Research paper

Structure and properties of new eco-material obtained by phosphoric acid attack of natural Tunisian clay

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ABSTRACT

In this work, new three dimensional geopolymer materials based on dehydroxylated natural kaolin and phosphoric acid were synthesized.

The effects of Si/P molar ratio and curing time were studied. The structures of raw, calcined kaolin and geopolymers synthesized were investigated using X-ray diffraction analysis, IR spectroscopy, scanning electronic microscope, ^{31}P, ^{29}Si and ^{27}Al MAS-NMR and by mechanical measurements.

The mechanical strength of geopolymers is maximum when Si/P molar ratio, equal to 2.25, which corresponds to Al/P ratio = 1. The mechanical properties are correlated with the amount of amorphous phase in geopolymer which is determined by the Rietveld method. In addition to metakaolin, illite mineral contributes to geopolymerization.

1. Introduction

In recent years, geopolymers, also known as eco-materials, have received considerable attention (Rowles and O'Connor, 2003; Vaou and Panias, 2010) because they could be consolidated at room temperature (Davidovits, 1991). These materials show a good chemical (Bakharev, 2005; Palomo et al., 1999) and thermal behavior (Al Bakri Abdullah et al., 2012; Cheng and Chiu, 2003) and also a good compressive strength (Lee and Van Deventer, 2002; Nugteren et al., 2009; Zhang et al., 2010). These properties give them a wide range of applications such as aviations (Davidovits, 1991), concrete products (Goung et al., 2012), refractory ceramics (Jonathan et al., 2008) and biomaterials (Derrien et al., 2004).

The geopolymers are generally obtained by activating an aluminosilicate mainly kaolinite and metakaolinite with alkali metal hydroxide (Na^+, K^+) (Davidovits, 1994a). Recent studies showed that such polymeric products could also be obtained by the phosphoric acid digestion of the same raw materials (Davidovits, 1994b) and have superior performance than those obtained by basic attack at ambient temperature (Le-ping et al., 2010).

Geopolymers are chains or networks of amorphous mineral molecules connected together via covalent bonds, which also contain three-dimensional semi-crystalline aluminosilicate polymers (Cui et al., 2011). These series are composed by molecular units (or chemical groups), such as $-Si-O-Si-O-$ siloxo, $Si-O-Al-O-$ sialate, $-Si-O-Al-O-Si-O-$ sialate-disiloxo, $-P-O-P-O-$ phosphate, $-P-O-Si-O-P-O-$ phosphor-siloxo, or $-P-O-Si-O-Al-O-P-O-$ phosphor-sialate (Davidovits, 1991, 1994a,b, 2008).

The geopolymerization mechanism, for the alkali-based geopolymers, is supposed to be a "bonding reaction" between the low-polymeric $Si-O$ tetrahedral units in sodium silicate solution and the active $Al-O$ layer in metakaolinite (Cao et al., 2004). In this case, the silicate network consists of SiO_4 and AlO_4 tetrahedral units, which were then linked to form three-dimensional structures. The balance of the negative charge on the AlO_4 tetrahedra, was achieved by Na^+ and K^+ ions (Davidovits, 1989).

The polymerization reaction of acid-based geopolymers is believed to be a bonding reaction between the active $Al-O$ in metakaolin and the low-polymeric $P-O$ tetrahedral units in phosphoric acid solution. Therefore, the low-polymeric $P-O$ tetrahedral units react with metakaolinite granules which adhere to each other inducing to the formation of $Al-O-P$ bonds (Cao et al., 2005). The positive charges on the $[PO_4]$ tetrahedral were balanced by the negative charges of the $[AlO_4]$ tetrahedral, so that neutrality could be maintained (Cao et al., 2005).

A large number of studies focused on the synthesis of geopolymers from metakaolinite (Cao et al., 2005; Le-ping et al., 2010). There is a lack of investigation on the elaboration of geopolymers based on natural clays. The aim of the present work is the synthesis of geopolymers based on raw clay from Tunisia. The latter is widely used in the ceramic

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industry and also as pozzolanic materials in cement industry. Today, materials such as geopolymers appear as an obvious alternative to re-place Portland cement.

2. Materials and experimental methods

The used Tunisian kaolin was collected from the Tabarka region (Northern Tunisia) and operated as an aluminosilicate source. This clay is ranked among the purest natural kaolin (Chakchouk et al., 2006). After being sieved at 140 μm, the clay is calcined at 700 °C for 5 h in a static bed (Essaidi et al., 2014), and then it is quenched by air to room temperature. Following formulations reported in Table 1, cal-cined kaolin, distilled water and phosphoric acid (PROLABO, 85%) were mixed for almost 3 min with ultrasonic waves in a flask to obtain an aqueous slurry. A series of seven sample compositions with different Si/P molar ratios were prepared. The chosen molar ratio and different formulations of the synthesized geopolymers are reported in Table 1. The synthesized geopolymer, identified as G^x, corresponds to that ob-tained from calcined kaolin with a Si/P molar ratio equal to x.

Because of the exothermic reaction between phosphoric acid and cal-cined kaolin, the samples were properly sealed to prevent water loss. They were kept at room temperature for 2 h before curing at 60 °C for 24 h in an oven. This step will accelerate the polycondensation of sam-ples and is believed to be sufficient to complete geopolymerization. Then the samples are stored at room temperature for 7, 14 and 28 days. Sample fragments, collected from compression tests, are con-served in acetone for 24 h and then dried in an oven at 60 °C for 5 h to stop geopolymerization (Alonso and Palomo, 2001) to be characterized by the different analyses.

The chemical composition of kaolin was determined by X-ray fluo-rescence (ARL 8400). The X-ray diffraction was carried out to determine the mineralogical qualitative composition of kaolin and of synthesized geopolymers (D8 ADVANCE, LynkEye detector-Bruker AXS, Germany) using CuKα radiation in the 10–80° 2θ range, scan rate of 0.02° (2θ), and 185 s equivalent per step. The quantification of the amorphous phase was performed using TOPAS 4.2-Bruker software following RIR (Reference Intensity Ratio) and Rietveld refinement techniques. The samples were admixed with 20 mass% Corundum as internal standard. Each X-ray powder diffraction pattern consists approximately of 7000 data point and 700 reflections; up to 40 independent variables were refined: phase fractions, zero point, 25–30 coefficients of the shifted Chebyshev function to fit the background, unit cell parameters, and profile coefficients (one Gaussian, Gw, and one Lorentzian term, Lx). The agreement indices, as defined in TOPAS, for the final least-squares cycles of all refinements are represented by Rp (%), Rwp (%), and GOF. The refined patterns were found in the following ranges: 2.5% < Rp < 4.0%, 3.0% < Rwp < 5.0% and 1% < GOF < 2%. The experimental error is within 5% relative. The (DTA/TG): differential thermal analysis/ thermogravimetry was carried out to establish the optimum range of calcination temperature for kaolin. The apparatus used was a SETARAM-SETSYS evolution S60-58292 and the heating rate was 10 °C/min with a helium purge. The infrared spectroscopy was carried

to find the different chemical bands of samples in the 400–4000 cm^{-1} spectral range. The apparatus used was a Perkin Elmer spectrum BX.

The kaolin was thermally treated in a programmable laboratory fur-nace. It was heated from ambient to 700 °C and was kept at the selected temperature for 5 h. The obtained specimen was quenched by air to am-bient temperature and was stored in a dry environment.

The mechanical properties of the synthesized geopolymers were measured by using the Brazilian test on cylindrical pellets (about 32 mm in diameter (D) and thickness (e) of about 7 mm). Five samples of each formulation were tested and the averaged values were reported. The magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra of ^{29}Si, ^{27}Al and ^{31}P were performed out by using BRUKER 300 WB (7 T) for raw, calcined kaolin and geopolymers (which are synthe-sized at different Si/P molar ratios and different curing ages). ^{31}P, ^{29}Si and ^{27}Al shifts are given in ppm referenced to H_3PO_4, TMS and alumi-num chloride respectively.

3. Results and discussion

3.1. Raw material characterization

The chemical composition of the used natural kaolin, determined by X-ray fluorescence, is given in Table 1. It is clear that the clay is rich in silica, alumina, and contains also some iron and potassium (K_2O = 1.28 mass%) suggesting the presence of illite mineral. In the XRD pat-tern of kaolin, (Fig. 1) we notice mainly the presence of kaolinite with some illite, quartz and anatase (TiO_2) as the secondary minerals. In ad-dition, the comparison between X-ray patterns studied Tabarka's kaolin before and after calcination shows that all diffraction peaks correspond-ing to kaolinite disappeared after heat treatment and a diffuse reflection appears between 18 and 30° (2θ) (Chakchouk et al., 2006) which proves the transformation of kaolinite into metakaolinite while crystalline structure of quartz and illite persisted (Chakchouk et al., 2006). The per-sistence of illite has already been reported by He et al. (1995).

The differential thermal (DTA) and thermogravimetric analyses (TGA) of this kaolin are already reported by Chakchouk et al. (2006). They show: i) Endothermic release of the absorbed water at T < 100 °C; ii) endothermic phenomenon attributed to kaolinite de-hydroxylation and formation of metakaolin between 430 °C and 620 °C; and iii) exothermic reorganization of the structure at almost 950 °C. These results show that the thermal treatment of the used kao-lin transformed the kaolinite to metakaolinite while the associated min-erals (quartz, illite and anatase) remain unchanged.

The ^{29}Si NMR spectrum of kaolin (Fig. 2a) reveals the presence of a narrow signal at δ = −91.3 ppm. This signal is characteristic of tetrahe-dral silicon bonded through oxygen to four other silicons in clay mineral (Engelhard and Michel, 1987). A less intense peak at δ = −108 ppm, due to the presence of free quartz, was also depicted (Bich, 2005). In the ^{29}Si NMR spectrum we notice a shift of the initial narrow peak at δ = −91.3 ppm in the raw kaolin to a broad peak at δ = −99.2 ppm after calcination at 700 °C (Fig. 2b), due to the dehydroxylation phenomenon. In the ^{27}Al NMR spectrum of studied kaolin (Fig. 2c) two reflections are present: i) at δ = −3.6 ppm attrib-uted to kaolinite's hexacoordinated Al, and ii) less intense peak at δ = 10.0 ppm relative to octahedral Al in illite mineral (Akolekar et al., 1997). In calcined kaolin, the ^{27}Al NMR spectrum (Fig. 2d) reveals the presence of three peaks at 51.8, −1.2 and 23.2 ppm assigned to tetrahedral, octahedral and the pentacoordinated Al, respectively.

3.2. Geopolymer characterization

Fig. 3 illustrates the X-ray patterns of calcined clay and the geopolymer at different molar ratios. The comparison of the spectra of the calcined kaolin with those of synthesized geopolymers, shows a shift in the wide broad band from 18°–30° to 22°–35° in calcined kaolin and geopolymers, respectively. This is related to the presence of an

Table 1
Compositions of used materials and formulations of geopolymers.

	Compositions (mass%)								
	SiO₂	Al₂O₃	Fe₂O₃	MgO	K₂O	CaO	Na₂O	PO₃	LOI
Calcined clay	62.96	26.44	1.89	0.24	1.28	–	–	–	12.5
H₃PO₄	–	–	–	–	–	–	–	85	–

	Formulations						
	G¹·⁵	G¹·⁷⁵	G²	G²·²⁵	G²·⁵	G²·⁷⁵	G³
Molar ratio Si/P	1.5	1.75	2	2.25	2.5	2.75	3