

A STUDY ON THE EARLY-STRENGTH IMPROVEMENT OF SLAG
CEMENTS

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CEMENTS**

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ABSTRACT

A STUDY ON THE EARLY-STRENGTH IMPROVEMENT OF SLAG CEMENTS

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Use of alternative raw materials, especially industrial by-products, is necessary for a sustainable cement industry. By replacing clinker with industrial by-products, consumption of natural resources and energy is decreased. Therefore, both economical and environmentally friendly cements are produced. Several industrial by-products such as fly ash, silica fume, and slag, one of the most widely used industrial by-products, can be used to produce standard blended cements.

Besides its many advantages, slag cements are reported to have lower early compressive strengths. Therefore, the objective of this study is to investigate the early-strength improvement of slag cements. In the experimental study, in order not to change the cement type, the additives were incorporated within the minor additional constituent ranges, i.e. less than 5%. First, CEM III/A type control cement was prepared by blending clinker (K) and slag (S), which were separately ground in a laboratory type ball mill. Ground limestone (L) of varying fineness, silica fume (F), and sodium hydroxide (N) were prepared to be used as minor

additional constituent. The ground clinker, slag, and gypsum, and the additives at various ratios were blended to obtain 15 CEM III/A type slag cements other than the control. Finally, the fresh and the hardened properties of the cements were determined.

As a result of this experimental study, it was observed that addition of limestone generally increased the early compressive strength of slag cements. However, silica fume and sodium hydroxide either decreased or did not affect the early compressive strength of the slag cements.

Keywords: Slag, Slag Cement, Strength, Limestone, Fineness

ÖZ

CÜRUFU ÇİMENTOLARDA ERKEN DAYANIMIN İYİLEŞTİRİLMESİNE YÖNELİK BİR ÇALIŞMA

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Çimento endüstrisinde sürdürülebilirliği sağlamak için alternatif hammaddeler, özellikle endüstriyel yan ürünler, kullanılmalıdır. Çimento üretiminde, klinkerin cüruf ile yer değiştirmesi yöntemiyle, doğal kaynak ve enerji kullanımı azalmış olur. Bunun sonucunda da düşük maliyetli ve çevre dostu çimentolar üretilir. Uçucu kül, silis dumanı ve en çok kullanılan endüstriyel yan ürünlerden birisi olan cüruf, standart çimento üretiminde kullanılan endüstriyel yan ürünlerden bazılarıdır.

Cürufu çimentolar birçok avantaja sahip olmasına rağmen, erken basınç dayanımları düşük olmaktadır. Bu yüzden, bu çalışmanın amacı, cürufu çimentolarda erken dayanımın iyileştirilmesinin incelenmesidir. Deneysel çalışmada, üretilen çimento tipini değiştirmemek için katkılar minör oranlarda yani kütlece %5'ten az olarak eklendi. Öncelikle, laboratuvar tipi bilyalı değirmende ayrı ayrı öğütülen klinker ve cüruf karıştırılarak katkısız CEM III/A tipi kontrol çimentosu hazırlandı. Daha sonra, çeşitli inceliklerde öğütülen kalker (L), silis dumanı (F), ve sodyum hidroksit (N) hazırlandı. Daha sonra ise, öğütülen klinker,

öğütülen cüruf, öğütülen alçıtaşı ve katkılar değişik oranlarda karıştırılarak, kontrol çimentosu haricinde 15 adet CEM III/A tipi cürufllu çimento üretildi. Meydana getirilen bu çimento çeşitlerinin taze ve sertleşmiş özellikleri belirlendi.

Bu deneysel çalışma sonucunda, katkı maddesi olarak kullanılan kalkerin genel itibariyle cürufllu çimentoların erken basınç dayanımlarını artırdığı gözlemlendi. Silis dumanının ve sodyum hidroksitin genellikle erken basınç dayanımlarını ya düşürdüğü ya da etkilemediği görüldü.

Anahtar Kelimeler: Cüruf, Cürufllu Çimento, Dayanım, Kalker, İncelik

To My Parents

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LIST OF ABBREVIATIONS

K	:	Clinker
S	:	Slag
L	:	Limestone
F	:	Silica Fume
N	:	Sodium Hydroxide (NaOH)
G	:	Gypsum
OPC	:	Ordinary Portland Cement
PC	:	Portland Cement
BFS	:	Blastfurnace Slag
GGBFS	:	Ground Granulated Blast Furnace Slag
C₃A	:	Tricalcium Aluminate
C₃S	:	Tricalcium Silicate
C₂S	:	Dicalcium Silicate
CH	:	Calcium Hydroxide
C-S-H	:	Calcium Silicate Hydrate
Std. Dev	:	Standard Deviation
Av.	:	Average
No.	:	Number
Spec.	:	Specimens
DIFF.	:	Different
CV	:	Coefficient of Variation
XRF	:	X-Ray Fluorescence
ASTM	:	American Society for Testing and Materials
EN	:	European Standard
TS EN	:	Turkish Standard Harmonized to European Norms
TCMA	:	Turkish Cement Manufacturers' Association

CHAPTER 1

INTRODUCTION

1.1 General

Slag, an industrial by-product of steel production, is produced during the reduction of iron ore to iron in a blast furnace. Slag may show cementitious and pozzolanic properties if rapidly quenched with water, dried and ground to a fine powder (Shi and Qian, 2000; Özkan and Yüksel, 2007).

Slag cement, also known as ground granulated blast furnace slag cement, is a mixture of portland cement clinker and slag in varying amounts. Although slag cement has superior qualities such as low heat of hydration, and better durability than OPC in harsh environmental conditions, it suffers from lower early-strength. Since the clinker amount is less in slag cements, the rate of hydration is less (Khatib and Hibbert, 2005; Mun et al., 2007). Moreover, in the hydration of all pozzolanic cements, C_3S and C_2S compounds in portland cement starts to form C-S-H gels and CH. This CH later reacts with the pozzolanic material to produce new C-S-H gels. Therefore, the early-strength values are usually lower whereas the ultimate strength is similar or even higher with respect to ordinary portland cement (Binici et al., 2007; Chen and Brouwers, 2007; Dweck et al., 2003; Lin et al., 2004; Menendez et al., 2003; Mun et al., 2007; Wan et al., 2004; Lin et al., 2004; Çakır and Aköz, 2006).

Ground granulated blast-furnace slag (GGBFS) is well known material commonly used as a replacement material for portland cement in concrete for many applications. Concrete produced with GGBFS has many advantages such as higher

durability, workability and economic gains (Barnett et al., 2006; Yongde and Yao, 2000).

Even though slag cement usage is widespread in concrete around the world, its usage is quite low in Turkey (Turkish Cement Manufacturers' Association [TCMA, 2009]). The amount of slag cement produced (Table 1.1, Figure 1.1) reached a maximum level of 6.69% of total cement production in 1997, and a minimum level of 0.36% in 1999.

Table 1.1 Cement Production Amount in Turkey (TCMA, 2009)

Years	Cement Types	
	Portland (CEM I) (tons)	Slag (CEM II,III) (tons)
1996	5,592,260	1,356,161
1997	4,862,706	2,182,263
1998	6,880,484	745,734
1999	5,784,843	113,293
2000	8,022,184	644,768
2001	6,929,546	332,159
2002	8,507,887	292,261
2003	9,861,027	266,835
2004	12,469,727	395,165
2005	15,947,844	612,568
2006	17,931,554	884,077
2007	17,759,434	734,243
2008	16,238,626	686,919

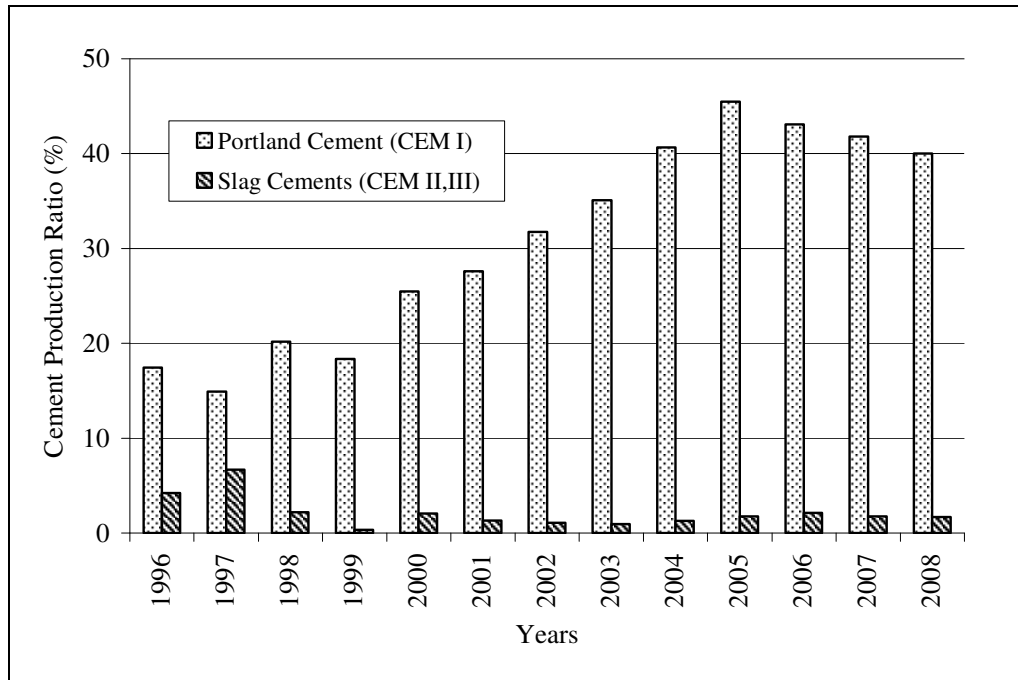


Figure 1.1 Cement Production Ratios in Turkey (TCMA, 2009)

1.2 Objective

The objective of this thesis is to investigate the effect of several additives on the strength improvement of slag cements. In this context three minor ingredients, limestone (L) with different fineness, silica fume (F) and sodium hydroxide (N) all with different ratios were used to produce 15 different slag cements. Then, the consistencies, initial and final setting times were determined as fresh properties. Hardened properties like the flexural and the compressive strength were determined at 2, 7, and 28 days. Briefly, the effects of these minor ingredients on cement properties were investigated.

1.3 Scope

This thesis consists of five chapters. Chapter 2 presents a literature review and gives a general background on cement production, the use of mineral additives for cement replacement, and slag cement types. In literature, usually limestone, NaOH, Na₂CO₃, and gypsum were used to increase the strength of slag cements.

Chapter 3 presents the experimental program such as the preparation of the materials used which are portland cement clinker, slag, limestone, silica fume, NaOH, and gypsum, and the cements, the test procedures like specific gravity, fineness, strength, consistency, and setting time, and the experimental data related with grinding, fresh and hardened properties of the slag cements.

Chapter 4 presents the results of the test program focusing on the fresh and hardened properties of slag cement. Moreover, the effect of mineral additive on the consistencies, initial and final setting times of slag cement are explained.

Chapter 5 gives a summary of the thesis and lists the result of this research. Furthermore, possible further research areas that will complement the findings of this thesis are also included.

CHAPTER 2

LITERATURE REVIEW AND BACKGROUND

2.1 Composition and Specifications for Common Cements

Although there are various construction materials, cement is the most widely used construction material all around the world. Cement is made from a mixture basically composed of limestone and clay. These materials are crushed and ground to generate the raw meal, a pale, flour-like powder and heated to around 1450 °C in rotary kilns to perform complex chemical alteration to be transformed into clinker which is rapidly cooled and stored. Finally, cement is produced by intergrinding of clinker and a small amount of gypsum (Erdoğan and Erdoğan, 2007; Günindi, 2005). This type of cement is known as Portland cement, discovered by Joseph Aspdin in 1824 (Yeğinoğlu, 2004). As defined by EN 197-1, upon mixing with water, cement compounds start to hydrate. After the hardening stage of paste, it gains strength and stability even under water.

Since 1970, many researchers have focused on the use of supplementary materials as partial replacement of portland cement. These materials are either natural resources such as pozzolan, limestone, and metakaolin or by-products like fly ash, slag from different metallurgical processes, and silica fume from other industries (Menendez et al., 2003).

Economical and environmental concerns have an essential part in the supplementary cementing material usage as well as better engineering and performance properties. From the viewpoint of the progress of high performance concrete and the recycle of industrial waste products, the application of blast-furnace slag (BFS) as a

cementitious ingredient in either cement or concrete compounds has been increasing (Güneyisi and Gesoğlu, 2007; Itoh, 2004).

Accordingly, limestone, clay, coal, and electricity are consumed to produce portland cement, and waste gases such as CO₂, SO₃, and NO_x, which cause greenhouse effect and acid rain, are released. To meet the increase of demand for cement and comply with the environmental regulatory, cement that presents less CO₂ emission during cement production should be developed. Therefore, it is feasible to produce cement with industrial by-products by reducing the amount of clinker. With the usage of by-products, added value is maximized for these industrial by-products, natural resources and energy are conserved, environmental pollution problems caused by CO₂ discharge are minimized, and the production cost is reduced (Dongxu et al., 2000; Erdoğan, 2002; Mun et al., 2007; Topçu and Karakurt, 2007).

Inorganic constituents of cements are termed either major or minor depending on the amount of additions in EN 197-1. It is called main constituent if inorganic material amount is more than 5% by weight of cement. In other words, if inorganic material amount is less than 5% by weight of cement, it is described as minor additional constituent.

Adding the constituents, such as blastfurnace slag, silica fume, pozzolan, etc., at the final grinding stage produces various cements for specialized uses. According to EN 197-1, there are 27 minor types of common cements assembled into 5 major cement types as follows:

- CEM I Portland cement
- CEM II Portland-composite cement
- CEM III Blastfurnace cement
- CEM IV Pozzolanic cement
- CEM V Composite cement

2.2 Composition and Specifications for the Additives

According to EN 197-1, limestone rocks are formed from calcite mineral (CaCO_3) which is the product of evaporated seas, lakes, and marine animal shells. Limestone fillers are used in cement production as a raw material and also as an additive (Lewis et al., 2003). Limestone is one of the most widely used mineral additives in cement especially because of European Cement Standards. In most European countries, limestone is used as a minor additional constituent (Erdoğan, 2002).

In the hydration of cements, addition of limestone (CaCO_3) increases the hydration rate by the formation of calcium monocarboaluminates ($\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$). C_3A is a possible reactive agent to use hydraulic reactivity of calcareous filler in cement. Therefore, CaCO_3 looks like a stabilizer of hexagonal hydrates, responsible for the mechanical structure of the hydrated mixture. In addition, monocarboaluminate has better combining property and more compacted formation than ordinary hydration products of C_3A . In other words, limestone and cement interact chemically to produce superior bond and strength result for cement. On the other hand, the effect of limestone on hydration rate increases with the amount of limestone addition especially in the first 2 days. In addition, heat of hydration results showed that reaction rate increases with the addition of limestone until first 12-16 hours time period. After 16 hours, there is no significant difference on the rate of heat of hydration generation (Erdoğan, 2002).

Silica fume is formed during the high-temperature lessening of quartz in an electric arc furnace where the major manufactured goods are silicon or ferrosilicon. Because of the enormous quantities of electricity required, the furnaces are placed in countries with plentiful electrical capacity including Scandinavia, Europe, the USA, Canada, South Africa and Australia. High-purity quartz is heated to about 2000°C with coal, coke or wood chips as fuel. Then an electric arc is introduced to divide the metal. Because the quartz is reduced, it gives out silicon oxide vapour. This combines with oxygen in the upper parts of the furnace. In the furnace, it oxidizes

and concentrates into microspheres of amorphous silicon dioxide. The fumes are emitted from the furnace throughout a precollector and a cyclone, which is used to eliminate the larger coarse units of incombusted wood or carbon. Later, the fumes are carried into special filter bags (Lewis et al., 2003; Massazza, 2003).

The terms silica fume, condensed silica fume, microsilica, and volatilized silica are frequently used to describe the by-products extracted from the exhaust gases of silicon, ferrosilicon and other metal alloy smelting furnaces. Nevertheless, the names microsilica and silica fume are used to describe those condensed silica fumes which are of high quality, for use in the cement industry (Lewis et al., 2003).

Silica fume was first produced in 1947 in Norway when environmental restraints made the filtering of the exhaust gases from the furnaces mandatory. The main fraction of these fumes was a very fine powder composed of a high proportion of silicon dioxide. Large-scale cleaning of gases started in the 1970s and the first standard for use in factory-produced cement was contracted in 1976 (Lewis et al., 2003).

Sodium hydroxide (NaOH), a white crystalline compound, is a chemical material. It is ready to absorb CO_2 and moisture from the air. It is generally known as caustic soda, and soluble in water. Sodium hydroxide is manufactured by electrolytic dissociation of sodium chloride. Moreover, it is produced in a small amount by soda-lime process where a concentrated solution of soda (sodium carbonate) is reacted with slaked lime (calcium hydroxide). During the soda-lime process, calcium carbonate precipitates and sodium hydroxide solution is produced. Sodium hydroxide is used for activation of slag in cement industry. Hydraulic property of slag is locked within glassy structure. Therefore, NaOH is used as an activator. NaOH reacts chemically with GGBS, and increase pH of the cement. Once a critical pH has been reached the glassy structure of the slag is harmed, and slag will begin to react with water producing its own cementitious gels (Shi et al., 2006; The

Columbia Encyclopedia, 2008; Collins and Sanjayan, 1998; Yongde and Yao, 2000; Dongxu et al., 2000).

Finally, the major constituent slag will be discussed in detail in Section 2.3.

2.3 Composition and Specifications for Slag Cements

As mentioned in the previous chapter, blastfurnace slag, a cementitious material, is produced as a by-product during the production of iron in a blastfurnace. Iron ore, limestone and coke are sent continuously to the blastfurnace, where they melt into two layers at 1500 °C. When the molten iron sinks, the blastfurnace slag floats on the surface due to its lower density. To process the slag into a form suitable for use as a cementitious material, one of two techniques, granulation or pelletization, can be employed. In both techniques, the slag is rapidly cooled to form a glassy disordered structure. If the slag is cooled too slowly, a crystalline well-ordered structure, which is stable and non-reactive, is formed. Rapid cooling causes the slag to cool rapidly into glassy granules no larger than about 5 mm in diameter. In most modern granulators, the temperature of water, which is used to cool the slag quickly, is kept below about 50 °C and the (water)/(slag) ratio is normally 10-20. Then, the slag is dried and ground to cement fineness in a conventional cement clinker grinding mill. On the other hand, pelletization involves pouting the molten slag onto a water-cooled steel-rotating drum. The drum has fins projecting from it, which throw the slag through the air inside a building where water is sprayed onto it for quick cooling. Pelletizing generates material from almost 100 mm down to dust; the coarser particles are likely to be crystalline in nature and have little or no cementitious property (Lewis et al., 2003; Lyons, 2006).

The chemical composition of slag can differ over a broad range depending on the natural history of the ore, the character of the limestone flux, the coke constitution and the type of iron being made. It can also transform over the years with alterations in the origin and kinds of ore being smelted. These variations have an effect on the

relative content of the four main components, which are lime, silica, alumina and magnesia, and also the amounts of the minor constituent, sulfur in the form of sulfide, and ferrous and manganese oxides (Regourd, 2003).

GGBFS-PC (ground granulated blast furnace slag-portland cement) type blended cements can be manufactured by intergrinding the two components (i.e. clinker and granulated slag) in the ball mills or by blending the two components at the cement plant or by blending in the mixer (Lewis et al., 2003; Lyons, 2006).

GBFS (granulated blast furnace slag) was used with lime in mortars as early as 1774. Moreover, the hydraulic property of GGBFS was first discovered as long ago as 1862 by Emil Langen in Germany. In 1865, lime-activated GGBFS began to be used commercially in Germany. Later, in 1889, it was used in the construction of the Paris metro. In addition, around 1880, GGBFS was first used in combination with Portland cement (PC). GGBFS-PC combination was used in 1892 in Germany and in 1896 in the USA. In the UK, in 1923, the first British Standard for Portland Blastfurnace Cement (PBFC) was generated. GBFS was used in cement production as a raw material until 1950s. After the late 1950s, it started to be used as a separate cementitious material in Australia, Canada, Japan, South Africa, UK, and US (Lewis et al., 2003; Lyons, 2006).

Depending on the amount of slag utilized, slag cements are labeled as CEM II, III or V. Table 2.1 lists the amounts of clinker and blast furnace slag that is specified in EN 197-1.

Although, slag cements have improved qualities such as low heat of hydration, admirable durability, and high standard strength, it is reported to present problems of reduction in early-strength (Dongxu et al., 2000; Erdoğan, 2002; Mun et al., 2007; Topçu and Karakurt, 2007).

Table 2.1 Slag Cement Types and the Compositions defined in TS EN 197-1

Cement Type	Cement Label	Composition (percentage by mass)				
		Main Constituent				Minor Addition
		Clinker	Blast-furnace Slag	Pozzolan	Fly Ash	
CEM II	CEM II/A-S	80-94	6-20	-	-	0-5
	CEM II/B-S	65-79	21-35	-	-	0-5
CEM III	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 V	CEM V/A	40-64	18-30	18 – 30		0-5
	CEM V/B	20-38	31-50	31 – 50		0-5

2.4 Previous Studies

A review of the literature revealed that research on the early-strength improvement of slag cements were focused especially by the end of 20th century. Collins and Sanjayan (1998) compared activated blast furnace slag with portland cement in terms of compressive strength at 1-day at normal curing temperatures. To activate blast furnace slag, NaOH (2%-3%-4%-5%-6%-7%) and Na₂CO₃ (0%-1%-2%-3%-4%) were used. According to the test results, 100% alkali-activated slag and ordinary portland cement has nearly the same compressive strengths at 1-day. Moreover, activation of slag with Na₂CO₃ is more effective than NaOH to reach the one-day strength value of portland cement. Furthermore, if Na₂CO₃ (4%) and NaOH (5%) are used together to activate slag, the compressive strength of slag at one day is equal to that of portland cement. However, compressive strength at 28 days is lower for activated slag than for portland cement.

In addition, Dongxu et al. (2000) studied high-content slag cement (70%-90% slag) by adding compound admixtures such as gypsum (5%), anhydrite gypsum (4%-5%), Na₂SO₄ (2%), and synthetic admixtures (4%-6%). The results showed that although the effects of anhydrite and Na₂SO₄ compound admixtures on the strength at early ages are noticeable, the effect is not so clear at 28 days. Moreover, when fineness increases from 300 m²/kg to 450 m²/kg, the strengths increase at 3, 7 and at 28 days. Furthermore, anhydrite and synthetic compound admixtures increase the compressive strength at 3, 7, and 28 days.

In another study conducted by Yongde and Yao (2000), combined-alkali-activated slag paste materials were examined. In the study, Na₂CO₃ and NaOH were used in combination or individually to activate the slag. The results of the study showed that better early-strength improvement is obtained when NaOH is used as an activator instead of Na₂CO₃. Besides, combination of NaOH and Na₂CO₃ provided higher early-strength.

In another study (Menéndez et al., 2003), binary or ternary mixtures of portland cement with limestone filler (10%-20%), and blast-furnace slag (10%-20%-35%) were used to investigate the strength improvements. The results indicated that limestone filler improves the early-strength of blended cements having 5 to 15 percent limestone filler and 0 to 20 percent blast-furnace slag at 1 and 3 days. Furthermore, the combination of portland cement, limestone filler, and blast-furnace slag increases early and ultimate compressive strengths.

In a study conducted by Demirboğa (2003), the effects of silica fume, class C fly ash, and blast furnace slag were investigated. Cement was replaced by the admixtures at the ratios of 10%, 20% and 30% by weight. According to the test results, compressive strength declined at early ages for all of admixtures, especially for fly ash as function of substitution ratio. On the other hand, silica fume (10%) usage increased compressive strengths of mortars at 7, 28 and 120 days. Similarly, fly ash (10%-20%) application increased compressive strength at 120 days.

Moreover, although blast furnace slag utilization decreases compressive strength at 28 days, it raised the strength at 120 days.

In addition, Barnett et al. (2006) investigated ground granulated blast-furnace slag cement and portland cement in terms of the strength improvement of mortars. The replacement amounts of ground granulated blast-furnace slag were 0%-20%-35%-50%-70% in the binder. Moreover, water–binder ratio and curing temperature were changed during the study. The study showed that curing temperature increases the early-age strength of mixtures containing ground granulated blast-furnace slag, especially for higher replacement levels.

In a similar study conducted by Çakır and Aköz (2006), ground granulated blast furnace slag (0%-30%-60% by weight) was used as a replacement material. In this study, curing temperature was changed from 20 °C to 40 °C temperatures. The study confirmed that slag cement mortars gained strength rapidly at early ages when curing temperature was higher.

In another study conducted by Mun et al. (2007), the strength of blast furnace slag cements were examined by adding inorganic activators. In the study, the quantities of commercial slaked lime, anhydrous gypsum, and limestone powder were at most 2.5%. The study showed that mortars with admixtures have higher compressive strengths at 3 days. The amount of the compressive strength increases are 30%, 24%, 13% for the materials gypsum (2.5%), slaked lime (0.5%), and limestone powder (2.5%) respectively. These results proved that suitable activators like lime, gypsum and limestone powder improves the compressive strength of slag cements at early age.

All of the studies mentioned above are summarized in Table 2.2.

Table 2.2 Materials Used in the Previous Studies

Material	Researchers														
	Collins& Sanjayan (1998)		Yongde and Yao (2000)		Dongxu et al. (2000)		Menéndez et al. (2003)		Demirboğa (2003)		Barnett et al. (2006)	Çakır and Aköz (2006)		Mun et al. (2007)	
	Q*	F*	Q*	F*	Q*	F*	Q*	F*	Q*	F*	Q*	Q*	F*	Q*	F*
Slag	50	4600	40-90	5000	70-90	3000-4500	10-35	4580	10-30	4000	0-70	0-60	4730	0-70	4600
	50	14960													
OPC	50	3420					45-100	3210	70-90	3410	30-100	40-100	3570	30-100	3300
NaOH	2-7		5												
Na ₂ CO ₃	0-4		5												
Clinker					2-25	3000-4500									
Gypsum					5	3000-3500									
Anhydrite					4 -5	3000-4500								0-2.5	
Na ₂ SO ₄					2	3000-4500									
Synthetic Admixture					4 -6	3750									
Limestone							10-20	7100						0-2.5	
C-Fly Ash									10-30						
Silica Fume									10-30						
Slaked Lime														0-0.5	

Q* : Quantity (%)
F* : Fineness (cm²/g)

CHAPTER 3

EXPERIMENTAL PROGRAM

The objective of this study is to investigate the effects of mineral additives, such as limestone, silica fume, and sodium hydroxide, on the fresh and hardened properties, especially early-strength improvement of slag cements.

First of all, CEM III/A type cement was produced by mixing 50% clinker (K) and 50% slag (S) as the control cement. Then, different cements were prepared by adding limestone (L) with different fineness, silica fume (F), and sodium hydroxide (N) to the control cement. Later, the fresh and hardened properties of produced cements were determined. Fresh properties included consistencies, initial and final setting times. Hardened properties included flexural and compressive strength tests at 2, 7, and 28 days.

3.1 Material Properties

This section presents the chemical and physical properties of all constituents. While producing the cements, portland cement clinker, granulated blastfurnace slag, silica fume, limestone, calcium sulfate, and sodium hydroxide were used. For each ingredient utilized, the properties of the materials are given in the following sub-sections.

Portland cement clinker, limestone, and gypsum were obtained from Set Italcementi Ankara Cement Plant, and slag was obtained from Set Italcementi Ambarlı Cement Plant. The chemical properties of ground clinker, ground slag, ground limestone, and silica fume are presented in Table 3.1. The chemical analyses were performed using XRF (X-Ray Fluorescence) technique in OYAK Bolu Cement Plant.

Table 3.1 Summary of the Chemical Properties of the Materials

Property	Clinker	Slag	Limestone	Silica Fume
SiO ₂ (%)	21.44	32.88	7.80	88.08
Al ₂ O ₃ (%)	5.89	15.97	2.36	-
Fe ₂ O ₃ (%)	4.25	2.89	0.72	0.33
CaO (%)	63.03	28.94	48.45	3.51
MgO (%)	2.27	8.27	1.12	0.72
SO ₃ (%)	0.80	-	-	-
K ₂ O (%)	0.76	0.82	0.25	0.55
Na ₂ O (%)	0.63	1.40	0.06	1.12

The sodium hydroxide was obtained from MERCK Company. The chemical properties of sodium hydroxide given in Table 3.2 were available on the box of the commodity.

Table 3.2 Chemical Properties of Sodium Hydroxide

Property	Sodium Hydroxide
Assay (acidimetric, NaOH)	> 97 (%)
Carbonate (as Na ₂ CO ₃)	< 1 (%)
Chloride (Cl)	< 0.01 (%)
Sulphate (SO ₄)	≤ 0.01 (%)
Heavy metals (as Pb)	≤ 0.02 (%)
Al (Aluminium)	≤ 0.02 (%)
Fe (Iron)	≤ 0.02 (%)

3.2 Experimental Procedures

3.2.1 Preparation of Slag Cements

Clinker, slag, limestone, silica fume, and gypsum were dried separately at least 24 hours in an oven at 100 °C. Since clinker, limestone, and gypsum particles were coarse, first they were separately crushed to 0.5-1.0 cm in a laboratory type jaw crusher (Figure 3.1). Slag was not crushed in the jaw crusher because it was finer than the discharge opening of the jaw crusher. The type of crusher was blake type jaw crusher. In this type of crusher, jaw is pivoted at the top, receiving area (A) is fixed, and discharge opening, also called set, (B = 0.5-1.0 cm) is variable.

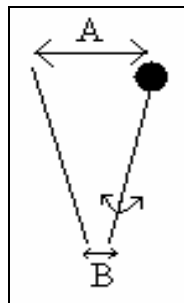


Figure 3.1 Crusher Mechanism

Then, all of the materials, except for silica fume and NaOH, were placed into a laboratory type ball mill (Figure 3.2) and were separately ground until the required Blaine fineness values were obtained. The required Blaine finenesses were 3500 cm^2/g for clinker, slag, and gypsum (but the fineness of gypsum was obtained as 5830 cm^2/g due to overgrinding). Moreover, limestone was ground to get 3500 cm^2/g , 7000 cm^2/g , and 10500 cm^2/g Blaine finenesses.

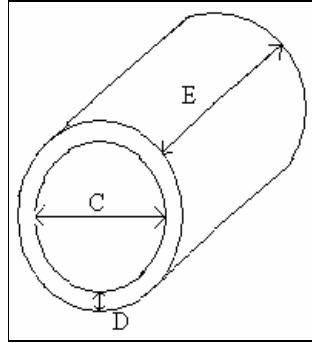


Figure 3.2 Ball Mill

The inside diameter (C) of the ball mill was 40 cm, the shell thickness (D) of the ball mill was 1 cm, and the length (E) of the ball mill was 46 cm. Therefore, the inside volume of the ball mill was approximately 57780 cm³.

Moreover, the grinding media were both steel balls and steel cylpebs. The bulk densities of the balls and the cylpebs were 4650 kg/m³ and 4700 kg/m³ respectively. The dimensions and the weights of the grinding media used in this thesis study are given in Table 3.3.

Furthermore, the bulk volume of the grinding media is calculated by using Equation 3.1

$$V = \frac{m}{d} \quad (3.1)$$

where V is the volume of the grinding media, m is the mass of the grinding media, and d is the bulk density of the grinding media. Therefore, the bulk volume of the grinding media was calculated as

$$V = \frac{84\text{kg}}{4650\text{kg/m}^3} + \frac{14\text{kg}}{4700\text{kg/m}^3} \rightarrow V \cong 21040 \text{ cm}^3$$

Since volume of the ball mill was 57780 cm³, and the bulk volume of the grinding media was 21040 cm³, the volume of the grinding media in the ball mill was approximately 36% of the inside volume of the ball mill.

Table 3.3 Size Distribution of the Grinding Media

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

On the other hand, grindability is affected by the properties which are hardness, elasticity, toughness, and cleavage of the materials. The hardness, a fairly good indication of the abrasiveness of a material, is determined by the Mohs scale. Materials may range from hard such as like quartz and granite, to soft such as talc and gypsum. The hardness of the materials in literature according to Mohs scale is

given Table 3.4 (Couper et al., 2005; Souza et al., 2008; Velez et al., 2001; Wang and Luer, 1998; He et al., 2006; Zhu et al., 2007; Güven and Özcan, 2005).

Table 3.4 Hardness of the Materials

	Clinker	Slag	Limestone	Gypsum
Hardness	4 - 5	6 - 7	3	2

Table 3.4 shows that hardnesses of the materials are ranked in decreasing order as slag, clinker, limestone, and gypsum.

After grinding operation, the materials were put into plastic bags separately to prevent exposure to humidity.

On the other hand, NaOH had a different sample preparation method. It was just crushed with a hammer and stored in plastic bags.

After the preparation of all materials, they were mixed in the proportions provided in Table 3.5 to produce the required cement types.

The manufactured cements were labeled systematically to identify the parameters involved. The first letter in the first column of Table 3.5 shows the type of addition, the first number shows the amount of addition, and the second number shows its fineness.

For example, in L-1-3500, L stands for limestone, 1 stands for 1.67% and 3500 stands for Blaine fineness in cm^2/g .

Table 3.5 Composition of Slag Cements with the Additives

Cement Type	Additive		Amount (%)				
	Name	Fineness	Clinker	Slag	Additive	Total	Gypsum
Control	-	-	50.00	50.00	-	100.00	3.50
L-1-3500	Limestone	3481	49.17	49.17	1.67	100.00	3.50
L-3-3500			48.34	48.34	3.33	100.00	3.50
L-5-3500			47.50	47.50	5.00	100.00	3.50
L-1-7000		6995	49.17	49.17	1.67	100.00	3.50
L-3-7000			48.34	48.34	3.33	100.00	3.50
L-5-7000			47.50	47.50	5.00	100.00	3.50
L-1-10500		10498	49.17	49.17	1.67	100.00	3.50
L-3-10500			48.34	48.34	3.33	100.00	3.50
L-5-10500			47.50	47.50	5.00	100.00	3.50
F-1	Silica Fume	*	49.17	49.17	1.67	100.00	3.50
F-3			48.34	48.34	3.33	100.00	3.50
F-5			47.50	47.50	5.00	100.00	3.50
N-1	NaOH	**	49.17	49.17	1.67	100.00	3.50
N-3			48.34	48.34	3.33	100.00	3.50
N-5			47.50	47.50	5.00	100.00	3.50
* : could not be detected with the Blaine apparatus.							
** : crushed by a hammer.							

3.2.2 Determination of Specific Gravity and Fineness of the Materials

To determine the specific gravities, Le Chatelier's principle was applied (ASTM C188, 2003). When finding the specific gravities of the materials, kerosene was used to prevent any reaction between the materials and the liquid in the flask. Kerosene was put into the flask to the level between 0 and 1 cm³. Then, the flask was placed into the temperature stabilizer to stabilize the temperature at 22 °C and

the level was measured. After the level was recorded, the solid material (64 grams) was poured into the flask and the new level was determined. The volume of the material was the change in the level. Therefore, density was found by dividing mass to volume of the materials. Since specific gravity is the comparison of the density of a material compared to the density of water (assumed 1.0 g/cm^3) at a specific temperature, it was represented as specific gravity in this study.

After determination of the specific gravities, finenesses of the materials were also determined using the Blaine air permeability method according to TS EN 196-6 (2002).

Later, the materials were sent to OYAK Bolu Cement Plant for particle size analysis with dry method. The sizes of the particles determined with laser beam which permits to measure the particle sizes between $1.8 \mu\text{m}$ and $350 \mu\text{m}$ when almost 1-2 grams of material sample is passing through the spout between the laser beam and the lens.

3.2.3 Determination of Consistency and Setting Time of Slag Cements

In order to determine consistency and setting time, pastes were prepared according to the procedures described in TS EN 196-3 (2002). The specimens were manufactured with 500 grams of cement, and different amounts of water to get the normal consistency. Normal consistency is the degree at which the plunger can penetrate into cement paste to a depth of $6 \pm 1 \text{ mm}$ from the base plate. After obtaining the normal consistency, the initial and final setting time is determined by the same apparatus. Penetration of the needle into the paste to a depth of $4 \pm 1 \text{ mm}$ from the base plate determines the initial setting. Then, the vicat mould is turned upside down to determine the final setting time. The penetration of the needle into the paste to a depth of 0.5 mm from the surface of the mould indicates the final setting.

3.2.4 Determination of the Strength of Slag Cements

In order to determine the strength of slag cement, cement mortars were prepared in accordance with TS EN 196-1. The types of the specimens were prisms having 40x40x160 mm dimensions. The amounts of cement, sand, and water were 450, 1350, and 225 grams respectively to produce one cement type (the ratio of cement/sand/water is 1/3/0.5 as given in TS EN 196-1).

After curing at 20 ± 2 °C in water, flexural and compressive strengths were determined at 2, 7, and 28 days with the equipment described in TS EN 196-1. Flexural strength was performed for 3 specimens for each type of cement. Specimens were supported from 2 points while loading from center-point at the rate of 5 ± 1 kgf/sec (Figure 3.3) (TS EN 196-1).

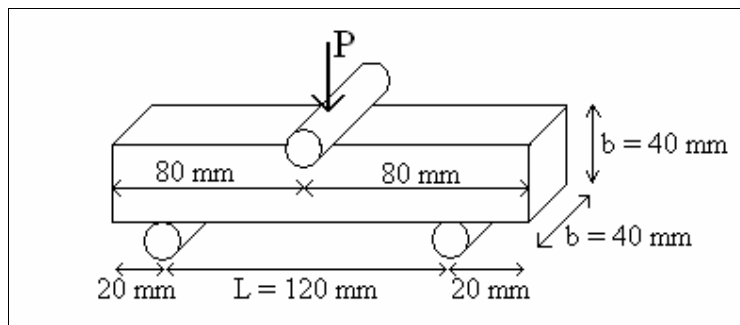


Figure 3.3 Flexural Strength Test

Then, the load that breaks the specimen at the mid point was recorded. The flexural strength was calculated using Equation 3.2 in accordance with TS EN 196-1:

$$R_f = \frac{1.5x F_f x L}{b^3} \quad (3.2)$$

where R_f is the flexural strength in MPa, F_f is the maximum load in Newton, L is the distance between the spans in mm, and b is the edge of the specimen in mm.

After the flexural strength test application, 2 specimens for compressive strength test were obtained. Load was applied at a relative rate of movement between the upper and lower platens, which were 40x40 mm metal plate, corresponding to a loading on the specimen with 90 kgf/sec. Then, the maximum load which breaks the specimens was recorded. The compressive strength was calculated using Equation 3.3 in accordance with TS EN 196-1:

$$R_c = \frac{F_c}{1600} \quad (3.3)$$

where R_c is the compressive strength in MPa, F_c is the maximum load in Newton, and 1600 is the are of the plates in mm^2 .

3.3 Experimental Data

One control and 15 cements with mineral and chemical additives were prepared to determine the strengths as shown in Table 3.5. The ratio of cement/sand/water was selected as 1/3/0.5 as given in TS EN 196-1.

3.3.1 Particle Size Reduction of the Materials

The specific gravities given in Table 3.6 are used to determine the Blaine values.

Table 3.6 Specific Gravities of the Materials Used

	Clinker	Limestone	Slag	Silica Fume	Gypsum
Specific Gravity	3.22	2.66	2.84	2.14	2.53

After crushing the materials in a laboratory type jaw crusher, the crushed material was charged into the laboratory type ball mill in 5 kg batches due to grinding capacity of the ball mill.

The strength performance of the cements depends on the fineness and the particle size distribution as well as the properties of the main components and their proportions in the cement. Therefore, the grinding process is one of the most important procedures to determine the cement performance (Bayburtlu, 2006).

The grinding durations to get the required Blaine values for the materials are given in Tables 3.7 through 3.9 for clinker, slag, and limestone. At each time interval, a sample was taken and the fineness was determined using the Blaine apparatus.

Grinding time for gypsum was determined as 7 minutes to obtain 5830 cm²/g Blaine fineness (due to overgrinding).

Table 3.7 Grinding Durations for Clinker

Time (min)	Blaine (cm²/g)
45	2572
75	3235
80	3465

Table 3.8 Grinding Durations for Slag

Time (min)	Blaine (cm²/g)
90	2734
105	2909
120	3168
135	3474

Table 3.9 Grinding Durations for Limestone

Time (min)	Blaine (cm²/g)
14	3481
35	5401
40	5685
50	6530
55	6615
60	6865
62	6995
80	7460
95	8341
110	8799
125	9088
140	9499
170	9604
185	10139
203	10498

The grinding durations for the required Blaine values for each material are summarized in Table 3.10.

Table 3.10 Summary of the Grinding Durations

	K	S	L (3500)	L (7000)	L (10500)	G
Quantity (kg)	5	5	5	5	5	5
Blaine (cm ² /g)	3465	3474	3481	6995	10498	5830
Time (min)	80	135	14	62	203	7

One of the most important physical properties of cementitious materials is particle size distribution (PSD). It mostly affects the setting time and the strength of the cements. There are a number of methods to determine PSD (sieving, cycloning, microscopy, etc.). Radically different information can be obtained by each of the techniques for particle size distribution investigation of the materials. Hence, the crucial aim of the classification determines the analysis technique. The results of a particle size distribution analysis may be represented in different techniques, by particle diameter pointing out the nominal mesh ranges, or by PSD, in grams, in percentage by weight of each fraction (differential distribution, either undersize or oversize). A number of mathematical models have been developed to get the distribution and density functions from investigational particle size distribution curves. One of the most commonly used methods is the Rosin Rammler Bennett (RRB) technique. The RRB distribution function has long been used to express the PSD of fine particles of a variety of types and sizes. The function is principally suitable to characterize fine particles prepared by grinding and crushing operations (Garcia et al., 2004).

The cumulative distributions are presented in Figure 3.4 for ground clinker, ground slag, ground gypsum and in Figure 3.5 for limestone. Moreover, particle size

distributions according to RRB method are presented in Figure 3.6 for ground clinker, ground slag, ground gypsum and in Figure 3.7 for limestone. However, the result of silica fume is not presented because the results were not reliable (because the measuring ranges of the equipment and the particle size are not in similar series).

The RRB distribution function is given in Equation 3.4.,

$$Y = 1 - \exp\left[-\left(\frac{d}{k}\right)^n\right] \quad (3.4)$$

where Y is the weight fraction of particles fine than size d, d is the particle size in microns, k is the position parameter, and n is the distribution modulus.

Moreover, in Figures 3.6 and 3.7, the slope (n) determines the proportion between the coarse and the fine ingredients of the cement, and the position parameter (k) determines the fineness level of the material. For the same Blaine fineness of the cements, if the slope is steeper, the size distribution is narrower. Because of the narrower particle size distribution, space volume gets larger. Therefore, the water requirement increases and the strength decreases. (Bayburtlu, 2006; Celik, 2009).

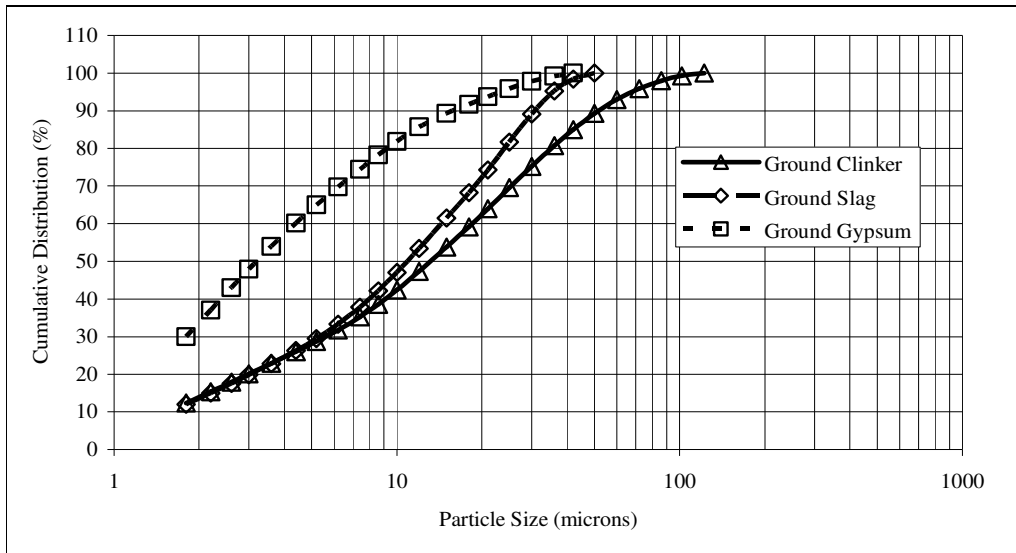


Figure 3.4 Particle Size Distribution for Ground Clinker, Slag, and Gypsum

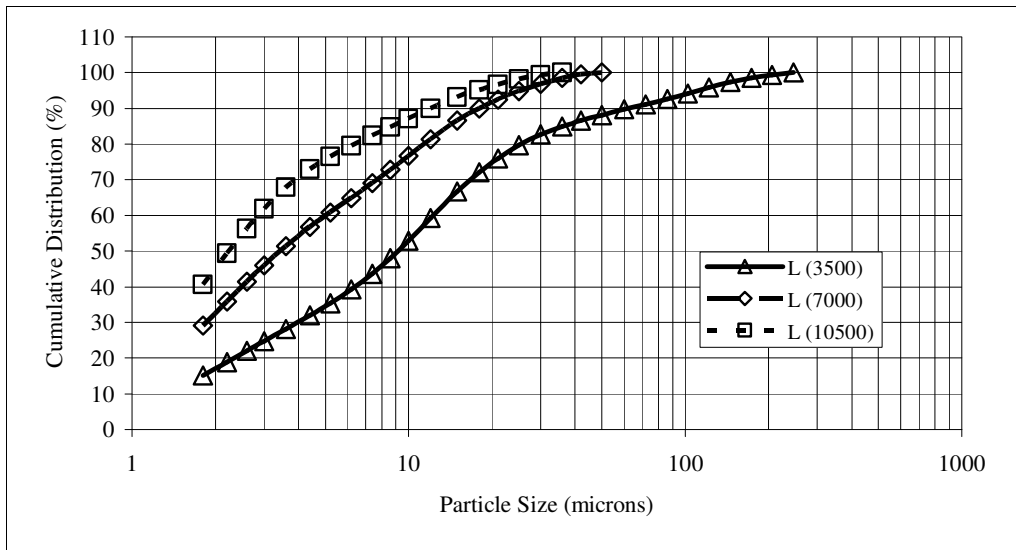


Figure 3.5 Particle Size Distribution for Ground Limestone

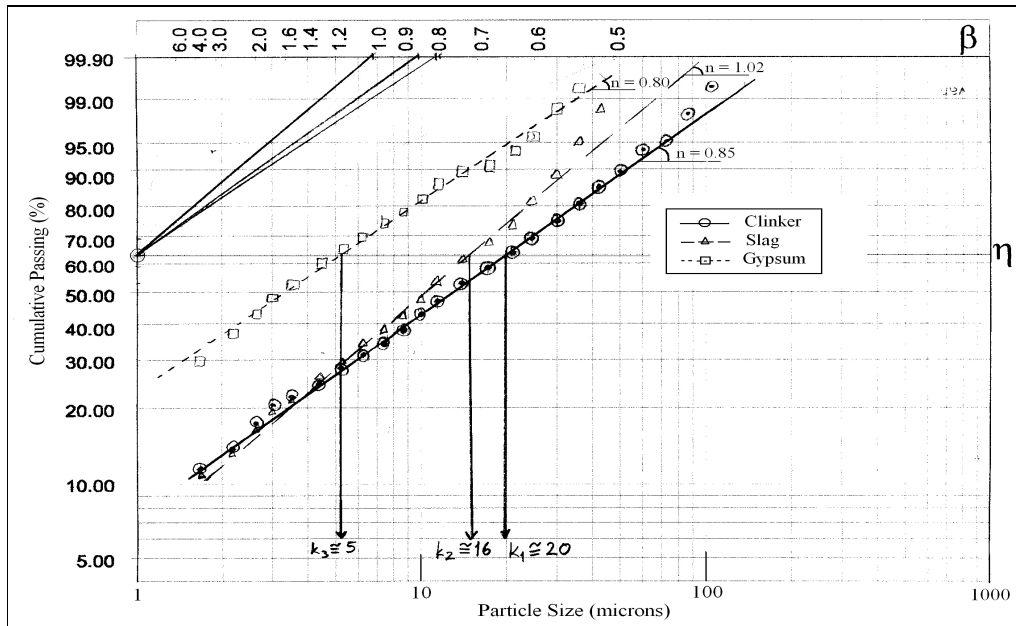


Figure 3.6 RRB Particle Size Distribution for Ground Clinker, Slag, and Gypsum

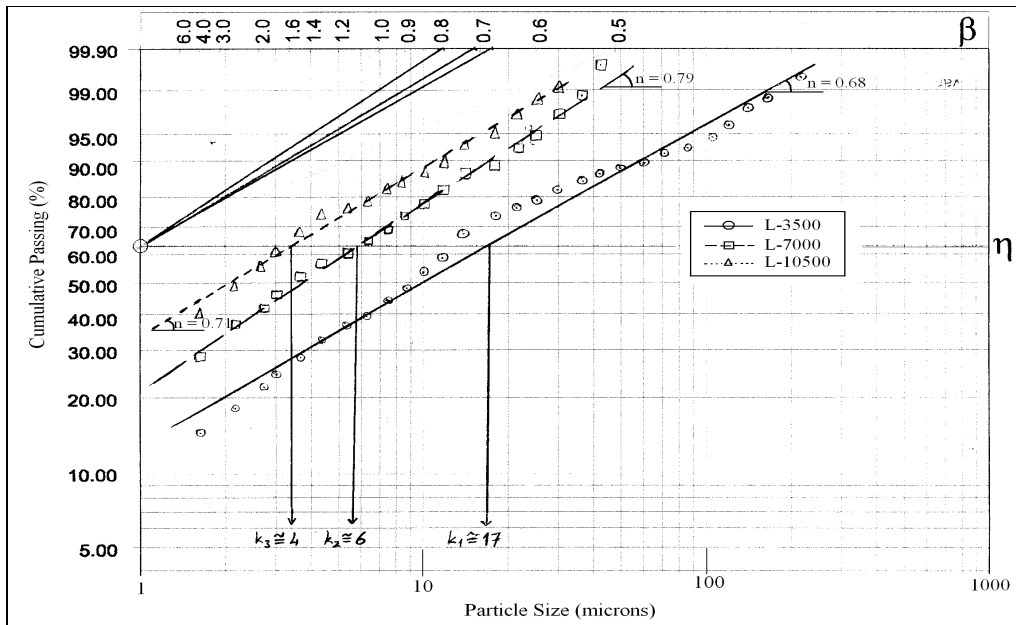


Figure 3.7 RRB Particle Size Distribution for Ground Limestone

Moreover, the slope, the k values of the distribution function according to Figures 3.6 and 3.7, and the particle sizes passing 50% and 100% of cumulative distribution according to Figures 3.4 and 3.5 are presented in Table 3.11 for ground clinker, ground slag, ground gypsum, and for ground limestone.

Table 3.11 Particle Size Distribution Parameters of the Ground Materials

	K	S	L (3500)	L (7000)	L (10500)	G
Distribution Modulus (n)	0.85	1.02	0.68	0.79	0.71	0.80
Position Parameter (k)	20	16	17	6	4	5
Particle Size in μm [< %50 cumulative]	14	11	9	4	2	3
Particle Size in μm [< %100 cumulative]	130	50	240	50	35	40

3.3.2 Fresh Properties of Slag Cements

Table 3.12 presents the tested fresh properties of the 6 cement types which have the highest strength values at 2, 7, and 28 days, control cement, and cement with NaOH. The table includes the required amount of water in grams and in percentage to achieve the consistency required by TS EN 197-1, and the initial and final setting times in minutes.

Table 3.12 Consistency and Setting Times of the Produced Pastes

Cement Label	Required Amount of Water for Consistency		Initial Setting Time (min)	Final Setting Time (min)	TS EN 197-1 Requirement for Initial Setting Time (min)
	(g)	(%)			
Control	145.0	29.0	173	262	≥ 75
L-1-3500	147.5	29.5	180	272	≥ 60
L-5-3500	150.0	30.0	179	267	≥ 75
L-1-7000	150.0	30.0	193	270	≥ 60
L-5-7000	160.0	32.0	174	306	≥ 75
L-3-10500	165.0	33.0	172	317	≥ 75
L-5-10500	165.0	33.0	177	280	≥ 60
N-1	165.0	33.0	172	245	≥ 75
N-5	180.0	36.0	15	95	-

3.3.3 Hardened Properties of Slag Cements

The hardened properties such as the flexural and the compressive strengths at 2, 7, and 28 were determined for all 16 cement types, including the control cement. Tables 3.13 through 3.16, related with strength results, present the individual values, averages, standard deviations and the coefficient of variations of the flexural strengths. In the tables, the italic and underlined values are the faulty results, out of 10% of the average value, according to TS EN 196-1, and they were not used in the calculations.

3.3.3.1 Flexural Strength Results

The flexural strength results are given in Table 3.13 for all ages. Since there are only 3 data for flexural strength test for each type of the cements, presentation of standard deviation and coefficient of variation in Table 3.13 is not appropriate.

Table 3.13 Flexural Strength at 2-7-28 Days in MPa

Cement Label	2 Days				7 Days				28 Days			
	Specimen No.			Av.	Specimen No.			Av.	Specimen No.			Av.
	#1	#2	#3		#1	#2	#3		#1	#2	#3	
Control	2.7	2.9	2.8	2.8	4.7	4.6	4.4	4.6	7.0	7.2	6.6	6.9
L-1-3500	3.0	2.9	2.8	2.9	4.4	4.5	4.9	4.6	6.7	7.4	7.1	7.0
L-3-3500	2.6	3.0	2.8	2.8	5.4	5.0	5.3	5.2	7.5	7.8	7.7	7.7
L-5-3500	2.9	2.7	3.1	2.9	5.2	5.0	5.0	5.0	7.6	7.6	8.1	7.8
L-1-7000	3.0	2.9	3.0	3.0	4.9	5.2	4.9	5.0	7.2	7.3	6.7	7.1
L-3-7000	2.6	2.8	2.8	2.7	5.5	5.6	5.6	5.6	9.0	8.4	8.3	8.6
L-5-7000	2.4	2.5	2.4	2.4	5.0	4.9	5.2	5.0	8.2	7.8	7.8	7.9
L-1-10500	2.4	2.6	2.5	2.5	5.3	5.6	5.5	5.4	7.4	7.2	6.6	7.1
L-3-10500	2.6	2.7	2.5	2.6	4.7	5.2	5.1	5.0	8.1	8.1	7.3	7.8
L-5-10500	2.7	2.6	2.6	2.6	5.6	5.4	5.6	5.6	8.4	7.8	8.1	8.1
F-1	2.4	2.4	2.3	2.4	5.0	4.6	5.0	4.9	6.6	6.2	6.6	6.4
F-3	2.6	2.5	2.5	2.5	4.7	4.9	4.9	4.8	6.5	6.9	6.9	6.8
F-5	2.0	2.2	2.4	2.2	4.5	4.4	4.8	4.6	6.5	7.0	6.9	6.8
N-1	4.0	3.5	3.5	3.7	6.2	6.1	6.0	6.1	7.7	7.6	7.8	7.7
N-3	3.5	3.5	3.8	3.6	5.7	4.9	5.7	5.4	6.7	6.3	6.3	6.4
N-5	3.8	3.5	3.7	3.7	<u>4.1</u> *	5.8	5.6	5.7	6.4	5.9	6.1	6.1

*: Disregarded as outlined in TS EN 196-1.

3.3.3.2 Compressive Strength Results

The compressive strength results of each cement type at 2, 7, and 28 days are given in Tables 3.14 through 3.16 respectively.

Table 3.14 Compressive Strength at 2 Days

Cement Label	Strength (MPa)						Av.	Std. Dev.	CV (%)
	Specimen No.								
	#1	#2	#3	#4	#5	#6			
Control	10.7	11.0	10.5	11.2	10.4	11.2	10.8	0.37	3.4
L-1-3500	<u>16.7*</u>	12.6	12.0	12.9	12.9	12.7	12.6	0.38	3.0
L-3-3500	11.6	11.5	11.6	11.6	11.2	11.9	11.6	0.22	1.9
L-5-3500	12.6	12.4	11.4	12.1	12.6	12.7	12.3	0.49	4.0
L-1-7000	12.6	12.7	12.5	12.3	13.2	13.4	12.8	0.44	3.4
L-3-7000	11.3	11.0	11.1	11.3	11.0	11.3	11.2	0.16	1.4
L-5-7000	10.1	10.1	10.6	9.6	9.6	11.0	10.2	0.55	5.4
L-1-10500	9.8	9.6	10.3	10.4	10.1	10.4	10.1	0.32	3.2
L-3-10500	10.5	10.6	9.9	10.9	10.3	11.0	10.5	0.38	3.6
L-5-10500	11.2	11.6	11.1	11.5	10.9	11.1	11.2	0.29	2.6
F-1	9.6	11.0	10.7	9.8	10.2	10.1	10.2	0.53	5.2
F-3	9.9	10.3	9.7	10.2	10.3	9.9	10.0	0.25	2.5
F-5	8.4	9.4	8.6	8.8	9.4	10.0	9.1	0.59	6.5
N-1	11.8	12.8	11.8	12.9	12.1	12.3	12.3	0.48	3.9
N-3	8.3	7.8	8.0	7.8	8.0	8.2	8.0	0.20	2.4
N-5	6.0	6.0	5.3	5.2	5.5	5.6	5.6	0.34	6.0
*: Disregarded as outlined in TS EN 196-1.									

Table 3.15 Compressive Strength at 7 Days

Cement Label	Strength (MPa)						Av.	Std. Dev.	CV (%)
	Specimen No.								
	#1	#2	#3	#4	#5	#6			
Control	20.2	21.3	19.7	18.8	19.7	19.4	19.9	0.82	4.2
L-1-3500	<u>26.8*</u>	23.6	22.9	23.1	23.3	22.3	23.0	0.51	2.2
L-3-3500	24.8	24.5	26.1	25.5	25.9	25.5	25.4	0.62	2.4
L-5-3500	23.9	24.0	23.4	22.7	23.1	22.9	23.3	0.53	2.3
L-1-7000	24.8	24.5	23.4	22.2	23.8	21.6	23.4	1.24	5.3
L-3-7000	26.5	26.2	26.2	27.0	26.6	27.3	26.6	0.43	1.6
L-5-7000	23.5	25.0	24.4	25.4	25.9	25.6	25.0	0.86	3.4
L-1-10500	24.8	25.8	25.2	24.5	25.6	27.0	25.5	0.89	3.5
L-3-10500	27.0	25.5	25.8	26.7	27.1	27.8	26.7	0.85	3.2
L-5-10500	26.4	26.4	24.3	26.4	25.6	24.6	25.6	0.94	3.7
F-1	22.2	20.4	20.0	20.5	19.0	19.5	20.3	1.10	5.4
F-3	19.9	20.9	20.2	20.1	20.0	21.1	20.4	0.51	2.5
F-5	18.9	19.3	19.4	19.0	19.9	19.5	19.3	0.37	1.9
N-1	23.9	24.5	23.4	24.1	23.9	24.8	24.1	0.50	2.1
N-3	14.5	15.5	14.0	14.7	14.5	15.5	14.8	0.58	3.9
N-5	12.0	12.5	12.5	11.7	11.9	11.8	12.1	0.36	3.0
*: Disregarded as outlined in TS EN 196-1.									

Table 3.16 Compressive Strength at 28 Days

Cement Label	Strength (MPa)						Av.	Std. Dev.	CV (%)
	Specimen No.								
	#1	#2	#3	#4	#5	#6			
Control	36.8	38.3	39.9	40.0	38.8	40.1	39.0	1.29	3.3
L-1-3500	41.9	43.6	43.7	45.7	42.1	43.1	43.3	1.38	3.2
L-3-3500	40.3	40.5	44.1	42.2	43.2	42.8	42.2	1.51	3.6
L-5-3500	38.3	38.8	38.5	40.2	38.6	37.2	38.6	0.99	2.6
L-1-7000	44.6	46.2	44.1	42.0	43.5	44.2	44.1	1.36	3.1
L-3-7000	39.6	40.6	41.8	40.8	42.7	40.9	41.1	1.07	2.6
L-5-7000	41.1	41.7	42.4	43.2	43.2	42.7	42.4	0.85	2.0
L-1-10500	38.9	40.0	40.5	39.7	39.8	39.5	39.7	0.55	1.4
L-3-10500	40.7	43.3	42.7	43.0	41.6	43.2	42.4	1.05	2.5
L-5-10500	41.0	42.8	44.4	43.3	43.2	42.7	42.9	1.12	2.6
F-1	39.5	41.7	39.5	41.6	41.5	42.7	41.1	1.29	3.1
F-3	39.4	39.1	38.4	40.2	38.1	40.6	39.3	0.97	2.5
F-5	<u>43.7*</u>	38.6	37.6	36.4	39.1	39.1	38.1	1.17	3.1
N-1	37.0	35.9	38.3	36.8	37.5	36.7	37.0	0.80	2.2
N-3	21.8	21.5	21.9	19.9	22.9	23.1	21.8	1.13	5.2
N-5	18.1	16.7	18.6	17.2	18.8	19.3	18.1	1.00	5.5
*: Disregarded as outlined in TS EN 196-1.									

CHAPTER 4

DISCUSSION OF RESULTS

4.1 Effects of Additives on Slag Cements

The effects of additives on the properties of slag cement were investigated on 15 types of mixtures. Fresh properties that were determined included the consistency and the setting time. Hardened properties included flexural and compressive strengths that were determined at 2, 7, and 28 days.

4.1.1 Fresh Properties

Fresh properties that include the consistency and the setting time of the pastes were not examined for all compositions as the additions were only minor additives. They were studied just for the compositions that had the highest three compressive strength values at 2, 7, and 28 days and for NaOH additive.

In section 3.3.2, Table 3.12 presented the tested fresh properties of the cement types which were produced with the additives. As seen in Figure 4.1, there is a tendency that, when fineness of the limestone increases in the same addition amount, required amount of water increases to obtain the required consistency. For example, L-1-7000 required more water than L-1-3500 for normal consistency. Moreover, the required amount of water for normal consistency increases when the addition amount increases for the same fineness of the material. For example, L-5-3500 required more water than L-1-3500 for normal consistency. It can be said that the results for required amount of water is as predicted because the required amount of water for normal consistency increases if the fineness of the material increases.

Indeed, there is more surface area for fine materials and more water is adsorbed by the surface of the materials (Yeğınobalı and Ertün, 2005).

Moreover, Figure 4.1 shows that the cements with NaOH, chemical additive, require highest amount of water to get the required consistency. The required amount of water is 165 grams (33%) for N-1 type and 180 grams (36%) for N-5. The study shows that the required water quantity for normal consistency increases rapidly for N-5. Moreover, it is obvious that when the amount of NaOH increases, the required amount of water for normal consistency increases. During the reaction between water and NaOH, heat is released. According to the study conducted by Zivica (2007), if the temperature of the mixtures increases, workability and also the consistency decrease. Because NaOH readily absorbs moisture as said in section 2.2, the results are reasonable.

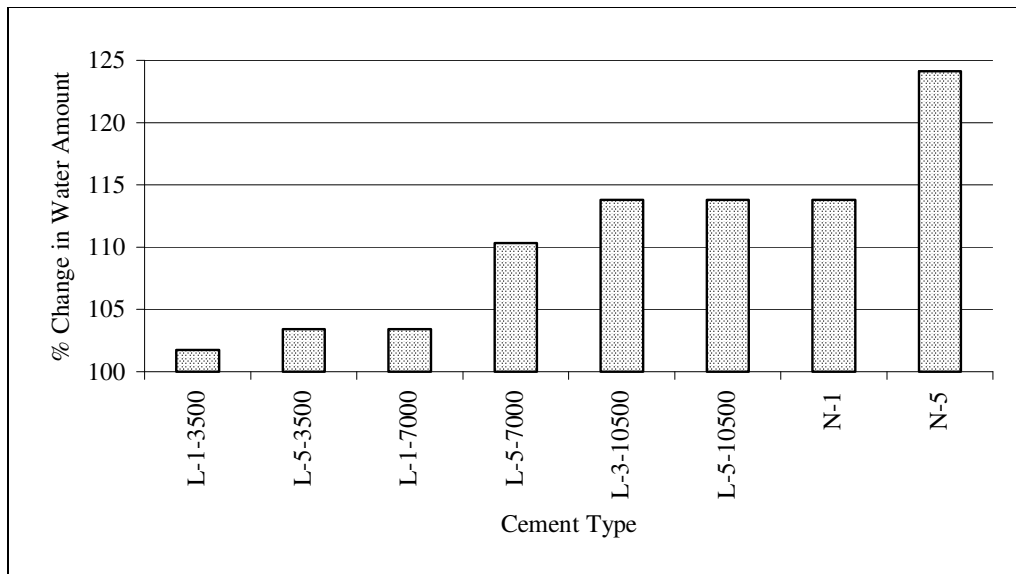


Figure 4.1 Water Amount for Required Consistency

Setting times are nearly the same when limestone with different fineness is used as an additive (Figure 4.2). Initial setting times are between 170 and 190 minutes, and final setting times are between 260 and 320 minutes when limestone with different fineness and amount is used. On the other hand, the initial setting time required by TS EN 197-1 is matched by the cements with limestone addition.

The possible reason why the change of setting times of the cements were not observed clearly is the amount of additions are small (up to 5%). If the addition amount of limestone was higher, the change of setting times would be observable.

Setting time of N-1 type is nearly the same when finest limestone is used as an additive (Figure 4.2). However, the setting time is too low when NaOH is used in higher amounts. While the initial setting time is 170 minutes for N-1 type, it is 15 minutes for N-5 type. Similarly, the final setting times are 245 minutes and 95 minutes for N-1 and N-5 types respectively. The required initial setting time according to TS EN 197-1 is not matched by the cements with NaOH addition.

The possible reason for lower setting time for cements with NaOH is higher temperature of mixtures. It was reported in literature that addition of NaOH as an activator increases the temperature of the mixtures, and decreases the setting time of the cements (Shi et al., 2006; Zivica, 2007).

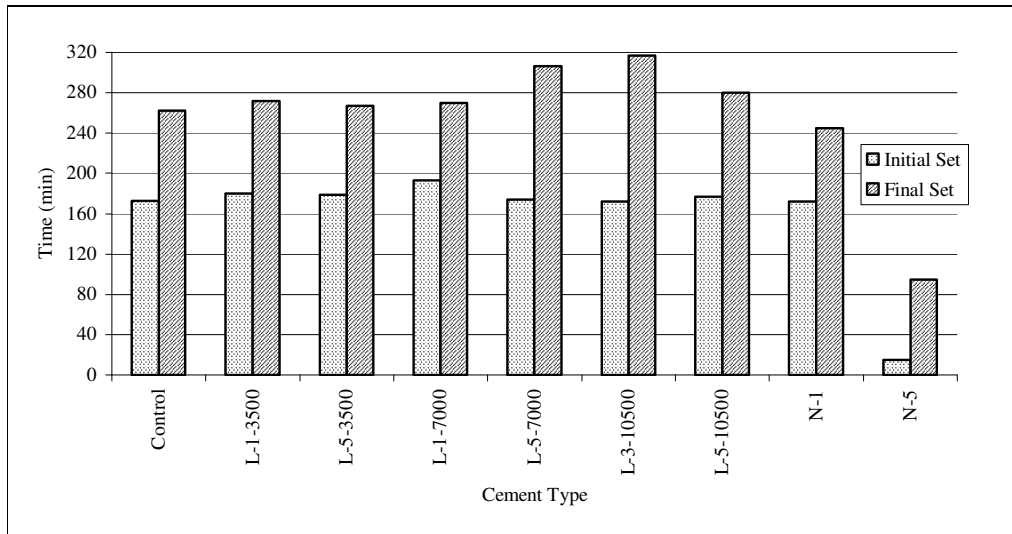


Figure 4.2 Initial and Final Setting Times

4.1.2 Hardened Properties

As for the hardened properties of slag cements, flexural and compressive strengths of the cements were determined at 2, 7, and 28 days. The effects of the mineral additives and NaOH on strength are presented in the following sections separately. Figures 4.3 through 4.16, which are about strength changes, show the comparison of the strengths according to the control cement. In the figures, control cement is represented as 100% change, and the lines below 100% represent reduction, and the lines above 100% represent an increase.

Furthermore, the strength changes according to the control cement are analyzed statistically to see whether there is a difference between the control cement and other types of cements or not. The statistical analyses were made by t-test (Two Sample Assuming Unequal Variances) using Microsoft Excel program with 95% confidence interval. The program provides an output, P-value, which corresponds to the probability that the two data sets are different or not. If the probability of the outcome is less than 5% (or $P < 0.05$) then it is acceptable to state that there is a

significant difference between data sets (Masse, 2006). In the study, P ($T \leq t$) two-tail is considered because it is desired that whether there is difference or not between the control cement and the others. The outputs of the program related with the statistical analyses are in the following sections in tables. The tables related with statistical analysis present the differences whether there is change (as DIFF.) statistically or not (as SAME). To understand the statistical analysis table, the example below can be helpful.

In Table 4.1, for Control and L-1-3500 columns at 2 days, the P($T \leq t$) two-tail result is 0.29 . Since the P value obtained is larger than 0.05, it can be said that L-1-3500 is not significantly different from control cement with 95% confidence interval.

4.1.2.1 Effects of Mineral Additives on Slag Cements

In section 3.3.3.1, Table 3.13 presented the flexural strength values of cement types which were produced with mineral additives at 2, 7, and 28 days.

In this section, statistical data and changes for flexural and compressive strength according to the control cement are available in tables and figures respectively for ages 2, 7, and 28.

According to the strength results, which are given in following parts, it can be said that addition of limestone to slag cement generally increases the strength for all ages especially for early age. Similar conclusion was achieved by Mun et al. (2007) for 50% slag amount. That study resulted that limestone addition increases the compressive strength producing carbonate crystal by replacing sulfate with ettringite. Then, the replaced sulfate is considered to facilitate the hydration in blast furnace slag. Moreover, Menendez et al. (2003) reported that limestone filler causes an increase of hydration and so increases the strength at early ages.

Moreover, addition of silica fume has no significant effect on the strength of slag cement for all ages. It is reported that addition of silica fume to cement decreases the pH value due to reaction of silica fume with CH, produced during hydration (Yeğınobalı, 2005; Xi et al., 1997). The pore solution with reduced pH and dense microstructure are responsible for the slow hydration. Therefore, the hydration of slag is slow due to the addition of silica fume to cement. Furthermore, silica fume is especially effective to increase the C₃S hydration. Therefore, silica fume can be more effective when used with the cements which have higher C₃S amount (Yeğınobalı, 2005; Xi et al., 1997). In addition, according to Demirboğa (2003), silica fume is more effective in production of concrete. The probable reason for that is an aggregate-paste bond development, which is related with structure of less porous transition zone in silica fume concrete. On the other hand, in this thesis study, the pozzolanic activity of silica fume was not determined. If the activity was determined, better explanation of the lower compressive strength results would have been possible.

Table 4.1 Statistical Analysis for Mineral Admixtures for Flexural Strength at 2-7-28 Days

		Control	L-1-3500	L-3-3500	L-5-3500	L-1-7000	L-3-7000	L-5-7000	L-1-10500	L-3-10500	L-5-10500	F-1	F-3	F-5
2 DAYS	Mean	2.8	2.9	2.8	2.9	3.0	2.7	2.4	2.5	2.6	2.6	2.4	2.5	2.2
	Variance	0.01	0.01	0.04	0.05	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.05
	No. of spec.	3	3	3	3	3	3	3	3	3	3	3	3	3
	P (two-tail)		0.29	0.90	0.47	0.07	0.38	0.01	0.03	0.14	0.13	0.01	0.04	0.03
	Conclusion		SAME	SAME	SAME	SAME	SAME	DIFF.	DIFF.	SAME	SAME	DIFF.	DIFF.	DIFF.
7 DAYS	Mean	4.6	4.6	5.2	5.0	5.0	5.6	5.0	5.4	5.0	5.6	4.9	4.8	4.6
	Variance	0.02	0.05	0.03	0.02	0.02	0.00	0.04	0.02	0.09	0.01	0.04	0.01	0.04
	No. of spec.	3	3	3	3	3	3	3	3	3	3	3	3	3
	P (two-tail)		0.91	0.01	0.01	0.02	0.01	0.03	0.00	0.10	0.00	0.12	0.09	1.00
	Conclusion		SAME	DIFF.	DIFF.	DIFF.	DIFF.	DIFF.	DIFF.	SAME	DIFF.	SAME	SAME	SAME
28 DAYS	Mean	6.9	7.0	7.7	7.8	7.1	8.6	7.9	7.1	7.8	8.1	6.4	6.8	6.8
	Variance	0.09	0.13	0.02	0.06	0.09	0.15	0.07	0.17	0.21	0.08	0.04	0.06	0.07
	No. of spec.	3	3	3	3	3	3	3	3	3	3	3	3	3
	P (two-tail)		0.63	0.03	0.02	0.51	0.00	0.01	0.53	0.06	0.01	0.09	0.52	0.71
	Conclusion		SAME	DIFF.	DIFF.	SAME	DIFF.	DIFF.	SAME	SAME	DIFF.	SAME	SAME	SAME

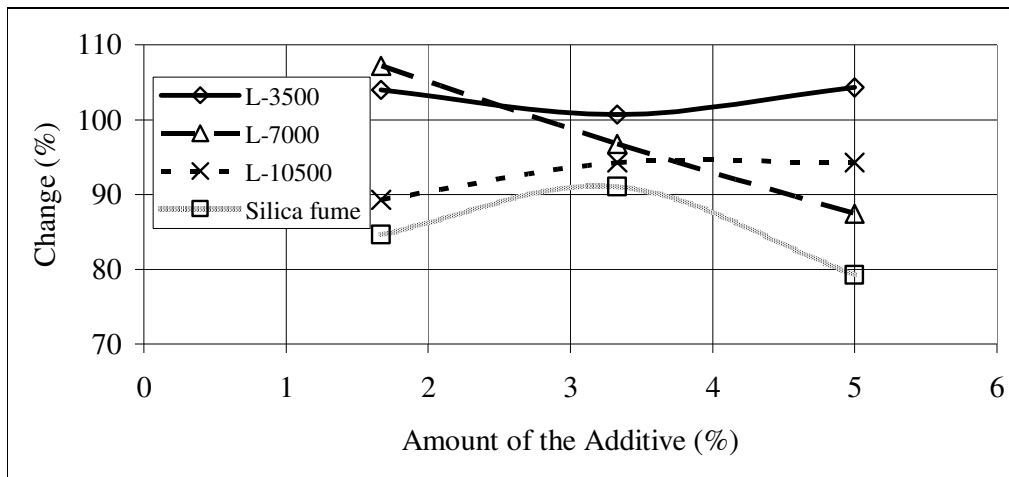


Figure 4.3 Flexural Strength for Mineral Additives at 2 Days

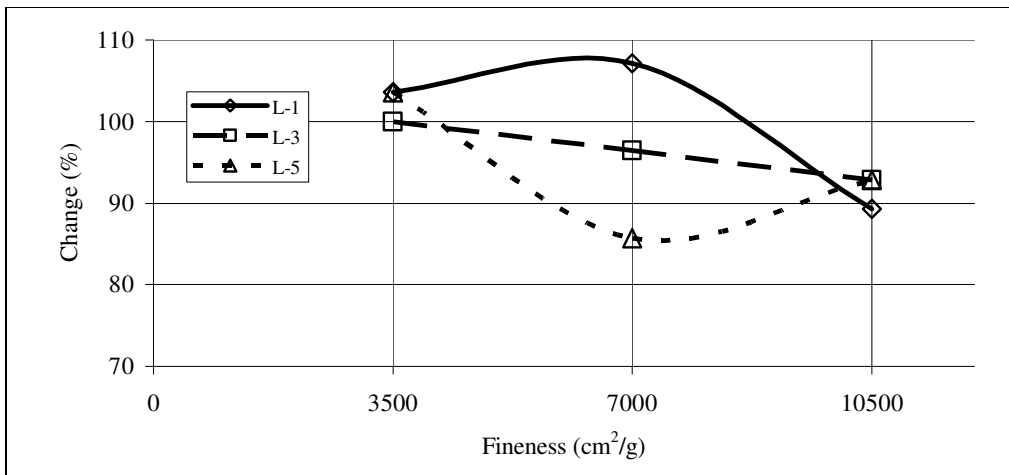


Figure 4.4 Flexural Strength for Limestone in terms of Fineness at 2 Days

According to Figures 4.3-4.4, and Table 4.1, limestone and silica fume decrease the flexural strength at 2 days for L-5-7000, L-1-10500, F-1, F-3, and F-5 types of cements. However, there is statistically no effect of the other types on flexural strengths at 2 days.

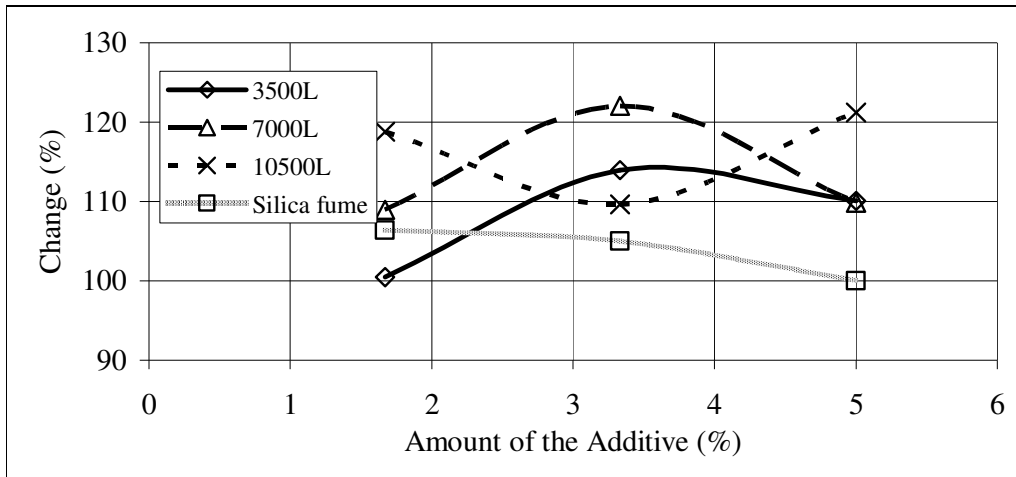


Figure 4.5 Flexural Strength for Mineral Additives at 7 Days

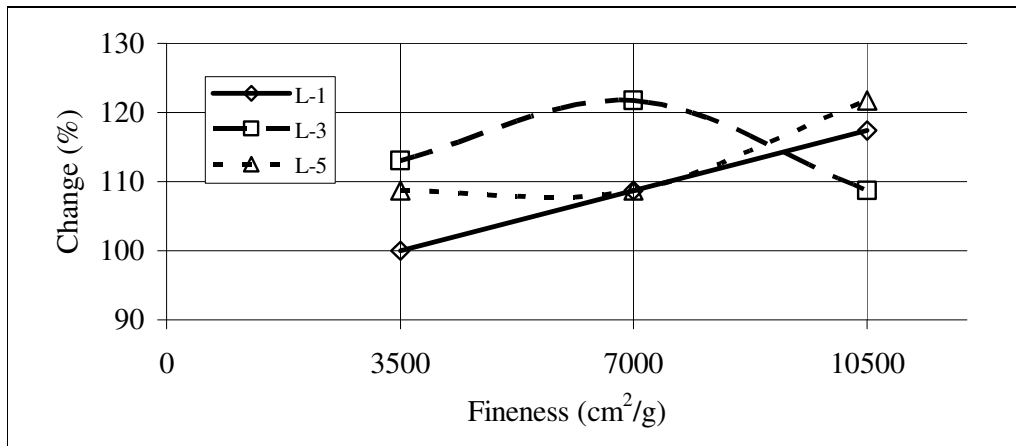


Figure 4.6 Flexural Strength for Limestone in terms of Fineness at 7 Days

On the other hand, Figures 4.5-4.6, and Table 4.1 show that all types of cements prepared with limestone apart from L-1-3500, and L-3-10500 have higher flexural strength values at 7 days. Likewise, cements with silica fume have no effect on the flexural strength statistically.

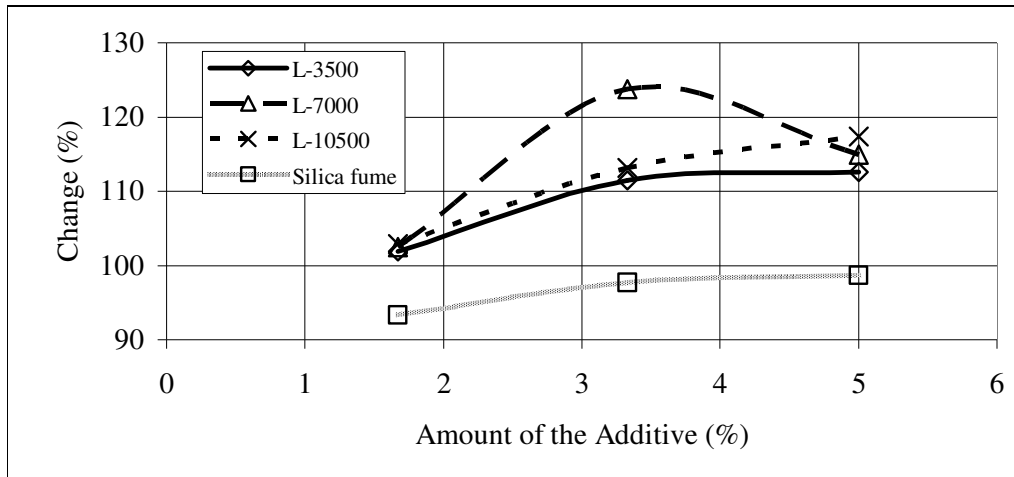


Figure 4.7 Flexural Strength for Mineral Additives at 28 Days

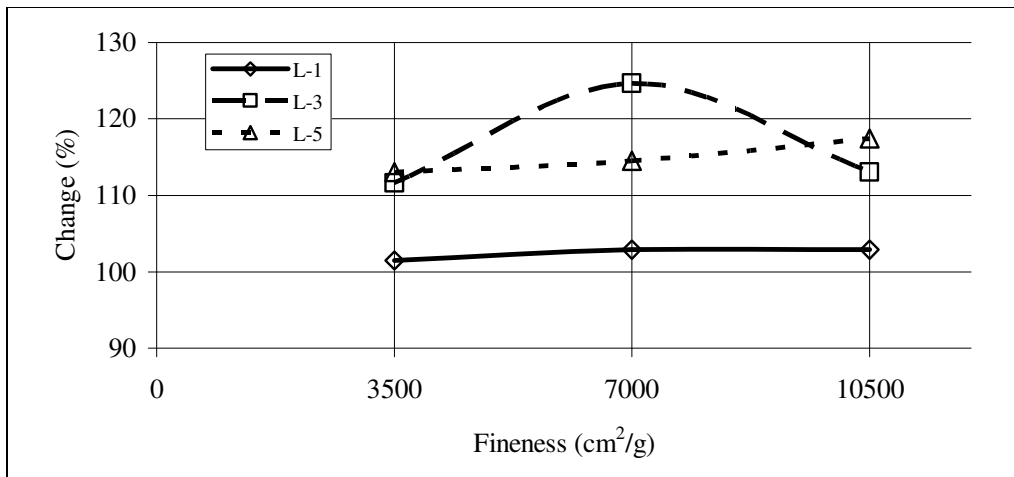


Figure 4.8 Flexural Strength for Limestone in terms of Fineness at 28 Days

At 28 days, Figures 4.7-4.8, and Table 4.1 show that there is an increase on the flexural strength for the types [L-3, L-5]-3500, [L-3, L-5]-7000, and L-5-10500. On the other hand, silica fume has no effect on the flexural strength statistically.

Table 4.2 Statistical Analysis for Mineral Admixtures for Compressive Strength at 2-7-28 Days

		Control	L-1-3500	L-3-3500	L-5-3500	L-1-7000	L-3-7000	L-5-7000	L-1-10500	L-3-10500	L-5-10500	F-1	F-3	F-5
2 DAYS	Mean	10.8	12.6	11.6	12.3	12.8	11.2	10.2	10.1	10.5	11.2	10.2	10.0	9.1
	Variance	0.13	0.11	0.05	0.24	0.19	0.03	0.30	0.10	0.14	0.08	0.28	0.06	0.35
	No. of spec.	6	6	6	6	6	6	6	6	6	6	6	6	6
	P (two-tail)		0.00	0.00	0.00	0.00	0.06	0.04	0.00	0.20	0.07	0.05	0.00	0.00
	Conclusion		DIFF.	DIFF.	DIFF.	DIFF.	SAME	DIFF.	DIFF.	SAME	SAME	DIFF.	DIFF.	DIFF.
7 DAYS	Mean	19.9	23.0	25.4	23.3	23.4	26.6	25.0	25.5	26.7	25.6	20.3	20.4	19.3
	Variance	0.68	0.21	0.38	0.28	1.54	0.18	0.74	0.79	0.73	0.89	1.20	0.26	0.14
	No. of spec.	6	6	6	6	6	6	6	6	6	6	6	6	6
	P (two-tail)		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.24	0.20
	Conclusion		DIFF.	DIFF.	DIFF.	DIFF.	DIFF.	DIFF.	DIFF.	DIFF.	DIFF.	DIFF.	SAME	SAME
28 DAYS	Mean	39.0	43.3	42.2	38.6	44.1	41.1	42.4	39.7	42.4	42.9	41.1	39.3	38.1
	Variance	1.67	1.90	2.29	0.98	1.85	1.15	0.72	0.31	1.11	1.26	1.66	0.94	1.10
	No. of spec.	6	6	6	6	6	6	6	6	6	6	6	6	6
	P (two-tail)		0.00	0.00	0.55	0.00	0.01	0.00	0.23	0.00	0.00	0.02	0.66	0.24
	Conclusion		DIFF.	DIFF.	SAME	DIFF.	DIFF.	DIFF.	DIFF.	SAME	DIFF.	DIFF.	DIFF.	SAME

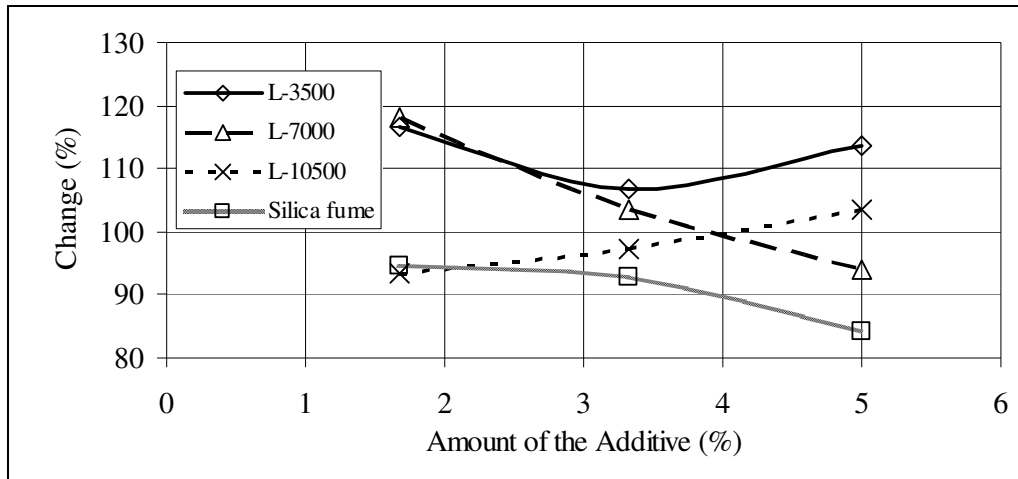


Figure 4.9 Compressive Strength for Mineral Additives at 2 Days

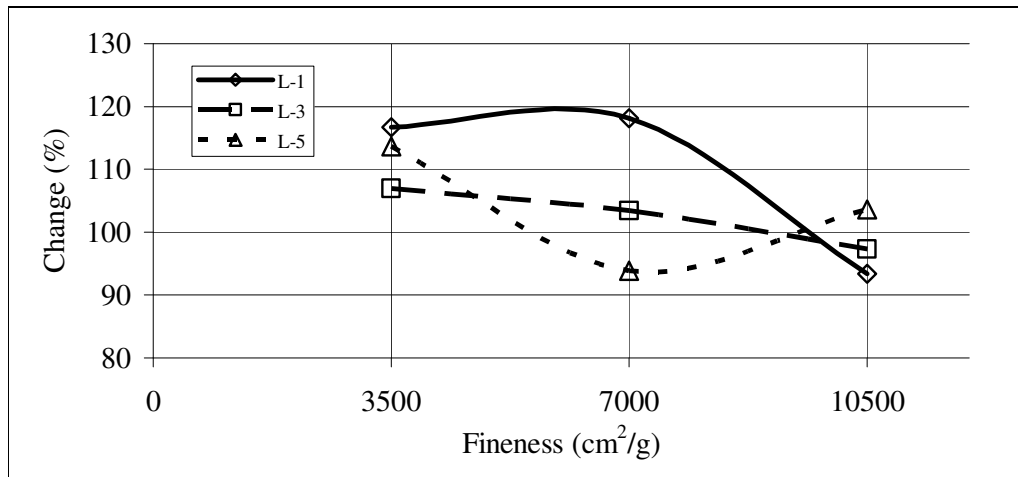


Figure 4.10 Compressive Strength for Limestone in terms of Fineness at 2 Days

Figures 4.9-4.10, and Table 4.2 show that compressive strength values are lower for types L-5-7000 and L-1-10500 at 2 days. However, there is no change statistically on the types L-3-7000, L-3-10500, L-5-10500 at 2 days. The other types of cements with limestone increase the compressive strength. Moreover, if silica fume is used as an additive for all ratios, the compressive strength is decreased.

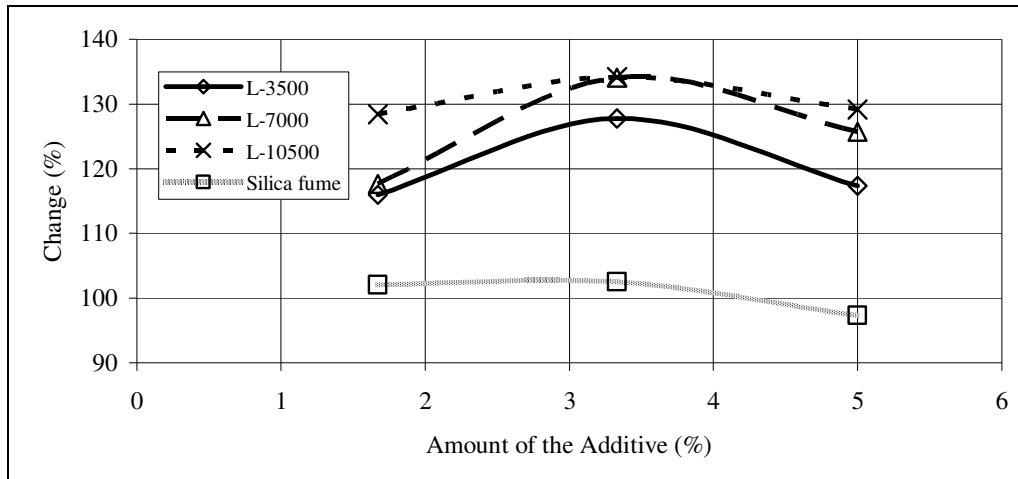


Figure 4.11 Compressive Strength for Mineral Additives at 7 Days

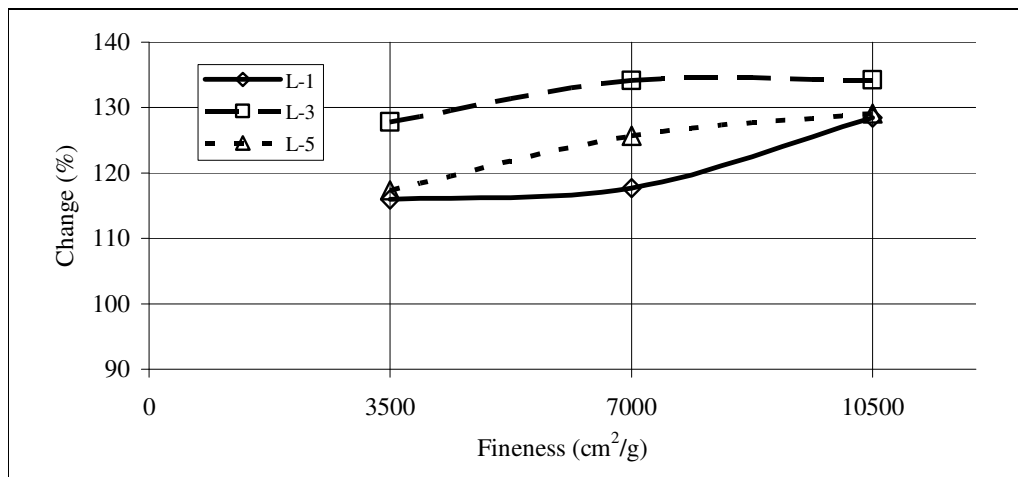


Figure 4.12 Compressive Strength for Limestone in terms of Fineness at 7 Days

On the other hand, at 7 days, Figures 4.11-4.12, and Table 4.2 show that there is an increase for all types of cements prepared with limestone. Nonetheless, compressive strengths of the cements prepared by silica fume have nearly no effect at 7 days.

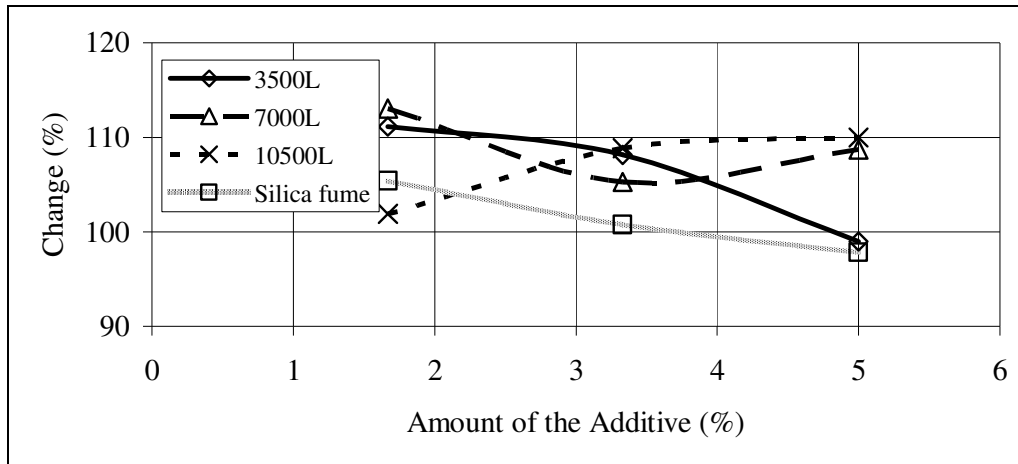


Figure 4.13 Compressive Strength for Mineral Additives at 28 Days

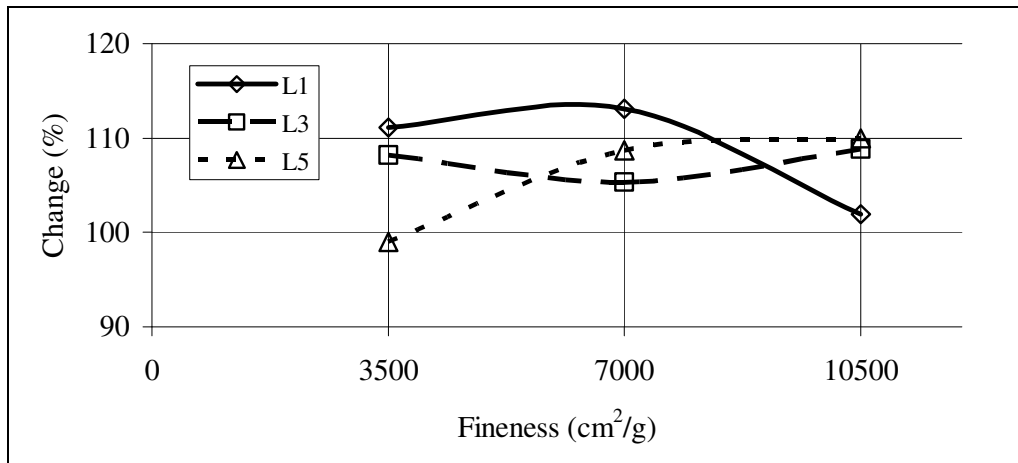


Figure 4.14 Compressive Strength for Limestone in terms of Fineness at 28 Days

At 28 days, according to Figures 4.13-4.14, and Table 4.2, for all types of mixtures prepared with limestone except for L-5-3500 and L-1-10500 types, have higher compressive strengths values. However, there is no effect of silica fume apart from F-1 type. If silica fume is used as 1.67% as an additive, the compressive strength increases nearly 5%, compared with the control cement.

4.1.2.2 Effect of NaOH on Slag Cements

In section 3.3.3.1, Table 3.13 presented the flexural strength values of the cement types which were produced with chemical additive NaOH at 2, 7, and 28 days respectively.

In this section, statistical data and changes for flexural and compressive strength according to the control cement are available in tables and figures respectively for ages 2, 7, and 28.

According to the strength results, which are given in following parts, it can be said that addition of NaOH to slag cement generally increases the flexural strength at 2, and 7 days. On the other hand, addition of NaOH at a ratio of 1.67% increases the compressive strength of the cements for each age. If the addition ratio is increased, the compressive strength values of the cements decrease. The reason for that may be due to the mixing water amount in the mortar. In the experiment, all of the mortars were prepared while keeping the amount of mixing water constant. In the previous sections, it was said that the required water amount increases with the increase of addition amount of NaOH. Probably, the amount of mixing water is absorbed by NaOH and so the hydration is not performed effectively.

Table 4.3 Statistical Analysis for N for Flexural and Compressive Strength at 2-7-28 Days

		2 Days				7 Days				28 Days			
		Control	N-1	N-3	N-5	Control	N-1	N-3	N-5	Control	N-1	N-3	N-5
Flexural Strength	Mean	2.8	3.7	3.6	3.7	4.6	6.1	5.4	5.7	6.9	7.7	6.4	6.1
	Variance	0.01	0.07	0.02	0.03	0.02	0.01	0.21	0.02	0.09	0.01	0.04	0.06
	No. of spec.	3	3	3	3	3	3	3	3	3	3	3	3
	P (two-tail)		0.01	0.00	0.00		0.00	0.09	0.00		0.04	0.09	0.03
	Conclusion		DIFF.	DIFF.	DIFF.		DIFF.	SAME	DIFF.		DIFF.	SAME	DIFF.
Compressive Strength	Mean	10.8	12.3	8.0	5.6	19.9	24.1	14.8	12.1	39.0	37.0	21.8	18.1
	Variance	0.13	0.23	0.04	0.11	0.68	0.25	0.33	0.13	1.67	0.64	1.27	1.01
	No. of spec.	6	6	6	6	6	6	6	6	6	6	6	6
	P (two-tail)		0.00	0.00	0.00		0.00	0.00	0.00		0.01	0.00	0.00
	Conclusion		DIFF.	DIFF.	DIFF.		DIFF.	DIFF.	DIFF.		DIFF.	DIFF.	DIFF.

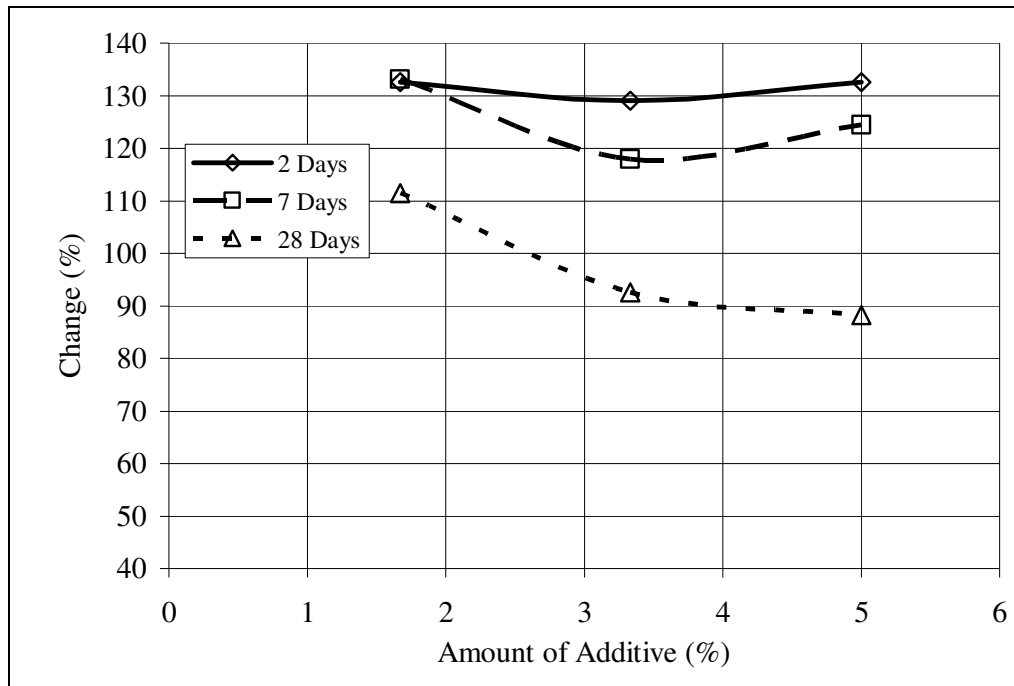


Figure 4.15 Flexural Strength for NaOH at 2, 7 and 28 Days

Figure 4.15 and Table 4.3 show that there is an increase at 2 days for all types of cements prepared by NaOH.

On the other hand, at 7 days, Figure 4.15 and Table 4.3 show that there is an increase for all types of cements prepared by NaOH apart from N-3 type.

At 28 days, Figure 4.15 and Table 4.3 show that NaOH increases the flexural strength for the type N-1, decreases the flexural strength for the type N-5. On the other hand, NaOH usage with 3.67% has no effect on the flexural strength statistically.

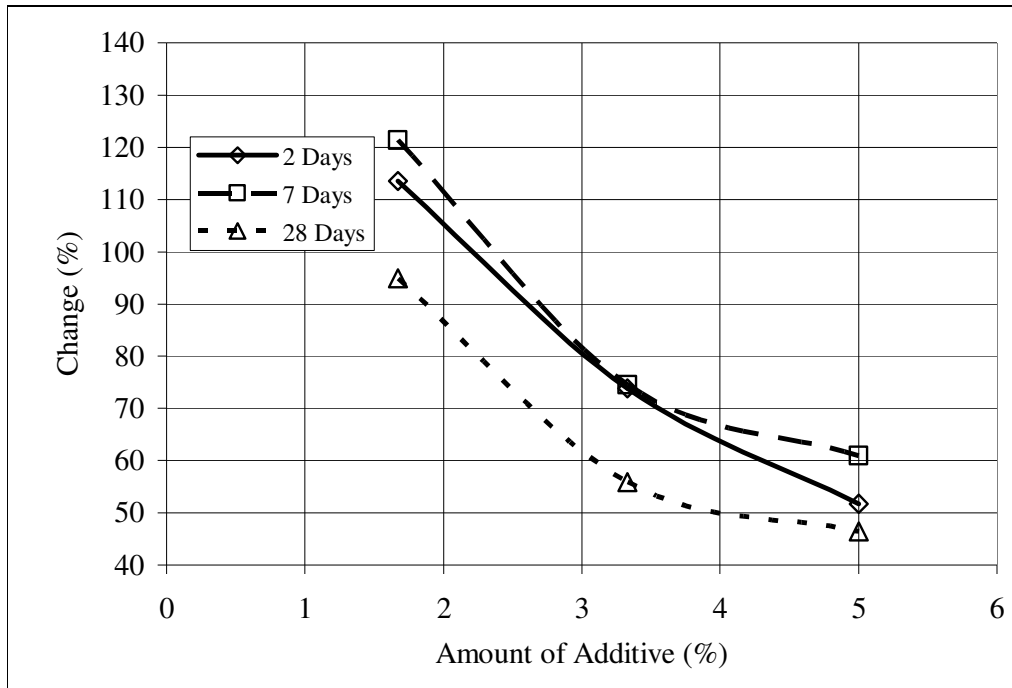


Figure 4.16 Compressive Strength for NaOH at 2, 7 and 28 Days

In section 3.3.3.2, Tables 3.14 through 3.16 presented the compressive strength values of the cement types which are produced with chemical additive NaOH at 2, 7, and 28 days. Figure 4.16 shows the comparison of the strengths according to the control cement.

Figure 4.16 and Table 4.3 show that the N-1 type of cement has higher compressive strength value at 2 and 7 days with respect to the control cement.

However, at 28 days, the compressive strength values are less for all types of cements prepared by NaOH according to Figure 4.16 and Table 4.3.

CHAPTER 5

SUMMARY AND CONCLUSIONS

5.1 Summary

In this study, 15 slag cement types were prepared using limestone, silica fume as mineral additives, and sodium hydroxide as chemical additive, and CEM III/A type control cement were produced to determine the fresh and hardened properties of the cements.

In the experimental study, in order not to change the cement type, the additives were incorporated within the minor additional constituent ranges, i.e. less than 5%. First, CEM III/A type control cement was prepared by blending 50% clinker (K) and 50% slag (S), which were separately ground in a laboratory type ball mill. Then, ground limestone (L) of varying fineness (3500 cm²/g, 7000 cm²/g, and 10500 cm²/g Blaine finenesses), silica fume (F), and sodium hydroxide (N) were prepared to be used as minor additional constituent (1.67%, 3.33%, and 5.00% of the cements). The ground clinker, slag, and gypsum, and the additives at various ratios were blended to obtain 15 CEM III/A type slag cements other than the control.

Finally, the fresh and the hardened properties of the cements were determined. Fresh properties included consistencies, initial and final setting times of the prepared pastes. Hardened properties included flexural and compressive strength tests at 2, 7, and 28 days for the produced mortars.

5.2 Conclusions

The following conclusions are obtained as a result of the thesis study:

1. The initial and the final setting times were nearly the same when limestone was used with different fineness as an additive. Moreover, the usage of NaOH as an additive decreased the setting times. The initial and the final setting times decreased rapidly with the usage of NaOH in higher amounts.
2. If fineness and also the amount of limestone in the same fineness in the cements increased, required water amount to obtain the normal consistency increased gradually. Furthermore, the cements with the NaOH particles required highest water amount to obtain the normal consistency.
3. Early compressive strength of slag cements increased by limestone usage. The cements with limestone increased the compressive strength except for L-3-7000, L-5-7000, L-1-10500, L-3-10500, and L-5-10500 types of cements at 2 days. Similarly, at 7 days, the compressive strength values were higher for all types of cements prepared by limestone. Furthermore, addition of silica fume either decreased or unchanged the compressive strengths at early ages. On the other hand, NaOH increased the compressive strengths when used at the ratio 1.67% at 2 and 7 days.
4. The cements with limestone increased the standard compressive strength apart from L-5-3500 and L-1-10500 types of cements. Moreover, addition of silica fume either increased or did not change the compressive strength at 28 days. Furthermore, NaOH decreased the compressive strengths at 28 days for all addition amounts.

5.3 Suggestions for Future Studies

As a result of this thesis study, the following suggestions could be made for future studies:

- In this study, the water amount was kept constant to determine the hardened properties of the cements. Instead of keeping the water amount constant, a constant flow for each cement type could be established and accordingly the hardened properties could be determined. This would especially be important to determine the hardened properties of cements prepared with NaOH.
- In the experimental study, addition of NaOH at the ratio 1.67% increased the compressive strengths at 2 and 7 days. Therefore, addition amount of NaOH up to 2% could be studied more in depth.
- In this study, the additives were used individually. The additives could be applied to the slag cement as binary or ternary mixtures, such as limestone with NaOH, limestone with slag, and slag with NaOH.
- Furthermore, the strength tests, conducted at 2, 7, and 28 days in the study, could be applied beyond 28 days to observe the effects of pozzolans.
- Amount of energy consumption could be determined and consequently a feasibility study could be performed.

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