HBRC Journal (2013) 9, 118–124

Housing and Building National Research Center

HBRC Journal

http://ees.elsevier.com/hbrcj

Hydration characteristics of Portland cement – Electric arc furnace slag blends

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Received 17 September 2012; accepted 4 December 2012

KEYWORDS

Electric arc furnace slag;
Portland cement;
Hydration;
Compressive strength

Abstract Utilization of electric arc furnace slag (EAF slag) as blending material for Portland cement has been examined. This was done via the investigation of the hydration characteristic of EAF slag – Portland cement blended mixtures. Various ratios of EAF slag were used namely; 5, 10 and 20 wt% of solid mix. The hydration properties investigated for the various mixtures were; compressive strength, chemically combined water and free lime contents as a function of hydration times. The hydration ages were; 1, 3, 7, 28 and 90 days. In addition, phase composition of the formed hydrates was examined using XRD technique as well as differential thermal analysis (DTA) for some selected samples. The results showed that as the ratio of EAF slag increases the values of compressive strength decrease at all the hydration ages. Hydration kinetics of the investigated mixes was followed by determining the variation of free lime and chemically combined water contents with time of hydration. It was observed that hydration proceeds in four different stages. The values of chemically combined water of the cement pastes blended with EAF slag were less than those of the neat Portland cement paste at all hydration ages. The mode of variation of free lime content with time was nearly similar to that of combined water content. The results of chemically combined water, free lime, XRD analysis as well as thermal analysis were correlated well with those of compressive strength. All these results indicate that the used EAF slag has no significant pozzolanic reactivity.

Introduction

Slag in general is a byproduct of various metals extraction and refining processes. In the specific case of making steels, the slag is generated at 3 different stages of processing and accordingly classified as: blast furnace slag, electric arc furnace slag and ladle slag [1]. It is well known that technical, economical and

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Peer review under responsibility of Housing and Building National Research Center.

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http://dx.doi.org/10.1016/j.hbrcj.2013.05.006

many environmental benefits are obtained from using alternative construction materials [1–2]. Since the Kyoto Protocol entered into force on February 2005, 35 countries have the obligation of reducing their gaseous emissions between 2008 and 2012 in order to achieve a target of greenhouse effect gas emissions of 8% reduction (CO_2, methane, nitrous oxide, etc.), including CO_2 which represents 80% of the total harmful gases.

Construction is one of the most affected industrial sectors because of its relationship with cement and concrete industries. The environmental regulations, that increase their severity day by day, have made these industries to put in a great effort to reduce their pollution, that is mainly caused by the process of calcite decarbonation that leads to the formation of about 480 kg of CO_2/ton of clinker.

Looking for a reduction of atmospheric contamination, has been and is the cause of looking for new complementary and alternative building materials to substitute traditional ones, this being a priority research line [3,4]. The building sector by their characteristics has enough capacity to recycle large volumes of by-products and wastes generated in different industrial activities, like silica fume, fly ash or blast furnace slag and electric arc furnace slags [5,6].

Several studies have been made to examine the characteristics of EAF oxidizing slag with respect to its application in the construction industry, in particular of its attributes as a material [7,8], its potential expansiveness [9] and its chemical reactivity [10]. The possibility of EAF slag being used satisfactorily in concrete has been demonstrated [11,12]. The principal problems in this field remain the durability of this type of concrete [13,14] and its environmental tolerance [15]. Correctly manufactured EAF slag concrete has good mechanical properties, and its high density is an advantageous property where weight is a key factor, in such constructions as breakwater blocks, foundations, shoring walls, noise barriers, and radiation insulators, among others.

A detailed study has been reported to define and analyze the properties of EAF oxidizing slag, its performance as an aggregate, and the attributes of the concrete in which it is a component [16]. The manufacturing process and results related to the physical and mechanical properties of this type of concrete have also been presented [17].

In the present paper, a further aspect is examined to evaluate the addition of EAF slag to Ordinary Portland cement for producing cement containing an industrial waste with the same specification and more environmental friendly products.

Materials and experimental

Materials

EAF slag

The EAF Slag used in this study was supplied from Ezz Flat Steel Company, Egypt, its chemical composition is shown in Table 1.

Ordinary Portland cement (OPC)

OPC was supplied from Suez Cement Company, Egypt, with a Blaine surface area of 2945 $cm^2\ g^{-1}$; its chemical oxide composition is given in Table 2.

Table 1 EAF slag chemical oxide composition, wt%.

Oxides	CaO	SiO_2	AL_2O_3	Fe_2O_3	MgO	SO_3
	33	13.1	5.51	36.8	5.03	0.14
Oxides	K_2O	P_2O_3	Cr_2o_3	Mn_2O_3	TiO_2	LOI
	–	0.7	0.8	4.18	0.6	–

Table 2 OPC chemical oxide composition, wt%.

Oxides	CaO	SiO_2	AL_2O_3	Fe_2O_3	MgO	SO_3
	61.28	20.46	5.14	3.53	2.80	2.82
Oxides	K_2O	P_2O_3	$Cr_2\ O_3$	Mn_2O3	TiO_2	LOI
	0.11	0.20	0.060	0.11	0.33	3.15

Experimental

Different pozzolanic cement pastes were prepared from different OPC–EAF Slag dry mixes. Table 3 shows the mix composition of the different mixes and their designations. Each dry cement blend was mechanically mixed in a porcelain ball mill for 1 h to ascertain complete homogeneity of the mix. Each paste was prepared by mixing the dry mix with the required amount of water, using the same water/solid (W/S) ratio of 0.50, for about 3 min continuously. After complete mixing, the resultant fresh paste was molded into cubic specimens by using one inch cubic molds. The molds, containing the pastes, were cured at about 100% relative humidity for 24 h to attain the final setting, and then, the cubic specimens were demolded and cured under water at room temperature for different time intervals of 3, 7, 28, and 90 days.

Compressive strength

At each time interval, compressive strength tests were performed on the hardened pozzolanic cement pastes using three cubic specimens at each hydration time, and the average value was recorded as kg cm^{-2}, This was performed using a Ton-industric machine (West Germany) for maximum load of 60 tons.

Stopping of hydration

The resulting crushed specimens of the hardened cement pastes, after measuring compressive strength were ground, and the hydration reaction was stopped using the method described in an earlier publication [18]. The samples were then dried at 90 °C for 3 h. In CO^2-free atmosphere and maintained

Table 3 Mix composition of EAF slag – OPC mixes, wt%.

Mix No.	EAF slag%	OPC%
Mix.0	0	100
Mix.1	5	95
Mix.2	10	90
Mix.3	20	80

in a desiccator containing soda lime and $CaCl_2$ until the time of testing was reached.

Hydration kinetics

Kinetics of the hydration reaction was studied by the determination of chemically combined water and free lime contents at the different ages of hydration using the ground dried samples.

The chemically combined water content, Wn (%), was determined by using Eq. (1) and the procedure of determination as follows: exactly about one gram of the dried sample was charged to a silica crucible and ignited in a muffle furnace for 1 h at 1000 °C (20 °C/min). The crucible containing the sample was cooled in a desiccator then weighed at room temperature. Duplicate measurements were carried out for each sample, and the mean value was recorded. The combined water content was calculated on the ignited weight looses.

$$\mathrm{Wn}(\%) = [(W_o - W_i)/W_i] \times 100 \quad (1)$$

where W_o = dried sample mass and W_i = ignited sample mass.

The free lime content, CaO (%), was determined by using the glycerol/ethanol extraction method, and the mean value of the two independent determinations was recorded [19].

Phase composition and thermal analysis

The phase compositions of the formed hydrates were investigated by means of X-ray diffraction (XRD) and differential thermal analysis (DTA). XRD was studied using copper target, wavelength = 1.54 Å under working conditions of 40 kV and 40 mA using Bruker D8 advance instrument Germany and thermal analysis was examined by using Setaram Labsys TG-DSC16 instrument France.

Results and discussion

Compressive strength

The results of the compressive strength of the hardened blended cement pastes made of Portland cement – *EAF Slag* blends are graphically represented as a function of hydration time in Fig. 1. For all of the pastes made, the compressive strength increases continuously with age of hydration. This increase in strength is mainly attributed to the formation and later accumulation of the hydration products which act as binding centers between the remaining unhydrated parts of the cement grains. The hydration products of both OPC and EAF slag blends are mainly calcium silicate hydrates and $Ca(OH)_2$ as well as hydrates of aluminate phase.

The paste containing EAF slag showed less values of compressive strength compared to the neat Portland cement pastes, as the ratio of EAF slag increase the values of compressive strength decreased. The reduction in the compressive strength was about 2.5%, 8.0% and 25% for the mix containing 5, 10 and 20 wt% EAF slag. This reduction in the compressive strength can be attributed to the less pozzolanic reactivity of EAF slag. Therefore, EAF slag can be used as blending material to Portland cement up to 10 wt%.

Hydration kinetics

Hydration kinetics of the investigated mixes was followed by determining the variation of free lime and chemically combined water contents with time. Fig. 2 shows the variation of combined water content as a function of hydration age. It can be noticed that hydration proceeds in four stages. The first stage was an accelerated stage within the early age of hydration up to 24 h. This was followed by a less accelerated stage in the period of 1–3 days. The third stage within the period of 3–7 days considered another accelerated one. The fourth stage showed a gradual and continuous hydration within the period 7–90 days. These stages of hydration are more obvious in the neat portland cement paste.

The paste blended with EAF slag showed less values of chemically combined water content compared to the blank paste. As the ratio of slag increases the combined water content decreases. This can be attributed to the less pozzolanic activity of EAF slag. The less pozzolanic activity of EAF slag may be due to the fact that it is not completely amorphous.

Free lime contents

Fig. 3 shows the variation of free lime content of the different mixes with age of hydration. All mixes show a continuous increase in the free lime content with the hydration time, This is

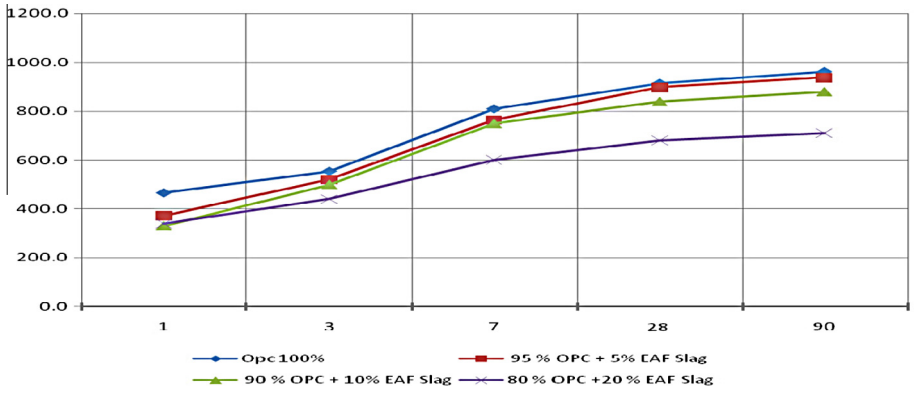

Fig. 1 The results of the compressive strength of the hardened Portland cement pastes in absence and presence of EAF slag as a function of hydration time.

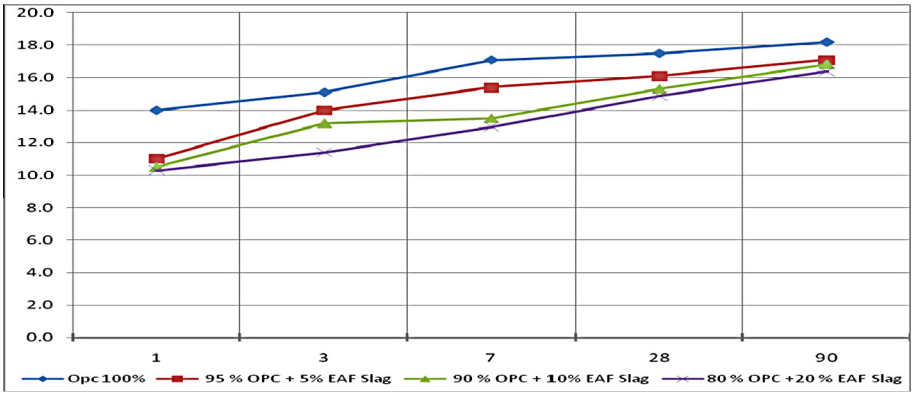

Fig. 2 The results of chemically combined water contents of the hardened Portland cement pastes in absence and presence of EAF slag as a function of hydration ages.

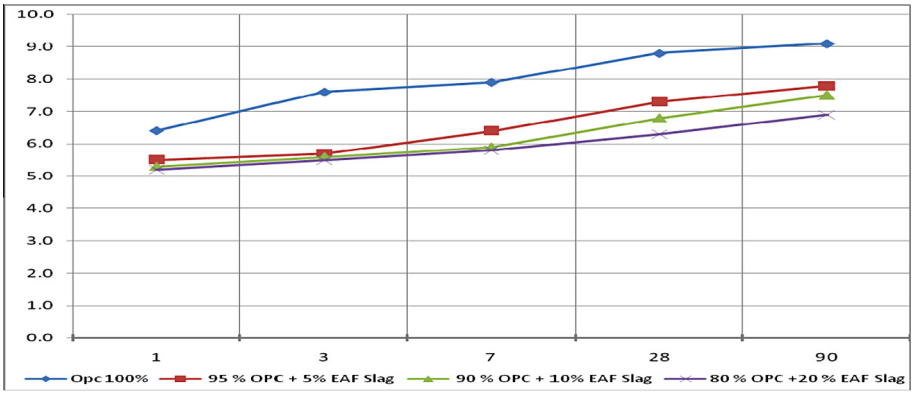

Fig. 3 The results of free lime contents of the hardened Portland cement pastes in absence and presence of EAF slag as a function of hydration ages.

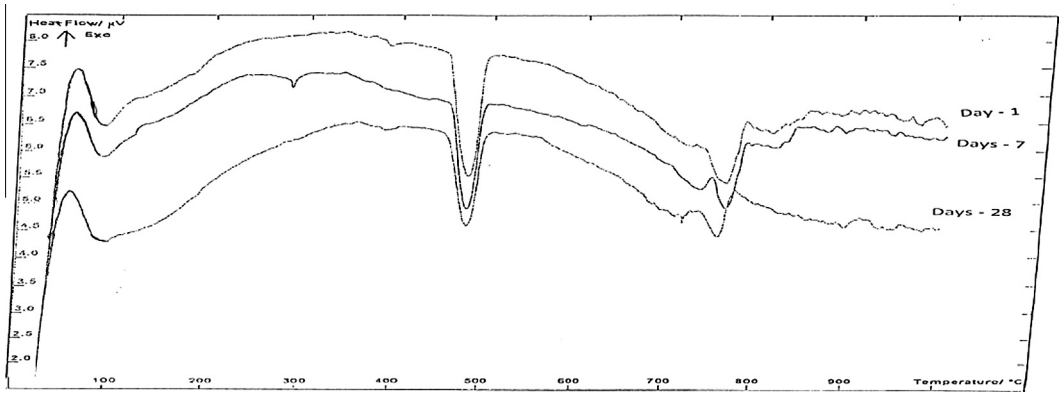

Fig. 4 DTA thermogram of the neat hardened Portland cement paste curved for 1, 7 and 28 days.

a result of the progress of the hydration process. The blended pastes with EAF slag show less values of free lime content compared with the blank mix. The increase of free lime content after hydration time is mainly due to the unhydration character of EAF slag. As the ratio of slag increases the values of lime content and the mode of the variation in the free lime contents are nearly similar to those of the combined water contents for all mixes. The results of both chemically combined water and free lime contents are in good agreement with those of compressive strength results

Thermal analysis

DTA Thermograms of the hardened Portland cement and blended cement pastes containing 5 and 10 wt% EAF slag are shown in Figs. 4–6 respectively. It can be noticed that

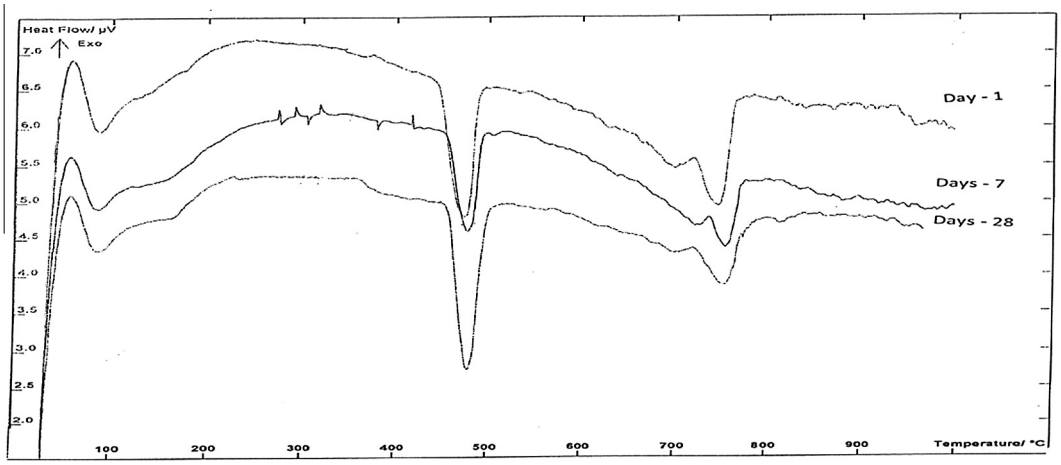

Fig. 5 DTA thermograms of the hardened Portland cement paste blended with 5% by weight EAF slag curved for 1, 7 and 28 days.

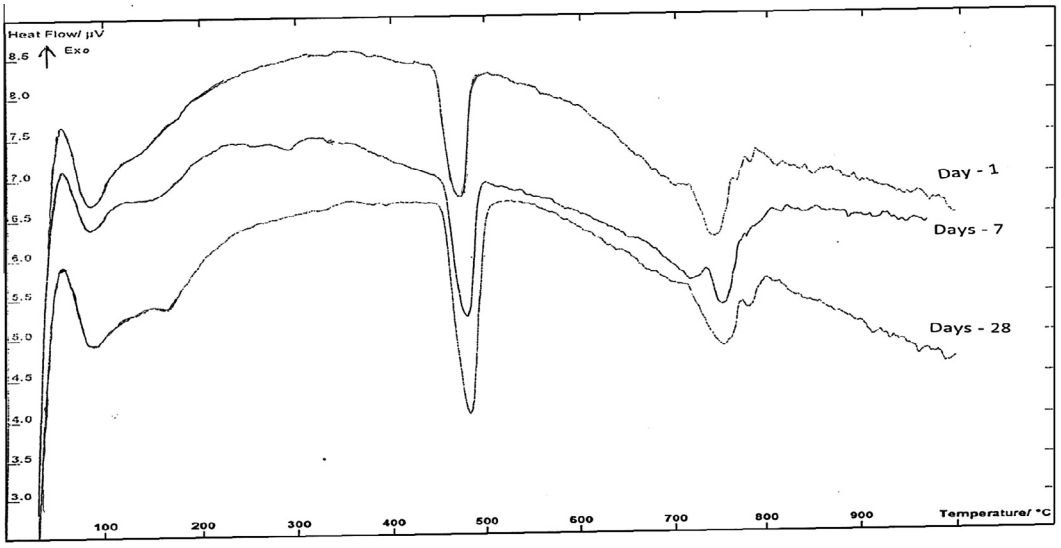

Fig. 6 DTA thermogram of the hardened Portland cement paste blended with 10 wt% EAF slag curved for 1,7 and 28 days.

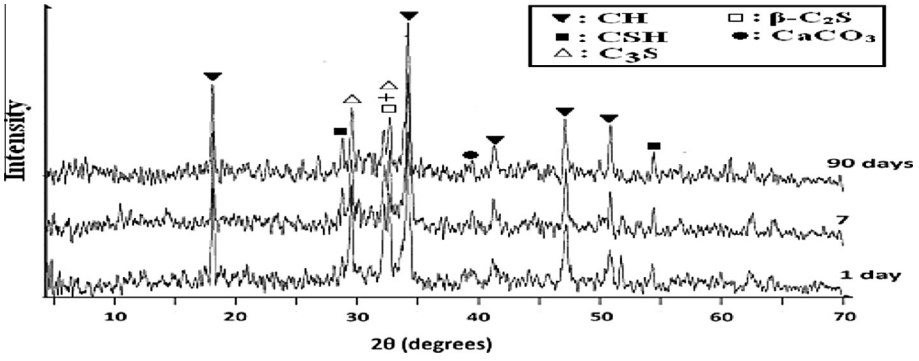

Fig. 7 X-ray diffraction patterns of the hydrated neat Portland cement paste curved for 1, 7 and 90 days.

the endothermic peaks in the ranges 60–120 °C and 450–480 °C are due to the decomposition of calcium silicate hydrate and calcium hydroxide respectively. The area of such peaks increases as the hydration age increases. On the other hand, the area of such peaks in the paste containing EAF slag is less compared to the neat Portland cement paste. The results of

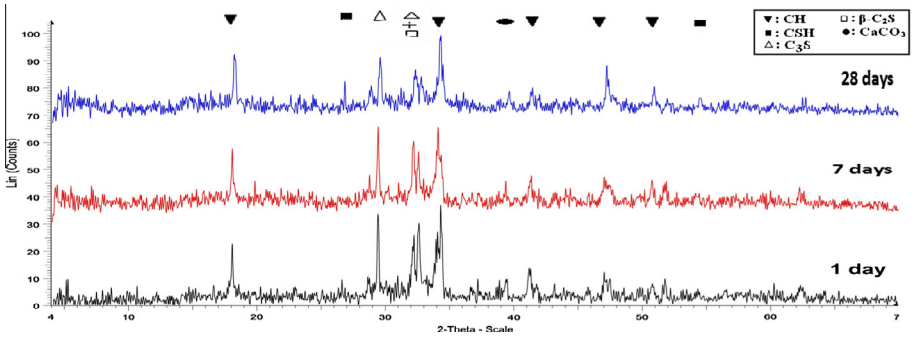

Fig. 8 X-ray diffraction patterns of the hardened Portland cement paste blended with 5 wt% EAF slag (Mix M1) curved for 1, 7 and 28 days.

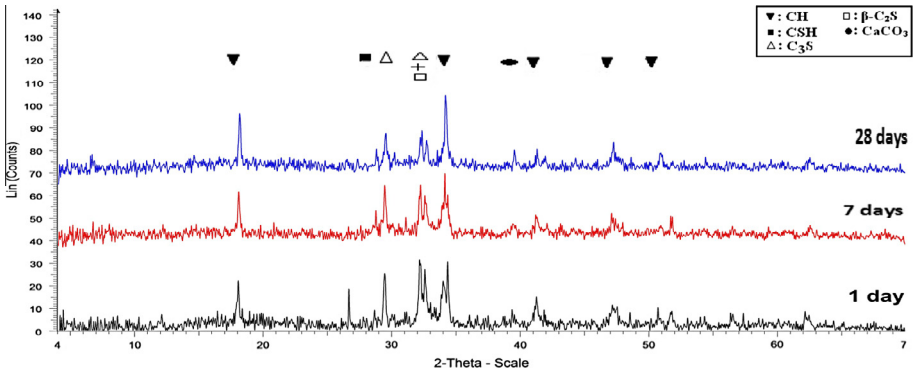

Fig. 9 X-ray diffraction patterns of the hardened Portland cement paste blended 10 wt% EAF slag curved for 1, 7 and 28 days.

XRD and DTA examinations are in good agreement with those obtained from measurements of compressive strength and hydration kinetics the endothermic peaks located in the range of 700–800 are due to the amorphous and crystalline $CaCO_3$.

Phase composition

Figs. 7–9 show the phase composition examined by XRD analysis of the hardened cement pastes; mixes; M0, M1 and M2. All the investigated samples show that with increasing hydration age the intensity of the peaks characteristic to reactants (C_3S & C_2S) decreases as a result of the progress of the hydration process while, the intensity of the peaks characteristic to the hydration products especially the more crystalline calcium hydroxide (CH) increases with hydration age.

The intensity of the peaks characteristic to (CH) in the sample containing EAF slag is less compared to the blank sample at all hydration ages. As the ratio of EAF slag increases the intensity of (CH) peaks decreases, On the other hand, the intensities of (C_3S & B-C_2S) peaks are higher than those in the blank sample. This indicates that the EAF slag has less pozzolanic reactivity. Such results are in good agreement with those of hydration kinetics and compressive strength results.

Conclusion

Concluding remarks derived from this study can be summarized as follows:

1. The values of compressive strength of the mixes containing 5 and 10 wt% EAF slag were near to those of the hardened neat Portland Cement Paste at most of the hydration ages especially at the later ages.
2. The values of compressive strength decrease with the ratio of EAF slag and the mix containing 20 wt% showed the least values of compressive strength at all ages of hydrations.
3. The results obtained from chemically combined water contents, free lime contents, XRD analysis and thermal analysis (DTA) were correlated well with each other and indicated that EAF slag has no considerable pozzolanic reactivity.

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