INVESTIGATION OF THE PROPERTIES OF PORTLAND SLAG CEMENT PRODUCED BY SEPARATE GRINDING AND INTERGRINDING METHODS

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INVESTIGATION OF THE PROPERTIES OF PORTLAND SLAG CEMENT PRODUCED BY SEPARATE GRINDING AND INTERGRINDING METHODS

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ABSTRACT

INVESTIGATION OF THE PROPERTIES OF PORTLAND SLAG CEMENT PRODUCED BY SEPARATE GRINDING AND INTERGRINDING METHODS

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In recent years, there has been a growing trend for the use of industrial by-products in the production of blended cements because of economical, environmental, ecological and diversified product quality reasons. Granulated blast furnace slag, a by-product of the transformation of iron ore into pig-iron in a blast furnace, is one of these materials which is used as a cementitious ingredient.

The aim of this study is to investigate the properties of Portland slag cement (CEMII/B-S) by using separate grinding and intergrinding of granulated blast furnace slag and Portland cement clinker.

For this purpose, granulated blast furnace slag was used as mineral admixture replacing 30% of the clinker. Clinker and granulated blast furnace slag were ground to four different Blaine fineness values of 3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g and 4500 cm^2/g by intergrinding and separate grinding in a laboratory ball mill. Then, eight Portland slag cement mixes and four Portland cement control mixes were prepared, in order to determine and compare 2-, 7-, 28-, and 90-day compressive and flexural strengths, normal consistencies and setting times.

It was found that for the Blaine fineness values of 3000 cm^2/g, 3500 cm^2/g and 4000 cm^2/g, the 2-, 7-, 28-, and 90-day compressive strength of the interground Portland slag cements had higher values than the separately ground Portland slag cements. However, for the Blaine fineness values of 4500 cm^2/g, separately ground Portland slag cement specimens had slightly higher 2-, 7-, 28-, and 90-day compressive strength values than the interground ones.

Keywords: Granulated Blast Furnace Slag, Portland Slag Cement, Intergrinding and Separate grinding

ÖZ

AYRI VE BERABER ÖĞÜTÜLMÜŞ PORTLAND CÜRUFLU ÇİMENTOLARIN ÖZELLİKLERİNİN İNCELENMESİ

GEVEN, Çağlar
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Son yıllarda çimento endüstrisinde ekonomik, çevresel, ekolojik ve çimentoya kattığı çeşitli üstünlükler göz önünde bulundurulduğunda, endüstriyel atıkların kullanımı giderek artmaktadır. Öğütülmüş fırın cürufu, demir çelik üretiminden oluşan bir ara ürün olarak yüksek orandaki silis ve aluminyum içeriği ile pozzolanik özellikler gösteren çimento harçlarında ve betonda katkı maddesi olarak kullanılmaktadır.

Bu çalışmanın amacı granüle yüksek fırın cürufunun klinker ile ayrı ayrı ve beraber olarak öğütülmesiyle oluşan Portland cüruf çimento (CEMII/B-S) harçlarının özelliklerinin incelenmesidir.

Bu amaçla, Set Ambarlı fabrikasından elde edilen granüle yüksek fırın cürufu, mineral katkı olarak ağırlıkça 30% oranında klinker ile laboratuvar boyutlarındaki bilyalı değirmende ayrı ve beraber öğütme yoluyla, dört ayrı Blaine inceliğine öğütülmüştür, 3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g ve 4500 cm^2/g. Daha sonra sekiz tip Portland cüruf çimentosu ve dört tip Portland çimentosu oluşturulup, 2, 7, 28 ve 90 günlük basınç ve eğilme dayanımları, normal kıvam ve priz başlangıcı ve priz sonu süreleri bulunmuş ve birbirleriyle karşılaştırılmıştır.

Bu çalışma sonucunda 3000 cm^2/g, 3500 cm^2/g ve 4000 cm^2/g Blaine inceliğinde, beraber öğütülerek hazırlanan Portland cüruf çimentolarının 2, 7, 28 ve 90 günlük basınç dayanımlarının ayrı öğütme yapılarak hazırlanan Portland cüruf çimentolarından daha yüksek olduğu görülmüştür. 4500 cm^2/g Blaine inceliğinde ise, ayrı öğütme yapılarak hazırlanan Portland cüruf çimentolarının 2, 7, 28 ve 90 günlük basınç dayanımlarının beraber öğütülerek hazırlanan Portland cüruf çimentolarından daha yüksek olduğu bulunmuştur.

Anahtar Kelimeler: Granüle Yüksek Fırın Cürufu, Portland Cüruf Çimentosu, Beraber ve Ayrı Öğütme.

To My Parents...

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I am grateful to my parents for their endless patience, encouragement, support and help all my life. I am especially grateful to my mom for cheering me up whenever I am down.

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TABLE OF CONTENTS

CHAPTERS

APPENDICES

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 1

INTRODUCTION

1.1. General

The cement industry is one of the largest energy intensive industries consuming about 1.5 % of the total world fuel production and about 2 % of the global electricity production [1]. The industry has been accused of wasteful energy use due to the low efficiency processes it employs, such as burning, cooling and particularly grinding. In these processes the efficiencies are said to be, at best, 67%, 70% and 1%, respectively [2].

Portland cement is a hydraulic binder, a finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water [3]. As explained in the previous paragraph, the manufacturing of Portland cement is an energy intensive operation so that mineral admixtures are generally used for partial replacement of Portland cement in order to have considerable savings in cost and energy consumption because of lower requirement of Portland cement clinker thus reduction in carbon dioxide emissions and conservation of natural resources. Moreover, ecological and environmental problems like air, soil, and surface, as well as ground water pollution associated with their disposal are minimized or eliminated [4]. These mineral admixtures could be natural pozzolans or industrial by-products such as fly ash, silica fume and granulated blast furnace slag.

Blast furnace slag is a non-metallic by-product produced in metallurgical furnaces producing pig iron, composed essentially of silicates and alumino silicates of calcium.

During the production of pig-iron, molten slag at a temperature of about 1400-1500°C is produced from blast furnace. Its conversion into products suitable for various uses depends on the process used in cooling the molten slag [3]. Granulation is the quenching of the molten slag; and the product is called granulated blast furnace slag. Granulated blast furnace slag behaves like a pozzolan with some cementitious properties and thus acquires the attributes of a suitable mineral admixture for use in concrete due to its amorphous structure gained during quenching [4]. The hydraulic reactivity of the rapidly chilled glassy ground granulated blast-furnace slag depends upon processing conditions, chemical composition and particle characteristics [4].

As a supplementary cementing material, slag can be used to replace a portion of Portland cement in concrete at ratios generally between 20 % and 80 % by mass of cementitious material, depending on application and desired properties [5]. This replacement can occur by adding slag as a separate material during concrete batching, or can be in the form of producing blended cements, namely; Portland slag cements, blast furnace cements and slag modified Portland cements such as Portland composite cements and composite cements according to TS EN 197-1 [6].

In the production of Portland slag cements two grinding methods can be used: The first one is intergrinding the granulated blast furnace with the Portland cement clinker and the second one is grinding of the granulated blast furnace slag separately and then blending it with Portland cement clinker. In both methods, the product particle-size distribution must remain relatively constant to assure product uniformity and conform to commercial specifications. In this case the comminution process is operated to achieve the desired goal of uniform particle-size distribution in the finished product [7].

1.2. Objective and Scope of the Thesis

This study consists of two main parts. The objective of the first part is to compare the grindabilities of separately ground and interground Portland slag cements (CEMII/B-S) with 30 % by weight of granulated blast furnace slag by using a laboratory type ball mill. For this purpose, the Blaine air permeability apparatus is used for determining of the four different Blaine fineness values of 3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g and 4500 cm^2/g of the granulated blast furnace slag and Portland cement clinker, and a laser diffraction particle size analyzer is used for determination of the particle size distribution of the separately ground and interground granulated blast furnace slag and Portland cement clinker particles.

In the second part, Portland slag cement (CEMII/B-S, with 30% by weight of granulated blast furnace slag) specimens are prepared to compare 2-, 7-, 28-, and 90- day compressive and flexural strengths, cement pastes are prepared to compare the normal consistencies and setting times of Portland slag cements in relation with the grinding method and Blaine fineness of the cements incorporating 3.5 % gypsum and same water/slag+cement ratios 1/2. Finally, not only the comparison between Portland slag cements produced by separate and intergrinding methods, but also the comparison of these cements with Portland cements having four different Blaine fineness values of 3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g and 4500 cm^2/g with the same gypsum amount (3.5%) and same water/cement ratios (1/2) are made for all of the tests mentioned above.

This thesis consists of six chapters:

Chapter 1 gives a brief introduction about the importance of grinding in the cement industry, definition of Portland cement, importance of using by-products in cement production and their benefits to the economy and environment, definition of blast furnace slag and brief production processes of ground granulated blast furnace slag and Portland slag cements, and finally, gives the objective and scope of this thesis.

Chapter 2 presents the manufacturing of Portland cement, chemical composition of Portland cement, hydration of Portland cement, definition and types of pozzolans, pozzolanic reaction, definition and types of blast furnace slag, production of blast furnace slag, chemical composition of blast furnace slag and hydration of ground granulated blast furnace slag, use of ground granulated blast furnace slag in the cement industry, literature review about Portland slag cements and effects of ground granulated blast furnace slag on mortar and concrete properties.

Chapter 3 presents the properties of materials used in the study, the experimental program followed, the grinding procedure, preparation of the Portland slag cements, slag activity index determination, preparation and curing of the specimens, and finally tests performed on Portland slag cement mortars and pastes.

Chapter 4 presents the comparisons of the test results of separately ground and interground Portland slag cements such as, slag activity indices, normal consistency and setting time of the pastes, flexural and compressive strength of the Portland slag cements, statistical analysis of the flexural and compressive strength of the separately ground and interground ground Portland slag cements.

Chapter 5 presents the conclusions of the thesis resulting from the findings of the tests and observations.

Chapter 6 presents recommendations for future researchers.

CHAPTER 2

THEORETICAL CONSIDERATIONS

2.1. Portland Cement

Cement is a material that essentially consists of compounds of lime with silica, alumina and iron oxide with adhesive and cohesive properties which make it capable of bonding mineral fragments such as stones, sand, bricks or building blocks. The cements of interest in making concrete have the property of setting and hardening under water by virtue of a chemical reaction with it and are, therefore, called hydraulic cements [8]. The hydraulic cements include pozzolanic cements, slag cements and hydraulic limes. The most commonly used hydraulic cement is Portland cement.

Portland cement, whose name was given originally due to the resemblance of the color and quality of the hardened cement to Portland stone, is a cement obtained by intimately mixing together calcareous and argillaceous, or other silica-, alumina-, and iron oxide-bearing materials, burning them at a clinker temperature of about 1450°C, and grinding the resulting clinker with 3-5% gypsum [8].

2.1.1. Manufacturing of Portland Cement

The raw materials for the manufacture of Portland cement contain, in suitable proportions, calcium oxide (lime), silica, aluminum oxide and ferric oxide. The source of lime is calcareous ingredients such as limestone or chalk and the source of silica and aluminum oxide are shales, clays or slates. The iron bearing materials are iron and pyrite. The cement clinker is produced by feeding the crushed, ground and screened raw mix into a rotary kiln and heating to a temperature of about 1300-1450°C (Fig. 2.1). The sequences of reactions in the kiln are as follows: in the drying zone (100°C), free water is expelled. In the preheating zone (100-750°C), firmly bound water from the clay is lost. In the calcining zone (750-1000°C), calcium carbonate is dissociated. In the burning zone (1000-1450°C), partial fusion of the mix occurs, with the formation of tricalcium silicate (C_3S), dicalcium silicate (C_2S) and clinker. In the cooling zone (1450-1300°C), crystallization of melt occurs with the formation of tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). After firing the raw materials for the required period, the resultant clinker is cooled and ground with about 3-5% gypsum to a specified degree of fineness. Finally, the resulting product is commercial Portland cement so widely used throughout the world [4].

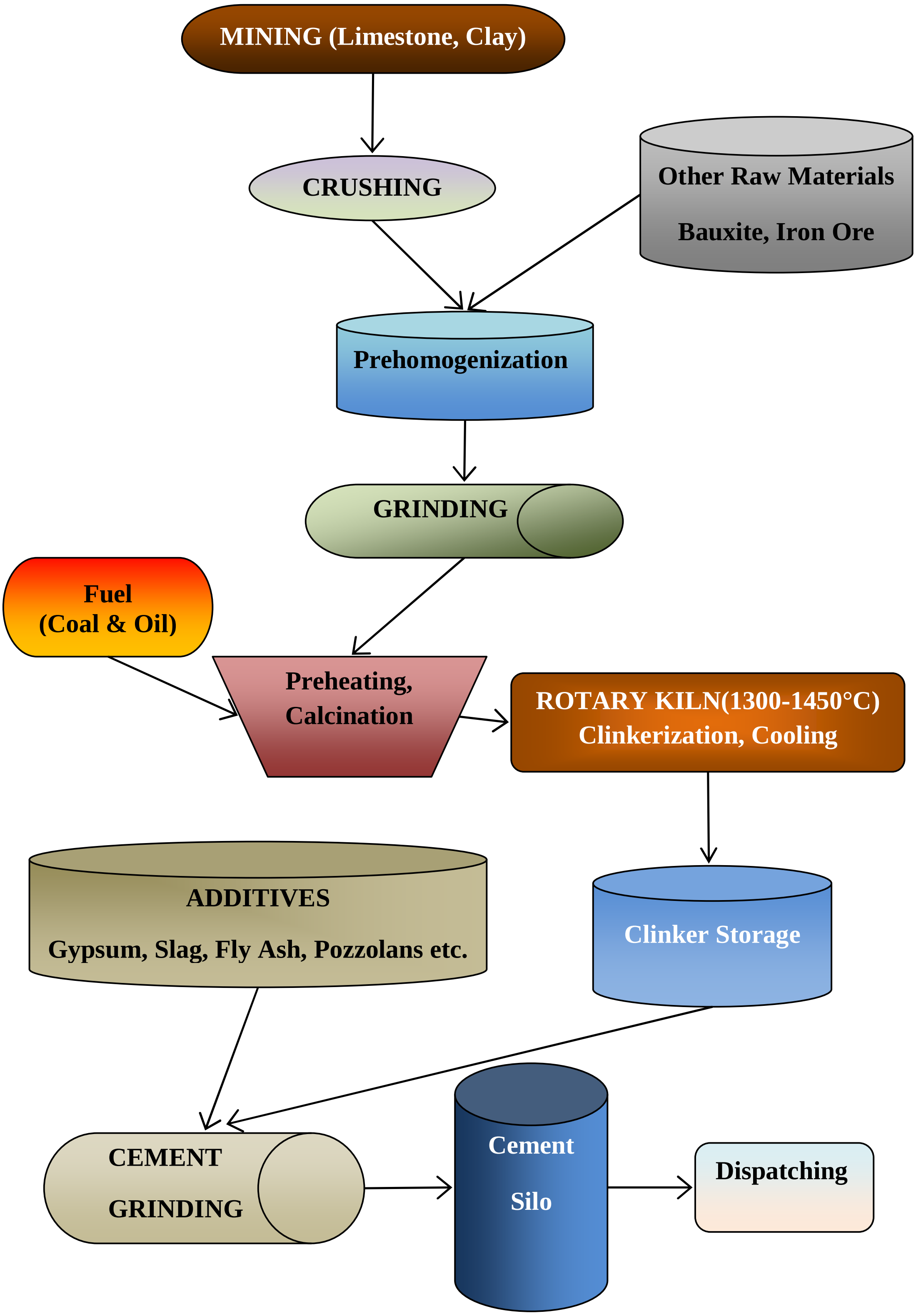


Figure 2.1. Flowsheet of Cement Production

2.1.2. Chemical Composition of Portland Cement

Determination of the exact chemical composition of cement is a very complex procedure. However, a general idea of composition for Portland cement can be obtained from its oxide analysis and is tabulated in Table 2.1.

Table 2.1. Typical Oxide Composition in Portland Cement [8]

Oxide	Limit Value (wt. %)	General (wt. %)
CaO	60-67	65
SiO_2	17-25	22
Al_2O_3	3-8	6
Fe_2O_3	1-8	3
MgO	< 5	2
SO_3	< 3	1
K_20+Na_2O	< 2	1

Four compounds are typically considered as the major constituents of cements: they are listed in Table 2.2 together with their abbreviated symbols, chemical formulas and contents.

Table 2.2. Main Compounds of Portland Cement and their Compositions [8]

Name of Compound	Chemical Formula	Abbreviation	Content (wt. %)
Tricalcium Silicate	$3CaO.SiO_2$	C_3S	35-60
Dicalcium Silicate	$2CaO.SiO_2$	C_2S	15-35
Tricalcium Aluminate	$3CaO.Al_2O_3$	C_3A	4-15
Tetracalcium Aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	8-13

2.1.3. Hydration of Portland Cement

The series of reactions of cement with water that causes setting and hardening of concrete is referred to as hydration. The major compounds of cement contact water molecules and become hydration products which in time produce a firm and hard mass the hydrated cement paste [8].

A basic view of the behavior and hydration of the four major compounds are as follows: Tricalcium silicates (C_3S) and dicalcium silicates (C_2S) which make up together 75-80 % of the all Portland cement are the strength-giving compounds which react with water to produce calcium silicate hydrate gel (C-S-H) and calcium hydroxide (CH). The hydration reactions of the two calcium silicates are similar. However, C_3S hydrates more rapidly than C_2S and therefore contributes more to high early strengths, while the reaction of dicalcium silicate is far slower, happening at ages beyond one week.
Calcium silicates hydrate as follows [9]:

$$\underset{\substack{\text{Tricalcium}\\\text{Silicate}}}{2C_3S} + \underset{\text{Water}}{6H} \rightarrow \underset{\text{C-S-H Gel}}{C_3S_2H_3} + \underset{\substack{\text{Calcium}\\\text{Hydroxide}}}{3CH} \tag{1}$$

$$\underset{\substack{\text{Dicalcium}\\\text{Silicate}}}{2C_2S} + \underset{\text{Water}}{4H} \rightarrow \underset{\text{C-S-H Gel}}{C_3S_2H_3} + \underset{\substack{\text{Calcium}\\\text{Hydroxide}}}{CH} \tag{2}$$

The calcium silicate hydrate (C-S-H) gel represents a high percent age of the total solids in a fully hydrated cement system. However, its exact chemical composition is variable. The ratio of C/S in the gel varies between 1.5 and 2, and depends on many factors such as temperature, water-cement ratio, and impurities [8]. In the hardened paste, the tiny C-S-H particles grow, forcing the adjacent particles like the remaining unhydrated cement grains and aggregates to interlock to form dense, bonded aggregations. The development of this structure is the paste's cementing action and is responsible for the setting, hardening and strength development of the concrete [8].

The next cement compound of particular importance is tricalcium aluminate (C_3A). C_3A content in Portland cement is comparatively small but has significant influences. The hydration reaction of C_3A with water is very rapid, but does not contribute to the ultimate strength of cement considerably [4, 8]. Higher amounts of C_3A in Portland cement may pose durability problems; therefore in order to control the hydration of C_3A gypsum is added. The C_3A phase, which reacts with gypsum in a few minutes to form ettringite and causes great expansion in volume is shown below [4]:

$$\underset{\substack{\text{Tricalcium}\\ \text{Aluminate}}}{C_3A} + \underset{\text{Gypsum}}{3C\overline{S}H_2} + \underset{\text{Water}}{26H} \rightarrow \underset{\text{Ettringite}}{C_6A\overline{S}_3H_{32}} \tag{3}$$

If the sulfate supply from the gypsum is consumed entirely before the C_3A is completely hydrated, a second reaction may occur to form another calcium sulfoaluminate hydrate containing fewer sulfates [9]:

$$\underset{\substack{\text{Tricalcium}\\ \text{Aluminate}}}{2C_3A} + \underset{\text{Ettringite}}{C_6A\overline{S}_3H_{32}} + \underset{\text{Water}}{4H} \rightarrow \underset{\substack{\text{Calcium Alumino}\\ \text{Monosulfo Hydrate}}}{3C_4A\overline{S}H_{12}} \tag{4}$$

The hydration of ferrite phase (C_4AF) yields the same sequence of products as C_3A; however, the reactions are much slower in the presence of gypsum. In the presence of water, C_4AF reacts as follows [9]:

$$C_4AF + 3C\bar{S}H_2 + 21H \rightarrow C_6(A,F)\bar{S}_3H_{32} + (A,F)H_3 \qquad (5)$$

C_4AF	$3C\bar{S}H_2$	$21H$	$C_6(A,F)\bar{S}_3H_{32}$	$(A,F)H_3$
Tetracalcium Aluminoferrite	Gypsum	Water	Calcium Trisulfo Aluminate	(Iron,Aluminium) Hydroxide

If the sulfate is all consumed and some C_4AF remains:

$$C_4AF + C_6(A,F)\bar{S}_3H_{32} + 7H \rightarrow 3C_4(A,F)\bar{S}H_{12} + (A,F)H_3 \qquad (6)$$

C_4AF	$C_6(A,F)\bar{S}_3H_{32}$	$7H$	$3C_4(A,F)\bar{S}H_{12}$	$(A,F)H_3$
Tetracalcium Aluminoferrite	Calcium Trisulfo Aluminate	Water	Calcium Monosulfo Aluminate	(Iron,Aluminium) Hydroxide

2.2. Pozzolans

According to ASTM C618 [10], pozzolans are defined as “Siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties”.

2.2.1. Classification of Pozzolans

Pozzolans can be divided into two groups according to their origin, namely; natural and artificial: Natural pozzolans are naturally occurring materials such as volcanic ashes and tuffs, pumicite, diatomaceous earth, opaline cherts, clays and shales. Natural pozzolans used in cements usually require grinding to cement fineness and may need to be calcined (e.g. clays&shales) in order to maximize their pozzolanic activities [9].

Artificial pozzolans are obtained as industrial by-products, such as fly ashes, silica fumes and granulated blast furnace slags. Fly ash is a finely divided, glassy material which is precipitated electrostatically or mechanically from the exhaust gases of thermal power stations; it is the most common artificial pozzolan. Silica fume is by-product of the manufacture of silicon and ferrosilicon alloys from high purity quartz and coal in a submerged-arc electric furnace. Granulated blast furnace slag is obtained as a by-product generated by rapid cooling of non-ferrous substances in iron ore separated from the hot metal in a blast furnace [4, 8]. Granulated blast furnace slag will be explained in detail in section 2.3.

2.2.2. Pozzolanic Reaction

The chemical reactions of finely divided pozzolans with calcium hydroxide (CH) in the presence of moisture are called pozzolanic reactions. It is essential that pozzolans be in finely divided form as it is only then that silica can combine with calcium hydroxide which is produced by the hydration of the Portland cement, in the presence of water to form stable calcium silicate hydrates which have cementitious properties [8]. The main chemical reaction that takes place between the silica of pozzolans and calcium hydroxide can be shown as below [11]:

$$\underset{\substack{\text{Calcium}\\\text{Hydroxide}}}{\text{CH}} \quad + \quad \underset{\text{Silica}}{\text{S}} \quad + \quad \underset{\text{Water}}{\text{H}} \quad \rightarrow \quad \underset{\substack{\text{Calcium Silicate}\\\text{Hydrate}}}{\text{C-S-H}} \tag{7}$$

Calcium silicate hydrate is the main product of pozzolanic reaction. This reaction will result in both a decrease in the amount of free calcium hydroxide (Figure 2.2), and an increase in the amount of calcium silicate hydrate and other products of low porosity, such as calcium carboaluminate, ettringite and calcium alumino monosulfate [11].

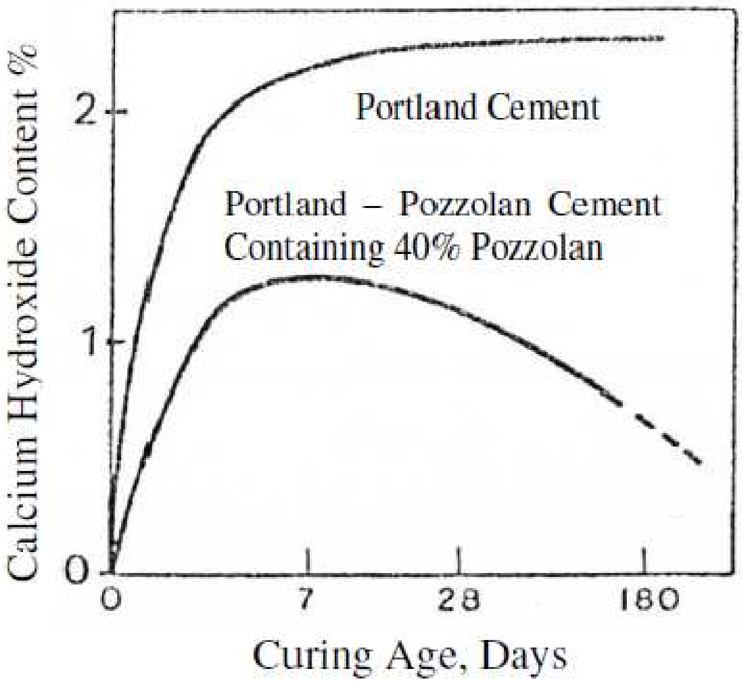


Figure 2.2. Changes in the Calcium Hydroxide Content of Hydrating Portland - Pozzolan Cement [12]

2.3. Blast Furnace Slag

2.3.1. Definition and Classification of Blast Furnace Slag

Blast furnace slag is defined as ‘the nonmetallic product, consisting essentially of silicates and alumina-silicates of calcium and of other bases, that is developed in a molten condition simultaneously with iron in a blast furnace’ [13].

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

Air-cooled blast furnace slags result from slow solidification of molten slag under atmospheric conditions. Because of the slow cooling process, crystalline forms of calcium silicates occur in the slag and this type of structure does not show hydraulic binding property. When air-cooled blast furnace slag is subsequently crushed and screened to appropriate sizes, it can be used as an aggregate for concrete [11] (Fig. 2.3).

Figure 2.3. Air-Cooled Blast Furnace Slag [14].

If the molten slag is cooled and solidified by adding controlled quantities of water, air, or steam, the process of cooling and solidification can be accelerated, increasing the cellular nature of the slag and producing a lightweight expanded or foamed blast-furnace slag when crushed to appropriate sizes. Expanded blast furnace slag is distinguishable from air-cooled blast furnace slag by its relatively high porosity and low bulk density [15].

Pelletized blast furnace slag can be produced if the molten slag is cooled and solidified with water and air in a spinning drum. By controlling the process, the pellets can be made more crystalline, which is beneficial for aggregate use, or more vitrified (glassy), which is more desirable in cementitious applications (Fig. 2.4). More rapid quenching results in greater vitrification and less crystallization [15].

Figure 2.4. Pelletized Blast Furnace Slag [14].

Granulated blast furnace slag is formed when the molten slag is cooled and solidified by rapid water quenching to a glassy state and the process is called granulation. In this system high pressure water jets are used to solidify the molten slag with water/slag ratio of about 10 to 1 by mass and this results in the formation of sand size (or frit-like) fragments, generally smaller than 4 mm, composed of predominantly noncrystalline friable clinker-like material [11] (Fig. 2.5). The physical structure and gradation of granulated blast furnace slag depend on the chemical composition of the slag, its temperature at the time of water quenching, and the method of production. When crushed or milled to very fine cement-sized particles, granulated blast furnace slag has cementitious properties, which make it a suitable partial replacement for or additive to Portland cement [15].

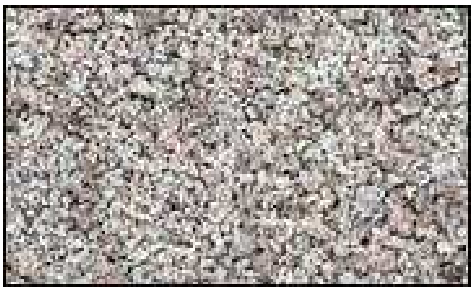


Figure 2.5. Granulated Blast Furnace Slag [14].

2.3.2. Production of Blast Furnace Slag

In the production of iron, the blast furnace is continuously charged from the top with iron oxide (ore, pellets, sinter, etc.), fluxing stone (limestone and dolomite), and fuel (coke). Two products are obtained from the furnace: molten iron that collects in the bottom of the furnace (hearth) and liquid iron blast furnace slag floating on the pool of iron. Both are periodically tapped from the furnace at a temperature of about 1500 °C [13] (Fig.2.6.). The cementitious activity of slag for use in mortar or concrete is determined by its composition, the rate of cooling and the cooling methods explained in the previous section.

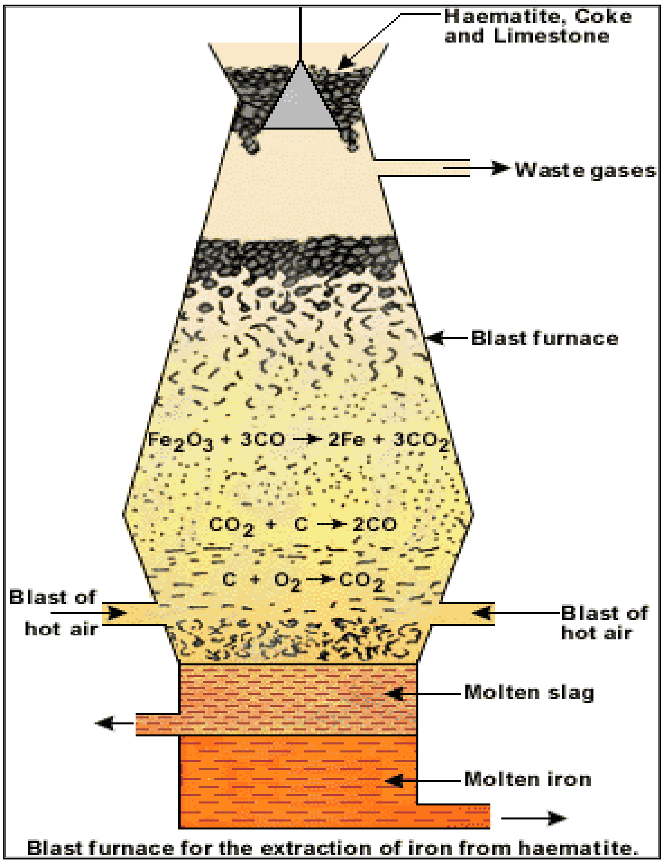


Figure 2.6. Production of Iron in a Blast Furnace [16].

2.3.3. Chemical Composition of Blast Furnace Slag

The composition of blast-furnace slag is determined by the nature of the iron ore, fluxing stone, and impurities in the coke charged into the blast furnace. The chemical compositions of some slags that are produced in some countries are given in percent by weight in Table 2.3.

Table 2.3. Chemical Composition of Blast Furnace Slags [11].

Compound	Turkey	U.S. and Canada	Australia	South Africa
CaO	34-41	29-50	39-44	30-40
SiO_2	34-36	30-40	33-37	30-36
Al_2O_3	13-19	7-18	15-18	9-16
Fe_2O_3	0.3-2.5	0.1-1.5	0-0.7	-
MgO	3.5-7	0-19	1-3	8-21
MnO	1-2.5	0.2-1.5	0.3-1.5	-
S	1-2	0-2.0	0.6-0.8	1.0-1.6
SO_3	-	-	-	-

2.3.4. Hydration of Ground Granulated Blast Furnace Slag

When granulated blast furnace slag is mixed with water, it shows limited hydraulic binding properties so that granulated blast furnace slag needs to be activated by alkaline compounds, which can be either soluble sodium salts, such as NaOH, Na_2CO_3, or calcium hydroxide [9]. The main reactions of slag are greatly enhanced in the presence of calcium hydroxide that is produced as a result of hydration of Portland cement, and also in the presence of some alkalis. In general, the hydration mechanism of ground granulated blast furnace slag involves a two stage reaction. Initially and during the early hydration, the predominant reaction is with alkali hydroxides, but subsequent reaction is predominantly with calcium hydroxide resulting in hydration products such as calcium-silicate-hydrates having strong hydraulic binding characteristics [11].

2.3.5. Use of Ground Granulated Blast Furnace Slag in the Cement Industry

Ground granulated blast furnace slags are used as cementitious ingredients in mortars also containing some limes, as additions in producing blended cements or as admixtures in concretes because of their pozzolanic characteristics. Another method of using ground granulated blast furnace slag is in place of clay or shale as a raw material for the manufacturing of the Portland cement clinker [3].

2.3.5.1. Use as Cementitious Ingredients in Mortars

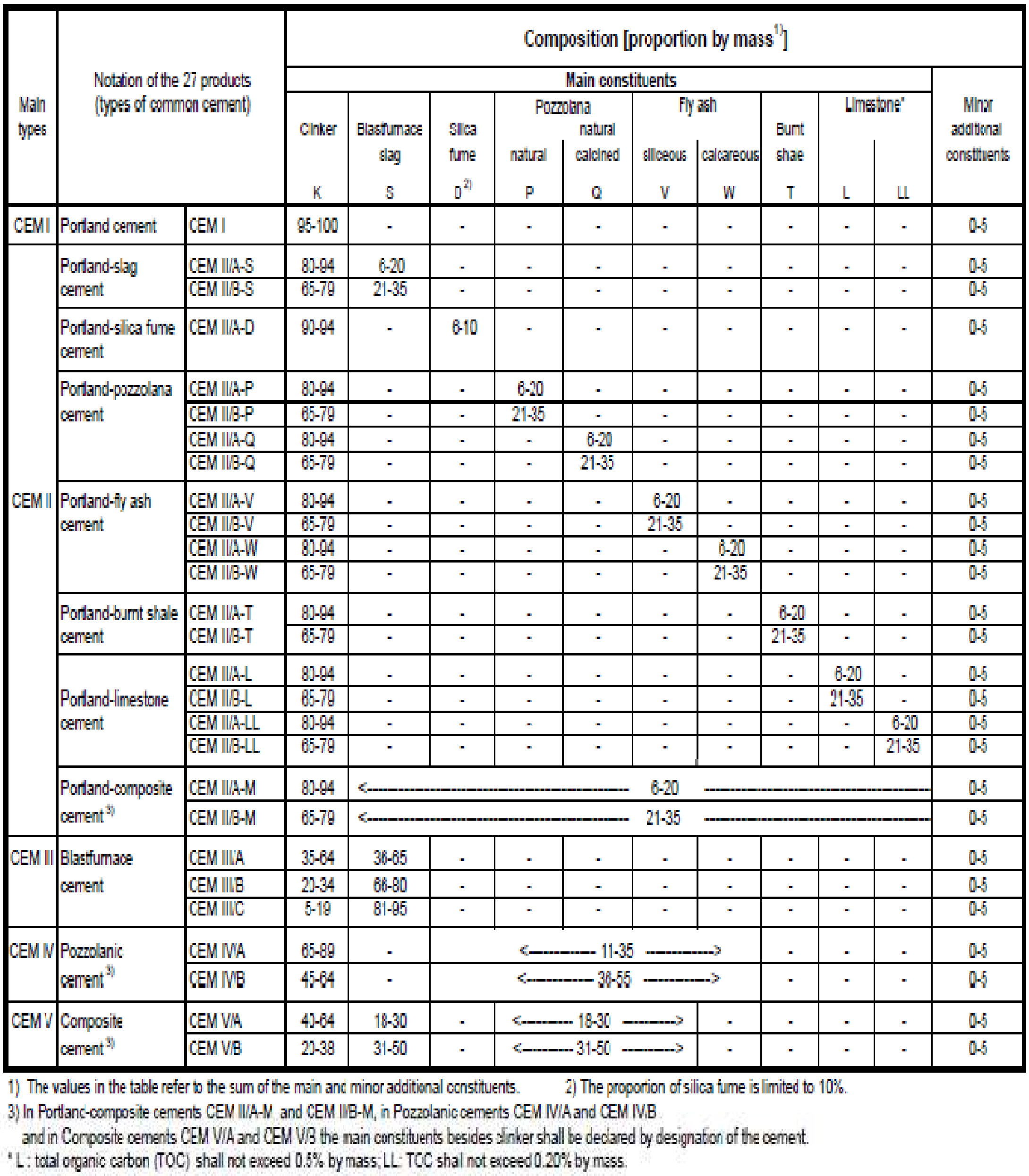
The use of ground granulated blast furnace slag as a cementitious material dates back to 1774 when Loriot made a mortar using ground blast furnace slag in combination with slaked lime [13]. When finely divided blast furnace slags are used with hydrated lime, the silica and alumina of the slag in noncrystalline state react with the calcium hydroxide leading to the formation of compounds possessing hydraulic binding characteristics and the cement is called lime-slag cement [11]. The first commercial use of slag-lime cement started in 1865 in Germany and after that their use spread too many other countries like France, Belgium, United Kingdom and the United States [3].

Lime-slag cements have especially been used for seawater and underground foundation works because of their resistance to attack by sulfates and their good plasticity. Metropolitan railway in Paris in 1900 and the seawater jetty in Yorkshire, England which was built about 100 years ago are the civil constructions made using lime-slag cements and are still in good conditions [3].

2.3.5.2. Uses as an Addition in Producing Blended Portland Cements

Blended cements such as Portland slag cements, CEMII/A containing 6-20% granulated blast furnace slag, CEMII/B containing 21-35% granulated blast furnace slag, blast furnace cements, CEMIII/A containing 36-65% granulated blast furnace slag, CEMIII/B containing 66-80% granulated blast furnace slag, and CEMIII/C containing 81-95% granulated blast furnace slag, and slag modified Portland cements such as Portland composite cements and composite cements are tabulated in Table 2.4 according to TS EN 197-1 [6]. The granulated blast furnace slag percentages in blended Portland cements vary from standard to standard and depending on the application and the properties of concrete desired. The first recorded production of Portland blast furnace slag cement in Germany and in United States was in 1892 and1896, respectively [13].

Table 2.4. Cement Types According to TS EN 197-1 [6].



Main types	Notation of the 27 products (types of common cement)		Composition [proportion by mass[1]] Main constituents: Clinker K	Blastfurnace slag S	Silica fume D[2]	Pozzolana natural P	Pozzolana natural calcined Q	Fly ash siliceous V	Fly ash calcareous W	Burnt shale T	Limestone* L	Limestone* LL	Minor additional constituents
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[3]	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[3]	CEM IV/A	65-89	-	<——— 11-35 ———>					-	-	-	0-5
		CEM IV/B	45-64	-	<——— 36-55 ———>					-	-	-	0-5
CEM V	Composite cement[3]	CEM V/A	40-64	18-30	-	<——— 18-30 ———>			-	-	-	-	0-5
		CEM V/B	20-38	31-50	-	<——— 31-50 ———>			-	-	-	-	0-5

1) The values in the table refer to the sum of the main and minor additional constituents. 2) The proportion of silica fume is limited to 10%.

3) In Portland-composite cements CEM II/A-M and CEM II/B-M, in Pozzolanic cements CEM IV/A and CEM IV/B and in Composite cements CEM V/A and CEM V/B the main constituents besides clinker shall be declared by designation of the cement.

* L : total organic carbon (TOC) shall not exceed 0.5% by mass; LL: TOC shall not exceed 0.20% by mass.

2.3.5.3. Use as an Admixture in Concrete

Starting in the early 1950s, granulated blast furnace slag was ground separately to an appropriate fineness and was mixed with Portland cement, aggregates and water in the concrete mixer. Depending on the particular performance demand on the concrete, ground granulated blast furnace slags have been used in proportions of 20 to 80 percent by mass of the total cementitious material [11]. All available granulated blast-furnace slag in South Africa and the greatest volume of slag produced in the United States are used as mineral admixtures for concrete. Moreover, this process is applied in many other countries including Canada, Australia, United Kingdom, France, Japan and Turkey.

Concrete incorporating ground granulated blast furnace slag cement sets more slowly than concrete made with ordinary Portland cement depending on the amount of ground granulated blast furnace slag in the cementitious material, but also continues to gain strength for longer periods of time in production conditions. This results in lower heat of hydration and lower temperature rises, and makes avoiding cold joints easier, but may also affect construction schedules where quick setting is required. Furthermore, use of ground granulated blast furnace slag significantly reduces the risk of damage caused by alkali-silica reaction, provides higher resistance to chloride ingress, reducing the risk of reinforcement corrosion, and provides higher resistance to attacks by sulphate and other chemicals [17]. Table 2.5 shows typical replacement rates for various concrete applications.

Table 2.5. Suggested Slag Cement Replacement Ratios for Various Concrete Applications [5].

Concrete Application	**Slag Cement (% by Weight)**
Concrete Paving	25–50
Exterior and Interior flatwork	25–50
Basement floors	25–50
Footings	30–65
Walls and columns	25–50
Prestressed concrete	20–50
Precast concrete	20–50
Concrete blocks	20–50
Concrete pavers	20–50
High strength concrete	25–50
Alkali-silica reaction mitigation	25–70
Sulfate resistance, Type II Equivalence	25–50
Sulfate resistance, Type V Equivalence	50–65
Lower permeability	25–65
Marine exposure	25–70
Mass concrete (heat mitigation)	50–80

2.3.6. Factors Determining Cementitious Properties of Ground Granulated Blast Furnace Slag

The cementitious properties of ground granulated blast furnace slag are determined by:

- 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

The slag's chemical composition has been used as an indicator of product quality. As a means of reducing slag composition data to one parameter, a hydraulic index is defined as [18];

$$\text{Hydraulic Index, } I_h = \frac{CaO + 1.4\ MgO + 0.56\ Al_2O_3}{SiO_2} \tag{8}$$

Hamling and Kriner found that for physical and chemical product quality control (percent glass, hydraulic index, hydraulic activity, and median particle size), the hydraulic index is found to be the best indicator of slag quality [19]. Slags with a hydraulic index of 1.0 or higher are recommended [20, 21].

As the interrelation of all the above factors is very difficult to determine, the best way to analyze the suitability for use in cement combination of any blast furnace slag is to conduct performance tests with the appropriate criteria for strength or durability [11].

Slag activity index for ground granulated blast furnace slag to be used as a concrete admixture is found by applying the test method described in ASTM C 989 [22]. The reference cement to be used for slag activity test should comply with the requirements of standard specification for Portland cement and its total alkali percentage (Na_2O+0.658K_2O) should be in the range of 0.60 to 0.90. The minimum 28 days compressive strength of the reference cement must be 35 MPa [22].

According to ASTM C 989 [22], slag is classified into three grades, 120, 100, and 80, depending upon the mortar strengths when mixed with an equal weight of Portland cement, and compared to that of pure Portland cement mortar. The corresponding slag activity index standards are presented in Table 2.6 [4].

Table 2.6. ASTM C 989 Slag-Activity Index Standards for Various Grades [4]

	Average of Five Consecutive Samples	Any Individual Sample
Minimum 7-day Index, %		
Grade 80	--	--
Grade 100	75	70
Grade 120	95	90
Minimum 28-day Index, %		
Grade 80	75	70
Grade 100	95	90
Grade 120	115	110

2.3.7. Production Methods of Portland Slag Cements

There are two alternatives in manufacturing Portland slag cements and blast furnace slag cements called the intergrinding method and the separate grinding method. In the intergrinding method, Portland cement clinker and granulated blast furnace slag are mixed and ground in the mill whereas in the separate grinding method Portland cement clinker and granulated blast furnace slag are ground separately in the mill and then mixed together. After the grinding operation is finished, for both methods 3-6 % gypsum mineral is used as a set retarder [5].

Historically, Portland slag cement has been produced using the intergrinding method. In this process, granulated blast furnace slag with the Portland cement clinker and gypsum are ground together in the tube mills. Although this method is less energy demanding than the separate grinding method [23], the main drawback of this method is that the particle size distributions of the slag and clinker materials are different [24]. This phenomenon was explained by the fact that hardness of granulated blast furnace slag is higher than clinker so that clinker particles are usually ground more easily than the granulated blast furnace slag particles and they show additional abrasive effect to the clinker particles [25]. Unfortunately, this is not the treatment required for the optimum performance of slag.

On the other hand, another scientific study has shown that intergrinding of granulated blast furnace slag and Portland cement clinker consumes more energy than separate grinding to reach 3500 cm^2/g Blaine fineness. However, the lower energy consuming separately ground Portland slag cement with 25% by weight of granulated blast furnace slag shows lower strength values than higher energy consuming interground Portland slag cement (Table 2.7). This situation is explained by the fact that intergrinding provides more homogeneous product and particle size distributions of the separately ground and interground Portland slag cements are not same [26].

Table 2.7. Compressive Strength of the Cements*[26].

Cement Type Code	Consumed Energy (kWh/ton)	1 day	2 days	7 days	28 days	90 days
P	52	13.1	22.5	40.2	53.6	59.6
PS	39	8.7	15.6	30.5	49.1	59.2
P+S	59•	8.0	15.0	29.3	48.1	60.4

P→ Portland cement

PS→ Intergrinding of Portland cement clinker and granulated blast furnace slag

P+S→ Separate grinding of Portland cement clinker and granulated blast furnace slag

•The consumed energies of separately ground cements were calculated by weighted average of consumed energies of the ingredients to reach 3500 cm^2/g

*All these cements have the same Blaine fineness (3500 cm^2/g ± 100 cm^2/g). Strengths of separately ground cements and were given as percentage of the strengths of interground cement of the same composition at the same age.

Although granulated blast furnace slag cements are known as produced by grinding granulated blast furnace slag together with Portland cement clinker and a small amount of gypsum, recent studies on separate grinding concluded that separate grinding should be preferred in view of lower specific energy consumption, ease of manufacture, higher addition of slag (i.e. fewer environmental hazards) on top of higher flexibility in product quality arrangement according to market requirements [27]. In order to prove these properties, Öner [28] compared separate grinding and intergrinding of granulated blast furnace slag cements with respect to their grindabilities, grinding kinetics and strength properties. Firstly, he concluded that the grindability of the slag is lower than clinker; slag is more resistant to grinding. Secondly, grindability of the mixture is not the weighted average of the component grindabilities but is even lower than the harder component slag [27]. This indicates that the specific grinding energy per specific surface necessary to produce blast furnace slag cement is greater when the components are interground [28]. Thirdly, he argued that when grindabilities of the components are different, their individual distributions are also different. The harder component, slag, tends to accumulate in coarse fractions having narrower size distribution, higher mean size and lower specific surface area and the softer component, clinker, being ground at a higher rate would accumulate in finer size fractions having a wider size distribution, lower mean size and higher specific surface area [28]. Because of these results, although the specific surface areas of the two blast furnace slag cements are the same, the slag in the interground blast furnace slag cement is relatively coarser than the slag ground separately. As the coarser slag would not take part in hydration reaction as fast as the fine slag, the compressive strength values of the blast furnace slag cement produced by intergrinding is lower than separately ground blast furnace slag cements, but no improvement has been seen for flexural strengths [28].

Separate grinding of ground granulated blast-furnace slag and Portland cement, with materials combined at the mixer, has two advantages over the interground blended cements;

i. Each material can be ground to its own optimum fineness,
ii. The proportions can be adjusted to suit the particular project needs [13].

Öner et al. [27] investigated the strength development of 1:1 mixes of clinker and granulated blast furnace slag with varying fineness of components from 3000 to 6000 cm^2/g Blaine. Overall results indicated that in manufacturing blended cements, it is not only the fineness of the clinker-slag mix but also of the individual components which govern the choice of the mix composition for a desired strength (Table 2.8). Moreover, initial setting times for blast furnace slag cements are higher than the initial setting time of the control cement. Finally, in manufacturing blast furnace slag cement, grinding the clinker component to a higher fineness should be practiced, as it is more effective in regulating the strength and it is also more cost-effective as given in Figure 2.7, clinker grinding is less energy consuming than grinding slag as expressed by shorter grinding times required for the same fineness levels [27].

Table 2.8. Fresh Properties for Different Slag-Clinker Mixes [27].

Compressive strength(MPa) Slag surface area (Blaine)	2 days	7 days	28 days	Normal Consistency (%)	Initial Setting (min)
Control sample (3000 Clinker)	24.0	35.0	46.1	25.0	170
3000 Clinker					
3000	5.6	13.4	30.8	22.5	195
4000	5.9	15.2	35.5	24.5	200
5000	7.5	18.0	41.2	23.5	170
6000	7.5	18.2	42.6	22.5	175
4000 Clinker					
3000	7.5	17.4	37.6	25.5	190
4000	8.9	19.1	42.3	24.0	190
5000	11.1	23.6	50.8	23.0	175
6000	12.4	24.7	52.3	22.5	175
5000 Clinker					
3000	12.1	20.8	39.2	25.0	170
4000	14.1	26.3	50.7	26.0	180
5000	14.7	29.3	55.2	27.0	180
6000	15.2	29.0	58.0	27.0	170
6000 Clinker					
3000	11.9	21.2	43.4	26.5	185
4000	12.5	24.4	50.7	27.0	210
5000	15.0	29.3	57.6	27.0	195
6000	15.0	31.9	58.8	27.0	190

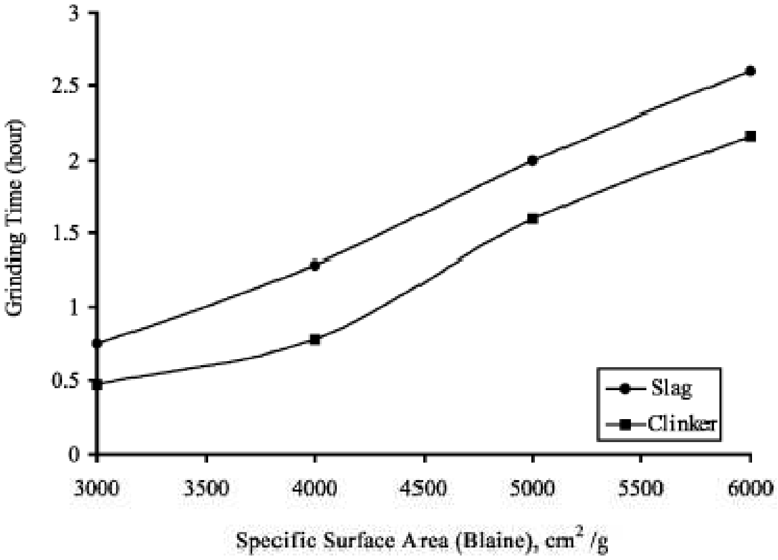


Figure 2.7. Grinding Periods Necessary to Obtain Desired Level of Fineness [27].

Another study was done by Binici et al. [29] about the effect of particle size distribution on the properties of blended cements incorporating granulated blast furnace slag and natural pozzolan. Pure Portland cement, natural pozzolan and granulated blast furnace slag were used to obtain blended cements containing 10, 20 and 30 % additives. The cements were produced by intergrinding and separate grinding and then blending. Each group had two different finenesses of 280 m^2/kg and 480 m^2/kg Blaine. According to the particle size distribution curves, the separately ground finer specimens, which had the highest compressive strength and sulfate resistance, had the highest percent passing for every sieve size [29]. They also observed that the compressive strength of all the blended cements was found to be higher than the minimum value stated by TS EN 197-1 [6]. Moreover, the average compressive strength of the separately ground blended cement specimens at 28 days was higher by about 8% than that of the interground ones. Finally, they showed that the strength of the mortars improves with an increase in the Blaine values of the cement [29].

Doğulu [30] studied the effect of fineness of İskenderun ground granulated blast furnace slag on its cementitious property when used as cement replacing material in Portland cement mortar with testing the 3-, 7-, 28- and 91-day flexural and compressive strengths of the mortars [30]. He used one type of Portland cement and five different fineness values of ground granulated blast furnace slag 3000, 3200, 3700, 3900 and 4400 cm^2/g Blaine and three different replacement amounts of 25, 35 and 45 percent of slag by weight of total cementitious material [30]. As a result of this study, he showed that as the fineness of the slag increases, the compressive strength of the mortar also increases (Table 2.8). However, the effect of the replacement amount to the strength development of the mortar depends on the time of testing. For the early days, the lower the slag content the higher is the strength development, but for later days (91) the higher the slag content, the higher is the strength development (Table 2.9) [30].

Table 2.9. Compressive Strengths of Portland Cement Mortar, Blast Furnace Slag Mortar and Slag-Portland Cement Mortar Specimens [30].

Mix	Blaine Value of Slag Ingredient (cm^2/g)	Compressive Strength (MPa) 3 Days	7 Days	28 Days	91 Days
PC	-	24.4	27.0	32.6	44.6
SC	-	19.0	23.0	33.8	48.2
S3000-25	3000	19.3	20.8	33.1	48.5
S3000-35	3000	14.9	20.6	32.4	49.5
S3000-45	3000	12.5	19.6	31.5	52.7
S3200-25	3200	19.3	22.9	34.7	48.8
S3200-35	3200	16.4	22.1	32.8	49.9
S3200-45	3200	14.0	20.5	31.8	52.7
S3700-25	3700	19.0	23.3	35.7	49.0
S3700-35	3700	16.9	22.6	33.7	50.9
S3700-45	3700	14.1	21.4	36.3	53.6
S3900-25	3900	19.3	23.8	36.3	49.8
S3900-35	3900	18.7	23.0	34.3	52.8
S3900-45	3900	15.1	22.2	37.5	54.9
S4400-25	4400	20.6	24.6	38.5	51.9
S4400-35	4400	19.5	24.3	39.4	53.2
S4400-45	4400	17.5	23.5	40.1	57.0

Hogan and Meusel [31] investigated the properties of granulated blast furnace slag produced by water granulation and they used a 4-by 11-m two-compartment cement grinding mill with the help of the Atlantic Cement company, in New York [31]. They reached some important conclusions which can be summarized as follows: Concrete strength development is slower for slag cement concretes at early ages, generally through three days of age; however, thereafter strengths for slag cement concretes were generally found to be greater, and the ultimate strength is usually significantly greater. Slag cement concretes subjected to elevated temperature (71.1 °C) curing exhibited greater strength development than the straight Portland cement concrete at all ages. On the other hand, slag cement concrete strength development is more adversely influenced by cold weather (4.4 °C) conditions than is the strength development of straight Portland cement concrete. Finally they stated that the optimum slag replacement for mortar strength development appears to be 50% replacement [31].

Dubovoy et al. [32] conducted more or less the same study as Hogan and Meusel [31]. They investigated the physical properties of pastes, mortars and concretes with using various granulated blast furnace slags and slag cement combinations. They have found that for both mortars and concretes, an optimum level of slag replacement exists for which strength is maximized and this level is approximately 50% of slag weight replacement. Moreover, at normal temperatures, early age strength development is retarded when slags are used and setting time of pastes is also retarded when a portion of the cement is replaced by slag. Finally, they have stated that strength of slag cement mixtures increases with an increase in slag fineness as it is in at later ages [32].

Öner and Akyüz [33] studied the optimum level of ground granulated blast furnace slag on the compressive strength of concrete. According to their test results, the compressive strength of ground granulated blast furnace slag concrete increases as the granulated blast furnace slag content is increased up to an optimum point about 55-59 %, after which the compressive strength decreases. Furthermore, they concluded that as the ground granulated blast furnace slag content increases, the water to binder ratio decreases for the same workability, and thus, the ground granulated blast furnace slag has positive effects on workability. Finally they stated that the early age strength of ground granulated blast furnace slag concretes was lower than the control concretes with the same binder content, but, as the curing period is extended, the strength increase was higher for the ground granulated blast furnace slag concretes. They explained this conclusion by the fact that the pozzolanic reaction is slow and the formation of calcium hydroxide requires time [33].

2.3.8. Effects of Ground Granulated Blast Furnace Slag on Mortar and Concrete Properties

2.3.8.1. Workability

Concrete containing ground granulated blast furnace slag increases the workability and placeability since the total volume of the fine particles become higher when compared with concrete not containing ground granulated blast furnace slag [13]. Moreover, it is also stated that the static electric charges of slag particles are much lower than those of the cement particles and this results in an easier dispersion in the mixture [11]. Finally, Fulton [34] investigated in detail the effect of ground granulated blast furnace slag on workability and he stated that cementitious matrix containing ground granulated blast furnace slags exhibited greater workability due to the increased paste content and increased viscosity of the paste.

2.3.8.2. Setting Time

When ground granulated blast furnace slag is used as a replacement for part of the Portland cement in concrete mixtures, an increase in time of setting can be expected [13]. Fulton [34] stated that the time of setting is dependent on the initial curing temperature of the concrete, the proportion of the blend used, the water to cement plus slag ratio, and the characteristics of the Portland cement.

2.3.8.3. Strength and Strength Gain

Hogan and Meusel [31] claimed that the compressive and flexural strength gain characteristics of concrete containing ground granulated blast furnace slag can vary over a wide range. Use of Grade 120 slag typically imparts reduced strength at early ages (1 to 3 days) and increased at later ages (7 days and beyond) compared to Portland cement concrete [13]. Generally, the strength of concrete containing ground granulated blast furnace slag depends on the water to cementitious material ratio, physical and chemical characteristics of the Portland cement, and curing conditions [13]. Hogan and Meusel stated that the optimum blend of ground granulated blast furnace slag should be 50 % of the total cementitious material [31].

CHAPTER 3

EXPERIMENTAL STUDY

3.1. Materials Used in the Study

One type of Portland cement clinker, one type of gypsum mineral and one type of granulated blast furnace slag were used to prepare the cements used in this study. The types of tests performed on these materials and the relevant test standards are given in Table 3.1.

Table 3.1. Tests Performed on Portland Cement Clinker and Granulated Blast Furnace Slag

Tests Performed on Portland Cement Clinker and Granulated Blast Furnace Slag	Relevant Standard
Chemical Analysis (X-Ray Fluorescence)	TS EN 197-1 [6]
Fineness by Blaine Air Permeability	ASTM C 204 [35]
Density	ASTM C 188 [36]

3.1.1. Portland Cement Clinker and Gypsum Mineral

For the production of cements, the Portland cement clinker of Set Cement from the Ambarlı İstanbul Plant was chosen. The clinker was first dried at a temperature of 100°C in the oven and then crushed before grinding operation to eliminate the very large particles. Like Portland cement clinker, the gypsum mineral was also obtained from the

Set Cement Ambarlı İstanbul Plant and dried at a temperature of 60°C and crushed before feeding to the ball mill. For all cements produced, the gypsum/clinker ratio was 3.5/96.5 by weight. The results of the chemical analysis of the Portland cement clinker are shown in Table 3.2. Finally the specific gravity of the Portland cement clinker was found to be 3.23.

Table 3.2. Chemical Composition of the Portland Cement Clinker

Oxides	Portland Cement Clinker, %
SiO_2	21.07
Al_2O_3	5.85
Fe_2O_3	4.35
CaO	64.13
MgO	2.03
Na_2O	0.94
K_2O	0.87
SO_3	0.78

The main compounds of the Portland cement clinker used in the study were calculated by using Bogue’s Equation [3] and shown in Table 3.3.

Table 3.3. Compound Composition of the Portland Cement Clinker

Compound	Content (%)
C_3S	53.22
C_2S	20.25
C_3A	8.14
C_4AF	13.24

3.1.2. Granulated Blast Furnace Slag

The granulated blast furnace slag used in this research was supplied by Set cement Ambarlı factory and produced by Ereğli Iron-Steel factory. The chemical composition of the granulated blast furnace slag is shown in Table 3.4.

Table 3.4. Chemical Composition of the Granulated Blast Furnace Slag

Oxides	Granulated Blast Furnace Slag, %
SiO_2	33.85
Al_2O_3	18.33
Fe_2O_3	2.95
CaO	33.71
MgO	9.47
Na_2O	-
K_2O	0.82
SO_3	0.87

The hydraulic index of the granulated blast furnace slag used in this study was calculated as 1.69 using Eqn. 8, thus exceeding the minimum of 1.00. Finally, the specific gravity of the granulated blast furnace slag was found as 2.84.

3.1.3. Standard Sand

Standard Rilem-Cembureau type sand, relevant to the TS EN 196-1 [37] was used in the preparation of all the mortars and pastes.

3.1.4. Water

The water used in this study was regular tap water in the construction materials laboratory which is connected to the campus water network system at METU.

3.2. Experimental Program

The experimental program of this study is composed of five major sections:

i. Determination of general chemical, physical and mechanical characteristics of the raw materials according to the related TS EN and ASTM standards.
ii. Determination of the slag activity indices of the slags having different Blaine fineness values in accordance with ASTM C 989 [22].
iii. Determination of the effect of separate grinding of Portland cement clinker, gypsum and granulated blast furnace slag with different Blaine fineness values on various properties of Portland slag cement mortars such as normal consistency, time of setting, flexural and compressive strengths in accordance with ASTM C 187 [38], ASTM C 191 [39], TS EN 196-1 [37], respectively.
iv. Determination of the effect of intergrinding of Portland cement clinker and granulated blast furnace slag with different Blaine fineness values on various properties of Portland slag cement mortars such as normal consistency, time of setting, flexural and compressive strengths in accordance with ASTM C187 [38], ASTM C191 [39], TS EN 196-1 [37], respectively.
v. Determination of the various properties of Portland cement such as normal consistency, time of setting, flexural and compressive strength with different Blaine fineness values in accordance with ASTM C187 [38], ASTM C191 [39], TS EN 196-1 [37], respectively.

3.3. Grinding of the Materials

Before the production of the Portland slag cements, the materials, Portland cement clinker, gypsum and granulated blast furnace slag had to be ground to the target Blaine fineness values by using separate grinding and intergrinding methods. For this purpose, Portland cement clinker and gypsum mineral were crushed to 0.5 to 1 cm by the laboratory type jaw crusher before feeding to the ball mill in order to eliminate the very large particles. Since the granulated blast furnace slag was fine enough for grinding operation it was not necessary to crush them in the jaw crusher. Grinding of all the materials to the desired Blaine finenesses was done by a laboratory type ball mill that was 460 mm in length and 400 mm in diameter and the revolution rate was 30 revolutions per minute. The grinding medium were both balls and cylpebs; having bulk densities of around 4650 kg/m^3 and 4700 kg/m^3, respectively. The sizes of the balls and cylpebs were selected small in size, ranging from 30 to 70 mm and 10 to 30 mm, respectively, in order to reach the high Blaine fineness values of the materials. The size distribution of the grinding media used in this study is given in Table 3.5.

Table 3.5. The Size Distribution of the Grinding Medium

Grinding Medium	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 × length)	10 × 10 20 × 20 30 × 30	14.00
TOTAL		98.00

The ball mill feed was selected as 8 kg for Portland cement clinker and granulated blast furnace slag in the separate grinding operation, and 10 kg for Portland cement clinker (70 % by weight) and granulated blast furnace slag (30 % by weight) mixture in the intergrinding operation. Gypsum was ground separately in the ball mill and added to every Portland slag cement mortar and paste in appropriate amounts so as to obtain 3.5 % gypsum in the mixture.

During the grinding operation, after the first 30 minutes the machine was stopped and a sample of about 70 g was taken in order to determine the specific gravity of the material using ASTM C 188 [36]. After this determination grinding was continued stopping the ball mill from time to time and taking a 10 g of sample in order to determine the target Blaine fineness values by using ASTM C 204 [35].

Finally, 13 different types of ground product were successfully produced from the ball mill grinding which are tabulated in Table 3.6. In all produced Portland cements and Portland slag cements, Blaine values in ±100 cm^2/g sensitivity were accepted as nominal.

Table 3.6. Grinding Details of the Materials

MATERIAL	Grinding Time (min.)	Exact Blaine Fineness (cm^2/g)	Assumed Blaine Fineness (cm^2/g)
Clinker (8 kg)	120	3026	3000
Clinker (8 kg)	170	3560	3500
Clinker (8 kg)	225	4080	4000
Clinker (8 kg)	315	4556	4500
Slag (8 kg)	150	3040	3000
Slag (8 kg)	180	3520	3500
Slag (8 kg)	240	3980	4000
Slag (8 kg)	330	4481	4500
Clinker (7 kg) + Slag (3 kg)	185	3056	3000
Clinker (7 kg) + Slag (3 kg)	240	3499	3500
Clinker (7 kg) + Slag (3 kg)	290	4035	4000
Clinker (7 kg) + Slag (3 kg)	420	4532	4500
Gypsum (8 kg)	5	6480	6500

In order to understand the difference on the particles in the separate grinding and intergrinding operations, particle size distribution of the Portland cement clinker and ground granulated blast furnace slag was determined by using a laser diffraction particle size analyzer which is the most efficient way of determining particle sizes over a wide range. The particle size distribution of each material are plotted on log-log graph papers in Appendix B using Rosin-Rammler-Bennett distribution function (Eqn. 9) which is one of the most frequently used particle size distribution model in the cement industry. The equation of the Rosin-Rammler-Bennett distribution is [40]

$$Y = \{1- \exp [-(d/k)^{n}]\} \quad (9)$$

where Y is the cumulative weight percent undersize, d is the particle size, in μm, k is the size modulus and n is the distribution modulus.

3.4. Preparation of the Portland Slag Cements

For the production of the Portland slag cements, ground granulated blast furnace slag was used as partial replacement of Portland cement clinker at 30 percent by weight in order to obtain CEMII/B-S containing 21-35 % ground granulated blast furnace slag by weight. Since materials were ground by using separate and intergrinding methods to four different Blaine fineness values, namely, 3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g and 4500 cm^2/g, eight types of Portland slag cements were prepared. For control purposes, with using Portland cement clinker samples having the same Blaine fineness values with the Portland slag cements, four types of Portland cements were prepared. All of the 12 cement mortar mixes and their cement labels used in the study are shown in Table 3.7.

Table 3.7. Cement Labels Used in the Study

Cement Label	Ingredients					
	Slag		Portland Cement Clinker		Gypsum Mineral	
	% by Weight	Blaine Fineness (cm2/g)	% by Weight	Blaine Fineness (cm2/g)	% by Weight	Blaine Fineness (cm2/g)
PC-3000	**—**	**—**	**100**	**3000**	**3.5**	**6500**
PC-3500	**—**	**—**	**100**	**3500**	**3.5**	**6500**
PC-4000	**—**	**—**	**100**	**4000**	**3.5**	**6500**
PC-4500	**—**	**—**	**100**	**4500**	**3.5**	**6500**
S S30/3000	**30**	**3000**	**70**	**3000**	**3.5**	**6500**
S S30/3500	**30**	**3500**	**70**	**3500**	**3.5**	**6500**
S S30/4000	**30**	**4000**	**70**	**4000**	**3.5**	**6500**
S S30/4500	**30**	**4500**	**70**	**4500**	**3.5**	**6500**
I S30/3000	**30**	**3000**	**70**	**3000**	**3.5**	**6500**
I S30/3500	**30**	**3500**	**70**	**3500**	**3.5**	**6500**
I S30/4000	**30**	**4000**	**70**	**4000**	**3.5**	**6500**
I S30/4500	**30**	**4500**	**70**	**4500**	**3.5**	**6500**

Table 3.8 describes the abbreviations used in labeling the cement types.

Table 3.8. The Description of the Abbreviations Used for the Cement Types

Type of Grinding:
S-Separate grinding
I-Intergrinding
First number following the source indicated:
Percent of slag by weight of Portland cement clinker
The last number following the dash sign:
Blaine fineness of the cement in cm^2/g

The ordinary Portland cement and Portland slag cement are denoted by the symbol of PC and S, respectively, followed by their finenesses such as PC/3000: ordinary Portland cement with a Blaine fineness value of 3000 cm^2/g.

3.5. Slag Activity Index Determination

Since ground granulated blast furnace slag was ground to four different Blaine fineness values, namely, 3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g and 4500 cm^2/g, four different slag activity index test were conducted by using ASTM C 989 [22] and ASTM C 109 [41].

For the determination of the slag activity index, two kinds of mortar mixes having the same workability (a flow of 110±5%) were prepared. The first one is the reference cement mortar, containing 500 g Portland cement and 1375 g standard sand, and the second one is slag-reference cement mortar, containing 250 g Portland cement, 250 g ground granulated blast furnace slag and 1375 g standard sand. Using ASTM C 109 [41], 5 cm cube specimens were cast with each of the mortars and their 7- and 28- day compressive strengths were determined using the formula:

$$\text{Slag Activity Index, \%} = (SP/P) \times 100 \qquad (10)$$

where SP is the average compressive strength of slag-reference mortar cubes at designated ages in MPa and P is the average compressive strength of reference cement mortar cubes at designated ages, in MPa.

3.6. Cement Mixes

For the purpose of investigating the effect of grinding technique on the Portland slag cements, 8 different mixes were prepared using one type of Portland cement clinker having four different Blaine fineness values (3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g and 4500 cm^2/g) and one type of granulated blast furnace slag having four different Blaine fineness values (3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g and 4500 cm^2/g) with one replacement amount (30% slag by weight). In addition to these, 4 different Portland cement control mixes were prepared using one type of Portland cement clinker having four different Blaine fineness values (3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g and 4500 cm^2/g) in order to compare with the Portland slag cements produced by separate grinding and intergrinding techniques. All the tested mortars including the control cement were designed to have the same workability, meaning that water/ (cement+slag) ratio and water/ cement ratio were kept constant in accordance with TS EN 196-1 [37] in order to compare the 2-, 7-, 28- and 90-day flexural and compressive strength values.

3.7. Preparation of the Specimens

The mortar specimens were prepared using laboratory mixer and then fresh mortars were placed into the rectangular mold prisms having dimensions of 40×40×160 mm for compressive and flexural strength development tests in accordance with TS EN 196-1 [37].

3.8. Curing of the Specimens

Specimens were placed into the moulds for 24 hours and then they were immersed in water at 20±1 °C temperature in the curing room having a humidity and the temperature around 90% and 20°C, respectively. The specimens were taken out of water 30 minutes before testing for flexural and compressive strength development.

3.9. Tests Performed on Portland Slag Cement Mortars and Pastes

3.9.1. Flexural and Compressive Strength Tests

For flexural strength tests, three specimens from each mix were prepared and tested. In flexural strength test, each specimen was supported from the two points each 2cm from the ends of the 16 cm length beam and the center-point loading was applied. The load was applied at the rate of 5±1 kgf/sec. The maximum load indicated by the testing machine, namely; Losenhausen having a capacity of 1 ton, was recorded and the tensile strength was calculated using the relation

$$\sigma = 1.5\, P\, L / b^3 \qquad (11)$$

where P is the average of the applied load for the specimen, in kilogram-force, L is the span length, in centimeters, b is the height of the specimen, in centimeters.

Since the specimen broke approximately at the midpoint, two identical specimens were obtained to be tested for compressive strength determination. A 4×4 cm metal plate was used to apply the compressive load to the specimen providing 4×4 cm cross-sectional area for the specimen. The load was increased 10-20 kgf/cm^2 every second by using Utest type compressive strength testing machine having a capacity of 30 tons. The compressive strength was calculated using the relation

$$\sigma = P / A \tag{12}$$

where P is the average load, in kilogram-force, and A is the cross-sectional area of the specimen, in square centimeters.

3.9.2. Normal Consistency and Setting Time

The normal consistency and setting time of cement pastes were determined using a Vicat apparatus according to the ASTM C 187 [38] and ASTM C 191 [39], respectively. For the normal consistency test, 650 g cement mixed with water in laboratory mixer and the prepared cement paste were molded in ball shape and tossed six times through a free path from one hand to another. Then, cement paste was pressed into the ring completely and located under the plunger of Vicat apparatus. Finally, the settlement of the plunger in the paste after 30 seconds was recorded in units of millimeters, which should be in the range of 10±1mm, in accordance with the ASTM C 187 [38]. For the setting time test, the cement paste preparation was the same as the normal consistency test procedure. Then, the cement paste was located under the needle of Vicat apparatus, and by gently releasing the weighted needle onto the surface of the paste, penetration in mm was recorded after 30 seconds. For initial setting the settlement of the needle should be in 25 mm penetration and for final setting it should be in 0-1 mm penetration.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Grinding of the Materials

The grinding time of the materials and the desired Blaine fineness to be reached are shown in Figure 4.1.

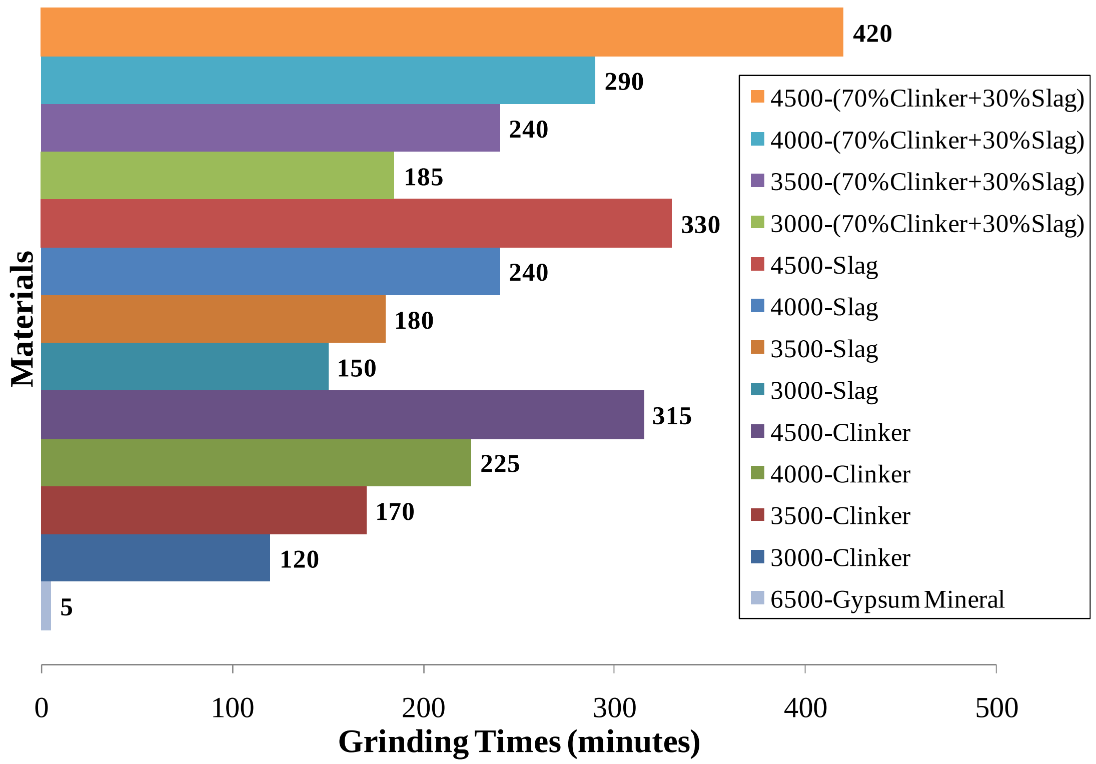


Figure 4.1. Grinding Times of Materials

From Figure 4.1, it can be clearly observed that as previous researchers indicated that the grindability of slag is lower than clinker, that is, slag is more resistant to grinding. This situation can be explained by the fact that the hardness of granulated blast furnace slag is higher than that of clinker so that clinker particles are usually ground more easily than the granulated blast furnace slag particles. For more information about grinding characteristics of each material, grinding times versus Blaine fineness values plots can be seen in Appendix A.

As it can be seen from the Rosin-Rammler-Bennett particle size distribution graphs given in Appendix B, the values of the distribution parameters "k" and "n" decrease with increasing Blaine fineness values for separately ground and interground Portland cement clinker and slag particles. This means that when the Blaine fineness increases, particles show narrower size distributions.

As seen from Appendix B.1 and B.2 graphs, separately ground Portland cement clinker particles have lower "n" values than the separately ground slag particles. This means that Portland cement clinker particles show wider size distribution than the slag particles. Appendix B.3 graph shows that "n" values of the interground Portland cement clinker and slag particles are in between the "n" values of the separately ground Portland cement clinker and the slag particles. This means that their particle size distribution is in between the slag and Portland cement clinker particles. However; it is not their weighted average values, it is closer to the "n" values of the slag particles.

4.2. Slag Activity Indices

The 7-day and 28-day compressive strength values for 5 cm cubic mortar specimens were determined according to the ASTM C 989 [22] and the slag activity indices were calculated by using Eqn. 10 and were tabulated in Table 4.1.

Table 4.1. 7- and 28-Day Compressive Strengths of Specimens and Their Slag Activity Indices

Mortar Mix	7-Day Compressive Strength (MPa)	7-Day Slag Activity Index (%)	28-Day Compressive Strength (MPa)	28-Day Slag Activity Index (%)
RCM(3500)	31.5	—	43.2	—
S-RCM(3000)	23.6	75	41.8	97
S-RCM(3500)	25.9	82	43.9	102
S-RCM(4000)	28.0	89	46.2	107
S-RCM(4500)	29.7	94	48.8	113

The results indicated that the grade of the mortar mixes having different Blaine fineness values had the same grade 100. However, increasing the Blaine fineness values of the mortar mixes improved both the 7-day and 28-day slag activity indices. This means that in order to increase the quality of the slag, in other words, to increase the grade of the slag, the granulated blast furnace slag particles should be ground much finer.

4.3. Normal Consistency and Setting Time

Normal consistency tests were performed on the cement pastes in order to determine the requirement of water amount for different Blaine fineness of Portland slag cements prepared using separately ground and intergrinding techniques. The test results are given in Figure 4.2.

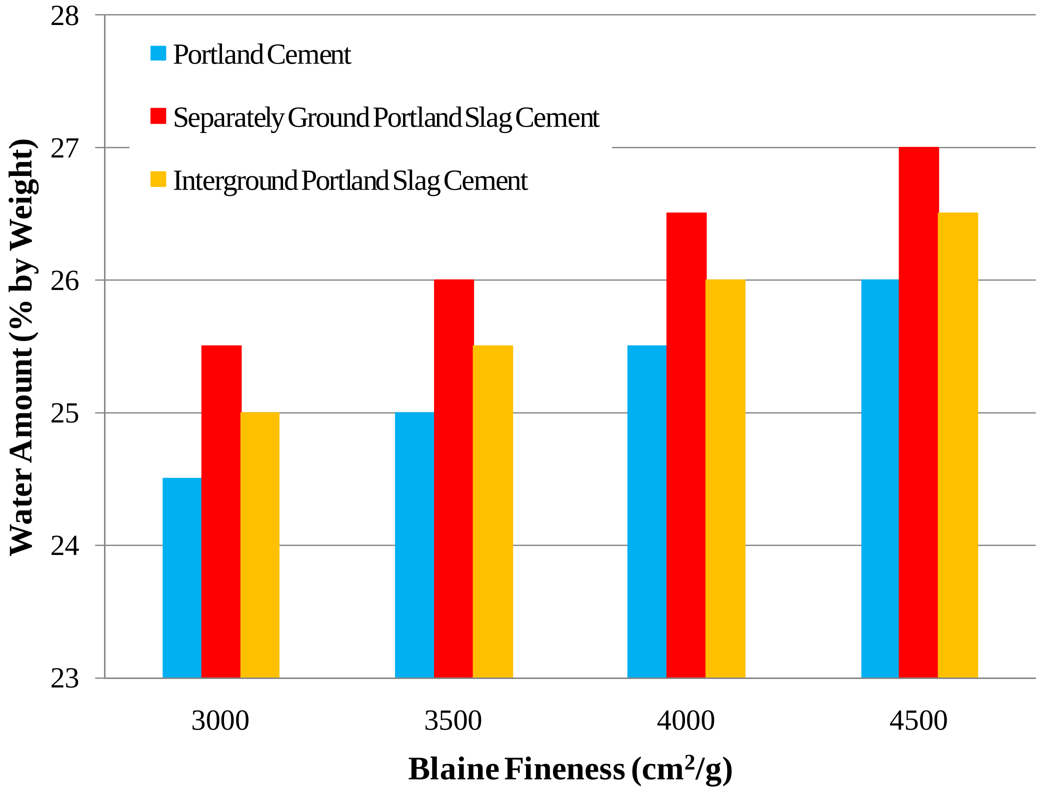


Figure 4.2. Normal Consistency of Cement Pastes

In Figure 4.2 it is clearly seen that Portland slag cement pastes require slightly higher water amount for normal consistency relative to Portland cement pastes. The reason of this may be the lower specific gravity of the slag particles (2.84) when compared to the Portland cement particles. Portland slag cements produced with separate grinding method requires slightly higher water amount than the Portland slag cement produced by intergrinding method for all the tested Blaine fineness values. This may be due to the more homogeneous particle size distribution of the interground materials. Finally, for all of the cement pastes, increasing the Blaine fineness of the particles increases the water demand for normal consistency circumstances.

The initial and final setting time test results are plotted in Figures 4.3 and 4.4, respectively. The initial and final setting times of each cement paste satisfy the limits according to ASTM C 1157 [42] which are 45 minutes and 420 minutes, respectively. In Figures 4.3 and 4.4, it is seen that the initial and the final setting times of all the Portland slag cement pastes are higher than the Portland cement pastes for all the tested Blaine fineness values. Moreover, the initial and the final setting times of separately ground Portland slag cement pastes are shorter than those of the interground Portland slag cement pastes. It is also observed that, as the Blaine fineness values increase, the initial and final setting times shorten because the rate of hydration of the cement paste increases when the Blaine fineness values increases. Finally, for all of the cement pastes, the initial and final setting times are inversely proportional to their water demand for normal consistency.

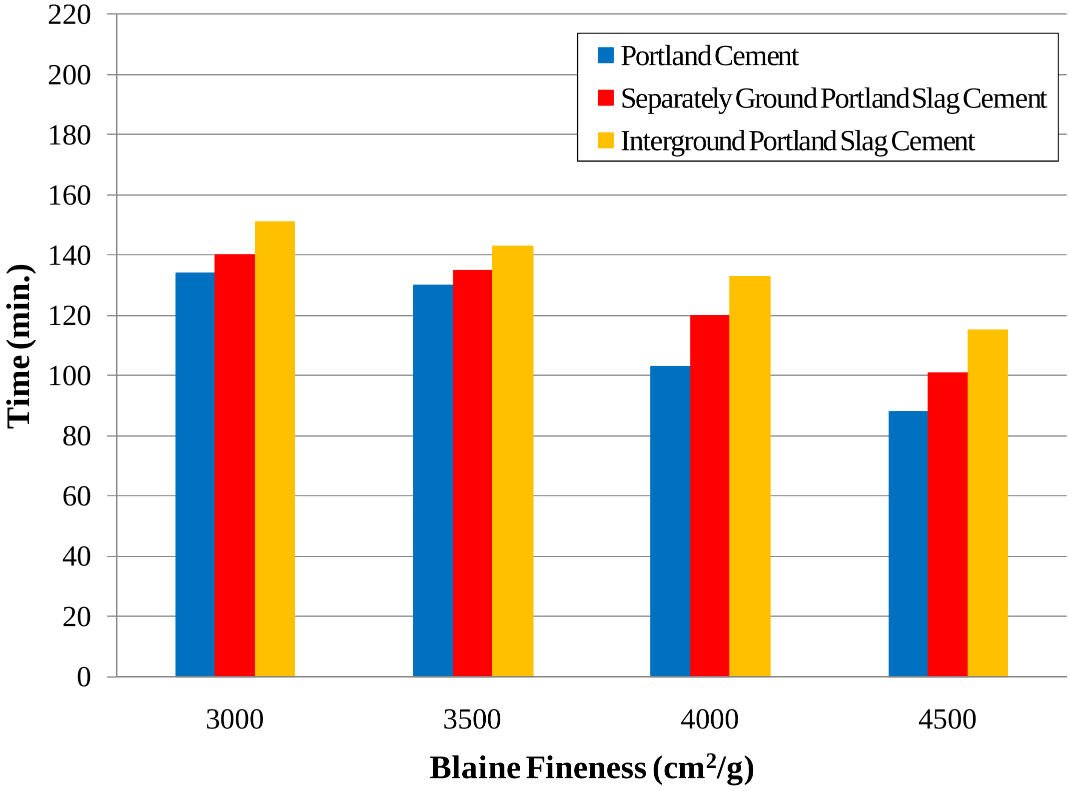


Figure 4.3. Initial Setting Times of Cement Pastes

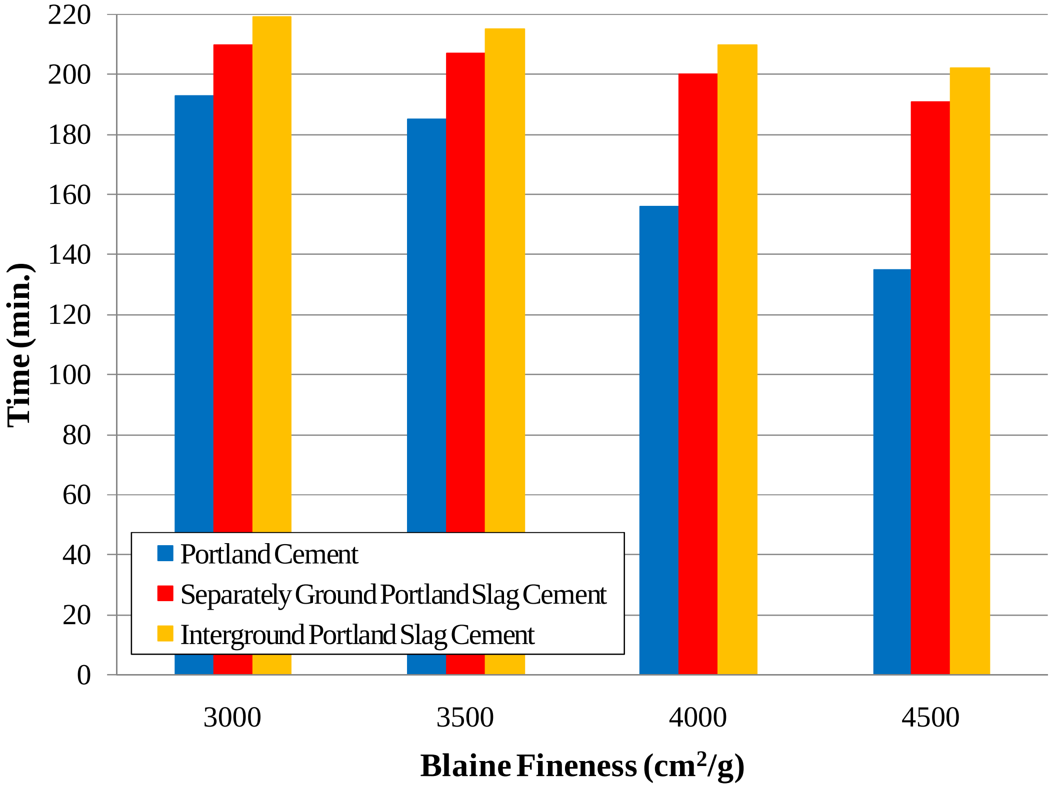


Figure 4.4. Final Setting Times of Cement Pastes

4.4. Flexural Strength of Cements

The flexural strength of the Portland slag cements produced by separate grinding and intergrinding and the control Portland cements were determined by using Eqn. 11 for 2, 7, 28, and 90 days and are given in Table 4.2.

Table 4.2. Flexural Strength Values of Portland Cement Control and Portland Slag Cement Specimens

Cement	Flexural Strength (MPa)				Coefficient of Variation (%)			
	2 Days	7 Days	28 Days	90 Days	2 Days	7 Days	28 Days	90 Days
PC-3000	5.6	7.3	7.8	9.2	4.1	1.8	1.0	9.8
PC-3500	6.4	8.0	8.7	9.5	0.8	1.3	4.6	2.2
PC-4000	7.2	8.0	8.9	9.6	4.0	1.1	2.5	3.2
PC-4500	7.5	8.0	9.1	10.4	4.1	3.0	1.2	4.5
S S30/3000	4.1	5.9	8.1	8.6	12.3	5.2	3.1	4.7
S S30/3500	4.9	6.3	8.3	9.2	7.0	6.1	1.7	3.8
S S30/4000	5.2	6.9	8.3	9.3	6.3	2.1	2.4	0.6
S S30/4500	5.4	7.1	8.3	9.4	10.5	2.4	1.0	1.8
I S30/3000	4.5	6.1	8.2	8.3	7.7	4.1	1.6	1.4
I S30/3500	5.0	6.6	8.3	8.4	7.3	1.5	2.8	1.5
I S30/4000	5.1	6.8	8.4	8.7	3.9	1.8	3.6	0.6
I S30/4500	5.4	6.9	8.5	8.9	3.7	1.8	3.4	1.3

As seen in that table, the interground Portland slag cements show higher strength values than the separately ground ones for the Blaine fineness values of 3000 cm^2/g and 3500 cm^2/g at 2 and 7 days. However, for Blaine fineness values of 4000 cm^2/g and 4500 cm^2/g, the separately ground Portland slag cements have higher strength values than the interground ones at 2 and 7 days. For 28 days, the flexural strength of the interground Portland slag cements show more or less the same values with the separately ground ones for all of the Blaine fineness values. Finally, the flexural strength of the separately ground Portland slag cements show higher values than the interground ones again for all of the Blaine fineness values at 90 days.

4.4.1. Statistical Analysis of the Flexural Strength Values of Separately Ground and Interground Portland Slag Cements

The program SPSS was used in order to statistically analyze the mean values of flexural strength of the separately ground and interground Portland slag cements. For normal distribution of the samples, q-q plots were plotted on SPSS and the results showed that the normality of the each sample size was not valid. In order show this conclusion with an example, Q-Q plots of the flexural strength of separately ground and interground Portland slag cements having Blaine fineness values of 3000 cm^2/g for 2 days of age were selected and were plotted in Figures 4.5 and 4.6, respectively.

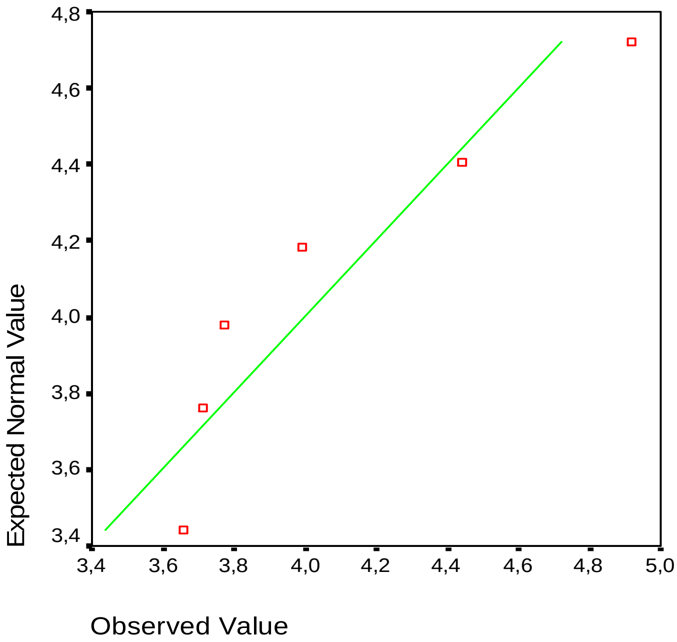


Figure 4.5. Q-Q Plot of Flexural Strength Values of Separately Ground Portland Slag Cements Having Blaine Fineness Values of 3000 cm^2/g for 2 Days of Age

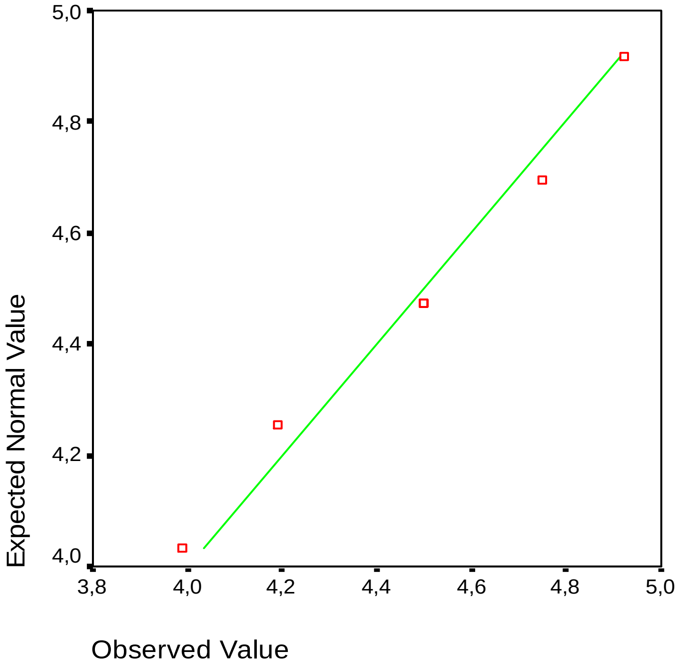


Figure 4.6. Q-Q Plot of Flexural Strength Values of Interground Portland Slag Cements Having Blaine Fineness Values of 3000 cm^2/g for 2 Days of Age

Since the sample size of the flexural strength tests is not higher than 30, a non-parametric test for 2-independent samples with Mann-Whitney test was chosen and in order to compare the flexural strength values of the separately ground and interground Portland slag cements with 95% confidence intervals, P values are calculated by using SPSS program. The null hypothesis and the alternative one are specified as follows:

H_0: The average of the flexural strength of the separately ground Portland slag cement values are equal to the average of the flexural strength of the interground Portland slag cement values.

H_1: The average of the flexural strength of the separately ground Portland slag cement values are not equal to the average of the flexural strength of the interground Portland slag cement values.

The results of the statistical analysis of the flexural strength comparison of the separately ground and interground Portland slag cements are tabulated in Table 4.3. According to the statistical test results, only four of the compared cements which are 7 and 90 days of Portland slag cements having Blaine fineness values of 3500 cm^2/g and 90 days of Portland slag cements having Blaine fineness values of 4000 cm^2/g and 4500 cm^2/g reject the H_0. This means that the average of the flexural strength of the separately ground Portland slag cement values are not equal to the average of the flexural strength of the interground Portland slag cement values and the rest of the all compared cements have the same flexural strength values statistically.

Table 4.3. Statistical Comparison of the Flexural Strength Values of Separately Ground and Interground Portland Slag Cements

Compared Cement Type	Days	P value	H_0
S S30/3000 vs. I S30/3000	2	0.107	Fail to reject
S S30/3500 vs. I S30/3500	2	0.407	Fail to reject
S S30/4000 vs. I S30/4000	2	0.378	Fail to reject
S S30/4500 vs. I S30/4500	2	1.000	Fail to reject
S S30/3000 vs. I S30/3000	7	0.127	Fail to reject
S S30/3500 vs. I S30/3500	7	0.043	Reject
S S30/4000 vs. I S30/4000	7	0.077	Fail to reject
S S30/4500 vs. I S30/4500	7	0.090	Fail to reject
S S30/3000 vs. I S30/3000	28	0.809	Fail to reject
S S30/3500 vs. I S30/3500	28	0.467	Fail to reject
S S30/4000 vs. I S30/4000	28	0.517	Fail to reject
S S30/4500 vs. I S30/4500	28	0.258	Fail to reject
S S30/3000 vs. I S30/3000	90	0.246	Fail to reject
S S30/3500 vs. I S30/3500	90	0.046	Reject
S S30/4000 vs. I S30/4000	90	0.043	Reject
S S30/4500 vs. I S30/4500	90	0.043	Reject

4.5. Compressive Strength of Cements

The compressive strength values of the Portland slag cements produced by the separate grinding and intergrinding methods and the control Portland cements were determined by using Eqn. 12 for 2, 7, 28, and 90 days as presented in Table 4.4.

The compressive strength development with respect to Portland cement control specimens for 2, 7, 28 and 90 days of Portland slag cements produced by separate grinding and intergrinding are plotted in Figures 4.7 through 4.10, respectively.

Table 4.4. Compressive Strength Values of Portland Cement Control and Portland Slag Cement Specimens

Cement	Compressive Strength (MPa)				Coefficient of Variation (%)			
	2 Days	7 Days	28 Days	90 Days	2 Days	7 Days	28 Days	90 Days
PC-3000	26.0	39.2	52.0	56.8	2.6	1.7	4.4	5.5
PC-3500	29.4	42.1	59.6	63.1	2.6	3.0	2.4	2.3
PC-4000	33.9	44.8	61.1	64.6	4.3	2.0	5.0	2.4
PC-4500	35.9	47.9	65.0	67.9	2.4	1.6	1.7	1.8
S S30/3000	17.5	26.7	47.0	55.2	6.8	3.8	5.2	2.8
S S30/3500	20.9	29.8	50.1	61.6	6.5	5.4	6.3	4.3
S S30/4000	22.7	33.6	55.5	67.2	7.5	5.1	4.1	2.3
S S30/4500	24.0	36.3	60.7	71.2	7.8	6.7	4.1	2.9
I S30/3000	19.3	28.2	48.0	60.1	7.4	2.6	2.4	3.3
I S30/3500	22.1	31.9	53.7	68.4	8.4	2.3	3.7	2.7
I S30/4000	22.9	34.2	56.0	69.2	2.9	3.0	3.4	4.7
I S30/4500	23.9	35.5	57.1	70.6	6.9	3.4	4.1	1.6

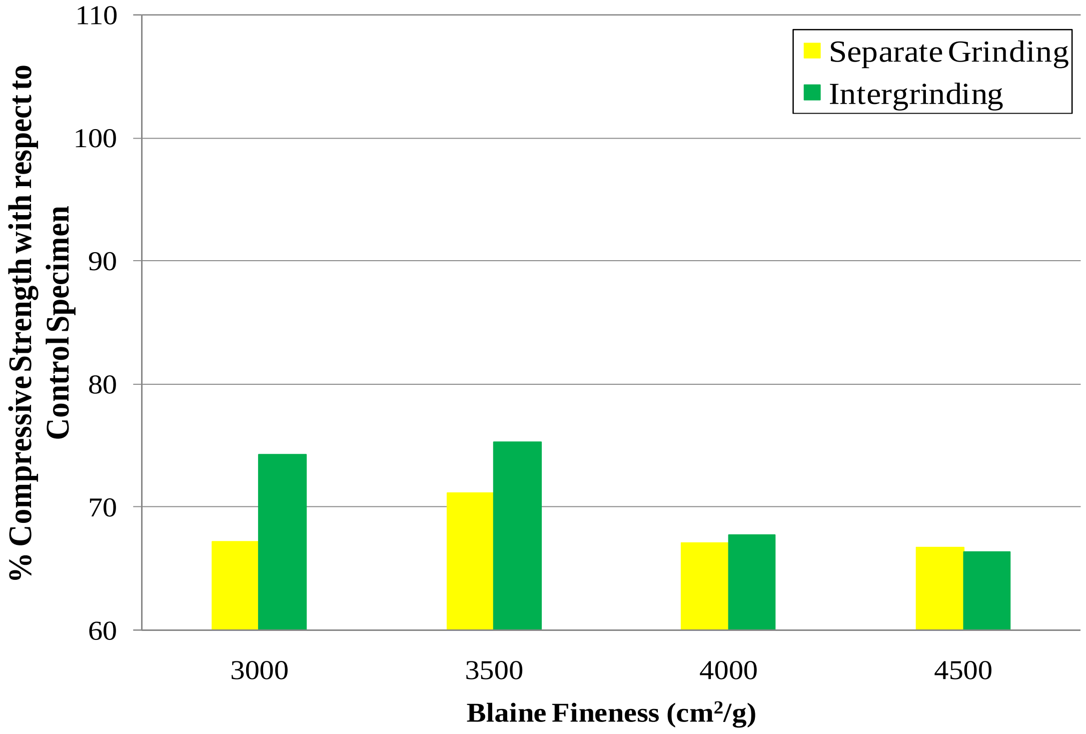


Figure 4.7. Compressive Strength at 2 Days

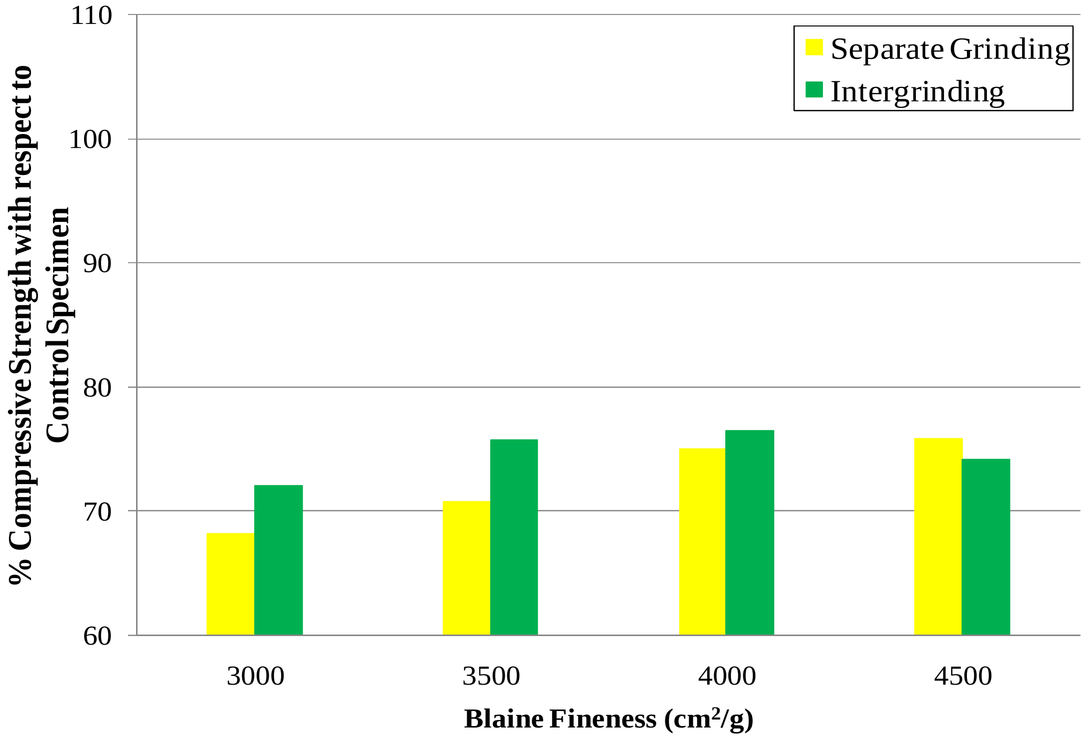


Figure 4.8. Compressive Strength at 7 Days

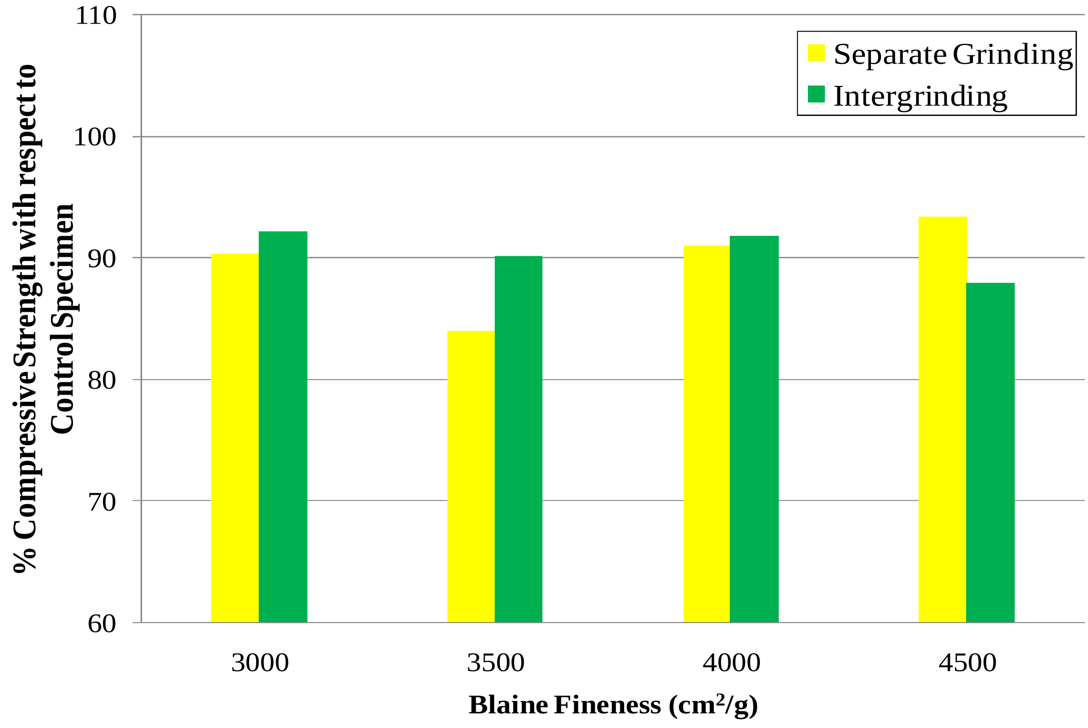


Figure 4.9. Compressive Strength at 28 Days

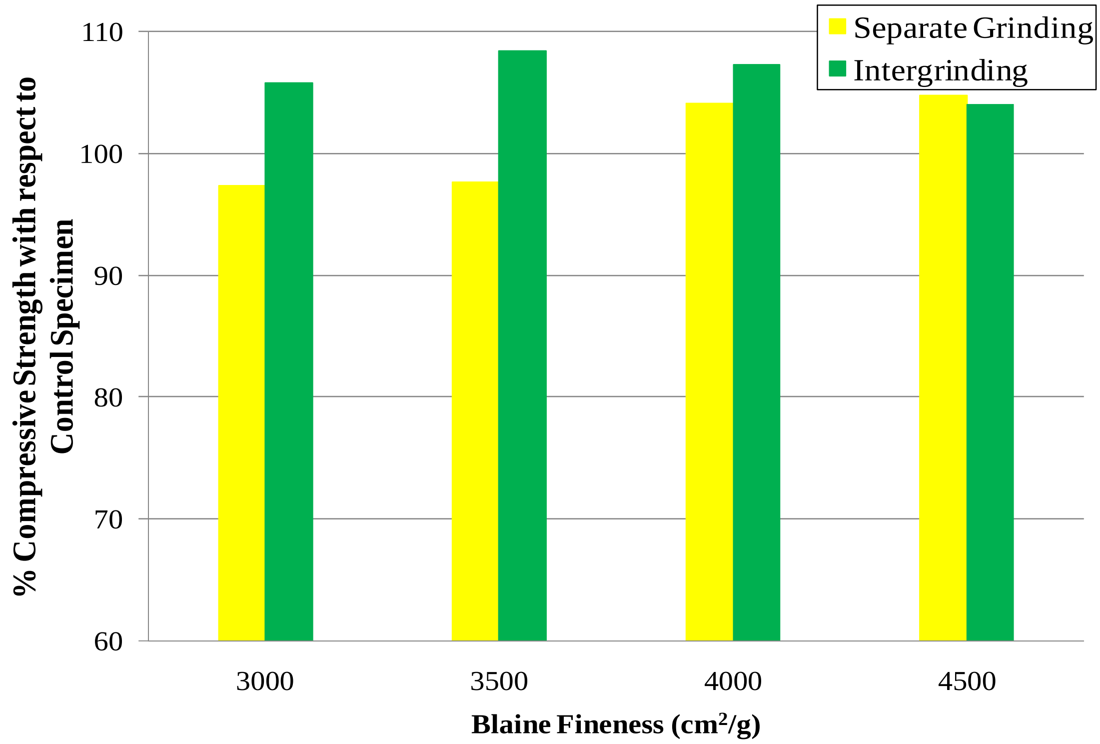


Figure 4.10. Compressive Strength at 90 Days

From Figures 4.7 through 4.10, it is seen that the 2-, 7-, 28- and 90-day compressive strength of the interground Portland slag cements have higher values than the separately ground Portland slag cements for the Blaine fineness values of 3000 cm^2/g, 3500 cm^2/g and 4000 cm^2/g. On the other hand, for the Blaine fineness values of 4500 cm^2/g, separately ground Portland slag cement specimens have a little bit higher 2-, 7-, 28-, and 90-day compressive strength values than the interground ones.

The compressive strength development of the separately ground and interground Portland slag cements with respect to Portland cement control specimens are plotted according to the Blaine fineness values, namely, 3000 cm^2/g, 3500 cm^2/g, 4000 cm^2/g and 4500 cm^2/g in Figures 4.11 through 4.14, respectively.

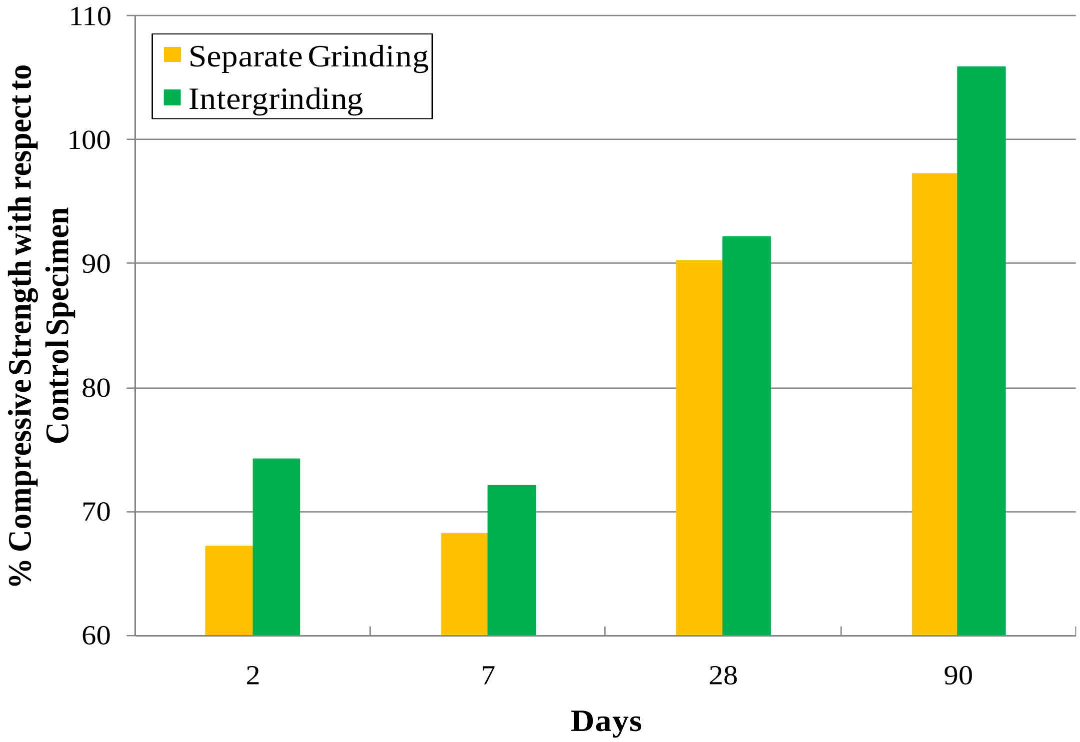


Figure 4.11. Compressive Strength Changes with respect to Control for 3000 cm^2/g Blaine Fineness

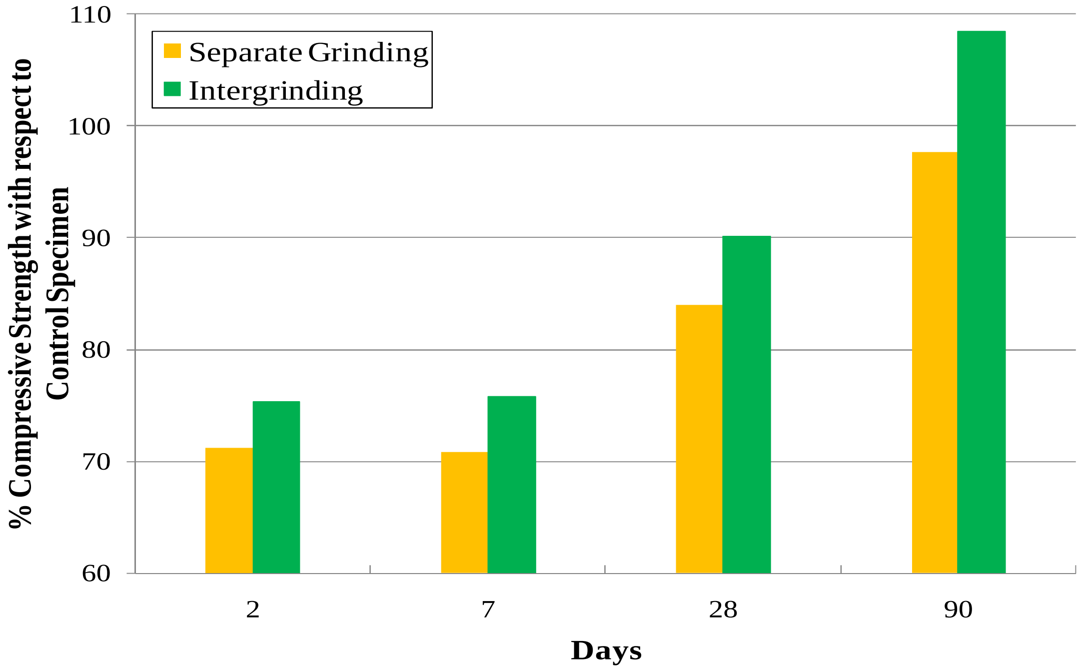


Figure 4.12. Compressive Strength Changes with respect to Control for 3500 cm^2/g Blaine Fineness

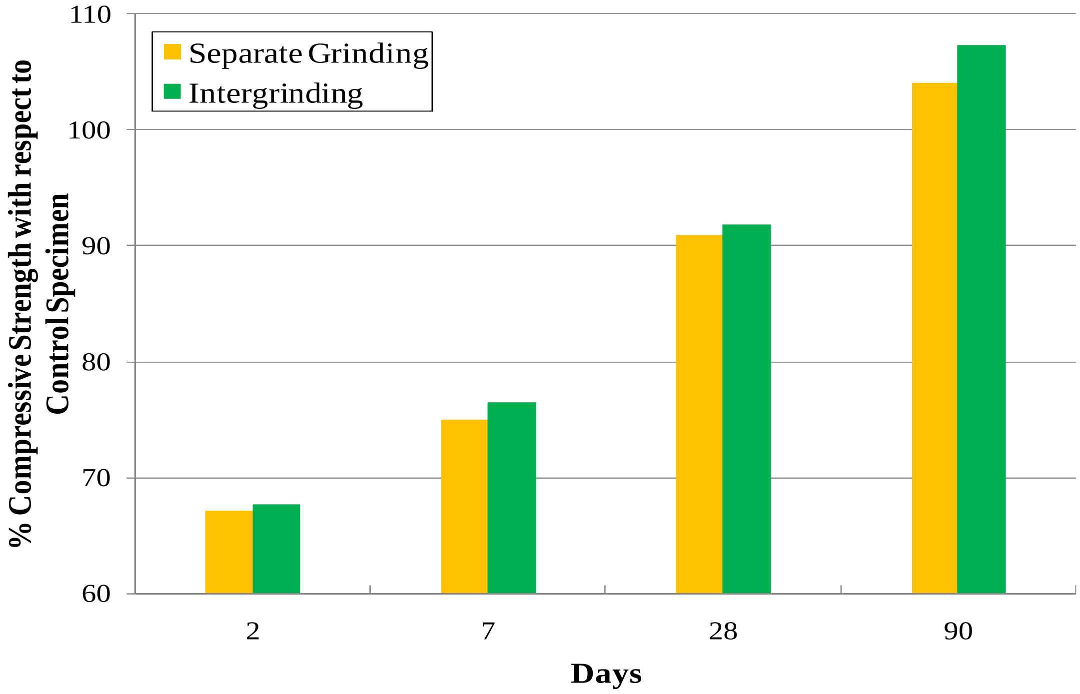


Figure 4.13. Compressive Strength Changes with respect to Control for 4000 cm^2/g Blaine Fineness

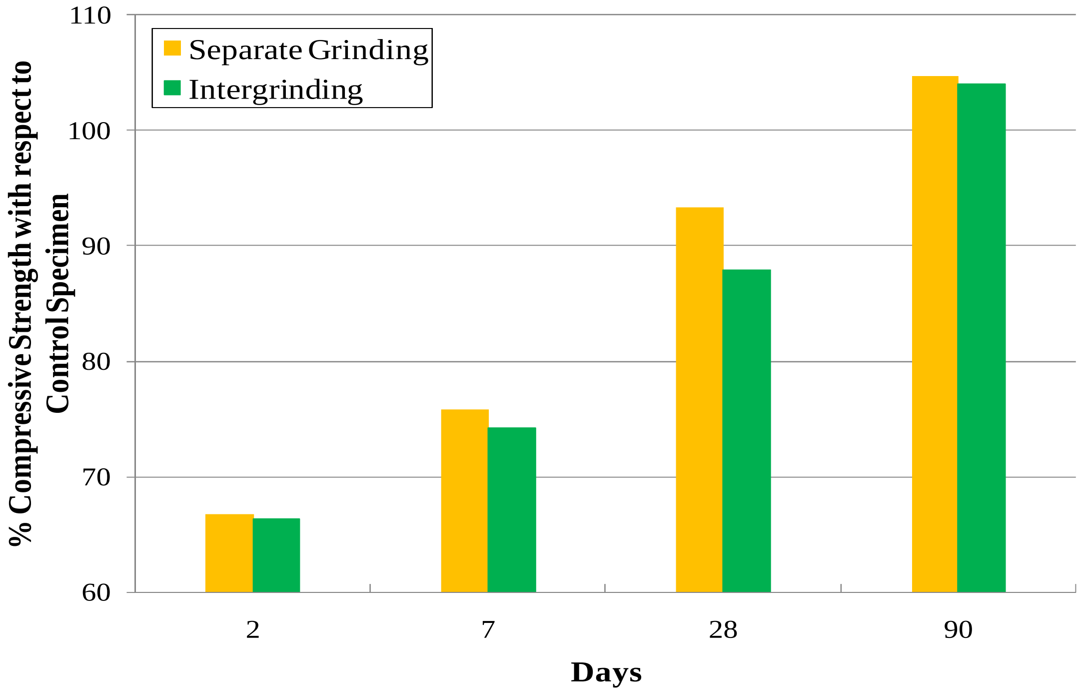


Figure 4.14. Compressive Strength Changes with respect to Control for 4500 cm^2/g Blaine Fineness

In Figures 4.11 through 4.14, it is seen that at early ages of testing (2 and 7 days) of compressive strength of the Portland slag cement specimens are much lower than the Portland cement control specimens. However, after 7 days, the compressive strength values of the Portland slag cements starts to increase and reaches about the 90% of the Portland cement control specimen values. For 90 days of testing, for interground Portland slag cements have higher compressive strength values than the Portland cement control specimens for all the Blaine fineness values. On the other hand, for separately ground Portland slag cement specimens, they have only passed the Portland cement control specimens for the Blaine fineness values of 4000 cm^2/g and 4500 cm^2/g.

4.5.1. Statistical Analysis of the Compressive Strength Values of Separately Ground and Interground Portland Slag Cements

For the statistical analysis of the mean values of the compressive strength of the separately ground and interground Portland slag cements, SPSS program was used and P values were calculated by using the same test (non-parametric test for 2-independent samples with Mann-Whitney test) with 95% confidence intervals as the same reason as the statistical analysis of the flexural strength values. In order show this conclusion with an example, the Q-Q plots of the compressive strength values of separately ground and interground Portland slag cements having Blaine fineness values of 3000 cm^2/g for 2 days of age were selected and plotted in Figures 4.15 and 4.16, respectively.

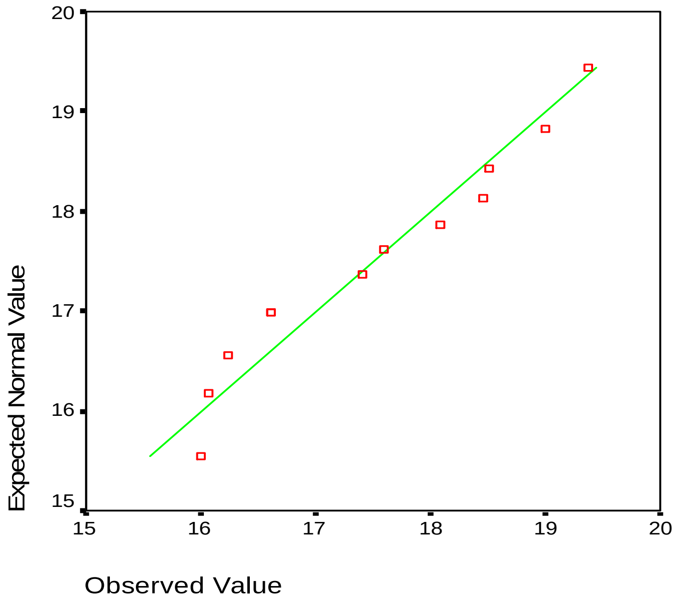


Figure 4.15. Q-Q Plot of Compressive Strength Values of Separately Ground Portland Slag Cements Having Blaine Fineness Values of 3000 cm^2/g for 2 Days of Age.

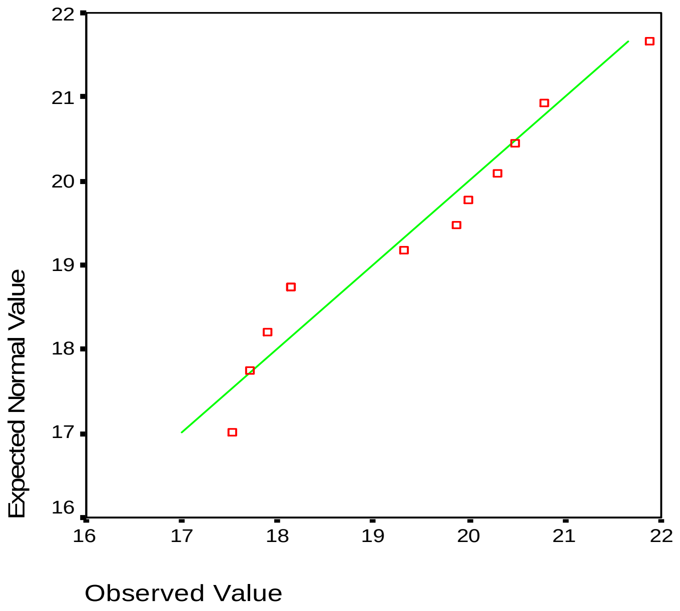


Figure 4.16. Q-Q Plot of Compressive Strength Values of Interground Portland Slag Cements Having Blaine Fineness Values of 3000 cm^2/g for 2 Days of Age.

The null hypothesis and the alternative one are specified as follows:

H_0: The average of the compressive strength of the separately ground Portland slag cement values are equal to the average of the compressive strength of the interground Portland slag cement values.

H_1: The average of the compressive strength of the separately ground Portland slag cement values are not equal to the average of the compressive strength of the interground Portland slag cement values.

The results of the statistical analysis of the compressive strength comparison of the separately ground and interground Portland slag cements are tabulated in Table 4.5. According to the statistical test results, 2, 7 and 90 days of Portland slag cements having

Blaine fineness values of 3000 cm^2/g, 7, 28 and 90 days of Portland slag cements having Blaine fineness values of 3500 cm^2/g and 28 days of Portland slag cements having Blaine fineness values of 4500 cm^2/g reject the H_0. This means that the average of the compressive strength of the separately ground Portland slag cement values are not equal to the average of the compressive strength of the interground Portland slag cement values and the rest of the all compared cements have the same compressive strength values statistically.

Table 4.5. Statistical Comparison of the Compressive Strength Values of Separately Ground and Interground Portland Slag Cements

Compared Cement Type	Days	P value	H_0
S S30/3000 vs. I S30/3000	2	0.007	Reject
S S30/3500 vs. I S30/3500	2	0.126	Fail to reject
S S30/4000 vs. I S30/4000	2	0.954	Fail to reject
S S30/4500 vs. I S30/4500	2	0.977	Fail to reject
S S30/3000 vs. I S30/3000	7	0.001	Reject
S S30/3500 vs. I S30/3500	7	0.000	Reject
S S30/4000 vs. I S30/4000	7	0.435	Fail to reject
S S30/4500 vs. I S30/4500	7	0.470	Fail to reject
S S30/3000 vs. I S30/3000	28	0.436	Fail to reject
S S30/3500 vs. I S30/3500	28	0.008	Reject
S S30/4000 vs. I S30/4000	28	0.470	Fail to reject
S S30/4500 vs. I S30/4500	28	0.007	Reject
S S30/3000 vs. I S30/3000	90	0.006	Reject
S S30/3500 vs. I S30/3500	90	0.004	Reject
S S30/4000 vs. I S30/4000	90	0.078	Fail to reject
S S30/4500 vs. I S30/4500	90	0.522	Fail to reject

CHAPTER 5

CONCLUSIONS

As a result of the experimental study, the following conclusions could be made:

1. The grinding time required for slag particles are higher than Portland cement clinker particles for all the tested Blaine fineness values; therefore, the grindability of the slag is observed to be lower than the grindability of the clinker.

2. According to the Rosin-Rammler-Bennett particle size distribution graphs, Portland cement clinker particles show wider size distribution than the slag particles. Moreover, the particle size distributions of the interground Portland cement clinker and slag particles are in between the particle size distributions of the slag and Portland cement clinker particles. However; it is not their weighted average values, it is closer to the slag particles.

3. Portland slag cements, whether separately ground or interground, require slightly more water than the Portland cements for normal consistency circumstances for all of the tested Blaine fineness values. The reason of this may be the specific gravity of the slag particles (2.84) which is smaller than that of the Portland cement particles.

4. The initial and final setting times of each cement paste satisfies the limits according to ASTM C 1157 which are 45 minutes and 420 minutes, respectively. Moreover, the initial and the final setting times of all the Portland slag cement

pastes are higher than the Portland cement pastes for all the tested Blaine fineness values.

5. The initial and the final setting times of separately ground Portland slag cement pastes are shorter than those of the interground Portland slag cement pastes. Furthermore, as the Blaine fineness values increase, the initial and final setting times shorten because the rate of hydration of the cement paste increases when the Blaine fineness values increase. Finally, for all of the cement pastes, the initial and final setting times are inversely proportional to their water demand for normal consistency.

6. The 2-, 7-, 28- and 90-day compressive strength values of the interground Portland slag cements are higher than the compressive strength values of the separately ground ones for the Blaine fineness values of 3000 cm^2/g, 3500 cm^2/g and 4000 cm^2/g. However, for the Blaine fineness value of 4500 cm^2/g, the compressive strength values of the separately ground Portland slag cements are a little bit higher than the interground ones.

7. The compressive strength development of Portland cement control specimens have higher values than those of the Portland slag cement specimens for 2,7 and 28 days. For 90-day testing, interground Portland slag cements have higher compressive strength values than the Portland cement control specimens for all the Blaine fineness values. On the other hand, for separately ground Portland slag cement specimens, they have only passed the Portland cement control specimens for the Blaine fineness values of 4000 cm^2/g and 4500 cm^2/g.

CHAPTER 6

RECOMMENDATIONS

According to the test results and observations derived from the study, the following recommendations could be made for other researchers:

1. Since grinding is the least efficient process among the cement manufacturing processes, the optimization of the grinding energy consumption should be made for blast furnace slag cements production by investigating separate grinding and intergrinding methods.

2. The durability characteristics, such as sulfate resistance, freezing and thawing and reaction with alkali-silica of the separately ground and interground Portland slag cements could be determined.

3. Low early strength development of the Portland slag cements could be investigated.

4. Comparison of the separately ground and interground blast furnace cements with different replacement amounts and different Blaine fineness values of slag could be investigated.

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APPENDIX A

GRINDING TIMES OF THE PARTICLES

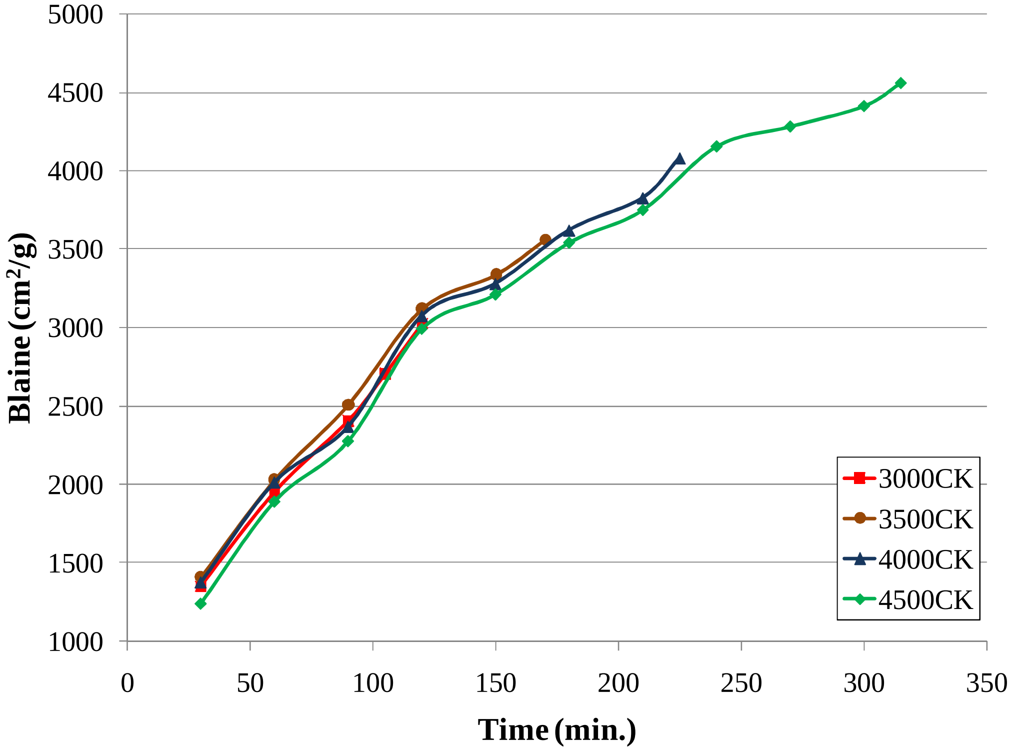

Figure A.1. Grinding Times of Portland Cement Clinker Particles

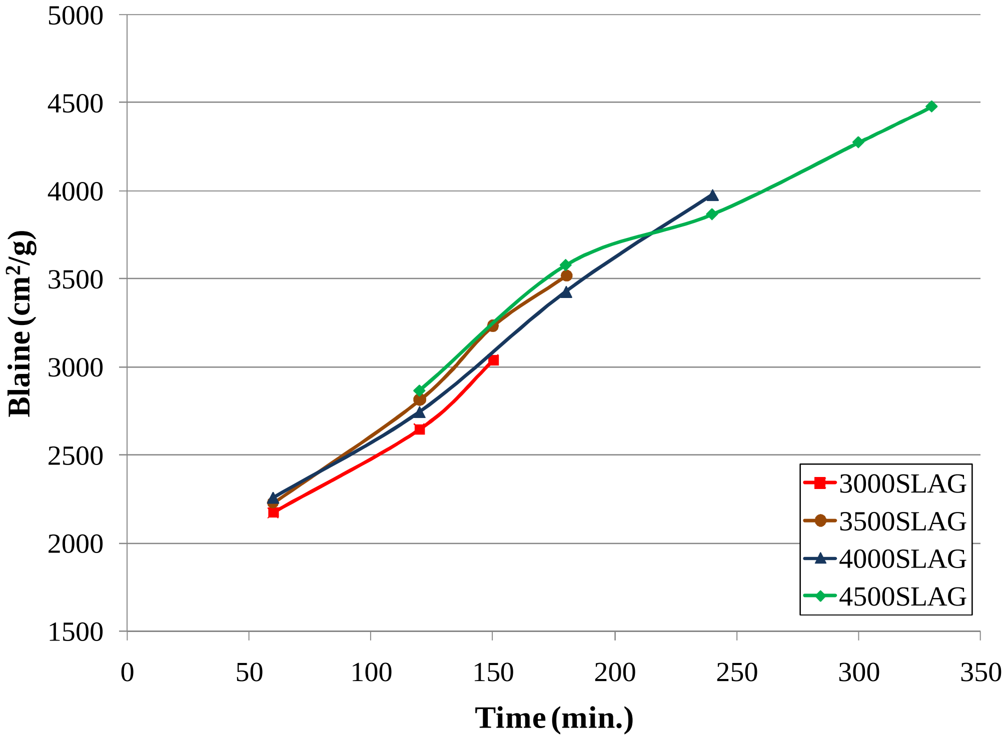

Figure A.2. Grinding Times of Granulated Blast Furnace Slag Particles

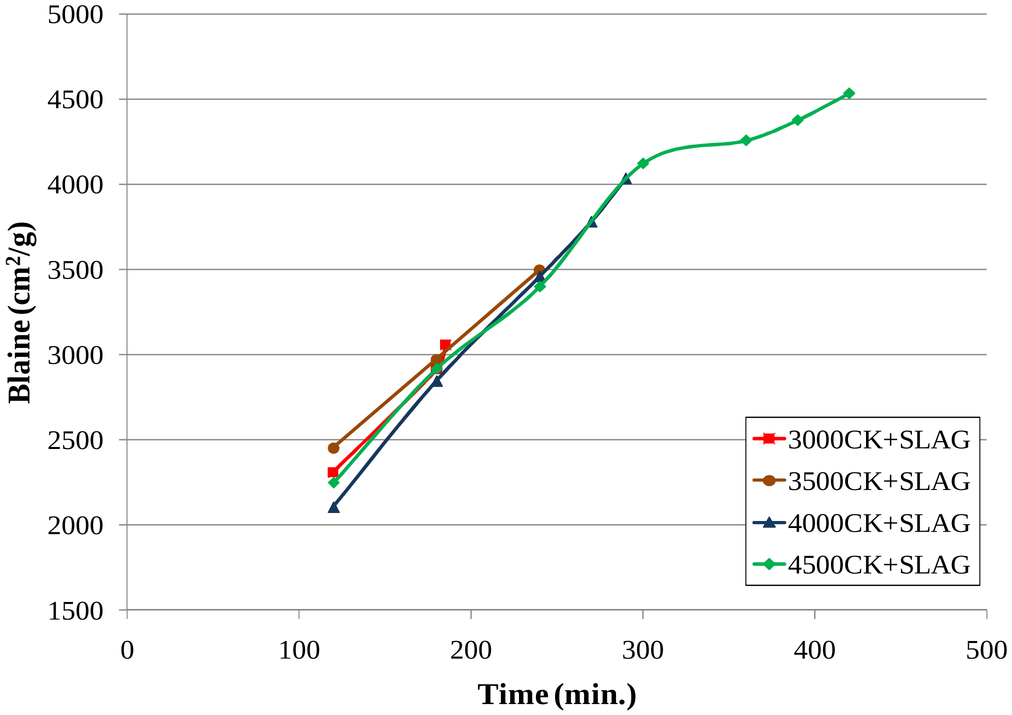

Figure A.3. Grinding Times of Interground Portland Cement Clinker and Granulated Blast Furnace Slag Particles

APPENDIX B

PARTICLE SIZE DISTRIBUTION OF THE PARTICLES

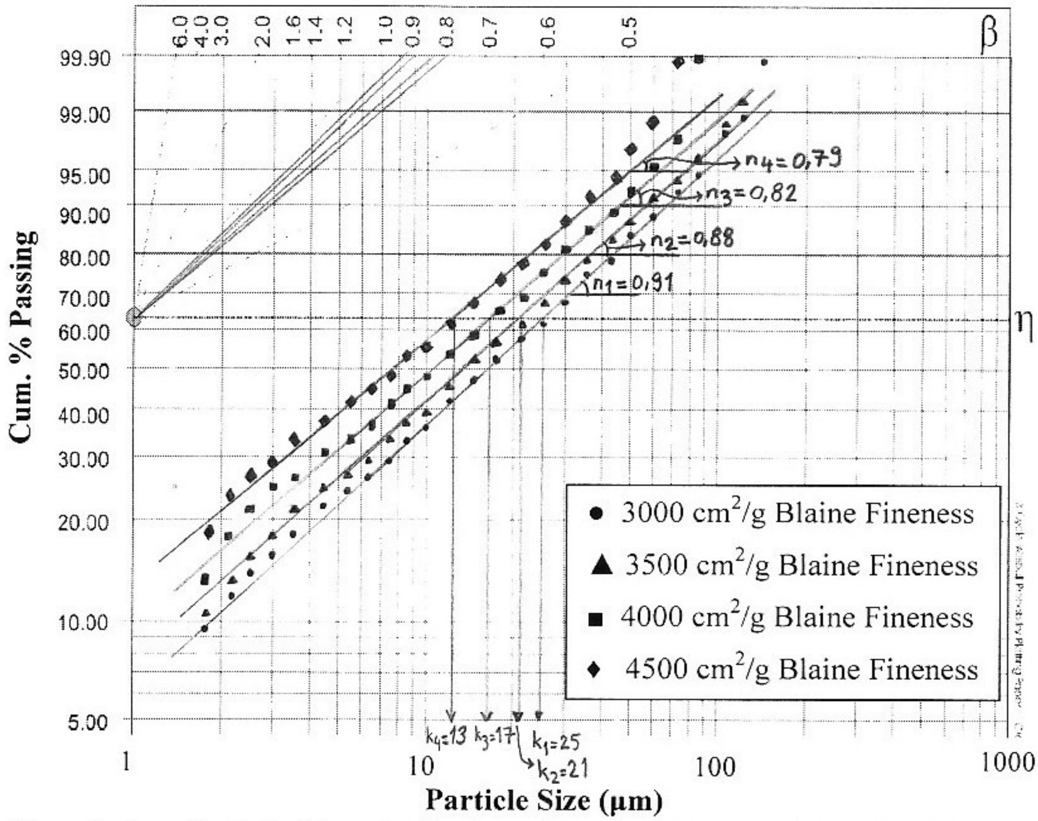

Figure B.1. Particle Size Distribution of Portland Cement Clinker Particles

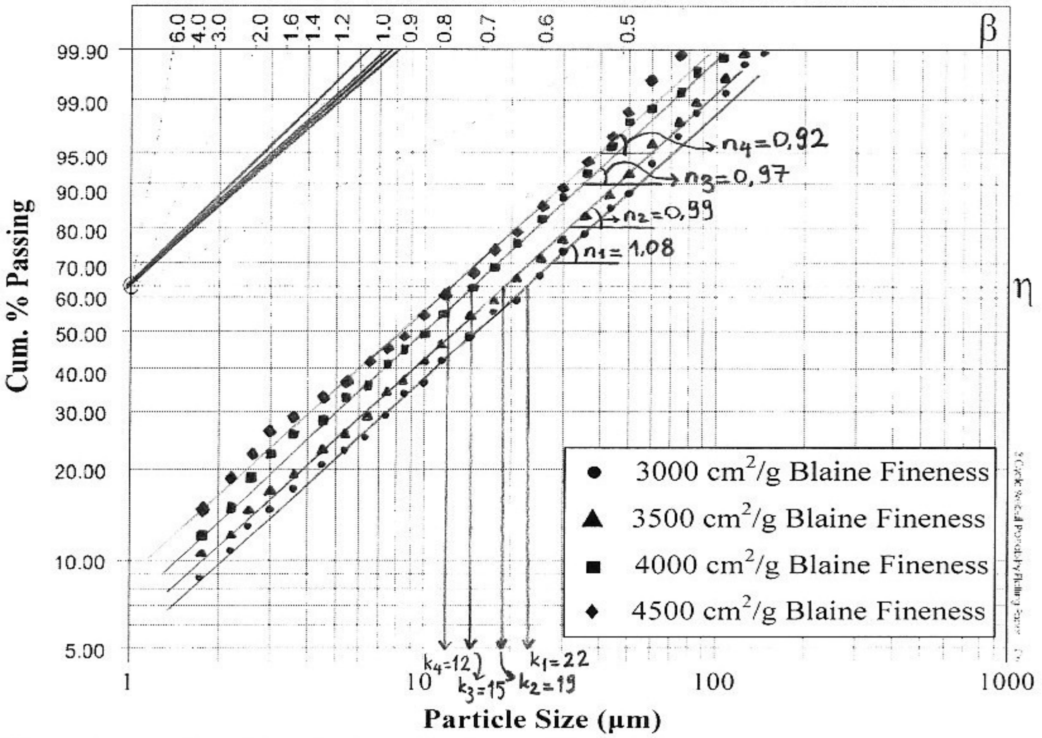

Figure B.2. Particle Size Distribution of Slag Particles

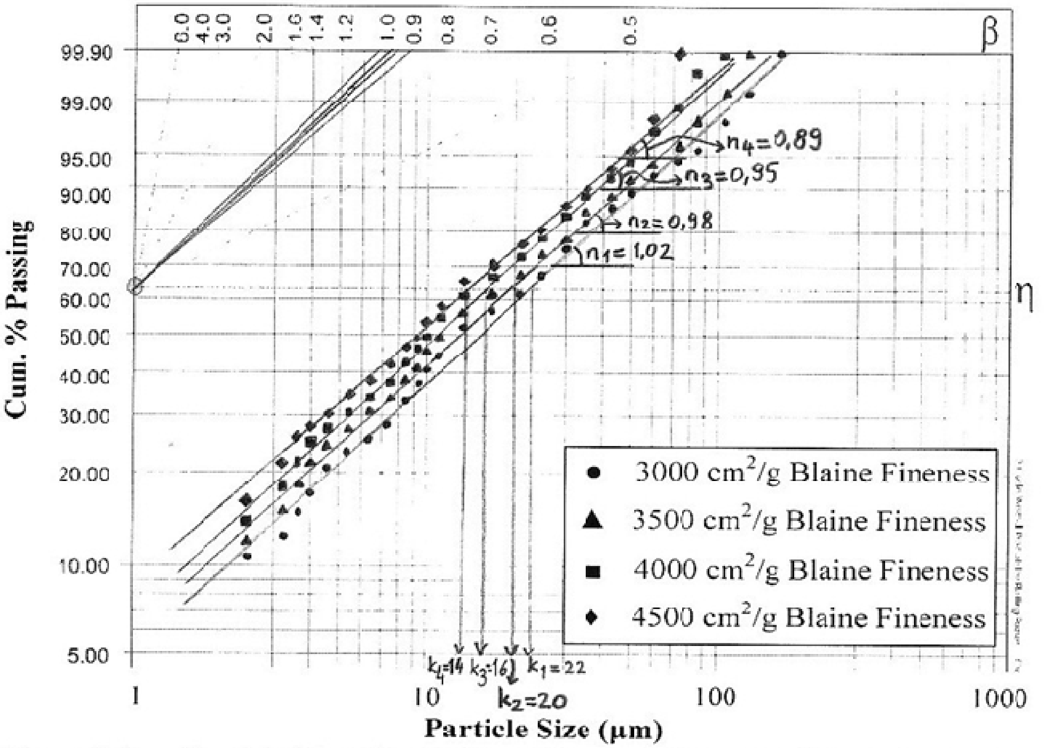

Figure B.3. Particle Size Distribution of Portland Cement Clinker+Slag Particles

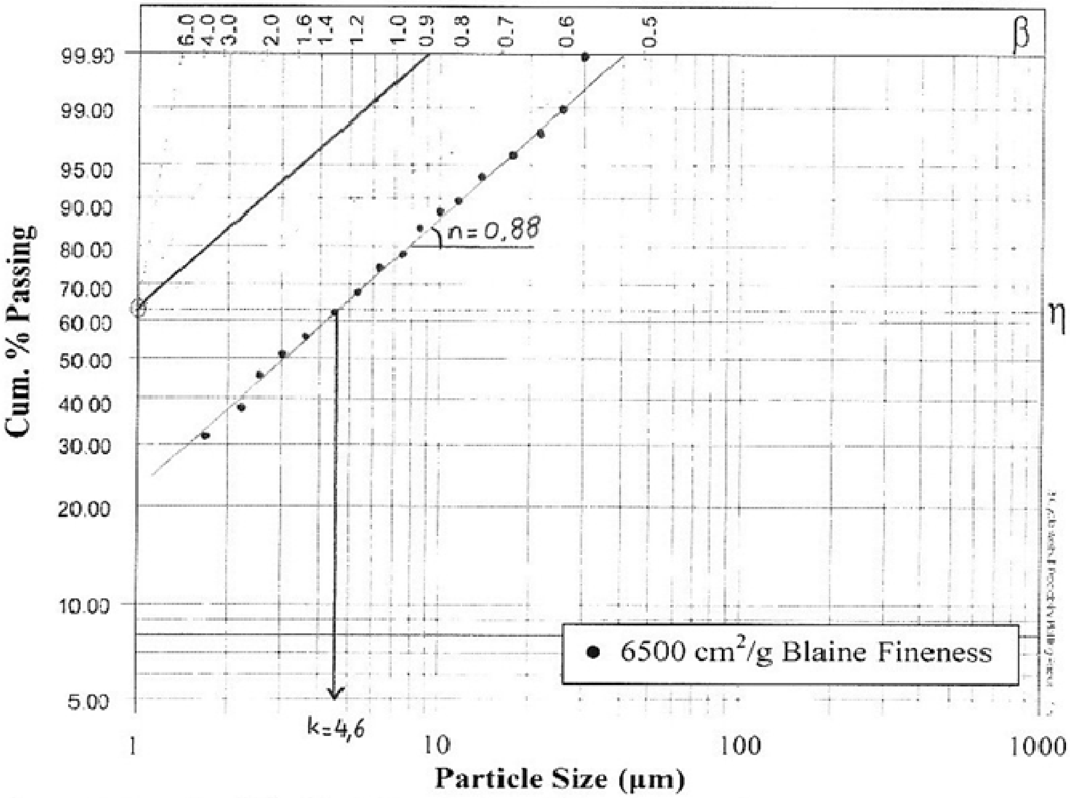

Figure B.4. Particle Size Distribution of Gypsum Particles