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Addition of low reactive clay into metakaolin-based geopolymer formulation: Synthesis, existence domains and properties

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ABSTRACT

This paper investigates the addition of low reactive Tunisian clay into metakaolin-based geopolymer as a valorization way in alkaline media. To conduct this investigation, the aluminosilicate precursors used were primarily characterized. Then, several samples were prepared by varying the amounts of metakaolin and clay in the mixture as well as the Si/K molar ratio of the alkaline solution. Correlations between (i) the polycondensation rate of the synthesized mixtures, followed by FTIR spectroscopy; (ii) the working properties, evaluated by the compression test; and (iii) the chemical composition were established, and a model of reactivity was proposed to elucidate the different networks formed for each sample. It appears that the Tunisian clay, after heat treatment, exhibits some reactivity that allows for the formation of consolidated materials. The associated minerals present in the clay seem not to participate in the polycondensation reaction and are simply agglomerated by the alkaline solution. However, the increase of the proportion of metakaolin in the mixture and the depolymerized species in the alkaline solution may improve the polycondensation rate and the working properties of the final materials. The optimal properties were obtained for a mixture of 50% low reactive Tunisian clay and 50% metakaolin and a Si/K ratio of the alkaline solution of 0.50.

1. Introduction

Tunisia is among the countries that have numerous large clay deposits that remain not fully exploited [1]. So far, Tunisian clays have been largely used in the traditional ceramic industry [2,3]. More innovative recent applications include the evaluation of the pozzolanic activity of Tunisian clays [4], the preparation of a clay-based micro-porous filtration membrane [5,6]and the mineralization of organic compounds in waste waters [7]. A novel application, yet not largely studied, is the use of Tunisian clays as an aluminosilicate source for the synthesis of geopolymer or geomaterial-based materials. This seems to be a potentially profitable application that allows not only reducing the cost of the raw materials but also valorizing natural resources.

Geopolymers are a promising and innovative new class of binders generated from the activation of an aluminosilicate source with an alkaline solution [8]. Their formation implies the dissolution of aluminosilicate species in an alkaline environment to form an amorphous three-dimensional geopolymer network by polycondensation reactions. The geopolymerization process is strongly influenced by the nature of the raw materials used [9]. Furthermore, depending on the raw material, geopolymers can exhibit various properties such as high compressive strength, low shrinkage, acid resistance, fire resistance and low thermal conductivity [10]. The aluminosilicate source, metakaolin, is one of the most commonly used raw materials because of its purity and high reactivity [11,12,13]. Autef et al., [12,13] have studied the behavior of three commercial metakaolins, which differ in terms of reactivity, dehydroxylation process and the amount of impurities, in the presence of an alkaline solution. It was demonstrated that, depending on the metakaolin used, one or several geopolymer networks are formed that govern the working properties. Despite the extensive use of metakaolin, research on low-cost and more available materials has encouraged many investigators [14,15,16,17,18] to turn to the use of common clays that display some reactivity that enables them to be suitable for producing geopolymer materials. Recently, two Tunisian clays, a kaolinitic clay from the region of Tabarka and an illito-kaolinitic clay rich in hematite from the region of Medenine, were tested as potential aluminosilicate precursors [15]. It appears that it is possible to obtain consolidated materials from fresh and calcined clays, although materials based on the calcined clays exhibit better mechanical strength. This fact highlights the effect of the heat treatment on the amorphization of clay minerals, and consequently, on the reactivity of the clay in an alkaline media.

Regardless of the aluminosilicate source, the alkaline solution plays an important role in the geopolymerization reaction [19]. In a previous work [20], the influence of the activating solution was elucidated.

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Indeed, the Si/K molar ratio was observed to control the degree of depolymerization of the silicate solution as well as the type and the amount of the siliceous species. Moreover, depolymerized species are highly reactive, which enables the fast formation of oligomers and leads to better mechanical properties of the resulting geopolymers.

In summary, both the aluminosilicate source and alkaline solution are key parameters in the geopolymerization reaction. Regarding the variability of the raw materials that can be used, the effect of the reactivity of each precursor is not fully understood. The objective of this work is to define consolidated materials ternary existence domains based on metakaolin mixture with poorly reactive clay and alkaline solution as a tool to predict geopolymer formation and then valorization way of low reactive clay. Tunisian clay was used as low reactive raw materials corresponding potentially to a large amount of deposits around the world. Moreover, this study aims to deeper comprehension of the effect of the aluminosilicate source reactivity as well as the effect of the activation solution on the geopolymer formation, final structure and working properties in order to define the key parameters controlling the polycondensation reaction when using not pure precursors. In fine, for this, a comparative study of the physical and chemical properties of the various aluminosilicate sources used was established. Then, several samples were prepared by varying the proportion of calcined Tunisian clay and metakaolin and/or the Si/K ratio of the alkaline solution. The structural evolution of the reactive mixtures was monitored by FTIR spectroscopy. Finally, the consolidated materials were characterized by compression tests, X-ray diffraction, and SEM.

2. Experimental

2.1. Raw materials and sample preparation

Two types of clays were used in this study, kaolin supplied by Imerys (France) and low reactive red Tunisian clay from the region of Medenine situated in the South of Tunisia. The two clays were sieved at 80 μm and calcined for 4 h at 700 °C with a heating rate of 5 °C/min. The obtained materials were used as aluminosilicate sources to elaborate geopolymer samples and were denoted as Me and MK for Medenine clay and metakaolin, respectively (Table 1).

Geopolymer samples were prepared by dissolving potassium hydroxide pellets, supplied by VWR (Belgium) (85.2% pure), into a commercial potassium silicate solution (Si/K = 1.7) supplied by ChemLab (Belgium). Then, Me clay and/or MK were added. Samples were placed in a closed sealable polystyrene mold at room temperature (25 °C) according to the procedure previously established by Autef et al. [12].

Table 1
Chemical and physical properties of the two MK and Me aluminosilicate precursors used.

Aluminosilicate precursors		Metakaolin	Calcined Medenine clay
Nomenclature		MK	Me
Color		White	Red
SiO_2	(wt.%)	53.30	59.80
Al_2O_3		45.50	21.84
Fe_2O_3		–	7.56
TiO_2		1.20	1.05
$K_2O + Na_2O$		–	4.34
CaO + MgO		–	5.37
d_{50} (μm)		8	10
BET value (m^2/g)		8	29
Initial kaolinite amount* (%)		99	27
Amorphous phase** (%)		98	25
Wettability (μL/g)		1010	600

* Determined from TGA analysis.
** Determined from Rietveld.

The mixtures were denoted as $^{Si/K}GM^{mMe/mMK}$, where Si/K refers to the Si/K molar ratio of the alkaline solution and mMe and mMK are the masses of Me and MK, respectively, for a total of 12 g of aluminosilicate sources. For example, $^{0.70}G^{9/3}$ corresponds to a mixture composed of 9 g of Me and 3 g of MK with a Si/K molar ratio of the alkaline solution of 0.70.

2.2. Sample characterization

The chemical composition of the raw materials was determined using X-ray fluorescence (ARL 8400, XRF 386 software).

The particle size distributions of the clays 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.

Powder BET surface areas were determined by N_2 adsorption at −195.85 °C using a Micrometrics Tristar II 3020 volumetric adsorption/desorption apparatus. Prior to the measurement, the samples were degassed at 200 °C under vacuum for 4 h.

The wettability value (μL/g) corresponds to the volume of water that can be adsorbed by one gram of powder until saturation.

X-ray diffraction patterns were acquired via X-ray diffraction (XRD) experiments on a Bruker-AXS D 5005 powder diffractometer using CuK α radiation (λKα = 0.154186 nm). The analytical range is between 5° to 60° (2θ) with a step of 0.04° and an acquisition time of 2 s for raw clays, and a dwell time of 0.5 s and a step size of 0.01° (2θ) for consolidated materials. JCPDS (Joint Committee Powder Diffraction Standard) files were used for phase identification.

FTIR spectra were obtained on a Thermo Fisher Scientific 380 infrared spectrometer (Nicolet) using the attenuated total reflection (ATR) method. The IR spectra were recorded over a range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. The atmospheric CO_2 contribution was removed via a straight-line fit between 2400 and 2280 cm^{-1}. To monitor the geopolymer formation, software was used to acquire a spectrum (64 scans) every 10 min for 13 h. To enable comparison, the spectra were baseline corrected and normalized [21].

The compressive strengths were tested using a LLOYD EZ20 universal testing machine with a crosshead speed of 0.1 mm/min. The compressive tests were performed on ten samples for each composition. The values of compressive strength represent the average of the ten obtained values. The test tubes used for the compression tests were cylindrical in shape with a diameter (Φ) of 15 mm and a height (h) of approximately 30 mm [22] and were aged for 7 days in a closed mold at room temperature.

The morphology of the final materials was observed using a Philips XL30 scanning electron microscope (SEM) at 15 kV. An Au/Pd fine layer was deposited on the samples before the observations.

3. Results and discussion

3.1. Aluminosilicate precursors and feasibility of consolidated materials

3.1.1. Investigation of the aluminosilicate precursors

To elucidate the main differences between the two aluminosilicate sources used, a preliminary characterization was performed. Me and MK were extensively studied using various characterization techniques described by Essaidi et al. [15] and Autef et al. [12], respectively. Therefore, only the main physical and chemical characteristics as well as the mineralogical analysis of these two precursors will be briefly described in this study. The chemical compositions of the studied precursors are detailed in Table 1. It clearly appears that MK is very pure because it contains only SiO_2 and Al_2O_3 with a Si/Al molar ratio near 1 (the theoretical value for kaolinite is Si/Al = 1, traducing the purity of the metakaolin). However, Me has a high amount of silica (59.86%) and a lower alumina content (21.84%), for a Si/Al ratio near 2.4. The presence of impurities is also evidenced in the Fe_2O_3 content (7.56%), which was