Sustainability of Iron and Steel Factory Wastes in Cement

Ömer Özkan
Department of Construction
Sakarya University
Sakarya, Turkey
omerozkan@sakarya.edu.tr

Muharrem Aktaş
Department of Civil Enginnering
Sakarya University
Sakarya, Turkey
muharrema@sakarya.edu.tr

Mehmet Sarıbıyık
Department of Construction
Sakarya University
Sakarya, Turkey
mehmets@sakarya.edu.tr

Abstract: This study reports the results of an experimental study conducted to determine sustainability development of composite cements manufactured with Basic Oxygen Furnace (BOF) Slag and Blast Furnace Slag (BFS) combination. The overall objective of this work is to determine whether a combination of BOF slag and BFS might be processed into a sufficiently cementitious material to produce Composite Portland Cement (CPC). Three group of cement are produced. First group is BOF slag, second group is BFS and the last group is the mixture of BOF slag and BFS. Physical properties and Alkali Silica Reaction (ASR) of those groups are evaluated. Result of BOF slag CPC showed the maximum ASR expansion. However; results of BFS composite portland cements showed minimum ASR expansion value.

Introduction

Industrial wastes sustainability is generally considered as a major source of environmental problems in the world. Reuse of some industrial waste materials has become very important during the past decade. The environmental regulations, requiring waste disposal minimization, force the reuse of waste materials. Land disposal that is a partial solution for this problem causes secondary pollution problems and extra costs. Therefore, more efficient solutions such as alternative recovery options need to be investigated. Solid wastes of iron and steel factories can be used as raw material in cement and concrete sectors. European Community (EU) has declared targets to protect the environment and to guarantee a cautious and efficient use of natural resources. Solid wastes should be reused in order to use natural resources efficiently and for sustainable development. Portland cement clinker production is expensive and ecologically harmful. For this reason, various studies have investigated about usage of wastes in cement production (Özkan and Yüksel, 2008). Fly ash, blast furnace slag, silica fume and steel slag are currently used in cement and concrete industry.

The BOF slag is a by-product that produced during the alteration of iron and steel. The BOF slag is comprise of calcium silicates and ferrite with oxides of aluminum, manganese, calcium and magnesium (Sahay et al, 2000). The mineralogical composition of BOF slag changes with its chemical composition. Olivine, merwinite, calcium silicates (C_2S, C_3S), C_4AF, C_2F, CaO–FeO–MnO–MgO in solid solution and free CaO are common minerals in steel slag (Shih et al, 2004). The attendance of C_3S, C_2S, C_4AF and C_2F confirms BOF slag cementitious properties. The free CaO content increased the basicity of the BOF slag that increased the reactivity of the BOF slag (Shi and Qian, 2000). However, high free CaO content in BOF slag has been shown to produce volume expansion problems (Ozkan, 2006). Many investigations were performed for using BOF slag as industrial raw material (Maotz and Geiseler, 2001). BOF slag was mainly used as a bulk material, asphalt aggregate, filling material, cement raw feed, railroad ballast, and in agriculture in the world. Nearly 12 million tons of BOF slag is produced in Europe per year. Today about 65 % of the produced BOF slag is used on qualified fields of application. The remaining 35 % of this slag was still dumped. It will need further intensive research work to decrease this rate as far as possible.

The BFS, a kind of industrial by-product, is also currently used in cement and concrete industry. The BFS is known to possess a latent hydraulic property. Ground BFS is used as an admixture in concrete or as an additive in the manufacture of Portland slag cements in countries where large amounts of BFS is available as by-product. When BFS is added to cement, it combines with the Portland (CH) released by cement hydration to give calcium silicate hydrate (CSH). Alkali silica activates this step, which increases the reaction rate. Some properties of the concrete containing BFS, such as creep, shrinkage, strength to freeze-thaw resistant are still under discussion, but the use of the BFS in cement and concrete has been proven to have many advantages (Sakai et al, 1993).

Alkali Silica Reaction (ASR) can cause serious expansion and cracking in concrete, resulting in major structural problems and sometimes necessitating demolition. ASR is the most common form of alkali-aggregate reaction (AAR) in concrete; the other, much less common, form is alkali-carbonate reaction (ACR). ASR and ACR are therefore both subsets of AAR. ASR is caused by a reaction between the hydroxyl ions in the alkaline cement pore solution in the concrete and reactive forms of silica in the aggregate (Ichikawa and Miura, 2007).

This work investigated ASR of mortars made with cements incorporating BOF slag and BFS as partial replacement of Portland cement clinker in different ratios of replacement. Specific weight, initial and final setting times, and expansion values of composite cements were investigated.

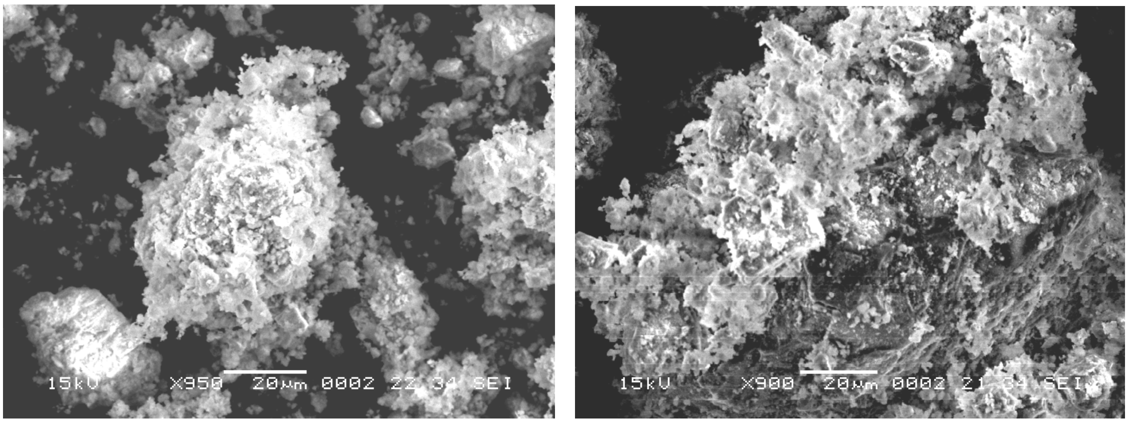
Materials and Procedure

Materials

Clinker and gypsum used in this study were provided from Lafarge-Ereğli (Karadeniz, Ereğli, Turkey) Cement Factory. BOF slag and BFS were provided from Ereğli Iron and Steel Works Company in Turkey. The chemical compositions of these materials are presented in [Table 1], which are acquired from the X-ray lab. The photographs of granule BOF Slag with a size of 90 µm both (a) under-griddle and (b) above-griddle showed in [Figure 1]. CEN standard sand was used to manufacture mortar specimens. Chemical composition and particle size distribution of the sand were presented in [Table 2] (TS-EN 196-1, 2009).

Table 1: Chemical compositions of BFS and BOF slag, clinker and gypsum (wt. %)

MATERIALS	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	SO_3
BFS	37.80	35.10	0.70	17.54	5.50	0.70
BOF slag	58.53	10.72	15.30	1.71	4.27	0.04
Clinker	66.11	21.57	3.17	5.09	1.74	1.35
Gypsum	32.57	0.67	0.24	0.21	2.20	46.56



(a) (b)

Figure 1: SEM photograps of BOF slags

Table 2: Sand gradient

Chemical compositions		Griddle pore size	Remaining
	%	(mm)	%
SiO_2	93.05	0.08	99.12
Al_2O_3	3.11	0.16	86.21
Fe_2O_3	0.37	0.5	65.74
CaO	0.17	1	33.02
MgO	0.03	1.6	5.23
SO_3	0.07	2	-
K_2O	1.5	Humidity	0.11
Na_2O	1.1		
LOI	0.57		

Procedure

BOF Slag and BFS are substituted together with the mixture of clinker-gypsum and then four main groups of cement are established on the base of these substitutions. The materials are supplied in granule size as are the outputs of factory. BFS, BOF Slag and Clikner-Gypsum were grounded in a ball mill to a specific surface area of about 2500 cm^2/g. The materials are mixed with each other in the amounts specified previously, and then grinded again to achieve specific surface value of 3100–3300 cm^2/gr, thus yielding the cements used in the tests. The first group is coded as the reference group and named as C, in the second group, coded as C1, Clinker-gypsum mixture is substituted with BOF slag, on the other hand Clinker-gypsum mixture is replaced with BFS in the third group C2, and the last group (C3) Clinker-gypsum mixture is substituted with the BFS-BOF slag composition that is arranged at a rate of 50% of BFS and 50% of BOF slag. Composition ratios of the mixtures used in the study is shown in the [Table 3]. All the main groups, except for the reference group C, are further divided into sub-groups and symbolized by suffixes (a, b, c, d) with respect to their changing ratios in compositions; for instance code C3c symbolize a material that is composed of 40% clinker-Gypsum, 30% BFS and 30% BOF slag.

Table 3: Composition of cement mixtures

Code	Materials	Clinker	Gyps.	BFS	BOF Slag
		%	%	%	%
C	100% Clinker-Gypsum	95	5	0	0
C1a	80% Clinker-Gypsum + 20% BOF Slag	76	4	0	20
C1b	60% Clinker-Gypsum + 40% BOF Slag	57	3	0	40
C1c	40% Clinker-Gypsum + 60% BOF Slag	38	2	0	60
C1d	20% Clinker-Gypsum + 80% BOF Slag	19	1	0	80
C2a	80% Clinker-Gypsum + 20% BFS	76	4	20	0
C2b	60% Clinker-Gypsum + 40% BFS	57	3	40	0
C2c	40% Clinker-Gypsum + 60% BFS	38	2	60	0
C2d	20% Clinker-Gypsum + 80% BFS	19	1	80	0
C3a	80% Clinker-Gypsum + 10% BFS + 10% BOF Slag	76	4	12	8
C3b	60% Clinker-Gypsum + 20% BFS + 20% BOF Slag	57	3	24	16
C3c	40% Clinker-Gypsum + 30% BFS + 30% BOF Slag	38	2	36	24
C3d	60% Clinker-Gypsum + 40% BFS + 40% BOF Slag	57	3	24	16

The physical properties of the produced cements are first examined after the tests conducted and then the weight percentages, specific surface values and specific gravities of cements remaining on the surface of sieves with 32 and 90µn pore sizes, according to the Turkish Standards (TS-EN 196-6, 2000). Moreover, the beginning and ending times of cement setting and expansion values of cements are also determined according to Turkish Standards (TS-EN 196-3, 2002).

The ASTM C1260 test is based on the assumption that a very high pH value of the pore solution initiates the reaction with potentially reactive aggregate. The intention was to create the most severe alkaline conditions as could be expected in the pore solution of mortar bars after hydrolysis, which is the interaction of alkalis and water. Therefore, test specimens are submerged in a hot and highly alkaline sodium-hydroxide solution (1 N). Originally, the test was not designed to consider influences of other components of the mortar mix such as admixtures but solely to determine the reactivity of a given aggregate type (ASTM C-1260). Mortar bars used in this study are of 25x25x290 mm dimension. Cement, standard rilem combreau sand and tap water with the proportions of 1, 2.25 and 0.47 respectively.

Specimens are first cured in a fog room in molds at 20° C for 24 hours, remove the specimens from the molds, make an initial comparator reading and then demoulded and one day cured in water at 80± 3 °C. After remove from in water, take the zero reading and then immersion into a 1 M NaOH solution with a temperature of 80 °C during 14 days. A subsequent comparator reading of the specimens reads periodically, with at least three readings.

Result and Discussion

Physical Properties of Cements

The physical properties of produced cements are shown in [Table 4]. Fineness, specific surface and specific gravity are listed.

Table 4: Physical properties of cements

Cements	Fineness (wt.%)		Specific surface	Specific gravity
	>32 µm	>90 µm	cm^2/g	g/cm^3
C	21.00	0.90	3330	3.12
C1a	21.15	1.18	3214	3.06
C1b	22.10	1.00	3213	3.02
C1c	22.15	1.25	3152	2.97
C1d	22.10	1.20	3150	2.96
C2a	21.20	1.10	3115	3.05
C2b	21.90	1.15	3108	3.01
C2c	21.80	1.15	3090	2.95
C2d	21.90	1.10	3070	2.94
C3a	19.20	0.90	3450	3.12
C3b	18.60	0.90	3550	3.15
C3c	19.10	1.00	3650	3.12
C3c	18.20	0.80	3700	3.11

It is found that BFS has harder structure than BOF slag and hardly grinded slag. BFS of 2400-2500 cm2/g reaches the required fineness after 4 hours of grinding when BOF slag takes only 3 hours for this degree of fineness. The reference cement (C) produced as Portland cement has a softer structure than the rest of specimens. Thus, it can easily be said that BFS and BOF slag, ground separately, can attain the same granule size on the condition that they are grinded finely. When cement's specific gravity results are examined, it is found that waste materials (BFS and BOF slag) substituted with clinker have lower specific gravity values.

Volume expansion values of cements are found to be within the limits set by Turkish Standards (TS-EN 196-3, 2002). In the light of examining results one can observe that expansion of cements with BOF slag additive is higher than that of other cements. In BOF slag, when the volume is stable, the rate of free CaO and MgO is of great importance since the reaction between both oxides and water has an effect on volume stability (Altun and Yılmaz, 2002).

Alkali Silica Reaction

Mortar specimens are exposed to 1 N NaOH solution with a temperature of 80 °C during 14 days. The expansions of the mortar specimens exposed to NaOH solution are given in [Table 5].

Table 5: Alkali Silica Reaction Expansions of Cements

	ASR Expansion (%)			
	2	6	10	14
C0	0,096	0,146	0,176	0,184
C1a	0,094	0,137	0,169	0,186
C1b	0,096	0,149	0,187	0,208
C1c	0,110	0,163	0,182	0,222
C1d	0,114	0,169	0,192	0,212
C2a	0,040	0,066	0,086	0,107
C2b	0,034	0,056	0,080	0,104
C2c	0,032	0,052	0,080	0,097
C2d	0,032	0,061	0,075	0,100
C3a	0,083	0,123	0,154	0,170
C3b	0,089	0,112	0,143	0,160
C3c	0,098	0,125	0,136	0,160
C3d	0,109	0,134	0,156	0,170

The outcomes showed tht the ASR expansion values are lower than 0.2%, which is defined as a limit value on ASTM C-1260. ASR expansion value is increased by the increase of BOF slag percentage in the cement as shown C1 series sample (Table 5). However, the increase of BFS percentage in the cement resulted a decrease in ASR expansion value. The expansions of the BOF slag mortar specimens exposed to NaOH solution are given in [Figure 2].

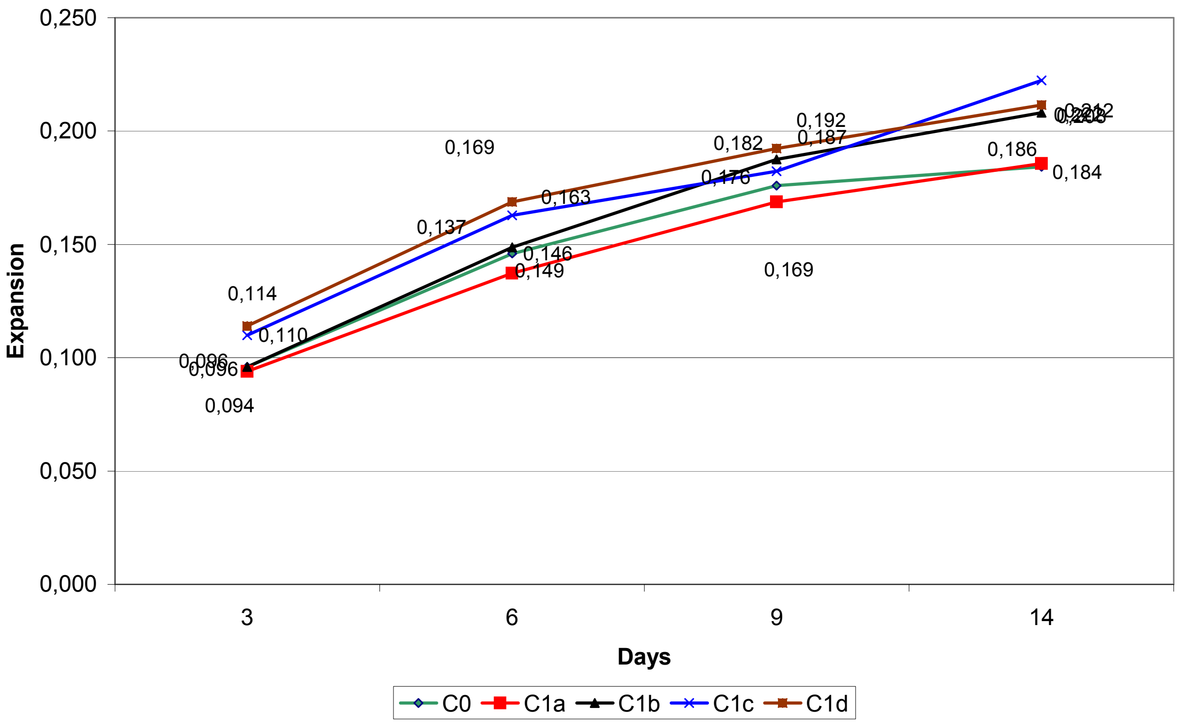


Figure 2: ASR Expansion of BOS slag

When C1 series ASR expansion value is investigated, the ASR expansion values found to be over than reference series. The reason for the high ASR expansion value is thought to be the ratio of CaO an MgO in BOF. BOF slag volumetric stability and leaching behavior caused the most concerns. The most important criterion is the volume stability, in which free CaO and MgO contents of the slag play an important role. The expansions of the BFS mortar specimens exposed to NaOH solution are given in [Figure 3].

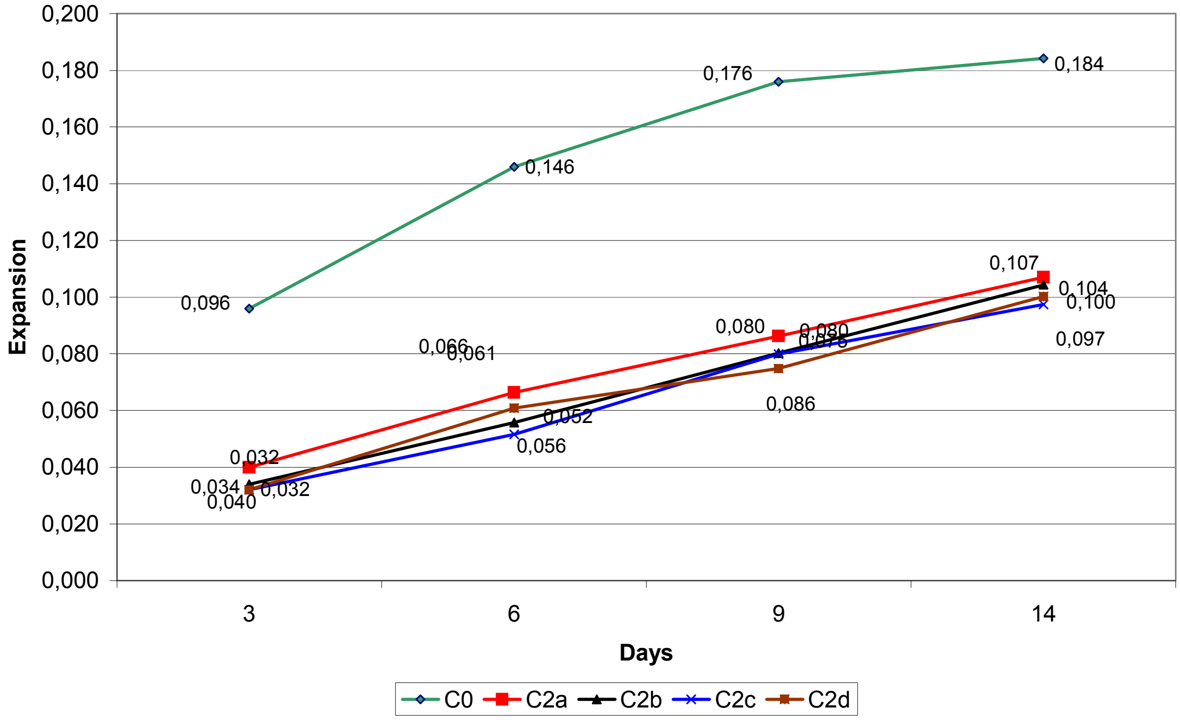


Figure 3: ASR Expansion of BFS

The value of ASR expansion is also below the limit value given by ASTM-C 1260. It is known that the existence of BFS reduced the ASR expansion value. Since puzzolans are less reactive and the reaction results include less amount of alkali than the Portland cement, they are addressed as solvent. Puzzolan cements have more effective W/C percentage than portland cement. Thus, the amount of alkali become more less, moreover puzzolans, decreases the amount of $Ca(OH)_2$ which also decrease the PH value. The expansions of the BOF slag and BFS mortar specimens exposed to NaOH solution are given in [Figure 4].

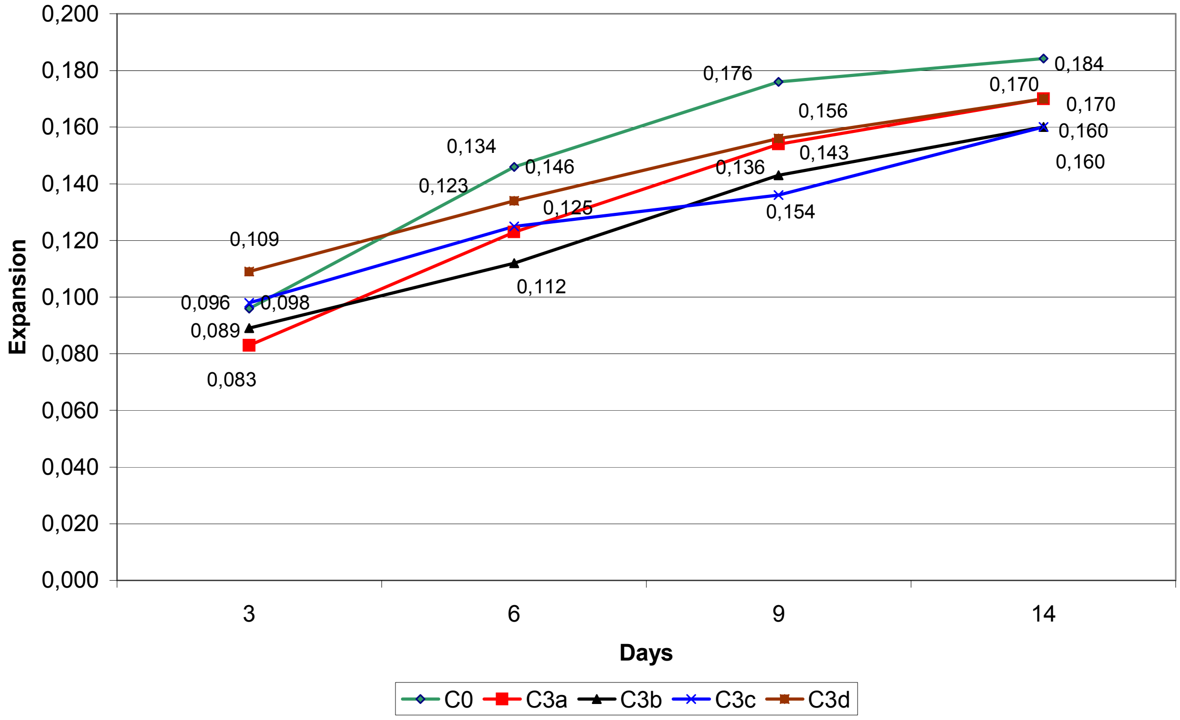


Figure 4: ASR Expansion of BOF slag and BFS

C3 Series resulted that existence of BFS eliminates the result of harmful effects of BOF slag. Also the ASR expansion values of C3 series are below the limit value of ASTM C-1260. In the literature there are studies which points out the harmfull effects of free CaO and MgO on expansion. This result also observed in this study. On the contrary, the existence of BOF slag has positive effects on durability properties of cement. Researchers especially emphasize that BOF slag effect are resistant to sulfates (Özkan, 2006; Özkan, 2008; Altun and Yılmaz, 2002). When cement-based materials are exposed to sodium sulphate attack, gypsum and ettringite are produced which can cause expansion in concrete. Formation of gypsum plays an important role in the damage of the material. Gypsum results in softening of the material. There is a close relationship between the $Ca(OH)_2$ content and gypsum formation (Torıı and Kawamura, 1994). Ettringite formation results in cracking and expansion of the material. Expansion is related to the water absorption of crystalline ettringite. The presence of a BOF slag results in an increase in the resistance to sodium sulphate attack (Özkan, 2008; Özkan and Yuksel, 2008).

Conclusion

BOF slag, which is environmentally dangerous material and has storage difficulties, has 65% usage in Europe, but in Turkey none. That it is really very important step to use environmental damaged BOF slag in other industries for sustainability point of view. Cement production can a new production line for BOF slag. This study shows that using BOF slag increase ASR expansion value of cement, which is harmful. But it has also has positive effects on the other durability properties of cement. In order to eliminate the harmful effects of BOF slag, other materials such as BFS can also be used in cement production. This study shows that durability properties of cement are at the required level when BOF slag and BFS are used together.
Using environmentally damaged BOF slag along with the other waste material, BFS, in production of cement material is very important in sustainability of waste management.

References

Altun I.A. & Yılmaz I. (2002). Study on steel furnace slag with high MgO as additive in portland cement. *Cement and Concrete Research.* 32, 1247–1249.
ASTM C-1260. Standard test method for potential alkali reactivity of aggregate, mortar-bar method.
Ichikawa T. and Miura M. (2007). Modified model of alkali-silica reaction. *Cement and Concrete Research*, 37, 1291–1297.
Sakai, K. Watanabe, H. Suzuki, M. Hamazaki, K. (1993). Properties of granulated last-furnace slag cement concrete, ACI Spec Publ SP, 132, 1367-1383.
Motz, H., Geiseler, J. (2001). Products of steel slags an opportunity to save natural resources. Waste Management, 21 (3), pp. 285-293.
Özkan, Ö. (2006). Heat effects on cements producing with GBFS and SS as additives. Journal of Materials Science, 41 (21), 7130-7140.
Özkan, Ö. (2008). Sulfate resistance of mortars produced with granulated blast furnace and steel slag additive cements. Gazi Üniversitesi Mühendislik Mimarlık Fakültesi Dergisi, 23(1), 1-8.
Özkan, Ö. & Yüksel, İ.(2008). Sulfate Resistance of Composite Potland Cements Containing Steel Slag and Granulated Blast Furnace Slag. 3rd International Symposium Sustainability in Cement and Concrete, 8-10 July, Dundee, Scotland.
Sahay, J., Nagpal, O. P. & Prasad, S. (2000). Waste management of steel slag, Steel Times International, 24 (2), 38-40.
Shi, C. & Qian, J. High (2000). Performance cementing materials from industrial slags- a review. Resources, Conservation and Recycling 29 (3), 195-207.
Shih, P.H., Wu, Z. Z. & Chiang, H.L. (2004). Characteristics of bricks made from waste steel slag. Waste Management. 24, 1043-1047.
Torii, K. & Kawamura, M. (1994). Effects of fly ash and silica fume on the resistance of mortar to sulfuric acid and sulfate attack. Cement and Concrete Research, 24, 361-370.
TS-EN 196-1. (2009). Methods of testing cement - Part 1: Determination of strength. Turkish Standards Institute, Ankara
TS-EN 196-3, (2002). Methods of testing cement-part 3: determination of setting time and soundness Turkish Standards Institute, Ankara.
TS-EN 196-6. (2000). Methods of testing cement;Part 6: determination of fineness. Turkish Standards Institute, Ankara.