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Heat effects on cements produced with GBSF and SS additives

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Abstract In this study, cement additives are developed by substituting granulated blast furnace slag and steel slag (SS) with the mixture of clinker–plaster. Mortar specimens of cement are prepared with these additives. Measurable properties of the series of cement additives such as the fineness moduli, Blaine values and specific gravities are computed before the casting. The Vicat setting times of specimens are determined according to the terms stated in TS EN 196-3 and the changes in their expansion levels are also detected. Furthermore, the cements produced and the mortar specimens casted are undergone thermal processes at the temperatures of 20, 100, 200, 300, 400, 500, 600, 700 and 800 °C, and mechanical and physical experiments are carried out for each series after the thermal processes. In all the series, sudden losses in strength are observed during the thermal process beyond 600 °C. Consequently, M3a series specimens that are produced with 80% clinker and gypsum in 12% blast furnace slag and 8% SS yield the best results in terms of compressive strength, elasticity modulus and decomposition.

Introduction

Occasionally, concrete structures are subjected to high temperatures (reactor vessels, thermal shock, fire, some industrial applications, coal gasification vessels, etc.). In most processes, such elevated temperatures seriously damage concrete structures and masonry walls [1]. By means of delaying heating, the basic components of the concrete (hydrate phase of CSH, calcium aluminates gels and CH) may be disintegrated, and this can result in deterioration of the physico-chemical properties of concrete [2].

As a result, many of the current studies focus on the effect of elevated temperatures on the mechanical properties of hardened concrete. Apart from the analyses regarding physical properties of concrete exposed to a medium temperature range [3], there are many articles investigating mechanical properties of the concrete heated to temperature levels up to 800 °C [4] or higher [5]. Previous studies have shown that strength and modulus of elasticity of hardened cement paste, mortar and concrete specimens decrease with the increase in temperature [6, 7]. Also searches have demonstrated that, at high temperatures beyond 300 °C, both strength and elastic modulus of hardened cement paste drop seriously [6]. In a recent study, Xu and Chung [7] have seen that addition of sand decreases the specific heat and increases the thermal conductivity of cement paste. Chan et al. [8] have shown that, at elevated temperatures, compressive strengths of both normal and high-strength concretes drop by more than 60% when the specimens are heated up to 800 °C. The effect of high temperatures on E-modulus is similar to the one on the compressive strength [9]. Flexural strength, on the other hand, is affected more by elevated temperatures than compressive strength [10].

The blast-furnace slag is a mineral by-product of the iron industry. It is used as a constituent of concrete and cement [11]. Granulated Blast Furnace Slag (GBFS) is

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known to possess a latent hydraulic property. The performance and use of ground GBFS have been studied for many years [12]. When GBFS is added to cement, it combines with the Portland (CH) released by cement hydration to give calcium silicate hydrate (CSH). Alkali salts activate this step, which increases the reaction rate. Some properties of the concrete containing GBFS, such as creep, shrinkage, strength to freeze-thaw resistant are still under discussion, but the use of the GBFS in cement and concrete has been proven to have many advantages [13]. Most of the properties of fresh and hardened concrete are enhanced by the addition of GGBFS to it [14]. GBFS's grinding technique affects geometric characteristics [15].

During the oxidation of steel pellets, steel slag (SS) is produced as a by-product in an electrical arc furnace. Steel slag, the residue of steel production process, is composed of silicates and oxides of unwanted elements in steel-chemical composition. Depending on the raw materials and the process, SS shows differences due to the phases of MgO, FeO and Fe_2O_3, which already exist in its structure [16]. This by-product, which mainly consists of calcium carbonate, is broken into smaller sizes to be used as aggregates in asphalt and concrete. They are especially useful in areas where good quality aggregate is hard to come by [17]. The most important criterion is the volume stability, in which free CaO and MgO contents of the slag play an important role. Both of these oxides can react with water. Hydration causes volume expansion and it affects volume stability [18].

In this study, a cement is produced by substituting GBFS and SS with clinker–gypsum. For this purpose, mortar specimens of the cement are prepared, and the mechanical and physical changes have also been observed when the specimens are exposed to temperatures from 20 to 800 °C.

Experimental study

Materials

Clinker and Gypsum are supplied from Lafarge–Ereğli (Karadeniz, Ereğli, Turkey) Cement Factory while SS and GBFS are provided by the Ereğli Iron and Steel Works Factory (Karadeniz, Ereğli, Turkey). Table 1 shows the chemical compositions of these materials, which are obtained in the X-ray lab. Figure 1 depicts the photographs of granule SS with a size of 90 μm both (a) under-griddle and (b) above-griddle, and XRD graph is given in Fig. 2. Clinker, gypsum, SS and GBFS used in the study are all in granule size.

From Fig. 2, it can be seen that metallic iron and ferric oxide (FeO and Fe_2O_3) phases are observed in the structure of SS despite the application of magnetic separation, and Ca–Si–Fe–O phases are also determined to be densely available in the structure.

Sand in rilem-cembureau standard is used in this study [19], and is silica sand whose gradient and chemical composition are presented in Table 2. As for the water, Zonguldak City tap water is utilized and is determined to have a pH value of 7.6 and a hardness of 12.8.

Methods

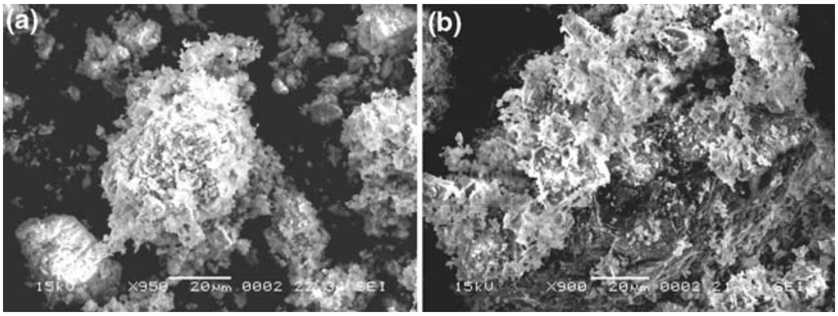
SS and GBFS are substituted first with the mixture of clinker–gypsum and then separately, and four main groups of cement are formed from these substitutions. The first group is coded as the reference group and named as M0, in the second group (M1) Clinker–gypsum mixture is substituted with GBFS, on the other hand Clinker–gypsum mixture is replaced with SS in the third group M2, and finally in the last group (M3) Clinker–gypsum mixture is substituted with the composition of GBFS 3/5 and SS 2/5. Table 3 shows the composition ratios of the mixtures used in our study. All the main groups, except for the reference group (M0), are also divided into sub-groups and symbolized by letters (a, b, c etc) with respect to changing ratios of compositions; for instance code M3c denotes that this material is composed of 40% of Clinker–gypsum, 36% of GBFS and 24% of SS.

The materials used in this study are supplied in granule size as are the outputs of factory. Each material is grinded for different time durations (Clinker for 3 h, GBFS for 4, and SS for 3 h) and specific surface value of 2400–2500 cm^2/g is achieved. The materials are mixed with each other in specified

Table 1 Chemical compositions of Clinker, Gypsum, GBFS and SS (wt.%)

Material	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	SO_3	P_2O_5	LOI
Clinker	66.11	21.57	3.17	5.09	1.74	1.35	–	0.77
Gypsum	32.57	0.67	0.24	0.21	2.2	46.56	–	22.98
GBFS	37.80	35.1	0.70	17.54	5.5	0.70	0.009	1.08
SS	58.53	10.72	15.30	1.71	4.27	0.04	0.92	1.11

Fig. 1 SEM photographs of steelworks slags (**a**) 90 µm under-griddle (**b**) 90 µm above-griddle



amounts, and then they are grinded again to achieve specific surface value of 3100–3300 cm^2/g, thus yielding the cements used in the tests. Experiments are conducted to determine Vicat time and the expansion amount of these cement mortars in compliance with TS-EN 196-3 [20].

Mortar specimens are produced in accordance with Turkish Standard TS EN 196-1 [19]. Mortar bars used in this study are of 40 × 40 × 160 mm dimension. They are prepared with cement mixtures given in Table 3, standard rilem-combreau sand and tap water with the proportions of 1, 3 and 0.5, respectively, The ratio of W to C is taken as 0.5 complying with TS EN 196-1. The ratio of W to C is taken as 0.5 complying with TS EN 196–1. Specimens were first cured in a fog room at 20 °C for 24 h, and then demoulded and cured in water at 20 ± 3 °C until 28th day.

Mortar specimens produced for this study are cured at 20 ± 3 °C for 28 days and kept at 60–70% relative humidity after curing until the 90th day. After 90 days these specimens are subjected to temperatures of 100, 200, 300, 400, 500, 600, 700 and 800 °C in a furnace with a volume of 9 (lt) dm^3 and the rate of heating of 6 °C/min until they reach the specified temperatures, except for one specimen, which is only kept at 20 °C, so that this can be the reference specimen.

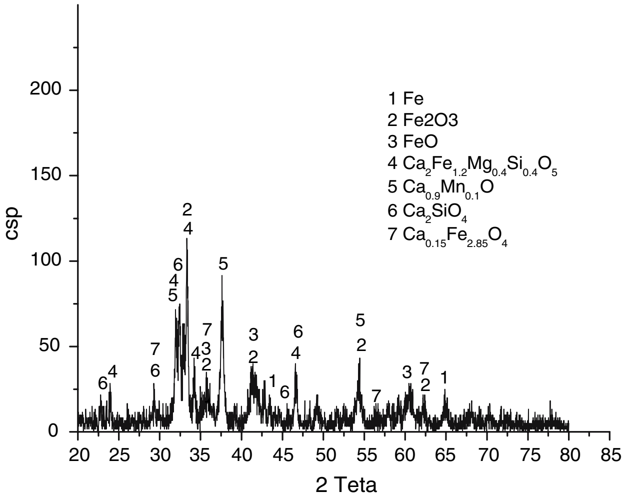


Fig. 2 XRD graph for SS after magnetic separation

The specimens are cooled in a laboratory (in air) with 60–70% relative humidity for 24 h after inflicting high temperatures to them. They are examined with respect to their compressive strengths and dynamic elasticity modulus. Compressive strength measurements are made by using computer controlled compression machine and the loading speed for this measurements is chosen to be 1 kN/s. Ultrasonic test apparatus is used for the computation of elasticity modulus and has a pulse generator with the frequency of 54 kHz.

Result and discussions

Physical properties

The physical properties of 11 different cements produced are shown in Table 4, and also Vicat setting time, end time and volume expansion values are illustrated in Table 5.

When specific surface values of the cements are examined, it is found that GBFS has much harder structure than SS and hardly grinded. GBFS 2400–2500 cm^2/g reaches the required fineness after 4 h of grinding when SS takes only 3 h for this fineness. The reference cement (M0) produced as Portland cement has a softer structure than the others. Thus, in grinding separately, it can easily be said that GBFS and SS 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 residue materials (GBFS and SS) replaced with clinker have lower specific gravity values.

It is strongly emphasized in the researches that volume expansion in SS may bring about undesired results. Amounts of free CaO and MgO in SS are of immense importance when volume is fixed. The reaction of both oxides with water has an effect on volume fixation [18].

Table 2 Sand gradient

Chemical compositions	%	Griddle pore size (mm)	Remaining %
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		

When the results are examined, it is seen that cements produced with SS has higher volume expansion values. Although the cements with SS additive cater for the largest volume expansion, this is still within the limits of the standard of TS EN 196-3.

When Vicat setting times and end times are taken into consideration that it is seen that cements with additives (M1, M2, M3) enter reaction slower than the reference cement (M0) does. As can be seen in Table 5, the control specimen M0 is obtained by clinker–gyps mixture, and has the shortest initial and final setting time. The setting times increase with the increase in the amount of additive. The initial and final setting times of M0 and M3d (30% Clin. + Gyps. 42% GBFS 28% SS) are measured to be $3^h\ 5^m$–$4^h\ 10^m$ and $4^h\ 20^m$–$5^h\ 40^m$, respectively. Both M1 (GBFS additive) and M2 (SS additive) specimens series have the similar effects on setting times when compared with each other. Chemical properties of the additives (MgO and Al_2O_3 content) and granule sizes may be the reason for this slow reaction [16, 18].

Compressive strength at 20 °C

Figure 3 illustrates the compressive strengths obtained at 20 °C for 90th day.

Table 4 Physical characteristics of cements

Specimen codes	Fineness (wt.%)		Specific surface cm^2/g	Specific gravity
	>32 μm	>90 μm		
M0	21.00	0.90	3,330	3.12
M1a	21.20	1.10	3,115	3.05
M1b	21.90	1.15	3,108	3.01
M1c	21.80	1.15	3,090	2.95
M2a	21.15	1.18	3,214	3.06
M2b	22.10	1.00	3213	3.02
M2c	22.15	1.25	3,152	2.97
M3a	22.25	1.25	3,138	3.05
M3b	22.50	1.45	3,028	3.01
M3c	22.55	1.55	3,055	2.96
M3d	22.40	1.45	3,077	2.93

In examining Fig. 3, it can readily be seen that M3a coded specimens have shown the best compressive strength level at 20 °C. In the analysis of 90th day compressive strengths, the better results are obtained from the series of M1b (40% GBFS replacement) than the control series. Pleasing results are not obtained from M2 series, which use SS alone. In M3b (60% Clin–Gyp. 24% GBFS 16% SS) series, using GBFS and SS together, the replacement yields better results than the control series. The series in which GBFS and GBFS–SS are replaced with clinker–gypsum, namely M1 and M3, produce the results with higher strength values than the reference, including the replacement ratio of 40%, while the series with replacement ratio of 60% yield the results with lower strength values than the reference. Also, the specific surface values of the cement decrease as the addition level increases and this situation is one of the reasons for the decrease in strength level. The strength development of the mortars at 20 °C depends primarily on the cement mixture compositions, and secondarily on the cements fineness. The replacement ratio can be taken to the levels of 60–70% with more grinding the GBFS and SS used in the replacement. Thus, higher compressive strength than

Table 3 Composition of cement mixtures

Specimen codes	Material composition	Clin. %	Gyps. %	GBFS %	SS %
M0	100% Clinker	95.0	5.0	0	0
M1a	80% Clin.–Gyps. + 20% GBFS	76.0	4.0	20	0
M1b	60% Clin.–Gyps + 40% GBFS	57.0	3.0	40	0
M1c	40% Clin.–Gyps + 60 %GBFS	38.0	2.0	60	0
M2a	80% Clin.–Gyps. + 20% SS	76.0	4.0	0	20
M2b	60% Clin.–Gyps. + 40% SS	57.0	3.0	0	40
M2c	40% Clin.–Gyps. + 60% SS	38.0	2.0	0	60
M3a	80% Clin.–Gyps. + 12% GBFS + 8% SS	76.0	4.0	12	8
M3b	60% Clin.–Gyps. + 24% GBFS + 16% SS	57.0	3.0	24	16
M3c	40% Clin.–Gyps. + 36% GBFS + 24% SS	38.0	2.0	36	24
M3d	30% Clin.–Gyps. + 42% GBFS + 28% SS	28.5	1.5	42	28

Table 5 Volume expansion and Vicat setting time of cements

Specimen codes	Vicat setting time (h:min)		Volume expansion (mm)
	Initial	Final	
M0	3:15	4:10	0.5
M1a	4:10	5:40	1.0
M1b	4:20	5:30	1.0
M1c	4:30	6:00	1.0
M2a	4:00	4:50	1.0
M2b	4:20	5:30	1.0
M2c	4:30	5:40	2.0
M3a	4:10	5:30	0.5
M3b	4:30	5:20	1.0
M3c	4:40	5:40	1.5
M3d	4:20	5:40	1.5
TS EN 196-3	1:00	10:00	max. 10

the reference specimen can be achieved in larger replacement ratios.

Compressive strength at elevated temperature

In 90th day, the mortar specimens are kept in the furnace at 100, 200, 300, 400, 500, 600, 700 and 800 °C. For the purpose of having a reference for the mortars kept at high temperatures, one group of mortar specimens is not subjected to these high temperatures. Specimens are taken out when the furnace has reached the desired temperature. These heated specimens are left to cool in a laboratory (in air) with a relative humidity of 60–70% for 24 h after which their compressive strengths are measured.

Figure 4 depicts the compressive strength test results for different temperatures.

In Fig. 4, M3a series supply the best compressive strength levels after the measurements carried out at all given temperatures. The strength levels tend to show similarities in all temperature groups.

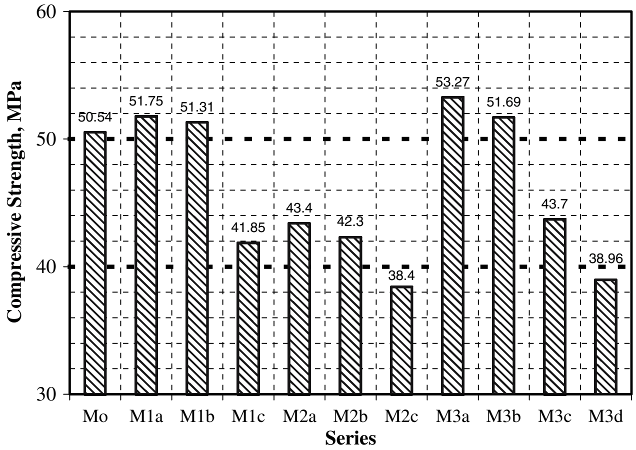


Fig. 3 Ninetieth day compressive strengths at 20 °C

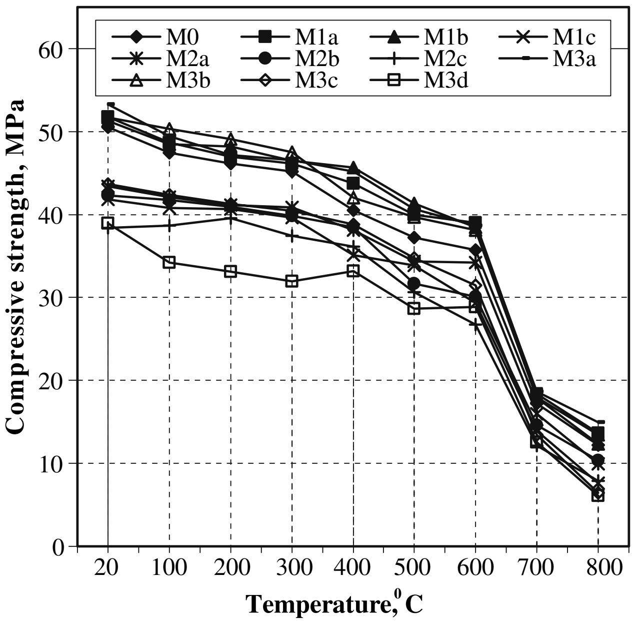


Fig. 4 Ninetieth day compressive strengths for different temperatures

Concrete contains capillary water, physically absorbed water and interlayer and chemically bound water in C–S–H and $Ca(OH)_2$. During the heating process, cement paste dries and consequently water makes its way out and evaporates. In other words, at 100 °C free water moves away from its medium [21].

Evaporated water is eliminated rigorously [22], otherwise it will affect the phases surrounding the cement paste. Evaporation creates a high pressure in the paste mainly due to flow resistance and high temperature.

Decomposition of $Ca(OH)_2$ begins at temperatures above 400 °C. At about 600 °C all the mixtures are almost completely dehydrated. At temperatures over 600 °C, as applied in this study, the C–S–H gels, used as the binders, which are the main source of concrete strength, undergo dehydration and lose cementing ability [22, 23]. $Ca(OH)_2$, one of the most important compounds in cement paste, turns into CaO at 530 °C. An almost 33% of shrinking is reported to be inevitable during this process [24].

The residual compressive strength following heating at different temperatures T is expressed as a ratio F_T/F_{20}, where F_T is the strength after heating at "T °C" and F_{20} is the initial strength of concrete at "20 °C". The strength ratio F_T/F_{20} as a function of the specimens' temperature T is shown in Table 6.

Table 6 Relative residual compressive strength of specimen series

	F_T/F_{20}								
	20 °C	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
M0	1.00	0.94	0.91	0.89	0.80	0.74	0.71	0.34	0.24
M1a	1.00	0.94	0.91	0.89	0.84	0.77	0.75	0.35	0.26
M1b	1.00	0.94	0.94	0.91	0.89	0.81	0.75	0.35	0.26
M1c	1.00	0.97	0.97	0.95	0.84	0.81	0.70	0.33	0.18
M2a	1.00	0.97	0.95	0.94	0.88	0.79	0.79	0.37	0.23
M2b	1.00	0.99	0.97	0.94	0.91	0.75	0.71	0.35	0.25
M2c	1.00	1.01	1.03	0.98	0.94	0.80	0.70	0.32	0.21
M3a	1.00	0.93	0.89	0.87	0.85	0.76	0.73	0.35	0.28
M3b	1.00	0.97	0.95	0.92	0.81	0.77	0.74	0.35	0.24
M3c	1.00	0.97	0.94	0.93	0.89	0.80	0.72	0.31	0.15
M3d	1.00	0.88	0.85	0.82	0.85	0.74	0.74	0.32	0.16

The specimens are taken out of the furnace when the internal temperature of furnace reaches 100 °C, and left to cool in air for 24 h. The residual compressive strengths at this temperature are measured and, as can be seen from Table 6, the value of 0.97 is obtained for M1c, 1.01 for M2c and 0.97 for M3c while the reference specimen reads out the value of 0.94. The lowest residual value, however, is attained by M3d series. As the researchers have underlined that the compressive strengths of specimens subjected to temperatures 100–200 °C are close to or higher than those subjected to 20 °C [21, 25]. Similar results are also observed in this study.

In investigating the residual values at 200 and 300 °C, M1c, M2c and M3c series are found to produce higher values than the reference series as is the case at 100 °C. This can be attributed to the deduction by Savva et al. [21] that for the pozzolanic material an additional to bermorite gel is formed as a result of the pozzolanic reaction of $Ca(OH)_2$ in OPC, with reactive silica in pozzolanic material. They also quote that the strength increases at temperatures up to 300 °C.

The researches conducted so far express that the decomposition of $Ca(OH)_2$ structure in cement initiates at temperatures above 400 °C [21, 25]. Aköz and co-workers [24] have stated that this disintegration materializes completely at 530 °C with a loss rate of about 33%. In this study, general loss rate is found to be 20% in view of examining the residual compressive strength values at 400 °C with M1b and M3d having the highest values. At 500 °C, however, the loss rate slightly goes up to 25% on average, approaching the rate found by the above researchers.

Structural damage is reported to be apparent due to the degradation of $CaCO_3$ at above 600 °C [25, 26]. It is observed in this study that the compressive strengths experience a loss of about 30% in mortar specimens subjected to 600 °C, and losses of 65% and 80% at 700 and 800 °C, respectively. Also observed in this study are the abrupt and large decreases in the residual compressive strengths above 600 °C due to the fact stated by many researches that C–S–H gels lose their cementing ability at above 600 °C.

In general point of view, all the specimen series exhibit similar tendencies. The series begin to lose out in the compressive strength at 400 °C and above, along with sudden losses above 600 °C. All the by-products show analogous attitudes in examining the effect of substituting materials on compressive strength. In detail, the residual compressive strength is observed to be higher at temperatures up to 500 °C than the reference in the series with 40–60% replacement values while it remains at the same level as the reference at 600, 700 and 800 °C.

E-Modulus at elevated temperature

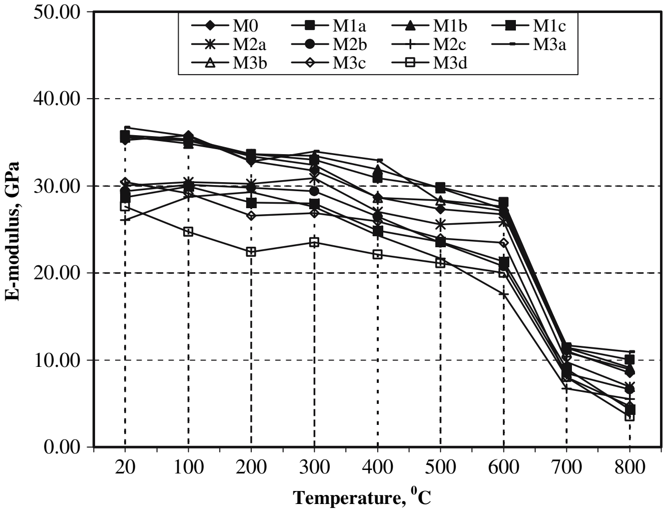
The modulus of dynamic elasticity of the mortar specimens, exposed to different temperatures, is computed using Eq. 1 by measuring the ultrasound penetration velocities of the specimen series and the results from this computation are charted in Fig. 5. The measurements are conducted on the specimens after they are taken out of the furnace and cooled in air for 24 h as in the compressive strength tests.

$$E_{\mathrm{d}} = 10^4 \times V^2 \times \frac{\beta}{g} \qquad (1)$$

E_{d} = Dynamic elasticity modulus
V = Ultrasound penetration velocity
B = Density
g = Gravitational force

It would be wrong to attribute the changes in concrete occurring owing to the effect of high temperature to solely compressive strength. The

Fig. 5 Ninetieth day E-modulus values for different temperatures



temperature-dependent damage to the hydration products integrity is caused by the hydrate phase dewatering with the consequent air voids formation inducing the pore structure coarsening. This is clearly confirmed by pore median radius increases with a rise in temperature. The higher the temperature, the more intense dewatering of hydration products and the more increase in large pore volume [25, 26]. Ghosh and Nasser [27] have found that a decrease in elastic modulus is due to a gradual deterioration of the binding matrix with a rise in temperature In the same work, the transformation of the matrix is seen to be purely physical at lower temperatures up to 71 °C, where small lumps of CSH gel are coalesced together to form a larger deforming gel mass. However, at further higher temperatures, chemical transformation of the gel is observed where the fairly dense lumps of CSH gel have undergone changes to form a loose white matrix that brings about loss of elasticity of the concrete.

In Fig. 5, E-modulus values are shown, and the results given here are analogous with those of compressive strength.

The residual E-modulus after heating at different temperatures T is expressed as a ratio E_T/E_{20}, where E_T is the strength after heating at "T" in °C and E_{20} is the initial strength of concrete at "20 °C". The strength ratio F_T/F_{20} as a function of the specimens' temperature T is shown in Table 7.

The highest residual E-modulus for the mortar specimens subjected to 100 °C is computed to be of M2c series with a value of 1.10. In conjunction with the compressive strength, E-modulus is obtained to be higher at 100 °C than that at 20 °C, which is also confirmed in literature [21, 25, 26]. Even though the compressive strengths are only higher at 100 and 20 °C, E-modulus is found to also have higher values at 200 and 300 °C, which M2 group mortars (SS replacement) produce higher E-modulus than that at 20 °C.

Table 7 Relative residual compressive strength of series

	E_T/E_{20}								
	20 °C	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
M0	1.00	1.02	0.93	0.90	0.81	0.77	0.76	0.31	0.24
M1a	1.00	0.99	0.94	0.92	0.86	0.83	0.78	0.32	0.28
M1b	1.00	0.98	0.94	0.94	0.89	0.83	0.77	0.32	0.26
M1c	1.00	1.04	0.98	0.97	0.87	0.82	0.74	0.31	0.15
M2a	1.00	1.01	1.01	1.03	0.90	0.85	0.86	0.33	0.23
M2b	1.00	1.03	1.01	1.00	0.90	0.80	0.71	0.29	0.22
M2c	1.00	1.10	1.12	1.06	0.93	0.83	0.67	0.26	0.21
M3a	1.00	0.97	0.89	0.93	0.90	0.77	0.74	0.32	0.30
M3b	1.00	0.99	0.94	0.91	0.81	0.80	0.78	0.31	0.25
M3c	1.00	0.96	0.87	0.88	0.85	0.79	0.77	0.26	0.15
M3d	1.00	0.89	0.81	0.85	0.80	0.76	0.72	0.29	0.13

E-modulus at 400 and 500 °C is on the decrease, which is emphasized in the literature [21, 25, 26] to be resulted from the pores in the structure of mortar. Decompositions in $Ca(OH)_2$ structure probably cause the E-modulus to a decrease, which reaches a level of 70% above 600 °C (i.e. 700 °C) as is the case in the compressive strength. Thus, this means that the cement loses its ability to form a mortar.

In the investigation of E-moduli on the by-products used in replacement after exposing to high temperatures, the M2 group mortars are found to yield higher residual values up to 300 °C than the others. Beyond this temperature, however, all the mortar series begin to demonstrate similar behaviour.

Microstructure examination

This section of the study focuses on structural variations of the reference and specimen groups with 40% replacement at the temperatures of 20, 600 and 800 °C by employing SEM photographs of the material. Figures 6, 7, 8 and 9 illustrate the SEM photographs of M0, M1b, M2b and M3b specimen series, respectively, enlarged 500 times (500×).

The reference concrete (M0) is seen to have evenly distributed in the matrix of hydration products and interlayer of aggregate matrix at normal medium temperature (Fig. 6a). In Fig. 6b (at 600 °C) it is observed that $Ca(OH)_2$ begins to degrade and to crack with the expansion of silica aggregate. At 800 °C (Fig. 6c), crak size in aggregate crack increases as well as in matrix crack. These observed cracks can be explained by the decrease in the compressive strength and E-modulus.

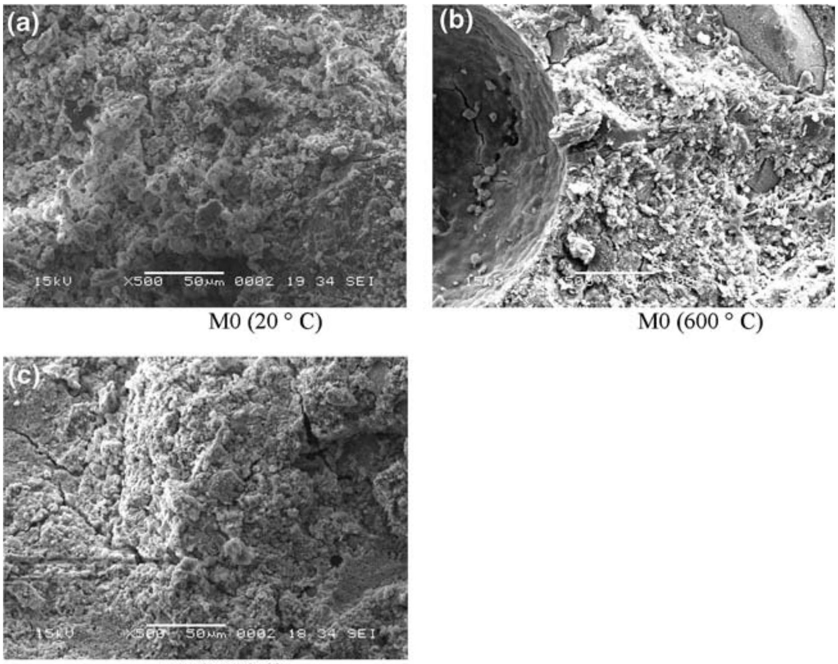
The crack size in M1b is observed to be smaller than the reference specimen after high temperature. Compared with the reference specimen, in terms of compressive strength and E-moduli, better results are achieved for this series in which GBFS is replaced at a rate of 40%. The photographs seem to support these findings.

At normal medium temperature (20 °C) M2b specimen is observed to form stratified and ettringite $Ca(OH)_2$ crystals in its structure. At 600 and 800 °C temperatures, it is found that $Ca(OH)_2$ is degraded, the water in its body dispersed, calcium silicate hydrate fibres formed and porous structure developed. This series of specimen produces craks as the reference specimen does at 600 and 800 °C, but not as large in size as those of the reference.

At normal medium temperature (20 °C) M3b specimen is also observed to have stratified and ettringite $Ca(OH)_2$ crystals in its structure as in the other series The mortar structures form calcium silicate hydrate fibres at 600 and 800 °C. This series of specimen produces smaller size of craks than the reference specimen after being exposed to high temperatures.

In all the SEM photographs, the decompositions are clearly observed to occur at 600 and 800 °C, and the cracks result from these decompositions. The crack

Fig. 6 SEM photographs of M0 reference specimen

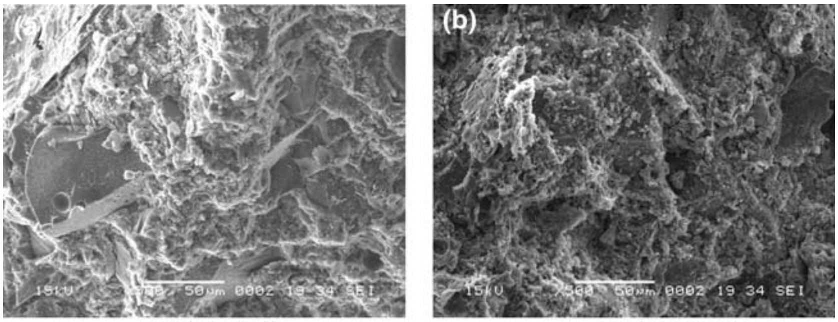


M0 (20 ° C)

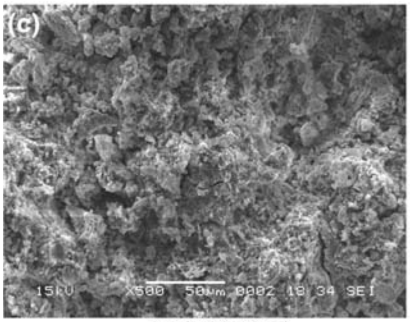
M0 (600 ° C)

M0 (800 ° C)

Fig. 7 SEM photographs of M1b specimen



M1b (20 ° C) M1b (600 ° C)

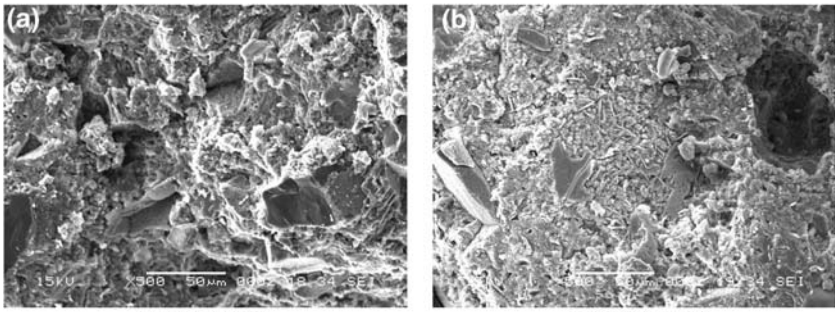


M1b (800 ° C)

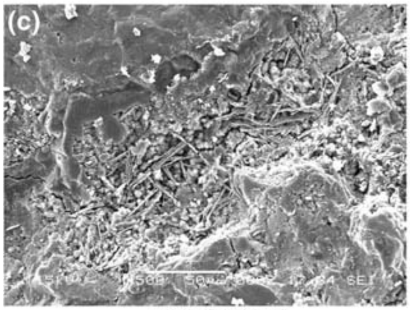
sizes generally are also examined in these tests, and of all the cracks, the largest size is found to come from the reference specimen. The above figures illustrating the SEM photographs support the residual compressive strength and moduli values.

GBFS and clinker interact each other. The ettringite amount formed during the hydratation is larger than the portland cement, and this difference is resulted from that the gypsum reacts with both C_3A found in clinker and alumina phase in slag. In XRD analysis of the cement with slag, the finding that the area under the C–S–H peak is 30% bigger than that under the portland cement indicates that C–S–H gel is formed by the hydratation of slag [28]. This can be attributed as

Fig. 8 SEM photographs of M2b specimen

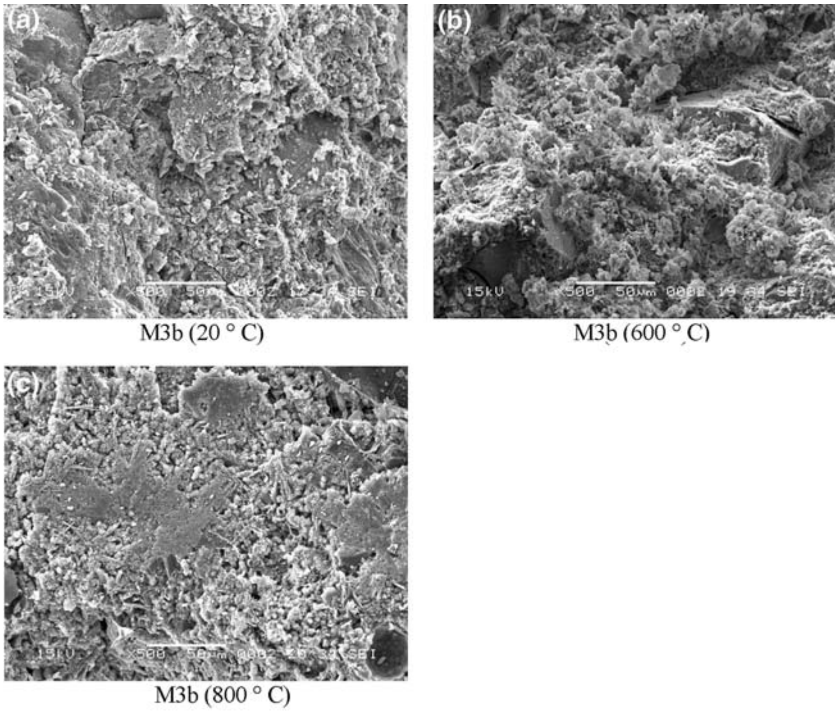


M2b (20 ° C) M2b (600 ° C)



M2b (800 ° C)

Fig. 9 SEM photographs of M3b specimen



the cause that the slag mixes, with up to somewhat a certain mixing ratio, increase compressive strength and strength at high temperatures.

In general the strength of cements with replacement ratios of below 70% reportedly depends on the characteristics of clinker while in the replacements of above this ratio it depends on the reactivity and fineness of slag [28]. In this study, it is found that the compressive strength and strength at high temperatures are reduced with the increase in replacement ratio, and this can be affiliated to the above-mentioned cause.

Conclusions

In this study, M3a series specimens are concluded to have the best values in terms of the criteria explained in the previous sections. These specimens (M3a) are produced by substituting GBFS and SS with clinker–gypsum additive (80% clinker–gypsum and 12% granulated blast furnace slag and 8% SS ratios to be exact) and have 3.05 specific gravity, 3,138 cm^2/g Blaine value, and proper plug duration and expansion change levels according to the standards and have 53.27 MPa compressive strength level at 20 °C.

It can also be concluded as follows:

- When GBFS and SS are used separately and together, they delay the plug duration.
- As the additive level increases, a decrease in the specific surface values of the cement is observed. This situation also affects the strength levels.
- M1 and M3 series with up to 40% replacement ratios give better result than the control series M0. As a result GBFS can be used both alone and together SS up to 40% replacement as an additive in cement production.
- GBFS and SS may be produced in a finer form by grinding them into powder in the grinding machine so that the loss of strength can be reduced.
- Residual compressive strength values are obtained to be higher at 100–200 °C than those at 20 °C in the mortars exposed to different temperatures, and to experience loss strength at 400 °C with a sudden decrease at 600 °C. At 800 °C, however, the specimens lose their mortaring characteristics.
- The E-moduli results are also consistent with the compressive strength results and support the findings from the SEM photographs.

This study underlines that, economic contribution can be achieved through using the recycled granulated blast furnace slag and SS that are otherwise industrial wastes in the process of cement production.

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References

1. Cülfik MS, Özturan T (2002) Cem Concr Res 32:809
2. Vodak F, Trtik K, Kapickova O, Hoskova S, Demo P (2004) Constr Build Mater 18:529
3. Mond Zain MF, Radin SS (2000) Cem Concr Res 30:1283
4. Saad M, Abo-El-Enein SA, Hanna GB, Kotkata MF (1996) Cem Concr Res 26:669
5. Chan YN, Luo X, Sun W (2000) Constr Build Mater 14:261
6. Dias WPS, Khoury GA, Sullivan PJE (1990) ACI Mater J 87:160
7. Xu Y, Chung DDL (2000) Cem Concr Res 30:59
8. Chan YN, Luo X, Sun W (2000) Cem Concr Res 30:247
9. Felicetti R, Gambarova P (1998) ACI Mater J 95:395
10. Zhang B, Bicanic N, Pearce CJ, Balabanic G (2000) ACI Mater J 97:556
11. Moranville-Regourd M (1998) Cements made from blast-furnace slag. Lea's Chemistry of Cement and Concrete Ed. P.C p 633
12. Tan K, Pu X (1998) Cem Concr Res 28(12):1819
13. Sakai K, Watanabe H, Suzuki M, Hamazaki K (1993) ACI Spec Publ SP 132:1367
14. Hogan FJ, Muesel JW (1981) Cem Concr Aggr 3(1):40
15. Wan H, Shui Z, Lin Z (2004) Cem Concr Res 34:133
16. Xuequan W, Hong Z, Xinkai H, Husen L (1999) Cem Concr Res 29:983
17. Maslehuddin M, Alfarabi M, Sharif M, Shameem M, Ibrahim MS (2003) Constr Build Mater 17:105
18. Altuna IA, Yılmaz I (2002) Cem Concr Res 32:1247
19. Turkish Standards (2002), TS-EN 196-1, Turkish Standards Institute, Ankara
20. Turkish Standards (2002), TS-EN 196-3, Turkish Standards Institute, Ankara
21. Savva A, Manita P, Sideris KK (2005) Cement Concr Compos 27:239
22. Castillo C, Durrani AJ (1990) ACI Mater J 87:47
23. Mehta PK, Monteiro PJM (1993) Concrete: structure, properties and materials. Prentice-Hall, Englewood Cliffs NJ
24. Yüzer N, Aköz F, Dokuzer Öztürk L (2004) Cement Concrete Res 34:1803
25. Janotka I, Mojumdar SC (2005) J Thermal Anal Calorimetry 81:197
26. Janotka I, Bágel L (2002) ACI Mater J 99:196
27. Ghosh S, Nasser K (1996) ACI Mater J (Jan–Feb): 51–60
28. Regourd M (1986) Slags and slags cements, cement replacement materials. Surrey University Press, p 73