Construction and Building Materials 37 (2012) 462–469

Contents lists available at SciVerse ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Portland cement-blast furnace slag mortars activated using waterglass: – Part 1: Effect of slag replacement and alkali concentration

E. Acevedo-Martinez, L.Y. Gomez-Zamorano, J.I. Escalante-Garcia *

Centro de Investigación y de Estudios Avanzados del IPN (Cinvestav), Unidad Saltillo, Apartado Postal 663, Saltillo, Coah, Mexico

HIGHLIGHTS

- The activation of mortars of Portland cement with slag was investigated to reduce the low early strength.
- For mortars with 50–30% slag, the activation with water glass (4–10%Na_2O) was not effective.
- For 80% slag the activation with 4–10%Na_2O was effective.
- The highest strengths were for activated 100% slag cements.

ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form 14 June 2012
Accepted 22 July 2012
Available online 5 September 2012

Keywords:
Hydration
Microstructure
Backscattered electron imaging
Alkali activated slag
Blast furnace slag
Nonevaporable water
Compressive strength

ABSTRACT

Mortars of PC replaced with 0% to100% blast furnace slag were activated by waterglass at 0–10 wt.% of Na_2O, aiming to investigate the effect of the alkaline activation in reducing the low early strength observed in Portland cement–slag blends. For the activated blended mortars, increased %Na_2O and slag contents favored strength; 80% slag showed favorable results with 6 and 10%Na_2O, while 30–50% slag, the presence of the alkaline activator was unfavorable relative to the non-activated Portland cement and slag mortars. The microstructures showed denser matrices of hydration products as the amount of slag and alkali concentration were increased, corresponding to the strength observations.

1. Introduction

Replacement of Portland cement (PC) by inorganic industrial by products has been the focus of much research in the interest of environmental protection from several perspectives. There is the need to reduce environmental liabilities by reutilizing byproducts to reduce pollution [1–6]; moreover, binders of an environmental impact lower than that of PC are also needed [7,8] in view of the impact of such industry in the CO_2 world emissions. Additionally, some by products improve specific properties to PC concretes, such as insulating, toxic waste encapsulation, and high strength.

Studies on the replacement of PC for blast furnace slag (BFS) are widely reported, and although many aspects still require investigation, it is widely accepted that the incorporation of BFS improves the long term strength and durability; other advantages are a lower heat of hydration, relatively lower cost, etc. [5,9,10,20].

Nonetheless, using BFS to replace PC in large proportions has the disadvantage of lower early strength and increased setting times compared to neat PC [10–13]; higher early strengths are desirable for such cements, especially when heat evolution is not a major concern. Such disadvantages origin from the slower BFS reactions to produce cementitious products, under the hydrated PC alkaline activating environment provided mainly by the $Ca(OH)_2$ (calcium hydroxide, CH) [14–16]. Various routes are available to enhance the reactivity of a predominantly glassy BFS in blends with PC, i.e. curing at higher temperatures [17,18] and increasing the surface area [19–21]. The former is not always possible for nonprecast products and the latter increases the cost of materials processing and potentially the water demand in detriment of the mechanical properties. Chemical activation is another possibility that has been successfully used for years to enhance the cementitious properties of BFS based cements [12]; among the various alkaline agents, sodium silicate (waterglass) is one of the most effectives for strength development [17,22,23].

---

* Corresponding author. Tel.: +52 844 4389600; fax: +52 844 4389610.
E-mail address: ivan.escalante@cinvestav.edu.mx (J.I. Escalante-Garcia).

0950-0618/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.conbuildmat.2012.07.041

However, the limited number of reports in relation to chemical activation of blends of BFS–PC report results that are not always consistent. Shi et al. [12] pointed that the addition of alkali silicates can be very effective in increasing the early strength of high volume BFS cements, they commented results for blends of PC with 50%BFS: the comparative activation with Na_2SiO_3, Na_2CO_3, NaOH and Na_2SO_4, indicated that Na_2SiO_3 and Na_2SO_4 were the most and least effective, respectively [24]. In contrast other authors reported that the use of 4%Na_2SO_4 significantly increased the strength of PC with 50%BFS [25], or 0.5%$NaSO_4$ and alum were effective for PC with 30%BFS [26].

Roy et al. [27] studied blends of clinker + gypsum + (20–80%) BFS and reported that activation with 1% waterglass (modulus $SiO_2/Na_2O = 3$) favored strength development, especially during the first few days of curing. Increased BFS contents reduced the strengths during the first 28 days for activated and non-activated cements, the strengths of pure PC were higher for up to 28 days, but after 90 days the highest strengths were those of activated blends with 40–50%BFS. Similar observations have been reported for non-activated systems PC–BFS [10]. Zivica [13] reported the use of an activator of an undefined mixture of pozzolan in an alkaline solution; such activator caused the 100%PC mortars to harden very fast and was only used on blends of PC–BFS. The addition of undisclosed amounts of the activator notably improved the strength of non-activated blends of PC with 70–100%BFS cured at 20 °C; the strength of the activated 90%BFS blend reached that of the 100%PC mortar. Ghosh et al. [28] investigated a 96% glassy BFS ($(C + M+.33A)/(S+.66A) = 1.03$), and used undisclosed amounts of waterglass of modulus equal to 3 (pH = 11) on blends of PC substituted with 55, 65, 75, 85%BFS and cured underwater at 27 °C. The waterglass was added in solution during grinding in a ball mill. For 55%BFS, the use of the activator was reported as favorable, but no reference data was provided for non-activated blends; on the other hand for BFS above 65% reactions slowed down specially after 7 days.

The results of Marciano and Battagin [29] contrast with the above, they used various alkaline agents at 1% on cements with 58 and 44%BFS and reported that sodium silicate was not effective and that the strengths were below those of non-activated cements for up to 28 days. On the other hand, Na_2SO_4 activation increased the early strength as the concentration was raised up to 2%; however, after 7 to 91 days the strengths were lower than the non-activated cements. Bakharev et al. [30] noted that for a PC substituted with 70%BFS activated at 4%Na with a sodium silicate with a modulus of 0.75; such mixture showed lower strength than activated BFS and non-activated PC–BFS blend and was disregarded for further investigation. A 7 day study of Sajedi and Razak [31] showed that for mixtures of CP with 60%BFS, the use of various alkaline agents, including sodium silicate of various moduli, reduced the strength of the activated blends in comparison to the nonactivated and 100%PC cements.

Soluble sodium silicate serves several functions as an additive to PC. It can be used as an effective set regulator, in freshly mixed PC rises the pH of the pore fluids and accelerates the hydration; however, elevated dosages does not proportionally further reduce the set times. Modest dosages of 2–4% of silicates can increase the strength of PC pastes, while higher dosages the rapid setting caused by the soluble silicates results in a more disordered structure and lower strengths. [32] In blends of PC–BFS there would be a competition for the WG and the overall effects are not understood in the literature.

Based on the above, this report presents the results of an investigation on the strength development and microstructures of mortars with binders of blends of PC with different contents of BFS activated with different concentrations of Na_2O using waterglass. The aim was to investigate whether the low early strength development observed for non-activated PC–BFS cements could be overcome by activation with concentrations of WG higher than those previously reported, and how such activation would affect the strength for up to 120 days.

2. Experimental

2.1. Materials

The materials used were an ordinary PC, a BFS and technical grade waterglass (WG) of modulus $SiO_2/Na_2O \approx 2$. The WG modulus was modified to 1.5 by adding NaOH pellets as described elsewhere [33,34], reducing the modulus allows a reduction in the viscosity of the solutions [35] and also increases the pH to enhance the activating efficiency. The BFS was ground to a blaine of 450 m^2/kg, the chemical composition of the materials is indicated in Table 1.

2.2. Mortar preparation

Different mortar mixes were prepared in the laboratory using standard Ottawa sand (ASTM C778) in a ratio sand:binder of 2.78:1, the water/binder ratio was kept at 0.5. The PC was replaced by BFS from 0% to 80% by mass, the dry powders were blended before the mortar mixing. The WG was added at 0, 4, 6 and 10 wt.% of Na_2O relative to the mass of BFS; the WG was homogenized with the required additional water before the mortar mixing. Table 2 presents the composition of the 16 mixes prepared. The powders and solution were mixed in batches of 8 kg in a laboratory blender for 3 min. Cubes of 50 mm were cast in sets of molds made of an alkali resistant polymer, the molds were covered with a damp cloth and plastic film, to avoid water evaporation, and transferred to an isothermal chamber at 20 °C for setting for 24 h. After demolding the cubes were submerged in water at 20 °C; time started to count from this stage. In agreement with other reports [12,13], the setting times of the activated blends were shorter than those of neat PC and non-activated PC–BFS, however this did not represent a critical problem. The workability of the blends allowed proper molding and vibrating of the mortars.

2.3. Characterization

After 1, 3, 7, 14, 28, 90 and 120 days 4 cubes were randomly selected and tested for compressive strength (CS) in a hydraulic testing machine (Controls model 50-C7024), the average was reported. From the fragments, lumps of about 30 g were sampled for nonevaporable water (NEW) measurements, the procedure as reported elsewhere [36]. Selected samples were cold mounted in epoxy resin; these were ground with succesively finer sandpaper grades and then polished with diamond pastes from 9 to ¼ μm using a non-water lubricant. The specimens were carbon coated to be observed under the scanning electron microscope (Jeol 6400) operated at 20 kV using backscattered imaging capabilities.

3. Results and discussion

3.1. Compressive strength

Fig. 1 presents the results of compressive strength vs time for all mortars investigated. The typical standard deviation was of 10 ± 5% relative to the mean of four samples; higher deviations were observed at lower CS. For non-activated mortars, the CS gradually reduced as the amount of BFS increased, after 28 days the values were 31, 25, 19 and 16 MPa for 0, 30, 50 and 80%BFS, respectively; this pattern persisted after 90 days and after 120 days the CS of 30 and 50%BFS blends reached values close to the 100%PC mortar. This behavior is commonly reported [10,37]. Although the use of large amounts of BFS results in better ultimate CS, the early CS development becomes inconveniently slower as the %BFS increases; in

Table 1
Chemical composition of starting materials.

	Oxide (wt.%)										
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	H_2O	LOI	Total
OPC	19.2	4.4	60.4	2.8	1.1	3.4	1.0	0.3	–	7.4[a]	100
BFS	31.9	10.6	36.4	6.5	9.3	3.0	0.8	0.9	–	0.8	100
Waterglass[b]	30.4							15.6	54.0		100

LOI = loss on ignition.

[a] Calcite used as admixture in the plant.

[b] Modulus ≈ 2.