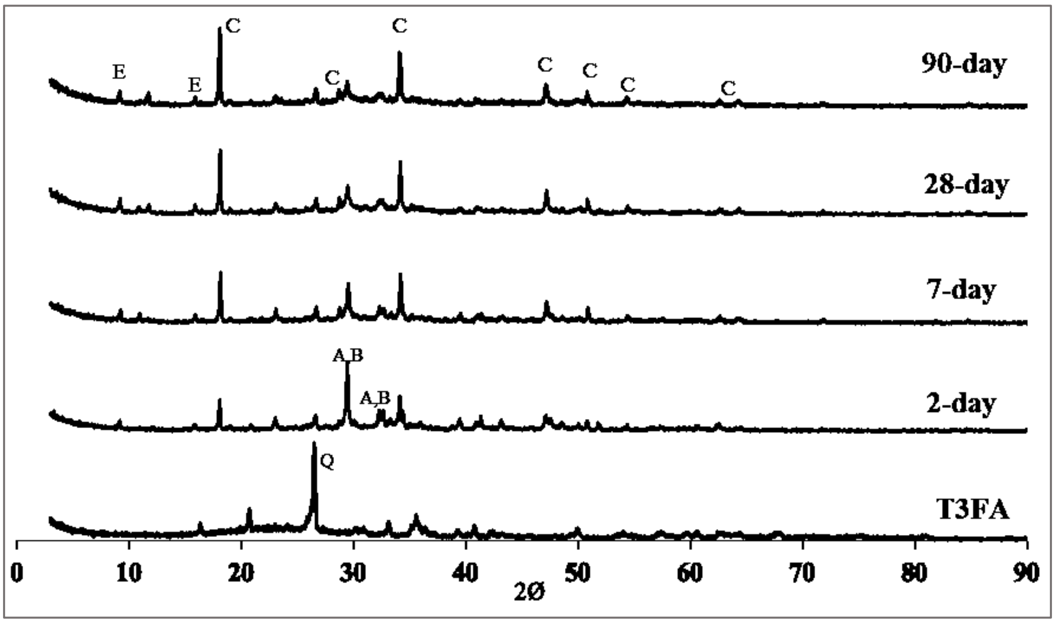

Figure 4.37 XRD patterns of hydrated 75%PC-25%T3FA paste at the different days.

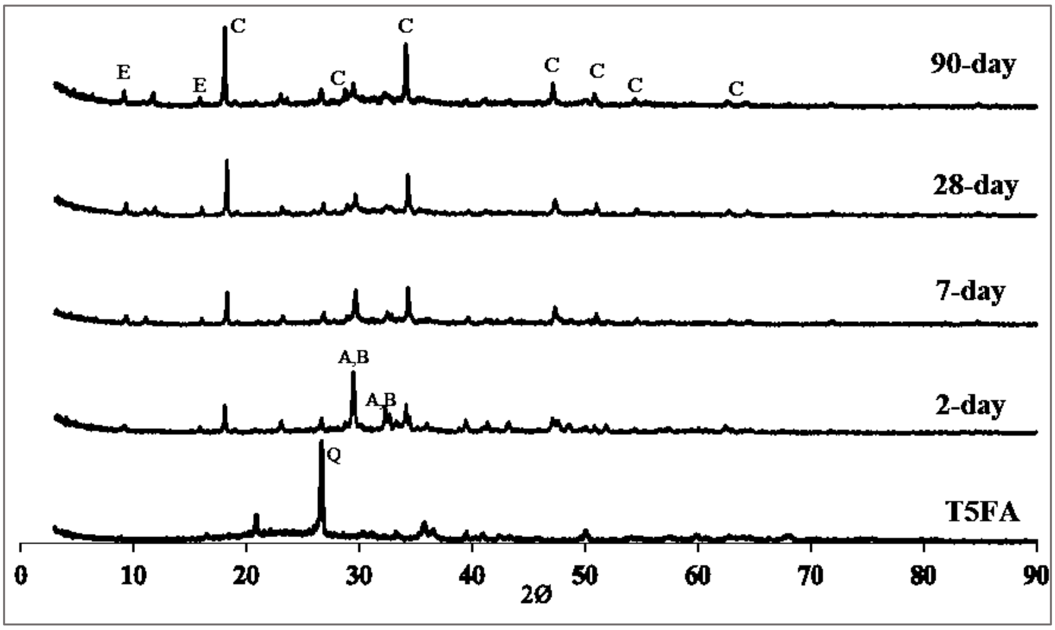

Figure 4.38 XRD patterns of hydrated 75%PC-25%T5FA paste at the different days.

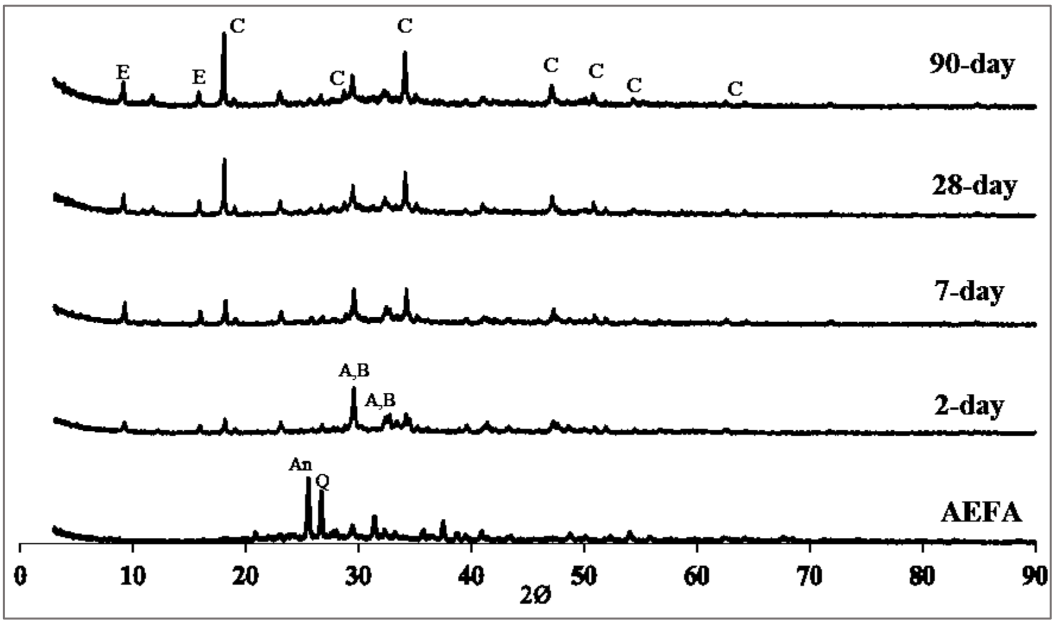

Figure 4.39 XRD patterns of hydrated 75%PC-25%AEFA paste at the different days.

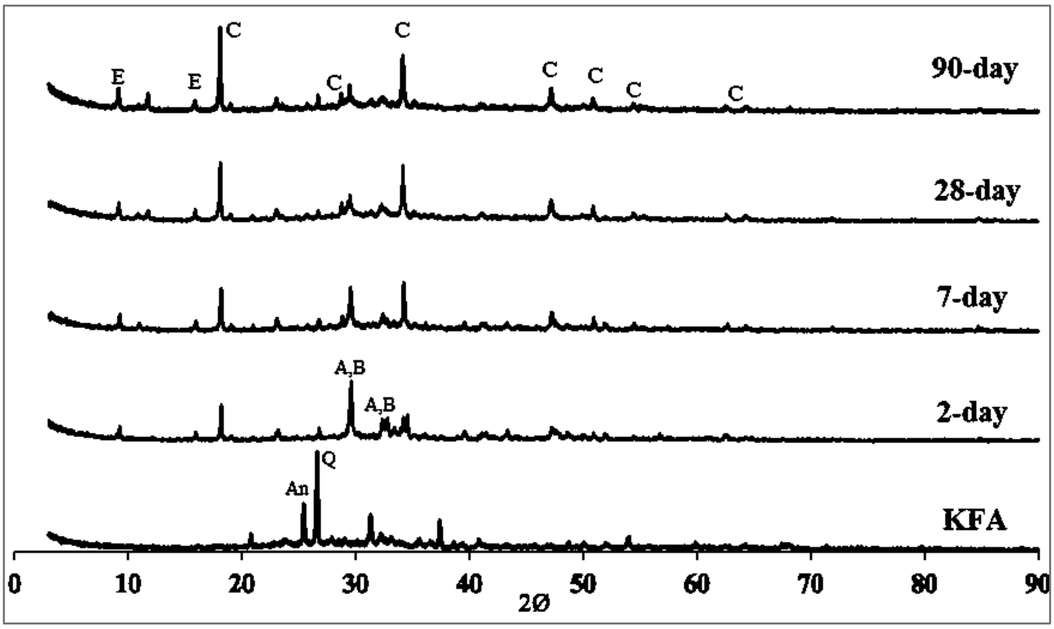

Figure 4.40 XRD patterns of hydrated 75%PC-25%KFA paste at the different days.

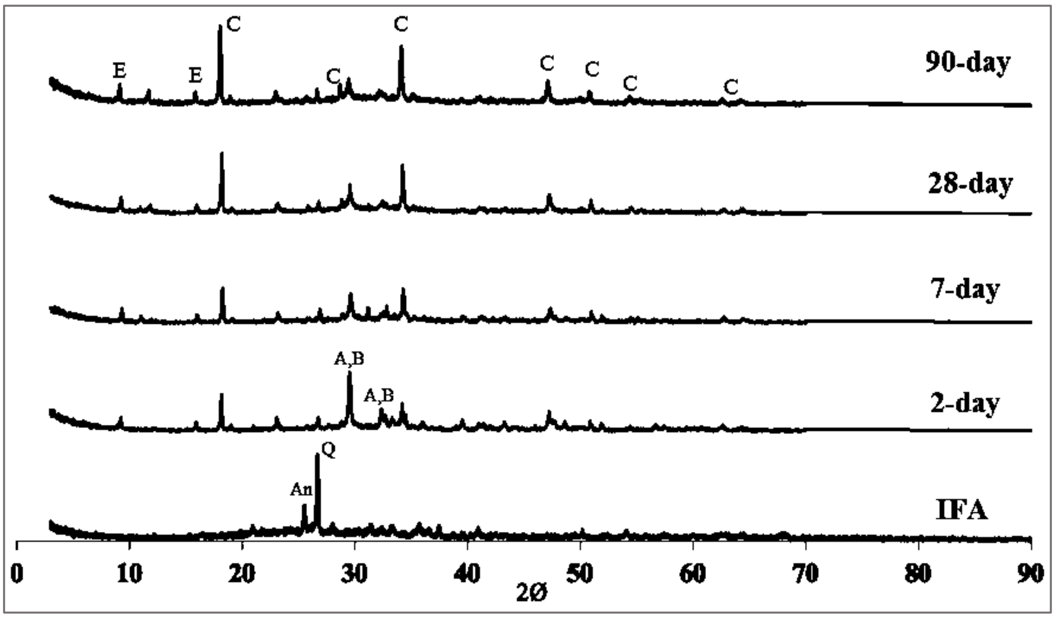

Figure 4.41 XRD patterns of hydrated 75%PC-25%IFA paste at the different days.

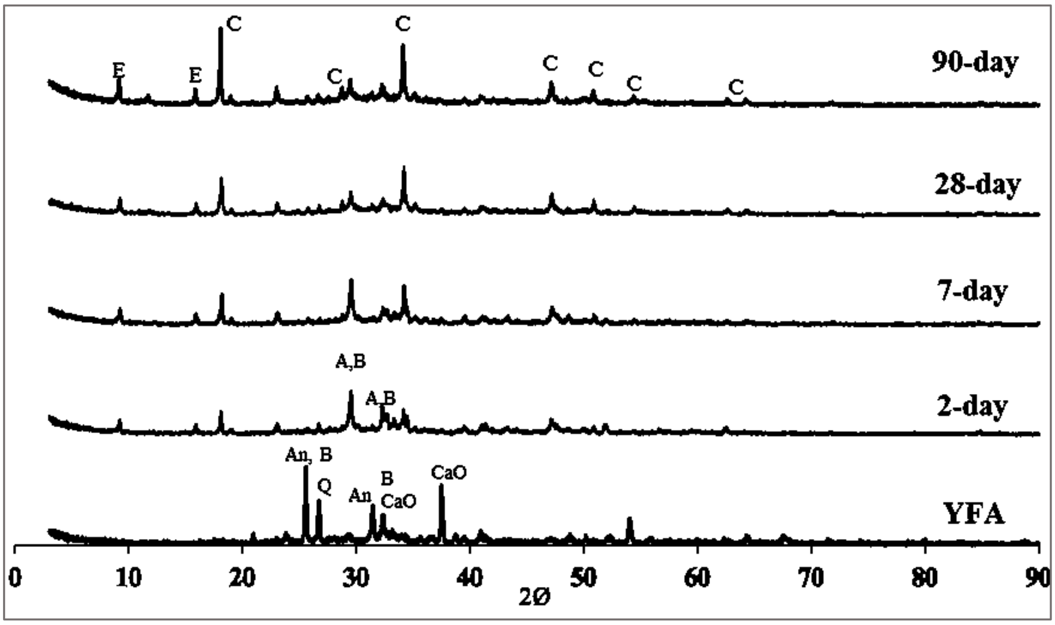

Figure 4.42 XRD patterns of hydrated 75%PC-25%YFA paste at the different days.

Figure 4.43 shows the x-ray diffraction patterns of hydrated PC and 75%PC-25%FA (Class V) pastes at the 90 days. Also, the x-ray diffraction patterns of hydrated 75%PC-25%FA (Class W) pastes at the 90 days are presented in Figure 4.44. The focus was on the portlandite (CH) phase. However, there was no significant degree of CH depletion observed. In the scope of this thesis, the comparison between the CH peaks was conducted only in the terms of intensity (counts) visually. To make the comparison more accurate detailed Rietveld analysis needs to be conducted.

Moreover, the fact that depletion of CH was not that clear can be due to curing conditions of the paste used in the XRD analysis (the paste were not immersed in water, but stored in closed molds at ambient conditions), and the tests were conducted only up to 90-days. 180-days and 360-days samples are going to be tested as a future work. In addition to that, increasing the replacement level (possibly up to 50%) might lead to more clear depletion that can be easily observed in the XRD analysis. Measuring the compressive strength test on the pastes or corresponding mortars can give a better understanding of the progression of the pozzolanic reaction. A detailed analysis combining the obtained strength values of mortars to the mineralogical changes in the pastes will be conducted in the future.

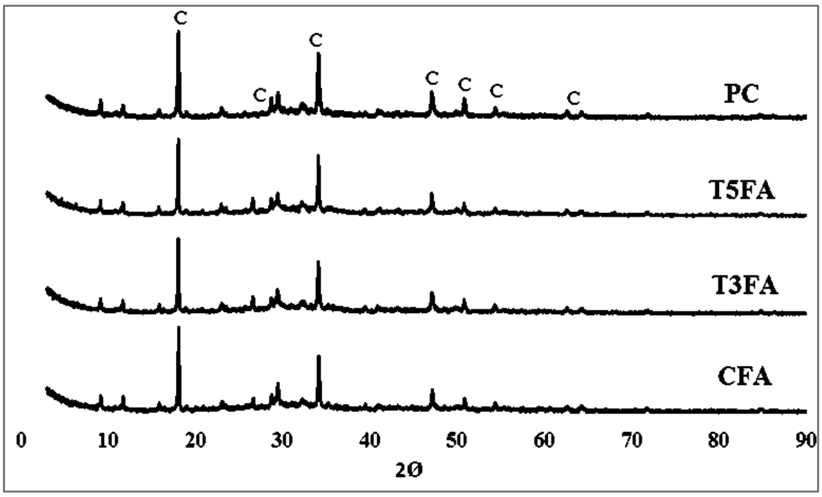

Figure 4.43 Comparison of XRD patterns of hydrated PC and PC-Class V FA at the 90 days.

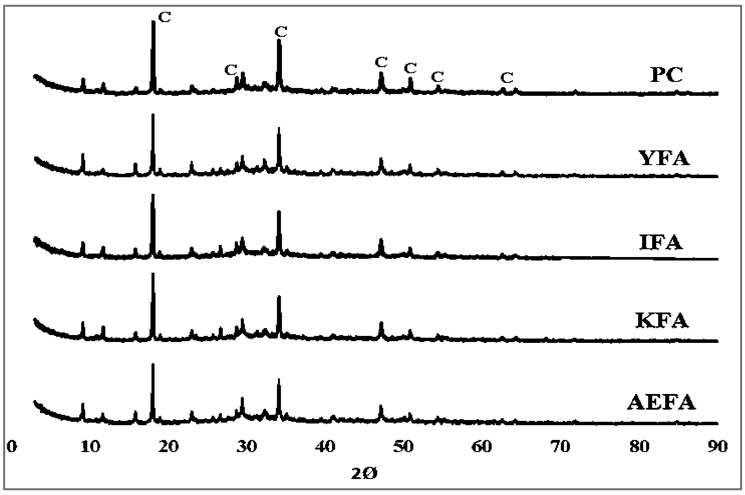

Figure 4.44 Comparison of XRD patterns of hydrated PC and PC-Class W FA at the 90 days.

4.9.3 Flexural and Compressive Strengths of Mortars

The strength development is affected by many factors such as the chemical and mineralogical composition of the fly ashes, the fineness of fly ashes, the level of fly ash substitution, curing conditions (Siddique, 2007); therefore, the impact of fly ashes on the cement based composites vary considerably. Generally, the PC replacement with FA leads to a strength reduction at early-ages, and comparable or higher strength at later ages (90 days or further) (Celik et al., 2014b).

The flexural and compressive strengths at the ages of 2, 7, 28, 90 and 180 days for mortar specimens prepared with 100% PC (control sample) and with 75% PC+25% FA are all given in the above tables (Table 4.38, Table 4.39). The compressive strengths of the mortars are also presented in the Figure 4.45 graphically. AEFA showed the lowest compressive strength at all ages. At the 90 days, except AEFA the strength results showed that the contribution of Class W fly ashes to the strength development is higher than Class V fly ashes especially for 28, 90 and 180 days. The mortars are labeled with the fly ash used.

Table 4.38 Flexural strength of mortars (N/mm^2).

Sample	**Day**				
	2	**7**	**28**	**90**	**180**
Control	5.23	7.78	8.60	9.36	9.45
CFA	3.98	5.26	6.77	8.09	8.51
T3FA	3.21	5.00	7.42	9.12	9.30
T5FA	3.60	5.70	7.17	8.83	8.72
AEFA	1.60	3.78	5.39	7.32	7.45
KFA	3.68	5.45	7.53	9.05	9.29
IFA	4.03	5.89	7.39	9.49	9.50
YFA	3.77	4.16	7.02	8.77	9.18

Table 4.39 Compressive strength of mortars (N/mm^2).

Sample	**Day**				
	2	**7**	**28**	**90**	**180**
Control	28.07	41.84	48.07	53.84	59.34
CFA	18.44	27.26	35.92	44.28	51.47
T3FA	14.48	25.74	36.73	50.55	54.54
T5FA	14.98	29.83	37.66	47.31	51.97
AEFA	10.04	20.25	24.82	40.86	42.85
KFA	16.89	32.38	42.96	53.00	58.43
IFA	18.21	32.83	43.07	56.23	61.79
YFA	13.50	26.49	44.22	52.11	59.87

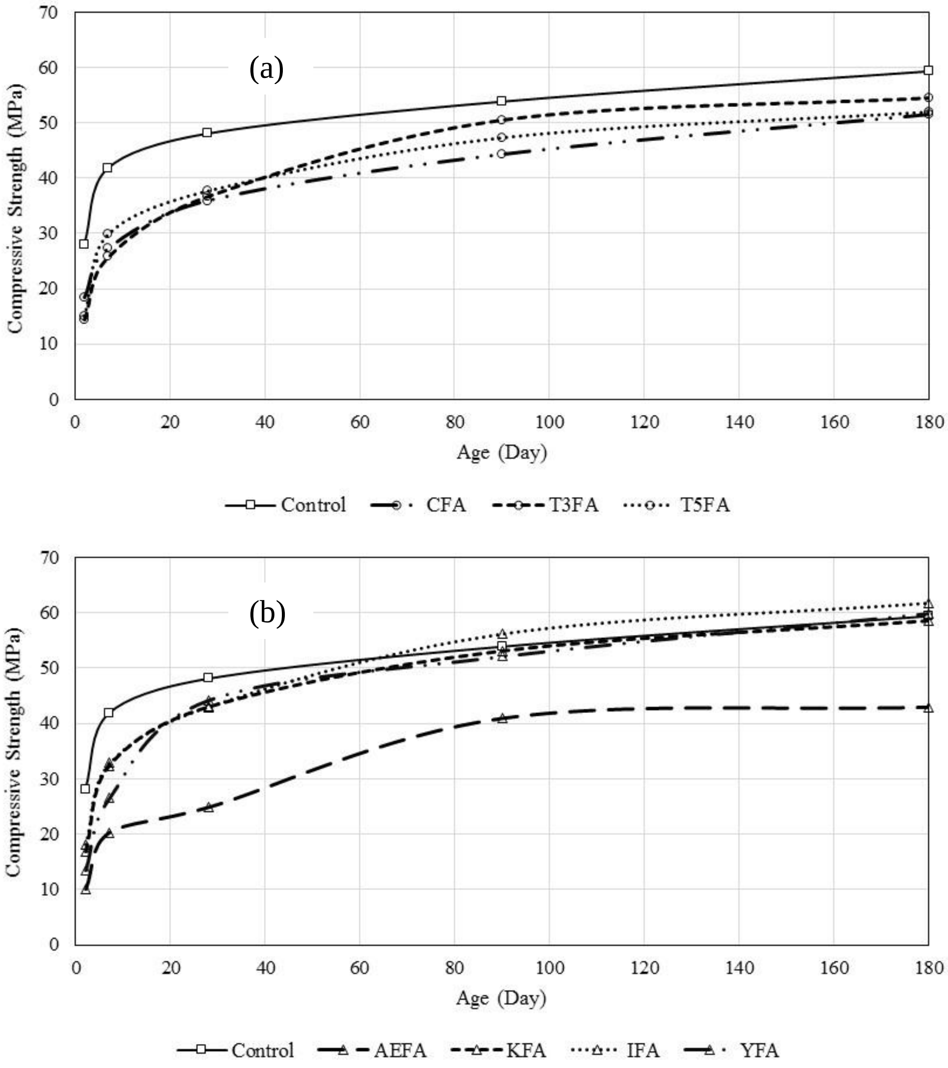

Figure 4.45 Compressive strength of mortars with FAs (a) Class V and (b) Class W.

As it is expected, the highest compressive strengths at the ages of 2, 7 and 28 days belong to control samples. 25% FA replacement with PC resulted in a reduction in the early-age strength for all FAs. The activity index of the FAs used in this study in terms of compressive strength are also presented in Figure 4.46.

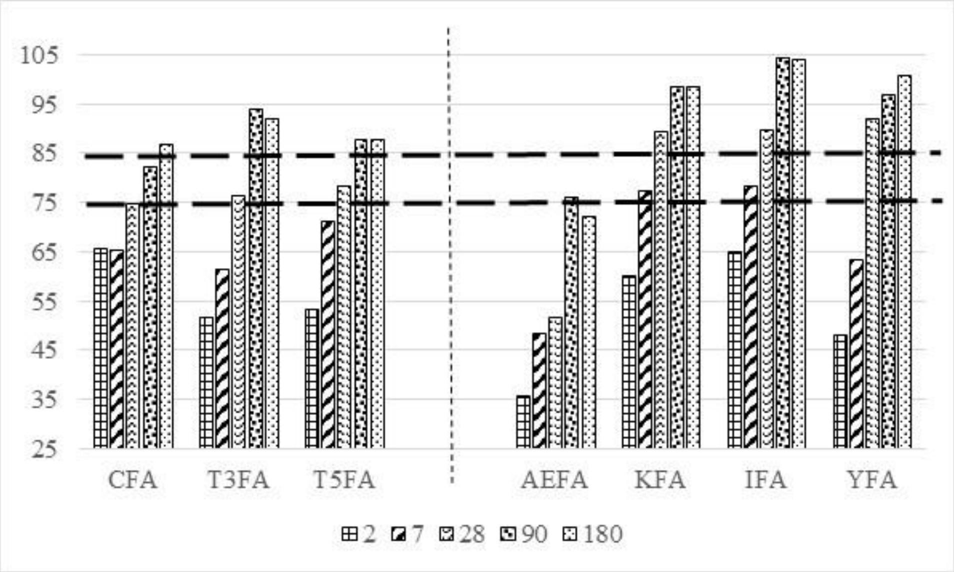

Figure 4.46 Activity index (%) of both Class V and Class W fly ashes in terms of compressive strength.

At the 2nd day, CFA resulted in about 35%, T3FA and T5FA resulted in about 47% strength reduction. The strength reduction at the end of 90 days was about 17% for CFA, 6% for T3FA and 12% for T5FA. When Class W fly ashes are examined, KFA and IFA showed similar strength values especially up to 28 days. Both of them showed about 37% strength reduction at the 2nd day, about 22% at the 7th day, about 11% at the 28th day. At the 90th and 180th days, the compressive strength of IFA surpassed that of the control sample. KFA showed comparable strength. The early-age performance of YFA was lower compared to KFA and IFA. However, at the 28th day YFA has reached the performance of the KFA and IFA. YFA showed comparable strength at the 90th day and higher strength at the 180th day compared to the control sample. It can be said that in the first seven days all the compressive strengths declined owing to the fact that the pozzolanic reaction is slow for both low calcium and high calcium fly ashes. (Malhotra and Ramezanianpour, 1994; Wesche, 2004). However, the mortars with Class W fly ashes achieved higher early-age strength due to their both pozzolanic and cementitious properties except AEFA (Mehta and Monteiro, 2006). After the 28th day the performance of Class W fly ashes (except AEFA) was higher than Class V fly ashes which have only pozzolanic property. Although that this trend in the result is generally expected, a detailed analysis needs to be conducted to correlate the physical, chemical and mineralogical characteristics of the studied fly ashes.

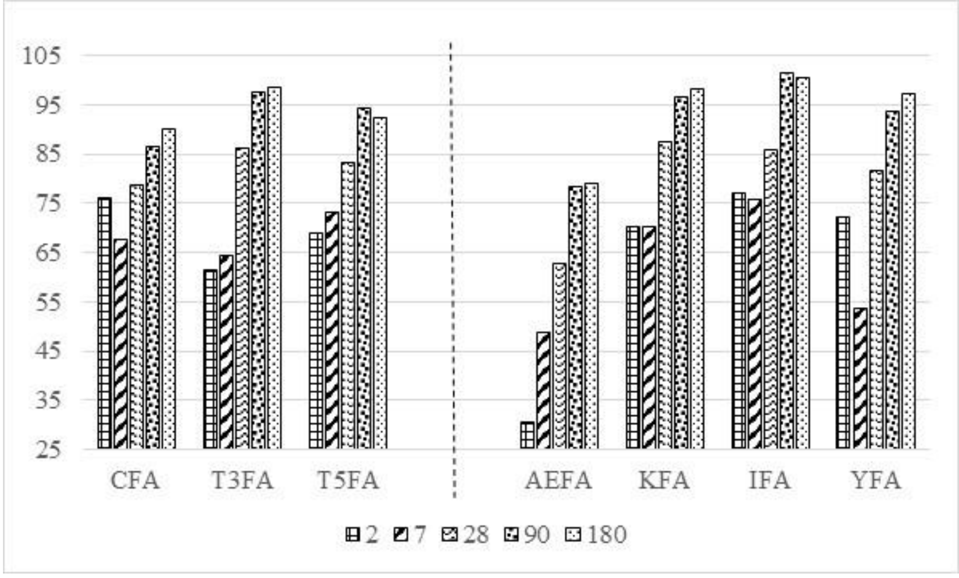

Figure 4.47 Activity index (%) of both Class V and Class W fly ashes in terms of flexural strength.

In the terms of flexural strengths, AEFA showed the lowest flexural strength at all ages as in compressive strength. There is no big difference between the behavior of the other Class W and Class V fly ashes. After 90-days, Class W fly ashes (KFA, IFA, YFA) resulted in slightly higher flexural strength compared to Class V fly ashes (CFA, T3FA, T5FA). Except AEFA and CFA, all the other fly ashes showed comparable flexural strength with the range of 93-97% of the control after 90-days. Moreover, at the 90th day IFA reached the performance of the control sample.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Concluding Remarks

In this thesis fly ashes obtained from Çatalağzı, Tunçbilek Unit 3 and 5, Afşin Elbistan, Kemerköy, Yeniköy, İçdaş Biga coal-fired TPPs were classified according to TS EN 197-1 and evaluated according to TS EN 450-1. For the chemical characterization the results were compared to the requirements of ASTM C 618. Beside the basic chemical and physical tests, heavy metal concentration, mineralogical and morphological properties of the ashes were also investigated. In addition to those, heat evaluation of the 75%PC-25%FA pastes (up to 7 days) and strength development 75%PC-25%FA mortars (up to 180 days) were investigated. Finally, hydration of the binary 75%PC-25%FA pastes were followed by XRD analysis (up to 90 days).

The following can be concluded from this study:

In terms of chemical composition;

- According to TS EN 197-1, due to the reactive CaO content CFA, T3FA, T5FA are siliceous fly ash (V) and AEFA, KFA, YFA and IFA are calcareous fly ash (W)
- According to both TS EN 197-1 and TS EN 450-1 standards, the requirement of more than 25 wt% reactive SiO_2 content was satisfied by all FAs except YFA (20.84%).

- According to TS EN 450-1, the requirement of more than 70 wt% SiO_2 + Al_2O_3 + Fe_2O_3 content was satisfied by CFA, T3FA, T5FA and IFA whereas AEFA, KFA and YFA did not satisfy this requirement.
- According to TS EN 450-1, the requirement of less than 4 wt% MgO content was satisfied by all FAs except T5FA and IFA.
- According to TS EN 450-1, the requirement of less than 3 wt% SO_3 content was satisfied by siliceous fly ashes. On the other hand, calcareous fly ashes did not satisfy this requirement.
- The requirements related to alkalis (Na_2O, K_2O), chloride, phosphate and soluble phosphate content given in TS EN 450-1 were satisfied by all fly ashes.
- According to TS EN 450-1, the requirement of less than 1.5% free CaO content was not satisfied by calcareous fly ashes except IFA. However, they satisfied the requirement for the soundness in the case of more than 1.5% free CaO.
- According to TS EN 450-1, the category of loss on ignition for all fly ashes is category A (<5%).
- According to ASTM C 618, CFA, T3FA and T5FA are Class F since their total amounts of SiO_2, Al_2O and Fe_2O_3 are more than 70 wt% and the total CaO contents are very low. On the other hand, AEFA, KFA and IFA are Class C since the total amounts of SiO_2, Al_2O and Fe_2O_3 are more than 50% and the total CaO contents are high. YFA did not met the requirement of more than 50% SiO_2+Al_2O+Fe_2O_3 amount. However, YFA is more suitable to be classified as Class C fly ash due to its very high CaO content.
- According to ASTM C 618, the requirement of less than 5% SO_3 content was satisfied by CFA, T3FA and T5FA which are Class F fly ashes. AEFA and YFA did not satisfy this requirement whereas KFA and IFA satisfied.
- According to ASTM C 618, the requirement of less than 6% loss on ignition was satisfied by all fly ashes.

- All the FAs had various amounts of toxic elements. According to the limit values in soil given by the “Regulation on Control of Soil Pollution” for Turkey, the FAs satisfied the limit values for lead, cadmium and zinc content; however, they exceeded the limits of chromium and nickel.

In terms of physical properties;

- According to TS EN 450-1, T3FA, KFA, IFA and YFA can be grouped as Category N in terms of fineness. CFA, T5FA and AEFA didn’t satisfy the maximum of 40% requirement on 45 μm sieve. According to wet sieve analysis results, the fly ashes can be sorted from coarser to finer as AEFA, T5FA, CFA, KFA, YFA, T3FA, and IFA.
- Although the values from the wet sieve analysis and the values of 45 μm from the laser diffraction are not equal, the results of the two tests were parallel to each other suggesting that both methods can be used to indicate the relative size of the fly ashes.
- The Blaine values of the FAs range from 2224 to 5214 cm^2/g.
- The 75%PC-25%FA mortars results in flow diameters in the range of 68% to 106% relative to that of control mortar of 100%PC. For Class V fly ashes, as the coarser and the smoother the FA becomes the higher the flow diameter. However, a consistent relationship between the change in the flow diameter, the Blaine values and PSD parameters of FA was not observed. This might be due to the higher SO_3 content of the Class W FAs and errors in the test method used.
- 25% FA replacement with PC caused to a delay in the initial setting within the range of 5 and 35 minutes. A relation was not observed between in the initial setting time and type of fly ash even though the SO_3 content of Class W FAs were considerably higher than that of Class V.
- The densities of the FAs were in the range of 1.99-2.75 g/cm^3. Calcareous fly ashes had higher density (2.41-2.75 g/cm^3) compared to siliceous FAs (1.99-2.21 g/cm^3).

- According to TS EN 450-1, the soundness requirement was satisfied by all fly ashes. Although the content of free CaO of calcareous fly ashes was higher than that of siliceous fly ashes a difference was not observed between the soundness measurements results according to type of fly ash.
- According to TS EN 450-1, the requirements of minimum 75% activity index at 28th day and 85% activity index at the 90th day were not satisfied by AEFA. CFA had the limit value at 28 day but at the 90 day it didn’t meet the 85% activity index criterion. Except those two, other fly ashes satisfied the activity index requirements.

In terms of mineralogical and morphological composition;

- All FAs had amorphous and crystalline phases. The amorphous phases, represented by broad humps in the XRD patterns, were more prominent in the siliceous fly ashes.
- All FAs had quartz and hematite phases. The siliceous FAs showed also some mullite and magnetite phases. The calcareous FAs showed calcium oxide and anhydrite phases. Some calcareous FAs showed also gehlenite or C_2S phases.
- According to SEM images, all fly ashes had both spherical and angular particles. The particle size of the FAs ranged from 1 to 150 μm. Small particles with a diameter of 1 μm to 15 μm were generally spherical in shape.

In terms of heat evolution of PC-FA pastes;

- Isothermal calorimetry studies on 75%PC-25%FA pastes showed that the subsitution of PC with FA resulted in retardation of the heat flow peaks and reduction of the cumulative heat.

In terms of strength development of PC-FA mortars;

- PC replacement with FA led to reduced early-age strengths for all FAs. The contribution of Class W fly ashes (except AEFA) to the strength development is higher than Class V at later ages (28, 90 and 180 days) possibly due to pozzolanic and cementitious properties of Class W fly ashes.

In terms of XRD analysis of PC-FA pastes;

- When the XRD patterns of PC-FA pastes were examined over time (2, 7, 28 and 90 days), a significant CH depletion was not observed.

5.2 Future Works and Recommendations

This thesis is a part of an ongoing project between METU and Turkish Cement Manufacturers Association. The ongoing tasks are listed below:

- The experiments for all of the collected FAs will be completed.
- Different fly ash replacement ratios and water-to-binder ratios will be used for the tests performed in this study for better understanding of the fly ash effect on the strength and the hydration reaction.
- In order to precisely quantify the mineral phases Rietveld analysis will be conducted.
- Durability tests such as alkali silica reaction or corrosion tests will be performed.
- The acoustical (in collaboration with Mezzo Studio) and radiological (in collaboration with Muğla Sıtkı Koçman University) measurements will be finalized.
- The chemical reactivity indices defined by the standards might be favorited for other activation methods (such as alkaline activation), but not for portland cement based systems. The alkali activation tests on FAs will be completed.
- The life cycle assessment (LCA) analysis on the PC-FA mortars and activated FA systems will be finalized.
- The experimentally obtained data on the characteristics and performance of Turkish FAs will be compared to fly ashes worldwide.

- A detailed analysis will be conducted to find a correlation between the physical, chemical and mineralogical characteristics of the fly ashes and their performance indicators such as compressive strength, heat of hydration and global warming potential.
- An artificial neural network model will be prepared from the experimentally obtained data set in conjunction with the data sets collected from literature to predict the above mentioned performance indicators from the characterization parameters.

For further research, the following are recommended:

- The BSE and EDAX analysis of the collected FAs can be conducted systematically to see the chemical variation within the FA grains.
- Characterization of the coal burnt at the TPP. The burning process used along with this characterization will provide a better understanding of the kind of changes or improvements that can be done to obtain better fly ashes to be used in the cement and concrete production.
- The utilization of biomass as a supplementary energy source in coal-fired thermal power plants has been steadily increasing. The fly ash from the joint combustion of biomass and coal could be investigated.
- In order to better explain the hydration reactions at early ages (from few hours to few days) and to correlate them to isothermal calorimetry results, in-situ XRD measurements can be performed at a synchrotron facility.
- The performance of PC-FA systems can be investigated by selecting various cements from different types and manufacturers.
- The in-situ heat evolution tests on PC-FA pastes can be conducted for the first 3 hours. This might be critical for effective utilization of high SO_3 FAs.

REFERENCES

ACI 232.2R, *Use of Fly Ash in Concrete*. American Concrete Institute, Farmington Hills, MI, USA, 2003.

Ahmaruzzaman, M. (2010). A review on the utilization of fly ash. *Progress in Energy and Combustion Science,* 36, 327-363.

ASTM C 618, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*. ASTM International, 2012.

Benscheidt, N., vom Berg, W., Feuerborn, H.-J., Heinz, D., Hohberg, I., Hugot, A., Lutze, D., Mengede, M., Pierkes, R., Schneider, E., & Wiens, U. (2010). *Handbook on fly ash in concrete* (2nd Ed.). Verlag Bau+Technik GmbH, Duesseldorf.

Bentz, D., Peltz, M., Duran-Herrera, A., Valdez, P., Juarez, C. (2010). Thermal properties of high-volume fly ash mortars and concretes. *Journal of Building Physics,* 34(3), 263-275.

Blissett, R. S., & Rowson, N. A. (2012). A review of the multi-component utilisation of coal fly ash. *Fuel,* 97, 1-23.

Bosbach, D., & Enders, M. (1998). Microtopography of high-calcium fly ash particle surfaces. *Advances in Cement Research,* 10(1), 17–23.

Bullard, J. W., Jennings, H. M., Livingston, R. A., Nonat, A., Scherer, G. W., Schweitzer, J. S., Scrivener, K. L., & Thomas, J. J. (2011). Mechanisms of cement hydration. *Cement and Concrete Research*, 41, 1208–1223.

Celik, K., Meral, C., Gursel, P., Mehta, P., Horvath, A., & Monteiro, P. J. M. (2014). Mechanical properties, durability, and life-cycle assessment of self-consolidating concrete mixtures made with blended portland cements containing fly ash and limestone powder. *Cement and Concrete Composites*, 56, 59-72.

Celik, K., Meral, C., Mancio, M., Mehta, P. K., & Monteiro, P. J. M. (2013). A comparative study of self-consolidating concretes incorporating high-volume natural pozzolan or high-volume fly ash. *Construction and Building Materials*, 67, Part A, 14-19.

Elektrik Üretim A.Ş. (EÜAŞ), (2011). *Electricity Generation Company 2011 Annual Report*, 1-75.

Erdoğan, T. Y. (1997). *Admixtures for Concrete*. Ankara: Middle East Technical University Press.

Gürsel, A. P., & Meral, Ç. (2012). Türkiye’de Çimento Üretiminin Karşılaştırmalı Yaşam Döngüsü Analizi. In *2. Proje ve Yapım Yönetimi Kongresi, İzmir Yüksek Teknoloji Enstitüsü*, İzmir.

Joshi, R. C., & Lohtia, R. P. (1997). *Fly Ash in Concrete: Production, Properties, and Uses*. Amsterdam: Overseas Publishers Association.

Kosmatka, S. H., Kerkhoff, B., & Panarese, W. C. (2002). *Design and Control of Concrete Mixtures*. Skokie, IL: Portland Cement Association.

Langan, B., Weng, K., & Ward, M. (2002). Effect of silica fume and fly ash on heat of hydration of Portland cement. *Cement and Concrete Research*, 32, 1045-1051.

Lloyd, R. R., Provis, J. L., & van Deventer, J. S. J. (2009). Microscopy and microanalysis of inorganic polymer cements . 1: remnant fly ash particles. *Journal of Materials Science*, 44(2), 608-619.

Malhotra, V. M., & Ramezanianpour, A. A. (1994). *Fly Ash in Concrete*. Canada: CANMET.

Mehta, P. K. (2001). Reducing the environmental impact of concrete. *Concrete International*, 23(10), 61-66.

Mehta, P. K. (2002). Greening of the Concrete Industry for Sustainable Development, *Concrete International*, July, 23-28.

Mehta, P. K., & Monterio, P. J. M. (2006). *Concrete:Microstructure, Properties, and Materials*. McGraw-Hill Education.

Mostafa, N. Y., & Brown, P. W. (2005). Heat of hydration of high reactive pozzolans in blended cements: Isothermal conduction calorimetry. *Thermochimica Acta*, 435(2), 162–167.

Odler, I. (2004). Hydration, setting and hardening of Portland cement. In: Hewlett, P. C. (Ed.), *Lea's Chemistry of cement and concrete* (4th Ed.). Elsevier Science & Technology Books.

PANalytical B.V. (2003). *X'Pert HighScore Sotfware (Version 1.0d).* Almelo, the Netherlands.

Pane, I., & Hansen, W. (2005). Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. *Cement and Concrete Research*, 35(6), 1155–1164.

Pyle, S. M., Nocerino, J. M., Deming, S. N., Palasota, J. A., Palasota, J. M., Miller, E. L., Hillman, D. C., Kuharic, C. A., Cole, W. H., Fitzpatrick, P. M., Watson, M. A., & Nichols, K. D. (1995). Comparison of AAS, ICP-AES, PSA, and XRF in determining lead and cadmium in soil. *Environmental Science & Technology*, 30(1), 204–213.

Ramachandran, V. S. (1996). *Concrete Admixtures Handbook: Properties, Science, and Technology* (2nd Ed.). Park Ridge, New Jersey: Noyes Publications.

Regulation on Control of Soil Pollution (2005). *Toprak Kirliliğinin Kontrolü Yönetmeliği.* Türkiye, Resmi Gazete Tarihi: 31.05.2005, Resmi Gazete Sayısı: 25831.

Siddique, R. (2007). *Waste Materials and By-Products in Concrete*. Springer Science & Business Media.

Smith, F. (1999). *Industrial Applications of X-Ray Diffraction*. Boca Raton, FL: CRC Press.

Sushil, S., & Batra, V. S. (2006). Analysis of fly ash heavy metal content and disposal in three thermal power plants in India. *Fuel*, 85(17-18), 2676-2679.

Tangüler, M., Gürsel, A. P., & Meral, Ç. (2015). Türkiye' de Uçucu Küllü Betonlar İçin Yaşam Döngüsü Analizi. In *9. Ulusal Beton Kongresi*, Antalya.

Tangüler, M., Meral, C., & Gursel, A. P. (2014). Merging Mechanical and Environmental Performance of Turkish Fly Ash-Portland Cement Mortars. In *11th International Congress on Advances in Civil Engineering,* 21-25 October, İstanbul.

Tangüler, M., Meral, Ç., & Aslam, I. (2014). Early-Age Performance of Binary Fly Ash- Portland Cement Blends. In *Eurasia 2014 Waste Management Symposium,* 28-30 April, İstanbul, Türkiye.

Taylor, H. F. W. (1997). *Cement Chemistry*. London: Academic Press.

Türkiye Elektrik İletim A.Ş. (TEİAŞ), (2014). *2014 Yıl Sonu Kurulu Güç Değerleri*. Yük Tevzi Dairesi Başkanlığı İşletme Faaliyetleri Raporları.

Tokyay, M., & Erdoğdu, K. (1998). *Türkiye Termik Santrallerinden Elde Edilen Uçucu Küllerin Karakterizasyonu*. Ankara: TÇMB / AR-GE / Y 98.3.

TS EN 196-1, *Methods of testing cement - Part 1: Determination of strength*. Turkish Standards Institution, March 2002.

TS EN 196-3, *Methods of testing cement - Part 3: Determination of setting times and sondness*, Turkish Standards Institution, March 2002.

TS EN 197-1, *Cement- Part 1: Compositions and conformity criteria for common cements,* Turkish Standards Institution, March 2002.

TS EN 450-1 *Fly ash for concrete - Part 1: Definition, specifications and conformity criteria*, Turkish Standards Institution, 2008.

Turkish Statistical Institute, *Mineral wastes generated by thermal power plants*, Turkey, 2008.

Türker, P., Erdoğan, B., Katnaş, F., & Yeğinobalı, A. (2003). *Türkiye'deki Uçucu Küllerin Sınıflandırılması ve Özellikleri*. Ankara: TÇMB / AR-GE / Y03.03.

U. S. Department of Transportation - Federal Highway Administration (2012a). *User Guidelines for Waste and Byproduct Materials in Pavement Construction* (Publication Number: FHWA-RD-97-148).

U. S. Department of Transportation Federal Highway Administration (2012b). *Evaluation of High-Volume Fly Ash Mixtures (Paste and Mortar Components) Using a Dynamic Shear Rheometer and an Isothermal Calorimeter* (Publication Number: FHWA-HRT-12-062).

WaveMetrics, Inc. (2014). *IGOR Pro Sotfware (Version: 6.3.7.2).* Lake Oswego, Oregon / USA.

World Business Council for Sustainable Development (WBCSD) (2009). *The Cement Sustainability Initiative: Recycling Concrete,* Klee, H. (Ed.). Geneva, Switzerland.

Wesche, K. (2004). *Fly ash in Concrete: Properties and Performance* (Vol. 7). CRC Press.

Yao, Z. T., Xia, M. S., Sarker, P. K., & Chen, T. (2013). A review of the alumina recovery from coal fly ash, with a focus in China. *Fuel*, 120, 74-85.

APPENDIX A

SELECTION OF REFERENCES

During the isothermal calorimetry experiments, the total solid amount (FA + PC) was kept constant for each paste at 4 g. The PC replacement ratio was 25% for all FAs. Powdered cement was chosen as reference sample. Reference ampoules which have same specific heat of the paste were prepared according to specific heat values of materials. The specific heats of PC, FA and water was taken as 0.74, 0.73 and 4.18 J/(g.K) respectively (Bentz et al., 2010). The weight of reference material was calculated according the formula below:

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

$$wreference = \frac{3 * 0.74 + 1 * 0.73 + 4\,.18 * 2}{0.74} = 11.31\ g$$

APPENDIX B

XRD RESULTS

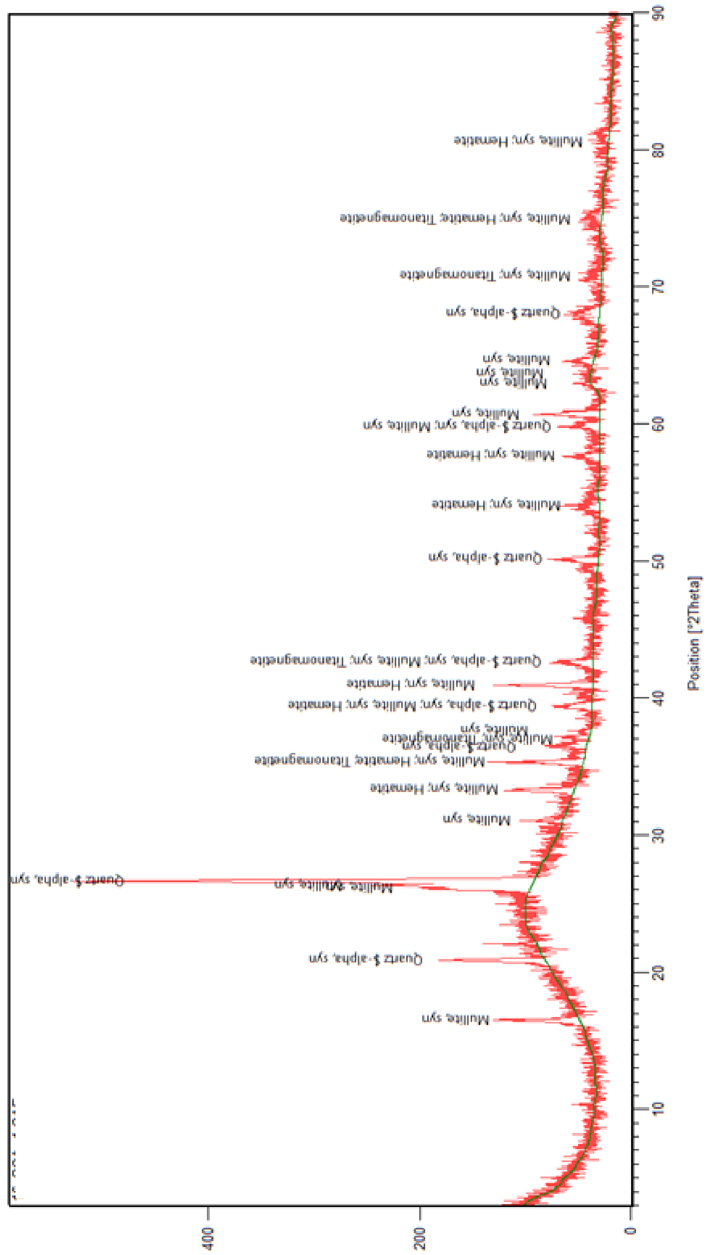

Figure B.1 X-ray diffraction pattern of CFA with major peak labels**.**

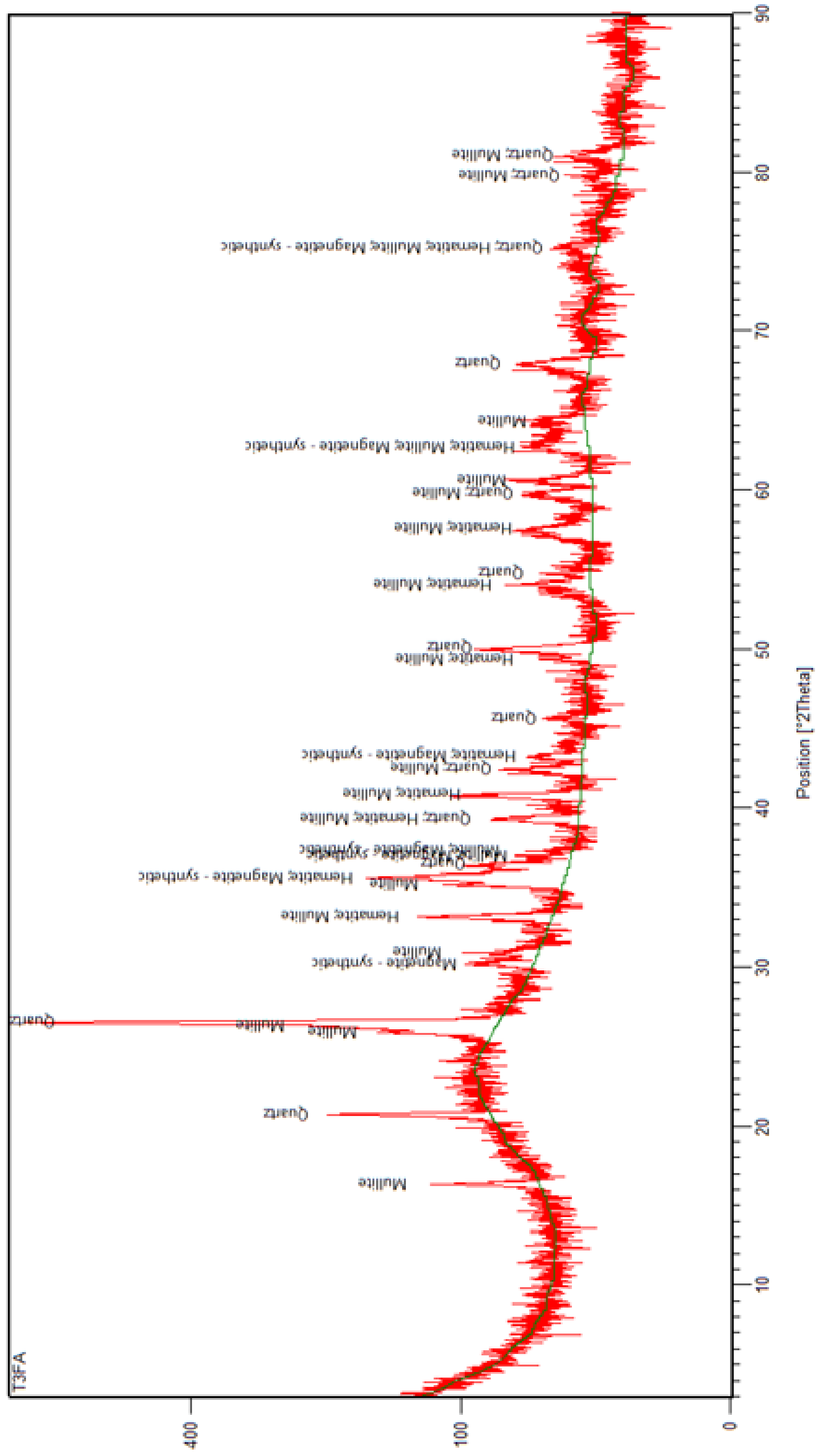

Figure B.2 X-ray diffraction pattern of T3FA with major peak labels**.**

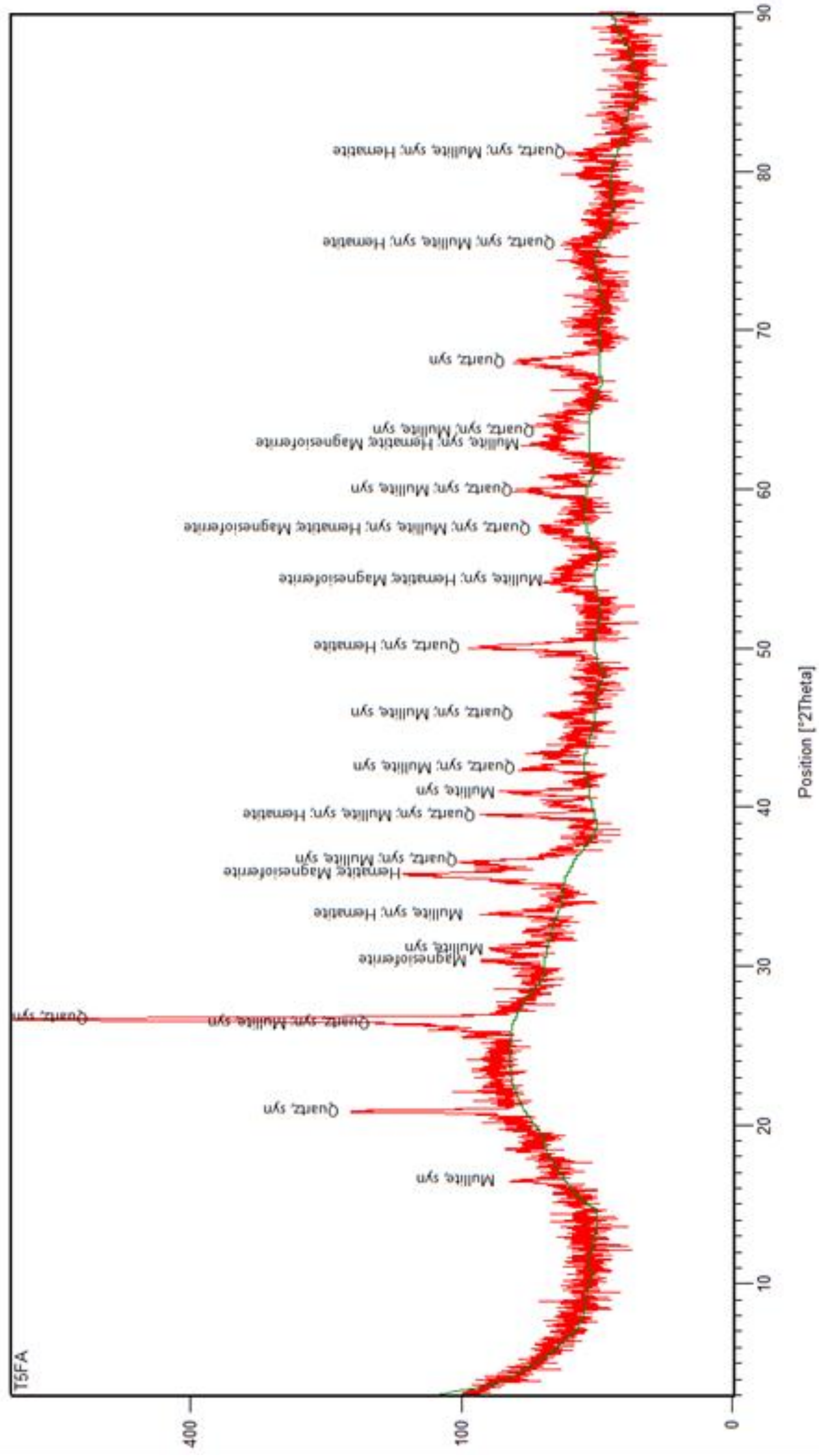

Figure B.3 X-ray diffraction of T5FA with major peak labels.

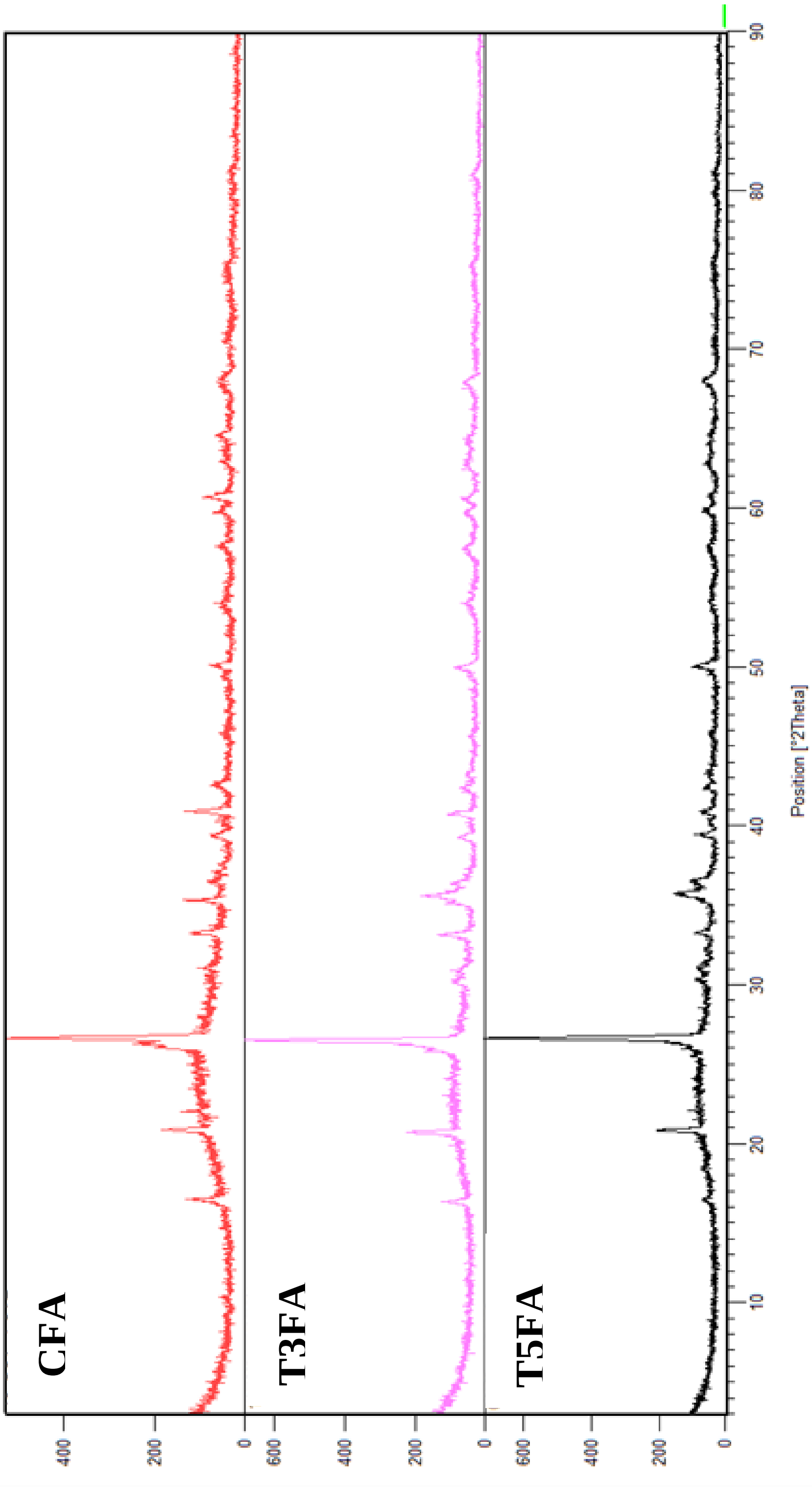

Figure B.4 Comparison of the x-ray diffraction of Class V fly ashes.

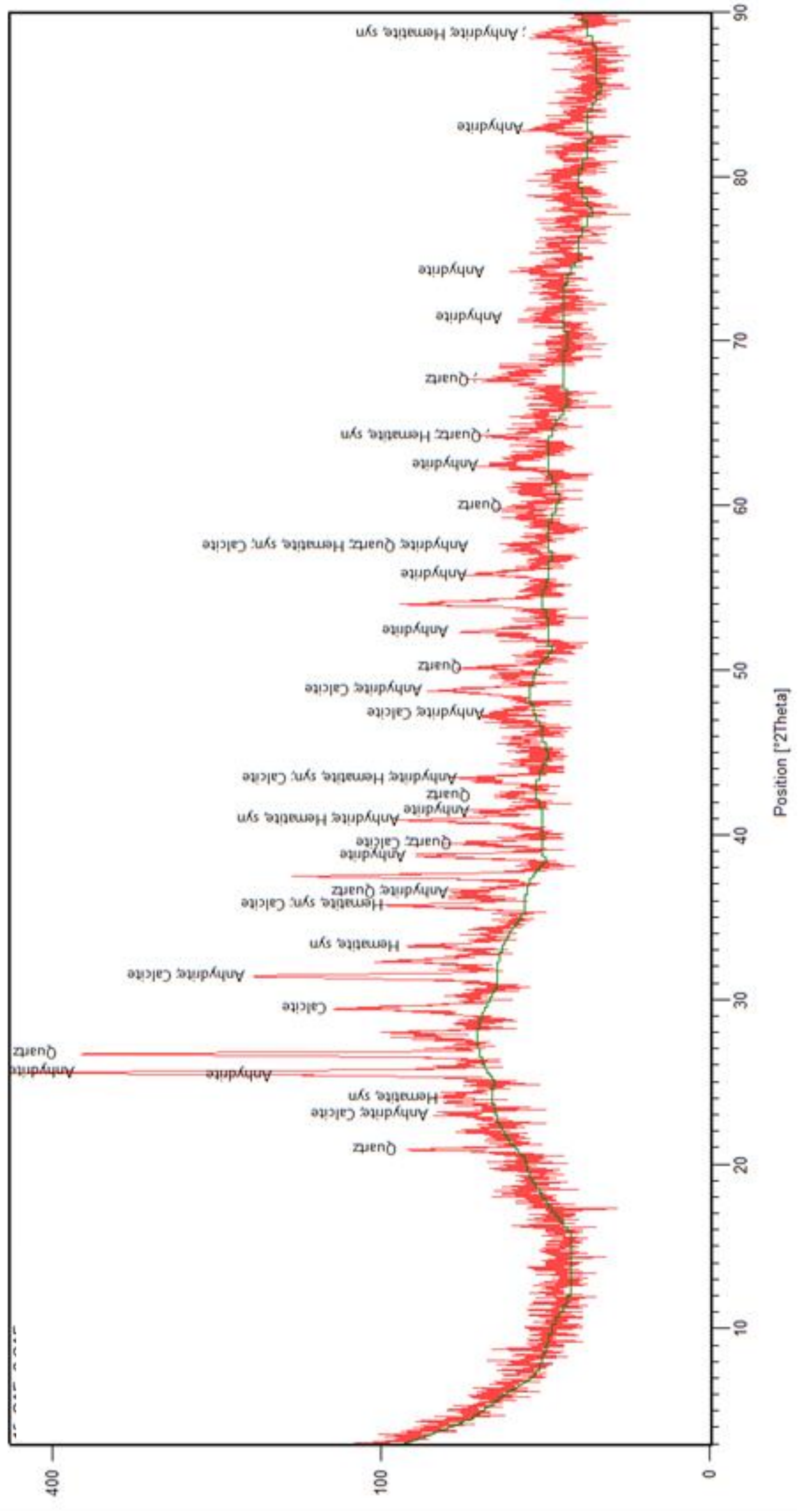

Figure B.5 X-ray diffraction of AEFA with major peak labels**.**

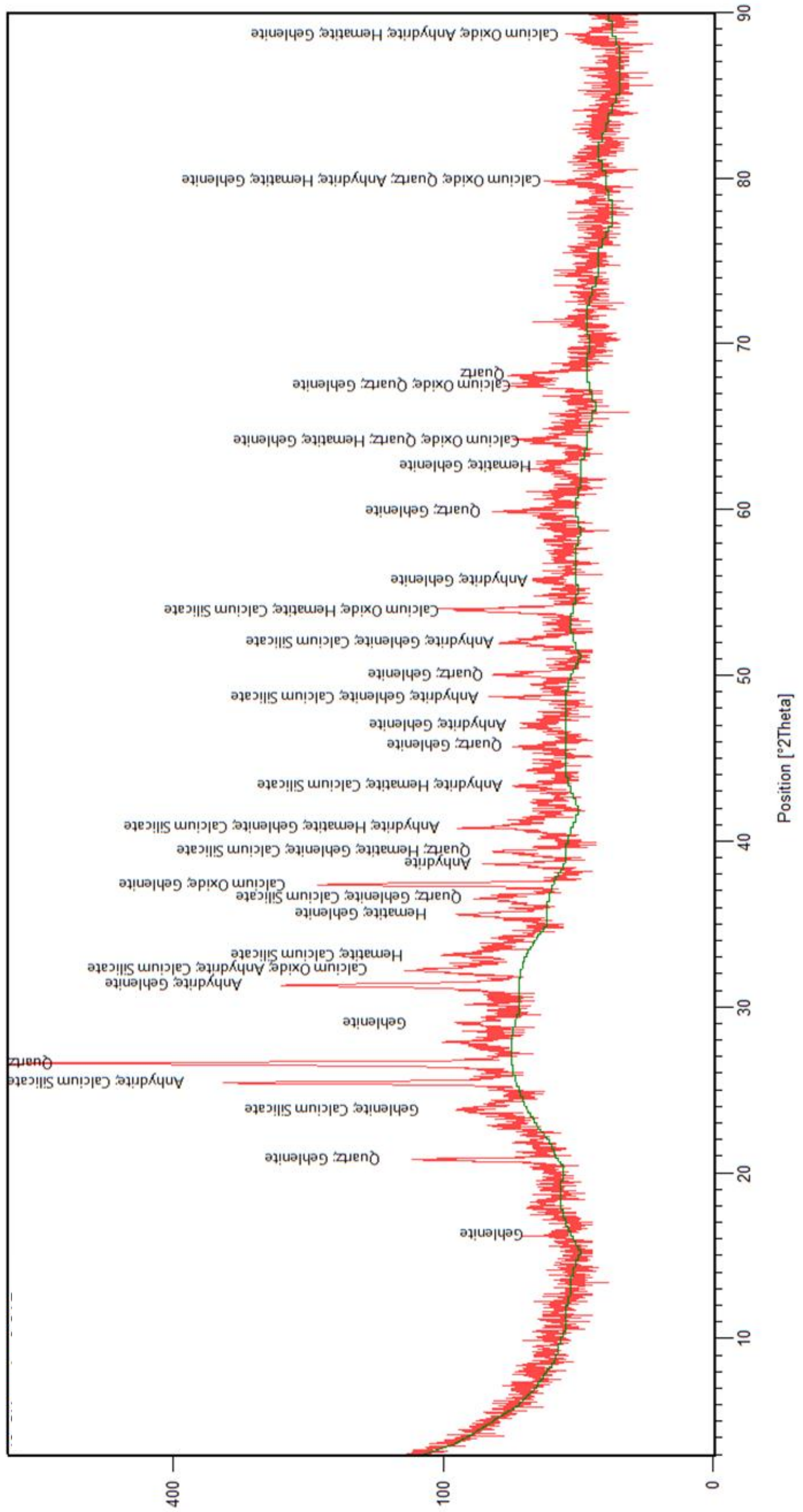

Figure B.6 X-ray diffraction of KFA with major peak labels**.**

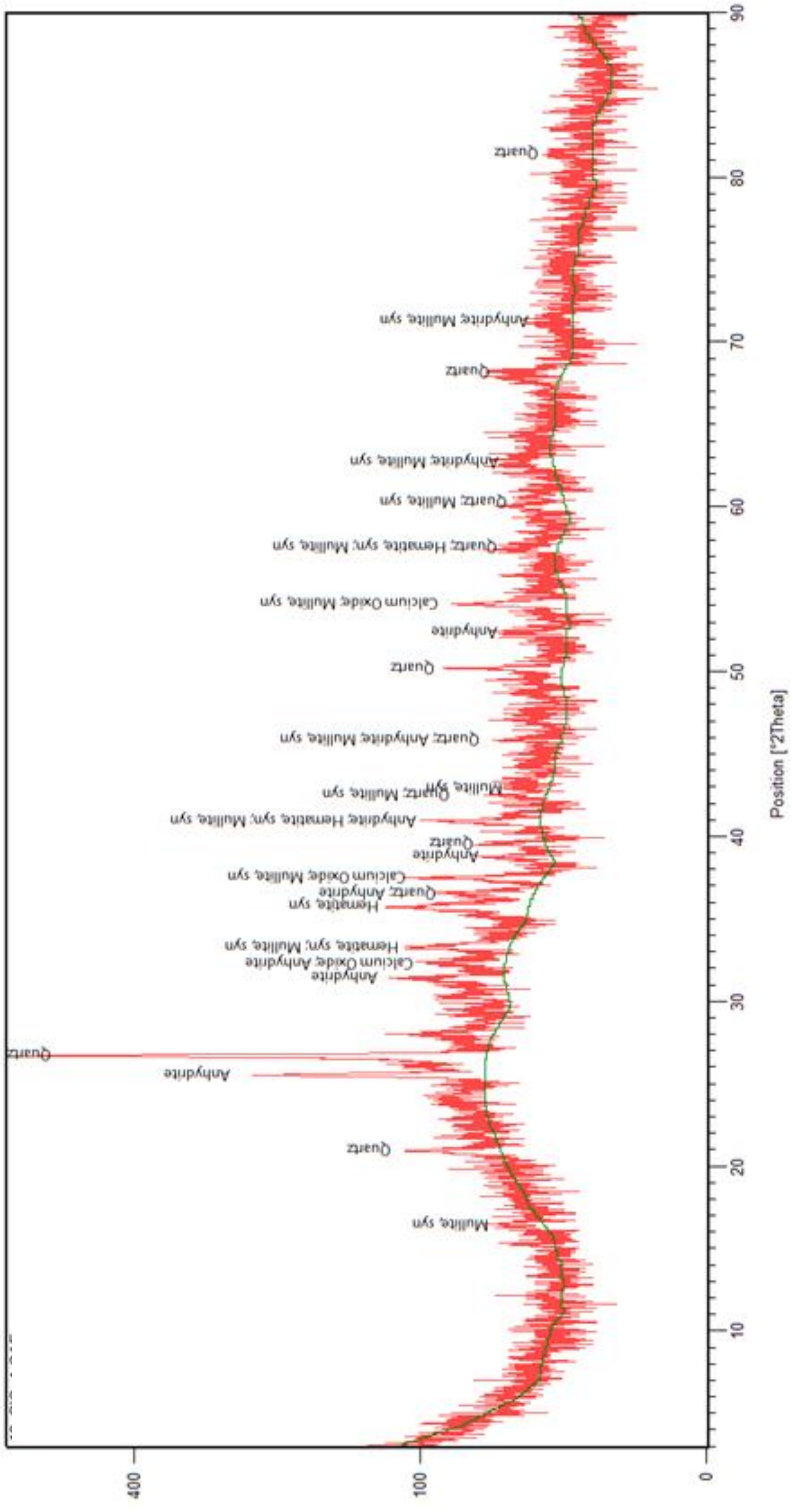

Figure B.7 X-ray diffraction of IFA with major peak labels**.**

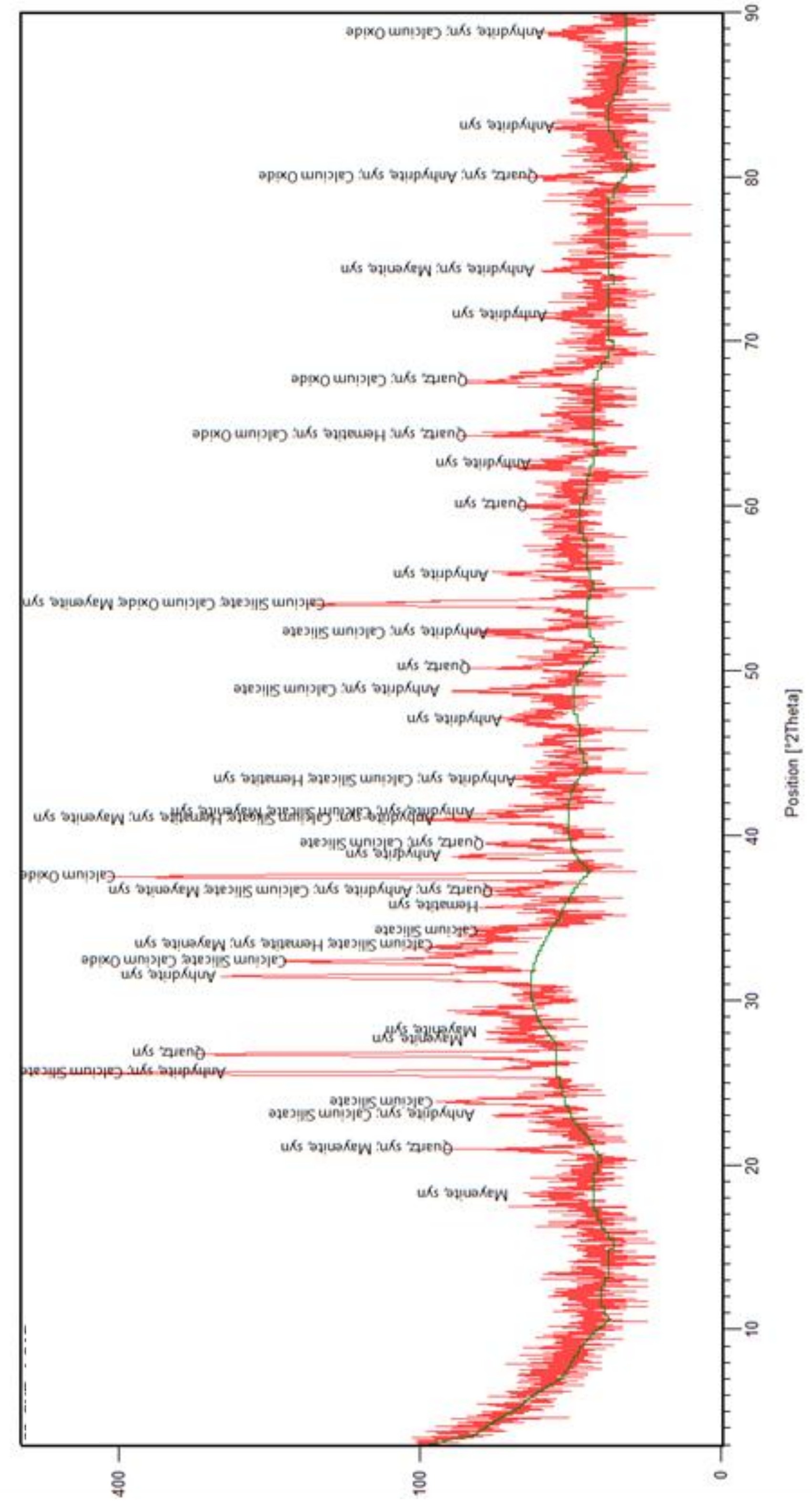

Figure B.8 X-ray diffraction of YFA with major peak labels**.**

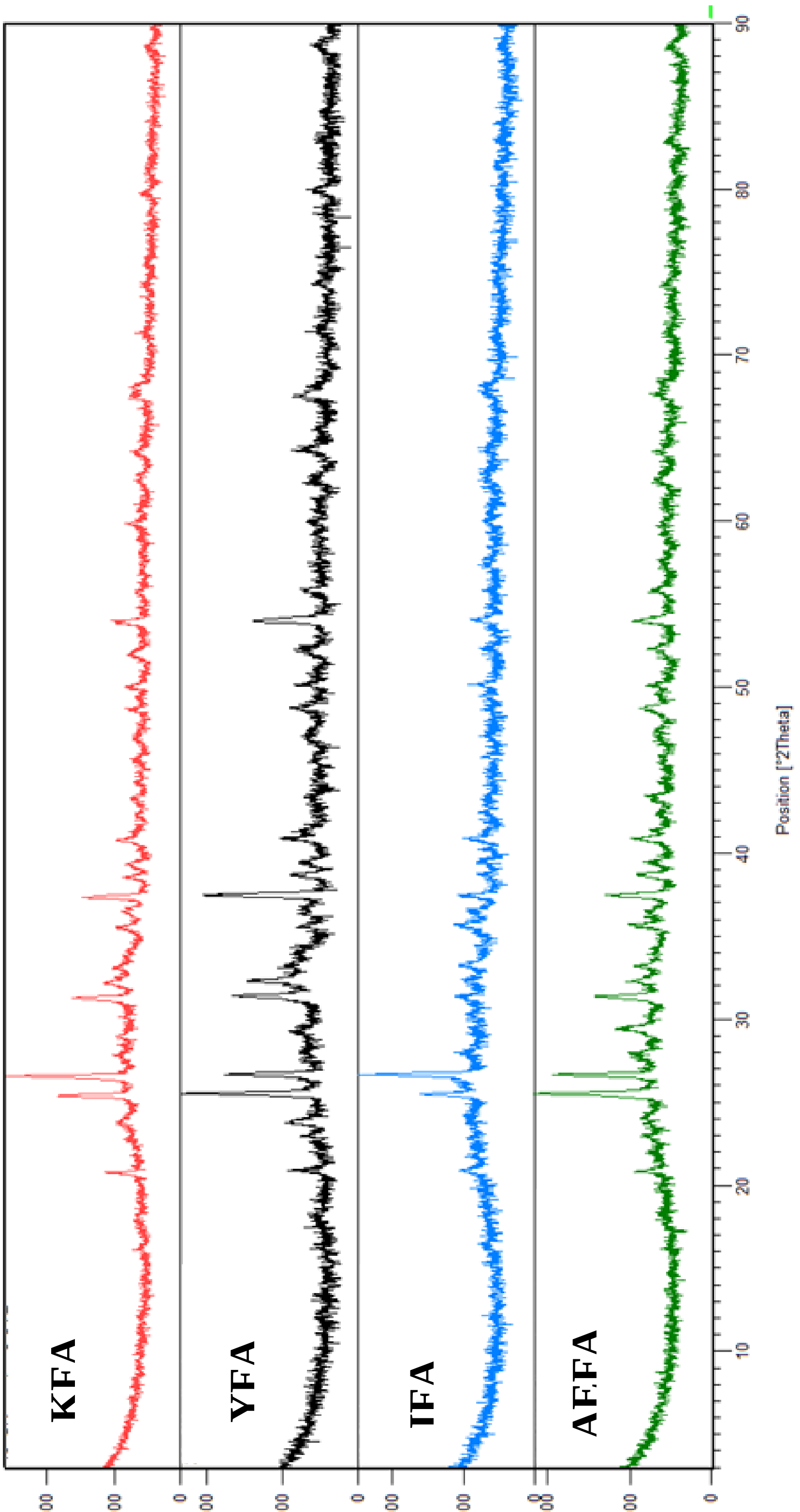

Figure B.9 Comparison of the x-ray diffraction of Class W fly ashes**.**