Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 34 (2004) 1103–1109

CEMENT AND CONCRETE RESEARCH

Effect of CO_2 on leaching from a cement-stabilized MSWI fly ash

Tom Van Gerven[a,*], Johnny Moors[a], Veroniek Dutré[b], Carlo Vandecasteele[a]

[a]*Department of Chemical Engineering, Katholieke Universiteit Leuven, De Croylaan 46, 3001 Louvain, Belgium*
[b]*VITO, Boeretang 200, 2400 Mol, Belgium*

Received 29 May 2003; accepted 26 November 2003

Abstract

A cement-stabilized MSWI fly ash w as leached according to the diffusion test NEN 7345. The influence of carbonation during leaching was tested by bubbling N_2, air or CO_2 through the leachant. The original test, where no gas is bubbled, was used as a reference. The periodically renewed leachant was analysed for its ionic concentrations. Porosity measurements, XRD and scanning electron microscopy (SEM) analysis were performed.

For some metals, leaching is seriously underestimated when precipitation on the tank walls is not included. Thus, the sum of the dissolved portion and the precipitated portion has to be taken into account. Diffusion tests with N_2 and air bubbling gave results that were not significantly different from those obtained in the reference test. Bubbling of pure CO_2, however, influenced leaching profoundly. This was mainly due to the lowering of pH. The reaction of hydroxides to carbonates—another effect of CO_2 bubbling—had a negligible effect on leaching.

Keywords: Carbonation; Heavy metals; Waste management; Leaching

---

1. Introduction

More and more countries allow and even promote reuse of waste in construction materials. To this end, release of contaminants must be controlled by a set of leaching tests and must comply with leaching standards [1]. In Flanders (the northern part of Belgium) the Dutch semidynamic batch test NEN 7345 [2], from here on called the diffusion test, is applied for monolithic materials.

In the diffusion test, CO_2 uptake from air is not controlled. The reaction of portlandite, $Ca(OH)_2$, and calcium silicate hydrate, C-S-H, the main constituents of a hydrated cement matrix, with CO_2 from the air (the carbonation reaction) results in the formation of calcite, $CaCO_3$ [3]. The carbonation reaction has three effects on the cement matrix and its pore water [4]: lowering of the pH of the pore water; change of metal solubility due to the presence of carbonate, which may result in metal carbonate formation; and decrease of the matrix porosity because of the formation of calcite, which is a larger molecule than portlandite, thereby clogging pores.

Carbonation is one of the important topics in recent research on long-term leaching of heavy metals. Carbonation and leaching occur intermittently during the life cycle of a monolith. Most research focuses on leaching *after* (accelerated) carbonation (e.g., Refs. [5–7]), and few results have been published on carbonation *during* leaching [8,9]. Sanchez et al. [8] apply a batch-leaching procedure interrupted by storage periods in a controlled atmosphere with known levels of CO_2 and humidity. In the approach of Andac and Glasser [9] the diffusion test is applied, with bubbling of gaseous CO_2 through the leachant. In the present paper a similar approach is followed. The purpose of the present study was to evaluate the influence of the uncontrolled uptake of CO_2 on the existing leaching test and to examine whether carbonation during leaching can be simulated by saturating the leachant with CO_2. Whereas Andac and Glasser applied leaching with CO_2 [9] and air [10] bubbling but on two different specimen types (cement paste and mortar), the present paper compares two extreme conditions (bubbling N_2 and CO_2) as well as a realistic intermediate condition (bubbling air) on the same cement paste with 25% of the cement replaced by a MSWI fly ash. The original leaching test with no bubbling is performed as a reference. In all diffusion tests, leaching tanks were rinsed with acid before

---

* Corresponding author. Tel.: +32-16-32-23-42; fax: +32-16-32-29-91.
E-mail address: thomas.vangerven@cit.kuleuven.ac.be
(T. Van Gerven).

0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2003.11.022

leachant renewal to dissolve precipitations on the wall of the tanks. Analyses of the leachates are combined with mineralogical and petrographical examination of fresh and leached monoliths to evaluate the influence of the formation of carbonates on leaching.

2. Materials and methods

2.1. Preparation of specimens

Cement pastes were prepared by mixing 1186.5 kg/m^3 of Portland cement (CEM I 42.5 R) with 395.5 kg/m^3 of fly ash from an electrostatic precipitator of a municipal solid waste incinerator and adding 455 l/m^3 of distilled water. The fresh pastes were poured in moulds (4 × 4 × 16 cm) and, after 2 days, the hardened pastes were demoulded and stored in a humid room (20 °C, >95% RH) during 28 days for curing. The bars were then sawn in cubes of 4 × 4 × 4 cm by a dry cutting technique and stored in airtight bags to prevent carbonation.

2.2. Diffusion test

The Dutch NEN 7345 diffusion test extended up to 121 days was used as reference test. The cubes were immersed in distilled water brought to pH 4 with nitric acid, which was intermittently renewed (after 6, 24, 54, 96, 216, 384, 864, 1536, 1944, 2400 and 2904 h). The volume of the leachant equals five times the volume of the cube. The pH and conductivity of the leachate after each renewal were measured. To include precipitation on the walls of the leaching tanks in the leaching results, all tanks were rinsed with 5 ml of concentrated HNO_3 after each renewal, an action that is at variance with the original NEN test. This washing solution was diluted with distilled water and analysed. Chlorides and sulphates in the leachates were measured by capillary zone electrophoresis, using a Waters Quanta 4000 CZE system with online UV detection at 254 nm. Acidified leachate samples were analysed for cations using a VG PlasmaQuad PQ-2 Plus ICP-mass spectrometer. Results of the 11 consecutive renewals were added to obtain cumulative leaching results and expressed as mass leached per sample surface (mg/m^2).

The same diffusion test was also performed while bubbling CO_2, N_2 or air through the leaching vessel. Bubbled CO_2 had a purity of 99.90%. Compressed N_2 gas contained only 40 ppm of impurities of which 30 ppm Ar. The used dry air consisted of 78% N_2, 21% O_2 and 0.035% (350 ppm) CO_2. The flux of the gases was about 200 ml/min. For CO_2 bubbling this lead to a near-constant pH of about 6.4 in the leachate from around the fourth renewal on.

For the leaching tests, specimens were used that had two cut sides and four mould sides. Three specimens were tested for each of the four leaching conditions.

2.3. Mineralogical and petrographical examination of the monoliths

Powdered samples of fresh and leached cement paste were analysed with a Philips PW1130/90 X-ray diffractometer with Co lamp.

The open bulk porosity of the samples is calculated according to Eq. (1). Three samples of each leaching condition were therefore dried at 105 °C until constant weight, weighed (dry mass), immersed in water (density = 1 g/cm^3) under vacuum until constant weight and weighed again (wet mass).

$$\text{Porosity (\%)} = \frac{\text{wet mass (g)} - \text{dry mass (g)}}{\text{volume of the cube (cm}^3\text{)}} \times 100 \qquad (1)$$

Specimens for scanning electron microscopy (SEM) were cut into samples of 1 × 1 × 1 cm. These were embedded in an epoxy resin, polished and coated with a silver layer. A Philips XL30 FEG-EDAX scanning electron microscope was used. Microphotographs were taken, along with line scans and mappings of selected elements.

3. Results and discussion

3.1. pH and conductivity of leachates

The pH measurements of the consecutive leachates are shown in Fig. 1 and indicate that pH decreases slowly from above 12 to below 10 in the reference test due to exhaustion of $Ca(OH)_2$. With N_2 and air bubbling, pH is also in the range 11–12, but $Ca(OH)_2$ exhaustion is delayed. The pH of the leaching test with CO_2 bubbling remains constant at about pH 6.4, the first leachates giving a slightly lower pH due to the short leaching periods so that no equilibrium is reached. According to Hewlett [12] the pH of water at 18 °C in equilibrium with atmospheric CO_2 is 5.7. In equilibrium with 100 vol.% of CO_2, the pH reaches 3.9. In the conducted leaching tests the pH values are higher because of the alkaline components present in hardened cement. These results confirm earlier measurements by Andac and Glasser [9,10], except for the air-bubbling test where they noted a pH that remained constant after 1 week at about 9. Probably, this is due to the low acid-neutralisation capacity of the mortars they tested. Mortars consist of a large portion of inert sand and thus have a low $Ca(OH)_2$ content, leading to rapid exhaustion of leachable alkaline components. In the present study the specimens are cement pastes (without sand) that have a high $Ca(OH)_2$ content.

Conductivity results show the same trend for all leaching conditions. The conductivity increases as the leaching periods become longer, until around the fifth renewal the conductivity decreases again due to exhaustion of leachable compounds. The higher conductivity measurements for the N_2- and air-bubbling tests compared to the refer-

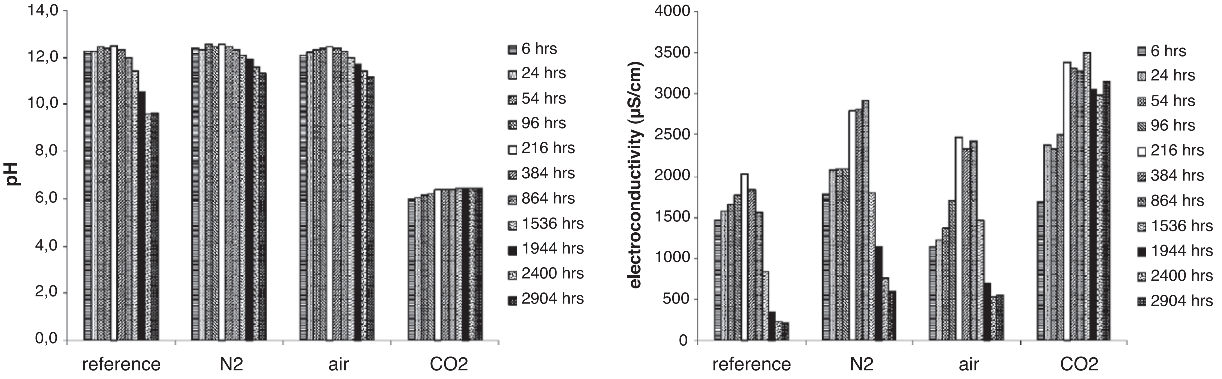

Fig. 1. pH and conductivity measurements of the 11 consecutive leachates for the four leaching conditions.

ence test seem to indicate an effect of the bubbling action on leaching.

3.2. Dissolution and precipitation

During diffusion tests, precipitation is sometimes noticed on the wall of the leaching tank or on the water surface [13]. The presence of these precipitates will influence leaching results, as they are not taken into account when analysing the leachate and also may influence the leaching of ions in later renewals: in fresh leachant old precipitates may partly dissolve and cause a lower concentration gradient between the pore water in the cement matrix and the leachant. In the diffusion tests performed in this study, precipitation of carbonates occurred. Therefore, the original diffusion test was adapted by rinsing the tanks with acid and analysing the washing water. The total (cumulative after 121 days) concentration of each cation leached (i.e., the sum of dissolved and precipitated) is shown in Table 1, together with the percentage of dissolved cation to total leached cation.

Almost no Na and K precipitate, as expected for these highly soluble ions. Leached Ca, Mg, Zn and Cr occur to a larger extent in the dissolved form with CO$_2$ bubbling than with air, N$_2$ or no bubbling. Al has an opposite behaviour. These results may be explained by the pH dependence of the ions [1]. At pH 6.4 Ca, Mg, Zn and Cr are much more soluble than at pH 10–12, while Al is less soluble at pH 6.4 than at pH 10–12.

Table 1
Cumulative concentration of leached cations and percentage of dissolved amount in relation to total leached amount

	Cumulatively leached (mg/m^2)				Percentage dissolved (%)			
	Reference	N$_2$	Air	CO$_2$	Reference	N$_2$	Air	CO$_2$
Na	16,418	17,423	16,841	17,384	99.5	99.1	99.1	99.2
K	33,814	35,416	34,411	32,235	99.8	99.4	99.5	99.5
Ca	27,326	30,203	22,413	247,741	63.0	92.6	91.1	97.2
Mg	19	17	19	3,578	80.8	78.5	84.2	98.9
Al	730	935	928	65	99.1	98.1	98.6	15.7
Cr	4	3	3	10	97.3	96.3	96.7	97.8
Zn	4	4	4	60	48.2	36.3	32.1	90.1
Mn	dl	dl	dl	35	–	–	–	93.5
Ni	dl	dl	dl	19	–	–	–	94.7
Co	dl	dl	dl	4	–	–	–	96.1

dl = below detection limit (0.5 mg/m^2).

An unexpected result is the low percentage of dissolved Ca in the reference leaching test. Although the total leached amount is roughly the same as in the tests with N$_2$ or air bubbling, a large fraction of the leached Ca precipitates on the wall of the tank. This may be caused by the absence of bubbling and hence stirring of the leachate, leading to locally exceeding the solubility of calcium-containing precipitates.

The results in Table 1 show that for some metals leaching will be seriously underestimated when the precipitation on the walls of leaching tanks is not dissolved before sampling. Leachates should therefore be acidified while they are still in the leaching tanks and walls should be scrubbed to ensure complete dissolution of present precipitates. This should be standard practice when performing the diffusion test.

3.3. Leaching results

Fig. 2 shows the cumulative leached concentrations for the different test conditions. Because sulphate, manganese, nickel and cobalt concentrations were below the detection limit (350 mg/m^2 for sulphate, 0.5 mg/m^2 for cations) for the reference, N$_2$ and air conditions, results for these components are shown only for the CO$_2$ bubbling test.

The results indicate that the reference test does not differ much from the N$_2$- and air-bubbling tests. At the end of the reference test only aluminium and chloride leaching is significantly different ($P < .05$) from the corresponding results of the two bubbling tests. The bubbling effect as noticed in the conductivity measurements (see Section 3.1) seems to originate from the leaching of hydroxide (see pH), aluminium and chloride ions but has no influence on leaching of other ions. This effect is therefore considered to be negligible for most ions. The presence of CO$_2$ in air also has a negligible influence on leaching in the diffusion test. This is in contrast with Andac and Glasser [10] who, for cement mortars, argue that air bubbling does have a significant influence on leaching. In their case this influence is mainly due to the decrease of pH (see Section 3.1).

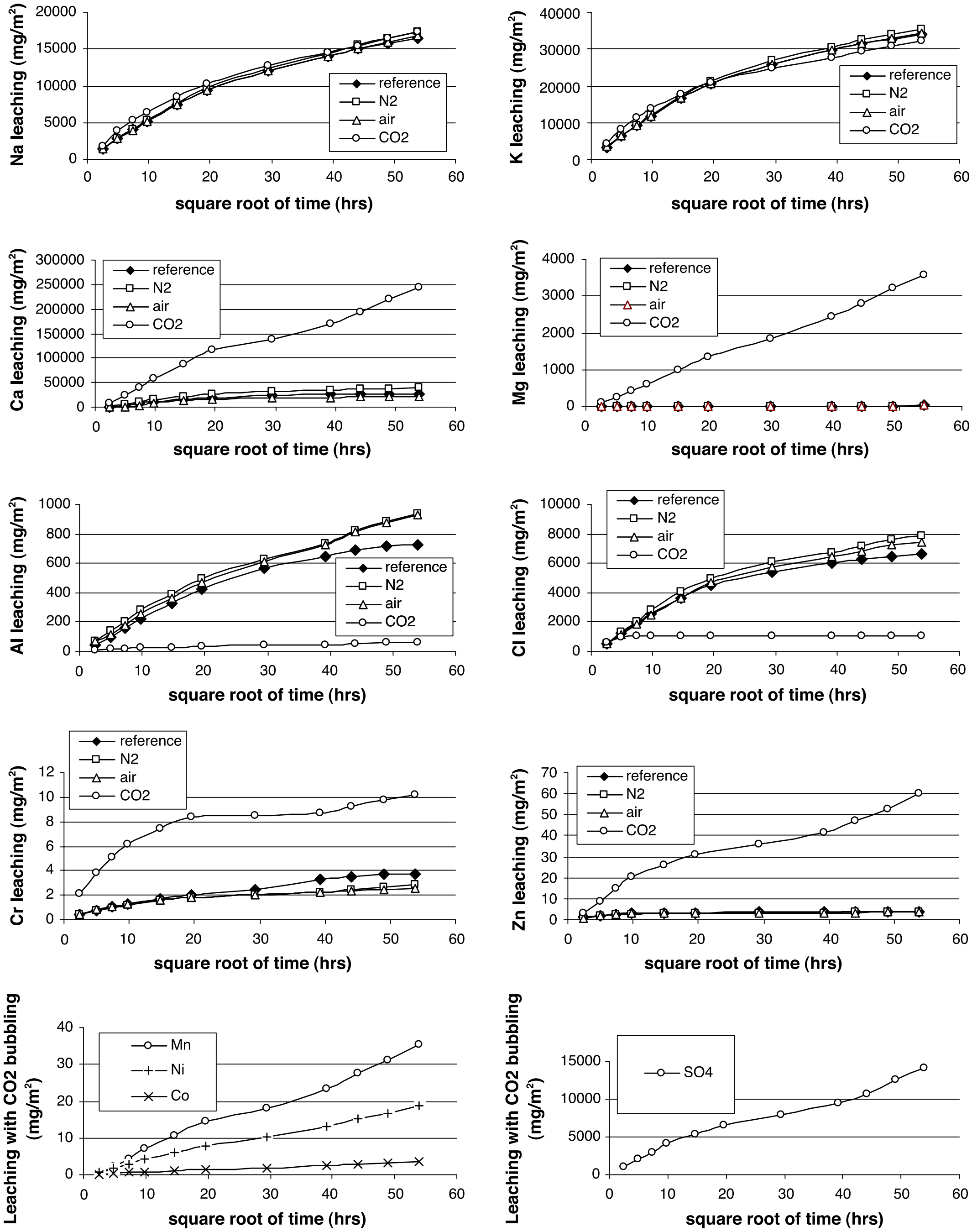

Fig. 2. Cumulative leaching for selected ions for the four leaching conditions.

Bubbling of CO_2 during leaching does affect leaching considerably. Ca, Mg, Cr, Zn, Mn, Ni, Co and sulphate leach to a significantly larger extent; Al and chloride leach significantly less. Na and K are unaffected by CO_2 bubbling. Again the pH influence may explain these results.

3.4. Physical examination of leached specimens

The porosity measurements (Table 2) indicate that the differences between the leached specimens are not significant (P>.05). X-ray diffractograms also showed limited differences between powdered material of specimens leached under different conditions. Only when sampling the surface of a specimen leached with CO_2 bubbling was a diffractogram obtained that differed from that from other

Table 2
Porosity (%) of the specimens at the end of the leaching test

Reference	N_2	Air	CO_2
34.06 (0.30)	34.57 (0.23)	34.02 (0.26)	34.67 (0.34)

Standard deviation between brackets (based on three samples each).

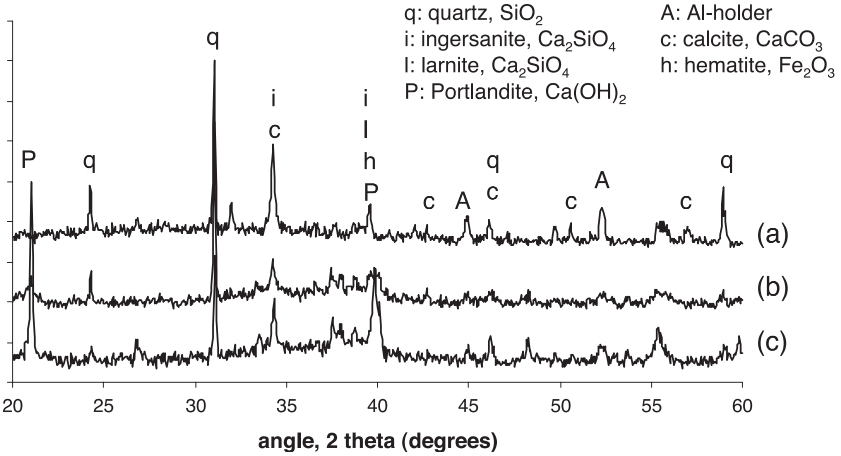

Fig. 3. X-ray diffractograms (relative intensity) of (a) the surface of a CO_2-bubbled specimen, (b) the surface of a reference-leached specimen and (c) the core of a nonleached specimen.

parts of leached specimens. Fig. 3 shows this diffractogram together with one of the outer surfaces of a specimen leached using the reference test and one of the cores of a nonleached specimen. In the surface of the CO_2-bubbled sample less Portlandite is present and slightly more calcite. This suggests that carbonation of specimens took place, but was limited to a very small part of the specimen.

These results were confirmed by SEM measurements. In an air-bubbled specimen no carbonated shell could be observed, in contrast to a CO_2-bubbled specimen where a small carbonated front was present. Fig. 4 shows a microphotograph of a section of a CO_2-bubbled specimen with line scans of carbon and calcium superimposed. The enrichment of carbon shows that the carbonated shell has a thickness of 600–800 μm. The carbonated zone is depleted in calcium. The concentration of calcium and carbon (225 and 125 cps, respectively) in the uncarbonated region corresponds with measurements in the core of a nonleached sample.

SEM mappings of a CO_2-bubbled specimen qualitatively visualize the elemental compositions near the surface (Fig. 5). The enrichment of oxygen confirms the carbonation of the specimen surface. Potassium and silicon are depleted in the carbonated region. No gradient can be seen for aluminium, magnesium and sodium. The concentration of heavy metals was too low to measure with SEM. Andac and Glasser [9] describe a complex zonal structure in a cut cross section of a CO_2-bubbled cement paste. The sequence of five zones is not really visible in our results.

3.5. Decrease of pH versus the reaction of hydroxides to carbonates

The bubbling of a CO_2-containing gas (air or pure CO_2) through the leachant could have an influence on metal leaching by three effects:

1. decrease of the porosity by formation of calcite. This effect was not observed in the porosity results.
2. decrease of the pH. A large pH decrease was observed in the CO_2-bubbling test, while the air-bubbling results show no pH decrease.
3. change of the metal solubility due to precipitation of metal carbonates. This effect can be expected to be negligible, both in bubbling with air and in bubbling with CO_2. In the air-bubbling test pH is 11–12, and the dissolved carbon dioxide is mainly present as the

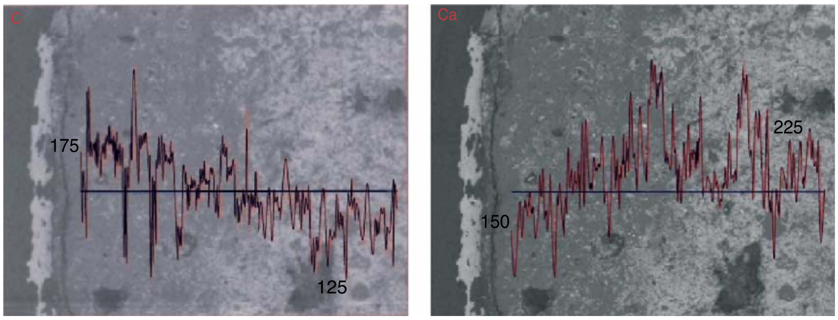

Fig. 4. SEM line scans of carbon (left) and calcium (right) with visual image underneath. Surface of specimen is on the left side. Scanning was performed along the horizontal line.

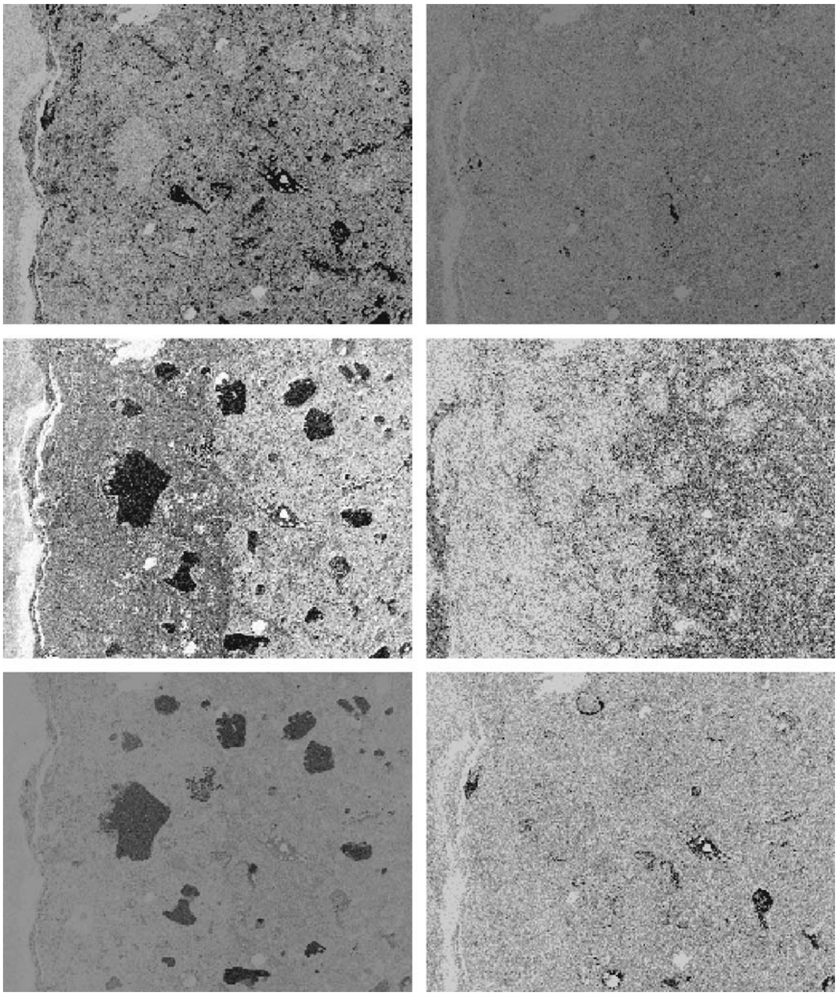

Fig. 5. SEM microphotograph with mappings of aluminium, magnesium, oxygen, potassium, silicon and sodium. Surface of specimen is on the left side.

carbonate ion (Fig. 6), which may form relatively insoluble carbonate salts, and to a very small extent as the bicarbonate ion, the salts of which are highly soluble. Nevertheless, no precipitation is observed in SEM measurements indicating that the amount of CO_2 trapped in the solution (renewed 11 times over a period of 121 days) is insufficient. In the CO_2-bubbling test high amounts of CO_2 are made available. However, at the pH reached (pH 6.4) CO_2 occurs as a combination of about as much bicarbonate ion as carbonic acid. In this case, much CO_2 is present but the species distribution is unfavourable for precipitation of carbonate salts. SEM measurements show a very thin shell of carbonate formation.

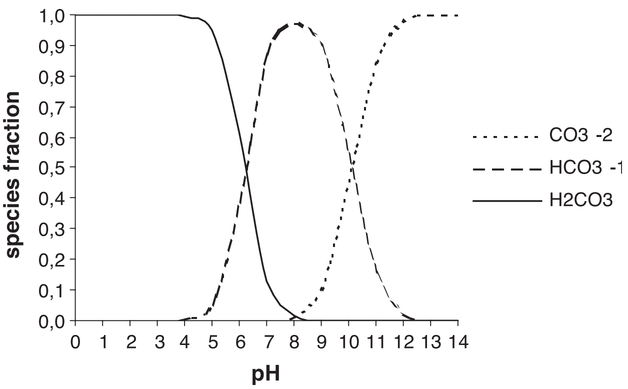

Fig. 6. Speciation of dissolved carbon dioxide as a function of pH.

3.6. Simulation of carbonation during leaching

The use of carbonated leachant largely increases release of most pH-dependent ions. Saturating the leachant with carbon dioxide through bubbling induces a large drop in pH, causing increased leaching, but almost no carbonates precipitate. Porosity decrease due to calcite formation and change in metal solubility due to formation of carbonates, both consequences of natural carbonation, are not simulated with this setup. Moreover, the pH drop witnessed in this setup is much larger than the decrease down to about pH 8 in specimens that are thoroughly carbonated before leaching [4], thereby overstressing the impact of pH in natural conditions.

CO_2 bubbling during the batch-leaching test can, however, be an interesting option when assessing release of contaminants from monoliths applied in construction works underground. Due to organic matter decomposition and other biological activity, CO_2 concentration in soil air is shown to increase to several hundred times higher than in air above ground. Concentrations up to 0.5–1% at a depth of 0.5 m and 5–10% at a depth of 1.5 m have been reported. Under the groundwater table alkaline water is neutralized because of the combined effect of this CO_2 production and the reducing conditions that arise due to progressing O_2 depletion [14]. Biological activity may be less abundant in the direct surroundings of concrete constructions where sand and gravel are used to stabilize the construction site, but cannot be neglected.

The Flemish and Dutch interpretations of the NEN 7345 batch-leaching test already distinguish between monoliths continuously submerged in groundwater and monoliths that are mainly in contact with water through rain, but these interpretations only take the wetting period into account. In Belgium it rains about 10% of the time. In order to transfer laboratory results to field results, a correction factor of 1 (for always submerged applications) and 0.1 (for applications in contact with rainfall in Flanders) or 0.14 (for applications in contact with rainfall in the Netherlands) is used to multiply the leached emission determined with the laboratory test. The results of this study, however, indicate that groundwater buffered to neutral pH will leach some metals 2 to 50 times more than predicted in the reference leaching test. The pH buffering capacity of the leachant in situ therefore needs to be taken into account when evaluating leachability. This could be done by saturation of the leachant with carbon dioxide by bubbling pure CO_2 during the diffusion test.

4. Conclusion

This study shows the importance of dissolving precipitates that occur on the walls of the leaching tanks. Not including the precipitated portion of leached metals would in some cases significantly underestimate leaching results.

The results of the diffusion tests with N_2 and air bubbling show that the uncontrolled uptake of CO_2 in the existing NEN 7345 test has a negligible effect on leaching conditions. Bubbling of pure CO_2, however, influenced leaching profoundly. It appeared that this was mainly due to the decreased leachate pH of 6.4. Precipitation of metal carbonates was negligible. Therefore, this setup does not simulate natural carbonation. Only in specific cases can bubbling of CO_2 during the diffusion test be an interesting option.

References

[1] IAWG, Municipal solid waste incinerator residues, Studies in Environmental Science, vol. 67, Elsevier, Amsterdam, The Netherlands, 1997.

[2] Nederlands Normalisatie Instituut (NNI), NEN 7345, Uitloogkarakteristieken van vaste grond- en steenachtige bouwmaterialen en afvalstoffen—Uitloogproeven—Bepaling van de uitloging van anorganische componenten uit vormgegeven en monolithische materialen met de diffusieproef, Delft, The Netherlands, 1995.

[3] M.S. Bin Shafique, J.C. Walton, N. Gutierrez, R.W. Smith, A.J. Tarquin, Influence of carbonation on leaching of cementitious wasteforms, J. Environ. Eng. 124 (5) (1998) 463–467.

[4] T. Van Gerven, D. Van Baelen, V. Dutré, C. Vandecasteele, Influence of carbonation method on leaching from cementitious matrices spiked with heavy metals, Cem. Concr. Res. 34 (1) (2004) 149–156.

[5] L.C. Lange, C.D. Hills, A.B. Poole, Preliminary investigation into the effects of carbonation on cement-solidified hazardous wastes, Environ. Sci. Technol. 30 (1996) 25–30.

[6] S. Valls, E. Vazquez, Accelerated carbonation of sewage sludge–sand–cement mortars and its environmental impact, Cem. Concr. Res. 31 (2001) 1271–1276.

[7] M.A. Venhuis, E.J. Reardon, Vacuum method for carbonation of cementitious wasteforms, Environ. Sci. Technol. 35 (2001) 4120–4125.

[8] F. Sanchez, C. Gervais, A.C. Garrabrants, R. Barna, D.S. Kosson, Leaching of inorganic contaminants from cement-based waste materials as a result of carbonation during intermittent wetting, Waste Manage. 22 (2002) 249–260.

[9] M. Andac, F.P. Glasser, Long-term leaching mechanisms of Portland cement-stabilized municipal solid waste fly ash in carbonated water, Cem. Concr. Res. 29 (1999) 179–186.

[10] M. Andac, F.P. Glasser, The effect of test conditions on the leaching of stabilised MSWI-fly ash in Portland cement, Waste Manage. 18 (1998) 309–319.

[11] P.C. Hewlett (Ed.), Lea's Chemistry of Cement and Concrete, Arnold, London, UK, 1998.

[12] V. Dutré, C. Vandecasteele, An evaluation of the solidification/stabilisation of industrial arsenic containing waste using extraction and semi-dynamic leach tests, Waste Manage. 16 (7) (1996) 625–631.

[13] G.H. Bolt, M.G.M. Bruggenwert, Soil chemistry, basic elements, Developments in Soil Science, vol. 5A, Elsevier, Amsterdam, The Netherlands, 1976.