A STUDY ON THE UTILIZATION OF STEEL SLAG IN CONCRETE

EHAT GİRAY ARSLAN

BOĞAZİÇİ UNIVERSITY

2007

A STUDY ON THE UTILIZATION OF STEEL SLAG IN CONCRETE

by

Ehat Giray ARSLAN

B.S. in C.E., Yıldız Technical University, 1999

Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Master of Science

Graduate Program in Civil Engineering

Boğaziçi University

2007

to my mother and father

Fikriye and Numan ARSLAN

ACKNOWLEDGEMENTS

I am deeply grateful to Prof. Dr. Turan Özturan, from his valuable support and suggestions in all phases of the research.

I would like to express my sincere gratitude to Prof. Dr. M.Ali Taşdemir for his invaluable guidance and help during the preperation of this dissertation. I would like to mention his patience, giving me inspiration and hope when I was stuck at dead-ends.

I would also like to thank İSTON A.Ş. and especially R&D Department staff, for supplying materials and for their help with conducting tests.

Finally, I would like to thank my family for their continuous support and encouragement.

ABSTRACT

A STUDY ON THE UTILIZATION OF STEEL SLAG IN CONCRETE

Steel slag is a by-product of the steel production. The scope of this thesis is to investigate the effect of steel slags, using as replacement of Portland cement, on the physical and mechanical properties of mortars and concretes. Four different types of steel slags were used in this study, all of them were obtained from Basic Oxygen Furnace of ERDEMİR- Ereğli Iron and Steel Plant as a by product. Steel slags were ground into cement fineness at Akçansa Cement Laboratory. These ground steel slags replaced standard portland cement in specified ratios (20, 40 and 60 % in mass) and 12 types of slag added cements were gained in total. First, the cementitious properties of Erdemir steel slags and the effect of steel slag addition on the properties of Portland cement were investigated in accordance with relevant codes. Density, w/c ratio, setting time, soundness, activity indices and strengths of slag added cements were determined. Then, concretes with a constant water/binder ratio and similar type aggregates were produced with 12 slag added cements. Physical and mechanical tests were conducted on concretes produced with steel slag added cements. Both cement and concrete tests were conducted compared with reference cement and concrete samples and all results are given in comparison.

According to the test results, it was seen that the ERDEMİR steel slags did not meet the required activation properties. In cement tests, as ratio of the replacement of Portland cement by steel slags increased, it was observed that, water requirement, setting times, compressive and flexural strengths decreased, however, soundness values increased. Similar to that, in concrete tests, it was determined that as the ratio of the replacement of portland cement by steel slags increased, compressive and flexural strengths decreased dramatically, however, rapid chloride diffusion, probably because of the metal content in steel slag, increased. Only in two types of steel slag with a replacement ratio of 20%, results mentioned above had the nearest values to the reference mortar and concrete samples. Also it wass examined that the type of steel slag or the replacement ratio did not have any effect on fracture energy.

ÖZET

ÇELİKHANE CÜRUFUNUN BETONDA KULLANILMASI ÜZERİNE BİR ÇALIŞMA

Çelikhane cürufu çelik üretiminin bir yan ürünüdür. Bu çalışmanın amacı Portland çimentosu ile ikame edilen çelikhane cürufunun harç ve betonların fiziksel ve mekanik özelliklerine etkisini incelemektir. Bu çalışmada ERDEMİR- Ereğli Demir ve Çelik İşletmeleri'nden tedarik edilen dört tip çelikhane cürufu kullanılmıştır. Bu cüruflar Akçansa Çimento Laboratuarında çimento inceliğinde öğütülmüştür. Bu öğütülen cüruflar standart Portland çimentosu ile belli oranlarda (%20,40 ve 60) ikame edilerek toplam 12 adet çimento karışımı elde edilmiştir. İlk olarak, çelikhane cürufunun çimentolama özellikleri ve çelikhane cürufu ilavesinin Portland çimentosu üzerindeki etkileri incelenmiştir. Çelikhane cürufu katkılı çimento karışımlarının özgül ağırlık, kıvam suyu, priz süresi, hacimsel genleşme, aktivite endeksi ve dayanım değerleri tespit edilmiştir. Daha sonra, bu 12 tip çimento ile su/bağlayıcı oranı sabit ve aynı tür agrega kullanılarak beton numuneler üretilmiştir. Üretilen bu betonlara fiziksel ve mekanik deneyler uygulanmıştır. Hem çimento hem de beton deneyleri şahit numuneler üzerinde de yapılmış, ve tüm sonuçlar karşılaştırmalı olarak sunulmuştur.

Elde edilen deney sonuçlarına göre ERDEMİR çelikhane cürufunun istenen aktivasyon özelliklerine sahip olmadığı görülmüştür. Çimento ile ikamesinde, ikame oranı arttıkça çimentonun kıvam suyu, priz süresi, basınç ve eğilme dayanımları düşmüş, hacimsel genleşmesi armıştır. Benzer şekilde betonda da cüruf ikame oranı arttıkça basınç ve eğilme dayanımları düşmüş, hızlı klor difüzyonu, muhtemelen çelikhane cürufunun metal içeriğinden dolayı, artmıştır. Sadece iki tip cürufun %20 ikame edildiği denemelerde bahsedilen özellikler şahit numune değerlerine yaklaşmıştır. Cüruf tipinin ya da ikame oranını kırılma enerjisi üzerinde olumlu, olumsuz herhangi bir etkisi gözlenmemiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

Slag is the molten by-product of many metallurgical and special operations, that is subsequently cooled (air, pelletized, foamed or granulated) for use, or in many cases stored indefinitely on site. It is formed as the lime flux reacts with molten iron ore, scrap metal or other ingredients in the steel furnace at melting temperatures.

Until current decade the main objective of the steel makers was the production of steel. Steel slag was treated as a by-product for disposal until the quantity of slag in the slag storing yards has reached to enormous amounts. A large amount of steel slag was deposited in slag storing yards, occupied farmland, silted rivers and polluted the environment for many years. Rising costs and decreasing capacity at landfills have forced the steel industry to change this view. Nowadays the effective utilization of waste steel slag became an important part of the steel manufacturing process . The resulting large quantities of slags produced and their potential impact on the enviroment have also prompted materials scientists and civil engineers to explore the technically-sound, cost-effective and enviromentally-acceptable use of a wide range of slags.

Globally, approximately 0.23 tonnes of blast furnace slag are produced for every tonne of iron and 0.1-0.2 tonnes of steel slag are produced for every tonne of steel. Minor efficency improvements can be achieved around these figures but dramatic reductions can not be achieved [1]. The IISI (The International Iron and Steel Institute) recently announced that global steel production exceeded 1200 million tones in 2006 [2]. Theoretically this would have resulted in generation of approximately 120-240 million tones of slag globally, however the exact figure is unknown.

Resource recovery and reuse of waste materials have become very important within the past decade because of the increased number of environmental regulations that force minimizing waste disposal. The utilization of steel slag is important for environmental protection and resource reuse in Turkey and abroad.

The possibilities for the recycling of steel slag differ from country to country, depending on the chemical composition of the slags, steel making process, the national and local environmental regulations. First, it was usual to recycle 30 per cent of the steel slag production internally in the steel works to the sinter and BOF plants. Nowadays, recycling slag via the sinter plant has declined because of the higher quality demands on steel production. Outside the steel works, steel slags have several applications including: road building, civil and marine engineering and agricultural use.

In ERDEMİR-Ereğli Iron and Steel Works Co. 350,000 tonnes of steel slag is produced annually during the process of steelmaking. This steel slag is processed at crushing-sifting plant and its metallic part is used in convertors as scrap material. Steel slag having particle size of 0-10 mm is utilized in sinter production in 100-110 kg/tonne (sinter: iron ore that has been baked into lumps with coke or coal to ensure it meets the specific properties required for steel production; recycled iron-containing dust and other residue from the steelmaking process can also be added to the mix.). Because of the increase in phosphor per cent it has a limited use in sinter. In our country except the limited use in sinter plant (the "oven" where iron ore and coke or coal and other residue from the steelmaking process is baked to form sinter), steel slag do not have a utilization area. Only in ERDEMİR 6.5 million tonnes of steel slag exists and stored as waste material [3].

Steel slag does not have an effective use in our country presently. Although lots of academic studies and application projects have been done on blast furnace slag, there are limited number of studies on steel slag.

This thesis studies whether the Erdemir steel slags might be used as a secondary binder material by replacing ordinary Portland cement in concrete. The convenience of steel slag is basicly dependent on its chemical properties. The chemical and mineralogical properties were investigated in detail in a research project by The Scientific and Technical Council of Turkey – Marmara Research Center. In this thesis, it is aimed to investigate the effects of steel slags on physical and mechanical properties of cement and concrete. All of the tests were conducted at İSTON (İstanbul Concrete Elements and Ready-Mixed Concrete Factories Corporation) and İstanbul Technical University Structural Materials laboratories.

2. STEEL SLAGS: A LITERATURE REVIEW

2.1. Definitions

Slag is a product of the iron and steel making process. Once scorned as a useless by-product, it is now accepted and, often, preferred and specified as it is known to be a valuable material with many and varied uses. There are mainly two types of slags.

2.1.1. Ferrous Slags

Ferrous slags are siliceous or alumino-siliceous by products of metallurgical processes. These slags possess little or no cementitious value, but in finely divided form and in the presence of the moisture they react with alkali and alkaline earth hydroxides (NaOH, KOH and $Ca(OH)_2$) at ordinary temperatures to form compounds possessing cementitious properties [4]. There are two types of ferrous slags classified according to iron or steel production:

2.1.1.1. Blast Furnace Slag: Blast-furnace slag is defined by the American Society for Testing and Materials as "the non-metallic product consisting essentially of silicates and alumino-silicates of calcium and other bases that is "developed in a molten condition simultaneously with iron in a blast furnace." Blast-furnace slag is formed when iron ore or iron pellets, coke and a flux (either limestone or dolomite) are melted together in a blast furnace. When the metallurgical smelting process is complete, the lime in the flux has been chemically combined with the aluminates and silicates of the ore and coke ash to form a non-metallic product called blast furnace slag. Molten iron collects in the bottom of the furnace and the liquid slag floats on it. Both are periodically tapped from the furnace.

The iron blast-furnace operation is a continuous process. The blended raw materials (burden) and coke are introduced at the top and as the materials move down through the furnace, they are heated from below. Air is injected near the bottom of furnace and the ignited coke eventually supplies enough heat to melt the burden. The slag results from the fusion of the fluxing stone (limestone or dolomite) together with the gangue (silicious and aliminous residues from the iron ore) and coke ash in the blast furnace. The molten slag floats on the top of the molten iron and below the unmelted burden. Both molten materials are drawn off at regular intervals from the continuous-process furnace. Blast-furnace slag is tapped from modern blast furnaces using high-quality ore burdens at a rate of 280-340 kg per metric ton of hot metal [5].

Blast-furnace slag exhibits cementitious properties and can be used as hydraulic binders in concrete with or without Portland cement. The hydraulic activity of these glassy materials is, however, generally too low for total replacement of Portland cement, and chemical activators must be introduced to catalyse the hydrolysis/hydration reactions. Strong alkalies [e.g., NaOH) are effective in increasing the hydration rate and hydraulic activity [6].

The physical state of the slag is fundamental to its cementitious properties. To cool the blast-furnace slag slowly in pits (referred to as air-cooled slag) allows sufficient time for the molecules to arrange themselves into crystalline mineral compounds as the slag solidifies. Unfortunately, these crystalline compounds have little or no cementitious value [7].

During the period of cooling and hardening from its molten state, blast furnace slag can be cooled in several ways to form any of several types of blast furnace slag products.

Air-cooled Slag: Blast furnace slag is allowed to slowly cool by ambient air, processed through a screening and crushing plant and processed into many sizes for use primarily as a construction aggregate or granular base. However, since energy savings have become a more important consideration in the manufacture of cements, the production of hydraulically inert, air-cooled slag has decreased. [8].

Foamed Slag: Foamed slag (sometimes referred to as expanded slag), which is used as a lightweight aggregate, is produced by introducing a limited amount of water to the molten slag. The water vaporizes and the escaping bubbles catch in the solidifying product resulting in a lightweight, porous product. Disadvantages of this process include the high emissions of hydrogen sulphide during foaming and the high absorption of water by the product when used as an aggregate [9].

Pelletized Slag: Pelletized Slag is quickly cooled using water to produce a lightweight aggregate that can be used for high fire-rated concrete masonry, lightweight fill applications, or for use to grind into a cement product. Pelletized slag is produced by expanding molten blast-furnace slag under water sprays, and than by passing the flow of this pyroplastic material over a spinning drum. On the drum are mounted fins, which break up the slag and fling it in the air for a sufficient time (and distance of about 15 m) that surface tension forms pellets. The action of throwing these particles through the air a distance of 15 m. also shapes them in spheres with each particle having a relatively smooth surface. This was a major improvement on the rough vesicular product produced by all other methods of expanding slag [10]. From the point of view of slag handling, the pelletizer takes the molten material, which would normally require several days of air cooling, and turns it into an easily handled product that can be immediately removed from the blast-furnace area. This quick-cooling aspect of peleltizing is important in situations where only limited space is available for slag handling adjacent to the furnace [11].

Granulated Blast-Furnace Slag: Molten slag is tapped from blast furnace and rapidly cooled by large quantities of water to produce a glassy, non-crystalline material called “granulate”. This is then ground to a fineness similar that of Portland cement, commonly known as GGBS (Ground Granulated Blast-Furnace Slag). The most commonly employed method of quenching slag is by water granulation. The molten slag is usually broken up by water jets and is then immediately immersed in water, but several variations are used [7].

The granulated blast-furnace slag glass contains the same major oxides as does Portland cement, but with considerably different proportions of lime and silica. Like Portland cement, it has excellent hydraulic properties and, with a suitable activator (such as calcium hydroxide) will set in a similar manner. Granulated slags may be crushed, graded or ground for specific applications [12].

2.1.1.2. Steel Furnace Slag: The American Society for Testing Materials (ASTM) defines Steel Slag as a non-metallic product, consisting essentially of calcium silicates and ferrites combined with fused oxides of iron, aluminum, manganese, calcium and magnesium, that is developed simultaneously with steel in basic oxygen, electric arc, or open hearth furnaces. Hot iron and/or scrap metal are the primary metals to make steel in each process. Lime is injected to act as a fluxing agent. The lime combines with the silicates, aluminum oxides, magnesium oxides, manganese oxides and ferrites to form steel furnace slag, commonly called steel slag. Slag is poured from the furnace in a molten state. After cooling from its molten state, steel slag is processed to remove all free metallics and sized into products [13]. In BOF, a blast furnace uses coke (carbon) to reduce iron to a high carbon molten iron, called "hot metal". This hot metal is then sent to the steel-making shop's Basic Oxygen Furnace (BOF) where it is combined with steel scrap, various metallic elements, additional lime or dolomitic lime fluxes and is injected with oxygen to produce steel (Figure 1.1). In this process, the BOF uses oxygen to remove carbon and oxidizing reactions to provide heat.

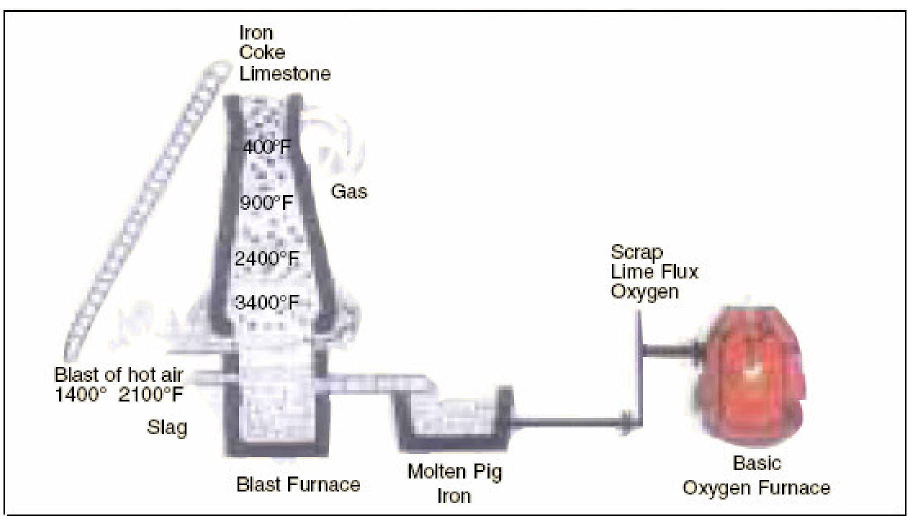

Figure 1.1. Typical basic oxygen furnace production scheme

In an Electric Arc Furnace (EAF) steel-making operation (Figure 1.2), steel scrap is melted in an electric arc furnace along with fluxing agents to produce similar products as that of a Basic Oxygen Furnace; steel and steel slag.

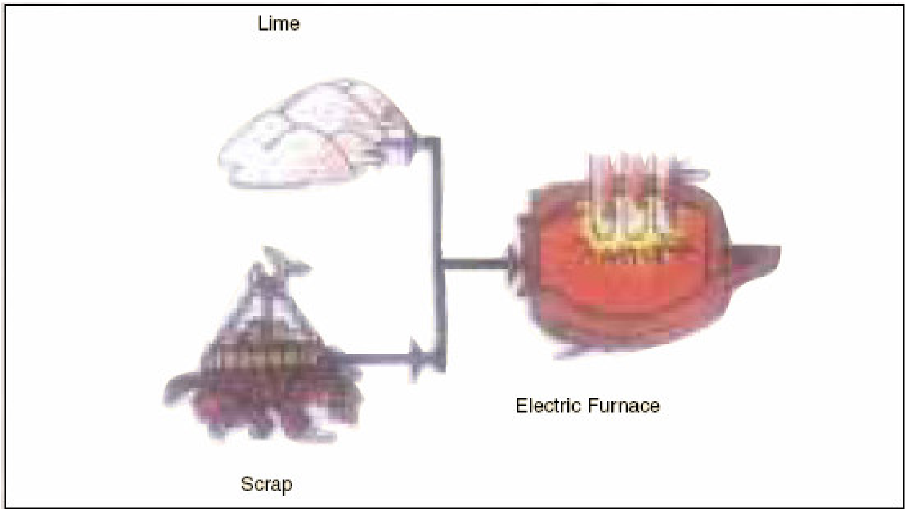

Figure 1.2. Typical electric arc furnace production scheme

The integrated (BOF) route uses raw materials (that is, iron ore, limestone and coke) and scrap to create steel. The electric arc furnace (EAF) method uses scrap as its principal input. The EAF method is much easier and faster since it only requires scrap steel. Steel can be produced by other methods such as open hearth. However, the amount of steel produced by these methods decreases every year. Of the steel produced worldwide in 2005, 65.4 per cent was produced via the integrated route, 31.7 per cent via EAF and 2.9 per cent via the open hearth and other methods [2].

In the basic oxygen process the manufacture of steel involves the removal of excess quantities of carbon and silicon from the iron by injection of oxygen and the addition of small quantities of other constituents that are necessary for imparting special properties to the steel. A lime or dolomite flux is used which combines with the oxidized constituents to form a slag. BOS slag is decanted off from the surface of the molten steel and is normally cooled slowly, by air cooling or water quenching, in pits or bays prior to being dug and transported to holding areas.

The process of making steel is by the melting of furnace charge into two mutually insoluble liquid phases at elevated temperatures, i.e., liquid metal phase and liquid oxide phase. The slag phase is the solution of additives and products of oxidation reactions.

Of the total solid waste generated in an integrated steel plant, b1ast furnace and steelmaking slags account for about 90 per cent of the material followed by about 10 per cent of oxide wastes from blast furnace, steelmaking and mills [14]. Slag is generated by the steelmaking process at a rate of approximately 100-200 kg per tonne of product in integrated plants using basic oxygen furnaces and 50 kg per tonne in electric arc furnace plants (mini-mills) [15].

2.1.2. Non-Ferrous Slags

Non-ferrous slags are copper, nickel and lead slags. Copper and nickel slags are extracted from sulphide concentrates by pyrometellurgical treatment. The process includes three different operations:

- roasting, in which sulphur is eliminated as SO_2 and iron is oxidized,
- smelting, in which the product of roasting is melted with a siliceous flux, forming a liquid iron-silicate slag which floats on the heavier, molten sulphide,
- converting, in which sulphur is driven of the sulphide melt and the remaining iron is oxidized and fluxed for removal as a silicate slag.

Converter slag is usually returned to the smelter because it is rich in metal content, whereas smelter slag is either discarded without further treatment or is granulated with excess water. These slags posseses a high degree of hardness and porosity and vary in unit weight and in chemical composition because of differences in ore type, furnace or smelter operations, and slag-cooling procedures [9].

Although the technology of utilization of granulated ferrous slags as cementing materials has been developed in Europe and Noth America, the utilization of non-ferrous slags as cementitious materials is not well established in concrete manufacture. The use of copper slags in mine backfill is current practice in Australia, where about 50 per cent of the Portland cement used in mine backfill has been replaced by ground granulated copper slag, resulting in lower production costs [16].

In Europe, Australia and Canada some copper, nickel and lead slags have been evaluated for performance as cementitious componenets in mine backfill [17, 18] and in concrete [19].

2.2. Physical, Chemical and Mineralogical Properties of Steel Slags

Compositions of steel slag are highly variable. Chemical composition, mineralogical composition and structure of slag vary with steel making processes (open hearth, converter and arc furnace) and with the furnace charge and steel types remelted. But the composition of steel slags with the same kind of steel is similar to each other. Main compositions of the slag are CaO, SiO_2, MgO, FeO, Fe_2O_3, Al_2O_3, MnO, P_2O_5, etc. The chemical composition of steel slag is quite similar to the composition of silicate cement clinker, but the low content of the CaO and high content of FeO, MgO, MnO, of the steel slag are the important difference between them [20].

The mineralogical phases of steel slags reflect their chemical analysis in being much more variable than blast furnace slags and higher in lime content. Typical phases occurring in ERDEMİR slags are Ca_2SiO_4, $CaFeO_2$, $3Ca_2Fe_2O_5$ and they were similar to overseas slags. The chemical analysis and its comparison to some overseas steel slag were given in Table 2.1.

As seen in Table 2.1 the chemical compositions of the slags vary a good deal. This is a main characteristic of steel slags, which shows compositional variation in the same process in a particular works. This is in contrast with blast furnace slags where the compositions vary relatively less. The CaO/SiO_2 ratio also vary a good deal and are on average much higher than those of the blast furnace slags.

The mineralogical composition of steel slag depends mainly on its chemical composition. The activity of steel slag is mainly dependent on its minerals namely the kinds of minerals and the amount of each mineral it contains. The formation of the minerals depends on many factors, such as the raw meal fed to converter the kind of steel manufactured and the kind of metallurgical technology employed, but mainly on the basicity (alkalinity) of the slag that can be expressed as $CaO/(SiO_2+P2O_5)$ [21].

Table 2.1. Chemical analysis of some steel slags [3]

Compound	ERDEMIR-Turkey [per cent weight]	USA [per cent weight]	Canada [per cent weight]	Germany [per cent weight]
CaO	45.68	40.3	41.3	59.9
SiO_2	12.11	21.7	15.6	13.8
MnO	4.02	4	10	3
Al_2O_3	2.38	3.8	2.2	2.10
MgO	2.74	4.4	6.9	0.9
P_2O_5	1.3	-	-	-
Na_2O	0.054	-	-	< 0.10
TiO_2	0.32	-	0.5	-
SO_3	0.11	-	-	< 0.25
K_2O	< 0.12	-	-	< 0.10
Fe_2O_3	30.63	16.3	20	10.5
CaO_{free}	6.47	-	3.3	13.3
CaO/SiO_2	3.77	1.85	2.65	4.3

The following mineralogical phases are formed according to their different basicities. When the basicity is low, usually there are olivine ($CaO.RO.SiO_2$) rhodonite ($3Ca.RO.SiO_2$) and RO phase (solid solution of MgO.MnO.FeO), whereas there are bicalcium silicate ($2CaO.SiO_2$) and tricalcium silicate ($3CaO.SiO_2$) only when the basicity is high. Steel slag often contains calcium ferrite ($2CaO.Fe_2O_3$ and $CaO.Fe_2O_3$). Depending on the basicity slags are divided into three types: (1) Low active slag which has the olivine, hydropite and RO phase content as main mineralogical composition with the basicity less than 1.8; (2) Medium active slag which has the C_2S and RO phase content with the basicity of 1.8-2.5; (3) High active slag has the C_3S and C_2S with the basicity more than 2.5 [22]**.**

Similar to Portland Cement clinker, hydraulic binding properties of steel slag come from its silicate (C_2S and C_3S) and ferrite-aluminate minerals. So steel slag can be considered as Portland Cement clinker of poor quality. Thus, steel slag is an inexpensive raw material of cement [23].

Steel slag has excellent skid resistance, high bulk density and a potential expansive nature because of the compounds such as free lime and magnesia [24]. The content of free lime and free MgO is the most important component for the utilization of steel slags for civil engineering purposes with regard to their volume stability. In contact with water these mineral phases will react to hydroxides. Depending on the rate of free lime and/or free MgO this reaction causes a volume increase of the slag mostly combined with a disintegration of the slag pieces and a loss of strength. Therefore, the volume stability is a key criterion for using steel slags as a construction material.

Table 2.2. Chemical analysis of ggbs, steel slag and high alumina [25]

Constituent	Portland cement	Blast furnace slag	Steel slag	High alumina
Cao	64.1	36-45	35	37.7
SiO_2	22	33-42	18	5.3
Al_2O_3	5.5	10-16	3.6	38.5
Fe_2O_3	3.0	0.3- 2.0	8.8	12.7
MgO	1.4	3-12	11.5	0.1
SO_3	2.1	-	-	0.1
MnO	-	0.2-1.5	6.5	-
FeO	-	-	18	3.9

A comparison of the compositions of different slags and cements is presented in Table 2.2. Steel stag, like most metallurgical slags, has a chemical composition similar to that of Portland cement. However, as seen in Table 2.3., there are significant differences, not only in the overall composition, but in the mineralogical species present in each material, The main compositional differences in the steel slag are the high iron oxide content, which exists in both the di-and trivalent states, and the presence of substantial free lime.

Table 2.3. Predominant mineral phases associated with steel slag [26]

Formula	Name	Synonym	Melting point (C)
$3CaO*SiO_2$	Alite	Tricalcium silicate	1900
$2CaO*SiO_2$	Belite	Dicalcium silicate	2130
β-$2CaO*SiO_2$	Belite	Dicalcium silicate (β)	
α-$2CaO*SiO_2$	Bredigite	Dicalcium silicate (α)	
$2CaO*Fe_2O_3$	Dicalcium ferrite	Calcium ferrite	1430
$4CaO*Al_2O*Fe_2O_3$	Brown millerite	Tetracalcium alumino ferrite	1410
FeO	Wustite	Iron oxide	
MgO	Periclase	Magnesia	2800
CaO	Lime	Calcia	2570

The mineralogical composition of steel slag at the beginning of melting is quite different from that at the end. It was realized through a great deal of experiments that due to the content of the two calcium silicate and three calcium silicate the steel slag possesses the binding character. Formation and quantity of C_2S and C_3S depend on the basicity of slag [20]. Steel slag has limited cementitious properties due to both a lack of tirialcium silicate and the presence of wustite solid solutions as a predominant mineral phase**.**

It is well known that steel slag contains similar mineral composition to that of OPC clinker; however, because of composition fluctuations, the slag may become unstable due to excess free CaO. The primary minerals in ordinary Portland cement are tricalcium silicate $3CaO$. SiO_2 (C_3S), dicalcium silicate $2CaO$. SiO_2 (C_2S), tricalcium aluminate $3CaO$. Al_2O_3 (C_3A), and tetracalcium alumino ferrite $4CaO$. Al_2O_3 . Fe_2O_3 (C_4AF). Each of these compounds plays a specific role in the production of a quality cement [24].

$2(3CaO.SiO_2)+6H_2O \rightarrow 3CaO.2SiO_2.3H_2O+3Ca(OH)_2$

$2(3CaO.SiO_2)+4H_2O \rightarrow 3CaO.2SiO_2.3H_2O+Ca(OH)_2$

$3CaO.Al_2O_3)+6H_2O \rightarrow 3CaO.Al_2O_3.6H_2O+CaO.Fe_2O_3.H_2O$

Table 2.4. Comparison of the chemical composition of steel slag with OPC clinker [27]

Chemical composition (by weight per cent)					
Material	CaO	$Al_2 0_3$	$Si0_2$	FeO / $Fe_2 0_3$	$P_2 0_5$
Steel slag	>35	<5	<20	<25	trace
OPC clinker	<60	4-10	18-24	<5	none

Despite differences in respective quantities of the chemical and mineral constituents that exist between steel slag and OPC clinker, steel slag can be considered comparable with OPC clinker. These differences do not affect the potential use of steel slag as an active material. The main differences are as listed in Table 2.4.

lt has been proven from different approaches that the effect of free CaO on the stability of steel slag itself not only depends on the amount, but also on the form and grain size of the free CaO. Analysis has shown that there exist two types of free lime in steel slags, the pure one and the solid solution. The former is free CaO and the latter CaO + x FeO (O < x < 10 per cent by weight). They can be distinguished in XRD patterns [27].

Geiseler [28] reported that, from microscopic investigation, it is evident that the free lime can exist in the form of residual lime and lime precipitated during solidification and subsequent cooling. In both categories, forms exist which are different in appearance and particle size. All types of free lime can hydrate; however, the most significant is the so-called spongy free lime with grain size up to 50 inch and which is a form of residual lime.

It would appear that the permissible content of free CaO is dependent on the end-use of the materials. For example, it has been reported that the use of steel slag in an experimental road has shown that slag with contents of free lime less than seven per cent causes no damage [22] and that a high free lime content of the steel slag (11.6 per cent) does not cause unsoundness of blended mortars. With regard to the stability of steel slag itself, a content of 4 - 5 per cent free CaO has been considered by many researchers to be the upper limit for stability [29]. From this, it is suggested that it is important to consider the condition for use of steel slag and the properties of the matrices in which steel slag exists when it is a component material in a composite. Varying free CaO contents may be acceptable, depending on the end-use of the material.

Murphy et al. [15] reported that the cooling rate had a significant effect on the final structure of the solidified slag. The XRD analysis indicated that controlled cooling of the liquid slag promoted the formation of the main cementitious minerals: alite, belite, calcium aluminate and calcium alumino-ferrite. However, by rapidly quenching the liquid slag it was possible to produce a predominantly glassy material that possessed inherent cementitious potential.

2.3. Worldwide Utilization of Steel Slag

As early as 350 B.C., the Greek physician, Aristotle, referenced iron-making slags for healing wounds. In the centuries to follow, additional applications for slag would be discovered, such as mosaics and even cannonballs. However, it was not until the early twentieth century, when the modern processes for iron and steel production were developed, that the commercial use of iron making slags became acceptable on a larger scale. In contrast, Steel Slag’s commercial introduction took significantly longer, as this product was thought to have little value beyond its use as an iron containing burden feed for the Basic Oxygen Furnace (BOF) steel making process and later as a sinter feed ingredient for the blast furnace iron making process.

While widespread use of slag in its many contemporary applications is a fairly recent development, the material itself is as old as the smelting process which produces it. As early as 1589, the Germans were making cannon balls cast from iron slag. And records are available which indicate that cast iron slag stones were used for masonry work in Europe of the 18th century.

Roads made from slag were first built in England in 1813 and, just seventeen years later, the first slag road was laid in this country. By the year 1880, blocks cast of slag were in general use for street paving in both Europe and the United States. A major city under the American flag with a long history of slag-paved streets is San Juan, Puerto Rico [13].

Use of slags developed in iron making dates back many centuries; in the U.S. blastfurnace slag had been used in road building as long ago as 1830, as railroad ballast since 1875, use as concrete aggregate began in the 1880's and in bituminous surfaces in the early 1900's. Major development of slag uses was in the construction aggregate applications, with much smaller amounts going into more specialized applications such as cement manufacture and agricultural applications. The first cements were produced from granulated blast-furnace slag in Europe by Langan in 1863 [5]. A history of slag cement production North America was written by Lewis [30]. For the past 25 years essentially all the blast-furnace slag produced in the nation has been used. This level of commercial application has been reached on a competitive basis with other materials; the slag has been used either because it can provide equal performance at a lower cost, or better performance for similar cost [12].

Even though slag was demonstrating its versatility well before the 20th century, for a long time, its principle use in United States was as track ballast for the railroads. As production grew, so did the need to find new applications [13].

The steel industry has traditionally produced co-products, which have been successfully used in many fields of application. Since then the steel industry has investigated their slags continuously, taken care of suitable processing and if necessary modified the iron and steelmaking processes to get slag products, which fulfill the requirements of the specific standards and regulations.

Table 2.5. Common Uses for Slags [13]

BF Air-Cooled	BF Expanded	BF Granulated	Steel Slag
Asphalt aggregate	Concrete masonry	GGBS cement	Asphalt aggregate
Concrete aggregate	Lightweight concrete	Soil cement	Fill
Insulation/mineral wool	Lightweight fill	Roller compacted concrete	Cement raw feed
Cement raw feed	Insulation	Fill	Agriculture
Agriculture	Fill	Fill	Environmental App.
Fill	Fill	Fill	Railroad ballast
Roof aggregate	Fill	Fill	Fill
Railroad ballast	Fill	Fill	Fill
Glass manufacture	Fill	Fill	Fill
Environmental App	Fill	Fill	Fill

In most of the countries there are extensive legislation controllig the disposal of wastes, including iron and steel making wastes. Many countries have specified procedures for operation monitoring and control of disposal plants and lanfill sites and have incorporated these in the waste disposal acts. These countries have set the direction which others will need to achieve.

Many steel plants have already taken up innovative waste recycling technologies with the ultimate objective of zero waste or 100 per cent recycling. These efforts have already paid dividends, with many plans crossing the level of 90 per cent recycling. Turkish steel plants have a long way to go to bridge the gap from the present recycling level which averages around 10 per cent. The main reasons for the lower usage/recycling rate in Turkish plants can be attributed to abundant dumping sites, lack of awareness of environmental protection needs, paucity of funds and socio-economic considerations [20].

As seen from the Figure 2.1 [20], the utilization of steel slag is very low in Turkey compared to other countries.

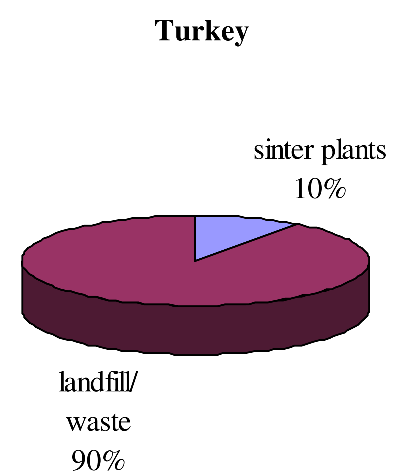

Figure 2.1.a

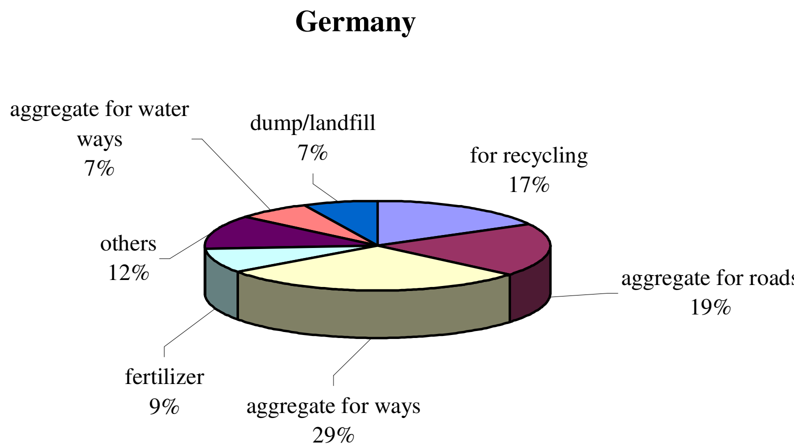

Figure 2.1.b

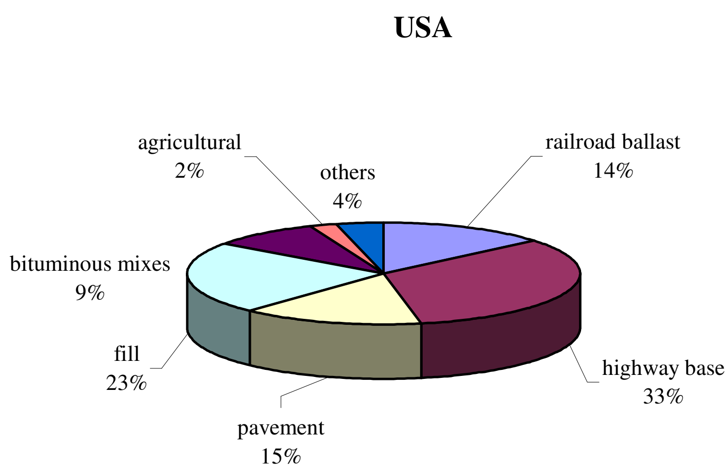

Figure 2.1.c

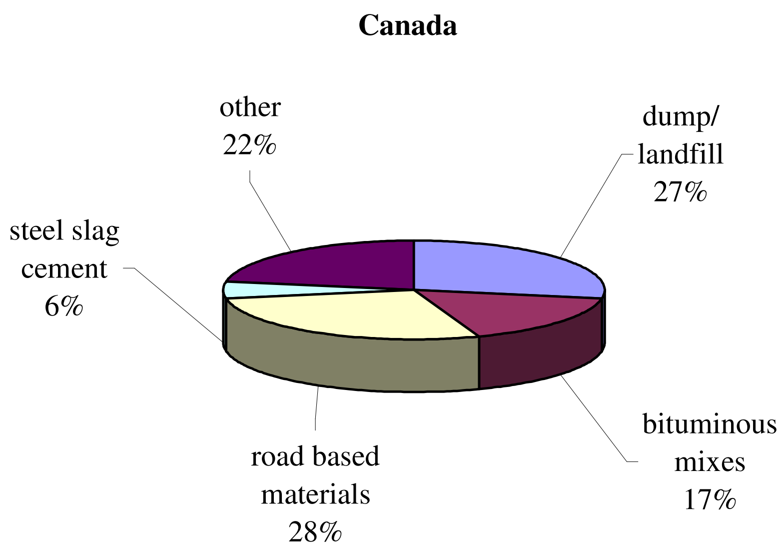

Figure 2.1.d

Figure 2.1. Utilization of steel slags in the world a-Turkey, b-Germany, c-USA, d-Canada

The recycling of steel slag worldwide has been mainly as aggregate in road bed construction and, to a leser extent, as a substitute for gravel on unpaved roads. Neither application involves any significant value added benefits for the steel manufacturer. The decisive criterion for the use of any material as aggregate in road construction is its volume stability in situ [28]. Steel slags have been used as aggregate in hot mix asphalt for many years, representing a subtantial outlet for recycle [31].

In Europe and most other continents there is a great demand for aggregates mainly from civil engineering industry, especially in the field of road and concrete constructions as well as for hydraulic purposes like stabilization of riverbanks. In Europe every year nearly 12 million tons of steel slags are produced. Owing to the intensive research work during the last 30 years, today about 65 per cent of the produced steel slags are used on qualified fields of application. But the remaining 35 per cent of these slags are still dumped.

The high bulk density of steel slags > 3.2 g/cm^3 qualifies steel slags as a construction material for hydraulic engineering purposes. In Germany about 400,000 tons per year are used as aggregates for the stabilization of river banks and river beds against erosion [24].

Table 2.6. Technical properties of processed BOF slags, in comparison with established natural aggregates

Characteristics	BOFslag	EAF-slag	Granite	Fine gravel
Bulk density (g/cm^3)	3.3	3.5	2.5	2.6
Shape – thin and elongated pieces (%)	<10	<10	<10	<10
Impact value (per cent/wt.)	22	18	12	21
Crushing value (per cent/wt.)	15	13	17	21
10 per cent Fines (KN)	320	350	260	250
Polishing (PSV)	58	61	48	45
Water absorption (per cent /wt.)	1.0	0.7	<0.5	<0.5
Resistance to freeze-thaw (per cent /wt.)	<0.5	<0.5	<0.5	<1
Binder adhesion (per cent)	>90	>90	>90	>85

Steel slags have been produced and used successfully in different European countries as a road construction material because of their advantageous technical properties. More than 25 years ago in Germany test roads were built using steel slags as an aggregate for unbound and bituminous bound mixtures. The test results, confirm these good properties to the present day. The asphaltic layers had been resistant to deformation, rutting and polishing over this long-term period.

In the field of hydraulic structures steel slags are mostly used for:

1. Dams and dikes;
2. Stabilisation of river bottoms;
3. Refilling of erosion areas on river bottoms; and
4. Stabilisation of river banks.

Aggregate sizes greater than 10 mm are usually used to prevent an erosion of fine particles. Mainly the high density, the high level of strength and abrasion as well as the rough texture of processed steel slag aggregates ensure a long-term resistance to dynamic forces coming from waves and river flow. The properties of steel slag are comparable to those of natural stones.

The engineering and ecological properties of steel slags are accepted in many countries and so steel slags are widely used as a construction material. In Germany the fields of road and waterway construction have made a very significant contribution to the present utilization rate of about 93 per cent. Thus, the use of steel slags saves existing resources of natural aggregates [24].

The comprehensive utilization of steel slag is a key research project in the field of environmental protection and resource reuse in China. China is reported to be the pioneer in using steel slag for cement production.

Since the 1960's, the central Research Institute of Building and Construction (CRIBC) of The Ministry of Metallurgical Industry (MMI) has concentrated on the search, production, utilization and development of steel slag cement and has solved many key technical problems for the production of steel slag cement. At the present time, more than 50 steel slag cement plants have been built in China, a total annual production has reached 3 million tones. As statistics show in China, up to the present time, nearly 25 million tones of steel slag cement has been produced for various engineering construction projects [23].

Steel slag is being used for many applications depending upon the specific situation of the individual plant. Plants in China, for example, have laid emphasis on cement production. Some of the Japanese plants are fucusing on road construction. POSCO steel Works of South Korea is paying more attention to utilize slag as part or full replacement in blast furnace and sinter plants. In Europe, slag has been used as a fertiliser and soil conditioner, recycled through blasts furnaces and land reclamation. Indian plants are already using steel slag in blast furnace and sinter plants. They have also gained confidence in using the slag as balast for railways, land reclamation, construction of local roads, etc.

Steel slag aggregate has been used in asphaltic mixtures since the early 1970's in Canada. The total generation rate in Canada is approximately one million tonnes per year. Except for using in asphaltic mixtures, this slag is stored indefinitely on site at some plants, shipped as fill from others, or, to a very limited extent, sold to cement manufacturers as a raw material source of iron and lime. In all instances, revenue from the sale of steelmaking slag is low and often there is a net cost associated with sending the material off-site [15].

2.4. Steel Slag Cement

The term "slag cement" is a very general one that can include many types of materials and combinations. "Slag cement" is also used at times to refer to a very specific material, as it is in ASTM Standards C219 and C595. In C219, slag cement is defined as a "blend of granulated blast-furnace slag and hydrated lime in which the slag constituent is more than a specified minimum percentage." C595 gives the minimum percentage applicable in that particular specification. In recent years, "slag cement" has been commonly used to refer to either combinations of Portland cement and ground slag or to the ground slag alone. It is possible at times to find varying opinions as to the proper classification for the latter - cement or mineral admixture.

One option for the recycling of steel slag, is to use it as an additive to portland cement clinker. Since these slag consist mainly of burnt lime and calcium silicates, (constituents of portland cement clinker), it might be expected that with same beneficiation, these slags could be useful cement additives downstream of the energy intensive clinkering operation. To date, steel slag has been used only as a minor raw material additive in the manufacture of portland cement, upstream of the clinkering process, because the form and variability of the chemical composition have caused difficulty in ensuring quality in the final cement product.

The clinkering process is energy intensive, requiring over 4 gigajoules per tone of product [25]. During the calcinations of limestone ($CaCO_3$) to lime (CaO) which is an integral part of the clinkering process, considerable amount of CO_2 is released into the atmosphere. Moreover, the combustion of large amounts of fossil fuel to drive the clinkering process means that substantial CO_2 generation is associated with cement manufacture. Simply reducing the total amount of raw material to be clinkered could abate these negative environmental factors. Since, on a mass basis, slag generation is about 10 per cent of cement clinker production rate, addition of slag to cement clinker in a 1: 10 ratio could effectively recycle all of the steelmaking byproduct, while reducing the material flow through the cement clinkering kiln by about 10 per cent [15].

There are two ways of incorporating steel slag in cement manufacture. One involves the use of the slag as a raw material for cement clinker, that is, steel slag is calcined in the kiln together with other raw materials, the other being a non-calcining process.

Calcining

Steel slag is treated as one of the raw materials to be calcined with other raw materials, such as clay and limestone. This can be regarded as a partial substitution of limestone.

Non-calcining

(1) Non-clinker (no OPC clinker blended), steel slag ground with GBF slag and gypsum;

(2) Low-clinker (low quantities of OPC clinker blended; usually less than 50 per cent by weight), steel slag ground separately, then addition of ground OPC clinker as a blend;

(3) Low-clinker, steel slag interground with OPC clinker.

Sersale et al.[32] used steel slag as one of the raw materials of cement clinker. It has been demonstrated that such a substitution (10 per cent steel slag content) appears to be effectual, without detriment to be technical behaviour of the resultant cements and with energy saving during the cilinkering process.

Due to the potential for energy saving, the noncalcining process is generally preferred. Normally, steel slag, GBF slag, OPC clinker and gypsum are mixed and ground together. An activator may be added in order to stimulate slag activity. The activators used maybe NaOH, $CaCl_2$, $Ca(OH)_2$, $CaSO_4$, $2H_2O$, and KF. The materials are generally ground to Blaine fineness greater than 3500 cm^2/g. Most of the published literature have indicated the use of four basic materials (steel slag, GBF slag, OPC clinker and gypsum) as the component materials of Steel Slag Blended Cement.

The physical and mechanical properties of steel slag cement are similar to those of blast furnace Portland cement. Steel slag cement has the following special features which the other kinds of cement do not have [3, 23].

1. High Late-Stage Strength: The late-stage strength of steel slag cement increases faster than that of ordinary cement.
2. Low heat of hydration: The heat of hydration of steel slag cement is less than that of Portland cement and blast furnace slag cement for dam construction.
3. Good abrasion resistance: Steel slag contains more iron and manganese than clinker. Besides there are some olivine and solid solution in steel slag cement. The hydraulicity of olivine and solid solution is very poor and they play a role of micro-aggregate during cement hydration.
4. Rate of Abrasion (per cent): Steel slag cement has good abrasion resistance (1.77 for grade 425).
5. Good impermeability: The impermeability of steel slag cement is excellent. At the water pressure up to 3 Mpa no permeability is observed for steel slag cement concrete with a grade of C20, which is made in the same way with ordinary cement.
6. Microexpansion: Steel slag cement shows microexpansion under the condition of standard curing.
7. Good frost and corrosion resistance: No strength loss is observed for steel slag cement in 100 cycles of freeze-thaw at -15 to -20 ^{0}C. Its surface remains intact and strength develops when it is immersed in sea water, 1 per cent H_2SO_4 or 20 per cent NaOH and sulphate solution for one year respectively. Strength develops under the action of CO_2.

Steel slag cement is suitable for industrial applications and civil construction, hydaulic works, road building and massive construction.

The cementitious properties of steelmaking slag may suffer due to the differences in mineralogy relative to Portland cement. The key to this deficiency is a lack of tricalcium silicate, which is the primary strength contributing phase during Portland cement hydration. In addition wustite solid solutions, which are the predominant mineral phases in steel slag, do not occur in Portland cements. These solid solutions have no inherent cementitious properties and do not combine to form hydraulic minerals during cooling from the melt. Wustite has the ability to take up to 27 per cent calcium into solution, thus using up calcium which could combine to form hydraulic tricalcium silicate [33]. In contrast to wustite, hematite will given suitable processing conditions, form calcium ferrites, calcium alumina ferrites, or go into solution replacing alumina. All of these ferritic minerals are hydraulic in nature [15]. The valence state of the iron oxide present in the slag can significantly influence the morphology and cementitious properties of the final material.

The physical and mechanical properties of Steel Slag Cement are similar to that of Portland cement. These are given in Table 2.7.

Table 2.7. Physical and mechanical properties of SS Cement vs BF Portland cement [14]

Properties	BF Portland Cement	SS Cement
Density (g/cm3,)	2.9-3.2	2.9-3.2
Bulk density (g/cm,)	0.9-1.2	0.9-1.2
Intitial setting time, min	>45	>45
Final setting time, hours	<12	<12
Fineness (m^2/kg)	300	<350

Two different approaches exist for the incorporation of steel slag in cement production. The first involves a simple substitution of slag into the raw material feed to the cement kiln by blending with limestone and clay. There is no energy savings as the slag must be clinkered and no direct economic benefit because one inexpensive material is substituted for another. A more attractive approach involves incorporating the slag downstream of the clinkering operation by blending with Portland cement clinker, gypsum, and, possibly, blast furmace slag. These blended cements haave a clear economic advantage due to the substantial savings in energy costs which can be realized [27]. Several studies have been performed in which ground steel slag has been blended with a variety of different materials resulting in limited success.

Wang and Li [21] reported that the result of large numbers of experiments shows that the steel slag blended cement with 50-60 per cent of Portland cement clinker posseses a 28 day compressive strength equivalent to that of Portland cement and its later age strength can be greater than that of Portland cement.

Other properties of steel slag blended cement, such as modulus elasticity, corrosion resistance, abrasion resistance, permeability resistance and the others are equal to or even better than those of Portland cement, among all the properties the permeability. Abrasion and corrosion resistances are excellent.

3. EXPERIMENTAL STUDY

This study was carried out to investigate the effects of ERDEMİR steel slags on the physical and mechanical properties of cement and concretes. Four different steel slags were used to replace portland cement in specified ratios; tests were done on cement and concrete samples produced with slag added cements and results were compared.

3.1. Methodolgy

The steps given below were followed:

1.All steel slags were ground to same fineness (at least 3000-4000 cm²/g).

2. Unit weights of the slags were determined.

3. Activity indices of slags were determined.

4. Following tests were done with steel slag added (20-40-60 per cent in mass) cements ;

    - Time of setting
    - Volumetric expansion due to temperature
    - Flexural and compressive strengths

5. Following tests were conducted for the concrete samples produced with steel slag added (20-40-60 per cent in mass) cements;

    - Flexural strength
    - Compressive strength
    - Splitting tensile strength
    - Fracture energy
    - Rapid chloride diffusion

All of the tests mentioned above were conducted on 13 sets of (one control concrete sample and three different replacement ratios (20-40-60 per cent) for four types of slags) concrete mixtures. All of the values were presented comparatively with diagrams and charts.

3.2. Materials

3.2.1. Steel Slag

Steel slags used in this study were obtained from Basic Oxygen Furnace of ERDEMİR- Ereğli Steel and Iron Plant as a by product. Four types of steel slags, according to their cooling process, were used:

1. Rapid cooled steel slag
2. Slow cooled steel slag with water
3. Slow cooled steel slag in air*
4. Slow cooled steel slag in air

* This is slow cooled steel slag sample but also kept in the factory stock yard for a short time.

3.2.1.1. Chemical Analysis: Wet chemical analysis was done with Perkin Elmer 2380 Atomic Absorption Spectrometer at TÜBİTAK Marmara Research Center (MRC) laboratories and results are given in Table 3.1.

Table 3.1. Wet chemical analysis of ERDEMIR steel slag [6]

per cent Weight	No. 1 Rapid Cooled Slag	No. 2-Slow Cooled Slag	No. 3*-Air Cooled Slag	No. 4-Air Cooled Slag
Cr_2O_3	0.1	0.1	0.1	0.1
MnO	3.2	3.3	3.5	3.9
TiO_2	0.6	0.6	0.6	0.5
SiO_2	12.2	10.6	11.7	10.1
S	0.1	0.06	0.1	0.08
CaO	40.3	39.2	42.7	38.0
MgO	5.9	7.9	6.5	8.5
Na_2O	0.1	0.06	0.04	0.03
K_2O	0.04	0.02	0.04	0.02
P_2O_5	1.1	1.0	1.0	0.9

Elemental analysis of samples was carried out in ERDEMIR with X-Ray Floresan Spectrometer and results are given in Table 3.2.

Table 3.2. XRF Spectrometer results of ERDEMIR steel slags

Element (per centWeight)	Rapid cooled (No -1)	Slow cooled (No-2)	Slow cooled in air (No-3*)	Slow cooled in air (No-4)
Fe	18.3	20.0	18.4	22.4
FeO	17.1	19.4	11.9	17.9
SiO_2	13.5	12.5	12.8	11.3
MnO	3.4	3.7	3.8	4.3
Al_2O_3	3.0	3.1	2.9	4.0
CaO	49.6	47.0	48.3	44.9
MgO	3.5	6.0	5.0	6.4
P_2O_5	1.0	1.1	1.0	1.0
S	0.1	0.1	0.1	0.1
Na_2O	0.001	0.001	0.001	0.001
K_2O	0.05	0.04	0.07	0.03
TiO_2	0.3	0.3	0.3	0.3
Cr_2O_3	0.1	0.1	0.1	0.1
Base 1	3.7	3.8	3.8	4.0
Base 2	3.2	3.4	3.4	3.4

Base 1=CaO/SiO_2

Base 2=$(CaO+MgO)/(SiO_2+Al2O_3)$

The amount of FeO and Fe^{+2} was determined of steel slag samples with 0-7 mm particle size according to ASTM D 3872-79 standard. The amount of free CaO analyzed according to TS 687 standard. Results are given in Table 3.3.

Table 3.3. FeO and Free CaO Analysis Results of Steel Slags [6]

Sample No	Type	FeO	Fe^{+2}	Free CaO
1	Rapid cooled steel slag	20.26	15.75	5.46
2	Slow cooled steel slag with water	19.68	15.30	5.94
3*	Slow cooled steel slag in air*	14.08	10.94	4.96
4	Slow cooled steel slag in air	20.83	11.27	6.08

3.2.1.2. Phase Analysis: Phase analysis was carried out with SHIMADZU XRD-6000 in TUBITAK-MRC on the Erdemir steel slags which chemical analysis are given above. Comparative X-ray diffraction patterns are given in Figure 3.1 and phases are given below:

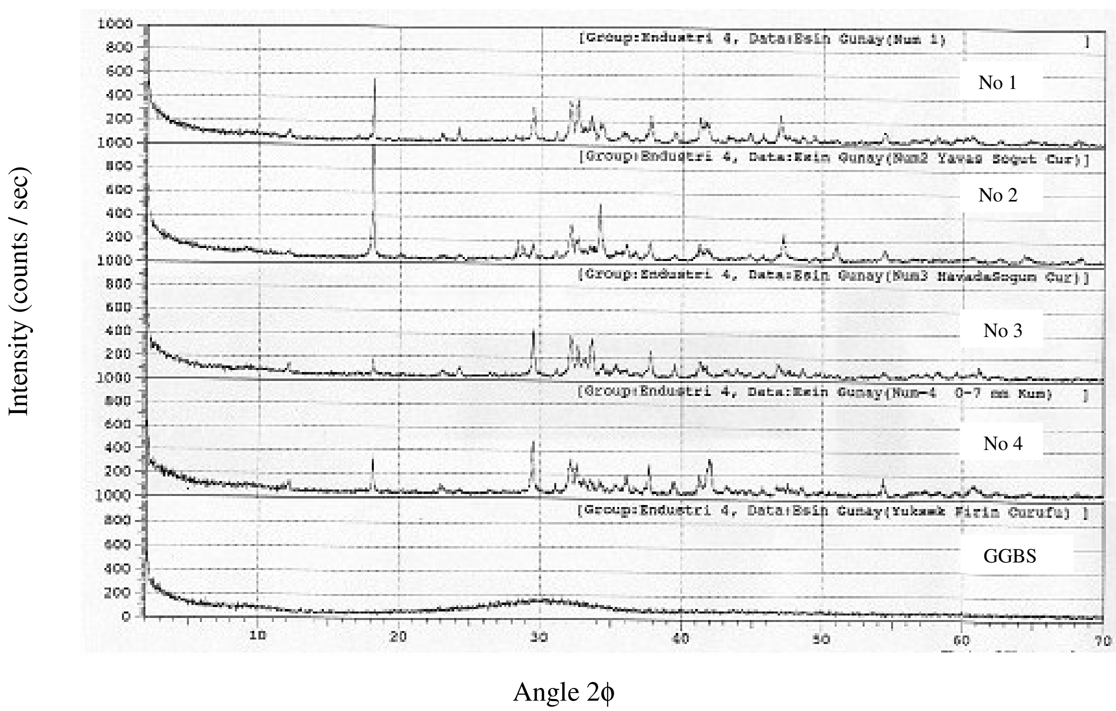

Figure 3.1. The comparison of ERDEMİR slags XRD Patterns

1) Larnite, Ca_2SiO_4

2) Calcite, $CaCO_3$

3) Calcium iron oxide, $CaFeO_2$

4) Portlandite, $Ca(OH)_2$

5) Calcium iron oxide, $Ca_2Fe_2O_5$

6) Hematite, Fe_2O_3

7) Wustite, FeO

From X-ray difractogram patterns it was determined that the steel slags contained similar compounds, but the quantitative ratios were differing. Compunds found in the samples were arranged in order according to approximate peak intensities. In all of Erdemir Steel slags Ca_2SiO_4 and Fe_2O_3 , that are required to be in cement clincker, were determined. However, FeO, which is not wanted to exist, was also determined in steel slag samples.

3.2.1.3. Structural Analysis: Metallographic investigation was done on micro and macro structures. Optic microscope photographs of steel slags are given in Figure 3.2-3.5.

Figure 3.2. Optical macrograph of No.1 slag. (2.25 X).

Figure 3.3. Optical macrograph of No.2 slag (2.25X).

Figure 3.4. Optical macrograph of No.3* slag (2.25X).

Figure 3.5. Optical macrograph of No. 4 slag(2.25X).

3.2.1.4. Grinding Properties: Steel slags were ground at Akçansa Cement Industry. Steel slags included some coarser steel particles, some of them were removed before grinding. Grinding periods and fineness values are given in Table 3.4.

Table 3.4. Grinding periods and fineness values of steel slags

Slag Code	Blaine Fineness	Grinding Period
	cm^2/gr	hour
NO 1	3930	7
	4070	7
NO 2	5020	8.5
	4970	4
NO 3	3910	7
	3900	9
NO 4	3700	7.5
	3700	7

Before grinding, steel slags were crushed and magnetically separated. Because the hardness of steel slag is high it was difficult to grind. Suitable grinding machine was selected for securing the quality and energy saving. Pre-separation of iron was carried out especially in steel slag with large particles (12/50 mm). These slags were pulverized to maximum 4 mm in jaw crusher.

3.2.2. Cement

Ordinary Portland cement comforming to TS EN 197-1 CEM I 42.5 was used. Data showing the physical and chemical analysis results supplied by the cement producer is given in Table 3.5.

Cement mixtures and their codes used in this study are as follows:

Reference : 100 per cent Portland Cement [reference]
No 1 – 20 % : 20 per cent Rapid cooled slag + 80 per cent Portland Cement
No 1 – 40 % : 40 per cent Rapid cooled slag + 60 per cent Portland Cement
No 1 – 60 % : 60 per cent Rapid cooled slag + 40 per cent Portland Cement
No 2 – 20 % : 20 per cent Slow cooled slag with water + 80 per cent Portland Cement
No 2 – 40 % : 40 per cent Slow cooled slag with water + 60 per cent Portland Cement
No 2 – 60 % : 60 per cent Slow cooled slag with water + 40 per cent Portland Cement
No 3 – 20 % : 20 per cent Slow cooled slag in air* + 80 per cent Portland Cement
No 3 – 40 % : 40 per cent Slow cooled slag in air* + 60 per cent Portland Cement
No 3 – 60 % : 60 per cent Slow cooled slag in air* + 40 per cent Portland Cement
No 4 – 20 % : 20 per cent Slow cooled slag in air + 80 per cent Portland Cement
No 4 – 40 % : 40 per cent Slow cooled slag in air + 60 per cent Portland Cement
No 4 – 60 % : 60 per cent Slow cooled slag in air + 40 per cent Portland Cement

* This is slow cooled steel slag sample but also aged for a short time.

Table 3.5. Chemical, Physical and Mechanical Properties of PC 42,5

Analysis		Test Results
Insoluble Residue	(per cent)	0.51
SO_3	(per cent)	2.63
Loss in Ignition	(per cent)	1.28
Cl^-	(per cent)	0.0385
Specific Gravity	(gr/m^3)	3.16
Setting Time Initial/Final	(min)	148/196
Soundness Le Chatelier	(mm)	2
Specific Surface	(cm^2/gr)	3680
Residue on 45 µm sieve	(per cent)	14.2
Residue on 90 µm sieve	(per cent)	1.9
Early Strength - 2 day	(MPa)	28.4

3.2.3. Aggregate

In cement tests RILEM-Cembureau standard sand was used. In concrete tests quarry sand (0-4 mm) and fine crushed stone (0-4 mm) were used as fine aggregate, fine gravel (4-8 mm) and coarse gravel (8-16 mm) were used as coarse aggregate. The maximum particle size of aggregate was 16 mm. Before the casting of concretes, sufficient amounts of aggregates were totally dried in the laboratory conditions. After this, all concrete productions were conducted subsequently. Sieve analysis of the aggregates used in this experimental investigation are given in Table 3.6. The sieve analysis results of the final mix designs are given in Figure 3.6.

Table 3.6. Grading of aggregates used in the mixtures

Sieve Size	Fine Gravel	Sand	Coarse Gravel	Crushed Stone	Mixture per cent
0.125	0	1	0	1	0
0.25	0	11	0	3	4
0.5	0	39	0	8	14
1	0	67	0	26	26
2	0	88	0	56	37
4	0	99	0	92	44.68
8	45	100	2	100	60
16	100	100	50	100	88
31.5	100	100	100	100	100
Unit Weight	2.7	2.548	2.71	2.74	
Mixing Ratios per cent	30	34	24	12	

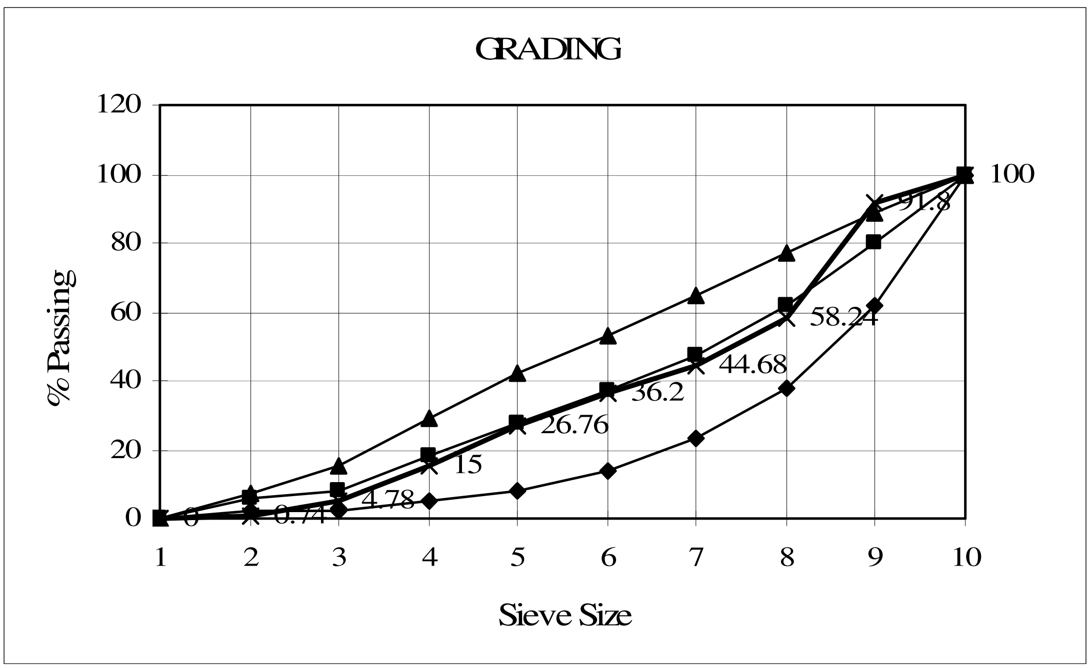

Figure 3.6. Grading curves of aggregate mixtures and standard curves

3.2.4. Superplasticizer

Chyrsofluid 854 type of superplasticizer was used. The properties of the superplasticizer is given in Table 3.7.

Table 3.7. Superplasticizer specification

Colour	Brown
State	Liquid
Density	1.247
Soluble Chlor (Cl^-)	<0.08
pH	7.11
Additive Material	42.03

3.3. Mixtures

In this study tests were conducted on cement pastes, mortars and concrete mixtures. In all of these stages, four different steel slags that replaced with ordinary portland cement in three different ratios (20,40 and 60 per cent) in mass, were used. Using these cement mixtures, mentioned above, test specimens were prepared accordance with the relevant codes.

3.3.1. Cement Mortar Mixtures

Cement pastes were prepared for water content, time of setting and soundness tests; mortar specimens of 40x40x160 mm were prepared for activation and hardened properties of mortar tests. A total of 13 mixtures were produced; 12 of them contained different types of steel slags in different ratios, the other was the reference. Reference cement mortar and cement with steel slag mortars were prepared in accordance with test method ASTM C 109 using a Tonindustrie mixing machine. The proportions of the mortars were as follows:

Reference cement mortar:

500 gr Portland cement

1375 gr graded standard sand

Slag-reference cement mortar:

250 gr Portland cement

250 gr steel slag

1375 gr graded standard sand

3.3.2. Concrete Mixtures

A total of 13 different concrete mixes were produced, one of which was reference mix. Portland cement was replaced with four different steel slags in 20,40 and 60 per cent in mass in C 30/37 conventional ready-mixed concrete mixture. Thus 12 different concrete mixes were produced using four types of steel slags. The water/(cement+steel slag) ratio of the mixtures were 0,52. Concrete mixtures were designed to provide a slump of 16 – 20 cm for ease of handling, placing and workability. Superplasticizer and water amount were kept constant for each mixture. Details of the mixtures are given in Table 3.8.

Table 3.8. Mixture proportioning of concretes in kg/m^3

	Reference	Steel Slags Replacement Ratio		
		20per cent	40per cent	60per cent
w/(cement+steel slag)	0,52	0,52	0,52	0,52
Water	182	182	182	182
Cement (PC 42,5)	350	280	210	140
Grinded Steel Slag	0	70	140	210
Fine Gravel (No I)	563	563	563	563
Sand	603	603	603	603
Coarse Gravel (No II)	452	452	452	452
Crushed Stone	225	225	225	225
Superplasticizer	4,91	4,91	4,91	4,91

3.4. Casting and Curing of Test Specimens

In mortar tests;
12 40x40x160 mm prismatic specimens were prepared for each 13 cement mixtures, to determine the activity indices and hardened properties of mortars. According to TS EN 196-1 mortars were casted into the moulds on an automatic vibrating table with standard vibrating time. Casting was conducted in two layers. After casting, test specimens were finished with a steel trowel. All specimens were kept in their molds for 24 hours and stored at temperatures of about 21ºC ± 1ºC and relative humidity of 60±5 percent. After demoulding, the specimens were cured in water at 23±2°C until tested.

In concrete tests;
Two different types of moulds were used in this study;

1) 70x70x280 mm prismatic mould
2) Ø 100/200 mm cylinder mould

Six 70x70x280 mm prismatic and one Ø 100x200 mm cylinder specimens were cast from each batch of concrete. Casting was conducted in three layers, with each layer compacted on a vibrating table for a few seconds. After casting, all test specimens were finished with a steel trowel. Immediately after finishing, the specimens were covered with plastic sheet to minimize their moisture loss. All specimens were kept in their molds for 24 hours and stored at temperatures of about 21ºC ± 1ºC and relative humidity of 60±5 percent. After demoulding, the specimens were cured in water at 23±2°C until tested.

3.5. Test Procedures

3.5.1 Cement and Mortar Tests

3.5.1.1 Cement Properties: Unit density of slags, water requirements in pastes, setting time of cement pastes with steel slags, soundness of cement pastes with steel slags and steel slag activity indices were determined for each cement mixture.

Density of the steel slags were determined according to TS EN 196-6. According to TS EN 196-3 by using Vicat device and mixing different amounts of water the optimum water content of the pastes were determined. The time that cement paste started to loose its plasticity (initial time of setting) and the time passed till the final time of setting were determined by using the Vicat device. Cement paste samples were exposed to water cure for 24 hours, and kept in boiling water for 3,5 hours. Expansion of the paste was determined by measuring the needle ends of the Le Chatelier device. The difference between the first and the last measurements shall not exceed the limit specified in TSE EN 196-3 which is 10 mm.

Activation tests were conducted on four types of steel slags and the reference mortars in accordance with ASTM C 989. Six prismatic 40x40x160 mm specimens were prepared for each steel slag type. Half of these specimens were tested for compressive strength at 7 days while the other half were tested for compressive strength at 28 days. Slag activity index is calculated using following expression;

$$Slag\ Activity\ Index,\ \% = \frac{SP}{P} x100 \tag{3.1}$$

where, SP and P are average compressive strength of slag-reference cement mortar and average compressive strength of reference cement mortar, respectively.

The test results were then evaluated using the classification given in Table 3.9.

Table 3.9. Min activity indices in ASTM C 989

ASTM C989	Slag Activity Index, min per cent	
Grades	7-Day Index	28-Day Index
Grade 80	-	75
Grade 100	75	95
Grade 120	95	115

3.5.1.2. Hardened Mortar Properties: 40x40x160 mm prismatic mortar samples were prepared for each type of slag. Flexural and compressive strength tests were done at 7 and 28 days in accordance with TS EN 196-1. Flexural and compressive strengths were calculated using formulas (3.2) and (3.3) respectively.

$$R_f = \frac{1.5xF_f xl}{b^3} \tag{3.2}$$

where, R_f, b, F_f and l are flexural strength, edge length of square cross section of prism, force applied and distance between the support cylinders, respectively.

$$R_c = \frac{Fc}{1600} \tag{3.3}$$

where, Rc, Fc and 1600 are compressive strength, maximum load and the area of the plates, respectively.

3.5.2. Concrete Tests

3.5.2.1. Fresh Concrete Properties: The fresh mixed concretes were tested for slump, air content and unit weights were determined according to TS EN 12350.

3.5.2.2. Hardened Concrete Properties:

a) Mechanical Properties: Compressive and net bending srengths were determined for each mix type at the age of 7 days. According to 7 day hardened properties of concretes two best and a worse concrete and the reference concrete were selected for the mechanical tests. All mechanical tests (compressive strength, splitting tensile strength, net bending srength and fracture energy) were obtained for these four types of concretes (No1%20, No2%20, No2%60 and reference) at about 120 days. Standard compression tests were conducted in accordance with the European Standards (EN 206 and EN 12390) on 70x70x70 mm cubic specimens. The tests were performed using an Amsler press with a capacity of 500 kN. Net bending stregth tests were conducted on 70x70x280 mm notched prismatic specimens. Compressive strengths and net bending strengths were calculated using the relations (3.4) and (3.5) respectively.

$$R_c = \frac{Fc}{A} \tag{3.4}$$

where R_c, F_c and A are compressive strength, maximum load and area of the plates, respectively.

$$\sigma = \frac{(PxL)}{(bxh^2)/6} \tag{3.5}$$

where, σ, P, L, b and h are net bending strength, maximum load, length of beam between supports, width of beam and net height of the beam at the notched section, respectively.

The tests for determining the fracture energy (G_F) were performed in accordance with the recommendation of RILEM 50-FMC Technical Committee. As schematically shown in Figure 3.7, the deflection was measured using a linear variable displacement transducer (LVDT). The load was applied using a closedloop testing machine (Instron 5500R) with a maximum capacity of 100 kN.

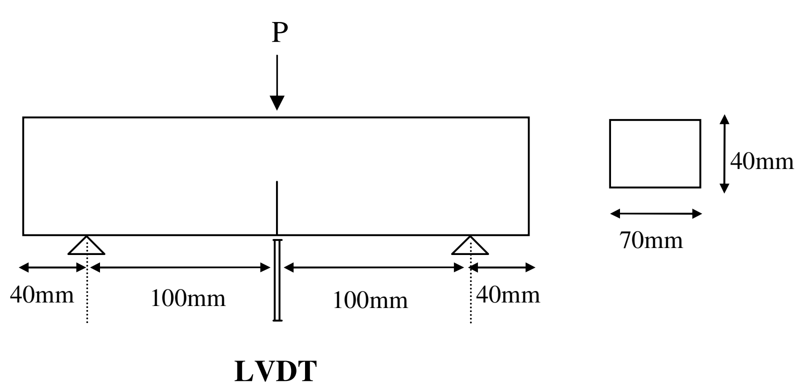

Figure 3.7. Schematic representation of the three point bending test

The beams prepared for the fracture energy tests were 280 mm in length and 70 × 70 mm in cross section. The notches were formed using a diamond saw. The effective cross section was reduced to 70 × 40 mm, and the length of support span was 200 mm. Thus, load versus displacement at the midspan (δ) curves were obtained for each specimen.

Fracture energy is the energy absorbed in a unit area of crack surface. Fracture energy of the matrix is based on the area under the complete load versus displacement at mid span curve. Fracture energy shematic load versus displacement curve is given in Figure 3.8.

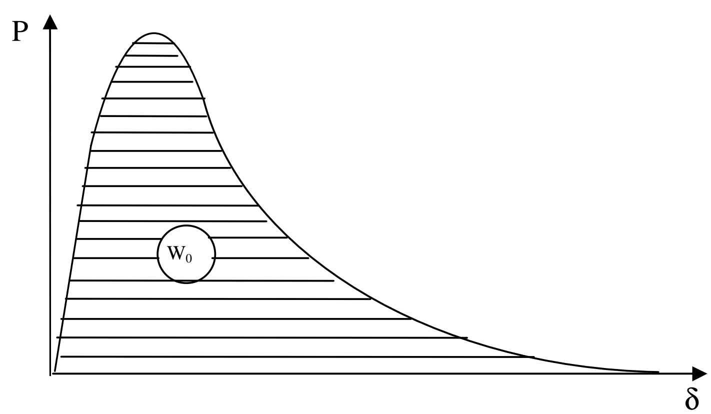

Figure 3.8. Schematic representation of load versus displacement at the midspan (δ) curve

The fracture energy was determined using the following expression

$$G_f = \frac{W_0 + mg\frac{S}{U}\delta s}{B(D\text{-}a)} \tag{3.6}$$

where, B, D, a, S, U, m, δs, and g are the width, depth, notch depth, span, length, mass, specified deflection of the beam and gravitational acceleration, respectively. At least three specimens of each mixture were tested at the 120th day. All the beams were loaded at a constant rate of 0.02 mm/minute.

Splitting Tensile Strength Test was performed in accordance with the specification of ASTM C 496. The tensile strength was calculated using the relation

$$f_t = \frac{2P}{\pi.D.L} \tag{3.7}$$

where, P, D and L are maximum load, diameter and length of specimen, respectively.

b) Chloride Ion Permeability: Chloride ion penetration test according to ASTM 1202 (Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration) was conducted at 120 days. This test was based on electrical conductivity of concrete.

This test method consists of monitoring the amount of electrical current passed through specimens during a 6-h period. Ø 100x200 mm cylinderic samples were prepared for each concrete with slag. Three 50 mm thick specimens were cut from each cylinder. Then, specimens allowed to surface dry in air about 1 hr. A sufficient amount of rapid setting coating was applied onto the side surface of each specimen. After allowing coating to cure, all specimens were subjected to a vacuum-saturation procedure for 3 hr. After that, the specimens were kept in water for 18±2 hr. After conditioning, the specimens were transferred to a test cell. Then, one side of the cell (+) was filled with 0,30 N NaOH solution, while the other side of the cell (-) was filled with 3 percent NaCl solution. Then a direct voltage of 60.0±0.1 V was applied across the two faces. The current passing through concrete was registered at every 30 minutes. Terminating the test after 6 hours, current (in amperes) versus time (in seconds) were plotted for each type of concrete and the area underneath the curve was integrated to obtain the ampere-seconds, or coulombs, of charge passed during the 6 hours test period. The total charge passing through at the end of 6 hours was measured using formula (3.8) and expressed in terms of Coulomb.

$$Q = 900\,(I_0 + 2I_{30} + 2I_{60} + \ldots\ldots. + 2I_{300} + 2I_{330} + I_{360}) \tag{3.8}$$

where, Q, I_o and I_t are charge passed (coulombs), current (amperes) immediately after voltage is applied and current (amperes) at t min after voltage is applied, respectively. The test results were then evaluated using the qualitative classification given in Table 3.10.

Table 3.10. Chloride Ion Permeability Based on Charge Passed in ASTM C 1202

Charge Passed (coulombs)	Chloride Ion Permeability
>4,000	High
2,000–4,000	Moderate
1,000–2,000	Low
100–1,000	Very Low
<100	Negligible

4. TEST RESULTS and EVALUATION

4.1. Cement Properties

4.1.1. Density

Density of the steel slags were determined according to TS EN 196-6, and results are given in Table 4.1. As it is seen, density of all of the slags are greater than Portland cement. Although the magnetic separation was conducted before grinding slags, there still exists some pieces of steel particles.

Table 4.1. Density of steel slags

Slag Code	Density gr/cm³
NO 1	3.27
NO 2	3.33
NO 3	3.33
NO 4	3.50

4.1.2. Water / (Cement+Steel Slag) Ratios in Pastes

According to TS EN 196-3 by using Vicat device and mixing different amounts of water the optimum water content of the pastes were determined. As seen in Table 4.2, it was observed that with increasing steel slag content, the water requirement of cement pastes decreases. The same behavior can be seen in each slag.

Table 4.2. Water / (cement+steel slag) ratios in pastes

Slag Code	Water/(Cement+Slag)		
	20 per cent	40 per cent	60 per cent
NO 1	0.27	0.23	0.21
NO 2	0.27	0.25	0.22
NO 3	0.25	0.24	0.21
NO 4	0.26	0.23	0.21
Reference	0.28		

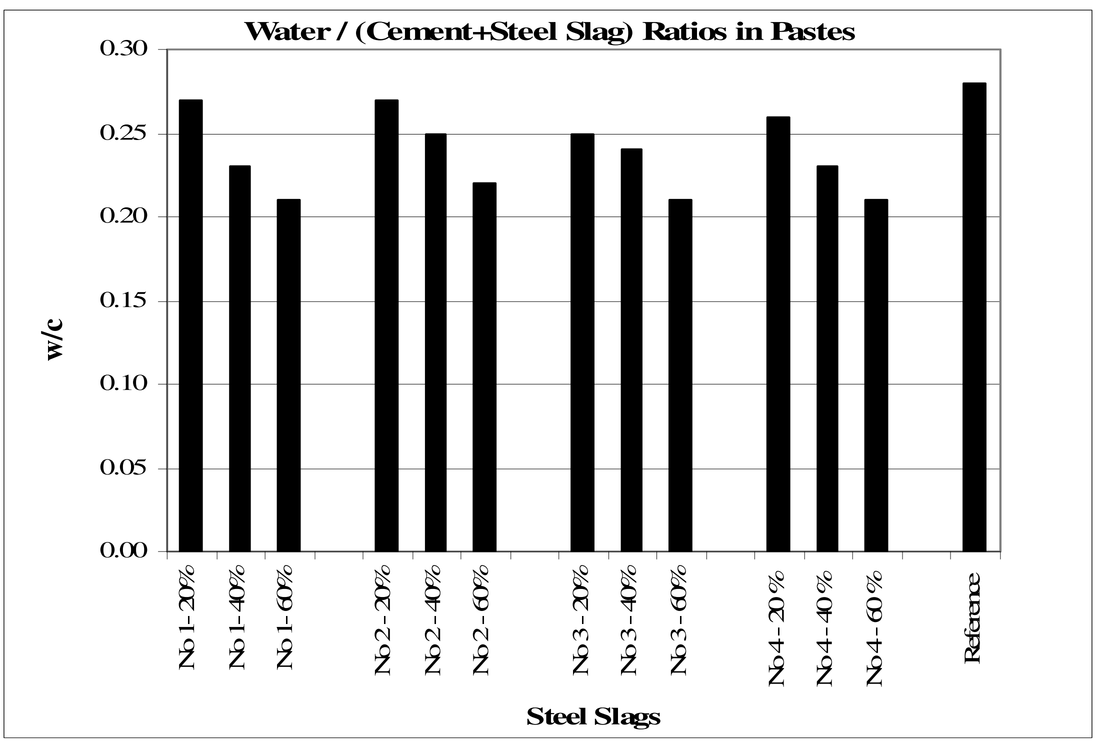

Figure 4.1. Water/(Cement+Steel Slag) ratios of pastes

4.1.3. Time of Setting

Setting times of cements with or without steel slags were determined using Vicat device, in accordance with TS EN 196-3. The results are given in Table 4.3 and depicted in Figure 4.2. As the amount of steel slag increases, the initial time of setting decreases. Especially for 40 and 60 per cent of No 3 and No 4, this period dramatically decreases .

Table 4.3. Time of settings for steel slags

Slag Code	Replacement of Cement by steel slag	Initial Setting Time	Final Setting Time
	(per cent)	(min)	(min)
NO 1	20	140	300
	40	130	260
	60	30	110
NO 2	20	120	260
	40	100	292
	60	70	260
NO 3	20	40	310
	40	20	290
	60	10	80
NO 4	20	70	280
	40	20	180
	60	10	40

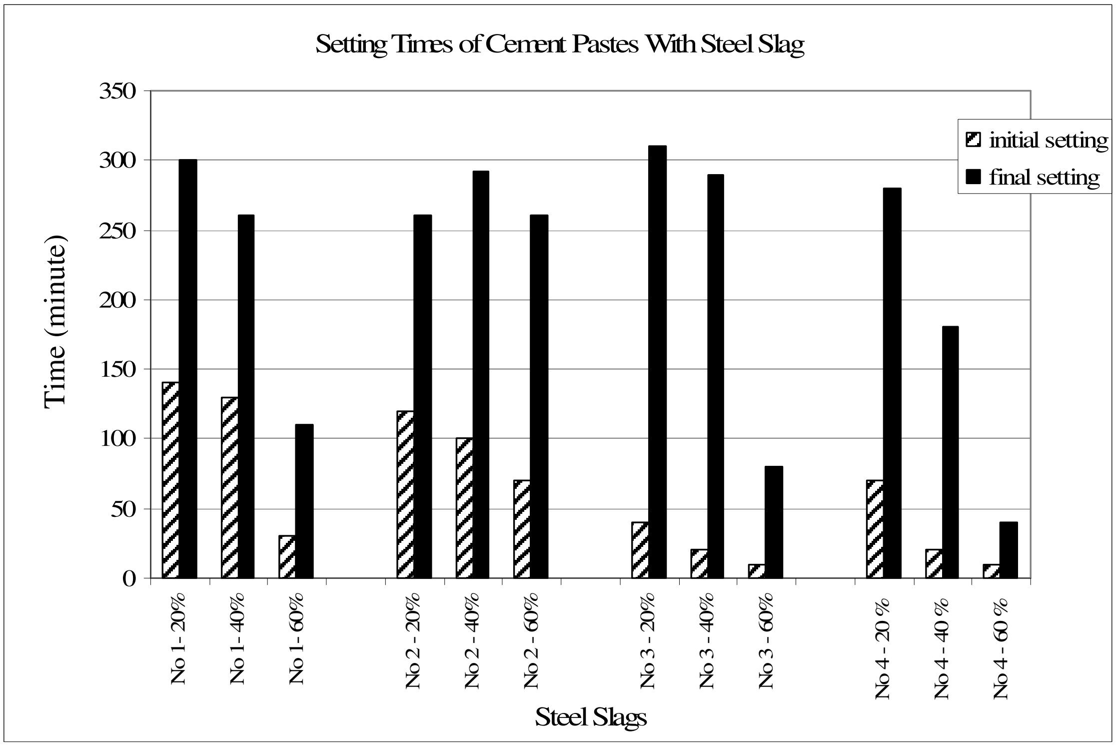

Figure 4.2. Setting times of cement pastes with steel slag

4.1.4. Soundness

Soundness of cements with or without steel slags were determined using Le Chatelier device, in accordance with TS EN 196-3. The results are given in Table 4.4 and depicted in Figure 4.3. The difference between the first and the last measurements shall not exceed the limit specified in TSE EN 196-3 which is 10 mm.

As it is seen from Figure 4.3, expansion increases proportional to the amount of steel slag in the pastes. 60 per cents have the highest values. While No 4-60% is very near to the 10 mm limit, No 3-60 % exceeds it.

Table 4.4. Soundness of cement pastes with steel slag

Slag Code	Replacement of Cement	A (mm)	B (mm)	B - A (mm)
NO 1	20	36.0	38.0	2.0
	40	20.3	25.3	5.0
	60	21.9	27.2	5.3
NO 2	20	29.5	30.1	0.6
	40	30.6	32.0	1.4
	60	23.1	26.2	3.1
NO 3	20	22.6	23.1	0.5
	40	19.9	22.0	2.1
	60	39.8	51.1	11.3
NO 4	20	35.3	37.2	1.9
	40	33.6	35.1	1.5
	60	22.7	32.3	9.6

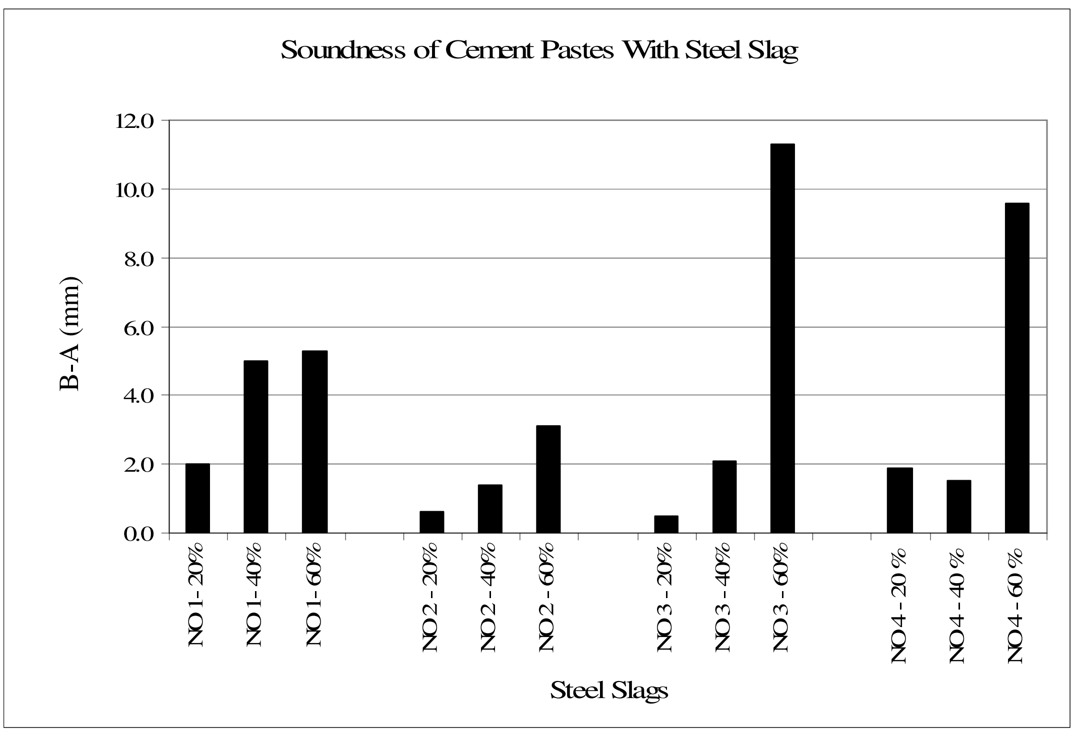

Figure 4.3. Soundness of cement pastes with steel slag

4.1.5. Activity Indices

Activity index of cements with or without steel slags were determined in accordance with ASTM C 989. The results are given in Table 4.5 and depicted in Figure 4.4.

Table 4.5. Steel slag activity indices

Slag Code	7 DAY		28 DAY	
	Compressive Strength	Slag Activity Index	Compressive Strength	Slag Activity Index
	(MPa)	(per cent)	(MPa)	(per cent)
NO 1	13.8	44.1	23.5	50.8
NO 2	16.4	52.4	27.2	58.7
NO 3	15.1	48.2	22.6	48.8
NO 4	15.5	49.5	28.9	62.4
Reference	31.3	100.0	46.3	100.0

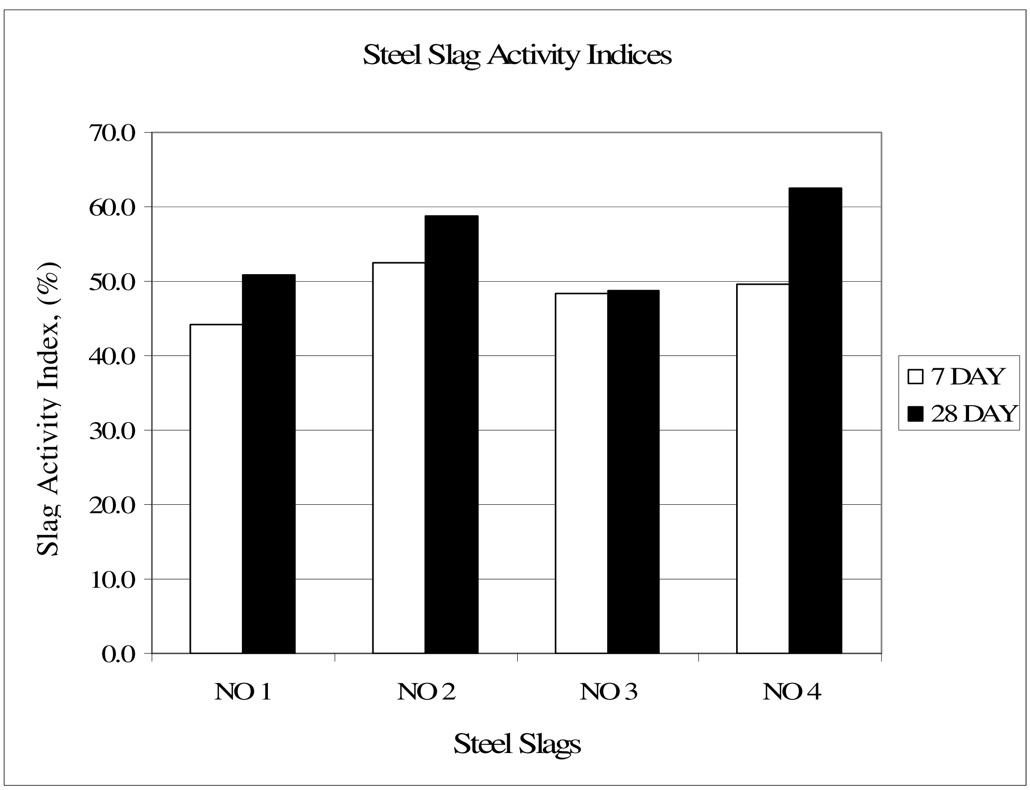

Figure 4.4. Steel slag activity indices

ASTM C 989 mentions three grades for slags: Grade 80, Grade 100 and Grade 120. As seen from Table 4.5, steel slags do not meet the required activity indices in the standard. Even the best active one can not meet the lowest grade, Grade 80.

4.2. Hardened Mortar Properties

Flexural and compressive strengths of mortars with or without steel slag were determined at 7 and 28 days. The results are given in Table 4.6 and depicted in Figures 4.5 and 4.6.

Table 4.6. Hardened proporties of mortars with or without steel slag

			7 DAY				28 DAY			
			FLEXURAL		COMPRESSION		FLEXURAL		COMPRESSION	
Slag Code	Replacement of Cement by steel slag	Unit Weight	Average Flexural Strength	Percentage of reference cement mortar	Compressive Strength	Percentage of reference cement mortar	Average Flexural Strength	Percentage of reference cement mortar	Compressive Strength	Percentage of reference cement mortar
	per cent	(kg/m³)	(MPa)	per cent	(MPa)	per cent	(MPa)	per cent	(MPa)	%
NO 1	20	2313	0.12	96	27.1	86	0.15	90	42.8	92
	40	2301	0.08	70	20.1	64	0.12	73	28.9	62
	60	2266	0.05	41	10.2	33	0.08	48	17.4	38
NO 2	20	2273	0.12	96	29.2	93	0.17	97	42.1	91
	40	2328	0.09	75	21.9	70	0.13	75	29.9	65
	60	2316	0.06	47	11.6	37	0.09	52	19.9	43
NO 3	20	2281	0.10	85	26.3	84	0.15	86	38.7	84
	40	2313	0.08	67	18.0	57	0.11	67	25.8	56
	60	2277	0.05	38	9.1	29	0.07	41	15.3	33
NO 4	20	2344	0.11	90	23.4	75	0.15	89	38.2	83
	40	2297	0.09	72	18.1	58	0.13	74	30.7	66
	60	2250	0.05	43	10.3	33	0.08	49	19.1	41
Ref.	Standard Cement Mortar	2320	0.12	100	31.3	100	0.17	100	46.3	100

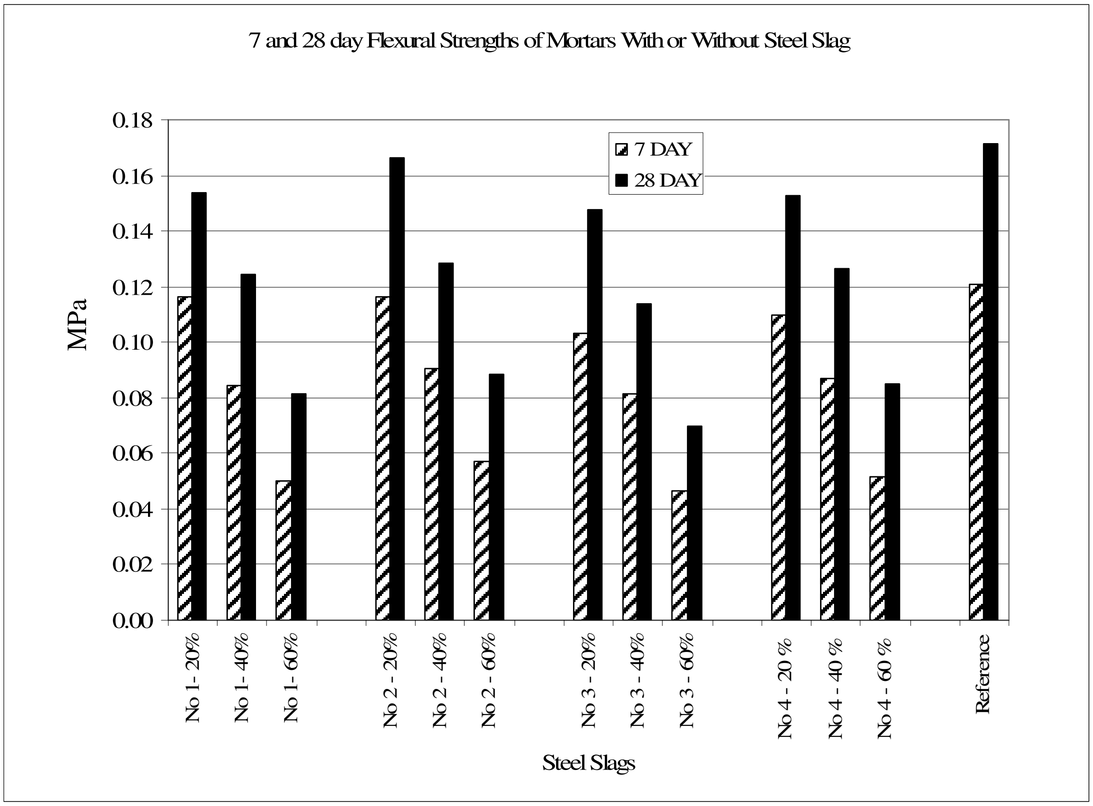

Figure 4.5. 7 and 28 day flexural strengths of mortar with or without steel slag

As the amount of steel slag increased both the flexural and compressive strength decreased. Almost none of the cement mixtures had the limit compressive strength of 42.5 MPa, No 1-20% exceeded and No 2-20% got very close to 42.5 MPa. The other two 20 per cent mixtures were not too lower than 42.5 with 38.7 and 38.2 MPa. As the percentage increased to 40 and 60 per cent compressive strengths decreased significantly.

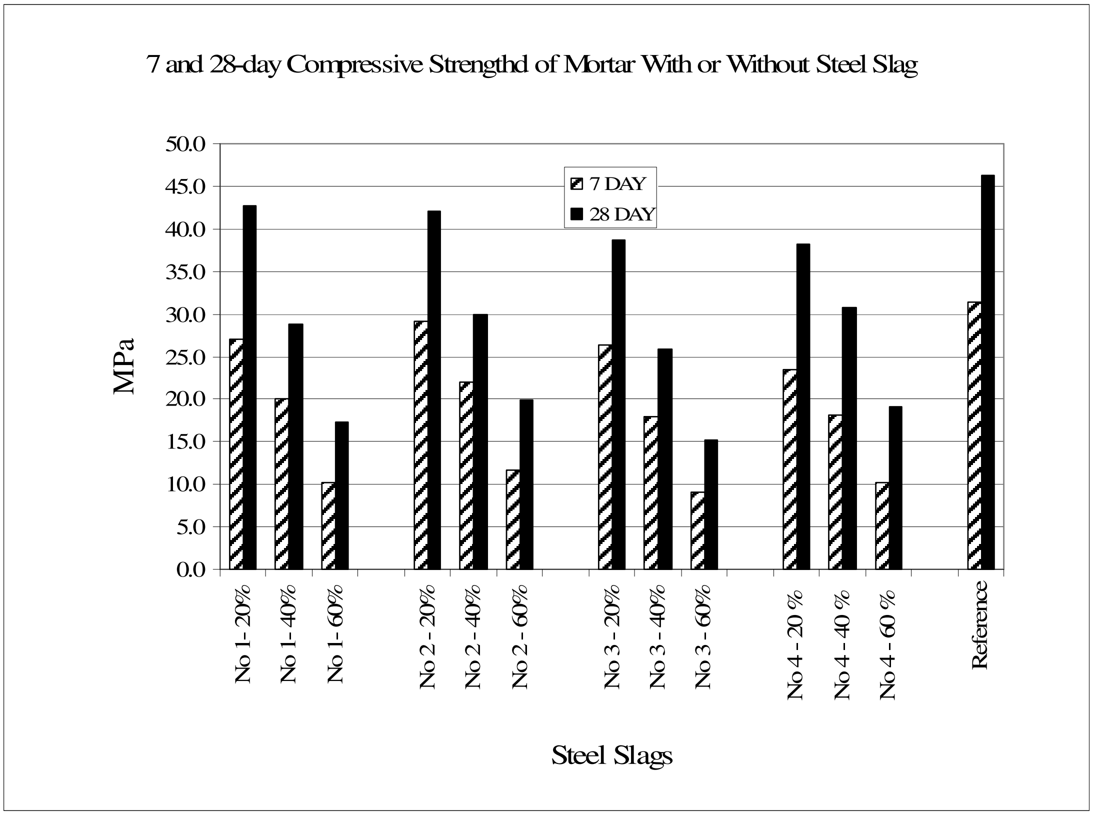

Figure 4.6. 7 and 28 day compressive strengths of mortar with or without steel slag

4.3. Concrete Properties

4.3.1. Fresh Concrete Properties

Fresh concrete properties such as slump, unit weight and air content are given in Table 4.7. Concretes with a w/c of 0.52 had slumps, very similar to each other, ranged between 16-19 mm. The unit weights ranged from 2429 to 2587 kg/m^3.

Table 4.7. Fresh properties of concretes with or without steel slag

Slag Code	Replacement of Cement by Steel Slag (per cent)	w/(c + ss)	Slump (cm)	Unit Weight (kg/m³)	Air Content (per cent)
NO 1	20	0,52	18	2587	9.3
	40		18	2536	7.7
	60		18	2458	4.9
NO 2	20	0,52	16	2461	4.9
	40		19	2469	5.3
	60		18	2450	4.7
NO 3	20	0,52	18	2455	4.6
	40		16,5	2470	5.3
	60		19	2449	4.6
NO 4	20	0,52	17	2471	5.4
	40		18	2429	3.9
	60		17	2590	10.1
Reference Concrete		0,52	16	2452	4.2

4.3.2. Hardened Concrete Properties

4.3.2.1. Compressive and Flexural Strength: The flexural and compressive strength tests data of 7-day specimens are given in Table 4.8 and depicted in Figure 4.7 and 4.8 to show the effects of steel slags at 7 days. The findings were the followings:

The flexural strength ranged from 1.2 to 6.6 MPa and the compressive strength ranged from 6.8 to 34.1 MPa at 7 days. The best values were get in 20 per cent replacements. However, none of them reached to the reference concrete values. As seen in Table 4.8, flexural and compressive strength values decreases with increasing steel slag content, because their activity indices are low.

Table 4.8. Hardened properties of concrete with or without steel slag at 7 days

Slag Code	Replacement of Cement	Age	w/c	Flexural Strength	Compressive Strength
	per cent	(day)		MPa	MPa
NO 1	20	7	0.52	6.6	31.0
	40			4.9	20.2
	60			1.9	8.3
NO 2	20	7	0.52	5.5	34.1
	40			4.2	19.6
	60			2.4	10.3
NO 3	20	7	0.52	5.3	27.4
	40			4.2	19.3
	60			1.2	4.4
NO 4	20	7	0.52	5.4	24.4
	40			3.7	19.3
	60			1.5	6.8
Reference Concrete		7	0.52	6.9	36.8

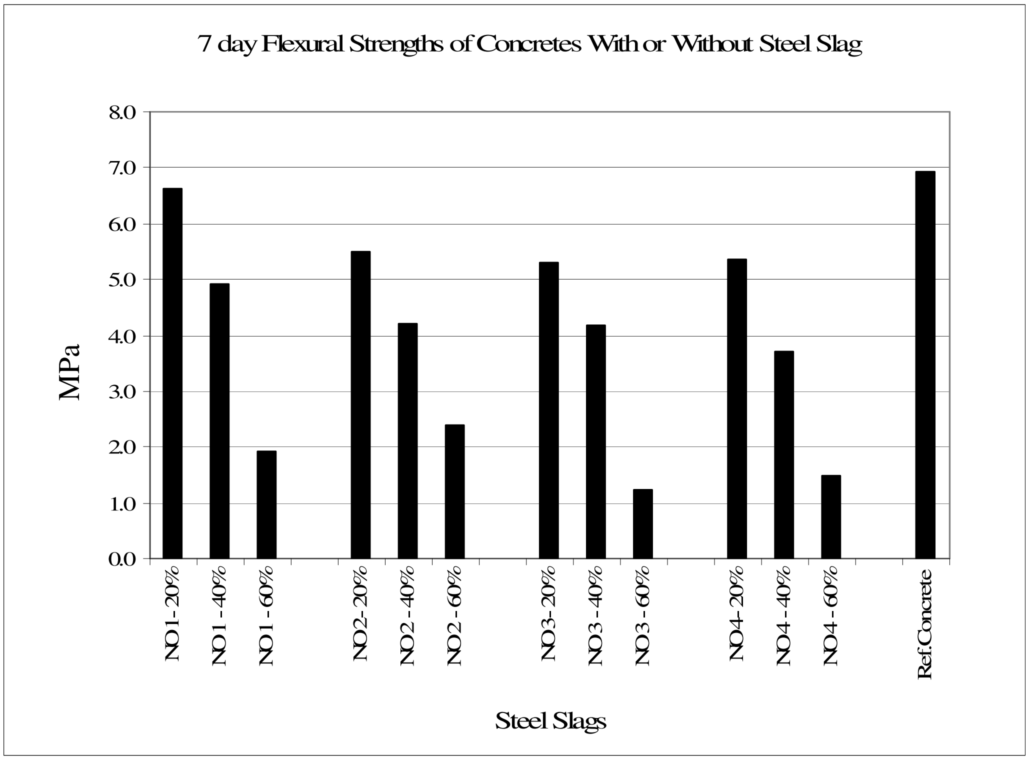

Figure 4.7. 7 day flexural strengths of concretes with or without steel slag

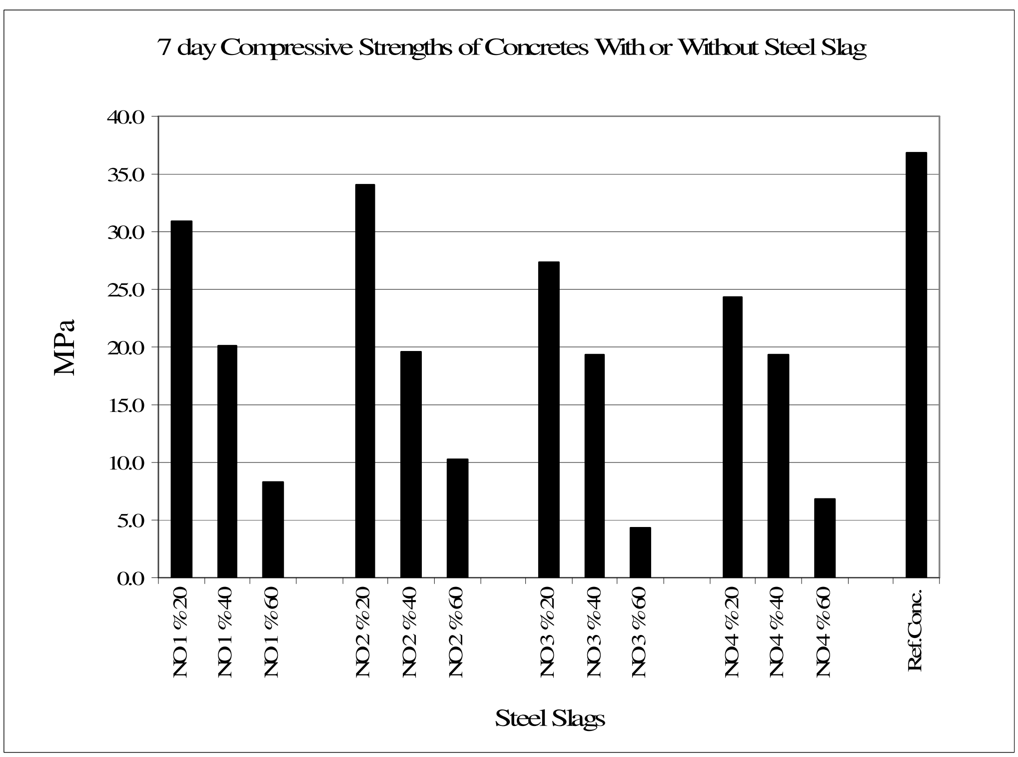

Figure 4.8. 7 day compressive strengths of concretes with or without steel slag

The compressive and net bending strength of selected concrete samples at 120 days are given in Table 4.9 and depicted in Figure 4.9 and 4.10.

Table 4.9. Compressive and net bending strengths of selected concrete samples at 120 days

Slag Code	Compressive Load	Compressive* Strength	Pmax	h	Net Bending Strength
	(kN)	(MPa)	(N)	(m)	(MPa)
No 1 % 20	278	56.7	2455	0.0423	5.89
No 2 % 20	279	56.9	2642	0.0426	6.26
No 2 % 60	184	37.5	1951	0.0425	4.63
Reference	316	64.5	2350	0.0418	5.77

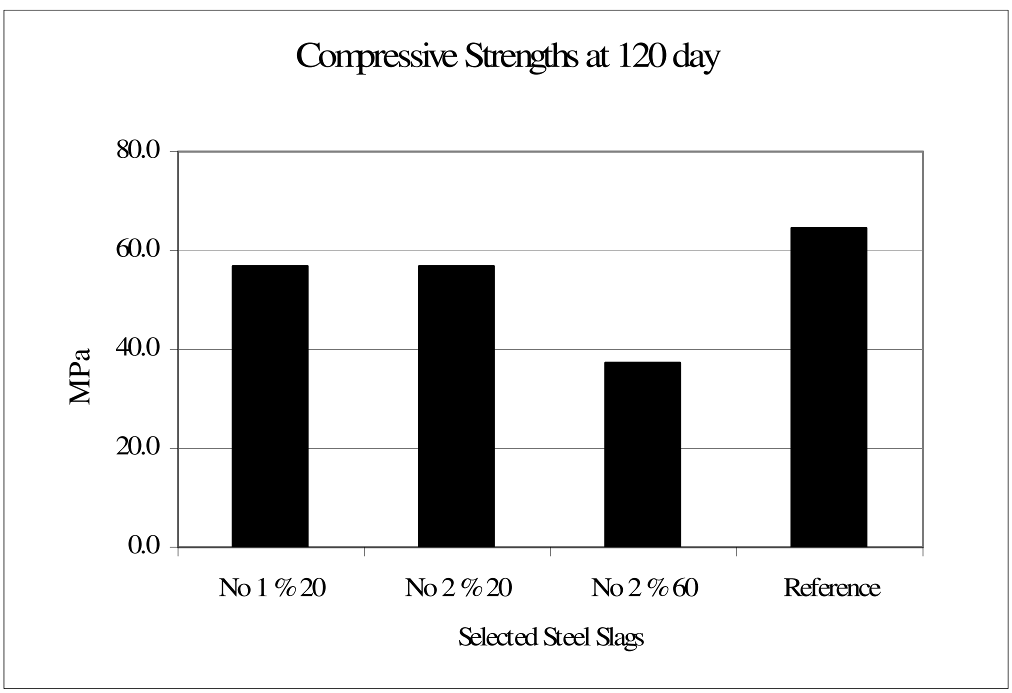

Figure 4.9. 120 day compressive strengths of selected concretes with or without steel slag.

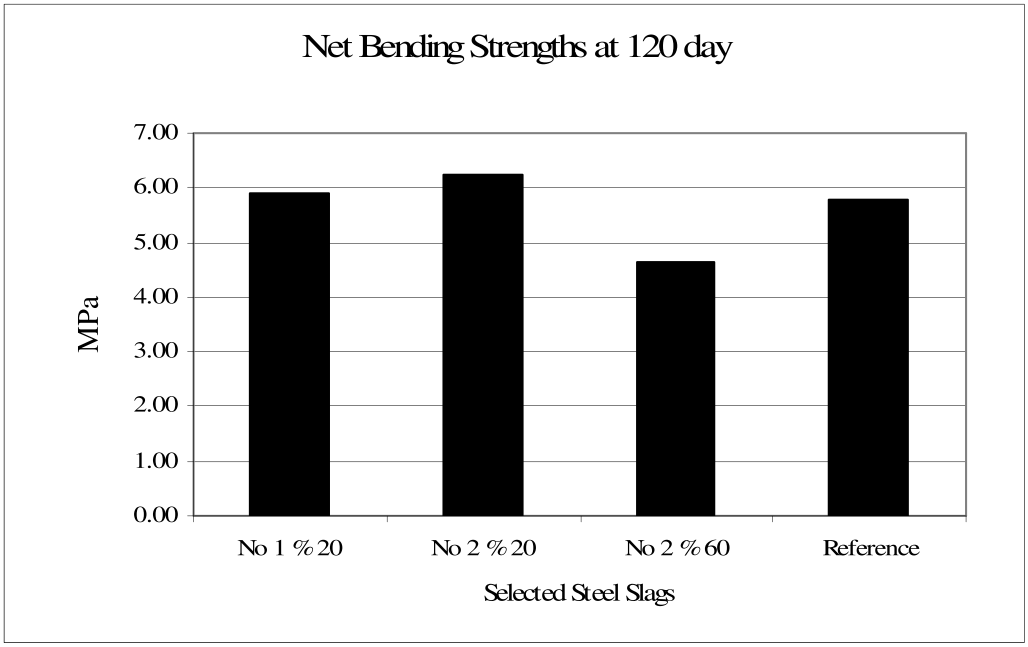

Figure 4.10. 120 day net bending strengths of selected concretes with or without steel slag

As seen in Table 4.9 compressive strength of concrete with slag of 20 per cent decreases slightly compared to the reference concrete. The significant reduction in compresive strength was obtained in concrete containing slag of 60 per cent. However net bending strength of concretes with slag of 20 per cent is slightly higher than that of reference concrete. These results can be attributed to the scatter in bending test results. As expected the net bending strength decreases significantly in concrete with slag of 60 per cent.

4.3.2.2. Splitting Tensile Strength: The splitting tensile strength of selected concrete samples at 120 days are given in Table 4.10 and depicted in Figure 4.11.

Similar to compressive strength results, splitting tensile strength of concrete with slag of 20 per cent decreases slightly compared to the reference concrete. The significant reduction in splitting tensile strength was obtained in concrete containing slag of 60 per cent.

Table 4.10. Splitting tensile strengths of selected concrete samples at 120 days

Slag Code	Splitting Load	Splitting Tensile Strength
	(kN)	(MPa)
No 1 % 20	45,5	5,91
No 2 % 20	46,3	6,01
No 2 % 60	35,3	4,59
Reference	56,7	7,37

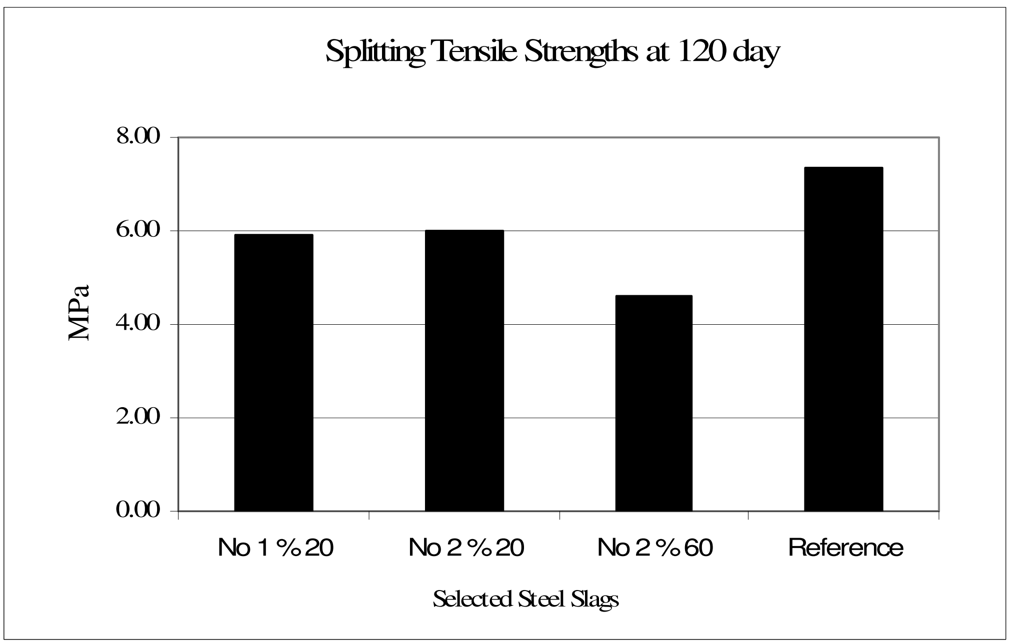

Figure 4.11. 120 day splitting tensile strengths of selected concretes

4.3.2.3. Fracture Energy: For each mixture the typical load versus displacement at the mid span curves in bending are shown in Figures 4.13, 4.14, 4.15 and 4.16. For the comparison some typical load versus displacement at mid span curves are also shown in Figures 4.17 and 4.18. As seen in Figure 4.17 ascending branches of concretes are close to each other; because the initial compliance (i.e. modulus of elasticity) is insensitive property to the mixture composition. As the bending strength of concrete increased, descending branch became steeper and more brittle behavior was obtained. However, as the strength decreased, the descending branch decreased slowly with a long tail, and material became less brittle (or more ductile).

As seen in Table 4.11 it can be said that there is no difference in fracture energies between the concretes with and without steel slag. Fracture energy was insensitive to the mixture composition, it was because, while the bending strength decreased, a long tail was obtained in the descending branch. Thus, it can be concluded that there was no significant effect of slag content on the fracture energy of concrete.

Table 4.11. Fracture energies of selected concrete samples

Slag Code	W	Weight of Beam	δ	Specific Fracture Energy Gf
	(Nm)	(kg)	(m)	(J/m)
No 1 % 20	0,2685	3,341	0,000538	96
No 2 % 20	0,2673	3,347	0,000420	94
No 2 % 60	0,2680	3,375	0,000565	96
Reference	0,2624	3,362	0,000474	93

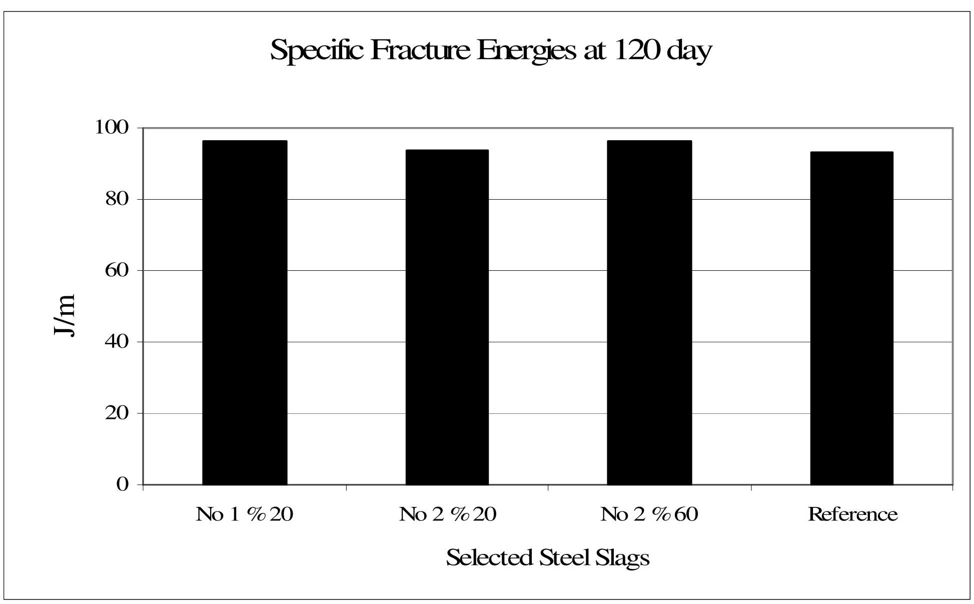

Figure 4.12. Specific fracture energies of selected concretes with or without steel slag.

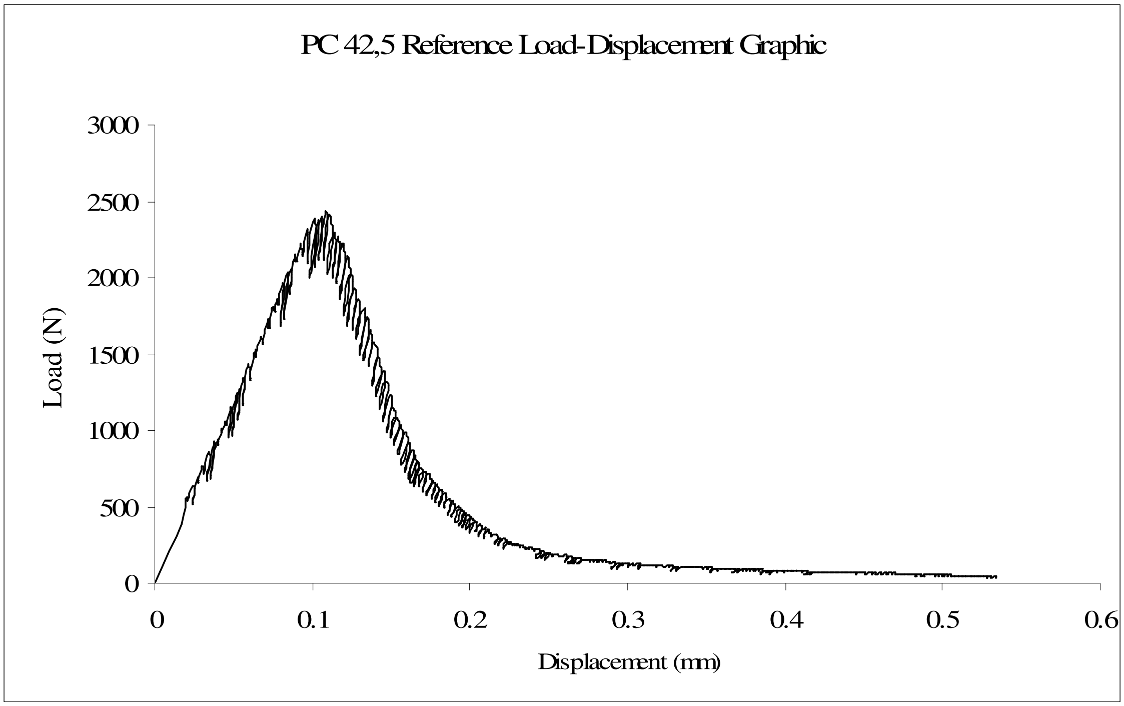

Figure 4.13. A typical curve of load - displacement at mid span (reference specimen 1)

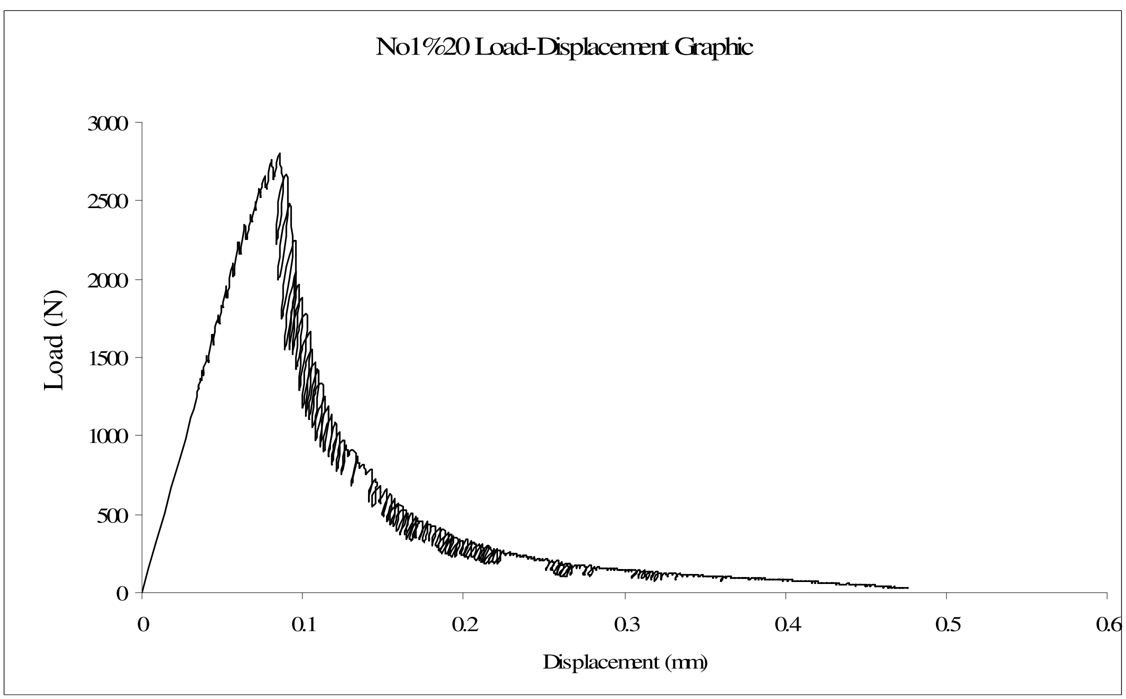

Figure 4.14. A typical curve of load - displacement at mid span (No1%20 specimen 1)

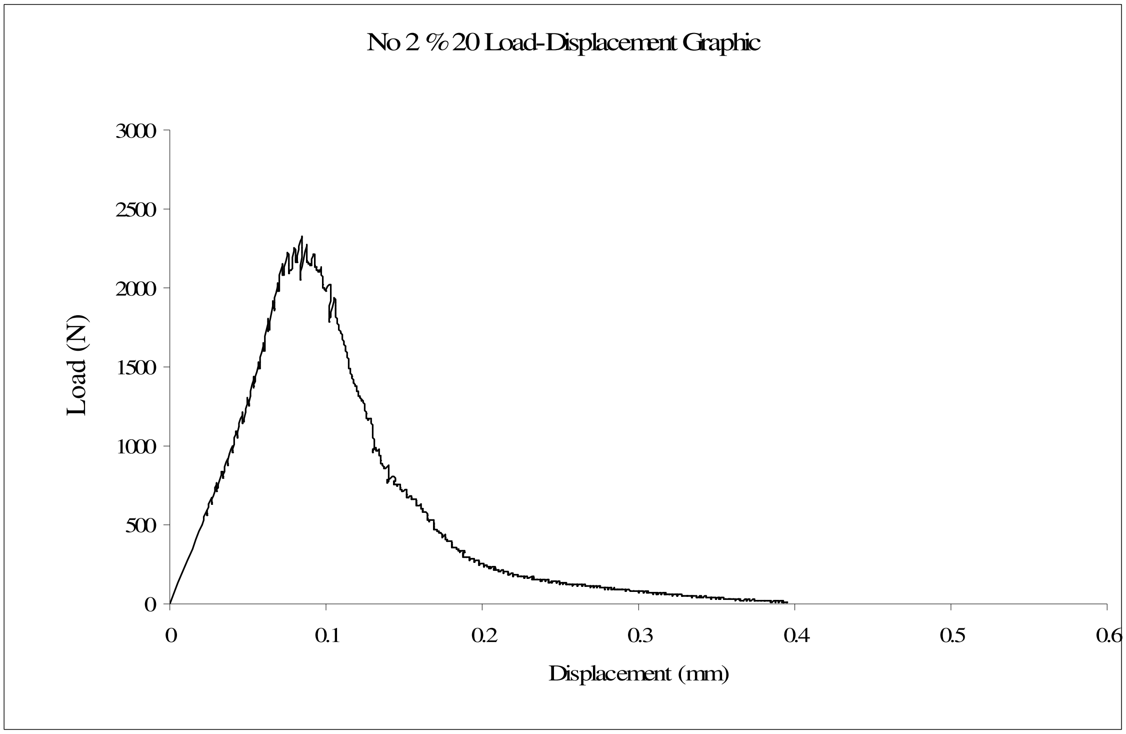

Figure 4.15. A typical curve of load - displacement at mid span (No2%20 specimen 3)

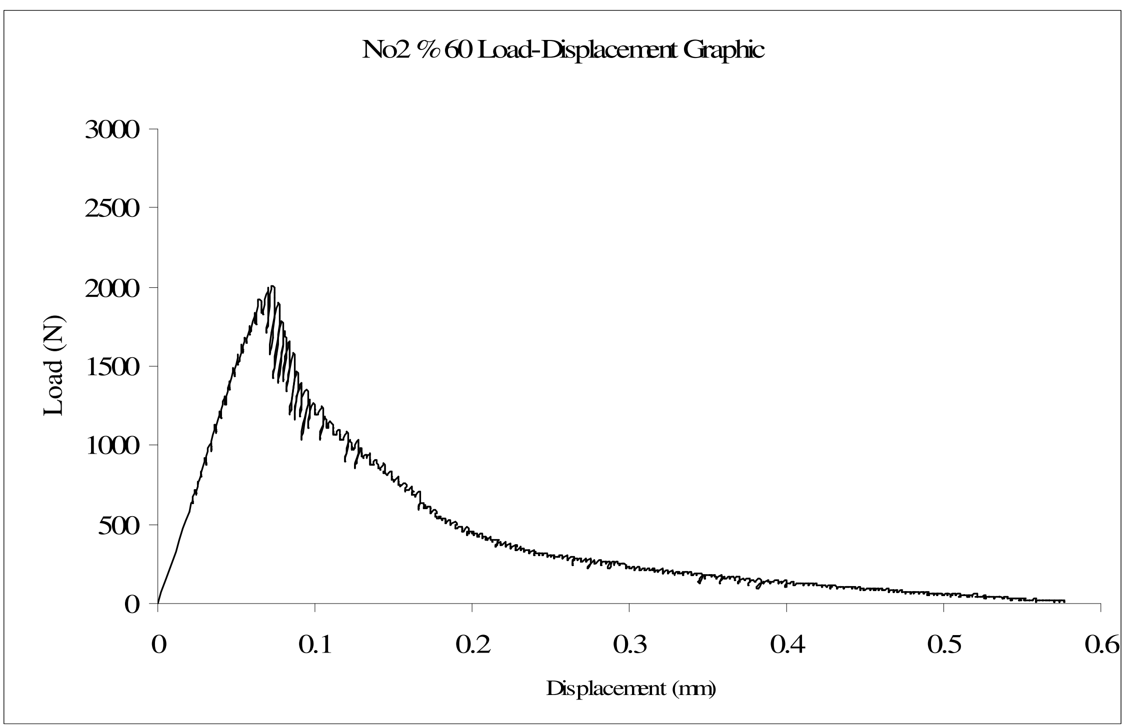

Figure 4.16. A typical curve of load - displacement at mid span (No2%60 specimen 1)

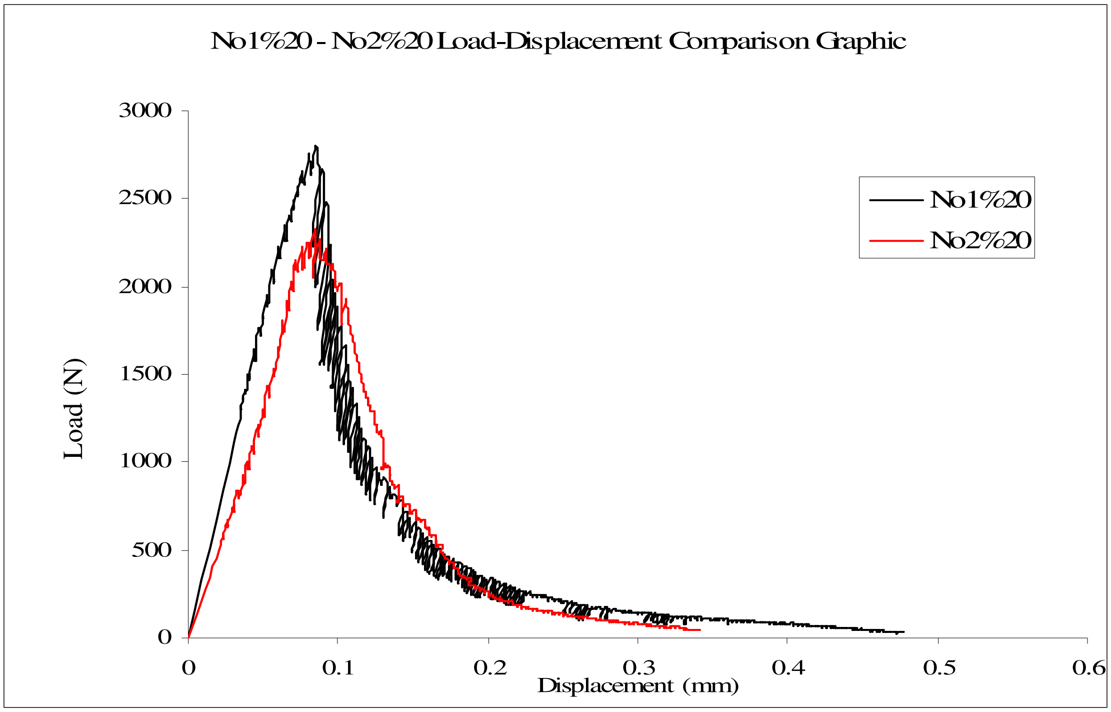

Figure 4.17. Comparison of the load-displacement curve of No1%20 and No2%20

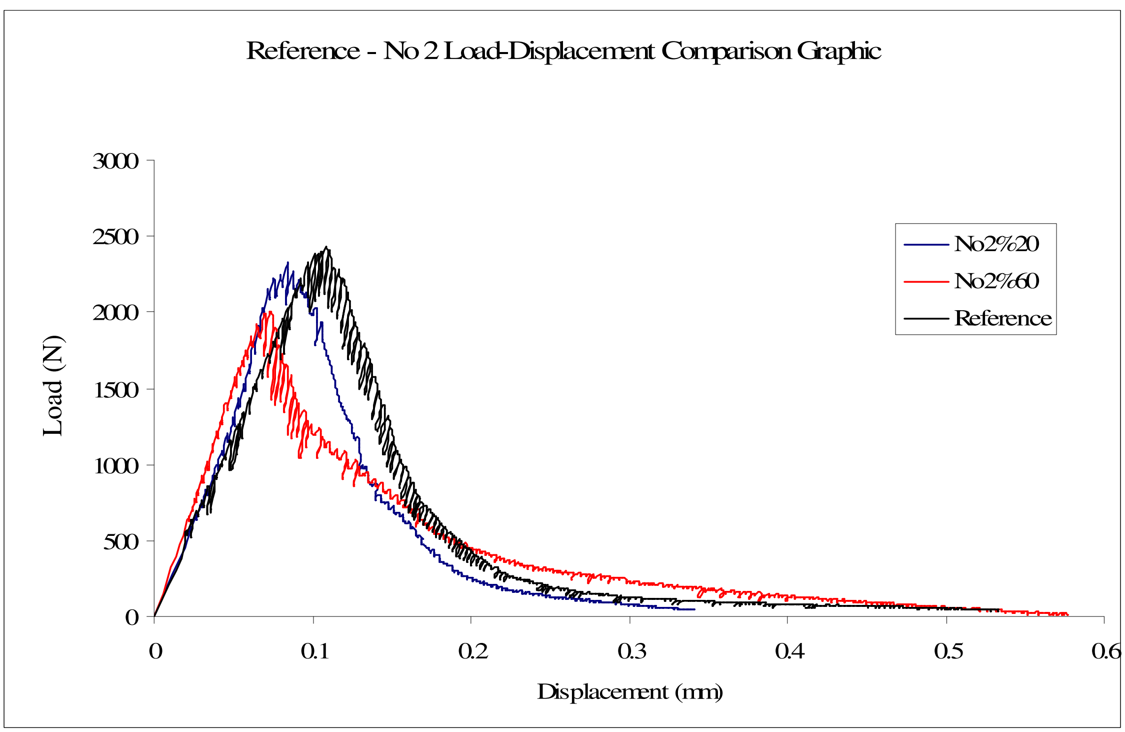

Figure 4.18. Comparison of the load-displacement curve of Reference and No2 (both %20 and %60).

<u>4.3.2.4. Chloride Ion Permeability:</u> The effect of steel slag on the rapid chloride permeability of concrete was more significant in case of slag content of 20 per cent. As seen in Table 4.12 the steel slag caused reduction in the chloride ion penetration for the low slag content such as 20 per cent replacement. The results obtained were evaluated according to values indicated in ASTM C 1202.

Table 4.12. Rapid Chloride Permeability Test Results

Slag Code	Replacement of Cement (per cent)	Charge Passed (coulombs)	Chloride Permeability Rating
No 1	20	2460	Moderate
	40	5373	High
	60	6564 *	High
No 2	20	1762	Low
	40	4921	High
	60	5576	High
No 3	20	2737	Moderate
	40	6646	High
	60	9317 *	High
No 4	20	3154	Moderate
	40	3043	Moderate
	60	5406 *	High
Reference		4551	High

* The tests could not be finished because of extreme heat increase in the solution.

The total charge passing through the concrete without steel slag (reference) was 4551 Coulombs, which corresponds to high ion permeability indicated in ASTM C 1202. As seen in the same table as the slag content increased further, the rapid chloride ion penetration increased significantly; because pieces of irons may cause the increase in the rapid chloride permeability.

Thus, it can be concluded that the higher chloride permeability of high volume steel slag concrete was due to the large amount of iron pieces.

5. CONCLUSION

Based on the results obtained in this study, the following main conclusions were drawn.

1. Waste management of steel slag must be taken seriously in Turkey where only 10 per cent is utilized. Based on this study, it is aimed to show if it is compatible or not to utilize steel slag in concrete.

2. Although some coaser steel particles were removed before grinding, it was difficult to grind steel slags. After grinding operation their Blaine Fineness are almost close to each other. So the fineness effect could not be investigated.

3. In the pastes with steel slag, water requirement of the paste decreased with increasing steel slag. Similar trends can be seen in the pastes with ground granulated blast furnace slag.

4. As the amount of steel slag increased, the setting time decreased dramatically.

5. Volumetrix expansion of cements increased dramatically with increasing steel slag content. Because free CaO and MgO were very high in each slag sample.

6. Based on the ASTM C 989, pozzolanic activity of steel slag was even lower than Grade 80. Thus, the activity indices found were not comparable with the ground granulated blast furnace slag.

7. The effect of steel slag content on the mechanical properties of concrete was low at the 7 days old specimens.

8. Both compressive and bending strengths of mortars with steel slag decreased with increasing slag, because their pozzolanic activities were very low. Almost none of the steel slag added cement mixtures have the limit compressive strength of 42.5 MPa.

9. A significant effect of the slag type and the replacement ratio by Portland cement on the fresh concrete properties was not observed. Concretes prepared with a constant water/(cement+slag) ratio had similar slumps and unit weights.

10. Similar to mortars, compressive and bending strengths of concretes prepared with steel slags at 7 days decreased with increasing slag amount. All results were lower than the reference sample. Same trend was observed in 120 day test results.

11. There was no difference between the fracture energies. It was observed that the type and the replacement ratio of steel slags did not have an effect on fracture energy. The area under load versus displacement at mid span curves were almost same.

12. Despite of magnetic separation before grinding, steel slags contain metal particles. This physical case had a significant effect on chloride ion permeability test. As the slag content increased the rapid chloride ion penetration results increased dramatically.

REFERENCES

1. Gale, S., "CemStar^{SM} Revolutionises Slag Disposal", *South East Asian Iron and Steel Institute (SEAISI) Conference*, Bangkok, Thailand, September 2003.

2. International Iron and Steel Institute website, www.worldsteel.org

3. TÜBİTAK Materials Institute Report No ME.1.04.001, 2004 Project Report On The Economical and Ecological Utilisation OF Selected Residual Materials For Landscape Creation E!2936-ECOUTIRESMAT, 2004.

4. ASTM C 593 Standard Specification for Fly Ash and Other Pozzolans for Use With Lime for Soil Stabilization

5. Schröder, F., "Slags and slag cements", *in Proceedings of Fifth International Symposium on the Chemistry of Cement*, pp.149-199, Tokyo, 1969.

6. Malhotra, V.M., Advances in Concrete Technology, CANMET, Energy, Mines and Resources Canada, pp.483-496, Second Edition, Ottawa, 1994.

7. Lea, F.M., "The Chemistry of Cement and Concrete", Chemical Publishing Co. Inc., pp. 687, Third Edition, New York, 1971.

8. Emery, J.J., Slags as Industrial Minerals, in Proceedings of Third Industrial Minerals International Conference, pp. 127-142, Paris, 1978.

9. Malhotra, V.M., Supplementary Cementing Materials for Concrete, CANMET, Energy, Mines and Resources Canada, Ottawa, 1987.

10. Cotsworth, R.P., Use Of Pelletized Slag In Concrete Masonry Unıts, National Slag Ltd, Prepared for ASTM Masonry Symposium, Chicago, IL, June 29, 1976.

11. Emery, J.J., C.S. Kim and R.P. Cotsworth, "Base stabilization using palletized blast-furnace slag", Journal of Testing and Evaluation, pp. 94-100, 1976.

12. Lewis, D. W., Properties And Uses Of Iron And Steel Slags, National Slag Association Presented at Symposium on Slag National Institute for Transport and Road Research South Africa, February, 1982.

13. National Slag Association website, http://www.nationalslagassoc.org

14. Sahay, J., O.P. Nagpal and S. Prasad, Waste Management of Steel Slag, *Steel Times International*, 38-41,March 2000.

15. Murphy, J.N., T.R. Meadowcroft and P.V. Barr, "Enhancement Of The Cementitious Properties of Steel Making Slags", *Canadian Metallurical Quarterly,* Vol.36, No.5, pp. 315-331, Great Britain, 1997.

16. Thomas, E.G., "Cemented Fill Practice and Research at Mount Isa", Proceedings of the Austrilian Institute of Mining and Metallurgy, 240: 33-51, 1971

17. Laneuville, J., Portland Cement-Slag Binders, Canadian Patent No.963482, Patent Office, Ottawa, Canada, 1975.

18. Thomas, E.G. and R. Cowling, "Pozzolanic Behaviour of Ground Isa Mine Slag in Cement Hydraulic Mine Fill At High Slag/Cement Ratios", 12^{th} Canadian Rock Mechanics Symposium, CIM Special Volume 19, pp. 129-132, 1980.

19. Higgins, L.M. and W.H. Bauer, "Utilization of Lead and Zinc Slags in Ceramic Construction Products", Conservation and Recycling, pp. 375-382, Pergamon Press, London, 1980.

20. TÜBİTAK Materials Institute Report No ME.1.05.003, Final Project Report On The Economical and Ecological Utilisation OF Selected Residual Materials For Landscape Creation E!2936-ECOUTIRESMAT, 2005.

21. Wang, Y. and D. Lin, “Steel Slag Blended Cement”, *Silicates Industriels*, Vol.6, 1983, pp. 121-126.

22. Sun, S. and Y. Yuan, ”Study of Steel Slag Cement”, *Silicates Industriels*, Vol.2, pp.31-34, 1983.

23. Li, Y., S. Sun, J. Wang and G. Zhu, “Steel Slag Cement”, Conference Proceedings of The McMaster Symposium on Iron and Steelmaking, Hamilton, Ontorio, Canada, 11-13 May 1994.

24. TÜBİTAK Materials Institute Report No ME.1.04.009, 2004 Project Report On The Economical and Ecological Utilisation OF Selected Residual Materials For Landscape Creation E!2936-ECOUTIRESMAT, 2004.

25. Lea, F.M., *“The Chemistry of Cement”*, 3rd edition, Edward Arnold Publishers Ltd, Glasgow, UK, 1970.

26. Monaco, A. and W.K. Wu, “The Effect of Cooling on The Mineralogical Characterization of Steel Slag”, In Proceedings of the International Symposium on Resource Conservation and Environmental Technologies, 1994, pp. 107-116.

27. Montgomery, D.G. and G. Wang, ”Preliminary Laboratory Study of Steel Slag for Blended Cement Manufacture, *Materials Forum*, Vol.15, 1991, pp. 374-382.

28. Geiseler, J. and R. Schlosser, Proceedings of The 3rd International Conference on Molten Slag and Fluxes, Glasgow, UK, 1988, pp. 27.

29. Luo, S., Proceedings of the The International Congress on The Chemistry of Cement, Paris, 1980, Vol.3, pp. 25.

30. Lewis, D.W., “History of Slag Cements”, Preprint, Presentation at the University of Alabama Slag Cement Seminar, pp. 7, 1981, (available from the National Slag Association).

31. Emery, J.J. and B.L. Ferrand, “Recent Improvements in The Quality of Steel Slag Aggregate”, *in Proceedings of The International Symposium on Resource Conservation and Environmental Technologies*, Aug., 1994, pp. 99-106.

32. Sersale, R., V. Amicarelli, G. Frigione and P. Ubbriaco, in Proceedings of The International Congress on The Chemistry of Cement, Rio de Janerio, 1986, pp. 194.

33. Nelson, L.R., “Determination of The Possible Causes of a Foaming Slag by Its Mineralogical and Textural Characterization, *in Extraction and Processing for The Treatment and Minimization of Wastes*, 1993, pp. 1041-1062.

34. ASTM C 989 Standard Specification for Ground Granulated Blast-Furnace Slag for Use in Concrete and Mortars, 1994 Annual Book of ASTM Standards, Vol.04.02

35. ASTM C 109 Standard Test Method for Compressive Strength of Hydraulic Cement Mortars, 1993 Annual Book of ASTM Standards, Vol.04.01

36. ASTM C219 Standard Termninology Relating to Hydraulic Cement

37. ASTM C595 Standard Specification for Blended Hydraulic Cements

38. RILEM 50-FMC Technical Committee

39. TS EN 196 Methods of Testing Cement-Parts 1,3 and 6

40. TS EN 12350 Testing Fresh Concrete