

EFFECTS OF SILICA MODULUS AND ALKALI CONCENTRATION ON ACTIVATION OF BLAST-FURNACE SLAG

A. Allahverdi, E. Najafi Kani and S. Esmaeilpoor

ali.allahverdi@just.ac.ir

Date of Receive: August 2007

Date of Acceptance: May 2008

Department of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran

Abstract: The use of alkali-activated cementitious materials especially over the past decades has significantly been increased. The goal of this research is to investigate the effects of silica modulus and alkali concentration on alkali-activation of blast-furnace slag. In this research, the most important physical characteristics of cementitious systems, i.e. the 28-day compressive strength and final setting time, were studied by changing influencing parameters such as silica modulus, i.e. $\text{SiO}_2/\text{Na}_2\text{O}$, (0.44, 0.52, 0.60, and 0.68) and Na_2O concentration (4, 6, 8 and 10% by weight of dry binder) at a constant water-to-dry binder ratio of 0.25. Final setting time of the studied systems varies in the range between 55-386 minutes. The obtained results show that systems cured at an atmosphere of more than 95% relative humidity at room temperature exhibit relatively high 28-day compressive strengths up to 107 MPa.

Keywords: Alkali-activation, Blast-furnace Slag, Setting Time, Compressive Strength.

1. INTRODUCTION

The goal of sustainable development of the cement industry is very important, and one important effort is utilization of the cementitious by-products produced in metallurgical industries. Blast-furnace slag is a by-product of the steel production industry [1, 2]. It has a latent hydraulic reactivity, which can be catalyzed by proper activators such as alkali metal hydroxides to form cementitious materials. Alkali-activated slag cement (AASC) provides a number of advantages over ordinary Portland cement including superior durability in aggressive environments, low energy consumption and low greenhouse gas emission in production process [3, 4, 5]. However, due to the numerous influencing factors, such as the chemical and mineral composition of the slag, the amount of glassy phase as well as the type and concentration of used activator, alkali activation of slag is still an insufficiently defined process requiring further research [2, 6, 7]. The goal of this research is to investigate the effects of silica modulus and alkali concentration on alkali-activation of blast-furnace slag.

2. EXPERIMENTAL

2.1. Raw Materials

Granulated blast-furnace slag was prepared from Isfahan steel complex located in Isfahan province, Iran. The prepared slag was firstly ground in a laboratory ball mill to attain a Blaine specific surface area of $340 \text{ m}^2/\text{kg}$. Table 1 presents the chemical composition of the used blast-furnace slag sample. Industrial sodium silicate solution (weight ratio $\text{SiO}_2/\text{Na}_2\text{O}=0.86$, $\text{SiO}_2=34.32 \text{ wt}\%$) and industrial-grade NaOH (99% purity) were used throughout all experiments.

2.2. Specimens Preparation

Commercial sodium silicate was used for preparing alkali activators. Enough sodium hydroxide was added to sodium silicate solution for preparing four different alkali-activators having silica moduli ($M_s=\text{SiO}_2/\text{Na}_2\text{O}$) of 0.68, 0.60, 0.52, 0.44. The sodium oxide-contents of systems were adjusted at four different levels of 4, 6, 8 and 10 % (by weight of dry binder). A water-to-dry binder ratio of 0.25 was used to prepare pastes.

Table 1. Chemical composition of Isfahan blast-furnace slag.

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2
wt %	36.06	9.16	0.70	36.91	10.21	1.15	0.70	0.48	3.50

Sodium oxide content and silica modulus of designed systems are presented in table 2. The pastes were then cast into 2×2×2 cm molds. The molds were held at an ambient of nearly 95% relative humidity for preventing drying and giving enough time (24 hrs) to the pastes to set and harden at ambient temperature, i.e. 25 °C. After demoulding, the specimens were cured using two different curing regimes including 28 days in an atmosphere of 95% relative humidity at 25°C and hydrothermal curing for 8 hours at 80°C. The hydrothermal curing procedure was 24 hrs in molds at 95% relative humidity at 25°C, demoulding and keeping the specimens at the same conditions for 6 days, then heating up to 80°C during 1 hr in a steam saturated atmosphere. The specimens were held at the final temperature for an additional 8 hrs. After that the specimens were stored dry in an open air atmosphere at 25°C and 40-50% relative humidity.

Table 2. Sodium oxide content and silica modulus of designed systems (W/C=0.25).

System No.	Na ₂ O (wt %)	Ms
1	4	0.44
2	6	0.44
3	8	0.44
4	10	0.44
5	4	0.52
6	6	0.52
7	8	0.52
8	10	0.52
9	4	0.60
10	6	0.60
11	8	0.60
12	10	0.60
13	4	0.68
14	6	0.68
15	8	0.68
16	10	0.68

3. RESULTS AND DISCUSSION

3.1. Final Setting Time

Fig. 1 shows the effects of Na₂O concentration on final setting time at different silica moduli. As seen, Final setting time of the studied systems varies in the range between 55 – 386 minutes. Such final setting times, however, are almost acceptable compared to usual values reported for ordinary Portland cement, i.e. more than 180 minutes. As shown in Fig. 1, at constant silica

modulus, the final setting time reduces when Na₂O concentration is increased. Increasing the Na₂O concentration from 4 to 6% could effectively accelerate activation reactions which in turn results in a significant decrease in final setting.



Fig. 1. Effect of Na₂O concentration on final setting time.

3.2. Compressive Strength

Before measuring the 28-day compressive strength, the specimens were observed visually for any possible crack. They were quite sound and no crack was observed visually. Figures 2 and 3 show the effects of Na₂O concentration on compressive strength at different curing conditions and different silica modulus. As seen, different curing conditions change the effect of Na₂O concentration on compressive strength development of specimens. The strength increase at relatively lower Na₂O concentrations, i.e. in the range between 4 to 8%, is much steeper and at relatively high concentrations, i.e. in the range between 8 to 10%, becomes gradually. Increasing the Na₂O concentration up to 8% generally results in an increase in 28-day compressive strength irrespective of curing regime. At higher concentrations of Na₂O, the 28-day compressive strength decreases due to excess sodium oxide.

Both sodium hydroxide and sodium silicate play important roles in geopolymerization reactions. Sodium hydroxide provides both hydroxide anion (OH⁻) which is very important for dissolution of the aluminosilicates in the first stage and sodium cation (Na⁺) which is important for charge balance of the aluminosilicate network formed in the last stage.

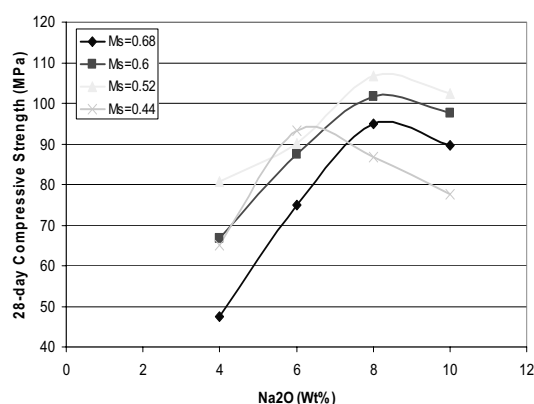


Fig. 2. Effects of Na_2O concentration on 28-day compressive strength development at 95% R.H. at 25°C .

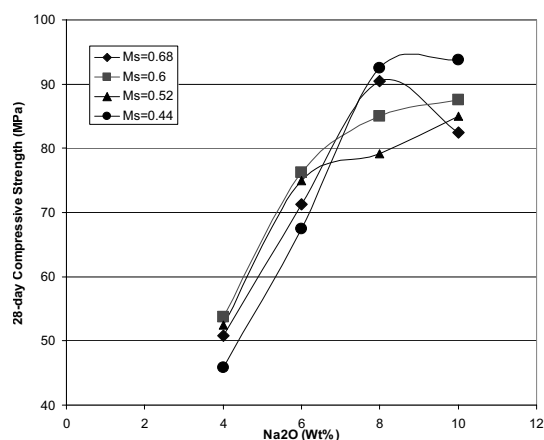


Fig. 3. Effects of Na_2O concentration on compressive strength development at hydrothermal curing condition.

Solubility of aluminosilicate increases with increasing OH^- concentration. Utilization of too much sodium hydroxide in preparation of alkali-activator, however, is not beneficial. Sodium silicate also provides good interparticle bonding and therefore mechanical strength of the material by synthesizing aluminosilicate gel [5,7,8]. The maximum achievable 28-day compressive strengths are 107 MPa and 94 MPa respectively at curing conditions of 95% R.H. at 25°C and hydrothermal curing for 8 hours at 80°C .

3.3. Efflorescence

To investigate any possible efflorescence from each system, a 28-day hardened specimen was placed in a given volume of water, i.e. 50 ml, and kept in an open-air atmosphere at ambient temperature i.e. 25°C until the water was dried completely. The results of efflorescence test were obtained qualitatively by just comparing

the specimens visually. Table 3 presents the obtained results. The severity of the efflorescence has been differentiated by letters A, B, and C. Systems exhibiting no efflorescence are shown by letter A. Those showing slight and severe efflorescence are distinguished by letters B and C respectively. Experiments showed that increasing the amount of alkali-activators in specimens increase the severity of efflorescence. The severity of efflorescence decreases in most systems by applying hydrothermal curing conditions.

Table 3. Results of efflorescence test (A: Slight, B: Moderate, C: Severe).

Curing at 95% R.H. at 25°C		Hydrothermal curing	
System No.	Severity of efflorescence	System No.	Severity of efflorescence
-	A	1,2,5,6,9,10	A
1,2,5,6,9,13	B	3,4,7,8,11,12,13,14	B
3,4,7,8,10,11,12,14,15,16	C	15,16	C

3.4. X-Ray Diffraction Analysis

X-ray patterns of slag and systems exhibiting the highest compressive strengths are presented in Fig. 4. As seen, the original crystalline phase of the starting material, i.e. blast furnace slag, has not been changed and remained the same. The crystalline phases present in slag and the tested systems are calcite, akermanite, and quartz. Calcite is the major product of a secondary reaction between the lime content of slag and carbon dioxide from atmosphere. It should be noted that X-ray diffractometry technique is not useful in tracing and identifying the binding compounds produced in the course of chemical reactions occurring in the material.

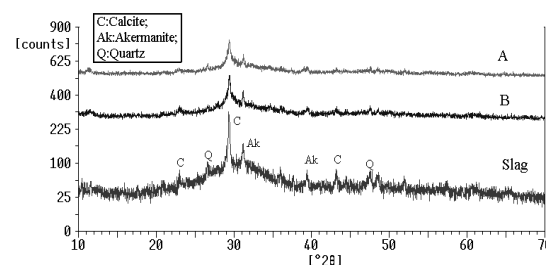


Fig. 4. X-Ray diffraction patterns of Slag, specimen cured at 95% R.H. at 25°C (specimen A), and specimen cured hydrothermally (specimen B) showing maximum compressive strength.

As seen, there is no indication from such compounds in the produced patterns. This means that the reaction products exhibiting binding properties are present in completely amorphous states.

3.5. FTIR Analysis

Fig. 5 displays the infrared spectra of slag and systems exhibiting the highest compressive strengths. As seen, in each spectra, there exist a main broad and strong absorption peak appearing at about 1000 cm^{-1} , a fairly broad and relatively strong peak at about 460 cm^{-1} , and a number of very weak peaks in the range $500 \sim 900\text{ cm}^{-1}$. The first of these bands that is the most intensive is usually a superposition of some bands situated close to each other. The main peaks of interest are peaks at $\sim 460\text{ cm}^{-1}$ assigned to the in-plane bending of Al-O and Si-O linkages, while the peaks at around 1000 cm^{-1} have been attributed to asymmetric stretching of Al-O and Si-O bonds [7].



Fig. 5. Infrared spectra of slag and system cured at 95% R.H. at 25°C (specimen B), and specimen cured hydrothermally (specimen A) showing maximum compressive strength.

The peaks at $\sim 1000\text{ cm}^{-1}$ are a major fingerprint for alkali-activated materials representing the fusion of both Al-O and Si-O asymmetric stretching and can indicate the extent of aluminum incorporation with a lowering in the energy of the peak. Octahedrally co-ordinated aluminium if present can be detected by a peak at 540 cm^{-1} while tetrahedral aluminium shows a weak peak at about 800 cm^{-1} , which is due to symmetric Al-O stretching.

4. CONCLUSIONS

Results obtained from activating blast-furnace slag using proportioned mixture of NaOH and Na_2SiO_3 prove the possibility of producing relatively high compressive strength alkali-activated slag cement. Systems cured at an atmosphere of more than 95% relative humidity at room temperature could exhibit relatively high 28-day compressive strengths up to almost 107 MPa. Final setting time of different systems studied varies in the range between 55-386 minutes which are almost acceptable to usual values reported for ordinary Portland cement.

REFERENCES

1. D. M. Roy, G.M. Idorn J. ACI 1982;79:444-457.
2. D. Krizan and B. Zivanovic Cem. & Concr. Res. 2002;32:1181-1188.
3. T. Bakharev, J. G. Sanjayan, Y. B. Cheng Cem. & Concr. Res. 1999;29:113-120.
4. J. Schneider, M. A. Cincotto, and H. Panepucci Cem. & Concr. Res. 2001;31:993-1001.
5. I. G. Richardsture, A. R. Brough, , G. W. Groves, and C. M. Dobson Cem. & Concr. Res. 1994;24:813-829.
6. T. Bakharev Cem. & Concr. Res. 2005;35:1233-1246.
7. I. Lecomte, C. Henrist, F. Liegeois, A. Maseri, R. Rulmont J. European Ceramic Society, 2006;26:3789-3797.
8. V. Zivica, Constr. Build. Mat. 2007; 21:1463-1469.