



# Extensive reuse of soda-lime waste glass in fly ash-based geopolymers

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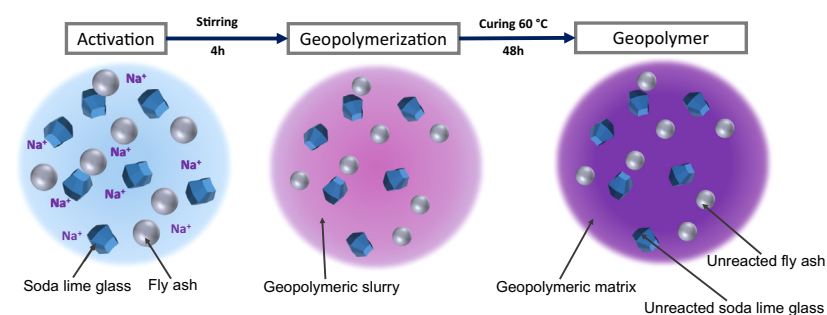
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## HIGHLIGHTS

- Waste-derived geopolymers synthesized using waste glass instead of sodium silicate.
- Mechanically competent materials achieved with high incorporation of waste glass.
- Formation of a geopolymeric gel confirmed by FTIR and EDX analysis.
- Leaching tests demonstrated sufficient stabilization of heavy metal ions.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The possibility of extensive incorporation of soda-lime waste glass in the synthesis of fly ash-based geopolymers was investigated. Using waste glass as silica supplier avoids the use of water glass solution as chemical activator. The influence of the addition of waste glass on the microstructure and strength of fly ash-based geopolymers was studied through microstructural and mechanical characterization. Leaching analyses were also carried out. The samples were developed changing the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio and the molarity of the sodium hydroxide solution used as alkaline activator. The results suggest that increasing the amount of waste glass as well as increasing the molarity of the solution lead to the formation of zeolite crystalline phases and an improvement of the mechanical strength. Leaching results confirmed that the new geopolymers have the capability to immobilize heavy metal ions.

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## 1. Introduction

It is well known that, according to pioneering work by Davidovits [1], the dissolution of aluminosilicate raw materials in highly alkaline solutions, followed by condensation reactions, leads to products generally known as geopolymers. These products possess a three-dimensional network structure, consisting of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra, connected by means of oxygen atoms, analogous to that of natural zeolites.  $\text{Na}^+$  and  $\text{K}^+$  ions, embedded in the cavities,

allow the tetrahedral coordination of  $\text{Al}^{3+}$  ions with oxygen, analogous to that of  $\text{Si}^{4+}$  ions [2].

Geopolymers have been primarily proposed for the construction industry as substitute for cement. Considering that each ton of produced cement determines the remarkable release of 1 ton of  $\text{CO}_2$  [3], any substitute with lower associated  $\text{CO}_2$  emissions is highly attractive. Geopolymers, with comparable or better performances than those of traditional construction materials, actually allow for reduction of greenhouse emissions, thanks to their capability to harden at room temperature, starting from precursors in turn derived from low temperature treatments, such as dehydration of kaolinite into metakaolin [4]. In addition, geopolymers may be even more advantageous in terms of low  $\text{CO}_2$

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emissions, if formulated replacing metakaolin with inorganic waste, otherwise landfilled [5,6,7]. The reduction of emissions is consequently coupled with the preservation of valuable resources, moving forward sustainable development [7].

The most significant waste-derived material used in geopolymerization consists of fly ash, a by-product generated by coal fired-power plants [8]. Fly ash is widely available worldwide and it mainly consists of an alumina- and silica-rich amorphous phase [9]. Thanks to the appropriate chemical composition along with favorable size and shape, fly ash is considered a suitable raw material for geopolymer technology [10]. The activation is due to the use of sodium or potassium hydroxide solutions; sodium or potassium silicate solutions (water glass) may be used as well, to balance the silica content.

The present study is essentially aimed at evaluating the feasibility of fly ash-based geopolymers using waste glass as silica source instead of water glass, normally used as alkaline activator. More precisely, we considered a soda-lime glass residue coming from urban waste collection in Italy. This material is an important kind of inorganic waste, since it corresponds to the fraction of glass cullet in which plastic or ceramic impurities are concentrated, so that it remains practically unemployed and mostly landfilled [11]. The use of waste glass, instead of sodium silicate, is expected to provide extra environmental advantage because it avoids the energy demand and CO<sub>2</sub> emissions associated with sodium silicate production, where temperatures around 1300 °C are required in order to melt sodium carbonate and silica mixtures [12].

Torres Carrasco et al. [13] and Martinez-Lopez et al. [14] have already tested the use of urban glass instead of waterglass but filtering the solution (in the first case) and using a solution of NaOH and Na<sub>2</sub>CO<sub>3</sub>. It was shown [14] that the presence of CaO in the glass is not problematic since the addition of the glass in fact decreased the Ca/Si ratio as more Si was available after the incorporation of glass in the matrix.

## 2. Experimental procedure

### 2.1. Materials

Low calcium fly ash (FA), class F (ASTM C 618) [15], provided by Steag Power Minerals (Gladbeck, Germany), with a mean particle size of 20 μm, and soda-lime glass waste (SLG), coming from municipal waste collection and provided by SASIL S. p. a. (Brusnengo, Biella, Italy) in the form of fine powders with particle size <30 μm, were used as raw materials.

Table 1 summarises the chemical composition of fly ash and waste glass determined by means of X-ray fluorescence (XRF, Spectro Analytical Instruments GmbH with a Spectro Xepos He energy-dispersive X-ray fluorescence spectrometer). The alkaline activator was a sodium hydroxide solution, prepared at 5, 8 and 10 M, using sodium hydroxide flakes (Merck 99.5%) dissolved in distilled water.

### 2.2. Sample preparation

In order to assess the possibility of making geopolymers using recycled waste glass instead of water glass, a systematic study was carried out varying the concentration of NaOH solution and the theoretical molar ratio between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

The initial mixtures were produced fixing the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> theoretical molar ratio of the final geopolymers at 5, 6 and 7, which rep-

**Table 1**  
Chemical composition of raw materials (wt%) determined by XRF.

wt%	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
FA	54.36	24.84	0.83	3.03	2.56	2.06	8.28	1.07
SLG	70.5	3.2	12	1	10	2.3	0.42	0.07

resents mixtures of FA/SLG (in wt%) of 76/24, 64/36, 54/46, respectively. NaOH aqueous solutions with molarity 5, 8, and 10 were used as alkali activation in all the mixtures, while the liquid solid ratio was fixed at 0.45 to obtain a good workability. The sample labeling for further characterization was established as xSyM where “x” is associated with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio, while “y” refers to the molarity of the activating solution.

To synthesize geopolymer samples, the raw materials were kept under mechanical stirring for 4 h in order to obtain an homogeneous slurry of partially dissolved glass powders and activated fly ash. From the study of Torres-Carrasco et al. [13], 4 h was considered a sufficient time to achieve suitable silica dissolution from the glass.

The mixture was cast into polyethylene-sealed moulds and vibrated for 3 min to remove trapped air before curing in an oven at 60 °C for 48 h to complete the polycondensation reaction. After curing the samples were stored in plastic bags.

### 2.3. Test and analysis methods

Fourier transform infrared spectroscopy (FTIR) studies were performed on powder by using a Shimadzu model IRAffinity-1S, Duisburg, Germany. The spectra were collected in transmittance mode with a resolution index of 4 and 24 numbers of scan.

The mineralogical analysis was conducted by X-Ray diffraction (XRD) on powdered samples (Bruker D8 Advance, Karlsruhe, Germany – CuKα radiation, 0.15418 nm, 40 kV–40 mA, 2θ = 10–70°, step size 0.05°, 2 s counting time). The phase identification was performed by means of the Match!® program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA).

The geometric density was evaluated by considering the mass to volume ratio of samples. The apparent and the true density were measured by using a helium pycnometer (Micromeritics AccuPyc 1330, Norcross, GA), operating on bulk or on finely crushed samples, respectively. The three density values were used to compute the amounts of open and closed porosity.

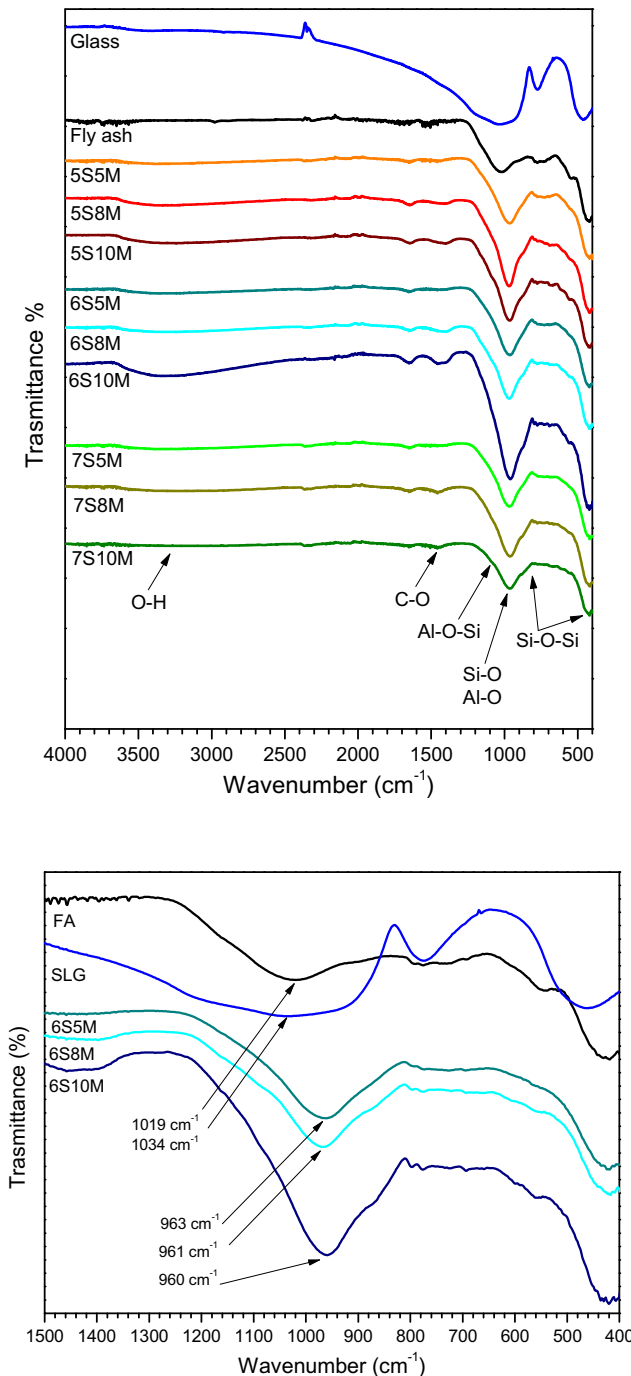
The compressive strength of cylindrical samples was measured by using a universal testing machine (Zwick Roell, Ulm, Germany Series Z050) with a load speed of 0.5 mm/min. A minimum of 10 samples for each batch was tested to evaluate the 28 days strength of the specimens. A qualitative morphological evaluation of the raw materials and final geopolymer samples was performed via scanning electron microscopy (LEO 435, LEO Electron Microscopy Ltd., Cambridge, UK and Ultra Plus, Zeiss, Jena, Germany) in order to assess, in the case of the geopolymer samples, their microstructural homogeneity. Pieces of samples after compression test (fracture surfaces) were used to analyse the microstructure by SEM observations.

The release of heavy metals was evaluated according to European Standard for waste toxicity evaluation (EN 12457-2). Fragments under 4 mm were placed in an extraction solution consisting of distilled water, with a pH value of ~7, for a liquid/solid ratio of 10, and softly stirred at 25 °C for 24 h. The resulting solutions were filtered through a 0.6 μm filter and analysed using inductively coupled plasma (ICP-OES; SPECTRO Analytical instruments GmbH, Kleve, Germany).

## 3. Results and discussion

### 3.1. Fourier transform infrared spectroscopy

Fig. 1 shows FTIR spectra of geopolymer samples with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio and dissolved with different molarity. The bands between 3000 and 3700 cm<sup>-1</sup>, assigned to stretching



**Fig. 1.** (a) FTIR spectra of geopolymer samples and raw materials; (b) plot with focus placed in the low wavenumber range. The relevant peaks are discussed in the text.

vibration of O–H groups, and those between  $1600\text{ cm}^{-1}$  and  $1650\text{ cm}^{-1}$  are associated with O–H bending [16]. As shown in Fig. 1a, these bands increased in intensity with increasing molarity, likely due to an enhanced dissolution of the initial materials, leading to the formation of more hydrated compounds. The presence of weak carbonate traces at  $1515\text{ cm}^{-1}$  is identified by the C–O bond stretching [17]. This band is typical of  $\text{CO}_3^{2-}$  vibration groups which are present in inorganic carbonates [18].

Bands at  $420\text{ cm}^{-1}$  and  $690\text{ cm}^{-1}$  are attributable to Si–O–Si bending vibrations and symmetric stretching [19]. The bands detected between  $1200\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  are associated with

the Si–O–Si asymmetric vibration and Al–O–Si symmetric bending vibration, respectively [20,21].

The geopolymerization reaction could be followed by the shift and the increase of intensity of the Si–O stretching vibration. Fig. 1b focuses on this band for the initial raw materials and selected samples with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 6, at different molarities. It can be noted that the SLG broad signal became narrower in the geopolymeric sample due to the more ordered structure, while the FA Si–O stretching vibration initially situated at  $1025\text{ cm}^{-1}$  shifted to lower frequencies [22]. This shift indicates the activation of the fly ash amorphous phase with the formation of the alumina-silicate gel. Torres Carrasco et al. [23] suggested that the band shifts to lower frequency due to the rise in tetrahedral aluminum content, for all the geopolymer samples this band was detected at around  $960\text{ cm}^{-1}$ . The intensity of the band is also attributable to the amount of Si–O or Al–O in tetrahedral configuration [17]. The lowest and the highest intensities correspond to geopolymers activated with 5 M and 10 M NaOH, respectively. These results are consistent with previous studies on the variation of NaOH solution in geopolymerization [24].

### 3.2. X-ray diffraction analysis

X-ray powder diffraction patterns for raw materials and geopolymeric samples, with different molarity but the same  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio, are represented in Fig. 2. A diffuse halo between  $25^\circ$  and  $45^\circ$  appears in all XRD patterns; the shift of the halo to higher angles may be considered as a further proof of the geopolymeric reaction between fly ash and recycled glass [25]. The crystalline phases, quartz ( $\text{SiO}_2$ , PDF#086-1560) and mullite ( $\text{Al}_4\text{SiO}_8$ , PDF#073-1389), detected in the original fly ash, remained apparently unaltered with activation.

The presence of zeolitic phases, such as sodalite ( $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$ , PDF#037-0476) and cancrinite ( $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{OH})_{2.04}(\text{H}_2\text{O})_{2.66}$ , PDF#078-2494), identified in the geopolymer samples, demonstrates the effective formation of an aluminosilicate 3D structure. The relative peak intensity of these crystalline phases increases with higher molarity of the alkaline solution. Sample 7S5M presents very limited traces, while samples prepared by increasing the molarity from 8 to 10 shows more intense and defined peaks. A higher alkalinity of the solution evidently promoted a more substantial silica dissolution from the waste glass during the geopolymer synthesis, inducing enhanced zeolite formation. The same trend was detected also for the mixture at  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 5 and 6.

### 3.3. Compressive strength

Fig. 3 shows the compressive strength values after 7 and 28 days by changing NaOH solution molarity and silica to alumina molar ratio. The dashed line shows the evolution trends depending on the molarity of the sodium hydroxide solution.

The molarity and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio affect the mechanical properties of the geopolymers. The compressive strength tends to rise as the molarity of the solution as well as the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio increase. This behavior is verified with solutions having a NaOH molarity up to 10, where the geopolymers with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  show compressive strength values similar to each other. Samples tested after 7 and 28 days show no significant variation with time, except for the sample 7S10M, confirming the short setting time characteristic of the geopolymer material [26].

When the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of the mixtures is enhanced, a higher replacement level of glass is introduced in the samples. Glass is partially dissolved under alkaline conditions, developing a silica rich gel at the surface of the particles, hindering the complete dissolution of the initial waste glass [5]. The silica available

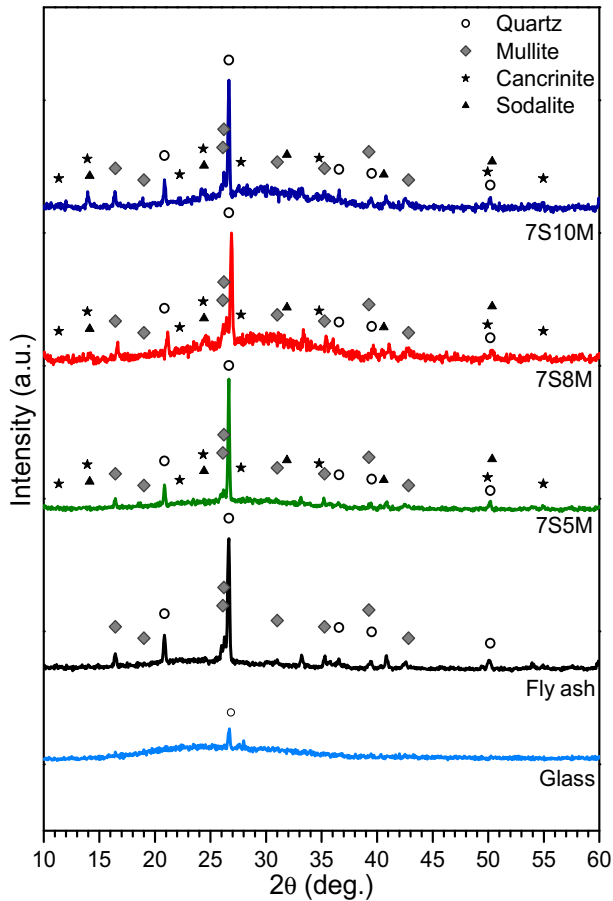


Fig. 2. XRD patterns of raw materials and geopolymers with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 7 at different molarities.

in the system is enhanced with increasing amount of glass in the formulation.

A NaOH solution at 5 M involves a low dissolution ratio of the raw materials, so that as a consequence a large amount of unreacted particles likely remained in the final material. On the other hand, solutions at 8 M and 10 M determined an increased dissolution of components leading to more geopolymeric precursors in the initial slurry and less unreacted particles.

Even if there are no significant differences in mechanical performance with time, sample 7S10M shows a strength loss. The value of 100 MPa achieved after 7 days decreases drastically to 36 MPa after a storage time of 28 days. The same behavior was detected by Novais et al. [20] who reported that a high alkalinity of the solution could disintegrate the aluminosilicate gel after a long period. This result indicates that the geopolymer network present after 7 days may decompose as an effect of alkali excess. A decrease in mechanical properties by increasing the alkalinity of the solution, although reported by different authors, is not clearly understood. Usha et al. [27] showed that an excess of  $\text{Na}^+$  and  $\text{OH}^-$  ions accelerates the dissolution of particles, but the rate of polycondensation decreased; on the other hand, Kamarudi et al. [28] stated that using a lower molarity implies more water in the system, which in turn eases the geopolymerization process by enhancing the ionic mobility. For the reasons above mentioned, it can be concluded that an alkali activation as strong as 10 M, not necessary to activate the raw materials, is not convenient from both economic and environmental points of view.

Samples 6S8M and 7S8M present outstanding mechanical properties reaching values as high as 45 MPa, even after setting time of 7 days and the values remain constant with time. These results suggest that a molarity of 8 is adequate to dissolve almost completely the initial raw materials, leading to a suitable ratio between silica and aluminum precursors in the geopolymeric gel.

These samples possess a compressive strength comparable to that of traditional Portland cement, normally used in construction industry [29]. Previous studies have already demonstrated the possibility to incorporate up to 30 wt% waste glass in the geopolymer network, but achieving compressive strength values not exceeding 20 MPa [30,31].

### 3.4. Density and porosity

The density and porosity values measured after 28 days of aging are reported in Table 2. The inherent porosity arises from the mesoporous nature of the geopolymeric gel, the unreacted fly ash particles or entrapped air. [32] All synthesized samples show high densities and low porosities, roughly between 20 and 35%, in agreement with other values found in literature [33]. We may observe that samples activated with low molarity present the highest total porosity values as a result of poor reaction of the initial materials and lack of cohesion between the unreacted particles, as the geopolymeric gel is not produced in sufficient extension.

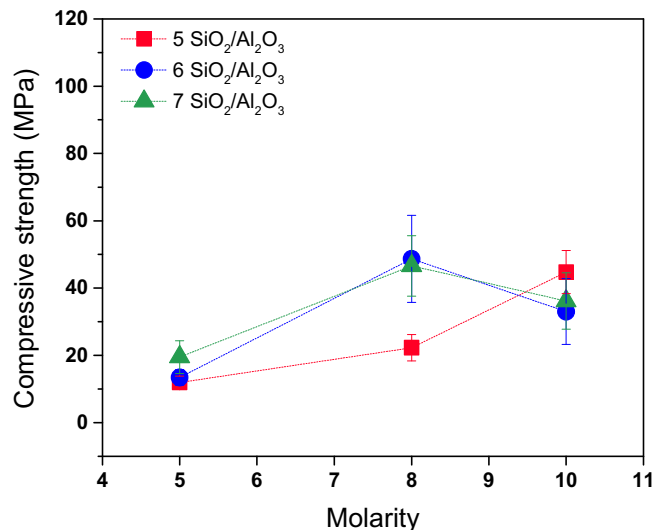
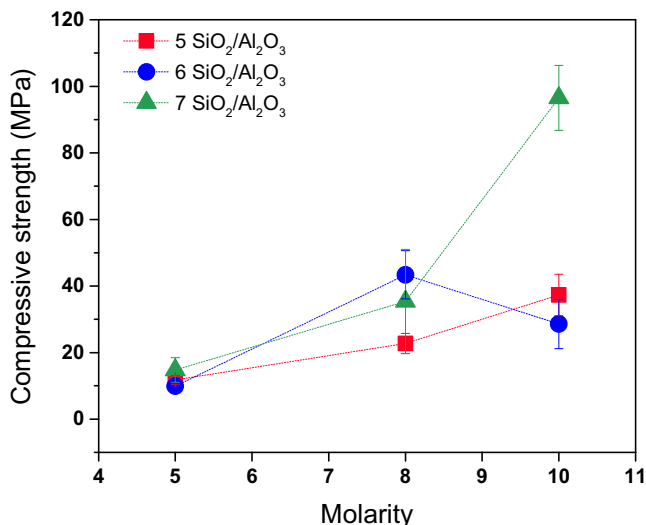


Fig. 3. Compressive strength of geopolymer samples after 7 (sx) and 28 (dx) days.

**Table 2**  
Density and porosity of fly ash based geopolymers after 28 days aging.

	Density (g/cm <sup>3</sup> )			Porosity (%)		
	Bulk [ $\rho_b$ ]	Apparent [ $\rho_a$ ]	True [ $\rho_t$ ]	Total [TP]	Open [OP]	Closed [CP]
5S5M	1.52 ± 0.01	2.27 ± 0.01	2.42 ± 0.01	37 ± 3	33 ± 2	4.1 ± 0.4
5S8M	1.63 ± 0.01	2.19 ± 0.01	2.33 ± 0.01	30 ± 1	26 ± 1	4.2 ± 0.7
5S10M	1.55 ± 0.01	2.20 ± 0.06	2.37 ± 0.01	21 ± 2	16 ± 3	6.0 ± 0.3
6S5M	1.51 ± 0.01	2.25 ± 0.01	2.39 ± 0.01	36 ± 1	32 ± 2	4.2 ± 0.3
6S8M	1.93 ± 0.01	2.06 ± 0.01	2.33 ± 0.04	17 ± 1	6.3 ± 0.2	11.0 ± 0.1
6S10M	1.18 ± 0.04	2.25 ± 0.06	2.32 ± 0.01	22 ± 2	19 ± 5	2.7 ± 0.3
7S5M	1.55 ± 0.02	2.30 ± 0.09	2.38 ± 0.01	34 ± 1	31 ± 6	3.5 ± 0.5
7S8M	1.80 ± 0.01	2.28 ± 0.01	2.35 ± 0.01	23 ± 6	21 ± 6	2.4 ± 0.1
7S10M	1.78 ± 0.01	2.33 ± 0.03	2.36 ± 0.01	24 ± 5	23 ± 9	1.1 ± 0.1

In these samples a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio increase produces a decrease in total porosity that could be seen as an indicator of enhanced geopolymerization. These results are in agreement with the slightly improvement of the mechanical properties.

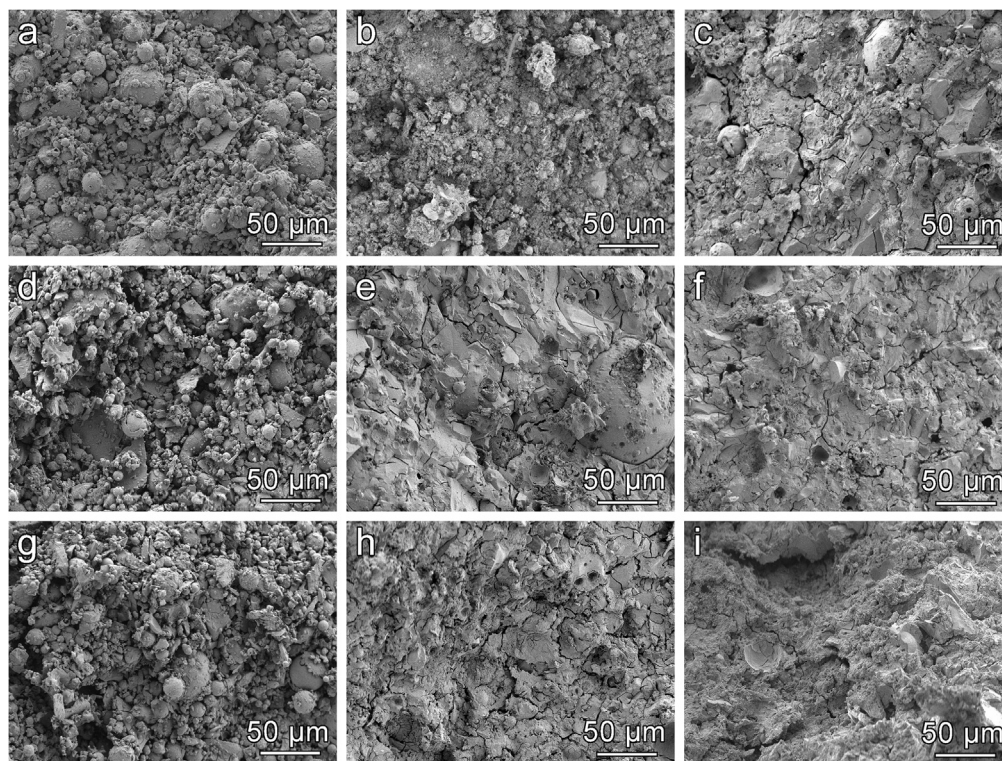
An increment in the NaOH solution molarity reduces the porosity of the geopolymer; the optimum molarity was found to be equal to 8 M; this reduced the porosity to 17% showing the best mechanical performance due to the formation of a flawless geopolymer structure.

### 3.5. Microstructure

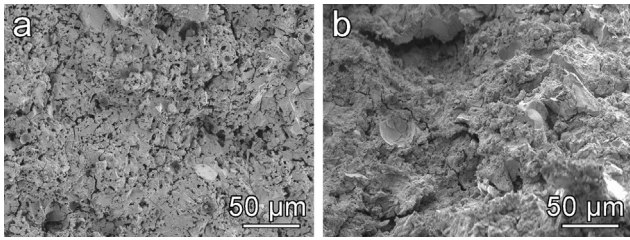
The mechanical properties could be correlated with the microstructure of the geopolymer samples, shown for different samples in Fig. 4. There are significant changes in microstructure with variation in molarity and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio. In all samples we can distinguish spherical particles as well as particles with sharp angles, that could be identified respectively as undissolved fly ash and unreacted glass [34]. These particles appear well distributed in the amorphous geopolymeric matrix. After dissolution with 5 M NaOH solution (Fig. 4a, d and g), a large amount of

unreacted particles remained poorly encapsulated by the geopolymeric gel. Working at low alkalinity solution implies a moderate reaction in the mixture so that there was poor adhesion between unreacted or partially reacted particles, leading consequently to low mechanical strength. In samples 5S8M and 5S10M (Fig. 4b and c respectively), although activated with a high molarity solution, limited silica precursors were involved in the geopolymerisation due to the lower amount of glass in the mixture, resulting in poor homogeneity. On the other hand, samples activated with 8 and 10 M NaOH solutions with theoretical SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratios of 6 and 7 (Fig. 4e, f, h and i), caused a more efficient dissolution, characterized by a largely homogeneous gel containing few unreacted particles and small micro-cracks in the matrix. The formation of a more compact matrix corresponds to a higher reaction degree that consequently results also in improved mechanical properties.

The decrease of the mechanical properties as function of time (Fig. 3), experienced by 7S10M sample, could be explained by the morphological changes occurring during aging. Fig. 5 compares the microstructure evolution from day 7 (Fig. 5a) to day 28 (Fig. 5b). The microstructure after 7 days, due to the excessive alkalinity, presents a sponge-like gel structure, already described in the



**Fig. 4.** Microstructure of fractured surfaces of geopolymers with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio and different NaOH molarity after 28 days of aging. 5S5M(a), 5S8M(b), 5S10M (c), 6S5M (d), 6S8M (e), 6S10M (f), 7S5M (g), 7S8M (h), 7S10M (i).



**Fig. 5.** SEM images of 7S10M after 7 (a) and 28 (b) days showing different microstructure.

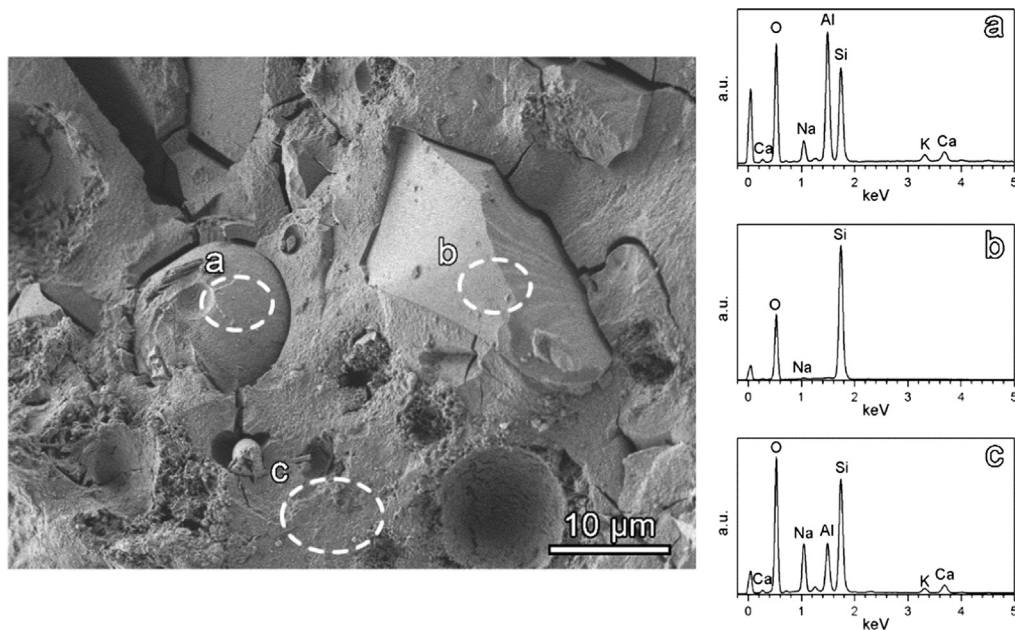
literature [28,35]. The uniformity of the gel could explain the good mechanical properties measured after short time. After 28 days of storage, the microstructure is more compact, however it also includes long visible cracks and pieces of unreacted glass. These defects inside the microstructure reasonably caused the strength decrease.

**Fig. 6** presents the EDX analysis of sample 6S8M (featuring the best overall properties), intended to clarify the nature of the developed geopolymeric gel. Spectrum (a), collected from the spherical particle, confirms the attribution to fly ash, according to the Si/Al ratio (in good agreement with the initial fly ash composition, shown in [Table 1](#)). The irregular particle with sharp angles

(identified by 'b') corresponds to an unreacted glass particle since the main signals in the EDX spectrum match the elements in a glass of soda-lime composition. From EDX analysis the detected amounts of silicon and aluminium were  $25 \pm 0.1$  wt% and  $10 \pm 0.1$  wt%, respectively. The actual composition of the geopolymer gel could not be measured but the silicon to aluminium molar ratio can be estimated to be in the range between 1 and 3, as expected from the formation of a geopolymer material [36]. The Na-related peak, nearly  $11 \pm 0.1$  wt%, is also consistent with a Al/Na molar ratio close to 1, in turn corresponding to the formation of  $\text{AlO}_4$  tetrahedra, mixed with  $\text{SiO}_4$  tetrahedra, with Na in a charge balancing role [37]. Furthermore, the amount of  $\text{Ca}^{2+}$  in the gel is limited, ideally in a charge balancing role similar to  $\text{Na}^+$  [38]. These results are in agreement with those reported by Cyr et al. [39] and Torres-Carrasco et al. [13], who demonstrated that CaO dissolution in mixed glass is fairly low and probably leads to the formation of a limited amount of hydrated calcium silicates (C-S-H), which can coexist with N-A-S-H.

### 3.6. Leaching test

Geopolymers may stabilize heavy metal ions within the polymeric network, although the immobilization mechanism is still in discussion [1]. The release of heavy metal ions upon leaching



**Fig. 6.** SEM image and EDX spectra of 6S8M geopolymer sample showing the composition of different phases.

**Table 3**

Leaching results from raw materials and geopolymer samples. Threshold values for inert and non-hazardous materials from Ref. [41].

Element (ppm)	As	Cd	Cr	Cu	Mo	Pb	Se	Zn
5S5M	0.63	0.005	0.035	0.098	0.86	0.152	0.066	<0.203
5S8M	1.177	0.003	0.0101	0.111	1.071	0.07	0.039	<0.203
5S10M	1.291	0.005	0.0101	0.154	1.187	0.056	0.041	<0.203
6S5M	0.174	0.007	0.0251	0.11	0.363	0.1	0.038	<0.203
6S8M	0.134	0.004	0.0101	0.115	0.143	0.078	0.048	<0.203
6S10M	1.587	0.08	0.0117	0.295	1.02	0.096	0.059	<0.203
7S5M	1.07	0.007	0.0059	0.271	0.792	0.079	0.044	<0.203
7S8M	0.147	0.008	0.0052	0.197	0.996	0.117	0.048	<0.203
7S10M	1.145	0.019	0.0073	0.188	0.924	0.14	0.044	1.1
FA	<0.049	<0.002	0.467	0.028	0.898	<0.047	0.022	<0.2
SLG	<0.049	0.001	0.043	0.036	0.007	0.018	0.018	0.088
Inert material	0.5	0.04	0.5	2	0.5	0.5	0.1	4
Non-hazardous material	2	1	10	50	10	10	0.5	50

tests under legislation limits represents a fundamental requirement for waste-derived marketable products [40]. The heavy metal release from geopolymer samples as well as from the initial raw materials (tested under the same conditions) is reported in Table 3.

The content of heavy metals in the initial soda-lime glass does not exceed the thresholds according to the normative EN 12457, while fly ash cannot be classified as being 'inert' concerning Mo.

In general, samples activated at low molarity are more prone to ion release since a limited geopolymeric gel was formed. The reduced leaching rate found in samples activated with molarity 8 is consistent with the effective formation of a geopolymer matrix that entraps heavy metals in three-dimensional zeolitic-like alumino-silicate 'cages'. Cr, released in high amount in fly ash, was successfully immobilized in the geopolymer network. Samples activated with 10 M show the highest leaching values in agreement with the previous observations on the depolymerisation caused by alkali excess. It may be concluded that the concentration of alkali activator plays a fundamental role in the immobilization efficiency.

The release of toxic elements still exceeds the limits for inert materials in all samples except 6S5M and 6S8M, however, all values are below the limits for non-hazardous materials. Geopolymers formed in these conditions present excellent chemical stability, confirming the capacity of geopolymer technology to produce a valuable product from waste materials.

#### 4. Conclusions

This study evaluated the possibility to replace water glass, normally used in geopolymer production, with soda-lime glass, in order to produce strong and chemically resistant fly ash-based geopolymers using NaOH solution as alkaline solution. This new approach could be an interesting way of recycling a fraction of glass currently landfilled, representing a significant economic advantage as well as an environmentally friendly solution to the landfill problems. Soda-lime glass cullet was proven to be a viable substitute for the commercial sodium silicate solutions commonly used to prepare geopolymers. In addition, the mechanical properties increased with increasing molarity of the activating solution, the same trend was observed with the increase of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  theoretical molar ratio. An excessive molarity of NaOH solution was found to induce strength loss as function of time, as an effect of ageing. The formation of the geopolymeric gel was confirmed by the formation of zeolite crystalline phases, detected by the XRD analysis. The leaching of heavy metals from selected compositions was found to meet the current regulatory thresholds for non-hazardous materials indicating that pollutants can be successfully stabilized in the geopolymeric matrix, despite the unconventional formulation.

#### Conflict of interest

The authors declare no conflict of interest related to this work.

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#### References

- [1] J. Davidovits, *Geopolymer Chemistry and Applications*, 3rd Edition., Geopolymer Institute, 2011.
- [2] R.H. Kupaei, U.J. Alengaram, M.Z. Jumaat, The effect of different parameters on the development of compressive strength of oil palm shell geopolymer concrete, *Sci. World J.* 2014 (2014) 898536.
- [3] T. Ostwal, M.V. Chitawadagi, Experimental investigations on strength, durability, sustainability and economic characteristics of geopolymer concrete blocks, *Int. J. Res. Eng. Technol.* 3 (2014) 115–122.
- [4] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J. Van Deventer, *Geopolymer technology: the current state of the art*, *J. Mater. Sci.* 42 (2007) 2917–2933.
- [5] N. Toniolo, A.R. Boccaccini, Fly ash-based geopolymers containing added silicate waste. A review, *Ceram. Int.* 43 (2017) 14545–14551.
- [6] A. Fernández-Jiménez, N. Cristelo, T. Miranda, Á. Palomo, Sustainable alkali activated materials: precursor and activator derived from industrial wastes, *J. Clean Prod.* (2017).
- [7] M. Safiuddin, M.Z. Jumaat, M. Salam, M. Islam, R. Hashim, Utilization of solid wastes in construction materials, *Int. J. Phys. Sci.* 5 (2010) 1952–1963.
- [8] N. Nordin, M.M.A.B. Abdullah, M.F.M. Tahir, A.V. Sandu, K. Hussin, Utilization of fly ash waste as construction material, *Int. J. Conserv. Sci.* 7 (2016).
- [9] E. Arioz, O. Arioz, O.M. Kockar, Leaching of F-type fly ash based geopolymers, *Proc. Eng.* 42 (2012) 1114–1120.
- [10] J. Feng, R. Zhang, L. Gong, Y. Li, W. Cao, X. Cheng, Development of porous fly ash-based geopolymer with low thermal conductivity, *Mater. Des.* (1980–2015) 65 (2015) 529–533.
- [11] A. Rincón, G. Giacomello, M. Pasetto, E. Bernardo, Novel 'inorganic gel casting' process for the manufacturing of glass foams, *J. Eur. Ceram. Soc.* 37 (2017) 2227–2234.
- [12] F. Puertas, M. Torres-Carrasco, Use of glass waste as an activator in the preparation of alkali-activated slag. Mechanical strength and paste characterisation, *Cem. Concr. Res.* 57 (2014) 95–104.
- [13] M. Torres-Carrasco, J. Palomo, F. Puertas, Sodium silicate solutions from dissolution of glasswastes. Statistical analysis, *Mater. Constr.* 64 (2014) 014.
- [14] R. Martínez-López, J.I. Escalante-García, Alkali activated composite binders of waste silica soda lime glass and blast furnace slag: Strength as a function of the composition, *Constr. Build. Mater.* 119 (2016) 119–129.
- [15] ASTM C. 618-03, Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete, 2003.
- [16] U. Rattanasak, P. Chindaprasit, Influence of NaOH solution on the synthesis of fly ash geopolymer, *Miner. Eng.* 22 (2009) 1073–1078.
- [17] V.F. Barbosa, K.J. MacKenzie, Thermal behaviour of inorganic geopolymers and composites derived from sodium polysialate, *Mater. Res. Bull.* 38 (2003) 319–331.
- [18] M. Ezzat, H. Khater, M. Abdeen, Enhanced characteristics of alkali activated slag/grog geopolymer bricks, *JSAER* 7 (2016).
- [19] Y. Lee, Y.L. Peng, M. Tomozawa, IR reflection spectroscopy of a soda-lime glass surface during ion-exchange, *J. Non Cryst. Solids* 222 (1997) 125–130.
- [20] G. Mucsi, R. Szabo, Á. Racz, Z. Molnar, F. Kristály, S. Kumar, Influence of red mud on the properties of geopolymer derived from mechanically activated lignite fly ash, 2015, 211–7.
- [21] M.A. Longhi, E.D. Rodríguez, S.A. Bernal, J.L. Provis, A.P. Kirchheim, Valorisation of a kaolin mining waste for the production of geopolymers, *J. Clean Prod.* 115 (2016) 265–272.
- [22] S. Kramar, V. Ducman, Mechanical and microstructural characterization of geopolymer synthesized from low calcium fly ash, *Chem. Ind. Chem. Eng. Quart.* 21 (2015) 13–22.
- [23] M. Torres-Carrasco, F. Puertas, Waste glass in the geopolymer preparation. Mechanical and microstructural characterisation, *J. Clean Prod.* 90 (2015) 397–408.
- [24] C. Heah, H. Kamarudin, A.M. Al Bakri, M. Bnhussain, M. Luqman, I.K. Nizar, et al., Kaolin-based geopolymers with various NaOH concentrations, *Int. J. Miner. Metall. Mater.* 20 (2013) 313–322.
- [25] R.M. Novais, G. Ascensão, M. Seabra, J. Labrincha, Waste glass from end-of-life fluorescent lamps as raw material in geopolymers, *Waste Manage.* 52 (2016) 245–255.
- [26] V. Živica, M.T. Palou, M. Križma, Geopolymer cements and their properties: a review, *Build. Res. J.* 61 (2014) 85–100.
- [27] S. Usha, D.G. Nair, S. Vishnudas, Feasibility study of geopolymer binder from terracotta roof tile waste, *Proc. Technol.* 25 (2016) 186–193.
- [28] H. Kamarudin, A.M. Al Bakri, M. Bnhussain, C. Ruzaidi, M. Luqman, C. Heah, et al. Preliminary study on effect of NaOH concentration on early age compressive strength of kaolin-based green cement, 2011, 10, 18–24.
- [29] J.L. Provis, J.S.J. Van Deventer, *Geopolymers: Structures, Processing, and Industrial Applications*, Elsevier, 2009.
- [30] A. Arulrajah, T. Kua, S. Horpibulsuk, C. Phetchuay, C. Sukiripattanapong, Y. Du, Strength and microstructure evaluation of recycled glass-fly ash geopolymer as low-carbon masonry units, *Constr. Build. Mater.* 114 (2016) 400–406.
- [31] C. Bobirić, J. Shim, J. Pyeon, J. Park, Influence of waste glass on the microstructure and strength of inorganic polymers, *Ceram. Int.* 41 (2015) 13638–13649.
- [32] J.S.J. Van Deventer, G.C. Lukey, H. Xu, Effect of curing temperature and silicate concentration on fly-ash-based geopolymerization, *Ind. Eng. Chem. Res.* 45 (2006) 3559–3568.
- [33] S. Tamburini, M. Natali, E. Garbin, M. Panizza, M. Favaro, M.R. Valluzzi, Geopolymer matrix for fibre reinforced composites aimed at strengthening masonry structures, *Constr. Build. Mater.* 141 (2017) 542–552.

- [34] D.L. Kong, J.G. Sanjayan, K. Sagoe-Crentsil, Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures, *Cem. Concr. Res.* 37 (2007) 1583–1589.
- [35] X. Ren, L. Zhang, D. Ramey, B. Waterman, S. Ormsby, Utilization of aluminum sludge (AS) to enhance mine tailings-based geopolymer, *J. Mater. Sci.* 50 (2015) 1370–1381.
- [36] M.R. Rowles, B.H. O'Connor, Chemical and structural microanalysis of aluminosilicate geopolymers synthesized by sodium silicate activation of metakaolinite, *J. Am. Ceram. Soc.* 92 (2009) 2354–2361.
- [37] W.E. Stone, G.M. El Shafei, J. Sanz, S.A. Selim, Association of soluble aluminum ionic species with a silica-gel surface: a solid-state NMR study, *J. Phys. Chem.* 97 (1993) 10127–10132.
- [38] I. Ismail, S.A. Bernal, J.L. Provis, R. San Nicolas, S. Hamdan, J.S. van Deventer, Modification of phase evolution in alkali-activated blast furnace slag by the incorporation of fly ash, *Cem. Concr. Compos.* 45 (2014) 125–135.
- [39] M. Cyr, R. Idir, T. Poinot, Properties of inorganic polymer (geopolymer) mortars made of glass cullet, *J. Mater. Sci.* 47 (2012) 2782–2797.
- [40] J. Xu, Y. Zhou, Q. Chang, H. Qu, Study on the factors of affecting the immobilization of heavy metals in fly ash-based geopolymers, *Mater. Lett.* 60 (2006) 820–822.
- [41] Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. *Official Journal of the European Communities* 2003, 16, L11.