

Pure $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ synthesized via a sol-gel technique as a raw material to replace metakaolin: chemical and structural characterization and thermal behavior

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Abstract:

The performance of alkali activated cements is strongly influenced by mineralogical composition and the impurity content of metakaolin, their aluminosilicate precursor. In this study, pure aluminosilicates were synthesized via the sol-gel technique and the possibility of using them to replace metakaolin was explored. The study of their thermal behavior by simultaneous Thermogravimetry/Differential Thermal Analysis allowed the best temperature for inducing their complete dihydroxylation to be determined. X-ray diffraction, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy showed that, after calcination, the materials are amorphous, homogeneous, and have a higher content of reactive Al(V) than metakaolin. The reactivity of the materials was ascertained by a leaching test carried out in strong alkaline solution. The quantification of the released aluminate and silicate species, carried out by inductively coupled plasma atomic emission spectroscopy, provide results which encourage the use of the synthesized materials in the preparation of alkali activated cements and geopolymers.

Keywords: Sol-gel method; $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ powder; thermal behavior; leaching test

1. Introduction

Metakaolin (MK) is a material used in the construction field, mainly as pozzolanic additive for modern cement and concrete. It is used as a raw material to produce alkali activated cements and geopolymers [1], which are three-dimensional alkali aluminosilicate binder materials, also prepared by alkaline activation of clays, natural minerals, industrial waste, fly ash and other aluminosilicate sources [2, 3]. In recent years, these inorganic polymers have attracted growing attention because they have performances comparable to those of Portland cement [4, 5], but are able to reduce CO₂ emissions [6, 7].

Metakaolin is unique as the only entirely natural supplementary cementitious material, which not is a by-product of an industrial process. It is obtained by calcination of kaolin clays [8], a hydrated aluminosilicate mineral clay. If heated between 100 and 200 °C it loses the adsorbed water, while at higher temperature (between 600 and 800 °C) it loses the chemically bonded hydroxyl ions through dehydroxylation [9]. Removal of these chemically bonded hydroxyl ions requires a large amount of energy and leads to the collapse of the kaolinite structure, thus leading to the formation of MK. This is an amorphous aluminosilicate more susceptible to alkaline attack than kaolin, because dehydroxylation leads to a change in the coordination number of Al; the Al IV-fold coordination of kaolin is converted into the more reactive Al(V) coordination of MK [1, 10]. Dehydroxylation conditions such as the temperature, heating rate and time, as well as cooling parameters (cooling rate and ambient conditions), significantly influence the process and, thus, the structure and the reactivity of the obtained MK. In particular, a nearly complete dehydroxylation without overheating leads to a pozzolan, whereas overheating can cause the formation of crystalline and non-reactive mullite [1, 10].

MK mainly consists of silica and alumina oxides, with variable contents of other oxides that can be considered as impurities (e.g. Fe₂O₃, CaO, MgO, K₂O, TiO₂ and Na₂O). The mineralogical composition of MK is also variable. Although an entirely amorphous structure

is desirable, secondary mineralogical phases are often detected, such as quartz, illite or muscovite. This variability is usually strongly dependent on the age of formation and the site of the kaolinite mine used and represents a drawback of the use of MK, because the impurity content, crystallinity and the presence of secondary phases are important factors that influence its pozzolanic activity and hydraulicity and, thus, the properties of the materials obtained by its alkali activation (e.g. mechanical properties of geopolymers) [11].

With the aim of overcoming the drawback represented by the non-homogeneous properties of natural MK due to significant variability of its structure, chemical composition and reactivity, four pure aluminosilicates with formula $Al_2O_3 \cdot 2SiO_2$ were synthesized and characterized in the present study, to be used as substitute for MK in the preparation of alkali-activated cements and geopolymers.

The pure aluminosilicates were synthesized by means of the sol-gel technique, a chemical method used to prepare glass and ceramics at low temperature [12]. The process starts by adding water to a solution of metal alkoxide precursors in alcohol. Hydrolysis and condensation reactions, which proceed through a second order nucleophilic substitution, lead to the evolution of a colloidal solution (called “sol”) into a rigid gel phase. This technique allows amorphous materials to be obtained which are characterized by high purity and homogeneity. Moreover, a fine control of the chemical composition and of the physicochemical properties (e.g. specific surface area, size and distribution of the pores, degree of cross-linking of the gel, etc.) of the synthesized materials is possible.

The thermal behavior of the fresh gels obtained is investigated with the aim to identify the most suitable temperature to be used in order to obtain a complete removal of the synthesis by-product and dehydroxylation of the synthesized precursor materials, avoiding their crystallization. Moreover, after their thermal treatment the samples have been characterized by several instrumental techniques, in order to study their chemical structure and

microstructures. Their ability to be dissolved in alkaline solution has also been studied and the results have been compared to those obtained with natural MK. This finding allowed us to evaluate the possibility of using the pure ‘sol-gel’ aluminosilicate as a substitute for the natural MK as a precursor in the production of alkali activated cements and geopolymers [13]. In the first step of their synthesis the aluminosilicate framework of the precursor was dissolved by alkali attack, thus producing aluminate and silicate species. In a second step those species link to each other to form a 3D-cross-linked polysilicate structure ($[-(\text{Si-O})_z\text{-Al-O-}]_n$) [3, 14] by means of polycondensation reactions occurring in the supersaturated alkaline solution. As a result, the microstructure of the final materials depends on the dissolution process of the used raw material, with particular reference to the concentration of the aluminate and silicate species in the alkaline solution.

The influence on the material structure and reactivity of the molar ratio between the metal alkoxide precursor of SiO_2 , (tetraethyl orthosilicate, TEOS) and the water used to hydrolyze it was also investigated. For this reason, samples with Si/Al atomic molar ratio fixed equal to 1 and with different TEOS/ H_2O molar ratios were synthesized. The results of the characterization were expressed as a function of this ratio and compared to the data recorded for natural MK.

2. Materials and Methods

2.1. $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ powder preparation.

Aluminosilicate gels were synthesized by means of the sol-gel method using aluminum nitrate nonahydrate (ANN, Sigma Aldrich) and tetraethyl orthosilicate (TEOS, Sigma Aldrich) as precursors of Al_2O_3 and SiO_2 respectively. Both precursors were dissolved in pure ethanol (EtOH, 99,8% Sigma-Aldrich). Moreover, distilled water was added to the solution of ANN in EtOH. Subsequently, the solution containing ANN and H_2O in EtOH was added drop by

drop under magnetic stirring to the solution of TEOS in EtOH. In the obtained sol, TEOS/ANN and TEOS/EtOH molar ratios are equal to 1 and 12 respectively, whereas four different TEOS/H₂O molar ratios were established, as shown in Table 1. The samples were labelled according to this latter molar ratio, which is 1:0 for sample C0-65° that was prepared without adding water to the ANN solution and, thus, using the salt hydration water to hydrolyze TEOS.

Table 1. Al₂O₃·2SiO₂ powder prepared for the study. H₂O_{add} = water added to ANN solution during the synthesis process. H₂O_{tot} = Sum of H₂O_{add} and ANN hydration water.

Sample Label	TEOS/H ₂ O _{add}	TEOS/H ₂ O _{tot}
C0-65°	1:0	1:9
C4-65°	1:4	1:13
C9-65°	1:9	1:18
C18-65°	1:18	1:27

After 30 minutes the stirrer was stopped and the prepared sols were left to gel in an oven at 65°C for 24 hours. Transparent and colorless gels were obtained. They were further dried in an oven at 120° for 1 h and subsequently heated up to 600°C in order to induce dehydroxylation. This temperature for the thermal treatment was chosen on the basis of the thermal analysis results (see below) by analyzing their thermal behavior. The samples were placed in the furnace and the temperature was increased at a rate of 9 °C/min. After 2 hours of heating, white powders were obtained. The described procedure was schematized in Fig. 1.

Metakaolin (MK, Neuvendis s.p.a, Italy) was used as a reference for natural aluminosilicate. Before performing their characterization, all the calcined samples were reduced to fine powders by grinding them in an agate mortar.

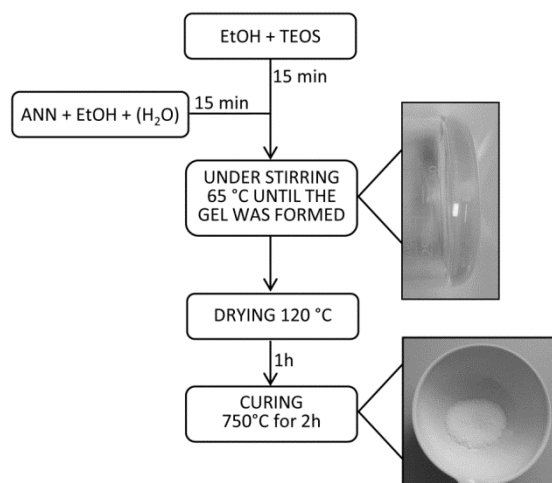


Figure 1. Flow chart of the sol-gel process.

2.2. Thermal analysis characterization

To choose the temperature inducing dehydroxylation and the removal of the synthesis by-products, the thermal behavior of the fresh gels was investigated using a Stanton Redcroft STA-1500 simultaneous TG/DTA apparatus, consisting of two Pt crucibles of cylindrical shape with Pt-Pt/Rh thermocouples. TG/DTA experiments were carried out using 20-25 mg of fine powders of sample (the same mass of alumina for the reference) under an inert 50 ml min^{-1} argon atmosphere at a heating rate of 10 K min^{-1} up to 1100°C. Calibration of the sample temperature was performed using very pure indium and zinc reference materials (whose melting temperatures and enthalpies of fusion are known from the literature [15]), and a final average temperature uncertainty $u(T) = \pm 0.5\text{K}$ was estimated over the whole temperature range.

2.3. Chemical, spectroscopic and structural characterization

The chemical structure of the synthesized powders before and after calcination was investigated by Fourier transform infrared spectroscopy (FT-IR) using a Prestige 21 (Shimadzu, Japan) system, equipped with a DTGS KBr -Deuterated Tryglycine Sulphate with

potassium bromide windows detector. KBr pelletised disks were prepared containing 1.0 wt% of the samples. The Prestige commercial software (IRsolution) elaborated the transmittance spectra recorded in the 400-4000 cm^{-1} region with resolution of 4 cm^{-1} (45 scans).

The chemical composition of the calcined materials was ascertained by means of Energy Dispersive X-Ray Fluorescence (EDXRF) spectroscopy using a Shimadzu Energy Dispersive X-Ray Fluorescence Spectrometer EDX-720 equipped with 50W Rh target x-ray tube, a high-energy resolution Si (Li) detector, and five primary x-ray filters.

The nature of the calcined powders was identified by X-ray diffraction (XRD) analyses using a Philips diffractometer equipped with a PW1830 generator, tungsten lamp and Cu anode, being a Cu-K α radiation ($\lambda=0.15418$ nm) the source of X-ray.

The morphological characterization was carried out using a scanning electron microscope (SEM, FEI Quanta 200) equipped with energy dispersive spectroscopy (EDS) after fixing the samples on stubs with colloidal graphite.

Finally, the chemical, spectroscopic and structural characterization was also carried out on the reference natural MK by means of the same above-cited instrumental techniques. The results obtained were compared in order to highlight the differences between the sol-gel obtained aluminosilicates and the natural MK.

2.4. Study of material dissolution in alkaline solution

The quantification of the aluminate and silicate species released from the samples in alkaline solution can be used as a reactivity index of the synthesized aluminosilicates [13].

To this end, a leaching test was carried out by soaking 200 mg of the sol-gel powders in 25 ml of an alkaline solution of NaOH with concentration 2, 5, and 10 M. The solutions were kept at room temperature under continuous magnetic stirring for 30 min, 1h and 24 h. After each period, the filtered solutions were analyzed by inductively coupled plasma atomic emission

spectrometer (ICPE-9000 Shimadzu, Tokyo, Japan) to estimate the amounts of Si and Al released.

3. Results and Discussion

3.1 Thermal Analysis

The TG/DTA curves of the four gel precursors are shown in Fig. 2.

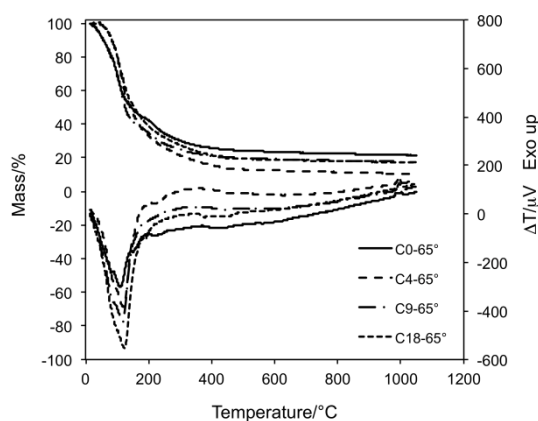


Figure 2. TG/DTA curves of the synthesized gel precursors at 10K/min under a stream of Ar.

The samples undergo a two-step dehydration process, characterized by a single TG mass loss up to 140 °C accompanied by two not completely distinguished endothermic DTA peaks. During the occurrence of this process they lose from 55 (in the case of C0-65° only) to about 60% of their initial mass (for C4-65°, C9-65° and C18-65°) for the removal of water physically bonded and possible trace amounts of alcohol (ethanol) derived by the synthesis of precursors. This result could be partly explained by the water amount used for the synthesis of the materials: the absence of water added to the ANN solution for the preparation of the sample C0-65° may reasonably limit the amount of crystalline water molecules retained by the material. Subsequently, all the gel precursors undergo the loss of crystallization water and water chemically bonded to the aluminosilicate network starting from 200 °C. This loss to depend on the amount of water added to the ANN solution in the synthesis process: the more

water added (increase of the ratio $\text{TEOS}/\text{H}_2\text{O}_{\text{add}}$), the higher the amount of chemically bonded water. The residual water is removed from the aluminosilicate structure at higher temperature (in the range 300-400 °C) with a low mass loss rate. Dehydroxylation, which represents the loss of water molecules obtained from condensation of the hydroxyl groups bonded to Al of the aluminosilicate structure [9], occurs in all the materials investigated in the range 500-850°C. In this temperature range this process shows a characteristic slow mass loss up to the final temperature investigated without any appreciable amount of heat adsorbed or released recordable by a DTA apparatus. In the temperature range between 250 and 600 °C the thermal decomposition of small amounts of nitrate cannot be excluded [16-18] even if the TG/DTA curves are not able to detect clearly. Finally, the crystallization of all the gel precursors is accompanied by an exothermic effect in the DTA curves at temperatures slightly lower than 1000 °C.

3.2 Characterization of precursor and thermally treated materials

FTIR analysis allowed the evolution of the material structure to be followed with increasing temperatures of the thermal treatment (Fig. 3) and of the $\text{TEOS}/\text{H}_2\text{O}$ molar ratio (Fig. 4). All the sample spectra recorded after the gelation show the peaks typical of the nitrate ions and are similar to the spectrum of $\text{Al}(\text{NO}_3)_3$ (Fig. 3a). Neither the Al_2O_3 peaks nor the SiO_2 peaks are visible (Fig. 3b). Some of them appear only after drying at 120 °C (Fig. 3c), probably because the thermal treatment allows the removal of a part of the nitrate ions that are not incorporated in the network. In particular, the band in the region between 1200 and 1000 cm^{-1} is typical for Si-O stretching [19, 20] and the weak peak at 923 cm^{-1} is ascribable to the Al(VI)-OH bond stretching [21]. After thermal treatment at 600 °C all the peaks characteristic of nitrate disappear from the spectra (Fig. 3d) due to their degradation observed with the TG/DTA. Moreover, the sample spectra change and became similar to that of MK (Fig. 3e).

This trend is recorded for all the samples, regardless of the TEOS/H₂O molar ratio. Therefore, only the spectra of C18-65° before (Fig. 3b) and after heating at 120 and 600°C (Fig. 3c-d) are reported as representative of all the samples.

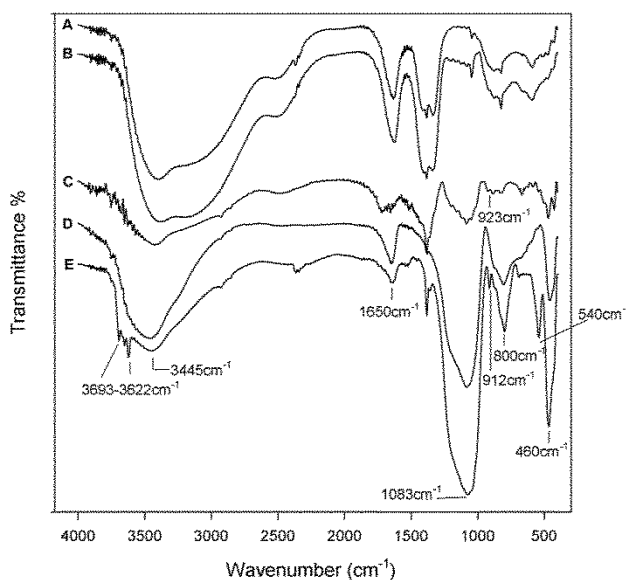


Figure 3 FTIR spectra of: (a) ANN, (b) fresh gel, (c) gel after heating at 120°C, (d) gel after heating at 600°C and (e) MK.

Fig. 4 (curves b-e) shows the FTIR spectra of all the synthesized samples after heating at 600°C compared to that of MK (Fig. 3e as well as Fig. 4a). In all these spectra, broad absorption bands at about 3445 and 1650 cm^{-1} are visible due to hydration water absorbed after the heat treatment. The spectrum of MK also shows sharp peaks in the range 3622- 3693 cm^{-1} and a weak band at 912 cm^{-1} , ascribed to the stretching of hydroxyl groups and of Al(VI)-OH bonds in the kaolinite residues [22], thus suggesting that an incomplete dehydroxylation of kaolin occurred during the calcination process. However, the presence of the band around 800 cm^{-1} , due to the stretching of the Al(IV)-O bond, which is absent in the kaolin spectrum, proves that the conversion occurred [23]. Moreover, the strongest vibrations typical of all the aluminosilicates, which are assigned to internal vibrations of Si-O-Si and Si-

O-Al bonds, are visible, such as the strong Si-O-Si asymmetrical stretching and bending vibrations, at about 1083 cm^{-1} and at about 460 cm^{-1} [24-27] respectively, and the Si-O-Al bending vibrations at about 540 cm^{-1} . All the described peaks are also observed in the spectra of the synthesized sol-gel precursors. Those spectra are very similar to each other and to that of the natural MK, except in the region between 800 and 500 cm^{-1} . In the spectra of the sol-gel powders, three shoulders at about 870 , 670 and 590 cm^{-1} are visible. These bands can be ascribed to the Al-O stretching vibrations of different AlO_x polyhedral species, according to what has been previously reported by Poe et al [28]. With the support of the results derived by both FTIR and ^{27}Al -NMR experiments they proved that the Al-O stretching vibrations of AlO_4 , AlO_5 and AlO_6 moieties are visible in the regions 700 - 900 , 600 - 700 , 500 - 6000 cm^{-1} , respectively. Therefore, the analysis of the FTIR spectra suggests that in the synthesized powder a different amount of AlO_x polyhedral species is present and, in particular, that a higher amount of Al(V)-O (band at 870 cm^{-1}) is present in comparison with what has been found in the natural MK.

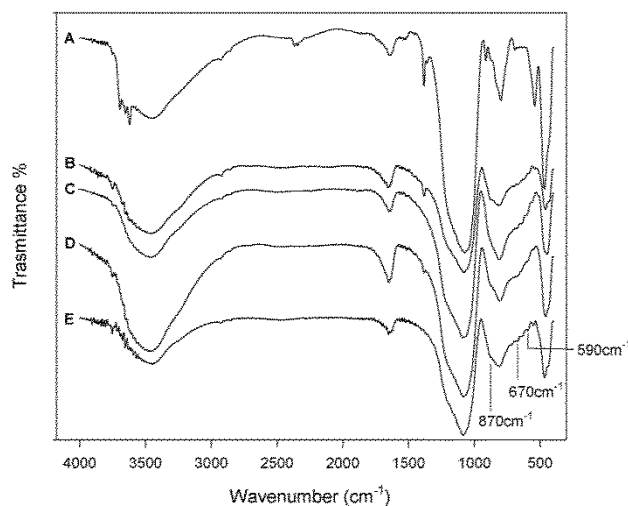


Figure 4. (a) MK FTIR spectrum compared with FTIR spectra of the synthesized samples after heat treatment at 600°C : (b) C0- 65° , (c) C4- 65° , (d) C9- 65° and (e) C18- 65° .

The chemical composition of the calcined powders and their purities has been ascertained by EDXRF analysis and the results were summarized in Table 2. No impurities were detected in the sol-gel powders whereas in natural MK impurities are present, though in small amount. The color of the powders confirm the result of the XRF analysis: MK is grey (mainly due to the presence of Fe_2O_3) whereas all the sol-gel powders are white.

Table 2 Chemical analyses of both the synthesized powders and MK performed by XRF

Analytes (wt%)	MK	C0-65°	C4-65°	C9-65°	C18-65°
Al_2O_3	41.90	40.71	43.38	46.94	47.16
SiO_2	52.90	59.29	56.62	53.06	52.84
K_2O	0.80	--	--	--	--
Fe_2O_3	1.10	--	--	--	--
TiO_2	1.80	--	--	--	--
MgO	0.18	--	--	--	--
CaO	0.13	--	--	--	--

The XRD spectra of all the calcined samples and of the fresh MK shown in Fig. 5 revealed that they are completely amorphous.

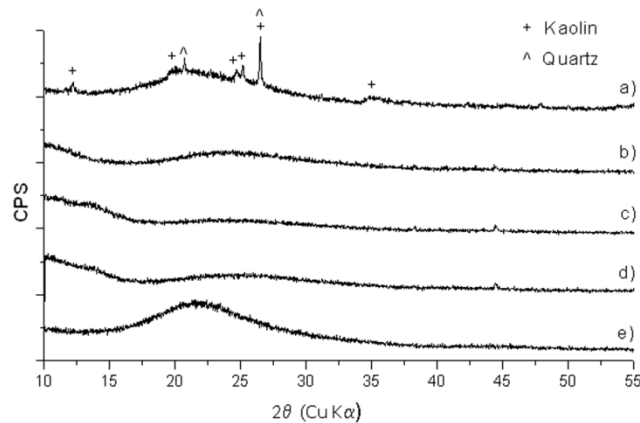


Figure 5. XRD spectra of the materials after the thermal treatment at 600°C. (a) fresh MK, (b) C0-65°, (c) C4-65°, (d) C9-65° and (e) C18-65°. (Λ) quartz and (+) kaolin.

By contrast, some sharp peaks attributed to the presence of residual crystalline kaolinite [29] and quartz were observed in the spectrum of MK, in addition to the typical amorphous band of the MK in the region 17-27° [30]. The last band is also evident in the sample C0-65° and, to a lesser extent, in C18-65°.

SEM analysis was performed on all the samples after their thermal treatment and the corresponding images show in Fig. 6 that all the samples are homogeneous and compact, regardless of the water content.

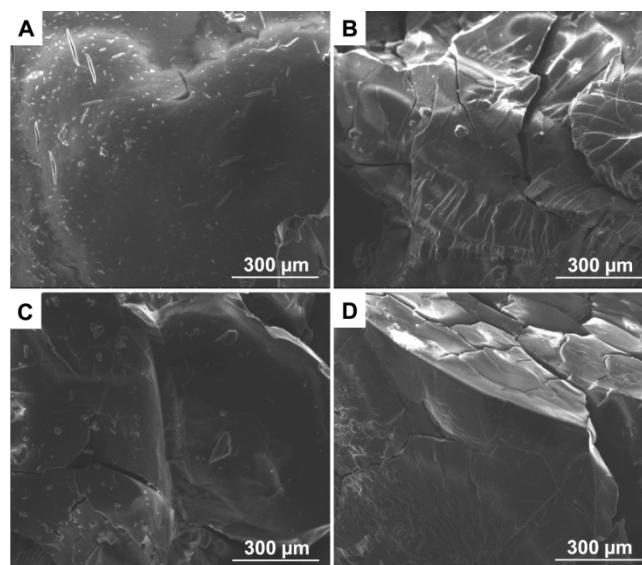


Figure 6. SEM micrograph of the synthesized samples after heat treatment at 600°C: (a) C0-65° (b) C4-65°; (c) C9-65°; (d) C18-65°.

3.3 Leaching of Si and Al in alkaline solutions

After each period of soaking of the calcined materials (30 min, 1 h and 24 h) in the alkaline solutions (2, 5 and 10M), they were filtered and analyzed by ICP in order to quantify the amount of silicate and aluminate species released from the materials. The amount of Si and Al released from the alkaline solutions expressed as mol/L are given in Figures 7-9.

The results show that the synthesized aluminosilicates release a higher amount of Al and Si than natural MK, regardless the TEOS/H₂O molar ratio. Therefore, synthetic materials are

more reactive than MK in alkaline solution. The concentration of the Al and Si released increases with the concentration of the NaOH solutions and with the exposure time.

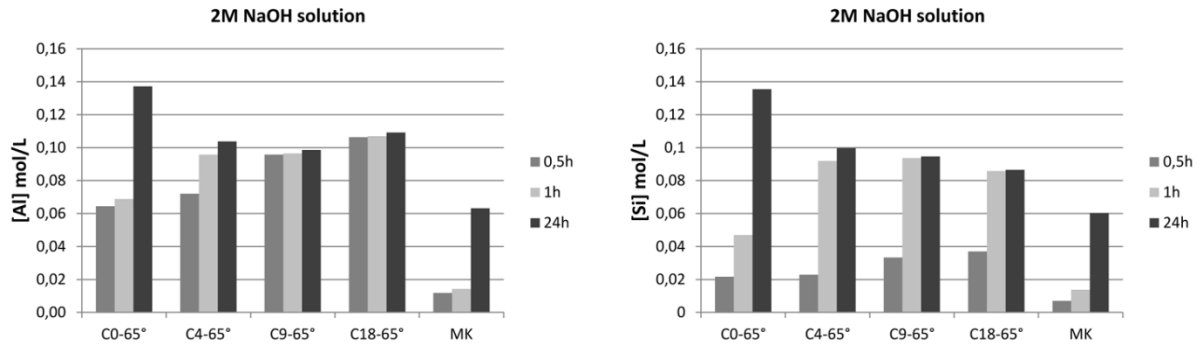


Figure 7. ICP analysis of NaOH 2M solution after material soaking.

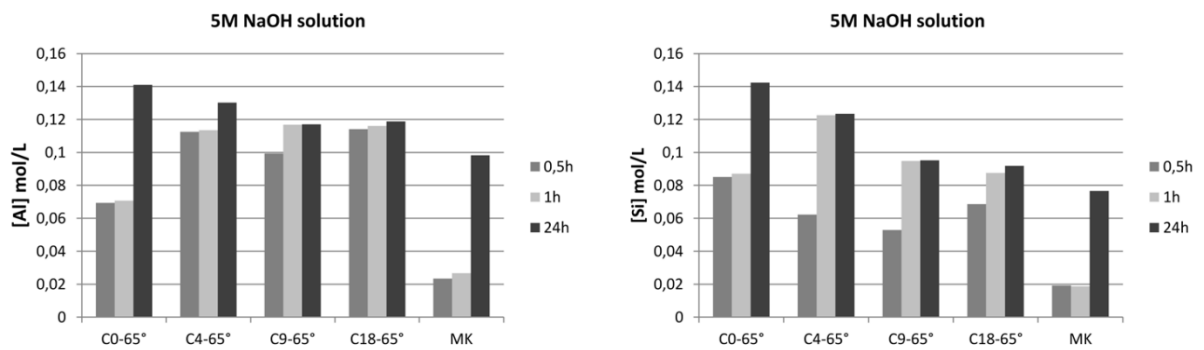


Figure 8. ICP analysis of NaOH 5M solution after material soaking.

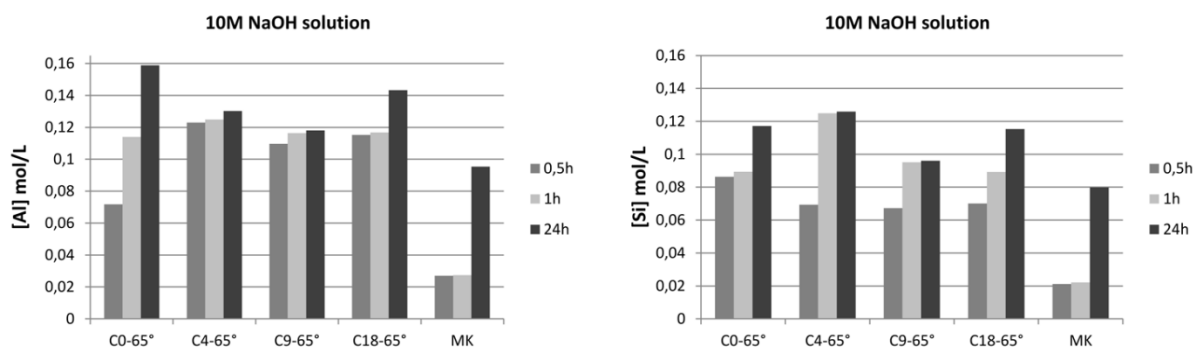


Figure 9. ICP analysis of NaOH 10M solution after material soaking.

4. Conclusions

In this study, four aluminosilicates with a general formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ were synthesized by means of the sol-gel technique using different TEOS/ H_2O molar ratios, in order to study the effect of increasing the content of water on the materials structure. Therefore, the chemical structure and the thermal behavior of the synthesized materials and of a reference 'natural' MK were investigated and the results were compared.

Thermal analysis allowed the most suitable temperature to be selected for the thermal treatment of the gel precursors. The results showed that dehydroxylation (which leads to the conversion of Al(VI) into the more reactive Al(V)) begin to occur at around 500 °C. For this reason the aluminosilicate gels were heated at 600°C. XRD spectra showed that the sol-gel aluminosilicate precursors are entirely amorphous whereas the 'natural' MK showed the presence of kaolinite residue. FTIR analysis showed that a higher amount of reactive Al(V) is present in the synthesized material compared to natural MK. ICP analysis detected a massive release of silicate and aluminate species from the sol-gel materials when they are soaked in an alkaline solution. These results suggest that the synthetic materials are more reactive than 'natural' MK and can be suitably used as raw materials, as a MK substitute.

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