# Coal fly ash-slag-based geopolymers: Microstructure and metal leaching

Maria Izquierdo [a,*], Xavier Querol [a], Joseph Davidovits [b], Diano Antenucci [c], Henk Nugteren [d], Constantino Fernández-Pereira [e]

[a] Institute of Earth Sciences "Jaume Almera"–CSIC, Lluis Solé Sabaris s/n 08028 Barcelona, Spain
[b] Cordi-Géopolymère, Espace Créatis, Z.A. Bois de la Chocque 02100 Saint-Quentin, France
[c] Institut Scientifique de Service Public (ISSeP) 200, rue du Chéra, B-4000 Liège, Belgium
[d] Delft University of Technology, Faculty of Applied Sciences, DelftChemTech, Particle Technology Group, Julianalaan 136, 2628 BL Delft, The Netherlands
[e] University of Seville, School of Industrial Engineering, Department of Chemical and Environmental Engineering, Camino de los Descubrimientos s/n, 41092 Seville, Spain

## ARTICLE INFO

## ABSTRACT

This study deals with the use of fly ash as a starting material for geopolymeric matrices. The leachable concentrations of geopolymers were compared with those of the starting fly ash to evaluate the retention of potentially harmful elements within the geopolymer matrix. Geopolymer matrices give rise to a leaching scenario characterised by a highly alkaline environment, which inhibits the leaching of heavy metals but may enhance the mobilization of certain oxyanionic species. Thus, fly ash-based geopolymers were found to immobilise a number of trace pollutants such as Be, Bi, Cd, Co, Cr, Cu, Nb, Ni, Pb, Sn, Th, U, Y, Zr and rare earth elements. However, the leachable levels of elements occurring in their oxyanionic form such as As, B, Mo, Se, V and W were increased after geopolymerization. This suggests that an optimal dosage, synthesis and curing conditions are essential in order to obtain a long-term stable final product that ensures an efficient physical encapsulation.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Over 40 million tonnes per year of fly ash are produced in Europe [1]. As far as the environment is concerned, the disposal of fly ash should not be regarded as a sustainable management strategy. Given the EU regulations, it is crucial to develop new technologies that allow the recycling of coal fly ash into added-value products. In this regard, the synthesis of geopolymer binders may be a successful alternative, resulting in low-cost and environmentally friendly materials with cementing properties resembling those of OPC [2].

Geopolymers were introduced by Davidovits in the early 1970s to describe inorganic materials obtained from the chemical reaction of alumino-silicate oxides with alkali silicates, yielding polymeric Si—O—Al bonds [3]. The network consists of $SiO_4$ and $AlO_4$ tetrahedra linked alternately by sharing all the oxygen. The $Al^{3+}$ in IV-fold coordination demands the presence of cations in the framework to balance the negative charge. According to Davidovits [2], the empirical formula of geopolymers, also known as poly(sialates) is as follows Eq. (1):

$$M_n\{-(SiO_2)_z-AlO_2\}_n\cdot wH_2O \qquad (1)$$

where M is a cation such as $K^+$, $Na^+$ or $Ca^{2+}$; $n$, the degree of polycondensation and $z$ is 1, 2 or 3. Other cations such as $Li^+$, $Ba^{2+}$, $NH_4^+$ and $H_30^+$ may also be present.

Research on the geopolymer green-chemistry conducted in recent years has resulted in the development of new cements based on natural materials (mainly kaolinite and metakaolin) or industrial wastes, with particular emphasis on pulverised coal combustion (PCC) fly ash [4–16]. Geopolymerization of fly ash may involve environmental benefits such as (1) the reduction in consumption of natural resources and (2) the decrease in the net production of $CO_2$ since it is estimated that the geopolymer cement synthesis emits 5–6 times less $CO_2$ when compared with Portland cement [11].

Given the physical performance of the final product, geopolymerization has become a promising technology that offers attractive possibilities for commercial applications, i.e. fast hardening, high and early compressive strength, optimal acid resistance and long term durability [17]. The synthesis of geopolymer matrices has proved to be an optimal and feasible option to stabilize certain metallic and radioactive wastes [18–20] or industrial wastewater [21].

Although the microstructure, chemistry and mechanical properties of fly ash-based geopolymers have been extensively studied, less attention has been paid to the leaching behaviour. The leaching properties have been assessed mainly on pulverised material under acidic conditions and essentially focused on Cd, Cr, Cu and Pb [9–10,12–14,22]. It could be expected that the acidic conditions and the size reduction could overestimate the releases of a number

of elements, which would provide safe-side predictions. However, predicted releases could underestimate the actual releases of certain elements when the pH is governed by the material itself, i.e. highly alkaline conditions. Moreover, other potentially harmful trace pollutants such as As, Mo, Sb or V have been overlooked in prior studies despite their environmental concern.

As for the environment, the leaching behaviour of fly ash-based geopolymer binders should be addressed with a view to its application. This is of particular significance in geopolymers synthesised by means of a user-friendly procedure, i.e. low-alkaline and low-temperature, such as those used in this study. Despite the evident economic and environmental benefits, the mild conditions of activation should not compromise the retention of trace pollutants. This study seeks to (1) determine the effect exerted by a user-friendly geopolymerization procedure on the microstructure, particle morphology and leaching properties of the final product and (2) identify the elements of environmental concern of fly ash/slag/K-silicate/$H_2O$ geopolymer systems and their retention efficiency.

## 2. Experimental

### 2.1. Starting fly ash samples

This study was conducted on 11 class F fly ash samples from different power plants located in Spain (A1, C1–C4), The Netherlands (T1–T5) and Belgium (I6). The sampling was performed within the framework of an EU R+D project (GEOASH, RFC-CR-04005). Six

samples were obtained from the combustion of coal, whereas the 5 others are co-fired fly ash obtained from the combustion of coal (>75%) with minor amounts of alternative fuels such as petroleum coke, sewage sludge and olive waste (Table 1). Fly ash samples were acid-digested by using a special two-step digestion method devised for the analysis of trace elements in coal and combustion wastes by Querol et al. [23]. An additional hydrofluoric acid digestion described by Thompson and Walsh [24] was carried out to determine the silica contents by ICP–AES. The fly ash and coal international reference materials NBS 1633b and SARM 19, respectively, were also digested to check the accuracy of the analytical and digestion methods. A chemical and environmental characterisation of a number of these fly ash samples was previously published by the authors [25]. Major, minor and trace element concentrations in solid samples were determined by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

### 2.2. Synthesis

The synthesis of geopolymer bodies was performed by following the method based on the fly ash/slag/K-silicate/$H_2O$ system reacting without thermal activation. Fly ash was mixed with blast furnace slag from a steel plant in the Czech Republic (Table 1), water and an activator solution. This consists of a potassium silicate and potassium hydroxide solution with $SiO_2/K_2O = 1.25$. The use of KOH accounts for a marked alkalinity in the geopolymer system, with consequences on the mobility of trace pollutants.

**Table 1**
Concentrations of a number of elements in fly ash samples, composition of the feed fuel blend and dosages of constituents used in geopolymer synthesis.

| Sample, fuel blend, coal, others | I6 90% Biomass | A1 100% | C1 100% | C2 100% | C3 76% Petcoke | C4 96% Petcoke | T1 86% Biomass | T2 90% Biomass | T3 100% | T4 100% | T5 100% | Slag – |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Composition (wt%)* | | | | | | | | | | | | |
| $SiO_2$ | 50 | 58 | 54 | 43 | 52 | 51 | 49 | 50 | 47 | 53 | 52 | 39 |
| $Al_2O_3$ | 29 | 23 | 23 | 26 | 25 | 26 | 28 | 21 | 25 | 27 | 29 | 11 |
| CaO | 5.2 | 3.5 | 3.5 | 5.3 | 3.0 | 2.9 | 6.4 | 4.5 | 6.9 | 3.1 | 1.7 | 41 |
| $Na_2O$ | 0.3 | 0.6 | 0.9 | 0.1 | 0.7 | 0.7 | 0.3 | 0.6 | 1.2 | 0.1 | 0.5 | 0.3 |
| $K_2O$ | 1.4 | 1.6 | 3.2 | 1.2 | 3.6 | 3.6 | 0.8 | 4.3 | 1.9 | 0.5 | 2.3 | 0.4 |
| MgO | 1.2 | 1.8 | 2.0 | 1.2 | 1.8 | 1.8 | 1.7 | 1.9 | 3.8 | 0.6 | 1.0 | 7.0 |
| MnO | 0.04 | 0.1 | 0.1 | 0.04 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.03 | 0.3 |
| $TiO_2$ | 1.4 | 1.1 | 1.0 | 0.9 | 1.0 | 1.0 | 1.8 | 0.5 | 0.9 | 1.8 | 1.5 | 0.5 |
| $SO_3$ | 0.7 | 0.2 | 0.4 | 0.9 | 0.5 | 0.5 | 0.4 | 0.9 | 1.0 | 0.5 | 0.4 | 2.2 |
| $P_2O_5$ | 2.2 | 0.5 | 0.8 | 0.5 | 0.6 | 0.5 | 1.1 | 0.8 | 0.7 | 1.6 | 0.2 | <0.02 |
| $Fe_2O_3$ | 5.8 | 6.1 | 8.5 | 19 | 7.0 | 6.9 | 4.3 | 8.0 | 9.3 | 7.4 | 8.3 | 0.3 |
| *Composition (mg/kg)* | | | | | | | | | | | | |
| As | 38 | 24 | 73 | 133 | 91 | 98 | 66 | 45 | 48 | 55 | 109 | 2 |
| B | 239 | 217 | 66 | 396 | 81 | 100 | 396 | 328 | 297 | 255 | 97 | 27 |
| Ba | 2293 | 1287 | 1009 | 684 | 1324 | 1412 | 1811 | 1370 | 2037 | 2182 | 1757 | 680 |
| Cd | 3 | 3 | 4 | 2 | 2 | 2 | 4 | 6 | 2 | 2 | 1 | 0.5 |
| Co | 44 | 33 | 29 | 35 | 40 | 38 | 64 | 50 | 55 | 112 | 72 | 0.4 |
| Cr | 221 | 167 | 156 | 182 | 231 | 210 | 204 | 200 | 140 | 196 | 171 | 16 |
| Cu | 189 | 97 | 87 | 62 | 112 | 113 | 112 | 106 | 186 | 154 | 254 | 5 |
| Li | 244 | 153 | 166 | 283 | 238 | 241 | 186 | 149 | 167 | 79 | 268 | 76 |
| Mo | 12 | 17 | 11 | 15 | 27 | 14 | 15 | 17 | 13 | 7 | 14 | <0.01 |
| Ni | 131 | 102 | 65 | 97 | 882 | 158 | 139 | 131 | 152 | 377 | 136 | 4 |
| Pb | 146 | 47 | 71 | 94 | 152 | 130 | 90 | 72 | 208 | 54 | 102 | 1 |
| Rb | 45 | 78 | 154 | 96 | 198 | 207 | 42 | 100 | 108 | 22 | 127 | 11 |
| Sb | 23 | 6 | 20 | 6 | 19 | 19 | 5 | 6 | 17 | 2 | 9 | <0.01 |
| Se | 14 | 19 | 2 | 35 | 23 | 22 | 44 | 34 | – | – | – | 2 |
| Sn | 21 | 6 | 7 | 12 | 12 | 12 | 11 | 7 | 10 | 9 | 10 | 0.1 |
| Sr | 1258 | 1017 | 396 | 978 | 577 | 595 | 1717 | 1116 | 1189 | 988 | 1920 | 951 |
| U | 11 | 7 | 10 | 19 | 7 | 7 | 13 | 11 | 25 | 5 | 17 | 13 |
| V | 125 | 248 | 218 | 202 | 3894 | 401 | 286 | 231 | 325 | 226 | 323 | 20 |
| Zn | 392 | 136 | 110 | 217 | 193 | 185 | 121 | 177 | 200 | 153 | 143 | 47 |
| *Dosage (%)* | | | | | | | | | | | | |
| Fly ash | 59 | 57 | 68 | 68 | 70 | 68 | 59 | 59 | 63 | 63 | 61 | – |
| Slag | 18 | 17 | 13 | 13 | 12 | 12 | 18 | 18 | 16 | 16 | 17 | – |
| Water | 12 | 14 | 11 | 11 | 11 | 11 | 12 | 12 | 11 | 11 | 11 | – |
| K-Sil | 12 | 11 | 9 | 8 | 8 | 8 | 12 | 12 | 11 | 11 | 11 | – |
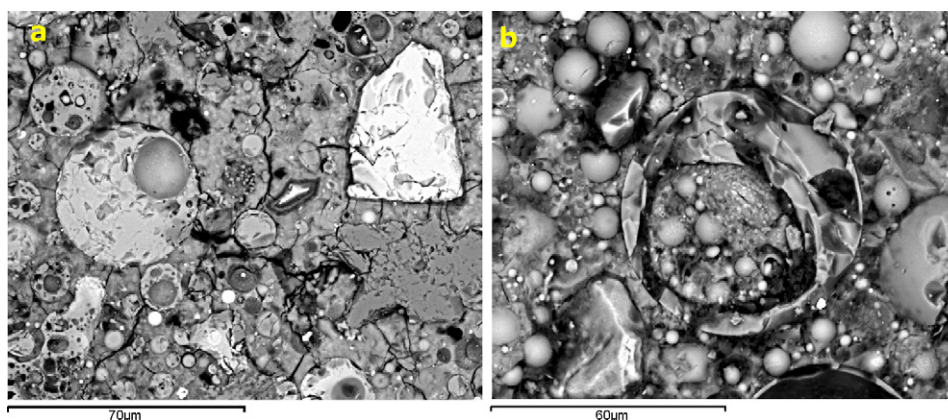
**Fig. 1.** Scanning electron photomicrographs in back-scattered and secondary electron (b) modes of fly ash-based geopolymer samples.

The chemical and physical properties exert a major influence on the tixotropic behaviour and consequently on the workability of the paste. For this reason, the fly ash proportions used in the synthesis differ between samples, ranging from 57% to 70% of the geopolymer mass (Table 1). Geopolymer pastes were vibrated by means of a vibrating table, then poured into cylindrical containers (diameter 29 and 39 mm height) and cured in the closed container at room temperature for 28 days.

### 2.3. Microstructure

The microstructure, occurrence and distribution of major elements over the geopolymer matrices were investigated by means of S-360 Stereoscan Scanning Electron Microscope coupled with EDX micro-analysis. A Cameca SX-50 Electron Microprobe allowed us to determine the quantitative composition of the geopolymer matrix.

### 2.4. Leaching

The EN 12457-2 [26] single batch leaching test was applied to determine the leachable contents of elements in fly ash, in the steel slag and in the fly ash-based geopolymer. Geopolymer bodies were crushed and size-reduced down to 200 μm. The leaching test was performed at a L/S ratio of 10 L/kg dry matter and deionised water as leachant. The agitation was applied with a vertical rotary shaker (10 rpm) for 24 h. Analyses were performed in duplicate in all cases. Major, minor and trace element concentrations in leachates were determined by means of ICP-AES and ICP-MS.

It should be borne in mind that the EN 12457-2 leaching test conducted on pulverised material may lead to overestimated predictions of geopolymer leaching as the surface area available for leaching is considerably higher. Such aggressive conditions do not resemble a real scenario of application. However, it is not the main purpose of this study to assess the environmental impact that arising from this utilization of fly ash, but rather to ascertain whether chemical immobilisation of trace pollutants occurs. To this end, geopolymer samples were size-reduced prior to the leaching test with the result that the physical retention effects were minimised.

## 3. Results and discussion

### 3.1. Geopolymer microstructure

Fly ash-slag-based geopolymers are a multi-component system mainly made up of the following constituents: (1) a relatively dense packing of relict particles from the starting materials, namely fly ash and slag, (2) the geopolymer matrix, i.e. the undifferenti-

ated and homogeneous mass surrounding and cementing particles and (3) porosity, present as interstitial and intra-particular porosity (Fig. 1a). The observed heterogeneity is consistent with other studies [16].

A similar microstructure was observed in all the samples, which suggests that geopolymerization reactions may be similar regardless of the sample. In agreement with the findings of other authors, relict fly ash particles are the main constituent [8,16], characterised by spherical-shaped particles of aluminosilicate glass and magnetite in minor proportions. This indicates that only the external rim of the particles may play a role in the development of the binder. The weak dissolution observed is consistent with a low-temperature and low-alkaline activation geopolymerization procedure. However, hollow cenospheres with geopolymer matrix grown within the intragranular pores (Fig. 1b) provided evidence of a partial corrosion [7] enabling the entry and growth of the newly formed binder. In contrast, magnetite (small, bright spherical shapes in Fig. 1a) and mullite (acicular crystals on glassy spheres) particles are embedded in the matrix with no clear signs of apparent corrosion [15] and appear to remain unreactive during the geopolymerization process. Inert particles could be regarded as disruptive components that should be minimised in order to ensure the quality of the final product.

SEM observations also revealed the significant degree of isolated porosity in geopolymer microstructure, which is consistent with other studies [15]. The occurrence of cenospheres accounted for most of the subspherical isolated vesicles, but an additional contribution consisted of interstitial spherical gas cavities distributed randomly.

Microprobe analysis allowed the determination of the contents of major elements in the newly formed geopolymer matrix surrounding the relict particles (Fig. 2). The major composition of the geopolymer matrix is relatively similar among samples, regardless of the fly ash composition used as reagent. Moreover, it was observed that the proximity of other particular constituents to the measurement area did not exert a significant impact on the matrix composition.

$SiO_2$ is the most abundant constituent of the geopolymer cement (around 50%), followed by $Al_2O_3$ (20–25% range) and CaO (12–15%). It is worth noting that the proportion among these main constituents varied little, particularly the silica content (Fig. 2). Other constituents also present in minor amounts were $K_2O$ (3–8%), followed by $Fe_2O_3$ (4%), MgO (1–4%), $SO_3$ (1.5%) and $Na_2O$ (0.6%). Based on the above results and given that the molar proportions of $Fe_2O_3$, $SO_3$ and $Na_2O$ are very low, the geopolymer composition may be summarised as follows Eq. (2). The glassy particles of fly ash mainly provide silica and alumina to the geopolymer system. The activation solution supplies silica and potassium while slag accounts for
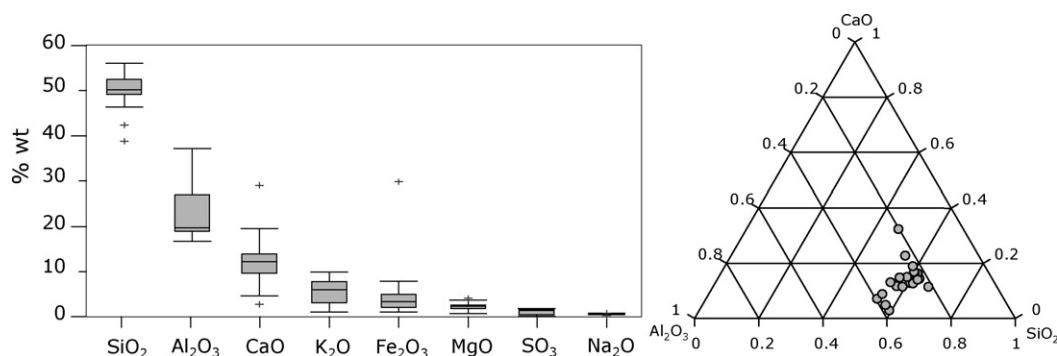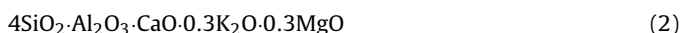
**Fig. 2.** Composition of geopolymer matrix ($n = 25$ in different geopolymer bodies).

the relatively high calcium and magnesium contents.

$$4SiO_2 \cdot Al_2O_3 \cdot CaO \cdot 0.3K_2O \cdot 0.3MgO \qquad (2)$$

The overall particle morphology of fly ash was not markedly modified during the geopolymerization process, but the main difference was the binder development cementing particles. Hence, the geopolymerization without thermal activation could be regarded as a superficial reaction based on diffusion mechanisms rather than on a complete dissolution and subsequent formation of species. With such a weak dissolution, a strong assimilation of trace pollutants within the binder structure is not expected.

### 3.2. Comparison between leachable contents in fly ash and fly ash-based geopolymer

Results of leaching of a given geopolymer were compared with the leaching of the corresponding starting fly ash in an attempt to ascertain whether the geopolymerization enhances or inhibits the mobility of certain elements. Although fly ash is the main constituent of the geopolymer system, the remaining constituents may exert a dilution effect on trace pollutants. For this reason, in Fig. 3 the releases of a number of elements in the geopolymer leachates are plotted against the releases in the corresponding fly ash but weighted in the fly ash dosage of each geopolymer. The steel slag is depleted in trace pollutants (Table 1) and the overall solubility is very low, as deduced by the low leachable concentrations determined. Therefore, its contribution to the geopolymer leaching is extremely low.

The pH of fly ash-based geopolymer leachates is clearly alkaline, ranging from 10.5 to 12.6 (12.2 on average). These values differ from those observed in fly ash leachates (8–11). The higher alkalinity is mainly attributable to the addition of KOH to the activation solution and may have an impact on the mobility of metals with a strong pH-dependent solubility.

As shown in Fig. 3, water leachable contents of geopolymer bodies are different from those observed in fly ash. The leachable levels of Ca, Sr and Ba decreased about one order of magnitude after geopolymerization, which is in line with the findings of Bankowski et al. [7]. These elements could have been dissolved from slag and fly ash (presumably in sulphate form) and subsequently act as charge-balancer of the system, occurring in cavities of geopolymer framework. However, a subsequent precipitation occurring in highly insoluble modes of occurrence, e.g. $BaSO_4$ or $SrCO_3$ [27] may also account for the lower mobility. Bearing in mind the high ionic radii of $Sr^{2+}$ and $Ba^{2+}$, the precipitation of insoluble salts under highly alkaline geopolymerization conditions could be the prevailing immobilization mechanism for the above elements.

Cd, Cu and other trace pollutants not depicted in Fig. 3 such as Be, Bi, Cd, Co, Cu, Nb, Ni, Pb, REE, Sn, Th, Y and Zr showed very low leachable concentrations in the starting fly ash remaining at very low levels after geopolymerization (<0.05 mg/kg and in a number of cases below the detection limit) in all samples. The releases of Zn slightly increased in certain samples after geopolymerization but values were of little significance (<0.2 mg/kg). Other major elements such as Fe, Mg and P were retained and their leachable contents were below the detection limit. It should be noted that I6 fly ash was obtained from the co-firing of sewage sludge with
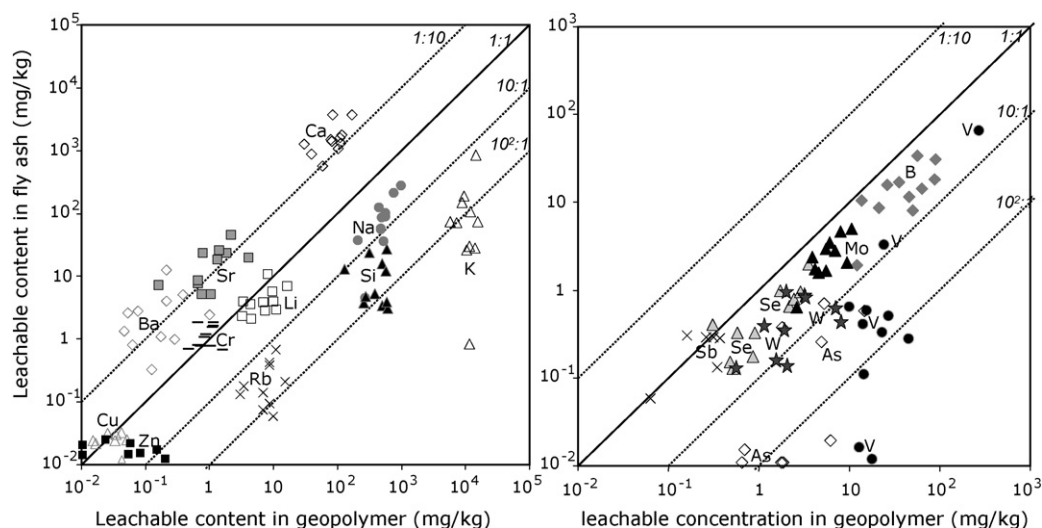


**Fig. 3.** Leachable concentrations of a number of elements in fly ash (weighted in the dosage used in the synthesis) and their derived fly ash-based geopolymers.

coal resulting in a slight enrichment of elements such as P, Cu, Zn or Sn [25]. However, this enrichment did not lead to higher leachable contents in the derived geopolymer sample but these elements remained highly immobile. Hence, the aforementioned elements should not be regarded as a matter of concern in the geopolymers studied.

As shown in Fig. 3, a number of elements displayed higher releases in the geopolymer leachates with respect to their corresponding releases in the fly ash leachates. These may be subdivided into 2 main groups according to their main source.

### 3.2.1. Elements supplied by the activation solution and the slag

The K-silicate-hydroxide solution may not completely react with fly ash but a remaining proportion could precipitate during the curing period as highly soluble salts. The subsequent remobilization in contact with the leachant resulted in very high leachable concentrations of K (up to 14.8 wt%) and Si (125–600 mg/kg). This reagent could also account for minor releases of elements with similar geochemical behaviour of K such as Na, Rb or Li, probably present as impurities in the K-silicate–hydroxide solution. Furthermore, significantly high releases of $SO_4^{2-}$ were determined (up to 17,600 mg/kg), with values higher than the bulk content of this major element in fly ash. As stated above, slag is partially dissolved to provide the required elements in order to form the geopolymer binder. However, in contrast to Ca, S present in slag is released without being subsequently assimilated in the geopolymer network but remaining easily leachable. This would account for the large leachable concentrations, in addition to those arising from fly ash.

### 3.2.2. Elements supplied by fly ash

Particular emphasis should be laid on As, B, Mo, Se, V and W, which have higher concentrations in the geopolymer leachates than in fly ash leachates and are regarded as being of major concern in fly ash owing to their mobility. Assuming that their bulk content in the geopolymer is similar to or lower than in the starting fly ash (main source), higher releases cannot be correlated with higher contents in the geopolymer. Rather, they could be linked to changes in the speciation or mode of occurrence during the geopolymerization reactions. Moreover, the mobility could be enhanced by the new leaching conditions after geopolymerization, i.e. a highly alkaline environment. It could be expected that the mild activation applied may not drastically modify the speciation or mode of occurrence of elements in fly ash during the treatment. It is therefore reasonable to assume that the different leaching behaviour could be mainly attributed to the effect of different leaching conditions, particularly the higher pH.

V and As revealed a mobility particularly sensitive to the pH. The leachable concentrations of V showed a 2 order-of-magnitude increase after geopolymerization. This may lead to potentially harmful releases in geopolymer matrices synthesised using V-enriched fly ash samples, such as those obtained from the co-firing of petroleum coke with coal (C3 fly ash). Thus, the resulting geopolymer showed a leachable content of V reaching 260 mg/kg. The V releases of the remaining fly ash-based geopolymer samples were lower but still of concern (12–43 mg/kg). The leachable concentrations of As increased after geopolymerization with the result that the values were one order of magnitude higher in the geopolymer than in the starting fly ash. In this case this increased mobility gave rise to values of environmental concern, ranging from 1 to 14 mg/kg. The leaching behaviour of As in alkali-activated matrices has been carefully studied by Fernández-Jiménez et al. [28]. According to these authors, the immobilization is hindered by higher Fe contents in the starting material, but a clear correlation between As releases and Fe concentrations in the fly ash could not determined in our study.

Geopolymer samples revealed higher leachable concentrations of B, Se and W. Although Se was not leached in large amounts (0.3–3.3 mg/kg) the relatively low toxicity threshold of this element should be borne in mind. Geopolymerization also promoted the mobility of Mo. The relatively soluble mode of occurrence of Mo yielded releases achieving 10 mg/kg. Other elements occurring as oxyanionic species under alkaline conditions showed a different trend. The leachable concentrations of Sb in geopolymers were very close to those of fly ash while the releases of Cr were slightly reduced and U releases remained below the detection limit. It can be deduced that, with the exception of Cd, Sb and U, the mobility of the oxyanionic species was raised after the geopolymerization of fly ash. This could be attributed to the fact that (1) these elements may not play a major role in the geopolymer formation, remaining relatively available for leaching, and that (2) the mobility of these species is enhanced by highly alkaline conditions.

### 3.3. Retention of trace pollutants

Results from the leaching test provided valuable information on the relative availability of trace pollutants and, hence, on the extent of retention.

### 3.3.1. Framework retention

The weak dissolution occurring under the studied geopolymerization conditions hinders the complete assimilation of trace pollutants as matrix forming elements. Thus, the effect of the retention of trace pollutants within the geopolymer structure is of little significance, with the exception of Ca.

### 3.3.2. Chemical retention

The synthesis of geopolymers could be a feasible option to chemically immobilise high Ba, Ca, Cu, Cd, Fe, Ni, P, Pb, Sr, Sn and Zn wastes. Some of these elements could display a certain geopolymer framework retention and may be partially assimilated by the geopolymer structure [10,12]. However, the alkaline conditions provided by geopolymer synthesis may strongly contribute to the inhibition of metal mobility. This behaviour could be regarded as a strong chemical retention together with an additional physical micro-encapsulation mechanism [10]. In this regard, it may be deduced that the environmental properties of certain metallic wastes could be considerably improved after geopolymerization. This chemical retention efficiency is consistent with other studies on heavy metal immobilization, particularly for Cd, Cu, Cr (III) and Pb [13–14,22].

In contrast, the relatively high solubility of As, V, Mo, Se and W provides evidence that the chemical immobilisation is weak. Consequently, geopolymerization may not be a successful treatment for materials enriched in these species unless a strong and long-term durable physical encapsulation is ensured. Nevertheless, it should be borne in mind that the chemical retention efficiency is highly dependant on several factors, namely (1) the metal content, (2) the evolution of the material and (3) the derived leaching conditions (mainly the pH), with the result that the long-term leaching behaviour could be different.

### 3.3.3. Physical retention

It goes without saying that the development of the geopolymer binder inhibits percolation and decreases infiltration, resulting in a lower overall leaching with respect to the pulverised material. In the case of oxyanionic species, the results obtained indicated that this encapsulation effect may be virtually the sole retention mechanism. Nevertheless, specific leaching tests are envisaged in future research, particularly monolithic leaching tests to accurately assess the degree of physical retention of oxyanionic species.

The results obtained stressed the crucial role played by physical properties and durability aspects in the leaching properties. The above observations highlighted the need for an optimal dosage, manufacturing and curing of pastes in order to synthesise geopolymer bodies with low porosity and a long-term stability. The foregoing should be taken into account given that the efficiency of heavy metal immobilization is strongly related to the binder microstructure [14] and composition [10,12]. Thus, the optimisation of dosages and synthesis conditions is required to ensure the environmental quality of the final product without compromising mechanical performance and long-term durability.

## 4. Conclusions

The user-friendly geopolymerization conditions applied to the system fly ash/slag/K-silicate/$H_2O$ yielded geopolymer bodies resembling concrete product, since the geopolymer product acts as a binder of enclosed relict fly ash and slag particles. The alkaline conditions of synthesised fly ash-based geopolymer inhibit the metal mobility with the result that a number of trace pollutants such as Ba, Be, Bi, Cd, Co, Cr, Cu, Nb, Ni, Pb, REE, Sr, Sn, Th, U, Y and Zr are retained. A minor assimilation as charge-balancing elements within the geopolymer framework could also contribute to the very low leached levels, but this may be of little relevance given the weak dissolution observed. At the same time, the high pH values enhance the oxyanionic mobility, increasing the releases of As, B, Mo, Se, V and W. Oxyanionic elements are not assimilated within the geopolymer structure but remain presumably encapsulated although the physical retention degree should be corroborated by means of specific leaching tests. Thus, the main mechanism of immobilization in the studied fly ash/slag/K-silicate/$H_2O$ geopolymers could be essentially physical encapsulation rather than chemical stabilization. This underlines the fact that an optimal dosage, the synthesis and the curing conditions are crucial for the environmental properties of the final product.

## Acknowledgements

## References

[1] Ecoba, 2005, http://www.ecoba.com.
[2] J. Davidovits, Geopolymers: inorganic polymeric new materials, J. Therm. Anal. 37 (1991) 1633–1656.
[3] J. Davidovits, SPE PACTEC '79, Society of Plastic Engineers, Brookfield Center, USA, 1979, p. 151.
[4] J.G.S. van Jaarsveld, J.S.J. Van Deventer, The effect of metal contaminants on the formation and properties of waste-based geopolymers, Cement Concrete Res. 29 (1999) 1189–1200.
[5] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, G.C. Lukey, The effect of composition and temperature on the properties of fly ash- and kaolinite-based geopolymers, Chem. Eng. J. 89 (2002) 63–73.
[6] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, G.C. Lukey, The characterisation of source materials in fly ash-based geopolymers, Mater. Lett. 57 (2003) 1272–1280.
[7] P. Bankowski, L. Zou, R. Hodges, Using inorganic polymer to reduce leach rates of metals from brown coal fly ash, Miner. Eng. 17 (2004) 159–166.
[8] J.S.J. van Deventer, J.L. Provis, P. Duxson, G.C. Lukey, Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products, J. Hazard. Mater. 139 (2007) 506–513.
[9] M. Mináriková, F. Škvára, Fixation of heavy metals in geopolymeric materials based on brown coal fly ash, Ceramics—Silikaty 50 (2006) 200–207.
[10] J.W. Phair, J.S.J. Van Deventer, Effect of silicate activator pH on the leaching and material characteristics of waste-based inorganic polymers, Miner. Eng. 14 (2001) 289–304.
[11] J. Davidovits, Geopolymer chemistry and sustainable development. The Poly(sialate) terminology: a very useful and simple model for the promotion and understanding of green-chemistry, in: J. Davidovits (Ed.), Proceedings of the World Congress Geopolymer, Saint Quentin, France, 28 June–1 July, 2005, pp. 9–15.
[12] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, L. Lorenzen, The potential use of geopolymeric materials to immobilise toxic metals. Part II. Material and leaching characteristics, Miner. Eng. 12 (1999) 75–91.
[13] J.Z. Xu, Y.L. Zhou, Q. Chang, H.Q. Qu, Study on the factors of affecting the immobilization of heavy metals in fly ash-based geopolymers, Mater. Lett. 60 (2006) 820–822.
[14] J. Zhang, J.L. Provis, D. Feng, J.S.J. van Deventer, Geopolymers for immobilization of $Cr^{6+}$, $Cd^{2+}$, and $Pb^{2+}$, J. Hazard. Mater. 157 (2008) 587–598.
[15] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes. A cement for the future, Cement Concrete Res. 29 (1999) 1323–1329.
[16] T. Bakharev, Geopolymeric materials prepared using Class F fly ash and elevated temperature curing, Cement Concrete Res. 35 (2005) 1224–1232.
[17] J. Davidovits, Geopolymeric reactions in archaeological cements and in modern blended cements, in: J. Davidovits, J. Orlinski (Eds.), Proceedings of the First International Conference on Geopolymer '88, vol. 1, Compiegne, France, 1–3 June, 1988, pp. 93–106.
[18] E. Hermann, C. Kunze, R. Gatzweiler, G. Kieβig, J. Davidovits, Solidification of various radioactive residues by Géopolimère® with special emphasis on long-term stability, in: Proceedings of the Second International Conference on Geopolymer '99, June 30–July 2, 1999, pp. 211–228.
[19] T. Hanzlicek, M. Steinerova, P. Straka, Radioactive metal isotopes stabilized in a geopolymer matrix: determination of a leaching extract by a radiotracer method, J. Am. Ceram. Soc. 89 (2006) 3541–3543.
[20] C. Fernández-Pereira, Y. Luna, X. Querol, D. Antenucci, J. Vale, Waste stabilization/solidification of an electric arc furnace dust using fly ash-based geopolymers, Fuel, in press, doi:10.1016/j.fuel.2008.01.021.
[21] D. Tavor, A. Wolfson, A. Shamaev, A. Shvarzman, Recycling of industrial wastewater by its immobilization in geopolymer cement, Ind. Eng. Chem. Res. 46 (2007) 6801–6805.
[22] Y. Zhang, W. Sun, Q. Chen, L. Chen, Synthesis and heavy metal immobilization behaviors of slag based geopolymers, J. Hazard. Mater. 143 (2007) 206–213.
[23] X. Querol, M.K.G. Whateley, J.L. Fernandez-Turiel, E. Tuncali, Geological controls on the mineralogy and geochemistry of the Beypazari lignite, Central Anatolia, Turkey, Int. J. Coal Geol. 33 (1997) 255–271.
[24] M. Thompson, N. Walsh, Handbook of Inductively Coupled Plasma Spectrometry, Chapman and Hall, Inc., New York, USA, 1989.
[25] M. Izquierdo, N. Moreno, O. Font, X. Querol, E. Alvarez, D. Antenucci, H. Nugteren, Y. Luna, C. Fernandez-Pereira, Influence of the co-firing on the leaching of trace pollutants from coal fly ash, Fuel 87 (2008) 1958–1966.
[26] European Committee for Standardisation, EN 12457–2:2002. Characterisation of waste–Leaching–Compliance test for leaching of granular waste materials and sludges–Part 2: one stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm.
[27] M.G. Blackford, J.V. Hanna, K.J. Pike, E.R. Vance, D.S. Perera, Transmission electron microscopy and nuclear magnetic resonance studies of geopolymers for radioactive waste immobilization, J. Am. Ceram. Soc. 90 (2007) 1193–1199.
[28] A. Fernández-Jiménez, A. Palomo, D.E. Macphee, E.E. Lachowski, Fixing arsenic in alkali-activated cementitious matrices, J. Am. Ceram. Soc. 88 (2005) 1122–1126.