Available online at www.sciencedirect.com
ScienceDirect
Microporous and Mesoporous Materials 108 (2008) 41–49
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso

Alkaline activation of metakaolin–fly ash mixtures: Obtain of Zeoceramics and Zeocements

A. Fernández-Jiménez [a,*], M. Monzó [b], M. Vicent [b], A. Barba [b], A. Palomo [a]

[a] Instituto de Ciencias de la Construcción Eduardo Torroja (CSIC), 28033 Madrid, Spain
[b] Instituto de Tecnología Cerámica (ITC), Campus Universitario de Riu Sec, 12006 Castellón, Spain

Received 22 August 2006; received in revised form 26 January 2007; accepted 19 March 2007
Available online 28 March 2007

Abstract

This study examines the variation in physico-mechanical properties and mineralogical and microstructural characteristics of the alkaline inorganic polymers obtained by alkaline activation, with a mixture of sodium silica solution and sodium hydroxide, of two different starting materials: matrix M (metakaolin) and matrix FM (50% fly ash and 50% metakaolin). The activation process was conducted at different temperatures (85 °C, 150 °C, and 200 °C). The highest strength values were obtained for the FM matrix at 150 °C. The main reaction product was a sodium aluminosilicate gel in every case. Zeolites formed as by-products. The quantity and type of arising zeolites (sodalite, zeolite A, and faujasite) depended on the nature of the starting material and on the curing conditions used.

Keywords: Metakaolin; Fly ash; FTIR; SEM; ^{29}Si MAS-NMR; Alkaline activation; Zeolites

1. Introduction

Alkaline activation is a chemical process in which a powder material of an aluminosilicate nature, such as metakaolin or fly ash, is mixed with an alkaline activator to produce a paste that is able to set and harden in a short time [1–7]. The properties and characteristics (strength, shrinkage, acid and fire resistance, etc.) of the resulting materials depend on the nature of the raw materials and on the process variables (activator, temperature, time, etc.). These materials, frequently termed alkaline inorganic polymers, geopolymers, hydroceramics, etc., constitute a new family of products which, among other interesting properties, are able to combine qualities peculiar to cements with those of traditional ceramics and zeolites. Because of that authors are now proposing a new generic name to these materials: ''Zeoceramic'' or ''Zeocement'' (depending on the main application)

Much of the work reported in the literature has been based on the study of metakaolin activation [8–15] and, more recently, on the activation of F-type fly ash [16–20]. Metakaolin is essentially an anhydrous aluminosilicate produced by the thermal decomposition of kaolin, a naturally occurring clay basically containing kaolinite [$Al_2Si_2O_5(OH)_4$] and trace amounts of silica and other minerals. In kaolinite, the hydroxyl ions are strongly bonded to the aluminosilicate framework structure and can only be eliminated at temperatures above 550 °C. During the dehydroxylation process, considerable atomic rearrangement occurs [10,21,22]. The result is a partly ordered structure that cannot rehydrate in the presence of water (or does so very slowly). Owing to its disordered nature (X-ray amorphous), it has a huge reactive potential in the presence of an alkali /alkaline earth-containing solution.

Class F fly ash is a finely divided mineral residue resulting from the combustion of ground or powdered coal (ASTM C 618). Fly ash particles are generally spherical in shape, though they are not necessarily homogeneous. The bulk of the ash is made up of silicon, aluminium, and iron oxides. The amount of crystalline and glassy

* Corresponding author. Tel.: +34 91 302 04 40; fax: +34 91 302 60 47.
E-mail address: anafj@ietcc.csic.es (A. Fernández-Jiménez).

1387-1811/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2007.03.024

phase depends largely on the combustion and gasification process used at each power plant. When the maximum temperature of the combustion process is above 1200 °C and the cooling time is short, the ash produced is mostly glassy phase material [23]. Previous studies have established the main characteristics that class F fly ash needs to exhibit for being potential Zeocements (liable of alkaline activation) [16].

Although the alkaline activation of metakaolin and fly ash yields an alkaline aluminosilicate gel as main reaction product in both cases, differences in the composition and microstructure of the starting material affect the microstructure of the end product. Thus, metakaolin gives rise to a very homogeneous matrix, a gel with a low Si/Al ratio [24], and a high degree of zeolitisation (Zeoceramic), while fly ash gives rise to more heterogeneous matrices (larger percentage of unreacted ash particles), a gel with a higher Si/Al ratio, and a smaller percentage of zeolites (Zeocement) [25,26].

However, no thorough study is available on the mixture of these two materials. The present study has been undertaken, therefore, to determine the behaviour of mixtures of fly ash and metakaolin, under alkaline activation, and the effect of curing temperature on the mechanical properties and nature of the resulting reaction products. In this study, the metakaolin matrix has been used as the reference material.

2. Experimental

The raw materials used in this study were metakaolin (kaolin supplied by CAOBAR, S.A., calcined at 750 °C for 20 hours [10,11]) and an class F fly ash (ASTM C618) from the power station at Lada (Spain) [16]. The chemical composition of both materials (see Table 1) was determined by X-ray fluorescence spectrometry with a PHILIPS PW 2400 spectrometer with PW 2540 VTC sample changer. The physical characterisation is presented in Table 2.

Two matrices were studied: matrix M (metakaolin) and matrix FM (50% fly ash and 50% metakaolin, by weight). The alkaline solution used as activating agent was a mixture of sodium silicate and sodium hydroxide, with a molar composition of 7.4% Na_2O, 1.5% SiO_2, and 91.1% H_2O, and density of 1.35 g/cm^3. The liquid/solid ratio used (matrix M or FM : Activating solution) was determined by the minislump method [27], in order to obtain good paste workability. The ratio was 1.250 and 0.875 by weight, respectively for the cases of matrices M and FM.

Table 2
Physical characterization of raw materials

	Particle size		ρ_{real} (g/cm^3)	S_{esp} (m^2/g)
	$d < 45$ μm	$d < 45$ μm		
Metakaolin (MK)	100%	–	2.57	7.7
Fly ash	78.5%	21.5%	2.26	0.8

Prism-shaped test specimens of $10 \times 10 \times 60$ mm were made to determine compressive strength. All test specimens were submitted to a preliminary curing regime of three hours at 85 °C and 98% relative humidity. The specimens were then demoulded and immediately submitted to a second curing stage of five hours at different temperatures: T1 = 85 °C, T2 = 150 °C, and T3 = 200 °C. After the curing process, the test pieces were kept for 24 hours at room temperature and relative humidity >90%. Their compressive strength was then determined. The load rate was 2.4 kN/s. Porosity was also determined by mercury intrusion porosimetry (Micromeritics 9320).

The degree of the reaction progress (%) was determined by chemical attack with a 1:20 solution of HCl by volume. This solution dissolved the reaction products (inorganic polymer and zeolites), leaving the unreacted material as insoluble residue [28].

The following techniques and instruments were used for the mineralogical and microstructural analysis of the hardened materials: X-ray diffraction (XRD) with a Philips PW-1730 instrument; Fourier transform infrared spectroscopy (FTIR) with an Ati Mattson Genesis Series FTIR instrument, with a scan frequency of 4000–400 cm^{-1}; Scanning Electron Microscopy (SEM) with a JEOL 5400 instrument and corresponding energy-dispersive analysis with an OXFORD Instruments LINK-ISIS EDX system and solid state detector; and ^{29}Si MAS-NMR with a MSL-400 Bruker apparatus. The resonance frequency used in this study was 79.5 MHz, with spinning rate of 4 kHz. All measurements were made at room temperature with TMS (tetramethylsilane) as external standard. The estimated errors in chemical shift values were lower than 0.5 ppm [25,26].

3. Results

3.1. Compressive strength and degree of reaction progress

Fig. 1 displays the compressive strength and the porosity test results. These results show that, independently of the curing process used, the FM matrix gives rise to higher

Table 1
Chemical analysis of raw materials

	Oxides, weight (%)										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	LoI[a]
Metakaolin (MK)	57.0	41.0	0.48	0.10	0.10	<0.01	0.50	0.24	<0.01	0.05	0.44
Fly ash	52.7	26.4	7.45	4.53	1.93	0.53	3.56	0.96	0.05	0.28	1.6

[a] LoI: loss on ignition, 1025 °C.