



Alkali activation of mortars containing different replacement levels of ground granulated blast furnace slag

Cahit Bilim^{a,*}, Cengiz Duran Atiş^{b,c}

^a Mersin University, Engineering Faculty, Department of Civil Engineering, Mersin, Turkey

^b Abdullah Gul University, Engineering and Architecture Faculty, Department of Civil Engineering, Kayseri, Turkey

^c Erciyes University, Engineering Faculty, Department of Civil Engineering, Kayseri, Turkey

ARTICLE INFO

Article history:

Received 30 June 2011

Received in revised form 23 September 2011

Accepted 2 October 2011

Available online 29 November 2011

Keywords:

Alkali-activated mortars

Ground granulated blast furnace slag

Liquid sodium silicate

Mechanical properties

Carbonation

ABSTRACT

The aim of the present study is to investigate some properties of alkali-activated mortars containing slag at different replacement levels. Ground granulated blast furnace slag was used at 0%, 20%, 40%, 60%, 80% and 100% replacement by weight of cement, and liquid sodium silicate having three different Na dosages was chosen as the alkaline activator. In this research, carbonation resistance measurements and compressive and flexural strength tests were performed on the mortar specimens with size of $40 \times 40 \times 160$ mm. The findings obtained from the tests showed that carbonation depth values of the mortars decreased with the increase of activator dosage. Additionally, compressive and flexural strength values increased with the increase in activator concentration and slag replacement level. Portland cement/slag mortars activated by liquid sodium silicate exhibited lower strength than the slag alone activated by the same activator.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Most cement plants consume large amounts of energy and produce a number of undesirable products which negatively affect the environment. For this reason, the extensive investigations on alternative inorganic materials which could replace conventional cement have been recently conducted to reduce greenhouse gas emissions from cement kilns. In this regard, blast furnace slag (BFS) plays a very important role. BFS refers in particular to the slag produced from the manufacture of pig iron. If the molten slag is quenched sufficiently rapidly it forms a glassy material, when finely ground, that is called “ground-granulated blast-furnace slag” or GGBS [1]. GGBS is often used in concrete as a supplementary cementitious material with partial replacement to ordinary Portland cement (OPC). However, the low early strength of the GGBS concretes constitutes an obstacle for many applications. This problem can be overcome by using alkali-activated slag (AAS) as the type of binder which can potentially yield early high-strength concrete [2].

AAS is a blend of a vitreous blast furnace slag and activators, which are chemical species capable of enhancing slag reactivity during hydration [3]. When compared with traditional cements and concretes, AAS binders present some advantages such as earlier and higher mechanical strengths, lower heat of hydration

and stronger resistance to chemical attack [4]. Many valuable research results have been reported on AAS binders which have recently received much attention from the academic field. Bakharev et al. [5] studied alkali activation of Australian slag cements. They reported that liquid sodium silicate provided the best activation compared to sodium hydroxide and sodium carbonate activators in terms of compressive strength. Liquid sodium silicate with a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio (modulus, Ms) of 0.75% and a 4% sodium concentration was recommended for use in AAS concrete. Bakharev et al. [6], studying the effect of elevated curing temperature on properties of AAS concrete, concluded that heat treatment considerably accelerates strength development, but at later ages the compressive strength was reduced compared to concrete cured at room temperature. They also concluded that heat curing considerably reduces shrinkage of AAS concrete, making it comparable to OPC concrete. Collins and Sanjayan [7,8] studied early age strength, workability and mechanical properties of AAS concrete. They concluded that one day compressive strength comparable to OPC concrete was achievable with AAS as the sole binder. Jimenez et al. [9], who studied the flexural and compressive mechanical strength of alkali-activated slag mortar, reported that liquid sodium silicate gave the highest mechanical strengths. Another important factor was the concentration of the activator, followed by curing temperature, and the fineness of the slag. Atiş et al. [10], who studied influence of activator on the strength and drying shrinkage of AAS mortar, concluded that there was an optimum $\text{SiO}_2/\text{Na}_2\text{O}$ ratio for liquid sodium silicate to obtain the highest compressive and

* Corresponding author.

E-mail address: cbilim@mersin.edu.tr (C. Bilim).

flexural tensile strength. They also reported that slag mortar made with liquid sodium silicate had a high drying shrinkage, and AAS mortar was more brittle than OPC mortar. Bakharev et al. [11] and Puertas et al. [12] also found that alkali silicate- or hydroxide-activated slag mortars and concretes are more rapidly carbonated than comparable OPC mixes, and that this degradation can lead to an important decrease in compressive strength. Byfors et al. [13] noted that AAS concrete exhibited a higher carbonation rate than Portland cement concrete for the equivalent compressive strength grade. On the other hand, Bernal et al. [14] reported that alkali-activated binders were, on the whole, highly resistant to carbonation contrary to some claims in the literature.

This investigation is focused on the effect of the GGBS replacement on carbonation and mechanical strength (flexural and compressive) properties of mortars activated by liquid sodium silicate with 4%, 6% and 8% Na.

2. Properties of materials used

2.1. Cement

The cement used was ASTM Type I normal Portland cement (42.5 MPa) with a specific gravity of 3.16 g/cm³ and a Blaine specific surface area of 325 m²/kg. The chemical composition is given in Table 1.

2.2. Ground slag

Ground slag was obtained from the Iskenderun Iron–Steel Factory in Turkey. Its chemical oxide composition is given in Table 1. The specific gravity of the slag was 2.81 g/cm³ and its Blaine specific surface area was about 425 m²/kg. It is classified as a category 80 slag according to ASTM C 989 [15] hydraulic activity index.

2.3. Alkali-activator

Liquid sodium silicate (obtained from Sisecam Soda Industrials Corp., Mersin Soda Factory) was used as the alkali activator. Liquid sodium silicate had a SiO₂/Na₂O ratio (modulus, Ms) = 2, and 38–40 Bé.

2.4. Sand

The sand was uncrushed, quartzitic, natural sand with maximum size of 4 mm. The grading complied with the requirements of ASTM C33 [16]. The absorption value of the sand was 1.2% and the relative density at saturated surface dry condition was 2.67.

2.5. Experimental program

The mortar mixture proportions were 1:2.75:0.5 by weight of cement, sand and water, respectively. GGBS was used at 0%, 20%, 40%, 60%, 80% and 100% replacement by weight of cement. For liquid sodium silicate activator, a SiO₂/Na₂O ratio (modulus, Ms) of 0.75 was chosen, and this ratio was obtained by adding NaOH to liquid sodium silicate. Sodium concentration in the mixture proportions were also chosen as 4%, 6%, and 8%. The amount of water was adjusted to obtain a 0.5 water/binder

ratio for all the mortar mixes. The amount of water in the activator was taken into account. Prismatic specimens with 40 × 40 × 160 mm dimensions were prepared from both OPC and OPC/slag mortar mixtures for all the testing measurements. After 24 h, the prisms were demoulded and placed in a humidity cabinet at 65% ± 5 relative humidity and 23 ± 2 °C temperature. A summary of the experimental program is presented in Table 2.

The flexural strength measurements were performed on three prismatic specimens using a third point loading test. The compressive strength measurements were carried out using six broken pieces of the prism specimens obtained from flexure test. The strength tests of the specimens were conducted at 7, 28, 90 and 180 days of age according to TS EN 1015-11 [17].

A phenolphthalein method was used to monitor the pH of mortar specimens in the carbonation experiments and the tests were conducted at 7, 28, 90 and 180 days of age. In this method, phenolphthalein is used as an indicator of the pH change in the mortar pore solution. The usual method of studying carbonation is to measure the depth of neutralisation as indicated by a phenolphthalein solution, which has been sprayed onto the fractured concrete surface. This indicator shows a magenta coloured region on the concrete where the pH value exceeds about 9 and a colourless 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 mortar prism after flexural strength test, and the depth of neutralisation was measured. The values were expressed by taking the average of three prismatic specimens.

3. Results and discussion

3.1. Flexural strength

The flexural strength of the mortars was determined at 7, 28, 90 and 180 days, and the test results were presented in Table 3.

As seen in Table 3, the control mortar achieved a flexural strength of 5.1 MPa at the age of 7 days, 4.8 MPa at the age of 28 days, 5.5 MPa at the age of 90 days and 6.0 MPa at the age of 180 days. The flexural strength of liquid sodium silicate-activated mortars containing different replacement levels of GGBS varied between 1.6 MPa and 6.4 MPa at the age of 7 days, 2.2 MPa and 6.7 MPa at the age of 28 days, 2.8 MPa and 6.8 MPa at the age of 90 days, and 2.9 MPa and 7.0 MPa at the age of 180 days. The flexural strength grew with an increase in the Na content in the mix for a constant replacement level of GGBS. On the other hand, a rise in the replacement level of GGBS increased flexural strength for a particular Na dosage, and the maximum flexural strength was obtained from liquid sodium silicate-activated mortars containing 100% slag. However, it was seen that flexural strength of GGBS100 mortar activated by liquid sodium silicate with 8% Na was lower than that of GGBS80 mortar activated by liquid sodium silicate at the same Na concentration. This phenomenon could be attributed to the crackings dependent on the high shrinkage deformations resulting from high Na concentration as discussed in the literature before [18]. Also, it is thought that dry curing conditions in which mortar specimens are kept, could play an important role in the development of these cracks.

Table 1
Physical, chemical and mechanical properties of cement and GGBS.

Chemical composition (%)	Cement	GGBS	Physical properties of Portland cement	
SiO ₂	19.71	36.70	Specific gravity	3.16
Al ₂ O ₃	5.20	14.21	Initial setting time (min)	150
Fe ₂ O ₃	3.73	0.98	Final setting time (min)	210
CaO	62.91	32.61	Volume expansion (mm)	1.0
MgO	2.54	10.12	Specific surface (Blaine) (cm ² /g)	3250
Na ₂ O	0.25	0.42	<i>Compressive strength (MPa) of cement</i>	
K ₂ O	0.90	0.76	2 Days	29.9
SO ₃	2.72	0.99	7 Days	41.4
LOI	0.96	NA	28 Days	52.2
			<i>Physical properties of GGBS</i>	
			Specific gravity	2.81
			Specific surface (Blaine) (cm ² /g)	4250
			<i>Pozzolanic activity index (%) of GGBS</i>	
			7 Days	57
			28 Days	85

Table 2
Summary of the experimental program.

Mixture name	GGBS (%)	Type of activator	Ms (SiO ₂ /Na ₂ O)	Sodium concentration (%)
Control	–	–	–	–
GGBS20	20	Liquid sodium silicate	0.75	4, 6, 8
GGBS40	40	Liquid sodium silicate	0.75	4, 6, 8
GGBS60	60	Liquid sodium silicate	0.75	4, 6, 8
GGBS80	80	Liquid sodium silicate	0.75	4, 6, 8
GGBS100	100	Liquid sodium silicate	0.75	4, 6, 8

Table 3
Flexural strength of liquid sodium silicate-activated OPC/slag mortars.

Mixture name	Activator concentration	Flexural strength (MPa)			
		7-Days	28-Days	90-Days	180-Days
Control	–	5.1	4.8	5.5	6.0
GGBS20	4% Na, Ms = 0.75	2.0	3.1	3.5	3.6
	6% Na, Ms = 0.75	1.7	2.7	2.8	3.0
	8% Na, Ms = 0.75	1.6	2.5	3.0	3.5
GGBS40	4% Na, Ms = 0.75	1.8	2.2	4.2	4.2
	6% Na, Ms = 0.75	1.9	2.6	4.2	4.3
	8% Na, Ms = 0.75	2.0	2.8	4.4	4.4
GGBS60	4% Na, Ms = 0.75	1.9	2.4	2.8	2.9
	6% Na, Ms = 0.75	2.7	2.4	4.1	4.2
	8% Na, Ms = 0.75	3.0	3.4	5.3	5.3
GGBS80	4% Na, Ms = 0.75	2.7	2.8	3.1	4.8
	6% Na, Ms = 0.75	4.5	5.9	6.2	6.6
	8% Na, Ms = 0.75	6.4	6.7	6.8	7.0
GGBS100	4% Na, Ms = 0.75	3.0	3.2	3.1	3.7
	6% Na, Ms = 0.75	5.9	6.1	6.2	6.3
	8% Na, Ms = 0.75	5.9	6.2	6.4	6.5

3.2. Compressive strength

The compressive strength of the mortars was determined at 7, 28, 90 and 180 days, and the test results were presented in Table 4.

As seen in Table 4, the control mortar achieved a compressive strength of 36.4 MPa at the age of 7 days, 40.8 MPa at the age of 28 days, 40.4 MPa at the age of 90 days and 41.9 MPa at the age of 180 days. The compressive strength of liquid sodium silicate-activated mortars containing different replacement levels of GGBS varied between 11.8 MPa and 67.0 MPa at the age of 7 days, 17.5 MPa and 81.1 MPa at the age of 28 days, 20.8 MPa and 84.2 MPa at the age of 90 days, and 21.7 MPa and 85.1 MPa at the age of 180 days. As expected, the compressive strength increased with age, and depending on the acceleration in the activation reactions, the compressive strength values increased with an increase in the Na content in the mix for a constant replacement

level of GGBS. On the other hand, an increase in the replacement level of GGBS increased compressive strength of the mortars for a constant Na dosage, and the maximum compressive strength was obtained from liquid sodium silicate-activated mortars containing 100% slag, similar to flexural strength results. Accordingly, the control mortar cured at the same conditions as slag-incorporated mortars showed less compressive strength than GGBS100 mortar activated by liquid sodium silicate at 6% and 8% Na concentrations, especially.

According to the strength test results, the flexural and compressive strength of the slag/cement blend activated by liquid sodium silicates was found to be lower than liquid sodium silicate-activated cementless slag mortar (GGBS100). It can be due to the effect of alkaline activator on Portland cement hydration, which results in formation of a significant amount of calcium hydroxide and Na-substituted C–S–H (N–C–S–H), which was reported to be less

Table 4
Compressive strength of liquid sodium silicate-activated OPC/slag mortars.

Mixture name	Activator concentration	Compressive strength (MPa)			
		7-Days	28-Days	90-Days	180-Days
Control	–	36.4	40.8	40.4	41.9
GGBS20	4% Na, Ms = 0.75	18.2	25.1	23.4	26.9
	6% Na, Ms = 0.75	15.6	19.7	20.8	21.7
	8% Na, Ms = 0.75	13.3	17.5	21.5	22.3
GGBS40	4% Na, Ms = 0.75	11.8	21.9	23.6	24.3
	6% Na, Ms = 0.75	13.1	24.0	27.8	28.9
	8% Na, Ms = 0.75	17.6	29.2	31.1	33.1
GGBS60	4% Na, Ms = 0.75	14.7	23.3	24.8	25.4
	6% Na, Ms = 0.75	18.1	28.6	39.7	41.9
	8% Na, Ms = 0.75	25.6	39.3	50.6	51.7
GGBS80	4% Na, Ms = 0.75	18.4	27.5	35.1	37.8
	6% Na, Ms = 0.75	45.3	57.1	60.0	62.1
	8% Na, Ms = 0.75	58.3	70.1	69.0	73.1
GGBS100	4% Na, Ms = 0.75	31.1	35.5	37.6	38.4
	6% Na, Ms = 0.75	62.7	71.7	74.4	77.6
	8% Na, Ms = 0.75	67.0	81.1	84.2	85.1

Table 5
Carbonation depths of liquid sodium silicate-activated OPC/slag mortars.

Mixture name	Activator concentration	Carbonation depths (mm)			
		7-Days	28-Days	90-Days	180-Days
Control	–	0.38	0.81	3.14	4.20
GGBS20	4% Na, Ms = 0.75	0	1.60	6.23	9.53
	6% Na, Ms = 0.75	0	1.44	5.29	9.08
	8% Na, Ms = 0.75	0	1.12	5.11	8.00
GGBS40	4% Na, Ms = 0.75	0	1.60	6.29	11.25
	6% Na, Ms = 0.75	0	1.45	5.08	9.41
	8% Na, Ms = 0.75	0	1.09	4.85	8.70
GGBS60	4% Na, Ms = 0.75	0	1.28	5.49	9.59
	6% Na, Ms = 0.75	0	0.81	4.21	6.57
	8% Na, Ms = 0.75	0	0.19	3.44	5.80
GGBS80	4% Na, Ms = 0.75	0.13	1.08	4.58	7.15
	6% Na, Ms = 0.75	0	0.70	4.08	5.73
	8% Na, Ms = 0.75	0	0.55	3.20	4.81
GGBS100	4% Na, Ms = 0.75	0.25	2.15	7.14	12.25
	6% Na, Ms = 0.75	0	0.58	3.96	5.26
	8% Na, Ms = 0.75	0	0.50	1.85	4.30

dense and has lower strength than hydration product of cement and water [5,19,20].

3.3. Carbonation

The evolution of the depth of the carbonated layer in time for the mortars was given in Table 5.

Concrete has naturally high pH due to $\text{Ca}(\text{OH})_2$ formed when Portland cement reacts with water. The pH of the ionic water solution present in the pores of fresh concrete may be over 14. When concrete is exposed to the atmosphere or when ground waters that contain some CO_2 seep into concrete, a reaction takes place between CO_2 and $\text{Ca}(\text{OH})_2$ of the hydrated cement paste leading to the formation of CaCO_3 . This situation can reduce the pH to 9, although that reaction usually is restricted to a thin layer at the surface and causes a decrease in the alkalinity of the concrete, which makes the steel reinforcement more vulnerable to corrosion [21]. As seen in Table 5, carbonation depth of the mortars increased with age since CO_2 penetrates from the surface to the interior of mortar in time. The carbonation depths of the control mortar were 0.38 mm at the age of 7 days, 0.81 mm at the age of 28 days, 3.14 mm at the age of 90 days and 4.20 mm at the age of 180 days. The carbonation depths of liquid sodium silicate-activated mortars containing different replacement levels of GGBS varied between 0 and 0.25 mm at the age of 7 days, 0.19 mm and 2.15 mm at the age of 28 days, 3.20 mm and 7.14 mm at the age of 90 days, and 4.30 mm and 12.25 mm at the age of 180 days. For a constant replacement level of GGBS, an increase in the Na content in the mix decreased the carbonation depths of mortars activated by liquid sodium silicate. This behaviour could be relevant to the more compact structure of binding paste occurring with an increment in the Na content which is responsible for the acceleration of the hydration reactions. The experimental results showed that the carbonation depth of liquid sodium silicate-activated mortars containing slag was higher than that of the control mortar at longer term ages even though showing less carbonation depth at 7 days. After 180 days of exposure to carbonation, it was found that the resistance of AAS mortar to carbonation was lower than that of OPC mortar, and AAS mortar had higher depth of carbonation than OPC mortar. This situation may be explained in this way: when AAS concrete is exposed to CO_2 , C–S–H reacts producing calcium carbonate, decalcified C–S–H and aluminosilicate gel. Because in slag concrete the Ca content is low, deposits of CaCO_3 are rare. As a result of the carbonation reaction, porosity in the matrix may increase. This increases the diffusivity of the concrete and

the access of HCO_3^- and CO_2 to the interior. Therefore, the reaction front may proceed more rapidly inward [11]. Thus, AAS binders present a potentially higher susceptibility to carbonation as compared with conventional cements.

4. Conclusions

It was concluded from the test results that flexural and compressive strength of the slag-incorporated mortars increased with an increase in the Na content of liquid sodium silicate used for alkali activation. Similarly, an increase in the replacement level of GGBS increased flexural and compressive strength of the mortars activated by liquid sodium silicate, and the maximum flexural and compressive strength was obtained from the GGBS100 mortars activated by liquid sodium silicate. Accordingly, OPC/slag mortars activated by liquid sodium silicate showed lower strength than the slag alone activated by the same activator. On the other hand, the findings obtained from the carbonation tests showed that an increase in the Na content in the mix decreased the carbonation depths of mortars activated by liquid sodium silicate, and AAS mortar had higher depth of carbonation than OPC mortar. As per the carbonation test results, it is considered that an effective curing procedure could be useful for the reduction of high carbonation rates seen in these binders.

According to the results of the tests performed within the scope of this study, a low performance obtained from OPC/slag mortars is not encouraging for further use of this type of binder. For this reason, it is considered to be more suitable that the researches on the mixtures containing slag alone activated by an alkaline solution should be carried out.

Acknowledgment

The authors would like to thank Çukurova University Scientific Research Projects Directorate (Project number: MMF 2004 D16).

References

- [1] Neville AM. Properties of concrete. 4th ed. Longman; 1995.
- [2] Collins FG, Sanjayan JG. Workability and mechanical properties of alkali activated slag concrete. *Cem Concr Res* 1999;29:455–8.
- [3] Neto AAM, Cincotto MA, Repette W. Drying and autogenous shrinkage of pastes and mortars with activated slag cement. *Cem Concr Res* 2008;38:565–74.
- [4] Puertas F, Amat T, Jiménez AF, Vázquez T. Mechanical and durable behaviour of alkaline cement mortars reinforced with polypropylene fibres. *Cem Concr Res* 2003;33:2031–6.

- [5] Bakharev T, Sanjayan JG, Cheng Y. Alkali activation of Australian slag cements. *Cem Concr Res* 1999;29:113–20.
- [6] Bakharev T, Sanjayan JG, Cheng YB. Effect of elevated temperature curing on properties of alkali-activated slag concrete. *Cem Concr Res* 1999;29:1619–25.
- [7] Collins F, Sanjayan JG. Early age strength and workability of slag pastes activated by NaOH and Na₂CO₃. *Cem Concr Res* 1998;28:655–64.
- [8] Collins FG, Sanjayan JG. Workability and mechanical properties of alkali-activated slag concrete. *Cem Concr Res* 1999;29:455–8.
- [9] Jimenez AF, Palomo JG, Puertas F. Alkali-activated slag mortars mechanical strength behaviour. *Cem Concr Res* 1999;29:1313–21.
- [10] Atiş CD, Bilim C, Çelik Ö, Karahan O. Influence of activator on the strength and drying shrinkage of alkali-activated slag mortar. *Constr Build Mater* 2009;23:548–55.
- [11] Bakharev T, Sanjayan JG, Cheng YB. Resistance of alkali-activated slag concrete to carbonation. *Cem Concr Res* 2001;31:1277–83.
- [12] Puertas F, Palacios M, Vázquez T. Carbonation process of alkali-activated slag mortars. *J Mater Sci* 2006;41:3071–82.
- [13] Byfors K, Klingstedt V, Lehtonen PYY, Romber L. Durability of concrete made with alkali activated slag. In: *Proceedings of the 3th international conference on fly ash, silica fume, slag and natural Pozzolans in concrete*. American Concrete Institute. Trondheim, Norway; 1989.
- [14] Bernal SA, Gutierrez RM, Provis JL, Rose V. Effect of silicate modulus and metakaolin incorporation on the carbonation of alkali silicate-activated slags. *Cem Concr Res* 2010;40:898–907.
- [15] ASTM C-989. Standard specification for ground granulated blast furnace slag for use in concrete and mortars. *Annual book of ASTM Standards*; 1994.
- [16] ASTM C33. Standard specification for concrete aggregates. West Conshohocken, USA: *Annual Book of ASTM Standards*; 2005.
- [17] TS EN 1015-11. Mortar testing method. Part 11: Measurement of compressive and flexural tensile strength of mortar. TSE, Ankara; 2000.
- [18] Krizan D, Zivanovic B. Effects of dosage and modulus of water glass on early hydration of alkali-slag cements. *Cem Concr Res* 2002;32:1181–8.
- [19] Way SJ, Shayan A. Early hydration of a Portland cement in water and sodium hydroxide solutions: composition of solutions and nature of solid phases. *Cem Concr Res* 1989;19:759–69.
- [20] Alexander KM, Davis CES. Effect of alkali on the strength of Portland cement paste. *Aust J Appl Sci* 1960;11:146–56.
- [21] Bilim C. Properties of cement mortars containing clinoptilolite as a supplementary cementitious material. *Constr Build Mater* 2011;25:3175–80.