Construction and Building Materials 150 (2017) 248–251

Contents lists available at ScienceDirect

Construction and Building Materials

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

Technical Note

The behaviour of iron in geopolymer under thermal shock

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HIGHLIGHTS

- Iron oxides accumulate in several points of thermally shocked geopolymers.
- Iron oxide particles tend to diffuse into interior section of a geopolymer being solidified.
- A model proposed to justify the behaviour of iron in geopolymer under severe thermal shock.

ARTICLE INFO

Article history:
Received 20 February 2017
Received in revised form 30 May 2017
Accepted 31 May 2017

Keywords:
Diffusion
Solidification
Alkali-activated fly ash
Iron accumulating
Microstructural analysis

ABSTRACT

In this paper, alkali-activated fly ash (geopolymer) samples were microstructurally analysed after thermal shock. The prepared samples were heated at 1000 °C, and then quenched in water to room temperature. X-ray diffraction (XRD), and energy dispersive spectroscopy (EDS) were used to analyse the samples. The colour of the interior and exterior section of samples were different, where the former was darker than the latter. XRD results showed that hematite forms in small quantities in both interior and exterior sections. EDS analyses showed the presence of iron-rich points in both sections; however, there were many accumulated iron points in the interior section. It was concluded that, to reduce free energy of the system, dissoluble iron during geopolymerisation diffuses through molten channels when geopolymer is being heated and forms accumulated iron regions.

1. Introduction

To implement geopolymer as a fire-resistant material it is essential to evaluate its heat resistance and thus investigate its properties [1]. There has been extensive research into the field in relation to the mechanical and durability properties of geopolymer, but there has been a lack of research on the analysis of geopolymer under high temperatures when subjected to thermal shock [2].

A number of studies have been conducted on the effect of elevated temperatures and subsequent thermal shock (air-cooling) on geopolymer. Timakul et al. [3] have studied thermal shock resistance of geopolymers due to the addition of TiO_2 particles. They have found TiO_2 a suitable material to increase thermal resistance of geopolymers. Sarker et al. [1] have studied properties of air-cooled geopolymer samples after fire exposure and found loss in compressive strength. Fernández-Jiménez et al. [4,5] have explored mechanical performance of air-cooled geopolymers and related them to microstructural properties of the corresponding samples.

This paper aims to evaluate microstructure of heated geopolymer samples after quenching in water. The samples were heated at 1000 °C and then water-cooled to room temperature. The behaviour of iron in alkali-activated slag has been investigated by Bernal et al. [6]. This paper, more or less, confirms their theory that iron has a different destiny that that available in the literature.

2. Experimental procedure

2.1. Materials

Gladstone fly ash, sodium silicate and sodium hydroxide were the materials used for preparing geopolymer samples. Gladstone fly ash is the most common type available in Australia, which its chemical composition has been given in Table 1; other properties could be found in Ref. [7]. D-Grade sodium silicate and analytical grade NaOH solid were sourced from PQ Australia and Sigma Aldrich respectively [7].

2.2. Sample preparation

Alkali activator was prepared by mixing sodium hydroxide and sodium silicate with the weight ratio of 1:1. After the alkali-activator cooled down, it was mixed with fly ash. The mix

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http://dx.doi.org/10.1016/j.conbuildmat.2017.05.223
0950-0618/

Table 1
Chemical composition of the starter materials.

Material	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	P_2O_5	K_2O_5	MnO	SO_3	TiO_2
Fly ash	51.1	25.6	4.30	1.45	12.5	0.77	0.89	0.70	0.15	0.24	1.32
Sodium silicate	29.4	–	–	–	–	14.7	–	–	–	–	–

contained 80 wt.% fly ash and 20 wt.% alkali activator. The mixture was stirred for 3 min by an industrial mixer.

The prepared mix was poured in cylindrical samples with the height of 100 mm and the diameter of 50 mm. The moulds were first half-filled by the geopolymer sample, vibrated for 30 s on a vibrating table and then completely filled followed by another 30 s vibration. The samples were then placed in a cool and dry place for three days while polythene sheets had covered them. After air curing, samples were demoulded and furnace-cured for 2 h at 70 °C to be ready for further thermal shock and microstructural analyses.

2.3. Testing procedure

The heating of the specimens to high temperatures was done via the use of an industrial furnace. Geopolymers were placed in circular alumina dishes (with the diameter of 60 mm) as directly gripping the heated samples with the industrial tongs would have led to structural deformation. The specimens were placed in the furnace and heated to 1000 °C. Once the specimens reached the desired temperature, they were left for a further 2 h at that temperature before their removal. The samples were safely removed from the furnace using industrial tongs and immediately placed into buckets filled with room temperature water for 4 min. These samples were then removed from water and left to cool for at least 2 h.

X-ray diffraction (XRD) analyses were conducted on both control (not heated) and thermal-shocked samples using a Bruker D8 Advance X-ray diffractometer.

Scanning electron microscopy (SEM) micrographs and energy dispersive spectroscopy (EDS) analyses were achieved using a Gemini apparatus. Secondary electrons with 5.0 kV energy were selected to acquire the results [7]. To make the sample conductive, gold coating was performed using a sputter deposition technique.

3. Results and discussion

One of the main observations during the testing was the discolouration and deforming of the geopolymer concrete samples. They changed to a brown colour through the heating process. The colour becomes darker as the heating temperature increases [5,6]. The other interesting result we found was the difference between interior and exterior colour of the quenched samples. The interior section was totally black/dark brown as it is not observed in any other heat-treated geopolymer samples available in the literature. Colour change of geopolymer due to heat exposure is attributed to the presence of iron in the matrix and its degree of oxidation [8]. The darker interior might show the accumulation of more iron oxides in the middle of geopolymer samples. Bernal et al. [6] have found that iron in alkali-activated materials should be considered as a metallic component rather than a dispersed one throughout the alkali-activated glass. Therefore, the particles do not dissolve during alkali activation of aluminosilicate source and hence remain in the final geopolymer structure unreacted. On the other hand, Pan and Sanjayan [9] reported that heating geopolymer above 680 °C makes it thixotropic. In thixotropic materials, molten phases appear within a solid matrix. Fig. 1 shows the changes in the shape of the samples subjected to elevated temperatures. This change in the shape of the samples can be due to either the thermal shock or the thixotropic behaviour of geopolymers.

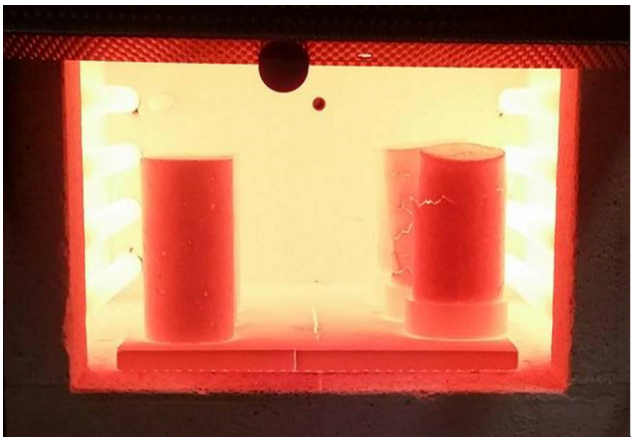

Fig. 1. Changes in the shape of specimens exposed to the temperatures above 800 °C.

We suggest a model based on these results [6,9] where by heating to high temperatures (here, 1000 °C), iron oxides diffuse through molten geopolymer channels to decrease free energy of the system (Fig. 2a). When the sample is quenched in water, the exterior section of the sample cools much faster than its interior one. Iron oxide particles that float within the molten geopolymer channels can be trapped by the paste being solidified or move in by the solidification front (Fig. 2b). The degree of entrapment or movement of these foreign solid inclusions depends on the temperature and viscosity of liquid [10]. Temperature of molten geopolymer at solidification front could follow one of the I or II paths for exothermic or endothermic reactions respectively. We believe that this reaction is exothermic and makes the molten geopolymer at solidification front less viscose; therefore, more iron oxides diffuse into the middle of geopolymer sample and make it darker. Fig. 3 shows the samples subjected to heating at 1000 °C and subsequent cooling. Changes in the colour of the core part of the samples with respect to the exterior side of them can be clearly noticed by the red markers.

Fig. 4 shows XRD results of both heat-treated and normal geopolymer samples. As there was a colour difference between interior and exterior sections of heated geopolymer, XRD tests were taken for both sections. A quartz peak is present at $2\theta = 26°$ and $2\theta = 50°$ in control sample, and, with the exception of $2\theta = 26°$ for exterior section, no apparent peaks are present after the geopolymer is subjected to thermal shock. Furnace-cooling of heated geopolymer has resulted in appearance of quartz peaks [11]. The figure also shows the presence of zeolite at $2\theta = 27°$ after thermal shock in both exterior and interior sections. However, crystalline phase formation is not apparent for the control geopolymer sample. This means that by quenching, quartz transforms to crystalline zeolite that is energetically unstable at room temperature.

Garronite is another phase that is present at $2\theta = 32°$ in exterior section. Mullite structural characteristics are different in all three