Role of the morphology and the dehydroxylation of metakaolins on geopolymerization

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ABSTRACT

Two commercial metakaolins were tested during partial geopolymerization with potassium silicate in order to emphasize the different surface reactivities. Both manual and short-term mechanical stirring were used for slurry preparation, while radiation, infrared, and microwave heating were used for curing. The metakaolins had similar compositions and specific surface areas, but different morphologies and dehydroxylation degrees due to different calcination kiln technologies. The degree of geopolymerization was checked by SEM and N_2 adsorption (BET), FTIR and ^{27}Al MAS NMR spectroscopy. While the dehydroxylation degrees were different, the metakaolins had similar reactivity. The metakaolin powder with rounded agglomerates and lower water demand was more sensitive to the various geopolymerization conditions than the fine dispersed lamellar one, thus giving rise to very different micro- and macrostructures of the partially geopolymerized samples. IR heating seemed to increase the geopolymerization degree slightly, while MW heating induced the fast evaporation of the water, forming porous samples.

1. Introduction

Differences in the durability of ancient cements and modern concretes have been investigated by Glukhovsky et al. (1980). This work led to the synthesis of various aluminosilicate binders from clays, feldspars, volcanic ashes and slags. Later, Davidovits used the word "geopolymers" for a similar class of inorganic polymeric materials (Davidovits, 1991; Davidovits, 2002), as an alternative to organic matrices for composites.

Geopolymers can be generally defined as amorphous to semi-crystalline materials with a three-dimensional aluminosilicate network formed by condensation polymerization. Polymeric bonds of Si–O–Al–O form under alkaline conditions in the presence of aluminosilicate oxides. The final microstructure of a fully reacted geopolymeric resin consists of nanoparticulates ranging from 5 to 15 nm, separated by nanopores of 3 to 10 nm (Kriven et al., 2003).

At the atomic scale, the geopolymer amorphous network is formed by SiO_4 and AlO_4 tetrahedra connected by oxygen corners. Recent results indicate that these tetrahedra form rings of various sizes in the network and endow the geopolymer matrix with ion exchange properties (Dedecek et al., 2008). All monovalent cations balancing the negative charge of AlO_4 tetrahedra (Na^+ or K^+) can be replaced by small monovalent (Li^+ and NH_4^+) or divalent (Co^{2+}) ions. On the other hand, large cations as Cs^+ can replace Na^+ or K^+ ions only partially. The ion exchange properties of geopolymers, together with the spectra of dehydrated Co(II) exchanged geopolymers in visible region, resulted in the suggestion that their network is formed predominantly by six-member, eight-member, and larger rings (Dedecek et al., 2008). Therefore, from some standpoints, geopolymers may be regarded as X-ray amorphous analogues and precursors of tetrahedral aluminosilicate framework zeolites.

To produce a geopolymer, the aluminosilicate raw materials are mixed with an alkaline aqueous solution, usually a sodium or potassium hydroxide and/or silicate aqueous solution (Kriven et al., 2003; Panagiotopoulou et al., 2007; Nair et al., 2007). The geopolymerization mechanism is quite complex (Davidovits, 2008), but may be simplified into a few steps (Duxon et al., 2007a): dissolution (consuming water); speciation equilibrium; gelation; reorganization; polymerization, and hardening. The first step is the dissolution of the solid aluminosilicates by alkaline hydrolysis, producing aluminate and silicate species. Small size cations such as Na^+ increase the dissolution rate (Panagiotopoulou et al., 2007; Xu and Van Deventer, 2000), while alkaline metal cations with a larger atomic size (such as K^+) stimulate condensation and promote the geopolymerization to a stage of completion (Comrie and Kriven, 2003).

Many Al–Si containing source materials may be used to produce geopolymers (Xu and Van Deventer, 2000; Panagiotopoulou et al., 2007; Duxon et al., 2007b; Fletcher et al., 2005; Rahier et al., 1996). When aluminosilicates come into contact with alkaline solutions,

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leaching (dissolution) of both Al and Si species starts. The extent of leaching depends on the concentration of the alkaline solution, nature of the alkali cations, stirring speed, leaching period, and structure and composition of Al–Si source materials. The leaching ability of raw materials in alkaline conditions is: metakaolins>zeolites>slags>fly ashes>pozzolana>kaolins (Panagiotopoulou et al., 2007). However, metakaolins designate different calcined kaolinite species, some of which react, whereas others do not, during geopolymerization (Davidovits, 2008).

In light of this fact, two commercial metakaolins with similar composition and specific surface areas, but with different morphologies and dehydroxylation degree due to different kiln technologies for kaolin calcination, were studied as raw materials for geopolymerization with potassium silicate alkaline solution. Manual and mild mechanical stirrings are used in a partial geopolymerization to emphasize the powder surface reactivity. The duration and intensity of stirring are dominant factors during the first stage of geopolymerization, when Al and Si species are leached by the alkaline solution from the surface of Al–Si particles and diffuse into the gel phase: longer leaching periods and a more intense stirring can maximally dissolve Al and Si complexes from the surface and break the barrier between the Al–Si particle surface and gel phase, so as to accelerate diffusion (Comrie and Kriven, 2003). Different heating systems (laboratory heater, infrared furnace, microwave oven) are used for curing. Metakaolins and geopolymeric structures belonging to the two metakaolins have been checked by SEM and N_2 adsorption (BET), FTIR and ^{27}Al MAS NMR spectroscopy.

2. Experimental procedure

2.1. Materials

Metakaolins were purchased from AGS Minéraux, Clérac, France, under the brand names M1000 and M1200S. Table 1 reports the chemical composition and characteristics (specific surface area and water demand estimated by Marsh cone) of the two metakaolins from the technical data sheets of the producer. Calcination technology is also reported in Table 1. For both metakaolins the calcination temperature range is 750–850 °C.

Potassium silicate solutions with molar ratios of SiO_2:$K_2O = 2$ and H_2O:$K_2O = 13$ (M1000) and 23 (M1200S) were prepared by dissolving KOH pellets (purity >99%, Merck, Darmstadt, Germany) into distilled water and adding fumed silica powder (99.8%, Sigma-Aldrich, Steinheim, Germany) under magnetic stirring. The different H_2O:K_2O ratios were chosen on the basis of the different water demand which is 1.8 times greater in M1200S than in M1000 (Table 1).

2.2. Geopolymer synthesis

The molar ratios are $SiO_2/Al_2O_3 = 4$ and $Al_2O_3/K_2O = 1$. Geopolymer samples were prepared by manual mixing or mild mechanical mixing (Yellow line OST 20 basic, IKA-WERKE GmbH & Co., Staufen, Germany) at 10 rpm. After 5 min of mixing, the slurry was vibrated to remove entrapped air before being transferred into polyethylene molds, which were sealed. After a maturation at room temperature, the samples were cured at 40 °C and/or 80 °C either in a laboratory heater (radiation heating) or infrared (IR) furnace with a permanence

of either 24, 48 or 72 h at each curing temperature. The curing was performed also in a microwave (MW) oven.

2.3. Analytical techniques

Metakaolins and partially geopolymerized samples were examined by XRD (Bruker D8 Advance diffractometer and CuKα radiation, Karlsruhe, Germany) and SEM (SEM, Cambridge S360, Cambridge, UK; EDS, INCA Energy 300, Oxford Instruments, Oxford, UK); samples were non-conductive and were coated using a gold sputter coater. Granulometric distribution analyses of the metakaolin powders were performed by SediGraph 5100, Micromeritics Instrument Corporation, Norcross, USA. BET analyses were performed using SORPTY 1750, Carlo Erba Instruments, Milan, Italy.

The transformation of metakaolins to geopolymers was monitored by ^{27}Al MAS NMR spectroscopy using a Bruker Avance 500 MHz (11.7 T) Wide Bore spectrometer with 4 mm o.d. ZrO_2 rotors with a rotation speed of 12 kHz. High-power decoupling pulse sequences with π/12 (0.7 μs) excitation pulse spectra was applied. The ^{27}Al NMR observed chemical shift referred to an aqueous solution of $Al(NO_3)_3$. For detail and quantitative analysis, spectra were simulated using Dmfit software.

Antisymmetric T–O vibrations in the TO_4 unit of the geopolymer were applied to monitor networking of the geopolymer, in the same way as with zeolites. The IR spectra of powdered geopolymers were recorded using ATR technique by a Nicolet 6700 (ThermoScientific) with nitrogen-cooled MCT-A detector and SmartMIRacle ATR adapter with Si plate. 64 scans were collected to record one spectrum with resolution 4 cm^{-1}. For details, see Dedecek et al. (2008).

The exchange of geopolymers by $CsNO_3$ and $Co(NO_3)_2$ was applied to monitor accessibility of geopolymer inner volume. Unlike other Al species, networked tetrahedral aluminum exhibits a negative charge which has to be balanced by solvated non-network cations located in the vicinity of networked Al. Therefore, the charge balance (sum of the non-framework cations balancing Al) of the geopolymer may serve as a measure of geopolymerization of the network. The experimental details are reported by Dedecek et al. (2008).

3. Results and discussion

3.1. Metakaolin characterization

Although with similar specific surface areas, these two metakaolins had different morphology (Fig. 1) due to different kiln technologies used for kaolins calcination: M1000 metakaolin due to calcination in a rotary kiln was characterized by rounded massive aggregates of lamellar particles; M1200S from calcination in a flash kiln was made up of fine lamellar particles with lower agglomeration. Granulometric distributions were broad and multi-modal for both metakaolins (Fig. 2). M1000 particles were coarser with a mean grain size D50 = 6.5 μm, while M1200S had a D50 = 1.7 μm, confirming SEM observations in Fig. 1.

XRD analyses (Fig. 3) showed that M1000 still contained traces of original kaolinite, as the dehydroxylation was not complete, and quartz and small amounts of a high-temperature form of muscovite as inert impurities that were also present in M1200S. However, the two metakaolins are not prepared from the same raw materials since the

Table 1
Chemical composition and characteristics of the two metakaolins from the technical data sheet of the producer, AGS Minéraux, Clérac, France.

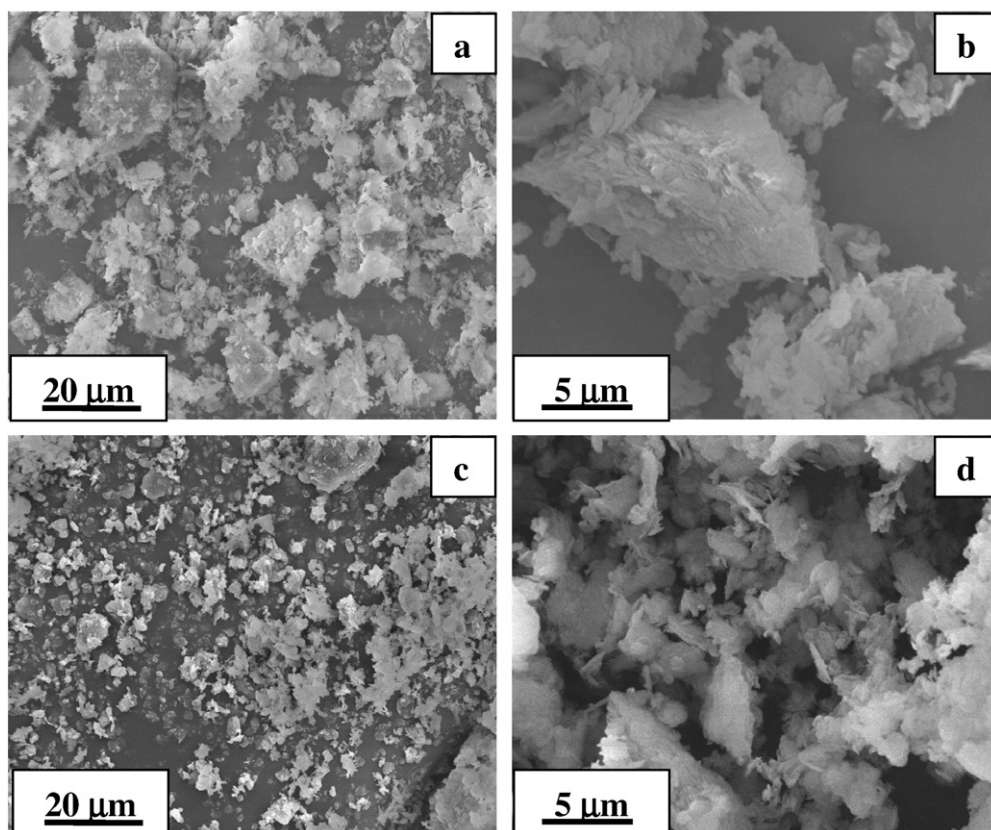| Brand name	Specific surface area (m²/g)	Chemical analysis (%)						Water demand Marsh cone (g/kg)	Bulk density (kg/m³)	Calcining kiln
		Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O/Na_2O	CaO/MgO			
M1000	17	40.0	55.5	1.4	1.5	0.8	0.3	900	400	Rotary
M1200S	19	39.0	55.0	1.8	1.5	1.0	0.6	1650	250	Flash

Fig. 1. SEM micrographs of the metakaolins M1000 (a, b) and M1200S (c, d).

relative amounts of the inert phases differ. In particular, in M1000 the relative amount of quartz is greater than in 1200 S (Fig. 3). According to Zibouche et al. (2009), the presence of inert secondary phases does not influence and/or prevent the geopolymerization reaction.

The most important information about metakaolin reactivity came from their ^{27}Al MAS NMR spectra (Fig. 4). Spectra of both M1000 and M1200S samples exhibit a broad complex band between 80 and −40 ppm and are similar to the spectra well known for metakaolins. Three broad resonances with the centre of gravity at 3, 27 and 59 ppm were identified according to the spectra simulation (not shown in

Fig. 2. Granulometric distribution of the metakaolins M1000 and M1200S.

the figure). Resonance at 3 ppm corresponds to the octahedral Al (Al$_{VI}$), resonance at 27 ppm reflects penta-coordinated Al (Al$_V$) and resonance at 59 ppm reflects tetrahedral coordinated Al atoms (Al$_{IV}$) in oxidic environment (MacKenzie and Smith 2002). It is evident that there is no difference between both metakaolins in the nature of Al structural units and both samples differ only in the relative concentration of Al atoms with different coordination numbers. Metakaolin M1000 exhibits higher concentration of octa-hedrally coordinated Al atoms (resonance at 3 ppm) but quantitative analysis is necessary. ^{27}Al MAS NMR single pulse spectra recorded using short excitation pulses (0.7 μs) reflects all Al atoms with the same probability. Thus, they can be used for quantitative analysis of the concentration of Al atoms in different co-ordinations. The simulation of the spectra using three resonances with the centres of gravity at 3, 27 and 59 ppm showed that the relative concentration of octahedral Al (Al$_{VI}$, resonance at 3 ppm) in M1000 is 35%, of penta-coordinated Al (Al$_V$, 27 ppm) 50% and of tetrahedral Al (Al$_{IV}$, 59 ppm) 15%. In the case of M1200S, these concentrations are 25, 55, and 20%, respectively. Sanz et al. (1988) studied the kaolinite−mullite transformation by ^{27}Al MAS NMR. They observed that at $T > 400$ °C, i.e. during the dehydroxylation of the kaolinite to form metakaolinite, in addition to the line at 0 ppm of the original Al in octahedral coordination with –OH groups (typical of kaolinite), two new lines appeared at 25–30 ppm and 55–60 ppm, and were attributed to penta-coordinated Al from intra-dehydroxylation and Al in tetrahedral coordination from inter-dehydroxylation (Davidovits, 2008). Intra-dehydroxylation refers to a dehydroxylation occurring between adjacent –OH groups of the same Al atom in the kaolinite structure, while inter-dehydroxylation occurs when water is expelled by dehydroxylation of –OH belonging to two neighbouring Al atoms. The penta-coordinated Al (–Al O) exhibited the highest reactivity in alkaline conditions (Davidovits, 2008). Thus, the optimal kaolin calcination temperature for the geopolymerization range is 700–
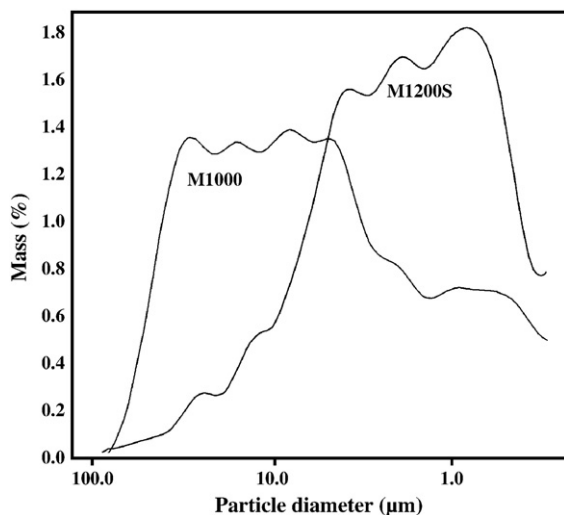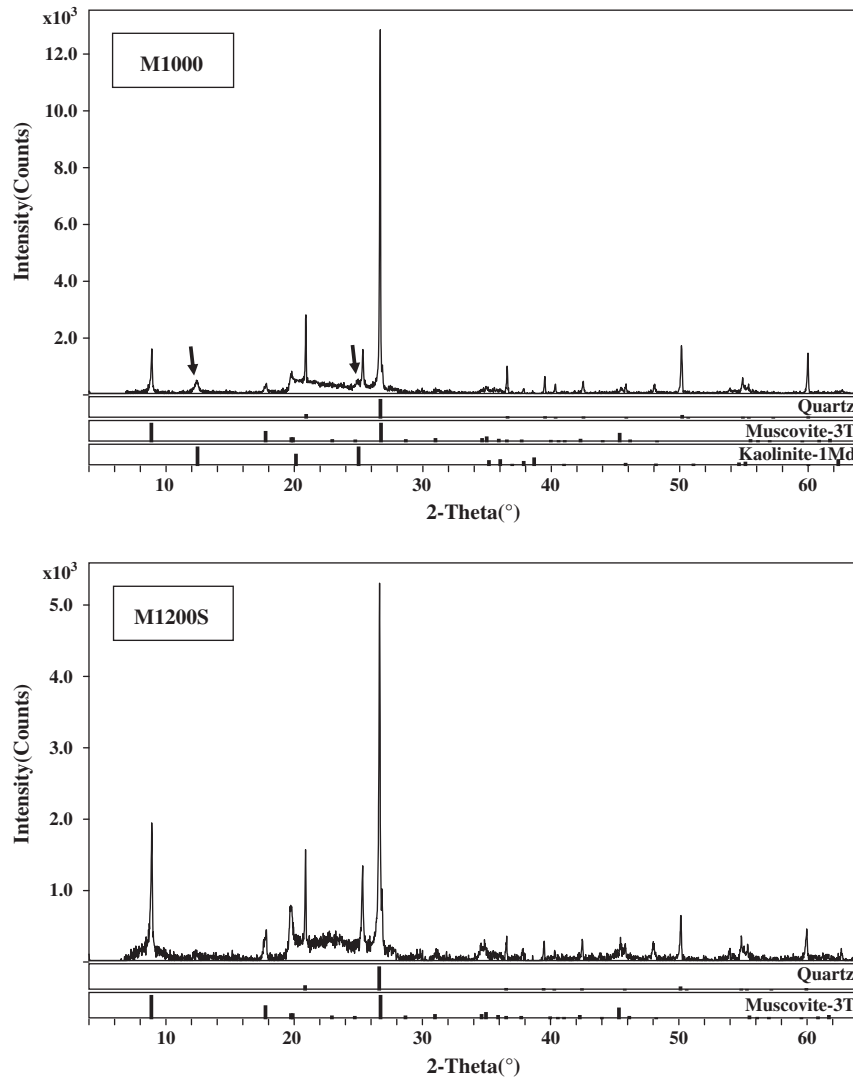
Fig. 3. XRD spectra of the two commercial metakaolins M1000 and M1200S. The arrow indicates the residual kaolinite. The amorphous and continuous background was subtracted in both spectra.

800 °C, where the highest intra-dehydroxylation followed by highest formation of penta-coordinated Al was reached.

Although the calcination range was between 750 °C and 850 °C for both metakaolins, the NMR spectra (Fig. 4) showed that the dehydroxylation was not complete, and the relative concentration of

octahedral Al atoms (Al_{VI}) in M1000 and M1200S is 35 and 25 rel.%, respectively. This may result in the low reactivity of the two metakaolins and M1000 should be considered less reactive than M1200S. As the calcination range was the same for both metakaolins, the kiln technology greatly affected the resulting morphology and dehydroxylation, and as a result, the reactivity of metakaolins. In particular, vertical or flash kilns maintain low vapor pressure during calcination, thus promoting dehydroxylation, while rapid calcination in rotary kilns gives rise to low Al penta-coordination (Davidovits, 2008).

3.2. Geopolymerization and curing

Various preparation and curing conditions were checked to highlight the difference between the two metakaolins in terms of morphology and reactivity. In particular, manual and mild mechanical stirrings were used to induce a partial geopolymerization to emphasize the different powder surface reactivities.

Curing at 80 °C was necessary for the set quantities of reagents and water medium. Actually, during geopolymerization, water is only a vehicle for the reaction to take place and does not remain in the final structure (Duxon et al., 2007a; Davidovits, 2008). When fine raw powders (such as metakaolins) are used, the need for a high amount of water affects the curing temperature greatly. As an example, when
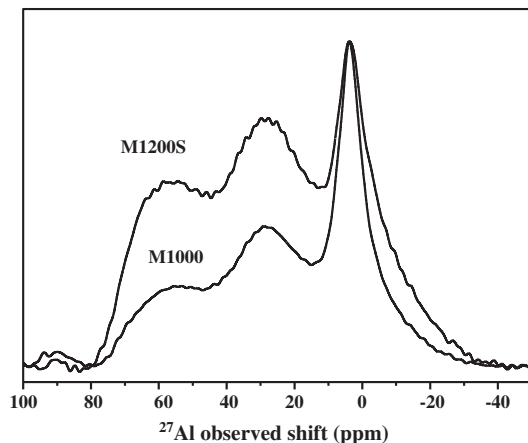

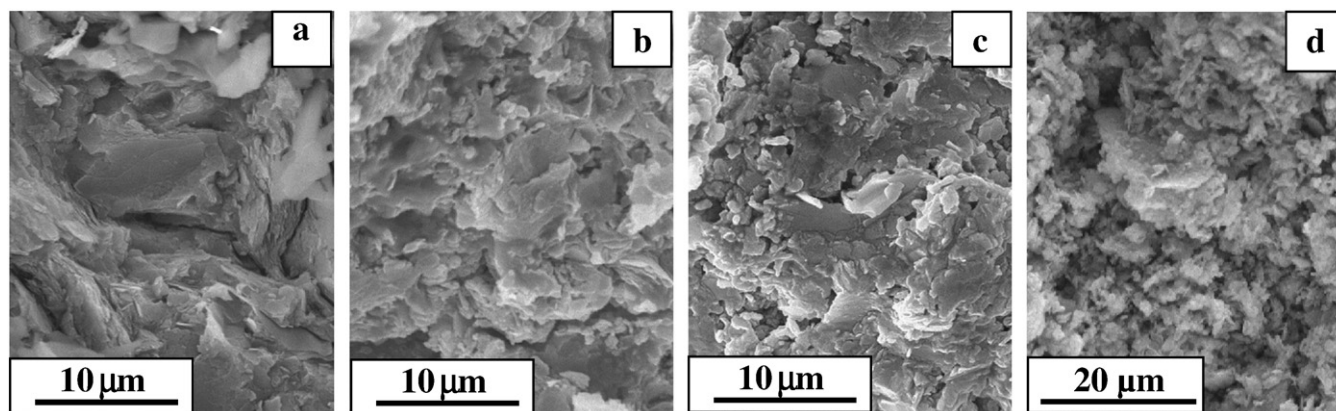**Fig. 4.** ^{27}Al MAS NMR spectra of the metakaolins M1000 and M1200S.

Fig. 5. SEM micrographs of M1000 (a, b, c) and M1200S (d) samples according to stirring methods and procedure in a heater: samples were prepared with potassium silicates by manual (a, c, d) or mechanical (b) mixing, then matured for 24 h and cured at 40 °C and 80 °C for 24 h (a, b, d) or 72 h (c).

the curing temperature was set at 40 °C, it was not sufficient to remove the entrapped water, and the samples from both metakaolins were still moist. Moreover, the maturation stage, i.e. the permanence at room temperature, was necessary because it triggered the transformation. When samples were directly heated at 40 or 80 °C, the phase segregation took place, i.e. the sedimentation of the powder occurred with the subsequent enrichment of the binder solution in the upper part of the sample.

Due to the agglomeration of M1000, a lower amount of water than in M1200S (H_2O: $K_2O = 13$ instead of 23) was necessary to prepare moldable slips, as reported by the Marsh cone test, which estimates both the water demand (Table 1) and the pastes' rheological behavior (Aïtcin and Baalbaki, 1994; Agullo et al., 1999; Le Roy and Roussel, 2005). Actually, the water demand is determined by fixing the viscosity and consequently the time it takes a known volume of paste to flow from the base of the cone through a short tube (the Marsh cone). Water demand depends both on the morphology and the chemical interaction in the liquid medium of the powder. As the chemical behavior in water of the two metakaolins is supposed to be quite similar although a different content of inert phases, the difference in water demand of M1000 and M1200S is mainly due to the powders morphology and consequently to their agglomeration state.

The morphology, rich with hard agglomerates, and the lower dehydroxylation degree made M1000 less reactive, with a need for a longer curing time. When the curing treatment in the heater was maturated at r.t. for 24 h, then cured during 24 h at 40 °C and during further 24 h at 80 °C, no clear presence of geopolymeric precipitates

was found in the microstructure (Fig. 5a); moreover the porosity was very low as the samples were still moistened. The extension of the curing from 24 to 72 h in the heater at 40 °C and 80 °C led M1000 to form geopolymeric precipitates (Fig. 5c), and resulted in complete water removal. The mild mechanical mixing helps geopolymerization, by homogenizing the slips and renewing the reactive surface of the powders, thus leading to samples with no sedimentation and with a clear presence of geopolymeric precipitates but also of un-reacted potassium silicate (Fig. 5b).

The effects of heating systems on M1000 sample micro- and macro-structures during curing are shown in Fig. 6. After a maturation stage of 24 h, infrared heating at 80 °C for 24 h induced the formation of rounded particles with a diameter of less than 1 μm and an almost complete water removal. Microwave heating after a maturation of 48 h at 80 W for 1 h induced the formation of macro-porous samples, due to the fast evaporation of water, but geopolymerization did not occur, and after a few weeks samples were fully covered by potassium silicate filaments. This foaming effect was not observed on mechanically mixed samples, thus indicating the effectiveness of mechanical stirring to promote the geopolymeric reaction.

As for M1200S, no significant microstructural differences appeared between samples which underwent manual or mild mechanical mixing and different curing conditions. Fig. 5d shows the microstructure of the sample prepared by manual mixing and set with a maturation of 24 h and cured in a heater at 40 °C for 24 h and 80 °C for 24 h. In spite of the higher water content in the starting slip, no water presence was detected in samples after curing. Moreover, microwave heating never induced foaming in these samples. These features
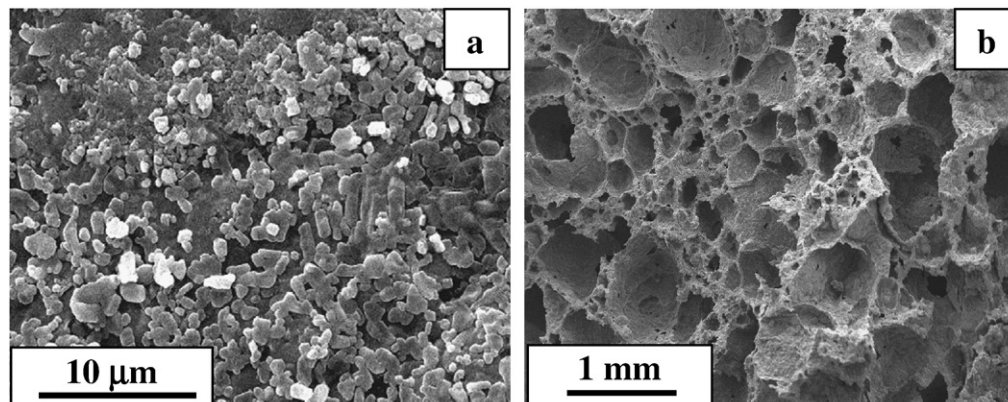

Fig. 6. SEM micrographs M1000 samples prepared by manual mixing and curing in IR kiln (a) and microwave oven (b).

indicate that water was quickly removed from the M1200S sample structure because of the lower powder agglomeration and the higher dehydroxylation, as compared to M1000.

N_2 adsorption (BET method) was used to estimate the surface area of prepared samples. The specific surface areas were significantly smaller (2–5 m^2/g) compared to the starting metakaolin powders, and even dramatically smaller compared to values reported in literature (20–140 m^2/g, Davidovits, 2008). These extraordinarily small surfaces may be explained by the presence of un-reacted potassium silicate, i.e. water glass that fills the mesopores and, mainly, surrounds the geopolymeric precipitates and unreacted metakaolin particles. This results in a decrease of the specific surface areas of partially geopolymerized samples.

3.3. Structural analysis of geopolymer samples

^{27}Al MAS NMR spectra of geopolymer samples are depicted in Fig. 7a and b. Four resonances at 3, 28, 57 and 67 ppm can be distinguished in the spectra according to the spectra simulation. Tetrahedral Al in the network of geopolymer is characterized by a narrow resonance at 57 ppm. The resonances at 3, 28 and 67 ppm can be attributed to unreacted metakaolin (see Fig. 4). Spectra simulation made it possible to quantify the Al concentration reflected in individual resonance (an example is reported in Fig. 8). The degree of geopolymerization was calculated as the ratio of Al in the geopolymer network showing resonance at 57 ppm to the total intensity of ^{27}Al spectrum (Table 2). The obtained results indicate a
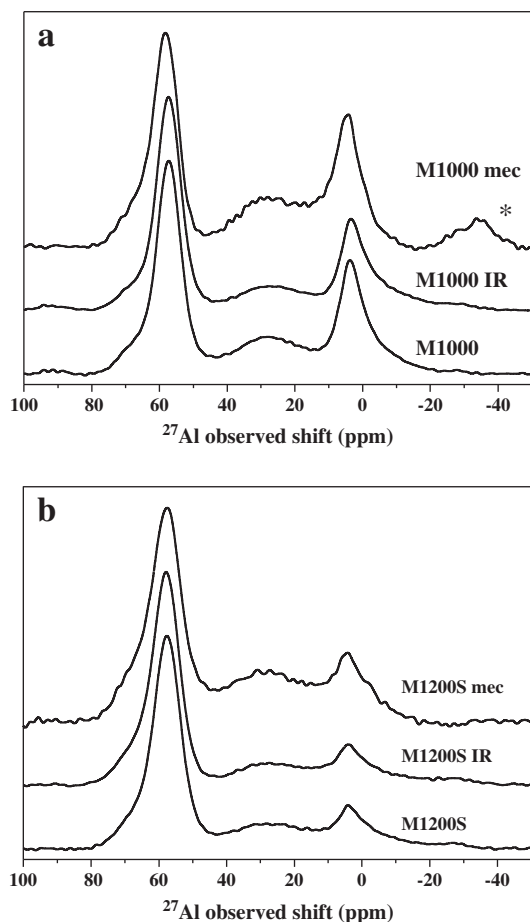

Fig. 7. ^{27}Al MAS NMR spectra of geopolymer samples prepared from M1000 (a) and M1200S (b) metakaolins by manual or mechanical mixing and cured in heater – coded respectively M1000, M1200S, M1000mec, and M1200Smec – and prepared by manual mixing and cured in IR kiln. Rotational sideband (*).
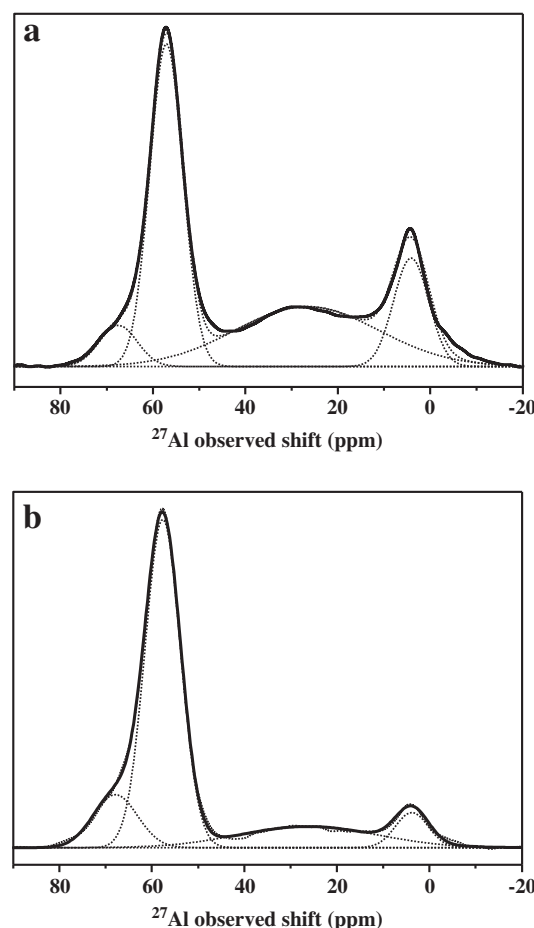

Fig. 8. Simulation of the ^{27}Al MAS NMR spectra to Gaussian lines of the M1000mec (a) and M1200Smec (b) samples prepared by mechanical mixing.

low geopolymerization degree of prepared samples. Nevertheless, it should be noted that, in the case of geopolymer/metakaolin composite, the degree of geopolymerization should be significantly overestimated due to the overlap of the 57 ppm resonance of network Al with the residual signal corresponding to tetrahedral Al of metakaolin. Therefore, other methods for the estimate of the geopolymerization degree must be applied.

It is possible to follow the degree of geopolymerization via the geopolymer IR spectra. There is a nonsymmetric wide band at 1000 cm^{-1} (antisymmetric T–O vibration in TO_4 unit), which contains two components ascribed as a low-frequency band (LF) at

Table 2
Comparison of the degrees of geopolymerization estimated by ^{27}Al MAS NMR and ion exchange of geopolymer samples prepared from M1000 and M1200S metakaolins by manual or mechanical mixing and cured in heater – coded respectively M1000, M1200S, M1000mec, and M1200Smec – and prepared by manual mixing and cured in IR kiln.

Sample	Geopolymerization degree ^{27}Al MAS NMR[a] (%)	Geopolymerization degree ion exchange[b] (%)
M1000	35	16–24
M1200S	45	18–26
M1000 IR	45	17–26
M1200S IR	50	17–25
M1000mec	45	18–26
M1200Smec	65	20–28

[a] The degree of geopolymerization was calculated as the ratio of ^{27}Al characterized by resonance at 57 pp to the total intensity of ^{27}Al MAS NMR spectrum; see Fig. 8.
[b] Limits of geopolymerization were estimated using ion exchange of geopolymers; see text and Table 3.
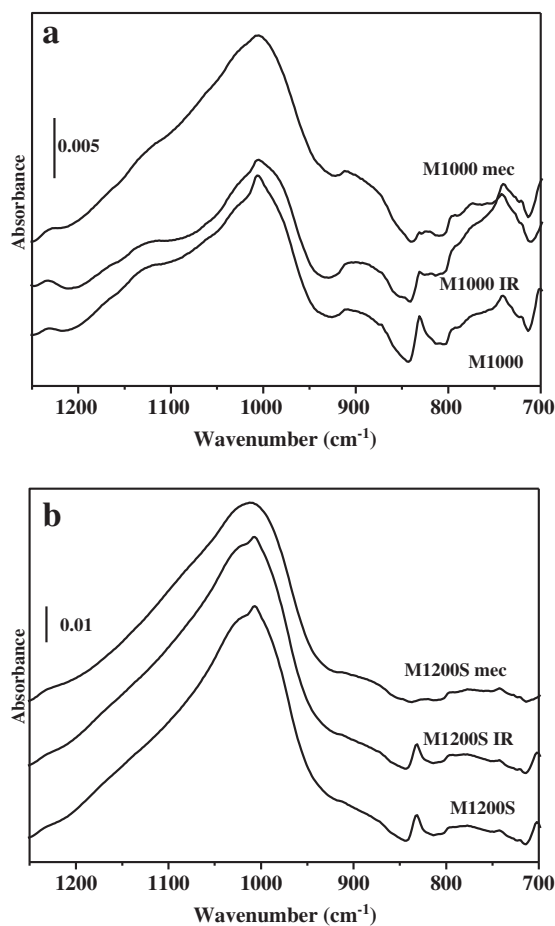
Fig. 9. FTIR spectra of geopolymer samples prepared from M1000 (a) and M1200S (b) metakaolins by manual or mechanical mixing and cured in heater – coded respectively M1000, M1200S, M1000mec, and M1200Smec – and prepared by manual mixing and cured in IR kiln.

Ion exchange in geopolymers was recently developed as a reliable measure of the geopolymerization degree of geopolymers. This approach is based on the fact that tetrahedral Al in the geopolymer network bears a negative charge, which must be balanced by non-network cations. Thus, the molar ratio of cations (Na and K) that balance both the network negative charge and Al represents the measure of geopolymerization of the sample. Moreover, the non-network cations are mobile and can be replaced by others (Dedecek et al., 2008). This makes it possible to distinguish between cations that balance the network negative charge and cations in residual salts in the geopolymer material. Small divalent cations such as Co(II) are applied to minimize steric limits of the ion exchange. The ion exchange of large monovalent cations may serve as a measure of aluminum atoms which are accessible through large (at least ten-member) rings (Dedecek et al., 2008).

The chemical composition of Cs and Co(II) ion exchanged samples is provided in Table 3. The ion exchange degree of the studied samples with Cs and Co(II) and, mainly, the total ion balance of the samples are low, and indicate the low polymerization degree of the studied samples; it is worth noting that one Co(II) balances two network Al atoms. Because the presence of potassium silicate was evidenced (see above), the nature of the K ions is not clear. K ions reflected in chemical analysis may correspond either to the potassium silicate or to cations that balance the network negative charge. In the studied samples, part of the Na ions may also be present in the form of salt. However, the resistance of Na ions against ion exchange by Cs and Co(II) ions may be explained by transport limitations due to the presence of potassium silicate. As was shown above, the presence of potassium silicate significantly decreases the surface area of geopolymer samples formed, and therefore the ion exchange to the geopolymer fraction may be limited. The restriction in the ion transport may explain the lower ion exchange degree of Co(II) compared to Cs ones in the case of non-mechanically mixed samples. Typically, the ion exchange capacity of geopolymers for Co(II) ions is higher than for Cs ions, because Cs ion exchange is limited by the size of the rings in the geopolymer structure (Dedecek et al., 2008). In the case of the potassium silicate barrier for ion exchange, the protons present in slightly acidic solutions of cobalt nitrate may also penetrate the geopolymer. Such combined Co(II)/proton ion exchange is well known for silicon rich zeolites. Nevertheless, the discrepancy described may also reflect the experimental error connected with the characterization of such a complex non-homogeneous system.

We can conclude that the ion exchange properties of even partially geopolymerized samples may be exploited to estimate the limits of sample geopolymerization. Cs/Al or Co/Al molar ratios represent the lower limit while (Cs + K + Na)/Al or (2*Co + K + Na)/Al ratios are the upper limit of the geopolymerization degree. Values corresponding to the studied samples are summarized in Table 2. It can be clearly seen that the geopolymerization degrees estimated by ^{27}Al MAS NMR and from ion exchange properties exhibit similar trends, but

$970\ cm^{-1}$, whose position is sensitive to amounts of Al in alumino-silicates, and a high-frequency band (HF) at $1100\ cm^{-1}$. The ratio of these bands determines the degree of geopolymerization, as was shown for zeolites by Bortnovsky et al. (2005). This approach represents an analogy for methods used in zeolite science (Coudurier et al., 1982). The FTIR spectra of investigated samples in the region of antisymmetric T–O vibrations are depicted in Fig. 9. Both LF and HF bands are poorly developed and reliable simulation of the spectra cannot be obtained. Therefore, in our case, the geopolymerization degree cannot be quantified by this method. Nevertheless, a low degree of the geopolymerization of investigated samples is clearly evidenced by the shape of the bands.

Table 3

Geopolymerization degree and chemical composition of Cs and Co exchanged geopolymer samples prepared from M1000 and M1200S metakaolins by manual or mechanical mixing and cured in heater – coded respectively M1000, M1200S, M1000mec and M1200Smec – and prepared by manual mixing and cured in IR kiln.

Atomic ratio	Cs-geopolymer						Co-geopolymer					
	M1000	M1200S	M1000 IR	M1200S IR	M1000mec	M1200Smec	M1000	M1200S	M1000 IR	M1200S IR	M1000mec	M1200Smec
Cs/Al	0.16	0.18	0.17	0.17	0.10	0.12	–	–	–	–	–	–
K/Al	0.05	0.05	0.05	0.05	0.05	0.05	0.03	0.04	0.04	0.05	0.04	0.04
Na/Al	0.03	0.03	0.04	0.03	0.03	0.03	0.03	0.04	0.03	0.04	0.04	0.04
Co/Al	–	–	–	–	–	–	0.06	0.07	0.07	0.06	0.09	0.10
(2*Co)/Al	–	–	–	–	–	–	0.12	0.14	0.14	0.12	0.18	0.20
(Cs + Na)/Al	0.19	0.21	0.21	0.20	0.13	0.15	–	–	–	–	–	–
(Cs + K + Na)/Al	0.24	0.26	0.26	0.25	0.18	0.20	–	–	–	–	–	–
(2*Co + Na)/Al	–	–	–	–	–	–	0.15	0.18	0.17	0.16	0.22	0.24
(2*Co + K + Na)/Al	–	–	–	–	–	–	0.18	0.22	0.21	0.21	0.26	0.28

the application of ^{27}Al MAS NMR significantly overestimated the geopolymerization degree of samples prepared from substrates containing tetrahedral Al atoms. This is also in agreement with results of FTIR. Overall, 30% of Al atoms were incorporated into the geopolymer network, more than 70% of Al atoms belong to Al atoms in both M1000 and M1200 metakaolins, while prepared samples represent the geopolymer/metakaolin composite.

4. Conclusions

M1000 and M1200S metakaolins from AGS Minéraux, Clérac, France, had similar compositions and specific surface areas, but different calcination kiln technologies which resulted in significantly different morphologies and dehydroxylation degrees.

Different dehydroxylation degrees of metakaolins usually control the metakaolin reactivity in geopolymerization. However, in our case, two metakaolins with significantly different morphologies and dehydroxylation degrees showed similar reactivities. Only a low polymerization degree, not exceeding 20–30%, was reached for both parent metakaolins. Similarly, different conditions of preparation (manual or mild mechanical mixing) and curing affected the degree of geopolymerization only slightly.

On the other hand, the metakaolin morphology, induced by different calcination kiln technologies, significantly affected micro- and macro-structures of prepared partially polymerized geopolymers. The metakaolin powder with rounded agglomerates and lower water demand was more sensitive to the various geopolymerization conditions than the fine dispersed lamellar powder, giving rise to very different micro- and macro-structures of the partially geopolymerized samples. When IR heating was used instead of the heater, a slight increase in the geopolymerization degree was observed but samples were completely dry; MW heating induced the fast evaporation of the water still contained in the manually mixed porous samples, but not in the mechanically mixed samples.

Acknowledgments

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