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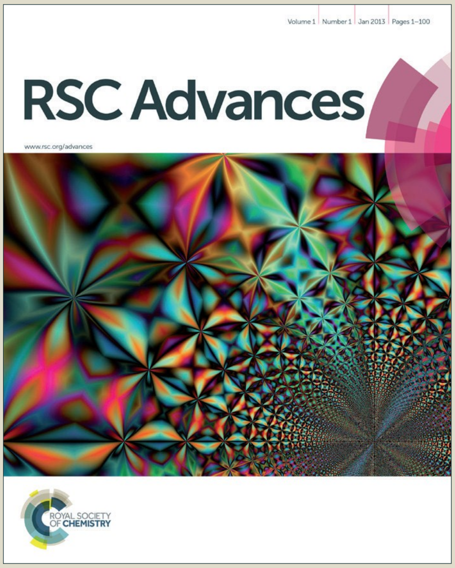

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CLAY SEDIMENT GEOPOLYMERIZATION BY MEANS OF ALKALI METAL ALUMINATE ACTIVATION

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Abstract

In this work a clay sediment from a reservoir was employed for the synthesis of geopolymers. The sediment was calcined at 650 and 750°C for 1 h to ensure the conversion of aluminium coordination from octahedral to tetrahedral. The sediment was characterized by means of X-ray fluorescence, X-ray diffraction, thermogravimetry, mercury intrusion porosimetry and scanning electron microscopy. After calcination, the sediment was submitted to X-ray diffraction, mercury intrusion porosimetry and scanning electron microscopy. Strongly alkaline sodium and potassium aluminate solutions were used to start the polycondensation reaction responsible for geopolymer formation. The initial alkali metal hydroxide concentrations of these solutions were 17, 15 (only Na), 13, 11 and 8.5 M. Polycondensation was carried out at 60°C for times ranging from 15 min to 28 d. The geopolymer products obtained in all the experimental conditions tested were submitted to the quantitative determination of the extent of polycondensation through mass increase and loss on ignition, as well as to qualitative characterization by means of FT-IR spectroscopy. A reduced set of samples activated with solutions corresponding to initial [NaOH] 13 M and [KOH] 11 M and cured at 60°C for 3 and 14 d were used for the determination of apparent density and unconfined compressive strength. These samples were also characterized by means of mercury intrusion porosimetry and scanning electron microscopy. The results have indicated that the development of preformed building materials starting from reservoir sediment, although requiring accurate mix design, can be possible by means of alkali metal aluminate activation.

Keywords: Geopolymer; Clay sediment; Aluminate activation; Polycondensation kinetics; Physico-mechanical characterization; Matter recovery.

1. Introduction

It is well known that many silico-aluminates undergo polycondensation by means of alkali metal silicate activation to form geopolymers. This synthesis was first described by Davidovits[1] who classified geopolymers into three classes based on the following different monomeric units: (–Si–O–Al–O–), polysialate (PS), $SiO_2/Al_2O_3=2$; (–Si–O–Al–O–Si–O–), polysialatesiloxo (PSS), $SiO_2/Al_2O_3=4$; (–Si–O–Al–O–Si–O–Si–O–), polysialatedisiloxo (PSDS), $SiO_2/Al_2O_3=6$. When the polycondensation is carried out in the temperature range 20-90°C, amorphous geopolymers are formed, while processing in autoclave at 150-200°C leads to the formation of crystalline geopolymers whose structure resembles that of zeolite A.[2]

The polycondensation responsible for geopolymer synthesis can be carried out starting from a wide range of raw materials that include metakaolinite,[2-8] natural silico-aluminates and alumino-silicates[9-13] and solid wastes such as coal and fuel oil fly ash,[14-20] reservoir sediments,[21] municipal solid waste incinerator fly and bottom ash,[22-24] bagasse bottom ash.[25] In all these cases polycondensation is promoted by adding highly alkaline aqueous solution of sodium or potassium silicate to the solid raw materials.

Geopolymer-based materials are of great interest because some excellent properties can be achieved among which mechanical properties and durability[4,26] as well as thermal stability[8] and resistance to acid attack.[16] Furthermore, geopolymer-based materials are more attractive than Portland cement-based ones because their manufacture requires much less energy and involves a strongly reduced greenhouse gas emission.[27] Due to the above mentioned properties, geopolymer-based materials have found application within the fields of new ceramics, cements, matrices for hazardous waste stabilization, fire-resistant materials, asbestos-free materials and high-tech materials.[2,28-33]

In addition to the above potentiality of geopolymer-based materials, it has been recently demonstrated that a calcium loaded porous geopolymer can act as a highly active catalyst for biodiesel production.[34] In this case the starting geopolymer was obtained by means of potassium silicate activation of metakaolinite.

In contrast to silicate activation, aluminate activation has received much less attention and few papers can be found in the literature on this type of alternative activation. As for silicate activation, systems containing different starting materials have been tested in the case of aluminate activation. Phair and van Deventer synthesized geopolymers starting from fly ash, kaolinite, K-feldspar and blast furnace slag by means of both silicate and aluminate activations.[35] They found that in some cases aluminate activated geopolymers were mechanically superior to the silicate activated ones. Systems composed of silica fume and sodium aluminate solution were used by Brew and MacKenzie to obtain geopolymers by means of sol-gel condensation.[36] The products showed all the peculiar characteristics of aluminosilicate geopolymers, including good compressive strength. Hajimohammadi et al. used a mixture of geothermal silica and solid sodium aluminate to obtain geopolymers by just adding water.[37] Their work was also useful for providing a better understanding of the fundamental chemistry of geopolymerization. In an interesting paper by Oh et al., class C fly ash alone or partially replaced by Na-aluminate was used for geopolymerization with NaOH solutions, proving the co-existence of geopolymers and C-S-H(I).[38]

Aluminate activated geopolymers have been also successfully used for hazardous waste stabilization. This is proved by the work by Ahmari et al. and Ogundiran et al., who employed geopolymeric matrices obtained via aluminate activation to incorporate copper mine tailings and lead smelting slag, respectively.[39,40]

As previously outlined, the management of silico-aluminate containing wastes often takes advantage from the potentialities of manufacturing geopolymer-based materials. To this regard, among the wide range of suitable wastes, reservoir sediments are worthy of consideration. In most cases these sediments contain clay minerals (mostly illites and smectites), chlorites and kaolinites. The nature of the clay minerals reflects the nature of the parent rocks.[41,42] These sediments, if not periodically removed, cause the progressive reduction of reservoir capacity. Once removed, the sediments must be properly managed and their recycling for the manufacture of geopolymer-based materials can be environmentally sound.[41] The occurrence of more than 7000 large reservoirs in the European Union, of which 564 Italy,[43] makes it clear that the management of reservoir sediments is a problem of major environmental relevance.

The silting of the Occhito reservoir (Carlantino, Foggia, Italy) has been recorded from 1972 to 2007 and the data show that, on average, the yearly increase of sediment amount is as high as 500 m^3 per km^2 with a total quantity of about 19 Mm^3 in 2007. These data clearly show that regular desilting operations can make available huge quantities of sediments that should be properly disposed of. In Italy, the Environmental Ministry Decree of 30 June 2004 faces this problem and states the criteria for disposal, recovery and recycling of this waste. To this regard, some matter recovery proposals can be found in the pertinent literature. These proposals are related to applications as raw materials for the manufacture of artificial aggregate, bricks and cement clinker.[44-48] The extension of matter recovery to the synthesis of geopolymer-based materials via aluminate activation of the Occhito reservoir sediments has been studied in this paper.

2. Materials and methods

The sediment employed in the present study comes from the Occhito reservoir and is the same as that used in a previous work by Ferone et al.[49] for geopolymer polycondensation via silicate activation. The Occhito reservoir is the largest artificial lake in Italy and the second in Europe. It is located at the border between the Italian regions of Molise and Puglia. Sediment sampling was carried out by coring in three different places. The three cores (10 cm in diameter and 1 m in height) were crushed in a jaw crusher, milled in a ring mill, sieved to pass a 180 µm sieve and carefully mixed to get a unique, homogeneous sample.

Extensive sediment characterization carried out by means of several analytical techniques can be found in the paper referred to above by Ferone et al.[49] Specifically, a specimen of the sediment sample was dried in oven at 105°C and then submitted to X-ray fluorescence, X-ray diffraction, thermogravimetric analysis, infrared spectroscopy and Blaine specific surface determination.[49]

The quantitative chemical composition of the sediment was obtained through X-ray fluorescence and is reported in Table 1.[49] It is seen that the prevailing components are silica and alumina, then making the available sediment a potential geopolymer precursor. However, within the wide range of natural and artificial silico-aluminates, the SiO_2/Al_2O_3 ratio is quite high, such to make the aluminate activation more attractive than the silicate one. In addition, the relatively high CaO content also suggests that submitting the sediment to the aluminate activation can be worthy of consideration. In fact, in the case of silicate activation, the added silica (as alkali metal silicate) could be only partially available for the polycondensation reaction, due to the parallel and competitive pozzolanic reaction.

The mineralogical characterization of the sediment was carried out from both the qualitative and semi-quantitative points of view.[49] The results showed that the sediment is mainly composed by clay minerals such as kaolinite, smectite and illite (62% total), quartz (18%), calcite (17%) and feldspars (3%). Of all these phases, only kaolinite disappeared after calcination at 650 and 750°C to form metakaolinite. The formation of metakaolinite is of fundamental importance for geopolymerization to take place, because aluminium is converted from octahedral coordination into the more reactive tetrahedral coordination. This was proved in a previous paper,[21] where ^{27}Al MAS NMR analysis was carried out on the sediment after firing at 650 and 750°C for 1 h. The results showed that the conversion from octahedral aluminium to tetrahedral aluminium is almost complete at 750°C and slightly lower at 650°C.

In addition to the above characterization, the sediment, as received and after calcination, was submitted to mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) in this paper. The employed apparata were a Micromeritics AutoPore IV porosimeter and a FEI Inspect scanning electron microscope.

Geopolymer synthesis was carried out using the sediment after calcination at 650 and 750°C for 1 h. Sodium and potassium aluminate solutions (one at a time) were used for activating the calcined sediments to get polycondensation. In both cases, these solutions were obtained by dissolving pulverized $Al(OH)_3$ into 17 M hydroxide solutions. Molar ratios of Al/Na=0.647 and Al/K=0.53 were obtained. Other characteristics of these solutions were as follows. Sodium aluminate: density=1550 g L^{-1}; $[NaAlO_2]$=7.35 M; [NaOH]=4.05 M; $[H_2O]$=44 M. Potassium aluminate: density=1610 g L^{-1}; $[KAlO_2]$=6.5 M; [KOH]=5.8 M; $[H_2O]$=36 M. In addition, diluted solutions corresponding to hydroxide initial concentrations of 15 (only NaOH), 13, 11 and 8.5 M were used. In all cases the ratio between the activating solution volume and the sediment mass was 0.42 mL g^{-1}. Mixes of the sediment plus the activating solution were polycondensed in sealed polyethylene cylinders (d×h=2×3 cm^2) at 60°C for times equal to 6 h, 1, 3, 7, 14 and 28 d. In some cases additional polycondensation times of 15, 30, 45 and 60 min were employed. At each of the above times, the samples were removed from the polyethylene cylinders, ground under acetone, vacuum filtered, rinsed with diethyl ether, dried and eventually stored in a desiccator. These samples were submitted to quantitative and qualitative characterization. All the recovered solid was weighed to get the mass increase upon polycondensation, representative of the total amount of reacted alkali metal aluminate and water. Then, the amount of reacted water was given by the weight loss upon firing. By difference between these two data, the amount of reacted alkali metal aluminate was obtained. In addition, the qualitative characterization of the samples after polycondensation was carried out by means of Fourier Transform Infra-Red (FT-IR) spectrophotometry using a Jasco FT/IR-430 spectrophotometer.

Different cylindrical samples (d×h=3×6 cm^2) activated with diluted solutions corresponding to initial [NaOH] 13 M and [KOH] 11 M, cured at 60°C for 3 and 14 d, then dried in oven at 40°C, were used for the determination of apparent density and unconfined compressive strength (UCS). The former data were obtained by weighing, while the latter by means of a Controls 50-C1201/FR press. These samples were also characterized by means of MIP and SEM.

3. Results and discussion

3.1. Sediment microstructural characterization

The microstructure of the sediment did not change very much upon firing. Once submitted to SEM, the sediment as received and after firing at 650 and 750°C revealed to be composed of irregularly shaped particles with rough surface in all cases.[50] Some noticeable differences were found in relation to porosity. The sediment as received and after firing at 650 and 750°C submitted to MIP showed porosity values of 513, 531 and 663 mm^3 g^{-1}, respectively. It is seen that the porosity increase is moderate at 650°C, while becomes much more significant at 750°C. The MIP traces showed that firing at the higher temperature causes the microporosity to decrease, likely due to sintering phenomena, and the meso- and macroporosity to increase as a result of the more extended decomposition.[50]

3.2. Geopolymer synthesis

The occurrence of the polycondensation reaction with formation of geopolymers can be proved by means of FT-IR analysis. Fig. 1, where the FT-IR traces are reported for the sediment calcined at 750°C and the products of geopolymerization carried out from 15 min to 28 d with an activating solution containing NaOH at 11 M initial concentration, is emblematic of all the cases studied. It shows that, as expected, the absorption band centred at 1038 cm^{-1} in the trace of the sediment calcined at 750°C (ν_1 in Fig. 1), corresponding to the Si–O asymmetric stretching in tetrahedral,[11,35] is shifted to lower wavenumbers (990±8 cm^{-1}, ν_2 in Fig. 1) as a consequence of polycondensation with alternating Si–O and Al–O bonds. Another fingerprint of geopolymers that can be seen in Fig. 1 is the absorption band at 694±2 cm^{-1} (ν_3 in Fig. 1) corresponding to the Al–O–Si bending. The other significant absorption band located at 459 cm^{-1} in the unreacted sediment trace and at 465±2 cm^{-1} in the polycondensed systems traces (ν_4 and ν_5 in Fig. 1) is related to the Si–O–Si and O–Si–O bending.

The qualitative data of Fig. 1 show that the polycondensation reaction is very fast, as the absorption bands at ν_2 and ν_3 are seen as early as after 15 min polycondensation. Furthermore, the intensities of these bands are considerably high after only 6 h polycondensation and do not increase very much up to 28 d, the longest polycondensation time tested. This is true even for the other experimental conditions tested.[50]

Data on geopolymerization kinetics in the case of aluminate activation have only been obtained by other researchers in few cases. These findings agree with those presented in this paper. Hajimohammadi et al.[37] found very fast geopolymer formation at 40°C after 1 d by means of FT-IR analysis. Oh et al.[38] found that at 80°C the development of UCS is equally very fast, and also that crystalline geopolymers are formed with high crystallinity degree as early as after 1 d (data obtained by XRD).

Finally, Ogundiran et al.[40] found an unfavourable effect of temperature on the development of UCS due to not so fast geopolymer formation at room temperature.

Quantitative data relative to the amounts of reacted water and alkali metal aluminate are reported in Tables from 2 to 5. Specifically, the results for sodium aluminate activation are reported in Tables 2 and 3, while those for potassium aluminate activation are reported in Tables 4 and 5.

As far as reacted water is concerned, the following considerations can be drawn from the data of Tables 2 and 4. Its amount decreases with polycondensation time in all the cases. This is in agreement with what is known on the reaction mechanism.[10] In fact, the geopolymer precursors that are formed at short times carry a considerable amount of water that is partially expelled when polycondensation takes place with geopolymer formation. The effect of alkali metal hydroxide initial concentration is such that its increase makes the reacted water increase in any case. Obviously, this is due to the more favourable geopolymer precursors formation when the alkali metal hydroxide concentration increases. In most cases the amount of reacted water decreases as the sediment calcination temperature increases from 650 to 750°C; this effect can be due to sintering that takes place to a greater extent at the higher temperature. The effect of the nature of the alkali metal hydroxide is such that KOH is, in general, favoured in respect to NaOH. In fact, up to 13 M concentration the data for KOH are greater, often considerably, than those for NaOH, and at 17 M concentration only there seems to be no definite difference between the two groups of data.

The amount of reacted aluminate is reported in Tables 3 (sodium) and 5 (potassium). The data reported in these tables show that most of the aluminate reacts within the polycondensation time of 6 h in all the cases. Then, these quantitative data confirm that polycondensation is very fast, as previously drawn from the qualitative data of Fig. 1. The effect of alkali metal hydroxide initial concentration is the same as for reacted water, that is the amount of reacted aluminate increases as the hydroxide concentration increases. Evidently, the more favourable geopolymer precursors formation has also a positive effect on the reacted aluminate. The effect of sediment calcination temperature as drawn from the data of Tables 3 and 5 is erratic. In fact, there are cases in which the data for 650°C are greater than those for 750°C, cases in which are lower and cases in which are almost the same. So, no definite conclusion can be drawn from the combined data relative to reacted water and aluminate on the effect of the sediment calcination temperature. More clear is the effect of the nature of the alkali metal hydroxide on the amount of reacted aluminate. In fact, the data for KOH are greater than those for NaOH when the other conditions are left unchanged. This result is in contrast with that obtained in a previous paper in which coal fly ash was activated by means of an alkali metal silicate solution at temperatures between 25 and 85°C.[17] In that occasion, a definite effect of the nature of alkali metal hydroxide was found at 25°C only (NaOH better than KOH).

To get more in-depth data on the polycondensation kinetics, some selected conditions were tested at times shorter than 6 h, that is 15, 30, 45 and 60 min. Specifically, these tests were carried out starting with the sediment calcined at both the temperatures (650 and 750°C) and the activating solution obtained with NaOH and KOH at 11 and 17 M initial concentrations. In all but two of these cases the data obtained at 15, 30, 45 and 60 min were not very different from those obtained at 6 h polycondensation time, confirming that the kinetics of aluminate activated geopolymer formation is very fast. The two cases for which this consideration does not apply are those corresponding to geopolymers obtained starting with the sediment calcined at 650°C activated with sodium aluminate. The data for these two cases are reported in Fig. 2 in which steadily growing reacted aluminate can be clearly seen. Anyway, even in these two cases the data at 15 min polycondensation time denote very fast kinetics.

3.3. Geopolymer physico-mechanical characterization

The samples polycondensed for times from 6 h to 28 d were qualitatively evaluated from the point of view of mechanical strength. This evaluation was based on the manual energy required for grinding the samples (see Materials and methods section) and the results are reported in Tables 6 (sodium aluminate activation) and 7 (potassium aluminate activation). These data show that, as expected, in any polycondensation condition the mechanical strength increases with time. Specifically, the qualitatively detected mechanical strength increases up to 3 d in the case of NaOH and up to 7 d in the case of KOH. The sediment calcination temperature seems to have no effect on this property, while significant effects can be observed when the nature and initial concentration of the alkali metal hydroxide are taken into consideration. In fact, the data obtained when the activating solution contains NaOH are considerably better than those relative to KOH, and this is in contrast with what is known in relation to silicate activation. In such a case, K-based geopolymers behave better than Na-based ones from the point of view of mechanical strength.[6,10,14,29]

Optimum initial concentrations of the alkali metal hydroxide can be identified from the data of Tables 6 and 7. These are 13 M for NaOH, as no evident improvement is observed beyond this value, and 11 M for KOH, as the qualitatively detected mechanical strength decreases beyond this value. For this reason, the quantitative determination of UCS was limited to the above two conditions.

The results of UCS determination are reported in Table 8 (average of three replicates) and agree with the considerations resulting from the qualitative determination. The results for NaOH are much better than those for KOH and, although not very high, can be considered as a good starting point for the development of preformed building materials. Of course this would require accurate optimization of the mix design from both the qualitative and quantitative points of view. For example, polycondensed materials could take considerable advantage from a limited addition of kaolinite, due to the formation of metakaolinite upon calcination at 650/750°C.[6]

The samples employed for the determination of UCS were also used for the determination of apparent density and for microstructural characterization.

The results of apparent density determination are reported in Table 9 (average of three replicates) and show to be not significantly affected by the polycondensation conditions. Furthermore, the values are of the same order as those of cementitious materials (2.0-2.4 g cm^{-3}).

The microstructural characterization was carried out by means of MIP and SEM. The results of MIP testing are reported in Fig. 3 and show that mesopores prevail in all cases, with macropores being much less abundant. The values of total porosity are much lower than those of raw and calcined sediment; then polycondensation makes the structure become more compact, which is desirable in view of building materials manufacture. When activation is based on sodium aluminate, the two curves relative to the sediment calcined at 650°C are almost the same up to 100 nm, and so are those relative to the calcination temperature of 750°C. Some difference can be observed between the two groups of curves (the samples derived from the sediment calcined at 750°C being more rich in mesopores than those at 650°C) and from case to case beyond 100 nm. However, these differences have no great influence on UCS (see Table 8). In the case of potassium aluminate activation, greater differences can be observed; specifically, the sample obtained starting from the sediment calcined at 750°C after a polycondensation time of 3 d shows the largest mesopores volume. This was the sample for which UCS was not detectable.

Figs 4 and 5 show the micrographs (1000×) resulting from SEM characterization. In the case of sodium aluminate activation (Fig. 4) these micrographs show that the structure is considerably more compact than in the case of potassium aluminate activation (Fig. 5). Furthermore, the sample obtained starting from the sediment calcined at 750°C after a polycondensation time of 3 d and activated with potassium aluminate (Fig. 5b) is evidently less compact than the homologous calcined at 650°C and shows several fracture lines. In the case of sodium aluminate activation, neither the calcination temperature, nor the polycondensation time have a noticeable influence on the microstructure of the samples. These considerations are in good agreement with the results of UCS determination. Most likely, it is just the higher compactness that keeps the values of UCS higher in the case of sodium, despite the lower aluminate conversion degree in respect to potassium. The other variables (sediment calcination temperature and polycondensation time) have a limited effect (except for the case mentioned above) on the microstructure.

4. Conclusions

This work has proved that aluminate activation of calcined reservoir sediment is effective to start polycondensation responsible for geopolymer synthesis. As for silicate activation, the polycondensation kinetics has proved to be very fast. The most important process variable that has been found to influence the quantitative results of reacted water and alkali metal aluminate is the initial concentration of the hydroxide. Specifically, the polycondensation degree strongly increases as this concentration increases. In relation to the influence of the nature of the alkali metal hydroxide (NaOH or KOH), it has been found that polycondensation takes advantage from the presence of KOH instead of NaOH. The sediment calcination temperature has been found to have an erratic effect.

The physico-mechanical characterization of the geopolymeric products has shown that the proposed system can be worthy of consideration for the development of pre-formed building blocks, although an accurate mix design making use of more valuable materials would be required. This is true when activation is carried out by means of sodium aluminate, despite the greater polycondensation degree observed in the case of potassium aluminate. Scanning electron microscopy has shown that the development of a more compact microstructure in the case of sodium can be responsible for this.

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Table 1 – Sediment composition, wt%.

SiO_2	47.5
Al_2O_3	15.6
CaO	10.2
Fe_2O_3	6.7
MgO	2.4
K_2O	1.9
Na_2O	0.3
L.O.I.	15.4
Total	100.0

L.O.I.: Loss on ignition

Table 2 – Amount of reacted water, wt%. Sediment calcined at 650/750°C.

[NaOH]	Polycondensation time					
	6 h	1 d	3 d	7 d	14 d	28 d
8.5	18.06/15.60	16.14/14.97	14.60/14.10	13.40/13.38	14.60/14.60	13.46/13.57
11	20.00/20.05	18.57/18.14	13.44/12.80	13.10/12.62	13.63/12.79	12.81/12.89
13	22.49/17.00	21.48/16.44	17.22/14.47	15.65/14.21	11.27/11.62	11.86/11.43
15	23.00/18.48	21.80/18.41	18.54/16.98	16.14/15.52	12.32/12.56	12.49/12.42
17	31.42/34.90	31.32/25.90	31.07/24.57	22.23/21.16	22.26/21.73	21.19/18.53

Table 3 – Amount of reacted sodium aluminate, wt%. Sediment calcined at 650/750°C.

[NaOH]	Polycondensation time					
	6 h	1 d	3 d	7 d	14 d	28 d
8.5	10.63/10.03	15.00/10.48	14.07/10.26	14.75/10.85	12.83/8.93	13.90/9.70
11	12.64/14.54	14.42/14.48	16.04/15.78	14.54/15.02	15.93/14.90	14.59/14.85
13	15.46/17.88	16.62/18.75	17.13/17.17	18.40/17.60	19.86/17.35	19.22/17.77
15	17.84/20.76	18.89/22.28	18.50/22.25	19.38/21.16	21.71/22.56	21.77/20.63
17	22.24/22.71	23.53/22.68	22.58/21.65	20.37/23.35	25.19/23.36	24.33/23.37

Table 4 – Amount of reacted water, wt%. Sediment calcined at 650/750°C.

[KOH]	Polycondensation time					
	6 h	1 d	3 d	7 d	14 d	28 d
8.5	19.79/16.28	19.75/15.72	20.16/15.66	20.80/15.65	18.24/14.46	18.14/14.66
11	24.57/22.01	23.50/20.02	26.74/17.61	19.13/14.67	20.48/17.68	19.16/18.50
13	32.26/29.54	31.66/27.70	24.33/23.64	25.84/21.54	26.08/20.39	23.56/20.97
17	32.40/32.91	23.17/30.19	22.73/25.30	25.27/24.16	23.24/26.48	24.41/22.78

Table 5 – Amount of reacted potassium aluminate, wt%. Sediment calcined at 650/750°C.

[KOH]	Polycondensation time					
	6 h	1 d	3 d	7 d	14 d	28 d
8.5	12.20/11.97	11.67/12.40	14.09/13.97	12.92/12.97	13.85/12.46	13.90/12.61
11	16.75/18.18	16.83/16.30	15.90/19.11	16.50/18.63	16.42/19.50	17.63/18.00
13	21.54/21.48	20.12/21.00	19.61/21.15	20.74/22.24	19.08/21.19	21.54/21.78
17	28.48/31.77	26.03/30.02	25.77/32.36	27.51/31.38	32.20/25.41/	27.59/33.01

Table 6 – Qualitative evaluation of mechanical strength. Sediment calcined at 650/750°C.

[NaOH]	Polycondensation time					
	6 h	1 d	3 d	7 d	14 d	28 d
8.5	L/FG	FG/FG	G/G	G/G	G/G	G/G
11	L/FG	FG/FG	G/G	G/G	G/G	G/G
13	VL/VL	FG/FG	VG/VG	VG/VG	VG/VG	VG/VG
15	VL/VL	FG/FG	VG/VG	VG/VG	VG/VG	VG/VG
17	VL/VVL	G/L	VG/VG	VG/VG	VG/VG	VG/VG

VVL=very very low; VL=very low; L=low; FG=fairly good; G=good; VG=very good.

Table 7 – Qualitative evaluation of mechanical strength. Sediment calcined at 650/750°C.

[KOH]	Polycondensation time					
	6 h	1 d	3 d	7 d	14 d	28 d
8.5	L/L	L/L	L/L	FG/FG	FG/FG	FG/FG
11	L/L	L/L	FG/L	G/G	G/G	G/G
13	VL/VL	VL/VL	VL/VL	L/L	L/L	L/L
17	VVL/VVL	VVL/VVL	VVL/VVL	VL/VL	VL/VL	VL/VL

VVL=very very low; VL=very low; L=low; FG=fairly good; G=good.

Table 8 – Unconfined compressive strength, MPa. Sediment calcined at 650/750°C.

	Polycondensation time, d	
	3	14
NaOH 13 M	6.6±1.1/7.1±0.4	6.7±0.7/7.1±1.3
KOH 11 M	2.8±0.3/Not detectable	4.9±0.6/6.4±1.2

Table 9 – Apparent density, g cm^{-3}. Sediment calcined at 650/750°C.

	Polycondensation time, d	
	3	14
NaOH 13 M	2.02±0.03/1.98±0.02	1.97±0.03/1.94±0.04
KOH 11 M	2.00±0.02/1.96±0.04	1.96±0.0.01/1.98±0.03

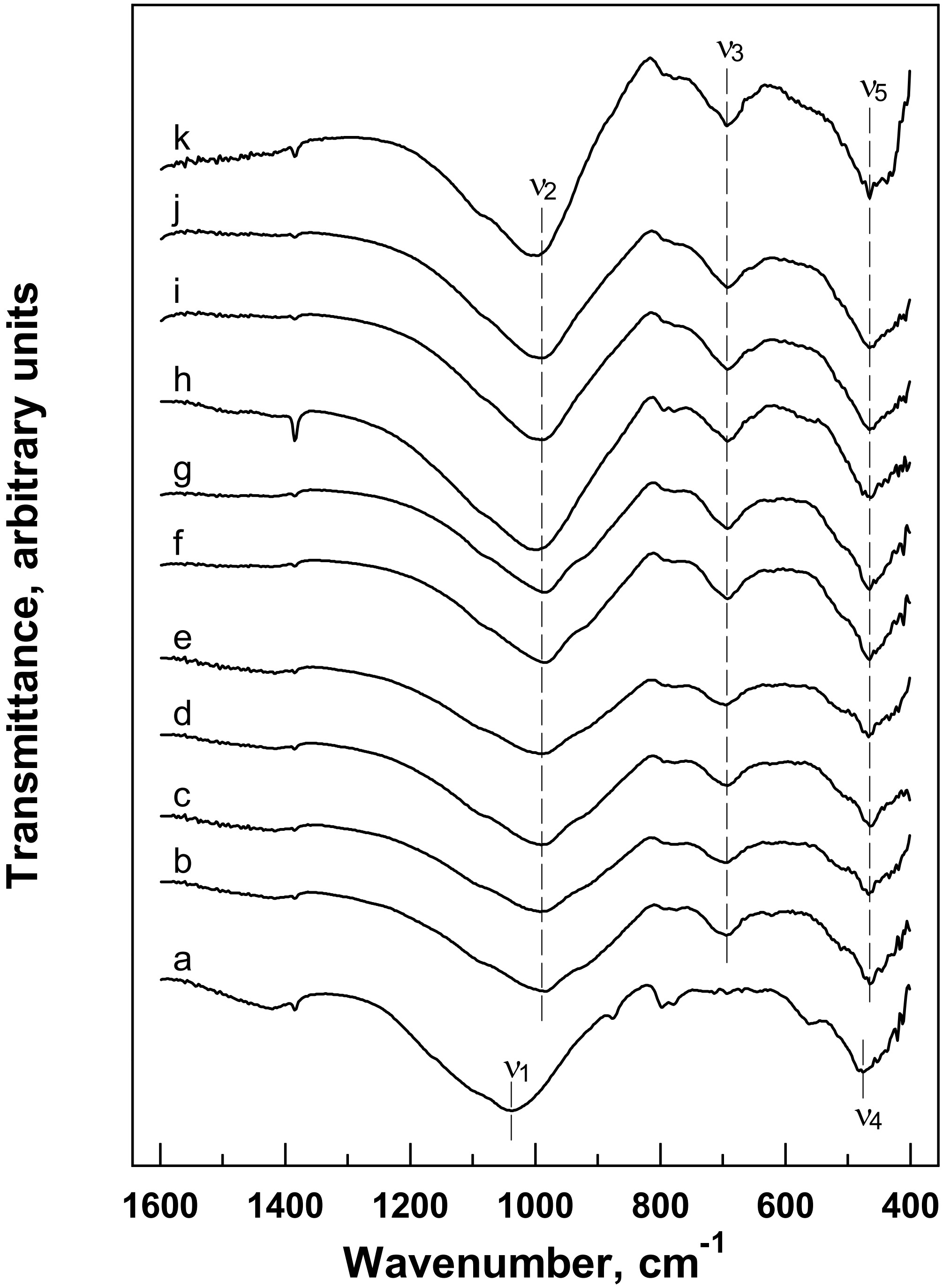

Fig. 1 FT-IR traces of (a) sediment calcined at 750°C and polycondensed systems for (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) 6 h, (g) 1 d, (h) 3 d, (i) 7 d, (j) 14 d and (k) 28 d. [NaOH]=11 M. ν_1=1038 cm^{-1}, ν_2=990±8 cm^{-1}, ν_3=694±2 cm^{-1}, ν_4=459 cm^{-1}, ν_5=465±2 cm^{-1}.

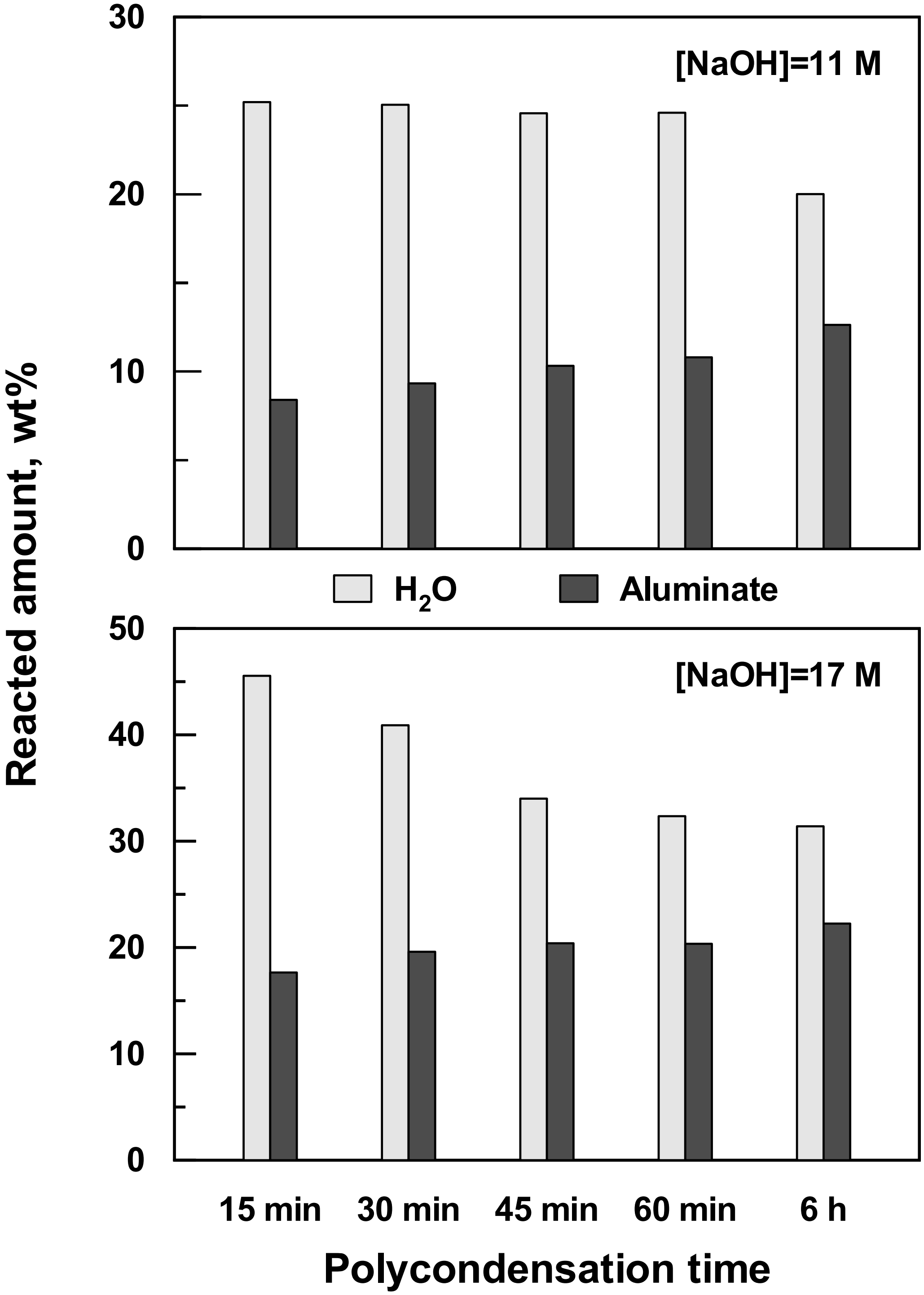

Fig. 2 Amount of reacted water and sodium aluminate for polycondensation carried out starting from the sediment calcined at 650°C.

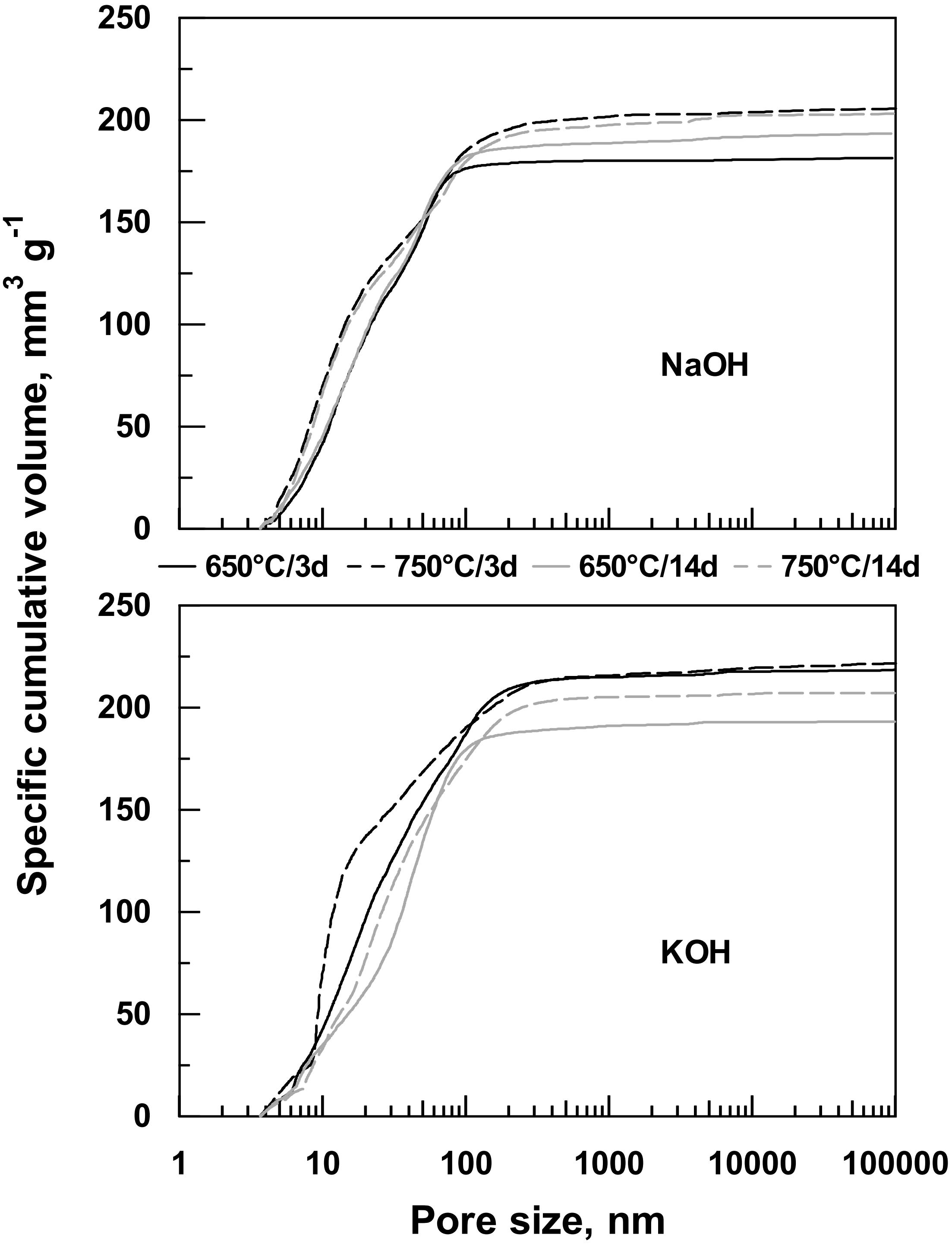

Fig. 3 Results of MIP testing for the samples polycondensed for physico-mechanical characterization.

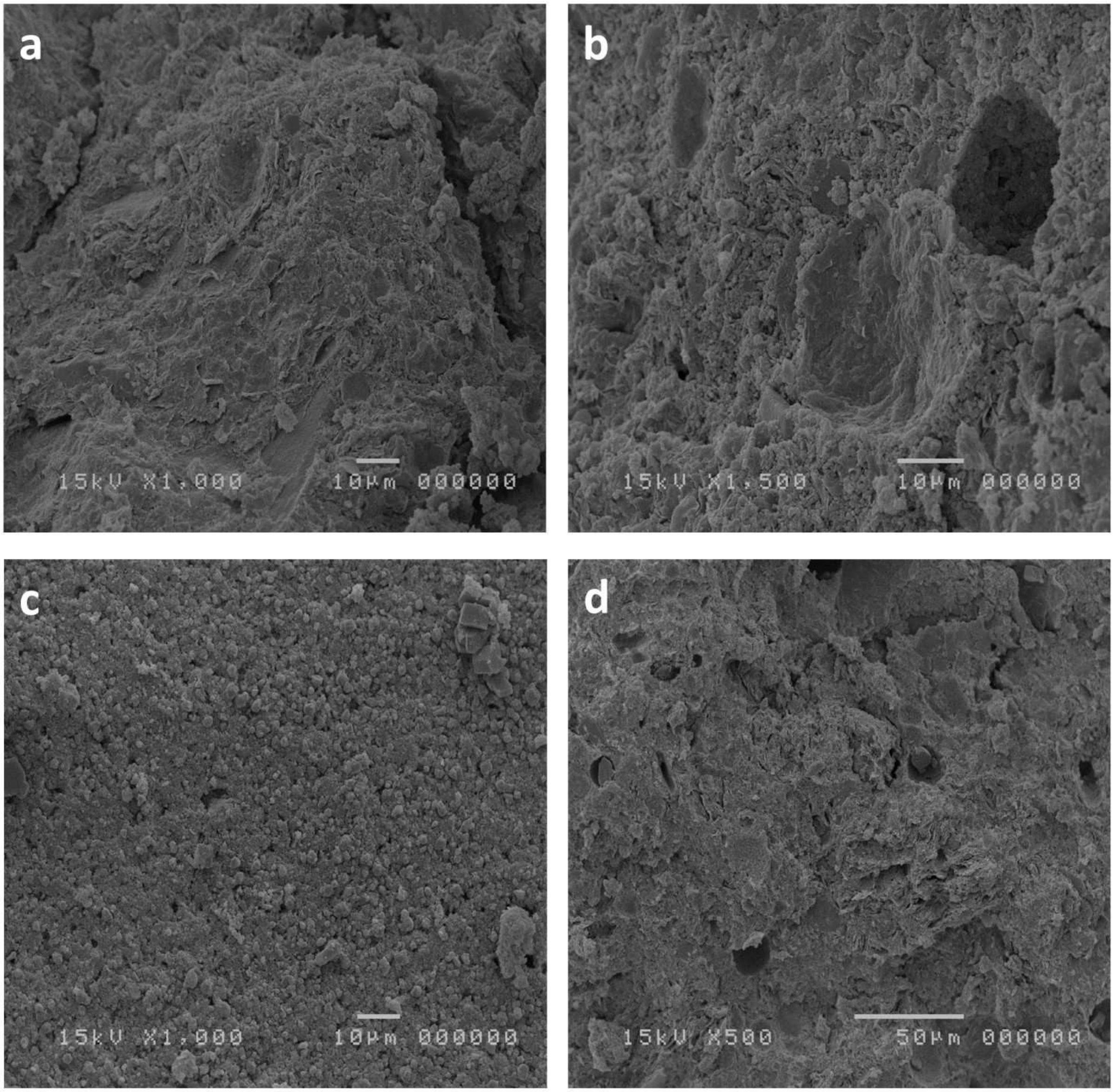

Fig. 4 SEM micrographs of the samples polycondensed for physico-mechanical characterization (sodium aluminate activation): (a) 650°C/3 d; (b) 750°C/3 d; (c) 650°C/14 d; (d) 750°C/14 d.

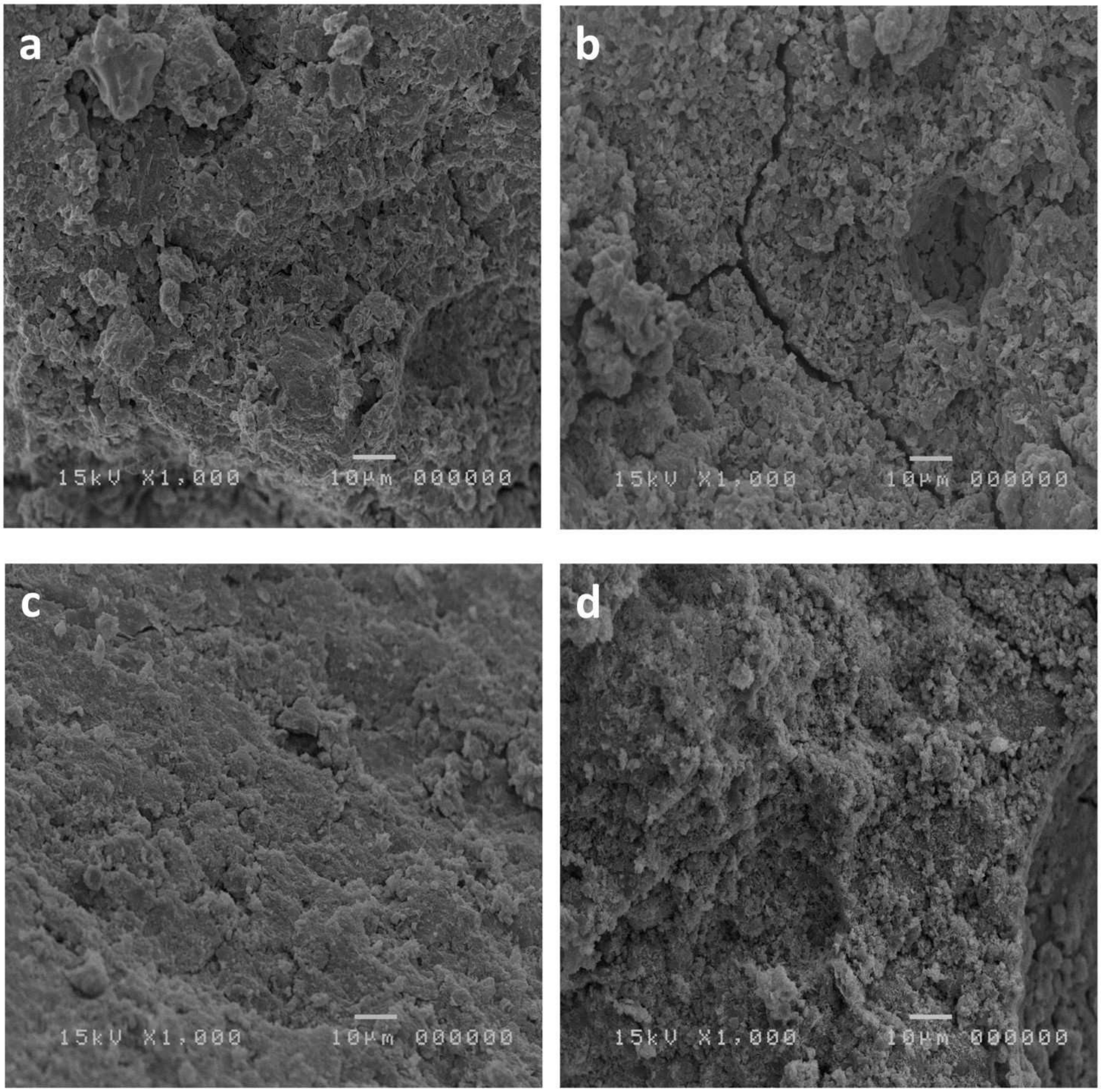

Fig. 5 SEM micrographs of the samples polycondensed for physico-mechanical characterization (potassium aluminate activation): (a) 650°C/3 d; (b) 750°C/3 d; (c) 650°C/14 d; (d) 750°C/14 d.

Alkali metal aluminate activation of a lake sediment has proved to be successful for the formation of geopolymer-based materials.