Cement and Concrete Composites 84 (2017) 157–166

Contents lists available at ScienceDirect

Cement and Concrete Composites

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

Comparative performance of alkali activated slag/metakaolin cement pastes exposed to high temperatures

Oswaldo Burciaga-Díaz*, José Iván Escalante-García

Cinvestav Saltillo, Ceramics Engineering Group, Av. Industria Metalúrgica No. 1062, Parque Industrial, Ramos Arizpe, Coahuila, MX C.P. 25900, Saltillo, Coahuila, Mexico

A R T I C L E I N F O

Article history:
Received 15 March 2017
Received in revised form
2 September 2017
Accepted 11 September 2017
Available online 13 September 2017

Keywords:
Alkali-activated composites
Slag
Metakaolin
Structural evolution
Thermal stability

A B S T R A C T

This paper presents a study on the effect of temperature exposure of binders of blast furnace slag (BFS) and metakaolin (MK) in BFS-MK weight ratios of 100-0, 50-50, and 0-100 activated with sodium silicate of modulus $Ms = SiO_2/Na_2O = 1$ and 5, 10 and 15% Na_2O. A blended ordinary CPC-30R Portland cement reference was used. Pastes were subjected to exposure up to 1200 °C and the performance was evaluated in terms of compressive strength, residual strength, volumetric shrinkage, physical appearance and microstructural changes at different temperatures. All the binders retained more than 30 MPa after exposure to 800 °C for 4 h; specimens of MK and CPC-30R experienced the highest strength losses of 42 and 56% respectively, while those of 100-0 and 50-50 showed minor losses of ~20%. After heating at 1200 °C the samples showed microstructural damage and more than 65% of strength losses. XRD indicated that the 100-0 and 50/50 binders are prone to form crystalline phases as akermanite, nepheline and nosean at temperatures greater than 1000 °C, while 0-100 geopolymeric binders preserved mostly an amorphous structure even at 1200 °C with some traces of mullite. The dehydration of C-A-S-H and N-A-S-H altogether with the crystallization of the binder gel induced the formation of highly porous microstructures.

1. Introduction

Although the concrete of Portland cement (PC) is an incombustible material, it may suffer serious damage upon heating during fire exposure [1–3]. Exposure to high temperature leads to deterioration through the increase of the pore pressure by evaporation of free and bonded water, as well as by the occurrence of thermal stresses due to differences in the thermal expansion coefficients among the anhydrous and hydrated phases as well as the aggregates [1]. The loss of water from the C-S-H is a continuous process that occurs from 105 °C onwards, while for $Ca(OH)_2$ the process takes place at 400–550 °C forming lime (CaO) and water vapor [1,4,5]. The degradation after exposure to high temperatures results in the formation of porosity, nucleation of cracks, spalling and in significant strength losses [6,7].

In alkali activated binders of blast furnace slag (BFS) or metakaolin (MK) (i.e NaOH and sodium silicate "waterglass"), the degradation upon heating follows a different route compared to PC, in that there is no $Ca(OH)_2$ or its dehydroxylation [8]; thus, the alkali-activated cements have been reported to be thermally more resistant than the PC [9]. For alkali-activated BFS pastes, Bernal et al. [10], found that binders produced from silica fume and rice husk ash activators, retained strengths greater than 50 MPa after exposure to 600 °C, where a slight depolymerization of the C-A-S-H gel became noticeable. In agreement with the above, Rovnaník et al. [11], also reported a partial decomposition of C-A-S-H at 600 °C, while the main changes in the microstructures of alkali activated slag occurred between 600 °C and 800 °C, when the dehydration of C-A-S-H phase was complete and new phases started to crystallize, among which akermanite was dominant. Additionally, Mejia de Gutierrez et al. [12], reported residual strengths, after treating at 500 °C, of 45% and 75% for mortars of PC and alkali-activated slag, respectively. In a report from Puertas et al. [13], alkali-activated slag mortars showed up to 50% higher residual strength than PC mortars after treatment at 500 °C; however in the range of 25–500 °C, the former exhibited greater weight losses. From the referred reports, it appears that the stability of alkali-activated slag binders is limited

---

* Corresponding author. Present address: Tecnológico Nacional de México, Instituto Tecnológico de Saltillo, Blvd. Venustiano Carranza # 2400, Col. Tecnológico, C.P. 25280, Saltillo, Coahuila, Mexico.

E-mail address: oburciaga@itsaltillo.edu.mx (O. Burciaga-Díaz).

http://dx.doi.org/10.1016/j.cemconcomp.2017.09.007
0958-9465/

to about 500°C–600 °C, which can be disadvantageous for mortars and concretes exposed to fire, where temperatures of approximately 800 °C can be reached after 30 min of starting the fire [14].

Binders of alkali activated MK (geopolymers) have also better temperature stability than PC and alkali activated slag binders; residual strengths of 88% and 41.7% have been reported after treating at 850 °C for binders formulated with ratios Si/Al = 1.54 and Si/Al = 1.40 respectively [15–17]. This was attributed to the presence of a highly crosslinked N-A-S-H gel that incorporates a low content of chemically bonded water and to the absence of calcium bearing phases as reaction products in its structure [18,19].

Although the atomic structure of geopolymers can be stable up to ~1000 °C, the thermal exposure alters the microstructure in a number of ways [19–22]. Dehydration by water evaporation promotes the first microstructural changes, which in turn causes a strong lineal shrinkage at ~200 °C [23]. The volume left after the evaporation of water takes shape into various microstructural features, such as cavities, cracks and pores, by the effect of expansion and contraction forces acting in the interior of the samples [15,24]. At temperatures greater than 800 °C, the sintering of the geopolymer paste alters the morphology, resulting in a microporous amorphous material with low mechanical properties [15]. Therefore, for applications that involve exposure to high temperatures, it is desirable to synthesize materials containing the least structural water possible, which can benefit from using less water during the preparation of the pastes. One option to reduce the water demand can be a reduction of the surface area of the MK and/or to add a coarser alternative precursor such as BFS; the latter demands considerably less water to prepare fluid pastes while being sufficiently reactive to enhance the strength [25]. Studies of thermal performances of binders of alkali activated blends of BFS and MK are scarce in the literature. In this regard Bernal et al. [26], observed that the inclusion of 20% BFS in MK-based geopolymers improved the residual compressive strength when exposed to temperatures of 200°C–800 °C. The loss of structural integrity was suggested to be the result of the C-S-H gel dehydration, which consequently induced a greater extent of volumetric contraction leading to the cracking of the samples.

Consequently, in view of the few reports on the high temperature performance of alkali-activated BFS or MK binders and their blends, the interest of this study is to provide new results essential to encourage the implementation of such materials in applications of exposure to high temperatures, which might not be limited to construction applications. The results are of great value considering that previous papers have studied separately the thermal performance of geopolymers or alkali-activated slag cements, which were also exposed to lower temperatures compared to this study.

2. Experimental procedure

2.1. Materials

The raw materials (precursors) used were a granulated blast-furnace slag (BFS) and a metakaolin (MK). A blended ordinary Portland cement designed as CPC-30R was also used as reference, which may include 6-35%BFS, 6–35% $CaCO_3$ and 1–10% of silica fume as defined in the national standard NMX-C-414-ONNCCE [27]. The chemical composition of the starting materials as determined by X-ray fluorescence is shown in Table 1. The BFS presented a mean particle size, determined through laser diffraction, of (d_{50}) = 11.77 μm and 10% finer than 2 μm with a Blaine fineness of 4653 cm^2/g. The metakaolin (MK) was prepared in the laboratory by calcination of commercially available high purity kaolin, at 800 °C for 6 h; its Blaine fineness was of 9469 cm^2/g with a mean particle size (d_{50}) of 7.6 μm and 10% finer than 2 μm.

Both precursors BFS and MK as shown Fig. 1 were predominantly amorphous to X-ray diffraction and showed traces of crystalline phases as akermanite ($Ca_2MgSi_2O_7$), gehlenite ($Ca_2Al_2SiO_7$), and merwinite ($Ca_3MgSi_2O_8$) for the BFS, and of quartz (SiO_2) and anatase (TiO_2) for the MK. For the CPC-30R cement the results showed alite (C_3S), belite (C_2S), gypsum ($CaSO_4$), aluminate (C_3A), and brownmillerite (C_4AF). Calcite ($CaCO_3$) and quartz (SiO_2) are common impurities contained in the gypsum added to clinker during the manufacture of the PC to regulate the setting time, which explains their presence in the XRD pattern [1].

The alkaline activators consisted of blends of sodium silicate (SiO_2 = 29.5%, Na_2O = 14.7% and H_2O = 55.8%) solution modulus SiO_2/Na_2O = Ms = 2 and sodium hydroxide flakes, both of industrial grade.

2.2. Sample synthesis

Pastes were formulated in mixes of BFS-MK in weight proportions of 100-0, 50-50 and 0-100, which is the nomenclature used throughout this paper. The alkaline activators had a Ms = 1 and were added at Na_2O concentrations of 5, 10 and 15 wt% relative to the mass of BFS + MK. A paste of CPC-30R with a ratio water/solids = 0.35 was used as reference. A summary of mixture compositions studied is given in Table 2.

The alkaline solutions were prepared dissolving NaOH flakes in water and then mixing with sodium silicate and the solutions were left to cool down to 20 °C before mixing with the powders. For the fabrication of the pastes, the alkaline solutions and the powders were mixed for 3 min in a planetary mixer and then cast into cylindrical molds of 5 cm of height by 2.5 cm of diameter, which were vibrated for 45 s to eliminate the entrapped air; the molds were covered with plastic cling film to minimize the moisture loss. The cylindrical geometry of the samples was adopted to promote an even heat transfer from the surface to the core of the specimens during the exposure to high temperatures.

2.3. Curing regime

Previous to the high temperature exposure, all specimens, including the reference CPC-30R and the alkali-activated binders, were isothermally cured as follows: 24 h at 20 °C and 80% RH, then 48 h at 60 °C in dry conditions. At the end of those 3 days, the specimens were removed from their molds and allowed to cool before the initial physical properties were tested.

Table 1
Chemical composition of the BFS, MK and CPC-30R used, from X-ray fluorescence analysis.

Material	Component (mass % as oxide)										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	Na_2O	K_2O	MgO	MnO	SO_3	Blaine(cm^2/g)
BFS	33.4	11.3	0.3	37.8	1.4	0.5	0.9	8.9	0.5	3.4	4653
MK	51.05	45.26	0.34	0.10	1.76	0.06	0.15	–	–	–	9469
CPC-30R	18.59	4.57	2.49	69.23	0.22	0.12	0.67	1.46	–	2.46	4100