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Dissolution of aluminosilicate minerals and by-products in alkaline media

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Abstract In this work, the leaching behaviour of six aluminosilicate industrial minerals and by-products (kaolin, metakaolin, fly ash, natural pozzolana from Milos, zeolite and furnace slag) in alkaline solutions is investigated. The variables studied are the kind of alkali metal (K, Na), the concentration of the alkaline solution (2.5, 5 and 10 M) and the time of dissolution (5, 10 and 24 h). The solid residue after the leaching was examined by means of XRD and FTIR. As it is concluded, the leaching ability of Al and Si is according to the following descending order: Metakaolin > Zeolite > Slag > Fly Ash > Pozzolana > Kaolin. The extent of dissolution is higher in NaOH than in KOH solutions, especially when the most reactive materials are concerned. Finally, Si and Al seem to have a synchronized leaching behaviour in both alkaline solutions.

Introduction

Synthesis of geopolymers is based on the activation of aluminosilicate materials by an alkali metal hydroxide and an alkali metal salt and their transformation into a three-dimensional inorganic amorphous structure [1]. The synthesis and chemical composition of geopolymers are similar to those of zeolites, but their microstructure is amorphous to semi-crystalline. During the last decades, geopolymers have drawn the attention of the scientific community throughout the world, due to their excellent mechanical properties and their high fire and acid resistance.

Theoretically, any aluminosilicate material can undergo geopolymerization under certain conditions. Previous works have reported the formation of geopolymers from natural minerals [2–4], calcined clays [5, 6], industrial by-products [7–10] or a combination of them [11–15].

The formation of geopolymers involves a chemical reaction between an aluminosilicate material and sodium silicate solution in a highly alkaline environment. According to Hua Xu and Van Deventer [2], geopolymerization process can be represented schematically according to Eqs. (1) and (2).

The exact mechanism of geopolymerization is not yet fully understood, but it is believed to consist of four main stages: (1) the surface dissolution of Al and Si in a highly alkaline solution, (2) the diffusion of the dissolved species through the solution, (3) the polycondensation of the Al and Si complexes with the added silicate solution and the formation of a gel and (4) the hardening of the gel that results to the final geopolymeric product. Stages (2) to (4) cannot be monitored since the procedures cannot be stopped and the products cannot be isolated. Therefore, the dissolution stage is the only one that can be quantitatively studied. A lot of papers have been published on the dissolution of aluminosilicate compounds, especially in

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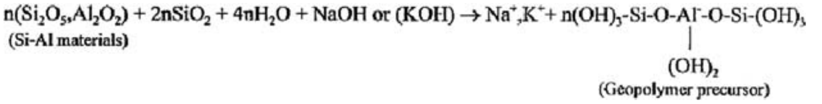
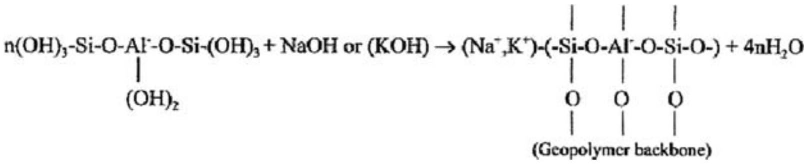


$$n(Si_2O_5,Al_2O_2) + 2nSiO_2 + 4nH_2O + NaOH \text{ or } (KOH) \rightarrow Na^+,K^+ + n(OH)_3\text{-}Si\text{-}O\text{-}\underset{\underset{\text{(Geopolymer precursor)}}{(OH)_2}}{Al^-}\text{-}O\text{-}Si\text{-}(OH)_3 \quad \underset{\text{(Si-Al materials)}}{} \tag{1}$$



$$n(OH)_3\text{-}Si\text{-}O\text{-}\underset{(OH)_2}{Al^-}\text{-}O\text{-}Si\text{-}(OH)_3 + NaOH \text{ or } (KOH) \rightarrow (Na^+,K^+)\text{-}(\text{-}\underset{O}{\overset{|}{Si}}\text{-}O\text{-}\underset{O}{\overset{|}{Al^-}}\text{-}O\text{-}\underset{O}{\overset{|}{Si}}\text{-}O\text{-}) + 4nH_2O \quad \text{(Geopolymer backbone)} \tag{2}$$

the geochemical literature [16–19]. Babushkin et al. and McCormick et al. proposed a dissolution scheme for zeolitic synthesis, consisting of 13 reactions [20, 21], while Hu and Van Deventer examined the dissolution of fifteen pure Al–Si minerals in alkaline media [2]. However, there is a lack of data concerning the dissolution of the materials that can actually be used for the preparation of geopolymers at an industrial scale. Yet, as it is indicated by the proposed mechanisms, the extent of their dissolution is crucial since the amount of Si and Al initially dissolved is substantial for the following polycondensation.

In this work, the alkaline dissolution of three Al–Si rocks (kaolin, natural pozzolana and zeolite), one calcined clay (metakaolin) and two industrial by-products (fly ash and furnace slag) is studied. The chosen materials vary as far as origin, chemical composition, mineralogy and pre-treatment (calcined or non-calcined) are concerned. This work is part of a research project concerning the exploitation of Greek minerals and by-products in geopolymer technology.

Table 1 Chemical composition of raw materials (% w/w)

	Pozzolana	Fly ash	Slag	Kaolin	Metakaolin	Zeolite
SiO_2	66.33	47.86	36.67	47.85	54.56	67.24
Al_2O_3	11.41	23.54	12.20	38.20	43.56	12.66
Fe_2O_3	3.81	7.15	0.82	1.29	1.47	0.15
CaO	6.41	10.56	41.10	0.03	0.03	3.01
MgO	1.30	2.28	5.45	0.04	0.04	0.49
K_2O	1.89	1.58	0.25			1.62
Na_2O	1.50		0.33			0.48
SO_3		2.50	2.17			
L.O.I.	7.38	4.30	0.84	12.30	0.70	13.92

Table 2 Mineral composition of raw materials

Materials	Mineral phases
Pozzolana	Cristobalite, feldspars, K-alunite, quartz
Fly ash	Quartz, feldspars, anhydrite, hematite, calcite
Slag	Amorphous
Kaoline	Kaolinite, illite, feldspars, quartz
Metakaoline	Mainly amorphous, illite, feldspars, quartz
Zeolite	Heuladite, feldspars, cristobalite, quartz

Experimental

The experimental part comprises three stages: the chemical and mineral characterization of the studied materials, the recording of their dissolution rate under varying conditions and the examination of the solid residue after the leaching of the starting materials.

The natural zeolite and the natural pozolana come from Thrace and Milos island, Greece, respectively. The kaolin and the metakaolin are commercial products of high purity. The fly ash comes from the power station at Megalopolis, Greece. The chemical and mineral composition of the above materials is presented in Tables 1 and 2, respectively. All the materials were previously ground and their mean particle size (d_{50}) was approximately 10 μm. This is the typical fineness of these materials when they are used in construction technology (as main constituents in blended cements). The used metakaolin is a commercial product (Metastar) of high purity with a mean particle size of 5.1 μm.

The leaching of the raw materials was conducted by mixing 0.5 (± 0.0001) g of solid with 20 ml of alkaline solution for certain hours under continuous stirring. The variables studied are the kind of alkali metal (K, Na), the concentration of the alkaline solution (2, 5 and 10 M) and the time of dissolution (5, 10 and 24 h). After filtering, the liquid part is diluted to 250 ml, the pH is adjusted to $pH < 1$ by adding concentrated HCl acid and AAS is used in order to determine the Al and Si concentration. The solid part is examined by means of XRD and FTIR in order to evaluate the effect of Al and Si leaching on the structure of the starting material.

X-ray powder diffraction patterns were obtained using a Siemens D-5000 diffractometer, $CuK_{\alpha1}$ radiation ($\lambda = 1.5405$ Å), operating at 40 kV, 30 mA. The IR measurements were carried out using a Fourier Transform IR (FT-IR) spectrophotometer (Perkin

Elmer 880). The FTIR spectra in the wavenumber range from 400 to 4,000 cm^{-1} were obtained using the KBr pellet technique. The pellets were prepared by pressing a mixture of the sample and dried KBr (sample:KBr approximately 1:200) at 8 tons cm^{-2}.

Results and discussion

Extent of dissolution

Tables 3 and 4 present the concentration of Al and Si, respectively, in the solutions in relation to the starting material, the time of leaching and the alkalinity of the leaching solution. These values are the measured concentrations, after the leaching of 0.5 g of the solid material and the dilution of the liquid to 250 ml.

Figures 1 and 2 present the percentage of dissolved Al and Si after leaching, for 24 h, in 10 M NaOH and 10 M KOH, respectively. Since the starting materials have a varying content of Al and Si, Figs. 1 and 2 present the percentage of the total Al and Si of the starting material that has been dissolved. In this way, we can evaluate how extensively the starting material has been affected by the attack of the alkaline solution. As it is seen, the starting materials are affected according to the following decreasing order: Metakaolin > Zeolite > Slag > Fly Ash > Pozzolana > Kaolin

This order stays the same in the case of shorter leaching time (5 and 10 h).

Table 3 Extent of Al dissolution in relation to time and alkalinity of the solution (ppm)

		Pozzolana	Fly ash	Slag	Kaoline	Metakaoline	Zeolite
NaOH	5 h	1.81	4.57	2.50	2.93	17.29	6.10
2 M	10 h	7.00	27.74	4.89	6.57	107.95	17.94
	24 h	7.32	42.61	17.96	8.21	118.71	32.33
NaOH	5 h	4.60	19.83	5.20	5.72	31.18	7.81
5 M	10 h	7.49	24.18	8.06	7.52	268.16	26.32
	24 h	9.17	45.62	20.34	9.07	336.65	41..26
NaOH	5 h	6.71	14.02	17.49	11.21	42.36	9.45
10 M	10 h	9.45	30.00	13.13	13.35	297.47	22.48
	24 h	10.67	46.89	42.11	13.01	344.32	56.92
KOH	5 h	1.06	2.68	1.04	2.27	64.81	11.45
2 M	10 h	4.21	20.13	6.96	6.87	77.82	13.64
	24 h	4.17	20.91	15.72	7.27	63.68	19.19
KOH	5 h	3.59	5.41	2.92	3.63	130.01	16.03
5 M	10 h	5.04	19.78	9.83	6.64	136.94	18.79
	24 h	5.29	29.82	12.68	8.22	154.83	28.34
KOH	5 h	6.80	5.35	6.11	9.36	123.42	21.86
10 M	10 h	7.45	25.68	26.50	17.11	137.64	36.83
	24 h	10.75	41.40	31.51	18.09	213.47	51.82

Table 4 Extent of Si dissolution in relation to time and alkalinity of the solution (ppm)

		Pozzolana	Fly ash	Slag	Kaoline	Metakaoline	Zeolite
NaOH	5 h	17.25	12.04	9.20	7.29	36.19	52.97
2 M	10 h	20.59	53.29	15.82	16.71	97.19	88.14
	24 h	26.70	70.59	20.47	27.81	143.73	181.44
NaOH	5 h	29.09	16.41	27.13	11.15	62.36	64.79
5 M	10 h	50.86	54.21	54.20	14.59	304.25	210.94
	24 h	51.95	78.34	63.96	25.81	386.81	348.88
NaOH	5 h	41.76	23.30	62.91	17.09	81.37	82.31
10 M	10 h	52.50	57.66	106.13	16.78	314.35	243.51
	24 h	53.35	87.65	185.31	29.92	394.50	322.77
KOH	5 h	11.94	7.22	4.72	7.13	79.41	50.99
2 M	10 h	16.62	33.97	39.68	18.55	71.11	67.56
	24 h	20.27	38.78	63.82	25.67	84.23	86.29
KOH	5 h	23.91	10.06	12.66	8.71	148.26	71.58
5 M	10 h	30.87	40.14	58.48	14.33	164.57	90.44
	24 h	34.29	54.33	82.76	31.61	188.55	131.10
KOH	5 h	37.09	10.71	23.85	15.38	131.28	98.65
10 M	10 h	48.14	58.81	94.57	26.48	173.35	127.64
	24 h	56.76	75.64	123.87	32.49	240.91	226.52

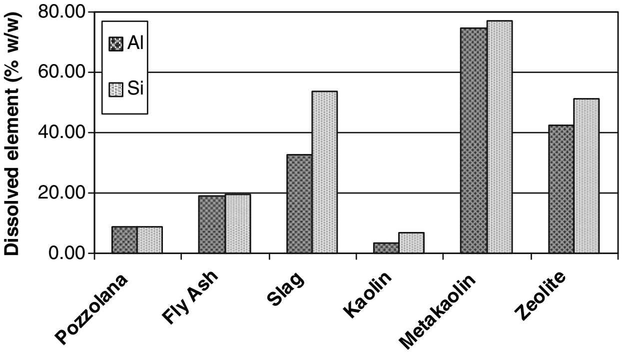


Fig. 1 Dissolved Al and Si after leaching, for 24 h, in 10 M NaOH (% w/w)

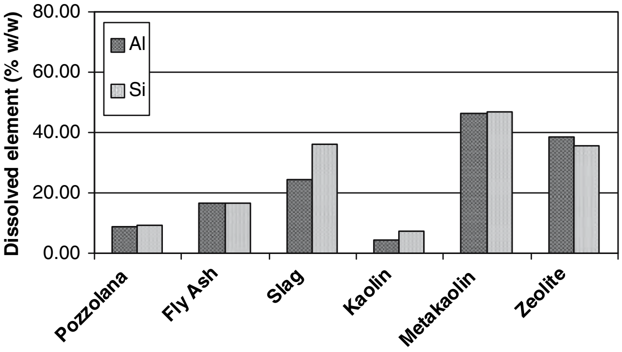


Fig. 2 Dissolved Al and Si after leaching, for 24 h, in 10 M KOH (% w/w)

The metakaolin is the most affected material. Almost 75% of Al and Si have been removed from the solid in the case of NaOH and 45% in the case of KOH. On the other hand, kaolin is the less affected material (approximately 6% of Al and Si were leached). The reactivity of metakaolin and slag must be associated with the thermal history of these materials. As it has been previously reported, the calcinations of materials improves their reactivity especially if their crystalline structure is changed in order to store the extra energy [22]. Besides, it must be noted that the high reactivity of metakaolinite is also connected to the change of Al^{+3} coordination from octahedral in kaolinite to tetrahedral in metakaolinite (tetrahedral Al^{3+} is generally more reactive than octahedral Al^{3+}) [23]. It must be noted, also, that metakaolin is the finest material and this is expected to increase, the rate of dissolution. The zeolite also shows a high reactivity, although it has an almost perfect crystalline structure. This may be due to the correlation between the reactivity and the capability of cation exchange. Materials, capable of cation exchange, are found to be, in some cases, more reactive than those containing vitreous constituents [24].

Si and Al seem to have a synchronized leaching behaviour in both alkaline solutions. This is very clear in the case of metakaolin, which consists mainly of metakaolinite. The ratio Si:Al in the solid is almost the same as the ratio Si:Al in the liquid. This indicates that Si and Al may be dissolved in some kind of linked form, at least in concentrated alkaline solutions. The other starting materials consist of more than one aluminosilicate phases, having varying degrees of dissolution, and therefore it is not possible to extract safe conclusions. However, other researchers have also reported a simultaneous leaching of Al and Si in the case of pure mineral phases [25].

Effect of alkalinity

Figures 3 and 4 present the effect of the alkalinity on the extent of Si dissolution in the case of NaOH and KOH, respectively. In the case of NaOH and as far as the most reactive materials (metakaolin and zeolite) are concerned, the increase of alkalinity from 2 to 5 M

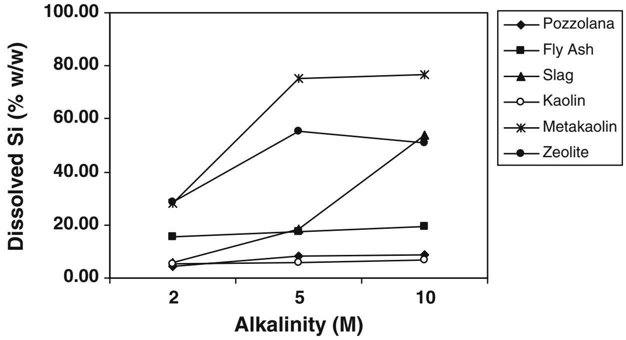


Fig. 3 Effect of the alkalinity on the leaching of Si in NaOH solution for 24 h

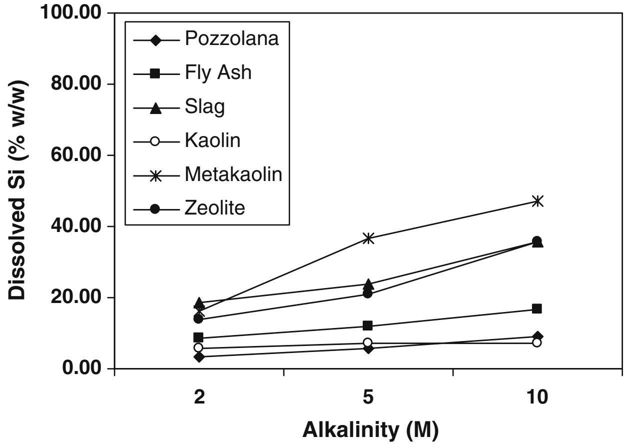


Fig. 4 Effect of the alkalinity on the leaching of Si in KOH solution for 24 h

causes a considerable increase of the amount of dissolved Si, while further increase of the alkalinity, has only a slight effect. In the case of KOH, however, the extent of dissolution is proportional to the alkalinity of the solution. This may indicate that, in the case of NaOH, equilibrium between dissolved species and undissolved solid is obtained at lower alkalinity, probably due to the higher leaching ability of NaOH. On the other hand, in both cases, the dissolution of slag mostly increases as the alkalinity of the solution increases from 5 to 10 M. For the rest of the materials the effect of alkalinity is only marginal. The leaching behaviour of Al in relation to the alkalinity of the solution is very similar to the behaviour of Si.

Effect of alkali ion

Figures 5 and 6 present the effect of the kind of alkali ion on the dissolution of Al and Si, respectively, after 24 h in 10 M solutions. In almost every case, and especially when the higher reactive materials are concerned, the dissolution is higher in NaOH than in KOH. The same effect has been also observed by other researchers and was associated with the smaller size of Na^+ which can better stabilize the silicate monomers and dimers in the solution, increasing in this way the dissolution rate of the minerals [2, 4].

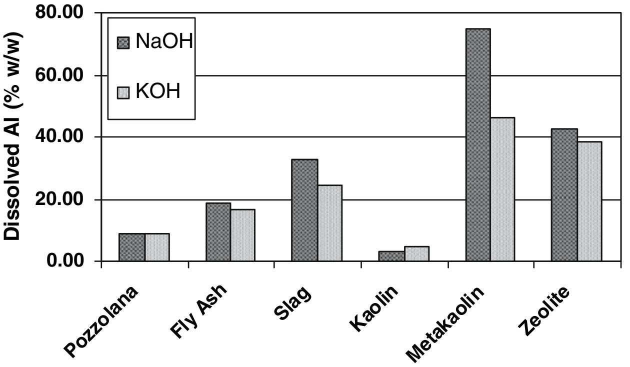


Fig. 5 Effect of alkali ion on the dissolution of Al in 10 M solutions for 24 h

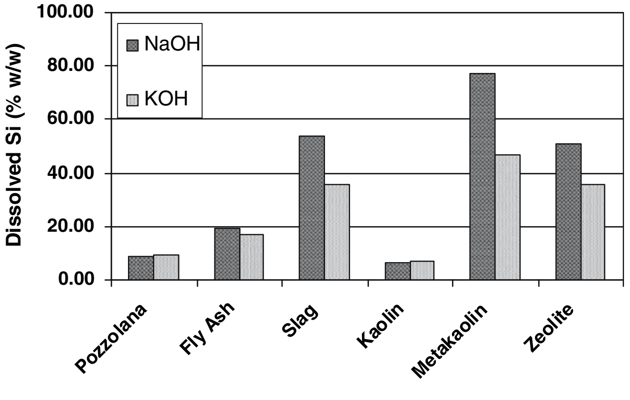


Fig. 6 Effect of alkali ion on the dissolution of Si in 10 M solutions for 24 h

Characterization of solid residue

Figures 7, 8 and 9 present the XRD patterns of the starting materials and their solid residues after leaching in 10 M NaOH for 24 h. As it is shown, zeolite is transformed to an almost amorphous material with some traces of heulandite and quartz. Although slag is completely amorphous, its solid residue contains the crystalline phase of portlandite (Fig. 7). It must be noted that slag has a high percentage of CaO (41.10% w/w) and as the aluminosilicate network of the material starts decomposing under the attack of the highly alkaline solution, Ca^{2+} moves in the solution and precipitates as $Ca(OH)_2$. For this reason, geopolymers based on slag are expected to contain calcium silicate hydrated phases (C–S–H), similar to those found in hydrated cement.

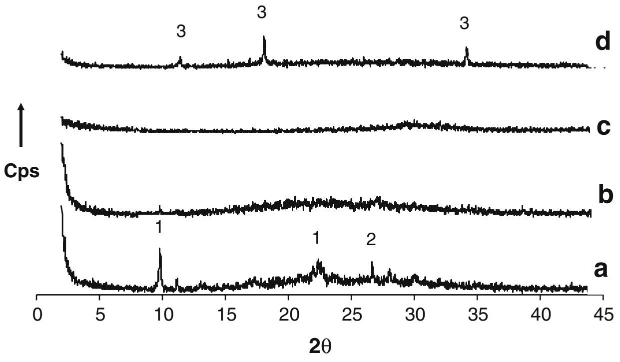


Fig. 7 XRD patterns of starting materials and solid residues. *a* zeolite, *b* solid residue of zeolite after leaching in 10 M NaOH for 24 h, *c* slag, *d* solid residue of slag after leaching in 10 M NaOH for 24 h. *1* Heulandite, *2* feldspars, *3* portlandite

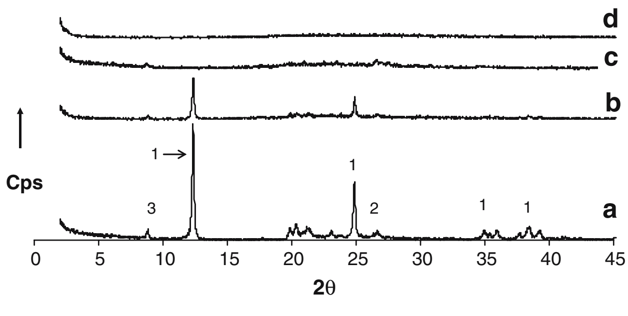


Fig. 8 XRD patterns of starting materials and solid residues. *a* kaolin, *b* solid residue of kaolin after leaching in 10 M NaOH for 24 h, *c* metakaolin, *d* solid residue of metakaolin after leaching in 10 M NaOH for 24 h. *1* Kaolinite, *2* quartz, *3* illite

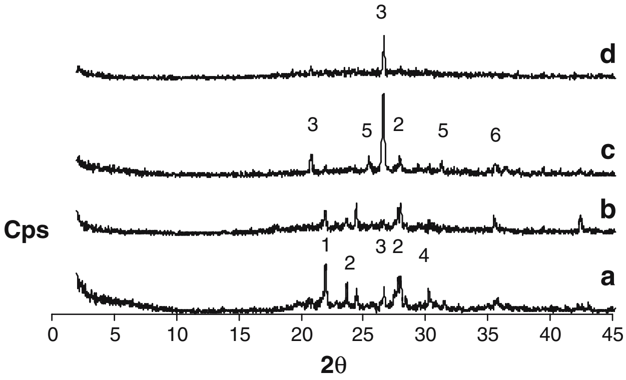


Fig. 9 XRD patterns of starting materials and solid residues. *a* pozzolana, *b* solid residue of pozzolana after leaching in 10 M NaOH for 24 h, *c* fly ash, *d* solid residue of fly ash after leaching in 10 M NaOH for 24 h. *1* Cristobalite, *2* feldspars, *3* quartz, *4* K-alunite, *5* anhydrite, *6* hematite

The solid residues of kaolin and natural pozzolana contain the same crystalline phases as the starting materials but in lesser amount as indicated by the decrease of the corresponding peaks. In the case of metakaolin, the solid residue is completely amorphous. Lastly, the solid residue of fly ash still contains quartz but feldspars seem to be completely dissolved (Figs. 8, 9).

The FTIR spectra of the starting materials and their solid residues confirm the above remarks. As an example, Fig. 10 presents the spectra of slag before and after leaching in 10 M NaOH for 24 h. The broad peak around 1,000 cm^{-1}, in the starting material, is associated with the Al–O and Si–O stretching vibrations in a disordered aluminosilicate framework. This peak is considerably decreased in the solid residue due to the removal of Al and Si after the leaching. The peak at 3,640 cm^{-1}, in the solid residue is assigned to the $_{v}$(OH) band of Ca(OH)$_2$. The new peaks at around 1,440 and 900 cm^{-1} have also been observed by other researchers and were attributed to the precipitation of some kind of hydrated carbonates or aluminates on the surface of the material [3].

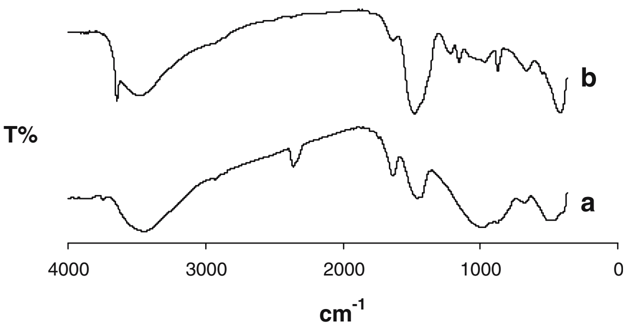


Fig. 10 FTIR spectra of the slag and the solid residue after leaching in 10 M NaOH for 24 h *a* slag, *b* solid residue

This work shows that some of the most common industrial minerals and by-products in Greece can be considered as potential raw materials for geopolymerization. However, it must be noted, that the leaching behaviour of Al and Si cannot predict by its self the quality of the produced geopolymers. Further experiments concerning the preparation and properties of geopolymers from these raw materials are now in progress. In any case, their efficiency as raw materials for geopolymers, is to be evaluated on the basis of strength and durability of the final products.

Conclusions

The leaching behaviour of six aluminosilicate industrial minerals and by-products (kaolin, metakaolin, fly ash, natural pozzolana from Milos, zeolite and furnace slag) in alkaline solutions is investigated. The following conclusions can be drawn from the present study:

The examined materials showed a varying degree of dissolution in alkaline solution. The leaching ability of Al and Si is according to the following descending order: Metakaolin > Zeolite > Slag > Fly Ash > Pozzolana > Kaolin

The extent of dissolution is higher in NaOH than in KOH solutions, especially when the most reactive materials are concerned.

Si and Al seem to have a synchronized leaching behaviour in both alkaline solutions. This is more evident in the case of kaolin and metakaolin, which consist mainly of one aluminosilicate phase.

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