



# The role of open and closed curing conditions on the leaching properties of fly ash-slag-based geopolymers

Maria Izquierdo<sup>a,c,\*</sup>, Xavier Querol<sup>a</sup>, Charles Phillipart<sup>b</sup>, Diano Antenucci<sup>b</sup>, Mark Towler<sup>c</sup>

<sup>a</sup> Institute of Environmental Assessment and Water Research, Jordi Girona 18, 08034-Barcelona, Spain

<sup>b</sup> Institut Scientifique de Service Public (ISSeP), 200, rue du Chêra 200, BE-4000 Liège, Belgium

<sup>c</sup> Clinical Materials Unit, Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

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## ABSTRACT

This study deals with the synthesis of geopolymers from co-fired fly ash and blast furnace slags. Geopolymer bodies were simultaneously synthesized in open and closed curing conditions in order to elucidate the role of this parameter on their resultant properties. Open curing conditions produce solid bodies characterized by high porosity, low compressive strength and exacerbated leaching of certain oxyanionic metalloids. By contrast, protected curing promotes the binder development, giving rise to higher strength and less porous systems. This imposes physical restrictions to leaching which decreases and/or retards releases of oxyanionic metalloids in comparison to open curing conditions. Fly ash-slag-based geopolymers may immobilize a number of trace pollutants such as Be, Bi, Cd, Co, Cr, Cu, Nb, Ni, Pb, REE, Sn, Th, U, Y and Zr, regardless of the curing conditions. Due to geopolymers displaying weak assimilation capacity for oxyanionic species, their successful regarding oxyanionic retention is strongly dependent on porosity and therefore on curing conditions applied.

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## 1. Introduction

Over 40 million tonnes of fly ash are produced annually in Europe [1]. European Union regulations are focused on the recycling of pulverised coal combustion (PCC) fly ash into added-value products. One method of addressing this is the synthesis of geopolymer binders; economically and environmentally low-cost materials which offer cementing properties close to those of ordinary Portland cement [2].

The term 'geopolymer' was first used in the early 1970s to describe inorganic materials with polymeric Si–O–Al bonds, obtained from the chemical reaction of aluminosilicate oxides with alkali silicates [3]. The network is composed of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra linked alternately by sharing all the oxygens. The Al<sup>3+</sup> in IV-fold coordination creates a local charge deficit that must be balanced with counter ions. According to Davidovits [2] the empirical formula of geopolymers or poly (sialates) may be written as follows (1):



where M is a cation such as K<sup>+</sup>, Na<sup>+</sup> or Ca<sup>2+</sup>; n is the degree of polycondensation and z is 1, 2 or 3. Other cations such as Li<sup>+</sup>, Ba<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup> may be also present.

Studies on geopolymer green-chemistry have resulted in the development of alternative cements based on natural materials or industrial wastes; particularly coal combustion fly ash [4–14]. The geopolymerization of fly ash offers environmental benefits, such as lower consumption of natural resources and a decrease in the net production of CO<sub>2</sub>; around 17% of that emitted by the Portland cement industry [15].

Geopolymers have other properties that make them attractive for cementation such as fast hardening, high and early compressive strength, optimal acid resistance and long term durability [16]. Geopolymer matrices have been proven to stabilize, solidify and encapsulate metallic and radioactive wastes and industrial wastewater [17–20].

A number of studies have focused their attention on the microstructure, chemistry and mechanical properties of fly ash-based geopolymers, but less attention has been paid to their leaching behaviour. Furthermore, the leaching properties have been assessed mainly under acidic conditions, on pulverised material and based mostly on Cd, Cr, Cu and Pb mobility [3,8–11,21], while other leaching conditions and elements of environmental concern in PCC fly ash have been overlooked. It is for these reasons that, for environmental applications, the leaching behaviour of fly ash-slag-based geopolymer binders needs to be addressed more comprehensively.

\* Corresponding author at: Materials and Surface Science Institute, University of Limerick, Limerick, Ireland. Tel.: +353 061 234170.

E-mail address: [maria.izquierdo@ul.ie](mailto:maria.izquierdo@ul.ie) (M. Izquierdo).

Alongside the issue of leaching, it is necessary to stress that optimal dosage, synthesis and curing conditions are critical issues to obtain a geopolymer that ensures efficient immobilization of pollutants. Previous studies [5,22–34] on the impact of the curing conditions on geopolymer properties have been mainly focused on the reagent composition, concentration, temperature and time of curing, but so far the effect of open and closed curing conditions on the properties of the final product has been scarcely studied.

This study seeks to: (1) assess the leaching behaviour of fly ash-slag-based geopolymer systems, and (2) determine the effect of open and closed curing on the performance of geopolymer-like bodies.

## 2. Materials and methods

### 2.1. Fly ash and slag samples

Three fly ash samples labelled I1, I5 and I6 were collected via different combustion technologies and feed fuel blends (Table 1), within the framework of an EU project (GEOASH, RFC-CR-04005). I1 and I5 were obtained at 850 °C by the co-combustion of Belgian coal tailings, French wood pellets and Polish coal using an atmospheric fluidised bubbling bed combustor boiler [25]; I6 fly ash was generated at 1200–1300 °C by the co-combustion of coal and biomass, using a PCC process. I6 is enriched in Cu, Ni, P, Sn and Zn due to the co-firing of sewage sludge, while wood pellets and coal tailings do not supply significant additional amounts of elements of environmental concern [26].

A blast furnace slag sample was supplied by a steel plant from the Czech Republic (Table 1). The grain size distribution was determined by means of the laser method using a laser Microtac S3500 analyser and is depicted in Fig. 1. The slag shows a relatively fine and well graded particle size distribution, ranging from 0.4 to 100 µm and with a mode around 20 µm.

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. [27]. An additional hydrofluoric acid digestion described by Thompson and Walsh [28] was undertaken in order to determine silica contents. 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.

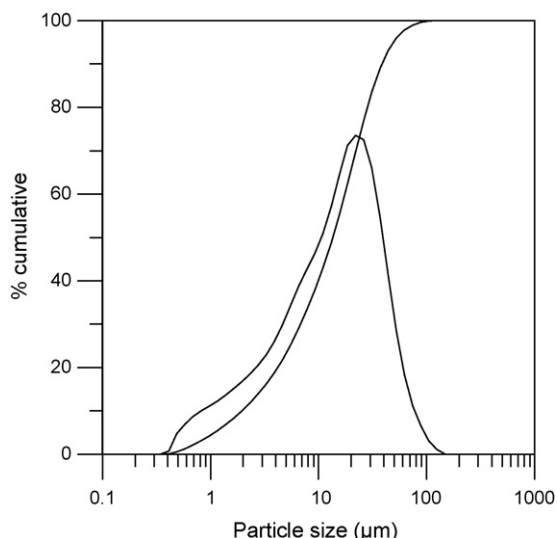


Fig. 1. Particle size distribution of blast furnace slag used in this study.

Table 1

Concentrations of a number of elements in fly ash samples and slag, composition of the feed fuel blend, and formulations used for geopolymer synthesis.

	I1	I5	I6	Slag
<i>Technology</i>	FBC	FBC	PCC	–
<i>Fuel blend (wt%)</i>				
Coal	–	73	90	–
Coal tailings	55	27	–	–
Wood pellets	45	–	–	–
Sewage sludge	–	–	5	–
Olive waste	–	–	5	–
<i>Composition (wt%)</i>				
SiO <sub>2</sub>	52	51	50	39
Al <sub>2</sub> O <sub>3</sub>	23	20	29	11
CaO	3.5	4.1	5.2	41
Na <sub>2</sub> O	0.5	0.4	0.3	0.3
K <sub>2</sub> O	3.3	2.6	1.4	0.4
MgO	1.7	2.1	1.2	7.0
MnO	0.10	0.10	0.04	0.3
TiO <sub>2</sub>	0.9	0.8	1.4	0.5
SO <sub>3</sub>	1.1	1.4	0.7	2.2
P <sub>2</sub> O <sub>5</sub>	0.3	0.2	2.2	<0.02
Fe <sub>2</sub> O <sub>3</sub>	4.7	5.2	5.8	0.3
<i>Composition (mg/kg)</i>				
As	22	17	38	2
B	97	91	239	27
Ba	990	526	2293	680
Cd	1	4	3	0.5
Co	29	25	44	0.4
Cr	188	158	221	16
Cu	110	144	189	5
Li	163	163	244	76
Mo	6	5	12	<0.01
Ni	94	98	131	4
Pb	97	173	146	1
Rb	156	126	45	11
Sb	8	7	23	<0.01
Se	8	25	14	2
Sn	6	8	21	0.1
Sr	229	190	1258	951
U	1	9	11	13
V	207	165	125	20
Zn	210	252	392	47
<i>Dosage (wt%)</i>	GI1	GI5	GI6	
Fly ash	37.2	30.7	53.0	–
Slag	27.9	29.7	21.0	–
K-silicate <sup>a</sup>	18.6	19.8	13.0	–
Added water	18.6	19.8	13.0	–
Total water <sup>b</sup>	27.3	29.1	19.1	–

<sup>a</sup> The K-silicate solution contains 47% of H<sub>2</sub>O.

<sup>b</sup> Added water + water contained in K-silicate solution.

### 2.2. Geopolymer synthesis

Two sets of geopolymer-like solid samples were synthesized at room temperature using the system fly ash/slag/K-silicate/H<sub>2</sub>O. Fly ash was mixed with the blast furnace slag, water and a potassium silicate activator solution. An activator is first prepared using a potassium silicate solution (K-silicate) to which an accurate quantity of KOH is added in order to get a user-friendly SiO<sub>2</sub>/K<sub>2</sub>O = 1.25 [29], which is the best molar ratio for the reactions desired. Then, on the one hand, extra water is added to this solution up to a K-sil solution/water ratio = 1 (blend 1). On the second hand, the fly ash and the slag are mixed together (blend 2). Finally, the blend 2 is progressively added to the blend 1. Such a procedure promotes the production of a paste with an optimal workability. The formulations used are summarized in Table 1.

The paste workability is strongly influenced by both fly ash content and its physicochemical properties, e.g. chemical composition, particle size distribution or morphology. I1 and I5 accounted for 36 wt% of the geopolymer paste, but I6 was increased up to

**Table 2**

Density and compressive strength values at 28 days of synthesized geopolymer-like solids.

	Density (kg/m <sup>3</sup> )				Compressive strength (MPa)		
	GI1	GI5	GI6		GI1	GI5	GI6
Closed curing	1827	1780	1881	Closed curing	50	52	49
Open curing	1349	1256	1381	Open curing	26	16	18
Increased porosity	48%	52%	50%				

53% while maintaining an optimal workability. The blends were stirred for 5 min by spatula and then poured in cubic moulds (50 mm). Identical replicates were simultaneously cured for 28 days in uncovered and covered moulds. Thereafter, samples were demoulded and submitted to a battery of tests.

### 2.3. Physical characterization

Density measurements were performed in line with the European standard EN 1936 [30]. Compressive strength was determined as described in the European standard EN 14617-15 [31].

### 2.4. Leaching properties

The physical retention features and the leaching of inorganic components as a function of time were assessed by means of the diffusion test EA NEN 7375 [32]. Solid cubic bodies were submerged in deionised water and the eluate was replenished at increasing periods of time (0.25, 1, 2.25, 4, 9, 16, 36 and 64 days). The concentrations of the leached components in the successive eluate fractions were measured.

Geopolymer-like solids were size-reduced (<200 µm) to minimize the physical retention effects and thereafter submitted to the single batch leaching test EN 12457-2 [33] performed at L/S = 10 L/kg, with an agitation time of 24 h and deionised water as a leachant. In both leaching tests, the pH at which leaching takes place is governed by the material itself.

All analyses were carried out in duplicate. Major and trace element contents in solid samples and eluates were determined by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES).

## 3. Results and discussion

### 3.1. Effect on the physical properties

The density of geopolymer-like bodies based on the fly ash/slag/K-silicate/H<sub>2</sub>O system (Table 2) do not significantly differ from that of OPC pastes, usually above 1800 kg/m<sup>3</sup>, but slightly lower (about 1750 kg/m<sup>3</sup>) for OPC with high fly ash contents.

Solid bodies cured in covered moulds displayed a density significantly higher than those cured in uncovered moulds. Since reagents and dosages are identical, this difference should be attributed to a higher porosity of uncovered curing solid bodies. The open air curing allowed water to evaporate, which reduced the water availability for geopolymer matrix to grow. An increase in porosity of around 50% was inferred by the variation in the density values. Nevertheless, it should be borne in mind that the higher porosity after an open curing is probably not homogeneously distributed over the sample. It can be expected it is primarily concentrated near the uncovered surface due to the air exposure. This assumption could be validated by extracting sections at increasing depths and comparing their porosity. Further research will be devoted to studying the gradient in the amount of porosity and the critical

depth at which air exposure effects on binder development inhibition are minimized. This may be of relevance for further efficient design of geopolymer blocks.

Compressive strength values sharply decreased after curing in open conditions (Table 2). This suggests that covered moulds promote the reactions responsible for matrix formation. Such curing conditions are favourable to the process of hydration that, at least in the case of slag-based systems, may play a critical role. This optimal situation may not be satisfied when the curing is performed in uncovered moulds, as the system is quickly dried.

Thus, it can be stated that, when using the fly ash/slag/K-silicate/H<sub>2</sub>O system, open curing conditions reduce the mechanical performance of produced geopolymer-like solids.

### 3.2. Effect on leaching properties

#### 3.2.1. Single batch leaching test (EN 12457)

The pH values are highly alkaline, as would be expected by the use of KOH, and are similar regardless of curing conditions (12.2–12.4). Thus, differences in leaching cannot be attributed to pH variation.

The comparison of leachable concentrations from open air cured geopolymers with those cured in protected conditions highlighted the impact of this parameter on the environmental performance of the final product (Fig. 2). Similar behaviour was recorded, regardless of the composition of the fly ash reagent and its combustion characteristics.

Curing in open air increased the leached quantities of K, by around 2000 mg/kg, and doubled Si release. Given the lack of physical restrictions to leaching, the increased leaching should not be ascribed to a higher porosity but rather to a higher K-silicate availability. Bearing in mind that dosages in both samples are identical, the reactivity must have been lower since some K-silicate has precipitated instead of reacting to develop the binder. Open curing conditions enable high and quick evaporation of water with the result that K-silicate may partially precipitate, being thus available for leaching instead of involved in polymerization reactions. The deduced lower reactivity is in line with the above observations on mechanical performance, indicating the critical role that dissolved silica from the K-silicate solution plays in promoting the formation of the first silicate units essential for subsequent polymerization. The high release of K (~2%) under all curing conditions suggests the occurrence of significant amounts of residual and unreacted K-silicate activator. Accordingly, formulation could be modified in further studies, reducing the K-silicate proportion.

Special attention should be paid to the release of elements that may behave as oxyanionic species in alkaline conditions. Prior studies dealing with fly ash-based geopolymers suggested that oxyanionic metalloids are the major environmental concern due to their leaching, significant mobility and toxicity threshold [26].

Table 3 shows extractable proportions of several trace pollutants, inferred from their contents in fly ash and slag and weighed to their respective dosages in the geopolymer paste. Up to 75% of the total Mo content is water extractable, which points to an occurrence in highly soluble salts. The highest Mo releases reached 5 mg/kg and are linked to the higher content in I6 fly ash and its higher loading in this particular geopolymer (53%). As, B, Se and V displayed a significant mobility exceeding 10% of their total content in the initial product. Cr and Sb were slightly mobile. With the exception of Cr and Sb, and bearing in mind the leaching conditions (grinded material), the above observations suggest that As, B, Se and V occur more probably in leachable salts precipitated during the curing process, rather than within the binding matrix framework. Therefore, geopolymers exert a weak chemical retention of the concerned oxyanionic metalloids.

**Table 3**

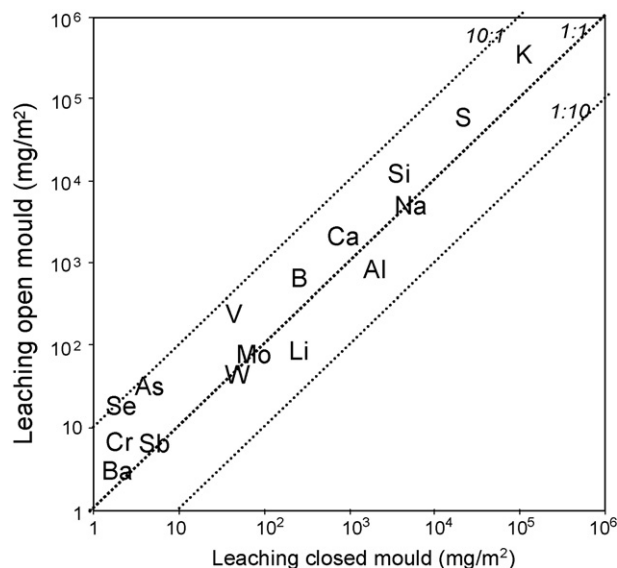
Water extractable proportions of oxyanionic metalloids in the synthesized geopolymers-like bodies.

	Extractable (%)					
	GI1		GI5		GI6	
	Cover	Open	Cover	Open	Cover	Open
As	7	17	8	18	3	9
B	16	18	18	16	12	14
Cr	0.1	0.4	0.3	0.7	0.5	1.2
Mo	49	36	78	72	74	75
Sb	2	1	2	1	1	2
Se	16	16	9	9	6	8
V	14	15	20	26	14	17

Assuming that (1) no physical retention occurred in this experiment and (2) covered curing favoured a better development of the binding matrix, the lower extractable fractions when cured in covered moulds suggest that a certain proportion of As, Cr and V could be incorporated in the neoformed binder. Although this hypothesis needs further specific studies beyond the scope of this paper, it would be consistent with the literature [34]. A partial Si substitution for the above species may account for the chemical retention, although it is difficult to clearly elucidate their crystallochemical status in the silicate binding polymers given the lack of data regarding these elements.  $S^{2-}$  in blast furnace slag may also provide an additional retention effect, as it generates reducing conditions promoting Cr to occur in highly insoluble Cr (III) form [35].

Leaching of Al, S, Na and Li increased when the curing was conducted in covered conditions (Fig. 2), as these promote polymerization and the dissolution of starting materials. Si, Al, S, Na, Li and other elements are partially removed from the glassy fly ash and slag particles but not all them subsequently behave as framework-forming elements of the geopolymer-like matrix produced. Protected curing might lead to an excess of aluminate ions  $[Al(OH)_4]^-$  that cannot be assimilated into the neoformed binding matrix. Na and Li are also released, probably because they occur in readily leachable species.

The measured mobility of the remaining elements, including some regarded as of environmental concern (i.e. Ba, Be, Bi, Cd, Co, Cu, Ni, Hf, Nb, Ni, Pb, rare earth elements, Sn, Ta, Th, Tl, U, Y, Zn and Zr) was very low ( $<0.01$  mg/kg) regardless of curing conditions. I6 fly ash was enriched in several trace pollutants, but their leachable contents in the I6-based geopolymers remained at very low levels. This may not necessarily mean assimilation within the neoformed matrix. Rather, such a strong chemical retention is probably favoured by high pH stability of these element-bearing



**Fig. 3.** Leachable contents according to EA NEN 7375 test after open and closed curing conditions of the GI6 geopolymer. Elements not depicted were leached in levels  $<1$  mg/m<sup>2</sup>.

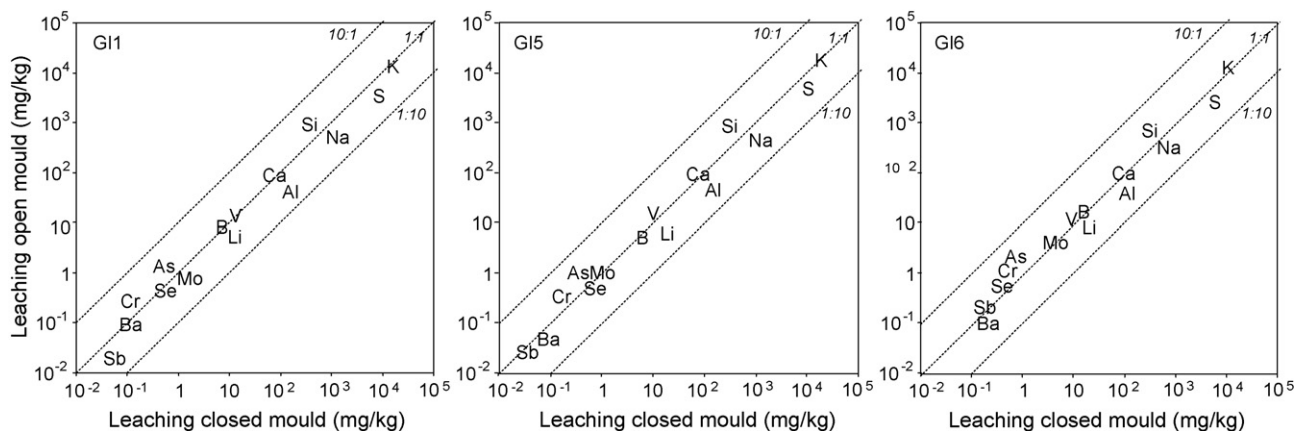
minerals. This is of particular significance for further valorization of fly ash enriched in the aforementioned trace pollutants, such as those obtained from the (co)-firing of certain alternative fuels, as well as for metallic waste encapsulation/stabilization purposes.

### 3.2.2. Tank leaching test (EA NEN 7375)

The different leaching units do not allow a straightforward comparison between EN 12457 and 7375 leaching test results (mg/m<sup>2</sup> and mg/kg, respectively) but general trends are consistent. Emission values revealed marked differences in the element mobility as a function of curing. K and Si were released more prominently in open air cured geopolymer bodies (Fig. 3).

Cumulative leaching of a number of trace pollutants (i.e. Be, Bi, Cd, Co, Cu, Hf, Mn, Nb, Ni, Pb, REE, Sn, Ta, Th, Tl, U, Y, Zn and Zr) after 64 days exposure was systematically low or below the detection limit (1 mg/m<sup>2</sup>), probably due to their strong retention in stable mineral phases under alkaline conditions.

The mobility of As, B, Cr, Se and V was largely enhanced when samples were cured in uncovered moulds, while the mobility of Mo, Sb and W was not affected by curing conditions. Their weak chemical and physical retention and the highly alkaline conditions



**Fig. 2.** Leachable contents (mg/kg) according to EN 12457-2 test in open curing and closed curing geopolymer samples. The log-scale should be noted. Elements not depicted were leached in levels  $<0.01$  mg/kg.



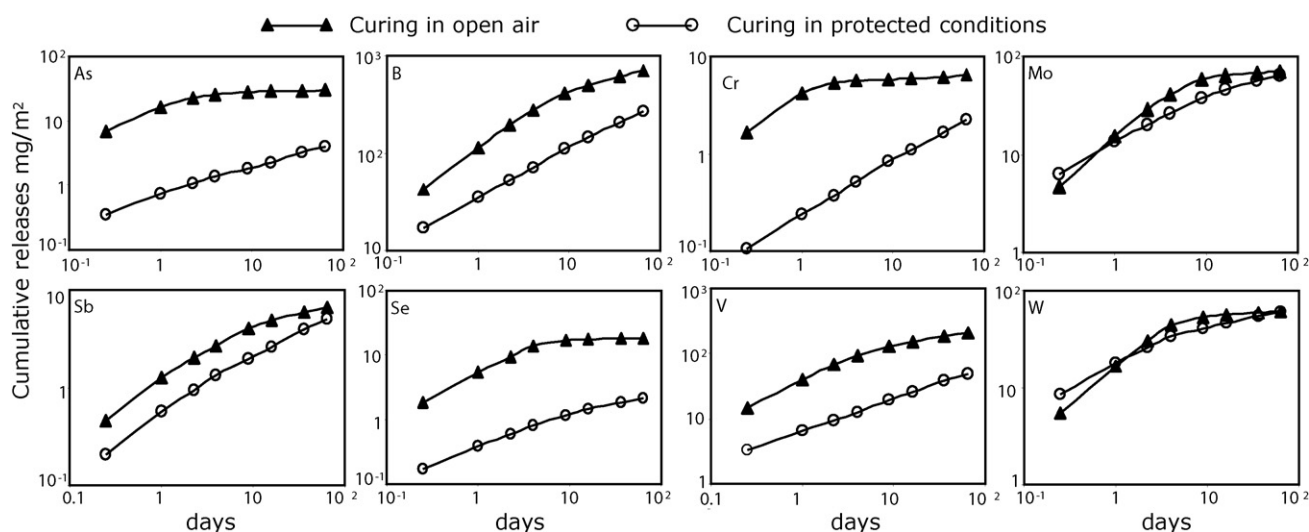


Fig. 4. Cumulative leaching curves of oxyanionic metalloids elements according to EA NEN 7375 test in open curing and closed curing GI6 geopolymer.

render these the most troublesome elements in geopolymers, given their significant mobility and the toxicity.

Leachable levels of As, B, Se and V from the open curing monolithic bodies were up to 1 order of magnitude higher than those from covered cured bodies, but a narrow difference was observed when the ground material was tested. This behaviour should be explained in terms of porosity and density of solid bodies, given that the monolithic leaching test induces a physical restriction to leaching.

Release patterns of oxyanionic species provide further insight into the influence of curing conditions. As depicted in Fig. 4, curing conditions and the subsequent degree of reactivity are key parameters in release dynamics. Open air curing geopolymers exhibited higher and faster release. According to the asymptotic trends of emission curves at the latest stages, a near depletion of the soluble fraction may be assumed.

Lower reactivity resulted in a porous internal structure, favouring the occurrence of connected pores forming channels by which metals are released. By contrast, protected curing promotes the binder development, giving rise to low porous systems. Such condition decreases the surface available for leaching and wash-off processes, with the result that physical retention mechanisms of the binder are stronger. Thus, the soluble fraction in protected curing geopolymers tends to be lower and progressively released, probably governed by diffusion-type mechanisms. Nevertheless, an additional contribution could be attributed to a certain chemical retention within the neoformed geopolymer matrix, particularly for As, Cr and V, when closed curing conditions are applied. The leaching curves of open curing geopolymers suggest, though, that cumulative releases could resemble those easily reached in uncovered curing geopolymers over an extended time frame. From this, it can be stated that, despite the fact that the leaching of oxyanionic species may not be avoided over the long term, their release can be delayed. The release patterns of Mo and W are not sensitive to curing conditions.

#### 4. Conclusions

The synthesis of geopolymer-like solids at room temperature using the fly ash/slag/K-Sil/H<sub>2</sub>O system, clearly indicates that the discussed curing condition exerts a significant effect on several properties of the bodies formed. Open curing conditions enable water evaporation and, as a consequence, the amount of alkaline solution available for the reaction was reduced and K-salt

precipitation increased significantly. This leads to solid bodies displaying higher porosity and lower strength than those produced in closed curing conditions. Should fly ash-slag-based geopolymers be widely used, the marked sensitivity of mechanical properties to the curing conditions must be borne in mind.

The low mobility of a large number of trace elements offers a promising opportunity to use fly ash as a starting material for further immobilization of hazardous wastes enriched in Cu, Pb, Zn or Bi, among others. Such strong retention regardless of the curing conditions renders fly ash an added-value raw material for geopolymer synthesis for the purposes of metallic-bearing waste management. Geopolymers displayed a weak chemical retention of As, B, Cr, Mo, Sb, Se, V and W, although the leaching tests suggest that the binder could incorporate As and V within the structure. The physical retention efficiency is strongly dependent on the porosity of the solid body, which is directly linked to the curing conditions. When cured in closed conditions, the binding matrices develop less interstitial porosity. Consequently, the release of oxyanionic metalloids is retarded when compared with the release measured after curing in open conditions.

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