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Utilization of secondary lead slag as construction material

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Abstract

Secondary lead slag, a waste product from battery smelting using $CaCO_3$ as flux, has been investigated for its use as an admixture and/or aggregate in the production of concrete blocks. The slag was added as partial replacements of cement and/or aggregate. The results revealed that the oxide components of the slag were similar to those of ordinary Portland cement (OPC). The CaO content in the slag is 6.2 times less than that in OPC, while its iron content, as FeO, is 15.1 times higher. Interestingly, it also possesses magnetic property. All samples exhibited higher compressive strengths than that of the sample without slag (STD) which increased with increasing the slag contents and ages. The highest compressive strength was of the sample containing 20% slag as cement substituent and 100% slag as aggregate replacement owing to 259% of that of the STD at 60 days. All samples showed higher water absorption than that of the STD. The higher the slag contents, the more the water absorption. The absorption was, as expected, decreased with ages. Magnetic property of the slag plays an important role in the properties of the concrete blocks. For environmental concern, leachability of lead (Pb) from all samples was also carried out.

Keywords: Slag; Magnetic property; Compressive strength; Water absorption; Porosity

1. Introduction

Due to environmental and economical reasons, there has been currently a growing trend for the use of industrial wastes or by-products as supplementary materials or admixtures in the production of composite cements. Blast furnace slag (BFS), for example, is one of these materials which is used in cement manufacture as blast furnace slag cement [1,2].

Secondary lead slag is a waste product of the transformation of lead sulfate ($PbSO_4$) and lead oxides (PbO and PbO_2) from expired batteries into metallic lead (Pb) using a rotary furnace. In this process, calcium carbonate ($CaCO_3$) is used as flux, while coal char and iron scraps are added as reducing agents. Sand is particularly put in the process to fix impurities or unwanted species (mostly iron ions) into calcium–silicate matrix as CaO–FeO–SiO_2. This makes this kind of slag unique [3]. From phase diagram, it may be in ternary compound, CaO.$(FeO)_2$.$(SiO_2)_2$, or in pseudobinary compound, 2CaO.SiO_2–FeO, owing to properties such as magnetic, hard as rock, and high resistant to acid and base.

Since oxides containing in the slag are similar to those of Portland cement, the application of the slag for construction material is fully attractive. As well, slag is known for a good aggregate substitution. Use of hard slag aggregate in concrete will be beneficial, particularly in areas where good-quality aggregates are not easily available.

The paper presents the preliminary investigation of the use of slag for the production of concrete blocks. In this work, powder slag was used to partially replace the ordinary Portland cement type I (OPC) to evaluate its pozzolanic reactivity. For a high volume of waste disposal viewpoint, the slag was also prepared and used in partial replacement of aggregate. Their compressive strength and water absorption were determined. Leachability of Pb from samples containing slag was also carried out to level its available toxicity. The influence of magnetic property in the slag on the properties of concrete blocks is discussed.

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2. Experimental

2.1. Materials

Secondary lead slag was prepared into two different sizes. The fine slag (*F*) was the content passing sieve no. 200 using as a partial substituent of OPC, while the aggregate slag (*A*) was that passing sieve no. 4 and used to partially replace crushed limestone aggregate. The cement used for comparison was the OPC commercially produced in Thailand.

2.2. Characterization of slag

An energy dispersive X-ray spectroscope was performed to analyze the chemical compositions of the materials. Loss on ignition (LOI) was obtained according to ASTM C114. A scanning electron microscope (SEM) was used to investigate microstructure of the ground slag. Fineness modulus and specific gravity were determined according to ASTM C136 and C188, respectively.

2.3. Methods

The material components are listed in Table 1. The *F* and/or *A* were added to the samples on the basis of OPC and/or crushed stone aggregate compositions, respectively. A type of hollow non-load-bearing concrete block with dimensions of 70×190×390 mm was used in the study. All concrete block samples were prepared at constant water to binder ratio (w/b) of 0.63 by weight where the workability required was met. For mixing binder, sand and crushed stone aggregate, a constant by weight ratio of 1:4.3:5 was used. The samples were demoulded after 24 h of casting and then cured under tap water at room temperature (ca.28 °C). Test for compressive strength was performed after the samples have been cured for 28, 60, and 90 days. Same as the strength test, all concrete block samples underwent the test of water absorption by measuring the decrease in mass of a saturated and surface-dry sample after oven drying for 24 h. The results were compared to the standard sample (0% slag, STD). Mortar specimens (5-cm cubes) were prepared to investigate its compressive strength and porosity to study the influence of the magnetic property of the slag towards strength. After strength test at required ages, the fracture pieces of samples were soaked in an isopropanol solution for stopping the hydration reaction [4], and the porosity of the samples were then determined by a mercury pore sizer. A leachate extraction is performed according to US-EPA SW846 to examine the leachability of Pb from all samples. Fracture pieces of the samples at 28 days were ground and then soaked in an acidic solution at pH 5 for 18 h. The slurry was filtered, and the supernatant was analyzed for Pb by an atomic absorption spectrometer.

Table 1
Component proportion

Sample	Binder (%)		Aggregate (%)	
	OPC	*F*	Crushed stone	*A*
STD	100	–	100	–
F20	80	20	100	–
F40	60	40	100	–
A20	100	–	80	20
A40	100	–	60	40
A60	100	–	40	60
A80	100	–	20	80
A100	100	–	–	100
F20A50	80	20	50	50
F30A50	70	30	50	50
F20A100	80	20	–	100
F30A100	70	30	–	100

Table 2
Chemical composition of slag and OPC (wt.%)

Constituent	Slag	OPC
CaO	10.53	64.26
SiO_2	24.40	20.39
Al_2O_3	3.44	5.16
Iron oxide	46.81 (as FeO)	3.10 (as Fe_2O_3)
MgO	1.28	0.90
K_2O	0.48	0.50
Na_2O	4.12	0.07
SO_3	6.64	2.67
TiO_2	0.19	–
PbO	1.37	–
others	0.74	1.87
LOI	(+) 7.48	1.12

3. Results and discussion

3.1. Chemical and physical characteristics of materials

The chemical composition and physical properties of the slag comparing to those of OPC are given in Tables 2, 3. Fig. 1 showed the microstructure of the slag.

It can be seen that the oxides of the slag are similar to those of OPC. However, the CaO content in slag is 6.2 times less than that in OPC, whereas its iron content, as FeO, is 15.1 times higher. Evidence from a Raman spectroscope shows as well that there is magnetite ($Fe^{2+}Fe_2^{3+}O_4$) other than FeO containing in the slag.

According to the LOI analytical method, this value, which indicates the amount of unburned compounds (mainly carbons) contained in the material, is normally a weight loss. However, in the case of the slag, the value obtained is a weight gained instead. This confirms that iron

Table 3
Physical properties of materials

Property	OPC	*F*	Crushed stone	*A*
Specific gravity	3.15	3.62	2.71	3.62
Blaine fineness (cm^2/g)	3380	3333	–	–
Fineness modulus	–	–	4.74	4.70

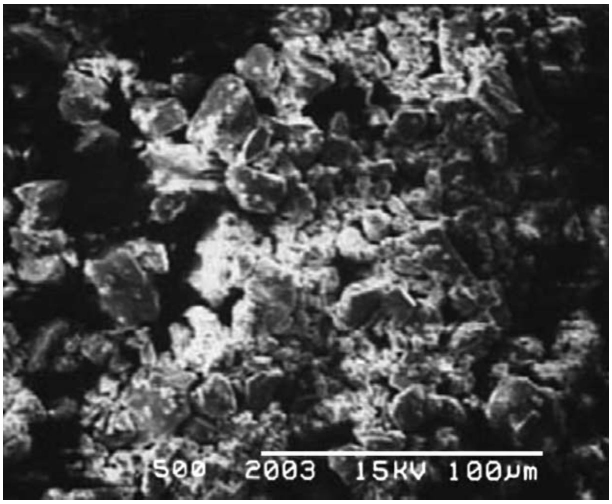

Fig. 1. SEM of the ground slag.

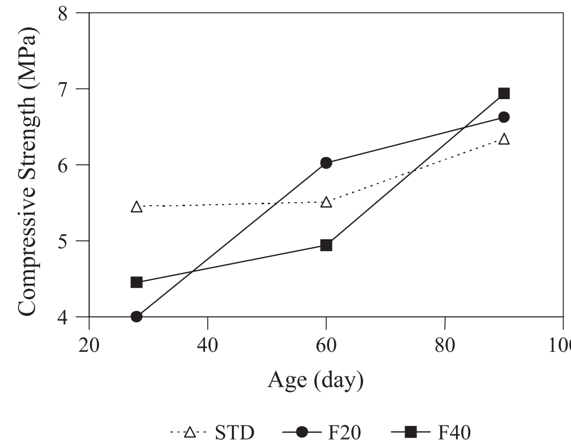

Fig. 2. Compressive strength of the samples at various ages and slag contents when using the slag to replace OPC.

oxide of this kind of slag is in reducing form (FeO) rather than oxidizing form (Fe_2O_3) [3]. Oxidation of FeO proceeds during the burning step of the LOI analysis following Eq. (1). From calculation, the oxygen required for the oxidation of 46.81% of FeO is 6.71%. The different percentage between 7.48 and 6.71 could be the O_2 amount required for the oxidations of some other reducing species since the refining process is in reducing condition. It is therefore confirmed that the iron oxide in the slag is as FeO and not Fe_2O_3. At room temperature, FeO is paramagnetic and becomes antiferromagnetic at temperature below -70°C, while Fe_2O_3 is antiferromagnetic [5].

$$4\ FeO + O_2 \rightarrow 2\ Fe_2O_3 \tag{1}$$

As shown in Fig. 1, slag particles are angular, which is generally found in crushed slag [6]. This certainly affects properties of the concrete blocks, such as physical property and mechanical property.

3.2. Influence of slag contents on compressive strength

The test results of the compressive strengths are shown in Figs. 2–4. Surprisingly, the fracture pieces of samples with high slag contents (A80, A100, F20A100, and F30A100) responded to a magnet. How this affects the use and durability of concrete is much interesting. It is currently under research by the author's group.

As can be seen from Fig. 2, the strength development of the STD has almost completed since 28 days, while those of the samples containing slag still undergo their development even after 90 days. The strength development of the samples during the first month period was slow comparing to that of the STD due to the slag replacement. However, after 90 days, all samples exhibited higher compressive strength than the STD.

It is well known that replacing cement by pozzolanic materials with low calcium, such as BFS and fly ash, would lower the early strength (generally up to 28 days) [2,7,8, and, reference therein]. An increasing rate of strength would occur after prolonging the curing due to pozzolanic reaction [6]. Portlandite ($Ca(OH_2)$) produced from the OPC hydration reaction is particularly required for dissolving the glassy phase of the slag, as a result, providing a route to the pozzolanic reaction [9]. This explains very well the result obtained. Pozzolanic activity of the slag *F* was also carried out. According to the ASTM C311 test method, the strength activity index (in percent) was used to evaluate the pozzolanic activity. The result obtained was 89.72% at curing age of 28 days.

Since the CaO content of the slag is 6.2 times less than that of the OPC (see Table 2), a higher replacement of the OPC by the slag would bring to a lower ultimate strength. On the contrary, in this work, the strength increases with increasing the slag contents. This is believed to be due to some properties of the slag other than its CaO content, such as magnetic property, size, and shape.

In general, admixtures have very little effect on the ultimate strength of concrete except when they affect the

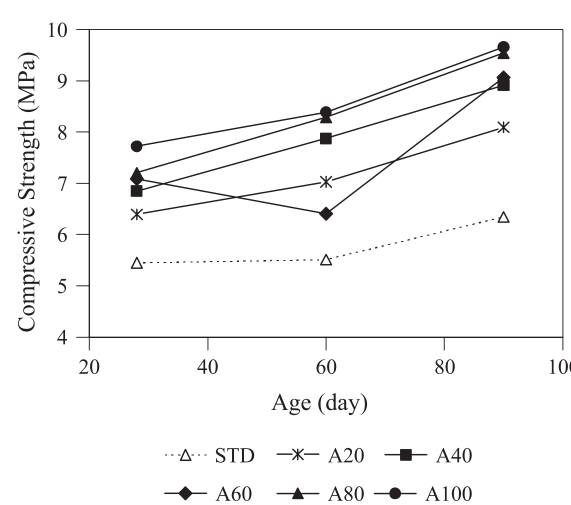

Fig. 3. Compressive strength of the samples at various ages and slag contents when using the slag to replace crushed stone aggregate.

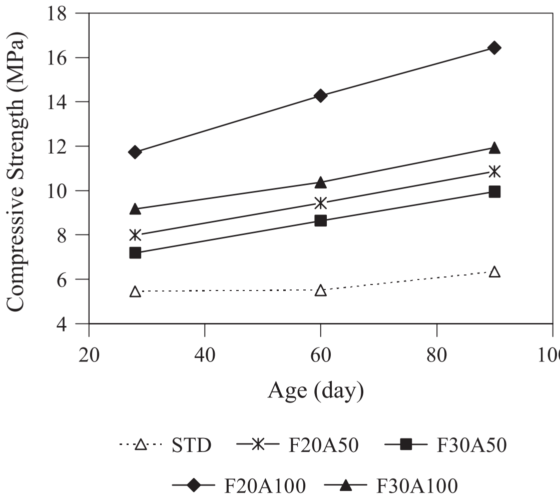

Fig. 4. Compressive strength of the samples at various ages and slag contents when using the slag to replace both OPC and crushed stone aggregate.

w/c ratio or the porosity of the concrete. In this work, it is explained that, due to its texture, the fine slag functions as filler to reduce the porosity. This in turn upgrades the strength of the samples (filler effect) [10,11]. Isaia et al. [12] recently proved that pozzolanic and filler effects increased as the mineral addition increased in the mixture. They also concluded that the filler effect, however, increased more than the pozzolanic effect.

The magnetic of the slag is proposed to be another factor responsible to the higher strength. It strengthens the microstructure of the paste by magnetic force, as well as induces the absorbed water to become magnetized water. Su et al. [13] reported that the compressive strength of the BFS concrete prepared with magnetized water (water flowing through a magnetic field) increased 10–23% more than that of the tap water samples. Similar result was also reported when applying the magnetized water to fly ash concrete [14]. It was explained that magnetic force can break apart water clusters into single molecules or smaller clusters, therefore, the activity of water is improved [15]. The magnetized water molecules can then easily penetrate into the cement particles where a thin layer of hydration product, $Ca(OH)_2$, firstly formed and hindered further hydration [13,14, and, reference therein]. This in turn improves concrete strength. Hence, it is the magnetic and filler effects that are believed to be responsible for the results in this case.

As can be seen in Fig. 3, when replacing crushed stone aggregate with A, the result shows that the strength of the STD from 28 to 90 days is the lowest among all samples. As the slag was added at a higher content, the higher strength was observed. Since the amount of OPC in each sample is the same at 0.68 kg, it is thus contributed this to the magnetic and packing effects, as described above. Moreover, in this case, the hardness of the slag aggregate could be taken into account since slag aggregate is known for better physical and mechanical characteristics than those of crushed limestone aggregate [16]. According to the ASTM C131, the loss by abrasion and impact in the Los Angeles machine of the slag A was 6.4%, while that of the crushed stone aggregate was 8.9%.

When replacing OPC and aggregate with F and A, respectively (see Fig. 4), the result clearly shows that all samples exhibit higher strength than the STD. At constant F, the higher strength is of the sample with more A content. When the same amount of A is used, the sample with 20% F shows better performance than 30% F. Sample F20A100 possesses the highest compressive strength owing to 215%, 259%, and 260% of the STD at 28, 60, and 90 days, respectively. A much higher strength of the sample comparing to the STD is believed to be the combined effects of hydration effect, pozzolanic effect, filler effect, magnetic effect, and the slag hardness. Experiments to differentiate all these effects from each other are under study.

3.3. Influence of slag contents on water absorption

The test results of the water absorption of all samples are illustrated in Figs. 5–7. The results clearly show in the figures that all samples absorb more water than that of the STD. At the same age, the absorption increases with increasing the amount of the slag. All samples show, as expected, lower absorption when aging.

It is well known that the primary factor governing the strength of materials is porosity. The higher the strength, the lesser its porosity. Before hydration begins, the available space is that occupied by the mixing water. After hydration has proceeded, the available space is then filled with the calcium–silicate–hydrate (C–S–H) network, more and more to lower porosity, and ended up to a dense framework [6].

Water absorption is a simple test for the permeability of hardened cements and concretes in relation to their porosity. A higher absorption implies more porosity. From Figs. 5–7, the lower absorption in each sample through the curing

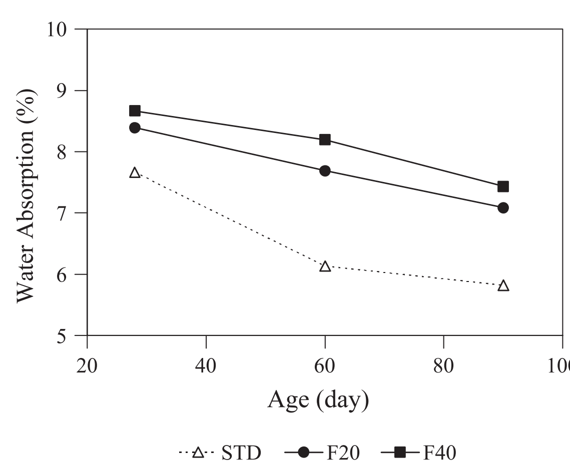

Fig. 5. Water absorption of the samples at various ages and slag contents when using the slag to replace OPC.

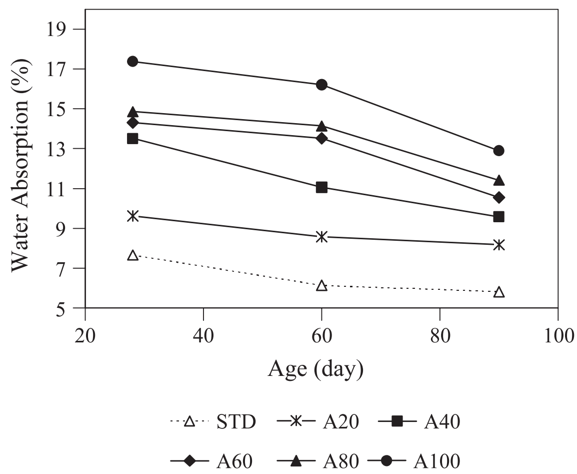

Fig. 6. Water absorption of the samples at various ages and slag contents when using the slag to replace crushed stone aggregate.

indicates, of course, its lower porosity by time. This also corresponds to the higher compressive strength, as evidenced in Figs. 2–4. However, the test results of the absorption of all samples containing slag at any ages showed the higher absorption than the STD and increased with increasing the slag contents. It is proposed the high water absorption to the magnetic property of the slag. The magnetic property induces water to penetrate into the porosity, as well as to bind the outer surface of the samples, by the magnetic force. Comparing F20A50 and F20A100 at the same age, for example, the result showed that the absorption of the former was lower than that of the latter due to less slag content and, hence, weaker magnetic force. Through comparison of the absorption and the compressive strength among the three samples that contained similar amounts of the slag, A100 (3.42 kg slag), F20A100 (3.56 kg slag), F30A100 (3.63 kg slag), it was found that their compressive strength was considerably different, while the absorption of three samples was similar. If the magnetic property of the slag really affects the water-bound surface as proposed, the finding will be advantageous to solving out problems, such as drying shrinkage and freeze-thaw resistance of concrete, as previously reported [17].

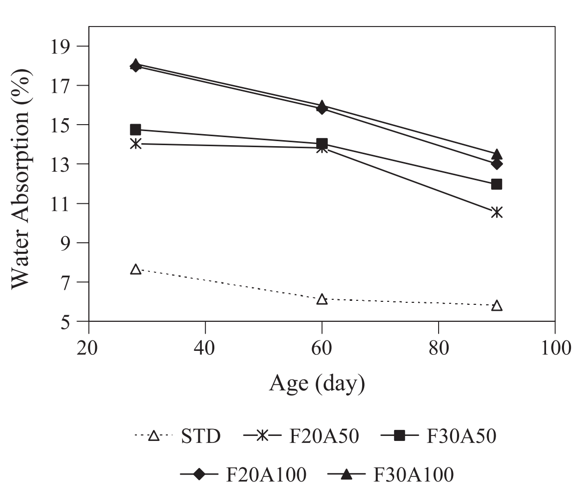

Fig. 7. Water absorption of the samples at various ages and slag contents when using the slag to replace both OPC and crushed stone aggregate.

3.4. Influence of the magnetic of lead slag towards strength

A mortar test of three samples, STD, A100, and F20A100, were selected to further study the relationship between their compressive strength and their porosity. The result is shown in Fig. 8.

Fig. 8(a) shows the typical relationship between porosity and strength. Sample A100 was conducted as a control sample for leveling the percentage of porosity required for a mortar when crushed stone aggregate was replaced by the slag *A*. As can be seen in Fig. 8(b), its porosity is almost constant since 7 days of age, while its compressive strength develops by time. It is explained that a kind of permanent

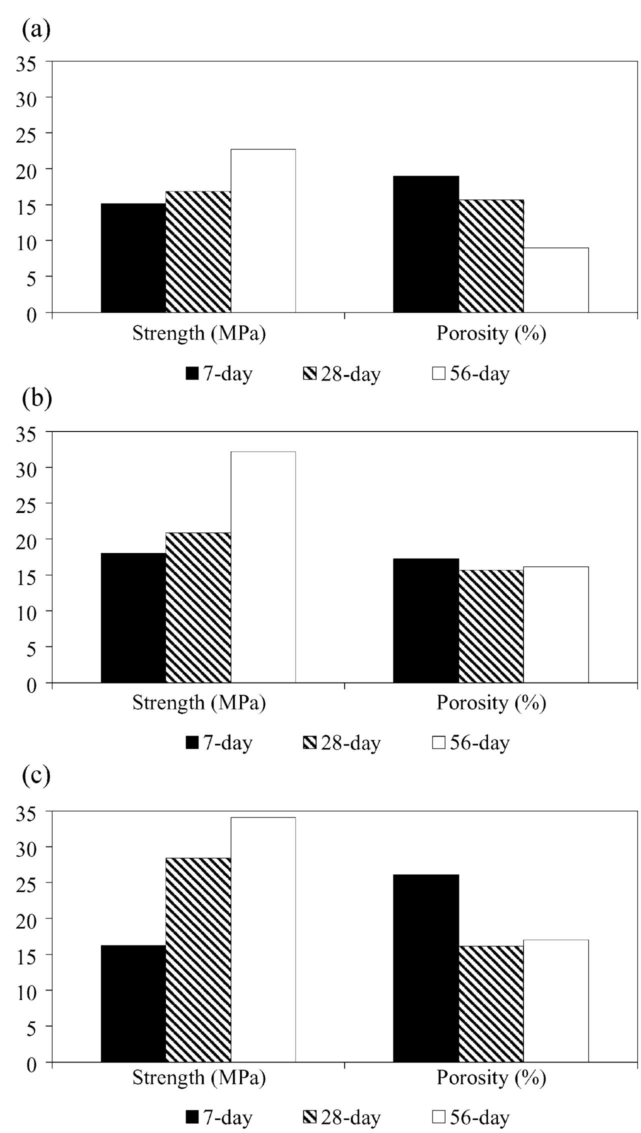

Fig. 8. Relationship between compressive strength and porosity at various ages of the samples: (a) STD, (b) A100, and (c) F20A100.

pores has been created where the C–S–H network is unable to fill them up. It is believed that the pores are the space occupied by magnetized water as strong adsorbed water and not free water where the hydration can occur. From Fig. 8(c), it clearly shows that the amount of porosity of the sample F20A100 at 7 days, as well as its compressive strength, are obviously high comparing to the sample STD and A100. The much higher porosity is contributed to the much more magnetized water created and adsorbed by the slag *F*. This amount of water rapidly decreases to the similar level of that required for A100 after 28 days due to the more effective hydration reaction and, hence, higher compressive strength.

3.5. Leachability of Pb from concrete blocks

Leaching of the Pb could be observed only for the samples with high slag content: A100, F20A100, and F30A100. The amounts detected were only 0.060, 0.065, and 0.067 ppm, respectively. It is, however, much lower than the acceptable limit (5 ppm) for the requirement of Thai hazardous waste disposal standard.

4. Conclusion

It can be concluded here that the secondary lead slag using limestone as flux can be used as admixture and/or aggregate for the production of concrete blocks.

The slag possesses magnetic property due to its CaO–FeO–SiO_2 structure. The magnetic plays an important role in the properties of the samples, particularly in terms of the strength. Other effects, such as filler effect and pozzolanic effect, were also observed.

5. Further works

Due to high contents of FeO and SO_3, chemical resistance and durability of concrete using the slag as admixture and/or aggregate need to be further studied, especially for corrosion and rust processes. Although aggregates do not generally contribute to the durability of concrete, deterioration of concrete is particularly noted when the aggregates are not chemically inert.

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