EFFECTIVENESS OF SET ACCELERATING ADMIXTURES WITH DIFFERENT CEMENT TYPES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
THE MIDDLE EAST TECHNICAL UNIVERSITY

BY

DİDEM TUĞBA ÜSTÜNER

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CEMENT ENGINEERING

SEPTEMBER 2009

Approval of the thesis:

EFFECTIVENESS OF SET ACCELERATING ADMIXTURES WITH DIFFERENT CEMENT TYPES

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ABSTRACT

EFFECTIVENESS OF SET ACCELERATING ADMIXTURES WITH DIFFERENT CEMENT TYPES

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September 2009, 114 pages

Accelerating and mineral admixtures, one of the major ingredients in concrete, are primarily used to modify the properties of both fresh and hardened concrete.

Within the scope of this thesis, there were four types of cements having almost identical fineness. The mixes were prepared by using natural pozzolan, blast furnace slag and limestone conforming to TS EN 197-1 and two types of accelerating admixtures, namely triethanolamine (TEA) and calcium formate (CF).

The effect of set accelerating admixtures with different cement types on the setting time, water demand and compressive strength has been analyzed by an experimental study in accordance with relevant ASTM standards.

Finally, it has been observed that the amount of the accelerating admixtures used is suitable because of their effects on the water demand, setting and strength. Due to the density difference of mineral admixtures and clinker, the normal consistency and 110% flow water content should be considered on a volumetric basis. The effectiveness of the accelerating admixtures on the normal consistency water, 110% flow water content and setting time depends on the type and amount of mineral admixtures. The increase caused by CF in the normal consistency and 110% flow water content is higher than that by TEA. The accelerating effect of TEA and CF on the setting times is more significant for cements incorporating 6% mineral admixture. The effects of accelerating admixtures on the compressive strength change with specimen age, type and amount of mineral admixtures. Generally, for all cement types, early age compressive strengths increase with the increase of TEA, however long term strengths increase by increasing CF.

Keywords: Calcium formate, triethanolamine, mineral admixtures, normal consistency, setting time, compressive strength

ÖZ

FARKLI ÇİMENTO TİPLERİ İLE PRİZ HIZLANDIRICI KATKILARIN ETKİNLİLİĞİ

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Eylül 2009, 114 sayfa

Betondaki ana bileşenlerden biri olan priz hızlandırıcı ve mineral katkılar, esasen hem taze hem de sertleşmiş betonun özelliklerini düzeltmek için kullanılırlar.

Bu tezin kapsamında hemen hemen aynı inceliğe sahip 4 çeşit çimento bulunmaktadır. Karışımlar, TS EN 197-1 standardına uygun olarak doğal pozzolan, yüksek fırın cürufu ve kireçtaşı ile iki çeşit priz hızlandırıcı katkı, trietanolamin (TEA) ve kalsiyum format (CF), kullanılarak hazırlanmıştır.

Priz hızlandırıcı katkılar ile farklı tip çimentoların priz süresine, su ihtiyacına ve basınç dayanımına olan etkisi ilgili ASTM standardlarına uygun olarak deneysel bir çalışma ile araştırılmıştır.

Sonuç olarak, su ihtiyacına, prize ve dayanıma olan etkileri nedeniyle deneyde kullanılan priz hızlandırıcı katkıların miktarlarının uygun olduğu gözlenmiştir. Mineral katkılar ile klinkerin yoğunluk farkından dolayı normal kıvam ve %110 akma için su gereksiniminde volümetrik bazda düşünülmelidir. Normal kıvam ve %110 akma için su ihtiyacı ile priz süresinde, priz hızlandırıcı katkıların etkinliği mineral katkının türüne ve miktarına bağlıdır. Normal kıvam ve %110 akma için su ihtiyacında CF'nin yol açtığı artış, TEA'ya göre daha fazladır. Priz sürelerinde TEA ve CF'nin hızlandırıcı etkisi %6 mineral katkı içeren çimentolarda daha belirgindir. Priz hızlandırıcı katkıların basınç dayanımına etkisi ise numune yaşı, mineral katkıların türü ve miktarı ile değişiklik göstermektedir. Genellikle tüm çimento tipleri için erken dayanım TEA’nın artışı ile artarken uzun dönem dayanımı ise CF’nin artışı ile artmaktadır.

Anahtar Kelimeler: Kalsiyum format, trietanolamin, mineral katkılar, normal kıvam, priz süresi, basınç dayanımı

ACKNOWLEDGEMENTS

In this section of the study, I owe my thanks to the people who never withheld their help from me.

It is my obligation to mention those people by their names here since they were continuously eager to help and inform me about the experimental studies throughout and wherever I had difficulty.

I’m grateful to the staff of Material Construction Laboratory for their contribution and support in the completion of experimental study.

Moreover, I would like to express my sincere thanks to the authorities of Set Ankara Cement Factory, Bolu Cement Factory and Sika Group for providing materials for the experimental study.

Finally, I would like to thank my advisor Prof. Dr. Mustafa Tokyay for his help and advice throughout the study.

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ABBREVIATIONS

Common Name	***Chemical Formula***	***Cement Chemistry***
Lime	CaO	C
Silica	SiO_2	S
Alumina	Al_2O_3	A
Iron	Fe_2O_3	F
Magnesia	MgO	M
Sodium Oxide	Na_2O	N
Potassium Oxide	K_2O	K
Water	H_2O	H
Sulfur trioxide	SO_3	$\bar{S}$
Tricalcium silicate	Ca_3SiO_5 or $3CaO \cdot SiO_2$	C_3S
Dicalcium silicate	Ca_2SiO_4 or $2CaO \cdot SiO_2$	C_2S
Tricalcium aluminate	$Ca_3Al_2O_6$ or $3CaO \cdot Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$Ca_4Al_2Fe_2O_{10}$ or $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF
Gypsum	$CaSO_4.2\ H_2O$	$C\bar{S}H_2$
Ettringite	$6CaO.\ Al_2O_3.\ 3SO_3.\ 32\ H_2O$	$C_6A\bar{S}_3H_{32}$ / Aft
Monosulfate Aluminate Hydrate	$4CaO.\ Al_2O_3.3SO_3.12\ H_2O$	$C_4A\bar{S}_3H_{12}$/AFm
Triethanolamine	$N(C_2H_4OH_3)_3$	TEA

CHAPTER 1

INTRODUCTION

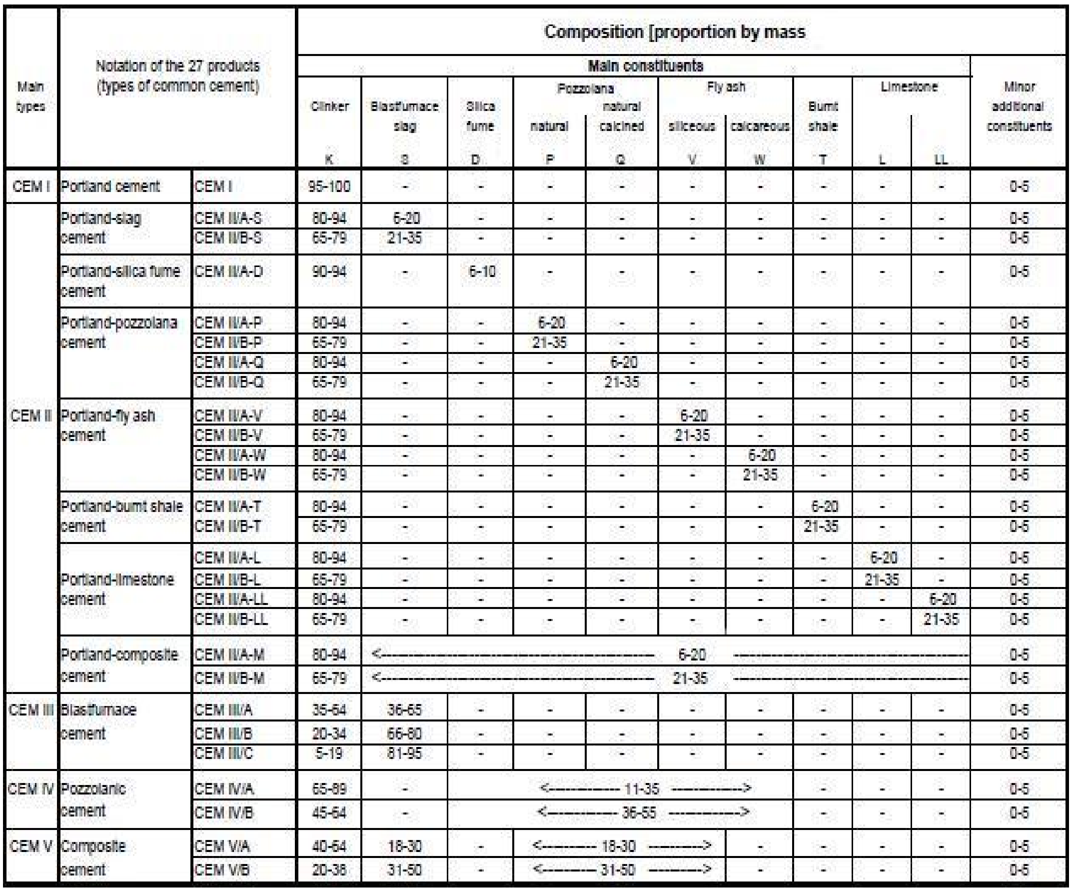
1.1 General Information

Accelerating agents increase the rate of setting and hardening of cementitious systems. They are used to speed up the concrete construction by making earlier finishing of the surfaces, earlier form removal and earlier development of strength possible. Accelerating agents are beneficial in cold weather concreting, also. They partially overcome the slow rate of hydration due to low temperature and shorten the period of protection of concrete against freezing damage.

Accelerating agents are usually grouped into two as (1) soluble inorganic salts and (2) soluble organic compounds. Although most inorganic salts like sodium carbonate, sodium aluminate, calcium fluoroaluminate and calcium sulfoaluminate have an accelerating effect on the setting and hardening of the concrete, calcium salts are the most effective. Among them calcium chloride had been the most commonly used accelerating agent due to its relatively low cost and ability to give more acceleration for a given amount of use. However, recently the use of calcium chloride in concrete has been restricted due to its corrosive effect on reinforcement (1). A variety of organic compounds are being used as accelerators or secondary accelerating constituents of various other chemical admixtures. Triethanolamine, calcium formate and calcium acetate are the common commercial organic accelerating agents (2). Besides these main groups of accelerating agents, various finely ground mineral substances such as calcium or magnesium carbonates, silicate minerals and silicas which are used to seed the concrete are reported to increase the rate of hydration and thus decrease the setting times (1). The accelerating agents belonging to the first group increase the rate of hydration of tricalcium silicate whereas the organic accelerators act by increasing the rate of hydration of tricalcium aluminate (1, 2).

Most of the research done so far on the use of accelerating agents in cementitious systems was carried out using Portland cements. However, due to ecological, economical and technical reasons, nowadays cements containing considerable amounts of mineral admixtures such as natural and artificial pozzolans, ground granulated blast furnace slag, limestone, etc. are being manufactured. According to TS EN 197-1 “Cement- Part 1: Compositions and Conformity Criteria for Common Cements”, there are five categories of cements as Portland Cements (CEM I), Portland Composite Cements (CEM II), Blast Furnace Slag Cement (CEM III), Pozzolanic Cements (CEM VI) and Composite Cements (CEM V). In all of these standard types of cements varying amounts of mineral admixtures are present either as one of the major constituents besides the Portland cement clinker or as a minor additional constituent [(3)]. TS-EN 197-1 cement types and their ingredient types and proportions are given in Table 1.1.

Table 1.1: Cement Types [(3)]



Main types	Notation of the 27 products (types of common cement)		Composition [proportion by mass										
			Main constituents										Minor additional constituents
			Clinker	Blastfurnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		
						natural	natural calcined	siliceous	calcareous				
			K	S	D	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21-35	-	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-burnt shale cement	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	-	0-5
	Portland-limestone cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	21-35	0-5
	Portland-composite cement	CEM II/A-M	80-94	<------------------ 6-20 ------------------									0-5
		CEM II/B-M	65-79	<------------------ 21-35 ------------------									0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement	CEM IV/A	65-89	-	<---------- 11-35 ---------->					-	-	-	0-5
		CEM IV/B	45-64	-	<---------- 36-55 ---------->					-	-	-	0-5
CEM V	Composite cement	CEM V/A	40-64	18-30	-	<-------- 18-30 -------->			-	-	-	-	0-5
		CEM V/B	20-38	31-50	-	<-------- 31-50 -------->			-	-	-	-	0-5

1.2 Object and Scope

The object of this thesis is to determine the effectiveness of accelerating agents when used with TS EN 197-1 CEM II cements. For this purpose, two soluble organic compounds namely triethanolamine (TEA) and calcium formate (CF) were used in three different amounts together with the laboratory-prepared Portland-pozzolan, Portland-slag and Portland-limestone cements which contained 6, 20 and 35% (by weight) mineral admixtures. TEA was used at dosages of 0.25, 0.50 and 1.00 % and CF was used as 1.00, 2.00 and 3.00% by weight of the cement. Normal consistency and setting time measurements of the cement pastes and flow and compressive strength determinations of standard mortars were carried out in the experimental part of the investigation. The results were analyzed and compared both within the mineral admixture-incorporated cements and with the ordinary Portland cement used as control.

1.3 Outline

There are six chapters in this thesis. The first chapter presents general information about cement and its properties, also aim and scope of the study.

The second chapter mentions the literature review and basic accumulation of knowledge about the mineral admixtures and accelerating agents.

The third chapter describes the properties of the materials used and the experimental procedure used throughout the study.

The fourth and fifth chapters give the results of this study by analyzing and interpreting the effectiveness of accelerating admixtures with blended cements with respect to some fresh and hardened properties of cement pastes and mortars.

The sixth chapter mentions the conclusions drawn from this study. Also, in this chapter, based on the outcomes of the study, possible new research topics are suggested.

CHAPTER 2

LITERATURE REVIEW AND BACKGROUND

2.1 Sustainable Development

Cement is a basic material of engineering construction. Output from the cement industry is directly related to the state of the construction business in general and therefore tracks the overall economic situation closely. The demand on the cement manufacture is continuously increasing worldwide. The demand in the Turkish domestic market has risen since 2003. In 2005, the domestic consumption grew to 35 million tons and it was 43.5 million tons in 2006. In Turkey the cement consumption per capita had reached 600kg in 2006 and it is forecasted that the domestic consumption will have an annual growth rate of 5-8% until 2015(4). Parallel to this situation, consumption of raw materials and fuels increased considerably. Cement industry, being an energy-intensive industry, results in a product for which the energy cost may be as high as 50-79% of the overall cost (4). Thus, in the recent years most investments or expenses were made towards energy reduction and ecological considerations. Therefore, in the recent years the sustainable development which means ‘the development that meets the needs of the present without compromising the ability of future generations to meet their own needs’ has become a very important issue in the cement manufacturing sector. Parallel to this, the cement industry is continuously seeking the possibilities of using alternative materials as a substitute for natural conventional raw materials. As a result, the industry expanded the use of blast furnace slag, fly ash, silica fume, natural pozzolans, limestone fines etc. The use of these materials, besides lowering the costs has positive environmental consequences, as well. That is, they reduce the quarrying of primary materials, energy consumption, and emissions of dust, CO_2 and acid gases. Fly ash and blast furnace slag are accepted as the most common industrial by-products that can be used in cement manufacturing. Their consumption in the cement sector increases daily. To promote a numerical example, the total fly ash in Turkey is 18 million tons, 700-800,000 ton of this amount is used in the plants (5). Moreover, the average production of slag is known to be 600,000-650,000 ton/year, and 500,000-550,000 ton/year of that is given to cement factories (5).

2.2 Hydration of Portland Cement (6, 7, 10, 16)

Portland cement consists of five major compounds and a few minor compounds or oxides. The major constituents of a typical Portland cement are tricalcium silicate, C_3S (also named alite); dicalcium silicate, C_2S (also named belite); tricalcium aluminate, C_3A; tetracalcium aluminoferrite, C_4AF (also named, more correctly ferrite solid solution, Fe_{ss}) and gypsum. When Portland cement is mixed with water its constituents undergo a series of chemical reactions. Reactions of cement with water are named hydration. Hydration covers the setting and hardening of Portland cements.

It is customary to consider the hydration reactions of the major cement compounds independently although there are always interactions between the hydrating compounds and these interactions have important consequences.

The hydration products of the two calcium silicates, C_3S and C_2S, are same, differing in the amounts of hydration products and rate of hydration, only. The principal hydration product of both calcium silicates is calcium silicate hydrate gel (CSH gel) which has a variable composition during the course of hydration. It has an amorphous or poorly crystalline structure and is formed of particles of colloidal dimensions. The other hydration product is calcium hydroxide (CH). The hydration reactions of C_3S and C_2S upon full hydration are given below. However, during the hydration process the lime-silica ratio of the CSH gel changes between 2.0 and 1.5.

For Alite $2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$
For Belite $2C_2S + 4H \rightarrow C_3S_2H_3 + CH$

The difference between the hydrations of the two calcium silicates lies firstly in the greater quantity of calcium hydroxide released by C_3S, and secondly in that the rate of reaction for C_3S is much greater than that for C_2S.

The formation of pores is shown in Figure 2.1 while calcium silicate hydrate is formed. ‘In (a) hydration has not yet occurred and the pores (empty spaces between grains) are filled with water. (b) represents the beginning of hydration and (c) shows the continuing hydration. Although empty spaces still exist, they are filled with water and calcium hydroxide. (d) shows the almost completely hydrates hardened cement paste. The majority of space is filled with calcium silicate hydrate. That which is not filled with the hardened hydrate is primarily calcium hydroxide solution. The hydration will continue as long as water is present and there are still unhydrated compounds in the cement paste.'

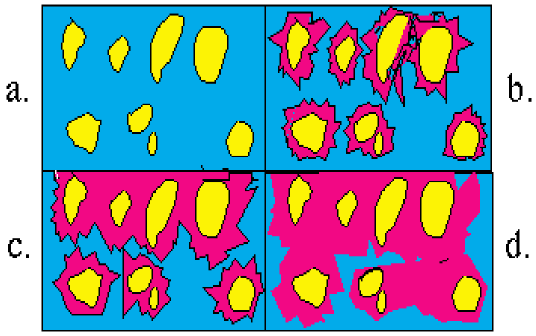


Figure 2.1: Schematic Illustration of the Pores in Calcium Silicate through Different Stages of Hydration (6).

The reaction of C_3A with water leads to the formation of calcium aluminate hydrates.

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

Since calcium aluminohydrates are not stable, their conversion into a stable form,C_3AH_6, occurs rapidly. This causes quick set or flash set. In order to prevent the flash set, some small amount of gypsum ($C\bar{S}H_2$) is added. In the event of C_3A hydration with the presence of gypsum, in Portland cement, two calcium sulfoalumino hydrates may form based on the gypsum amount. Generally, ettringite known as a primary hydration product, forms as a result of the reaction between C_3A + gypsum and water as shown in below:

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32}$$

However, before C_3A hydration has not completed, if the gypsum amount is not sufficient, ettringite may transform into the monosulfate form following the equation given:

$$2C_3A + C_6A\bar{S}_3H_{32} + 4H \rightarrow 3C_4A\bar{S}H_{12}$$

Yet, monosulfate form ($C_4A\bar{S}H_{12}$) may reconvert into ettringite when contacted with more sulfate ions.

$$C_4ASH_{12} + 2C\bar{S}H_2 + 16H \rightarrow C_6A\bar{S}_3H_{32}$$

After ettringite forms, very high amount of heat evolution occurs and the cement paste expands. Therefore, there is an optimum gypsum content that must be added to the clinker during the production of cement.

The hydration reactions of C_4AF are slower and include less heat compared to C_3A. Also, the retardation effect of gypsum on the quick stiffening is more significant on C_4AF.

When C_4AF hydrates in the presence of gypsum the following reactions take place:

$$C_4AF + 3C\bar{S}H_2 + 21H \rightarrow C_6(A, F)\bar{S}_3H_{32} + (A, F)H_3$$
$$C_4AF + C_6(A, F)\bar{S}_3H_{32} + 7H \rightarrow 3C_4(A, F)\bar{S}H_{12} + (A, F)H_3$$

Heat is evolved with cement hydration. This is due to the breaking and making of chemical bonds during hydration. The heat generated is shown below as a function of time (Figure 2.2).

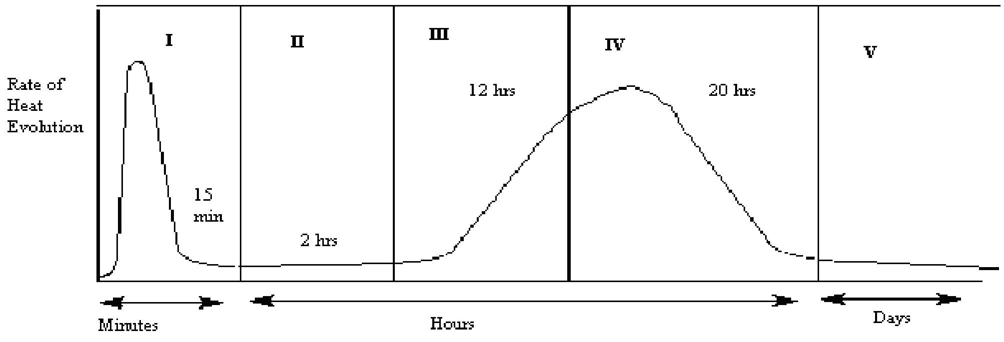


Figure 2.2: Rate of Heat Evolution during the Hydration of Portland Cement (6, 8)

The hydration of cementitious materials is exothermic. Monitoring the heat evolution, the process of hydration can be followed. Figure 2.2 shows a typical heat evolution curve. This curve can be divided into 5 stages as follows:

Pre-induction stage: In the stage 1, hydrolysis of the cement compounds occurs rapidly with a temperature increase of several degrees (6). In this stage, as a result of the reaction with gypsum and C_3A, ettringite and CH forms (8).

Dormant stage (9)*:* In this stage, cement has a low reactivity. The heat evolution slows significantly. During this period, because the concrete is in a plastic state, the concrete can be transported and placed without any major difficulty (6, 8).

Acceleration stage and *Post-acceleration stage* (6, 8)*:* In stages III and IV, 'the concrete starts to harden and the heat evolution increases due primarily to the hydration of tricalcium silicate.' The hydration of C_3S leads to the peak in the stage IV. CSH and CH are the main products of these stages.

Final Stage: The hydrate products form slowly and this process continues in the presence of water and unhydrated silicates are present (6).

As a result, the general properties of clinker phases are given in Table 2.1.

Table 2.1: The General Properties of Clinker Phases

Property		The General Properties of Clinker Phases			
		C_3S	C_2S	$C_3A + C\overline{S}H_2$	$C_4AF + C\overline{S}H_2$
Rate of reaction		Moderate	Slow	Fast	Moderate
Heat of Liberation		High	Low	Very high	Moderate
Contribution to strength	Early	High	Low	Low	Low
	Ultimate	High	High	Low	Low

2.3 Pozzolans

A Pozzolan is one of the mineral admixtures. 'It is a siliceous or siliceous/aluminous material that, when mixed with lime and water, forms a cementitious compound (7)'.

The use of different blending materials in different mineral composition causes important variations in the cementing system. Because of the production process and the properties of the raw materials used, there occur changes in their physical, chemical, and mineralogical compositions which causes different effects on the cement properties. For example, the permeability and the rate of diffusion of moisture and aggressive species into the steel-concrete interface decreases drastically when pozzolanic materials are used in concrete.

Pekmezci et Akyüz (11) investigated the effect of a natural pozzolan on the properties of concrete. According to their study, the optimum pozzolan/cement ratio to obtain the maximum strength is approximately 0.28.

Pozzolanic Reaction (5, 7)

When finely divided pozzolans contact calcium hydroxide in the presence of moisture, some chemical reactions occur. The main reaction between silica of the pozzolan and calcium hydroxide in the presence of moisture;

$$\text{CH} + \text{S} + \text{H} \rightarrow \text{C-S-H}$$

The products of these types of reactions are like that;

- Calcium silicate hydrate (C-S-H);
- Calcium alumino hydrate (C_4AHx) $9 \leq x \leq 13$,
- Hydrated gehlenite (C_2ASH_8)
- Calcium carboaluminate ($C_3A.CaCO_3H_{12}$)
- Ettringite ($C_6AS_3H_{32}$)
- Calcium aluminate monosulphate (C_4ASH_{12})

Pozzolanic Activity (7)

The activity of a pozzolanic material with hydrated lime that is how good a pozzolan will behave in mortar or concrete is expressed as its "pozzolanic activity". In other words, pozzolanic activity refers to the reaction of alumina-silicate with calcium hydroxide to form cementitious products.

- In the short term, the activity of pozzolan depends on specific surface area, in the long term it is based on its chemical and mineralogical compositions (12).

- The amount of CH which pozzolans react with is related with the amount of S in the active phases within the pozzolan (12).

Pozzolans are divided into two main groups namely (7)*;*

- Natural Pozzolans
    - Natural Pozzolans of Volcanic Origins: Volcanic Glasses, Volcanic Tuffs, Volcanic Ashes
    - Thermally Treated Clays, Shales and Diatomaceous Earths.

- Artificial Pozzolans
    - Fly Ashes
    - Silica Fumes
    - Granulated Blast Furnace Slags

2.3.1 Natural Pozzolans

"The most common types of them are volcanic ashes, volcanic tuffs, and thermally treated clays, shales and diatomaceous earths (7)".

Natural Pozzolans of volcanic origin (13)

'Natural Pozzolans of volcanic origin were formed from minerals ejected from volcanoes in the form of very finely divided vitreous material. These minerals are composed of mainly silica and alumina with smaller and variable quantities of other minerals containing calcium, magnesium, iron, potassium, and sodium).'

The alumino silicates, present in these types of pozzolan, can react with Ca ions in the presence of water because of large surface area and disordered structure. Volcanic ashes, volcanic glasses, volcanic tuffs and trass are the major pozzolanic materials that belong to the volcanic-originated natural pozzolans group.

Thermally treated clays, shales and diatemaceous earths (13)

“Clays and shales in raw form do not possess pozzolanic properties because they have a crystal structure. However, clays and shales become highly pozzolanic by heat treatment such as calcining at 700 to 900°C.”

The chemical requirements for Natural Pozzolans According to ASTM C 618 “Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete” and TS 25 “Natural Pozzolan (Trass) for Use in Cement and Concrete-Definitions, Requirements and Conformity Criteria” are described below Table 2.2 (7).

Table 2.2: Chemical Requirements for Natural Pozzolans (7)

	ASTM C 618	TS 25
S+A+F , min %	70	70
$\bar{S}$, max %	4	5
Moisture content, max %	3	3
Loss on ignition, max %	10	10
M, max %	-	5
Available alkalies as N, max % (Optional requirement)	1.5	1.5

The effects of natural pozzolans on some properties of cement have been studied extensively. One of the study about the influence of natural pozzolans on setting time, compressive strength, normal consistency and alkali silica activity of concrete have been executed by Turanlı et al. (14). According to the experiment results; the standard consistency water requirement increased with the increase of pozzolan content in the blended system. For example, when the pozzolan content increased from 35% to 55%, the water demand increased by approximately 14%. On the other hand, the blended cement was observed to have different setting times based on the pozzolan content. For instance, the initial and final setting times of 55% natural pozzolan incorporated cement were shorter compared to that of

Portland cement. However, 35% pozzolan incorporated cement showed longer initial and final setting times. Also, 45% pozzolan incorporated cement exhibited similar initial setting time with Portland cement, but delayed the final setting time. On the contrary, the compressive strength of mortars for all tested ages decreased by increasing the pozzolan content. Also, large amount of natural pozzolans cements decreased expansion comparing with Portland cement.

Turanlı (15) studied the effects of pozzolan content on fresh properties like slump, air content and hardened properties of concrete namely compressive strength by using Portland cement at different fineness and Portland-pozzolan cement at different pozzolan ratios (8.43, 20, 25 and 30 % pozzolan) and different fineness. Some results of his study are as follows;

Figure 2.3 shows CH amount formed as a result of the hydration reactions in the different cement types. According to that, as the proportion of pozzolan increased, CH content decreased.

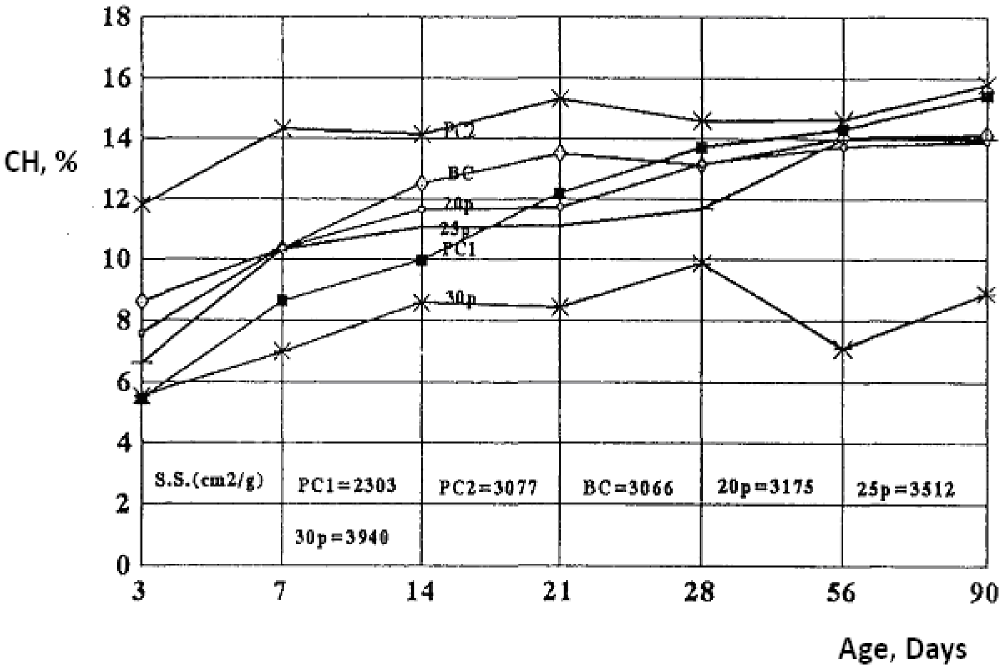


Figure 2.3: CH Contents of Hydrated Portland Cements and Portland-Pozzolan Cements (15)

Figure 2.4 demonstrates the effect of pozzolan and fineness of cement on the Normal consistency. Firstly, the normal consistency of Portland-pozzolan cement pastes increased with the increase in pozzolan content. Secondly, the water requirement of cement paste was affected by fineness of cement. That is; cements having same Blaine specific surface, demanded approximately same amount of water.

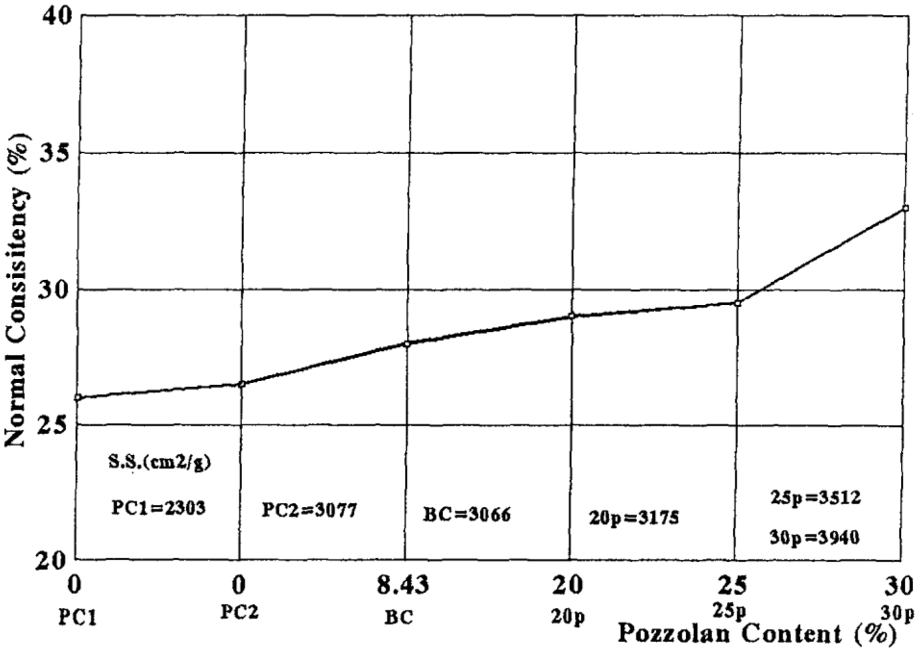


Figure 2.4: The Normal Consistency of Cement Pastes (15)

Figure 2.5 indicates the change in the initial and final setting times related with different cement pastes. According to that; Blaine specific surface area of Portland cements did not have a significant effect on the setting times of cement. Only, the cements with coarser size had longer setting time comparing with the cements with finer size. Also, the setting time increased by increasing the pozzolan content and fineness. Figure 2.6 indicates that with the addition of pozzolan, the heat of hydration reduces. Also, the Blaine specific surface had a significant effect on the heat of hydration. The hydration heat of finer cements was slightly higher heat of hydration than that of coarser cements.

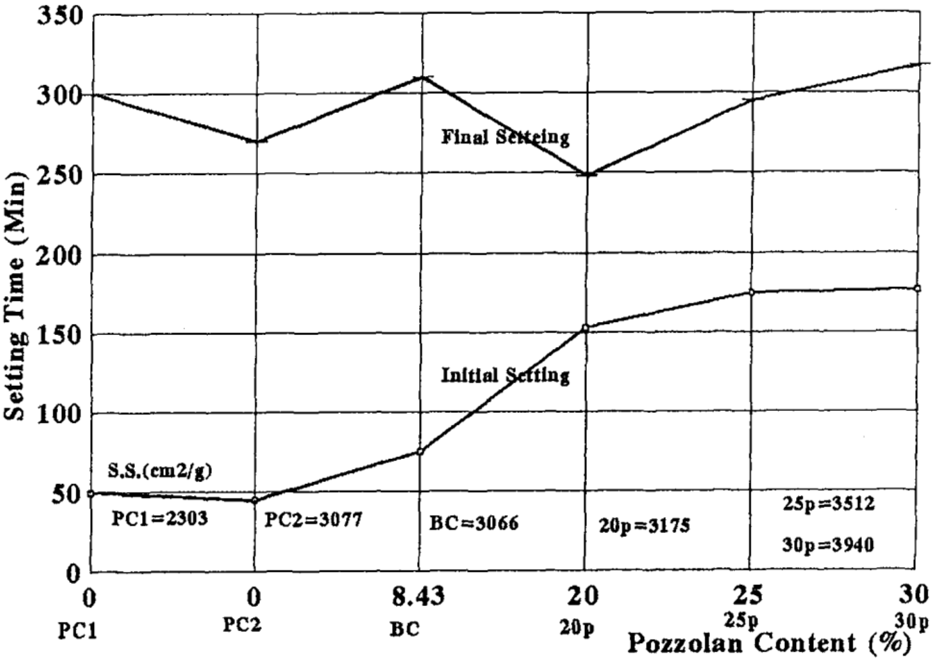


Figure 2.5: The Initial and Final Setting Times of Cement Pastes (15)

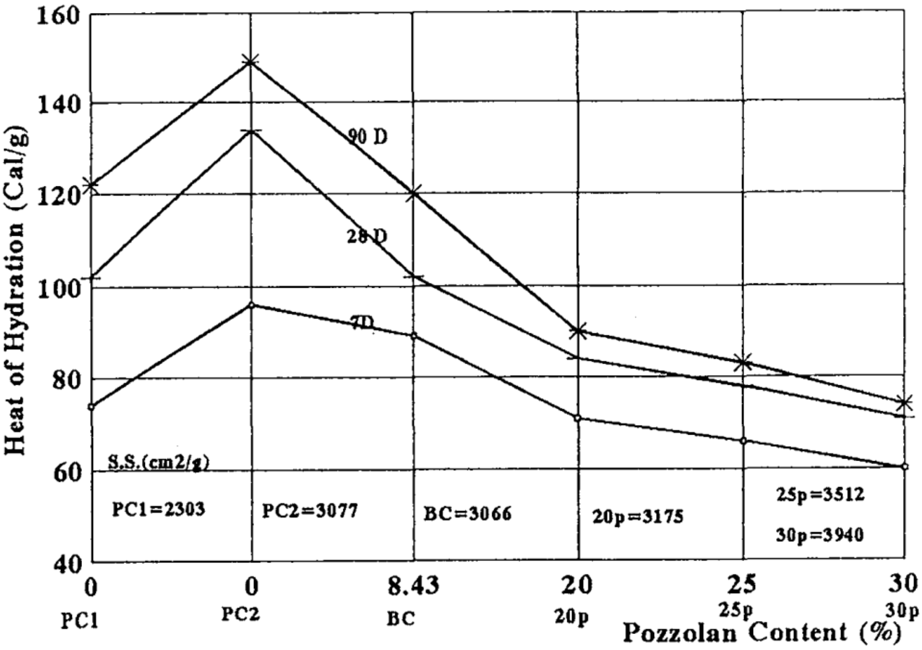


Figure 2.6: Heat of Hydration of Cement Pastes (15)

Generally, the compressive strength decreased with the increase in pozzolan content at all ages as shown in Figure 2.7. The compressive strength values were affected by the specific surface area of the cements. The finer cement types had higher compressive strengths at all ages than the coarser cement types. The increase or decrease of the CH produced by the hydration of each type of cement and the heat of hydration values lead to the increase or decrease in the strength values. The compressive strength vs. the pozzolan content curve is parallel with the pozzolan content vs. the CH produced by the hydration curve and the pozzolan content vs. the heat of hydration values curve.

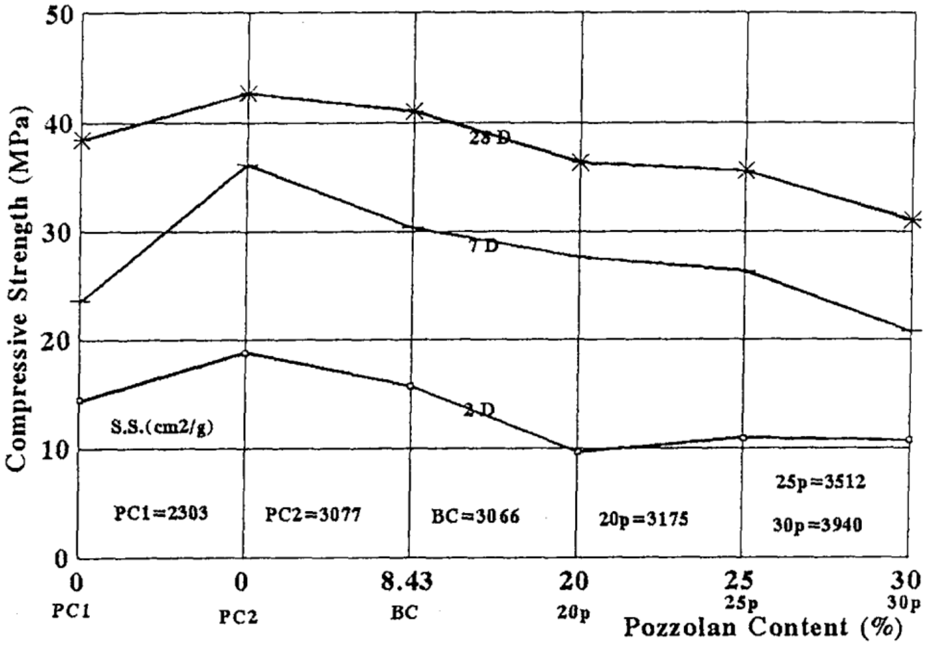


Figure 2.7: Compressive Strength of Cement Pastes (15)

Yetgin and Çavdar (16) determined the compressive strength by using the cements including 0%, 10%, 20%, 25%, 30%, 35% mass ratios via fixing trass type and trass fineness.

Table 2.3: The Experimental Results of the Study (16)

Sample	Compressive Strength (MPa)				Setting Time		Water Consistency %
	1 Day	*2 Days*	*7 Days*	*28 Days*	*Initial (min)*	*Final (min)*	
DP00	12.0	21.3	40.1	60.8	115	185	28.00
DP10	9.9	18.1	36.1	55.2	125	190	28.00
DP20	7.4	13.2	30.5	49.6	145	185	31.00
DP25	6.5	11.9	27.2	45.6	125	205	29.00
DP30	5.9	11.3	23.4	41.7	135	195	29.25
DP35	5.3	10.8	22.0	37.8	120	210	31.75

As seen from the test results in Table 2.3, the early compressive strength reduced with the increase of natural pozzolan amount. This is caused by the limited hydration of natural pozzolan. That is; the natural pozzolan is not able to hydrate completely in 28 days. Natural pozzolan reacts and the strength difference decreases after sufficient time passed. The strength of Portland cement mortar was higher than that of 35% trass incorporated cement mortar. This difference was 56% in the 1st day, 49% in the 2nd days, 45% in the 7th days and 38% in the 28th days. According to this, the strength gaining rate of trass incorporated cement was found to be slower comparing with Portland cement. On the other hand, workability and the amount of water required for normal consistency increased relatively when the amount of trass increased. This increase was smaller compared to addition of trass. As for setting time, the amount of natural pozzolan affected the setting properties of cement mortar. The retardation of setting time in the beginning of the experiment changes with time. With the delay in the setting time, hydration rate slows down and hydration heat and temperature decreases. This prevents shrinkage.

According to experimental tests conducted (12), there are some effects of natural pozzolans on the fresh and hardened properties of concrete and cement.

- Bleeding (12): Usage of little amount of pozzolan in cement or concrete instead of using only Portland cement reduces bleeding significantly.

- Sulfate and Chloride Attack (17): Natural pozzolan increases resistance to sulfate and chloride attack.

- Alkali-Aggregate Reaction (17): Natural pozzolan reduces alkali-aggregate reaction because natural pozzolan is shattered into such a fine particle size resulting in dramatically increased reactive surface area it can react quickly with calcium hydroxide and can trap the alkalis inside the cement paste.

2.4 Blast Furnace Slag

“The Blast furnace slag is a nonmetallic co-product produced in the process in which iron, iron ore, iron scrap, and fluxes (limestone and/or dolomite) are charged into a blast furnace along with coke for fuel. Then, the coke is combusted to produce carbon monoxide, which reduces the iron ore to a molten iron product. This molten iron product can be cast into iron products, but is most often used as a feedstock for steel production” (18).

Figure 2.8 presents a general schematic which depicts the blast furnace feed stocks and the production of blast furnace co-products like iron and slag.

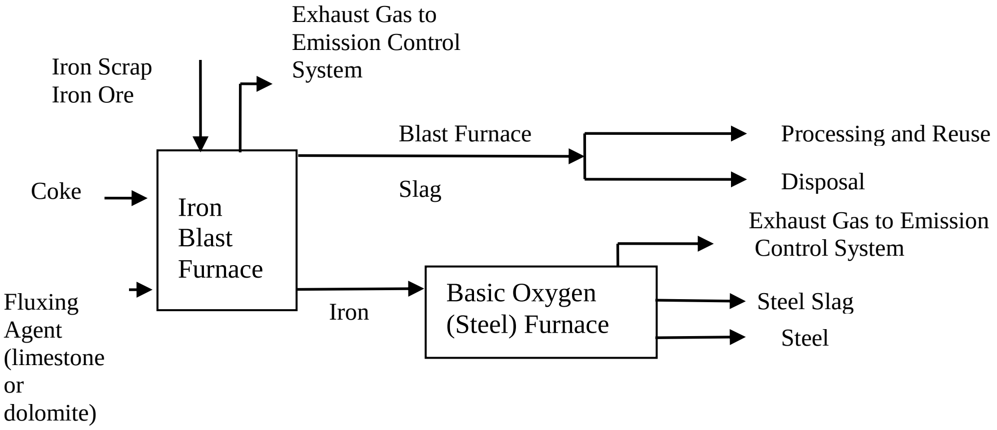


Figure 2.8: General Schematic of Blast Furnace Operation and Blast Furnace Slag Production (18)

The reactions occurring in this process are as follows (9);

$C + O_2 \rightarrow CO_2$
$C + CO_2 \rightarrow 2CO$ (CO is the main reducing agent)
$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

Due to some rocky materials in the composition of iron ore which not melt at the temperature of the furnace, it is not pure. Therefore, these materials congest the furnace. To convert this into slag, limestone is used. Limestone decomposes as follows; clog up

$CaCO_3 + S \rightarrow CaSiO_3$
$C + S \rightarrow CaSiO_3$

The $CaSiO_3$ melts and runs to the bottom of the furnace to form a layer on top of the molten iron. It can be tapped off from time to time as slag.

The blast furnace slag consists primarily of silicates, aluminosilicates, and calcium-alumina-silicates. The molten slag, which absorbs much of the sulfur from the charge, comprises about 20 % by mass of iron production.

Types of Blast Furnace Slag (19, 20, 21)

"Different forms of slag product are produced depending on the method used to cool the molten slag. These products include air-cooled blast furnace, expanded or foamed slag, pelletized slag, and granulated blast furnace slag."

- "When the liquid slag is poured into beds and slowly cooled under ambient conditions, a crystalline structure is formed, and then a hard, lump slag is produced, which can subsequently be crushed and screened. This structure is called *Air Cooled Blast Furnace Slag*."

- *"Expanded or Foamed Slag* is produced with the help of acceleration of the process of cooling and solidification and increase in the cellular nature of the slag after the molten slag is cooled and solidified by adding controlled quantities of water, air, or steam. Foamed slag is distinguishable from air-cooled blast furnace slag by its relatively high porosity and low bulk density."

- *"Pelletized Blast Furnace Slag* is produced when the molten slag is cooled and solidified with water and air quenched in a spinning drum, pellets, rather than a solid mass."

- "If the molten slag is cooled and solidified by rapid water quenching to a glassy state, little or no crystallization occurs. This process results in the formation of sand size (or frit-like) fragments, usually with some friable clinker like material. This material is *Granulated Blast Furnace Slag*."

When crushed or milled to very fine cement-sized particles, ground granulated blast furnace slag (GGBFS) has cementitious properties, which make a suitable partial replacement for or additive to Portland cement.

The main factors that determine the cementitious properties of GGBFS are chemical composition of the slag, alkali concentration of the reacting system, glass content of the slag, fineness of the slag, temperature during the early phase of the hydration process (7).

In general, the cementitious properties of GGBFS increase with the increase of C/S ratio up to a limit value. But, in the case of high C/S ratio, its cementititous properties decrease due to hard granulation. Also, the cementititous properties of GGBFS increase with increase in A content at constant C/S ratio (19).

- Separate grinding is a more efficient grinding process (7).
- The average composition of blast furnace slag produced in Turkey was given in Table 2.4;

Table 2.4: The Typical Chemical Composition of Blast Furnace Slag in Turkey (7);

	C	S	A	F	M	MnO	S	$\bar{S}$
Value, %	34-41	34-36	13-19	0.3-2.5	3.5-7	1-2.5	1-2	-

There are some factors affecting the physical structure and gradation of granulated slag namely the chemical composition of the slag, its temperature at the time of water quenching, and the method of production (7).

There exists only one standard for GGBFS namely ASTM C 989 ‘Standard Specification for Slag Cement for Use in Concrete and Mortars’ as shown in Table 2.5. According to ASTM standard, there are three grades of granulated blast furnace slag. There is no Turkish specification for blast furnace slag to be used as admixtures (7).

Table 2.5: Requirements of GGBFS According to ASTM C 989 (7)

Fineness *(Amount ret. on 45µm, max %)*	Air Content of Slag Mortar, max %	Sulfide sulfur, S, max %	Sulfate ion reported as $\overline{S}$, max %
20	12	2.5	4.0

The particle size of GGBFS should lie between 10 µm and 45µm with a considerable proportion of particles below 10µm. It’s reported that slag particles less than 10µm contribute to early strength development in concrete up to 28 days, whereas 10 µm and 40 µm particles contribute to long-term strength (21).

Mechanism of Action

When GGBFS is mixed with water some immediate reactions start to take place. These reactions are as follows (7);

- “At the beginning of hydration process, blast furnace slag only reacts with water for a short time and then stops. The reason for this phenomenon is the formation of a water impermeable layer on the blast furnace slag particle surface (8)”. Actually, the reaction between slag and water does not provide strong cementitious results.

- With the hydration continues there is need for activators like solutions of alkalis or sulphate for the latent hydraulicity of blast furnace slag (8).

- Then, two main products named calcium-silicate-hydrate gels (C-S-H gels) and calcium hydroxide form as a result of the reaction between calcium silicates compounds (C_3S and C_2S) of Portland cement and water. They both have strong cementitious properties.

Bouzoubaâ et Foo (20) studied the general effects of granulated blast furnace slag and fly ash on cement mortar and concrete. The results related with the effects of granulated blast furnace slag are given in Table 2.6.

Table 2.6: General Effects of Granulated Blast Furnace Slag (20)

Fresh Properties	Comments
Water Demand	do not have a strong effect on water demand.
Workability	do not have a strong effect on slump, but increases pumpability.
Bleeding	do not have a strong effect on bleeding.
Setting Times	its effect on setting time is less
Mechanical Properties	*Comment*
Compressive Strength	slag concrete has higher early age mechanical properties and lower long term mechanical properties comparing with fly ash concrete.
Flexural Strength	
Drying Shrinkage	appears to reduce creep and has no effect on drying shrinkage.
Creep	
Durability	*Comments*
Permeability	reduces water and chloride-ion permeability, especially at later ages, if well cured.
Corrosion Resistance	increases the protection of reinforcing steel from corrosion if well cured.
Sulfate Resistance	the content required should be investigated (usually more than 35% is required)
Alkali Silica Reaction Resistance	the amount required is usually more than 35%.
Carbonation Resistance	concrete resistance to carbonation decreases with increasing content.

The compressive strength development of cement mortar incorporating 20, 40 and 60 % replacement of GGBFS for standard sand was investigated (22). Table 2.7 demonstrates the percentage and amount of the consistency. According to the results; as the amount of slag increases, the consistency increases.

Table 2.7: Mix Design Details (22)

Sample	Cement (%)	Slag (%)	Consistency (%)	Consistency (ml)
Standard	100	0	27.0	78
1	80	20	28.5	81
2	60	40	29.5	83
3	40	60	31.0	86

The compressive strength of cement mortar was obtained at the ages of 3, 7, 28, 56, 90, 150 and 180 days. As a result, the strength at all ages decreased with the increase in the consistency. The compressive strength of slag incorporated mortar is lower than that of the PC mortar as illustrated in Figure 2.9. However, the compressive strength increases consistently with time independent of the cement types.

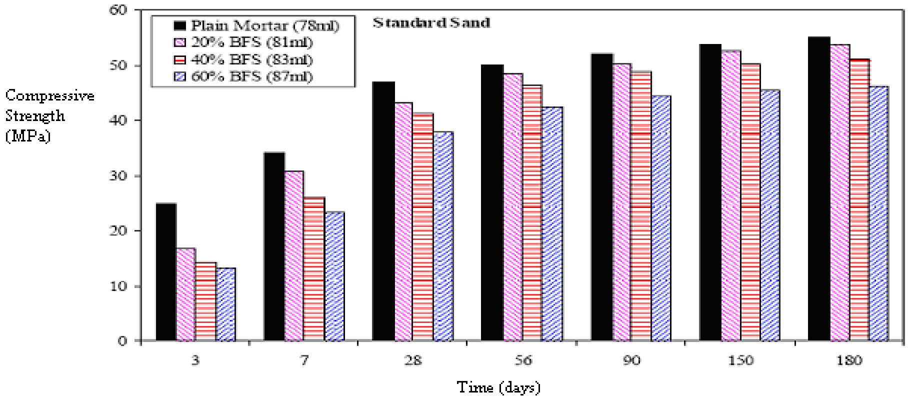


Figure 2.9: The Effect of Slag Addition on the Compressive Strength at Different Ages (22)

Another study related with the effect of blast furnace slag on Portland cement performed by Mobasher et al. (23) who prepared paste, mortar, and concrete samples containing up to 15% copper slag as a cement replacement. According to the study; the initial and final setting times of the cement paste was delayed when slag used, but these retarding effects are negligible.

When monitoring the hydration reactions of control and 10% slag incorporated cement paste at ages of 1, 7, and 28 days, semi-quantitative X-Ray diffraction method was used. The results showed that there is a slight increase in the CH peaks of 10% slag incorporated samples comparing with the control sample.

The compressive strength values of mortar slag incorporated and control sample are shown in Figure 2.10. According to that, the 1-day compressive strength decreased with the use of copper slag, whereas the 28 and 90-day compressive strength increased for all amounts of slag studied. The long term strength of slag incorporated mixtures was significantly high comparing with the control specimens.

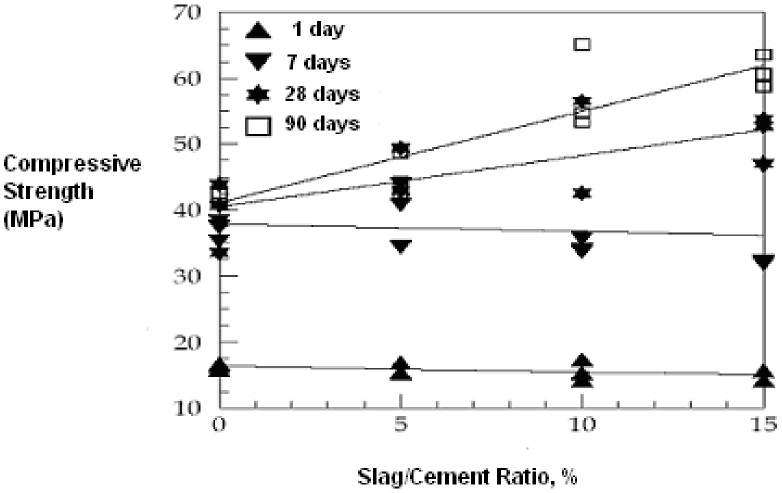


Figure 2.10: Effect of Copper Slag on the Compressive Strength of Concrete (23)

2.5 Limestone Powder (LP)

Limestone powder is one of the recent mineral admixtures produced by grinding limestone finely. The replacement of limestone powder with PC is beneficial from the economical and environmental points of view. Also, it has a positive effect on the concrete properties such as early compressive strength, durability and workability. TS EN 197-1 (3) permits that 6 to 20% of LP is inter-ground with the clinker in Type II cement types.

Portland limestone cements have been widely used for many years in some counties, such as France, Sweden and Spain (8). TS EN 197-1 (3) requires that, in Portland limestone cement, the limestone contains at least 75% $CaCO_3$ by weight. Also, total organic carbon (TOC) content should conform to below criteria suggested by TS EN 197-1;

LL; TOC not exceed 0.2 % by mass,
L ; TOC not exceed 0.5 % by mass

The addition of limestone in cement leads to the some physical and chemical effects within the hardening binding system. The first one is the filling of the intergranular spaces in the hardening water–cement system with limestone. The second one is the participation of limestone in hydration of the silicate and aluminate phases. This leads to the calcium hydrocarbonate aluminate and possibly calcium hydrocarbonate formation. The third one is the replacement of CO_3^{2-} ions with SO_4^{2-} ions in the emerging ettringite (24).

Hydration of Portland Cement with Limestone Powder

The principal hydration products in composite cements are essentially similar to those found in pure Portland cement. However, in composite cements CH content is lowered, both by the dilution of clinker and the pozzolanic reaction. The effect of limestone on C_3S and C_3A hydration was given respectively.

- The effect on C_3S hydration

According to Kakali et al. (8), the hydration of C_3S is accelerated with the use of limestone. The calcium carbosilicate hydrate is formed as a result of this. In addition, based on the study of Pera et al. (8), limestone changes the C_3S hydration and forms calcium carbosilicate hydrate by reacting with C_3S. On the other hand, the heat evolution rate of C_3S with 50% limestone is higher comparing with pure C_3S which shows the mass of clinkers.

- ❖ The effect on C_3A hydration

Voglis et al. (25) showed the results of hydration in limestone cement pastes, according to that carbonate ions are incorporated in calcium aluminate hydrates and carboaluminates are formed. Based on the study of Kakali et al. (8), limestone was found to prevent the conversion of AFt to AFm and to react with C_3A o form monocarbonate hydrate from the beginning in the C_3A+ $CaCO_3$ system.

Figure 2.11 (8) demonstrates the differences between Portland cement and limestone blended cement hydration periods. According to Barker, Pera and Voglis (8); in limestone blended cement, the formation of AFt is accelerated, but the conversion of AFt into Afm is delayed or stopped with the use of limestone. In Figure 2.11, Ettringite abbreviated as E, Gypsum as G, Monocarboaluminate as Mc, Calcium Carbonate as CC, Monosulfoluminate as Ms.

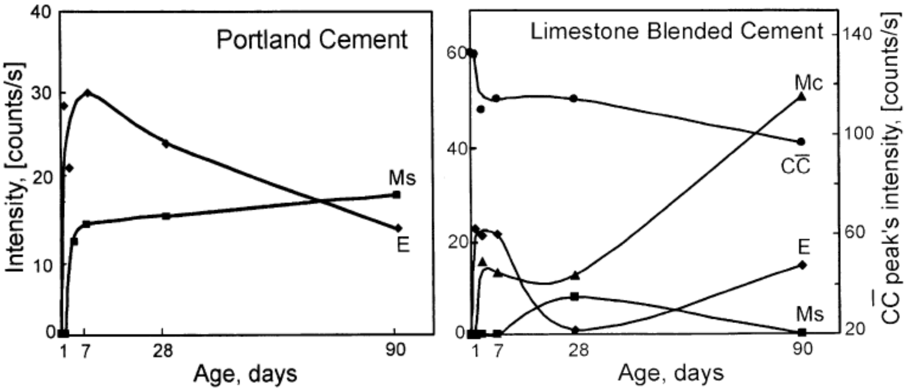


Figure 2.11: Evolution of Hydration Products in PC Paste with and without LP (8)

The rate of heat evolution of PC incorporating limestone with the w/s ratios of 0.4 and 0.5 at 20°C and 30°C has been performed by Zhou (8). According to experiment results, the Portland cements reaction mechanism changed with the addition of limestone. For example, the dormant stage became shorter and the hydration of C_3S and C_3A occurred at early times. The dormant stage became shorter when the temperature and the limestone content increases at certain w/s ratio. Based on XRD studies of Zhou; with the absence of gypsum, limestone was observed to react with C_3A to produce calcium monocarboaluminate. On the other hand, with the addition of gypsum, ettringite first formed as a result of the reaction between C_3A and gypsum. Then, limestone converts ettringite into calcium monocarboaluminate.

Pera et al.(27) have studied the effects of limestone on cement hydration by using limestone at ratios of 0, 10, 20, 30, 40 and 50 % of cement. According to them, the strength of pastes containing 10% $CaCO_3$ is higher or equal comparing with Portland cement. With the increase in limestone content, the compressive strength decreases. This indicates that the strength development of Portland cement pastes containing $CaCO_3$ is different from that of Portland cement. In Portland cement, as a result of the interactions between C_3A and $CaCO_3$, calcium carboaluminate hydrate forms and ettringite modified. On the other hand, in blended C_3S pastes only calcium carbosilicate hydrate is produced. Yet, the strength is in the acceptable limit when 50% limestone incorporated cement used.

Another study is by Belie et al. (28) who performed an experiment to evaluate the sensitivity to changes in accelerator type and dosage, and the effect of accelerators in combination with different cement types. In this experiment, two types of cement, namely CEM I 42.5 R and CEM II/A-LL 42.5 R and two types of accelerating admixtures such as alkaline aluminate based and alkali free $Al_2(SO_4)_3$ based solutions were used. According to their study, the ultrasound measurements were significantly affected by the effect of cement type, accelerator type and dosage on the setting behavior of mortar. The accelerating effect of alkaline accelerator on the microstructure development is higher than that of the alkali-free accelerator, especially at ages below 90 min. At very early age, the alkali free accelerator has a larger effect on mortar containing CEM I comparing with CEM II. On the other hand, the effect of the alkaline accelerator was more pronounced on mortar containing CEM II.

Caldarone (29) studied the effect of limestone on the compressive strength at ages 1, 3, 7, 14 and 28 days by using limestone at different amounts (3.4, 3.7 and 4.4%) and at different fineness (3,500-4,100 cm^2/g). According to the results given in Table 2.8, the inclusion of at 5% or less limestone was observed not to affect the water demand or flow significantly. On the other hand, at all ages the compressive strength of cements containing limestone are similar or higher comparing with that of non-limestone cements.

Table 2.8: Experimental Results of Compressive Strength (29)

Blaine	Limestone, % by mass	Normal Consistency, %	Compressive Strength (MPa)		
			3 days	*7 days*	*28 days*
3530	-	26.2	28.6	43.6	55.3
4120	3.7	26.3	33.3	47.1	56.7
3810	-	27.4	36.5	41.7	49.2
4060	4.4	27.5	36.2	42.6	46.4
4090	-	26.5	31.8	25.8	45.4
4050	3.4	26.9	31.8	36.2	47.0

Vuk et al. (30) evaluated the effect of 5% limestone addition on various properties of cement like compressive strength, workability in relation to clinker type and fineness. Based on the results given in Table 2.9, limestone addition considerably influences some characteristics of cement, but this influence depends also on other factors namely clinker type and fineness.

Table 2.9: Experimental Results of the Study (30)

Clinker Type	Limestone (%)	Blaine (cm^2/g)	Water Dem. (%)	Init. Set. Time (min)	Fin. Set. Time (min)
A(low C_3S)	0	4,040	25.0	255	345
A	5	4,370	25.3	205	300
A	0	3,070	24.5	300	400
A	5	3,670	24.1	250	340
B(high C_3S)	0	3,950	26.3	190	280
B	5	4,380	25.8	170	240
B	0	3,130	24.3	210	300
B	5	3,540	23.8	180	250

The standard consistency water decreased by an average of 0.5% in absolute scale with the use of 5% limestone incorporated cement. The fineness of limestone was effective on the water demand. That is; the water demand decreased by approximately 1.5% in absolute scale when fineness changed from 2% to 5% residue on the 90-mm sieve. Also, both the initial and final setting decreased when limestone used. However, the clinker type is important in its effect on the initial setting time. The initial setting time decreased by approximately 50 min when limestone incorporated clinker A (low C_3S) used. On the other hand, the initial setting time reduced by 25 min with the use of limestone incorporated clinker B (high C_3S). The fineness and lime standard of clinker used decreases both setting times however, the clinker type was more pronounced in combination with low fineness of cement. It seems that the effect of clinker composition on setting time becomes stronger when the fineness of cement is lower. The influence of limestone on the compressive strength depends on clinker type used. The addition of limestone to clinker having high lime standard influenced predominantly early compressive strength, while the addition of limestone to clinker having low LSF influenced mostly the compressive strength after 28 days and the initial setting time (Figure 2.12).

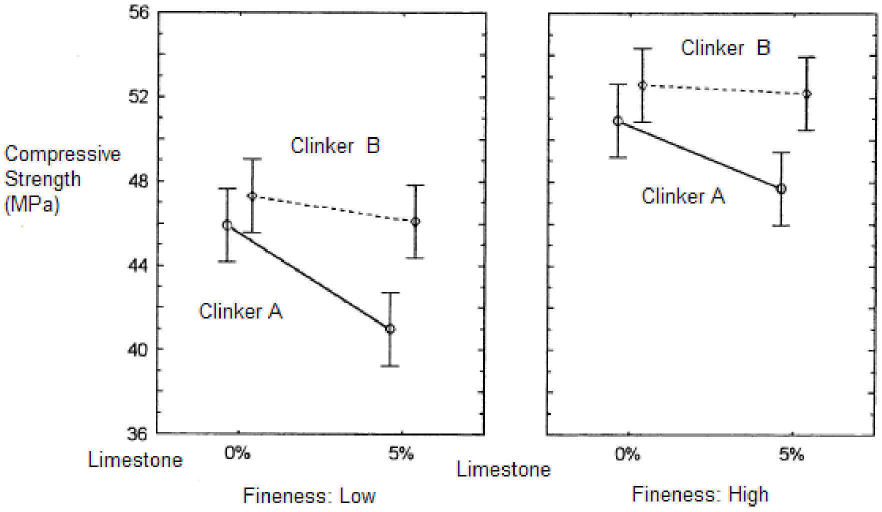


Figure 2.12: The Effect of Limestone Addition on Compressive Strength at 28 days (30)

Tsivilis et al. (31) investigated the parameters affecting the properties of Portland limestone cements at different fineness and limestone content. Three types of limestone have been used in this study. The first one has the higher content of calcite while the second and the third contain significant amounts of dolomite and quartz/clay respectively. According to this study; the clinker quality, the limestone quality, the percentage of contents and the cement fineness are important parameters for Portland limestone cements. As for water demand, the limestone cements, despite their higher fineness, generally have lower paste water demand than the corresponding pure cements. In limestone cements based on clinker Cl, and containing 10% limestone, there is a reduction of water demand from 26% to 24%-25%. Also, the increase of the limestone content to 20% and 35% causes a decrease of the water demand to 24-22.5%. On the other hand, the compressive strength of limestone cements having up to 10% limestone content and fineness up to a limit value is almost same comparing with that of the corresponding pure cements. Also, the setting time and soundness of Portland limestone cements are satisfactory and similar to those observed in Portland cements.

Another study by Voglis et al. (25) investigated the mechanical and physical properties of the cements by using limestone and pozzolan at 15%. The results of their study are given in Table 2.10.

Table 2.10: The Mechanical and Physical Properties of Cements Used in the Study (25)

Cement Type	Grinding Time (min)	Specific Surface (cm^2/g)	Paste Water Demand (%)	28-day Compressive Strength (MPa)	Setting Time (min)	
					Initial	Final
PC	41	3,030	24.3	40.3	125	170
PLC	60	5,110	24.5	40.5	90	170
PPC	52	4,180	26.2	41.2	95	140

In this study, there are some variations in the specific surface areas of cements. The results of this study can be summarized as follows; the water demand increased when 15% limestone and pozzolan incorporated cement used. However, the increase in the water demand was more pronounced in pozzolan incorporated cements. According to study, up to 7 days, the compressive strength of limestone cement was observed to be higher because of filler effect of the fine particles of limestone, the higher clinker fineness in Portland limestone cement and the low rate of pozzolanic reaction. But then, especially after 28 days the strength development rate of Portland limestone cement was low comparing with that of

Portland cement. Also, the 28-day compressive strengths of Portland limestone cement and Portland pozzolan cement were higher than that of Portland cement.

Dumitrescu and Menicu (24) researched the effects of the replacement the cement clinker with some mineral admixtures like limestone and blast furnace slag at 20-35%. In that study, the composite cements were obtained either by intergrinding the Portland cement clinker with the desired addition (A) or by separate grinding followed by mixing (B). Based on the study, the setting time decreased with the addition of limestone. Also, the long term compressive strength decreased when the limestone content increased from 20% to 35%. On the other hand, the 2-day compressive strength increased with the addition of 20% limestone.

Effect of Limestone on Cement Durability Properties

- Permeability:

The permeability of concrete is controlled by capillary pores. The permeability depends mostly on water/cement ratio, age and degree of hydration. In general the higher the strength of cement paste, the higher is the durability and the lower is the permeability (9).

“Moir and Kelham (26) reporting results from a Building Research Establishment study, found that the permeability to oxygen for a series of concretes made with cements with or without 5% or 25% limestone was slightly reduced by the presence of limestone. Porosity was very similar for the control and 5% limestone cements.”

- Drying & Carbonation Shrinkage

“Almost all concrete is mixed with more water than is needed to hydrate the cement much of the remaining water evaporates, causing the concrete to shrink. Restraint to shrinkage, provided by the subgrade, reinforcement, or another part of the structure, causes tensile stresses to develop in the hardened concrete. On the other hand, carbonation shrinkage forms as a result of the reaction between CH and CO_2.”

The results of the effect of limestone on drying shrinkage and carbonation are different, while in some situations it has positive effects on them, sometimes having negative effects on that. There are some studies regarding these properties.

“Adams and Race (26) studied the effect of blended limestone on the drying shrinkage of Type I (11.4% C_3A) and Type II (6.4% C_3A) cements. They found slight increases in drying shrinkage also between cement types there exists a small difference.”

“Barker and Matthews (26) studied the durability of two series of concretes having different cement composition and properties. They found that regardless of the composition of the cement, the depth of carbonation correlated well with the strength of the concrete.”

- Freezing & Thawing

In concrete, water when freezes expands in volume. This causes internal hydraulic pressure and cracks the concrete.

“Sprung and Siebel (26) found that in general concretes made with Portland limestone cement showed reduced resistance to frost damage as compared with those made with Portland cements, even when the strengths were the same. They tested Portland limestone cements containing 15% limestone by the cube method. The most important criterion for limestone quality as related to frost resistance is the clay content, since clays can adsorb moisture which expands on freezing. The specimens made from Portland limestone cement (13% to 17% limestone) performed as well as or slightly better than those made from Portland cement.”

- Sulfate Attack

Sulfate attack is defined as the result of the event in which deleterious chemical and/or physical re-action between sulfates in ground water or soil and certain constituents in cement. It causes expansion and disruption of the concrete.

“Soroka and Stern (26) studied the effect of reagent-gade $CaCO_3$ on the sulfate resistance of Portland cement mortars having a water/cement ratio of 0.75. According to this study; the $CaCO_3$ has a beneficial effect beyond the reduction of the C_3A content of the cement.”

“Gonzáles and Irassar (26) also evaluated effects on sulfate resistance (ASTM C 1012) of mortars made with Type II and Type V cements with 0%, 10%, and 20% limestone. Their results indicate no significant difference in sulfate resistance of low C_3A cements with or without 10% limestone; however, for 20% replacement levels, the sulfate resistance was lowered.”

In summary, the accumulation of knowledge on the effects of natural pozzolans, blast furnace slag and limestone powder on fresh and hardened properties of cementitious systems leads to the following generalizations:

Natural Pozzolan

- The water-to-cement ratio required for standard consistency of the cement pastes increased with increased pozzolan content in the blended system. This increase is smaller compared to addition of trass.

- The blended cements cause quite different setting times according to pozzolan content. In some circumstances, pozzolan content increases the setting time. This effect is increased by increasing pozzolan content level and fineness.

- In hydration process, as the proportion of pozzolan increases, CH content decreases. Also, with the addition of pozzolan, heat of hydration reduces. The compressive strength of the mortars made with blended cements decreases with the increasing pozzolan content for all tested ages.

- Usage of little amount of pozzolan in cement or concrete instead of using Portland cement reduces bleeding significantly.

- The blended cements containing large amount of natural pozzolans showed much reduced expansions when compared with the reference Portland cement.

- Natural pozzolan increases resistance to sulfate and chloride attack. On the other hand, it reduces alkali-aggegate reaction.

Blast Furnace Slag

- Blast furnace slag does not have a strong effect on water demand. However, in some conditions as the percentage of blast furnace slag replacement increases, the consistency of blended cement also increases.

- Blast furnace slag does not have a strong effect on slump, but increases pumpability.

- Blast furnace slag does not have a strong effect on bleeding.

- Blast furnace slag delays both initial and final setting times of the cement paste. Such retarding effects are characteristic of many pozzolanic reactions, and are usually negligible.

- The compressive strength increases with time independent of the slag content. However, slag concrete has lower early age and higher long term mechanical properties comparing with Portland cement concrete. However, if slag incorporation increases the water requirement of the fresh concrete, strength will consequently be lowered.

- It appears to reduce creep and has no effect on drying shrinkage.

- It increases the protection of reinforcing steel from corrosion if well cured.

- Its effect on sulfate and alkali-silica resistance depends on the content of it. The amount required is usually more than 35%.

- The resistance to carbonation decreases with increasing blast furnace slag content.

Limestone

- Increasing limestone content reduces both the rate and total amount of heat released.

- Limestone addition considerably influences some characteristics of cement like compressive strength, but this influence depends also on other factors namely clinker type and fineness. For example, lower strengths are obtained with higher $CaC0_3$ levels, the addition of at or below 5% by mass limestone into samples caused to obtain equivalent or higher compressive strengths than samples without limestone.

- Limestone decreased both setting times namely initial and final setting times, but the effect on the initial setting depended on clinker type.

- The water demand also related with its content. For instance, in limestone cements based on clinker Cl, and containing 10% limestone, there is a reduction of water demand from 26% to 24%-25%. However, the increase of the limestone content to 20% and 35% causes a decrease of the water demand to 24-22.5%. On the other hand, with using limestone at 15% in cement increases water demand.

- Drying shrinkage and carbonation depths show mixed results, in some cases being increased and in some decreased in limestone Portland cements when compared to control Portland cements. The differences are of limited practical significance in the context of overall concrete mix variations.

- The permeability to oxygen for a series of concretes was slightly reduced by the presence of limestone.

- Freeze/thaw resistance is equivalent in Portland and limestone Portland cements if the amount of entrained air or more specifically, the air void system is controlled.

- The use of limestone improves the sulfate resistance of mortars, but not to such an extent as to produce sulfate-resistant mortars.

2.6 Accelerating Admixtures

"Accelerating admixtures are added to concrete either to increase the rate of early strength development or to shorten the time of setting, or both, or reduces the quantity of the mixing water required to produce concrete of a given consistency (32)."

According to TS 3452 "Chemical Admixtures for Concrete" and ASTM C 494 "Standard Specification for Chemical Admixtures for Concrete", accelerating admixtures are divided as accelerating and water reducing-accelerating admixtures. Accelerating admixtures can be separated into two groups; water-soluble inorganic salts and water soluble organic salts (7).

- ***Water Soluble Inorganic Salts:*** In this group, there are a lot of water soluble organic salts like chlorides, bromides, carbonates, nitrates, fluorides, silicates, aluminates and alkali hydroxides. Their function is to accelerate the setting and hardening of Portland cements. Calcium chloride is the most common one which is a byproduct of the Solvay process for sodium carbonate manufacture. Calcium chloride has two forms namely solid form (flake, pellet or granular calcium chloride) and liquid form (water solutions of $CaCl_2$ in various concentrations). Despite its positive effects on the setting time, fresh concrete properties like workability and also on early compressive strength and flexural strength development, it has a tendency to promote the corrosion. Its corrosion-related problem limited its use and other alternatives which demonstrate similar properties with $CaCl_2$ without having corrosive effect are started to search.

- ***Water Soluble Organic Salts:*** Most water soluble organic salts act as retarders, but there are some exceptions. The most common ones used as accelerating admixtures are calcium formate and triethanolamine. Also, there are a lot of types for the accelerating purpose namely calcium acetate, calcium propionate, calcium butyrate and etc.

There are some studies related with the results of the relationship between alkali free and alkaline admixtures with cement.

Maltese et al. (33) studied to determine the effect of moist ageing of cement on reaction with an alkali-free accelerator. They executed many experiments at 20°C and 95% relative humidity; such as the accelerating effect of alkali free accelerators, the influence of ageing time and the amount of water absorbed by the cement. In this research, they utilized Type I cement and aluminum sulfate based alkali-free accelerator at 2% and 7% by cement mass. They observed the formation and the growth of ettringite crystals affects significantly the action mechanism of alkali-free accelerators. Ettringite (in amorphous or crystalline state) is formed immediately as a result of the reaction between Al^{3+} and SO_4^{2-} coming from the accelerator and C_3A and Ca^{2+}. There is at least 32 moles of water in each mole of ettringite. In other words, the final setting time becomes shorter when the amount of ettringite is higher. Therefore, the solid/liquid ratio and the viscosity of the cementitious system determining a setting time shortening is enhanced by the ettringite formation and water reduction. In addition, the final setting time of cement pastes containing accelerator affects the early strength of the sprayed concrete. In particular, the final setting time decreases with the increase in the early bond strength.

Paglia et al. (34) studied to investigate the influence of alkali-free and alkaline accelerators on the setting behavior of cement. They used Ordinary Portland Cement, alkali free calcium-sulfoaluminate based accelerator, alkali free sulfoaluminate based accelerator and $KAl(OH)_4$ based alkaline accelerator. According to study; the setting of cement was strongly accelerated by the alkali free accelerators because of their aluminium sulfate content which promotes the formation of ettringite prisms on the clinker surface. The acceleration in the setting of cement with the help of the alkaline accelerators was caused by the combined action of hydrates such as KCAASSH, CH and thin ettringite rods precipitated from the pore solution. The initial and final setting time decrease with the use of the alkali free and the alkaline admixtures. The shortest setting times were obtained by the addition of the alkaline admixtures. This is due to the amorphous phase KCAASSH and CH crystallization rather than the formation of ettringite rods. Also, the early hydration of C_3A and C_3S is promoted by the alkali free accelerating admixtures and the alkaline admixtures.

2.6.1 Triethanolamine

‘Triethanolamine (TEA) is one of the most common water soluble admixtures which commonly are used to offset the retarding effect of water reducing admixtures or to provide non-corrosive acceleration. TEA is produced between ammonia and ethylene oxide as illustrated in Figure 2.13 (2).

$$NH_3 + 3\overset{O}{CH_2 - CH_2} \rightarrow N\,(CH_2CH_2OH)_3 \text{ or } (N\,(C_2H_4OH)_3)$$

Figure 2.13: Formation of Triethanolamine (2)

TEA is an oily, water-soluble liquid with a fishy odor. Depending on the cement type and the addition rate, TEA can either accelerate or retard the setting. At an addition rate of 0.02% to the type I Portland cement, TEA acts as a set accelerator, at 0.25% it acts as a mild set retarder, at 0.5% TEA acts as a severe retarder, and at 1% it is a very strong accelerator (Figure 2.14) (38). Also, the fact that the dosage rate of TEA is more than 0.5% by weight of cement, leads to strength reduction (7).

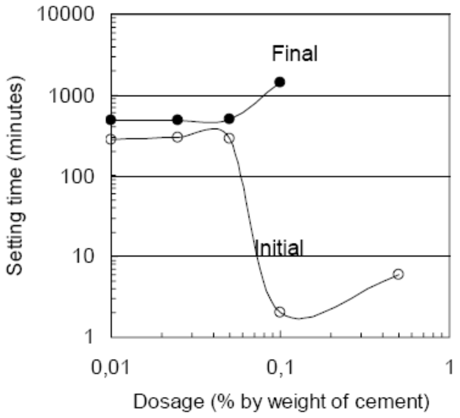


Figure 2.14: Effect of TEA Dosage on the Initial and Final Setting of OPC Mortar (38)

Hydration

"TEA is a surface active substance which is absorbed on surface of cement particles and cement hydrated products. TEA enables the solution of some metallic ion like Fe^{3+} and Al^{3+} thus increases the activity of C_4AF compound and inhibits the formation of $Fe\,(OH)_3$ and Al

$(OH)_3$ on surface of cement particle. This action can facilitate the hydration rate of silicate and aluminate phases in cement particle (37)".

Besides, TEA can also reduce to some extort the surface tension of water that enables the cement powder wetting and dissolving highly reactive cement compounds (37). The effects of TEA on cement constituents are described below.

- The Effect of TEA on C_3A Hydration (2, 41)

In the absence of gypsum, there are some differences in the effect of TEA on the hydration of C_3A. Without TEA, C_3A firstly hydrates to hexagonal aluminate hydrate before transforming to cubic form. With the use of TEA, the reactions associated with the hydration are accelerated. For example, TEA accelerates the subsequent conversion of the ettringite to monosulphate by reaction with C_3A. The C_3A hydration with 5 or 25 % gypsum, with or without 1 % TEA, shows some difference. In the absence of TEA, gypsum reacts initially to form ettringite; with TEA, the formation of ettringite is accelerated.

- The Effect of TEA on C_3S & C_2S Hydration (2, 41)

There is some evidence of the formation of some complex surface compounds on the initial hydrates of C_3S when TEA is used. TEA promotes the formation of C-S-H with a high C/S ratio and enhances the formation of non-crystalline CH. The amount of CH found at 1, 3, 7 or 28 days was in the order C_3S + 0 % TEA > C_3S + 0.1 % TEA > C_3S + 0.5 % TEA > C_3S + 1.0 % TEA, independent of the method adopted for estimation. The behavior of C_2S is similar to that of C_3S except that the reaction proceeds more slowly.

The early rate of heat of hydration curves with varying amounts of TEA as shown in Figure 2.15 indicates that hydration is somewhat retarded due to the formation of complex surface compounds as the peak of the curve is moved to the left. On the other hand, much higher heat evolution of TEA incorporated pastes indicates that TEA accelerates mainly the C_3A + gypsum hydration (2).

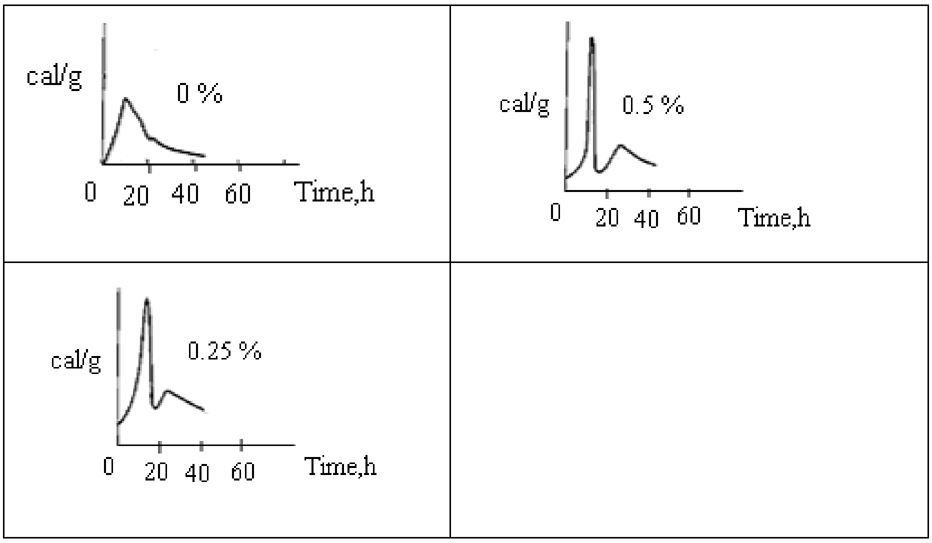


Figure 2.15: The Hydration Curves with TEA (2)

Therefore, TEA is usually not considered as a very effective accelerating agent when used alone (2). It's generally used as a secondary ingredient in some chemical admixture formulations.

Ramachandran (38) demonstrated the effects of TEA on setting and strength properties of cement. The initial setting time retards and the induction period of the hydration of C_3S slightly extends with at or below 0.05 % TEA. In addition, at 0.1 and 0.5 % TEA, however, rapid setting occurs as shown in Table 2.11. The second experiment has been made to determine compressive strength as shown in Figure 2.16.

Table 2.11: The Setting Time Changes Depending on the Different Ratio of TEA (38)

% TEA	Initial Setting Time (min)	Final Setting Time (hr)
0.000	258	8.3
0.010	282	8.1
0.025	294	8.1
0.050	288	8.4
0.100	~ 2	24
0.500	~ 6	-

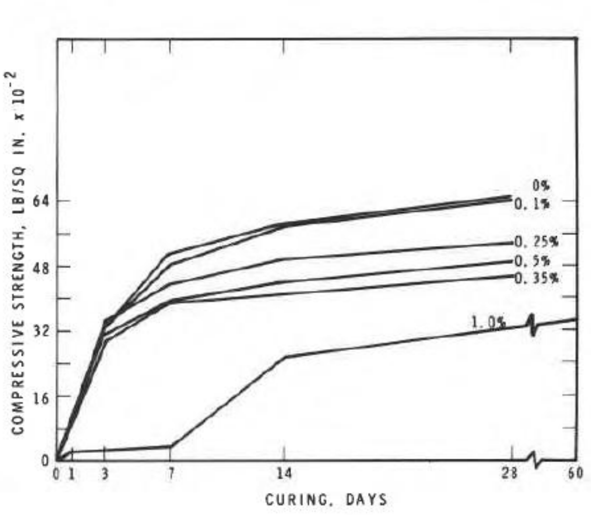


Figure 2.16: The Effect of TEA on the Compressive Strength (38)

The compressive strengths of samples when TEA used are lower at all periods comparing with that of standard specimen. In other words, the compressive strengths decrease when the amount of TEA increases. Especially, the early compressive strength decreases drastically when the sample with 1.0% TEA used. Very low amounts of TEA (<0.1%) do not significantly alter strength (38).

Quy and Lam (37) executed experiments by using limestone powder additive concrete and TEA. They concluded that TEA affects significantly both the concrete strength development and the formation of hardened Portland cement structure. Also, according to the results of the experiment, the initial set was delayed but the final set remained the same as for control sample.

In addition, the dosage rate of TEA is important from the point of strength reduction. The experiment made by using 30% Portland cement, 70% slag and 0.5% TEA, has showed that 7 day strength increased by 40% (21).

Aggoun et al. (35) investigated the effect of TEA at 0.05%, on the setting and hardening process of different cement pastes at 20°C. In this study, there were two samples containing 0.05% TEA namely M12 samples formed with C1 cement type and M22 samples prepared by using C2 cement type. Both C1 and C2 cements have similar C_3S content and fineness, but C2 has lower amount of C_3A contents than C1. Table 2.12 shows the setting times and the compressive strength values when M12 and M22 samples used. The setting time of M12 mix slightly affected with the use of 0.05% TEA with C1 types. However, it increased the compressive strength at 1 and 3 days by 50%, at 28 days by 20%. As for C2 cement, the final setting time of M22 was decreased by approximately 25% compared to control sample. In addition, the 1 and 3-day compressive strength values increased significantly by about 50%, but the 7 and 28-day compressive strength by 15, 20% respectively. According to the results; TEA was observed to be a hardening accelerator regardless of the cement type used.

Table 2.12: The Results of Experimental Setting Time and Compressive Strength (35)

Samples	Setting Times (± 10 min)		Compressive Strength (MPa)			
	Initial	*Final*	*1 day*	*3 days*	*7 days*	*28 days*
M 10 (control)	137	205	18	25	38	60
M12	150	235	28	36	45	70
M 20 (control)	188	330	11	17	35	50
M22	190	240	17	25	40	62

2.6.2 Calcium Formate

Calcium Formate (CF) is one of the most common water soluble admixtures which commonly are used to offset the retarding effect of water reducing admixtures or to provide non-corrosive acceleration.

CF is a by-product produced in the manufacture of the polyhydric alcohol. The formation is given on Figure 2.17 (2); it’s obtained as a fine powder and is supplied normally in this form as accelerating admixture because of its limited solubility in water (about 15% at normal room temperature).

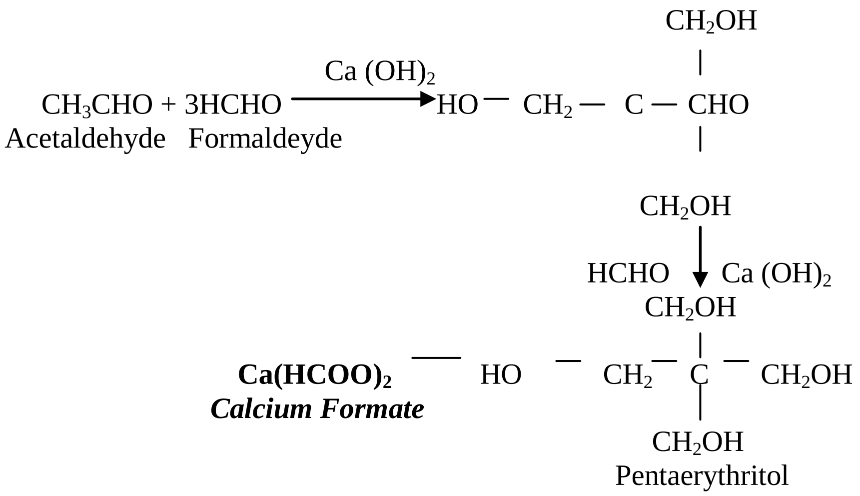


Figure 2.17: Formation of Calcium Formate (2)

Hydration

In the hydration of Portland cement, although initially larger amounts of heat are developed in the presence of CF, at later ages the heat may be slightly lower or equal to that of the reference material. The hydration of C_2S is accelerated by calcium formate (39).

At equal concentration, CF is less effective in accelerating the hydration of C_3S than calcium chloride and a higher dosage is required to impart the same level of acceleration as that imparted by $CaCl_2$ (32).

Singh and Abha (40) have reported the rate of hydration of tricalcium silicate in the presence of different amount of calcium formate (0.5-6%). Table 2.13 shows the degree of hydration obtained with different amounts of calcium formate at different times. According to that, calcium formate accelerates the tricalcium silicate hydration but beyond 2% addition, especially with respect to the effect at 24 hours, is not significant.

Table 2.13: The Degree of Hydration of Tricalcium Silicate in the Presence of CF (40)

% CF	Degree of Hydration, %			
	Time (2 hrs)	Time (4 hrs)	Time (8 hrs)	Time (24 hrs)
0	11.03	12.73	39.36	59.95
0.5	-	-	46.08	59.95
1.0	-	-	52.85	69.78
2.0	17.76	45.24	66.08	80.33
4.0	17.80	42.71	-	82.88
6.0	18.39	44.82	-	82.71

The utilization of calcium formate as an accelerating agent has been studied several times. Some of them are as follows:

According to a study of calcium formate conducted by Gebler (32), the composition of cement, in particular gypsum content had a major influence on the compressive strength development of concretes containing calcium formate. Results showed that the ratio of C_3A to $\overline{S}$ should be greater than 4 for CF to be an effective accelerating admixture; and that the optimum amount of calcium formate to accelerate the concrete compressive strength appeared to be 2-3% by weight of cement.

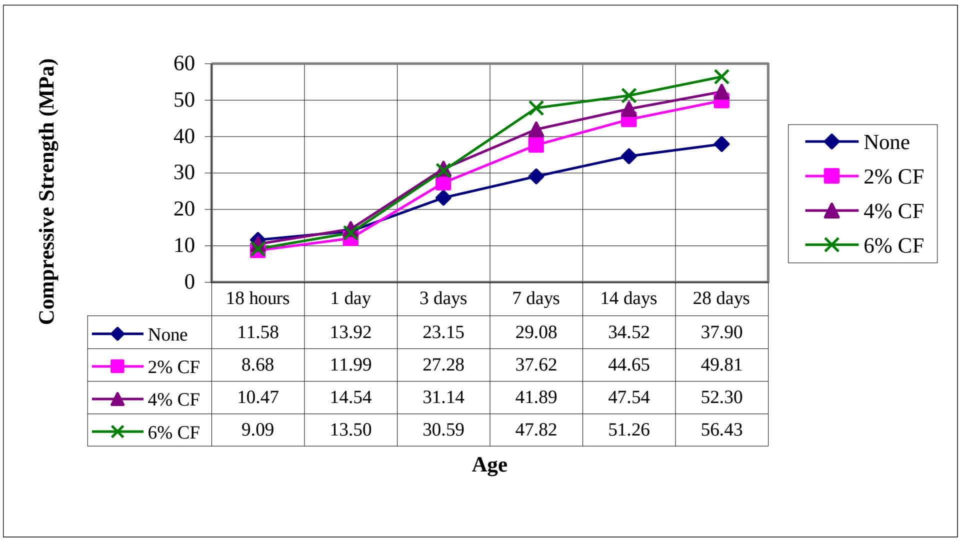
Another study about optimum amount of calcium formate was executed by Singh and Abha whose experiments have indicated that calcium formate acts as an accelerator up to 2%, but above this concentration, the excess of it has practically no effect (40).

Ramachandran (21) demonstrated that concrete setting time is accelerated with the use of calcium formate. However, to reach the same acceleration level obtained by $CaCl_2$ a higher dosage of CF is required. Table 2.14 compares the initial and final setting times of cement containing 2% $CaCl_2$ and CF. The effectiveness of CF is known to be valid for setting times at different temperatures.

Table 2.14: Setting Characteristics of Cement Containing 2% $CaCl_2$ and CF (21)

Admixture	Initial Setting Times (min)	Final Setting Times (min)
None	185	225
Calcium chloride	65	75
Calcium formate	80	90

Also, he showed that CF increases the early strength of concrete. In Figure 2.18, the results on the effect of 2% and 4% CF indicate that the strengths are increased in the first 24 hrs. At lower dosages, the strength development may not be very significant.



	18 hours	1 day	3 days	7 days	14 days	28 days
None	11.58	13.92	23.15	29.08	34.52	37.90
2% CF	8.68	11.99	27.28	37.62	44.65	49.81
4% CF	10.47	14.54	31.14	41.89	47.54	52.30
6% CF	9.09	13.50	30.59	47.82	51.26	56.43

Figure 2.18: Compressive Strengths of Mortars Containing CF (21)

Heikal (41) who made experiments related with the effects of calcium formate on Portland cement and pozzolanic cements containing 80 % Portland cement and 20 % silica fume (SF) or 20 % ground clay bricks (GCB) by mass reported that the use of CF decreased both the initial and final setting times. In addition, CF promoted the ettringite formation no matter that it's either pure C_3A or the one present in cement and increases the rate of C_3S and β-C_2S hydration reactions. Also, according to results, the compressive strength increased with the use of CF at 0, 0.25, 0.5, and 0.75% by mass because of the acceleration effect of CF. The early and later compressive strength increased and the formation of C-S-H accelerated when CF used. However, the 28-day compressive strength was not decreased and this means that there is no risk of reinforcement corrosion.

In the influence of CF on silicate phases, the diffusion rates of formate ions ($HCOO^-$) and Ca^{2+} are significant. If the diffusion rate of $HCOO^-$ is much higher than Ca^{2+} $HCOO^-$ can penetrate into the hydrated layers covering C_3S and β-C_2S gains. As a consequence, CH precipitation and calcium silicates decomposition accelerate. The C_3A content can be one of the important factors in the effect of CF on the cement paste strength, especially on the acceleration of it. The C_3A content of cement may affect the influence of CF on the cement paste strength. That is; the strength development accelerated with low C_3A content.

CHAPTER 3

EXPERIMENTAL STUDY

3.1 Materials Used in the Study

3.1.1 Cement

Three blended types of cements having similar fineness values were used in the experimental work. The amounts of mineral admixtures used to prepare these blended cements were 6, 20 and 35%. These amounts were chosen such that the resulting cements would be in accordance with the limits given in TS EN 197-1(3) for Portland pozzolan cements CEM II/A-P, CEM II/B-P; Portland slag cements CEM II/A-S, CEM II/B-S and Portland limestone cements CEM II/A-L and CEM II/B-L which contain 6-20% and 21-35% mineral admixtures, respectively. The cements were prepared in the laboratory by taking the Portland cement clinker, the pozzolan and the slag from Set Cement Ankara Factory and the limestone from Bolu Cement Factory. From here on Portland cement is named as PC, Portland-Pozzolan Cement as PPC, Portland-Blast Furnace Slag Cement as PSC and Portland-Limestone Cement as PLC.

The Portland cement used as the control cement in this investigation conforms with TS EN 197-1 CEM I 42.5N requirements. Its oxide composition, physical and mechanical properties are given in Table 3.1.

The oxide composition of cement was determined by X-Ray Fluorescence (XRF). In this analysis, ARL XRF 80-86 system was used. The concept of XRF is the emission of characteristic X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays.

The abbreviations used in the subsequent table were explained in the section of Abbreviations.

Table 3.1: Physical and Chemical Properties of the Portland cement Used

Oxide Composition, %							
S	A	F	C	M	$\bar{S}$	K	N
21.12	5.87	4.33	63.17	2.07	0.91	0.86	0.76

Physical and Mechanical Properties					
Fineness (Blaine), cm^2/g	Initial Set, min.	Final Set, min.	Compressive Strength, MPa		
			2 Days	7 Days	28 Days
3,500	271	363	20.8	30.7	37.2

3.1.2 Mineral Admixtures

In this investigation, there were three types of mineral admixtures used namely natural pozzolan, granulated blast furnace slag and limestone.

The oxide compositions of mineral admixtures were obtained by X-Ray Fluorescence (XRF) and their particle size distributions were measured by a laser particle sizer which uses dry dispersion.

The natural pozzolan used in this investigation is of volcanic origin. It is commonly named as trass. It conforms to ASTM C 618 and TS 25 (7). The granulated blast furnace slag and the limestone used in this investigation conform to TS EN 197-1 (3).

The oxide compositions & physical properties of mineral admixtures are given in Table 3.2. Also, their particle size distributions are shown in Figure 3.1. The particle size analysis revealed similar results to the Blaine’s fineness results.

From here on natural pozzolan is named as pozzolan and ground granulated blast furnace slag as slag.

Table 3.2: Oxide Composition & Physical Properties of Mineral Admixtures

Mineral Admixtures	Oxide Composition, %								Blaine	Density
	S	A	F	C	M	$\bar{S}$	K	N	(cm^2/g)	(g/cm^3)
Pozzolan	51.75	14.29	4.46	0.38	-	-	2.94	6.30	3,690	2.42
Slag	31.47	16.10	2.88	31.60	5.88	-	0.57	0.26	3,080	2.80
Limestone	11.87	3.91	1.07	45.60	1.04	-	0.20	-	3,480	2.66

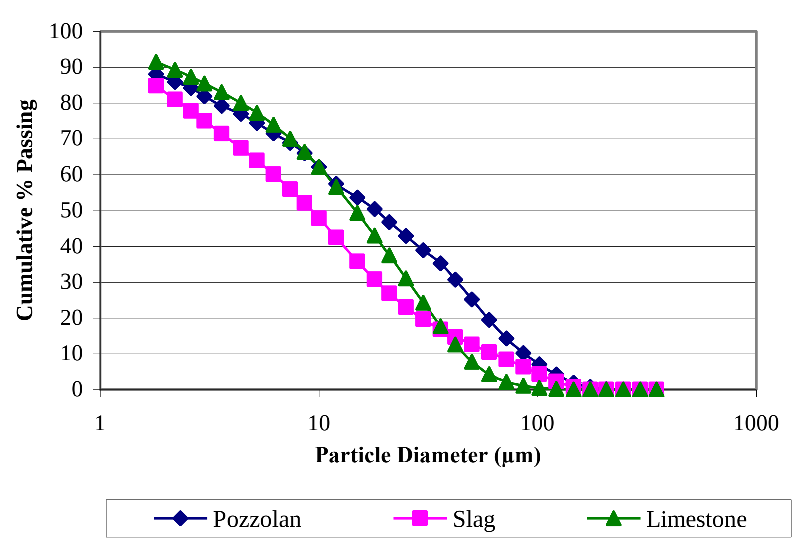


Figure 3.1: The Particle Size Distribution of Mineral Admixtures

3.1.3 Accelerating Admixtures

In these investigation two types of accelerating admixtures, namely triethanolamine (TEA) and calcium formate (CF) were used. The amounts of TEA and CF incorporated in the mixes were 0.25, 0.50, 1.00 and 1.00, 2.00, 3.00 by weight percentage of cement, respectively. These amounts were also the commonly used values given in the literature (7).

Neither TEA nor CF used in this investigation is being marketed as accelerating agents, alone. Instead, they are being used as secondary ingredients in various other commercial chemical admixtures.

In this study, both accelerating agents were added directly to the mixes prepared by dissolving them in the mixing water.

3.1.4 Water and Standard Sand

In this investigation, tap water and CEN 196-1 Standard sand conforming to TS EN 196-1 “Methods of Testing Cement-Part 1: Determination of Strength” (44) were used.

3.2 Experimental Procedure

The experimental part of this investigation consisted of three parts, namely (1) preparation of the cements through drying, grinding and blending; (2) measurement of normal consistency and setting time, and (3) preparing the mortar specimens with 110% flow and determination of compressive strength. The procedure was conducted conforming to mainly relevant ASTM standards.

3.2.1 Drying & Grinding

The mineral admixtures were dried up to 24 hours until the specimen reached a constant weight. After drying the materials were ground in a laboratory type ball mill. The fineness values of the samples were measured by Blaine method according to TS EN 196-6 “Methods of Testing Cement; Part 6: Determination of Fineness” (45).

3.2.2 Measurement of Normal Consistency and Setting Time

The normal consistency water and setting time of cement pastes were determined via Vicat method explained in ASTM C 403 “Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance” (43).

3.2.3 Flow Measurement

The measurement of flow was made by the method described in ASTM C 124 “Method of Test for Flow of Portland-Cement Concrete by Use of the Flow Table” (46). The diameter of mortar spreading at the end of experiment was measured and compared with the specified value in the standard.

3.2.4 Compressive Strength Measurement

The compressive strength measurement was carried out according to the method defined in ASTM C 109 “Standard Test Method for Compressive Strength of Hydraulic Cement Mortars” (47) which describes the procedure to determine the strength of mortar specimens that have been molded in place using special molds attached to formwork. According to ASTM C 109 (47), at least three specimens were prepared for each period of test specified.

The compressive strength determinations were made for 2, 7 and 28 days. Three specimens were used for 2 and 7-day compressive strengths and six mortar specimens were used for 28-day compressive strengths. The mortar specimens were cured in water of $23 \pm 1.7^{o}C$ in a curing room until the age of test.

CHAPTER 4

RESULTS

In this investigation, the effectiveness of accelerating admixtures with blended cements containing natural pozzolan, granulated blast furnace slag and limestone on the water demand for the normal consistency and 110% flow, initial and final setting times, 2, 7 and 28 days cube compressive strength was analyzed. From here on natural pozzolan is named pozzolan and ground granulated blast furnace slag as slag.

The Blaine fineness values of the blended cements prepared in the laboratory were calculated as the weighted average of those of mineral admixtures and that of the portland cement used. Although there are other parameters affecting the Blaine fineness such as the density and the particle shape of the powder, this approximation may lead to an overall view of the fineness of blended cements. The estimated Blaine fineness values of the cements are given in Table 4.1.

Table 4.1: Estimated Fineness Values of the Blended Cements

Amount of Mineral Admixtures, %	Fineness of Pozzolan, cm^2/g	Fineness of Slag, cm^2/g	Fineness of Limestone, cm^2/g
0	3,500	3,500	3,500
6	3,511	3,475	3,499
20	3,538	3,416	3,496
35	3,567	3,353	3,493

The normal consistency water (NCW) by volume was calculated based on the densities of mineral admixtures and PC as shown in Tables 4.2-4.5 respectively.

Table 4.2: Normal Consistency Water of PC and Mineral Admixture Incorporated Cements (by volume).

Amount of Mineral Admixture, %	Water Demand by Volume for Different Mineral Admixtures		
	Pozzolan	*Slag*	*Limestone*
0	0.816	0.816	0.816
6	0.806	0.813	0.808
20	0.790	0.810	0.797
35	0.774	0.807	0.787

Table 4.3: Normal Consistency Water of PPC (by volume)

Type of Accelerating Agents	Amount of Accelerating Agents,%	Water Demand by Volume for Different Pozzolan Contents			
		0%	6%	20%	35%
TEA	0.00	0.816	0.806	0.790	0.774
	0.25	0.816	0.816	0.800	0.786
	0.50	0.816	0.820	0.804	0.788
	1.00	0.829	0.825	0.808	0.791
CF	1.00	0.820	0.811	0.794	0.778
	2.00	0.834	0.815	0.796	0.782
	3.00	0.848	0.819	0.801	0.787

Table 4.4: Normal Consistency Water of PSC (by volume)

Type of Accelerating Agents	Amount of Accelerating Agents,%	Water Demand by Volume for Different Slag Contents			
		0%	6%	20%	35%
TEA	0.00	0.816	0.813	0.810	0.807
	0.25	0.816	0.817	0.814	0.811
	0.50	0.816	0.821	0.818	0.813
	1.00	0.829	0.824	0.821	0.815
CF	1.00	0.820	0.817	0.814	0.810
	2.00	0.834	0.821	0.818	0.812
	3.00	0.848	0.825	0.823	0.820

Table 4.5: Normal Consistency Water of PLC (by volume)

Type of Accelerating Agents	Amount of Accelerating Agents,%	Water Demand by Volume for Different Limestone Contents			
		0%	6%	20%	35%
TEA	0.00	0.816	0.808	0.797	0.787
	0.25	0.816	0.809	0.801	0.806
	0.50	0.816	0.817	0.806	0.823
	1.00	0.829	0.826	0.811	0.842
CF	1.00	0.820	0.813	0.802	0.808
	2.00	0.834	0.817	0.807	0.830
	3.00	0.848	0.822	0.812	0.854

Also, Tables 4.6-4.9 demonstrate the water demand by volume for 110% flow of PC, PPC, PSC and PLC respectively.

Table 4.6: Water Demand for 110% Flow of PC and Mineral Admixture Incorporated Cements (by volume)

Amount of Mineral Admixture, %	Water Demand by Volume for Different Mineral Admixtures		
	Pozzolan	*Slag*	*Limestone*
0	1.662	1.662	1.662
6	1.637	1.676	1.710
20	1.600	1.660	1.815
35	1.566	1.644	1.890

Table 4.7: Water Demand for 110% Flow of PPC (by volume)

Type of Accelerating Agents	Amount of Accelerating Agents,%	Water Demand by Volume for Different Pozzolan Contents			
		0%	6%	20%	35%
TEA	0.00	1.660	1.637	1.600	1.566
	0.25	1.710	1.636	1.605	1.572
	0.50	1.720	1.647	1.611	1.577
	1.00	1.730	1.654	1.619	1.583
CF	1.00	1.690	1.644	1.614	1.590
	2.00	1.690	1.648	1.619	1.595
	3.00	1.700	1.652	1.622	1.601

Table 4.8: Water Demand for 110% Flow of PSC (by volume)

Type of Accelerating Agents	Amount of Accelerating Agents,%	Water Demand by Volume for Different Slag Contents			
		0%	6%	20%	35%
TEA	0.00	1.660	1.676	1.660	1.644
	0.25	1.710	1.681	1.666	1.649
	0.50	1.720	1.687	1.671	1.655
	1.00	1.730	1.692	1.677	1.661
CF	1.00	1.690	1.681	1.665	1.640
	2.00	1.690	1.695	1.670	1.645
	3.00	1.700	1.700	1.675	1.650

Table 4.9: Water Demand for 110% Flow of PLC (by volume)

Type of Accelerating Agents	Amount of Accelerating Agents,%	Water Demand by Volume for Different Limestone Contents			
		0%	6%	20%	35%
TEA	0.00	1.660	1.710	1.815	1.890
	0.25	1.710	1.714	1.821	1.894
	0.50	1.720	1.717	1.824	1.897
	1.00	1.730	1.721	1.827	1.900
CF	1.00	1.690	1.713	1.817	1.892
	2.00	1.690	1.715	1.819	1.894
	3.00	1.700	1.717	1.821	1.896

CHAPTER 5

DISCUSSION OF RESULTS

In this study, all accelerating and mineral admixtures were added in specified amounts to find out the effectiveness of accelerating agents when used with TS EN 197-1 CEM II cements. The comparison of the effects of accelerating admixtures on nine different blended cements with each other and the control Portland cement was thus made possible.

5.1 Water Demand

The effects of mineral admixtures on the water demand change depending on their type and amounts. Normal consistency water (NCW) increases by the use of mineral admixtures similarly as many studies reported previsously (16, 22, 25).This is illustrated in Figures 5.1 and 5.2. The increase in NCW is linearly proportional with the amount of mineral admixture used, as shown in Figure 5.3.

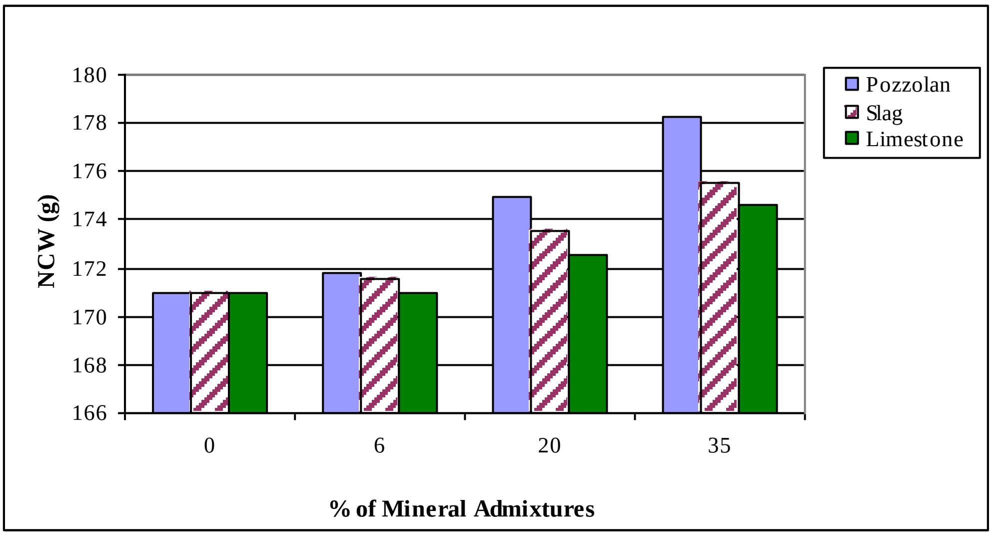


Figure 5.1: Effect of Different Mineral Admixtures on NCW Requirement as weight

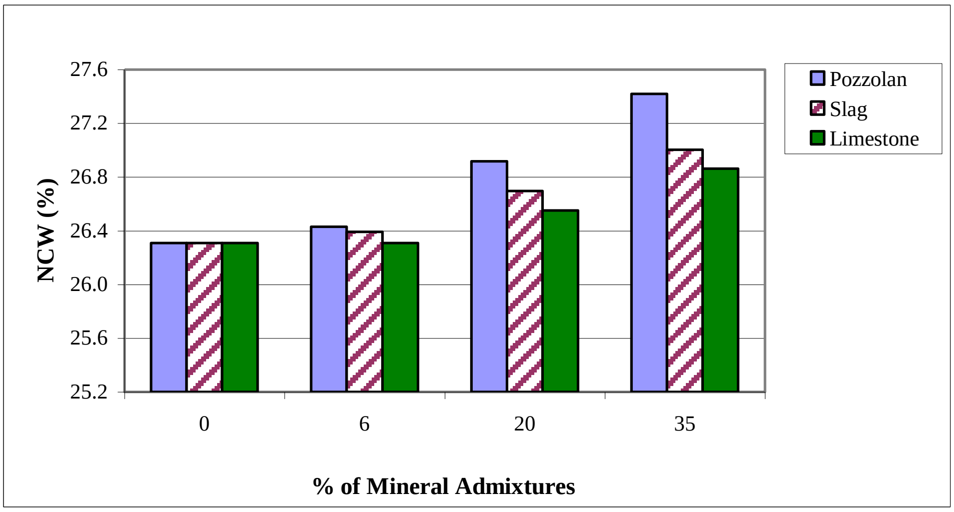


Figure 5.2: Effect of Different Mineral Admixtures on NCW Requirement as Percentage

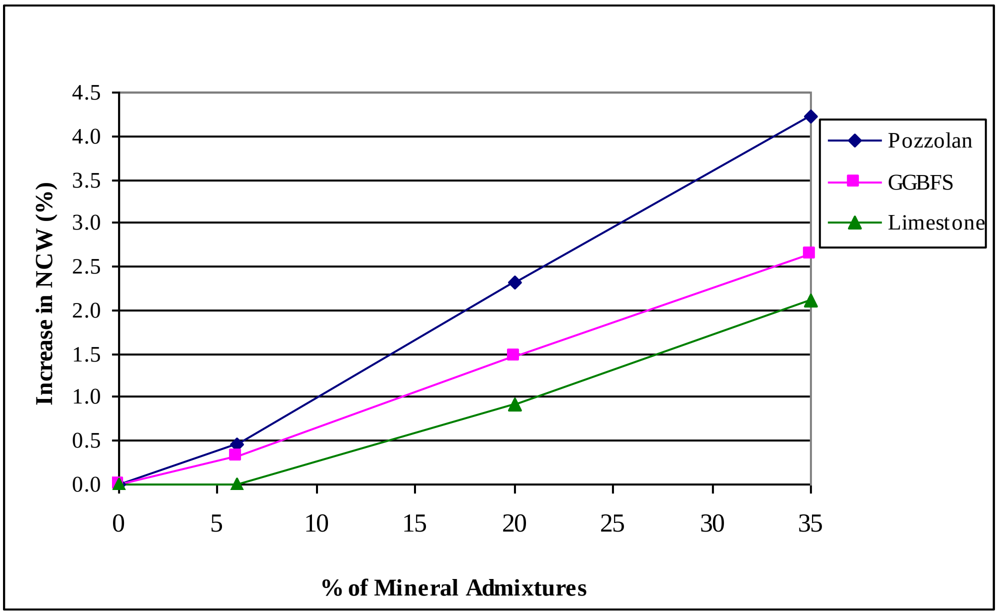


Figure 5.3: Effect of Different Mineral Admixtures on the Increase in NCW

Volume of the binder was calculated as the weighted average of the Portland cement and the mineral admixtures used in the experiment. In Figures 5.1-5.3, the relationship between normal consistency water (NCW) and amount of mineral admixture used is based on the weight of the paste samples prepared. However, due to the differences of the densities of the Portland cement and the mineral admixtures used, volume based calculations lead to another point of view: Considering the volume of the pastes and calculating normal consistency water requirement on volumetric basis, it is observed that water requirement decreases with the use of mineral admixtures as shown in Figure 5.4.

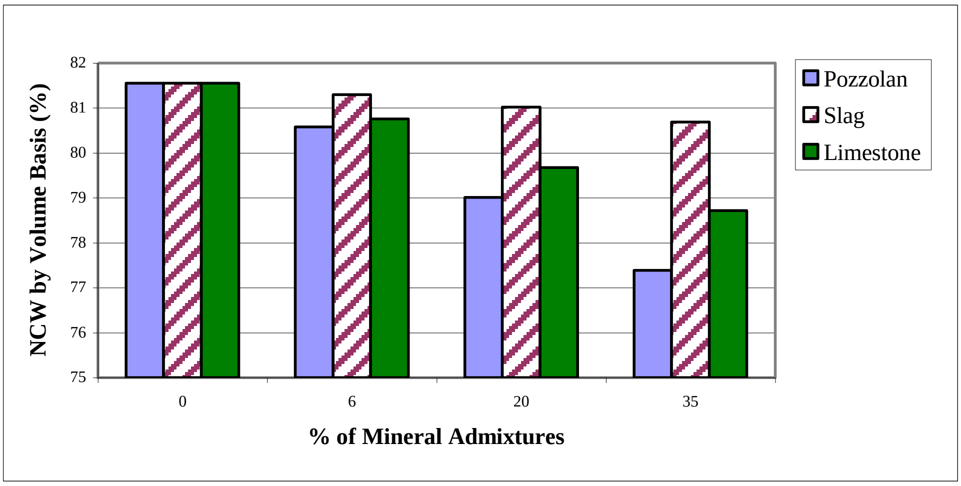


Figure 5.4: Effect of Different Mineral Admixtures on NCW by volume basis

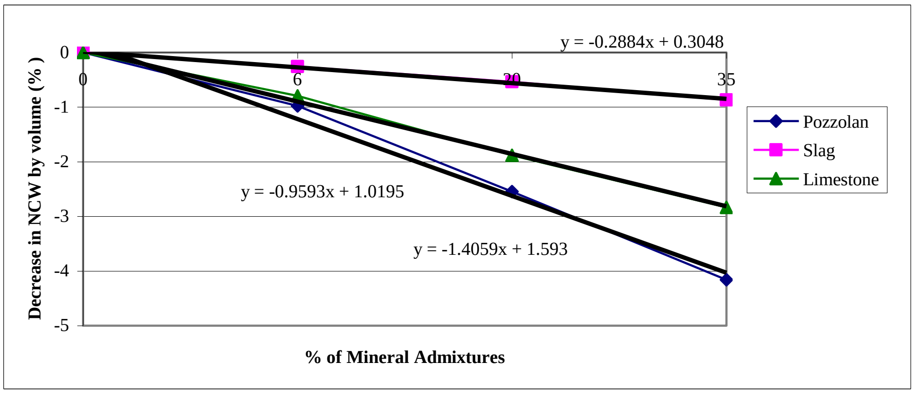


Figure 5.5: Effect of Mineral Admixtures on the Decrease in NCW by volume basis

As the amount of mineral admixture used increases, water reduction increases too. There is a linear relationship between the amount of mineral admixture used and the reduction in normal consistency water requirement as shown in Figure 5.5. Pozzolan has the largest water reduction effect whereas slag has the smallest.

Furthermore, the fineness values of the cement and the mineral admixtures used were slightly different from each other. For a specified consistency, as the fineness of the binder increases, also the water requirement increases since the specific surface area to be wetted increases. Therefore, the increase in normal consistency water (on weight basis) is not only related with the amount of mineral admixtures used but also with the fineness of the binder prepared. Calculating the fineness of each binder specimen prepared as the weighted average of the fineness values of the Portland cement and the mineral admixtures, linear relationships between the fineness of the binder and the normal consistency water requirement were determined. Among these mineral admixtures used in the study, pozzolan was the finest (3,690 cm^2/g) and slag was the coarsest (3,080 cm^2/g). Limestone and the Portland cement had almost the same fineness values (3,480 and 3,500 cm^2/g, respectively). This is shown in Figure 5.6.

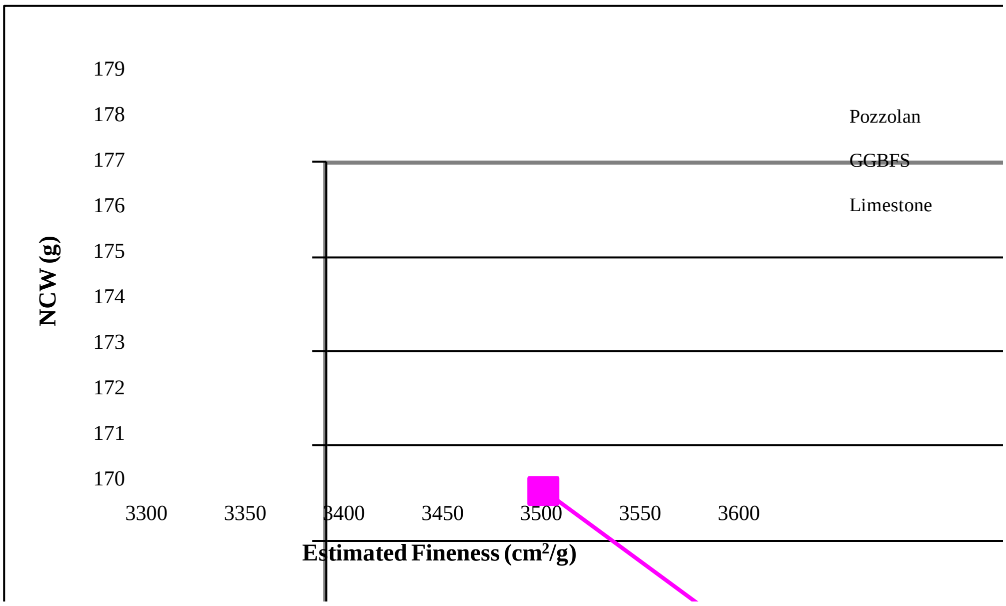


Figure 5.6: Effect of Fineness on Normal Consistency Water

The effects of accelerating agents change according to cement types. For PPC, the normal consistency water (NCW) on weight basis increases by the increase in the amount of the accelerating agents as shown in Table 5.1. Among them, the highest increase in the normal consistency water was obtained with the use of PPC containing 35% pozzolan and 3% CF.

Table 5.1: Normal Consistency Water of PPC

Type of Accelerating Admixtures	Amount of Accelerating Admixtures, %	NCW of PPC for Different Pozzolan Contents, gr			
		0 %	6 %	20 %	35 %
TEA	0.00	171.0	171.8	175.0	178.2
	0.25	171.0	174.0	177.1	181.0
	0.50	171.0	174.8	178.1	181.5
	1.00	173.8	175.9	179.0	185.2
CF	1.00	172.0	172.9	175.9	178.2
	2.00	175.0	173.8	176.3	179.2
	3.00	177.9	174.7	177.3	180.1

The normal consistency water (NCW) on volumetric basis increases by increasing the content of accelerating agents regardless of their type as shown in Figures 5.7 and 5.8.

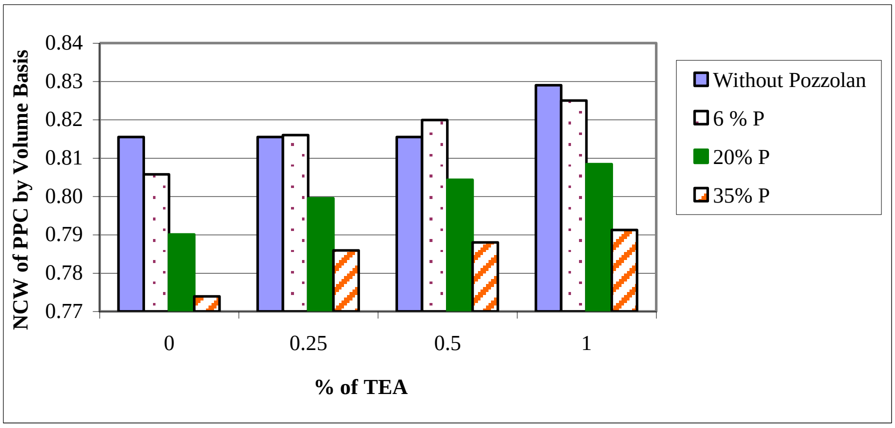


Figure 5.7: NCW of PPC on Volumetric Basis Depending on TEA content

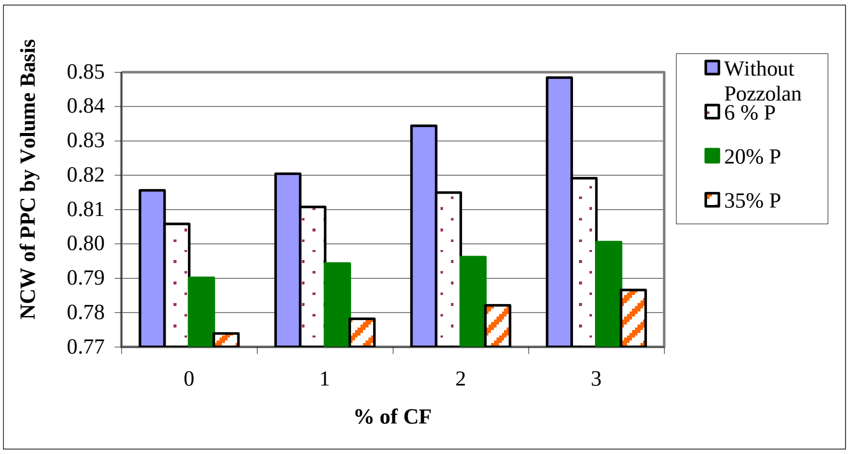


Figure 5.8: NCW of PPC on Volumetric Basis Depending on CF content

The increase in the normal consistency water (NCW) by weight is linearly proportional with the amount of CF used whereas in the case of TEA there is a logarithmic relationship between NCW and the amount of accelerating admixtures, as demonstrated in Figures 5.9-5.11. This shows that by using CF, the normal consistency water will increase more comparing with the use of TEA.

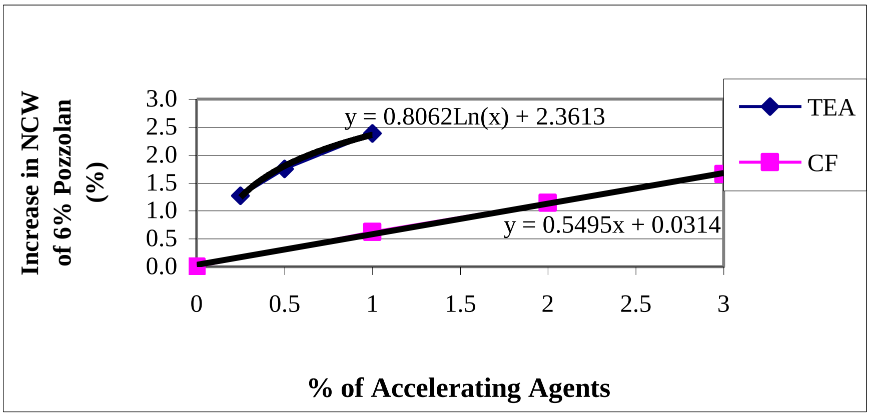


Figure 5.9: Effect of TEA and CF on the Increase in NCW of PPC Containing 6% Pozzolan

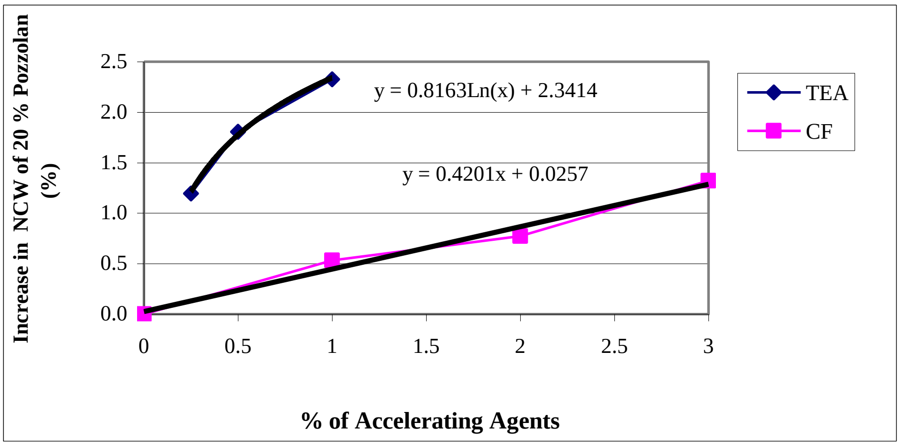


Figure 5.10:Effect of TEA and CF on the Increase in NCW of PPC Containing 20%Pozzolan

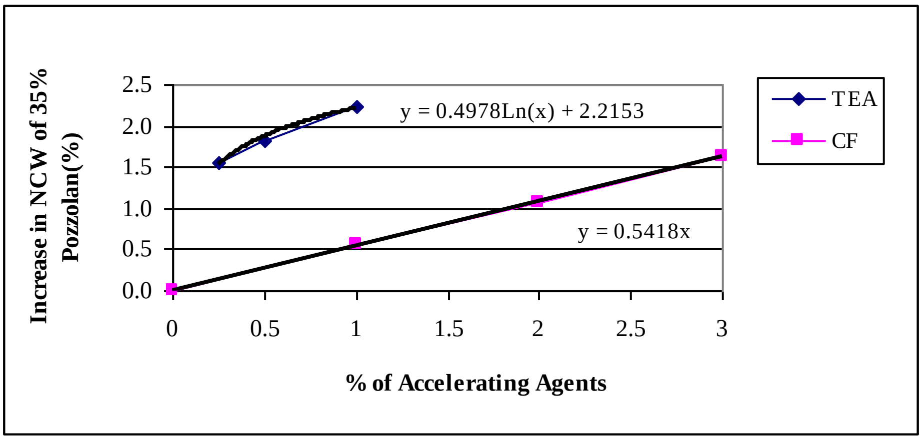


Figure 5.11:Effect of TEA and CF on the Increase in NCW of PPC Containing 35%Pozzolan

As for PSC, the effects of TEA and CF on the normal consistency water of PSC containing different amounts of slag are given in Table 5.2. The highest increase in the normal consistency water was obtained with the use of PSC containing 35% slag and 3% CF.

However, the normal consistency water of PSC based on volume of the samples increases with the amount of accelerating agents as in the case of pozzolan as shown in Figures 5.12 and 5.13.

Table 5.2: Normal Consistency Water of PSC

Type of Accelerating Admixtures	Amount of Accelerating Admixtures, %	NCW of PSC for Different Slag Contents, gr			
		0 %	6 %	20 %	35 %
TEA	0.00	171.0	171.6	173.5	175.5
	0.25	171.0	172.3	174.3	176.4
	0.50	171.0	173.2	175.1	176.9
	1.00	173.8	174.0	175.9	177.3
CF	1.00	172.0	172.4	174.3	176.1
	2.00	175.0	173.2	175.2	176.7
	3.00	177.9	174.2	176.2	178.3

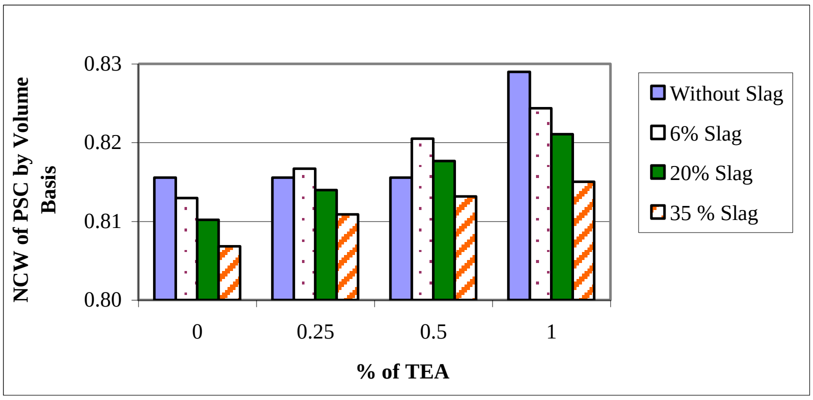


Figure 5.12: NCW of PSC on Volumetric Basis Depending on TEA content

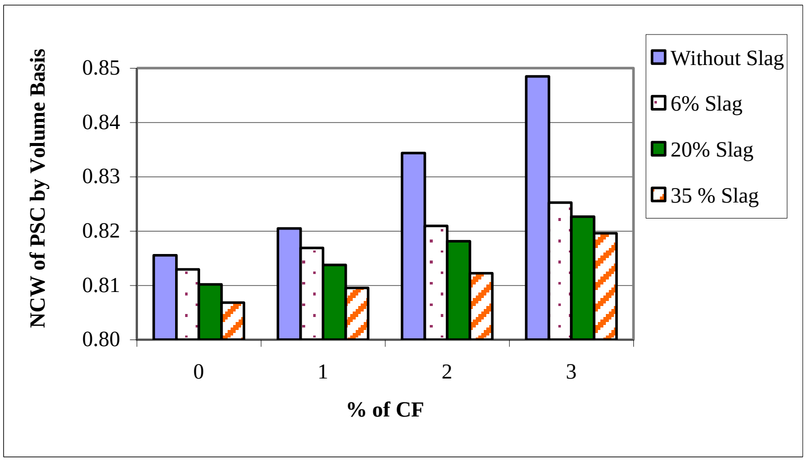


Figure 5.13: NCW of PSC on Volumetric Basis Depending on CF content

The relationship between the increase in normal consistency water of PSC and the use of CF and TEA in the investigation depends on the amount of slag used. At 6 and 20% slag incorporated cements, the increase in the normal consistency water is linearly proportional with the amount of CF, and there is a logarithmic relationship between the normal consistency water and the amount of TEA, as demonstrated in Figures 5.14-5.16.

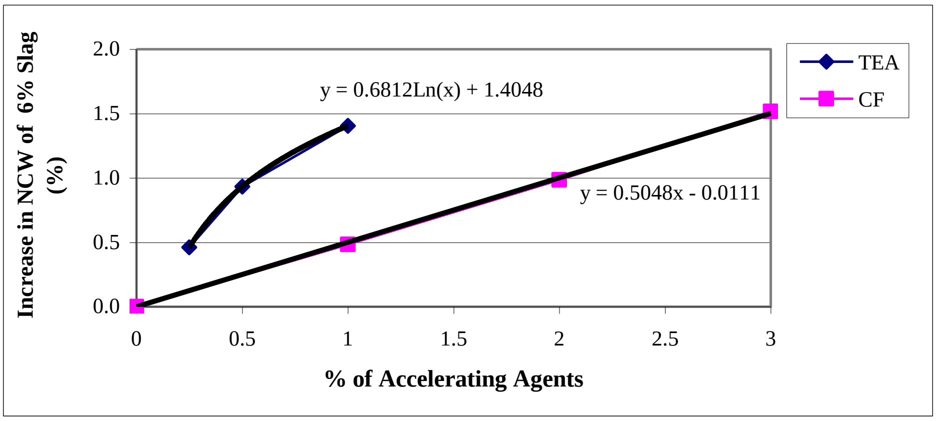


Figure 5.14: Effect of TEA and CF on the Increase in NCW of PSC containing 6% Slag

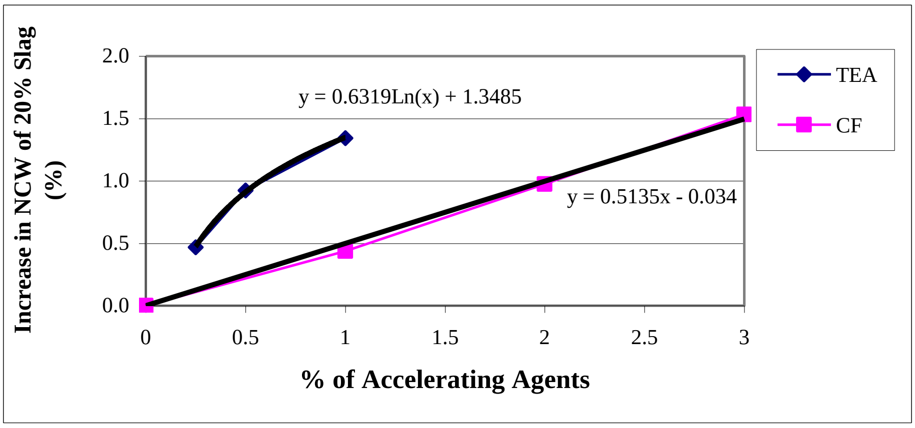


Figure 5.15: Effect of TEA and CF on the Increase in NCW of PSC containing 20% Slag

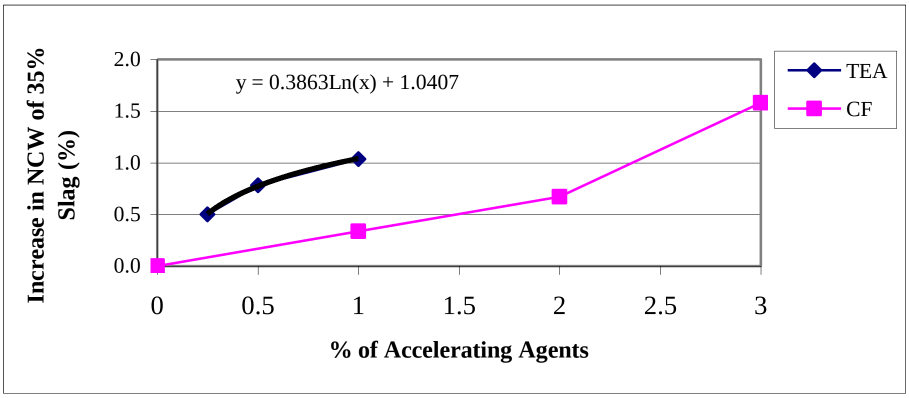


Figure 5.16: Effect of TEA &CF on the Increase in NCW of PSC containing 35% Slag

Regarding with PLC, the normal consistency water increases by increasing the contents of accelerating agents as shown in Table 5.3. The highest increase in the normal consistency water is seen in the use of PLC containing 35% limestone and 3% CF.

Table 5.3: Normal Consistency Water of PLC

Type of Accelerating Admixtures	Amount of Accelerating Admixtures, %	NCW of PLC for Different Limestone Contents, gr			
		0 %	6 %	20 %	35 %
TEA	0.00	171.0	171.0	172.6	174.6
	0.25	171.0	171.4	173.5	178.7
	0.50	171.0	173.0	174.6	172.6
	1.00	173.8	174.8	175.8	176.8
CF	1.00	172.0	172.2	173.8	179.2
	2.00	175.0	173.0	174.9	184.0
	3.00	177.9	174.2	176.0	189.5

On the other hand, the volumetric basis water requirement decreases up to limestone content of 20%, but between the range of 20 and 35% limestone incorporated cements, it increases with the amount of limestone as shown in Figures 5.17 and 5.18.

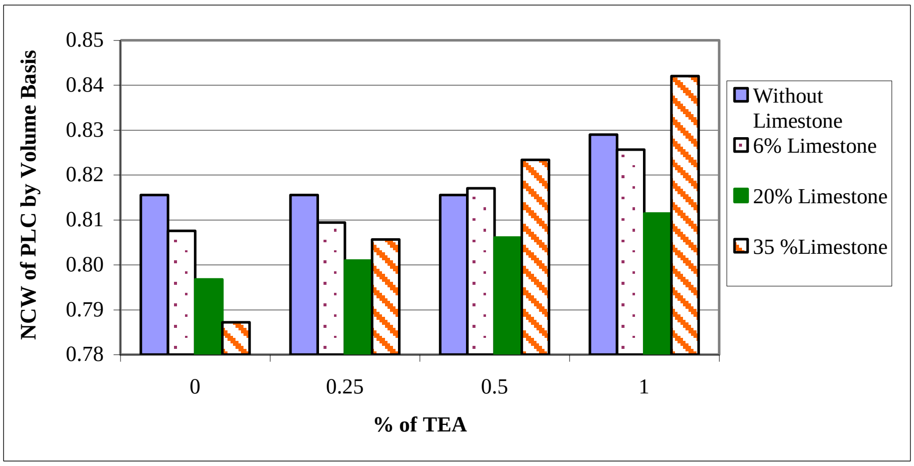


Figure 5.17: NCW of PLC on Volumetric Basis Depending on TEA content

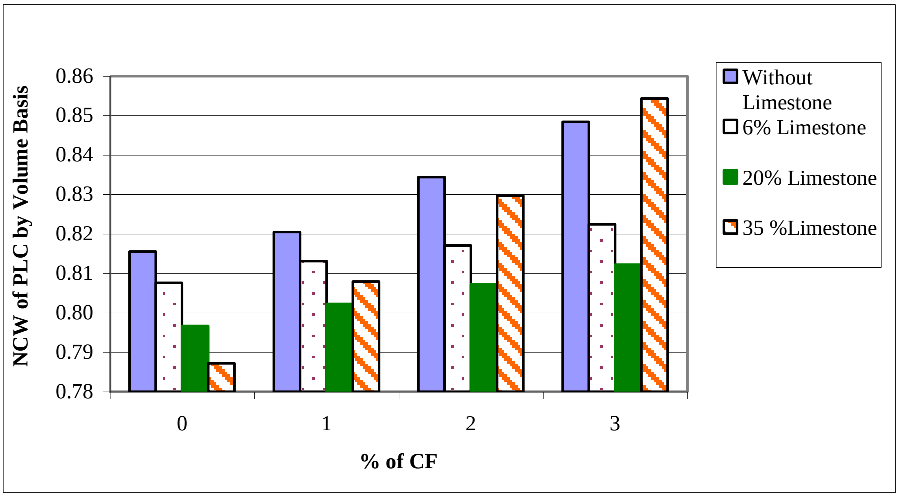


Figure 5.18: NCW of PLC on Volumetric Basis Depending on CF content

Figures 5.19-5.21 show the formulas related with the effectiveness of accelerating agents depending on the effect of PLC on the normal consistency. According to these figures, in the case of CF, the normal consistency water increase is linearly proportional with the amount of accelerating admixtures used, on the other hand in the use of TEA there is a logarithmic relationship between the normal consistency water and the amount of TEA.

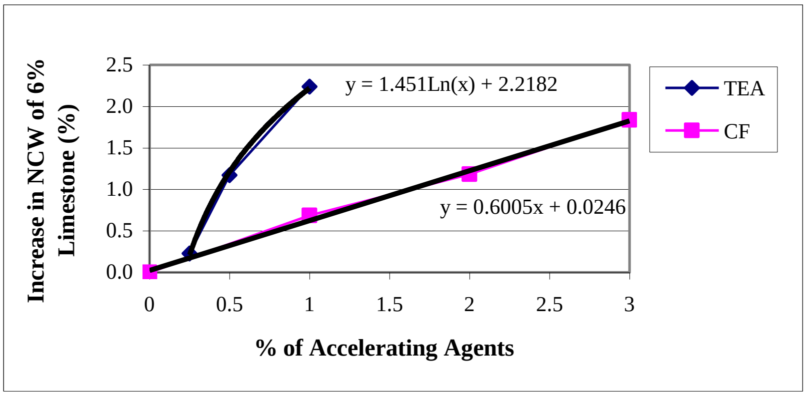


Figure 5.19:Effect of TEA and CF on the Increase in NCW of PLC containing 6%Limestone

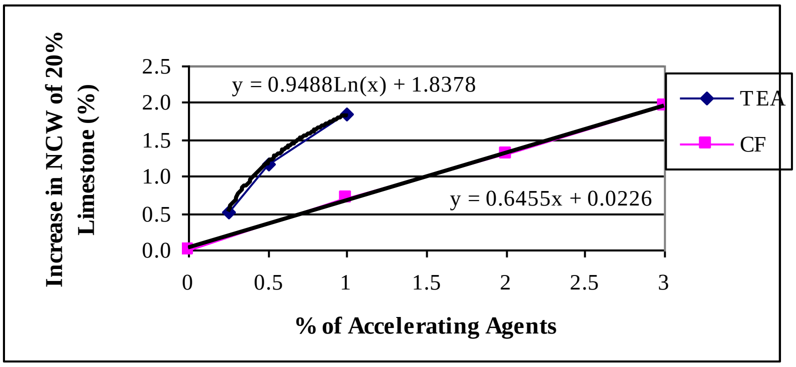


Figure 5.20:Effect of TEA and CF on the Increase in NCW of PLC containing 20%Limestone

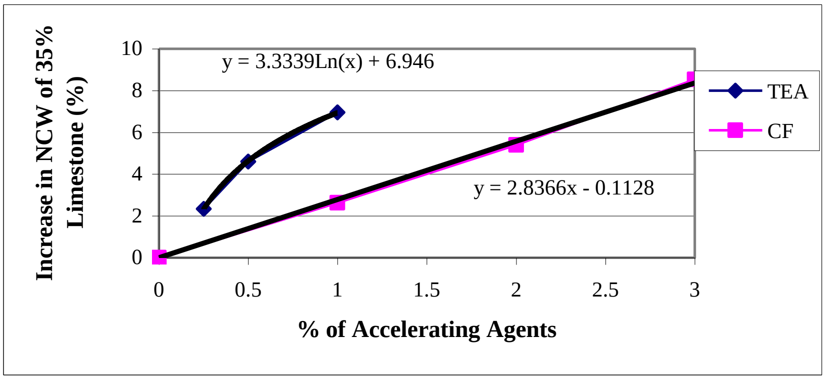


Figure 5.21: Effect of TEA and CF on the Increase in NCW of PLC containing 35% Limestone

5.2 Setting Time

In analyzing the setting times, it can be stated that besides the water content of the pastes, the fineness, type and amount of mineral admixtures used and type and dosage of accelerating agents are main parameters.

The initial and final setting times of PC (Portland Cement), PPC (Portland-Pozzolan Cement), PSC (Portland-Slag Cement) and PLC (Portland-Limestone Cement) are given in Tables 5.4-5.7.

Table 5.4: The Final and Initial Setting Times of PC

Accelerating Agents	Amount of Accelerating Agents, %	Final Setting Time, min	Initial Setting Time, min
TEA	0.00	363	271
	0.25	337	242
	0.50	340	198
	1.00	309	189
CF	1.00	328	213
	2.00	220	162
	3.00	124	75

Table 5.5: The Final and Initial Setting Times of PPC

Acc. Agents	Amount of Accelerating Agents, %	Final Setting Time, min				Initial Setting Time, min			
		Amount of Pozzolan, %				Amount of Pozzolan, %			
		0 %	6 %	20 %	35 %	0 %	6 %	20 %	35 %
TEA	0.00	363	270	255	263	271	173	189	225
	0.25	337	252	250	383	242	119	117	240
	0.50	340	228	207	387	198	94	67	322
	1.00	309	99	148	364	189	24	47	225
CF	1.00	328	266	221	222	213	206	165	166
	2.00	220	203	179	230	162	150	143	153
	3.00	124	137	145	195	75	98	95	126

Table 5.6: The Final and Initial Setting Times of PSC

Acc. Agents	Amount of Accelerating Agents, %	Final Setting Time, min				Initial Setting Time, min			
		Amount of Slag, %				Amount of Slag, %			
		0 %	6 %	20 %	35 %	0 %	6 %	20 %	35 %
TEA	0.00	363	308	294	289	271	242	206	214
	0.25	337	254	252	357	242	169	154	247
	0.50	340	254	265	394	198	161	149	332
	1.00	309	212	214	328	189	120	127	248
CF	1.00	328	245	202	258	213	179	162	169
	2.00	220	199	196	232	162	145	150	130
	3.00	124	141	148	179	75	80	100	78

Table 5.7: The Final and Initial Setting Times of PLC

Acc. Agents	Amount of Accelerating Agents, %	Final Setting Time, min				Initial Setting Time, min			
		Amount of Limestone, %				Amount of Limestone, %			
		0 %	6 %	20 %	35 %	0 %	6 %	20 %	35 %
TEA	0.00	363	243	245	197	271	149	84	86
	0.25	337	205	205	174	242	108	45	83
	0.50	340	210	198	163	198	100	52	49
	1.00	309	185	157	144	189	53	51	52
CF	1.00	328	202	170	160	213	138	52	100
	2.00	220	154	115	124	162	77	52	71
	3.00	124	117	97	95	75	50	20	55

The reduction in setting time increases with the use of mineral admixtures regardless of their type. Thus, the setting times of all mineral admixture incorporated pastes are shorter than those of control Portland cement paste. For PPC, according to pozzolan content, different setting times were obtained as shown in Figure 5.22. Upon using 6% by weight pozzolan, there occurs a drastic decrease in the setting times when compared with the control paste. Although the setting times of 20 and 35% pozzolan incorporated paste are still shorter than those of PC, they are longer than those of 6% pozzolan incorporated paste. The use of minimum amount of pozzolan which is finer than PC results in more rapid early hydration since the pozzolan particles behave as nuclei for the hydration process (42).

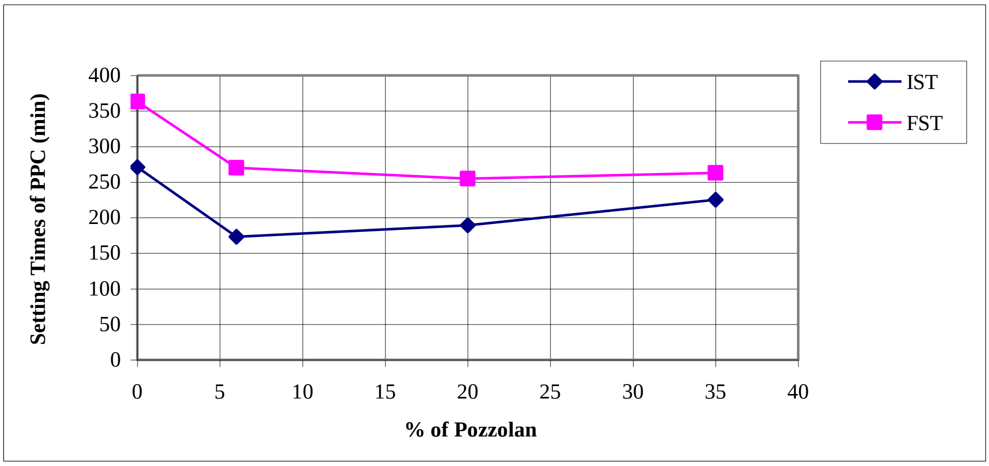


Figure 5.22: Effect of Pozzolan Content on the Setting Times

Considering the water requirement for the normal consistency on volumetric basis, increasing pozzolan content results in reduced water amount as mentioned before. This is most probably the reason why the setting times of pozzolan incorporated cements are shorter as shown in Figure 5.23.

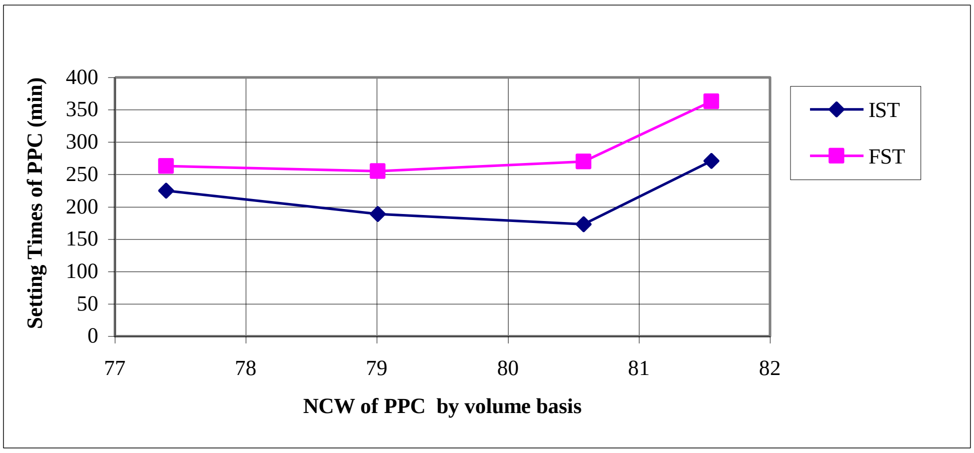


Figure 5.23: The Relationship between NCW and Setting Times of PPC

The reduction in the setting times increases with the increase in slag and limestone contents as shown in Figures 5.24 and 5.25. This result is in consistence with Vuk et.al. study (30).

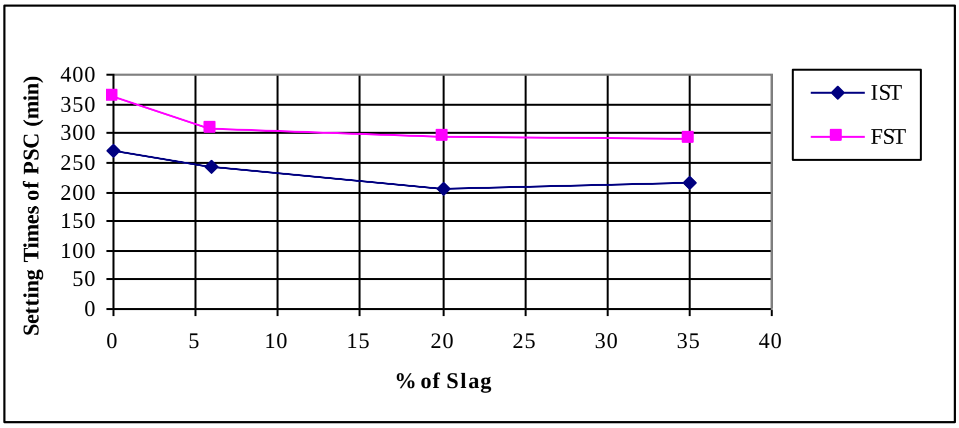


Figure 5.24: Effect of Slag Content on the Setting Times

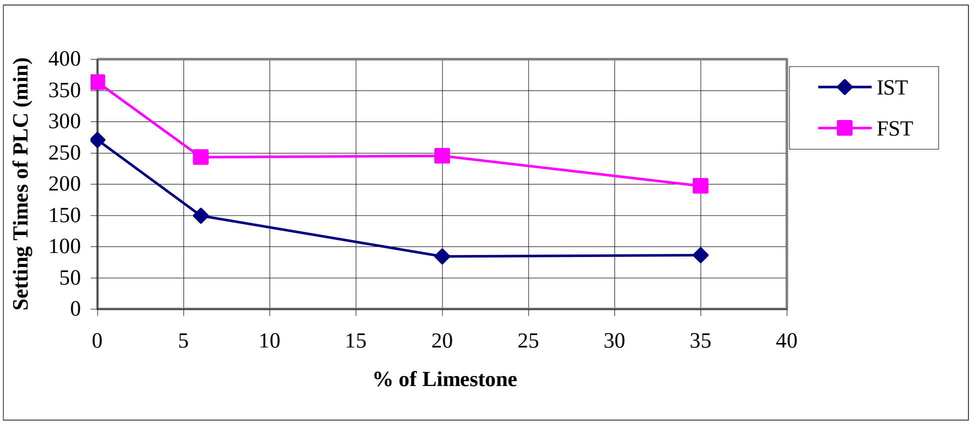


Figure 5.25: Effect of Limestone Content on the Setting Times

There are not any drastic decreases in the setting times with the use of PSC type comparing with PPC type as plotted in Figure 5.24. On the other hand, the limestone affects the setting times similarly comparing with the pozzolan as shown in Figure 5.25 because upon using limestone, the initial and final setting time reduce significantly especially at 6% incorporated limestone pastes.

From the point of the normal consistency water requirement by volumetric basis, increasing slag and limestone contents result in reduced water amount as mentioned before. However, the decreases in PSC and PLC are not high comparing with that in PPC. Figures 5.26 and 5.27 illustrate the relationship between the water demand by volume and the setting times of PSC and PLC types. This can be the reason for the differences among the setting times of PPC, PLC and PSC.

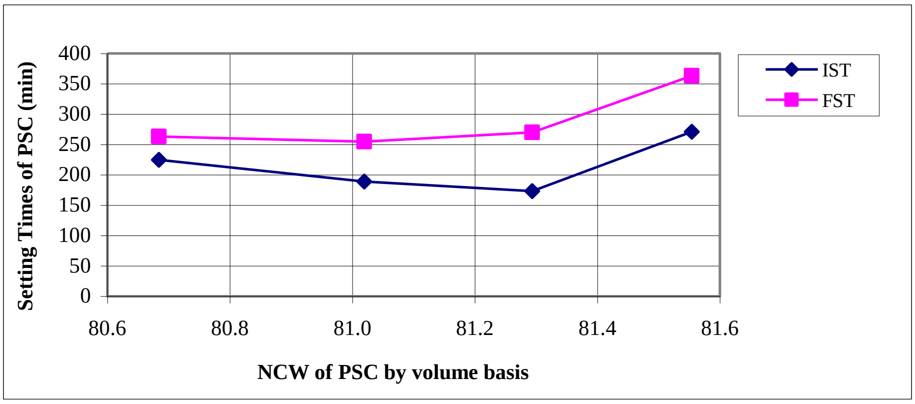


Figure 5.26: The Relationship between NCW and Setting Times of PSC

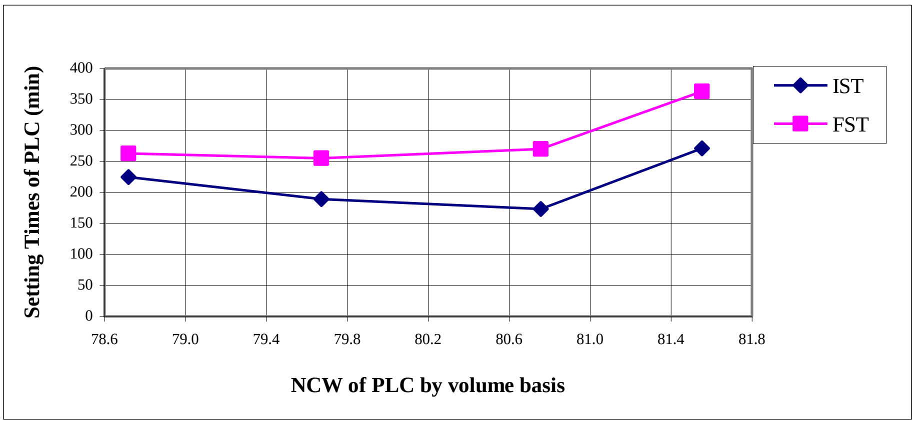


Figure 5.27: The Relationship between NCW and Setting Times of PLC

Among these mineral admixtures used in the investigation, the highest reduction in setting time occurs when limestone is used. Pozzolan comes as the second, and slag as third.

In this investigation, the fineness values of the mineral admixtures used were 3,600 cm^2/g, 3,480 cm^2/g and 3,080 cm^2/g for pozzolan, limestone and slag, respectively. Pozzolan and limestone have more or less the same fineness as the Portland cement. However, slag is considerably coarser when compared with the other mineral admixtures used. Since the fineness of the cementititous material is a major parameter affecting setting time due to the surface area available for hydration reactions, the setting times of slag incorporated pastes were longer than the other two mineral admixtures incorporated pastes.

As expected, accelerating agents regardless of their type decrease setting time (21, 38), but the decrease amount depends on some factors such as the water demand by volume and type and dosage of accelerating agents and mineral admixtures. Water requirement for normal consistency increases with the amount of accelerating agent used regardless of the type of cement.

Figure 5.28 shows the effect of accelerating admixtures on the normal consistency water of PC. The relationship between the increase in water requirement and accelerating agent content is a polynomial with the use of TEA, but there is a linear relationship between them when CF used.

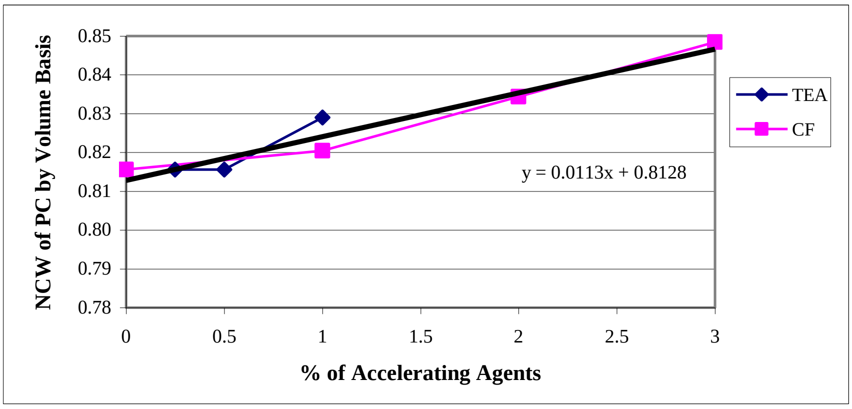


Figure 5.28: The Effects of Accelerating Agents on NCW of PC by Volume

For all types of cement, the maximum dosage of either accelerating agent leads to approximately the same increase in water demand on volumetric basis as shown in Tables 4.2-4.5. Although the water requirement increases with the use of TEA, the use of mineral admixtures reduces the water requirement by volume basis. Therefore, when interpreting the results of the water demand and setting time, the net effect of accelerating agents and mineral admixtures must be considered simultaneously.

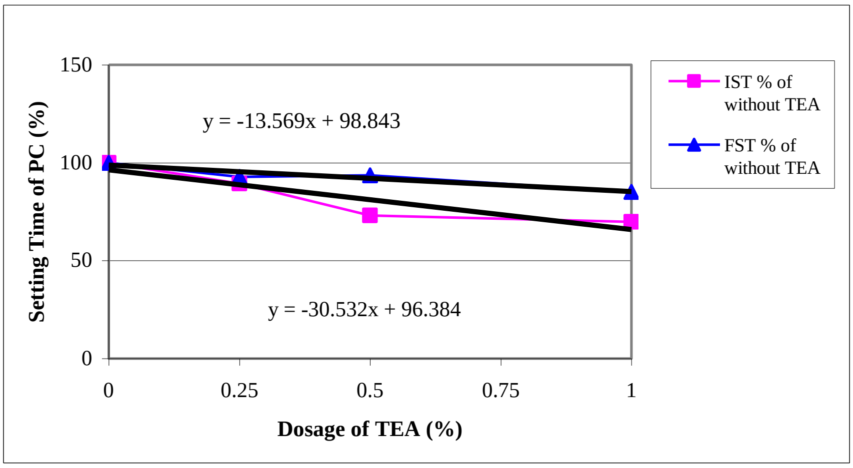


Figure 5.29: The Effect of TEA on Setting Time of PC

Both initial and final setting times of PC reduce linearly as the amount of TEA increases as shown in Figure 5.29.

According to Figures 5.30-5.32; similar relationship holds true for 6% and 20% pozzolan incorporated cements. However, no reasonable correlation between TEA content and the setting time was observed for 35% pozzolan incorporated paste. For both 6 and 20% pozzolan incorporated cements, the rates of reduction in setting times upon using TEA are higher than those of PC.

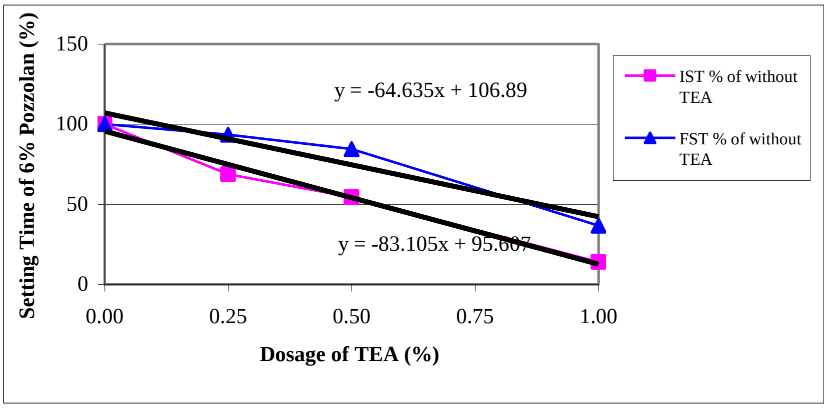


Figure 5.30: The Effect of TEA on Setting Time of 6% Pozzolan

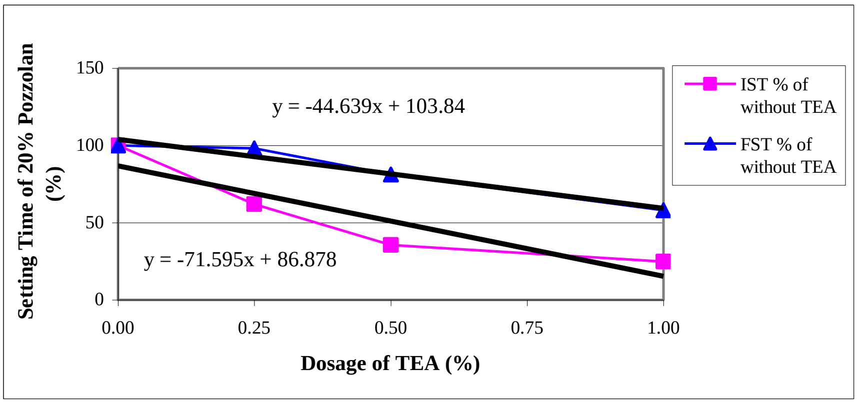


Figure 5.31: The Effect of TEA on Setting Time of 20% Pozzolan

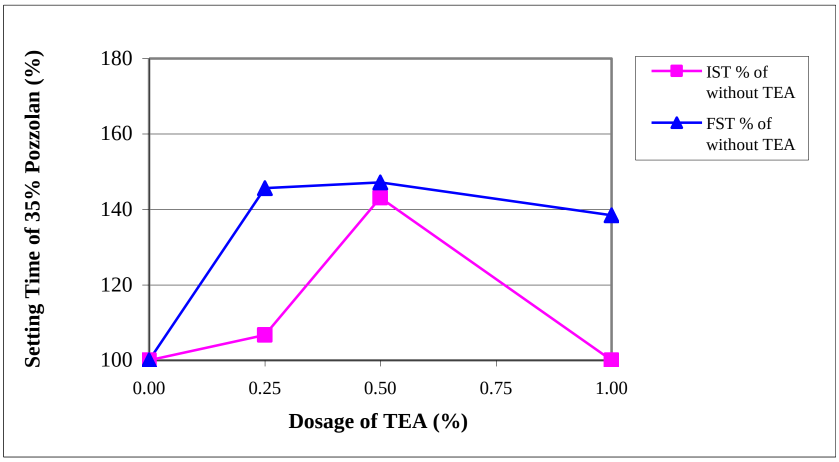


Figure 5.32: The Effect of TEA on Setting Time of 35% Pozzolan

The accelerating effect of TEA on the setting time of PSC is less pronounced comparing with PPC as shown in Figures 5.33-35.

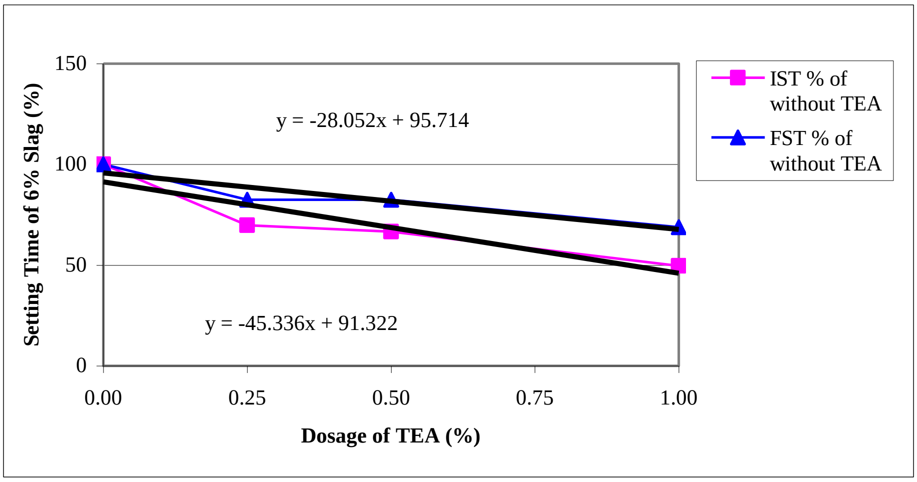


Figure 5.33: The Effect of TEA on Setting Time of 6% Slag

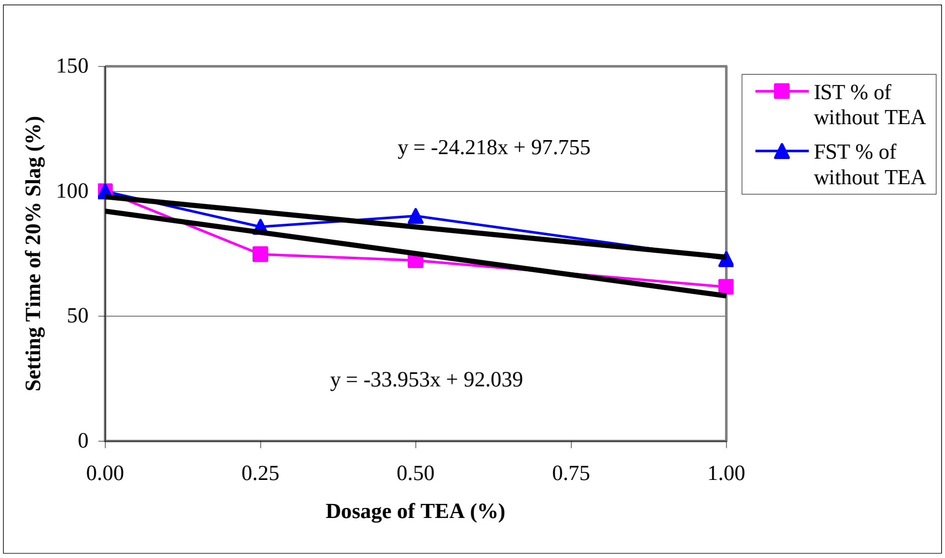


Figure 5.34: The Effect of TEA on Setting Time of 20% Slag

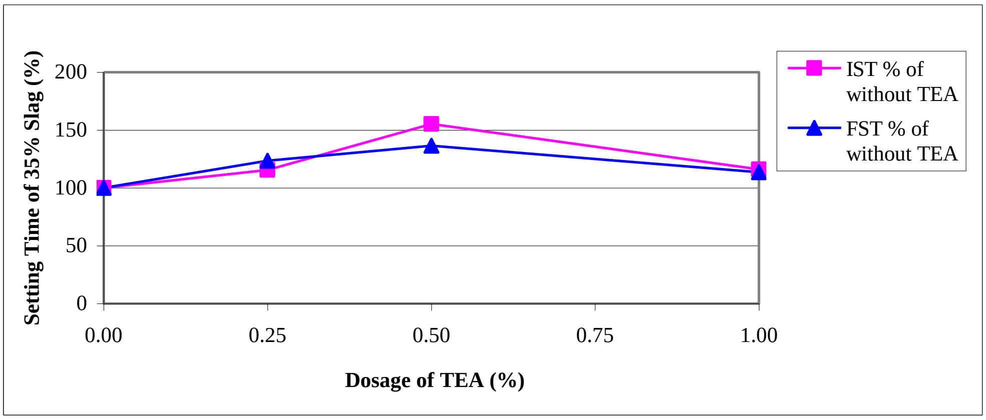


Figure 5.35: The Effect of TEA on Setting Time of 35% Slag

According to Figures 5.36-5.38; TEA reduced the setting times of PLC with respect to control cement. Also, its rate of accelerating effect is between those of pozzolan and slag. Unlike PPC and PSC, at 35% limestone incorporated cements there is a linear relationship between the amount of TEA used and setting times.

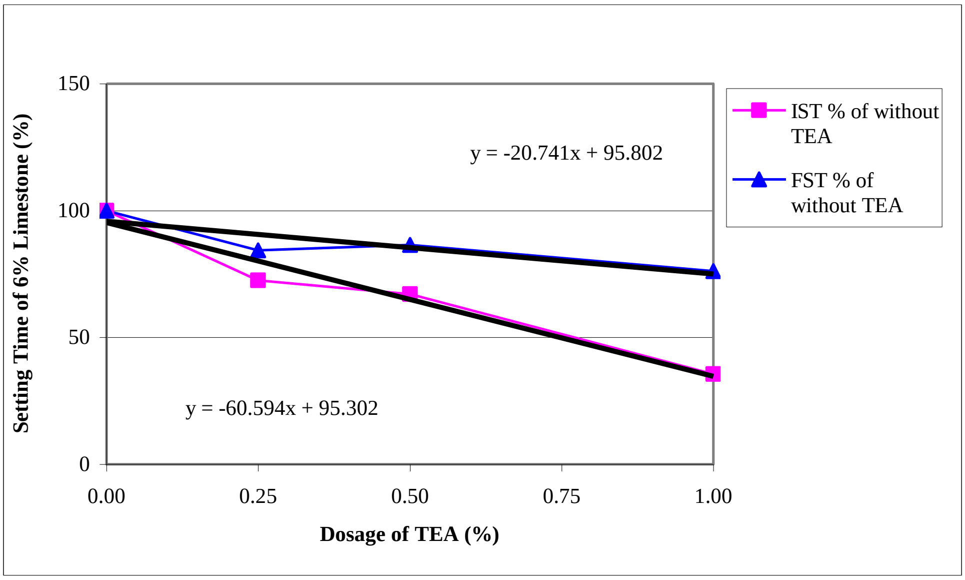


Figure 5.36: The Effect of TEA on Setting Time of 6% Limestone

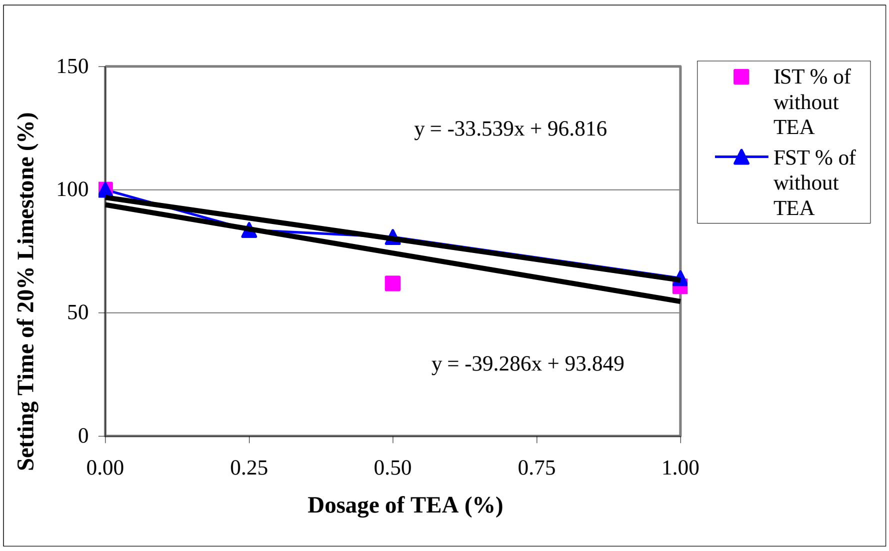


Figure 5.37: The Effect of TEA on Setting Time of 20% Limestone

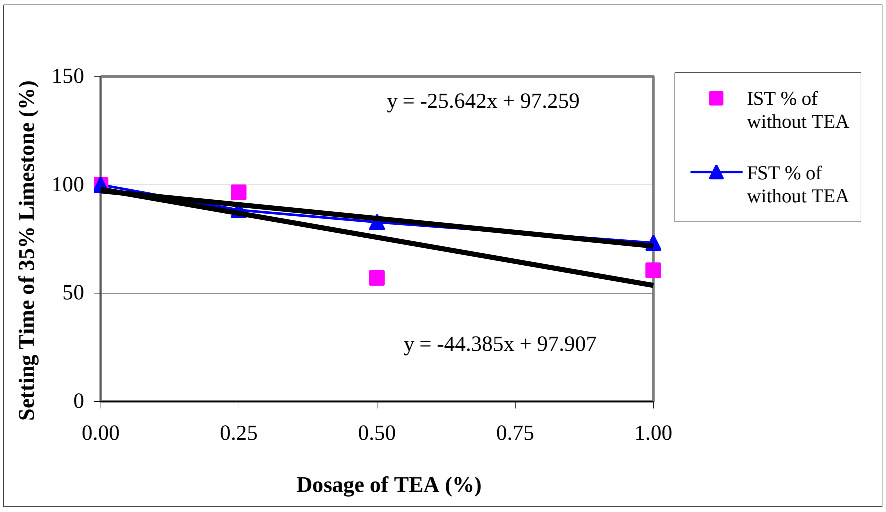


Figure 5.38: The Effect of TEA on Setting Time of 35% Limestone

The effectiveness of CF with all cement types for both the initial and final setting is similar. Its effect on both setting times of PC is given in Figure 5.39.

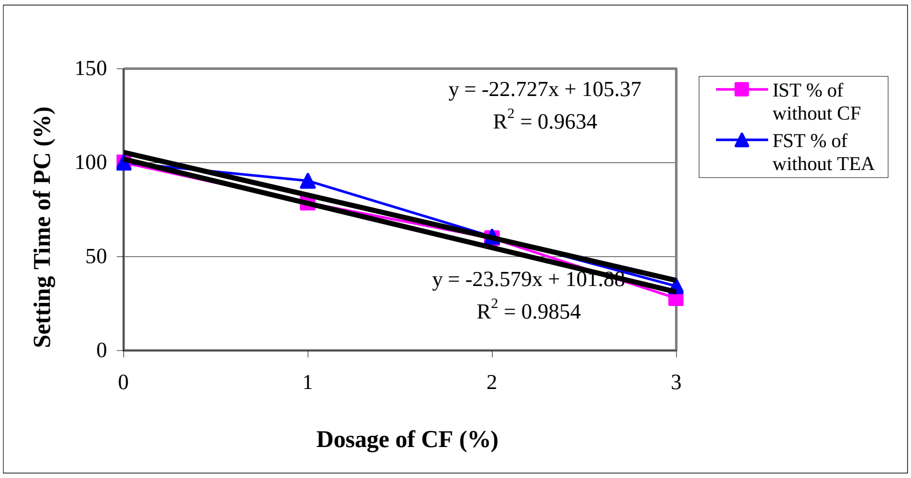


Figure 5.39: The Effect of CF on Setting Time of PC

There is a similar trend between CF dosage and 6% mineral admixtures incorporated cements is shown in Figures 5.40-5.42. Also, this is valid for control and cements containing 20 and 35% mineral admixtures.

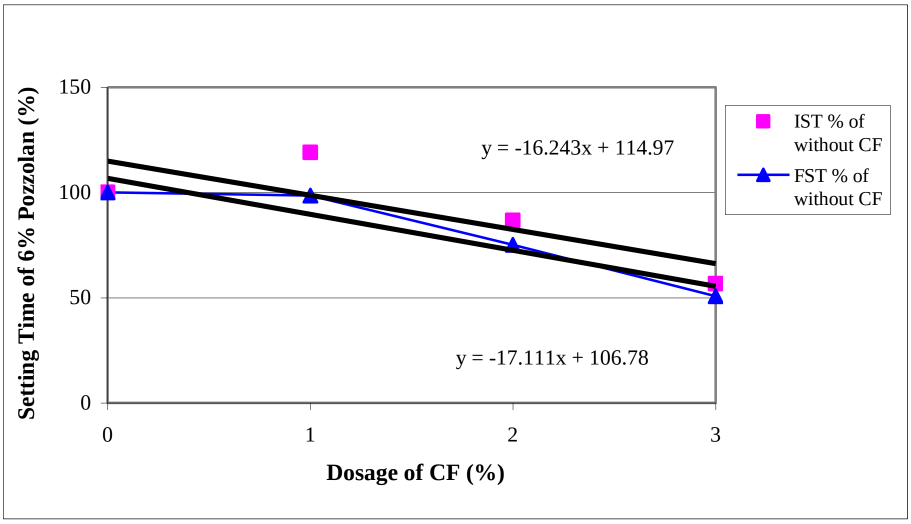


Figure 5.40: The Effect of CF on Setting Time of 6% Pozzolan

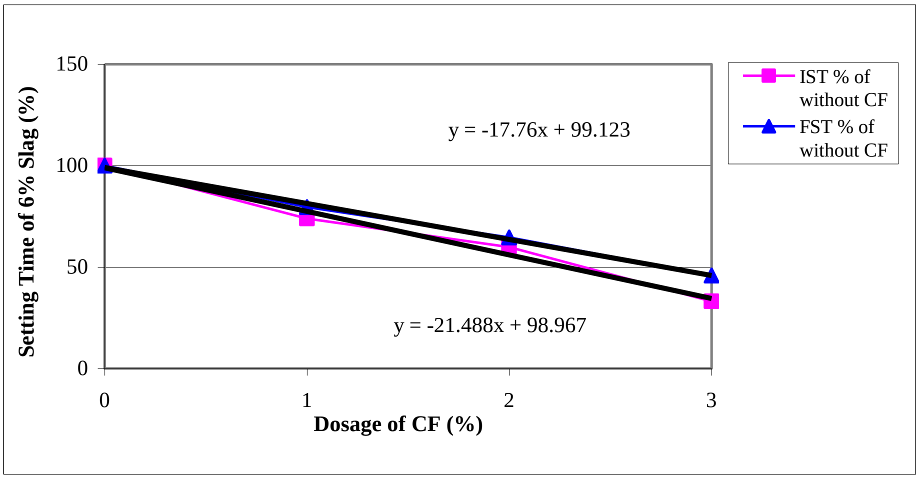


Figure 5.41: The Effect of CF on Setting Time of 6% Slag

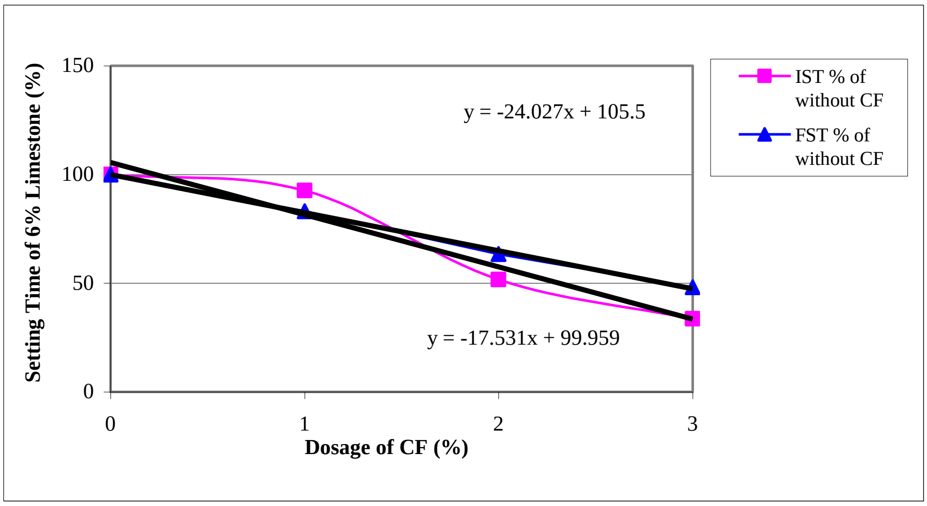


Figure 5.42: The Effect of CF on Setting Time of 6% Limestone

As mentioned before, the relationship between CF dosage and initial and final setting times is linear and the slopes of the linear equations obtained are given in Table 5.8. As can be observed from Table 5.8, the decrease in setting time with the increase in the amount of CF results in similar behavior for all mineral admixture types and amounts used, except for 35% pozzolan incorporated cements.

Table 5.8: The Slopes of The Graphs showing Setting Time vs CF

	The Slope of FST	The Slope of IST
PC	-22.727	-23.579
PPC		
6% Pozzolan	-17.111	-16.243
20% Pozzolan	-14.588	-16.085
35 % Pozzolan	-7.4525	-13.778
PSC		
6 % Slag	-17.760	-21.488
20 % Slag	-15.102	-16.012
35 % Slag	-12.318	-20.888
PLC		
6% Limestone	-17.531	-24.027
20 % Limestone	-20.367	-22.857
35 % Limestone	-17.360	-11.544

For all blended cements, the accelerating effect of TEA is more pronounced at lower mineral admixture contents. Also, comparing two accelerating agents used in this investigation, within the amount of ranges used, TEA is more effective than CF for all cement types.

5.3 Water Demand for 110% Flow

The water demand for 110% flow increases with the use of mineral admixtures as shown in Figure 5.43. However, the extent of the increase is based on the type of mineral admixtures. Among these mineral admixtures used, limestone leads to the highest increase in the water demand for 110% flow. On the other hand, the slag has the smallest effect on it.

There is a linear relationship between the amount of mineral admixtures used and the water demand for 110% flow for all cement types as shown in Figure 5.44.

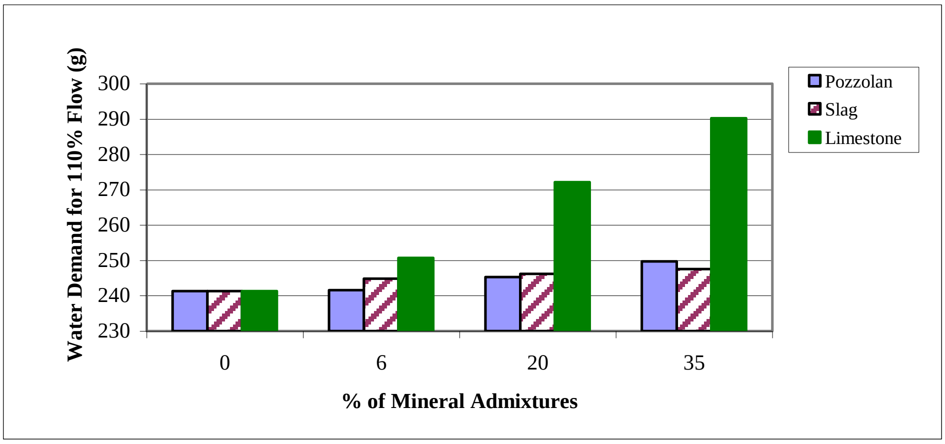


Figure 5.43: The Effect of Mineral Admixtures on Water Demand for 110% Flow

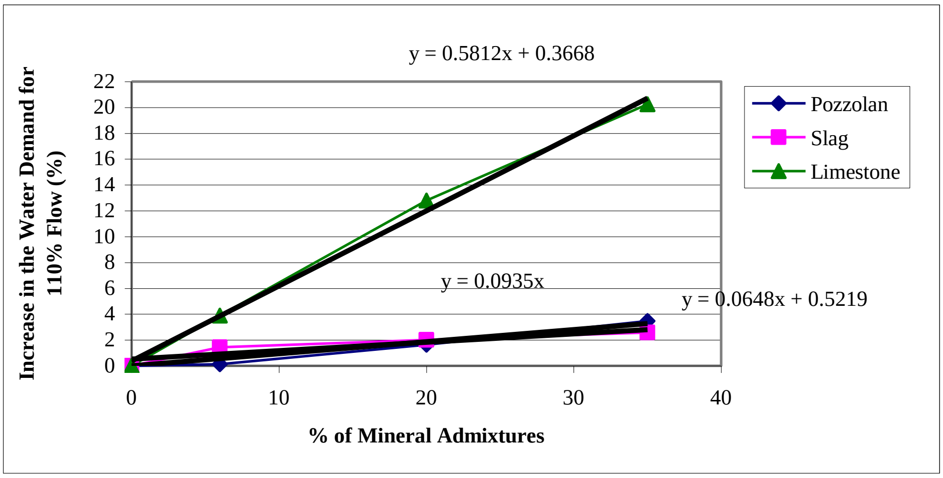


Figure 5.44: The Increase in the Water Demand for 110% Flow

Due to density differences of mineral admixtures, the water requirement for 110% flow was calculated by volume basis. According to the data plotted in Figures 5.45 and 5.46, for PPC and PSC the water demand for 110% flow decreases by increasing the content of pozzolan and slag, however there is an increasing trend in the water demand for 110% flow with the use of limestone in the study.

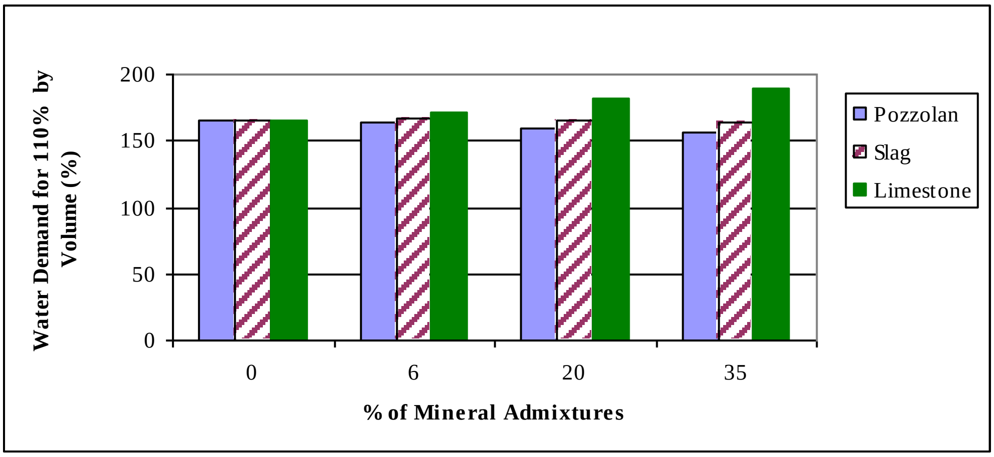


Figure 5.45: The Water Demand for 110% Flow by Volume

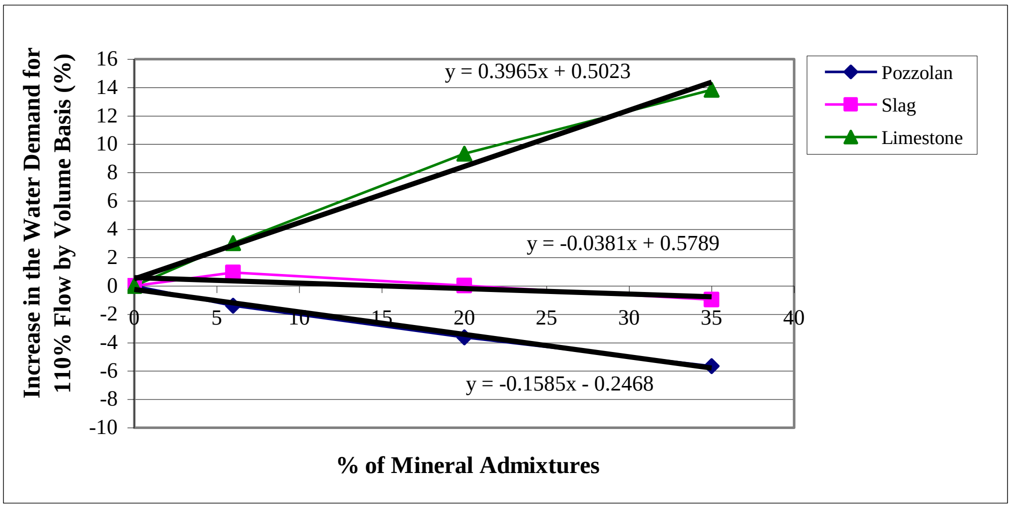


Figure 5.46: Increase in the Water Demand for 110% Flow by Volume

According to Figures 5.45 and 5.46, the most effective mineral admixture on the water demand for 110% flow is limestone, pozzolan and slag comes respectively.

Also, the effect of fineness on the water requirement for 110% flow was evaluated as shown in Figure 5.47. It was observed that the fineness has similar effects on the water requirement for 110% flow of mineral admixtures as in the case of normal consistency water demand.

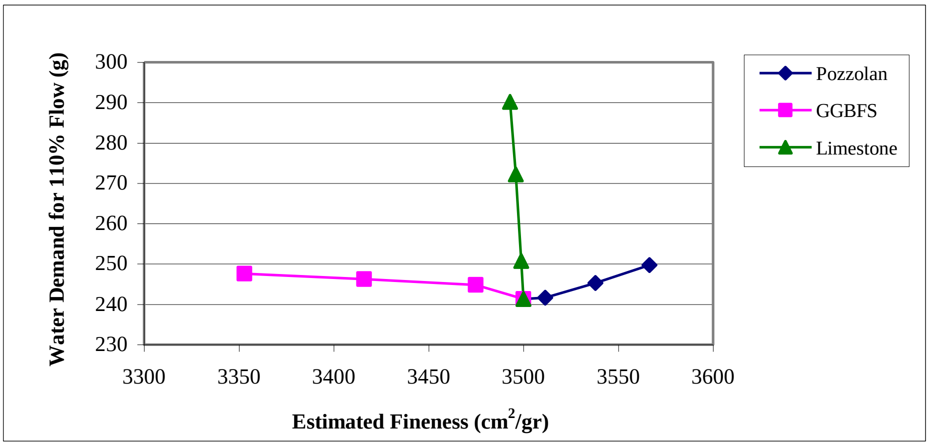


Figure 5.47: The Effect of Fineness on the Water Demand for 110 % Flow of Binders

Accelerating agents affect the water demand for 110% flow in a similar manner as in the normal consistency water. In other words, it increases regardless of the type of them, but the rate of increase especially depends on the type and dosage of mineral and accelerating admixtures. For PPC, the water requirement for 110% flow increases with the increase of pozzolan and accelerating agent contents as shown in Table 5.9.

Table 5.9: Water Demand for 110% Flow of PPC

Type of Accelerating Admixtures	Amount of Accelerating Admixtures, %	Water Demand for 110% Flow of PPC for Different Pozzolan Contents, gr			
		0 %	6 %	20 %	35 %
TEA	0.00	241.3	241.6	245.3	249.7
	0.25	248.4	241.5	246.1	250.6
	0.50	249.7	243.1	247.1	251.4
	1.00	250.5	244.2	248.3	252.5
CF	1.00	245.5	242.7	247.5	253.6
	2.00	245.8	243.2	248.2	254.3
	3.00	246.2	243.9	248.7	255.2

According to Table 5.9; the increase rate at 6 and 20% pozzolan incorporated cements is very low comparing with PC when TEA used. On the other hand, by using CF the increase rate at 6 % pozzolan incorporated cements is very low comparing with PC when TEA used, but when the pozzolan content is between 20 and 35%, the increase rate in water demand for 110% flow is higher than that in PC. By comparing the accelerating admixtures, CF is more effective on the water demand for 110% flow than TEA at high dosage of pozzolan.

The water requirement on volumetric basis for 110% flow increases by increasing the contents of accelerating agent as shown in Figures 5.48 and 5.49.

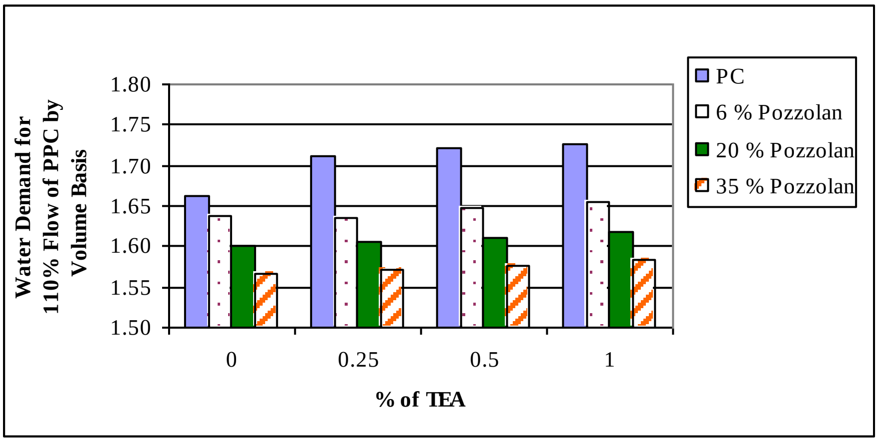


Figure 5.48: The Water Demand for 110 % Flow of PPC by Volume based on TEA

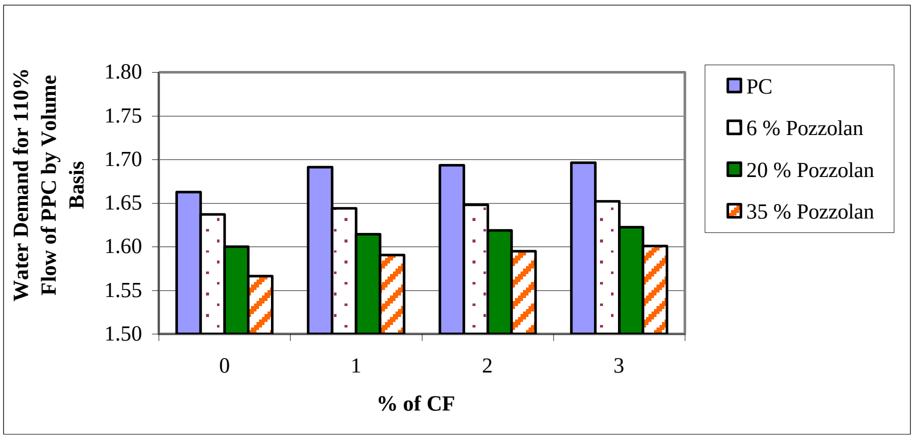


Figure 5.49: The Water Demand for 110 % Flow of PPC by Volume based on CF

Figures 5.50-5.52 show the relationships between the water demand for 110% flow of PPC and the accelerating admixtures.

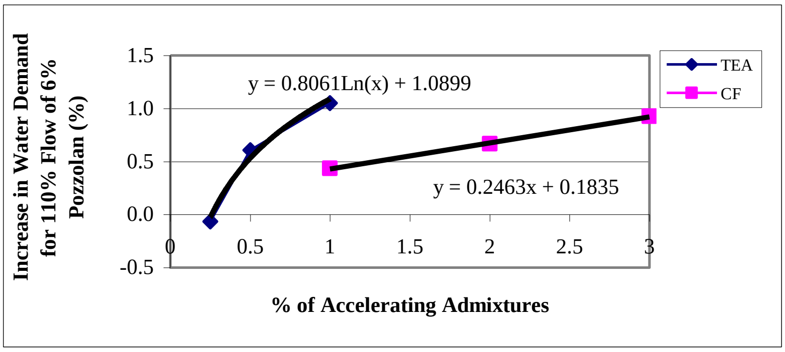


Figure 5.50: The Increase in Water Demand for 110% Flow of 6% Pozzolan

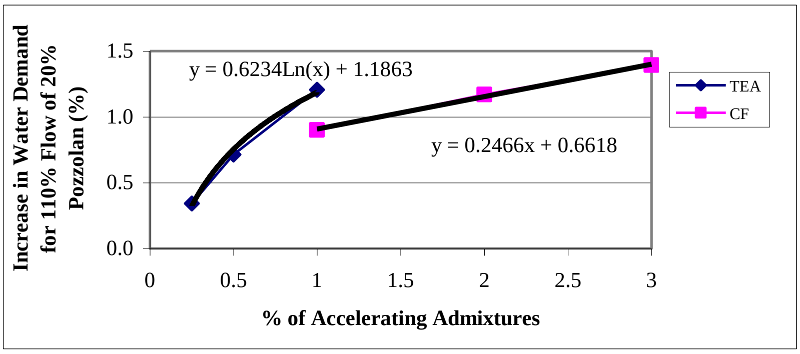


Figure 5.51: The Increase in Water Demand for 110% Flow of 20% Pozzolan

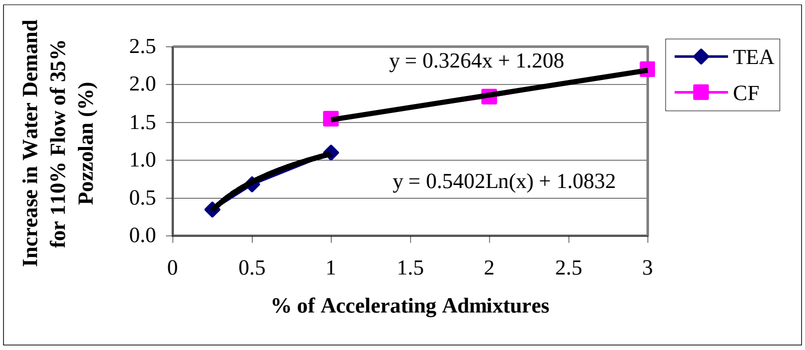


Figure 5.52: The Increase in Water Demand for 110% Flow of 35% Pozzolan

According to Figures 5.50-5.52, in the case of CF, the water increase is linearly proportional with the amount of accelerating admixtures used on the other hand in the use of TEA there is a logarithmic relationship between them.

For PSC, the water requirement for 110% flow increases by increasing accelerating agent contents as shown in Table 5.10, but the increase rate at all contents of slag is very low comparing with PC when TEA and CF used.

Table 5.10: Water Demand for 110% Flow of PSC

Type of Accelerating Admixtures	Amount of Accelerating Admixtures, %	Water Demand for 110% Flow of PSC for Different Slag Contents, gr			
		0 %	6 %	20 %	35 %
TEA	0.00	241.3	244.8	246.2	247.6
	0.25	248.4	245.6	247.0	248.4
	0.50	249.7	246.4	247.8	249.3
	1.00	250.5	247.2	248.7	250.1
CF	1.00	245.5	245.6	246.9	247.0
	2.00	245.8	247.6	247.6	247.8
	3.00	246.2	248.3	248.3	248.5

From the point of water demand on volumetric basis, the water requirement on volumetric basis for 110% flow decreases with increasing the slag content regardless of accelerating admixtures used in Figures 5.53 and 5.54. According to these figures, with the increase in TEA and CF content, the water requirement by volume increases. The effectiveness of TEA and CF depends on the slag content. At 6 % slag incorporated cement, the effect of CF on the water demand for 110% flow is more pronounced than that of TEA. On the other hand, at 20 and 35% slag incorporated cements, TEA is more effective on the increase in water demand for 110% flow.

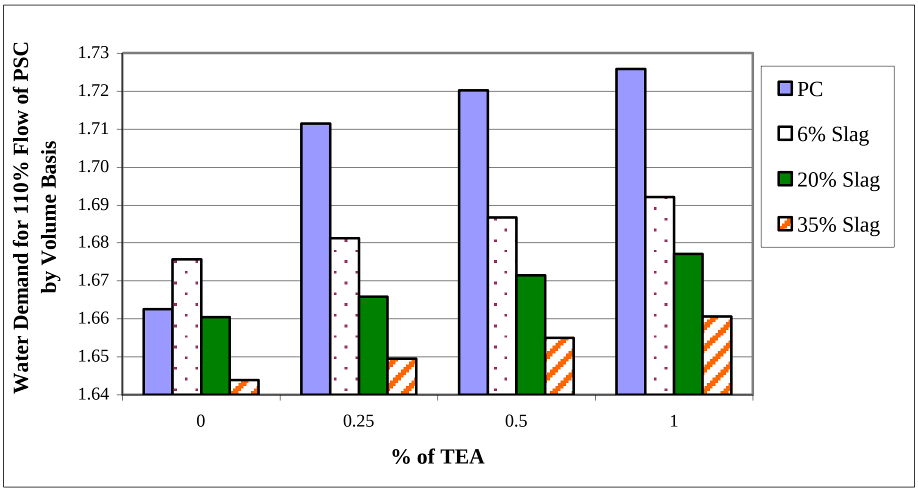


Figure 5.53: The Water Demand for 110 % Flow of PSC by Volume based on TEA

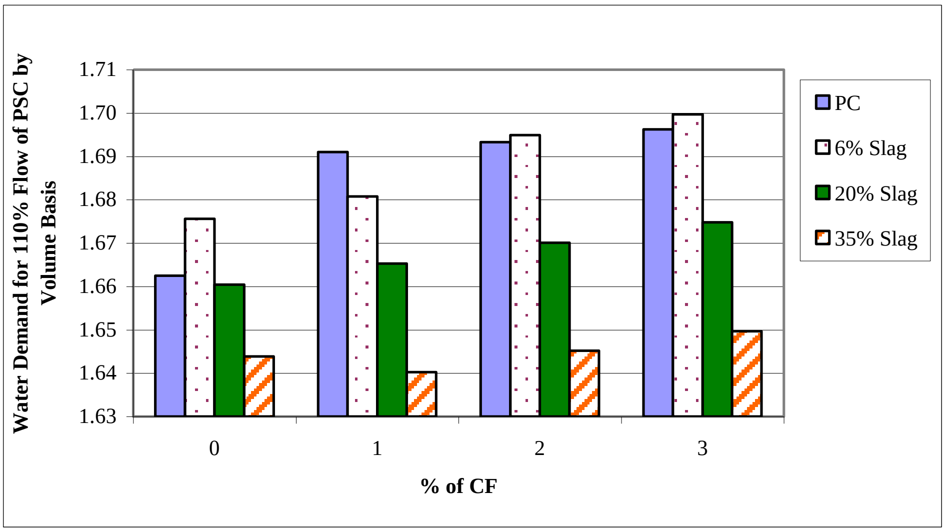


Figure 5.54: The Water Demand for 110 % Flow of PSC by Volume based on CF

The water demand for 110% flow and the accelerating admixtures depending on the slag content was formulated as shown in Figures 5.55-5.57. According to these figures, in the case of CF, the water demand for 110% flow increases linearly with the amount of accelerating admixtures used, on the other hand in the use of TEA there is a logarithmic relationship between them.

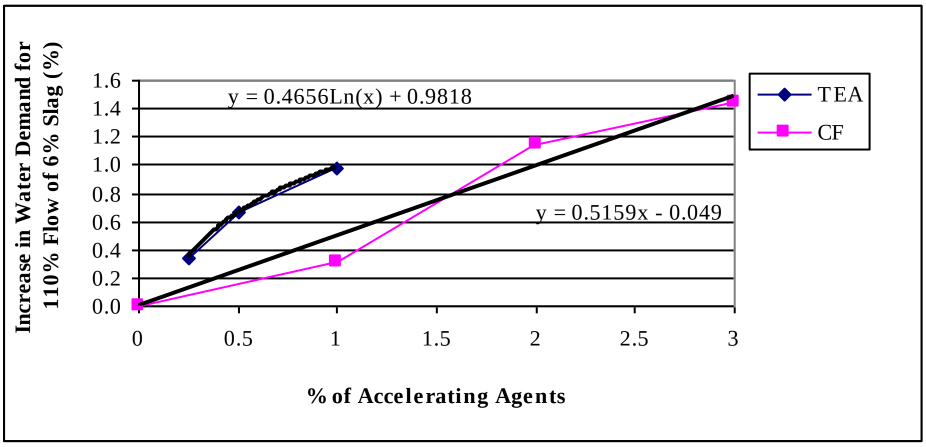


Figure 5.55: The Increase in Water Demand for 110% Flow of 6% Slag

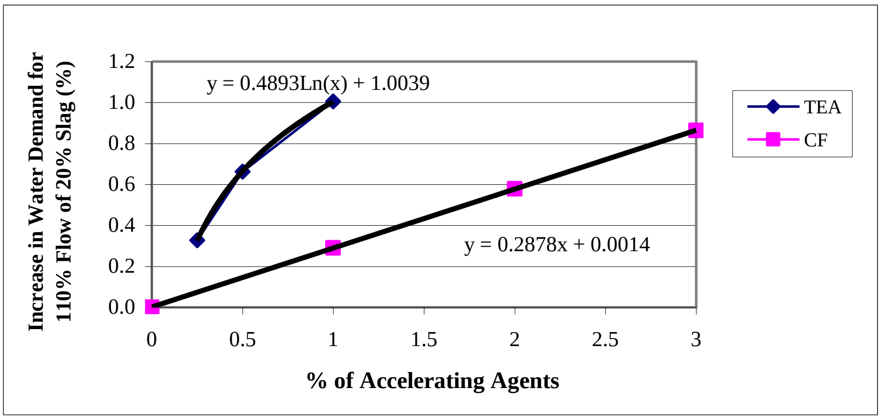


Figure 5.56: The Increase in Water Demand for 110% Flow of 20% Slag

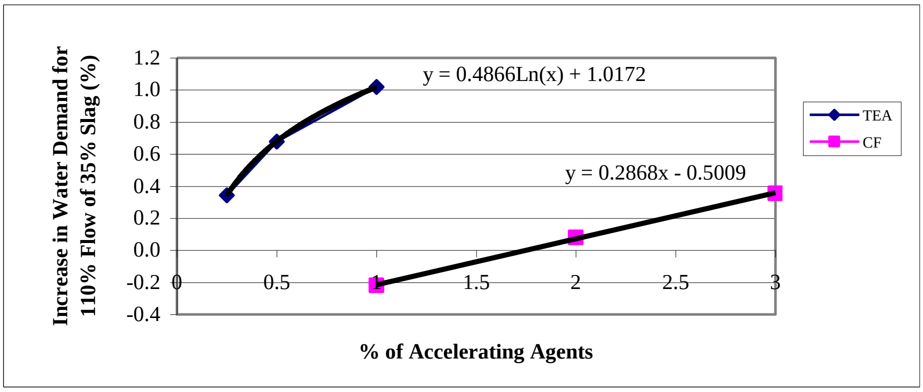


Figure 5.57: The Increase in Water Demand for 110% Flow of 35% Slag

For PLC, the water demand for 110% flow increases by increasing limestone and accelerating agent contents as shown in Table 5.11, but the increase rate at all contents of limestone is very high comparing with PC.

Table 5.11: Water Demand for 110% Flow of PLC

Type of Accelerating Admixtures	Amount of Accelerating Admixtures, %	Water Demand for 110% Flow of PLC for Different Limestone Contents, gr			
		0 %	6 %	20 %	35 %
TEA	0.00	241.3	250.7	272.2	290.2
	0.25	248.4	251.3	273.1	290.9
	0.50	249.7	251.8	273.5	291.3
	1.00	250.5	252.3	274.0	291.8
CF	1.00	245.5	251.1	272.4	290.6
	2.00	245.8	251.4	272.8	290.9
	3.00	246.2	251.7	273.1	291.2

From the point of water demand on volumetric basis, the water requirement on volumetric basis for 110% flow increases with increasing the content of pozzolan and accelerating admixtures used in Figures 5.58 and 5.59. The effects of TEA and CF on the increase in the water demand for 110% flow are similar.

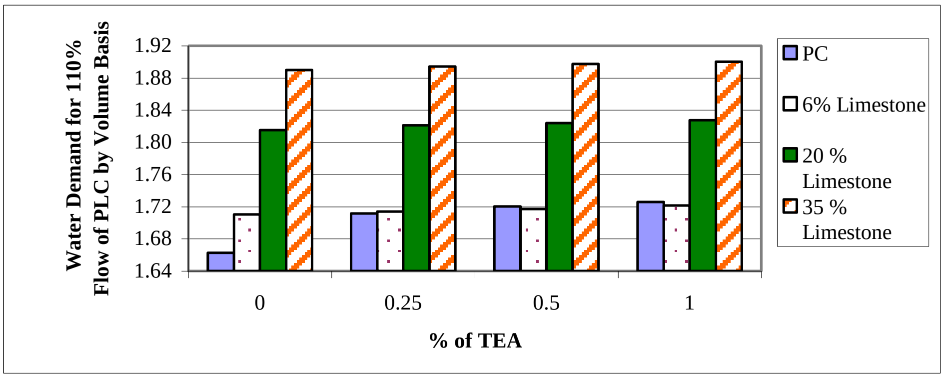


Figure 5.58: The Water Demand for 110 % Flow of PLC by Volume based on TEA

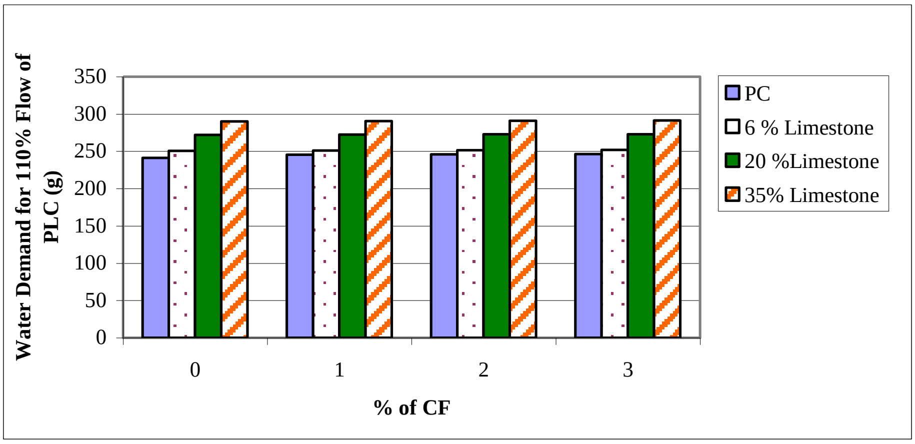


Figure 5.59: The Water Demand for 110 % Flow of PLC by Volume based on CF

The relationships between the water demand for 110% flow and the accelerating admixtures depending on the limestone content was determined as shown in Figures 5.60-5.62. According to these figures, in the case of CF, the water increase is linearly proportional with the amount of accelerating admixtures used on the other hand, in the use of TEA there is a logarithmic relationship between them.

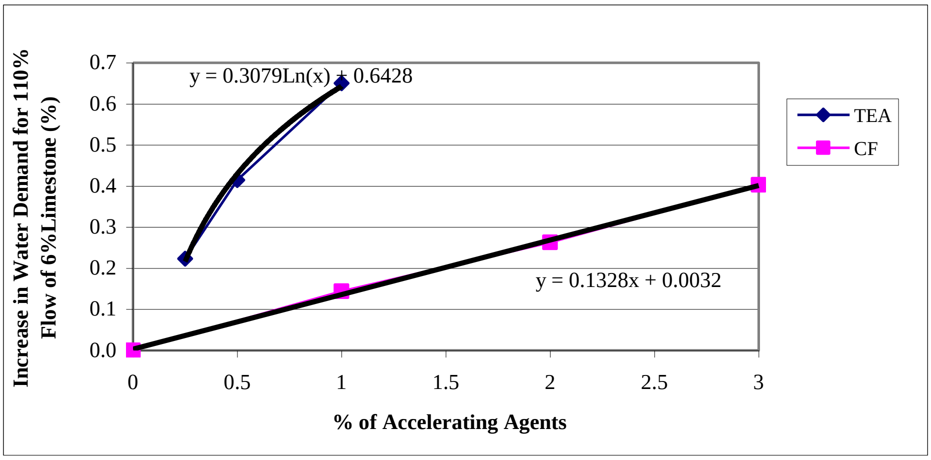


Figure 5.60: The Increase in Water Demand for 110% Flow of 6% Limestone

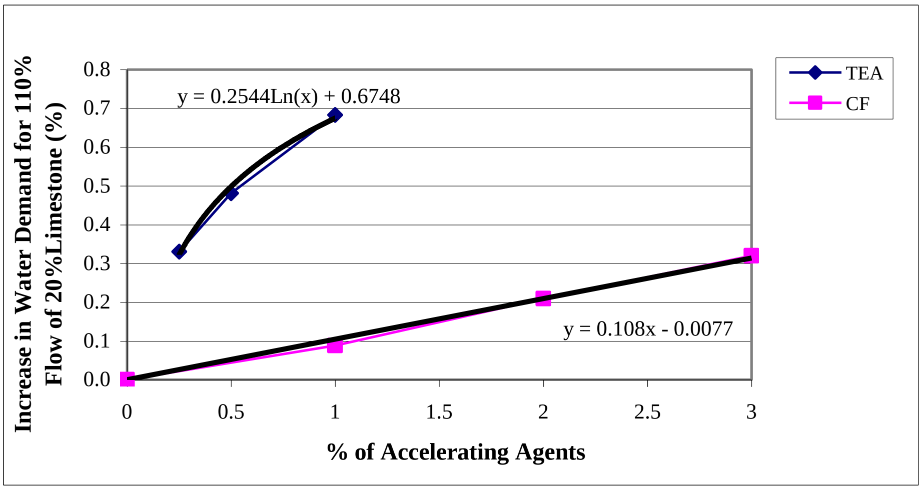


Figure 5.61: The Increase in Water Demand for 110% Flow of 20% Limestone

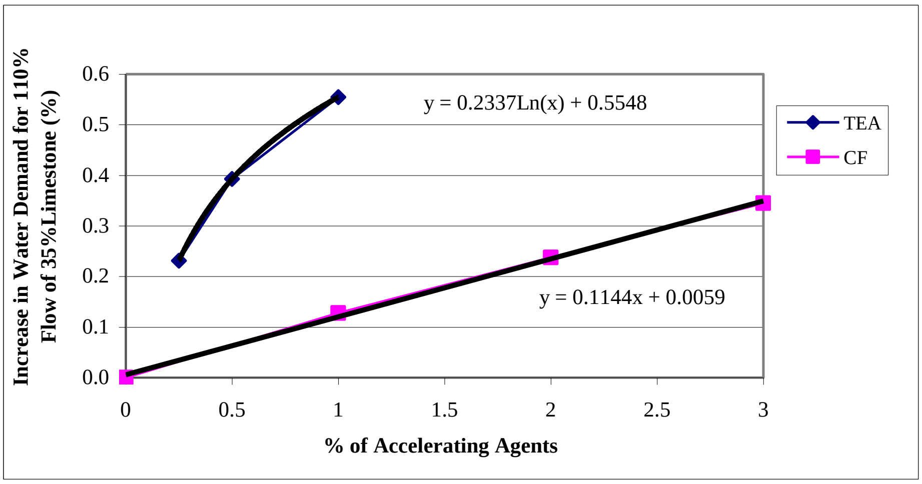


Figure 5.62: The Increase in Water Demand for 110% Flow of 35% Limestone

5.4 Compressive Strength

The compressive strength of cement types containing pozzolan, slag and limestone and TEA and CF are different from each other as expected. In this study, the 2, 7 and 28-day compressive strength measurement values were determined for each mix containing different amounts of mineral and accelerating admixtures and they are given in the Appendix. The compressive strength values in comparison with control sample change according to type, dosage of admixtures and age as shown in Tables 5.12-15.

Table 5.12: The Compressive Strength of PC

Accelerating Admixtures	Amount of Accelerating. Admixtures, %	Compressive Strength, MPa		
		2 days	*7 days*	*28 days*
TEA	0.00	20.8	30.7	37.2
	0.25	26.4	32.9	42.2
	0.50	22.1	32.2	42.6
	1.00	22.7	34.7	44.0
CF	1.00	20.1	31.5	44.8
	2.00	16.1	30.7	49.4
	3.00	15.7	39.9	47.0

Table 5.13.: The Compressive Strength of PPC

Pozzolan, %	Type of Acc. Adm.	Amount of Acc. Adm., %	Compressive Strength, MPa		
			2 days	*7 days*	*28 days*
6	TEA	0.00	14.3	27.7	38.2
		0.25	16.3	30.3	45.6
		0.50	15.3	29.8	39.8
		1.00	14.4	33.3	42.5
	CF	1.00	13.6	25.9	42.7
		2.00	13.6	35.9	43.3
		3.00	12.8	35.6	46.1
20	TEA	0.00	10.2	23.6	36.7
		0.25	13.1	28.8	35.6
		0.50	10.3	26.5	35.1
		1.00	10.4	24.6	31.8
	CF	1.00	9.9	23.4	41.7
		2.00	12.3	29.5	41.1
		3.00	13.7	29.3	41.6
35	TEA	0.00	10.6	19.3	30.1
		0.25	11.5	24.0	31.4
		0.50	9.7	20.0	29.1
		1.00	9.6	18.8	32.2
	CF	1.00	11.5	17.4	18.4
		2.00	9.4	19.4	19.6
		3.00	9.3	20.7	21.8

Table 5.14: The Compressive Strength of PSC

Slag, %	Type of Acc. Adm.	Amount of Acc. Adm., %	Compressive Strength, MPa		
			2 days	*7 days*	*28 days*
6	TEA	0.00	19.7	29.4	33.6
		0.25	18.3	29.1	32.9
		0.50	20.6	36.2	39.7
		1.00	19.8	34.1	34.9
	CF	1.00	16.6	19.2	48.9
		2.00	16.2	27.3	52.5
		3.00	17.4	23.0	50.2
20	TEA	0.00	13.2	19.5	37.1
		0.25	12.9	13.3	39.3
		0.50	13.7	21.4	43.0
		1.00	12.3	13.7	40.0
	CF	1.00	13.8	14.2	43.5
		2.00	12.2	29.4	45.1
		3.00	12.9	14.4	48.5
35	TEA	0.00	10.8	13.0	37.6
		0.25	11.4	15.5	38.4
		0.50	8.7	11.3	37.2
		1.00	7.8	14.4	39.2
	CF	1.00	10.0	13.4	39.5
		2.00	11.4	18.1	43.5
		3.00	9.9	13.0	43.9

Table 5.15: The Compressive Strength of PLC

Limestone,%	Type of Acc. Adm.	Amount of Acc. Adm., %	Compressive Strength, MPa		
			2 days	*7 days*	*28 days*
6	TEA	0.00	20.0	28.4	34.4
		0.25	20.9	30.5	44.4
		0.50	21.1	36.5	42.3
		1.00	18.7	32.4	40.0
	CF	1.00	19.6	33.7	42.1
		2.00	17.4	33.0	41.2
		3.00	18.6	34.0	40.3
20	TEA	0.00	11.9	19.9	28.2
		0.25	14.0	25.4	31.9
		0.50	11.7	23.1	29.1
		1.00	13.6	22.6	29.0
	CF	1.00	12.9	24.6	33.3
		2.00	11.4	21.9	29.7
		3.00	11.0	24.6	32.2

Table 5.15 (continued): The Compressive Strength of PLC

Limestone,%	Type of Acc. Adm.	Amount of Acc. Adm., %	Compressive Strength, MPa		
			2 days	*7 days*	*28 days*
35	TEA	0.00	7.6	11.1	18.2
		0.25	9.8	15.8	20.1
		0.50	7.7	14.0	16.9
		1.00	4.8	12.4	18.2
	CF	1.00	7.0	12.1	19.8
		2.00	6.5	11.6	18.5
		3.00	5.8	10.5	17.7

Generally, the compressive strengths for all tested ages decrease with increasing amount of mineral admixtures. This is an expected result since the cement is replaced by a less reactive material. However, there are some differences among them in the case of PSC and PLC. Figures 5.63-5.65 show the differences between the compressive strength of PC and blended cement types. The effects of mineral admixtures on the compressive strength change with the type and amount of mineral and chemical admixtures and ages.

As for PPC, with the increase of pozzolan content, the change in the 2 and 7-day compressive strength decreases, but the change in the 28-day compressive strength increases up to 6% pozzolan as shown in Figure 5.63.

Regarding PSC (Figure 5.64), the changes in the 2 and 7-day compressive strength increase at the same rate up to 20% pozzolan content, but between the range of 20 and 35% pozzolan content the change in the 7-day compressive strength is a bit higher than that in the 2-day compressive strength. On the other hand, the 28-day compressive strength increases at all slag contents.

Considering PLC, the change in the compressive strength all tested ages increase by increasing the content of limestone as shown in Figure 65. However, the change rate depends on the limestone content. Up to 6% limestone, the changes in the 7 and 28-day compressive strengths are higher than that in the 2-day compressive strength, but the change in the 2-day is more pronounced comparing with that in the 7 and 28-day compressive strengths between 6 and 35% limestone.

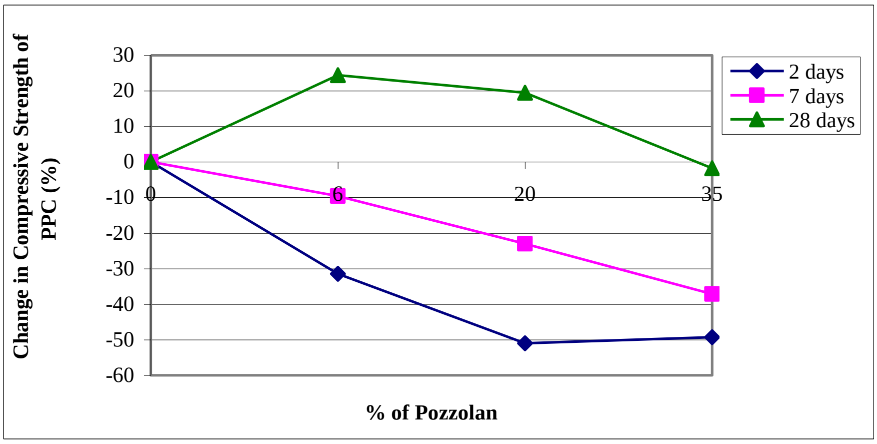


Figure 5.63: The Change in the Compressive Strength of PPC

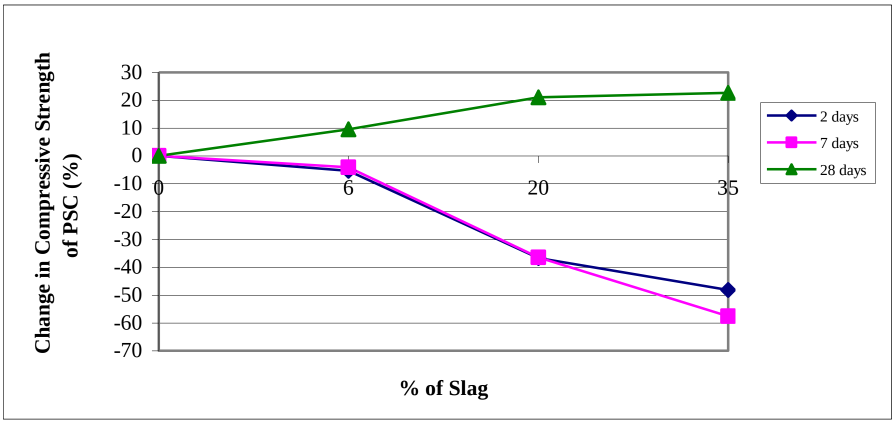


Figure 5.64: The Change in the Compressive Strength of PSC

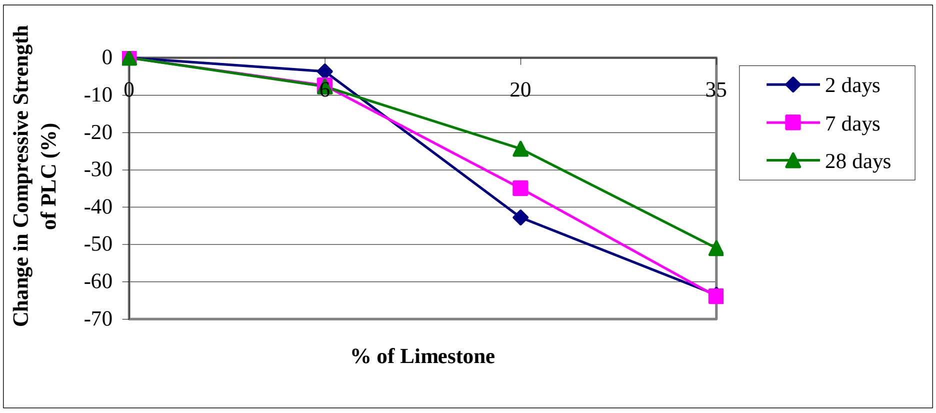


Figure 5.65: The Change in the Compressive Strength of PLC

The highest change occurs at limestone incorporated cements. This is an expected result because the water demand with the use of limestone is higher than other mineral admixtures as mentioned in the parts above.

The effectiveness of accelerating agents on the compressive strength of cement types depend on the dosage and type of accelerating agent, mineral admixture type and amount and age of testing as shown in Tables 5.12-5.15. Accordingly, the compressive strength of PC for all tested ages increases with the increase of TEA content. On the other hand, by increasing CF dosage, the 28-day compressive strength of PC increases, whereas the 2-day compressive strength of PC decreases. For the early compressive strength of PC, TEA is more effective, but for the long term strength, the effect of CF is more pronounced. While the 28-day compressive strength of PC containing 2%CF is almost %30 higher than that PC, the 7-day compressive strength of PC is approximately 30% higher than that of PC.

The effectiveness of CF with PPC types change with the amount of pozzolan and tested ages. For example, at PPC, CF increase the 28-day compressive strengths approximately by 20%, on the other hand at 35% pozzolan content, the 2 and 7-day compressive strengths decrease by increasing CF content. TEA generally increases the compressive strength for all tested ages except for 35% pozzolan incorporated cements. At low dosage of pozzolan CF is more effective in the increase of the long term compressive strength comparing with TEA.

Generally, the compressive strength of PSC at early ages, decreases with the increase of CF content, however, the 28-day compressive strength values of PSC containing CF are higher compared with PC. TEA was observed to increase the 2 and 7-day compressive strength at 6 and 20% slag incorporated cements when the amount of it is 0.5%. Also, it increases the 28-day compressive strength at all dosages.

There are various factors affecting the relationship between CF and PLC types such as dosage of CF, amount of limestone and age of testing. CF decreases the compressive strength of PLC for all tested ages at 20 and 35% limestone incorporated cements. On the other hand, it increases the 7 and 28-day compressive strengths at 6% limestone incorporated cements. The effect of TEA on the compressive strength values of PLC depends on the dosage of it and tested ages. The 2 and the 7-day compressive strength increase up to 0.5% TEA content, but then decreases with the increase of TEA content. On the other hand, the same situation holds true at 1%TEA content for the 28-day compressive strength.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Within the scope of this thesis the effectiveness of two common organic accelerating admixtures when used with blended cement types was studied. TEA and CF are water soluble organic salts which have a set-accelerating effect. The amounts of TEA and CF used in this study were 0.25, 0.50 and 1.00% and 1.00, 2.00 and 3.00%, by weight of cementitious material, respectively. These amounts were chosen since they were the commonly used minimum, average and maximum amounts stated in the literature. The mineral admixtures used in the blended cements were a natural pozzolan, ground granulated blast furnace slag and limestone. Their amounts were chosen as 6, 20 and 35%, by weight of cement, so as to represent CEM II/A and CEMII/B cements in TS-EN 197-1.

Based on the laboratory test results of both accelerating admixtures on the normal consistency water requirement and setting time of cement pastes and water requirement for 110% flow and 2-, 7- and 28-day compressive strengths of standard mortars the following conclusions are drawn:

- It is suitable to use the admixtures in the amounts used in this investigation. Both accelerating agents have led to approximately the same effects and the asymptotic character of the accelerating agent amount vs the dependent variable (water demand, setting time, strength) curves indicate that above the maximum dosage used in this study no further significant change would occur.

- Due to density differences of mineral admixtures and the Portland cement clinker, the water demand for normal consistency and 110% flow should be also considered on volumetric basis.

- The water demand for normal consistency and flow increases with the amount of mineral admixture used. In normal consistency water the highest increase is seen in pozzolan by weight and volume basis comparing with other binders. On the other hand, the effect of limestone on the water demand for 110% flow is more pronounced than the others by volume and weight basis.

- The increasing effect of CF on the normal consistency water is higher than that of TEA especially at 35% mineral admixtures incorporated cements. This is due to the linear relationship between CF and the normal consistency water for all cement types. On the other hand, there is a linear relationship between dosage of TEA and normal consistency water is logarithmic.

- TEA can be used as an accelerating agent for Type A PPC where the range of pozzolan content is between 6 and 20%. On the other hand, for Type B PPC the setting time increases with the use of TEA. As for PSC, the accelerating effect of TEA is less pronounced. However, for Type A and B PLC TEA can serve as an accelerator.

- In all blended cement types, the accelerating effect of TEA on the setting times is more pronounced especially at 6% pozzolan dosage. On the contrary, CF is more effective at 6 and 20% slag and limestone incorporated cements.

- Within the blended cement types, CF is more effective on the water demand for 110% flow than TEA at 35% pozzolan incorporated cements. However, for PSC types the increasing effect of CF on the water demand for 110% flow is more pronounced than that of TEA at 6 % slag incorporated cement. On the other hand, at 20 and 35% slag incorporated cements, TEA is more effective on the increase in water demand for 110% flow comparing with CF. Regarding with PLC, the effectiveness of CF and TEA on the water demand for flow is similar.

- The highest decrease in the compressive strength occurs at limestone incorporated cements.

- For the early compressive strength of PC, TEA is more effective, but for the long term strength, the effect of CF is more pronounced.

- At low dosage of pozzolan CF is more effective in the increase of the long term compressive strength comparing with TEA.

In addition to the results obtained from this investigation, there were some recommendations for further research given as follows;

- For other cement types similar studies should be carried out.

- The amounts of accelerating agents used in this investigation were chosen as the commonly used values given in literature. However, amounts exceeding the maximum values should also be investigated for a more thorough analysis.

- Besides the effects on the water requirement and setting time, probable effects on the other rheological properties such as yield value and viscosity of the fresh pastes and mortars should be carried out.

- Probable changes in the rate and mechanism of the hydration process upon accelerating agent usage should be investigated by microstructural research through various advanced means such as electron microscopy and X-ray diffraction.

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APPENDIX

COMPRESSIVE STRENGTH MEASUREMENTS

Table A.1: Compressive Strength of Different Cement Types

Type of Acc. Agents	Acc.Agents, %	Compressive Strength of PC with TEA, MPa					
		2 days	Ave.	7 days	Ave.	28 days	Ave.
TEA	0.00	19.0	20.8	28.7	30.7	35.1	37.2
		22.8		32.1		35.1	
		20.6		31.2		40.2	
						37.2	
						40.8	
						35.0	
	0.25	26.5	26.4	35.1	32.9	44.1	42.2
		25.3		31.5		42.4	
		27.3		31.9		40.4	
						45.1	
						39.2	
	0.50	22.8	22.1	29.2	32.2	43.4	42.6
		21.8		34.9		39.3	
		21.7		32.5		44.7	
						40.8	
						44.8	
	1.00	23.2	22.7	37.2	34.7	46.3	44.0
		20.6		35.2		44.9	
		24.2		31.7		44.2	
						43.4	
						41.2	
CF	1.00	20.8	20.1	31.6	31.5	44.8	44.8
		20.6		29.8		45.0	
		19.0		33.2		44.1	
						55.0	
						46.2	
						44.1	
	2.00	14.9	16.1	31.6	30.7	53.6	49.4
		17.4		27.9		44.5	
		16.1		32.5		51.9	
						45.1	
						47.2	
						53.8	
	3.00	15.5	15.7	39.4	39.9	50.5	47.0
		16.0		39.4		42.9	
		15.6		40.8		51.0	
						44.0	

Table A.1 (continued): Compressive Strength of Different Cement Types

Type of Accelerating Admixtures	Amount of Accelerating Admixture, %	Compressive Strength of PPC containing 6% Pozzolan, MPa					
		2 days	Average	7 days	Average	28 days	Average
TEA	0.00	14.4	14.3	28.2	27.7	34.9	38.2
		12.9		27.5		34.7	
		15.4		27.5		41.8	
						37.8	
						38.8	
						40.9	
	0.25	15.1	16.3	32.8	30.3	49.8	45.6
		17.1		28.4		42.9	
		16.7		29.7		50.0	
						44.9	
						42.8	
						43.4	
	0.50	14.4	15.3	31.0	29.8	39.9	39.8
		16.7		30.7		40.8	
		15.0		27.7		38.3	
						40.4	
						36.1	
						43.0	
	1.00	14.0	14.4	36.6	33.3	44.6	42.5
		15.8		32.1		43.1	
		13.5		31.2		42.4	
						41.6	
						39.6	
						43.8	
CF	1.00	13.9	13.6	24.4	25.9	46.7	42.7
		14.5		25.4		39.6	
		12.4		27.9		41.5	
						46.9	
						41.9	
						39.3	
	2.00	14.9	13.6	36.5	35.9	40.7	43.3
		12.8		33.9		42.5	
		13.0		37.3		46.0	
						40.8	
						46.9	
						42.7	
	3.00	12.8	12.8	34.3	35.6	44.3	46.1
		13.3		36.7		48.7	
		12.5		35.7		46.5	
						45.0	
						46.1	
						45.8	

Table A.1 (continued): Compressive Strength of Different Cement Types

Type of Accelerating Admixtures	Amount of Accelerating Admixture, %	Compressive Strength of PPC containing 20% Pozzolan, MPa					
		2 days	Average	7 days	Average	28 days	Average
TEA	0.00	10.7	10.2	24.1	23.6	35.9	36.7
		10.1		22.7		38.1	
		9.8		24.1		34.8	
						38.3	
						37.6	
						35.4	
	0.25	13.1	13.1	30.1	28.8	33.2	35.6
		14.1		29.7		37.0	
		12.0		26.8		37.7	
						34.5	
						33.0	
						38.3	
	0.50	10.2	10.3	24.5	26.5	37.0	35.1
		10.0		27.5		34.5	
		10.6		27.3		32.2	
						35.6	
						36.6	
						34.7	
	1.00	10.5	10.4	25.7	24.6	33.6	31.8
		10.0		23.0		28.6	
		10.7		25.1		30.8	
						34.1	
						28.8	
						35.0	
CF	1.00	9.8	9.9	23.1	23.4	44.0	41.7
		10.0		22.3		40.8	
		9.9		24.8		42.1	
						40.9	
						40.7	
						41.4	
	2.00	11.9	12.3	28.8	29.5	43.0	41.1
		13.5		29.5		40.3	
		11.5		30.3		37.8	
						38.1	
						45.1	
						42.3	
	3.00	13.9	13.7	27.6	29.3	41.0	41.6
		13.9		30.3		45.4	
		13.2		30.1		38.6	
						42.6	
						38.8	
						43.0	

Table A.1 (continued): Compressive Strength of Different Cement Types

Type of Accelerating Admixtures	Amount of Accelerating Admixture, %	Compressive Strength of PPC containing 35% Pozzolan, MPa					
		2 days	Average	7 days	Average	28 days	Average
TEA	0.00	10.8	10.6	19.0	19.3	28.4	30.1
		10.9		17.7		31.2	
		10.0		21.1		30.1	
						30.3	
						28.6	
						32.2	
	0.25	11.6	11.5	25.5	24.0	30.8	31.4
		11.4		25.6		31.7	
		11.3		21.0		30.5	
						31.1	
						34.5	
						29.7	
	0.50	10.5	9.7	18.6	20.0	26.6	29.1
		9.3		21.5		30.7	
		9.3		19.9		26.5	
						31.0	
						28.0	
						32.0	
	1.00	10.2	9.6	18.4	18.8	30.8	32.2
		9.3		20.4		29.9	
		9.4		17.6		34.5	
						35.4	
						31.4	
						31.0	
CF	1.00	10.6	11.5	17.7	17.4	18.4	18.4
		11.8		17.0		16.7	
		12.1		17.6		18.1	
						19.5	
						20.0	
						17.8	
	2.00	8.9	9.4	19.7	19.4	18.3	19.6
		9.9		18.7		19.2	
		9.3		19.9		20.5	
						21.6	
						18.5	
						19.8	
	3.00	8.8	9.3	19.4	20.7	23.9	21.8
		9.8		21.9		20.7	
		9.1		20.8		22.1	
						21.7	
						20.1	
						21.3	

Table A.1 (continued): Compressive Strength of Different Cement Types

Type of Accelerating Admixtures	Amount of Accelerating Admixture, %	Compressive Strength of PSC containing 6% Slag, MPa					
		2 days	Average	7 days	Average	28 days	Average
TEA	0.00	20.2	19.7	30.6	29.4	33.5	33.6
		19.7		30.2		35.7	
		19.2		27.4		32.8	
						35.5	
						31.8	
						32.4	
	0.25	19.0	18.3	27.4	29.1	30.1	32.9
		16.7		28.9		29.7	
		19.1		31.1		35.9	
						33.5	
						35.9	
						32.2	
	0.50	21.5	20.6	36.1	36.2	39.3	39.7
		21.3		34.6		38.8	
		19.0		37.9		38.7	
						39.6	
						41.3	
						40.4	
	1.00	20.1	19.8	33.1	34.1	32.6	34.9
		19.4		34.9		33.7	
		19.8		34.1		35.3	
						37.4	
						36.9	
						33.2	
CF	1.00	17.7	16.6	19.8	19.2	52.1	48.9
		16.8		18.5		53.6	
		15.4		19.4		44.3	
						53.8	
						44.7	
						44.9	
	2.00	17.1	16.2	25.2	27.3	54.7	52.5
		15.8		26.8		52.8	
		15.7		30.1		41.6	
						54.5	
						52.7	
						47.7	
	3.00	16.4	17.4	22.7	23.0	43.5	50.2
		17.6		21.1		46.7	
		18.2		25.3		49.2	
						51.4	
						53.0	
						50.6	

Table A.1 (continued): Compressive Strength of Different Cement Types

Type of Accelerating Admixtures	Amount of Accelerating Admixture, %	Compressive Strength of PSC containing 20% Slag, MPa					
		2 days	Average	7 days	Average	28 days	Average
TEA	0.00	14.2	13.2	19.5	19.5	40.8	37.1
		12.1		17.7		35.9	
		13.1		21.4		34.8	
						36.3	
						40.8	
						34.0	
	0.25	12.8	12.9	14.1	13.3	40.8	39.3
		12.1		13.8		43.2	
		13.7		12.0		43.2	
						37.5	
						35.6	
						35.7	
	0.50	13.7	13.7	22.5	21.4	38.8	43.0
		13.5		20.6		45.0	
		14.0		21.0		46.7	
						43.6	
						44.7	
						39.5	
	1.00	11.8	12.3	14.6	13.7	43.8	40.0
		13.4		12.6		36.8	
		11.7		13.8		43.9	
						36.2	
						37.5	
						41.6	
CF	1.00	13.7	13.8	15.2	14.2	44.2	43.5
		13.5		12.8		45.1	
		14.2		14.5		46.1	
						39.6	
						38.9	
						46.7	
	2.00	11.9	12.2	26.9	29.4	49.4	45.1
		12.0		30.7		45.0	
		12.8		30.6		43.4	
						41.3	
						48.5	
						43.0	
	3.00	12.0	12.9	15.0	14.4	51.0	48.5
		13.2		13.7		47.0	
		13.5		14.3		48.9	
						50.6	
						49.8	
						43.7	

Table A.1 (continued): Compressive Strength of Different Cement Types

Type of Accelerating Admixtures	Amount of Accelerating Admixture, %	Compressive Strenght of PSC containing 35% Slag, MPa					
		2 days	Average	7 days	Average	28 days	Average
TEA	0.00	10.4	10.8	11.8	13.0	39.8	37.6
		11.0		13.7		35.2	
		11.0		13.5		35.7	
						38.8	
						40.6	
						35.5	
	0.25	11.5	11.4	16.1	15.5	41.7	38.4
		11.6		14.9		38.5	
		11.0		15.5		34.9	
						40.7	
						37.3	
						37.2	
	0.50	9.1	8.7	12.4	11.3	39.2	37.2
		7.9		10.6		35.1	
		9.0		10.8		35.2	
						34.5	
						40.8	
						38.3	
	1.00	7.7	7.8	14.8	14.4	42.4	39.2
		8.3		13.7		36.6	
		7.3		14.9		40.6	
						36.1	
						44.7	
						40.1	
CF	1.00	10.9	10.0	13.3	13.4	36.5	39.5
		9.1		13.0		43.5	
		10.1		13.9		40.5	
						43.4	
						36.5	
						36.9	
	2.00	11.4	11.4	16.4	18.1	41.0	43.5
		12.4		18.1		43.9	
		10.4		19.9		44.9	
						40.8	
						45.5	
						44.8	
	3.00	10.5	9.9	11.9	13.0	41.6	43.9
		9.6		13.9		44.1	
		9.6		13.2		46.3	
						44.7	
						35.5	
						43.0	

Table A.1 (continued): Compressive Strength of Different Cement Types

Type of Accelerating Admixtures	Amount of Accelerating Admixture, %	Compressive Strength of PLC containing 6% Limestone, MPa					
		2 days	Average	7 days	Average	28 days	Average
TEA	0.00	19.7	20.0	29.5	28.4	31.5	34.4
		20.6		27.8		34.2	
		19.9		27.9		37.3	
						35.2	
						31.3	
						36.8	
	0.25	20.8	20.9	32.2	30.5	44.3	44.4
		20.4		27.7		41.4	
		21.7		31.6		47.9	
						41.4	
						45.5	
						45.6	
	0.50	19.1	21.1	37.2	36.5	39.4	42.3
		21.0		34.5		46.2	
		23.0		37.7		43.5	
						38.9	
						46.5	
						39.1	
	1.00	19.9	18.7	34.3	32.4	41.3	40.0
		17.7		31.3		40.0	
		18.4		31.7		37.0	
						40.5	
						40.7	
						40.3	
CF	1.00	19.0	19.6	34.0	33.7	43.5	42.1
		20.4		33.1		44.0	
		19.4		34.1		42.9	
						41.1	
						37.8	
						43.1	
	2.00	16.6	17.4	33.0	33.0	46.2	41.2
		17.2		32.2		38.8	
		18.4		33.8		39.8	
						37.4	
						45.8	
						39.4	
	3.00	19.6	18.6	36.2	34.0	40.1	40.3
		18.6		31.8		32.8	
		17.7		34.0		42.1	
						33.4	
						47.0	
						46.6	

Table A.1 (continued): Compressive Strength of Different Cement Types

Type of Accelerating Admixtures	Amount of Accelerating Admixture, %	Compressive Strength of PLC containing 20% Limestone, MPa					
		2 days	Average	7 days	Average	28 days	Average
TEA	0.00	11.8	11.9	21.2	19.9	29.5	28.2
		12.5		18.0		28.9	
		11.4		20.6		27.4	
						29.5	
						26.8	
						26.9	
	0.25	14.2	14.0	23.5	25.4	33.2	31.9
		13.0		25.8		32.7	
		14.7		27.0		31.4	
						32.5	
						31.5	
						30.2	
	0.50	12.8	11.7	24.2	23.1	26.9	29.1
		11.6		21.9		31.0	
		10.8		23.2		31.2	
						31.3	
						26.2	
						27.9	
	1.00	13.4	13.6	22.7	22.6	29.1	29.0
		13.5		23.7		31.0	
		14.0		21.3		25.1	
						31.9	
						27.7	
						28.0	
CF	1.00	13.8	12.9	22.2	24.6	31.5	33.3
		11.7		26.5		29.1	
		13.2		25.1		28.4	
						34.1	
						34.0	
						33.4	
	2.00	11.3	11.4	22.9	21.9	32.0	29.7
		11.4		22.4		26.7	
		11.5		20.3		28.9	
						30.5	
						29.0	
						30.9	
	3.00	12.0	11.0	24.4	24.6	26.3	32.2
		10.2		23.2		35.2	
		10.7		26.1		33.1	
						29.9	
						30.3	
						32.5	

Table A.1 (continued): Compressive Strength of Different Cement Types

Type of Accelerating Admixtures	Amount of Accelerating Admixture, %	Compressive Strength of PLC containing 35% Limestone, MPa					
		2 days	Average	7 days	Average	28 days	Average
TEA	0.00	8.0	7.6	10.9	11.1	15.5	18.2
		7.1		10.6		17.2	
		7.7		11.7		18.6	
						18.1	
						18.7	
						18.6	
	0.25	9.6	9.8	15.9	15.8	19.6	20.1
		9.7		15.2		19.4	
		10.0		16.1		19.7	
						19.2	
						21.2	
						21.6	
	0.50	7.7	7.7	14.6	14.0	16.6	16.9
		7.7		13.6		17.0	
		7.9		13.8		16.4	
						19.9	
						16.5	
						19.9	
	1.00	4.3	4.8	11.5	12.4	14.2	18.2
		5.0		13.6		17.7	
		5.1		12.1		16.2	
						18.3	
						18.3	
						18.6	
CF	1.00	7.3	7.0	12.0	12.1	19.6	19.8
		7.2		11.0		20.2	
		6.4		13.3		18.6	
						20.6	
						19.7	
						19.9	
	2.00	6.0	6.5	10.7	11.6	18.5	18.5
		6.6		11.7		18.4	
		6.7		12.5		19.4	
						20.0	
						17.1	
						17.8	
	3.00	6.0	5.8	9.5	10.5	18.2	17.7
		5.2		11.2		16.9	
		6.1		10.8		17.3	
						18.1	
						18.9	
						16.5	