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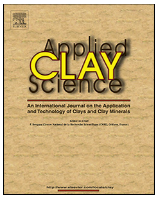

Research paper

Effect of structural and textural properties of a ceramic industrial sludge and kaolin on the hardened geopolymer properties

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ABSTRACT

This paper presents a comparative structural and textural study of an industrial sludge and commercial kaolin, in order to explain the transformation of the industrial sludge after calcination and to correlate the raw material properties to the hardened geopolymer products structure and compressive strength. The industrial sludge used in this study comes from a local factory manufacturing ceramic sanitary products. The amorphization and the dehydroxylation of the two materials were followed by X-ray diffraction, infrared spectroscopy and thermogravimetric method. The clay morphology was verified by scanning electron and transmission electron microscopies. The textural study of materials was carried out using two techniques, the mercury porosimetry and nitrogen adsorption. The chemical composition of the newly formed geopolymers phases was followed by FTIR spectroscopy. The XRD analysis revealed that the crystallinity of the industry sludge is lower than that of commercial Kaolin. The FTIR analysis confirmed that the dehydroxylation of the ceramic industrial sludge at the chosen temperature caused a total removal of hydroxyl groups. The N2 adsorption isotherms of the calcined industry sludge (MB) and the Metakaolin (MK) showed that the texture is formed by the agglomeration of aggregates. The maximum value of the compressive strength of MB-geopolymer is too close to that of MK-geopolymer (about 29 MPa), confirming therefore the great reactivity of the ceramic industrial sludge. We conclude that the industrial ceramic sludge appears to be a very efficient material that should find a niche in a market where kaolin clay is becoming scarce.

1. Introduction

Metakaolin is used as a pozzolan, added to Portland cement to improve its performances (Ambroise et al., 1994; He et al., 1995; Rashad, 2013; Sabir et al., 2001). In addition, Metakaolin is also used as a raw material in manufacturing geopolymer materials (Duxson et al., 2007a, 2007b; Wang et al., 2005). The ceramic industry sludge (regarded as a waste) includes kaolinite, which is the hydroxylated form of Metakaolin, could be used as a raw material by replacement of Metakaolin in the field of construction (Belmokhtar et al., 2016; Lamrani et al., 2016). The ceramic industry sludge is a solid waste obtained at the end of the wastewater treatment process carried out by some ceramic industries.

Due to depletion of natural kaolinite resources, the ceramic industrial waste area has exceeded the remediation of environmental impact of this kind of waste (Habert et al., 2011; Ortiz et al., 2009). Several studies have shown that the effectiveness of the pozzolanic reaction or the geopolymerization reaction is related to the dehydroxylation degree of raw material (Shvarzman et al., 2003; Tironi et al., 2012a, 2012b). Thus, the use of totally dehydroxylated and amorphous metakaolin or a ceramic industry sludge improves the cement and concrete performances more than partially dehydroxylated ones.

The dehydroxylation process starts by the migration of the proton from one hydroxyl group to another hydroxyl group, followed by the H_2O molecule formation and finishes by the removal of this molecule (H_2O) outside the lattice. The efficiency of this process depends on the duration of calcination (Ilić et al., 2010; Shvarzman et al., 2003; Vizcayno et al., 2010). According to Ptáček, the great mass loss observed in the TGA pattern at about 500 °C is due to the departure of the hydroxyl groups contained in the mineral (phenomenon of dehydroxylation) as H_2O molecules (Castelein et al., 2001; Chandrasekhar, 1996; Kakali et al., 2001; Ptáček et al., 2010b). Indeed, 4OH groups leave the layer to form 2 molecules of H_2O leaving 2 of residual oxygen according to the following equation(Ptáček et al., 2011):

$$4OH^{-} \rightarrow 2H_2O + 2O^{2-}$$

The transformations undergone in the crystal structure by the material during the calcination vary considerably as a function of several intrinsic parameters including the crystallinity of the starting material.

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The Stoch index (IK) calculated from the XRD pattern depends on the surface defects of materials (Bich et al., 2009; Dubois et al., 1995; Tironi et al., 2012a, 2012b). The higher the IK value, the larger is the number of surface defects of the mineral it contains. Moreover, when the (IK) value is lower than 0.7, the mineral is considered having a well crystalline network. Whereas, when the (IK) value is more than a unit the mineral is considered having a disordered network (Tironi et al., 2012a, 2012b).

Our paper presents a structural and textural study of a calcined ceramic industrial sludge in comparison with a commercial kaolin, in order to explain the transformation undergone on the ceramic industrial sludge after its calcination. Furthermore, this study aims to correlate the raw material properties to the hardened geopolymer products structure and compressive strength, in order to use this type of ceramic industrial sludge as a geopolymer cement raw material in the construction industry.

The term geopolymer describes all types of amorphous or semi-crystalline materials obtained by the reaction of an aluminosilicate powder and an alkaline solution at ambient or slightly elevated temperature (Davidovits, 1991). A large number of starting materials that are rich in alumina and silica can be used to produce geopolymer materials. Among these materials are, Metakaolin, flay ash, bottom ash and some kinds of ceramic industrials sludge (Belmokhtar et al., 2017; Longhi et al., 2016; Nimwinya et al., 2016; Zhuang et al., 2016).

Geopolymers structure consists mainly of SiO_4 and AlO_4 tetrahedra, where a number of the Si^{4+} positions are occupied by Al^{3+}, giving rise to a charge deficit that is balanced by the presence of positive ions such as Na^+ or K^+ (Davidovits, 1989, 1994). Several researchers have shown that the properties of geopolymers such as strength development, shrinkage, permeability, fire resistance and durability are related to the syntheses process, type of alkaline cations, setting conditions and Na_2SiO_3/MOH ratio (M = Na or K), the chemical and mineralogical composition of starting materials (Antunes Boca Santa et al., 2013; Bakri et al., 2012; Belmokhtar et al., 2016; Duxson et al., 2005; Duxson et al., 2007a, 2007b; Elimbi et al., 2011; Hounsi et al., 2014; Songpiriyakij et al., 2010; Xu and van Deventer, 2003).

The ceramic industrial sludge used in this study has more quantity of crystalline phases than kaolin. Theoretically, any type of alkaline solution can be used to synthesize a geopolymer cement. However, the mostly used one is that prepared from a combination of water glass and sodium hydroxide or from water glass and potassium hydroxide. The alkali cations affect the geopolymerisation reaction in different ways. The presence of Na^+ increases the dissolution of aluminosilicate source due to its small size by formation of a geopolymer with more ordered species. However, the presence of K^+ tends to increase the degree of polycondensation due to its large size, which favors the formation of larger silicate oligomers inducing a lower ability to the formation of crystalline phases. Consequently, the use of water glass/potassium hydroxide combination improves the mechanical property of geopolymer materials(Hounsi et al., 2014).

2. Materials and methods

2.1. Materials

The industrial sludge (B) used in this study was obtained from a local factory manufacturing sanitary ceramic products. A commercial kaolin (K) is also used in this study. The chemical composition was determined by X-ray fluorescence (Table 1). The molar ratio SiO_2/Al_2O_3 of B powder and K powder are respectively 3.82 and 2.16. The calcination temperature of the ceramic industrial sludge is 800 °C. Whereas that of Kaolin is 750 °C. Both raw materials were calcined for 2 h in tubular furnace in open mode with a ramp of 5 °C/min. When the calcination was completed, the samples were soaked in air, cooled at room temperature and placed in plastic bags. The BET surface area of calcined industrial ceramic sludge (MB) and Metakaolin (MK) determined by ASAP2010 instrument are 2.37 m^2/g and 4.72 m^2/g respectively, and the medium laser particle size (d50) is 7.12 µm for MB and 6.20 µm for MK.

The potassium hydroxide solutions are prepared by dissolution of KOH in distilled water. The potassium hydroxide solutions are cooled before adding sodium silicate solution in various mass ratios. The activated alkali silicate solutions in the appropriate Na_2OSiO_2/KOH mass ratios are prepared by adding potassium hydroxide solution (12 M) to diluted sodium silicate solution (Si = 32.48 mg/l, Na = 19.62 mg/l). The activated alkali silicate solutions are stored for 24 h prior to use.

2.2. Geopolymer synthesis

The samples were prepared by mixing raw materials and activated alkali silicate solutions for 10 min, the mix proportions of the synthesized geopolymers are shown in Table 2. The fresh pastes were casted into cylindrical molds (width = 20 mm and height = 40 mm) and they underwent twenty shocks for removing air bubbles trapped in the paste. The samples were cured at room temperature and normal pressure for 7 days, then at 80 °C for 20 h.

2.3. Characterization

The identification of the mineralogical phases is carried out using a Bruker D8 Advance diffractometer comprising a Debye-Scherrer assembly, operating in reflection and equipped with an INEL curve detector CPS 120 (Curved Position Sensitive Detector). This assembly, operating at 40 kV and 30 mA, is equipped with an X-ray source using Kα radiation from copper. The index of Stoch (IK) defined by the eq. (1) is calculated in order to compare the crystallinity of the kaolinite present in the kaolin clay and ceramic industry sludge.

$$IK = \frac{A}{B} \tag{1}$$

With A: the intensity of 020 reflection, B: the intensity of $1\bar{1}0$ reflection.

The infrared spectra in the wavelength range of 400 cm^{-1} to 4000 cm^{-1} were obtained using a Fourier Transform Infrared Spectrometer (PERKIN ELMER) using the standard KBr technique.

Thermogravimetric analysis was carried out using a NETZSCH STA 449F3 instrument (range: 105/3,0(K/min)/1200), under air sweeping for a heating rate of 5 °C/min to 1000 °C.

The textural study is carried out using two techniques. The first one is adsorption of nitrogen at 77 K using ASAP 2010 V5.02 instrument. The BET method is used to calculate the surface area. The pore size distribution is determined by the BJH method (Rouquerol et al., 2003). The second one is the mercury intrusion porosimetry technique using Autopore IV 9500 V1.03 instrument (Jozefaciuk, 2009).

The calcined and the non-calcined materials morphology is observed by the scanning electron microscopy (SEM: FEI Quanta 200)

Table 1
Chemical composition of the ceramic industrial sludge (B) and kaolin (K).

Oxides	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	ZrO_2	MgO	Fe_2O_3	ZnO	TiO_2	MgO
B (%)	57,4	26,3	2,42	1,68	1,29	0,82	0,46	0,45	0,35	0,30	–
K (%)	47.2	37.12	0.03	0.05	2.2	–	0.39	0.83	–	0.04	0.39