TO MY WIFE AND MY DAUGHTER

33609

EFFECTS OF TURKISH FLY ASHES ON THE PORTLAND CEMENT - FLY ASH SYSTEMS

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ABSTRACT

EFFECTS OF TURKISH FLY ASHES ON THE PORTLAND CEMENT-FLY ASH SYSTEMS

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Fly ash is no longer a waste by-product of the coal combustion in thermal power plants, but a well-established pozzolanic and/or cementitious concrete ingredient. Direct economic factors caused by energy conservation and the increasing awareness of the need to protect environment, as well as the modification of certain properties of fresh and hardened concrete are major reasons for using fly ash in concrete. However, the current use of fly ash as a concrete ingredient is negligibly small in Turkey. It seems that the utilization rate of fly ash in concrete can be much higher than the present value with a better understanding of the fly ash behavior in portland cement-fly ash (PC-fa) systems and by development of proper test methods and specifications for these systems.

In this study the effects of four lignite-originated fly ashes, produced in Turkey, on various properties of PC-fa systems were investigated. One of the fly ashes (Tunçbilek) was a low-lime fly ash and three others (Afşin-Elbistan, Seyitömer and Soma-B) were high-lime fly ashes. The fly ash substitution was 10, 20 and 40% by weight of cement. Fly ash inclusion was performed by both simple replacement and additional replacement method. The normal consistency, setting time, water requirement, flow, slump, air content and unit weight of fresh PC-fa systems, as well as their strength, pozzolanic activity index, modulus of elasticity, heat of hydration, sulfate resistance, drying shrinkage and carbonation in hardened state were investigated.

The results of tests and analyses, conducted on more than 90 paste, 750 mortar and 600 concrete specimens, revealed that the use of Tunçbilek and Soma-B fly ashes improved most of the properties of PC-fa systems even when the fly ash replacement level was as much as 40% by weight of cement. However, Afşin-Elbistan and Seyitömer fly ashes when used in excessive proportions affected almost all of the characteristics of the PC-fa systems adversely.

The first chapter of the text includes general information on fly ash, its worldwide production and utilization rates and object and scope of the study. The constitution and hydration of portland cement, nature and classification of pozzolans and fly ashes, as well as the mechanisms by which fly ash improves the properties of PC-fa systems are discussed in Chapters 2 and 3. Theoretical background together with a review of research on the effects of fly ash on various properties of concrete are given in Chapter 4. Experimental program and the tests and analyses carried out are explained in Chapter 5. Chapters 6, 7 and 8 are devoted to the results and discussions, conclusions drawn and recommendations for future research, respectively.

Key words: Fly Ash, Portland-Cement Fly Ash Systems, Water Requirement, Setting Time, Heat of Hydration, Strength, Pozzolanic and Strength Activity Index, Modulus of Elasticity, Sulfate Resistance, Drying Shrinkage, Carbonation.

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ÖZ

TÜRKİYE'DEKİ UÇUCU KÜLLERİN PORTLAND ÇİMENTOSU - UÇUCU KÜLLÜ SİSTEMLERİNE ETKİLERİ

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Uçucu kül, artık termik santrallarda taş kömürün yakılmasından açığa çıkan bir malzemeden ziyade, puzolanik veya bağlayıcı özelliğe sahip bir beton bileşiğidir. Enerji tasarrufundan kaynaklanan ekonomik kazanç gün geçtikce daha fazla hissedilen çevreyi koruma gereği, ayrıca uçucu külün taze ve sertleşmiş betonun birtakım özeliklerini iyi yönde etkilemesi, uçucu külün betonda kullanılmasının başlıca nedenleridir. Buna rağmen, Türkiye'de uçucu külün beton malzemesi olarak kullanılması yok sayılacak kadar azdır. Uçucu külün betonda kullanılmasını artırmak, bu malzemenin portland çimentosu-uçucu küllü (PÇ -UK) sistemlerde davranışını daha iyi anlamakla ve bu sistemler için daha uygun deney metodları ve şartnameler hazırlamakla mümkündür.

Bu araştırmada Türkiye'de üretilmekte olan ve linyitin yakılmasından elde edilen dört çeşit uçucu külün, PÇ-UK sistemlerinin özeliklerine etkisi incelenmiştir. Uçucu küllerden birisi (Tunçbilek) düşük-kireçli ve diğer üçü (Afşin-Elbistan, Seyitömer ve Soma-B) yüksek-kireçlidir. Karışımlarda çimento ağırlığının %10, 20 ve 40'ı kadar uçucu kül kullanılmıştır. Uçucu külün karışımlara eklenmesi, karışımdan alınan çimentonun ağırlığına eşit ve ondan daha fazla olmak suretiyle iki değişik yöntemle yapılmıştır. Taze karışımların normal kıvam, priz süresi, su ihtiyacı, akma, çökme, hava içeriği, birim ağırlığı ve sertleştikten sonra dayanımı, puzolanik aktivite indeksi, elastiklik modülü, sülfat direnci, büzülme ve karbonasyon özelikleri incelenmiştir.

90 adetten fazla çimento hamuru numunesi, 750'nin üstünde harç numunesi ve 600'ü aşkın beton numunesi üzerinde yapılan deneyler sonucu, Tunçbilek ve Soma-B küllerinin,çimentonun %40 oranında kullanıldıklarında bile, PÇ-UK sistemlerinin bir çok özeliğini iyi yönde etkiledikleri saptanmıştır. Bununla birlikte, Afşin-Elbistan ve Seyitömer külleri yüksek dozda kullanıldığı takdirde PÇ-UK'nın bir çok özeliğini olumsuz yönde etkilemektedir.

Tezin birinci bölümünde uçucu külün Türkiye ve dünyada üretimi ve tüketimi hakkında genel bilgi verilmiş ve çalışmanın amaç ve kapsamı açıklanmıştır. Portland çimentosunun yapısı ve hidratasyonu, puzolanların ve uçucu küllerin yapısı ve sınıflandırılması, ayrıca uçucu külün PÇ-UK sistemlerini etkileme mekanizmalarından 2. ve 3. bölümlerde bahsedilmiştir. Uçucu külün betonun değişik özeliklerine olan etkisi hakkında daha önce yapılmış olan araştırmaların sonucu dördüncü bölümde yer almıştır. Araştırmanın deneysel programı ve yapılan test ve analizler beşinci bölümde verilmiştir. Deney sonuçları ve bunların tartışması, varılan sonuçlar ve gelecekteki araştırmalar için öneriler sırasıyla altıncı, yedinci ve sekizinci bölümlerde sunulmuştur.

Anahtar kelimeler: Uçucu Kül, Portland Çimentosu-Uçucu Küllü Sistemler, Su İhtiyacı, Priz Süresi, Hidratasyon Isısı, Dayanım, Puzolanik Aktivite İndeksi, Elastiklik Modülü, Sülfat Direnci, Büzülme, Karbonasyon.

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CHAPTER I

INTRODUCTION

1.1 General

During the generation of electricity in coal-burning thermal power plants, as pulverized coal passes the high temperature zone of the furnace, the carbon and volatile matter are burned off; whereas, the mineral impurities deposited in the coal during its formation fuse and remain in suspension in the flue gas. Some of the mineral matter agglomerates to form bottom ash and the remaining is transported from the firebox by flue gas stream to form fly ash. Fly ash is subsequently removed from flue gas by mechanical separators, electrostatic precipitators, or by bag filters.

Since fly ash is a condensation product from droplets of molten coal, it is typically spheroidal, with individual particles ranging from less than 1μm to greater than 1mm. The granulometry of the particles of any particular fly ash is greatly affected by the fineness to which parent coal is ground, by the operating condition of the power plant, and by the type of the dust collection system.

There is a wide variation in the chemical compositions of fly ashes which is mainly governed by the source of the coal. Low-lime fly ashes, (<10% CaO content) usually formed by the combustion of anthracite or bituminous coal, consist of 45-65% SiO_2, 20-30 % Al_2O_3, 4-20 % Fe_2O_3. etc. On the other hand, high-lime fly ashes, (>10% CaO) formed by the combustion of subbituminous coals or lignite, typically contain 20-50% SiO_2, 15-20% Al_2O_3, 15-30 % CaO, 5-10% Fe_2O_3.

Owing to their fine particle size and generally non-crystalline character, fly ashes usually show satisfactory pozzolanic property, or in the case of high-lime fly ashes, both pozzolanic and cementitious properties. In other words, fly ashes possess no or some cementitious value when mixed with water alone, but in the presence of moisture, at ordinary temperatures, they may chemically react with calcium hydroxide to form cementitious compounds.

In fact, fly ash is used in concrete primarily for its pozzolanic and cementitious properties which contribute to strength gain and durability improvement. Direct economic factors caused by energy conservation, and increasing awareness of the need to protect the environment coupled with the modification of certain properties of fresh and hardened concrete are major reasons for using fly ash in portland cement concrete.

The suitability of coal ash as a pozzolanic ingredient for use in concrete was recognized as early as in 1914. However, the first data on its use in concrete was reported in 1937 by Davis and his associates [1]*. Considerable pioneering and developmental work in this field was conducted throughout 1940s and 1950s, particularly in mass concrete. During this period, usefulness of low-lime fly ash, the only available type at that time, was established [2].

The energy crisis of the 1970s led to the greater use of coal particularly low-rank coal (i.e. subbituminous and lignite containing calcium compounds in their incombustible fractions) to fire power plants. Concurrent with the availability of different fly ashes, a great deal of research aimed at understanding the properties of portland cement-fly ash (PC/fa) systems has been undertaken. During the last ten years a relatively large number of publications dealing with the subject have appeared. For example the proceedings of Second, Third and Fourth International Conferences on Fly Ash, Slag, Silica Fume, and Natural Pozzolans contain more than 250 papers in three Special Publications of the ACI (SP-91, SP-114 and SP-132). In addition to numerous research papers that are routinely published in technical journals, there are at least four books [3-6] and two committee reports [7,8] which attempt to cover the state of the art in a comprehensive manner.

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* Numbers in brackets refer to the reference numbers.

The 1984 production and utilization rates of fly ash in various countries are given in Table 1.1[8]. A comparison between the 1984 and 1980 statistics shows that, in some countries the annual rates of fly ash being produced and used in the cement and concrete industries have remained fairly stable. In various countries, the rate of fly ash utilization as a pozzolan vary from a high of about 20% to a low of about 1% [10], which is far lower than the value that can be efficiently utilized. In general, poor quality and lack of uniform composition are reported as the primary reasons for low utilization rates of fly ash. With a better understanding of technical requirements for satisfactory performance of fly ash in concrete, followed by development of proper test methods and specifications, it seems that the utilization rate of fly ash can be much higher than the present value.

The fly ash production in Turkey, from 15 different power plants was around 13.5 million tons in 1991 [11]. However, the current use of it is negligibly small [11,12]. The fly ash rate of production and utilization figures in Turkey in 1991 are given in Table 1.2.

Table 1.1. Annual Production and Utilization Rates of Fly Ash as a Pozzolanic Admixture in Various Countries in 1984 [8]

Country	Fly Ash Production ($t\times10^6$)	 Utilization (%)
Australia	3.5	7.2
Canada	3.3	24.2
China	35.0	20.6
Denmark	1.0	45.0
France	5.1	29.4
Germany	2.6	76.9
India	19.0	2.6
Japan	3.7	13.5
Netherlands	0.5	60.0
South Africa	12.9	0.8
Sweden	0.1	20.0
U.K.	13.8	9.4
U.S.A.	47	10.6

Table 1.2. Annual Production and Utilization Rates of Fly Ash in Turkey in 1991 [11]

Power Plant	Fly Ash (10^3 x tons)		
	Production	Utilization	
		1989	1990 (May)
Afşin-Elbistan	2434	-	-
Çatalağzı (A)	130	-	-
Çatalağzı (B)*	704	-	-
Çayırhan	420	-	-
Kangal *	576	-	-
Kemerköy*	1824	-	-
Orhaneli*	431	-	-
Seyitömer	980	-	-
Seyitömer IV.Group*	440	-	-
Soma (A)	84	14	3
Soma (B)	1312	-	-
Soma(B)V.VI.Group*	1248	-	-
Tunçbilek	607	1.4	0.3
Yatağan	1075.2	17.9	4.7
Yeniköy	1135.2	-	3.67

* These power plants are under construction and the values given are estimates

1.2 Object and Scope

Although the actual statistics from some countries are not available, it seems that the current worldwide fly ash utilization, despite the increasing trend toward its expanded use, is still less than 15% for all purposes. It is, thus, obvious that finding storage or disposal sites could become a serious problem unless the use can be increased significantly. In this way, it is possible to minimize or eliminate disposal costs and the area reserved for disposal to create financial returns from by-product sales and to replace some scarce or expensive natural resources.

Nowadays, fly ash is mostly used in fills and embankments. Problems associated with such use are different from the problems accompanied with marketing fly ash as a suitable pozzolanic ingredient for concrete; because, in the latter case, fly ash must perform as a reactive ingredient without harming concrete. Therefore, considerably more testing and monitoring of its characteristics is required as compared to other uses.

The object of this study was to determine the possibilities of the use of four fly ashes produced in Turkey as an ingredient in concrete and monitoring the effects of them on various properties of cement, mortar and concrete. For this purpose, three high-lime fly ashes obtained from Afşin-Elbistan, Seyitömer, and Soma(B) thermal power plants, and a low-lime one produced in Tunçbilek power plant were used. The fly ash production in these power plants accounts for approximately 40 % of the total fly ash production in Turkey. Fly ash substitution level ranged from 10% up to 40 % by weight of cement. Fly ash inclusion was adapted by both simple replacement method (i.e. replacing a known amount of cement with the same amount of fly ash) and by additional replacement method (i.e. the weight of added fly ash was two times or four times that of the removed cement). The effects of fly ashes on various physical and mechanical properties and durability characteristics of portland cement-fly ash systems containing various proportions of the ashes were compared with those of non-fly ash bearing counterpart materials.

CHAPTER II

MECHANISMS BY WHICH FLY ASHES MODIFY PORTLAND CEMENT SYSTEMS PROPERTIES

The incorporation of mineral admixtures in general and fly ash in particular in concrete leads to general improvement in most properties of concrete, provided that the process by which the properties improved are clearly understood, and a conscious effort is made in concreting practice to promote these processes. It is necessary to note that most of the improvements stated are based on the knowledge accumulated on low-lime fly ash incorporation.

The process by which fly ash is able to improve the rheological behavior of fresh concrete, and the engineering properties of hardened concrete are both physical and physico-chemical [9]. The physical effect is simply obtained by densely packing very fine particles of the fly ash between the relatively larger particles of the fine aggregate and cement resulting in a reduction in both water content and the size of the voids in fresh cement systems with a subsequent reduction in bleeding and segregation. Fly ash also contributes to pore refinement process by reducing the flocculation tendency of the cement grains and making a better dispersion of them in water-cement systems. In this regard, Helmuth reported that like conventional dispersing agents, the particles of fly ash are able to disperse a flocculated cement-water system and therefore will act as a water-reducer [14]. In deed, depending on the inclusion level, and particle size characteristics and mineralogical character, some fly ashes, may themselves require the application of a powerful dispersing [9]. Therefore, for the benefits to be realized from the fine grain size of the fly ash, the mere inclusion of the additive into cement systems is not enough. The additive must be well dispersed, with or without the aid of a conventional plasticizing agent, and by thorough mixing of concrete.

The effectiveness of the physical and chemical processes responsible for strengthening microstructure, and therefore the engineering properties of the hardened cement systems, is again largely dependent on the uniform distribution of fly ash particles throughout the mix. Two of these processes which are slow and take a long time to manifest may be highlighted as: (a) very fine particles of the fly ash not only result in pore refinement by physical densification effect but also cause an acceleration of cement hydration reactions, (b) the hydration reactions of pozzolanic and/or cementitious additive lead to further pore refinement, and also to grain refinement in the hydrated cement paste as well as in the interface between the cement paste and coarse aggregate in concrete. Since it is the aggregate-matrix interface that governs most of the important properties of concrete, such as strength, elastic modulus and permeability the beneficial effects of fly ashes cannot be fully demonstrated by determining their influence on the engineering properties of cement pastes and mortars. This is why Mehta [9] believes that direct tests with concrete mixtures are necessary to assess the effect of the mineral admixtures on concrete properties.

On the other hand, in spite of some researchers who underrate the chemical effects associated with pozzolanic and/or cementitious character of fly ash on the ultimate engineering properties of concrete, a relatively lower early strength and higher later strength of fly ash-cement systems with respect to cement systems show this effectiveness. Besides, the so called chemical effect can be observed by the influence of curing temperature which causes more than a proportional increase in the reaction rate and subsequent properties of concrete containing fly ash [7].

In the light of above discussion it seems that, a brief review of the physics and chemistry of portland cement and pozzolans along with their hydration and pozzolanic reaction processes will be helpful in understanding the mechanism by which the fly ashes are able to improve the properties of portland cement-fly ash systems, although there are still numerous vague points and uncertainties about these reactions.

2.1 Portland Cements

Cements for constructional purposes, can be described as siliceous and calcareous materials capable of bonding mineral fragments, stones, bricks or blocks to a compact whole. The cements of interest in making concrete have the property of setting and hardening under water, therefore, called hydraulic cements. Portland cements are one of the major types of hydraulic cements.

Portland cement is manufactured by clinkering an intimate mixture of calcareous and argillaceous materials, and grinding the resulting material with a small amount of gypsum to have particles ranging in size from 0.5 to 80μm and a Blaine specific surface area from 2400 to 5000 cm^2/g. Portland cement is mainly composed of crystalline minerals of calcium silicates and aluminates. The rheological behavior of fresh cement systems (i.e. consistency, cohesiveness, bleeding and segregation), and the engineering properties of hardened cement systems (i.e. strength, elastic modulus, impermeability, and durability) are controlled to a considerable degree by the relative proportions of the major compounds and by fineness of cement as well as the curing conditions.

2.1.1 The Constitution of Portland Cement

The raw materials fed into the cement kiln consist mainly of lime, silica, alumina, and iron oxide. These oxides interact with each other to form a series of more complex compounds, so that by applying a suitable rate of cooling, apart from a small residue of uncombined lime which has not sufficient time to react, a state of equilibrium is reached [15].

Four major compounds, tricalcium silicate (C_3S)*, dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF), are formed along with some minor compounds which amount to not more than a few percent of the weight of cement. In commercially available portland cements the compounds occur rarely in pure forms [15].

In C_3S, ions of Mg or Al may substitute Ca at random points. For this reason, the mineral name "alite" is preferred to tricalcium silicate [17].

C_2S may also occur in several polymorphic forms depending on the temperature level. Among them only β-C_2S, named as "belite" which is preserved in the clinker at the rates of cooling the commercial cement, has cementitious properties [16].

C_4AF, which really is not a compound, typifies a solid solution of composition lying between C_6AF_2, to C_6A_2F, but the description C_4AF is a convenient simplification [17].

The most common calcium aluminate phase in the portland cement is C_3A. However, depending on the alumina and lime contents of the raw materials, and on the clinkering temperature during cement production, other forms of it, such as $C_{12}A_7$ or C_5A_3 may occasionally be present [17].

Although the cement compounds do not exist as simple oxides, for the sake of simplicity, the results of the chemical analysis of portland cements are traditionally reported in terms of oxides of the elements present. A general idea of the composition of cement can be obtained from Table 2.1 which gives the oxide composition limits of portland cements [15].

---

* C, S, A and F denote CaO, SiO_2, Al_2O_3 and Fe_2O_3, respectively.

As it can be seen from Table 2.1, the amount of various oxides present only change between somewhat restricted limits. However, a relatively small change in the analytical composition of cement alters the compound content in a wide range with a consequent change in the properties of cement [17]; indeed, different types of cements are obtained by suitable proportioning of the raw materials.

Table 2.1. Approximate Composition Limits of Portland Cement [15]

Oxide	Content (%)
CaO	60-67
Si_2O	17-25
Al_2O_3	3-8
Fe_2O_3	0.5-6.0
MgO	0.1-4.0
Alkalis	0.2-1.3
SO_3	1-3

In spite of various uncertainties involved, the potential compound composition can be calculated, for assumed idealized conditions, by using "Bogue's equations" [15,16,17]. In addition to the computation method, the actual compound composition of cement can be determined by microscope examination of powder penetration and their identification by the measurement of the reactive index. Another method makes use of X-ray powder diffraction to identify the crystalline phase and also to study the crystal structure of some of the phases. Another development in estimating the compound composition of cement is aided by the use of the electron microscope which produces a high magnification by employing an electron beam instead of light waves [15]. The oxide and relevant compound compositions of a typical portland cement are given in Table 2.2.

Table 2.2. Oxide and Compound Compositions of a Typical Portland Cement [15]

Oxide composition (%)		Calculated compound composition Using Bogue's equation (%)	
C	63	C_3S	54.1
S	20	C_2S	16.6
A	6	C_3A	10.8
F	3	C_4AF	9.1
M	1.5	Minor	
$\bar{S}$	2	Compounds	-
N+K	1		
Others	1		
LOI	2		
IR	0.5		

C: CaO, S: SiO_2, A: Al_2O_3, F: FeO, M: MgO, $\bar{S}$: SO_3 K: K_2O, N: Na_2O, LOI: Loss on ignition, IR: Insoluble residue

2.1.2 Hydration of Portland Cement

Although there are several different theories related with the hydration of cement, the most relevant and generally accepted one is as follows: the anhydrous cement compounds when come into contact with water begin to ionize and form hydrated products of low solubility which precipitate out of the solution to deposit into previously water-filled spaces. Since the hydration products have a lower density as compared to the anhydrous minerals, the formation and deposition of them lead first to a progressive decrease in porosity with a subsequent increase in strength and impermeability as shown in Figure 2.1[10]:

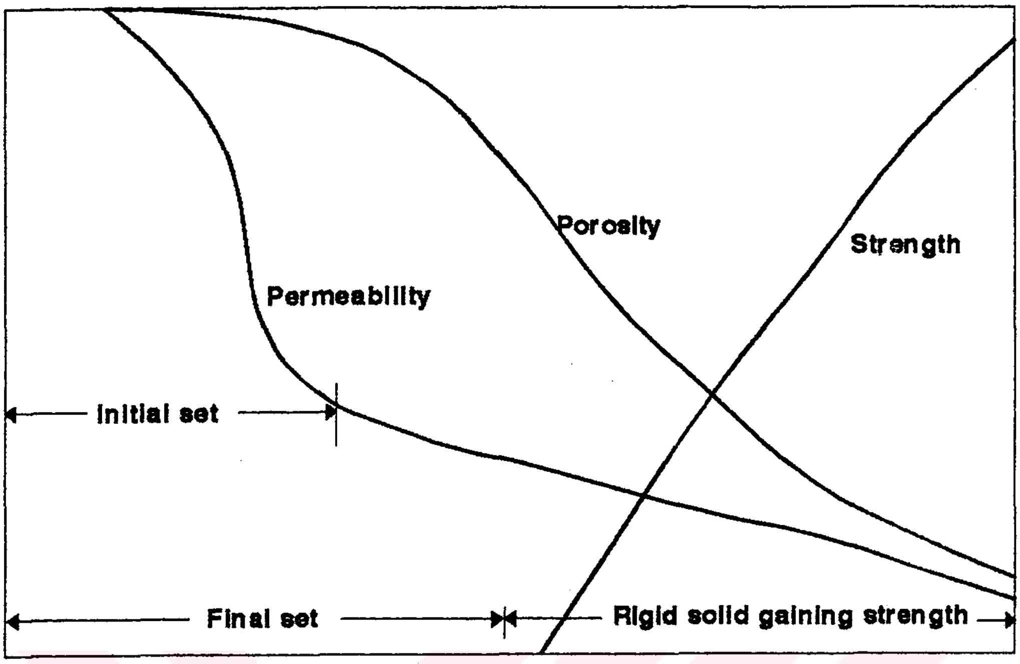


Figure 2.1. Change in Physical and Mechanical Properties of Portland Cement with Hydration [10]

The series of the reaction of cement with water is referred to as hydration process. The process is a complex one and does not proceed to completion. The complexity arises not only from the presence of several different compounds undergoing hydration simultaneously, but also from the interaction of the hydration products with one another and the physical nature of the products [16, 17].

Many attempts have been made to monitor the hydration reaction under the electron microscope. In spite of misgivings over the interpretation of observations, it is possible to distinguish four critical stages in the hydration process and formation of cement gel as shown diagrammatically in Figure 2.2 [18]:

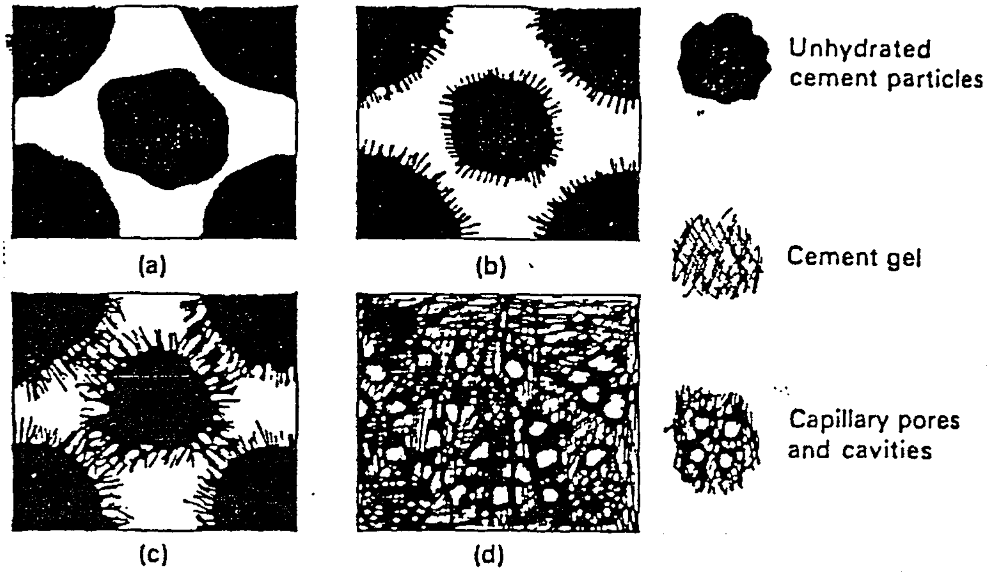


Figure 2.2. Diagrammatic Representation of the Cement Hydration Development [18].

a) Immediately after mixing, cement grains become dispersed in the mixing water, the interparticle spacing being determined by water-cement ratio. Sufficiently higher surface area of cement particles, within the range of practical water-cement ratios, prevent them from settling down and causing bleeding.

b) After a few hours, the paste loses some of its fluidity but can still be shaped. At this stage, the rods of ettringite are formed at the surface of particles. Meanwhile, the crumpled foils and needle like structure of calcium silicate hydrates are accumulated on the surface of cement grains and in the intergranular water, respectively.

c) After a day, cement paste sets but it has no real strength. The hydration on the surface improves further outwards and inwards. The hydrates in the intergranular space grow and become interconnected, forming a continuous solid skeleton which is further reinforced by C_3A and C_4AF hydration products and large crystals of CH.

d) After 7 days, although hydration reactions are not complete, the paste acquires considerable strength. The skeletal structure becomes denser and develops further by infilling original hydration link. However, some unfilled capillary pores and some unhydrated cement grains remain in the system. Nor are they ever likely to be [18].

The microstructure of the hydrated cement paste is more or less similar to those of silicate phases and a direct correlation may be made between the hydration of cement and that of pure C_3S. It is known that a thin film of C_3S hydration products get deposited on the surface of unhydrated own grains, resulting in a so called induction or dormant period of inactivity [16, 17, 19]. This leads to the hydration of aluminate phase to occur earlier than the silicate phase.

A simplistic view of the behavior and hydration of four major compounds are represented below to provide some idea about the composition of the hydrated products.

The C_3A is characteristically a fast-reacting compound with water and after passing through intermediate compositions such as C_4AH_{14}, C_2AH_{18}, reaches to a stable cubic crystalline form in which six molecules of water are taken up [17].

$$C_3A + 6H \Rightarrow C_3AH_6 \quad (2.1)$$

This rapid reaction leads to an immediate stiffening (i.e. flash setting) without strength development, since C-A-H phase prevents the hydration of C_3S and C_2S [19]. However, some of the gypsum ground in the clinker dissolves immediately in water and sulfate ions in the solution react with C_3A to form insoluble calcium sulfoaluminate hydrate often referred to as ettringite. Ettringite deposits on the surface of C_3A to form a protective colloidal membrane and thus retards the direct hydration reaction.

$$C_3A + 3C\bar{S}H_2 + nH \Rightarrow C_6A\bar{S}_3H_{32} \quad (2.2)$$

Ettringite is usually the first product to precipitate out of the system and is mostly responsible for the initial set and early strength development [10]. Lime may also take part as well as water in C_3A hydration:

$$C_3A + CH + nH \Rightarrow C_4AH_{19} \qquad (2.3)$$

Subsequently, depending on the availability and reactivity of the sulfate, alkali and aluminate bearing phases in the cement, either a monosulfate hydrate ($C_4A\bar{S}H_{18}$) or a mixture of monosulfate and calcium aluminate hydrate (C_4AH_{19}) may also form [10].

$$C_3A + C\bar{S}H_2 + nH \Rightarrow C_4A\bar{S}H_{18} \qquad (2.4)$$

Usually sufficiently added gypsum is consumed within 24 hours of mixing. After that straightforward hydration reaction takes over [18].

Although C_3A , acting as a flux, reduces the temperature of the kiln and facilitates the formation of calcium silicates, it is not desirable in cement due to its little contribution to strength and high susceptibility to sulfate attack [15]. It also evolves the largest heat of hydration [15, 17].

The rate of reaction of calcium aluminoferrites, typified by C_4AF, with water increases with the proportion of alumina in the aluminoferrite; therefore, hydration of C_4AF in portland cement is somewhat slower than C_3A [10, 17]. The straightforward hydration reaction of C_4AF is in doubt [18], but in some cases C_3AH_6 and C_3FH_6 may be formed [17]. However, it has been suggested that, like C_3A, lime and gypsum may take part as well as water in its hydration to form iron analogous of ettringite, monosulfate and calcium aluminate hydrates [10, 18].

$$C_4AF + 3C\bar{S}H + nH \Rightarrow C_6A(F)\bar{S}_3H_{32} \qquad (2.5)$$

$$C_4AF + C\bar{S}H + nH \Rightarrow C_4A(F)\bar{S}H_{18} \qquad (2.6)$$

$$C_4AF + CH + nH \Rightarrow C_4A(F)H_{19} \Rightarrow C_3AH_6 + C_3FH_6 \qquad (2.7)$$

There is a contradiction in C_4AF contribution to strength of hardened cement paste. Some of the researchers claim that, all of the reaction products of aluminum-sulfate iron analogous are capable of contributing strength [10]. However, others believe that, these products as well as hydration products of C_3A contribute little or nothing to the strength development of hardened cement paste [15,18].

In addition to above mentioned hydration products, C_3A and C_4AF hydrations result in the formation of various other compounds or solid solutions, such as hydrates of calciumferrite and calcium aluminate. C-A-S and C-F-S collectively referred to as hydrogarnets, after a natural mineral, may also be formed.

The hydration reactions of tri-ordi-calcium silicates can be shown as [10]:

$$C_3S \text{ and } C_2S + nH \Rightarrow C\text{-}S\text{-}H + CH \qquad (2.8)$$

The products of hydration of these compounds are C-S-H gel of a lower basicity with a C/S ratio between 1.5-1.8, depending on the free calcium hydroxide content [15,17]. There exists a considerable uncertainty as to whether C_3S and C_2S result in the same hydrates [15]. However, there is a strong evidence that, the ultimate hydration product of C_2S has a C/S ratio of 1.65 [15], closely similar to that of C_3S [17]. The difference between C/S ratio of early hydration products of calcium silicates may be arisen from lower rate of reaction of C_2S. Furthermore, temperature may affect the hydration products of silicate compounds, as the permeability of gel is affected by temperature.

The C-S-H gel is highly cementitious and constitutes about 60 to 65 % of the total solids in a fully hydrated cement system. On the other hand, CH forming about 20% of the silicate minerals hydration products, contributes little to the cementitious properties of the system. Furthermore, being more alkaline and soluble than other hydration products, it is readily attacked by water and acidic solutions, thus reduce the durability of portland cement systems to such environment.

As to summarize, at any stage of hydration, the hydrated paste consists of hydrates of various compounds, referred to as gel, of crystals of CH, some minor components, unhydrated cement, and the residue of previously water filled spaces, named as capillary pores. However, the relative amounts of so called hydration products change in time as shown in Figure 2.3.

The effect of the interaction of cement compounds and their hydration products on the rate of hydration of major compounds are shown in Figure 2.4 and Figure 2.5.

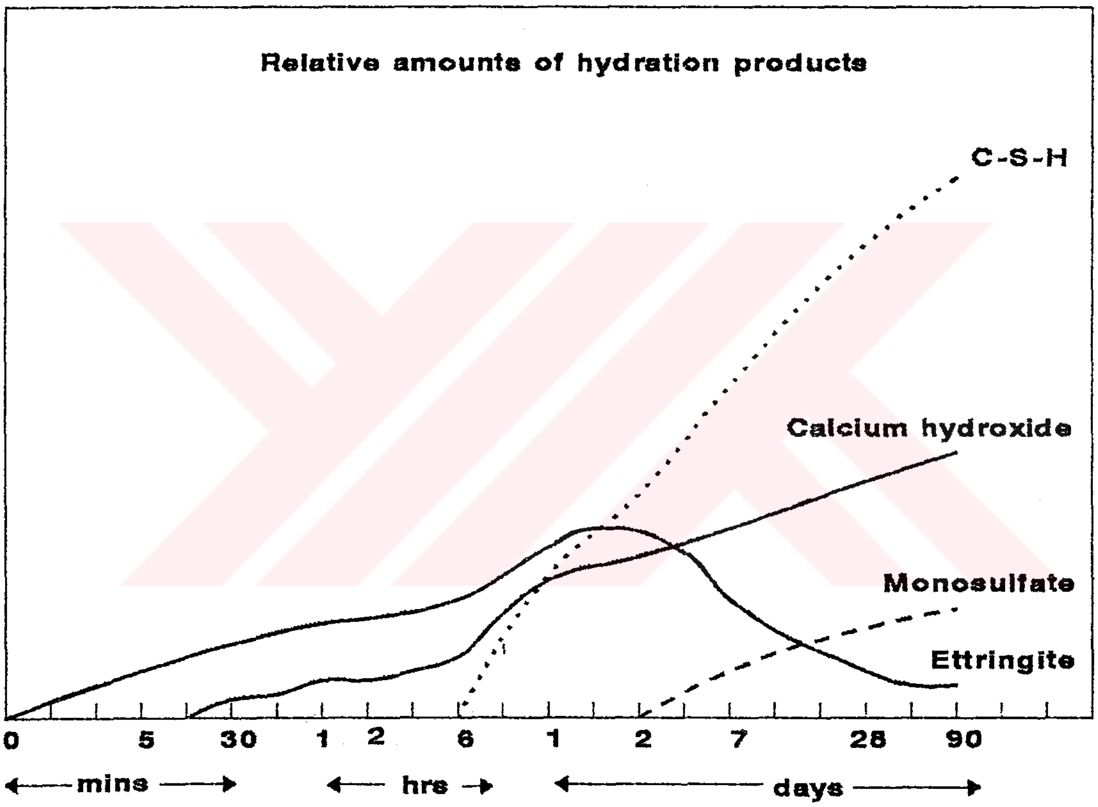


Figure 2.3. Changes in the Relative Amounts of Hydration Products in Time [10]

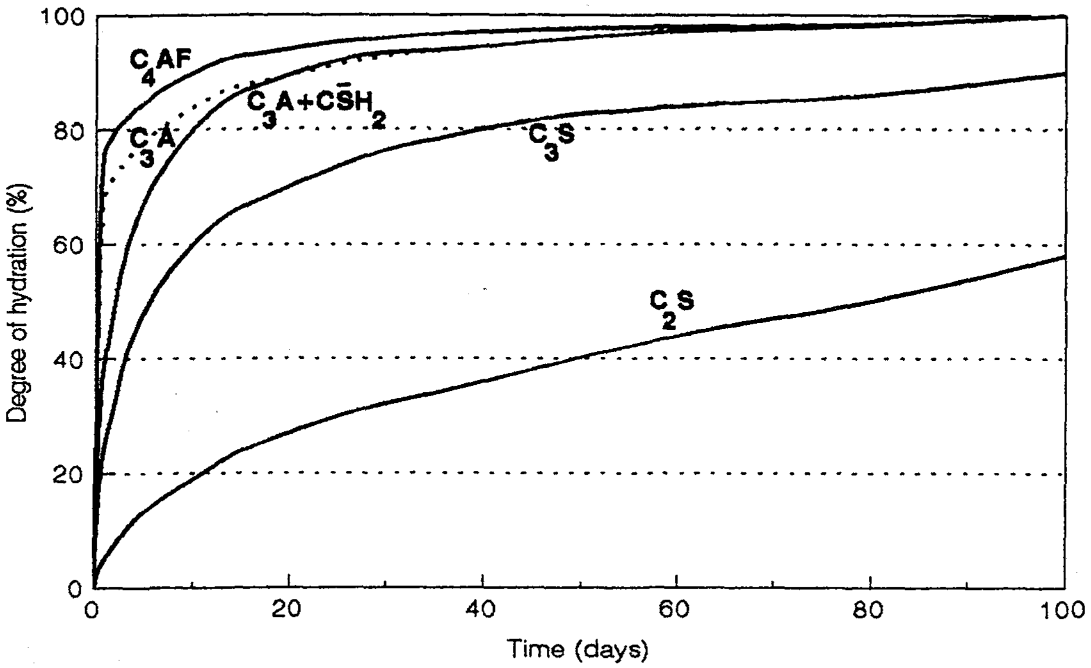


Figure 2.4. Rate of Reaction of Pure Cement Compounds [19]

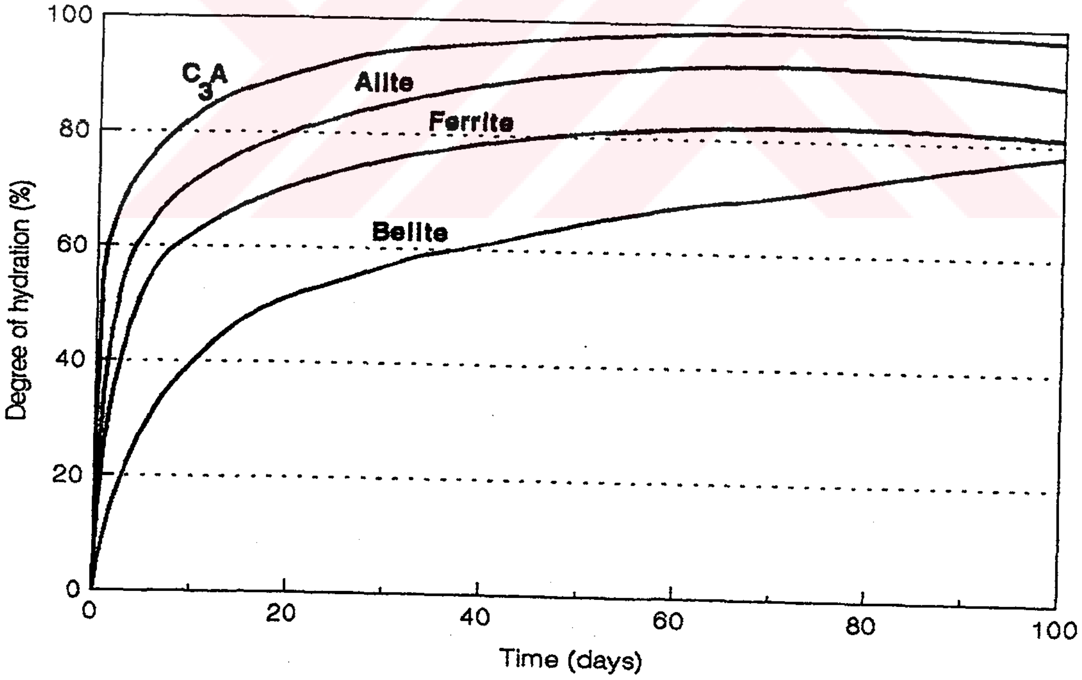


Figure 2.5. Rate of Hydration of Major Compounds in a Portland Cement [17]

2.2 Pozzolans

Portland cement minerals are not the only source of the cementitious compounds. There are many other natural and industrial materials capable of providing cementitious components, such as hydrates of calcium silicates, calcium sulfoaluminates, calcium aluminates, calcium aluminoferrites, and calcium sulfoaluminate ferrites. In fact, before the advent of the portland cement, mixtures of lime and volcanic ashes or calcined clays were employed as hydraulic cements for making mortars and concretes. These materials, which are mainly siliceous and aluminous, are called "pozzolans" and their reaction with lime, which is slow at ordinary temperature, is called "pozzolanic reaction".

According to ASTM C 595 "Standard Specification for Blended Hydraulic Cements" [20], a pozzolan is defined as "a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties".

Indeed, not all siliceous and aluminous materials are pozzolanic. It is known that, crystalline minerals, for instance silica as quartz, alumina as corundum, and aluminosilicates such as sillimanite (SA), and mullite (S_3A_2) are not lime combining materials at room temperature. Siliceous and aluminous materials may show pozzolanic properties when they are in divided and non crystalline form. Therefore, for the purpose of evaluating the mineral admixtures for use in cement and concrete, it is not the chemical composition of the mineral admixture, but its specific surface area and mineralogical composition which determine the rate of providing silica and alumina for reactions with lime released by decomposition of C_3S and C_2S [10].

2.2.1 Nature and Classification of Pozzolans

As it was mentioned earlier, the generic term "pozzolan" is used to describe materials which exhibit reactivity with lime and which set, harden and develop strength in the presence of water. However, due to wide variety of origin, structure, chemical and mineralogical compositions of these materials, Sersale [21] and Massazza [22] have expressed reservations in the use of word "pozzolan" as quoted by Swamy [4]. It is probably more correct to refer to these materials as mineral additives. Accordingly, classes of mineral additives would include natural pozzolans, calcined clay and shales, fly ash, silica fume, and ash from agricultural residues. However, since conventional use of the term pozzolan still prevails, it is also used in this study. Sersale, in general sense, taking into account the origins of the lime-combining materials, classifies them into natural and artificial groups [21].

One of the first classifications of natural pozzolans was proposed by Mielenz et al [23]. In this classification system, according to the activity type, natural pozzolans were divided into 5 groups and 5 subgroups ranging from volcanic glass to hydrated oxides of alumina as shown in Table 2.3.

In this classification types 1,2 and 4 are natural pozzolans and types 3 and 5 show lime combining property but are considered pozzolanic after they have been calcined [4]. A more recent classification has been proposed by Massazza as shown in Figure 2.6 [4].

In this classification natural pozzolans are divided into three main groups. The first group, pyroclastic rocks, are formed by violent ejection of the molten magma and its subsequent rapid quenching to produce a glassy material containing entrapped gas bubbles. Therefore, the chemical composition of these materials is dependent on the composition of the ejected magma. With respect to mineralogy, Sersale [25] notes that the quality of these pozzolans seems to be associated with a composition containing alkali feldspars in preference to anorthite, since the glassy phase decreases with an increase in the amount of anorthite.

The second group of natural pozzolans in Massazza's classification comprises altered materials with a high silica content. These pozzolans are formed by deposition of materials of different origins in stagnant water, leaching of the soluble oxides and chemical conversion to produce a generally light-colored and porous rock. These materials are generally mixed with clay, which reduces their pozzolanicity [4].

Table 2.3. Classification of Natural Pozzolans [4]

Activity Type	Essential Active Constituent
1	Volcanic glass
2	Opal
3a	Kaolinite-type clay
3b	Montmorillonite-type clay
3c	Illite type clay
3d	Mixed clay with vermiculite
3e	Attapulgite type clay
4	Zeolites
5	Hydrated oxides of alumina

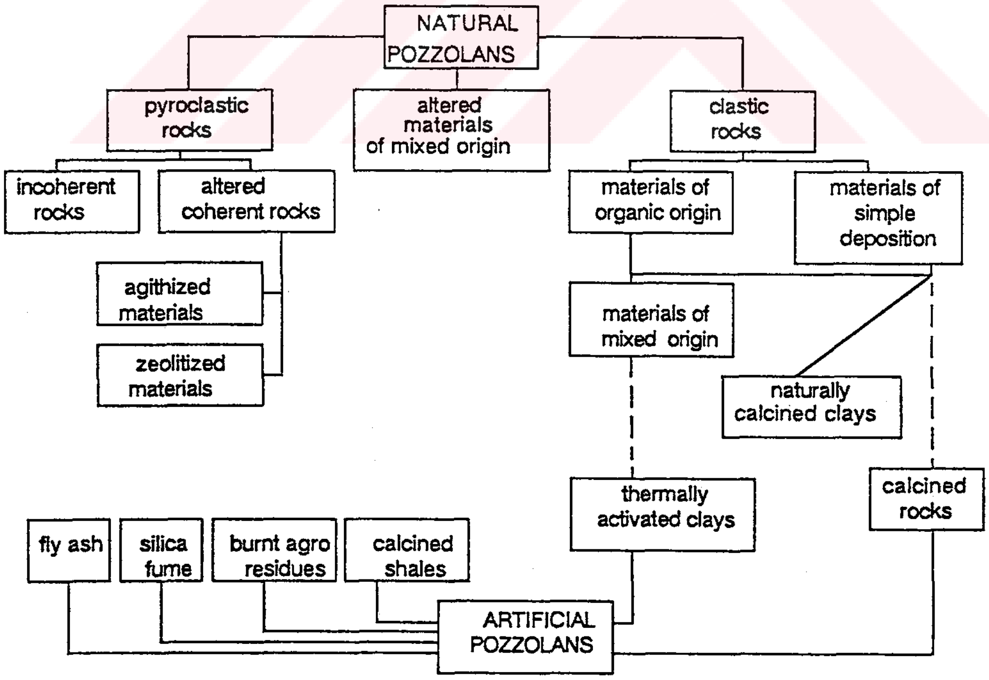


Figure 2.6. Classification of Pozzolanic Materials

The last group of natural pozzolans are of clastic origin including the clays and diatomaceous earths. It is well known that, clay can be fixed with lime to impact strength and stability but, due to the lack of pozzolanic activity, strength development is sufficiently small to preclude their use as a portland cement replacement. In fact, in this process clay minerals are not destroyed but are transformed by lime. However, calcination at appropriate temperature conditions can significantly promote the pozzolanicity of clay. Diatoms are siliceous organic residues with high silica content more frequently mixed with clay and other sediments. Diatomaceous soils can exhibit pozzolanic characteristics either before or after grinding, but due to the presence of clay, the soil needs calcination to show adequate pozzolanicity. Although calcined diatomaceous clays are used in construction of several dams [26] in 1950s, their exploitation for cement replacement is not extensive. Swamy has quoted Lea's view that, diatoms because of skeletal nature, increase the water demand of the mixes significantly resulting in a consequent disproportional strength reduction [4].

Artificial pozzolans or siliceous by-products, on the other hand, has been classified into five groups by Mehta on the basis of their cementitious or pozzolanic activity when used in combination with portland cement [9]. Mehta's proposal which has been approved by RILEM Technical Committee on the use of siliceous by-products in concrete [8] is given in Table 2.4 [9].

According to this system of classification, the cementitious mineral admixtures, to which some high calcium fly ash (> 20% CaO) and rapid-cooled blast furnace slag belong, essentially consist of fine particles of silicate glass considerably modified by calcium, magnesium and aluminum ions. Relatively small amounts of activators, such as portland cement, alkalies or gypsum are needed to accelerate the hydration and rate of strength gain of this class of mineral admixture.

The second category to which high-calcium fly ashes with 10-20% CaO belong, are partly cementitious and partly pozzolanic because of the non-uniformity of glassy phase. It is possible that, a part of

Table 2.4. Classification, Composition, and Particle Characteristics of Siliceous By-Products Used as Mineral Admixtures in Cement and Concrete Industries [9]

Classification	Chemical and Mineralogical Composition	Particle Characteristics
I. Cementitious Rapidly-cooled blast furnace slag	Mostly silicate glass contaninig calcium, magnesium, and aluminum. Crystalline compounds of melili group and merwinite may be present in small quantities.	Unprocessed material is granular or pelletized and contains 5 to 15% moisture. Before use it is dried and ground to particles mostly less than 45µm (400 to 500 m^2/kg Blaine). Particles have rough texture.
II. Cementitious and Pozzolanic High-calcium fly ash (> 10% CaO)	Mostly silicate glass* containing calcium, magnesium, and aluminum. The small quantity of crystalline matter present generally consists of quartz and C_3A; free lime and periclase may be present; $C\bar{S}$ and $C_4A_3\bar{S}$ may be present in the case of high-sulfur coals. Unburnt carbon is usually less than 2%.	Powder corresponding to 10-15% particles larger than 45µm (usually 300-400 m^2/kg Blaine). Most particles are solid and spheroidal with less than 20 µm diameter. Particle surface is generally smooth but not as clean as in low-calcium fly ash.
III. Highly Pozzolanic a. Condensed silica fume	Consist essentially of silica in non-crystalline form.	Extremely fine powder consisting of solid and spheroidal particles mostly less than 0.1µm diameter (about 20000 m^2/kg surface area by nitrogen adsorption).
b. Rice hust ash profduced by controlled incineration	Consist essentially of silica in non-crystalline form.	Particles are generally less than 45µm but they are highly cellular (about 60000 m^2/kg surface are by nitrogen absorption).
IV. Normal Pozzolanic Low-calcium fly ash (< 10% CaO)	Mostly silicate glass containing aluminum, and iron. The small quantity of craytalline matter present consists generally of quartz, mullite, hematite, and magnetite. Urburnt carbon is usually less than 5% but at times may be up to 10%.	Powder corresponding to 15-30% particles larger than 45 µm (usually 250-300 m^2/kg Blaine). Most particles are solid and spheroidal with average 20 µm diameter. Cenospheres and plerospheres may be present.
V. Others a. Slowly-cooled blast furnace slag b. Bottom ash, boiler slag, field-burnt rice hust ash.	Consist essentially of crystalline silicate minerals, and relatively small amount of non-crystalline matter.	The materials must be pulvarized to very fine particle size in order to develop satisfactory cementiticus or pozzolanic activity. Ground particles are rough in texture.

In fly ashes containing more than 20% CaO, the composition and reactivity of the glass are much different than the glass in low-calcium fly ash; the glass in high-calcium fly ash is more reactive.

the glass is essentially an aluminosilicate glass whereas, the remainder is a silicate glass, containing large amounts of calcium and magnesium.

By-products such as, low-calcium fly ashes, which consist mostly of silicate glass modified with aluminum and iron, are categorized as normal pozzolans. Compared to calcium-magnesium substituted silicate glass, the aluminum-iron substituted one appears to be less reactive.

The fourth group categorized as highly pozzolanic consist essentially of glassy silica exhibiting great pozzolanic activity. Condensed silica fume and controlled-burnt rice husk ash belong to this group.

The last category contains mineral admixtures of low reactivity, such as slowly cooled blast furnace slag and bottom ash, which must be sufficiently pulverized to very fine particles in order to develop acceptable levels of strength in combination with portland cement.

2.2.2 Pozzolanic Activity

The reaction of pozzolans with calcium hydroxide under moist conditions is referred to as pozzolanic reaction. The activity of a pozzolan with lime is related to some inherent characteristics of the pozzolan, such as vitreous compound content and fineness as well as, some external factors, such as presence of admixtures and thermal treatments.

It is necessary to mention that, pozzolanic reaction in cement or concrete is not merely a lime-silica interaction and includes all cementitious reactions in the system CaO-SiO_2-Al_2O_3-SO_3-H_2O. Therefore, the difference between pozzolanic reaction and cementitious reactions in the hydration of portland cement lies mainly in the reaction rates, not in the character of the hydration products [10].

Several investigators have studied the mechanism of pozzolanic activity [17, 22, 27]. The results are somewhat inconclusive and indicate that the lime-pozzolan reaction is still not well-understood.

As cited by Swamy [4], one proposal suggested that, lime-pozzolan reaction is due to presence of zeolites, which absorb lime through a base exchange mechanism. However, many pozzolans contain no zeolites and lime-pozzolan reaction results in new compounds which cannot be explained by this mechanism.

As quoted by Sersale [21], Dorn interpreted the pozzolanic reaction by considering the solubility of feldspar-like structures in a lime solution. He considered that, tetrahedral silica units are held in position in the interior of material by oxide ions at the apexes of the tetrahedron. At the surface, however, the oxide ions are converted to a hydroxyl group; that is:

$$O^{2-} + H_2O \Rightarrow 2(OH)^- \qquad (2.9)$$

This destroys the spatial equilibrium for the unit within the material allowing it to pass into the solution, where it reacts with calcium ions to form insoluble calcium silicate hydrates. The removal of one silica unit permits another to be in contact with lime solution, and hence the mechanism can continue. Sersale believes that, this mechanism can occur more easily in pyroclastic pozzolans, in which the bond between the silica tetrahedra is weaker. Besides, this mechanism would explain the faster rate of reaction for finely divided and porous pozzolans.

Swamy [4] has also quoted Takemoto and Uchikawas' [27] diffusion-controlled dissolution mechanism, according to which the pozzolanic particles are attacked by water in the highly alkaline lime solution, dissociating Si OH group on the particle surface to SiO_4^{4-} and H^+. As a result, the particle surface is negatively charged and absorbs Ca^{2+}. The Ca^{2+} at the particle surface reacts with silica and alumina to form a layer which thickens in time. Osmotic pressure resulting from the difference of concentration between the inside and outside of the layer causes it to rupture. As a result of differences in the diffusion characteristics of the calcium aluminate and calcium silicate hydrates, the former is nucleated in the matrix away from the pozzolan, while the latter precipitates at the surface of the pozzolan. This phenomenon is also suggested by SEM observations. The general concepts of diffussion-controlled dissolution mechanism is also observed for fly ash by Ghose and Pratt [28].

The pozzolanicity of a mineral is generally best determined through compressive strength tests conducted on mortars and concrete containing the mineral in accordance with standardized procedures, though a number of chemical methods (for instance solubility in cold hydrochloric acid or hydrofluoric acid or a mixture of hydrofluoric and nitric acid) and physical methods (such as quantitative X -ray powder diffraction) have been developed.

Although the assessment of pozzolanic activity based on mechanical properties, i.e. compressive strength is the most meaningful from the end users point of view, it suffers the disadvantage of relatively slow rate of strength development in both lime and portland cement-pozzolan systems. As cited by Swamy [4], Tea [29] has proposed an accelerated curing regime to overcome this shortcoming. In his method, the difference between 7-day compressive strength of mortar specimens cured at 50° and 18°C is regarded as a measure of pozzolanic reactivity.

As it was mentioned earlier, in addition to temperature, a number of chemicals, such as sodium hydroxide, sodium silicate sodium carbonate, and gypsum can affect the rate of strength gain of lime-pozzolan systems. As an example, the effect of sodium hydroxide on the strength development of a porous opalline pozzolan-lime mortar reported by Alexander [30] is given in Figure 2.7.

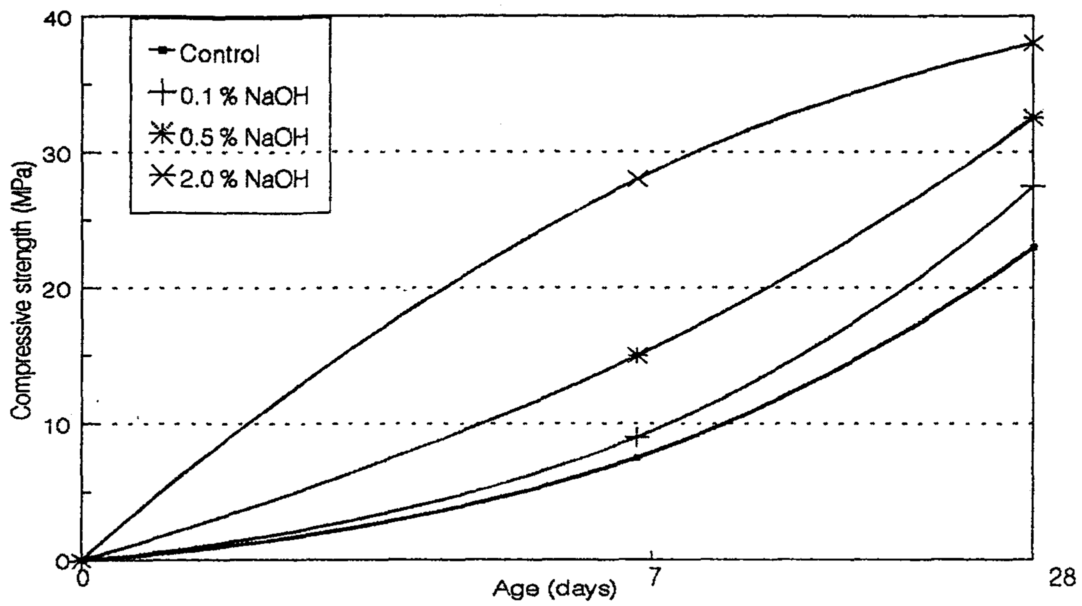


Figure 2.7. Effect of Sodium Hydroxide on the Compressive Strength of Lime-Pozzolan Mortars [30]

2.2.3 Products of Pozzolanic Reactions

It is commonly accepted that the products of lime-natural pozzolan reactions are as follows [21, 24, 25]:

a) Calcium silicate hydrate C-S-H,
b) Calcium aluminate hydrate of the form C_4AH_x with x varying from 9 to 13,
c) Hydrated gehlenite C_4ASH_8
d) Calcium carboaluminate $C_4A\bar{C}H_{12}$
e) Ettringite $C_6A\bar{S}_3H_{32}$
f) Monosulfate calcium aluminate $C_4A\bar{S}H_{12}$

However, all products will not be present at the same time and their presence depends on the chemical and mineralogical constituents of the pozzolan, the availability of lime, the extent of hydration reactions and ambient conditions during hydration.

CHAPTER III

NATURE AND CLASSIFICATION OF FLY ASHES

During the combustion of pulverized coal in the modern power plants, the carbonaceous content of the coal is burned off whereas, the remaining present as impurities in the coal, such as clays, quartz and feldspars, melt whilst in suspension in flue gases. The fused matter is quickly transported to lower temperature zone where it solidifies as spherical particles. About 80% of the coal ash flies out with the flue gas stream, and hence is called fly ash. This ash is subsequently removed from flue gases by a variety of dust collection systems before discharging into the atmosphere. There is a wide variation in the chemical composition of fly ashes which is mainly governed by the source of the coal. Generally 85% of the fly ash comprises SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO.

3.1 Classification of Fly Ashes

Traditionally, even though the fly ash constituents are not present as oxides, fly ashes are classified in accordance to their oxide compositions. In some countries, such as France and Spain, where there is no fly ash standard, lime and SO_3 content are taken into account to identify fly ashes [31]. Accordingly, fly ashes are said to be a) silico-aluminous, which are mainly composed of aluminum silicates and are generally obtained from bituminous coals, b) silico-calcic, which are generally formed by combustion of lignites containing high silica and lime contents, and c) sulfo calcic, which are again mainly lignite based with high SO_3 and lime content.

On the other hand, in recent years, fly ashes are divided into two distinct groups with particular regard to their use in concrete. i) Low-lime fly ashes, which possess truly pozzolanic properties, i.e. activators are required for these fly ashes to undergo reaction and produce cementitious properties. ii) High-lime fly ashes, some of which are self cementitious by themselves, in addition to pozzolanic properties.

This grouping is generally associated with the type of the coal and essentially coincides with the Class F, usually formed by combustion of bituminous coals, and Class C fly ashes, by products of subbituminous coals and lignite, respectively, as recognized by ASTM C 618 [32] "Standard Specification of Fly Ash and Raw or Calcined Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete". In this specification, fly ashes are designated on the basis of parent coal types with a min. 70 % and min. 50 % limitations on the sum of SiO_2, Al_2O_3 and Fe_2O_3 content for Class F and Class C fly ashes, respectively. This requirement tends to cause confusion because most of Class C fly ashes meet the requirements of Class F fly ashes.

More recently, Mehta [9] has proposed his system of classification of mineral by-products, based on their cementitious or pozzolanic activity. This classification, which transcends the traditional barriers of categorizing materials according to their sources of origin, is based on the performance of the mineral additive. In this grouping, in addition to low-lime fly ashes (<10 % CaO), which belong to normal pozzolans group and need an activator to undergo reactions and produce cementitious compounds, high-lime fly ashes with 10-20 % CaO content are regarded as cementitious and pozzolanic by-products whereas, high-lime fly ashes having more than 20 % CaO content are categorized as cementitious mineral additives.

However, the dependence of the fly ash nature to the geological history of the parent coal and to the processing conditions of the coal before and during burning, makes any classification attempt incompetent. Indeed, in spite of the wide range of existing categorized classes, there may be some fly ashes between or beyond the characteristic types [31].

It seems that, the most suitable way to describe a fly ash and its behavior in a system is to undertake a complete physico-chemical study hoping that, during the testing time, the coal or the lignite from which the fly ash is derived will not change too much, rather than making any attempt to oversimplify the actual nature of the fly ash by classifying it. In fact, there are fly ashes that exhibit some properties of more than one class, while others are so singular as to constitute a class by themselves. However, a regular check of chemical and physical characteristics of a specified fly ash obtained from a particular power plant is always necessary in order to note any change in its properties.

3.2 Characteristics of Fly Ashes

3.2.1 Chemical and Mineralogical Composition

The formation rate of cementitious products resulted from the interaction between fly ash and portland cement hydration products depends on the composition of cement, mineralogical composition and particle characteristics of the fly ash, reaction temperature, and ionic concentration of the solution phase in the system. Contrary to portland cement, in which generally a close relationship exists between chemical and mineralogical composition, in fly ashes, due to the presence of large glassy matter, there is no direct relationship between chemical and mineralogical composition which controls the reactivity of the fly ash [10]. Therefore, closer attention should be paid to the mineralogical character rather than to the chemical composition of the fly ash. However, traditionally oxide analysis is used to describe the chemical composition of fly ashes and the standard specifications emphasize chemical requirements which serve little or no useful information about the behavior of the fly ash in cement systems. Also, the assumption, in some standard specifications including ASTM C 618 [32], that all silica, alumina, and iron oxide present in a pozzolan is in noncrystalline form, and therefore potentially reactive with lime seems to be incorrect, since in actual practice substantial amounts of these oxides occur as non-reactive crystalline minerals.

Fly ashes are mainly composed of silica (SiO_2), alumina (Al_2O_3), iron oxides (FeO, Fe_2O_3, Fe_3O_4), lime (CaO), and sulfurtrioxide (SO_3). In addition to these, small amounts of magnesia (MgO), alkali oxides (Na_2O and K_2O) and titanium oxide (TiO_2), as well as unburned carbon may be found in fly ashes.

The carbon content of fly ash, generally reported as loss on ignition in chemical analysis, is related to the burning process in the furnace, and in modern power plants it is less than 3 %. Typical oxide composition ranges for both low-lime (< 10 % CaO) and high-lime fly ashes (> 10 % CaO), as well as for ordinary portland cement are given in Table 3.1.

From Table 3.1, wide variations in the chemical composition of different types of fly ashes, and even each type of fly ash become readily apparent. However, as it was mentioned earlier, there is little correlation between the oxide composition of the fly ash and its performance in concrete. From the standpoint of concrete behavior, the importance of chemical composition of fly ash is to the extent of its influence on the mineralogical character of the ash.In addition to chemical composition, the processing conditions also affect the mineralogical properties of the products and their subsequent performance characteristics in concrete [4, 10].

Although some of the crystalline components present in fly ashes have the ability to affect properties of concrete, most of them are inert or poorly reactive to water or cement systems at ordinary temperature. Therefore, their presence in large proportions, at the cost of the glassy phase, reduces the reactivity of the fly ash [10].

The principal crystalline minerals in low-lime fly ashes are generally composed of quartz (SiO_2), mullite (S_3A_2), sillimanite (SA), hematite (Fe_2O_3) and magnetite (Fe_3O_4) [33, 34, 10]. From these, mullite and sillimanite are generally cooled slowly as slender needles in the interior of large glassy aluminosilicate spheres [10]. In addition to quartz, the crystalline phase in high-lime ashes is known to include C_3A, C_4A_3S, CS, alkali sulfates and free CaO. The calcium compounds and alkali sulfates are reactive. In fact, quick setting and high heat of hydration of some fly ashes with large proportions of C_3A or free CaO is due to rapid formation of C_4AH_{13}, $C_4A\bar{S}H_{18}$, $C_6A\bar{S}_3H_{32}$ [10].

Table 3.1. Typical Oxide Composition Ranges of Fly Ash and Portland Cement [9], [15]

	Mass percentage		
Oxides	OPC	High-lime FA	Low-lime FA
SiO_2	17-25	20-50	45-65
Al_2O_3	3-8	15-20	20-30
Fe_2O_3	1-6	5-10	4-20
CaO	60-67	15-30	1-5
MgO	0.5-4	3-5	1-2
SO_3	1-3	1-6	1-2
Alkalis	0.5-1.5	1-8	1-3
LOI	0.5-2	1-2	3-5

The predominant constituent in fly ash is the non-crystalline silicate glass which is the source of pozzolanicity. There is a growing realization among the researchers that the key to differences in reactivity of fly ashes has to be sought in the characteristics of their glassy phase [9]. It will be helpful here to describe briefly the structure of glass, the major component of the fly ashes.

3.2.1.1 Structure of Glass in Fly Ash

Solid materials lacking long-range interatomic order are generally non-crystalline. Among these, glasses are the products of fusion of inorganic materials which have cooled to rigid condition without crystallizing. The degree of disorder in a non-crystalline material can be inferred by observation of its X-ray diffractogram, which shows a broad diffuse halo rather than sharp diffraction peaks as shown in Figure 3.1.

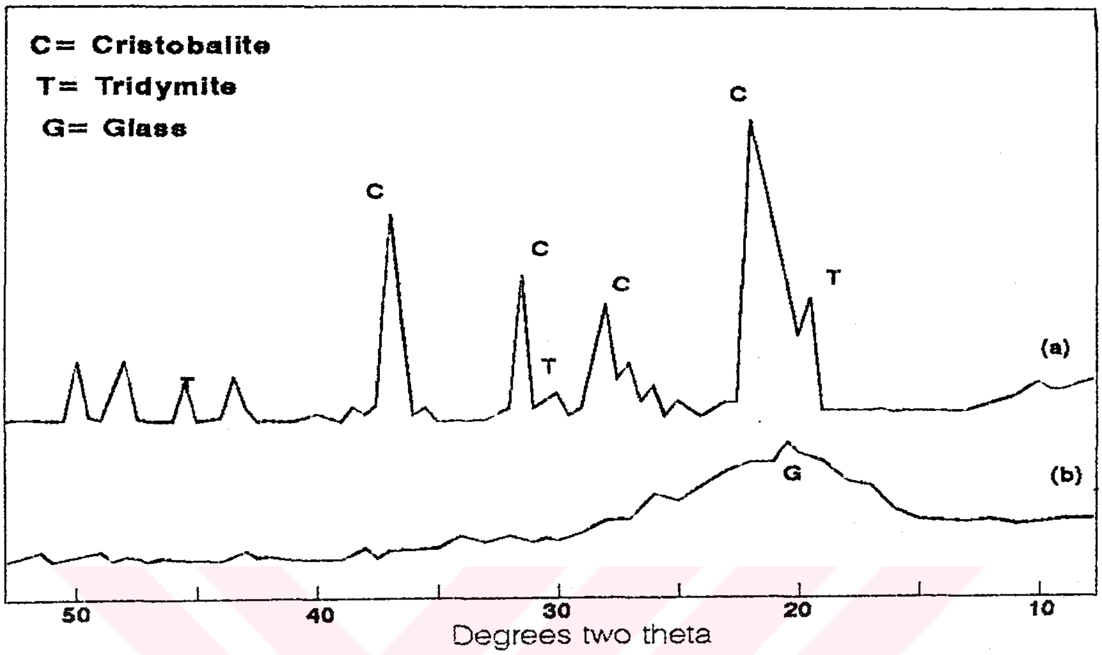


Figure 3.1. X-Ray Diffractograms of a) Crystalline Silica Cristobalite) and b) Glassy Silica [9]

According to Hemmings and Berry [35], in simple glass forming oxides, such as pure SiO_2, the integral structure lacks long-range order, but there is continuity in the chains of constituent atoms (Figure 3.2a). The disorder results from the difference in the size of the rings into which these chains are linked to form a structural network. More complex glasses are formed by introducing modifier cations, such as Na, K and Ca into the silicate structure. As a result, greater level of disorder occurs both through randomness of the size of chains and through chain breaking by the modifier cation to form non-bridging oxygen atoms (Figure 3.2b). As more constituents are introduced into the glass, further levels of disorder result from random replacement of Si by Al and Fe (Figure 3.2c). Most of the glasses of practical interest to the cement industry are disordered both by chain breaking through the presence of modifier cations and by random chemical disorder on chains resulted from substituted atoms [10].

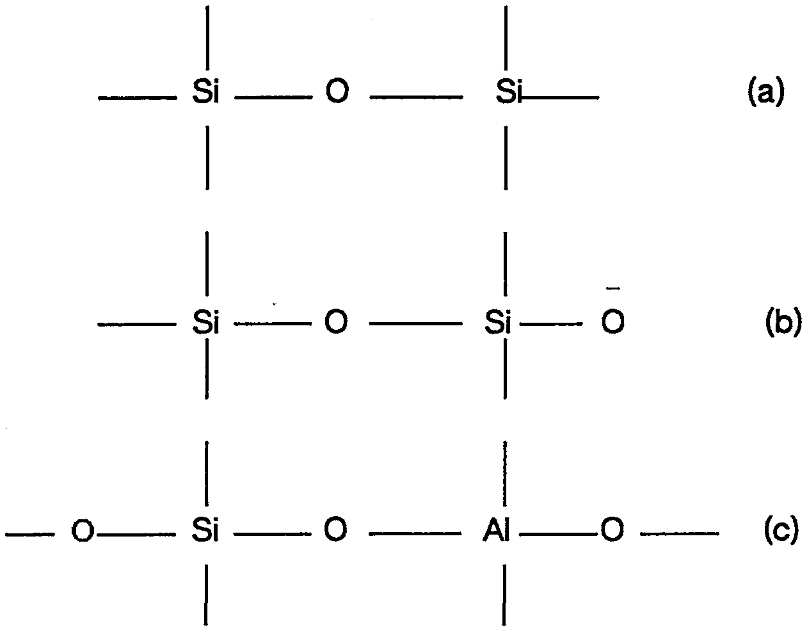


Figure 3.2. Structure of Silicate Glass [35] a) Typical Si-O Chain with Oxygen Bridging in Simple Glasses b) Non-Bridging Oxygens in Complex Glasses Containing Na^+ Ions c) Random Chemical Disorder Resulting from Replacement of Si by Al

The impetus for research on composition of glass in fly ash came from the general observation of different reactivities of low-lime and high-lime fly ashes. The former, due to the high proportions of silica and alumina, consist principally of aluminosilicate glass [10]. However, the glassy phase in the latter is quite different due to the presence of significant amounts of MgO, alkalis and sulfates, as well as CaO. Hence, the position of diffraction halo produced by X-ray scattering changes with the type of fly ash. Low-lime fly ashes show typically a diffuse halo maxima at 21-25° 2θ, and high-lime ones at 30-34° 2θ (Cu-Kα) [36].

There is no doubt that, the value of $2\theta_{max}$ on a typical XRD Pattern indicates the extent of glass modification [35, 36, 9]. Diamond [37], attributed 32° $2\theta_{max}$ (in high-lime fly ashes) to a calcium aluminate type glass, like $C_{12}A_7$. On the other hand, Mehta, [10] regarding the similarities in the XRD patterns of high-lime fly ash and granulated blast furnace slag, reported that the composition of the glass in these fly ashes is essentially melilitic, i.e. a silicate glass modified by calcium and aluminium. Roode [38], Hemmings and Berry [39], as quoted by Mehta, [9] support the conclusion made by Mehta [40]. They confirmed the general trend of increase in the $2\theta_{max}$ value with increasing CaO in fly ash, and concluded that, the composition of silicate glass in high-lime ashes is modified by Al, Ca, Fe, Na, and K substitutions. Hemmings and Berry [39] concluded that, an overlap in the XRD patterns of different glass types, co-existed within samples of fly ash from a single source, causes the asymmetry of the glass halo. Besides, they attributed the shift in the XRD halo to higher $2\theta_{max}$ values for different size fractions of a fly ash and to the increasing content of cation modifiers in essentially the same aluminosilicate matrix and not due to the formation of a new type glass such as $C_{12}A_7$. Typical mineralogical composition of fly ashes are given in Table 3.2. Also they are compared with other pozzolans and portland cement graphically in a ternary diagram in Figure 3.3.

Table 3.2. Typical Mineralogical Composition of Fly Ashes [43]

Mineral (%)	Silico-aluminous	Sulfo-calcic	Silico-calcic
Amorph and Glassy Phase	60	35	50
Mullite	20	1	5
Hematite	7	4	3
Magnetite	6	1	1
Quartz	5	5	5
Anhydrite	-	15	5
Free lime	-	20	10
Feldspats and gehlenite	-	≥20	≥15

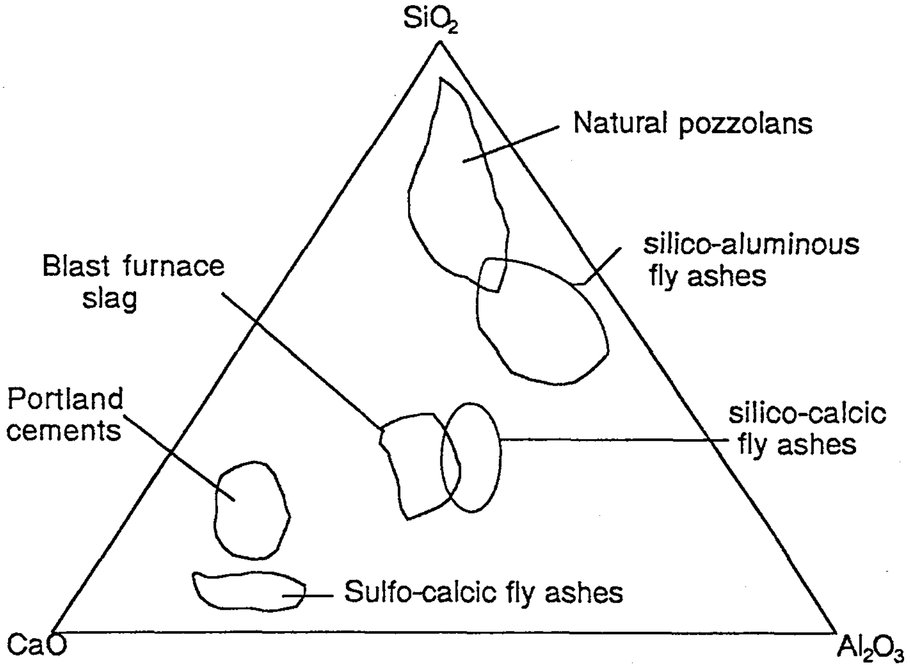


Figure 3.3. Presentation of Fly Ashes and Other Pozzolans as well as Portland Cement in a Ternary Diagram [43] After [31, 44].

3.2.2 Physical Properties

3.2.2.1 Morphology

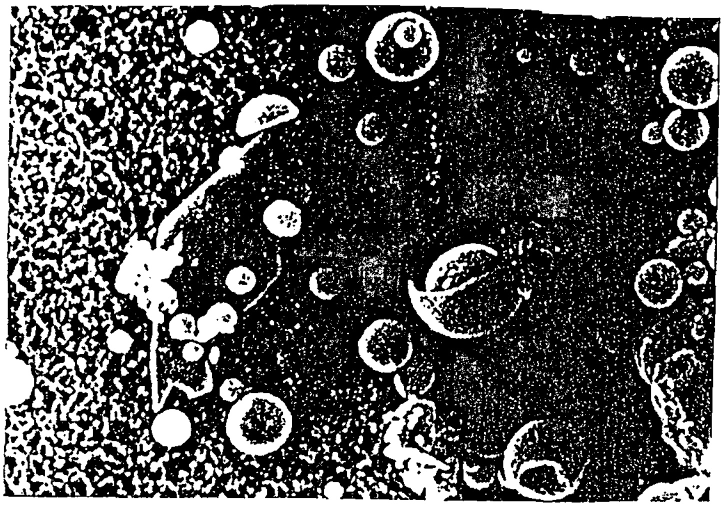
Particle size and shape characteristics of fly ash are dependent upon the source and uniformity of the coal, the degree of grinding prior to burning, the combustion environment (temperature level and oxygen supply), uniformity of combustion and the type of ash collection system [7]. Fly ash particles are mostly glassy, solid or hollow and spherical in shape. Hollow empty spheres are called cenospheres. Spheres that are packed inside with smaller particles are known as plerospheres. Dermospheres, which are relatively larger spheres, are formed on the surface of crystalline particles, as well as on porous clay residue and unburned carbon as shown in Figure 3.4.

It has been shown that, the intergrinding of fly ash with cement clinker in the manufacturing of blended cements has improved its contribution to strength. Grinding further reduces particle size, breaks up cenospheres and releases smaller particles contained in plerospheres. However, too fine grinding may increase water requirement of the blended cement [7]. Lane and Best [46] have reported that, the shape of fly ash particles is also a function of particle size.

The physical characteristics of fly ash, i.e. particle shape, surface texture and particle size distribution, account for its water reducing ability in portland cement concrete. The glassy, smooth, and non-absorbing surface texture of the fly ash is, in part, responsible for better workability and lower water requirement of portland cement-fly ash systems. Another reason seems to be the reduction in the volume of voids present in concrete through pore refinement [10]. Helmuth [47] believes that, water reduction in fly ash-portland cement systems is due to the absorption of small fly ash particles on the surface of electrically charged cement grains, causing a better dispersion of the cement particles in a manner similar to conventional water reducing admixtures.

3.2.2.2 Fineness

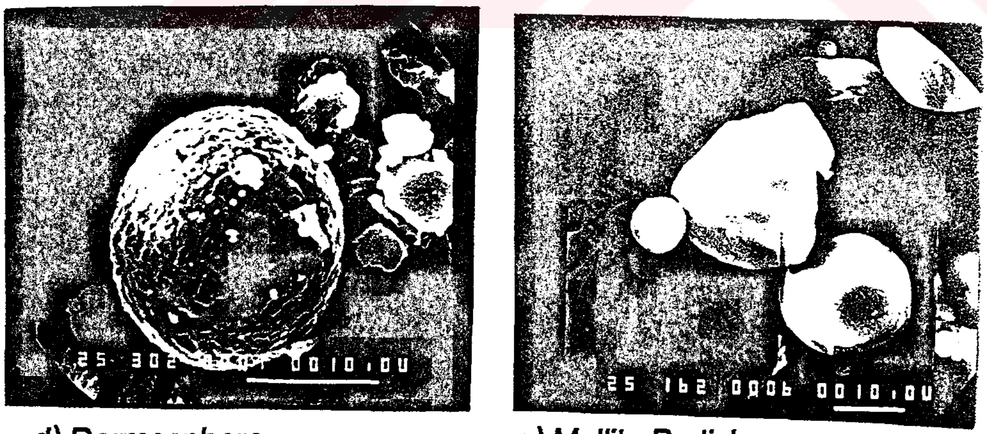
Individual particles of fly ash range in size from less than 1μm to greater than 1mm, the majority being less than 20μm. The particle size distribution of fly ash is dependent on the coal source, coal grinding, process operation and plant load. As shown in Figure 3.5, fly ashes collected by electrostatic separators are finer than those obtained by mechanical separators. In fact, the former one, in which majority of particles pass 45μm (No. 325) sieve is considered as a suitable siliceous mineral admixture to use in concrete.



a) Cenospheres and Plerospheres

b) Porous Clay Residue

c) Magnetite Spherical Particle



d) Dermosphere

e) Mullite Particle

Figure 3.4. SEM Photographs of Typical Fly Ash Particles [43]

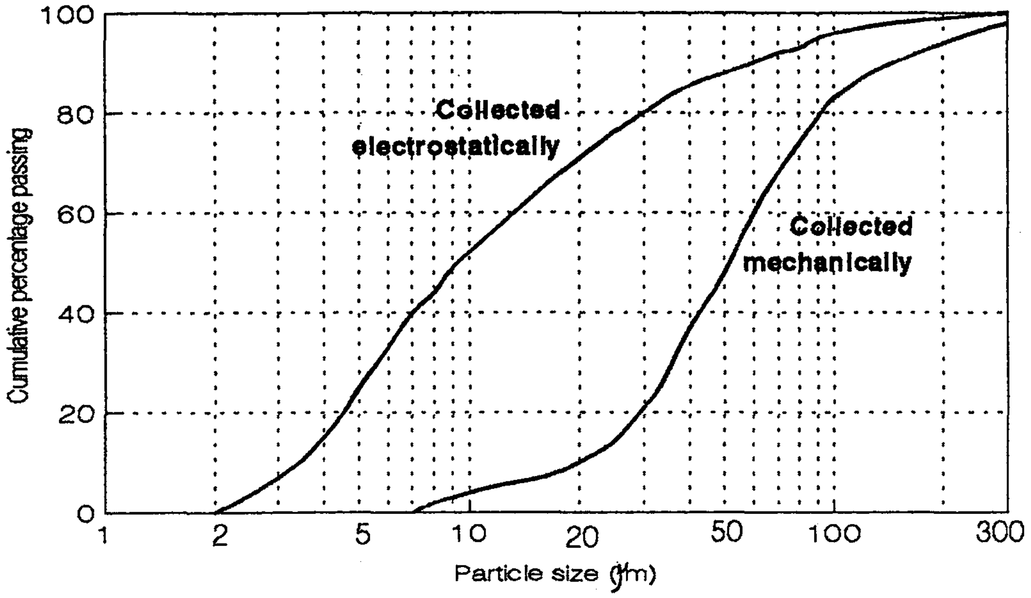


Figure 3.5. Typical Particle Size Distribution of Fly Ash [45]

It is generally accepted that, accompanied by mineralogical character, fineness of the fly ash has a significant effect on its performance in concrete. Lane and Best [46] have reported that, the fineness of fly ash directly influences certain aspects of fly ash concrete including strength, abrasion resistance and resistance to freezing - thawing. They concluded that fly ash performance in concrete improves with increased fineness. Mehta [48] has cited [9] his own research on several U.S. fly ashes reporting that, in general, probably due to the presence of larger amounts of alkali sulfates, the high-lime fly ashes tend to be finer than low-lime ones. Also the possibility of the relationship between the amount of < 10μm fly ash particles and the 7 and 28 -day compressive strength of fly ash bearing blended cements is shown. However, the same author [10] in his previous study confirms that particle size alone may not affect the potential reactivity of the ash. The measurement of fineness has attracted a great deal of attention, but controversy remains. The measurement of fineness as specific surface, originally applied on fly ashes is an acceptable method for portland cement. However, it seems to be an unreliable method for fly ashes due to several difficulties arising from wide density ranges and porosity of fly ashes [45]. The results of several studies give a 180-600 m^2/kg Blaine specific surface range for fly ashes [9, 12] as compared to that of portland cement which ranges from 240 to 280 m^2/kg.

Recently, there is a common trend to express the fineness of fly ash as percentage retained on 45µm sieve. Reactivity of fly ash has been found to be related directly to the quantity passing this sieve, since the coarse particles generally do not react efficiently in concrete [7]. Particularly, a good correlation exists between a multiple factor (product of fineness and loss on ignition) and consistency of concrete, measured as slump, in low-lime fly ashes having high loss on ignition value [7, 61].

3.2.2.3 Specific Gravity

The average specific gravity of fly ash ranges from 1.9 to 2.4 [45] somewhat less than the specific gravity of cement which is around 3.1. Some of fly ash particles, such as cenospheres, are capable of floating on water, indicating a specific gravity less than 1. However, specific gravity measured after grinding until no hollow particle remains, ranges between 2.6 and 2.8. High specific gravity is often an indication of fine particles. Besides, Roy et.al [49] indicate that fly ashes high in iron tend to have higher specific gravity whereas, those higher in carbon have lower specific gravity. High-lime fly ashes, owing to their finer particles and fewer cenospheres, tend to have higher specific gravities (2.4 to 2.8) [7]. The loose bulk density of dry fly ash is approximately 800 kg/m^3 [45].

3.2.2.4 Color

The color of fly ash ranges from almost light cream to brown and from gray to black depending on the proportions of unburned carbon present, as well as upon its iron content. The color of fly ash becomes generally darker with increasing its carbon content. Fly ash color is generally not an engineering concern except that a change in the color of an ash from a particular source may be an indicator of changed properties due to changes in coal source, loss on ignition, iron content, or burning conditions. Besides, fly ash concrete and the amount of used ash can influence the color of resulting concrete.

3.3 Fly Ash Specifications and Their Significance

The main physical and chemical fly ash requirements, specified in TS 639 [50] and other standards across the world, are summarized in Table 3.3. In the following section the significance of each of the required properties listed in Table 3.3. is briefly discussed.

3.3.1 Loss on Ignition (LOI)

This is essentially a measure of unburned carbon present in fly ash. A high carbon content is considered to influence the color of fly ash and to affect its quality adversely by increasing water demand and reducing fineness and pozzolanic activity. The great majority of fly ashes produced in modern power plants show LOI well below the given limitations, due to the efficiency of operations required to make economical use of coal as an energy source.

On the other hand, increased LOI results in an increase in the amount of required air-entraining agent to produce the same air content in the concrete. However, the phenomenon is not always considered to be simply related to carbon content.

In many countries, the loss on ignition of fly ash is limited by the standard specifications to values in the 5-12% range [45, 51, 52] as shown in Table 3.3. However, it is reported that the presence of high amounts of carbon in fly ash (up to 19% in certain cases) did not affect the microstructure and various properties of PC-fa mortars and concretes [53, 54, 55]. Besides, it is observed that, fly ashes having carbon contents up to 23% do not adversely affect the freezing-thawing resistance of concrete as long as a proper air bubble network is provided by increasing the air-entraining admixture dosage [55].

Table 3.3. Selected National Standard Specifications for Fly Ash Use in Concrete [3], [45]

Requirement	Australia (AS1129)	Austria Önorm(B3892)	Canada (Can3-A23.5-M82) Class		India (IS 3812)	Japan (JISA 6201)	Korea (K.S.L5405)	Turkey (TS 639)	UK (BS3892)	USA (ASTM C618) class		USSR (GOST 6269)
			F	C						F	C	
LOI, max %	8.0	5.0	12.0	6.0	12.0	5.0	12.0	10.0	7.0	12.0	6.0	10.0
SO_3, max %	2.5	3.5	5.0	5.0	3.0	-	5.0	5.0	2.5	5.0	5.0	3.0
MgO, max %	-	5.0	-	-	5.0	5.0	5.0	5.0	4.0	5.0	5.0	-
Available alkali as Na_2O, max %	-	-	-	-	1.5	-	-	-	-	1.5	1.5	-
Si_2O, min %	-	42-60	-	-	35	45	-	-	-	-	4.0	40
Al_2O_3, %	-	16-32	-	-	-	-	-	-	-	-	-	-
Fe_2O_3, %	-	3-12	-	-	-	-	-	-	-	-	-	-
$SiO_2+Al_2O_3+Fe_2O_3$, min %	-	-	-	-	70	70	70	70	-	70	50	-
C, max %	-	3.0	-	-	-	-	-	-	-	-	-	-
Cl, max %	-	0.1	-	-	-	-	-	-	-	-	-	-
Moisture, max %	1.5	1.0	3.0	3.0	-	1.0	3.0	3.0	0.5	3.0	3.0	-
Water Req.Max, %	-	-	-	-	-	100	102	105	95	105	105	-
PAI with cement min %	-	80	75	75	-	60-70	85	70	-	75	75	85
PAI with lime min. N/mm^2	-	-	-	-	3.9	-	5.5	-	-	5.5	5.5	5.5
Blaine specific surface min. cm^2/gr	-	4000-5000	-	-	2800	2400	-	3000	-	-	-	-
Fineness, max % Retained	on 45µm 50	-	on 45 µm 34	34	-	-	-	on 200µm0.3 on 90 µm 8	on 45 µm 12.5	on 45 µm 34	34	-

3.3.2 SO_3 Content

Virtually, all specifications have placed a maximum limit to SO_3 to avoid an excess of sulfate remaining in the hardened concrete which could contribute to harmful sulfate attack. High levels of SO_3 in concrete leads to volume instability and, thus, loss on durability through formation of ettringite. Besides, sulfate in fly ash can affect the optimum amount needed for maximum strength development and acceptable setting time for fly ash blended cements.

3.3.3 MgO Content

A maximum limit on magnesia content in fly ash is specified by standard requirements for durability; since, free MgO hydrates after hardening of concrete leading to volume expansion and eventual deterioration.

3.3.4 Alkali Oxides

The alkali metals may react with certain types of aggregate to produce an unlimited swelling alkali-silica gel, leading to an eventual deterioration of concrete. This is why some standards contain an optional chemical requirement on the amount of available alkalis expressed as Na_2O equivalent. However, it has been reported that, the fly ash inhibits alkali - silica reaction probably through increasing the quantity of C-S-H gel, thus making it more difficult for the hydroxyl ions to meet with the aggregate [51] as cited by Dhir [45]. Other investigators attribute the reduction in alkali-silica expansion by fly ash to the "alkali dilution" effect [52], as well as to the low permeability to ionic diffusion in systems containing fly ash [9].

3.3.5 Major Oxides

A minimum requirement for silica and/or the sum of SiO_2, Al_2O_3 and Fe_2O_3 are placed in some standards to ensure a sufficient potentially reactive glass constituent in fly ash. However, as it was mentioned earlier, analytical SiO_2 and Al_2O_3 content can be affected by several crystalline non-reactive minerals, also Fe_2O_3 does not play a direct part in the reactivity of fly ash. As a result, the major oxides requirement seems to be incorrect to evaluate fly ash performance. Indeed, no sensible connection between these oxides and fly ash performance has been substantiated [10]. This point is confirmed clearly by the strength test results of fly ash concretes reported by Dhir et al [58] and shown plotted in Figure 3.6 and Figure 3.7. [45].

3.3.6 Water Requirement

The water requirement of fly ash, measured on the mortar mixes of a known consistency (100-115 % flow), is used to ensure that the use of fly ash in concrete does not result in any significant reduction in strength through increasing mixing water content. However, the application of water requirement test value in determining water demand for a concrete mix may be of little help [60].

In most of the specifications, a reduction or a small increase in water demand of fly ash mortars is required. However, most of high lime fly ashes increase water requirement. Besides, no statistically acceptable correlation could be made between fly ash fineness and water requirement of the fly ash included systems. A relationship between water demand of fly ash concrete and water requirement of United Kingdom fly ashes, which are almost of bituminous coal origin, is reported by Dhir, [45] as shown in Figure 3.8.

In the same manner, in spite of the general trend to relate the water requirement to the fly ash fineness, no common correlation has been established in this matter [43].

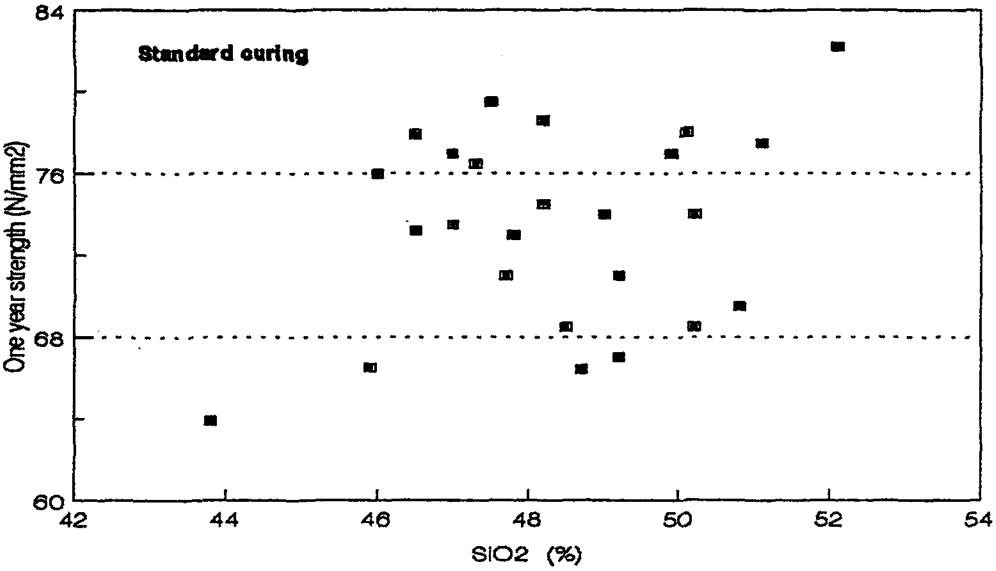


Figure 3.6. Effect of SiO_2 Content of Fly Ash on Concrete Strength Development [45]

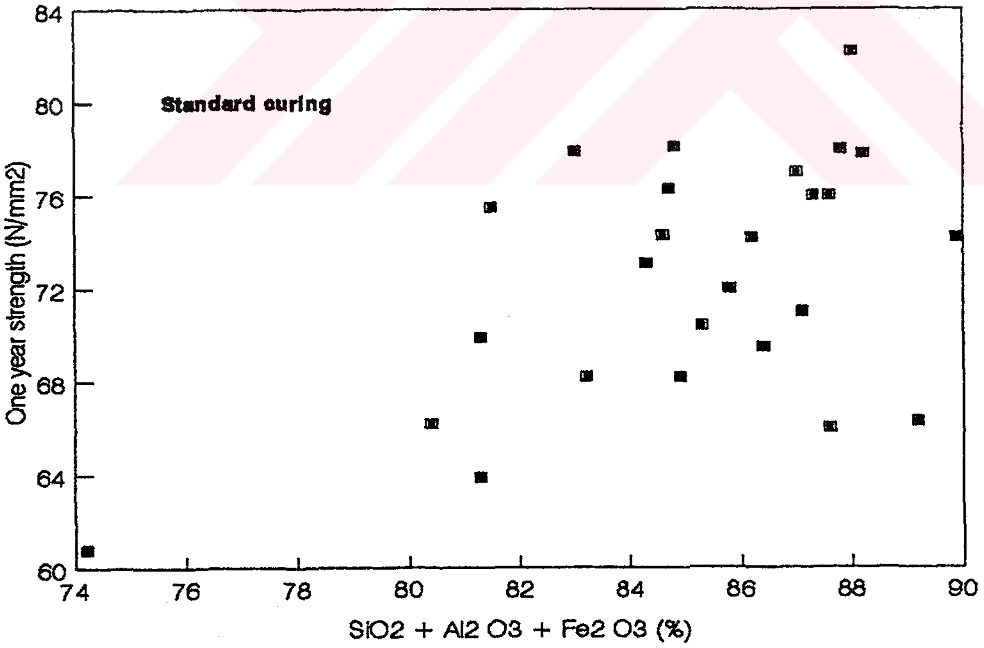


Figure 3.7. Effect of $SiO_2 + Al_2O_3 + Fe_2O_3$ Content of Fly Ash on Concrete Strength Development [45]

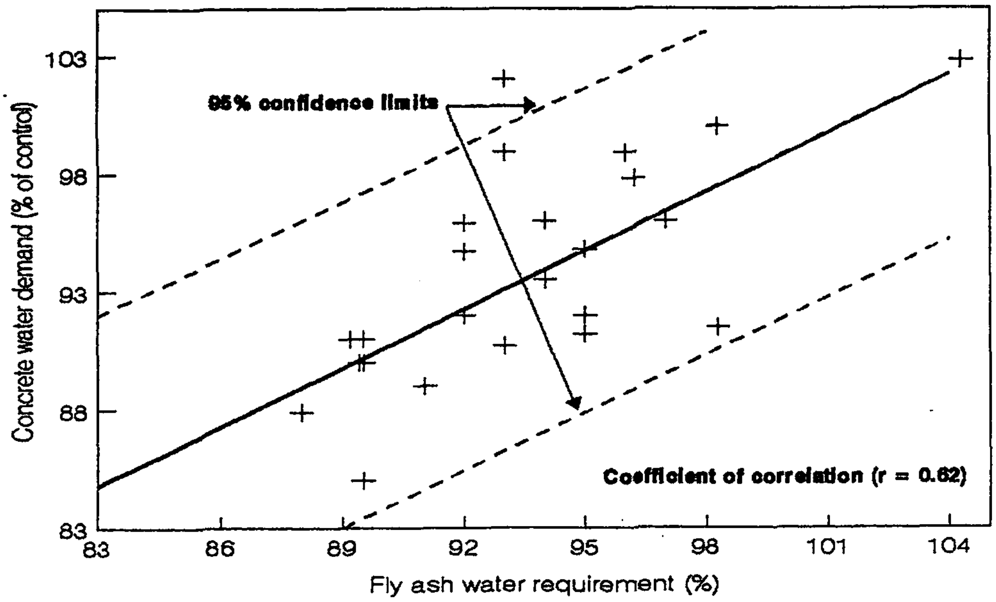


Figure 3.8. Relationship Between UK Fly Ashes Water Requirement and Concrete Water Demand [45]

3.3.7 Pozzolanic Activity Index (PAI)

The PAI is commonly considered as an indication of fly ash reactivity, although this is never substantiated. In fact, it has been reported that, PAI can neither be used to predict the ultimate strength of fly ash concrete [61], nor reflects the amount of reactive amorphous phase present in the fly ash [60]. The impossibility of establishing any relationship between vitreous phase of the fly ash and its PAI is graphically demonstrated in Figure 3.9 [45].

On the other hand , Dhir et al [61] have shown that, PAI responds to the physical, chemical and surface characteristics of low-lime fly ashes. They have established the relationship between fly ash fineness and its PAI as shown in Figure 3.10.

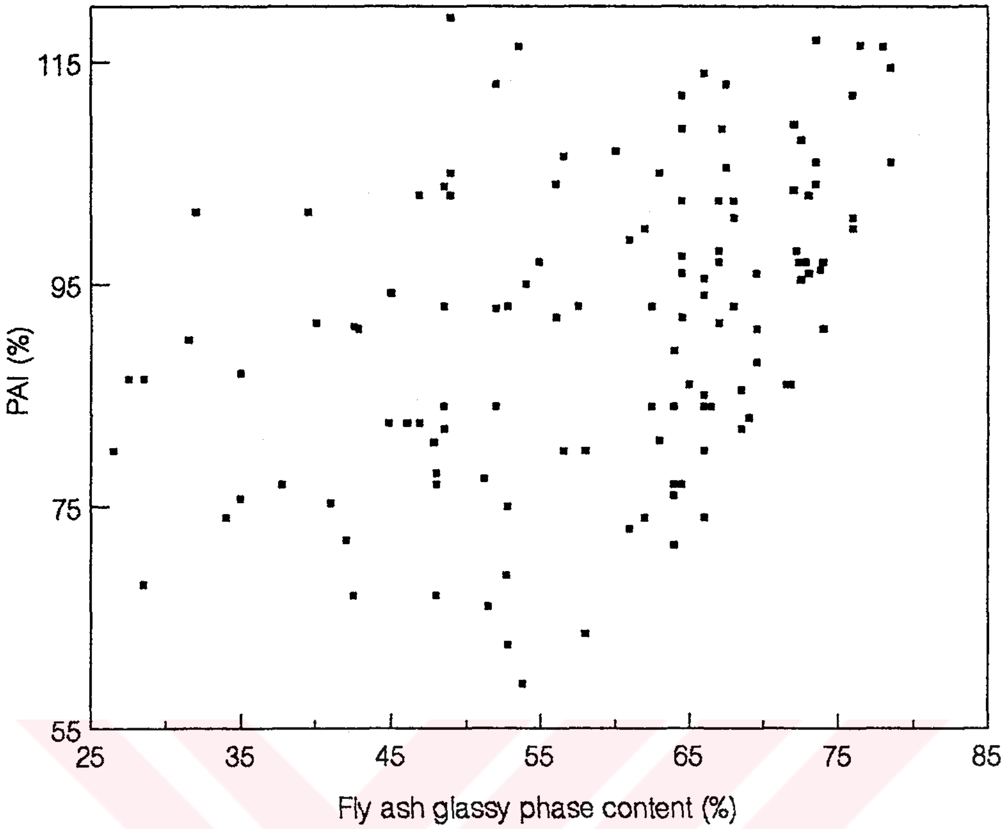


Figure 3.9. Relationship Between Fly Ash Amorphous Phase Content and Its Pozzolanic Activity Index [45]

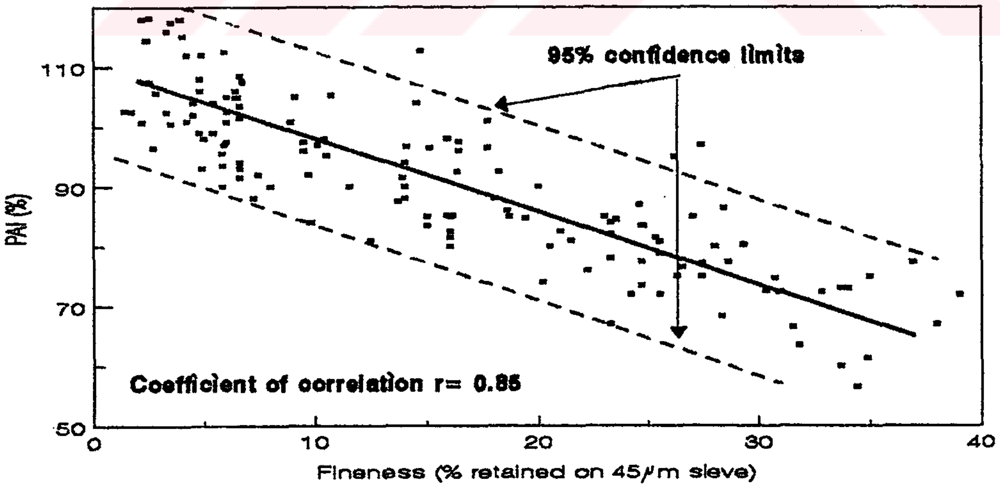


Figure 3.10. Relationship Between the Fineness of Low-Lime Fly Ashes and Their PAI [61]

However, no appreciable characteristics of self cementitious high-lime fly ashes can be reflected by PAI [10, 43]. This is why, there is a general consideration to refer fly ashes as "mineral admixtures" rather than "pozzolanic materials".

CHAPTER IV

REVIEW OF RESEARCH ON THE USE OF FLY ASH AS A CONCRETE INGREDIENT

The studies on the use of fly ash in concrete started as long ago as 1937 simultaneously with the recognition of its pozzolanic property. These studies revealed the effects of fly ash on almost all aspects of portland cement-fly ash (PC-fa) systems.

During the past ten years, a relatively larger number of publications dealing with the properties of pozzolan-bearing systems have appeared. For example, the proceedings of Second, Third and Fourth International Conferences on Fly Ash, Slag, Silica Fume, and Natural Pozzolans contain more than 250 papers in the three special publications of the ACI (SP-91, SP-114 and SP-132). About half of them is related with fly ash-containing systems. In addition to numerous research papers that are routinely published in scientific and technical journals, there are at least four books [3-6] and two committee reports [7-8] which attempt to cover the state of the art in a comprehensive manner.

It is impossible to cover up all of the past publications on the use of fly ash in concrete and this review is not intended to be a digest of the past investigations. Instead, it is aimed to review relatively new studies and highlight any new information which represents a significant advancement to the state of art.

Although the influences of fly ash on the hydration products of cement and various properties of cement systems both in fresh and hardened states are closely interrelated, for the sake of simplicity, these effects are discussed separately.

4.1 Influences of Fly Ash on the Hydration of Portland Cement

The effects of fly ash on the hydration of cement systems are still being explored, and no fully definitive summary can yet be made. The difficulty in generalizing the reactions in fly ash bearing systems arises, in part, from the variations between different fly ashes and between different particles within a fly ash and, in part, from the various types of the analysis used by the investigators in the interpretation of the microstructure of these systems.

Generally, these influences have been identified in three distinct areas [45]:

a) physical, by providing additional sites for portland cement hydration,

b) chemical, through preferential encouragement of portland cement silicate phase hydration and,

c) pozzolanic, due to lime-fly ash reaction.

The reactivity of fly ash in PC-fa mixture depends largely on dissolution of the glassy structure of the fly ash by hydroxide ions produced by portland cement hydration and fineness of fly ash, as well as, on the ambient or curing temperature. In this way, both the fineness and the structure of fly ash glassy phase control the activation energy available for the hydration reactions.

Thus, the activation energy involves chemical energy from the chemical reactants (i.e. chemical composition of non-crystalline phase and the solution chemistry of the contact fluid), mechanical energy from fine grinding and thermal energy from heat of hydration or an outside heat source [9]. The positive effects of fly ash particles smaller than 10µm on early strength development rates of PC-fa mixtures, which are due to the early development of pozzolanic reactions, have been reported by several investigators including Mehta [9] and Berry [62].

The hydration of fly ash in the presence of portland cement involves a three-stage reaction. Immediately after mixing with water, reaction rims of impermeable coatings surround the fly ash particles, which prevent occurrence of any further reaction until the availability of alkali or calcium hydroxide and sulfate ions, in sufficient concentration, in the solution phase. During the second stage, the hydroxide ions activate the hydration of glassy phase in fly ash. The third and main reaction stage is the slow pozzolanic reaction which continues to consume calcium hydroxide and form C-S-H as long as calcium and hydroxyl ions are available [9]. There is, however, some disagreement concerning the maturity at which these reactions occur [45, 63]. On the other hand, there is a general agreement among investigators that, the hydration products of PC-fa systems are similar to that of pure cement systems, regardless of the type of fly ash [13, 45, 63] as represented schematically in Figure 4.1 [64, 65].

As it was mentioned earlier, the presence of fly ash encourages the hydration of portland cement silicate phase [45], [66] through providing additional precipitation sites for C-S hydrates. This phenomenon is justified by the higher $Ca(OH)_2$ content in fly ash-bearing systems. Besides, an acceleration in the polymerization of the silicate phase has also been considered, depending on the reactivity and amount of silica in the fly ash . The type of C-S hydrates in PC-fa systems alters significantly and the molar ratio of C/S is suggested to reduce [63] from a value around 3 in pure portland cement system, to less than one in C-S hydrates near pozzolan particles [45].

The hydration of C_3A, in the absence of calcium hydroxide, has been shown to be accelerated by fly ash to form ettringite and monosulfate [13, 45, 62, 65]. However, there are several studies reporting the opposite [62, 67].

There is a reasonably consistent picture of the pozzolanic reaction between the glassy phase of fly ash and calcium hydroxide, by-product of portland cement hydration. However, the data in literature related to the rate of CH consumption is contradictory. Some of the

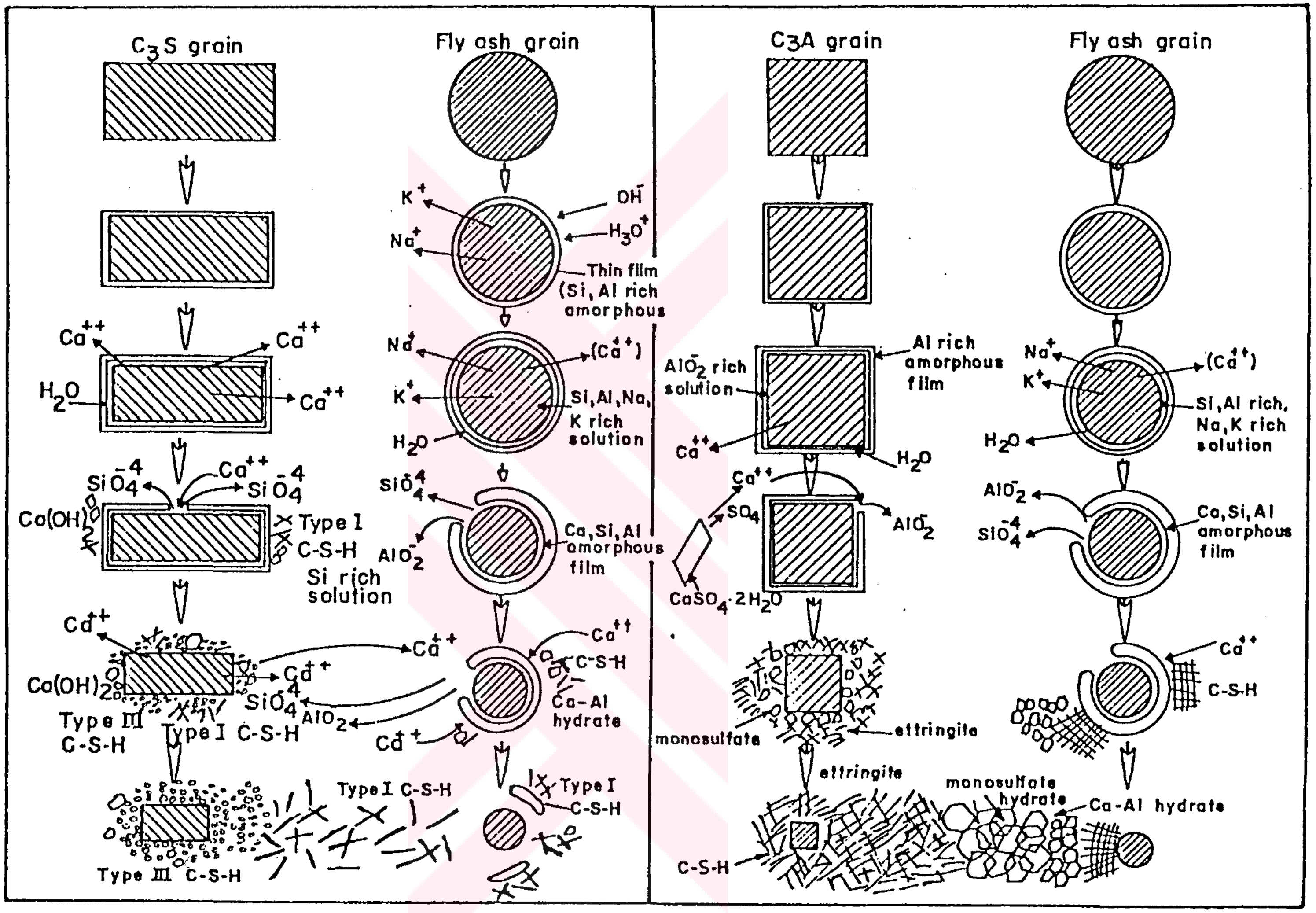


Figure 4.1. Schematic Representation of the Hydration Mechanism of C_3S-Fly Ash [64] and C_3A-Fly Ash [65] in PC-fa Systems.

investigators [13, 45, 66] have reported no appreciable reduction in CH content of the hydration products even up to 28 days. They have confirmed that either pozzolanic reaction in the PC-fa system is not sufficient to show a reduction in CH content, or the formation and consumption of CH in the system are occurring at similar rates, pointing out that, some of the CH is consumed for ettringite formation rather than C-S-H as follows:

$$\mathrm{CH} + \mathrm{SO}_4^{2-} + \mathrm{AlH} \Rightarrow \text{Ettringite [62]}$$

The others [62, 63], however, have confirmed that, beyond three days, even at ordinary temperatures, the amount of bound water in fly ash bearing systems is larger. This-in turn-indicates increased C-S-H production and is therefore an evidence of early pozzolanic activity. This confirmation is consistent with the observations from pore size and permeability determinations [13, 62].

In short, it is likely that, the physical and chemical effects of fly ash will dominate the early age strength up to around 21 days [45]. Although the pozzolanic reactions, in some cases, have been detected as early as a few hours after mixing [28, 62], its contribution to strength development may not be significant until 28 days [13, 68].

Berry et al [62] in their extensive study, using size fractions of the same fly ash, have shown that, the results of XRD, non-evaporable water content, Thermogravimetric Analysis (TGA), pore size distribution and water permeability considerations are not necessarily consistent with each other and the aspect of hydration mechanism of PC-fa systems requires further investigation.

4.2 Effect of Fly Ash on the Rheological Properties of Fresh Concrete

4.2.1 Workability and Water Requirement

The beneficial effects and the mechanism by which fly ash is capable to improve the rheological properties of concrete was shortly discussed previously (Chapter II). It was mentioned that, fine particulate structure of fly ash prevents the flocculating tendency of cement grains and provides a better dispersion of them in the water-cement system [9, 45]. This effect is analogous with the result of dosing a concrete mix with a conventional dispersing agent [14]. However, unlike a plasticizer, this dispersion is stable and can, therefore, create a more dense and uniform matrix by proceeding hydration as shown in Figure 4.2 [45].

Moreover, the increase of SiO_2 concentration over CaO produces an improved stability of the dispersion of the cement and fly ash particles in the highly alkaline fresh paste as quoted by ACI 226.3R-87 Committee Report [7]. Besides, weight-to-weight incorporation of fly ash as a partial cement replacement results in an increase in the volume of the paste in concrete due to the lower density of fly ash, than that of cement [7, 9]. While it depends on the proportions used, this increase in paste volume produces a concrete with improved plasticity and better cohesion [69, 70].

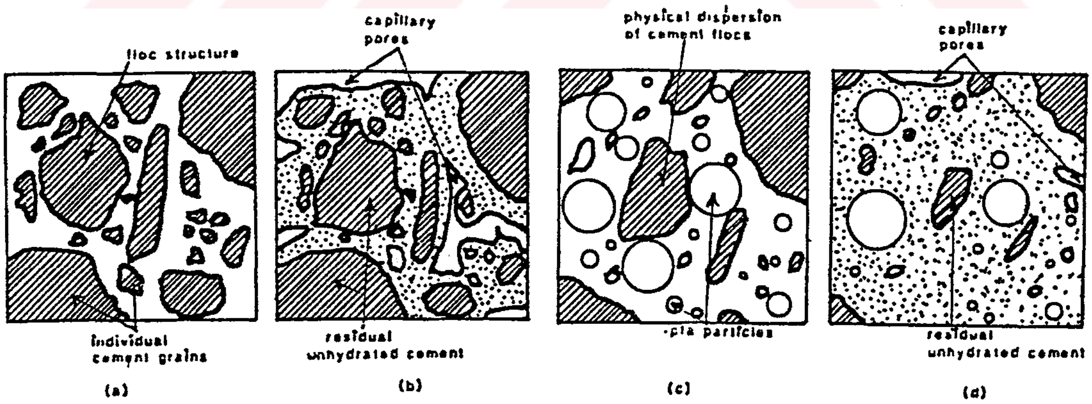


Figure 4.2. Idealized Model of the Effect of Fly Ash in the Freshly Mixed Concrete and the Consequent Hydrated Microstructure. (a) and (c) Freshly Mixed OPC Concrete and Fly Ash Concrete, (b) and (d) 28 Days Hydrated Microstructure of OPC Concrete and Fly Ash Concrete [45]

Although-unlike the other pozzolans the favorable influence of fly ashes on the water requirement reduction of concrete, for a known workability, is established as long ago as 1937 [1], the recent studies have shown that, the fineness of the fly ash and its carbon content, as well as the amount of fly ash in the mixture are the most important factors in this matter [71, 72, 73].

According to Ravina [71] fly ashes with high proportions of coarser particles increase concrete water demand. Owens [74], as cited by Berry and Malhotra [3], shares the same idea, stating that substitution of cement with high proportions (50 %) of fine particulate fly ash (<45 μm) can reduce the concrete water requirement in the order of 25 %. Minnick et al [72] have related the reduction in the water requirement of fly ash concretes to a multiple factor (LOI of fly ash x its % retained on No. 325 sieve), stating that the fly ashes having a multiple factor less than 100 result in a reduction in water requirement of the concrete for the same workability. ACI 226 committee [7] also reports the favorable effects of Class C fly ash having high proportions of particles less than 10 μm on concrete workability.

Samarin et al [69] have quoted the improvement of the rheological stability and resultant workability of the fly ash concretes using Australian fly ashes. The same results are reported by other investigators [76, 77, 78].

The beneficial influence of ball-bearing effect of fly ash particles on rheological stability and improved workability of high fly ash content concretes have been reported by Hague et al [73].

In spite of above mentioned investigations, there are, however, other studies confirming that some fly ashes may result in increased water demand or loss of slump at the same water content [3], [70, 75, 78, 80, 81].

4.2.2 Time of Set

There is a common agreement among the investigators that, fly ash incorporated mixtures set more slowly than corresponding non-fly ash systems, but the setting times are mostly within the usual specification limits unless very large amount of fly ash is used [10], [46]. The set retardation of fly ashes can be attributed to their higher water requirement [46], [72], or may be arisen from the fact that the soluble calcium and sulfate ions, from the surface of fly ash particles, can combine to form additional gypsum, which in turn, retards the hydration of C_3A [45], [65]. Obviously, this effect is more pronounced for high-lime fly ashes [63]. In addition, it has also been found that, Class C fly ashes may retard early C_3A hydration [64], [84]. It is necessary to point out, however, that some high-lime fly ashes, low in carbon and high in reactive constituents (crystalline or non-crystalline), may sometimes exhibit opposite behavior or have no significant effect on the time of set [75], [82].

It seems that, the effects of ambient and concrete temperature, cement type, content and fineness, water content of the paste, soluble alkalies, presence of other admixtures, as well as the amount of fly ash and its fineness and chemical composition must be considered simultaneously when setting time is regarded [83] as cited in ACI 226 Committee Report [7].

The set retardation in a reasonable limit is advantageous in mass concrete to prevent the formation of cold joints [55]. However, the increased pressure on the formwork due to improved workability, slower slump loss, and retarded setting characteristics of fly ash concretes must be taken in to consideration [7].

4.2.3 Bleeding

Fly ash concrete is generally reported to show reduced segregation and bleeding consistent with reduced water requirement and higher paste content than plain concrete.

The fine fly ash particles can carry an associated surface film of water, and act as a water-entraining agent through wide dissemination and retention of a significant proportion of the mix water through the plastic concrete, thus, reduce bleeding [45]. Linked with this effect fly ash, due to its pore refining property, can reduce the size of the bleed-water channels or even block them [10] to restrict the movement of free water in the plastic concrete, and consequently reduce bleeding. Figure 4.3 shows the typical effect of fly ash incorporation in reducing bleeding in concrete [85].

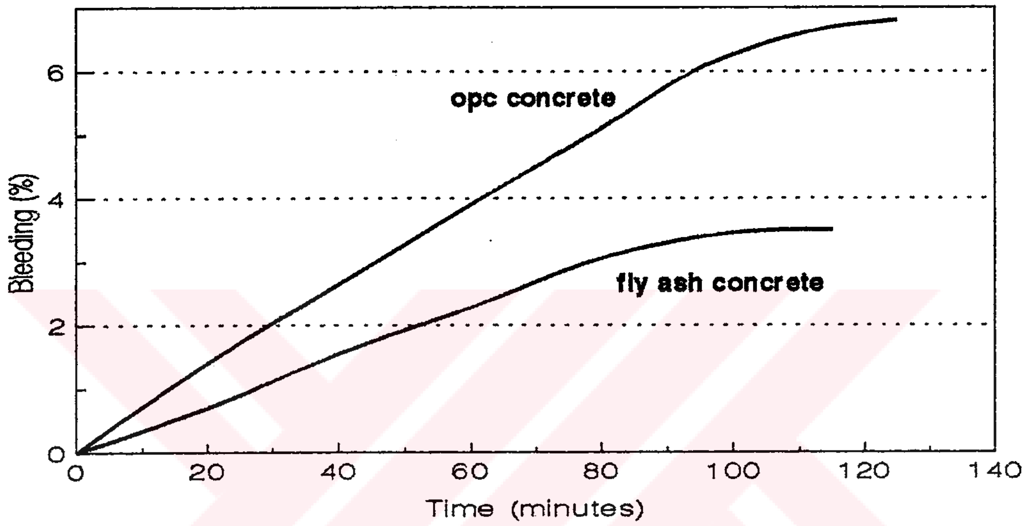


Figure 4.3. Effect of Fly Ash in Reducing Bleeding in Concrete [85]

In line with the improved rheological properties and placability and as a result of the fine particulate content, fly ash causes a marked improvement in pumpability and finishability of concrete when it is used as a replacement for either sand or cement. Effects such as these make apparent that, lean concrete mixes and those made with aggregate deficient in fines would benefit more from ash addition.

4.2.4 Influence of Fly Ash on Temperature Rise

The reaction of cement with water is exothermic and liberates a considerable quantity of heat. This heat generation can be classified into three stages by isothermal calorimetry as shown in Figure 4.4. Much attention has been paid to the temperature rise of concrete on account of its considerable importance in mass concrete construction. The principal causes of the serious cracking which has occurred in large concrete masses is the shrinkage which takes place as the mass cools from the high temperature attained during setting and early hardening.

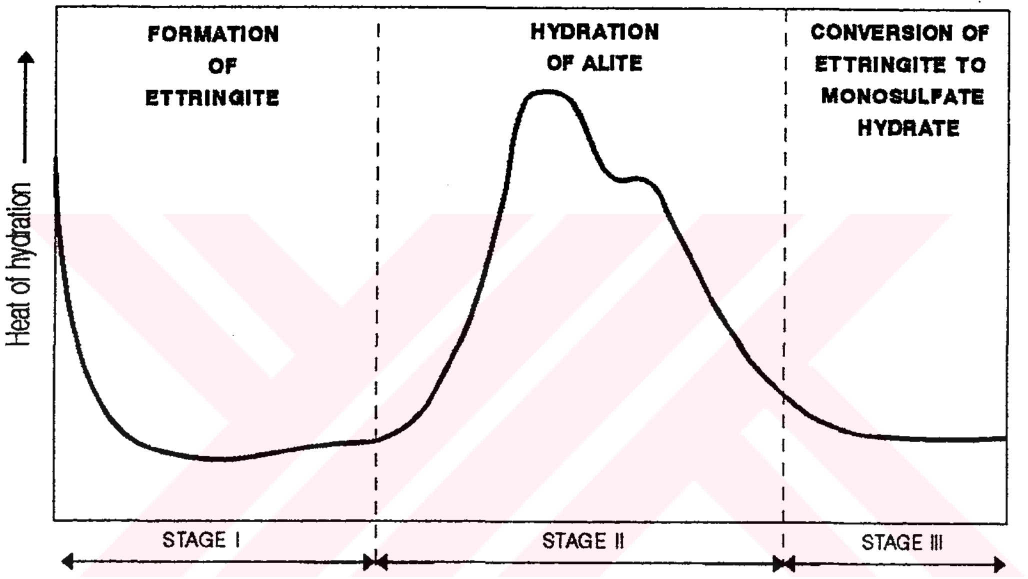


Figure 4.4. Classification of Cement Hydration Stages by Isothermal Calorimetry [63]

From the stand point of thermal stress on cooling, cement replacement by some fly ashes offers an obvious advantage [3, 10], and has long been exploited in mass concrete construction where low cement contents and as high as 100 %, by weight of cement, fly ash portions are often used to counteract thermal cracking.

Low-lime fly ashes are reported to reduce the temperature rise almost in the proportion in which they replace cement, since generally low-lime ashes do not react to any significant degree for several days. Berry and Malhotra [3] cite McInnis's work to show that, 30% cement replacement with fly ash resulted in a 30 % reduction in maximum temperature rise. Mehta [10] has quoted a field test carried out by Bamforth [86] to confirm a 15 % reduction in temperature rise at 30 % cement replacement level. Bamforth also reported that, compared to laboratory cured specimens, the early age heat cycle reduced the in situ 28-day strength of plain concrete up to 30% probably due to the less microcracking at lower thermal gradient in the laboratory. However, this was not the case in fly ash concretes where thermal gradient is lower and due to the accelerated healing of microcracks by fly ash-cement hydration products.

The advantages of temperature rise in concrete by replacing a part of cement with low-lime fly ash are clearly shown by several investigators [55, 75, 87]. The results of a recent case study, reported by Baoyu et al [88] show that, the concrete incorporating both silica fume (≈ 8 %) and low-lime fly ash (replaced for 25 % by weight of cement) resulted in a great decrease in the total heat of hydration.

High-lime fly ashes, on the other hand, due to their relative reactivity may not be as effective as low-lime ashes in reducing heat of hydration. Mehta [10] cited Vace and Robert's work showing that, the heat of solution by calorimetric method described in ASTM C 186 [89] was 422-507 cal/g for a number of high-lime ashes, whereas it was less than 405 cal/g for several low-lime ashes. Diamond et al [90], Tokyay [87], and Cook [91] have also shown that some high-lime fly ashes may contribute, to some extent, to early heat evolution of cement systems.

In a more recent study, Barrow et al [92] used two low-lime and two high-lime fly ashes to replace 20, 27.5, and 35 % by volume of cements. Three types of cements, Type I, Type II and Type III were tested to confirm a significant decrease in the temperature rise of the mortars containing low lime fly ashes regardless of the type of cement. This effect was more pronounced by increasing fly ash incorporation level. However, high-lime ash incorporated specimens attained the same, or even higher, maximum temperature rise than the control mix in all of the cements, except that the time to maximum temperature rise was delayed by approximately three to five hours. The contribution of these fly ashes to temperature rise increased at higher incorporation levels.

4.3 Effect of Fly Ash on the Engineering Properties of Hardened Concrete

The incorporation of fly ash in concrete leads to general enhancement in rheological behavior of fresh concrete and engineering properties of hardened concrete through both physical and physico-chemical mechanisms. Concrete mix proportions, rhelogical behavior of plastic concrete and degree of hydration are among the physical effects which are associated with particle size distribution of the fly ash. Strength, permeability and general durability are the main effects associated with the physico-chemical effects on pozzolanic and cementitious reactions of fly ash.

The physico-chemical process is responsible for the slow but long-term improvement of engineering properties of concrete due to: (a) acceleration of cement hydration as well as pore refinement because of physical densification derived from the presence of very fine fly ash particles in the mix and, (b) further pore refinement and also grain refinement in the hardened cement paste as well as paste-aggregate interface zone due to pozzolanic and cementitious reactions in portland cement-fly ash system [9].

Practical and laboratory studies, during the long history of the use of fly ash in concrete, have shown that, the improvements in properties of fly ash concrete depends not only on the particle size and mineralogical characteristics of fly ash, but also on the properties and relative proportions of other ingredients.

4.3.1 Methods of Fly Ash Inclusion as a Cementitious Material in Concrete

In practice, there are basically two approaches for fly ash inclusion in concrete, i) the use of a blended cement containing fly ash and, ii) the introduction of fly ash as a separate additional material at the concrete mixing plant.

The first method is simple and free from possible batching errors. Normal mix proportioning procedures can be applied and more uniform control may be assured. However, it is grossly inefficient for most structural applications where the early strength is a major design criteria. The second method is flexible and allows for more complete exploitation of the qualities of fly ash as a concrete component. This permits the most effective utilization of fly ash, and therefore, a great deal of effort has been devoted do develop suitable mix proportioning methods for this kind of fly ash concrete.

4.3.1.1 Mix Proportioning of Fly Ash Concrete

The main requirement of any concrete mix proportioning is to select the proportions of the constituent materials for a given set of conditions both in the freshly mixed state and in hardened state, at the lowest possible cost. The most commonly required concrete properties in this context are its workability, strength and durability, and in the case of mass concrete, the rate of temperature rise during first few days after placing.

In most applications, the objective in using fly ash in concrete is to achieve one or more of the following benefits [3]:

- Reducing the cement content to reduce cost and increase volume stability,
- Improving workability,
- Reducing heat of hydration,

- Attaining required levels of strength in concrete at ages beyond 90 days,
- Improving durability.

In common with the other constituent materials, the nature of any particular fly ash will greatly affect the properties of concrete in which it is used. It is the objective of the mix design method to minimize the unrequired effects of fly ash on concrete. Generally, two main assumptions are made in selecting an approach to mix proportioning fly ash concrete:

- Fly ash usually reduces the early age strength of concrete.
- For equal workability, fly ash concrete usually demands lower water than plain concrete.

As it was discussed earlier, neither of these two assumptions is universally true, and both are influenced by the characteristics and quantities of the other concrete components.

Throughout more than fifty years during which fly ash has been used in concrete, three basic mix proportioning approaches have developed [3, 45]:

a) Simple Replacement Method requires a direct partial replacement of cement with fly ash.
b) The Sand Replacement Method requires partial replacement of fine aggregate with fly ash.
c) The Additional Replacement Method and/or The Rational Method requires replacement of both a portion of cement and of fine aggregate with fly ash.

The fly ash concrete proportioned by simple replacement method, either based on equal volume or equal weight basis, exhibits lower early strength than the corresponding plain concrete, but depending on the replacement level, equal or higher strength may be achieved beyond three months. In this regard, high-lime fly ashes, due to their higher reactivity, differ greatly from low-lime ones [3]. Apart from its simplicity, this method provides a considerable cost reduction and results in a concrete of adequate quality particularly for mass concrete applications, where early strength is not a prime requirement. However, the main drawback is the considerable fluctuation in the pattern of strength development (and also durability) depending on the nature of cement, water demand of fly ash and its pozzolanicity, as well as the replacement level, as illustrated in Figure 4.5 [93].

In the second method, fly ash is added to the mix without corresponding reduction in cement quantity and necessary adjustments are usually made through changes in fine aggregate content. As a result of an increase in the effective cementitious material content of the mix, this method of inclusion provides higher strength values at all ages than corresponding non-fly ash concrete. However, the improvement at later ages is more pronounced and it is even greater than that obtained by an equal addition of cement as cited by Berry and Malhotra [3].

To overcome the deficiency of lower early strength of simply replacement designed fly ash concrete mixes, several additional replacement methods are proposed [93-98], by taking into account those properties of fly ash which affect the workability and strength of the concrete. All these methods have a common feature: the amount of fly ash put into the mix is greater than the amount of cement removed; the difference is accommodated by a simultaneous change in the aggregate proportions. It was shown that, the optimum fly ash-portland cement proportions and the actual quantity of fly ash in excess are dependent not only on the particle size and mineralogical characteristics of the selected fly ash but also on the type [94], quality and alkali content of the cement [95], the cement content of the original mixture [94] (with the extra required fly ash increasing as cement content decreased), the amount of cement removed [96], the presence of chemical admixtures, placement conditions and parameters, such as nominal design strength, curing conditions, and weather conditions at the time of placement [98].

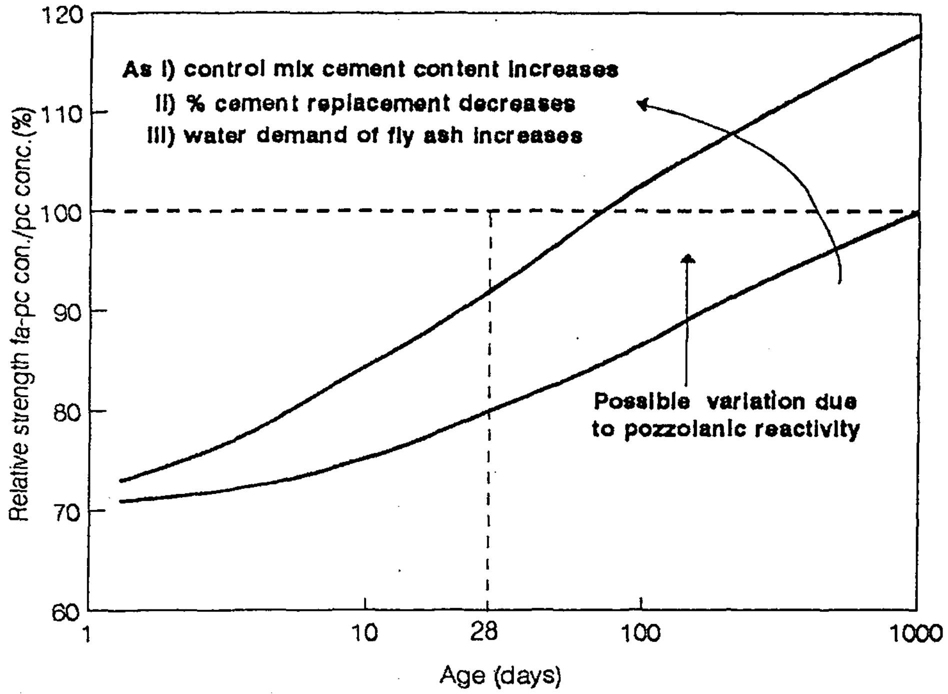


Figure 4.5. Strength Variation of Fly Ash Concrete Due to Different Mix Parameters [93]

In view of the long history of the use of fly ash in concrete, it seems that the most effective method for evaluating the performance of a given fly ash in concrete and establishing proper mix proportions for a specific application is by use of a trial batch and testing program. Since some fly ashes exceed the performance of others, the proportions established for a given fly ash and cement can not be applied for all materials and requirements. Therefore, a series of mixtures should be prepared and tested to determine the required total cementitious material content to obtain a specified strength with various percentages of fly ash rather than following any predetermined mix proportioning method [7, 91, 97].

4.3.2 Effect of Fly Ash Characteristics on Concrete Strength

There are a large number of studies showing the effects of fly ash on the strength of concrete at any given age and rate of strength gain of fly ash concrete. It is not possible to summarize all of these studies. Therefore, in this review, only selected investigations rather than extremely specified studies are considered and discussed.

There is a general agreement among the investigators that, the particle size and mineralogical characteristics (or type) of fly ash are the most important factors affecting the strength of concrete. The rate of strength development of high-lime fly ashes is comparable to that of control mix [78, 99]. However, cement replacement by low-lime fly ashes generally results in lower rates of strength gain up to even three months [70, 76], noting that in some exceptional studies, low-lime fly ash concretes have been reported to have comparable strengths with control concrete as early as three days age [100].

Carette and Malhotra [70], in their study on the performances of eleven Canadian fly ashes of different types and various origins, two lignitic, three subbituminous and six bituminous, have reported that, regardless of the type of fly ash, a 20 % cement replacement with fly ash resulted in a lower compressive strength up to 28 days age. At 28 days, except to one high-lime fly ash which showed an equal strength, the remaining fly ash concretes ranged from 70 to 95 % of that of control concrete. At 91 days, except for two low-lime fly ash and two high lime fly ash concretes, the remaining had still lower strength than plain concrete. Even after one year moist curing, only six of the eleven fly ashes had reached strengths exceeding that of control concrete whereas, the remaining had strength values lower than that of control concrete by 5 to 10% as shown in Figure 4.6.

Similar to what was observed with compressive strength, the flexural strength of eight fly ash concretes was consistently lower than that of the control concrete at the age of 28 days. At 91 days, except for two lignitic and one subbituminous fly ash included concretes which had strength values slightly exceeding that of control concrete, the others resulted in 5 to 10 % lower strength as illustrated in Figure 4.7.

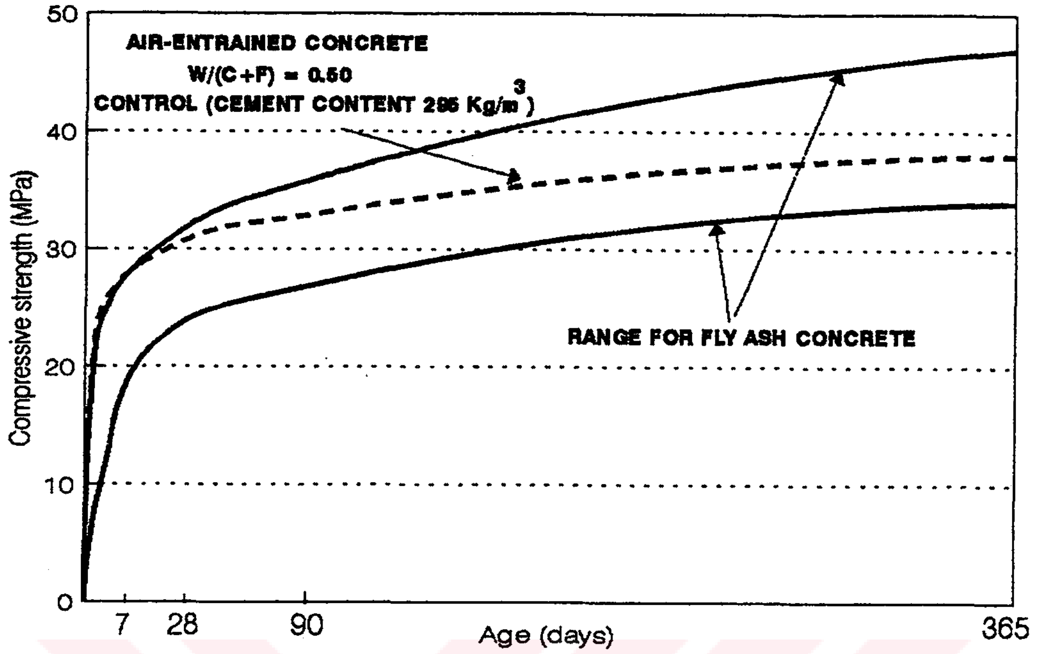


Figure 4.6. Compressive Strength Development of Fly Ash Concretes [70]

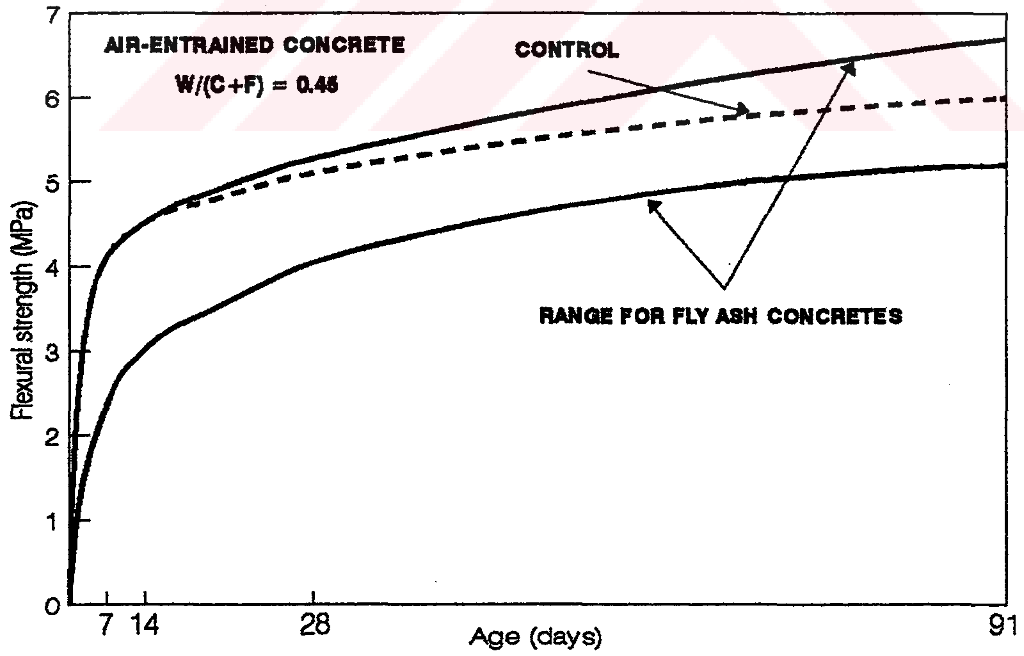
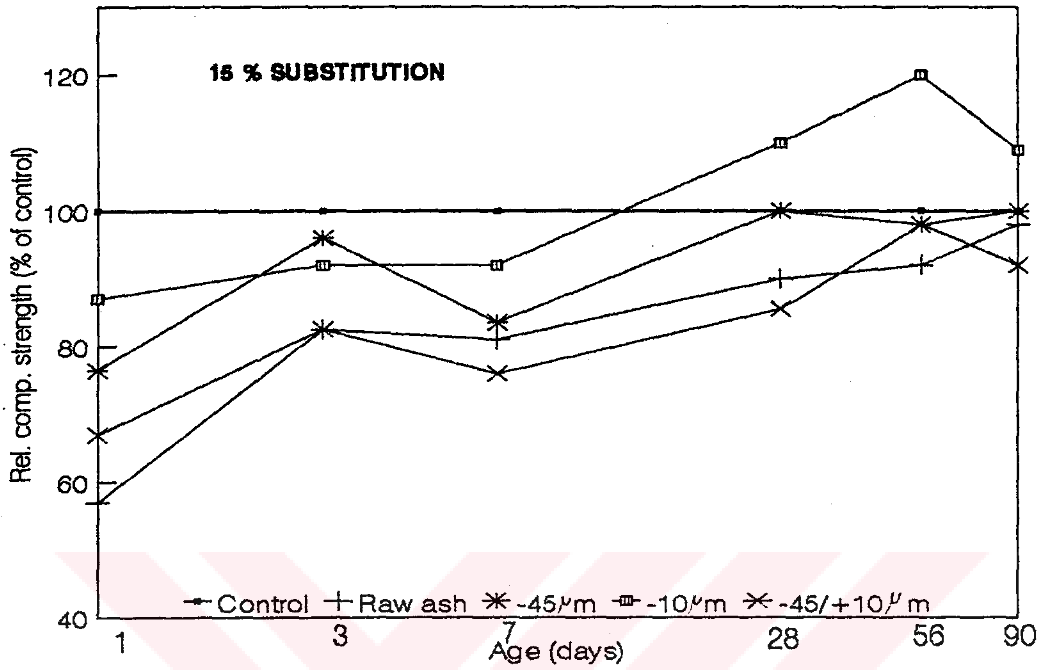


Figure 4.7. Flexural Strength Development of Fly Ash Concretes [70]

In another series of experiments conducted on ten different fly ashes, Gebler et al [78] have concluded that, moist cured concretes containing Class F fly ash, developed lower strength than either control concrete or Class C fly ash incorporated concrete at early ages. However, the long term (90-day and onwards) compressive strength of fly ash concretes was not significantly influenced by the class of fly ash. It is interesting to note that, one of the Class C fly ashes used in this study resulted in a superior compressive strength than control concrete even at one day age. In this study replacement level of cement with fly ash was 25 % by weight.

Berry et al [62] in their study on a low-lime fly ash have size separated the ash with nominal sizes of -45µm, -10µm and -45/+10µm. Then, the rate of strength development in PC-fa mortars of constant flow has been examined at 15 and 30% (by volume) ash substitution for portland cement. As it can be understood from Figure 4.8, the raw ash contained mortars, not surprisingly, reduced strength relative to the control mortar at all ages up to 90 days for both substitution levels. Mortars incorporating -45µm product reached equal strength with control mortar after 28 days and 56 days curing for 15 % and 30% replacement levels, respectively. The corresponding ages for -10µm products were shortly after 7 days and shortly after 28 days for lower and upper inclusion levels. The 90 day compressive strength, regardless of the inclusion level, for this size fraction was close to 110% of the control. Besides, it was observed that, incorporation of 30 % of -45µm fraction gave equivalent strength at all ages to 15 % raw ash incorporated mortars which indicates a significant potential for cement savings for finer sized fly ashes.

The results of all the above investigations are in agreement with the commonly reported fact that, high-lime fly ashes and very fine low-lime ones do contribute to substantial gain in strength at relatively early ages as opposed to most low-lime fly ashes whose contribution to strength becomes most significant only after age of 90 days or later. However, some high-lime ashes [70] may behave opposite to this. Using 28 days strength as a reference, strength increases of 50 % at one year for fly ash concrete as



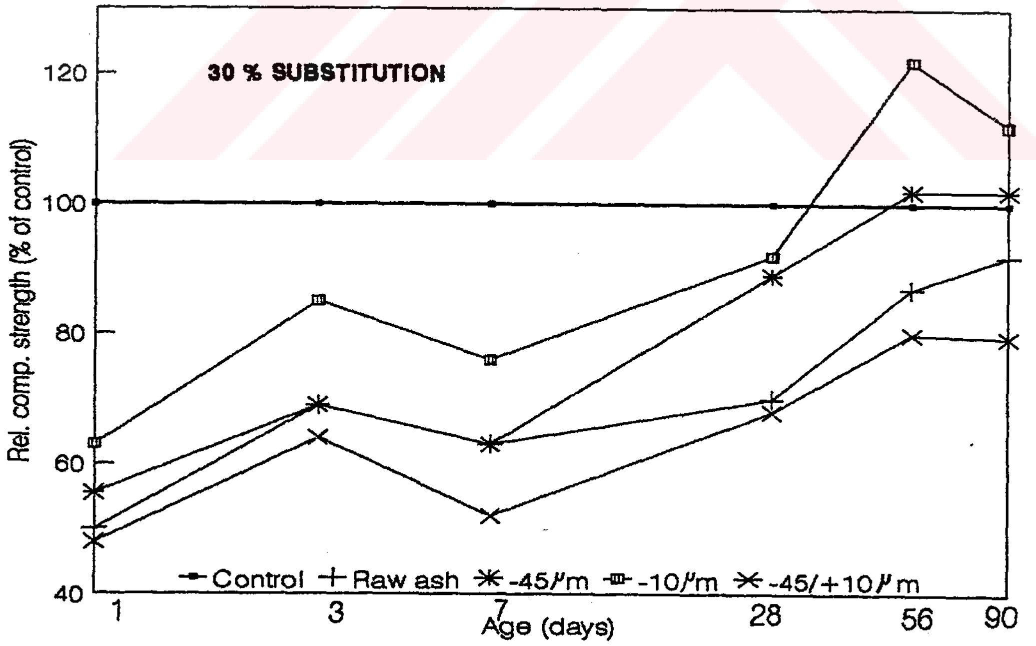


Figure 4.8. Relative Compressive Strength Development of Raw and Size Fractioned Fly Ash-Portland Cement Mortars [62]

compared with 30 % for corresponding non-fly ash concrete has also been reported [46].

Meanwhile, the ability of fly ash to aid in achieving high ultimate strengths or in rate of strength development depends on the composition of concrete. It is reported that, cements with alkali content of 0.6 % or more typically perform better with fly ash. However, when potentially alkali-reactive aggregates are used in concrete, low-alkali cement is generally specified, even if fly ash is also used [7].

There is a recent approach taken successfully by many investigators [101, 102] to enhance the low-early age strength of fly ash concretes by using fly ash and silica fume simultaneously. Carette and Malhotra [102] confirmed that, 30 % cement replacement by a low-lime fly ash in concretes containing 10, 15, and 20 % silica fume (by weight of cement) and a constant W/C ratio of 0.4 (by the use of plasticizer) was resulted in a higher strength value than plain concrete and almost twice that of concrete with fly ash alone at the age of 7 days. They also reported that at ages between 7 and 28 days, the loss in compressive strength of fly ash concrete was completely compensated by the addition of as little as 10 % silica fume. The same conclusions are also made by other investigators [88, 103].

In a more recent case study, Dunstan et al [104] reported the results of an investigation carried out to assess the conditions and properties of high-volume fly ash concretes, used in the construction of five different structures, after ten years of service and exposure. Low-lime fly ashes from seven different sources were used in these structures. The cement contents of the mixes were in between 175 to 290 kg/m^3 and fly ash inclusion levels were ranging from 50% to 125 % by weight of cement. The increase in compressive strength from 28 days to approximately 10 years was reported to be 10 to 40% in various structures. This is an indication of continuing contribution of fly ash to long-term strength development.

In another investigation [105], Bilodeau and Malhotra monitored the performance of high-volume fly ash concrete made with three different low-lime fly ashes. In this study, cementitious materials content of 300, 370 and 430 kg/m^3 and three water-to-cementitious materials ratio of 0.39, 0.31 and 0.27 were used. The percentage of fly ash used was 58 % of the total cementitious materials content. All the concrete mixes were air-entrained and superplasticized. They reported that, high-volume fly ash concrete with adequate early-age strength (up to about 13 MPa 7-day strength) and excellent later-age strength (up to about 42 MPa one year strength) can be produced with cement and total cementitious materials as low as 125 and 300 kg/m^3, respectively.

Papayianni [106] reported the use of a high-lime fly ash with a lime content of 42 % in roller compacted concrete. It was observed that, the fly ash when used in the range of 76 to 88 % of the total cementitious materials resulted in the highest strength values. Even in mixtures with only fly ash as cementitious material, strengths from 23.6 up to 33.7 MPa were obtained in 91 days. It is concluded that, this fly ash behaves as a hydraulic binding agent and its free lime reacts with SiO_2 without creating any volume instability.

4.3.3 Effect of Curing Condition on Fly Ash Concrete Properties

Adequate curing (i.e. availability of moisture and the prevailing temperature) is a key factor in the development of strength as well as in achieving impermeability and durability in both plain concrete and fly ash concrete. The ACI, Recommended Practice for Curing Concrete [107], suggests 7 days of moist curing for most structural concrete, or the time necessary to attain 70 % of the specified strength, whichever is less.

Curing time is expected to be larger if fly ash or any other pozzolan is to be used, to allow for the slower pozzolanic strength development [3, 107, 108]. However, some investigators including Dhir [58] do not share the same idea stating that, a properly designed fly ash concrete does not suffer from the lack of moisture any more than does the corresponding plain concrete as shown in Figure 4.9.

Concrete will hydrate even if it is not in a fully saturated condition. This is because, the cement can draw on water reservoirs held in large capillary pores by surface tension forces below 100 % relative humidity (R.H.), for further hydration. However, the rate of hydration will become slower, and when internal relative humidity drops below about 80 %, the binder reactions are ceased and strength development is arrested. In order to promote pozzolanic and hydration reactions and to decrease the volume of large pores, a 95 % or higher R.H. is required, at least during the early age curing [104, 110, 116, 117]. The presence of sufficient moisture for binder reactions of both cement and fly ash does become obvious. So, discussions in this part will be focused on the curing temperature.

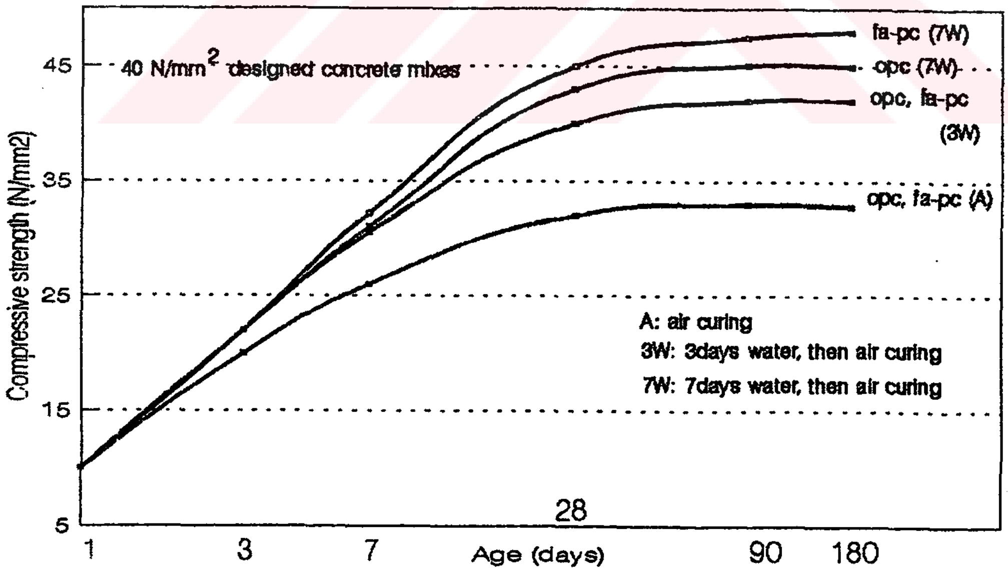


Figure 4.9. Strength Development of Concrete with Varied Duration of Initial Moist Curing [59]

Many investigators have shown that, curing temperature as well as fineness of fly ash play an important role on the reactivity of fly ash [9]. Besides, the products of hydration of fly ash-cement system do not exhibit the poor mechanical properties associated with curing plain cement systems at elevated temperatures. The detrimental effects of curing temperatures on the pore volume of plain cement paste and its beneficial effects on the pore volume of fly ash blended cement paste is also reported by Mangat and El-khatib [117]. These may be due to the difference in the relative proportions and the morphology of the hydration products of thermally accelerated cement with that of cement-fly ash system [3]. Mehta [9] has cited his own work [111] on several U.S. low-lime and high-lime fly ashes, to show that PC-fa mixtures cured at 50°C (a temperature easily available by massive concrete) produce similar level of strength in 7 days as normally cured (20°C) mixtures in 28 days. The effect of high temperature evolved in mass concrete or cement-rich concrete sections on the strength development of plain and fly ash concrete are also reported by Dhir et al [58] as shown in Figure 4.10:

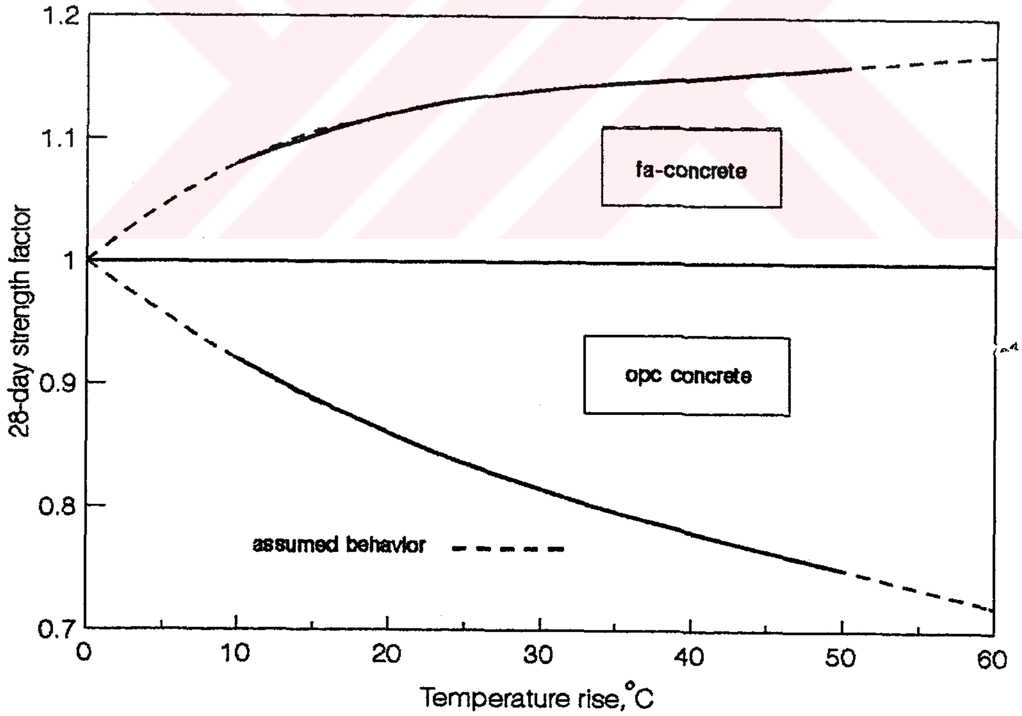


Figure 4.10. Effect of Early-Age Temperature Rise Due to Heat of Hydration on 28-Day Strength of Concrete [58].

Owens [112] reported that, temperature rise and fall of concrete at early ages, caused by cement hydration and referred to as in-situ temperature cycle (ITC), reduce the performance of plain concrete and that the performance can be improved by the inclusion of fly ash. Compared with standard curing, the effect of ITC on the plain concrete resulted in 22 % strength reduction, while fly ash concrete had an 18 % increase in strength. Bamforth [86] and Gopalan [113] as cited by Hague [110] made similar conclusions.

Hague and Gopalan [110] reported that, although a 10°C increase in curing temperature at 75 % R.H. increased the strength of both plain and fly ash concrete, the strength increment was more pronounced in fly ash concretes with higher replacement levels. However, the same increase in temperature at 50 % R.H. decreased the strength of all tested concretes. They concluded that, in addition to a high temperature, presence of sufficiently high relative humidity is also necessary for strength development of concrete.

Ravina [114] showed that, the rate of reaction of fly ash in cement systems is so significantly increased by temperature, that the effects of particle size on pozzolanic behavior are largely overcome. Besides, the pozzolanic reaction, once initiated by heat, continues even after removing the external heating source. The same results are also reported by Dalziel [115], Tokyay [13], Thomas [108] and Gebler et al [78].

4.3.4 The Effects of Fly Ash on the Elastic Properties of Concrete

Published data indicate that, in association with compressive strength, the modulus of elasticity of fly ash concrete is somewhat lower at early ages and a little higher at later ages (91 days and above) than corresponding plain concrete for a given variety of curing conditions [3, 4, 6, 70, 118]. In a more recent work, discussing the effects of Canadian fly ashes on various properties of concrete, Carette and Malhotra [70] found that 28 days modulus of elasticity of fly ash concrete varied between about 90 % and 110 % of the elastic modulus of control concrete. The obtained data in their experiments provided no clear indication of significant effect of fly ash or type of fly ash on the modulus of elasticity of concrete. They attributed the observed differences, if any, to the variability of the test, rather than the presence or the inclusion level of fly ash. ACI Committee 226 [7] makes the same statement and concurs that cement and aggregate characteristics have a greater effect on modulus of elasticity than the use of fly ash.

Sri Ravindrarajah and Tam [119] reported that at early ages the reduction in modulus of elasticity of low-calcium incorporated fly ash concrete, having different inclusion levels, with respect to control concrete, increased with the reduction in concrete grade and with the increase in the fly ash replacement level. However, at later ages, regardless of the above mentioned factors, the elastic modulus of fly ash concrete was comparable with that of control concrete.

Dhir [45] has cited the relationship between strength and modulus of elasticity of plain and fly ash concrete containing different fly ashes with fineness varying from 3 % -30 % retained on the 45µm sieve and loss on ignition varying up to 5 % and cured at four different regimes. The results as shown in Figure 4.11 are in a good agreement with other published data.

Bilodeau and Malhotra [105] obtained 91-day modulus of elasticity of high-volume fly ash concretes, containing 58 % fly ash by weight of total cementitious materials, from 37.3 to 43.7 GPa. Considering that, 91-day compressive strengths of these concretes range from 30.1 to 50.3 MPa, and regarding the equation proposed by ACI Committee 363 [189], these values are indeed high. They suggested that, this could be due to the unhydrated fly ash particles acting as fine aggregate and thus contributing to an increase in the modulus value.

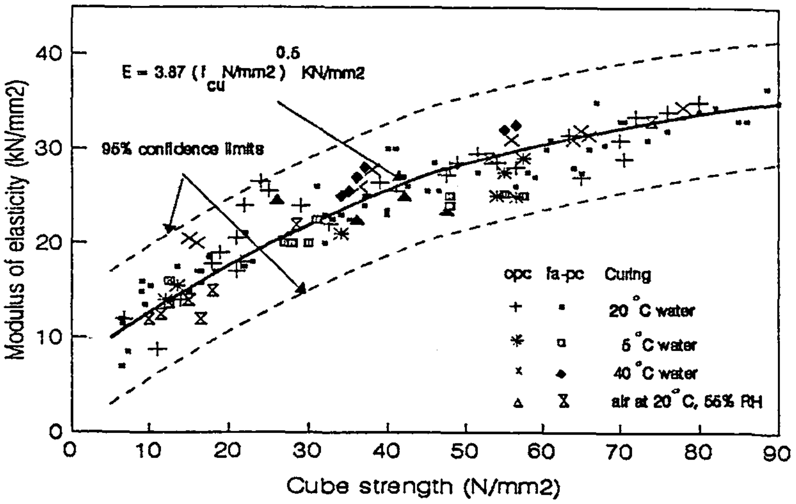


Figure 4.11. Relationship Between the Modulus of Elasticity and Strength of Concrete with and without Fly Ash [45]

4.3.5 Effect of Fly Ash on the Creep of Concrete

Creep is related to the removal of absorbed water from hydrated cement paste. In general, the rate and magnitude of creep deformation in fly ash concrete, same as plain concrete, depends on several factors; including strength of concrete (W/C ratio and curing condition), modulus of elasticity, aggregate content and aggregate stiffness, creep stress/strength ratio and age of concrete when loaded [3, 7, 9, 45]. These investigators agree that, the extend of fly ash incorporation effect on the creep strain can be limited to its influence on the strength development of concrete. Therefore, at early ages, fly ash concrete with a given volume of cementitious material (cement + fly ash) will normally exhibit lower strength and consequently higher creep strain than concrete having an equal volume of cement alone.

However, many investigators including Lane and Best [46], Dhir et al [61], Carette and Malhotra [70], Bamforth [86] and Ghosh and Timsuk [120] showed that fly ash concrete, having the same strength as plain concrete at the age of subjecting to a certain sustained loading, produced less creep strain at all subsequent ages. Carette and Malhotra [70] have attributed the reduction in creep strain, to the differences in the nature of hydrated cement-fly ash gel. Mehta [9], on the other hand, confirms that the improvement in the microstructure and strength of aggregate-cement paste transition zone (particularly in high-strength concrete) is responsible for creep strain reduction.

It should also be noted that, the conclusions made above are acceptable for reasonable fly ash inclusion levels ranging up to about 20 % by weight of cement. As shown in Figure 4.12, with higher levels of fly ash incorporation (30 % and above), considerably higher creep strains are reported [121, 122]. The higher paste volume, due to the lower density of fly ash compared to that of portland cement, coupled with the lower strength is responsible for this behavior. However, some individual studies have shown contradictory data [119, 123, 124], reporting lower creep strains even at 50 % inclusion levels. In a more recent study, Bilodeau and Malhotra [105] tested the creep of high-volume fly ash concretes containing 58 % fly ash by the weight of total cementitious materials content. They observed that, in spite of a much lower stress-strength ratio, the reference plain concrete showed creep strain similar or noticeably higher than those of most of the high-volume fly ash concretes. The investigators concluded that, the low creep strain of high-volume fly ash concretes could be the result of unhydrated fly ash particles in the concrete acting as fine aggregate, and thus providing restraint against creep.

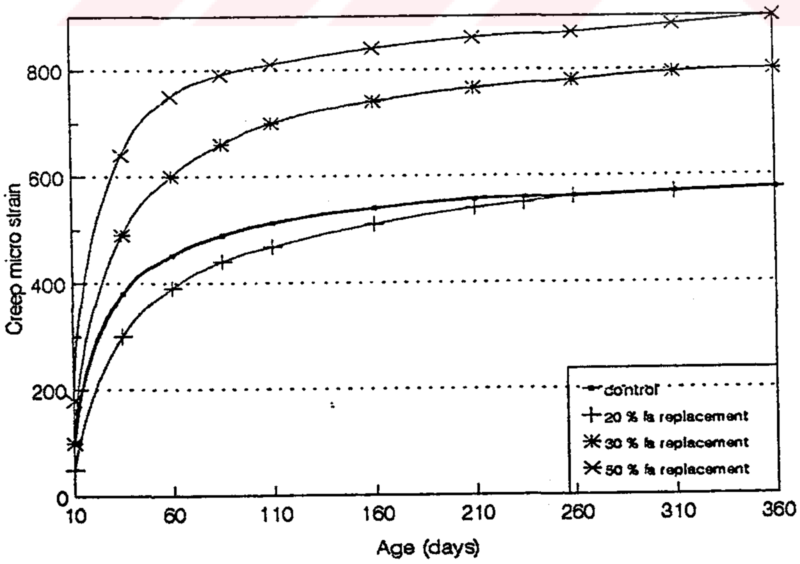


Figure 4.12. Creep of Fly Ash Concretes [121]

4.3.6 Effect of Fly Ash on Load-Independent Volume Changes of Concrete

There is no general agreement with regard to factors affecting the drying shrinkage of even non-fly ah concrete. However , it is commonly believed that, drying shrinkage is a function of the volume percentage of paste present in concrete [15, 45]. Since the replacement of cement by fly ash in concrete increases the paste volume, the drying shrinkage is expected to increase in fly ash concretes. However, this simple hypothesis is not supported by the data reported in literature [1, 5, 70, 119, 120, 121, 125]. In all of these investigations, it is found that, parallel to that observed for creep behavior of concrete, the use of fly ash in reasonable proportions (up to 25% by weight of cement) does not significantly influence the drying shrinkage of well-cured concretes.

Dhir [45] explained the reduction in drying shrinkage of fly ash concrete by the reduction in water demand of concrete and formation of a finer paste structure resulting in restricting the loss of pore water within the paste and consequently in reducing drying shrinkage.

As cited by Mehta [9], Munday et al [125], using a low-lime fly ash, found little differences between drying shrinkage values of several fly ash and non-fly-ash concretes for lower inclusion levels. However, when the cement replacement level was high (> 50 %), the drying shrinkage was significantly higher than control concrete. Nasser and Al-Manaseer [123] share the same idea using a lignite fly ash at 50% replacement level.

Sri Ravindrarajah and Tam [119] found that, the drying shrinkage is affected both by strength level of concrete and fly ash inclusion level, as well as curing regime. It was concluded that, fly ash concrete should be sufficiently cured in order to have similar or higher volume stability than plain concrete. The decrease in drying shrinkage of fly ash concrete with increased moist curing period is attributed to the decrease in porosity of concrete through pozzolanic reactions improvement.

Swamy and Mahmud [124] have compared the shrinkages of high-volume fly ash concretes (50 % fly ash replacement) having 20, 40 and 60 MPa 28-day design strength. Three different curing regimes, standard moist curing, uncontrolled laboratory condition and outside drying environment were applied. The highest shrinkage and swelling values were recorded to 20 MPa concrete. The 60 MPa samples showed marginally higher shrinkage values than 40 MPa ones under both exposure conditions. This fact was attributed to the higher (about 1.4 times) binder material content of the former mix by the authors. However, the final measured shrinkages of all mixes were below the predicted ultimate shrinkages. About 50 % and 90 % of the final shrinkages were likely occurred within 14 days and 90 days of drying respectively. Besides, the swelling strains of concrete, when exposed to continuous moist condition, amounted to 40-55 % of their shrinkage value. It was stated that, the tendency of fly ash concrete for higher water absorption compared to conventional concrete is an indication of its need for longer curing period to provide continued hydration and complete pozzolanic reactions.

Ukita et al [126] used a sized separated fly ash of nominal 20, 10 and 5μm maximum particle sizes to report that at 15 % replacement level and with finer fly ash, drying shrinkage was lower than that of plain concrete. Samples with higher fly ash content, regardless of the nominal size of fly ash particles, showed somewhat higher, but negligible, drying shrinkage compared to that of plain concrete. Besides, no relation was found between compressive strength and drying shrinkage of mixes and concluded that, it is better to correlate drying shrinkage with the aggregate content rather than the strength of concrete .

As quoted by Berry and Malhotra [5] and Dhir [45], some results are also available which show that the fly ash incorporation also does not significantly affect the wetting expansion, alternative wetting and drying expansion, or thermal expansion of concrete.

4.4 Effects of Fly Ash on Durability of Concrete

Absence of durability or deterioration of concrete during its service life, may be arisen from either external or internal causes. The external causes affecting the durability may be physical, chemical or mechanical. The internal causes include alkali-aggregate reaction, volume changes due to differences in thermal properties of aggregate and cement paste, and above all the permeability of concrete, which controls the vulnerability of concrete to external aggressive agencies.

In studying the durability of fly ash concrete, the effect of the intrinsic characteristics of fly ash itself in combination with other ingredients, as well as the improvement of concrete structure by fly ash and its consequent response to the external aggressive agencies should be considered simultaneously.

4.4.1 Effects of Fly Ash on Permeability of Concrete

It is well known that all the cementitious hydrates and some of the concrete aggregates are sensitive to attack by sulfates, chlorides, acids, organic agents and even by water. The movement of aggressive solutions into concrete and the removal of the dissolved reaction products out of concrete play a primary role in the rate of concrete deterioration caused by chemical attack. Therefore, the permeability of concrete mass is fundamental in determining the rates of mass-transport relevant to destructive chemical action or attack by pure water.

Whether the use of fly ash in concrete can effectively reduce its permeability, would in final analysis depend on the proportioning of the binder material, i.e. relative amounts of portland cement and fly ash in the mix, the age of concrete and its curing history [45].

The quantitative data from water permeability tests on concrete are generally not reliable because of experimental difficulties in achieving a steady state flow or other problems [9]. However, Berry and Malhotra [3] cited studies dated as far back as 1950's to show that well-cured fly ash concrete pipes, having 30 to 50% of cement replaced with fly ash, were approximately five times as impermeable as the corresponding plain concrete at six months age. The authors also quoted data from water permeability tests on cement pastes by Manmohan and Mehta [127], and chloride ion permeability tests by Short and Page [128], which confirm earlier work.

Gebler and Klieger [78] concluded that, regardless of the fly ash type, at 25 % replacement level, the air entrained fly ash concretes were as resistance to chloride ion penetration as corresponding air entrained plain concrete. The same result is confirmed by Plante and Bilodeau [129].

Ukita et al [126] used a raw low-lime fly ash and its classified separate grades with nominal sizes of -20, -10, and - 5µm at 15% and 30% replacement levels. They concluded that, 28-day cured fly ash samples having 15% replacement level were less permeable than plain concrete. At the same age, for 30% inclusion level, fly ash concretes showed lower water tightness compared to plain concrete, regardless of the fineness of fly ash. However, by increasing the curing period to 91 days, a sharp reduction was observed in the permeability of fly ash concrete, but it was still a little higher than control concrete as shown in Figure 4.13.

In another similar investigation, Berry et al [62] used classified fly ashes with nominal sizes of -45µm and -10µm. The inclusion levels of fly ash was again 15 and 30% by weight of cement, but tests were conducted on pastes. The porosity and water permeability of the samples were determined at several ages as shown in Table 4.1.

In this investigation, all pastes showed progressive decrease in permeability to water with curing age. At 1-day, the permeability of fly ash paste containing 15%, -10µm fly ash (1015) was approximately one half of the control sample, 1030, and 4515 pastes. At 7-day the 1015 paste and the control paste showed similar permeabilities which were considerably lower than the permeability of remaining pastes. However, at 28-day the 1030 paste had the lowest measured permeability of the set followed by

4530 paste. It was concluded that, PC-fa pastes containing 30% fly ash were considerably less permeable than control concrete at 28-day age. This was an evident indication of reasonably higher fly ash loading being beneficial in this respect.

In a more recent study, Marusin [130] measured the permeabilities of three concrete mixes in which 30% of cement was replaced by three types of fly ash, Class F, C and F/C, and a control concrete. For all four concretes, the chloride ion permeability decreased when the length of moist curing was increased from 7 to 28 days. However, after 12 months of testing the two mixes containing fly ashes Class F and F/C exhibited such low chloride ion contents at depths below 25 mm that, the length of moist curing had little influence in chloride ion reduction in contrast to that found for control concrete and, to a lesser extent, for concrete containing Class C fly ash. It was concluded that, use of all three fly ashes resulted in remarkable improvement in concrete impermeability when compared with control concrete.

4.4.2 Effect of Fly Ash on Freezing-Thawing Resistance of Concrete

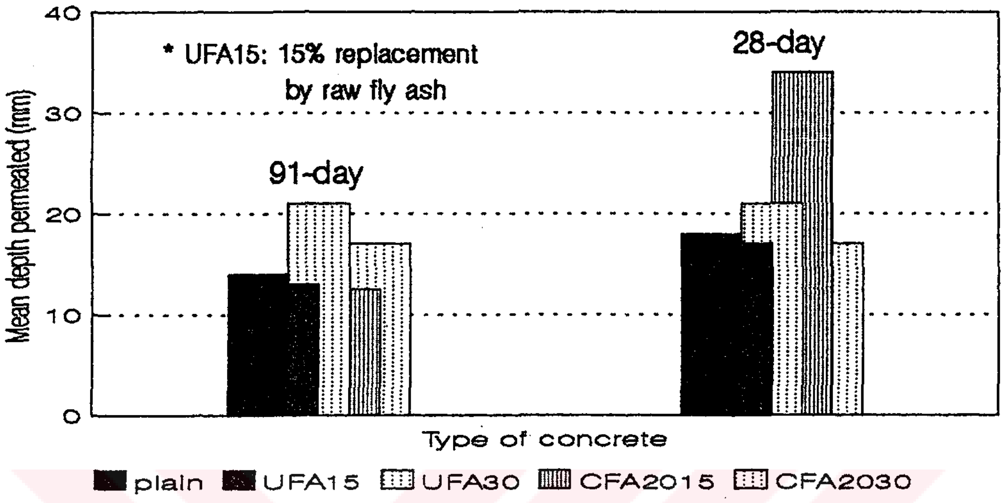
The resistance of concrete to damage from freezing and thawing depends on the air-void system, the soundness of the aggregate, age, degree of hydration, strength of cement paste and moisture conditions of concrete [131, 132]. When concrete is to be exposed to frost action, it must be protected from expansion and cracking by the use of air-entrainment. For satisfactory resistance to freezing and thawing, an air content of 4-7%, a bubble spacing factor of <200 µm and a bubble specific surface of > 24/mm are generally required [9].

The results of several studies [55, 70, 118] carried out on the frost resistance of fly ash concretes containing either low-lime [46] or high-lime fly ashes [98, 133] have shown that, the fly ash concrete represents no greater risk from frost attack than the corresponding plain concretes, as long as the concrete has sufficient strength and air content [9, 70, 121,134].

Table 4.1. Porosimetry and Permeability Data for PC-fa Pastes [70]

Paste	Age	Total Pore Area (m²/g)	Avg. Pore Diam (μm)	Bulk Density (g/cm³)	Skeletal Density (g/cm³)	Porosity (%)	Perme-ability (cm/sec)
Control	1d	38.3	0.035	1.37	2.50	47.4	1.2x10
	3d	53.4	0.022	1.45	2.54	42.5	4.9x10
	7d	53.9	0.019	1.47	2.39	38.4	6.5x10
	28d	50.7	0.018	1.51	2.33	35.0	6.2x10
4515*	1d	28.8	0.045	1.43	2.65	46.0	1.1x10
	3d	48.4	0.026	1.40	2.48	43.6	2.0x10
	7d	50.4	0.023	1.40	2.32	39.7	1.3x10
	28d	50.7	0.020	1.50	2.39	37.4	1.3x10
4530	1d	24.4	0.061	1.32	2.57	48.6	7.1x10
	3d	43.2	0.031	1.42	2.70	47.5	4.7x10
	7d	50.7	0.026	1.32	2.30	42.8	5.6x10
	28d	55.9	0.020	1.43	2.42	40.9	1.0x10
1015	1d	32.9	0.041	1.37	2.54	46.3	6.0x10
	3d	43.3	0.028	1.41	2.46	42.7	5.4x10
	7d	53.9	0.022	1.42	2.43	42.1	6.1x10
	28d	55.0	0.019	1.47	2.36	37.9	2.9x10
1030	1d	41.0	0.039	1.29	2.62	50.9	1.6x10
	3d	49.0	0.030	1.35	2.66	49.3	2.3x10
	7d	50.0	0.026	1.36	2.43	44.3	1.9x10
	28d	63.9	0.020	1.35	2.35	42.4	5.3x10

* 4515 for instance denotes that 15% of cement is removed by - 45 μm fly ash



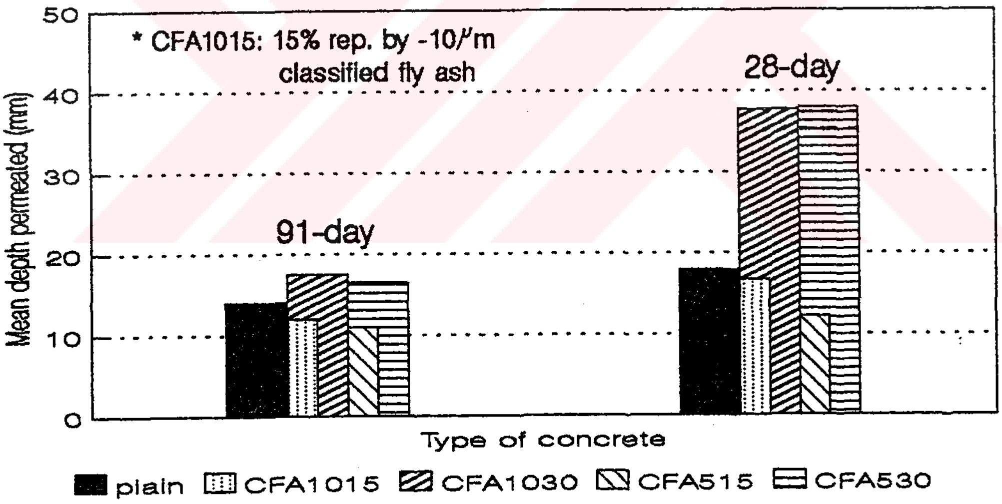


Figure 4.13. Comparison of Water Permeabilities of Plain Concrete, Raw Fly Ash Concrete and Classified Fly Ash Concretes [126]

However, the air entrainment in fly ash concrete may give rise to difficulties with the variability of air content, as well as void size and distribution. For example, because of the slower strength gain of low-lime fly ash concrete, more cementitious material (cement+fly ash) is normally used to achieve comparable maturity at 28 days. This increased amount of cementitious material requires an increase in the dosage of air-entraining agent used for unit volume of the concrete in order to obtain equivalent air content [7]. Besides, the increased dosage of air entraining admixture in fly ash concrete is also attributed to the organic matter, carbon and SO_3 content of the fly ash [54, 55, 86, 133].

It should also be noted that, there are no reports which show frost damage to concrete arising as a direct result of the fly ash. However, as cited by ACI Committee 226 [7], application of deicers were observed [135] to cause a slightly higher loss of surface mortar from fly ash concrete. This can be attributed, in part, to the suboptimal finishing or curing of the fly ash concrete surface, and in part, to the differences in carbonation due to a less amount of calcium hydroxide available in the mix [7].

Nasser and Lai [136] investigated the resistance of fly ash concrete containing 20, 35 and 50% Class C fly ash by weight of cement, to freezing and thawing. They showed that, the use of high percentage of fly ash in concrete (35 and 50 %) reduced its resistance to freezing and thawing even though it contained about 6 % air and was cured in water for 80 days. However, concrete containing 20 % fly ash gave satisfactory performance provided that, its air content and strength were comparable to control concrete which contained no fly ash. Results from SEM examination showed that, the decrease in resistance of fly ash concrete to freezing and thawing may be due to the slow migration of portlandite and ettringite crystals from the dense C-S-H zones to the air voids. Fly ash concrete was less susceptible to the migration of portlandite, but its air voids contained more fibrous hydrates which may have led to increase the paste porosity.

4.4.3 Effect of Fly Ash on Carbonation of Concrete

Carbonation is the reaction of CH, and to a less extent, the hydrated calcium silicates and aluminates with CO_2 from the atmosphere. The rate of carbonation depends on permeability, availability of CH in concrete mass, as well as on the relative humidity of the surroundings [3, 138].

A well compacted properly cured concrete at a low W/C ratio will be sufficiently impermeable to resist carbonation beyond the first few millimeters. The progress of carbonation into concrete mass may increase its permeability and shrinkage [3]. Besides, when carbonation proceeds, the pH value of concrete is lowered (concrete loses its basicity) so that reinforcement is more readily attacked by aggressive ions and corroded [139]. However, little is known about the relationship between carbonation and loss of functional efficiency of structural elements.

The results of several field observations [75, 137, 143], numerous laboratory studies [138, 139, 141, 142] extending as long as 20 years, and different investigations carried out using higher concentration of CO_2 to provide accelerated carbonation [140, 144] on the fly ash concrete can be summarized as follows:

- Initial curing period affects the carbonation of concrete and hence, it is necessary for fly ash concrete to have a long curing period at early ages.

- Carbonation will progress with advancement of age, and this effect is considered as proportional to the square root of age in some investigations.

- Carbonation is influenced by environmental conditions, i.e. relative humidity and concentration of CO_2. Depth of carbonation is reported to be the highest at a relative humidity of 65 % regarding other factors the same.

- The nature of cement plays an important part in the carbonation effect, ordinary portland cement with high C_3S content seems to be the most resistance against carbonation, although the rate of carbonation increases with the availability of CH in the system. However, fly ash inclusion at less than 20% (by weight of cement) has no significant effect on rate of carbonation, but at higher fly ash contents the carbonation is enhanced. Mehta [10] states that, reduction in the permeability of concrete through the formation of additional cementitious products improves the overall resistance of concrete to CO_2 attack.

- There is a linear relationship between 28-day compressive strength and depth of carbonation regardless of fly ash replacement. Therefore, it is possible to evaluate the potential depth of carbonation by knowing the 28-day compressive strength. This relationship is not valid under changing exposure conditions or initial water curing periods. It also changes with age as shown in Figures. 4.14 and 4.15.

- The addition of fly ash to concrete without cement reduction decreases the penetration of CO_2, whereas simple replacement of cement with fly ash accelerates the carbonation process. This is ascribed to the fact that when fly ash replaces cement, CH is reduced for both cement reduction and pozzolanic reaction which makes the carbonation process more rapid. The electrochemical measurements indicate that every process which is able to reduce the concrete alkalinity, such as the pozzolanic reaction due to the presence of fly ash, is a necessary condition but not a sufficient one to promote corrosion in reinforced concrete. Instead, rebars corrosion seems to be strongly affected by the concrete permeability, and then by concrete porosity [145].

- Fly ash concrete usually shows larger carbonation depth than plain concrete, but there is no evidence to suggest that corrosion of reinforcement is also higher in fly ash concrete, because, reinforcement in a carbonated concrete does not necessarily corrode unless depassivating ions are present. Furthermore, if cover requirements of structures are achieved during construction, the steel will continue to remain passive for the whole service life period even where fly ash is used.

- The depth of carbonation of concrete is related to cementitious material content, type of cement, slump and fly ash inclusion level by some researchers. However, the influence of these factors may be considered to be the effect of compressive strength at 28 days age. It is reported that [75], there is no significant difference between carbonation of fly ash and plain concrete as long as they are proportioned on the basis of equal slump and 28-day strength.

- The carbonation coefficient defined as depth of carbonation (in mm) divided by square root of exposure duration (in years) is proportional to air content of concrete independent of the fly ash replacement and fly ash type. However, the carbonation coefficient of concrete with the same air content depends on the fly ash replacement level.

- Accelerated tests give consistent results with the field observations or with the actual test with exposing concrete to atmospheric CO_2.

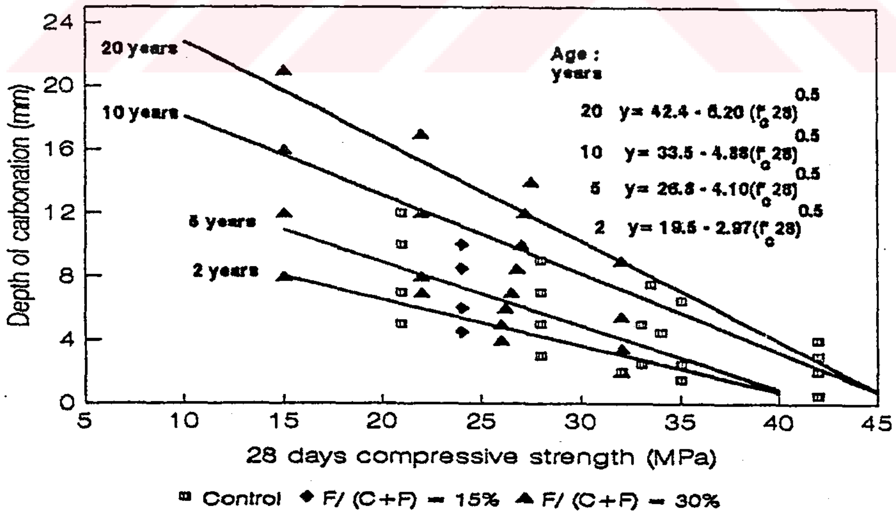


Figure 4.14. Relationship Between 28-Day Compressive Strength and Carbonation Depth Using Ordinary Portland Cement and a Low-Lime Fly Ash [141]

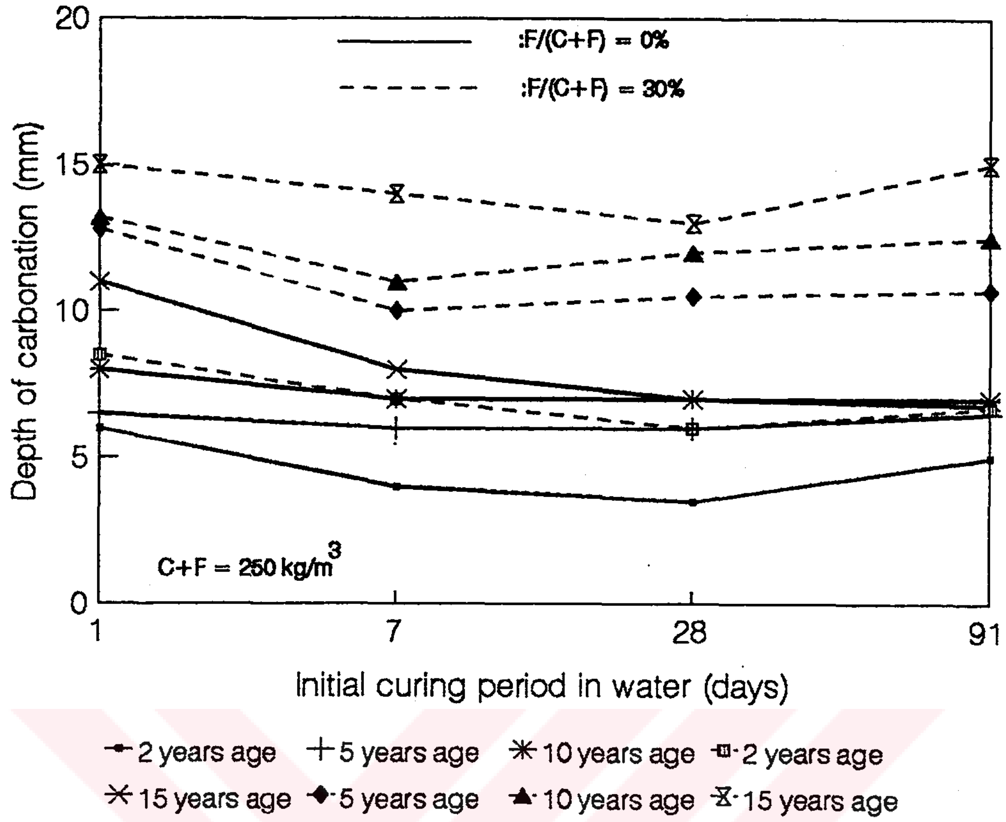


Figure 4.15. Effect of Initial Curing Period on Carbonation Depth of Fly Ash and Plain Concrete [141]

4.4.4 Effect of Fly Ash on Sulfate Resistance of Concrete

Water soluble sulfates, if present in excessive amounts, can damage concrete through reaction with certain constituents of hydrated cement paste. Typically, these constituents are monosulfate hydrate ($C_4A\bar{S}H_{12}$), calcium aluminate hydrate (C-A-H) and calcium hydroxide (CH). The chemical reactions between these constituents and sulfate ions are resulted in the formation of ettringite $C_6A\bar{S}H_{32}$, and gypsum ($C\bar{S}$), which occupy greater volume than the original reactants leading to excessive expansion, cracking and strength loss of concrete [10, 15, 29, 147].

The sulfate attack can be controlled when the presence of $C_4A\bar{S}H_{12}$, and C-A-H in a hydrated cement paste is reduced or even eliminated by either restricting the C_3A content of portland cement, or by substituting a part of the portland cement with a suitable blending material. The latter method can be effectively employed to reduce also CH content of the hydrated cement paste by using most of low-lime fly ashes as a pozzolanic additive [7, 45, 75].

Since 1937 [1], the ineffectiveness or even the contribution of some low-lime fly ashes to sulfate attack on concrete has been known. However, the beneficial effects of most low-lime fly ashes in improving sulfate resistance of concrete has also been confirmed in several investigations [1, 55, 75, 148].

The situation with high-lime fly ashes is somewhat less clear due to their free lime, anhydrite and reactive alumina contents, and there is considerable controversy with respect to sulfate resistance of these fly ashes [7]. For instance, Mather [149] has reported that, 30 % replacement of several high C_3A content cements with different high-lime fly ashes made the system less sulfate resistant. On the other hand, Mehta [147], Manz et al [133], and Hooton [150] showed that, some high-lime fly ashes may satisfactorily improve sulfate resistance of concrete.

ACI Committee 226 [7] affirms that, the sulfate resistance of either plain concrete or fly ash concrete is controlled by the same factors which are: curing conditions, exposure and water to cementitious-material ratio. The effect of fly ash on sulfate resistance is dependent upon the amount and individual chemical and physical characteristics of fly ash and cement used.

In a more recent study, Erdoğan et al [151] have shown that, the amount of incorporated fly ash in the system is a controlling factor in this consideration. There is a linear relationship between free CaO/Fe_2O_3 ratio of the PC-fa system and its potential sulfate expansion. Besides, they concluded that, the $(C_3A + \text{free alumina})/(\text{free CaO})$ ratio can be used for estimating the effect of fly ash incorporation on the sulfate resistance of the PC-fa system.

Dunstan [152] has suggested that, the CaO and Fe_2O_3 contents of fly ash are the main parameters affecting sulfate resistance or susceptibility of fly ash concrete to sulfates. The sulfate resisting factor proposed by Dunstan is calculated as: R = (C- 5/F), where C is CaO% and F is Fe_2O_3% in fly ash. At 25% cement replacement level, Dunstan found that, when R was less than 1.5, the sulfate resistance of concrete was improved, when R was more than 3.0, it was reduced. However, the results of later studies made by several investigators, including Mehta [147] and Manz et al [133], have confirmed that, Dunstan's R-factor is not reliable to predict the suitability of fly ash concrete for use in sulfate resisting concrete.

From microstructural examination of portland cement pastes containing a variety of fly ashes, Mehta [147] found that, a more rational correlation than that given by "R-factor" exists between sulfate resistance of paste and mineralogical composition of the fly ash-cement hydration products. Irrespective of R-factor, the amount of reactive alumina contributed by fly ash (from dissolution of aluminosilicate glass and the hydration of crystalline aluminum compounds, such as C_3A and $C_4A_3\bar{S}$), control the presence of the minerals highly vulnerable to sulfate attack (such as $C_4A\bar{S}H_{12}$ and C-A-H) and resultantly control the sulfate resistance of concrete.

Using 16 different fly ashes, both high-lime and low-lime, with widely varying R-factor, Mehta [9,147] has concluded that some lignite fly ashes, with high-lime and sulfate contents, upon interaction with cement in the presence of water, formed ettringite as a stable product of hydration before exposure to the sulfate action. Therefore, well-cured cement pastes containing these fly ashes showed no characteristic expansion and strength loss on sulfate exposure. On the contrary, some low-lime fly ashes, with high contents of reactive alumina in glass, formed the monosulfate hydrate as a result of fly ash-cement hydration, and therefore, the corresponding pastes showed considerable strength loss on sulfate exposure.

Freeman and Carrasguillo [153] tested the sulfate resistance of concretes containing 25 and 35 % (by volume) cement replacement with fourteen fly ashes, including six Class F and eight Class C fly ashes. Fly ashes were added as mineral admixtures at the concrete mixing stage and were interground with the cement clinker to obtain a blended fly ash cement. A Type II cement was used in this investigation. It was reported that, regardless of the fly ash inclusion method, Class F fly ashes resulted in better sulfate resistance than control concrete. However, the use of Class C fly ashes, either interground or as a mineral admixture, showed a highly variable effect on the sulfate resistance of fly ash concrete. This variability was attributed to the wide range of compositions and reactivities of Class C fly ashes. Besides, it was reported that, sulfate-related expansion of concrete mixes containing Class C fly ashes, with a total lime content of less than approximately 26 %, was reduced by intergrinding. These interground low-calcium Class C fly ash mixtures consistently expanded less than the control mix without fly ash.

4.4.5 Effect of Fly Ash on Alkali-Silicate Reaction (ASR) in Concrete

Since 1940, it has been known that the aggregate in concrete is often not inert. Alkali hydroxides derived from the alkalis (Na_2O and K_2O) present in portland cement, when exceeding a known limit (> 0.6 % equivalent Na_2O), may react with amorphous silica present in certain aggregates to form an unlimited swelling alkali-silica gel, thus resulting in expansion and cracking of concrete.

In numerous studies, a partial replacement of high-alkali cement with fly ash has been found to be effective in minimizing or even eliminating the risk of alkali-silica reaction in concrete [10, 55, 150, 154]. The exact mechanism by which the alkali-silica reaction causes expansion, and the mechanism by which fly ash is able to reduce expansion are still imperfectly understood. However, it is suggested that, the bonding in some silica or silicate structures can be destroyed by high alkaline solutions (pH >13), and the product thus formed can swell upon absorption of water [10].

Several reasons have been put forward for the beneficial effects of fly ash in this matter. First, straightforward dilution of the water-soluble alkali concentration occurs. Second, the reaction of fly ash with CH liberated by hydration of calcium silicates lowers the pH of the pore liquid, therefore reduces the reactivity between alkalis and active silica in aggregate. Third, the highly amorphous phase of fly ash itself may rapidly consume alkalis in cement paste and reduce their availability for further expansion reactions. Finally, any reduction in the permeability of concrete due to fly ash inclusion may beneficially reduce the moisture movement into concrete [3, 7, 10, 45, 155].

Meland [156] studied the effect of several factors, such as type of aggregate and amount of fly ash, as well as soluble alkali content of the system on alkali-silicate reaction. Besides, the degree of alkali released by fly ash has been studied extensively by pore fluid analysis [157, 147] as cited by Kollek [159] and Alasali [162], to show that the hydroxyl ion concentration extracted from blended cement systems can rise or fall as a result of portland cement replacement by a reactive fly ash depending on the relative alkali contents of the cement and fly ash and their mix proportions. Barlow [160] showed that the release of alkalis from fly ash can be changed by test conditions, hence, test conditions should reflect sufficiently well the conditions applying to the real concrete. Besides, it was observed that, the released alkalis which become bound up in the hydration products can again be easily made available in an aqueous extract.

Kollek [159] using beltan opal as reactive aggregate reported that, in a composite binder, the alkali contribution from the mineral additive must also be taken into consideration. In the case of fly ash or other artificial mineral additives, this contribution should be taken as 17 % of their total alkalis. Kobayashi et al [155], using all 14 types of low-lime fly ashes available in Japan and andesite as a reactive aggregate, have reported that, fly ash controls ASR in concrete due to not only the dilution effect but also due to its pozzolanic effect. They attributed the lower expansion of some blended systems, having higher alkali content than corresponding cement system, to the latter fact. It was also concluded that, fly ashes having higher alkali content tend to accelerate ASR. However, SiO_2 as quartz and mullite in fly ash tends to prevent ASR. Besides, the quantity of alkali in cement determines the effective amount of fly ash substitution. Higher alkali content cements require higher replacement levels. Ukita et al [126] recognized that, all fractions of a fly ash separated to maximum size fractions of 20, 10, and 5μm had the same alkali content. Even 15 % replacement level was observed to be efficient in suppressing alkali-silica expansion, emphasizing that finer particles of fly ash were even more effective.

Hooton [150] showed that, 25 % replacement of cement (1.17 % Na_2O eq.) with a lignite fly ash of 6.68 % alkali content (Na_2O equivalent) resulted in reduction of expansion of mortar bars containing pyrex glass as reactive aggregate. On the other hand, using the same aggregate and three Class C fly ashes with total alkali content varying from 2.3 to 7.4 %, Lee [161] reported that, 15 % replacement of high-alkali cement and up to 40 % of low-alkali cement with the fly ashes produced greater amount of mortar expansion than non-fly ash control mortars. It was also concluded that, in addition to replacement level, the composition of cementitious material plays an important role in fly ash effectiveness. Maximum expansion may be observed when the total equivalent Na_2O/SiO_2 (N/S) mole ratio of the cementitious material is at a critical value. This critical value seems to vary from fly ash to fly ash.

4.4.6 Effect of Fly Ash on the Corrosion of Reinforcing Steel

The reinforcing steel in concrete remains covered with a passive iron oxide film which protects it from corrosion. The depassivation of steel can occur in the presence of chlorides or when the pH of concrete is reduced to less than eleven by acid attack, such as by carbonation [9]. When passive iron oxide film is destroyed, the corrosion of reinforcement begins. The progress of corrosion is controlled by the rates of oxygen and moisture movement through concrete and the electrical resistivity of concrete [9, 141, 146].

Since fly ash incorporation in concrete affects the various factors involved in steel corrosion, such as permeability, resistivity and carbonation, it plays an important role in the corrosion of reinforcement.

Permeability of concrete is the key factor in this consideration, because it controls not only the rates of carbonation or chloride ingress required to initiate the corrosion process but also the rates of oxygen and moisture flow essential for the progress of corrosion process. The beneficial effects of fly ash inclusion on the permeability of concrete through pore refinement in cement paste and grain refinement by strengthening aggregate-cement paste interface zone was discussed earlier.

Also it was mentioned that, the common idea about the sensitivity of fly ash concrete to carbonation, due to the relatively lower amount of CH available in these concretes, is not shared by all investigators. Some researchers, including Mehta [9,10], believe that, owing to their lower permeability, fly ash concrete with a sufficiently long curing period (90 days) show comparable or less carbonation depth than an equivalent strength plain concrete. Kokubu and Nagataki [141] have shown that, same as carbonation, the corrosion of reinforcement is correlated with 28-day compressive strength. Besides, they have noted that, the thickness of cover is of great importance in this concern and should be increased with increasing W/C ratio to provide a sufficient protection against corrosion, because corrosion occurs before carbonation progresses to the thickness of cover (at the age of 20 years).

Al-Amoudi et al [146] showed that, reaction between fly ash and CH component of hydrated cement paste, at a 20 % replacement level, did not reduce the pH value below the alkalinity of pure saturated CH solution (pH= 12.5).

In conclusion, compared to normal concrete, a fly ash concrete would not decrease the corrosion protection of reinforcement, provided it contained good-quality fly ash, proper mix proportions, and has received adequate curing prior to environmental exposure.

CHAPTER V

EXPERIMENTAL STUDY

5.1 Experimental Program

The experimental program of this study consisted of four main parts:

a) Determination of general chemical, physical and mechanical characteristics of the materials according to the related ASTM standards.

b) Determination of the effects of fly ash type and fly ash content on various properties of PC-fa pastes, such as water requirement, normal consistency, setting time and heat of hydration.

c) Determination of the effects of fly ash type and fly ash content on various properties of fresh and hardened PC-fa mortars, such as flow, compressive strength, potential sulfate expansion and drying shrinkage.

d) Determination of the effects of the fly ash type and fly ash content on various properties of fresh and hardened PC-fa concretes, such as unit weight, air content, compressive and tensile strength, modulus of elasticity and carbonation depth.

5.2 Materials

One type of ordinary portland cement and four types of fly ashes were used for paste, mortar and concrete specimens. The natural aggregate used for making the concrete specimens was obtained from Zir Creek near Ankara. The tests performed on these materials and the relevant test standards are summarized in Table 5.1. The properties of these materials are described below.

Table 5.1. Tests Performed on Portland Cement, Fly Ashes and Aggregates

Tests Performed on	Relevant Standard
a) Portland Cement :	
Chemical analysis	ASTM C 114
Fineness by Blaine air permeability	ASTM C 204
Fineness by the # 100 and # 200 sieves	ASTM C 184
Density	ASTM C 188
b) Fly Ashes :	
Chemical analysis	ASTM C 311
Mineralogical composition by XRD	-
Fineness by Blaine air permeability	ASTM C 204
Fineness by the # 100 and # 200 sieves	ASTM C 184
Grain size distribution	ASTM D 422
Density	ASTM C 311
c) Aggregates :	
Sieve analysis of fine and coarse aggregate	ASTM C 136
Specific gravity and absorption of coarse agg.	ASTM C 127
Specific gravity and absorption of fine agg.	ASTM C 128
Soundness by use of sodium sulfate	ASTM C 88
Resistance to abrasion by use of the Los Ageles machine	ASTM C 131

5.2.1 Cement

An ordinary Turkish portland cement, PÇ 40*, from Adana Cement Plant was utilized. The physical properties and the chemical composition of the cement were determined according to the related ASTM standards. Table 5.2 summarizes the properties of the PÇ 40 cement used in the investigation and compares the values obtained with the requirement values of ASTM C 150 [163] and TS 19 [164].

5.2.2 Fly Ashes

Four types of Turkish fly ashes obtained from Tunçbilek, Soma-B, Afşin-Elbistan and Seyitömer power plants were used in this investigation. These are designated as T, SB, A and SR, respectively throughout this study. The first fly ash is a low-lime and the other three are high-lime fly ashes. Chemical and physical properties of these fly ashes and their mineralogical compositions were found.

5.2.2.1 Chemical Composition of Fly Ashes

The chemical composition of fly ashes were determined according to ASTM C311 [166]. Table 5.3 summarizes the test results and compares these results with the limiting values of ASTM C 618 [32] and TS 639 [50].

Among the four fly ashes used in this investigation, only T fly ash was found as conforming with the current Turkish Standard on Fly Ashes (TS 639) with $SiO_2+Al_2O_3+Fe_2O_3$ content greater than 70 %.

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* Turkish standard TS 19 defines PÇ 40 as a cement obtained by intergrinding portland cement clinker and gypsumrock and having a minimum 28 day compressive strength of 40MPa.

Table 5.2.a. Chemical Characteristics of the Portland Cement and Compliance with ASTM C 150 [163] and TS 19 [164]

Chemical Composition (%)	Test Result for Portland Cement PÇ 400	ASTM C 150 Limits [163]	TS 19 Limits [164]
SiO_2	19.02	-	-
Al_2O_3	6.54	-	-
Fe_2O_3	3.92	-	-
CaO (total)	60.38	-	-
MgO	2.86	max.6.0	max.5.0
SO_3	2.62	max.3.5*	max.3.5
Na_2O	0.16	Na_2O eq.	-
K_2O	0.50	max.0.6**	-
Loss on ignition (LOI)	1.45	max.3.0	max.5.0
Insoluble residue (IR)	1.81	max.0.75	max.1.5
Bogue Potential Compounds (%)			
C_3S	44.24	-	-
C_2S	21.16	-	-
C_3A	10.70	-	-
C_4AF	11.93	-	-

Table 5.2.b. Physical and Mechanical Properties of the Portland Cement and Compliance with ASTM C150 [163] and TS [164]

Specific gravity	3.15	-	-
Vicat setting time (min)			
- Initial	220	min.45	min.60
- Final	340	max.375	max.600
Blaine specific surface(m^2/kg)	303	min.280	min.240
Compressive strength (MPa)			
3 days	19.9	12.4	20***
7 days	33.8	19.3	31.5
28 days	48.3	27.6**	40

* When C_3A is more than 8%, otherwise SO_3 content is 3 %

** Optional requirement

*** 2-day strength

Considering the ASTM C 618 requirements, only A fly ash is not appropriate for use in concrete due to its comparatively low $SiO_2+Al_2O_3+Fe_2O_3$ content which is less than 50%, the minimum requirement in ASTM C 618. This standard classifies fly ashes into two according to their $SiO_2+Al_2O_3+Fe_2O_3$ content s and the coal from which they are originated. Fly ashes obtained from the combustion of bituminous coals and anthracite and having $SiO_2+Al_2O_3+Fe_2O_3$ >70% are named as Class F fly ashes, whereas those obtained from lignite or subbituminous coals and having $SiO_2+Al_2O_3+Fe_2O_3$ >50% are named as Class C fly ashes. Therefore, all the four fly ashes used can be considered as belonging to Class C according to ASTM C 618 since they are all obtained from lignite combustion. Besides, when Table 5.3 is analyzed it could be seen that, A and SR fly ashes exceed the SO_3 limit of the standards. Similarly, SR has greater MgO content than the maximum value given by the standards. Another classification of fly ashes is based on the relative proportions of SiO_2, Al_2O_3, CaO, and SO_3

Table 5.3. Chemical Composition of Fly Ashes and Their Compliance with ASTM C 618 [32] and TS 639 [50]

Oxide (%)	Tunçbilek (T)	Soma-B (SB)	Afşin-Elbistan (A)	Seyitömer (SR)	ASTM C 618 Limits		TS639 Limits
					Class F	Class C	
SiO_2	56.4	39.8	22.4	40.6	-	-	-
Al_2O_3	23.0	22.3	12.8	9.1	-	-	-
Fe_2O_3	10.0	4.4	5.5	7.7	-	-	-
$SiO_2+Al_2O_3+Fe_2O_3$	89.4	66.5	40.7	57.4	min.70	min.50.0	min.70
CaO	3.1	25.4	47.0	19.9	-	-	-
MgO	3.3	1.9	2.5	8.1	max.5.0	max.5.0	max.5.0
SO_3	0.5	4.8	6.2	11.6	max.5.0	max.5.0	max.5.0
TiO_2	n.d	0.6	0.7	n.d	-	-	
Na_2O equivalent	0.9	0.4	0.4	1.4	max.1.5*	max.1.5*	-
Loss on ignition	2.4	0.4	2.4	2.8	max.6.0**	max.6.0	max.10

* Optional requirement

** Up to 12 % may be approved if either acceptable performance records or laboratory test results are made available.

5.2.2.2 Mineralogical Composition of Fly Ashes

Mineralogical composition of fly ashes plays an important role in the behavior of fly ash bearing cementitious systems. Generally, the type of impurities present in the parent coal (that is the coal where the specific fly ash is produced from) and its combustion temperature are the main factors governing the mineral phases of fly ashes. Table 5.4 shows the main impurities present in the parent coals used for the production of the fly ashes that are used in this investigation [43]. The burning temperature of the coals in the power plants, from which the fly ashes used in this study were obtained, were 950-1050°C.

Table 5.4. Main Impurities in Parent Coals

Coal	Main impurities
Tunçbilek (T) Coal	Quartz, kaolinite, hematite, illite, pyrite, chlorite, gypsum.
Soma-B (SB) Coal	Quartz, chlorite, pyrite, illite.
Afşin-Elbistan (A) Coal	Montmorillonite, calcite, quartz, hematite, aragonite, pyrite.
Seyitömer (SR) Coal	Quartz, illite, feldspar, chlorite, pyrite, siderite, gypsum.

Since quartz and hematite are stable at this temperature, they pass directly from coal to fly ash keeping their original structure unchanged. Pyrite, upon oxidation, transforms to magnetite and sulfurdioxide.

$$3FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2 \uparrow \tag{5.1}$$

Aragonite impurities transform into calcite which decomposes into free lime and carbondioxide at 900°C.

$$CaCO_3 \xrightarrow{900°C} CaO + CO_2 \uparrow \qquad (5.2)$$

Presence of anhydrite in fly ash may be due to the presence of gypsum as an impurity in coal, or it may be due to the combination of sulfurdioxide, formed as a result of the transformation of pyrite during oxidation (equation 5.1), and some of the free lime produced as shown in equation 5.2.

$$CaO + SO_2 + \frac{1}{2} O_2 \longrightarrow CaSO_4 \qquad (5.3)$$

Although clay minerals behave differently at different temperatures depending on their composition, the effect of temperature level on clay minerals can be generalized as follows [43]:

150°C - Chemically unbound water evaporates and shrinkage occurs.
400-900°C - Chemically bound water evaporates
900°C - Crystalline structure is destroyed

Temp. increases ↓

- Amorphous phase is formed
- New crystalline phases such as mullite and cristobalite are formed
- Glassy phase is formed
- Melting occurs

The mineralogical composition of the fly ashes is given in Table 5.5. Quantification of mullite, quartz, magnetite, hematite and free lime contents of fly ashes was carried out by XRD modal analysis using calibration curves developed by Hubbard et al [169]. The quantity of anhydrite, due to its less crystallinity, was determined gravimetrically. The chemically bound CaO was determined by X - ray fluorescence and the obtained value was distributed stoichiometrically to estimate the plagioclase and gehlenite contents. The amorphous and glassy phase content was calculated by subtracting the amount of known minerals from the total weight of fly ash to obtain the values given in Table 5.5 [43].

Table 5.5. Mineralogical Composition of Fly Ashes [43]

Mineral	T	SB	A	SR
Quartz	13.9	5.1	4.5	5.6
Lime	0.9	9.8	18.5	5.5
Anhydrite	-	7.4	12.2	9.3
Plagioclase	-	~20	~28*	~15
Hematite	3.0	2.0	4.0	6.0
Magnetite	4.1	0.6	0.8	2.5
Mullite	8.8	4.3	1.0	1.2
Amorphous and glassy phase	~70	~50	~30	~50

*Includes gehlenite (C_2AS) also

For the X-ray diffraction (XRD) measurements, fly ash specimens were ground in order to obtain homogeneity of grain size in the range of 3-30 μm. Diffraction data were obtained using Philips PW 1050 diffractometer with Cu k radiation at generator settings of 40 kV and 30 mA. Phases were identified by reference to the JCPDS Minerals Powder Diffraction Files. The XRD traces of the fly ashes with major crystalline phases indicated are given in Figure 5.1. [43].

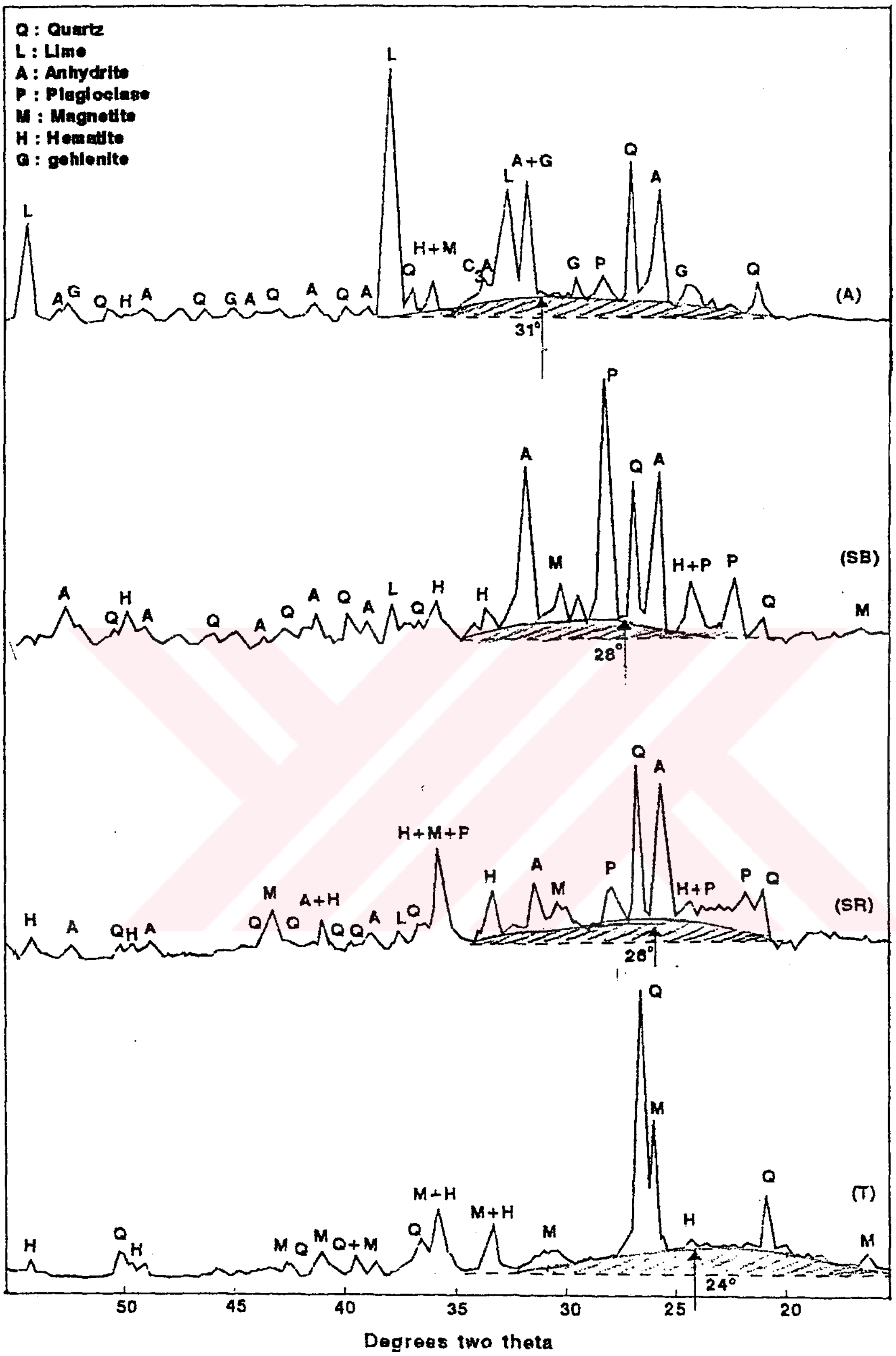


Figure 5.1. X-ray Diffractograms of Fly Ashes [43]

5.2.2.3 Physical Characteristics of Fly Ashes

For the four types of the fly ashes used in this investigation, fineness, grain size distribution, density, pozzolanic activity and water requirement were determined as their physical properties.

Fineness of fly ash is important as it affects the rate of pozzolanic activity and the workability of the concrete [7]. ASTM C 618 [32] requirement formerly based on the use of Blaine air permeability test has been deleted from the specification on the basis of failure of results to correlate with properties of concrete. Another measure of fineness which measures the amount of material retained by washing on the 45 μm (No. 325) sieve, ASTM C 430 [170], is the only method included in ASTM C 618 [32] requirements for fineness. According to ASTM C 618 [32], maximum amount of fly ash retained when wet-sieved on 45 μm sieve should be 34 %. On the other hand, fineness requirement as expressed on the basis of Blaine air permeability test is still present in most specifications, such as the Turkish Standard, TS 639 [50]. According to TS 639 [50], the Blaine fineness of fly ash should be minimum 3000 cm^2/g.

Table 5.6 shows the fineness values for the four types of fly ashes. The method given in ASTM C 204 [171], which is the same method as Turkish Standard, was used for the determination of Blaine specific surface of the ashes, sieve analysis of the ashes were conducted in accordance with ASTM C 184 (172), as well.

Due to the lack of the necessary equipment in the laboratory, fineness of fly ashes by wet sieving on 45 μm sieve could not be determined. However, the particle size distribution of the fly ashes were found by the hydrometer analysis, ASTM D 422 [165]. Thus, an idea about the distribution and fineness of the particles of the fly ashes could be obtained. Figure 5.2 shows the grain size distribution of the three fly ashes used in this investigation. Due to the rapid reaction of A fly ash with water and its consequent precipitation, the hydrometer analysis of A fly ash could not be performed. There is no requirement in the ASTM specification about the particle size distribution of fly ash as determined by hydrometer analysis.

Table 5.6. Sieve Analysis and Blaine Specific Surface of Fly Ashes

Fly Ash	% Retained on 150μm	% Retained on 75μm	Blaine Specific Surface(cm^2/g)
T	4.5	13.5	3370
SB	3.0	19.0	2530
A	3.0	14.9	3210
SR	1.0	3.0	9700

In general, the density of fly ash has little or no effect on the properties of concrete except that, it may indicate the particle size present in the ash. There is no requirement in ASTM specifications about the density of the fly ash. The densities of the fly ashes as determined in accordance with ASTM C 311 [166] are shown in Table 5.7:

Table 5.7. Densities of Fly Ashes

Fly Ash	Density (g/cm^3)
T	1.99
SB	2.42
A	2.63
SR	2.46

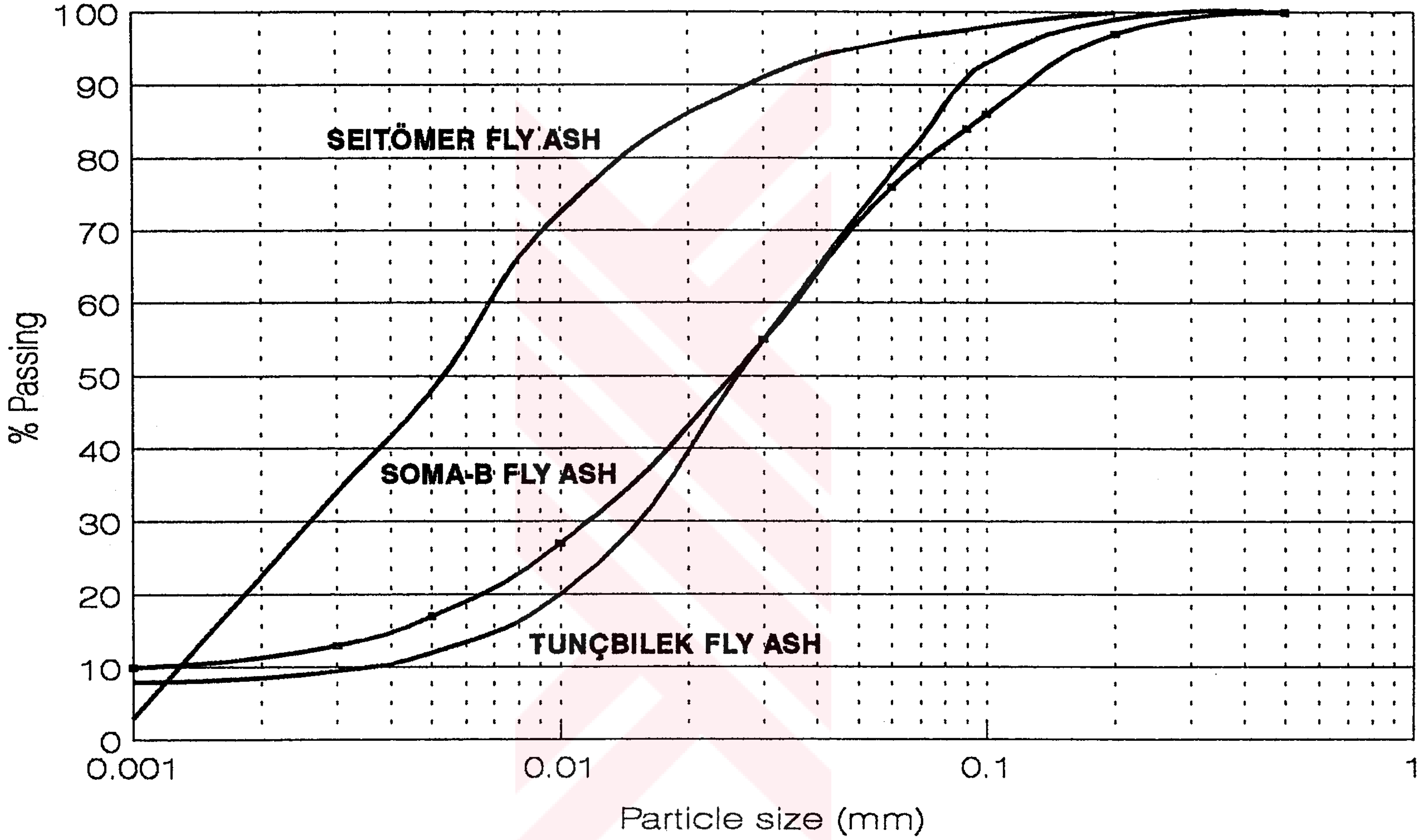


Figure 5.2. Grain Size Distribution of Fly Ashes Used in This Study

The strength activity indices of the fly ashes with portland cement and the pozzolanic activity indices (PAI) of the fly ashes with lime were determined according to ASTM C 311 [166]. The test results and their compliance with ASTM C 618 [32] are shown in Table 5.8:

Table 5.8. Strength Activity Index and Pozzolanic Activity Index of Fly Ashes and Their Compliance with the Requirements of ASTM C 618 [32]

	T	SB	A	SR	ASTM C 618 Requirement
Strength activity index with portland cement					
at 7 days, % of control	71.0	80.3	78.3	74.9	min.75%
at 28 days, % of control	72.5	94.5	86.4	79.8	min.75%
Pozzolanic activity index with lime at 7 days, MPa	3.4	5.3	5.0	4.4	min.5.5

The water requirements of fly ashes are given in Table 5.9. These values were found in accordance with ASTM C 311 [166].

Table 5.9. Water Requirements of Fly Ashes and Their Compliance with the Requirements of ASTM C 618 [32]

Fly Ash	Water requirement (% of control)	ASTM C 618 Limit (% of control)
T	104.2	
SB	105.6	max.105
A	110.0	
SR	116.4	

5.2.3 Aggregates

The fine and coarse aggregates were, washed and dried, natural sand and river gravel with maximum particle size of 30 mm, respectively. To keep the grading uniform for concrete mixture, the coarse aggregate was separated into two different size fractions, i.e. (7-15 mm) and (15-30mm), and recombined at a specific grading before feeding into the mixer. The grading and the physical properties of both aggregates are given in Tables 5.10 and 5.11, respectively.

As there is no standard specification related to combined aggregate in ASTM, aggregates were blended in accordance with TS 706 [173] requirements. The following proportions were found:

Fine aggregate : 45 %
(7-15 mm) Coarse aggregate : 20 %
(15-30 mm) Coarse aggregate : 35 %

The granulometry of blended aggregate and its compliance with TS 706 requirements are shown in Figure 5.3.

Table 5.10. Grading of Aggregates

	Coarse aggregates		Fine aggregate	
	% Cumulative retained			% Cumulative
Sieve size	15-30mm	7-15mm	Sieve size	retained
38.1 mm (1.5 in.)	0		9.50mm(3/8″)	0
25.4 mm (1 in.)	12		4.75mm(No.4)	13
19.1 mm (3/4 in.)	59	0	2.38mm(No.8)	36
12.7 mm (1/2 in.)	86	24	1.19mm(No.16)	58
9.5 mm (3/8 in.)	94	56	600μm(No.30)	75
4.75mm (No.4)	98	98	300 μm(No.50)	90
Pan	100	100	150 μm (No.100)	98
			Pan	100
			Fineness modulus : 3.7	

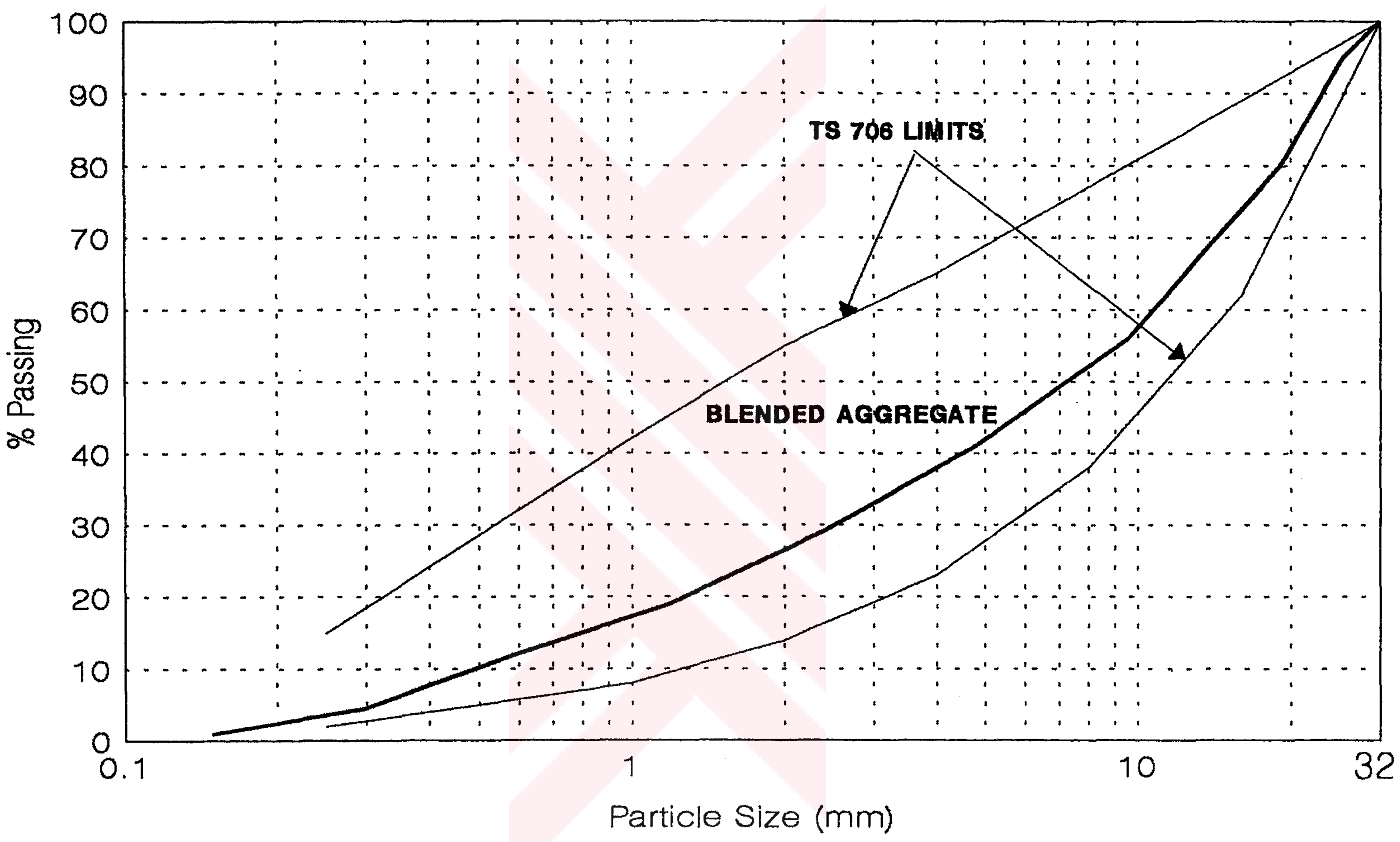


Figure 5.3. The Granulometry of Blended Aggregate and its Compliance with TS 706 [173] Limits

Table 5.11 Physical Properties of Aggregates

Property	Coarse Agg.	Fine Agg.	ASTM C 33 Limits
SSD Bulk specific gravity	2.54	2.54	-
Absorption (%)	2.32	3.23	-
Soundness (%) by sodium sulfate solution	3.89	-	max.12
Los Angeles abrasion (% wear) B-grading	20.7	-	max.50

5.3 Mortar and Concrete Mixture Proportioning

Fly ash mortar mixture and the control mortar mixture (the mortar mixture without any fly ash) were prepared in accordance with ASTM C 109 [174]. The water content of control mortar and fly ash mortar mixtures were adjusted for a flow value of 110 ± 5%. Fly ash inclusion was adapted by two methods: simple replacement and additional replacement. In simple replacement method, 10, 20 and 40 % (by weight) of cement was replaced by equal amounts of fly ash. These are designated as M_s mixes. In additional replacement, twice or four times (by weight) of fly ash was added for the amount of cement that was removed from each mix. These are designated as M_a mixes, where M_{a2} and M_{a4} represent twice or four times fly ash addition in place of the removed amount of cement, respectively. The type of mortar mixes and the percentage of materials replaced are summarized as follows:

Type of Mortar Mix	% Cement Removed (by weight)	% Fly Ash Included (by weight)
M_s	10	10
M_s	20	20
M_s	40	40
M_{a2}	10	20
M_{a2}	20	40
M_{a4}	10	40

As can be seen from the above summary, for each type of fly ash, six different mortar mixtures were cast. In this study, each mortar mixture is designated by the type of fly ash, type of mixture and the amount of cement removed. For example, T-M_s-10 identifies that, 10 % of cement is simply replaced by 10 % of Tunçbilek fly ash (T) in the mortar mixture and T-M_{a2}-10 identifies that, 10% of cement is additionally replaced by 20 % of Tunçbilek fly ash in the mortar mixture.

The control concrete mixture, having no fly ash inclusion, was designed for a 25 MPa 28-day compressive strength and a slump value of 50-80 mm using the ACI 211.1 [175] mix design recommendation. In the fly ash concrete mixtures, the method and amount of fly ash inclusion were the same as for the mortar mixtures. Concrete mixtures are designated as C_s, C_{a2} and C_{a4} . For example, T-C_s-10 identifies that, in the concrete mix 10% (by weight) of cement is simply replaced by 10 % of Tunçbilek fly ash and T-C_{a4}-10 identifies that, 10 % (by weight) of cement is replaced by 40 % of Tunçbilek fly ash. In all of the fly ash concrete mixtures, necessary adjustments were made for the relative proportions of the aggregate. Besides, the water content of the all mixes was adjusted to a 50-80 mm constant slump. The mix parameters and some of the characteristics of fresh concrete are given in Table 5.12.

5.4 Specimens

In all of the tests and analyses performed, specimen preparation was made with regards to the following considerations:

a) For the purpose of eliminating discrepancies that may arise from either a low or a high water content, uniformity in consistency was the prime consideration:

- all the paste specimens were prepared at normal consistency,
- all the mortar mixtures were prepared to have a 110 ± 5 % flow and,
- all the concrete mixtures were prepared to have a 50 - 80 mm slump.

Table 5.12. Mix Parameters and Some of the Characteristics of the Fresh Concrete

Mix	CA. kg/m^3	FA kg/m^3	C kg/m^3	Fly A. kg/m^3	W kg/m^3	$\frac{W}{C.Mat.}$	Slump (mm)	Air Cont(%)	U.Wgt. kg/m^3
Control	1209	653	274	-	168	0.61	60	1.1	2304
T-C$_s$-10	1201	646	247	27	167	0.61	60	1.0	2288
T-C$_{a2}$-10	1201	605	247	54	169	0.56	50	1.0	2276
T-C$_{a4}$-10	1201	518	247	108	178	0.50	80	1.3	2252
T-C$_s$-20	1201	645	219	55	165	0.60	60	1.5	2285
T-C$_{a2}$-20	1201	523	219	110	184	0.56	65	1.3	2237
T-C$_{a4}$-40	1163	627	164	110	175	0.64	60	1.7	2339
SB-C$_s$-10	1209	651	247	27	168	0.61	60	1.1	2302
SB-C$_{a2}$-10	1209	628	247	54	166	0.55	55	1.1	2304
SB-C$_{a4}$-10	1209	534	247	108	181	0.51	80	0.9	2279
SB-C$_s$-20	1212	651	219	55	165	0.60	75	1.2	2302
SB-C$_{a2}$-20	1212	567	219	110	175	0.53	80	1.4	2283
SB-C$_s$-40	1194	643	164	110	170	0.62	80	1.4	2281
A-C$_s$-10	1214	655	247	27	165	0.60	55	1.1	2308
A-C$_{a2}$-10	1214	612	247	54	172	0.57	60	1.2	2299
A-C$_{a4}$-10	1214	492	247	108	199	0.56	60	1.6	2260
A-C$_s$-20	1214	653	219	55	165	0.60	55	1.5	2306
A-C$_{a2}$-20	1214	526	219	110	194	0.59	50	1.7	2263
A-C$_s$-40	1191	641	164	110	175	0.64	75	1.9	2281
SR-C$_s$-10	1217	654	247	27	165	0.60	75	1.0	2310
SR-C$_{a2}$-10	1217	550	247	54	194	0.59	70	1.2	2262
SR-C$_{a4}$-10	1217	481	247	108	199	0.56	50	0.9	2252
SR-C$_s$-20	1196	645	219	55	173	0.63	60	0.8	2288
SR-C$_{a2}$-20	1196	528	219	110	197	0.60	70	0.9	2250
SR-C$_{a4}$-40	1186	638	164	110	175	0.64	60	1.1	2273

b) Each test was performed on at least three specimens to obtain a sufficient precision.

c) Size and shape of the specimens and methods of preparation were in accordance with the related standards. For example, 150x30mm cylindrical specimens were used for strength and carbonation tests of concretes, 50 mm cubic specimens were used for compressive strength, and 25x25x285 mm prismatic specimens were used for drying shrinkage and sulfate resistant tests of mortars.

5.5 Curing Condition

The test specimens were exposed to continuous moist curing at (23 ± 1.7)°C and 95 % relative humidity until the time of test.

5.6 Test Procedures

Except for carbonation depth determination test, that does not take place as a standard method in the ASTM Standards, all of the tests performed in this study were carried out according to the related ASTM Standards. Since the procedures of the routine tests are given in detail in the related standards, rather than re-explaining the whole procedures once again, reference is made to the number of standard test where necessary.

5.6.1 Tests Performed on PC-fa Pastes

The tests performed on PC-fa pastes and the relevant test standards are given in Table 5.13. The normal consistency and setting time of control cement paste and fly ash-cement pastes with 10, 20, and 40 % of cement simply replaced with fly ash were determined in accordance with ASTM C 191 [176] "Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle".

The normal consistency tests of PC-fa pastes were carried out for two reasons: a) to determine the changes in the water requirement of pastes upon fly ash substitution and b) for using these results in the specimen preparations of other related tests, such as setting time and soundness in order to obtain comparable results.

The heat of hydration of control paste containing no fly ash, and PC-fa pastes were carried out in accordance with the method described in ASTM C 186 [177] "Standard Test Method for Heat of Hydration of Hydraulic Cement", which consists of the measurement of the heat of solution of the dry cement and the heat of solution of a separate portion of the cement that was partially hydrated for 7 and 28 days, the difference between values being the heat of hydration for the respective hydrating period. Each heat of hydration test was performed at least two times unless the difference between two consecutive heat of hydration values were larger than 8 cal/g, or 10 cal/g, respectively as stated in ASTM C 186.

Table 5.13. Tests Performed on PC-fa Pastes

Test Performed	Relevant Standard
Normal consistency by Vicat apparatus	ASTM C 187
Time of setting by Vicat apparatus	ASTM C 191
Heat of hydration by use of calorimeter	ASTM C 186

5.6.2 Tests Performed on PC-fa Mortars

The tests performed on PC-fa mortars and the relevant test standards are given in Table 5.14. The compressive strengths of 50 mm cubic mortar specimens were determined in accordance with ASTM C 109 [174] at 7, 28, 90 and 180 days age. As it was mentioned earlier in section 5.3, in addition to control mortar specimen, for each fly ash, six different mortar mixes at three different cement replacement levels were prepared. Six specimens were tested at each age and the results presented are the average values.

The compressive strength tests were carried out in 100 ton universal testing machine, using 1/5 of its capacity. For the specimens having expected maximum loads more than 1350 Kgf, an initial loading up to one half of the expected maximum load at an arbitrary rate was applied. The remainder of the load (or the entire load in the case of expected maximum load less than 1350 Kgf) was applied at such a rate that the maximum load was reached in not less than 20 nor more than 80 seconds from the start of loading as stated in ASTM C 109.

The potential sulfate expansion of mortars were determined in accordance with ASTM C 452 [177] "Standard Test Method for Potential Expansion of Portland Cement Mortars Exposed to Sulfate". The potential expansion of mortar bars, having 25 x 25 x 285 mm initial dimensions, was measured at 14, 28, 90, and 180 days age.

The increase of drying shrinkage of mortar bars having 25 x 25 x 285 mm initial length was determined according to ASTM C 311 [166]. Two series of specimen were prepared. The first group was subjected to 7 days of moist curing (including the period in the molds). The second group was kept in moist condition for 90 days. The increase of drying shrinkage of the specimens was monitored after 28, 54 and 90 days of air storage at (23 ± 1.7)°C and 55 ± 5 % relative humidity.

Table 5.14. Tests Performed on PC-fa Mortars

Test Performed	Relevant Standard
Flow	ASTM C 109
Water requirement	ASTM C 311
Pozzolanic activity index with lime *	
Str. activity index with portland cement	ASTM C 311
Compressive strength	ASTM C 109
Potential sulfate expansion	ASTM C 452
Drying shrinkage	ASTM C 311

5.6.3 Tests Performed on PC-fa Concretes

The tests performed on PC-fa concretes and the standards used in these tests are summarized in Table 5.15. 150 x 300 mm cylindrical control and fly ash concrete specimens having proportions given in Table 5.12 were prepared in accordance with ASTM C 192 [178] "Standard Method of Making and Curing Concrete Test Specimens in the Laboratory". The mixer used was an electrically-driven tilting mixer of 0.06 m^3 capacity. Immediately after mixing, consistency (slump), unit weight and air content of the fresh concrete were determined in accordance with ASTM C 143 [179] "Standard Test Method for Slump of Portland Cement Concrete", ASTM C 138 [180] "Standard Test Method for Unit Weight, Yield, and Air Content of Concrete", and ASTM C 231 [181] "Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method".

The compressive strength of concrete specimens were obtained according to ASTM C 39 [182] "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens" at 7, 28, 90 and 180 days age.

In addition to the compressive strength of concrete specimens, their split tensile strength and modulus of elasticity were also determined in accordance with ASTM C 496 [184] "Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens" and ASTM C 469 [183] "Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression", respectively, at 28 days age.

Table 5.15. Tests Performed on PC-fa Concretes

Test Performed	Relevant Standard
Slump	ASTM C 138
Unit weight and yield	ASTM C 143
Air content by pressure method	ASTM C 231
Compressive strength	ASTM C 39
Static modulus of elasticity	ASTM C 469
Split tensile strength	ASTM C 496
Carbonation depth	-

5.6.3.1 Test Procedure for Carbonation Depth Determination

In ASTM specifications, there is no standard test method for determining carbonation depth of concrete. Therefore, in this investigation an accelerated carbonation test, similar to the one used by Ho and Lewis [144], and Ohga and Nagataki [140] was performed.

For this purpose, six 150 x 300 mm cylindrical specimens were cast for each concrete mixture. At the end of initial curing period, each specimen was sawn into two 150 x 150mm cylinders. First series of specimens (half of them) were moist cured for 7 days, then allowed to air drying in laboratory for 21 days. At the end of this period, half of the specimens (three 150 x 150 cylinder for each mixture) were stored in carbonation chamber where the level of carbon dioxide was maintained at 4% by volume. From then on, the specimens were splitted after four, eight and twenty weeks of storage. One percent phenolphthalein ethyl alcohol solution was used as an indicator and the average depth of uncolored portion was measured as carbonated portion. The second series of the specimens were given similar treatment except that they were initially moist cured for 90 days before exposure to laboratory air drying and accelerated carbon dioxide effect.

CHAPTER VI

TEST RESULTS AND DISCUSSIONS

For the particular fly ashes and the conditions employed in this study, the obtained test results and their discussions are presented in this chapter.

6.1 Results of Tests Performed on PC-fa Pastes

6.1.1 Normal Consistency

Normal consistency was determined for the neat portland cement and for the portland cement + fly ash pastes. In the fly ash pastes 10, 20 and 40% by weight of cement was simply replaced with fly ash. The water requirement values of the pastes, for 10 ± 1 mm penetration of Vicat plunger, were obtained. The results, given in Table 6.1 and graphically shown in Figure 6.1, are the average of three individual tests. The densities of the fly ashes are smaller than the density of cement. For the sake of comparison, water requirement for normal consistency are also calculated on volumetric basis.

The following comments can be made on the effect of fly ash substitution on the water requirement of pastes for normal consistency:

1. The normal consistency of fly ash pastes increases parallel to fly ash replacement level. However, the increase in water demand of fly ash incorporated pastes for normal consistency is not significant for small and medium inclusion levels.

2. SR fly ash, having the highest loss on ignition and highest specific surface among the fly ashes requires the greatest amount of water for normal consistency at all inclusion levels when considered at volumetric basis.

Table 6.1 Normal Consistency of Control and PC-fa Pastes

Fly Ash	Simple Repl. Level of Cement	Specimen	Water/Cementitious Mat. % by weight	 %by volume
-	0	Control	27.1	85.37
T	10	10T	29.18	88.53
T	20	20 T	31.32	91.39
T	40	40 T	35.47	95.27
SB	10	10 SB	27.38	84.30
SB	20	20 SB	28.50	85.73
SB	40	40 SB	30.21	86.58
A	10	10 A	28.50	88.29
A	20	20 A	29.53	89.95
A	40	40 A	33.16	97.56
SR	10	10 SR	29.71	91.53
SR	20	20 SR	30.42	91.63
SR	40	40 SR	34.89	100.27

3. The low lime T fly ash and high-lime A fly ash having the same loss on ignition and nearly equal Blaine specific surfaces show approximately equal water requirement values when compared on volumetric basis. It seems that, there is a close relationship between water requirement for normal consistency of the paste and a multiple factor (Blaine specific surface x loss on ignition of the fly ash). As it can be seen from Table 6.2, SR having the highest multiple factor shows the highest water requirement; T and A, having approximately the same multiple factors, show nearly the same water requirement for normal consistency. Finally, SB having the smallest multiple factor among the fly ashes requires the lowest amount of water for normal consistency. The relationship between Blaine specific surface x LOI of the fly ashes and their water requirements are given in Table 6.2 and graphically shown in Figure 6.2.

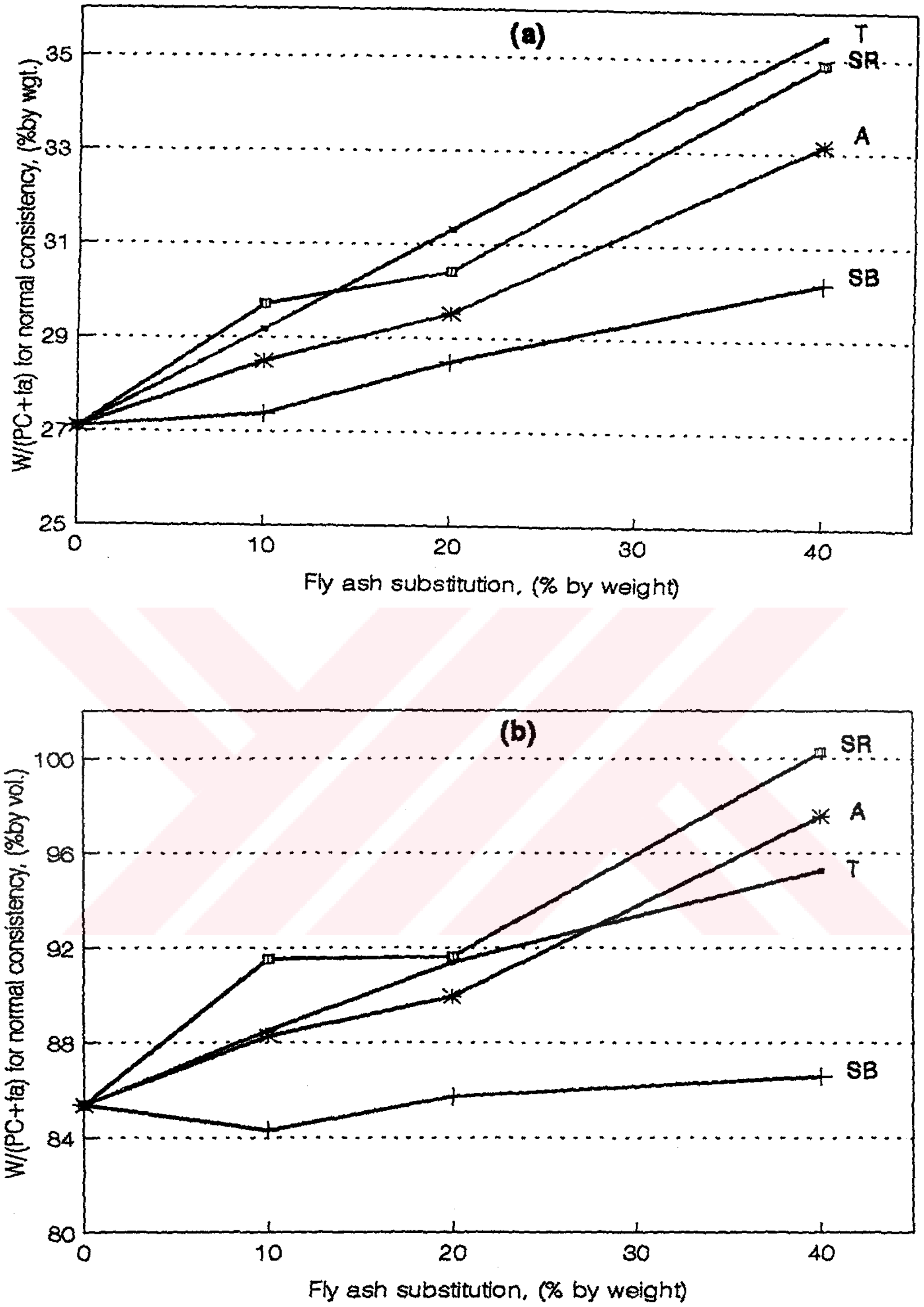


Figure 6.1. Changes in Water Requirement for Normal Consistency of Control and Fly Ash-Cement Pastes a) on Weight Basis b) on Volume Basis

Table 6.2. The Relationship Between Fineness x LOI of the Fly Ash and its Water Requirement

		Change in Water Requirement					
		(wgt. basis, %)			(vol. basis, %)		
	Blaine Fineness	Cement repl. level			Cement repl. level		
Fly Ash	XLOI	10%	20%	40%	10%	20%	40%
T	8088	7.7	15.6	30.9	3.7	7.1	11.6
SB	1012	1.03	5.2	11.5	-1.3	0.4	1.4
A	7704	5.2	9.0	22.4	3.4	5.4	14.3
SR	27160	9.6	12.3	28.7	7.2	7.3	17.5

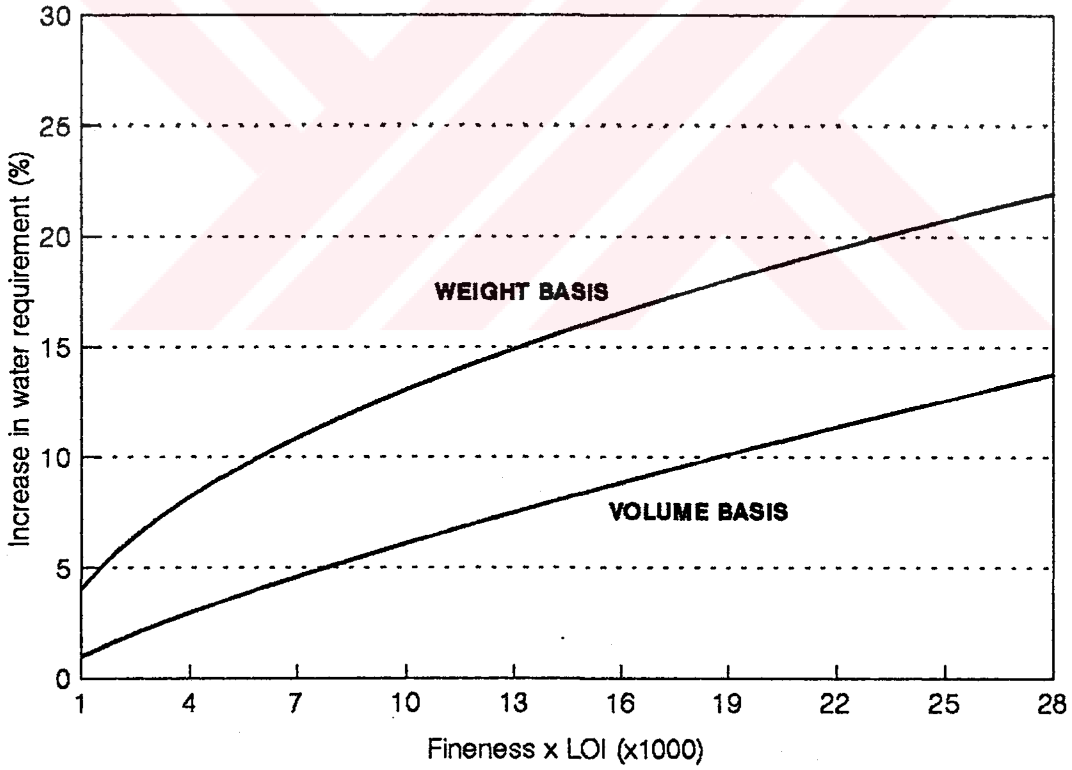


Figure 6.2. Relationship Between Fineness x LOI of the Fly Ash and the Increase in its Water Requirement

4. Considering the volumetric basis, when the water requirement for normal consistency of the control specimen is compared to those of the fly ash pastes, it could be seen that all the pastes except the one including SB show a higher water requirement. The increase is more pronounced for higher inclusion levels.

6.1.2 Setting Time

The initial and final setting times of control and fly ash pastes corresponding to 25 and 0 mm penetration of Vicat needle are given in Table 6.3. For setting time determination, pastes of normal consistency were prepared and tested.

Time of setting test results, presented in Table 6.3 show that:

1. Regardless of the type of fly ash, setting time is not significantly affected when fly ash inclusion level is 10%.

2. For higher inclusion levels, T, SB and SR fly ashes result in set retardation ranging from 0 to 100 minutes for initial set and from 15 to 170 minutes for final set. These can be attributed to higher water requirement of the fly ashes. Among these fly ashes, only the setting times of SB fly ash are within the limits given for portland cement in ASTM C 150 [163], which are minimum 45 minutes and maximum 375 minutes for initial and final setting times, respectively.

3. In contrast to the other three fly ashes, A fly ash accelerates the setting time. Not surprisingly, the acceleration effect is increased by increasing fly ash inclusion level. Since A fly ash contains larger amounts of free lime and anhydrite, the set acceleration effect may be due to the rapid transformation of these compounds into calcium hydroxide and gypsum.

Table 6.3. Setting Times of Control and PC-fa Pastes

Specimen	Vicat Setting Time (min)		Retardation Relative to Control Paste (min)	
	Initial	Final	Initial*	Final*
Control	220	340	-	-
10 T	230	405	10	65
20 T	275	450	55	110
40 T	330	490	110	150
10 SB	205	355	-15	15
20 SB	215	370	-5	30
40 SB	260	425	40	85
10 A	210	360	-10	20
20 A	140	285	-80	-55
40 A	105	205	-115	-135
10 SR	220	355	0	15
20 SR	285	480	65	140
40 SR	305	510	85	170

* minus sign means accelerated setting time compared to control

6.2 Effect of Fly Ash Type on the Hydration of PC-fa Systems

The X-ray diffractions of hydrated fly ashes or their mixture with CH were investigated at different ages to monitor the changes occurring in the course of hydration and types of hydration products. Besides, the investigation of hydration rate of PC-fa systems was carried out by monitoring the amount of evolved hydration heat of these systems at different time intervals.

6.2.1 Mineralogical Composition of Fly Ashes

It has been apparent in recent years that, the engineering properties of hardened concrete are controlled by the particle characteristics and mineralogy rather than the type of fly ash. This is because, the granulometry and mineralogy of the reactants influence the reaction rates, which determine the microstructure of the PC-fa interaction products and, hence, the engineering properties. Thus, from the stand point of the effect of fly ash on the properties of concrete, the type of fly ash is not significant. However, the fineness of fly ash and the activity of the noncrystalline phases present in fly ash are of importance.

The crystalline minerals in T fly ash are quartz, mullite and ferrite spinel (i.e. magnetite and hematite). In addition to these compounds, the crystalline phases in high-lime fly ashes SB, A and SR include anhydrite, free lime and plagioclase as shown in Table 5.5.

As it is apparent from Figure 5.1, the position of the X-ray diffraction diffuse halo maxima ($2\theta_{max}$), which is dependent on glass composition, is about 24° for T and ranges from 26° to 31° for high-lime fly ashes. There is no doubt that the values of $2\theta_{max}$ on the typical XRD pattern for fly ash indicate the extent of glass modification. Mehta [9, 10] confirms the general trend of increase in $2\theta_{max}$ value with increasing CaO in fly ash. The same trend was also observed for fly ashes used in this investigation.

Hemmings and Berry [39], as cited by Mehta [9] have attributed the asymmetric shape and shift in position of fly ash halo to any or all of the following: (a) different glasses with different modifier levels in different particles (inter-particle speciation), (b) different glasses in the same particle (intra-particle speciation), or (c) phase separation.

Unlike the low-lime fly ash T, high-lime fly ashes (SB, A, and SR) contain low proportions of glass component. One of the most important components of glassy phase is residual clay. Clay minerals lose their crystalline structure at high temperature during combustion and transform into highly reactive SiO_2 and Al_2O_3.

6.2.2 Hydration Products of Fly Ashes

XRD analysis of hydrated fly ashes at different ages reveals that, the reaction products of the fly ashes are mainly the same with slight differences between their types and rate of formations.

The high-lime SR fly ash has the lowest free lime content (5.5%) among the high-lime fly ashes. Free lime content has a marked effect on the hydration of fly ash. The examination of X-ray diffractograms of hydrated SR, given in Figure 6.3, shows that gypsum is the only detectable hydration product of this fly ash even up to 90-day hydration. However, the mixture of this fly ash with 20% (by weight) commercial lime accelerates the anhydrite-gypsum transformation and results in the formation of ettringite, C_4AH_{13} and its carbonate $C_4A\bar{C}H_{11}$ at later ages. These late forming calcium aluminate products are most probably resulted from the aluminous portion of glassy phase rather than the highly reactive free alumina of residual clay [186].

In contrast to SR, A and SB are highly reactive due to their larger free lime contents. Regarding the X-ray diffractograms of these fly ashes shown in Figures 6.4 and 6.5, the transformations of free lime and anhydrite into CH and gypsum occur at very early stages of hydration. Meanwhile, ettringite forms upon the reaction of these compounds with active alumina. Within a few days, ettringite formation consumes the existed CH and gypsum in the system completely so that no CH and gypsum remain in 7-day-old specimens.

C-S-H gel is not clearly detectable in these systems, because the usual peaks of this product at about 3.8, 2.8, and 1.8 A° are weak and diffuse. Furthermore, they may overlap by the peaks of calcite, resulting from CH carbonation and quartz impurity of fly ash. Tokyay [185] cites the assumption of Grudemo [186] to state that around 18° 2θ angle, due to structural similarities between CH and C-S-H peak, any additional peak or increase in intensity may be interpreted as the presence of C-S-H gel in the system. Accordingly, Tokyay confirms that, from 7-days onward, since there is no major CH peak (2.63 A°), the observed peak at 18° 2θ angle can be attributed to the presence of C-S-H gel. At 90 days age C_4AH_{13} and $C_4A\bar{C}H_{11}$ are also detectable.

Low-lime T fly ash upon mixing with 20 % commercial lime results in the same hydration products like other three fly ashes. However, the rate of formation of hydration products is slightly different. The diffractogram of T+CH mixture is given in Figure 6.6. In addition to peaks of quartz, magnetite and hematite, which are already present in the fly ash, peaks of ettringite and calcite are also detectable. However, due to the lack of anhydrite, gypsum is not present as a hydration product even as early as 7-days age.

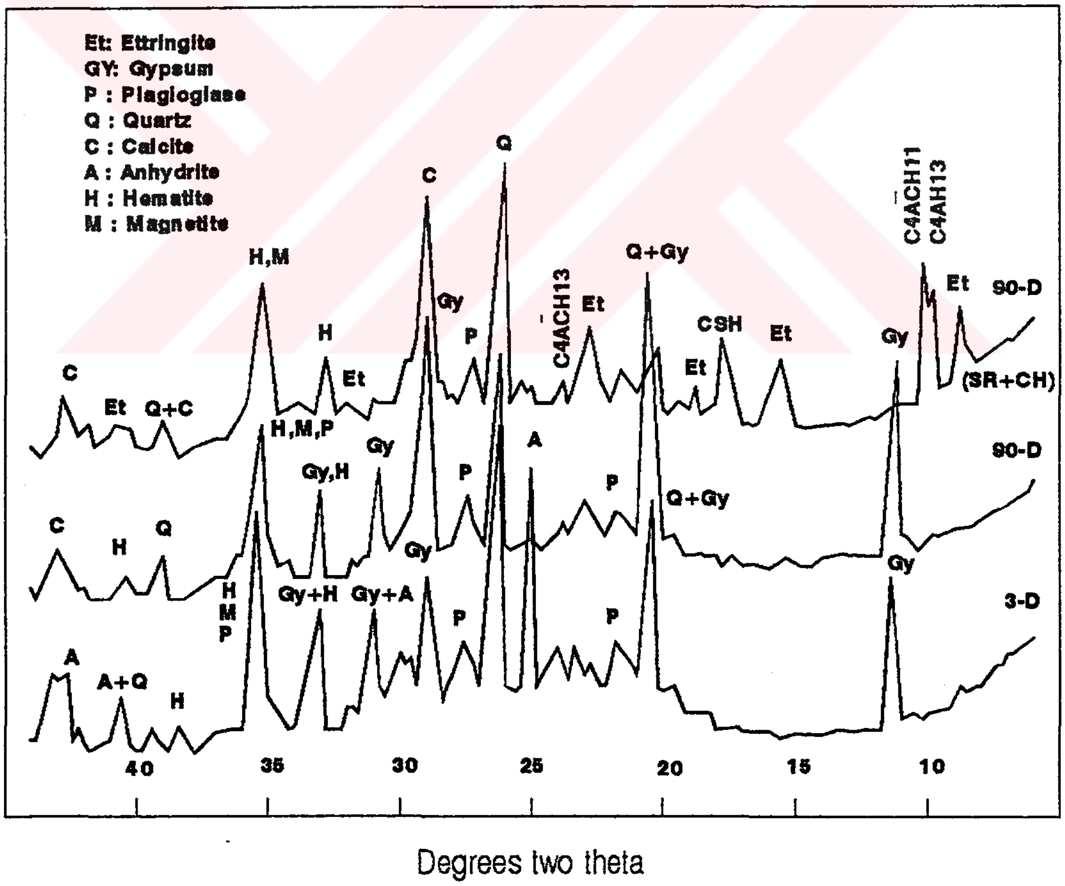


Figure 6.3. X-Ray Diffractograms of Hydrated SR Fly Ash and SR +CH [43]

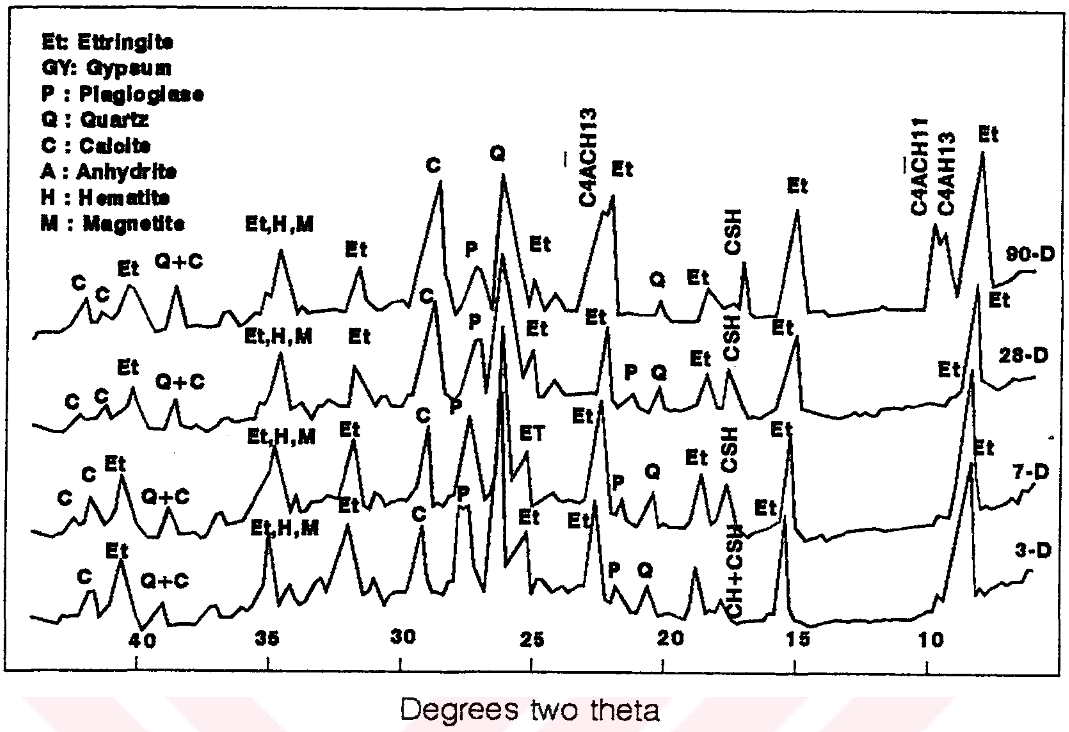


Figure 6.4. X-Ray Diffractograms of Hydrated SB Fly Ash [43]

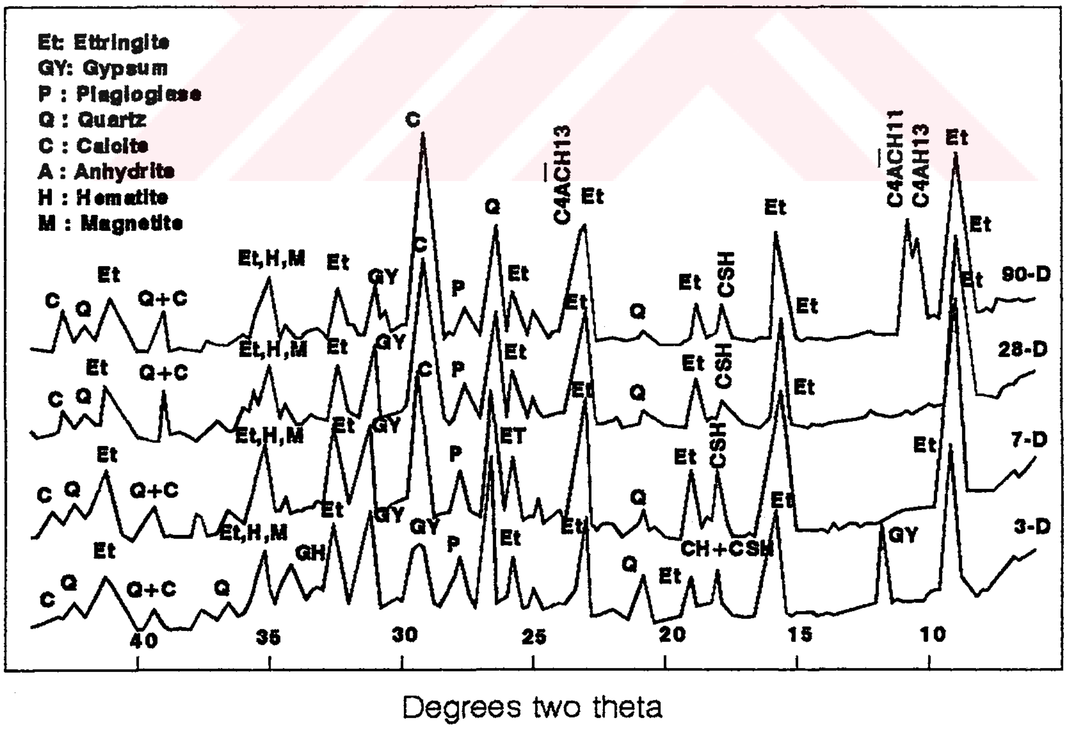


Figure 6.5. X-Ray Diffractograms of Hydrated A Fly Ash [43]

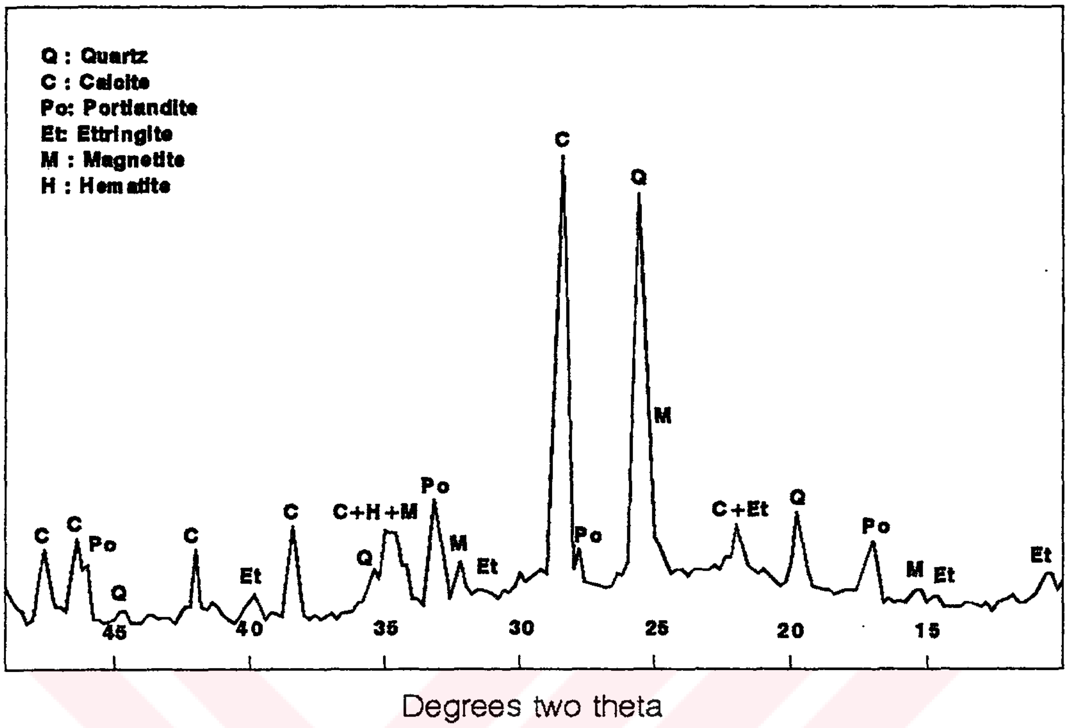


Figure 6.6. X-Ray Diffractograms of Hydrated T+CH [43]

6.2.3 Heat of Hydration

The hydration reactions of portland cement are exothermic. Portland cement evolves about 120 cal/g heat upon complete hydration. Not only in concrete dams, but also in large foundations, piers, columns and beams the heat of hydration, which can not be dissipated rapidly by radiation, may be of such magnitude as to require special attention. The attention is required to prevent excessive temperature rise followed by shrinkage and cracking when the structure cools down to ambient temperature. The cracks jeopardise the structural safety and, more importantly, increase the permeability of concrete which exposes the structure to other processes of deterioration. Depending on the size and shape of the structure, cement type and content, and concrete temperature at placement, adiabatic temperature rise of the order 30 to 60°C is not uncommon in massive structures made with ordinary concrete. Even higher temperatures may be experienced with high-strength concrete mixtures. In the case of plain concrete, the peak temperature may be reached within 2 to 5 days after placement, and the structure will develop thermal cracking due to either temperature gradient between the surface and the interior or volume changes during cooling to ambient temperature.

As described in several reports [3, 7, 9, 10], one of the ways to reduce the rate of temperature rise significantly is to replace a part of cement (commonly 25-35 % by weight) by fly ash, which provides an effective means of controlling thermal shrinkage cracking in concrete without compromising the ultimate desired strength.

In the United States, most concrete gravity dams built during last 30 years and several recently constructed roller-compacted dams are made from fly ash concrete. At 30% cement replacement level by fly ash, 15 % reduction in temperature rise of concrete is reported. Other advantages associated with the use of fly ash in mass concrete are its water-reducing ability and consequently further cement reduction at a given W/C radio, and the thermal activation potential of fly ash which is superior to portland cement. At high curing temperatures, not only the rate of hydration of even a coarse grained fly ash becomes high but also the microstructure and mechanical properties of the PC-fa paste are usually superior to the neat PC pastes [9, 13]. On the other hand, on cold-weather concreting, heat of hydration provides a degree of autoprotection against the ambient temperature which might otherwise cause freezing.

For both of the above mentioned cases, the information on the quantity of heat of hydration of cement should be available. Furthermore, quantity of evolved hydration heat, at known time intervals, is a good measure of the degree and the course of hydration reactions. The heat of hydration of plain cement and PC-fa mixtures at 7, 28, 90 days age are presented in Table 6.4. A comparison of the hydration heat of control and fly ash incorporated specimens are given in Figure 6.7.

Table 6.4. Heat of Hydration of Control and PC-fa Pastes at Various Stages of Hydration

Specimen	Heat of Hydration (cal/g) at		
	7 days	28 days	90 days
Control	85.5	99.9	113.4
10 T	82.6	85.4	105.6
20 T	74.9	83.1	104.0
40 T	59.8	77.1	99.7
10 SB	83.8	99.7	110.8
20 SB	80.1	88.2	108.0
40 SB	75.0	87.1	107.1
10 A	87.9	95.6	114.9
20 A	95.7	106.8	114.1
40 A	99.1	112.8	116.8
10 SR	89.3	95.2	113.0
20 SR	91.7	101.4	114.0
40 SR	96.9	109.7	113.8

The interpretation of the test results leads to the following:

1. As it can be seen from Table 6.4 and Figures 6.7 and 6.8 among the fly ashes used, low-lime T fly ash is the most effective one in reducing the heat of hydration. The reduction is more pronounced for 40% inclusion level and for early stages of hydration.

2. As illustrated in Figure 6.12, for 10% low-lime T fly ash substitution level, the reduction in 7-day heat of hydration (4%) is less than the reduction in 28-day heat of hydration (15%). This can be attributed to the amount of fly ash in the mix. The 10% replacement of cement with fly ash is not sufficient to offset the effects of early heat generating compounds (C_3A and C_3S) of cement. T fly ash can be successfully used to reduce hydration heat of concrete at substitution levels beyond 20% by weight of cement.

3. SB fly ash at 10% inclusion level has no marked effect on heat of hydration. However, at higher replacement levels, it decreases hydration heat of the system slightly as shown in Figures 6.9 and 6.13.

4. Both A and SR fly ashes result in an increase in hydration heat of the system at all substitution levels. The difference between heat of hydration values of A and SR bearing pastes and control paste is larger at early ages of hydration and increases with increasing the amount of fly ash in the mix as shown in Figures 6.7, 6.14 and 6.15. This is a measure of higher reactivity of these fly ashes either by themselves or in the PC-fa system.

5. It seems that free lime plus anhydrite content and fineness of fly ash play an important role in heat of hydration evolution of PC-fa pastes. Fly ash A, containing 30.7% lime bearing compounds (freeCaO+C$\bar{S}$) evolves the largest heat of hydration. SR, having a lower lime bearing compounds content (14.8%) than SB (17.2%), due to its extremely higher fineness (9700 cm^2/g), results in higher heat of hydration than SB fly ash. It seems that, very fine particles of SR fly ash encourage cement hydration by acting as additional sites for portland cement hydration at early ages [3, 10]. At 90 days, age the heat of hydrations of SR bearing pastes are approximately equal to control paste regardless of the inclusion level.

6. High-lime fly ashes used in this study, due to their higher reactivity arisen from the presence of lime compounds or due to their extremely high fineness, have either negligible effect on heat of hydration (SB) or increase it (A and SR). So, special care should be given when using these fly ashes in mass concrete.

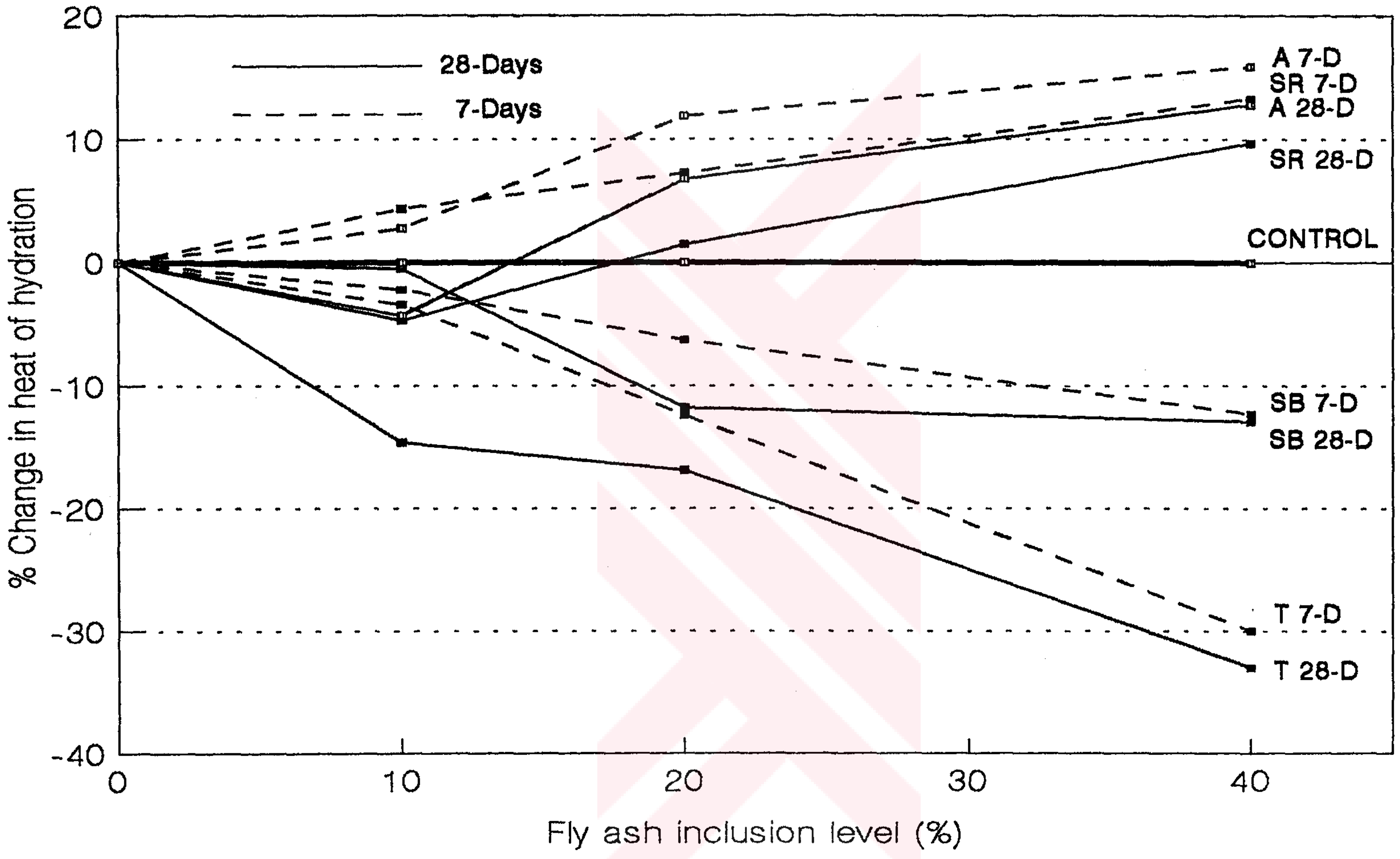


Figure 6.7. Changes in Heat of Hydration with Fly Ash Type and Fly Ash Inclusion Level

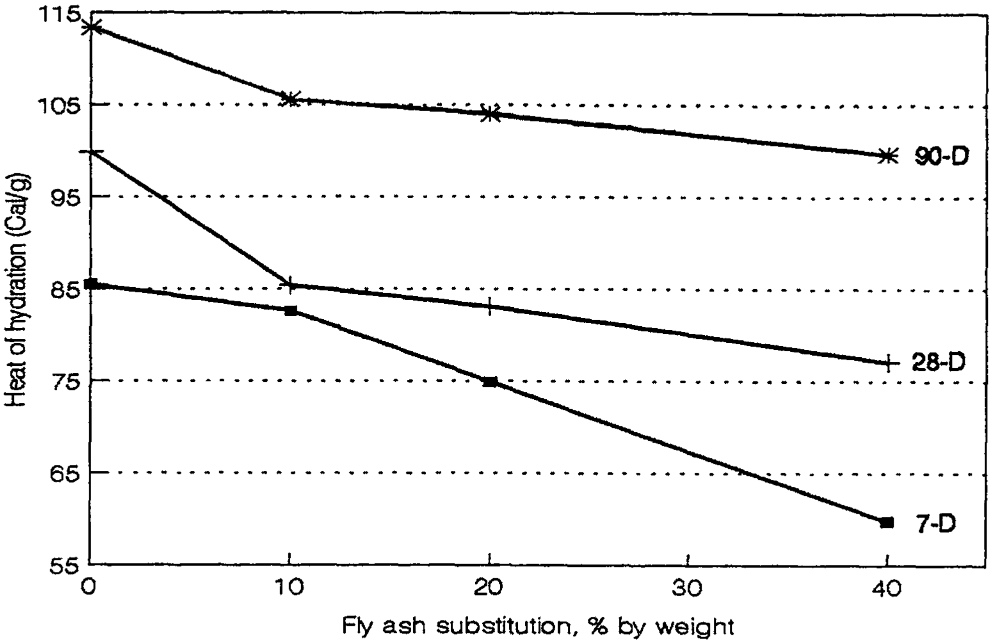


Figure 6.8. The Effect of T Fly Ash Substitution on the Heat of Hydration of PC-fa Pastes at Various Ages

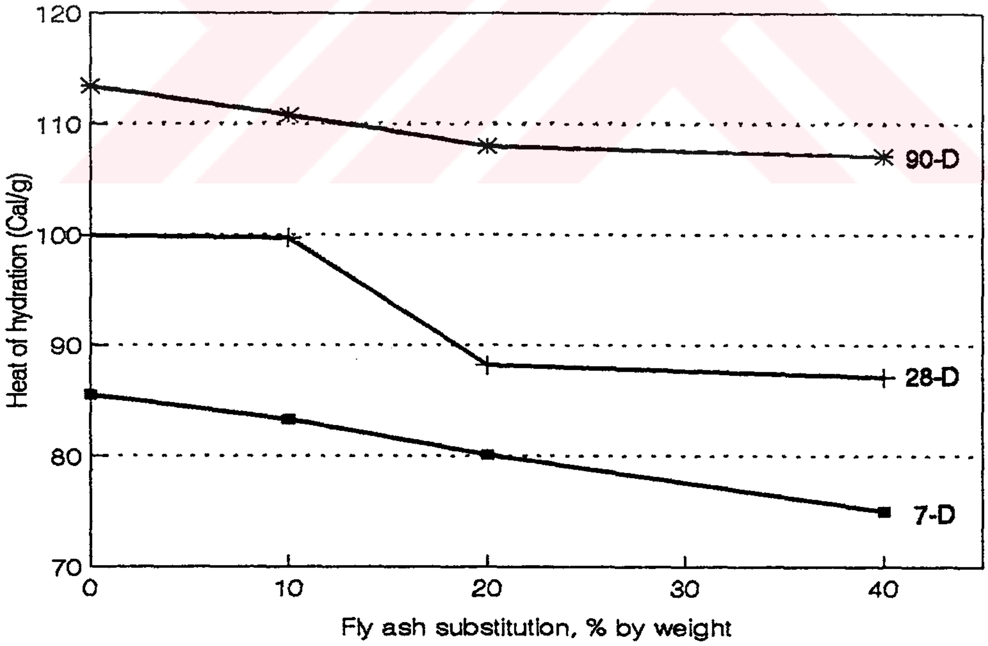


Figure 6.9. The Effect of SB Fly Ash Substitution on the Heat of Hydration of PC-fa Pastes at Various Ages

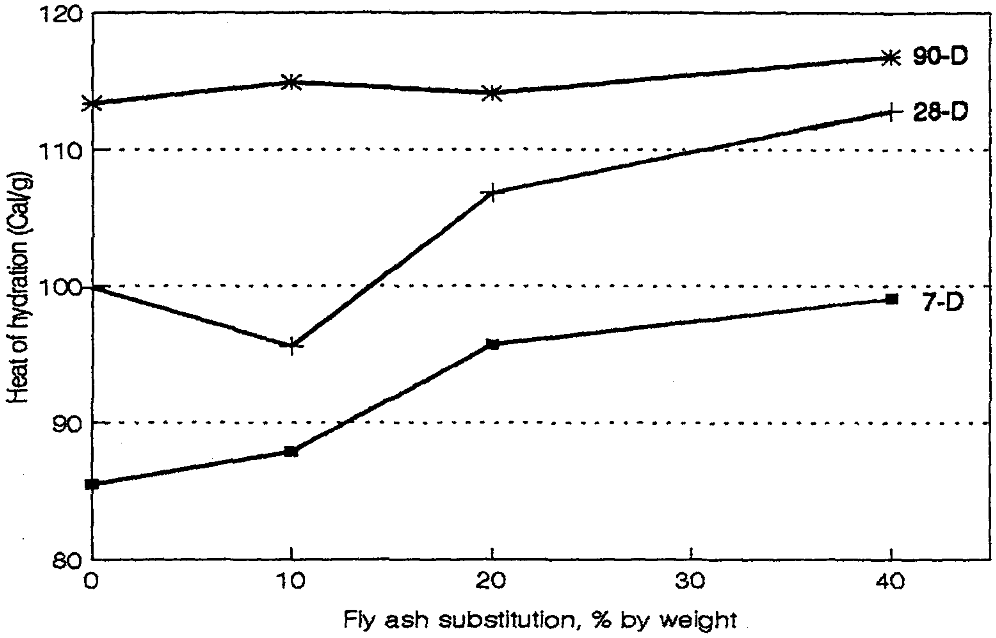


Figure 6.10. The Effect of A Fly Ash Substitution on the Heat of Hydration of PC-fa Pastes at Various Ages

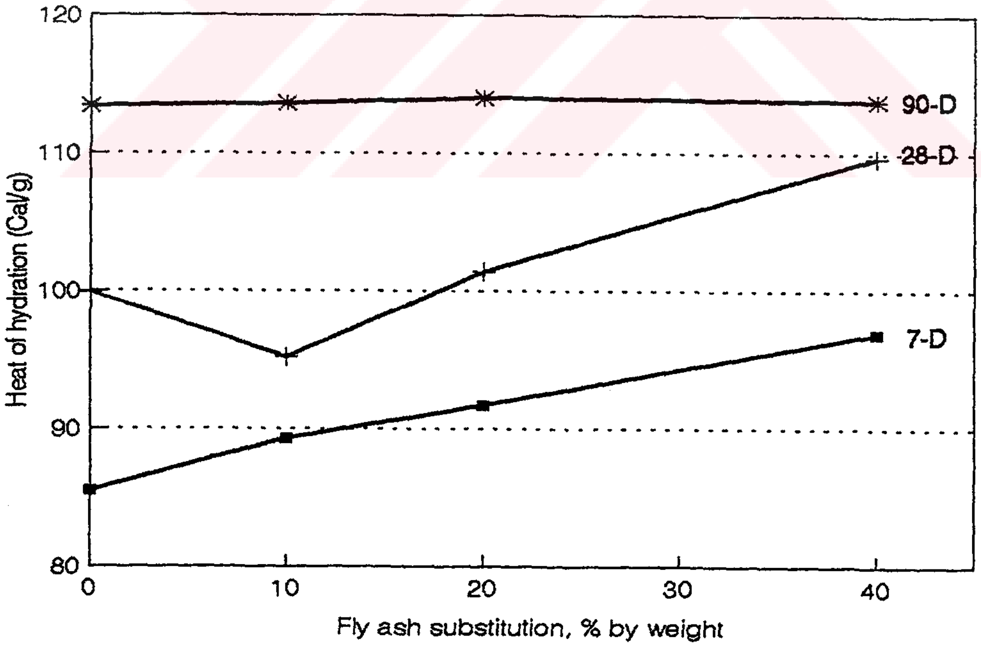


Figure 6.11. The Effect of SR Fly Ash Substitution on the Heat of Hydration of PC-fa Pastes at Various Ages

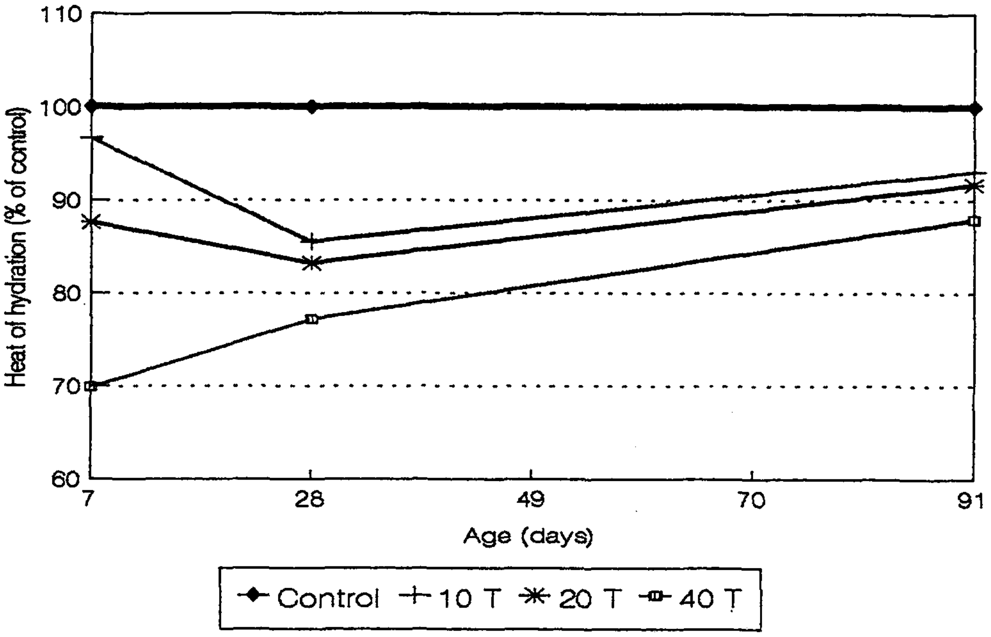


Figure 6.12. The Effect of T Fly Ash on the Heat of Hydration Evolution Rate

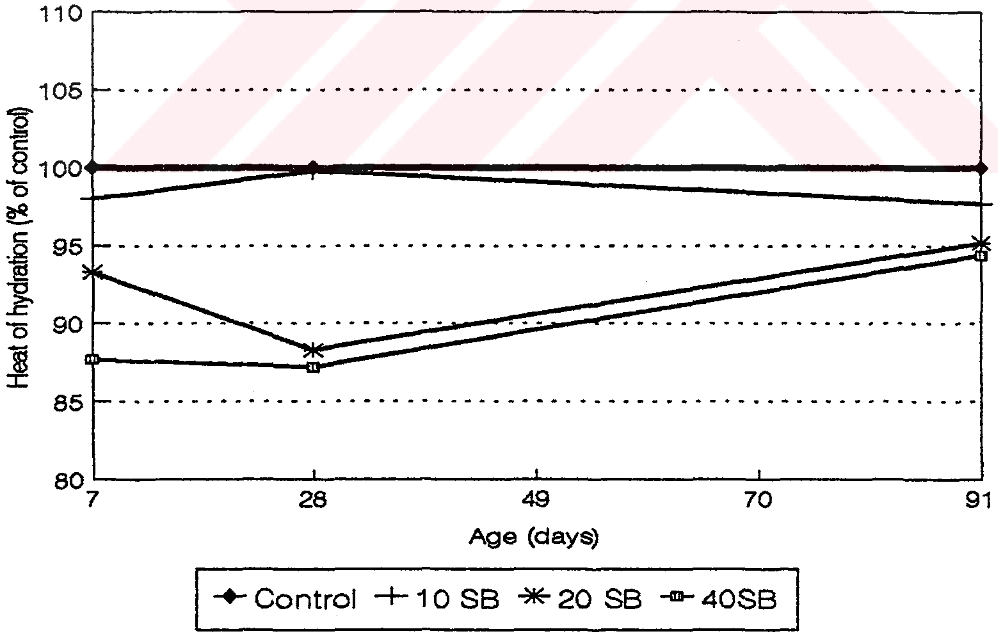


Figure 6.13. The Effect of SB Fly Ash on the Heat of Hydration Evolution Rate

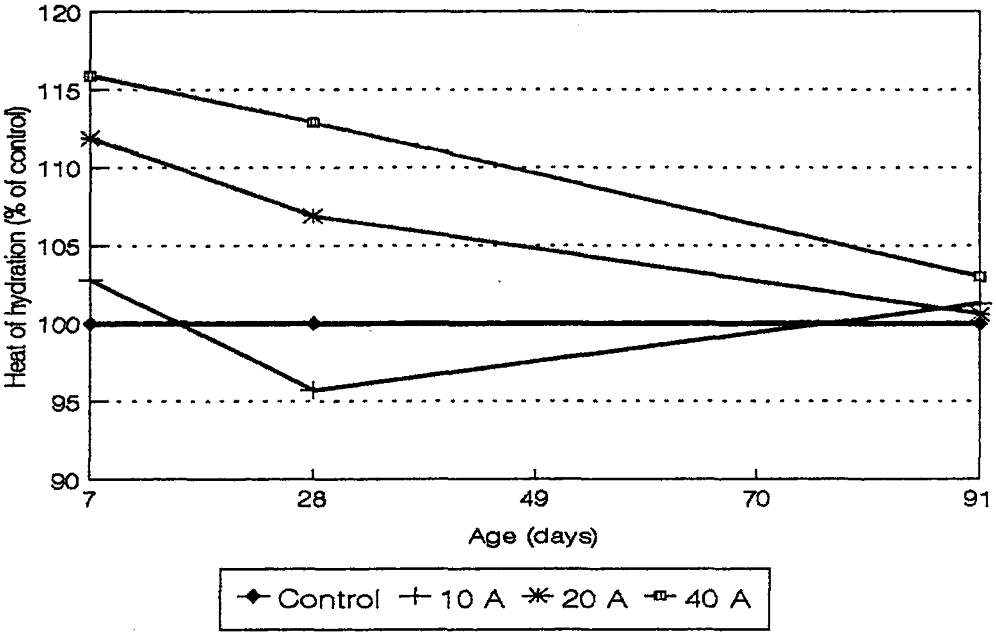


Figure 6.14. The Effect of A Fly Ash on the Heat of Hydration Evolution Rate

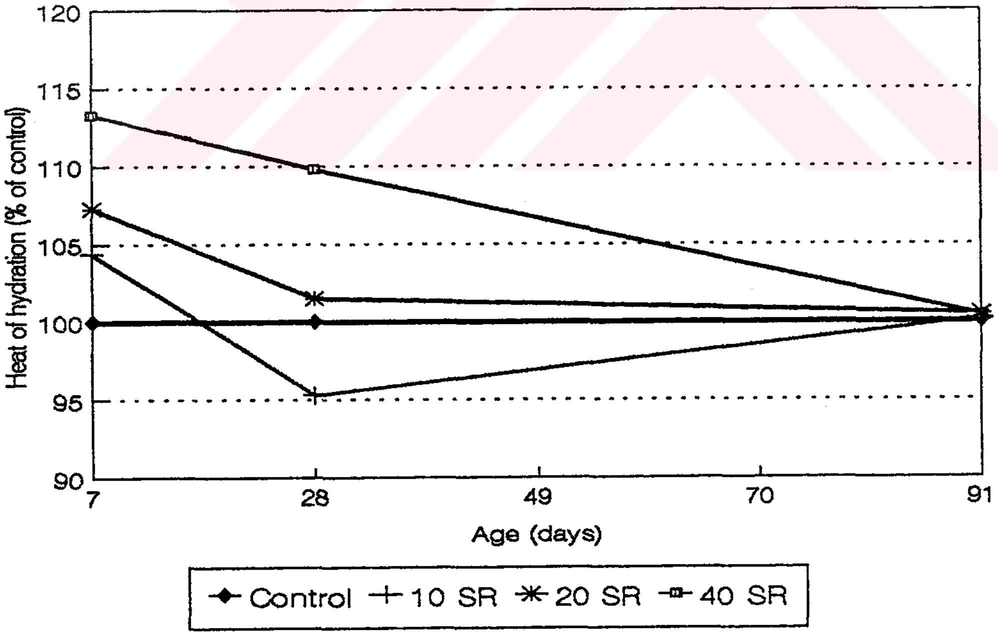


Figure 6.15. The Effect of SR Fly Ash on the Heat of Hydration Evolution Rate

6.3 Effects of Fly Ash on Flow and Water Requirement of PC-fa Mortars

The water requirement of PC-fa mortars is generally accepted as a measure of fly ash suitability to use in concrete. The water requirement of fly ashes were determined in accordance with ASTM C 311 [166] to obtain 100 to 115% flow in mortars. The results are given in Table 5.9. According to these results, T and SB fly ashes with 104% and 105% (of control) are in acceptable range (105% of control); however, the water requirements of A (110%) and SR (116%) exceed the acceptable limit.

In addition to determining the water requirement of fly ashes as a compliance test for fly ashes, the flow determinations were repeated during preparation of compressive strength test mortar specimens. The flow, water requirement and corresponding water-cementitious materials ratio both on weight basis and volume basis, given in Table 6.5, reveal that:

1. As it was expected from the results of water requirement tests on fly ashes, all of the fly ashes increase the water demand of mortars for a given consistency with respect to control mortar.

2. Owing to their lower specific gravity and the replacement of cement with fly ash on weight basis, the volume of fly ash bearing pastes is larger than that of control mortar. Thus, on volume basis, T and SB fly ashes result even in a slight reduction in water requirement. Whereas, A fly ash at 40% substitution level and SR fly ash at 20% and 40% inclusion levels result in higher water requirement.

3. The higher water demand of A fly ash may be due to its higher anhydrite and free lime contents which immediately, upon mixing with water, react with active alumina to form ettringite. Ettringite formation reduces the consistency of the mortar and consequently increases water requirement for a given flow.

4. SR fly ash contains lower proportions of anhydrite and lime than A and SB fly ashes. The higher water requirement of this fly ash is due to its extremely high fineness which provides larger surface area to be wetted with water.

6.4 Effects of Fly Ash on the Strength of Mortars

Since the fly ashes used in this study were examined as concrete-making materials, in addition to fly ash compliance tests, the rate of strength development in PC-fa mortars was also monitored.

The strength development rate of the mortars was examined for the fly ashes at 0, 10, 20 and 40% (by weight) cement replacement levels. Besides, for each fly ash, in three extra mixes, 10% of cement was replaced by 20% and 40% of fly ash, as well as 20% of cement was substituted by 40% of fly ash. In this way, in addition to control specimens, six different mortar mixtures were prepared for each fly ash, as shown in Table 6.5.

As it can be observed from Table 6.6, except for SB fly ash at 10% inclusion level, all of the fly ashes resulted in strength reduction of PC-fa mortars at all ages regardless of the fly ash substitution level. However, this reduction is more pronounced at early ages and for higher replacement levels. The early age strength reduction clearly results from the increase in water requirement of the mortars for a given consistency (Table 6.5). In this regard, it is valuable to consider the extent to which the chemical reactivity of the ash contributes to strength at different ages. Same as any potential pozzolan, when a fly ash is partly substituted for portland cement, it may function in one or more ways: a) It may be inert (non-pozzolanic) and merely dilute the portland cement, but at the same time influence the water demand, b) It may be weakly cementitious and thus, both dilute the portland cement and contribute to bonding action, c) It may be strongly cementitious.

The portland cement and fly ashes contribute to the binding action at different rates. So, portland cement may dominate at a particular

Table 6.5. Flow, Water Requipment and Water-Cementitious Material Ratio of PC-fa Mortars

Specimen	Flow (%)	Water Content (g)	PC+fa Content (g)	Water/Cementitious Material			
				by wgt.	%of control	by vol.	%of control
Control	112	238	490	0.486	100	1.53	100
T-M$_{s}$-10*	109	250	440+50	0.510	104.9	1.52	99.1
T-M$_{a2}$-10	105	285	440+100	0.528	108.6	1.50	98.1
T-M$_{a4}$-10	107	335	440+200	0.523	107.7	1.39	91.2
T-M$_{s}$-20	105	255	390+100	0.520	107.1	1.47	95.8
T-M$_{a2}$-20	114	325	390+200	0.551	113.3	1.45	94.7
T-M$_{s}$-40	106	300	290+200	0.612	126.0	1.56	101.8
SB-M$_{s}$-10	110	220	440+50	0.449	92.4	1.37	89.6
SB-M$_{a2}$-10	106	273	440+100	0.506	104.0	1.51	98.6
SB-M$_{a4}$-10	115	315	440+200	0.492	101.2	1.42	92.6
SB-M$_{s}$-20	109	243	390+100	0.500	102.0	1.47	96.2
SB-M$_{a2}$-20	106	300	390+200	0.508	104.6	1.45	95.0
SB-M$_{s}$-40	110	266	290+200	0.543	111.7	1.52	99.5
A-M$_{s}$-10	110	240	440+50	0.490	100.8	1.51	98.8
A-M$_{a2}$-10	104	280	440+100	0.519	106.7	1.58	103.0
A-M$_{a4}$-10	112	325	440+200	0.508	104.5	1.51	98.5
A-M$_{s}$-20	110	255	390+100	0.520	107.1	1.58	103.0
A-M$_{a2}$-20	110	312	390+200	0.529	108.8	1.56	102.0
A-M$_{s}$-40	115	275	290+200	0.561	115.5	1.64	106.9
SR-M$_{s}$-10	108	250	440+50	0.510	104.9	1.56	102.1
SR-M$_{a2}$-10	113	276	440+100	0.511	105.2	1.53	100.0
SR-M$_{a4}$-10	108	330	440+200	0.516	106.1	1.49	97.6
SR-M$_{s}$-20	102	270	390+100	0.551	113.4	1.64	107.2
SR-M$_{a2}$-20	110	318	390+200	0.539	110.9	1.55	101.3
SR-M$_{s}$-40	106	303	290+200	0.618	127.2	1.75	114.4

* T-M$_{s}$-10 denotes that, 10% of cement is simply replaced by 10% of Tunçbilek fly ash in the mortar mixture and T-M$_{a2}$-10 identifies that, 10% of cement is additionally replaced by 20% of Tunçbilek fly ash in the mortar mixture.

Table 6.6. Effect of Fly Ash on the Compressive Strength Development of 50 mm Cubic Mortar Specimens

Specimen	Ave.Compressive Strength(MPa)				Relative Comp.Str.(% of Control)				Feret ratio
	7 -D	28-D	90-D	180-D	7 -D	28-D	90-D	180-D	
Control	33.8	48.3	63.9	69.2	100	100	100	100	1.0
T-M_s-10	25.9	46.0	59.9	69.0	76.6	95.2	93.7	99.7	0.94
T-M_{a2}-10	24.3	40.5	56	67.2	71.9	83.8	87.6	97.1	0.69
T-M_{a4}-10	23.0	36.0	57.6	65.1	68.1	74.5	90.1	94.1	0.55
T-M_s-20	19.1	38.4	55.6	61.3	56.5	79.5	87.1	88.6	0.66
T-M_{a2}-20	20.8	33.4	54.8	62.5	61.5	69.2	85.6	90.3	0.49
T-M_s-40	13.1	24.1	40.4	44.4	38.8	49.9	63.2	80.1	0.35
SB-M_s-10	34.0	47.9	58.6	69.9	100.5	103.9	105.0	110.1	0.97
SB-M_{a2}-10	28.4	46.4	56.3	70.7	84.1	96.1	94.4	102.2	0.73
SB-M_{a4}-10	27	42.9	59.9	67.9	79.9	88.8	93.7	98.1	0.60
SB-M_s-20	26	42	61.3	64.5	65.1	86.9	95.9	99.0	0.73
SB-M_{a2}-20	29.8	46.7	62.1	68.9	76.3	96.7	97.2	99.6	0.55
SB-M-$_s$40	16.7	31.6	44.8	60	49.4	65.4	70.1	86.7	0.42
A-M_s-10	29.2	43	52.6	68	86.3	89.1	82.3	98.2	0.87
A-M_{a2}-10	12.8	38.5	58.5	67.1	37.9	79.7	91.5	97.0	0.71
A-M_{a4}-10	9.5	16.7	43.5	56	28.1	34.6	68.1	86.1	0.58
A-M_s-20	20.5	30.1	51	63.2	60.7	62.3	79.8	91.3	0.68
A-M_{a2}-20	7.5	15.1	38.4	49.6	22.1	31.3	60.17	1.7	0.52
A-M_s-40	8.9	13.9	30.4	39.2	26.3	28.8	47.6	56.6	0.40
SR-M_s-10	25.1	38.4	48.1	52.7	74.3	79.5	75.3	76.2	0.82
SR-M_{a2}-10	8.9	32	48.8	57.5	26.3	66.3	76.4	83.1	0.72
SR-M_{a4}-10	10.6	27	38.8	49.1	31.4	55.9	60.7	71.0	0.57
SR-M_s-20	17.7	28.8	46	52	52.4	59.6	72.0	75.1	0.63
SR-M_{a2}-20	7.2	20.4	32	41.3	21.3	42.2	50.1	59.7	0.50
SR-M_s-40	8	16.3	23.6	35.0	23.7	33.7	36.9	50.6	0.35

time of curing, while fly ash may be effective at an earlier or later age. Therefore, the strength development of fly ash bearing portland cement systems is a complex combination of chemical action (cementing value) and physical effect (water demand). In evaluating a fly ash, it is desirable to know : a) whether it contributes chemically to cementing action; b) at what age such a contribution becomes apparent; c) the extent of the contribution over a practical range of curing age and condition.

To obtain this information, Berry and Hemmings [62, 187] used a reduced form of the equation proposed by Feret [15] to relate the strength of the mortars to the absolute volumes of water (W_o) and portland cement (C_o) in the fresh mixture as follows:

$$\sigma_o = K\left(\frac{C_o}{C_o+W_o}\right)^2 \tag{6.1}$$

In this expression K is a constant determined by the properties of the portland cement. Regarding the fly ash as an inert ingredient substituted for portland cement, the above equation may be reproduced for PC-fa mixtures as follows:

$$\sigma_i = K\left(\frac{C_i}{C_i+W_i}\right)^2 \tag{6.2}$$

In this expression C_i and W_i are the portland cement and water absolute volumes in PC-fa mortar mixtures, respectively, and K is assumed to be unaffected by the presence of fly ash. The authors defined "Feret ratio" as the ratio between the strength of i-th PC-fa mixture and control mortar as follows:

$$F = \frac{\sigma_i}{\sigma_o} = \left\{\frac{C_o+W_o}{C_i+W_i}\,\frac{C_i}{C_o}\right\}^2 \tag{6.3}$$

Besides, the ratio of experimental compressive strength values of PC-fa mortar at time t (s_t) to that of control specimen at the same age (s_o) was defined as:

$$S_t = \frac{s_t}{s_o} \tag{6.4}$$

Berry et al [62] have stated that in any set of test data obtained under identical curing conditions using a single portland cement, if (S_t/F) >1, it is probable that the fly ash is contributing to cementing action. The larger the extend to which (S_t/F) ratio is greater than unity, the more effective is the pozzolan at curing time t. Thus, it was proposed to term (S_t/F) as the "Pozzolanic Effectiveness Ratio" (PER). Although PER is not a direct measure of the cementing activity of the fly ash, an increase in it is caused by the formation of hydration products additional to those formed by the portland cement alone.

The pozzolanic effectiveness ratio (PER) was calculated for mortars. However, in mortars containing larger volume of fly ash (i.e. at 40 % replacement level, as well as in additional replaced mortars in which extra placed fly ash increases the volume of the mortar) PER is not reliable; because, in these mixes, volume of fly ash (which is not inert actually) approaches to or even exceeds the volume of cement. For mortars containing lower proportions of fly ashes, in which PER is more accurately applicable, PER values are given in Table 6.7.

From these results it is clear that, T fly ash becomes effective after 90 and 28 days curing at 10% and 20% inclusion levels, respectively. However, SB is effective as early as 7 days for 10% and within 28 days for 20% inclusion levels. A fly ash is somewhat less effective than SB and its contribution to strength starts at later ages. SR fly ash at 10% substitution level has almost a constant pozzolanic effectiveness ratio. This may be arisen from the fact that, this fly ash has no chemical (cementing) contribution to strength; however, it becomes effective at 20% inclusion level and at later ages.

Table 6.7. Pozzolanic Effectiveness Ratio (PER) of Mortars

	PER			
Specimen	7-D	28-D	90-D	180-D
T-M_S-10	0.82	1.01	0.97	1.06
T-M_S-20	0.85	1.06	1.22	1.34
SB-M_S-10	1.03	1.07	1.08	1.14
SB-M_S-20	0.89	1.19	1.31	1.36
A-M_S-10	0.99	1.02	0.95	1.13
A-M_S-20	0.89	0.92	1.17	1.24
SR-M_S-10	0.90	0.96	0.92	0.93
SR-M_S-20	0.83	0.95	1.14	1.19

Regarding the Table 6.6 and Figures 6.16 to 6.19, which show the effect of fly ashes on the strength development of mortars, it is possible to conclude that:

1) The portland cement PÇ 40 used in this investigation conforms with the requirements of ASTM C 150 [163] from strength point of view. The required compressive strength limits at 3 and 7 days age for Type I cement are 12.4 and 19.3 MPa which are far lower than 19.9 and 33.8 MPa obtained in this study at the same ages.

2) Although T fly ash bearing mortars fulfill the 7 day strength requirements of ASTM C 150 at 10 and 20% substitution levels, their strength is lower than corresponding control specimen.

3) 10% replacement of cement with T fly ash reduces the strength at all ages. However, the reduction is not significant at later ages. Additional replacement of cement with T fly ash provides no further strength development.

4) A fly ash results in strength reduction at all ages and for all inclusion levels, but the reduction in strength is less pronounced at 10% replacement level. At 20 and 40% replacement levels, it takes 90 days and 180 days, respectively for A fly ash bearing mortars to attain equivalent strength as 28 days control specimen.

5) SR fly ash results in strength reduction for all cases, too. At 10% replacement level (SR-M_S-10), and even after 180-day curing the mortar shows 24% lower strength value than control specimen. It seems that, longer curing period provides no significant improvement in the strength of SR bearing mortars.

6) The strength reduction in mortars containing T, A, and SR fly ashes may be attributed to the higher water demand of these materials which couples with their lower activity index to minimize their binding value. This is why, SR fly ash having the largest water requirement and the lowest activity results in the highest strength reduction.

7) SB fly ash bearing mortars at 10% substitution level give superior strengths than control specimen as early as 7-day curing. However, additional replacement of 10% of cement by 20% and 40% of SB fly ash, due to higher water requirement of the resultant mortars for a constant flow, causes a progressive strength reduction.

8) At 20% substitution level, SB fly ash results in about 10% strength reduction in 28 days with respect to control specimen, and equivalent strength is attained after 180-day curing.

9) When fly ash substitution exceeds 20 % for SB, the strength of mortar is lowered more. However, the rate of strength gain is higher for this mortar and the strength difference is sharply reduced by time. (SB-M_S-40) mixes reach the 7-day strength and 28-day strength of control mortar after 28 days and 90 days curing, respectively. This observation indicates that a significant potential for cement saving exists for this fly ash at substitution levels up to 40%.

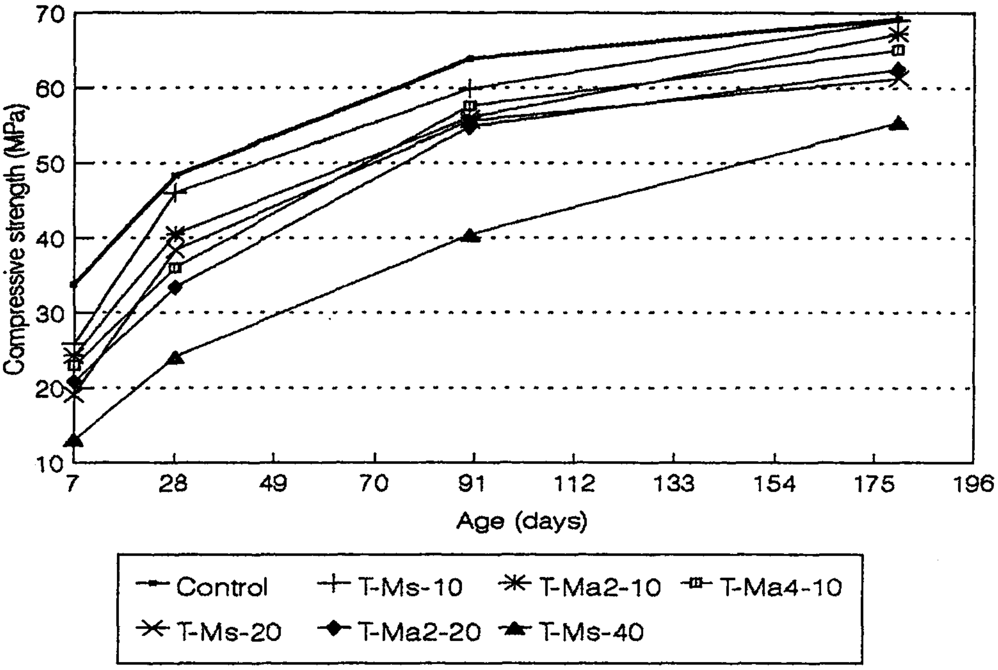


Figure 6.16. Effect of T Fly Ash on the Compressive Strength Development of Mortars

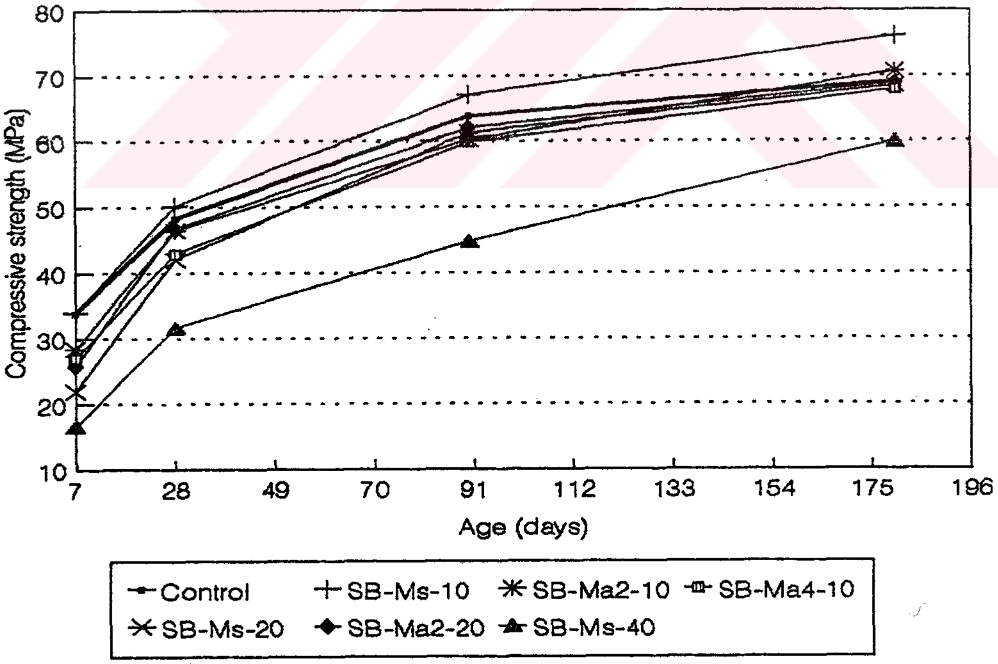


Figure 6.17. Effect of SB Fly Ash on the Compressive Strength Development of Mortars

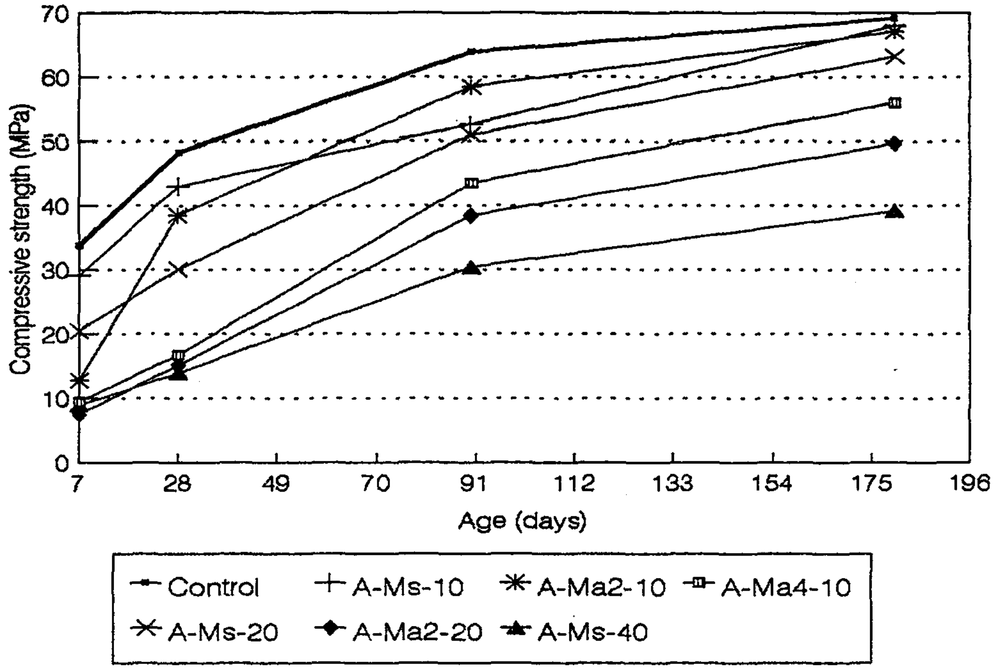


Figure 6.18. Effect of A Fly Ash on the Compressive Strength Development of Mortars

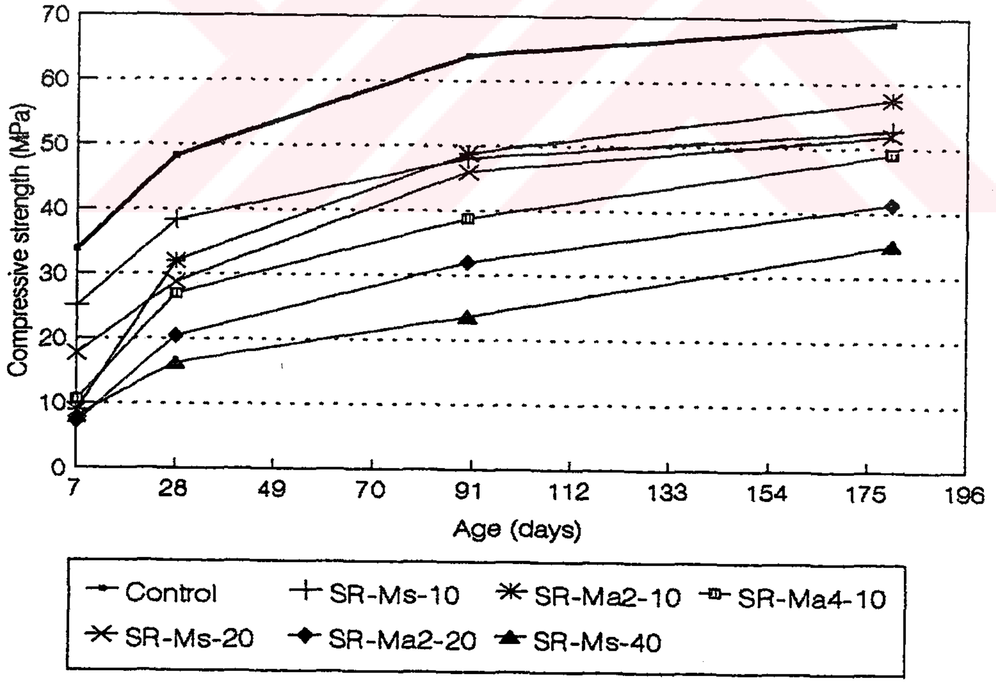


Figure 6.19. Effect of SR Fly Ash on the Compressive Strength Development of Mortars

6.5 Effects of Fly Ash on the Properties of Fresh Concrete

As it was mentioned in section 5.3 the control concrete mixture was designed for 25 MPa 28-day compressive strength and a slump value of 65 ± 15 mm. Fly ash inclusion to concrete mixtures was carried out both by simple replacement method and additional replacement method.

In simple replacement 10, 20, and 40% by weight of cement was substituted with fly ash. These mixtures are designated as C_s mixes throughout the study. In additional replacement, the weight of added fly ash was either two or four times that of removed cement. The resulting mixtures are designated as C_{a2} and C_{a4} respectively. For 10% replacement level both C_{a2} and C_{a4} mixes and for 20% replacement level only C_{a2} mixes were casted. In additional replaced samples simultaneous adjustments were carried out in the aggregate proportions, so that a fraction of sand having equal volume to the extra placed fly ash was removed from the mix. In all fly ash concrete mixtures the water content of the mix was arranged to obtain a 65 ± 15mm slump.

6.5.1 Effects of Fly Ash on the Water Content and Unit Weight of Concrete

It is apparent from the mix parameters, given in Table 5.12, that except for SR, at 10 and 20% replacement levels the water requirement of fly ash concrete mixtures remains approximately unchanged or reduces slightly for the same slump as control concrete. This may be due to the ball-bearing effect of fly ash particles and, hence, the increase in the workability of the mix.

However, at higher inclusion levels and in the mixes prepared by additional replacement method, as well as SR bearing mixes the water demand of concrete increases due to the increase in the volume of finely divided fly ash particles in the mix. The increment in water requirement is more pronounced in A and SR fly ash bearing mixes and reaches to about

20% of control concrete water demand in SR fly ash containing concrete mixes.

Owing to the higher water requirements of these fly ashes, represented in Table 5.9, it is possible to say that, in A fly ash bearing concrete mixtures the higher water demand may be arisen from the immediate formation of C_3A formed by the interaction of active alumina and free lime of fly ash and a consequent reduction in the consistency of the mix. However, the higher fineness and extremely larger surface area of SR fly ash particles seem to be responsible for larger water requirement. It should also be noted that, in spite of the increase in water demand, except for 40% inclusion level, the water-cementitious material ratio of fly ash concretes are still lower than that of control mix.

The unit weights of fly ash concretes, given in Table 5.12, are slightly lower than that of control concrete. This reduction is solely due to the differences between the specific gravities of the fly ash and cement or aggregate which are replaced by the fly ash. As a result, the highest reductions occur in T fly ash bearing mixes which have the lowest specific gravity among the fly ashes or in SR fly ash bearing mixes due to its relatively higher water demand.

6.5.2 Effects of Fly Ash on Air Content of Concrete

The air content of fresh concrete mixtures was measured by pressure method. The results presented in Table 5.12 indicate that, at lower inclusion levels, fly ash does not have a significant effect on the air content of non-air entrained concrete. However, T, SB and A fly ashes result in a slight increase in air content at 40% substitution level.

On the other hand, with regard to air-entrained concrete, it is reported that the presence of fly ash may give rise to difficulties with the variability of air content, as well as void size and spacing. These difficulties are generally suggested to be caused by the carbon content and fineness of fly ash. Thus, it is necessary to exercise greater control when fly ash is used in air-entrained concrete, and whenever possible, an air-entraining agent formulated specifically for fly ash applications should be used [7, 10, 45].

6.6 Effects of Fly Ash on the Strength of Concrete

6.6.1 Effects of Fly Ash on the Compressive Strength of Concrete

The compressive strength development of the 150 x 300 mm cylindrical, control and fly ash concretes was monitored at ages up to 180 days. Each value given in Table 6.8 is the average strength of three specimens. The interpretation of data graphically shown in Figure 6.20 to Figure 6.23 leads to the following:

- T and SB bearing concretes at 10% inclusion level using additional replacement method show equivalent strength values to control specimen as early as 7 days age.

- At 20 % inclusion level, T fly ash concrete acquires the same strength as control concrete at 90 days age. Additional replacement method is still effective in higher rate of strength gain. At 180 days age, the strength of (T-C_S-20) and (T-C_{a2}-20) mixtures is about 12% larger than control specimen.

- At 40% inclusion level, both T and SB bearing concrete mixes result in lower strengths than control one even after 180 days of curing. The 180-day strength of these mixtures is approximately equal to 28 day strength of control specimen. However, the difference between the strength of (T-C_S-40) and (SB-C_S-40) mixtures and control concrete decreases with age.

- At 20% inclusion level, regardless of the inclusion method, SB fly ash concretes reach the same strength as control concrete at 28 days age. These mixtures show approximately 5% and 15% higher strength values than control concrete at 90 days and 180 days age, respectively. Besides,

Table 6.8. Effect of Fly Ash on the Compressive Strength Development of Concrete

Specimen	Ave.Compressive Strength(MPa)				Relative Comp.Str.(% of Control)			
	7 -D	28-D	90-D	180-D	7 -D	28-D	90-D	180-D
Control	18.8	26.5	31.1	33.6	100	100	100	100
T-C_s-10	15.2	24.5	31.0	36.9	80.9	92.5	99.7	109.8
T-C_{a2}-10	18.0	28.6	39.2	47.5	95.7	107.9	126.0	141.4
T-C_{a4}-10	11.1	26.1	36.0	41.9	59.0	98.5	115.8	124.7
T-C_s-20	10.3	17.8	30.8	37.1	54.8	67.2	99.0	110.4
T-C_{a2}-20	12.8	23.9	31.7	38.1	68.1	90.2	101.9	113.4
T-C_s-40	5.8	12.1	18.5	27.7	30.9	45.7	59.5	82.4
SB-C_s-10	16.3	28.2	32.3	35.1	86.7	106.4	103.9	104.5
SB-C_{a2}-10	15.2	27.5	39.1	47.0	80.9	103.8	125.7	139.9
SB-C_{a4}-10	19.3	31.5	37.4	46.9	102.7	118.9	120.3	139.5
SB-C_s-20	17.6	27.6	34.0	36.8	93.6	104.2	109.3	109.5
SB-C_{a2}-20	16.2	26.8	31.2	40.0	86.1	97.4	100.3	119.0
SB-C_s-40	12.0	19.2	24.9	29.9	63.8	72.4	80.1	89.0
A-C_s-10	15.0	24.2	30.8	34.9	79.8	91.3	99.0	103.9
A-C_{a2}-10	11.0	24.6	29.1	32.0	58.5	92.8	93.4	95.2
A-C_{a4}-10	10.6	20.1	27.2	30.9	56.4	75.8	87.5	92.0
A-C_s-20	9.9	21.0	28.1	32.3	57.6	79.2	90.4	96.1
A-C_{a2}-20	8.2	17.0	23.1	31.1	43.6	64.2	74.3	92.6
A-C_s-40	7.1	11.1	20.5	27.3	37.8	41.9	65.9	81.3
SR-C_s-10	11.4	21.3	27.6	31.7	60.6	80.4	88.7	94.3
SR-C_{a2}-10	9.2	23.5	32.0	36.1	48.6	88.7	102.9	107.4
SR-C_{a4}-10	8.5	25.5	33.3	39.0	45.2	96.2	107.1	116.1
SR-C_s-20	11.0	23.6	30.1	34.0	58.5	89.1	96.8	101.2
SR-C_{a2}-20	7.2	24.5	29.9	35.5	38.3	92.4	96.1	105.7
SR-C_s-40	7.2	19.9	22.6	30.6	38.3	75.1	72.7	91.1

the trend of strength development shows that at ages beyond 180 days, even more superior results may be expected from these mixtures.

- The SB fly ash, due to its self-cementitious property, contributes to strength development at earlier ages. However, at later ages low-lime T fly ash bearing mixes, due to higher pozzolanicity of this fly ash, gain strength at a higher rate.

- The strengths of A and SR fly ash concretes are about 50 % that of control one at 7 days age. The concretes containing these fly ashes acquire equivalent strength to control concrete at 90 days or even 180 days for smaller inclusion levels. It seems that, additional replacement method plays no important role in early strength development of A and SR bearing concretes.

- Same as corresponding mortar specimens, the lower strength of A and SR bearing concretes lies in higher water requirements of these mixtures for the same consistency. In addition to this fact, relatively lower strength values at later ages arise from the lower pozzolanicity of these fly ashes.

- The amorphous phase of A and SR fly ashes are identical. However, SR, in spite of having higher fineness, has little cementitious or pozzolanic contribution to the strength. This may be attributed to the lower free lime content of this material which results in decrease in the reactivity of fly ash.

- Although all of the fly ashes used in this study satisfy the PAI as specified by ASTM C 618 [32], their performance in mortar or concrete is quite different. It seems that PAI is not a reliable measure of the fly ash activity.

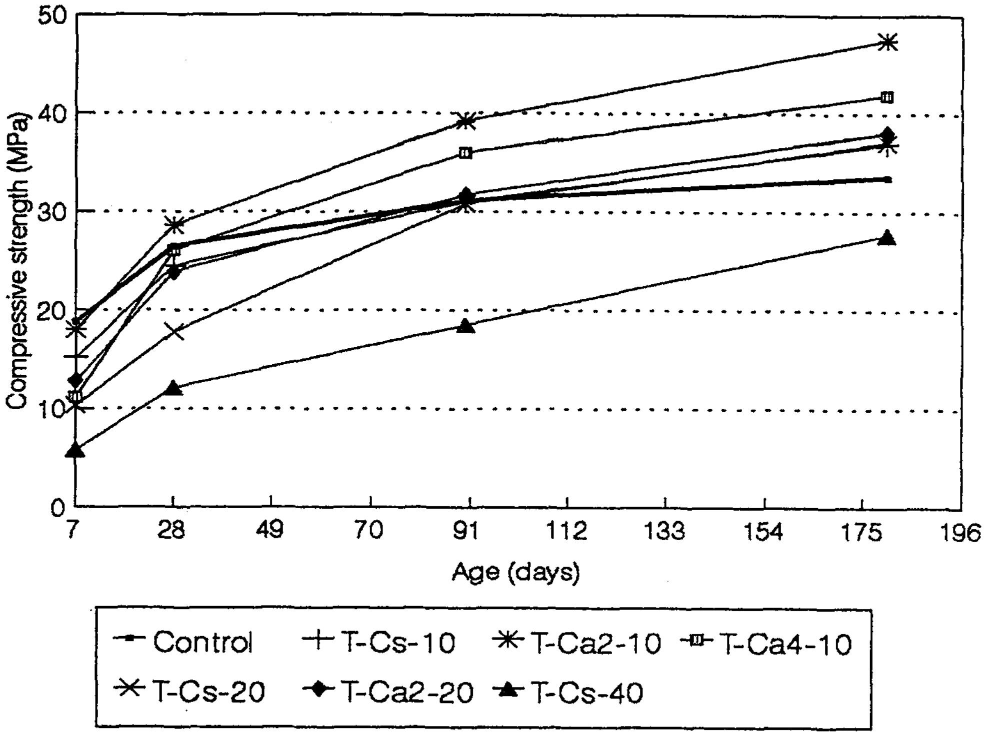


Figure 6.20. Effect of T Fly Ash on the Compressive Strength Development of Concrete

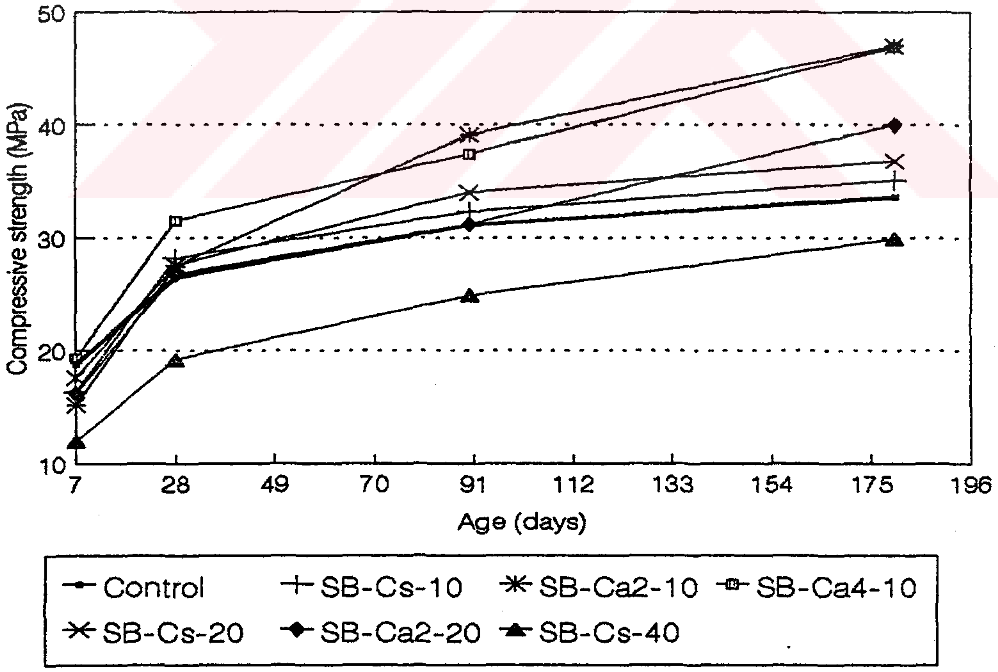


Figure 6.21. Effect of SB Fly Ash on the Compressive Strength Development of Concrete

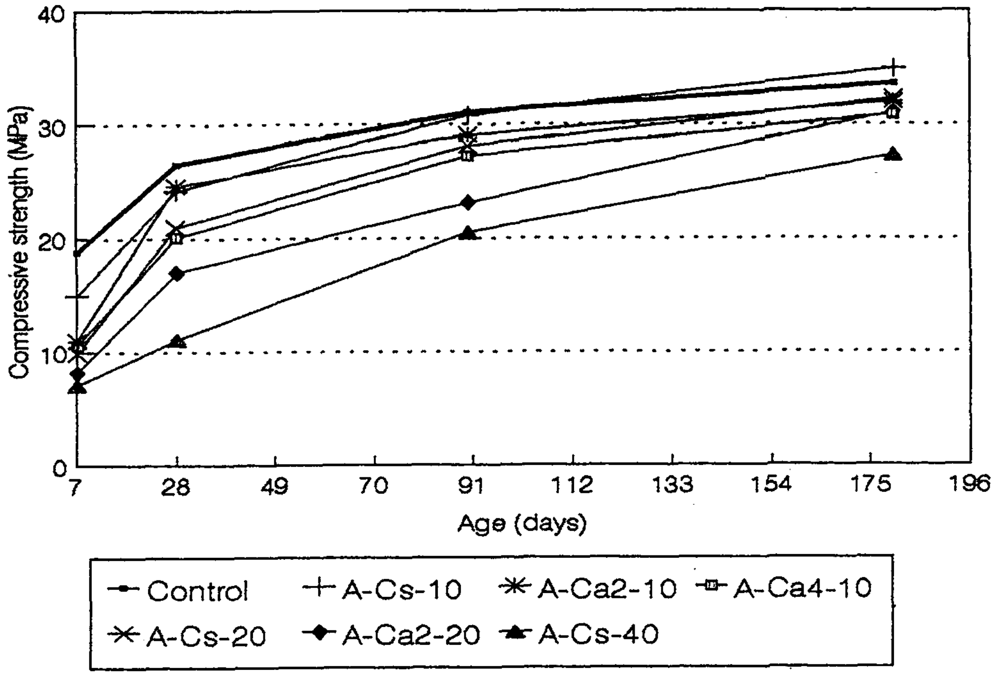


Figure 6.22. Effect of A Fly Ash on the Compressive Strength Development of Concrete

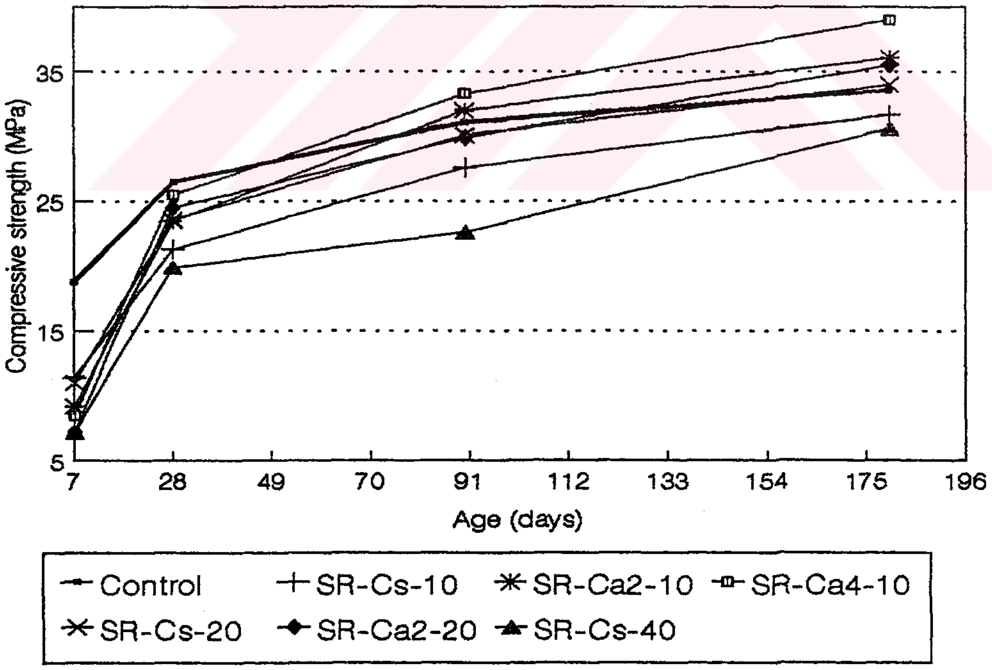


Figure 6.23. Effect of SR Fly Ash on the Compressive Strength Development of Concrete

- As it can be understood from Figure 6.24 to Figure 6.27, fly ashes having higher water requirement cause a considerable reduction in early and ultimate strength of the concrete for a fixed consistency with respect to control concrete. In this case, application of additional replacement method alone does not appear to be sufficient to increase the strength of fly ash concrete to the level of control concrete strength at early ages. Thus, other measures such as using water-reducer or plasticizer agents seem to be necessary to overcome this deficiency.

- Concrete compressive strength test results indicate that, an optimum replacement level exists for each fly ash. It is on the basis of trial batches and performance records that the optimum amount of fly ash for a given workability and strength can be determined.

6.6.2 Effects of Fly Ash on the Tensile Strength of Concrete

Although it is usually assumed in design that the concrete behavior is governed by its compressive strength, tensile strength is also a fundamental property of concrete. A knowledge of concrete tensile strength is necessary to predict the shear resistance of unreinforced sections and the resistance of concrete to shrinkage and temperature stresses. Tensile strength also has a significant influence on cracking of the concrete structures. Indeed, cracking can only occur after the tensile capability of concrete has been exhausted. Therefore, tensile strength of concrete is vital for appearance and durability of concrete structural members [15, 19].

It has been well established that, the splitting tensile test of the cylindrical specimens gives a more reasonable tensile strength estimation than the direct tensile test which underrates, or modulus of rapture test which overestimates the tensile strength of the concrete. The acceptance of the split tension test is based on the fact that the stress distribution is reasonably uniform along the vertical diameter of the cylinder, which has been shown to be the plane of principle tensile stress for about 80 % of its length [15, 188].

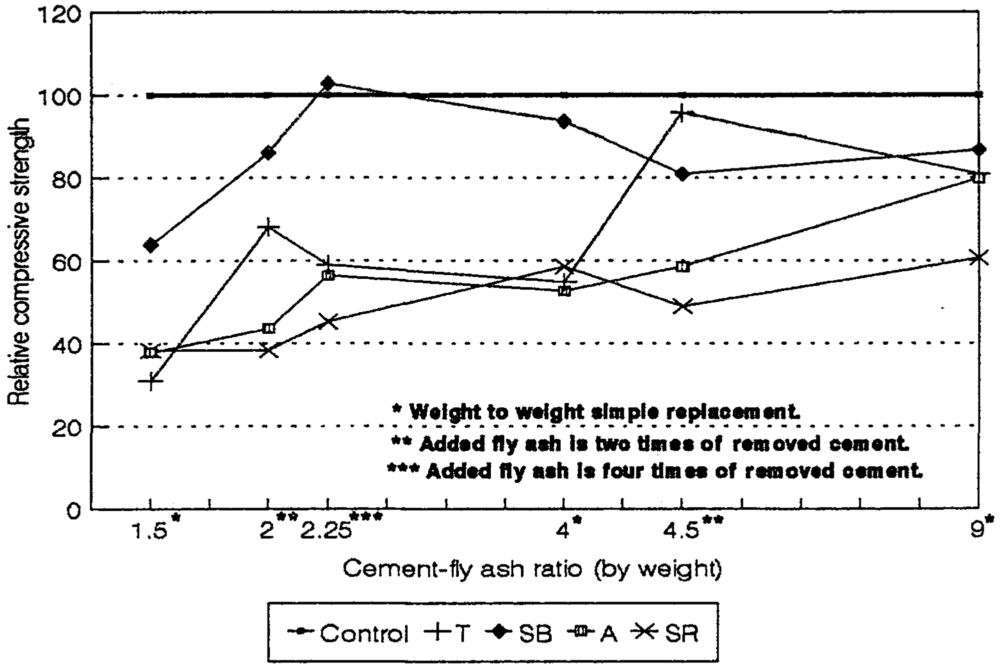


Figure 6.24. Relationship Between 7-D Concrete Compressive Strength-C/fa Ratio

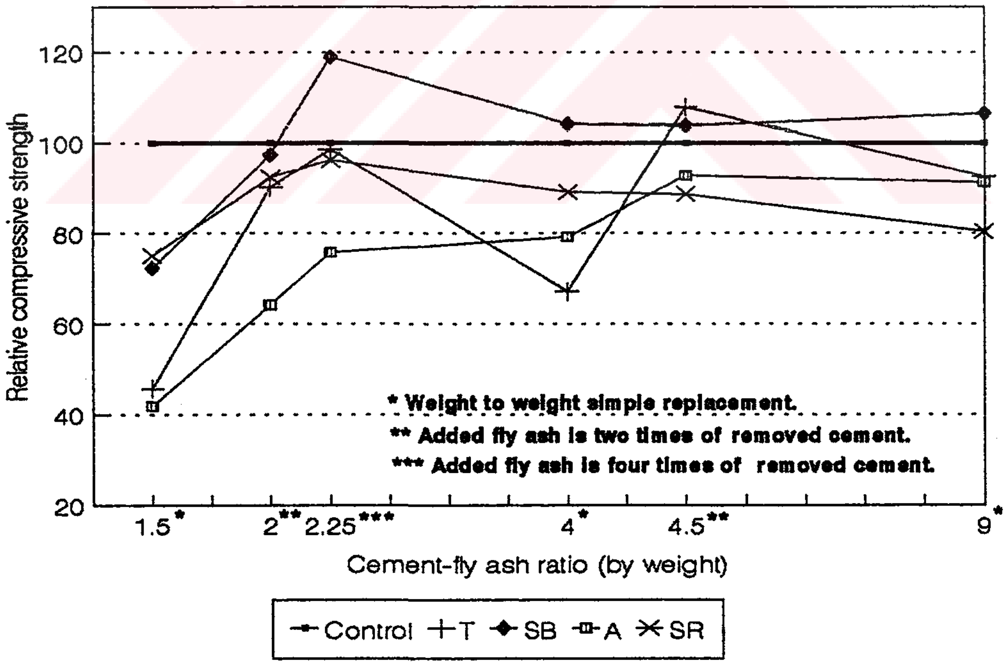


Figure 6.25. Relationship Between 28-D Concrete Compressive Strength-C/fa Ratio

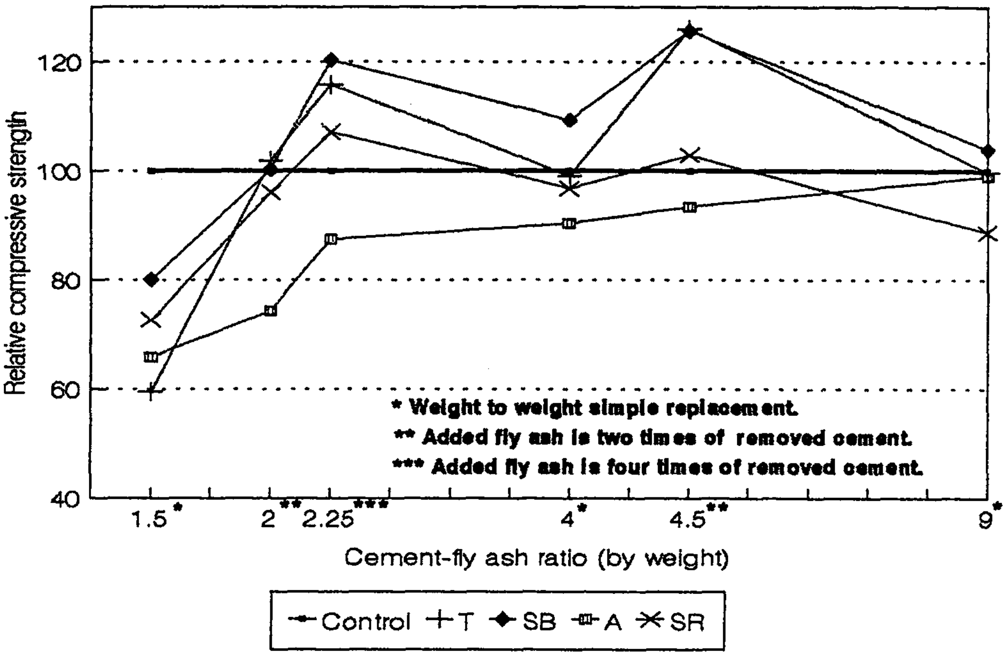


Figure 6.26. Relationship Between 90-D Concrete Compressive Strength-C/fa ratio

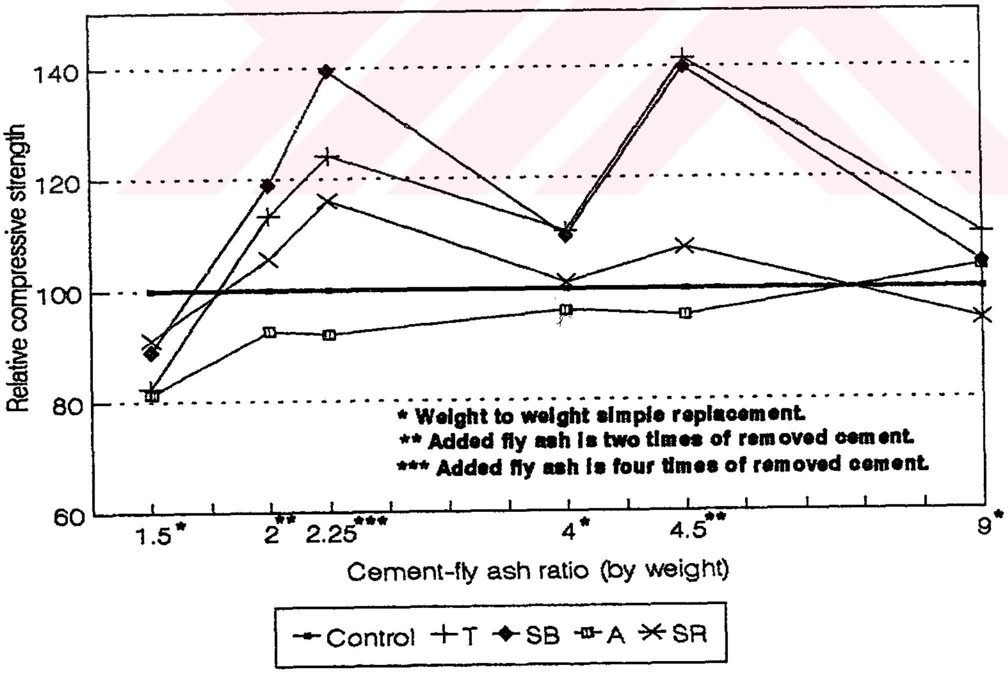


Figure 6.27. Relationship Between 180-D Concrete Compressive Strength-C/fa ratio

The split tension test was carried out on control and fly ash concretes at 28 days age. The results are given in Table 6.9. Each given value is the average of two tests. The obtained tensile strengths are also compared with the values estimated by the empirical relationship $\sigma_t = 0.56(\sigma_c)^{0.5}$ proposed by ACI Committee 318, Building Code [189]. In this expression, s_t is estimated tensile strength, and σ_c is the compressive strength of concrete in MPa.

As it is stated by several investigators [189, 190], the actual splitting tensile strength of both control and fly ash concretes are slightly lower than the estimated values. However, the difference is negligible. Thus, in estimating the tensile strength of concrete from its compressive strength, the normally accepted relationships can be applied to concrete with and without fly ash for the strength level employed in this study.

The interpretation of test results reveals that:

- Similar to what was observed with compressive strength, the 28-day split tensile strength of fly ash concretes was consistently lower than that of the control concrete. The only exceptions were, once again, T-C_{a2}-10 mixture and concrete made with SB fly ash at 10 and 20 % inclusion levels which show equivalent or superior tensile strengths than control concrete.

- 28-day split tensile strengths of fly ash concretes are nearly correlated with their compressive strengths at the same age. These results, once again, offer the validity for the specifications that accept the 28-day compressive strength as a standard strength for design.

6.7 Effect of Fly Ash on Modulus of Elasticity of Concrete

The modulus of elasticity of control and fly ash concretes determined in accordance with ASTM C 469 [183] at 28-days and 90 days age are given in Table 6.9.

Table 6.9. Effect of Fly Ash on Split Tensile Strength and Modulus of Elasticity of Concrete

	28-D Comp. Strength (MPa)	28-D Split Tensile Str.(MPa)		Modulus of Elasticity (GPa)	
		Average	Estimated	28-D	90-D
Control	26.5	2.7	2.9	25.7	28.2
T-C_s-10	24.5	2.7	2.8	26.0	27.1
T-C_{a2}-10	28.6	2.8	3.0	27.2	30.6
T-C_{a4}-10	26.1	2.6	2.9	24.9	29.0
T-C_s-20	17.8	1.9	2.4	20.1	22.0
T-C_{a2}-20	23.9	2.5	2.7	22.1	24.8
T-C_s-40	12.1	1.4	1.9	18.0	19.3
SB-C_s-10	28.2	2.9	3.0	25.6	30.1
SB-C_{a2}-10	27.5	2.8	2.9	26.6	30.3
SB-C_{a4}-10	31.5	3.0	3.1	28.2	31.0
SB-C_s-20	27.6	2.8	2.9	27.1	29.0
SB-C_{a2}-20	26.8	2.7	2.9	27.0	30.9
SB-C_s-40	19.2	2.0	2.5	25.0	28.6
A-C_s-10	24.2	2.4	2.8	26.3	27.0
A-C_{a2}-10	24.6	2.6	2.8	26.5	27.9
A-C_{a4}-10	20.1	2.2	2.5	23.0	24.1
A-C_s-20	21.0	2.2	2.6	21.8	22.0
A-C_{a2}-20	17.0	1.8	2.3	19.1	20.5
A-C_s-40	11.1	1.2	1.9	16.3	18.7
SR-C_s-10	21.3	2.1	2.6	22.9	23.9
SR-C_{a2}-10	23.5	2.2	2.7	23.3	24.1
SR-C_{a4}-10	25.5	2.4	2.8	23.8	24.3
SR-C_s-20	23.6	2.0	2.7	23.1	24.2
SR-C_{a2}-20	24.5	2.0	2.8	25.8	26.7
SR-C_s-40	19.9	1.6	2.5	18.1	19.7

The 28-day and 90-day Young's modulus of elasticity (E) values of SB bearing mixtures are larger than control concrete, whereas, SR fly ash, regardless of the substitution level, results in lower E values than control concrete. T fly ash causes a slight increase in modulus of elasticity at 10 % substitution level at both test ages. A fly ash at 10% inclusion level results in a slight increase in the modulus of elasticity at 28 days age, but there is a consequent reduction in it at 90 days age. Except for SB fly ash, all fly ashes result in a reduction in modulus of elasticity at 20 and 40 % substitution levels.

Although the modulus results obtained experimentally are in agreement with the modulus values calculated according to ACI Building Code 318 [189], the modulus value of the fly ash concretes at 10 and 20% replacement levels are somewhat higher than control concrete. The higher modulus is probably due to the densifying effect caused by the unhydrated fly ash particles acting as fine filler in the concrete.

The data provide no clear indication of significant effect of fly ashes on the modulus of elasticity. The effect, if any, may be masked by the variability of the test or by the conditions of the specimen, such as its moisture condition at the time of test.

6.8 Effect of Fly Ash on the Durability of PC-fa Systems

6.8.1 Effects of Fly Ash on the Sulfate-Resistance of PC-fa Mortars

One of the major durability problems encountered in cement systems is the damage caused by the reaction of sulfate ions and some hydration products of cement, such as CH, $C_4A\bar{S}H_{12}$ and C-A-H. These reactions result in the formation of ettringite ($C_6A\bar{S}H_{32}$) or gypsum ($C\bar{S}$), which occupy larger volume than the original reactants, and lead to excessive expansion, cracking and strength loss of the cement system.

In this study, the potential sulfate expansion of control and fly ash mortars was determined as described in ASTM C 452 [177]. Same as mortar strength test, the specimens of this experiment were prepared by replacing 10, 20, and 40 % (by weight) of cement with varying amounts of fly ash and six different sets of specimens were tested. The SO_3 content of the control specimen was adjusted to be 7%, as stated in ASTM C 452 [177], by adding a predetermined amount of a commercially available gypsum containing 51.77 % analytical SO_3. For fly ash mortars the SO_3 content of the mixes were kept constant. The length of the specimens were measured immediately after demolding at 24 hrs as initial length of the specimens. The 14-day potential sulfate expansion values of control specimen and of fly ash mortars were recorded. The measurements were continued until 180 days. The results are presented in Table 6.10 and graphically shown in Figures 6.28 to 6.31.

It was found out that the low-lime fly ash T, in all inclusion levels, and the three high-lime fly ashes only at 10% substitution level satisfy the 0.045 % expansion limit given in ASTM C 150 [163]. Except for T fly ash at 40 % substitution level, all of the fly ash mortars, regardless of the type of fly ash, showed higher expansion values than control specimen. However, at later ages, T bearing mortars showed equivalent or even lower expansion than control specimen. The lowest expansion values were recorded in T-M_S-40 mortars in which 40 % of the cement is simply replaced by T fly ash. In high-lime fly ash mortars the expansion was directly increased by the level of fly ash substitution in the mix. The largest expansion values were recorded for A fly ash bearing systems.

Dunstan's resistance factor (R) of the fly ashes were calculated as -0.19, 4.63, 7.64, and 1.94, respectively . It was noticed that the sulfate resistance of the fly ash mortars is in a good correlation with R-factor. However, Dunstan's conclusion stating that [152], when $R < 0.75$ fly ash greatly improves the sulfate resistance, when $0.75 < R < 1.5$ it results in a moderate improvement, when $1.5 < R < 3.0$ no appreciable change occurs, and finally when $R > 3.0$ sulfate resistance reduces, is not reliable for the fly ashes examined in this study.

Table 6.10. Potential Sulfate Expansion of Control and Fly Ash Mortars Determined According to ASTM C 452 [177]

Specimen	Expansion (mm/mm)			
	14-D	28-D	90-D	180-D
Control	2.96×10^{-4}	3.52×10^{-4}	8.89×10^{-4}	1.56×10^{-3}
T-M_s-10	3.01×10^{-4}	3.58×10^{-4}	8.56×10^{-4}	1.03×10^{-3}
T-M_{a2}-10	3.15×10^{-4}	4.84×10^{-4}	7.57×10^{-4}	7.74×10^{-4}
T-M_{a4}-10	3.30×10^{-4}	6.34×10^{-4}	9.48×10^{-4}	9.73×10^{-4}
T-M_s-20	3.16×10^{-4}	4.92×10^{-4}	8.75×10^{-4}	8.85×10^{-4}
T-M_{a2}-20	3.48×10^{-4}	7.1×10^{-4}	1.03×10^{-3}	1.09×10^{-3}
T-M_s-40	2.81×10^{-4}	3.41×10^{-4}	3.16×10^{-4}	8.64×10^{-4}
SB-M_s-10	3.95×10^{-4}	5.79×10^{-4}	9.65×10^{-4}	1.75×10^{-3}
SB-M_{a2}-10	8.09×10^{-4}	9.53×10^{-4}	1.64×10^{-3}	2.62×10^{-3}
SB-M_{a4}-10	6.37×10^{-4}	7.68×10^{-4}	1.33×10^{-3}	2.31×10^{-3}
SB-M_s-20	6.23×10^{-4}	7.6×10^{-4}	1.32×10^{-3}	2.35×10^{-3}
SB-M_{a2}-20	1.15×10^{-3}	1.45×10^{-3}	2.48×10^{-3}	4.04×10^{-3}
SB-M_s-40	1.23×10^{-3}	1.62×10^{-3}	2.8×10^{-3}	4.18×10^{-3}
A-M_s-10	3.51×10^{-4}	5.85×10^{-4}	1.21×10^{-3}	2.76×10^{-3}
A-M_{a2}-10	6.61×10^{-4}	8.48×10^{-4}	2.34×10^{-3}	failed
A-M_{a4}-10	1.08×10^{-3}	1.55×10^{-3}	5.14×10^{-3}	failed
A-M_s-20	1.19×10^{-3}	2.56×10^{-3}	5.7×10^{-3}	failed
A-M_{a2}-20	1.32×10^{-4}	1.57×10^{-4}	8.99×10^{-4}	failed
A-M_s-40	2.43×10^{-3}	3.02×10^{-3}	failed	failed
SR-M_s-10	3.98×10^{-4}	5.67×10^{-4}	8.73×10^{-4}	1.32×10^{-3}
SR-M_{a2}-10	6.22×10^{-4}	8.02×10^{-4}	1.19×10^{-3}	1.29×10^{-3}
SR-M_{a4}-10	5.55×10^{-4}	7.53×10^{-4}	8.39×10^{-4}	1.18×10^{-3}
SR-M_s-20	5.34×10^{-4}	6.12×10^{-4}	1.12×10^{-3}	1.17×10^{-3}
SR-M_{a2}-20	4.62×10^{-4}	6.13×10^{-4}	1.10×10^{-3}	1.14×10^{-3}
SR-M_s-40	5.73×10^{-4}	7.15×10^{-4}	9.67×10^{-4}	1.13×10^{-3}

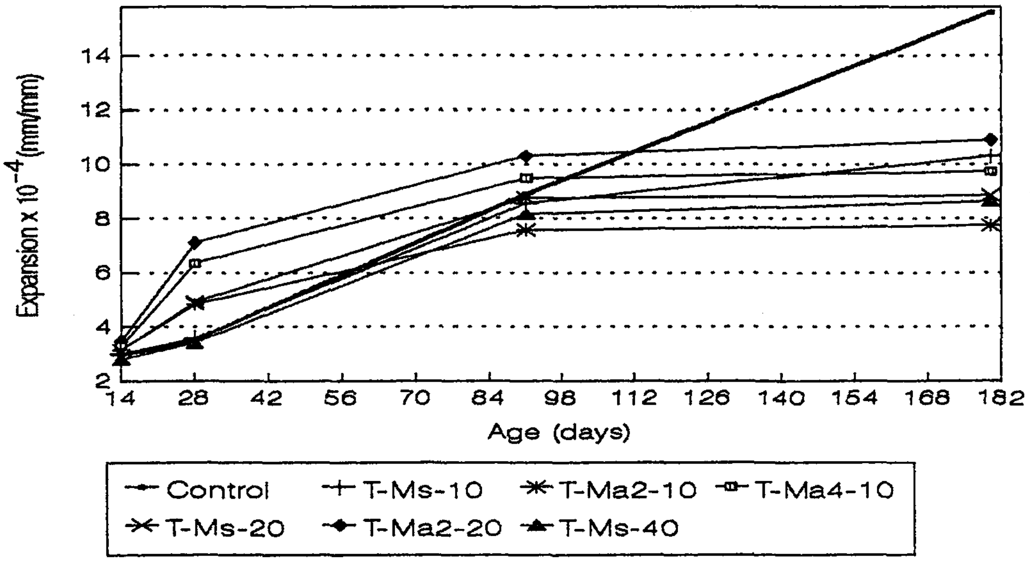


Figure 6.28. Potential Sulfate Expansion of T Fly Ash Bearing Mortars and Control Specimen

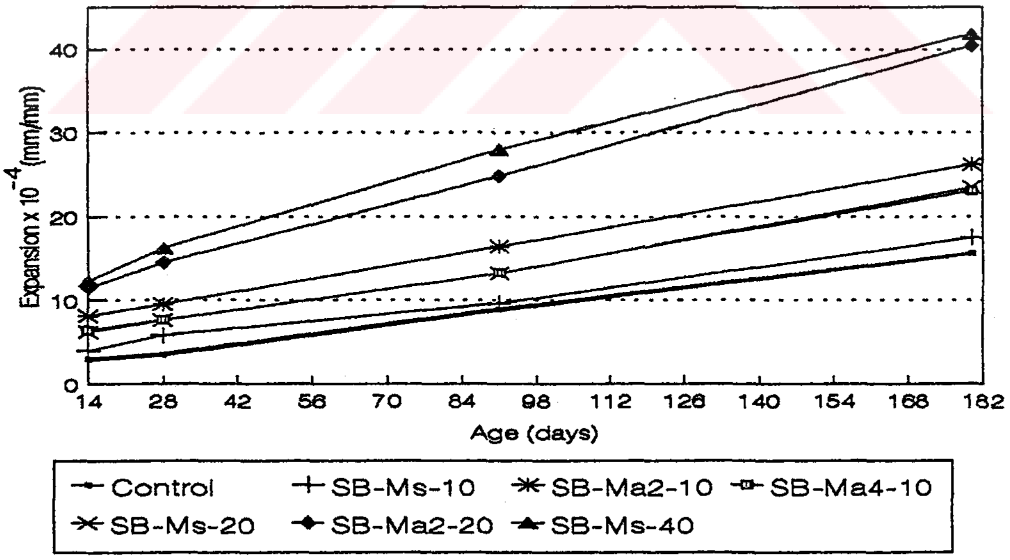


Figure 6.29. Potential Sulfate Expansion of SB Fly Ash Bearing Mortars and Control Specimen

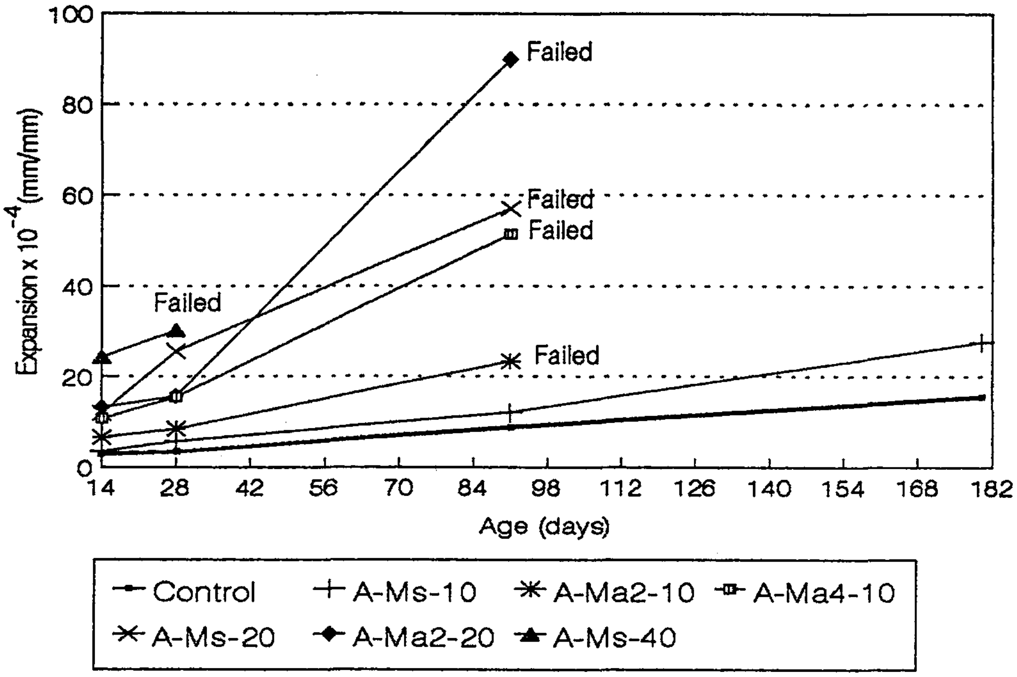


Figure 6.30. Potential Sulfate Expansion of A Fly Ash Bearing Mortars and Control Specimen

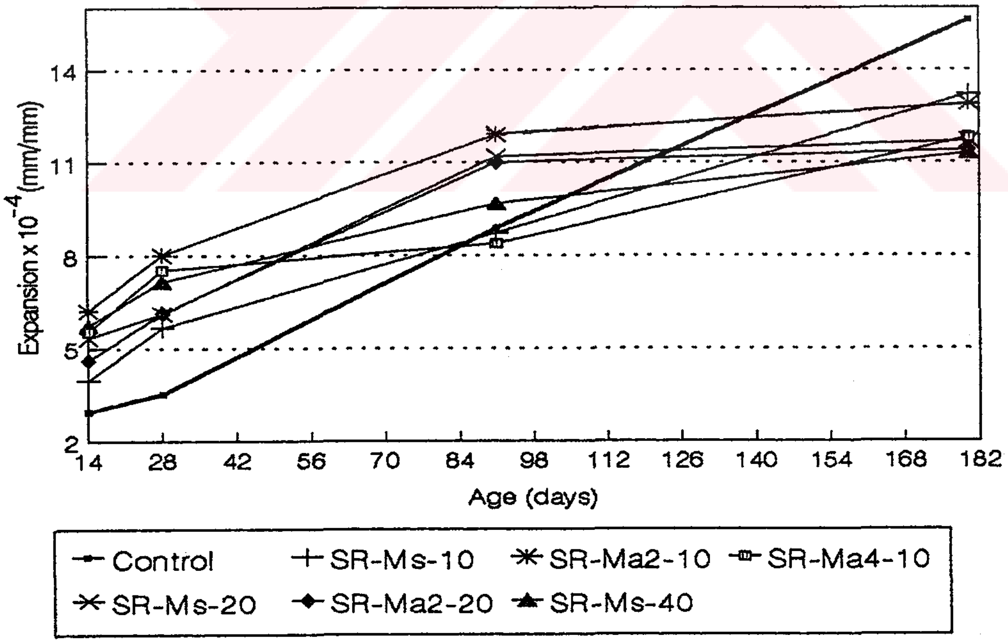


Figure 6.31. Potential Sulfate Expansion of SR Fly Ash Bearing Mortars and Control Specimen

A major criticism against using the R-factor of fly ash, which is an index of sulfate resistance of fly ash bearing systems is due to the failure of this factor not taking the alumina content of fly ash into account; particularly, the state of reactivity of alumina bearing phases present in fly ash. However, it is known that, when the reactive alumina content of the fly ash is high, the hydration of PC-fa system leads to the formation of considerable amounts of the compounds which are directly responsible for sulfate attack. Thus, such a system would not be expected to show any improvement in sulfate resistance, regardless of the CaO and Fe_2O_3 contents of the fly ash.

Thus, it seems that instead of using Dunstan's empirical R-factor to estimate the performance of the fly ash bearing binders in sulfate environment, it is more rational to consider those constituents of the ash which are relevant with sulfate resistance. These constituents of the fly ashes as well as the approximate estimate of their glass composition derived from their X-ray diffractograms (Figure 5.1) are presented in Table 6.11.

As it can be seen from Table 6.11, all three high-lime fly ashes used contain comparatively large amounts of free lime, anhydrite, and reactive alumina. The free lime forms by the decomposition of calcite in the coal during burning, the anhydrite forms by the reaction between the SO_2 evolved from pyrite and some of the free lime, and the reactive alumina is arisen from the decomposition of clay impurities in the coal during burning at about 1000°C, which is the combustion temperature of the power plants from which the fly ashes were obtained. The reactive alumina contents of the fly ashes are determined by treating the fly ash in HCl. This component is readily acid-soluble and the difference between Al_2O_3 contents of the raw and acid treated fly ashes gives the amount of reactive alumina in the mix [151].

Table 6.11. Chemical and Mineralogical Composition of Fly Ashes Relevant to Sulfate Resistance

Fly Ash	% CaO	% Al_2O_3	% SO_3	1 % Free CaO	2 % Reactive Al_2O_3	3 % Anhydrite	(1+2-3)	Comp. of Glass	Main Relev. Crystalline Minerals
T	3.1	23.0	0.5	0.9	n.d	-	-	A-S	Mullite
SB	25.4	22.3	4.8	9.8	5.3	7.4	7.7	C-A-S	$C_4A_3\bar{S}$,$C\bar{S}$
A	47.0	12.8	6.2	18.5	3.5	12.2	9.8	C-A-S	Mullite,CaO $C_4A_3\bar{S}$,$C\bar{S}$ CaO, C_3A
SR	19.9	9.1	11.6	5.5	4.0	9.3	0.2	C-A-S	$C_4A_3\bar{S}$,$C\bar{S}$ CaO

For glass type estimation, the location of the diffused band on the fly ash X-ray diffractograms were taken into consideration. Assuming that the glass with mainly aluminosilicate composition (A-S) is indicated by the presence of diffused band between 21-25 degrees 2θ; the glass with calcium aluminosilicate composition (C-A-S) is indicated by the diffused band between 31 to 34 degrees 2θ. Besides, fly ashes with less than 10 % total CaO mostly contain A-S glass, whereas those with more than 20 % CaO contain mainly C-A-S type glass [147].

The main alumina bearing crystalline phase in T fly ash is mullite (A_3S_2) which furnishes no reactive alumina for monosulfate or C-A-H formation. Besides, this fly ash contains less than 1 % free lime, so the CH content of the binder arisen from the presence of free lime in fly ash is negligible. In this way, the higher sulfate resistance of PC-T system may be attributed to two effects; the dilution effect (i.e., a reduction in C_3A content of the blended cement) and the interaction effect (i.e., formation of hydration products that are more stable to the sulfate environment).

Among the high-lime fly ashes, SR is the one having the highest sulfate resistance. This may be attributed to two facts: a) Its free lime content is about 1/2 and 1/3 of the other two high-lime fly ashes, thus, it supplies lower CH in the hydrated binder system b) As the anhydrite content of this fly ash is relatively high, the probability of ettringite formation during hydration, which is stable in sulfate environment, is larger than the formation of monosulfate and calcium aluminate hydrate.

Fly ash A, with the highest (free lime plus reactive alumina minus anhydrite) content, has the lowest sulfate resistance. Fly ash A bearing mortars at 40 % inclusion level disintegrated after about 60 days exposure to sulfate environment. The same behavior was also observed for 10 and 20 % substitution levels at later ages. The other reason for higher sulfate sensitivity of PC-A system may be arisen from the lower dilution effect of this fly ash. As it can be seen from X-ray diffractogram of fly ash A, presented in Figure 5.1, the fly ash introduces some C_3A to the system by itself.

Regarding the (free lime + reactive alumina-anhydrite) contents of the fly ashes and the potential sulfate expansion of PC-fa systems, it, once again, becomes evident that the value of it (free lime + reactive alumina - anhydrite) gives only a rough idea about the sulfate resistance of the system, and the test results are not in a good correlation with this value. Consequently, to have a more realistic idea in this subject, it is necessary to examine the hydration products and the interaction between different compounds in PC-fa system rather than taking the chemistry of fly ash alone into account for predicting the effectiveness of fly ash to improve the resistance of the system to sulfate attack.

6.8.2 Effects of Fly Ash on the Drying Shrinkage of PC-fa Mortars

The drying shrinkage tests were performed on mortar bars in accordance with ASTM C 311 [166] and ASTM C 157 [191]. The test specimens were moist cured for 7 days as stated in ASTM C 311, as well as 91 days in lime saturated water at room temperature. Following these periods, the specimens were transferred to drying room at 55 ± 5% relative humidity. In addition to length measurement, after 28-day air storage as required in ASTM C 311 [166], drying shrinkage data were obtained after 7, 14, 56, 90, and 180-day air storage. The results presented in Table 6.11 and graphically shown in Figures 6.32 and 6.33 are the average values of three specimens.

The drying shrinkage strains of control specimens and T bearing mortars following 7 days of water storage are comparable after 14-day air drying and on wards. In the same curing condition, SB fly ash mortars show somewhat higher drying shrinkage strains at early ages and comparable results with control specimen at ages beyond 28 days. The reduction in drying shrinkage of T and SB bearing mortars may be arisen from the formation of a finer paste structure which restricts the loss of pore water from the paste [45].

A and SR bearing mortars exhibited larger drying shrinkage values than control specimen at all ages for the first curing condition (i.e., 7 days moist curing). This may be attributed to their higher water requirement to produce 100-115 % flow.

The drying shrinkage of control mortar following 91 days of water storage is low at early ages of drying; however, it increases rapidly with time and approaches the shrinkage strain values of corresponding 7-day water-cured specimens. On the other hand, fly ash mortars stored in water for 91 days exhibit significantly lower drying shrinkage strains compared to corresponding specimens moist cured for 7 days. This, once again, shows the importance of longer curing period of fly ash bearing binder systems to improve their various properties.

Table 6.12. Drying Shrinkage of Mortar Bars After 7 and 91-day Initial Moist Curing

Curing Conditions	Type of Fly Ash	Drying Shrinkage Strain x 10^{-4} (mm/mm)					
		7-D	14-D	28-D	56-D	90-D	180-D
Air-dried at room temperature and 50 % RH, after 7 days of water curing	Control	2.66	3.81	4.83	5.95	6.01	9.24
	T	3.05	3.95	4.68	5.61	6.06	8.97
	SB	3.41	4.28	5.09	5.83	6.1	9.23
	A	5.01	6.20	7.07	7.95	8.36	12.2
	SR	6.43	7.63	8.82	9.95	10.4	14.2
Air-dried at room temperature and 50 % RH, after 91 days of water curing	Control	1.60	2.33	4.60	5.93	6.08	8.37
	T	1.59	2.0	2.75	4.21	4.71	6.21
	SB	1.72	2.23	2.71	2.99	3.38	7.1
	A	2.81	3.19	3.7	4.01	5.07	9.15
	SR	2.44	3.12	3.97	4.78	5.72	9.68

Under both curing conditions and almost at all ages of drying, T fly ash bearing mortars exhibit the lowest drying shrinkage strains. This effect is more pronounced for this fly ash, as well as the other three fly ashes following the 91-day moist curing. Although the drying shrinkage of A and SR bearing mortars reduces significantly by prolonged curing period, even after 91 days of moist curing, their drying shrinkage values approach or even exceed those of control specimen at later ages.

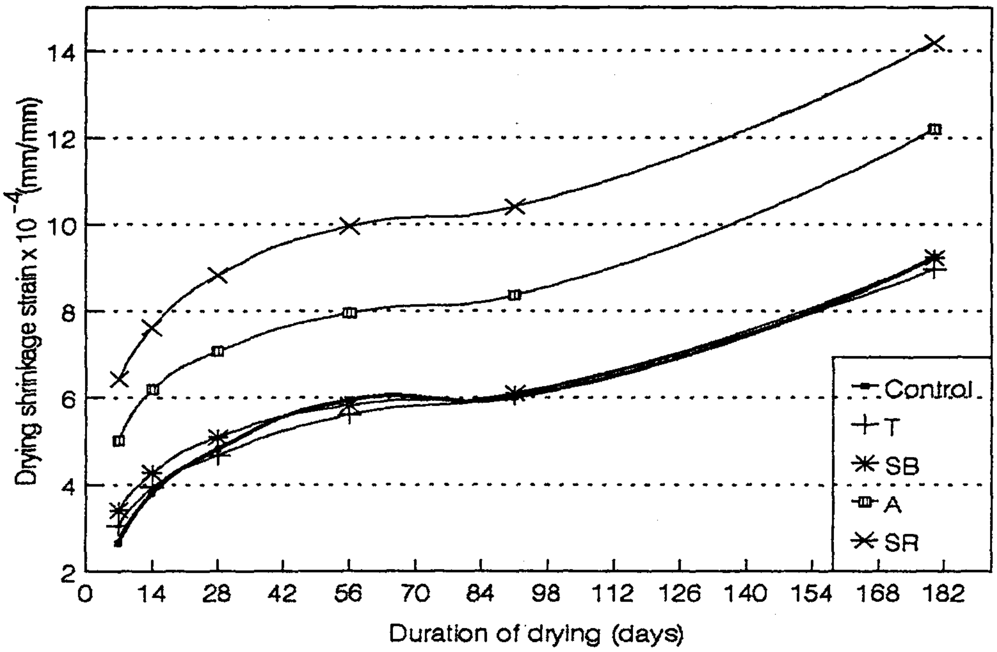


Figure 6.32. Drying Shrinkage Versus Age of Drying of Mortars After 7 Days of Initial Moist Curing

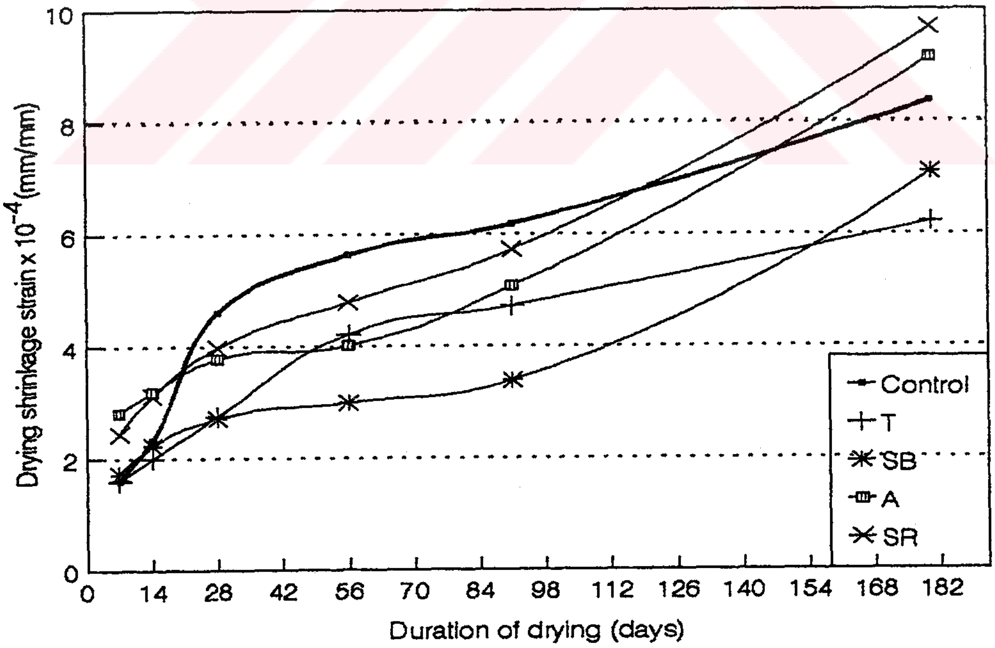


Figure 6.33. Drying Shrinkage Versus Age of Drying of Mortars After 91 Days of Initial Moist Curing

6.8.3 Effect of Fly Ash on the Carbonation of PC-fa Concretes

One of the main causes of concrete reinforcement corrosion is the loss of the efficiency of the concrete cover which has been known to protect the steel bars by keeping them in a passive state. The breakdown of the passivity may occur by carbonation which is the reaction of calcium hydroxide, and to a less extent, the other hydration products of cement with CO_2 from the atmosphere. As a result, the pH level of the concrete adjacent to the steel reduces to values which can no longer maintain passivation.

Aggressive environments in which concrete structures are subjected to hot weather have been found to cause higher rate of carbonation. It has further been observed that hot climate accompanied by the ambient relative humidity varying between 50 % to 75 %, as in some regions of the Middle East, encourages substantial increase in carbonation in comparison with wet and cool climate [192].

On the other hand, the increasingly common practice of including fly ash and other pozzolanic materials in concrete has prompted investigators to study the influence of such materials on the carbonation durability of concrete. It has been demonstrated that, fly ash concrete carbonates faster than plain concrete even though their strengths are similar [141]. This point, however, is controversial, and other investigators have found no indication of increased carbonation in equal strength concretes with and without fly ash [10, 75].

In this study, same as concrete strength specimens, six different concrete mixtures for each fly ash were prepared and cast in 150 x 300 mm cylindrical molds. The specimens were initially moist cured for 7 and 91 days before transferring to the following ambient conditions:

a) Carbonation chamber where a 4 % concentration of CO_2 at room temperature and 55 ± 5 % relative humidity were maintained.

b) Indoor laboratory condition where specimens were exposed to atmospheric CO_2 concentration (0.03 %) at room temperature and 55 ± 5 % relative humidity.

The amunt of neutralization of concrete was determined after four, eight, and twenty weeks of exposure by treating the freshly broken surface of the specimens with phenolphthalein, the free $Ca(OH)_2$ was colored pink, while the carbonated (neutralized) portion was uncolored. The mean depth of carbonation at the cross section was calculated by the following equation:

Depth of carbonation (mm) = $(\sqrt{A} - \sqrt{a})/2$
Where, A = area of cross section (mm^2)
a = area of colored portion (mm^2)

For the specimens exposed to atmospheric CO_2 concentration, not surprisingly, no depth of neutralization was observed even after 90 days of exposure. Because, carbonation in this condition occurs at a very low rate and becomes noticeable after several months or even years.

The test results of specimens exposed to accelerated carbonation testing are given in Table 6.13. The results reveal that, regardless of the type of fly ash, fly ashes reduce the rate of carbonation of concrete at 10 % inclusion level. This may be attributed to the physical pore refining effect of fly ashes at this substitution level, which reduces the size of the pores in the mix and, hence, results in the reduction of carbonation rate.

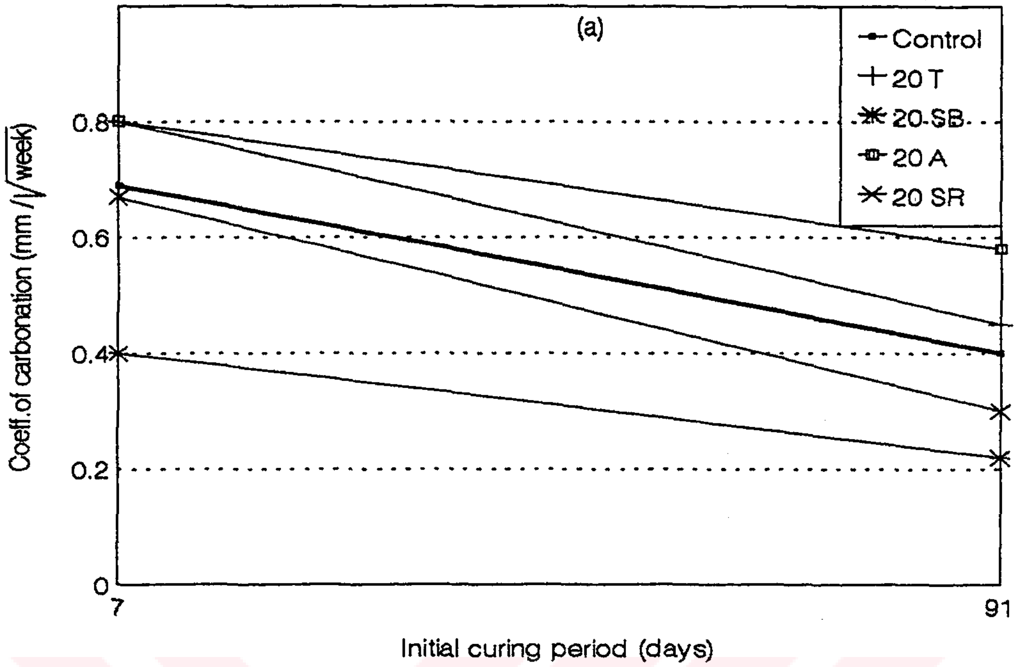
At 20 % inclusion level, fly ash substitution has no significant effect on the depth of carbonation, particularly for those specimens which were moist cured for 91 days before exposing to CO_2. However, at 40 % inclusion level, all of the fly ash concretes showed a considerable increase in carbonation depth. The effect of initial curing period in water on the carbonation coefficient, which is defined as depth of carbonation in mm divided by square root of exposure duration in weeks [140], is shown in Figure 6.34.

Table 6.13. Depth of Carbonation of Control and Fly Ash Concretes at Various Times in 4 % CO_2 Cabinet

Type of Mix	7 Days Initial Moist Curing Neutralization Depth(mm) Duration in Carbonation			Average Coeff.of Carbonation mm /√week	91 Days Initial Moist Curing Neutralization Depth(mm) Duration in Carbonation			Average Coeff.of Carbonation mm / √week
	4 weeks	8 weeks	20 weeks		4 weeks	8 weeks	20 weeks	
Control	-	2	3	0.69	-	1	2	0.40
T-C_s-10	-	-	-	-	-	-	-	-
T-C_{a2}-10	-	-	-	-	-	-	-	-
T-C_{a4}-10	-	-	2	0.45	-	-	1	0.22
T-C_s-20	-	2	4	0.80	-	-	2	0.45
T-C_{a2}-20	-	-	3	0.67	-	-	-	-
T-C_s-40	8	12	19	4.16	5	7	11	2.48
SB-C_s-10	-	-	-	-	-	-	-	-
SB-C_{a2}-10	-	-	-	-	-	-	-	-
SB-C_{a4}-10	-	-	-	-	-	-	-	-
SB-C_s-20	-	-	-	-	-	-	-	-
SB-C_{a2}-20	-	1	2	0.40	-	-	1	0.22
SB-C_s-40	4	6	12	2.27	2	3	5	1.06
A-C_s-10	-	-	-	-	-	-	-	-
A-C_{a2}-10	-	-	-	-	-	-	-	-
A-C_{a4}-10	-	2	4	0.80	-	2	3	0.69
A-C_s-20	-	2	4	0.80	-	2	2	0.58
A-C_{a2}-20	2	4	5	1.17	-	2	3	0.69
A-C_s-40	9	13	20	4.52	3	5	8	1.67
SR-C_s-10	-	-	-	-	-	-	-	-
SR-C_{a2}-10	-	-	-	-	-	-	-	-
SR-C_{a4}-10	-	-	2	0.45	-	-	-	-
SR-C_s-20	-	-	3	0.67	-	-	-	0.3
SR-C_{a2}-20	-	-	2	0.45	-	-	-	-
SR-C_s-40	5	7	12	2.55	2	3.5	5.5	1.06

It becomes evident from the Figure 6.34 that, the carbonation coefficient of fly ash concretes is more affected by initial curing period than that of control concrete. This is more pronounced for mixes in which fly ash has a 40% substitution level. The effect of initial curing period on the depth of carbonation of control and 40% fly ash concrete mixes are graphically represented in Figure 6.35.

Figure 6.36 shows the effect of fly ash replacement level on the carbonation coefficient of concrete. At lower substitution levels, fly ashes result in reduction or a negligible increase in carbonation coefficient. However, at 40% inclusion level, a sharp increase in carbonation coefficient is noticeable. This may be attributed to higher water/binder ratio, or consequently lower strength of these mixes with respect to control specimen.



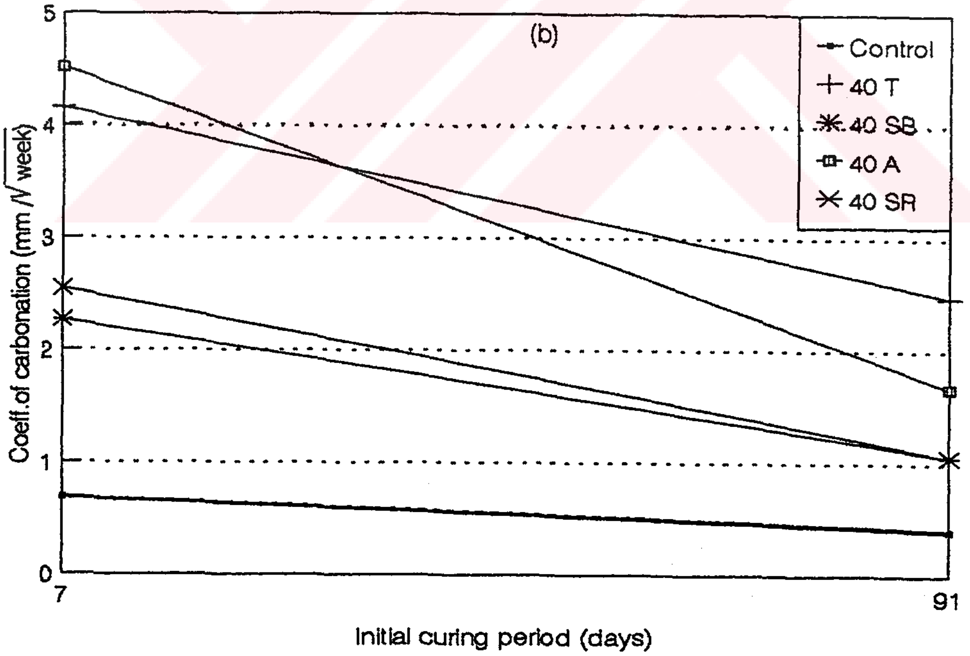


Figure 6.34. Effect of Initial Curing Period on the Carbonation Coefficient of Control and Fly Ash Concretes. a) 20 % Inclusion Level b) 40 % Inclusion Level

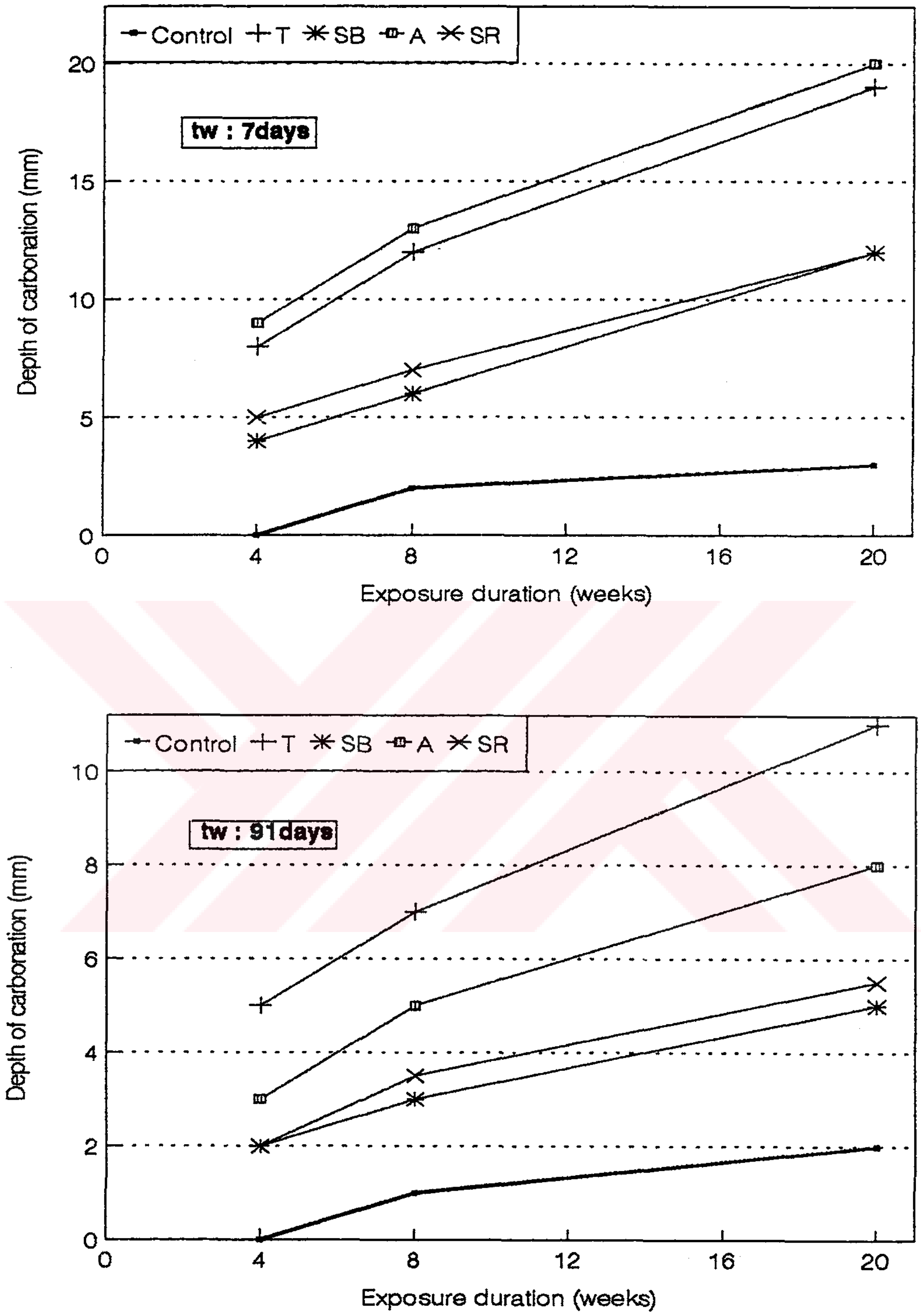
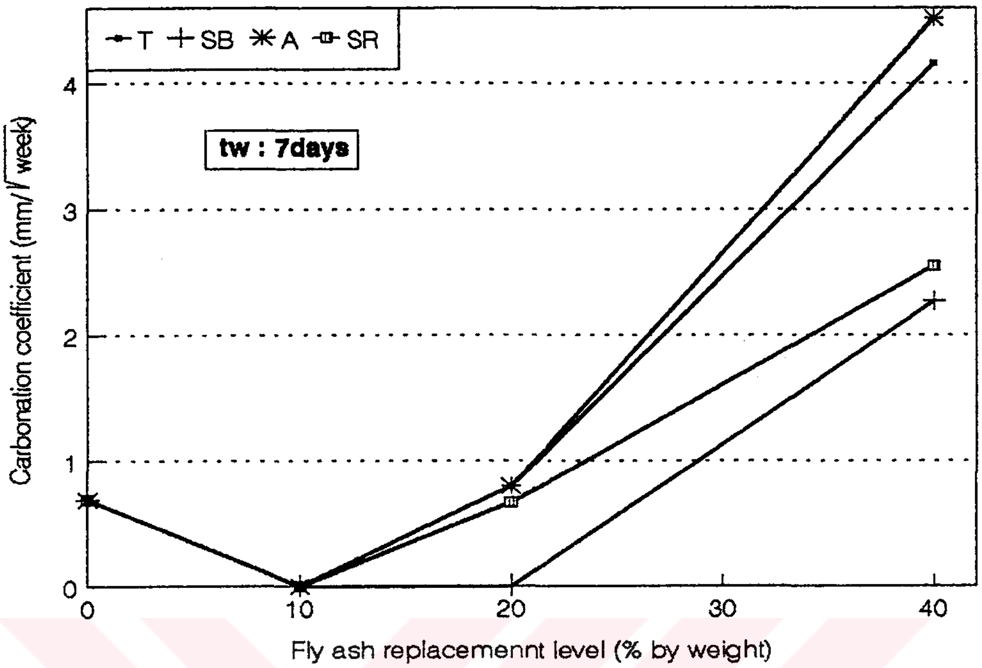


Figure 6.35. Relationship Between the Exposure Duration and the Depth of Carbonation in Accelerated Test (tw: Initial curing Period in Water)



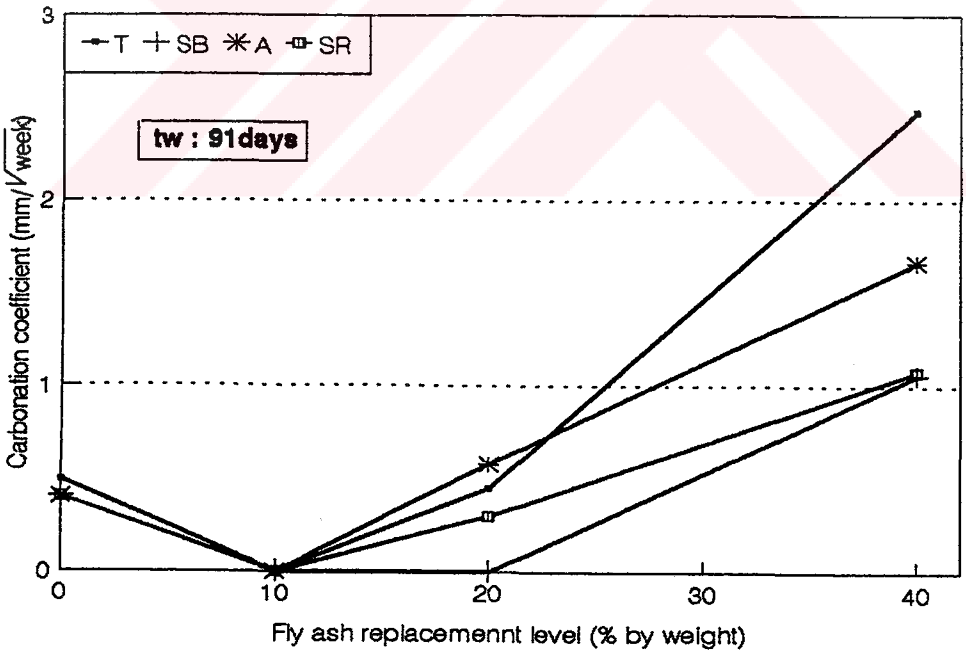


Figure 6.36. Relationship Between Fly Ash Replacement Level and the Carbonation Coefficient (tw: Initial Curing Period in Water)

CHAPTER VII

CONCLUSIONS

The suitability of fly ash as a pozzolanic ingredient for use in concrete was first demonstrated in 1937 [1]. During the next twenty years, considerable pioneering and development work in this field was conducted to show the usefulness of low-lime fly ash, which was the only available type at that time, in concrete production. This fly ash is obtained traditionally from bituminous coals. The oil crisis of the 1970s led to the greater use of coal for the production of electricity, particularly low-rank one to fire power plants. These are lignitic or subbituminous coals containing calcium compounds in their incombustible fraction resulting in the formation of high-lime fly ashes. These fly ashes have attracted the attention of researchers recently; and their behavior in portland cement-fly ash systems is relatively less known due to their wide variety.

Since 1970s direct economic factors coupled with an increasing awareness of the need to protect the environment and conserve energy have combined to focus attention on the utilization of fly ash in concrete. A formidable amount of research and field experience aimed at understanding the properties of PC-fa systems have been undertaken. It is now known that fly ash inclusion in cementitious systems affects almost all of their aspects. These effects are dependent on the mineralogical, physical, and chemical characteristics of the fly ash, as well as on the properties of cement, presence of other admixtures, curing condition, etc.

Although fly ash supplies throughout the world have increased and several countries have produced standard specifications for its use in concrete, the consumption of fly ash in cement and concrete industry is not as common as it should be. This is due to the non uniformity in the quality of fly ash produced in recent years resulting from the changes in the combustion systems of power plants and use of a large range of different types of coals. Thus, the recognition of the differences between the mineralogical composition and physical characteristics of various fly ashes necessitates further research to distinguish the ways in which they influence concrete properties.

Regarding the fact that most of the fly ashes produced in Turkey are high-lime fly ashes, in this investigation three high-lime fly ashes, Soma-B (SB), Afşin-Elbistan (A), and Seyitömer (SR), and a low-lime fly ash, Tunçbilek (T) have been used. The production of these fly ashes accounts for about 40% of the total fly ash production in Turkey. The effects of the type and amount of fly ashes on various properties of cement paste, mortar, and concrete were studied.

For the particular fly ashes used and test conditions employed in this study, the following conclusions appear to be justified:

1. The type of fly ash to substitute a part of cement weight-to-weight affects the water requirement of the paste for normal consistency:

a. Regardless of the fly ash type, the increase in water requirement of fly ash pastes for normal consistency is not significant for 10 % inclusion level.

b. The chemical compositions of fly ashes do not affect the water requirement for normal consistency. Due to the spherical shape of majority of the particles, it is generally stated that low lime fly ashes reduce the water demand. However, in this study, the low-lime fly ash, T, required more water than the control. Similarly, two of the high-lime fly ashes, A and SR, increased the water content for normal consistency. The other high-lime fly ash, SB, resulted in a slight water reduction. It seems that the water requirement of the fly ash pastes for normal consistency is closely related to a multiple factor (Blaine specific surface x loss on ignition of the fly ash). In this regard, SR fly ash, having the highest multiple factor, shows the highest water requirement, and SB fly ash with the lowest multiple factor among the fly ashes requires the lowest amount of water for normal consistency.

2. All of the fly ashes at 10 % weight-to-weight substitution level result in a slight reduction or a negligible increase in setting time. However, parallel with the water requirement of the pastes for normal consistency, at higher inclusion levels T, SB, and SR fly ashes result in increased setting time.

In contrast to the other three fly ashes, A accelerates setting. The set acceleration is more pronounced at 40 % inclusion level. This may be due to the larger free lime, and anhydrite contents of this fly ash which immediately transform to calcium hydroxide and gypsum, respectively or interact with reactive alumina to form calcium aluminate sulfates such as ettringite.

$$6Ca\,(OH)_2 + 3SO_4^{2-} + 2Al\,(OH)_3 \Rightarrow \text{Ettringite} \tag{7.1}$$

The initial setting times of PC-fa pastes conform with the ASTM standard limitations (45 minutes). However, the final setting time of T and SR fly ash bearing pastes at 20 and 40 % substitution levels and SB containing paste at 40 % inclusion level exceed the 375 minutes which is the maximum limitation for final setting time in ASTM C 150 standard.

3. The X-ray diffractograms of the hydrated fly ashes reveal that the hydration products of the fly ashes are mainly same, with slight differences between their types and rate of formation. Free lime content of the fly ash has a marked effect on the hydration rate of the fly ash.

4. The heat generated with the hydration and pozzolanic reactions involved in PC-fa systems is significantly affected by the mineralogical composition and fineness of the fly ash.

a. T fly ash reduces the heat of hydration proportionally with its substitution level. This reduction diminishes with age by the additional heat generated through pozzolanic reaction. However, regardless of the substitution level, T fly ash results in about 10 % reduction in heat of hydration even after 90 days.

b. SB fly ash has no significant effect on heat of hydration. At 10 % replacement level, it results in an equivalent heat of hydration to control specimen, but at 20 and 40 % substitution level, it causes a slight reduction in heat of hydration with respect to control specimen at all ages.

c. A and SR fly ashes at 10 % substitution level result in a slight increase in 7-day heat of hydration and a negligible reduction in 28 day heat of hydration. The amount of heat evolution in A bearing pastes is more than control specimen at higher substitution levels. However, the increment in generated heat diminishes with age. The hydration of lime-containing compounds, such as C_3A, CS and gehlenite (C_2AS), in these fly ashes seem to be responsible for the higher heat of hydration at early ages.

5. The water requirement of PC-fa mortar, for a known flow, is taken as one of the common measures of the suitability of the fly ash as a cement- replacing material. Direct weight-to-weight replacement of cement with all fly ashes increases the water requirement of the mortars. This can be attributed to the lower densities of the fly ash with respect to cement which results in an increase in the volume of total solid material in the mix. The water requirement of T fly ash (1.99 g/cm^3 density and 3370 cm^2/g specific surface) and SB fly ash (2.42 g/cm^3 and 2530 cm^2/g) bearing mortars are comparable with the maximum acceptable value given in ASTM C 618 standard. The water demand of A fly ash (2.63 g/cm^3 and 3210 cm^2/g) SR fly ash (2.46 g/cm^3 and 9.700 cm^2/g) bearing mortars exceed the ASTM standard limitation due to either higher free lime and anhydrite content or the extremely higher fineness of the ash which provides larger surface area to be wetted by water.

In the case of concrete specimens, simple replacement of cement with fly ash at small and medium levels causes a slight reduction or a slight increase in water demand. However, at 40 % simple replacement level, or when additional replacement methods are applied to replace a part of cement and a part of sand with fly ash, again due to a relative increase in the volume of solids in the concrete mix, its water demand for a constant slump increases, but the change in water/binder ratio is not significant even in these mixtures.

6. Fly ash substitution has no significant effect on the air content of non-air entrained fresh concrete mixtures. It seems that although the size of larger pores and capillaries reduce through physical densification or pore refinement, total porosity in fresh concrete remains nearly unchanged due to the decrease in spacing of the pores or the presence of porous particles, such as unburned carbon in fly ash itself.

7. The strength of fly ash bearing systems is controlled by the type of the fly ash as follows:

a. T bearing mortars show lower strength than control mortar at early ages proportional with the level of substitution. However, the reduction in strength diminishes with age, and becomes negligible after 28 days and 90 days for 10 % and 20 % replacement levels, respectively, through pozzolanic reactions. At 40 % substitution level, the strength of resultant mortar is about 80 % of control specimen strength even after 180-day curing. Substitution of higher amount of fly ash than removed cement in the mix causes a further reduction in strength at early ages.

b. 10 % SB bearing mortars give superior strength than control specimen as early as 7-day curing. At 20 % substitution level, SB results in about 10 % strength reduction at 28 days age compared to control specimen. Replacing 40 % of cement with SB causes a further reduction in the strength, particularly at early periods. However, the strength of this mortar which is about 60 % of control specimen at 7 days rapidly increases with time and reaches to about 90 % of control specimen after 180-day curing. Additional replacement of cement with SB has no significant effect on the strength development of resultant mortars. The results indicate that, a significant cement saving potential exists for this fly ash at substitution levels lower than 40 %.

c. A and SR fly ashes result in strength reduction parallel to the increase in water requirement for a constant flow. The strength reduction in A and SR bearing mortars may be further attributed to their lower pozzolanic activity index. The largest strength reduction is caused by SR fly ash which has the highest water requirement and lowest activity index among the fly ashes.

8. The concrete strength test results are not in a good correlation with mortar strength test results. However, the same trend of strength development, particularly at early periods of curing, can be observed between mortar and concrete specimens.

a. The amorphous phases of SB and SR fly ashes are identical. However, SR, in spite of having higher fineness, has little contribution to the strength. This can be attributed to the lower free lime content of this fly ash which results in decreasing the activity of the fly ash, as well as to the higher water requirement of SR bearing concretes for a constant slump.

b. Although all of the fly ashes satisfy the Pozzolanic Activity Index (PAI) with cement requirement, as specified in ASTM C 618, their performance in cement systems is quite different. The results obtained in this investigation are in conformance with the previous arguments on the doubtfulness of the PAI as a measure of the reactivity of fly ash.

c. Compared to control specimens, higher water requirement of the fly ash bearing mixes causes a considerable reduction in early and ultimate strength, particularly at higher inclusion levels. In such a case, using additional replacement method alone does not appear to be sufficient to provide an equivalent strength development at early ages.

d. Test results indicate that, an optimum replacement level exists for each fly ash. It is on the basis of trial batches and performance records that the optimum amount of fly ash for a given workability and strength can be determined. Besides, it is necessary to exercise greater control and longer curing period when fly ash is used in concrete.

e. Similar to compressive strength test results, with a few exceptions, the 28-day split tensile strength of fly ash concretes are somewhat lower than control concrete. Besides, there is a good correlation between the compressive and tensile strengths of the specimens at the same age. The test results offer the validity for the specifications that accept the 28-day compressive strength as the standard value for design.

9. The results of elastic modulus determination tests provide no significant effect of fly ash on the concrete modulus of elasticity. The effect, if any, may be masked by the variability of the test or by the conditions of the specimens, such as moisture condition at the time of test. The highest reduction in elastic moduli of fly ash concretes is recorded at 40 % fly ash substitution inclusion level.

10. The following conclusion can be arrived at by the results of potential sulfate expansion tests:

a. The sulfate resistance of PC-fa mortars is affected by the chemical composition of the fly ash. However, the chemistry of fly ash alone is not sufficient to predict the effect of fly ash on the sulfate resistance of the fly ash bearing system. In this regard, Dunstan's sulfate resistance factor, which is based on lime and iron oxide content of the fly ash, is not in a good correlation with the sulfate resistance of the fly ash bearing systems.

b. The type of hydration products and cement-fly ash interaction products control the behavior of the system in sulfate environment. Thus, the sulfate resistance of the PC-fa system is directly related to C_3A content of the cement and (free lime + reactive alumina - anhydrite) content of the fly ash. These may interact and hydrate to form constituents susceptible to sulfate attack.

c. Although fly ash inclusion increases the potential sulfate expansion of the mortars, regardless of the type of fly ash and its substitution level, the low-lime fly ash at all inclusion levels and three high-lime fly ashes at 10 % substitution level satisfy the 0.045 % expansion limit required in ASTM C 150.

d. Except for A fly ash bearing mortars, the rate of expansion in sulfate environment reduces with age in PC-fa mortars, whereas expansion continues at about the same rate in control mortar.

11. The main factors affecting the drying shrinkage of cementitious systems are the fractional volume of the paste and water content of the mix. The addition of fly ash to mortar increases both of these factors, thus, increases the drying shrinkage of the mix.

a. In addition to chemical composition, specific gravity, water requirement of the fly ash and the duration of initial moist curing period play an important role in drying shrinkage of PC-fa system.

b. The drying shrinkages of 7-day moist cured fly ash mortars are larger than that of corresponding control specimen at early ages. However, T and SB bearing mortars show equivalent or even lower drying shrinkage strains beyond 28 days of drying compared to that of control specimen.

c. The drying shrinkage of control mortar following 91 days of water storage is low at early ages; however, it increases rapidly with time and approaches the shrinkage strain values of corresponding 7-day water cured control bars. On the other hand, fly ash mortars wet cured for 91 days exhibit significantly lower drying shrinkage compared to corresponding specimens stored in water for 7 days. This shows the significance of longer curing period for PC-fa systems to improve their various properties.

12. Except for 10 % substitution level in which all fly ashes result in lower rate of carbonation, due to their physical pore refining effect, fly ash concrete carbonates faster than plain concrete even though their strengths are similar. This effect is more pronounced at 40% fly ash replacement level in which the strength of the fly ash concrete is also lower than the corresponding control concrete.

As in the case of drying shrinkage strain, depth of carbonation of fly ash concrete is largely dependent on the initial curing period. In fly ash concrete, the depth of carbonation of specimens initially moist cured for 91 days is about half or even one-third of the corresponding specimens cured initially in water for 7 days.

13. In the light of foregoing determinations it is possible to state that, T and SB - bearing cementitious systems give comparable or sometimes even superior results to corresponding control specimens. While in SB fly ash these positive effects can be detected both at early and later ages, in T fly ash the effects take place mainly at later ages. However, A and SR fly ashes affect most of the properties of the cementitious systems adversely. Besides, in order to improve various durability aspects, such as reducing shrinkage and carbonation, the necessity of applying longer curing periods to PC-fa systems as compared to neat portland cement system is observed.

CHAPTER VIII

RECOMMENDATIONS

The world wide increasing trend of fly ash production results in various undesirable ecological and economical problems. In Turkey the 1993 fly ash production is expected to be about 13 x 10^6 tons. However, the current use of fly ash as a construction material is negligibly small. This may be arisen from the lack of sufficient information about the characteristics of Turkish fly ashes and their behavior in concrete. Although since 1960s various researches have been carried out in various governmental institutes of Turkey, such as State Water Works (DSİ) and State Highway Department (TCK) and several universities including METU, on the use of fly ash in cement and concrete industry, still there are certain unresolved problems related to this by-product. Therefore, the following are recommended for future research on this subject:

1. The first recommended step is to establish a fly ash quality assurance program for each fly ash source. The quality history should be aimed at understanding the fly ash conformation to specification requirements and checking its uniformity during a known period of time. The quality control program should include the study of coal type, degree of its pulverization, operation system and amount of load on power plant, combustion temperature, collection system, etc. Besides, the critical characteristics of fly ash for the intended use and the general requirements of specifications for its use in concrete need to be included in testing program.

2. A complete revision of the existing TS 639-75 standard seems to be necessary. For many of the chemical and physical tests of fly ash contained in this standard, the precision and bias estimates should be established. Besides, the minimum requirement of major oxides

(SiO_2+Al_2O_3+Fe_2O_3) specified in TS 639 seems to be insufficient to evaluate the fly ash performance in concrete.

3. The use of fly ash in concrete together with other pozzolanic admixtures, such as silica fume, as well as some chemical additives such as superplasticisers may diminish the disadvantage of the low early strength of fly ash concrete and requires further investigation.

4. Freezing-thawing resistance of air-entrained and non-air entrained fly ash concrete, as well as other long term durability characteristics of fly ash bearing systems cured in various conditions should be studied.

5. The use of fly ash in "classified form" by dividing it into smaller size fractions is reported to improve its performance in concrete through increasing the glass content and the proportions of spherical particles in the fly ash. Such a research may be carried out for fly ashes produced in Turkey.

6. The exact mechanism of grain-refining effect of the fly ash is not clear yet. Further investigation on the changes in the microstructure and composition of PC-fa paste and aggregate interface region is also beneficial .

7. The use of fly ash in "high-strength" concrete and "high volume fly ash" concrete has attracted the attention of researchers in recent years. Further studies in these subjects may be helpful to create new fly ash utilization fields in Turkish concrete industry.

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