

Influence Of Curing Conditions on Geopolymer Leaching

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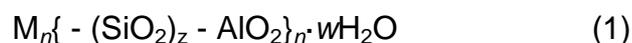
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INTRODUCTION

The worldwide production of PCC fly ash is estimated at achieving 800 million tonnes per year in 2010 [1]. European Union regulations aim at developing new technologies focused on the recycling of these large amounts of PCC fly ash into added-value products. The synthesis of geopolymer binders may be a successful alternative, giving rise to low-cost and environmentally friendly materials with cementing properties resembling those of OPC [2].

Geopolymers were firstly mentioned by Davidovits in the early 1970s to describe inorganic materials with polymeric Si-O-Al bonds, obtained from the chemical reaction of alumino-silicate oxides with alkali silicates [3]. The network is made up with SiO₄ and AlO₄ tetrahedra linked alternately by sharing all the oxygens. The Al³⁺ in IV-fold coordination becomes a network forming but requires extra charge to compensate, which forces the presence of cations in the framework to balance the structure. According to Davidovits [2], the empirical formula of geopolymers or poly(sialates) is as follows (1):



where M is a cation such as K⁺, Na⁺ or Ca²⁺; n, the degree of polycondensation and z is 1, 2 or 3. Other cations such as Li⁺, Ba²⁺, NH₄⁺ and H₃O⁺ may be also present.

The research on the geopolymer green-chemistry conducted over the last years aimed at developing alternative cements based on natural materials or industrial wastes, particularly on PCC fly ash.

The synthesis of geopolymer matrices is a feasible alternative to stabilize metallic and radioactive wastes [4-5] or industrial wastewater [6]. The fast hardening, high and early compressive strength, optimal acid resistance and long term durability [7] render geopolymerization a promising technology with attractive opportunities for commercial applications.

The microstructure, chemistry and mechanical properties of fly ash-based geopolymers have been widely studied, but less attention has been paid to the leaching behaviour. Moreover, this issue has been often addressed focusing on Cd, Cr, Cu and Pb mobility, under acidic conditions and based on pulverised material [8-12], which may not resemble a typical application scenario. As far as the environment is concerned, the leaching behaviour of fly ash-slag-based geopolymer binders is a key question to be comprehensively studied with views to its further extensive application.

An optimal dosage, synthesis and curing conditions are key parameters for the long-term performance of geopolymer bodies. Prior studies on the role of the curing conditions have mainly focused on the reagent composition and concentration, curing temperature and curing time, whereas the influence of open or closed curing conditions has been overlooked. This study seeks to determine the role that a curing in uncovered conditions may play on the environmental performance of geopolymer-like bodies.

MATERIALS AND METHODS

The fly ash, collected at a power plant from Belgium, was obtained after the co-firing of coal with biomass (5% sewage sludge and 5% olive waste). Two sets of geopolymer samples were synthesized according to the method based on the fly ash/slag/K-silicate/H₂O system reacting without thermal activation. Fly ash was mixed with a blast furnace slag from a steel plant in the Czech Republic, water and an activator solution consisting of a potassium silicate and potassium hydroxide solution with SiO₂/K₂O=1.25. Fly ash accounted for 53% of the geopolymer paste. Pastes were poured in cubic moulds (50 mm) and cured at room temperature for 28 days. Identical replicates were simultaneously cured in uncovered and covered moulds. Thereafter, samples were submitted to the different tests.

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 [13] leaching test. Solid cubic bodies were submerged in deionised water and the eluate was replenished at increasing periods of time over 64 days. The concentrations of the leached components in the successive eluate fractions were measured. Geopolymer samples were also size-reduced (<200 µm) to minimize the physical retention effects and thereafter submitted to the single batch leaching test EN 12457-2 [14]. The leaching test was performed at L/S=10 L/kg, with an agitation time of 24 hours and deionised water as a leachant. Leaching tests were carried out by duplicate and major and trace element contents in eluates were determined by means of ICP-AES and ICP-MS.

RESULTS AND DISCUSSION

Single batch leaching test (EN 12457)

Leachates are highly alkaline, with pH values are practically unchanged (12.2-12.4) whatever the curing conditions are. Differences in leaching cannot be then attributed to pH variations. The comparison of leachable concentrations of open air cured

geopolymers with those cured in protected conditions brings to light the impact of this parameter on the environmental performance of the final product (Table 1).

Table 1. Leachable contents according to the single batch (EN 12457-2) and tank (EA NEN 7375:2004) leaching test in open-cured and covered-cured geopolymer samples.

	Batch leaching test (mg/kg)		Tank leaching test (mg/m ²)	
	covered curing	uncovered curing	covered curing	uncovered curing
Al	106	49	1432	1200
Ca	95	108	994	2093
Fe	<2.5	<2.5	29	36
K	12491	14339	158296	232926
Mg	<5	<5	58	72
Na	479	419	6101	5540
P	<10	<10	116	234
S	4130	3220	33583	40752
Si	391	682	5215	8472
V	10	12	50	208
Cr	0.6	1.5	2.2	6
Co	<0.01	<0.01	<0.5	<0.5
Ni	0.01	<0.01	<0.5	<0.5
Cu	0.03	0.01	<0.5	1.1
Zn	0.08	0.08	<0.5	<0.5
As	0.7	1.8	4	30
Se	0.5	0.6	2.1	18
Mo	5	5	65	69
Cd	0.02	0.03	<0.5	0.5
Sn	<0.01	<0.01	<0.5	<0.5
Sb	0.2	0.2	5	7
Ba	0.2	0.1	2	3
W	108	54	60	61
Pb	<0.01	<0.01	<0.5	<0.5
Bi	<0.01	<0.01	<0.5	<0.5
Th	<0.01	<0.01	<0.5	<0.5
U	<0.01	<0.01	<0.5	<0.5

The leached quantity of K and Si is higher after curing in open air, the latter being doubled. If assumed that the size-reduction applied for the leaching test minimised the encapsulation effects, the increased leaching should not be ascribed to a higher porosity but rather to a higher K-silicate availability. As dosages are identical, the reactivity must have been lower since a certain K-silicate proportion has precipitated instead of reacting to give rise to the geopolymer matrix.

Open-curing conditions may allow high and quick evaporation of water with the result that K-silicate precipitates, remaining available for leaching instead of being involved in polymerization reactions. This indicates the critical role that dissolved silica from the K-Sil solution plays in promoting the formation of the first silicate units essential for the polymerization. Nevertheless, K is largely released (about 2% wt) at any curing, suggesting the occurrence of significant amounts of residual and unreacted K-silicate activator.

Particular attention should be deserved to the releases of oxyanionic metalloids. Prior studies dealing with fly ash-based geopolymers pointed to oxyanionic species as the major environmental concern in geopolymers in terms of leaching, due to their significant mobility and the toxicity threshold [15].

Up to 75% of the total Mo is water extractable (Table 2), which may support an occurrence in readily leachable salts. As, B, Se and V displayed a significant mobility that can surpass 10% of the total content in the initial product, while Cr and Sb were slightly mobile. Bearing in mind the leaching conditions (ground material), the above observations suggest a mode of occurrence in leachable salts precipitated during the geopolymerization process, rather than within the binding matrix framework. This would then be responsible of such a weak chemical retention. Moreover, values of extractable V and Mo depicted in Table 2 largely exceed the extractable proportions from the raw fly ash [16], providing evidence that geopolymerization reactions favours the mobility of oxyanionic species.

Table 2. Extractable proportions of oxyanionic metalloids in the synthesized geopolymers.

% extractable	As	B	Cr	Mo	Sb	Se	V
covered	3	12	0.5	74	1	6	14
uncovered	9	14	1.2	75	2	8	17

Only As and Cr were sensitive to the curing conditions. Assuming that 1) no physical retention applies in this test and 2) the protected curing favoured the geopolymer development, the lower extractable fractions when cured in covered moulds (Table 2) suggest that a certain proportion could have been assimilated by the neoformed binder. This is in line with the findings of other authors [1]. A partial Si substitution for As or V could account for the chemical retention.

Leaching of Al, S, Na and Li increased when the curing was conducted in covered conditions, given that these promote the geopolymerization and the dissolution of starting materials. Si, Al, S, Na, Li and other elements would be unlocked from the glassy fly ash and slag particles but not all them would subsequently behave as framework-forming elements of the geopolymer matrix. Results suggest that the protected curing leads to an excess of aluminate ions AlO_2^- that could not find a new stable mineralogical status at high pH (~12.3).

The mobility of the remaining elements, including some regarded as of concern, i.e. Ba, Be, Bi, Cd, Co, Cu, Ni, Hf, Nb, Ni, Pb, REE, Sn, Ta, Th, Tl, U, Y, Zn and Zr, was very low (<0.1 mg/kg) regardless of whether geopolymer bodies were protected or kept in open air throughout the curing time. 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/stabilisation purposes.

Tank leaching test (EA NEN 7375)

The different leaching units do not allow a straightforward comparison between EN 12457 and NEN 7375 leaching test results (mg/m^2 and mg/kg , respectively) but general trends are consistent. Emission values revealed marked differences in the element mobility as a function of the curing conditions. K and Si were largely released, more prominently in open air cured geopolymer bodies (Table 1).

The cumulative leaching of a number of trace pollutants after 64 days of exposure was close or below the detection limit. As a result of the aforementioned strong chemical retention, Be, Bi, Cd, Co, Cu, Hf, Mn, Nb, Ni, Pb, REE, Sn, Ta, Th, Tl, U, Y, Zn and Zr showed releases $<0.5 \text{ mg/m}^2$ and were highly immobile under the tank leaching test conditions. The mobility of As, Cr, Se and V was largely increased when samples were not protected during the curing, while Mo, Sb and W mobility remained insensitive to this parameter. The weak chemical and physical retention and the highly alkaline conditions render them the most concerning elements in geopolymers, given their significant mobility.

It is worth noting that As, B, Se and V leaching from the open-curing monolithic bodies was up to 1 order of magnitude higher than those cured protected conditions, whereas little difference was observed when testing the ground material. 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. The 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 washoff processes, with the result that physical retention mechanisms of the binder are stronger.

CONCLUSIONS

The studied curing condition exerts a significant influence on the behaviour of the resulting geopolymer matrices. The open air conditions enabled the water evaporation, with the result that the amount of alkaline solution available for reacting was reduced and the K-salts precipitation was markedly higher.

The low mobility of a large number of trace pollutants in both batch and monolithic leaching tests offers a promising opportunity to use fly ash as a starting material for further immobilisation of hazardous wastes enriched in Cu, Pb, Zn or Bi, among others. Such strong retention ability regardless of the curing renders fly ash an added-value raw material for geopolymer synthesis with views of metallic-bearing wastes containment.

Geopolymers displayed a weak chemical retention of oxyanionic metalloids. As, B, Cr, Mo, Sb, Se, V and W are highly mobile under highly alkaline conditions, although the binder may assimilate As and V within the structure. The physical retention efficiency is strongly dependant on the porosity of the solid body, which is directly linked to the curing.

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Part 2: one stage batch test at a liquid to solid ratio of 10 L/kg for materials with particle size below 4 mm.

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