Applied Clay Science 88–89 (2014) 221–227

Contents lists available at ScienceDirect

Applied Clay Science

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

Note

Feasibility of producing geopolymers from two different Tunisian clays before and after calcination at various temperatures

N. Essaidi [a,b], B. Samet [a], S. Baklouti [a], S. Rossignol [b]

[a] Laboratoire de Chimie Industrielle, Ecole Nationale d'Ingénieurs de Sfax, BP W 3038 Sfax, Tunisia

[b] Centre Européen de la Ceramique, Groupe d'Etude des Matériaux Hétérogènes, Ecole Nationale Supérieure de Céramique Industrielle, 12 rue Atlantis, 87068 Limoges, France

ARTICLE INFO

Article history:
Received 18 April 2012
Received in revised form 2 December 2013
Accepted 3 December 2013
Available online 31 December 2013

Keywords:
Clay
Calcination
Kaolinite
Surface defects
Consolidated material
Geopolymer

ABSTRACT

Two Tunisian clays, kaolinitic from the Tabarka (Clay T) region and illito-kaolinitic rich in hematite from the Medenine (Clay M) region, are tested as potential aluminosilicate sources for the synthesis of geopolymers. The raw clays and clays calcined at 700, 800, 850 and 900 °C were characterized using XRD, DTA/TG, and FTIR spectroscopy and ^{29}Si and ^{27}Al MAS NMR measurements. It was demonstrated that samples based on Clay M present more reactivity than those based on the Clay T because of the amorphization of clay minerals.

The structural evolution on calcination is studied in detail to predict the behavior of the clay during geopolymerization. Despite its lower content in kaolinite than Clay T, Clay M is capable of providing geopolymers.

1. Introduction

From the earliest days of civilization, natural clays have been well known and familiar to mankind. In recent years, there has been increasing interest in studying the use of natural clays in the synthesis of geopolymers because of their low cost and abundance in most countries. “Geopolymers” are ill-organized polymeric aluminosilicate materials obtained by alkaline or alkaline-earth activation of aluminosilicates (Davidovits, 2008). Geopolymers are currently of considerable interest because of their good thermal (Cheng and Chiu, 2003), chemical (Bakharev, 2005) and mechanical properties (Lee and Van Deventer, 2002) and their potential for use as a “green” cementitious binder. The raw materials commonly used to synthesize geopolymers are those rich in aluminosilicate, such as natural pozzolan, fly ash, blast furnace slag, and calcined kaolinite. A large number of studies have focused on the synthesis of geopolymers from metakaolinite, which is essentially an anhydrous aluminosilicate obtained from the calcination of clays. Metakaolinite possesses a huge reactive potential when activated in alkali solution because of its disordered structure (Davidovits, 2008). Many authors (Elimbi et al., 2011) have calcined kaolinite at various temperatures to produce geopolymers. Khale and Chaudhary (2007) reported that the usual thermal treatment range of kaolinite was approximately 600–800 °C and that metakaolinite persisted in Si and Al releasing ability until it was heated to approximately 900 °C. The structural changes associated with the dehydroxylation of kaolinite to metakaolinite have been widely investigated. More particularly, MAS NMR measurements on a thermal study of kaolin in metakaolin have revealed the existence of a disordered aluminosilicate compound (Massiot et al., 1995). In fact, they have evidenced for the aluminum species, the existence of four- and five-fold structural networks. This last coordination can be also considered as a third species of aluminum considered as an intermediate chemical shift among Al (IV) and Al (VI). Generally, it was accepted that thermal treatment results in the kaolinite phase being thermodynamically unstable and more reactive. It has been reported that calcined source materials display higher activities than non-calcined materials because the calcination process activates materials by changing the crystalline structures into amorphous structures, during which extra energy is stored and the structural stability declines (Lee and Van Deventer, 2002). Xu and Van Deventer (2003) also reported that un-calcined kaolinite could be used together with fly ash and albite to produce a high-strength low-cracking geopolymer. However, there are very few investigations on the synthesis of geopolymers from natural clays because clay generally contains a mixture of different clay minerals and associated non-clay minerals. The variability in clay composition and the parameters associated with the thermal activation process complicate the formation of a general statement about the suitability of clay resources for the production of geopolymers, as shown in different papers that have taken somewhat controversial positions (Buchwald et al., 2007; Kaps and Buchwald, 2002; Mackenzie et al., 2008).

The aim of the present research is to study the feasibility of producing geopolymers from two Tunisian clays. The first clay is a kaolinitic, and the second is an illito-kaolinitic clay that is rich in hematite. This work is based on the characterization of two clay samples, both before and after calcination at different temperatures, using several physicochemical analyses. The structural evolution of the calcined clays versus

0169-1317/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.clay.2013.12.006

calcination temperature is monitored using XRD, FTIR, ^{29}Si and ^{27}Al NMR.

2. Experimental

2.1. Raw minerals and consolidated materials

Two Tunisian clays are used in this study. One is in the north from Tabarka, mainly used in handmade pottery and the other, characterized by its red color, is in the south from Medenine, mainly used in the brick and ceramic industry. After sieving at 125 μm, the clays were calcined for 5 h in a static bed at a heating rate of 10 °C/min at the following temperatures: 700 °C, 800 °C, 850 °C and 900 °C. Consolidated materials were prepared by first dissolving potassium hydroxide in potassium silicate and then adding clay or calcined clay to the alkaline solution and mixing until the paste is homogenous according to the procedure established by Prud'homme et al., 2010. The various ratios are Al/Si = 1.4 and Si/K = 2.1.

After mixing, the paste specimens are poured into plastic containers 35 mm in diameter and 70 mm in height. The pastes are then cured at 70 °C for 48 h, followed by 21 days at ambient temperature. The samples are identified as $^{\theta}G^{M,T}$, where is the calcination temperature of the clay, G the mean geopolymer and M, T refer to the origin of clay.

2.2. Technical characterization

The chemical composition of the clays was determined using X-ray fluorescence (ARL 8400, XRF 386 software). The mineral phases were identified by XRD with a BRUKER AXS D8 Advance powder diffractometer using CuK_{α} radiation ($\lambda_{K\alpha} = 0.154186$ nm). The analytical range is between 5° and 70° in steps of 0.04° and an acquisition time of 2 s. JCPDS (Joint Committee Powder Diffraction Standard) files were used for phase identification.

The particle size distributions of these raw materials were measured using a laser particle size analyzer Mastersizer 2000. The powder is suspended by an air current flowing through a glass cell with parallel faces illuminated by a beam of laser light. The measurement is made at a pressure of 3 bars.

DTA and TG were performed with the samples held in a Pt crucible between 25 °C and 1200 °C using a SDTQ600 V20.9. The samples were heated at 10 °C min^{-1} in a dry air flow.

FTIR spectra were recorded on a ThermoFisher Scientific 380 infrared spectrometer (Nicolet). The IR spectra were scanned between 500 and 4000 cm^{-1}, with a resolution of 4 cm^{-1}. The commercial software, OMNIC (Nicolet Instruments), was used for data acquisition and spectral analysis.

^{27}Al and ^{29}Si MAS NMR analyses were performed on a Bruker ASX500 (7 T magnetic field) spectrometer spinning rates of 15 kHz for ^{27}Al and 8 kHz for ^{29}Si. ^{29}Si and ^{27}Al spectra were recorded, and the chemical shifts were referenced to tetramethylorthosilicate in $CDCl_3$ for the ^{29}Si nuclei and to aqueous $AlCl_3$ (1 M) for the ^{27}Al nuclei. The spectra are obtained after 40,960 scans.

3. Results and discussion

3.1. Characterization of the raw samples

The chemical compositions of the studied clay samples are presented in Table 1. Note that for both samples, the amount of silica is

Table 1
Chemical composition of the clays in mass percent.

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	K_2O	MgO	Na_2O
Clay (M)	2. 16	61.17	16.30	5.90	0.08	2.73	2.39	≤0.01
Clay (T)	–	61.84	25.95	1.85	–	1.25	0.23	–

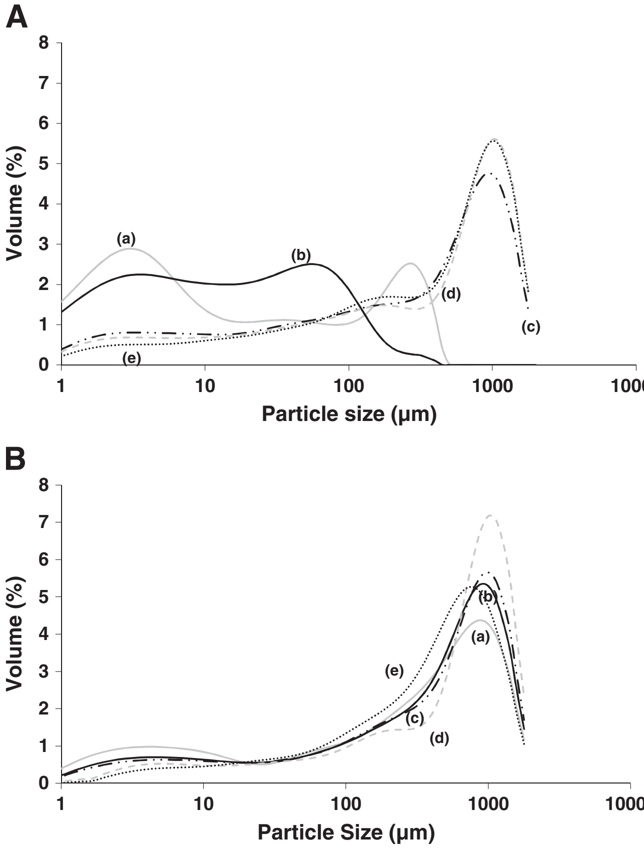

Fig. 1. Particle size distributions of (A) Clay T and (B) Clay M:(a) 25 °C, (b) 700 °C, (c) 800 °C, (d) 850 °C and (e) 900 °C.

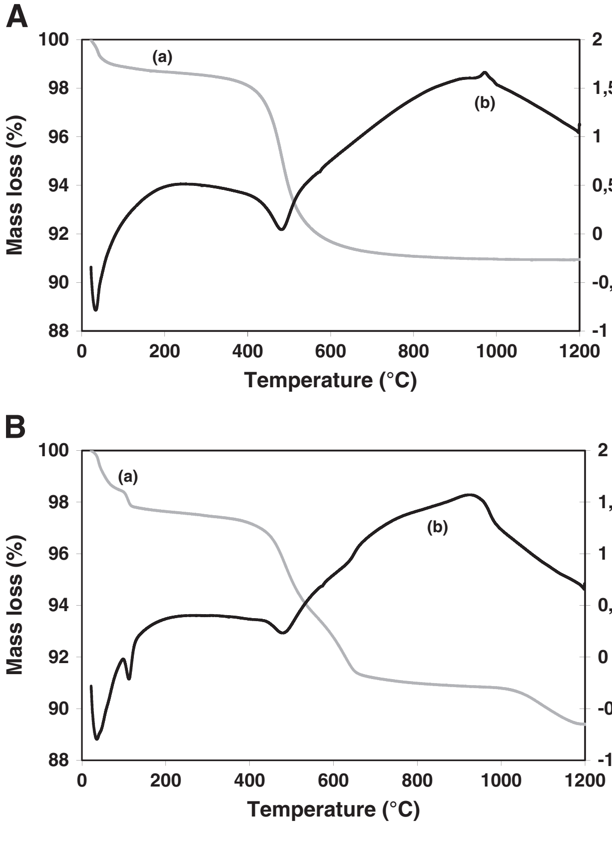

Fig. 2. Mass loss (a) and heat flow (b) curves of the raw (A) Clay T and (B) Clay M.