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Research Article

CARBONATION RESISTANCE OF SLAG MORTARS ACTIVATED BY DIFFERENT ALKALI ACTIVATORS

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ABSTRACT
In this study, the carbonation depths of slag mortars activated by sodium silicate (water glass), sodium hydroxide and sodium carbonate were investigated and the results were compared to those of control mortar with CEM I 42.5 R normal Portland cement. In the mixture, the sand/binder ratio was 2.75 and the water/binder ratio was 0.50. Na concentrations in the mixture proportions were determined as 4%, 6%, and 8% for all the activators. For liquid sodium silicate activator, SiO_2/Na_2O ratios (Ms) of 0.75, 1, 1.25, and 1.5 were also chosen. Prismatic specimens having 40 x 40 x 160 mm dimensions were prepared from both fresh Portland cement and slag mortar mixtures for the measurements. The day after the mortar casting, the prisms were demolded and placed in a humidity cabinet at 65% ± 5 relative humidity and 22 ± 2 °C temperature. The carbonation tests of mortars were conducted at 7, 28, 90 and 180 days. It was observed that the carbonation resistance of slag mortars activated by alkalis was lower than that of control mixture with Portland cement. However, it was also seen that an increment in the Na dosage of activator improved the resistance of the activated slag mortars to carbonation.

Keywords: *Carbonation, Mortar, Slag, Activator*

1. INTRODUCTION

The use of mineral admixtures in today's concrete technology has an important place because of the positive effects on strength and durability of concrete as well as reducing production costs. One of these mineral admixtures is the ground granulated blast furnace slag (GGBFS) which is by-product of the iron-steel industry. GGBFS consists mainly of lime and calcium–magnesium aluminosilicates and has the glassy granular structure which is formed when the molten blast-furnace slag is rapidly chilled by immersion in water (Erdoğan, 2010; Atiş *et al.*, 2009)

GGBFS, which is exhibiting pozzolanic properties when finely ground, is used in the production of slag cement in cement industry or in the production of concrete containing mineral admixture by replacing it with ordinary Portland cement (OPC). However, the low early strength seen in slag-added concrete limits the use of such binder due to the slow rate of hydration. For this reason, a number of researches which can speed up reactions by increasing the rate of this low hydration have been carried out. The studies have shown that when the slags are activated with alkali activators, they can bring about a strong paste structure that can be used in construction applications and thus provide high strength by solving the low early strength problem (Collins and Sanjayan, 1999).

Various studies on alkali-activated slag (AAS) showed that these binders exhibited superior performance even in aggressive environments such as high temperature, chemical attack and freeze-thaw cycles in comparison to OPC (Palacios and Puertas, 2007; Neto *et al.*, 2008; Bilim, 2016). Byfors *et al.* (1989) noted that AAS concrete had a higher carbonation rate compared to OPC concrete having the equivalent compressive strength grade. Bilim and Atiş (2012) studying on alkali activation of mortars containing different replacement levels of GGBFS reported that the carbonation depths for liquid sodium silicate-activated OPC/slag mortars were higher than OPC mortar. Bernal *et al.* (2010) reported that alkali-activated binders were, on the whole, highly resistant to carbonation contrary to some claims in the literature.

As seen in the literature, there are a lot of published papers about some properties of mortar containing AAS as the binder. However, there is no adequate information on the carbonation properties of AAS materials without OPC. Therefore, this study focuses on the investigating of carbonation properties of the slag mortars activated with some alkali activators such as liquid sodium silicate, sodium carbonate and sodium carbonate.

2. EXPERIMENTAL STUDY

The cement was ASTM Type I normal Portland cement (42.5 MPa) with a specific gravity of 3.16 g/cm^3 and a Blaine specific surface area of 325 m^2/kg. The chemical oxide composition is presented in Table 1. GGBFS was procured from the Iskenderun Iron–Steel Plant in Turkey. Its chemical composition is as shown in Table 1. The specific gravity of GGBFS was 2.81 g/cm^3 and its Blaine specific surface area was about 425 m^2/kg. Slag is classified as a category 80 in terms of hydraulic activity index according to the requirements of ASTM C 989 (1994). Sodium hydroxide and sodium carbonate (obtained from MERCK chemicals) and liquid sodium silicate (obtained from Mersin Şişecam Soda Factory) were used as activators. Liquid sodium silicate had a SiO_2/Na_2O ratio (Ms) = 2. The natural sand with maximum size of 4 mm was used. The grading complied with the requirements of ASTM C 33 (2005). The absorption value of the sand was 1.2% and the relative density at saturated surface dry condition was 2.67.

Table 1 Chemical composition of OPC and GGBFS (%)

Oxide	OPC	GGBFS
SiO_2	19.71	36.70
Al_2O_3	5.20	14.21
Fe_2O_3	3.73	0.98
CaO	62.91	32.61
MgO	2.54	10.12
SO_3	2.72	0.99
K_2O	0.90	0.76
Na_2O	0.25	0.42
LOI	0.96	-

Three different concentrations of sodium were selected for the activation of the mortars, 4%, 6% and 8% by weight of the slag. Liquid sodium silicate and sodium hydroxide were mixed at different ratios to obtain four Ms values (0.75, 1.00, 1.25 and 1.50) in solution. In order to keep the ratio of water/binder of 0.50, the amount of water to be added to the mortar mixtures is decreased by considering the amount of water in the solution. A summary of the experimental program is presented in Table 2.

Table 2 Summary of the experimental program

Mixture Name	Activator Type	Sodium Dosage
OPC Mortar	-	-
AAS Mortar	Sodium hydroxide	4%,6%,8%
AAS Mortar	Sodium carbonate	4%,6%,8%
AAS Mortar	Liquid sodium silicate (Ms=0.75, 1, 1.25, 1.5)	4%,6%,8%

Prismatic specimens having 40 x 40 x 160 mm dimensions were prepared from both fresh OPC and AAS mortar mixtures for the measurements. The day after the mortar casting, the prisms were demolded and placed in a humidity cabinet at 65% ± 5 relative humidity and 22 ± 2 °C temperature. The carbonation tests of mortars were conducted at 7, 28, 90 and 180 days.

The phenolphthalein method was used to watch the pH change of mortar specimens in carbonation experiments. The phenolphthalein indicator shows a magenta colored region on the concrete where the pH value exceeds about 9 and a colorless region at the originally exposed surface where carbonation has reduced the pH to below 9. At the time of measurement, a 1% phenolphthalein solution in alcohol was sprayed on a broken surface of the remaining mortar prisms from flexural strength test, and the depth of neutralization was measured. The values were expressed by taking the average of three prismatic specimens. The results of flexural and compressive strength for AAS mortars were earlier presented by Atiş *et al.* (2009).

3. RESULTS AND DISCUSSION

Carbonation is a durability problem that starts from the surface of the concrete and progresses to its interior. The most important process that needs to be done in order to prevent the carbonation which is important for the corrosion of the reinforcement is to produce the concrete as impermeable as possible.

The carbonation depths at 7, 28, 90 and 180 days for slag mortars activated by liquid sodium silicate (LNS) are given in Table 3. Table 3 also shows the carbonation values of OPC. Additionally, the results obtained from slag mortars activated by sodium hydroxide (NH) and sodium carbonate (NC) activators are presented in Table 4 and Table 5, respectively.

Table 3. Carbonation depth of slag mixes with LNS (mm)

	Activator Type	Activator Dosage	7	28	90	180
Cement	—	—	0.38	0.81	3.14	4.20
Slag	LNS	4% Na, Ms=0.75	0.25	2.15	7.14	12.25
	LNS	4% Na, Ms=1.00	0	1.74	6.50	11.69
	LNS	4% Na, Ms=1.25	0	1.35	5.27	8.59
	LNS	4% Na, Ms=1.50	0	1.09	4.73	7.78
	LNS	6% Na, Ms=0.75	0	0.58	3.96	5.26
	LNS	6% Na, Ms=1.00	0	0.29	3.39	6.35
	LNS	6% Na, Ms=1.25	0	0.21	2.93	5.90
	LNS	6% Na, Ms=1.50	0	0.14	1.66	4.34
	LNS	8% Na, Ms=0.75	0	0.50	1.85	4.30
	LNS	8% Na, Ms=1.00	0	0.35	0.71	3.63
	LNS	8% Na, Ms=1.25	0	0.25	0.53	2.33
	LNS	8% Na, Ms=1.50	0	0.18	0.40	1.78

Table 4. Carbonation depth of slag mixes with NH (mm)

	Activator Type	Activator Dosage	7	28	90	180
Slag	NH	4% Na	0.13	1.73	3.92	7.76
	NH	6% Na	0	1.41	3.04	5.59
	NH	8% Na	0	0.90	2.04	3.09

Table 5. Carbonation depth of slag mixes with NC (mm)

	Activator Type	Activator Dosage	7	28	90	180
Slag	NC	4% Na	0.26	4.04	10.47	17.80
	NC	6% Na	0	3.04	6.31	10.18
	NC	8% Na	0	2.25	5.62	9.25

The results show that an increase in the carbonation values of all mortars happened in time depending on the amount of CO_2 that permeates to the interior of specimen.

The highest carbonation values were obtained from the slag mortars activated by sodium carbonate activator due to calcium carbonate crystals that happens as a result of chemical reactions between CO_3^{2-} ions in the structure of Na_2CO_3 and Ca^{2+} ions coming from the slag.

Additionally, it is thought that there is a decrease in carbonation values with an increase in Na dosage, and this is probably due to the relatively higher level pH environment that occurs in the pore solution due to the increased Na dosage. Similarly, the rising silicate modulus (Ms) in the slag mortars activated with the sodium silicate solution produced the lower carbonation values.

From all the tables, it was seen that carbonation in AAS mortars had higher values compared to OPC mortar. This situation may be explained in this way: When AAS concretes are exposed to a carbon dioxide-rich medium, some chemical changes occur in the binder matrix such as the formation of calcium carbonate crystals, a decrease in the pH level of the pore solution, and a decomposition of the lime from the C-S-H gels. Because Ca^{2+} content in the slag incorporated concretes is lower than OPC concrete, $CaCO_3$ precipitation is rare. So, the diffusion of CO_2 into the interior of the concrete is easier since the porosity increases in the area where the $CaCO_3$ crystals occurs dependent on the carbonation reaction. This situation leads to the faster advancing of the carbonation reactions from the surface towards to interior increasing the carbonation.

On the other hand, OPC concretes have more Ca^{2+} content in comparison with AAS concretes. When the binder matrix comes into contact with CO_2, the $CaCO_3$ crystals precipitate in the pores, and thus produce a barrier which prevents the diffusion of CO_2 into the paste. Therefore, the carbonation reactions in OPC paste progress more slowly and the carbonation values of AAS concretes are higher than those of OPC concrete (Bilim, 2006).

The changes in the carbonation depths, which were measured over the 180-day time period for both OPC mortar and the slag mortars activated with different alkali activators, are shown in Fig. 1.

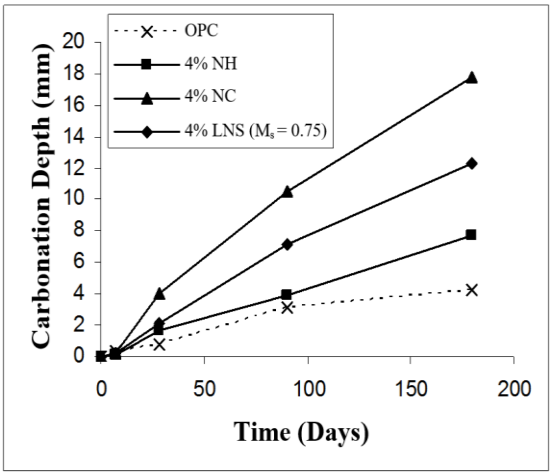

Fig. 1. The changes in carbonation depths of both OPC and AAS mortars

4. CONCLUSION

The following conclusions can be drawn from this study:

1. The findings obtained from the test results exhibited that the carbonation resistance of slag mortars activated by alkalis was lower than that of control mixture with OPC.
2. The highest carbonation values were obtained from the slag mortars activated by sodium carbonate activator.
3. An increment in the Na dosage of activator improved the resistance of the activated slag mortars to carbonation.
4. The rising silicate modulus (Ms) in the slag mortars activated with the liquid sodium silicate solution produced the lower carbonation values.

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