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Alkali-activated materials from different aluminosilicate sources: Effect of aluminum and calcium availability

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ABSTRACT

The present study aims to determine the influence of aluminum and calcium availability from two different aluminosilicate sources (COx argillite and sediment), thermally treated at 750 °C, on the formation, the structure and the working properties of the resulting alkali-activated materials. Despite their similar chemical composition, some differences in terms of aluminum coordination, amorphous phase and calcium availability were detected between the two studied aluminosilicate sources. Indeed, sediment sample exhibits higher reactive aluminum and lower reactive calcium compared to argillite sample. Moreover, FTIR spectroscopy has revealed that available calcium interacts with free silicon and aluminum and alkali cation in excess (sodium or potassium) leading to the formation of several networks (Si—O—Al and Si—O—Ca bonds). For both aluminosilicates, the calcium content ($0.33 < Ca/Si < 0.36$) seems to be not sufficient to produce C-S-H hydrated phases. It was also demonstrated that the low availability of aluminum in addition to the high availability of calcium favor the precipitation of secondary reaction products in the detriment of the geopolymer network. These products fill the voids inducing a decrease of the porosity and the pore size but also lead to higher heterogeneity that decreases the mechanical properties of the final material. However, the higher availability of aluminum and the lower availability of calcium in presence of high alkaline conditions favor the polycondensation reaction.

1. Introduction

The term geopolymer was introduced by Davidovits [1] to design materials resulting from the activation of an aluminosilicate source by an alkaline solution at ambient temperature. They can be defined according to their constituents, synthesis conditions, structure and working properties. Based on these criteria, a geopolymer is an amorphous three-dimensional aluminosilicate material resulting from the condensation of alumina and silica sources at high pH and at room temperature and characterized by high mechanical properties and thermal stability at high temperatures [2]. Geopolymers can be synthesized from a wide variety of aluminosilicate materials. They are generally synthesized from metakaolin or Ca free or low content aluminosilicate sources [3,4,5,6]. Other studies [7,8,9,10] have also demonstrated the suitability of other clay minerals with different mineralogies (illite-smectite clays, etc.) to produce geopolymer and have studied the influence of their composition on the performance of the obtained materials. It was shown that the heat treatment is essential to improve the reactivity of these precursors. The heat treatment temperatures range generally between 500 and 800 °C permitting the dehydroxylation of clay minerals and not achieving the recrystallization. Bushwald et al., [11] has shown with solubility tests in alkaline solutions that the highest amount of dissolved aluminate from an illite-smectite clay is released after heat treatment at 750 °C. Similarly, Ferone et al., [12] have demonstrated that a heat treatment of Italian sediment at 750 °C favors the dissolution of silicate and aluminate species and therefore enhances the geopolymerization and the mechanical properties of final materials. Other authors focused on the use of natural resources or industrial co-products containing a high amount of calcium (slags, fly ash…). In this case, attention should be paid to the designation of these materials. In fact, the term geopolymer cannot be used for any activated material with an alkali silicate regardless of its structure and properties. That is why their designation as alkali activated materials is more appropriate because it was demonstrated that the structure and nanostructure of the final materials strongly depend on the calcium content of the used raw precursor [13]. Indeed, geopolymers result from polycondensation reaction (dissolution of the aluminosilicate source and formation of the geopolymer network). The aluminum in the final structure is only in tetrahedral environment [14]. However, alkali activated materials are generated from different

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reactions such as polycondensation and hydration depending on the calcium content.

The available calcium may either precipitates as portlandite Ca$(OH)_2$ or reacts with the dissolved silicate and aluminates due to its strong polarizing power [15, 16]. Indeed, high calcium content leads to the coexistence of a C–S–H gel containing aluminum and an aluminosilicate gel containing some calcium [16,17]. Moreover, Yip et al., [18] highlighted also the crucial impact of the alkalinity of the used solution. Indeed, the coexistence of geopolymer and C-S-H is possible at low pH value. However, the geopolymer network is favored in detriment of C-S-H at higher alkali concentration ([Na] = 7.5 M) [18]. The calcium content influences also the mechanical strength. In fact, the formation of hydrated phases and unreacted particles lead to an increase of the mechanical strength of the final materials [19].

Recently, Peyne et al., [20] have studied the effect of alkali cation solutions on the formation and properties of brick clay (Ca content of 3 wt%) based geomaterials. It was evidenced that the polarizability of the alkaline and alkaline earth solutions modify the polycondensation reactions and the Si—O—Ca bond formation and therefore the final properties.

^{27}Al MAS-NMR spectroscopy was extensively used to study the structure and the reaction products of geopolymer and alkali activated materials [21]. In these materials, the aluminum is generally in tetrahedral environment Al^{IV} [22]. However, the unreacted used raw material leads to the presence of 4, 5 and 6 coordinated aluminum. ^{27}Al MAS-NMR was also useful to prove the incorporation of Al in the silicate chains of C-S-H or C-A-S-H gels in the case of alkali activated slags [23].

Despite the advances in the research on geopolymer and more generally on alkali-activated materials, the effect of calcium is not yet fully understood and strongly depends on the parent raw materials. Moreover, the interaction between alkali and alkali earth in the reactive mixture and the final reaction products are still ambiguous. In the present work, a comparative study between alkali-activated binders based on two different aluminosilicate sources containing calcium was undertaken in order to study the influence of calcium and aluminum availability on the formation, the structure and the working properties of the consolidated materials.

2. Experimental

2.1. Raw materials and sample preparation

Two types of aluminosilicate sources were used in this study (Table 1): Callvo-Oxfordian argillite [24] denoted A supplied by Andra[1] and dredged sediment called S and supplied by EDF.[2] The two aluminosilicate sources were dried, crushed and ground in order to obtain a particle size lower than 100 µm. Then, they were calcined, under static air, at 750 °C during 4 h with a heating rate of 5 °C/min.

Consolidated materials were synthesized by mixing A and S samples with either potassium silicate solutions with different Si/M molar ratios (Si/M = 0.6 and 0.7, respectively) and alkali concentrations ([M] = 5.2 and 4.1 mol L^{-1}, respectively) or a sodium silicate solution (Si/M = 0.7, [M] = 8.3 mol L^{-1}). Si/M was fixed at 0.7 in sodium alkaline solution and 0.6 in potassium one, being the optimal ratios for higher reactivity according to previous work [25]. A potassium alkaline solution with a Si/K ratio at 0.7 was also studied in order to understand the effect of cation nature.

The obtained mixtures were placed in a closed sealable polystyrene mold at room temperature (25 °C). Samples were denoted as A^{Mx} and S^{Mx} for samples based on A and S samples, respectively with M: alkali cation Na or K and x the Si/M molar ratio of the solution.

Table 1
Nomenclature, chemical and physical characteristics of used aluminosilicate sources.

Aluminosilicate source	A	S
Si/Al	2.49	2.48
Ca/Si	0.33	0.36
Mg/Si	0.08	0.08
Fe/Si	0.09	0.12
D_{50} (µm)	26	16
S_{BET} (m^2/g)	5	9
Wettability (µL/g)	535	900
Natural pH value	12	13
Ionic conductivity at pH = 13 ($*10^{-3}$ S/cm)	6.8	8.2

2.2. Sample characterization

The chemical composition of the three used aluminosilicate materials was determined using X-ray fluorescence (Zetium spectrometer, PANalytical).

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 (m^2/g) were determined by N_2 adsorption at −195.85 °C using a Micromeritics 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 1 g of powder before saturation. One gram of powder is deposited on a glass slide, water is then added to the powder using a micropipette until visual saturation [4]. The obtained value is the average of at least three experiments.

pH value and ionic conductivity were measured with sensors of an ESA analyzer (Acoustosizer II S flow through system, Colloidal Dynamics). In order to measure the ionic conductivity, a solution (water + KOH) with a pH value of 13. The use of silicate solution was not possible because the equipment did not allow to work with high alkaline solution (pH value > 13).

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed with a SDT Q600 apparatus from TA atd Instruments, in an atmosphere of flowing dry air (100 mL/min) in platinum crucibles. The signals were measured with Pt/Pt–10%Rh thermocouples. The samples were heated up to 800 °C with a rate of 5 °C/min.

FTIR spectra were obtained with a Fourier-transform infrared (FTIR) spectrometer. The IR spectra were recorded over a range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. Atmospheric CO_2 contribution was removed via a straight-line fit between 2400 and 2280 cm^{-1}. To enable comparison, the spectra were baseline corrected and normalized [26].

X-ray diffraction (XRD) patterns were acquired with a Bruker-AXS D8 powder diffractometer using Cu Kα radiation ($\lambda K\alpha = 0.154186$ nm). The analytical range is between 5° and 55° (2θ), with a step width of 0.02° θ and a dwell time of 1 s. Joint Committee Powder Diffraction Standard (JCPDS) files were used for phase identification. The quantification of the different phases is determined by the Rietveld method using Topas software (Bruker). A quantitative analysis was realized on all the present phases. For that, a standard phase (30% of ZnO) was added to the sample [4].

High-resolution NMR experiments were performed at room temperature using a Bruker AVANCE-400 spectrometer, operating at 104.26 MHz for ^{27}Al signals. ^{27}Al MAS-NMR experiments were carried out for aluminosilicate and consolidated materials, which were spun at 10 KHz. The number of scans was 400. In order to record the central transitions of aluminum (27Al) (I = 5/2), a π/8 (1.5 µs) pulse was

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