Influence of silicate solution preparation on geomaterials based on brick clay materials

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ABSTRACT

Brick clay mixtures are raw materials with the potential for use in geomaterials other than tiles or bricks. This study concerns the effect of mixed alkali cation solutions on the polycondensation reactions of geomaterials based on brick clay mixtures. To evidence the feasibility and the understanding of such effects, FTIR and Raman spectroscopy, thermal analyses and compressive tests were investigated to reveal the performance of the alkaline solution and aluminosilicate source. The various solutions used contained different siliceous species (rings, chains) that modified the polycondensation reactions and the Si-O-Ca bond formation. The effect of the polarizability of the alkaline and alkaline earth solutions must be controlled to enhance the final properties. Better mechanical properties were obtained with a low water content.

1. Introduction

Clay minerals are among the most abundant minerals on earth and are of considerable interest due to their low cost [1]. Therefore, they are widely used in a large range of industries [2,3]. Indeed, they exhibit outstanding properties, such as functional surface chemistry, cation absorption and adsorption [4], dry and fired strength [5], and swelling ability, as well as, more importantly, their various mineral and chemical compositions. Novel applications for the use of aluminosilicate materials have been developed during the last two decades of geopolymer synthesis.

Geopolymer materials are a promising and innovative new class of binders generated from the activation of an aluminosilicate source with an alkaline solution [9]. The increasing interest in these new materials in last two decades is attributed to their ability to be more environmentally friendly than classic binders [6,7] and their good working properties [8]. A 3D amorphous geopolymer network is formed by a polycondensation reaction [9,10]. The geopolymer synthesis simply requires the dissolution of aluminosilicate species in the alkaline environment. The polycondensation reaction mechanism and the final working properties of the geopolymer are totally dependent on the type of alkaline solution (Na or K solutions) used and on the type of aluminosilicate materials (metakaolin, fly ash, raw and calcined clay and blast furnace slag) used. Metakaolin is one of the most commonly used raw materials because its purity and high reactivity [11,12,13].

Recently, the search for alternative low cost and easily available materials has led to the development of geopolymers based on natural clays [14], which are more available. Indeed, in some country like Tunisia, clay is widely available, and could be very interesting to use in geopolymer materials. Then, Essaidi et al. [15] have demonstrated the use of two Tunisian clays, from two localizations (fresh and calcined), as potential aluminosilicate precursors.

It has already been demonstrated that the activation process of raw clay by a thermal treatment between 500 and 800 °C leads to more reactive clay minerals [16,17] and then to geomaterials presenting good mechanical properties or durability. A previous study demonstrated the feasibility of producing geomaterials made from a brick clay aluminosilicate source that was calcined at 750 °C [18,19], but they exhibited lower mechanical properties and water resistance than geopolymers from metakaolin. According to L. Reig's works [20], the use of red clay brick waste in alkali activated cement pastes leads to a compressive strength up to 50 MPa after curing for 7 days at 65 °C. Moreover, M. F Zawrah et al. [21] also showed that a mix of byproducts from brick production with granulated blasting led to an increase in the mechanical properties up to 83 MPa with 60% of the slag incorporated into the waste fired brick clay system. Thus, corroborating the literature, a previous study performed on geomaterials synthesized from calcined brick clay [19] demonstrated an increase in the mechanical properties (from 4 to up to 20 MPa) in the presence of red bricks, corresponding to the competition between the alkali cations

(Ca^{2+} and Na^+).

The influence of the alkali cations in the silicate solution as well as the preparation methods for the alkaline solutions lead to changes in the siliceous species of the silicate solutions [22]. For example, increasing the alkali cation size leads to both an increased amount of charged siliceous species and to a slightly higher amount of Q^{2C} and Q^{3C} siliceous species [23]. Moreover, Stephen D. Kinrade and David L. Pole [24] showed that the extent of polymerization increases ($Li^+ < Na^+ < K^+$) as the ion pair formation constants decrease. Plus, they also proved that the ion paired cations stabilize several specific oligomers by immobilizing their large ring structures. Finally, Melkior et al. [25] proved that K^+ cations exhibit a higher mobility than Na^+ cations due to their Stokes radius values, which are linked to the size of the hydration shell. Thus, all of these parameters could be responsible for affecting the polycondensation reaction for geomaterials. For example, McCormick and Bell [26] evidenced that the larger cations increase the extent of condensation during the formation of aluminosilicate structures due to their hydration spheres and the charge densities of the Na^+ and K^+ cations. All the effects of the alkali metals on the polycondensation process can lead to some structural changes. Indeed, H. Xu et al. [27] evidenced for the first time that for a kaolinite mixture, Na^+, compared to K^+, enhanced the dissolution of the aluminum and siliceous species, but the compressive strength remained higher with K^+ cations. The influence of mixed alkali cations on geomaterials based on low reactive aluminosilicate sources has not been yet studied.

This study aims at understanding the effects of mixed alkali cations solutions on polycondensation reactions for geomaterials based on a brick clay mixture. To achieve this goal, calcined brick clay was added into various sodium and/or potassium silicates from laboratory or commercial solutions. The influence of the alkali metals on the features of the silicate solutions was investigated by FTIR and RAMAN spectroscopy. Then, the structural evolution of the reactive mixtures was monitored by FTIR spectroscopy and thermal analyses. Finally, the consolidated materials were characterized by compressive tests.

2. Raw materials and characterization techniques

2.1. Raw materials

A brick clay mixture supplied by one of the main brick manufacturers in France was used for the geopolymer mixture synthesis as previously described [18]. The geopolymer was prepared from an alkali silicate solution, which was either prepared in a lab or from a commercial provider as described in Fig. 1. The lab-prepared solutions were obtained by the dissolution of KOH and NaOH pellets and amorphous silica in deionized water at room temperature as described in previous works [28]. The various silicate solutions are gathered in the Table 1. The final geomaterials are named according to the following nomenclature: $^a_{C/L}SiM_M$, where a is the Si/M molar ratio of the silicate solution, SiM represents the alkali cations (Na and/or K) of the starting solution, C/L is the manufacturing process (C: Commercial and L: Laboratory) and M is the alkali cation added in the starting silicate solution (Na or K). The lab-prepared solutions are characterized by the same chemical features of the commercial silicate solution (as seen in Table 1). Indeed, the Si/M molar ratio, alkali cation concentration and water content are similar.

2.2. Characterization techniques

FTIR spectroscopy in ATR (attenuated total reflectance) mode was used to characterize the silicate solutions and geopolymer mixtures. FTIR spectra were obtained using a ThermoFisher Scientific Nicolet 380 infrared spectrometer. The IR spectra were collected over a wavenumber range of 525 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. The atmospheric CO_2 contribution was removed by using a straight line

between 2400 and 2280 cm^{-1}. To allow comparisons between the spectra, they were corrected using a baseline and were normalized. To monitor the geopolymer formation, a programmed routine was used to acquire a spectrum (64 scans) every 10 min for 450 min.

Raman spectroscopy was performed on the silicate solutions using a T64000 Horiba-Jobin-Yvon spectrophotometer with 514 nm laser excitation operated at a power of 30 mW. Scattered light was collected in backscattering mode using a long working distance objective ($\times 50$) with a triple diffraction grating (1800 lines/mm). The spectral range was 300 to 1400 cm^{-1}, and the exposure times of the solutions were 15 s each for 60 accumulations. The acquired spectra were corrected by subtracting the baseline, which was modeled by a 5° polynomial curve. Then, the spectra were decomposed using Wire 4.0 software.

Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were performed in platinum crucibles on an SDT Q600 apparatus from TA Instruments in an atmosphere of flowing dry air (100 mL/min). Signals were measured with Pt/Pt-10%Rh thermocouples. To characterize the geomaterials, the samples were heated up to 1100 °C at a rate of 10 °C/min.

Compressive strengths were performed using an 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 the compressive strength represent the average of ten obtained values and are expressed in MPa. Test tubes used for the compression tests were cylindrical with a Ø/H ratio of 1/2 according to the standard. The samples were left in a closed mold at 70 °C for 24 h and then were left at room temperature for 28 days.

3. Results

3.1. Effect of the alkaline silicate solution preparation

To determine the role of the preparation of the alkaline silicate solutions on the polycondensation reaction, a preliminary study of the alkaline solution was performed using various spectroscopy techniques, such as FTIR and Raman spectroscopy.

The infrared spectra of all the alkaline solutions are presented in Fig. 2 (A,B – a-a′, b-b′, c-c′). The various bands and their attributions are shown in Table 2. All the spectra exhibit a contribution near 1640 cm^{-1} and a broad band near 1000 cm^{-1} due to the bending of water molecules (δ-OH) and the asymmetric stretching of Si-O-Si bonds (ν_{as} Si-O-Si), respectively, [29]. The majority of the species for these solutions are Q^2 species, with a high contribution near 980 cm^{-1}. For a the pure $^{0.58}_C SiK_K$ commercial alkaline solution (Fig. 2A-a), three peaks at 979, 921 and 823 cm^{-1} are observed and all attributed to the ν_{as} Si-O-Si [30]. The introduction of mixed alkali cations (Na^+) $^{0.58}_C SiK_{Na}$ (Fig. 2A-a) did not induce any important changes in the FTIR spectra. The intensity of the band at 921 cm^{-1} increased, whereas the band intensity of the band at 979 cm^{-1} decreased. Thus, the introduction of Na^+ in the commercial potassium silicate solution induced slight depolymerization phenomena. The same observations were noted for the lab-prepared solutions of $^{0.58}_L SiK_K$ and $^{0.58}_L SiK_{Na}$ (Fig. 2B-a). Nonetheless, the changes in the band intensity values at 921 and 979 cm^{-1} between the pure and mixed alkali solutions were more significant for the lab-prepared solutions.

For the pure $^{0.51}_C SiK_K$ and mixed $^{0.51}_C SiK_{Na}$ commercial alkaline silicate solutions (Fig. 2A-b), the same observations and contributions were observed, with the increase in the intensity of the bands attributed to the vibrations of ν_s Si-O-Si at 921 and 813 cm^{-1} due to the depolymerization phenomena. In addition, a weak shift in the ν_s Si-O-Si contributions toward lower wavenumbers was observed (968 to 914 cm^{-1}). The $^{0.51}_L SiK_K$ and $^{0.51}_L SiK_{Na}$ lab-prepared solution (Fig. 2B-b) spectra display the same contributions with, nonetheless, a significant decrease in the band intensity values at 914, 820 and 979 cm^{-1}. Finally, for the $^{0.72}_{C/L} SiNa_{Na}$ and $^{0.72}_{C/L} SiNa_K$ pure and mixed alkali cation commercial and laboratory silicate solutions (Fig. 2A, b – c), the