Physical–chemical characterization of Tunisian clays for the synthesis of geopolymers materials

S. Selmani [a,c,d], N. Essaidi [c], F. Gouny [c], S. Bouaziz [a], E. Joussein [b], A. Driss [d], A. Sdiri [a], S. Rossignol [c,*]

[a] University of Sfax, National Engineering School of Sfax, Laboratory Water, Energy, Environment (L3E), Tunisia
[b] University of Limoges, GRESE, 123 Avenue Albert Thomas, Limoges, France
[c] University of Limoges, Ceramic European Center, SPCTS UMR 7531, 12 rue de l'atlantis, France
[d] Technical Centre for Building Materials, Ceramics and Glass (CTMCCV), Tunisia

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ABSTRACT

Natural clay materials from Tunisia were examined as an aluminosilicate source for the synthesis of consolidated materials at low temperatures. Three clay samples were collected from the El Kef, Douiret and Gafsa basins and calcined at different temperatures. All of the samples were characterized using chemical and mineralogical analyses, thermogravimetry, dilatometry, and Fourier transform infrared spectroscopy (FTIR) measurements. The chemical (XRF) and mineralogical analyses (XRD and FTIR) indicated that all of the samples contained various amounts of kaolinite and quartz, followed by calcite, mica, palygorskite and gypsum. Curing produced a binder which did not significantly affect the physic-chemical properties of these clays. The obtained materials heterogeneous did not reach the geopolymerization stage, most likely because of their low kaolinite content. The addition of a suitable aluminosilicate to these clays is therefore recommended to produce homogeneous consolidated geopolymers. The synthesized materials obtained after the addition of metakaolin to the formulation to improve reactivity have interesting properties, thereby providing good potential for Tunisian clays in the synthesis of geopolymers.

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1. Introduction

Clay minerals are commonly used in various industrial applications due to their specific physic-chemical properties, such as their surface areas, ion exchange capacities and cation adsorption properties (Sdiri et al., 2011). As expected, the mineralogical composition of the clay strongly influences its physical and chemical properties Essaidi et al. (2013).

Clay minerals are generally used in a large number of applications, such as ceramics, rubber and porcelain manufacturing (Murray, 1991; Breen et al., 1997). Some clay deposits in Tunisia contain clays whose qualities are not easily utilized in the ceramics industry (due to the presence of iron oxide or anatase, for example). However, these low value deposits can be used for consolidated materials (Essaidi et al., 2014a,b). Kaolinitic clays are significant industrial raw materials used in various manufacturing applications, such as in the construction field, in ceramics processing and in many other sectors for diverse and varied applications (Murray, 2007). A strong interest in kaolin has recently developed,

particularly for its dehydroxylated form (metakaolin), which is very reactive (Autef et al., 2013a,b,c). Metakaolin is mainly used in traditional ceramics, as a pozzolanic additive for cement and concrete and as an aluminosilicate source in the synthesis of geopolymers (Davidovits, 2008).

One of the most innovative applications for kaolin's is their use as inexpensive raw materials in the synthesis of geopolymers. Indeed, there has been increasing interest are interested in producing eco-friendly geopolymers from natural, inexpensive clayey materials (Xu and Van Deventer, 2003; Lee and Van Deventer, 2002; Elimbi et al., 2011). Geopolymers are new materials that are obtained through the activation of aluminosilicates and alumina- and silica-rich materials such as calcined clays which are used as precursors (Davidovits, 2008) and appear to be a promising alternative for conventional cementitious materials due to their hydrothermal stability and resistance to acidic environments and/or reducing agents (Bakharev, 2005). They are also known for their promising mechanical and thermal properties (Duxson et al., 2007a,b). However, the presence of secondary minerals in the deposit can play a role in the preparation binders. For instance, Essaidi et al. (2013) recently investigated the role of iron oxides during the synthesis of geopolymer materials from calcined

* Corresponding author.
  E-mail address: sylvie.rossignol@unilim.fr (S. Rossignol).

Tunisian clays. Autef et al. (2013a,b,c) demonstrated the influence of impurities such as quartz and micas on the physico-chemical properties of potassium geopolymers, whereas Prud'homme et al. (2012) investigated the possibility of forming geopolymer foam from industrial waste. Those studies indicated that the dissolution of geopolymer precursors was closely related to temperature, which subsequently enhances the polycondensation rate (Duxson et al., 2007a,b). Moreover, the mineralogical composition and solubility in alkaline silicate solutions of aluminosilicate precursors affect the geopolymerization rate and the compressive strength of the obtained geopolymer. Xu and Van Deventer (2003) reported that the calcined raw materials, activated by a concentrated solution of silicate and potassium hydroxide, produce high strength materials. However, only a few studies have reported on the effects of impurities in clays on the dissolution of clay minerals in alkaline media and on the geopolymerization process. More than 65% of the Earth's surface is composed of aluminosilicate minerals, representing potentially important sources for the synthesis of geopolymers (Davidovits, 2008). Thus, it appears interesting to study the feasibility of producing geopolymer-type materials from various natural aluminosilicate sources and to compare the resulting materials with those obtained from more classical and well-known raw materials. Recently, Essaidi et al., demonstrated the possibility of using activated Tunisian clays (from Tabarka and Medenine deposits) calcined at different temperatures in the synthesis of consolidated materials. The compressive strength and the development of the geopolymeric structure are directly related to the presence of non-bonding silicate species generated by the thermal treatment of the clay.

This study was undertaken to evaluate the possibility of using natural clay materials from Tunisian in the synthesis of geopolymer-type materials. First, the physical and chemical properties of the clays were investigated, and then the clays were introduced in the geopolymer formulation. The feasibility of their use in synthesizing geopolymers and investigations of their properties were performed using FTIR, SEM, and thermal analyses, and their compressive stress were evaluated.

2. Experimental

2.1. Raw/calcined clays and consolidated materials

Three Tunisian clays (A1, A2 and A3) were used as aluminosilicate sources in the synthesis of consolidated materials. Their chemical compositions are presented in Table 1. Light brown clay (A1) was collected from the Kef study site, and it is currently used in the manufacturing of Portland cement; the second sample (A2) is a green illitic to kaolinitic clay from the Douiret area, which is currently used in ceramics; and the third clay sample (A3) was collected from the Gafsa district, also used in the ceramics field. These raw clay samples were dried at 105 °C overnight and then crushed and sieved to obtain the desired fraction (<125 μm) and calcined at 550 °C for 4 h under static air. Hereafter, we use A1^{25}, A2^{25} and A3^{25} to refer to the original A1, A2 and A3 samples, respectively, and A1^{550}, A2^{550} and A3^{550} to refer to their corresponding calcined samples (calcined at 550 °C).

The consolidated materials were prepared by mixing clays with KOH pellets (85.7% purity supplied by Aldrich) previously dissolved

in potassium silicate (SiO_2 = 16.37%, K_2O = 7.56%, density = 1.2,76% of water, supplied by Chemical Labs, USA). The reactive mixture was mixed for 5 min at 700 rpm and then placed in an opened polystyrene sealed mold in an oven at 70 °C for 24 h (He et al., 2012). Small amounts of clay samples (i.e., A1, A2 and A3) were added with 16% of two types of commercial metakaolin, M1 and MKI, which differ in terms of their reactivities: M1 is less reactive than MKI (Autef et al., 2013). The nomenclature adopted for the synthesized aluminosilicate materials is as follows: Axg^{550} for consolidated Tunisian-based calcined materials, Axg^{550+25} for the stoichiometric mixture ratio of raw and calcined clays, and AxgMKy^{550} for the calcined and MK mixture (see the previous discussion, where (x) and (y) are the names of the Tunisian sample and metakaolin).

2.2. Characterization techniques

Chemical analysis was performed 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 Cu Kα radiation ($\lambda K\alpha$ = 0.154186 Å) over the 2θ range from 5° to 70° with an acquisition time of 2 s and a step size of 0.04°. Files from the Joint Committee on Powder Diffraction Standards (JCPDS) were used for phase identification.

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

Thermogravimetric analysis (TG/DTA) was performed by heating the samples in a Pt crucible at 10 °C min^{-1} in a dry air flow between 25 °C and 1200 °C.

The dilatometry measurements were performed on a horizontal differential Dilatometer "NETZSCH" (Model 402PC DIL) heating from 25 to 1100 °C at a heating rate of 5 °C/min in air.

FTIR spectra were recorded on a Thermo Fisher Scientific 380 infrared spectrometer (Nicolet) by scanning 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.

The compressive strength of samples stored for 7 days were determined using LIyodEZ20 machine moving at constant crosshead displacement of 0.2 mm/min. Specimens were cylindrical, 15 mm in diameter and 30 mm in high. Samples surfaces were polished flat and parallel to avoid the requirement for capping. All values presented in the current work are an average of 10 samples. The experimental error is obtained from the average of standard deviation of the 10 samples.

3. Results and discussion

3.1. Characterization of raw samples

The three clay samples were characterized after sampling to determine their quality for use as a low-cost material. The particle size distributions (PSDs) of the raw clays, A1^{25}, A2^{25}, and A3^{25}, are shown in Fig. 1. The PSDs indicate the presence of three main fractions: (1) clay fraction (<2 μm), which represented approximately 8–10%; (2) silt fraction, known for its particle size ranging between 2 and 20 μm; and (3) the remaining fraction coarse than 20 μm. The silt fraction represented 53%, 56% and 48% of the A1^{25}, A2^{25} and A3^{25} clays, respectively. The coarse portion (i.e., >20 μm sized clays) represented 40%, 32% and 42% of the A1^{25}, A2^{25} and A3^{25} clays, respectively.

According to the BET and wet ability results (Table 2), the most reactive sample appears to be A2^{25}, which possessed the largest

Table 1
Chemical compositions of the Tunisian raw clays in molar percent.

Elements	Ca	Al	Si	Fe	K	S	Ti	P
A1^{25}	36.0	18.2	37.4	4.4	2.4	0.7	0.6	0.2
A2^{25}	2.3	25.1	54.7	7.3	9.2	0.6	0.8	–
A3^{25}	15.7	22.2	51.6	5.5	3.9	0.3	0.7	–