



# Geopolymers from Algerian metakaolin. Influence of secondary minerals

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## ABSTRACT

The influence of secondary phases (illite, quartz) on the geopolymerization reaction of metakaolin has been investigated by comparing two metakaolins, one prepared from a pure kaolinite and the other from illite- and quartz-containing Algerian kaolin from the Tamazert region, respectively. Geopolymerization was achieved by mixing the metakaolins with an alkaline sodium silicate solution at room temperature and curing at 50 °C. The products were characterized by X-ray diffraction and <sup>29</sup>Si and <sup>27</sup>Al MAS-NMR. The results show that the secondary phases, at the concentration used in this work, do not prevent the geopolymerization reaction.

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## 1. Introduction

“Geopolymers” are ill-organized polymeric aluminosilicate materials obtained by alkaline or alkaline-earth activation of aluminosilicates. They are currently of large interest, due to their good thermal, chemical and mechanical properties and their potential as “green” cementitious binder (Duxson et al., 2007a). Geopolymerization involves an exothermic reaction between an aluminosilicate precursor, such as a metakaolin for instance, and a highly alkaline silicate solution (Davidovits, 1994). According to Xu and Van Deventer (2002), the basic steps of geopolymerization are the dissolution of the solid aluminosilicate oxide in the MOH solution (M: alkali metal), the diffusion of dissolved Al and Si complexes from the particle surface to the inter-particle space, the formation of a gel phase resulting from the polymerization between the silicate solution and Al and Si complexes, and finally the hardening of the gel phase.

The SiO<sub>2</sub>/M<sub>2</sub>O molar ratio in the activating solution is one of the most critical factors for the synthesis of geopolymers because it controls the degree of polymerization of the dissolved species (Swaddle, 2001; Duxson et al., 2007b). Addition of an Al source like metakaolinite leads to a hydrated Na<sub>2</sub>O–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> system and is accompanied by the transformation of non bridging oxygen atoms of sodium silicate to bridging oxygen, i.e., oxygen atoms bonded both to Si and to Al atoms. The Na cations balance the negative charges created by the formation of the Al–O–Si bonds, or the remaining non-

bridging oxygen ions. The identification of structural subunits and topology of the polymer network have still not been clarified in detail. Clearly, out of equilibrium, in such system a great variety of different structural subunits and a complex network structure are to be expected (Davidovits, 1994; Barbosa and Mackenzie, 2003).

A large number of previous studies focused on the manufacture of geopolymeric products prepared from kaolinite or metakaolinite as the main precursor (Xu and Van Deventer, 2002; Barbosa and Mackenzie, 2003), in particular for applications as adhesives, coatings and hydroceramics (Duxson et al., 2007a). However, if geopolymers made from clays are to be used as construction materials, large volumes of precursor will be needed, likely to come from clay deposits containing secondary minerals. The objective of this study is to appreciate the impact of these secondary phases (illite, quartz) on the corresponding geopolymers, by comparing the products obtained from a pure kaolinite with those obtained from kaolin containing a large amount of secondary minerals, from Algeria. The products will be characterized by X-ray diffraction and solid-state NMR. Their behavior in water will also be determined.

## 2. Experimental

### 2.1. Materials and sample preparation

We used two kaolins as solid precursors. One of them (symbol KF3) is from the Tamazert deposit, East Algeria. It was obtained from the Algerian Company of Kaolin. The second one (symbol KF4) is a pure kaolinite purchased from Sigma-Aldrich. The metakaolins, MKF3 and MKF4, were prepared by heating KF3 and KF4 at 800 °C for 2 h in air (Table 1).

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**Table 1**  
Mineral phase composition of the KF3 and KF4 kaolin samples and silica/alumina molar ratio in the corresponding metakaolins, MKF3 and MKF4

KF3	KF4
Kaolinite (70%), illite (20%), quartz (10%)	Kaolinite (96%), quartz (4%)
MKF3	MKF4
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 2.5	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 2.1

Aqueous sodium hydroxide was prepared by dissolving NaOH (Reagent grade 98%, from Sigma-Aldrich), in water. It is the only source of Na<sub>2</sub>O in the geopolymerization reaction. The liquid precursor of geopolymerization, a sodium silicate solution of variable SiO<sub>2</sub>/Na<sub>2</sub>O ratio, was prepared by dissolving amorphous silica (40–63 μm, purchased from Merck) in the appropriate alkaline silicate solution with stirring. The solutions were stored for 24 h before use.

All the geopolymer samples were prepared at room temperature by mechanically mixing the metakaolin powder in the alkaline sodium silicate solution. The water content in all the sample preparations was kept the same with a molar ratio of H<sub>2</sub>O/Na<sub>2</sub>O = 11. The Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>O ratio was about 1. The SiO<sub>2</sub>/Na<sub>2</sub>O ratio varied from 0 to 3 and, in parallel, the Si/Al ratio from 1 to 2.5. The calculations of the Si/Al molar ratio in the geopolymer synthesis took into account the total numbers moles of silica contained in the metakaolins, including silica and illite phases. Once a homogeneous mixture was obtained, the samples were cast in moulds inside a sealed container and cured at 50 °C for 24 h.

## 2.2. Sample characterization methods

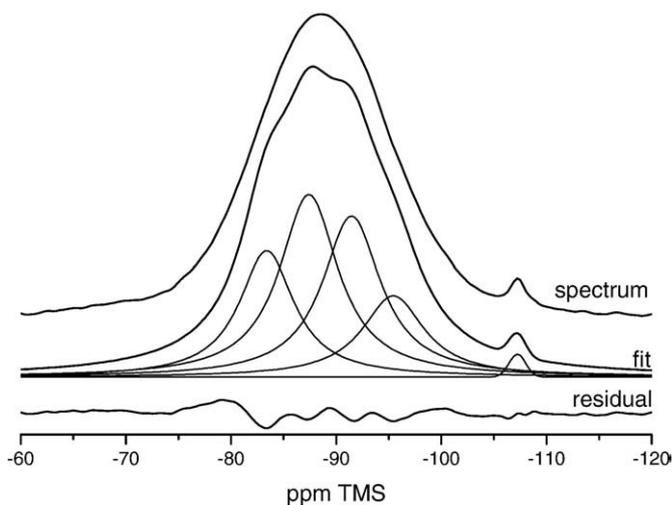
The mineral phases were identified by X-ray diffraction (XRD) using a Philips PW 1700 X-ray diffractometer with Cu Kα radiation, Ni filter and  $\theta$ -2 $\theta$  geometry, operated at 40 kV, 40 mA and a scanning rate of 0.25° min<sup>-1</sup>. Phase identification was made using the X'Pert Pro software from Panalytical. The <sup>27</sup>Al and <sup>29</sup>Si MAS NMR spectra were recorded using a Bruker ASX 500 (11.7 T magnetic field) spectrometer operating at 130.31 MHz for <sup>27</sup>Al and 99.36 MHz for <sup>29</sup>Si. The grinded samples were loaded in 4 mm zirconia rotors and spun at 12 and 10 kHz for the <sup>27</sup>Al (400 accumulations) and <sup>29</sup>Si (1800 accumulations) spectra, respectively. A  $\pi/2$  pulse was applied for <sup>29</sup>Si which is a nucleus with spin 1/2, whereas a  $\pi/12$  pulse was applied for <sup>27</sup>Al which is a nucleus of spin higher than 1/2, in order to excite only the central transition and to remain quantitative. The pulse duration was set at 2 μs and the delay time between successive pulses was 2 s in both cases. No proton decoupling was used. The chemical shifts were measured with respect to tetramethylsilane (TMS) for <sup>29</sup>Si, and Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> for <sup>27</sup>Al. <sup>27</sup>Al being a quadrupolar nucleus, only its resonance maxima are reported and no attempt is made to disentangle the true chemical shift from the second order quadrupolar shift.

All spectra are fitted with the freeware WINFIT using Gaussian lineshapes (Massiot et al., 2002). The resonances of silicium in tetrahedral environment was interpreted in terms of contributions of Q<sup>n</sup>(mAl) units, whose characteristics are reported in Table 2 (Duxson et al., 2005). Fig. 1 shows a typical <sup>29</sup>Si MAS NMR spectrum decomposition.

Leaching experiments were performed by putting small pieces of the geopolymer materials ( $\approx 1$  cm<sup>3</sup>) in 100 ml of water at room

**Table 2**  
<sup>29</sup>Si NMR parameters of the Q<sup>n</sup>(mAl) units (in ppm)

Q <sup>n</sup> (mAl)	Q <sup>4</sup> (4Al)	Q <sup>4</sup> (3Al)	Q <sup>4</sup> (2Al)	Q <sup>4</sup> (1Al)	Quartz
Position (+/-1 ppm)	-83	-88	-92	-97	-107
Width (+/-0.5 ppm)	6	7	7	7	2



**Fig. 1.** Example of <sup>29</sup>Si MAS NMR spectral decomposition: MKF3 based geopolymer with Si/Al = 1.75.

temperature. The samples were removed, surface-dried, and weighted at regular intervals.

## 3. Results and discussion

### 3.1. Precursor materials

The mineralogical composition of the KF3 and KF4 kaolin samples, determined by X-ray diffraction and chemical analysis, is summarized in Table 2. KF4 is an almost pure kaolinite material (4% quartz), whereas KF3 contains 20% illite and 10% quartz. The <sup>29</sup>Si and <sup>27</sup>Al MAS NMR data are summarized in Table 3. Both samples exhibit a <sup>29</sup>Si resonance centered at -91 ppm and assigned to Q3 species in tetrahedral layers (Fitzgerald, 1998). A weak Q4 resonance at -107 ppm assigned to quartz is also detected in the case of KF3. Both KF4 and KF3 spectra show one intense <sup>27</sup>Al resonance at 0 ppm, assigned to Al(VI) in the clay octahedral layers (Fitzgerald, 1998). An additional <sup>27</sup>Al resonance at 67 ppm, assigned to Al(IV) in hydroxylated aluminum tetrahedral layers, is also detected in the spectra of KF3.

The X-ray patterns of MKF3 and MKF4 metakaolins are shown on Fig. 2. For the samples obtained from the pure KF4 precursor, the main feature is by far the very broad reflection assigned to the amorphous metakaolinite structure. Expectedly, for the sample obtained from the impure KF3 precursor, sharp reflections due to the residual crystalline quartz, illite and kaolinite phases are also observed alongside the broad reflection. Illite is an aluminosilicate which can react in alkaline conditions. Its presence in the MKF3 material is therefore a significant feature which can affect geopolymerization.

The <sup>29</sup>Si MAS NMR spectra of MKF4 and MKF3 are shown in Fig. 3. In addition to the resonance at -107 ppm assigned to the residual quartz in MKF3, both metakaolin materials show a broad <sup>29</sup>Si resonance peak around -100 ppm with large FWHM assigned to Q3 "sheet-like" layers. However, the center of gravity of the resonance of the MKF3 sample is shifted significantly downfield. This can be explained by the contributions of the secondary phases such as illite in the MKF3 sample, phases

**Table 3**  
NMR Chemical shifts and abundance (%) of the Al and Si species in the KF4 and KF3 samples

	Al(VI) 0 ppm	Al(IV) 67 ppm	Si Q3 ordered -91 ppm	Si Q3 disordered -91 ppm	Quartz -107 ppm
%KF4	100	0	75	25	-
%KF3	94	6	70	28	2

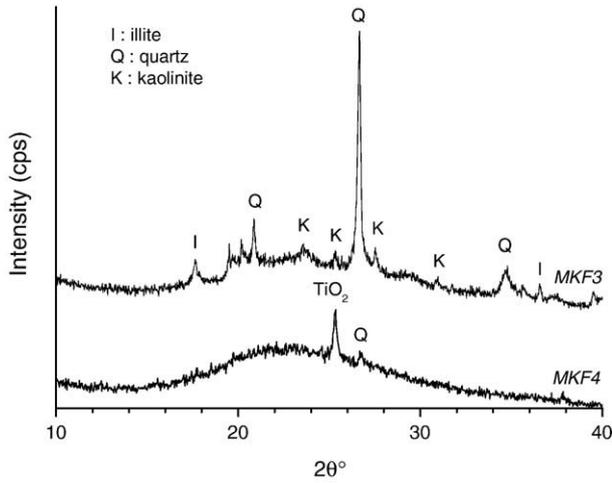


Fig. 2. X-ray diffraction patterns of the MKF3 and MKF4 metakaolin samples.

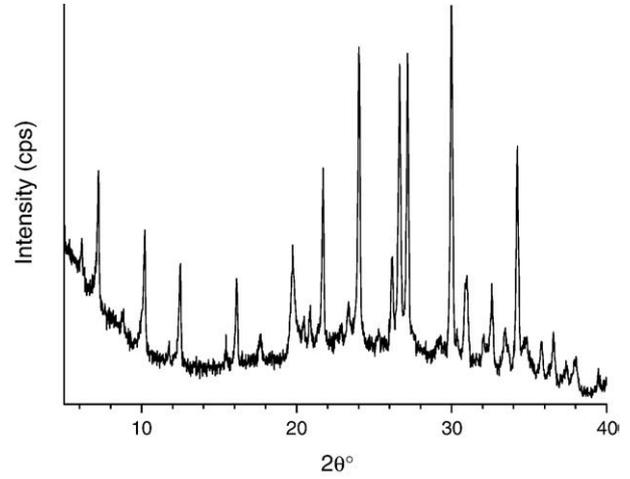


Fig. 5. X-ray diffraction pattern of a zeolite obtained from MKF3.

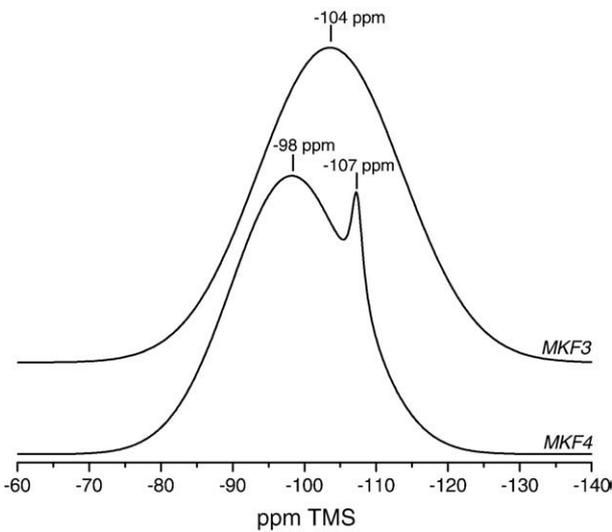


Fig. 3. <sup>29</sup>Si MAS NMR spectra of the MKF3 and MKF4 metakaolin samples.

for which the silicon coordinations are unaffected by the heat treatment. Indeed, the silicon NMR chemical shifts of pure illite reported by Carrolla et al. (2005) are Q3(1Al): -86.8 ppm, Si Q3(0Al): -92.0 ppm.

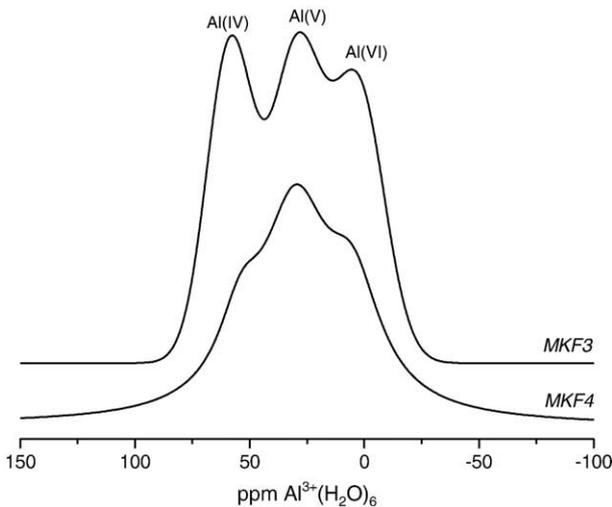


Fig. 4. <sup>27</sup>Al MAS NMR spectra of the MKF3 and MKF4 metakaolin samples.

The <sup>27</sup>Al MAS NMR spectra of MKF4 and MKF3 are shown in Fig. 4. The spectrum of the pure MKF4 sample is characterized by the appearance of overlapping resonances with maxima at 59 ppm, 28 ppm and 2 ppm corresponding to Al(IV), Al(V) and Al(VI) species, respectively. This is in agreement with the well studied dehydroxylation process of the kaolinite aluminum octahedra (Lambert et al., 1989). For the MKF3 sample the Al(V) signal is more intense than the two others. Again, this can be explained by the Al(IV) resonance of the persistent illite structure at 65.2 ppm (Carrolla et al., 2005) which superimposes itself on the resonances of the metakaolinite.

### 3.2. Geopolymerization

As a check, we performed our first geopolymerization attempts by reaction of the metakaolin precursor samples with NaOH at 50 °C. As illustrated by the product X-ray diffraction pattern in Fig. 5, only crystalline Faujasite-Na (Na<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>.40<sub>8,8</sub>.6.7 H<sub>2</sub>O) was obtained. The <sup>29</sup>Si MAS NMR spectra of the products show only one peak at -89 ppm which is characteristic of zeolite (Engelhardt and Michel, 1987). Expectedly, there was thus no formation of amorphous geopolymers.

Subsequent experiments were performed by reacting the metakaolin samples with alkaline sodium silicate solutions at different SiO<sub>2</sub>/Na<sub>2</sub>O and Si/Al molar ratios (between 0 and 3, and between 1 and 2.3, respectively; see Experimental section). As the Si/Al ratio is increased from 1 to 2.3, the X-ray diffraction patterns show the formation of an amorphous phase in addition to the zeolitic phase (Fig. 6 for MKF4 and

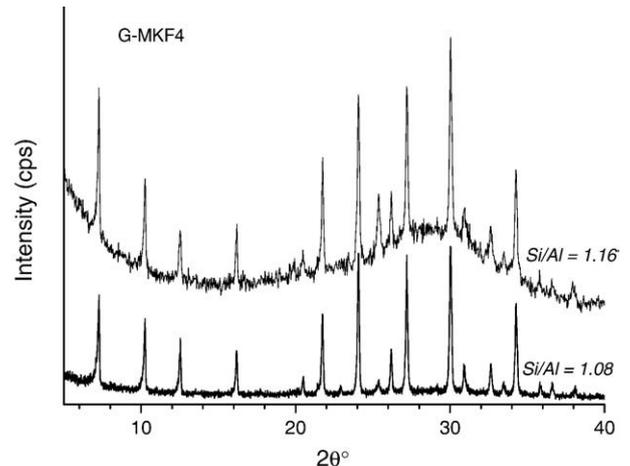


Fig. 6. X-ray diffraction patterns of geopolymers obtained from MKF4 at Si/Al = 1.08 and 1.16, respectively.

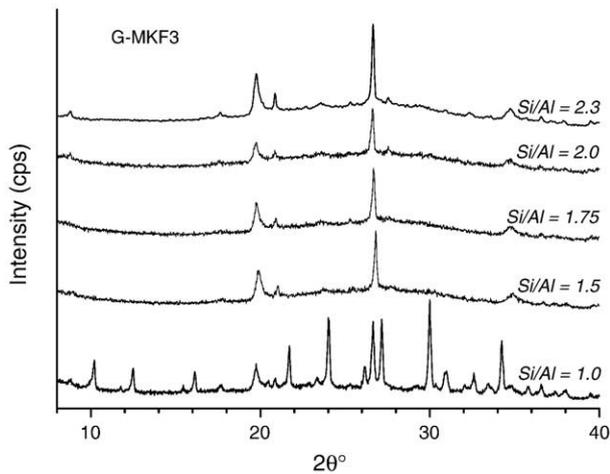


Fig. 7. X-ray diffraction patterns of geopolymers obtained from MKF3 at different Si/Al ratios.

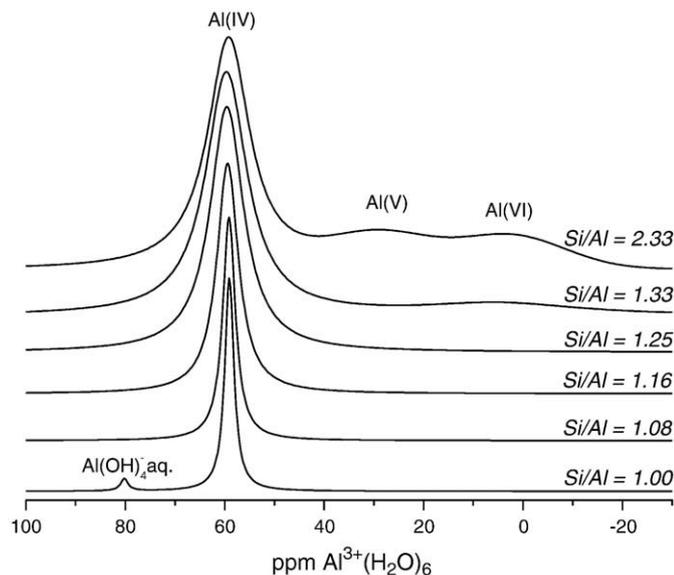


Fig. 8.  $^{27}\text{Al}$  MAS NMR spectra of geopolymers obtained from MKF3 at different Si/Al ratios.

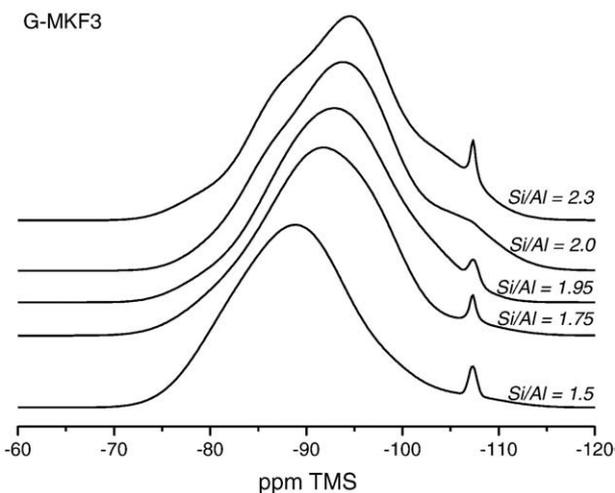


Fig. 9.  $^{29}\text{Si}$  MAS NMR spectra of geopolymers obtained from MKF3 at different Si/Al ratios, between 1.5 and 2.3.

**Table 4**  
Evolution of the  $^{29}\text{Si}$  NMR chemical shifts with the Si/Al ratio (ppm)

Si/Al	Q <sup>4</sup> (4Al)	Q <sup>4</sup> (3Al)	Q <sup>4</sup> (2Al)	Q <sup>4</sup> (1Al)	Q <sup>4</sup> (0Al)
1.5	-81.5	-87.5	-92.5	-98	-107
1.75	-81.5	-87.5	-92.5	-98	-107
1.95	-81.5	-87.5	-92.5	-98	-107
2	-81	-87	-92	-97.5	-105
2.3	-80	-86	-90.5	-96	-104

Fig. 7 for MKF3). In the case of the MKF3 precursor, some residual illite may also be detected. With both precursors, as soon as the Si/Al ratio is larger than 1.1, setting occurs. The mixture forms a cohesive and relatively hard solid. This is the signature of geopolymerization.

The  $^{27}\text{Al}$  MAS NMR spectra of the geopolymerized MKF3 materials (G-MKF3) are represented on Fig. 8. The main resonance line is centered around 59.5 ppm. This is characteristic of Al(IV) species and confirms that geopolymerization transforms octahedral aluminum layers into tetrahedral sites, in agreement with previous work (Puyam et al., 2005; Duxson et al., 2005). No significant evolution in chemical shift is observed with increasing Si/Al ratio. For high Si/Al ratios, two weak and broad bands are observed at 28 and 2 ppm, assigned to the Al(V) and Al(VI) species, respectively. The presence of these bands shows that for high Si/Al ratios, metakaolin dissolution is not total, in agreement with previous work (Provis and Van Deventer, 2007) concluding that high silica concentrations slow down the geopolymerization reaction.

At small Si/Al ratio (that is, Si/Al very close to 1), a weak  $^{27}\text{Al}$  resonance is observed at 80 ppm. This resonance may be assigned to the signal of aqueous  $\text{Al}(\text{OH})_4^-$  species released during dissolution of the metakaolin (Davidovits, 1994). This ion is supposed to react during geopolymerization. However, at low Si/Al ratios, it may not react completely and stay in the pores of the geopolymer material. According to the X-ray diffraction patterns, (Figs. 6 and 7), some samples also contain a crystalline zeolitic phase. This fact is also reflected in the  $^{27}\text{Al}$  spectra where the octahedral resonances appear less broad in the zeolite containing samples. Unfortunately, the  $^{27}\text{Al}$  MAS NMR spectra do not reveal the relative amount of zeolite in the sample since the Al(IV) resonance of the zeolite is not resolved from the one of the geopolymer.

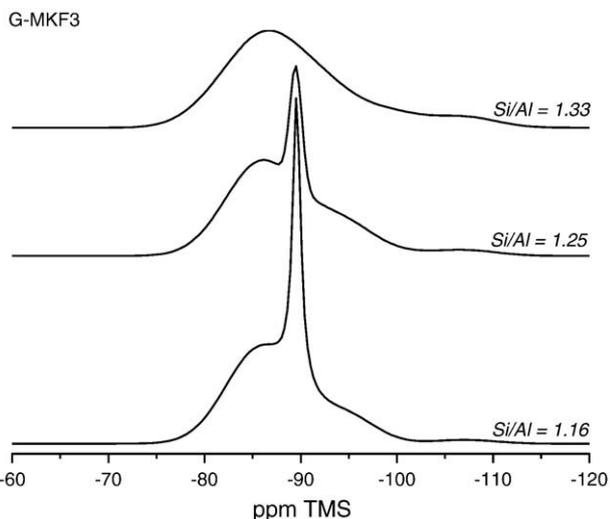
The  $^{29}\text{Si}$  MAS NMR provides additional information on the geopolymer materials. The spectra in Fig. 9 illustrate the influence of the Si/Al molar ratio on the solids obtained from the MKF3 precursor, in the range  $1.5 \leq \text{Si/Al} \leq 2.3$ . The main feature in all spectra is a strong and broad resonance shifted downfield from the MK resonances with a maximum evolving from -95 ppm for Si/Al=2.3 to -88 ppm for Si/Al=1.5. This is related to the replacement of Al as first neighbor of a Si Q3 nucleus by the other Si nuclei. The peak appearing at -107 ppm may be assigned to the unreacted quartz impurities in the parent KF3

**Table 5**  
Relative abundance (%) of the various Si species obtained from the  $^{29}\text{Si}$  NMR spectra, as function of the nominal Si/Al ratio

Si/Al	Q <sup>4</sup> (4Al)	Q <sup>4</sup> (3Al)	Q <sup>4</sup> (2Al)	Q <sup>4</sup> (1Al)	Q <sup>4</sup> (0Al)
1.5	16.4	41.3	29	10.3	0.5
1.75	11.8	24.9	36.2	22.6	1.8
1.95	7.8	22.6	34.5	26.9	8.2
2	4.6	19.1	34.1	32.3	9.9
2.3	9.8	16.5	25.3	35.2	12.1

**Table 6**  
Comparison of the nominal Si/Al ratios (sample preparation) with the Si/Al ratios calculated from the NMR peak areas

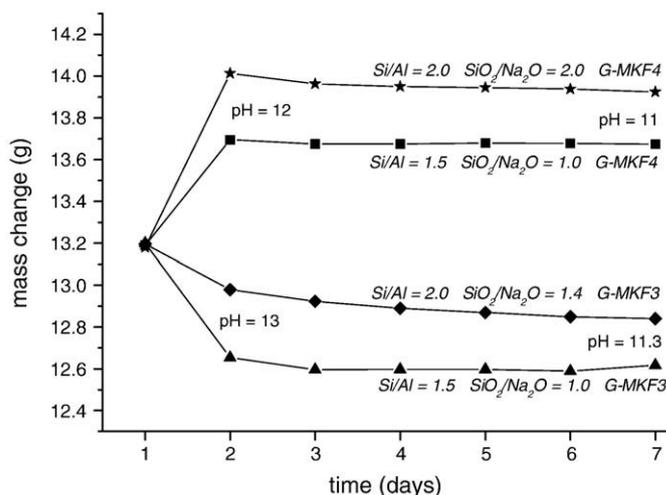
Introduced	Recalculated by areas	Difference in %
1.5	1.5	2
1.75	1.9	8
1.95	2.3	16
2	2.7	34
2.33	2.7	15



**Fig. 10.** <sup>29</sup>Si MAS NMR spectra of geopolymers obtained from MKF3 at different Si/Al ratios, between 1.16 and 1.33.

material, in agreement with other studies on geopolymer formation from impure waste precursors (Phair and Van Deventer, 2002).

The evolution of the Q<sup>4</sup>(4Al), Q<sup>4</sup>(3Al), Q<sup>4</sup>(2Al), Q<sup>4</sup>(1Al) and Q<sup>4</sup>(0Al) populations, as Si/Al increases, may in principle be followed quantitatively by decomposing the observed spectra into their components (Engelhardt and Michel, 1987). However, this decomposition is less straightforward than expected. Indeed, at the Si/Al increases, each component is slightly shifting up field. In addition the FWHM of each component is also changing. This introduces a rather large uncertainty in the results of the decomposition process. Tables 4–6 summarize the results of a decomposition in Q<sup>4</sup>(nAl) species, including the Q<sup>4</sup>(0Al) contribution of the residual quartz. Significantly, the effective Si/Al ratios so obtained by NMR are systematically larger than the nominal ones, and this despite the fact that they represent a lower limit since downfield shifts can result not only from Si by Al substitutions but also from Q<sup>3</sup> rather than Q<sup>4</sup> connectivity. This means that part of the aluminum from the precursor was not incorporated in the geopolymer tetrahedral network. This proves that the secondary aluminum bearing phases originally present in the KF3 kaolin (namely illite) did not fully participate to the geopolymerization process.



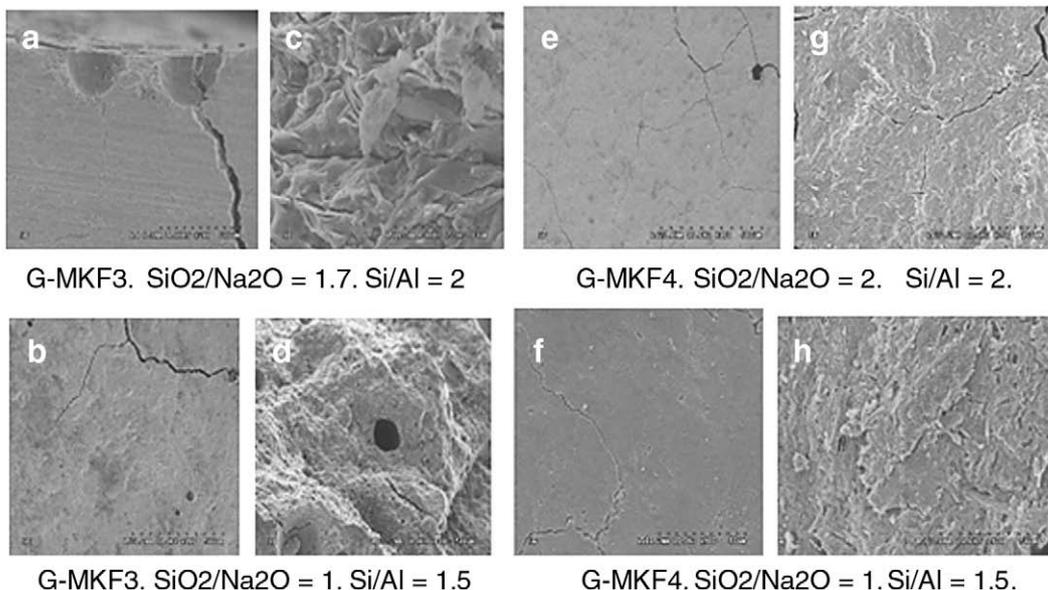
**Fig. 12.** Mass loss or mass gain of various geopolymer samples in water.

For Si/Al ratios very close to 1 (1.16 ≤ Si/Al ≤ 1.33), the <sup>29</sup>Si MAS NMR spectra exhibit, in addition to the broad band which was just discussed, a narrow and intense peak at -89 ppm, characteristic of Y-zeolite (Fig. 10), in agreement with the X-ray diffraction results (Fig. 6). The intensity of the zeolite band is decreasing when the Si/Al ratio increases, in favor of the broad band assigned to the geopolymer. It is virtually vanishing at Si/Al = 1.33.

### 3.3. Microstructure and leaching behavior

No obvious mechanical difference between the geopolymer materials obtained from the MKF3 and MKF4 precursors could be detected by handling the samples. Both materials are cohesive and hard solids, with a somewhat sticky surface. A noticeable difference between the products obtained from MKF3 and those obtained from MKF4 is the brownish color of the former, most probably due to the trace iron content.

Fig. 11 shows scanning electron micrographs of cast and fracture surfaces of two geopolymer samples obtained from MKF3 and MKF4, respectively. At first sight both samples look similar but more careful examination reveals significant differences. The cast surface of the G-MKF3 sample is more extensively cracked than the one of the G-MKF4 sample and its fracture surface is more heterogeneous. This may



**Fig. 11.** SEM micrographs of various geopolymer samples. (a), (b), (e) and (f), cast surfaces; (c), (d), (g) and (h), fracture surfaces.

be linked to the 30% of poorly reactive minerals (quartz, illite) in the precursor material (Table 2).

Another difference between the two families of geopolymer materials is their leaching behavior. As illustrated in Fig. 12, the geopolymers prepared from the pure precursor gain weight in water, whereas the materials prepared from the impure material loose weight ( $\approx 2\%$  at Si/Al=2 and  $\approx 4\%$  at Si/Al=1.5). The former behavior may be assigned to water penetration in the porosity, whereas the later behavior is obviously due to matter loss. This loss may be related to the fact that because some aluminum is not participating in the reaction, there is an excess in Na versus the stoichiometric ratio of Na/Al in the geopolymer phase. This sodium might form leachable sodium carbonate.

#### 4. Conclusion

The main result of the work presented in this paper is that kaolin deposits containing as much as 30% of secondary minerals are still suitable, after moderate heat treatment, for the synthesis of cohesive, yet castable, geopolymer-type solids by alkaline activation. Considering the large deposits of impure kaolins in many parts of the world, this opens the way to the large scale utilization of these mineral resources for the production of green construction materials. One source of concern though is the chemical lability of the products, especially at low Si/Al ratio in the reactive solution. Further work on the geopolymerization chemistry and its relation with mechanical setting is in progress.

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