Applied Clay Science 73 (2013) 11–16

Contents lists available at SciVerse ScienceDirect

Applied Clay Science

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

Research paper

Clay reactivity: Production of alkali activated cements

C. Ruiz-Santaquiteria [a,*], A. Fernández-Jiménez [a], J. Skibsted [b], A. Palomo [a]

[a] Eduardo Torroja Institute (CSIC), c/ Serrano Galvache, nº 4, 28033 Madrid, Spain
[b] Instrument Centre for Solid-State NMR Spectroscopy, Interdisciplinary Nanoscience Center (iNANO), Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

ARTICLE INFO

Article history:
Received 30 April 2012
Received in revised form 23 October 2012
Accepted 25 October 2012
Available online 18 March 2013

Keywords:
Alkali activation
Geopolymer
Clay
Reactive SiO_2/Al_2O_3 ratio
^{29}Si MAS NMR

ABSTRACT

This study has assessed the suitability of dehydroxylated (5 h at 750 °C) red, white and ball clays for the use as prime materials in the production of alkaline cements. The analytical methodology applied to quantify their potentially reactive phases included selective chemical attack, which was also used in conjunction with subsequent ICP analysis of the resulting leachate to determine their reactive SiO_2/Al_2O_3 ratios. These results were compared with compressive strength values of the respective pastes activated with an 8-M NaOH solution and cured at 85 °C and 90% RH for 20 h. It was observed that when the reactive phase content was above 50%, the reactive SiO_2/Al_2O_3 ratio in the starting materials had a larger impact than the amount of reactive phase on the developed strength of the cement material. In this context, fly ash was used as the reference material. Finally, to verify the accuracy of the results, a binder consisting of 70 wt.% fly ash and 30 wt.% dehydroxylated clay was activated with an 8-M NaOH solution. The reactivity of this cement was determined by chemical attack with 1:20 HCl (v/v) and the reaction products were characterised by powder X-ray diffraction and ^{29}Si MAS NMR spectroscopy.

1. Introduction

The key to ensure a good mechanical performance and durability in alkaline, Portland or any other type of cement lies in a strict control of the properties of the starting materials. The cements obtained from alkaline activation of aluminosilicates are known to be conditioned by factors such as particle-size distribution, reactive amorphous/vitreous phase content and the quantity of silica in the starting materials. More specifically, roughly 80 wt.% of the binder should have a particle size less than 45 μm and the amorphous/vitreous phase content should be over 50 wt.% (Fernández-Jiménez and Palomo, 2003; Kumar and Kumar, 2011; Provis et al., 2010). Similarly, many authors have reported that alkaline cements with SiO_2/Al_2O_3 ratios of two or above, yield better compressive strengths than alkaline cements with lower ratios (Duxson et al., 2005, 2007; Fernández-Jiménez et al., 2006a). Although all these factors have been shown to affect the strength development in alkaline cements, the relative impact of the individual factors in alkaline activation has never been assessed.

In a recent study (Ruiz-Santaquiteria et al., 2011), we showed that the reactive phase content under alkali activation conditions in a series of aluminosilicates was equivalent to the amount of material that dissolved in a 1% (v/v) HF solution and that the reactive SiO_2/Al_2O_3 ratio of these materials could be quantified by ICP analysis of the resulting leachates. The methodology proposed in that work, and the findings described above formed the basis for the present study, which focuses on whether the percentage of the potentially reactive phase prevails over the reactive SiO_2/Al_2O_3 ratio of the starting materials (or vice-versa) in the satisfactory mechanical development of alkaline cements, or whether their impacts are equally important. The present study also intends to confirm whether, on the basis of the before-mentioned findings, optimal aluminosilicate blends can be designed to guarantee good mechanical properties for the resulting cements.

2. Experimental

Three dehydroxylated (at 750 °C for 5 h) common clays, white clay (WC), ball clay (BC) and red clay (RC), and a fly ash were used in this study. The chemical composition of these materials (Table 1) was determined by X-ray fluorescence (XRF) on a PHILIPS PW-1004 X-ray spectrometer. The particle-size distribution was obtained by laser diffractometry, using a 0.90- to 175-micron SYMPATEC particle-size analyser, which showed that around 80 wt.% of the particles of all the materials used had a size below 45 μm.

The fraction of reactive phase and the reactive SiO_2/Al_2O_3 ratio of the starting materials were determined by means of selective chemical attack using a 1% (v/v) HF solution as illustrated in Fig. 1. The acid attack was conducted by subjecting 1.0 g of each aluminosilicate to 100 ml of a 1.0% by volume hydrofluoric acid solution for 5 h under stirring. After the chemical attack, the solid residue and the solution were separated by filtering using Albet® ash-less filter paper (% ash < 0.01) for retention of particles under 2 μm (ref. DP5893125). The resulting residue was washed with distilled water until neutral pH from the funnel was

---

* Corresponding author. Tel.: +34 91 302 04 40; fax: +34 91 302 07 00.
E-mail address: ruiz.cs@ietcc.csic.es (C. Ruiz-Santaquiteria).

0169-1317/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.clay.2012.10.012

Table 1
Chemical composition (XRF) of dehydroxylated three clays, fly ash and the blend 70F.

	Chemical composition (% oxides)									
	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	Others	LoI[b]
FA	51.78	27.80	6.18	0.06	1.52	4.59	0.59	2.51	2.75	2.23
WC	58.76	32.72	1.70	0.01	1.60	1.04	–	1.85	0.55	1.83
BC	51.15	39.53	5.51	0.023	0.61	0.57	0.14	1.50	0.98	0.00
RC	59.36	27.46	5.25	0.066	0.89	0.62	0.13	3.42	1.32	1.48
70F[a]	53.90	29.30	4.84	0.05	1.54	3.52	0.35	2.31	2.08	2.11

[a] 70F = 70 wt.% FA + 30 wt.% WC. The chemical composition of this blend was calculated from the XRF results for each individual component.

[b] LoI: Loss of ignition at 1000 °C.

achieved. Once the residue was completely dry, it was calcined together with the filter paper at 1000 °C in a platinum crucible for 1 h. The percentage of reactive phase content was quantified by subtracting the final mass of the residue from the initial mass of the aluminosilicate (see Fig. 1). The percentage of silica and alumina released during the selective chemical attack was determined in the leachates by means of ICP. The ICP-AES analyses were conducted on a Varian 725-ES ICP atomic emission spectrometer with the following characteristics: plasma power, 1.40 kW; plasma gas flow, 15.00 l/min; nebuliser gas flow, 0.85 l/min; read time, 5 s. The concentrations of soluble silicon and aluminium determined by the ICP-AES technique correspond to the average of three measurements for a given liquid sample. Moreover, this procedure was conducted in duplicate in order to verify the precision of the measurements.

The starting materials (dehydroxylated clays and fly ash) were alkali-activated with an 8-M NaOH solution at the alkaline solution/binder ratio (S/B, by weight) required to obtain satisfactory workability (S/B = 0.85 for WC, 0.55 for BC and RC and 0.35 for FA). The resulting pastes were moulded into prismatic specimens measuring $1.0 \times 1.0 \times 6.0\ cm^3$ and cured for 20 h at 85 °C and a relative humidity above 90% to avoid carbonation (Criado et al., 2005). The compressive strengths for the alkaline cement pastes were measured just after the curing process (~20 h) on an IBERTEST® press. The values given are the average over 12 measurements.

Based on the before-mentioned results, a 70:30 (wt.%) FA/WC blend (denoted 70F in Table 1) was activated with 8-M NaOH (S/B = 0.50) and cured for 20 h at 85 °C and a relative humidity above 90%. The cements obtained from the 70F blend (70F-N8) and WC (WC-N8) were characterised with XRD and ^{29}Si MAS NMR. The XRD mineralogical studies were conducted on a BRUKER AXS D8 ADVANCE diffractometer, employing Cu–$K_{\alpha1,\alpha2}$ radiation. The ^{29}Si MAS NMR spectra were obtained on a Varian Unity INOVA-300 spectrometer (7.05 T), using a home-built CP/MAS probe for 7 mm o.d. rotors, a spinning speed of $\nu_R = 7.0$ kHz, a 45° excitation pulse (for $\gamma B_1/2\pi \approx 40$ kHz), and a 30-s relaxation delay.

The percentage of reaction products generated during alkali activation of the WC and 70F binders (degree of reaction) was determined by selective chemical attack, using a 1:20 (v/v) HCl solution (Fernández-Jiménez et al., 2006b) as depicted in Fig. 2. The selective chemical attack was conducted by subjecting 1.0 g of each alkaline cement to 250.0 ml of a 1:20 (v/v) HCl solution for 3 h at room temperature under stirring. After the chemical attack, the solid residue and the solution were separated by filtering (same type of filter paper as used for the acid attack measurements). The resulting residue was washed with distilled water until neutral pH from the funnel was achieved and once the residue was completely dry, it was calcined together with the filter paper at 1000 °C in a platinum crucible for 1 h. The percentage of reaction products generated in both cementitious systems was quantified by subtracting the final mass of the residue from the initial mass of alkaline cement (see Fig. 2). The percentage of silicon and aluminium being a part of the reaction products was determined by analysis of the resulting leachates by means of ICP-AES, under the experimental conditions described above. Given the precision in the measurements found for the silicon and aluminium concentrations by means of ICP (see Table 2), no duplicate experiments were conducted in this case.

3. Results and discussion

3.1. Correlation of binder composition and reactivity with compressive strength

Table 2 gives the percentages of potentially reactive phase in the aluminosilicates studied along with their reactive SiO_2/Al_2O_3 ratios. For the purpose of comparison, bulk SiO_2/Al_2O_3 ratios calculated from the XRF results are also given in Table 1.

According to the findings given in the table, all the materials except red clay (RC) have potentially reactive phase contents above 50 wt.%, which would initially translate into high reactivity in the alkaline activation process (Fernández-Jiménez and Palomo, 2003). Note that the bulk SiO_2/Al_2O_3 ratios found by XRF differ significantly from the reactive SiO_2/Al_2O_3 ratios determined using selective chemical attack. The consequence of this observation, i.e., that neither all the silicon nor all the aluminium present in the materials is reactive, justifies the use of a specific methodology to determine this ratio.

The compressive strengths for all the cements obtained are shown in Fig. 3, along with the calculated potentially reactive phase content and reactive SiO_2/Al_2O_3 ratios. The graph was designed to illustrate how these factors correlate with the cement strength.

The results plotted in Fig. 3 show that higher reactivity does not necessarily induce a larger strength development, although it is generally expected that a higher reactivity of the starting material will generate a larger percentage of reaction products (N–A–S–H gel)

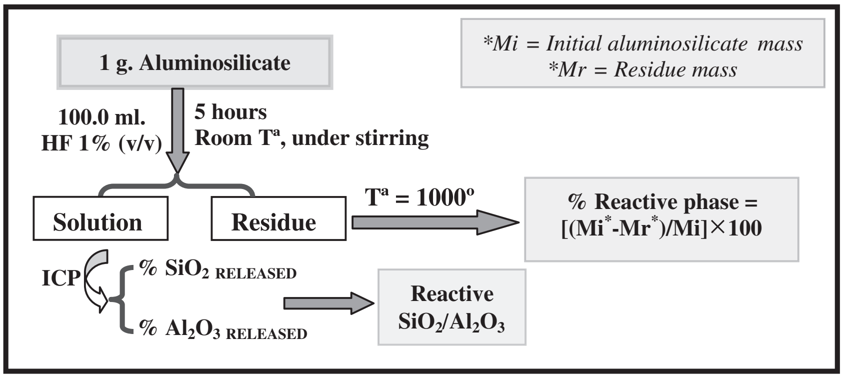

Fig. 1. Experimental procedure followed to quantify the percentage in weight of the potentially reactive phase and the reactive SiO_2/Al_2O_3 ratio in the starting aluminosilicates.