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Effect of the addition of ammonium molybdate on metakaolin-based geopolymer formation: Shrinkage and crystallization

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ABSTRACT

This paper focuses on the influence of the addition of ammonium molybdate to geopolymer mixtures to better understand the formation of geopolymer structural networks and the effect of Mo-based additive on the thermal behavior of material. Several geopolymers were synthesized between two metakaolins and various amounts of ammonium molybdate. The microstructure of samples was determined by SEM, the structural evolution (depending on the amount of molybdenum added) was investigated using Raman spectroscopy and XRD analyses, and the temperature behaviors of materials by DTA–TGA and dilatometric analyses. The results showed that (i) both metakaolins react differently in the presence of ammonium molybdate, (ii) molybdenum induces decrease of shrinkage value at high temperatures, and (iii) the crystallization seems to be favored with ammonium molybdate. This work shows that ammonium molybdate controls polycondensation reactions highlighting the modifier or former role played by the molybdenum atoms depending on the amount of ammonium molybdate added.

1. Introduction

Geopolymers are aluminosilicate materials synthesized at ambient temperature or slightly higher temperature by the alkaline activation of aluminosilicate sources. These materials were previously discussed in the 1960s by Glukhovsky [1]. Due to the high interest of geopolymer materials in industry, a large number of studies were conducted, and it was found that the main role of the aluminosilicate source was as the alumina source for Al–Si polycondensation, and the alkaline solution acted as an activating agent [2,3]. The aluminosilicate sources could be derived from natural clay minerals, calcined clays or industrial by-products [4]. Even if metakaolins are the major aluminosilicate source used around the world due to their high reactivities, it is also possible to work with other Al-rich sources, such as montmorilllonite, illite or non-dehydroxylated kaolin [5]. But it was shown that the geopolymerization is much less complete with unreactive non-dehydroxylated kaolinite or 2:1 clay minerals [6,7]. Previous studies on aluminosilicate sources showed the influence of the reactivity and purity of different metakaolins on the formation of various networks in the strengthened materials [8,9]. Thermal treatments were performed on various potassium-based geopolymers to identify these different networks, and the analyses highlighted the crystallization of compounds identified as leucite ($KAlSi_2O_6$) and kalsilite ($KAlSiO_4$) for all of the samples [10]. The various metakaolins used will lead to differences between the strengthened materials. Indeed, the authors demonstrated that a more reactive metakaolin will form a single geopolymer network due to the very fast dissolution of the metakaolin. A less pure and reactive metakaolin leads to two "geopolymer" networks: a Si-rich network and an Al-rich network with a partial dissolution of the metakaolin.

Concerning the alkaline solution, there are various parameters that could influence the polycondensation reactions such as the alkali cation, the water content, the Si/M ratio (where M = Na or K) or the siliceous species present in the solution. Indeed, Steins et al. [11] studied the influence of three cations (sodium, potassium and cesium) as alkali activators. They demonstrated that the dissolution of the metakaolin is more rapid with a small cation. They demonstrated that the alkali hydration sphere could play a role in the local organization and consolidation of the geopolymer. Moreover, other authors showed the influence of the silicate solution used [12,13]. Indeed, they studied two different potassium silicate solutions; the first one was prepared by adding KOH pellets to a commercial potassium silicate solution, and the second one was obtained by the dissolution of silica in a solution containing water and KOH pellets. The authors demonstrated that the second solution contained more Q^0 species than the first one. Because Q^0 species are more reactive than other Q^n species, this solution has a higher reactivity. So, these solutions will lead to different polycondensation reactions. According to this, the quality of the alkaline solution and therefore its reactivity are in accordance with the purity and the reactivity of the metakaolin (see before) because the various networks formed in these

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materials are essentially based on silicate compounds. So, the control of the siliceous species in the reaction mixture could influence the formation of a specific network.

Some studies highlighted that the formation of silicomolybdic entities was possible thanks to the reaction between siliceous species and ammonium molybdate ($(NH_4)_2Mo_2O_7$) [14]. The formation of α and β silicomolybdic acid ($H_4SiMo_{12}O_{40}$) was demonstrated by Truesdale and Smith [15]. These entities could be used for the determination of the silica thanks to a colorimetric method [16]. Indeed, in water, the reaction between silica and molybdate will form yellow or blue silicomolydic acid. The intensity of the color, measured by spectrophotometric analysis, allows the determination of the concentration of silicomolybdic entities in the material. Other authors determined the size of colloidal silica in alkali–silicate solutions depending on the pKa of $H_3SiO_4^-$ by a reaction with molybdic acid [17]. Some studies showed the stability of different molybdic species as a function of the pH value. Thus, Jiang et al. [18] determined that in the presence of phosphorus or zirconium, MoO_4^{2-} entities exist for pH values between 6 and 10.5 while $Mo_7O_{24}^{6-}$ species exist between pH values of 6 and 7.5. Others authors [19] showed the presence of $Ag_2Mo_2O_7$ for a pH value near 5 and the existence of Ag_2MoO_4 for pH values between 6.5 and 12. It was highlighted that alumina could react with molybdic species to change the isoelectric point whereas silica reacts with molybdic compounds to form various species. The interaction of the Oxo molybdenum species with alumina is irreversible, whereas with silica the species remain labile [20]. In some recent studies, the molybdate method and spectroscopic measurements were used to follow the various interactions between an alkaline solution and aluminosilicates [21]. They showed that the formation of different structural units depends on the reaction time. The same methods were also used to determine the structure of the geopolymer formed [22]. Studies on various types of silicate glass showed that crystallization in these materials is favored by these molybdic compounds [23]. In silicate glass, the molybdenum atoms are in a four-fold environment ($[MoO_4]^{2-}$). These tetrahedrons cannot bridge with silicon polyhedrons [24]. Thus, the molybdenum atoms are located in zones rich in alkali or alkaline earth metals. Therefore, the silica network is impoverished in alkaline cations and contains fewer non-bridging oxygen atoms. When potassium atoms are present in the system, the crystallization of potassium bimolybdate ($K_2Mo_2O_7$) and potassium molybdate (K_2MoO_4) occur at 460 °C and 925 °C, respectively, during thermal treatments [25,26].

The molybdate compounds could be used to modify siliceous species from the alkaline solution. Because geopolymers are alkaline activated materials based on silica species, the aim of this study is to control these siliceous species in the potassium silicate solution by adding ammonium molybdate. Finally, the role of molybdic species on the formation of different structural networks in geopolymer materials was determined. To do this, various geopolymer samples synthesized from two different metakaolin sources were realized with Mo-addition and were studied by spectroscopic, microscopic and dilatometric analyses.

2. Material and methods

2.1. Raw materials and sample preparation

Samples were synthesized using an alkaline silicate solution (Si/K = 0.7) and two metakaolins (denoted Mk1 and Mk2) from the supplier Imerys (Table 1) [27]. The alkaline silicate solution was obtained by the dissolution of KOH pellets (85.2% purity) and amorphous silica (99.9% purity) in osmotically purified water at room temperature as described in a previous work [28]. Syntheses were performed by mixing the alkaline silicate solution and metakaolins. Then, the samples were placed in a closed mold at room temperature (25 °C). The geopolymer characteristics are presented in Table 1. Other samples were realized with the addition of anhydrous ammonium molybdate (99.9% purity) to the alkaline solution before the addition of the metakaolins. The amounts added were between 0.08 and 1.57% molar of molybdenum.

Table 1
Chemical characteristics of raw materials and geopolymers.

	Raw materials		Geopolymers		
	Chemical composition (weight %)		Si/Al	Al/K	% H_2O
	SiO_2	Al_2O_3			
M1	55.0	40. 0	1.80	1.12	32.8
M2	55.0	39.0	1.84	1.09	32.8

Some of these samples were heated at 1400 °C using a 5 °C/min ramp after consolidation. The nomenclature used for the various samples is reported in Table 2.

2.2. Sample characterization

Raman spectroscopy was performed on powder samples using a T64000 Horiba–Jobin–Yvon spectrophotometer with 514 nm laser excitation operating at a power of 30 mW at the sample. Scattered light was collected in the backscattering mode using a long working distance objective (×50) with a triple diffraction grating (1800 lines/mm). The spectral range was 100 to 1200 cm^{-1}, and the acquisition time was 60 s.

X-ray patterns were collected from powder samples after they were crushed to 63 μm in size and were obtained from 5 to 80° (2θ) using a Brücker D8 apparatus equipped with a graphite-backed monochromator. The device was equipped with a cobalt anode (λ = 1.79026 Å). The XRD patterns were obtained using a dwell time of 0.5 s and a step size of 0.01° (2θ). The crystalline phases were identified by comparing the patterns with powder diffraction file (PDF) standards from the International Center for Diffraction Data (ICDD).

The morphologies of the final products were determined using a Cambridge Stereoscan S260 scanning electron microscope (SEM). The samples were broken and carbon coated.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on an SDT Q600 apparatus from TA Instruments in a flowing dry air atmosphere (100 mL/min) in platinum crucibles. The signals were measured using Pt/Pt-10% Rh thermocouples. Milligram aliquots of the samples were placed in platinum crucibles, and the analyses were performed from 30 to 1400 °C at 20 °C/min for the consolidated geopolymer samples obtained at room temperature. All of the samples were crushed prior to analysis.

Dilatometric measures were made under air, by means of a contact vertical dilatometer (TMA Setsys Evolution Setaram), on bulk samples with a cylindrical geometry (H = 7 mm; Ø = 6.5 mm). Two platinum holders were placed at the surface end contacts of the samples to avoid high-temperature diffusion between the samples and the alumina holders. A calibration cycle (without the sample) was performed and registered. The calibration data were then subtracted from the data collected for each sample to eliminate the contribution of the device. The thermal cycle used consisted of heating from 30 to 1400 °C and cooling from 1400 to 30 °C, both at a rate of 5 °C/min. Then, the $\Delta L_{sample}/\Delta L_{reference}$, where the reference is the sample without the addition of ammonium molybdate, was calculated for every composition. For example, for the $^{25}M2_{1.57}$ geopolymer, the total shrinkage is equal to 4.8%. The shrinkage of the reference ($^{25}M2$) is 20%. So, the $\Delta L_{sample}/\Delta L_{reference}$ value is equal to 0.24.

Table 2
Nomenclature of samples.

Molar % of Mo	Mk1		Mk2	
	25 °C	1400 °C	25 °C	1400 °C
0	$^{25}M1$	$^{1400}M1$	$^{25}M2$	$^{1400}M2$
0.40	$^{25}M1_{0.40}$	$^{1400}M1_{0.40}$	$^{25}M2_{0.40}$	$^{1400}M2_{0.40}$
1.57	$^{25}M1_{1.57}$	$^{1400}M1_{1.57}$	$^{25}M2_{1.57}$	$^{1400}M2_{1.57}$