



Effect of carbonation, chloride and external sulphates on the leaching behaviour of major and trace elements from concrete

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ABSTRACT

The effect of the exposure of concrete structural components to CO₂, chloride and external sulphates on the leaching of major and trace elements (Al, Ca, K, Na, S, Si, Ba, Sr, Cr and V) was investigated for concrete made with OPC and fly ash using a tank leach test and the Dutch availability test NEN 7341. Concrete specimens were carbonated under natural and accelerated conditions (2 vol.% CO₂) before testing. Exposure to chloride or external sulphates was simulated by adding NaCl (30 g/L) or Na₂SO₄ (3 or 30 g SO₄²⁻/L) to the tank leach test eluent. The results show that concrete leaching depends significantly on the abovementioned environmental factors. In particular, the cumulative release of Cr during the tank leach test increased proportionally to carbonation depth. More V was released from carbonated concrete. Replacement of the cement by a fly ash with more Cr and V had no discernible effect on Cr release, but resulted in additional V release in proportion to the level of cement replacement. Exposure of concrete to NaCl solution enhanced the release of Cr, but not V. Exposure to Na₂SO₄ solution increased the release of Cr and V considerably. It is suggested that the dissolution of CrO₄²⁻ and VO₄³⁻ substituted AFt/AFm governs the leaching of Cr and V.

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1. Introduction

At present, increasing attention is being paid to the potential leaching of heavy metals from concrete structural components, in particular, in view of the increasing use of secondary fuels in cement production and additions like fly ash or slag in concrete which generally lead to larger amounts of heavy metals in concrete. Heavy metals are leached into water in contact with concrete surfaces by direct dissolution of surface phases and/or diffusion through the pore solution to the concrete surface. The solubility of heavy metals depends on their bonding in the hydration products as well as their ability to form aqueous complexes and precipitate solubility-controlling phases. Thus van der Sloot [1] observed no distinct correlation between the total amounts of Cr, Mo, Pb, V and Zn in mortar and their availability as defined by the Dutch availability test NEN 7341 [2], i.e. their soluble content with respect to dry specimen weight. Consequently, the evaluation of environmental risks cannot be based on the total amounts of trace metals contained in concrete alone, but requires better understanding of the mechanisms involved in leaching. In addition to this, leaching is affected by the actual environmental conditions

at the surface of concrete structural components. These include exposure to CO₂ and NaCl. The latter is commonly used as a deicing agent for concrete highways in moderate and cold climates. Sometimes concrete is exposed to sulphates in groundwater or soil. Such effects are not considered by contemporary leach tests with water which are used to assess the release of environmentally relevant substances from concrete. Incorrect assessment may lead, on the one hand, to underestimation of the actual release of toxic substances or, on the other hand, to the restriction of otherwise useful construction materials.

Since carbonation results in a reduction in pH of the pore solution of concrete, dissolution of the hydration products as well as changes in porosity and pore size distribution, it is expected to affect the solubility and transport of major and trace elements in the pore solution and therefore their leaching behaviour. Despite this, relatively little is known about the effect of carbonation on the release of heavy metals from concrete. Andac and Glasser [3] and Van Gerven et al. [4] investigated the effect of CO₂ on the leaching of metals from cement-stabilized municipal solid waste incineration fly ash by bubbling pure CO₂ through the leachant. The latter authors noted a significant increase in the leaching of Cr, Zn, Ni and Co. However, CO₂ bubbling tends to produce very low pH values and amounts of dissolved CO₂ much in excess of those occurring naturally. Another approach is to compare the leaching of carbonated and non-carbonated specimens. Usually the carbonation process is accelerated in climatic chambers with high CO₂

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concentrations or by the use of super critical CO₂ [5–7]; the method chosen affecting the degree of carbonation and leaching behaviour. Van Gerven et al. [5] observed a reduction of the leaching of Ca, Ba, Cu and Pb from mortar specimens by carbonation.

Penetrating chloride is also expected to affect the solubility of major and trace elements in the pore solution. Thus, for example, according to You et al. [8] Cr may be released from ettringite which is able to incorporate Cr(VI). Opposed to this, it has been reported by Dai et al. [9] that Cr(VI) can be fixed by adsorption on Friedel's salt, an AFm phase formed in the presence of chlorides.

Exposure of concrete structural components to external sulphates leads to deterioration owing to the formation of the expansive phases, ettringite and gypsum, whereas portlandite, AFm phases and C–S–H tend to dissolve, see for example Müllauer et al. [10,11]. It is likely that external sulphates affect the solubility of trace metals and thus their leaching behaviour.

This paper focuses on the effect of carbonation, exposure to NaCl and Na₂SO₄ solutions on the leaching behaviour of Al, Ca, K, Na, S, Si, Ba, Sr, Cr and V from concrete made with OPC and fly ash. The Dutch availability test NEN 7341 and a German tank leach test [12] were used.

2. Materials and methods

The experiments were carried out with concretes made from OPC and a fly ash with the chemical compositions listed in Table 1. The materials were analysed by ICP-OES after digesting in nitric acid. This particular fly ash resulted in a marked increase in the amounts of V, Cr, Ba and Sr in the concrete.

Five different concrete compositions differing in the amount of fly ash were used, Table 2. The concretes were prepared at a total

binder content of 450 kg/m³ and an equivalent water binder ratio w/b_{eq} of 0.60. The equivalent water/binder ratio is used in German regulations for mixes with fly ash [13] where a factor k accounts for the amount of fly ash considered as binder, the rest being regarded as inert filler. The aggregate was Munich sand 0/4 mm and 4/8 mm gravel graded at A8/B8. Concrete cubes (100 mm) were cast from moulds lined with PTFE sheeting to avoid contamination of the concrete by a release agent. After 24 h at 20 °C and 98% RH in climatic cabinet, the samples were demoulded, tightly wrapped in polyethylene foil and stored over water for 90 d.

In order to investigate the effect of carbonation on leaching, the cubes were unwrapped and stored for 154 d at 20 °C in the following controlled conditions.

- (i) Argon for non-carbonated reference samples.
- (ii) 65% RH with ambient CO₂ concentrations for natural carbonation.
- (iii) 2 vol.% CO₂, 65% RH to accelerate the carbonation process.

Afterwards, carbonation depths were determined by spraying a phenolphthalein solution onto freshly fractured surfaces of companion specimens. The main specimens were all conditioned at 20 °C and 65% RH for a further 28 d before performing the tank leach tests. Two separate specimens were investigated for each concrete composition and storage condition. Each specimen was immersed in distilled water ($V_S = 90 \text{ L/m}^2$) in a polyethylene container and the space above the water flooded with argon to minimise carbonation during the experiments. After 1, 3, 7, 16, 32 and 56 d the concentrations of Ca, Na, K, Al, S, Si, Cr, V, Ba and Sr in the eluates were determined by ICP-OES, the pH determined by titration and the eluent renewed. After each step, the containers were flooded with argon again and resealed. An overview of specimen storage is given in Fig. 1.

To investigate the effect of penetrating chloride and external sulphates on leaching behaviour, the tank leach test was performed using concrete B1, following 90 d storage in a foil, with eluents containing NaCl (30 g/L) or Na₂SO₄ (3 and 30 g SO₄²⁻/L). The sulphate concentrations correspond to upper limit of exposure class XA2 according to EN 206 and the concentration of solutions often used to test the resistance of concrete to sulphate attack. The data were corrected for small quantities of Si, Al, Sr and Cr in the initial sulphate and chloride solutions.

The cumulative release of major and trace elements at end of the tank leach test (56 d) was calculated from the concentration of each substance j in the eluate after each elution step i and the eluent/concrete volume-to-surface ratio V_S .

$$E_{56,j} = V_S \sum_{i=1,6} c_{i,j} \quad (1)$$

Additional specimens of concretes B1 and B4 were stored under conditions (i) and (iii) after which pieces of concrete were dried at 40 °C, finely ground to <125 µm and analysed following the

Table 1
Chemical composition of the initial materials.

Substance	Unit	Cement	Fly ash	Sand	Gravel
SiO ₂	wt.%	13.95	50.40	26.66	14.34
Al ₂ O ₃		5.35	27.31	1.76	1.31
Fe ₂ O ₃		4.88	4.79	1.00	0.74
TiO ₂		–	1.50	0.09	0.07
CaO		61.44	7.29	30.85	36.24
MgO		1.20	1.49	6.89	8.59
MnO		0.55	0.06	0.04	0.03
SO ₃		2.95	0.46	0.01	0.01
K ₂ O		0.78	1.52	0.24	0.10
Na ₂ O		0.22	0.28	0.22	0.14
Na ₂ O _{eq}		0.73	1.28	0.38	0.20
P ₂ O ₅		0.17	1.06	0.00	0.00
LOI		1.21	2.48	32.11	38.31
Cr	mg/kg	97.7	343.6	31.0	44.0
V		41.0	336.0	5.0	6.0
Ba		217.0	1645.0	17.0	23.0
Sr		218.0	1723.0	127.0	129.0

Table 2
Concretes used in the experiments.

Concrete	Cement, kg/m ³ c	Fly ash, f		Aggregate ^a kg/m ³	w/b_{eq} ^b	w/b^c	Water, w kg/m ³
		%	kg/m ³				
B1	450	0	0	1551	0.60	0.60	270
B2	427.5	5	22.5	1566		0.58	262
B3	405	10	45	1581		0.56	254
B4	360	20	90	1611		0.53	238
B5	270	40	180	1730		0.41	183

^a 68% 0/4 mm sand, 32% 4/8 mm gravel.

^b Equivalent w/b ratio for mixes with fly ash, $w/b_{eq} = w/(c + kf)$, $k = 0.4$, $f/c \leq 0.33$ according to DIN 1045-2 [13].

^c $w/(c + f)$.

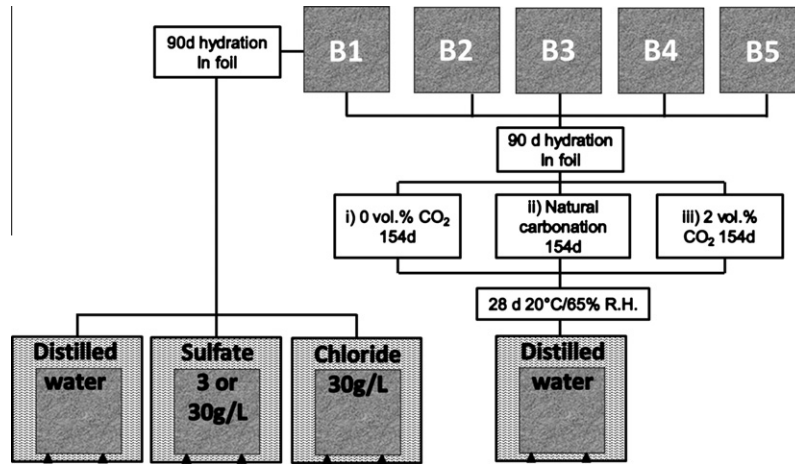


Fig. 1. Overview of specimen storage.

Table 3

Carbonation depth of specimens B1–B5 after 154 d (following 90 d initial storage in a foil).

Storage conditions, 20 °C	B1	B2	B3	B4	B5
(i) 0 vol.% CO ₂ , argon	0.0 mm	0.0 mm	0.0 mm	0.0 mm	0.0 mm
(ii) Natural CO ₂ conc., 65% RH,	2.3	1.8	1.8	1.5	1.2
(iii) 2 vol.% CO ₂ , 65% RH	16.7	16.5	15.7	15.5	12.0

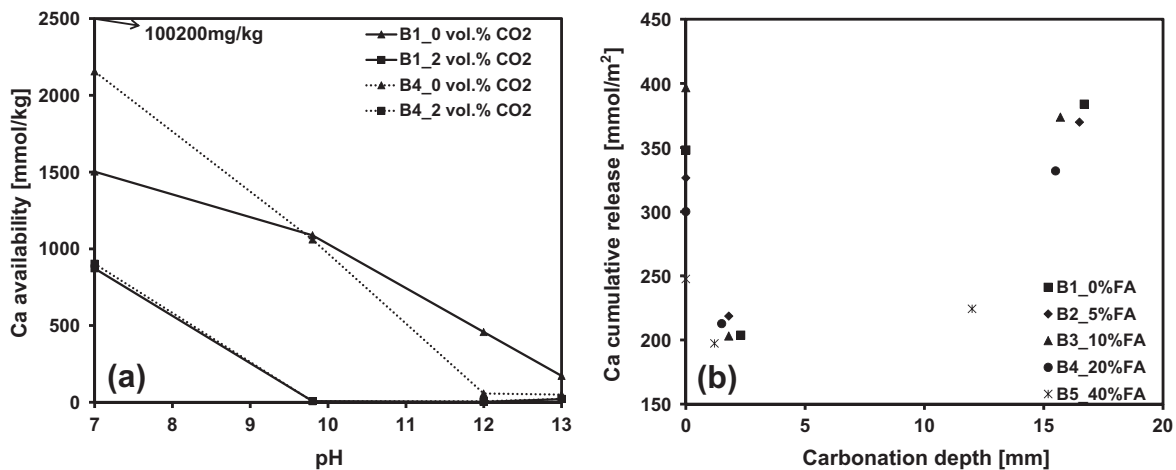


Fig. 2. Effect of carbonation and fly ash content on (a) availability and (b) cumulative release of calcium.

availability test NEN 7341 to assess the maximum leachability of major and trace element in the concretes at pH 4, 7, 9.8, 12 and 13. In the test, 5 g powder portions were mixed with 500 ml distilled water and, while stirring, the pH adjusted by titrating 1 mol/L HNO₃ or NaOH.

3. Results and discussion

3.1. Carbonation

The carbonation depths measured after 154 d are presented in Table 3. A decrease in carbonation depth with increasing fly ash content is apparent which is, as is well-known, due to the denser concrete pore structure obtained with fly ash. The phenolphthalein

test yielded no measurable carbonation depth for the specimens stored in argon.

The effect of carbonation on Ca availability is shown in Fig. 2a where the marked decrease in Ca availability is obviously due to the formation of CaCO₃ which has a low solubility at high pH; in fact the availability of Ca observed at pH ≥ 9.8 was negligible. A similar decrease in Ca availability was observed by Van Gerwen et al. [5] on carbonating mortar with super critical CO₂. In Fig. 2b, the cumulative release of Ca determined from the tank leach test is compared with the corresponding depths of carbonation. A similar dependence of release on carbonation was also observed for mortar by Van Gerwen et al. [5,6] who attributed the reduction in Ca release from slightly carbonated specimens to precipitation of CaCO₃ at the higher pH values of the eluate and the increase in Ca release from strongly carbonated specimens

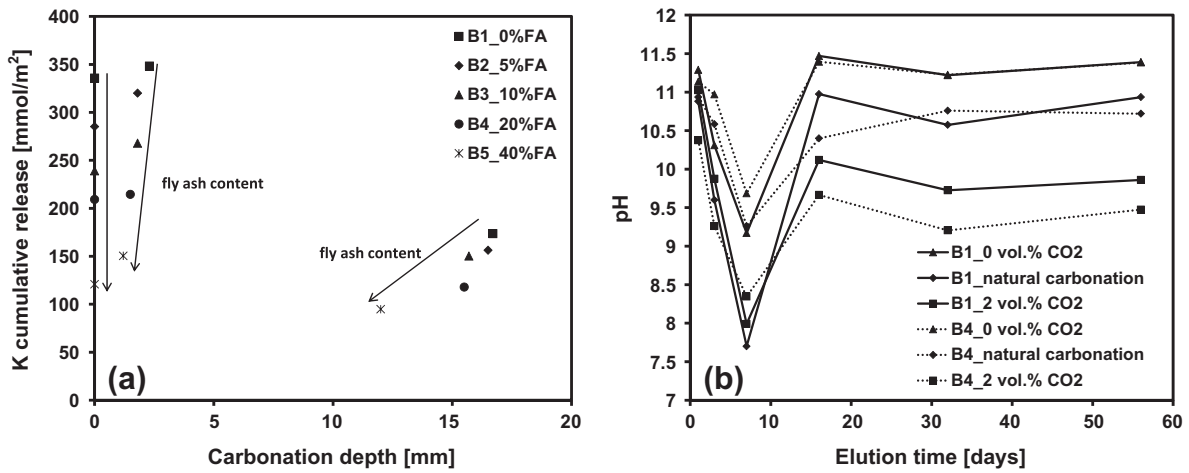


Fig. 3. Effect of carbonation and fly ash content on (a) cumulative release of potassium and (b) eluate pH during the tank leach test.

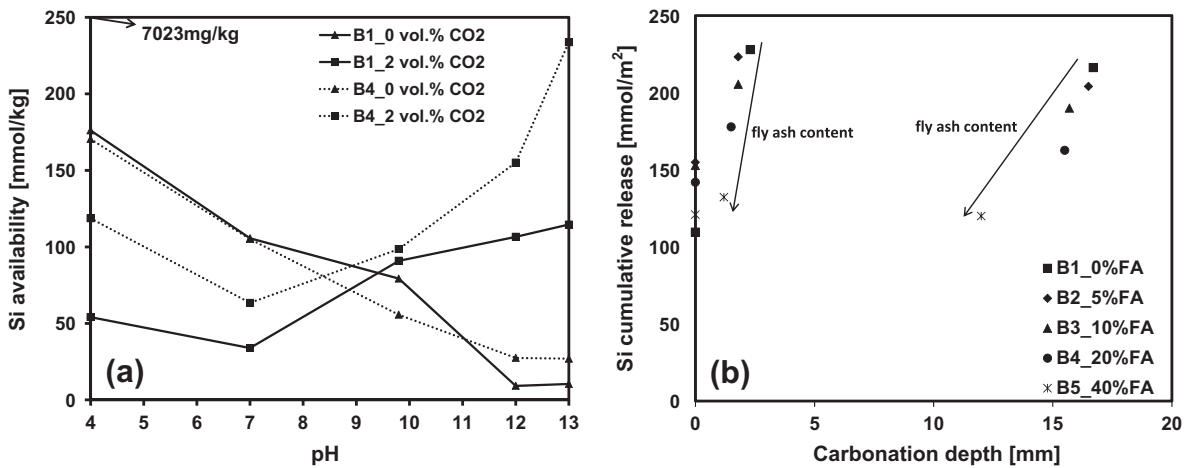


Fig. 4. Effect of carbonation and fly ash content on (a) availability and (b) cumulative release of silicon.

to the domination of bicarbonate at lower pH. Since CaCO_3 is relatively insoluble at the pH of the eluate, Fig. 3b, the higher Ca release produced by accelerated carbonation is probably connected with the dissolution of C–S–H; portlandite having already been converted to CaCO_3 .

Fig. 3a shows the effect of carbonation on the cumulative release of K. Similar results were obtained for Na. As also observed by Van Gerven et al. [5], alkali release tends to decrease with the severity of carbonation. Since alkalis readily dissolve in the pore solution, their release is mainly diffusion-controlled. Thus fewer alkalis are released from carbonated concrete owing to its denser microstructure. The replacement of cement by fly ash also reduces alkali release systematically according to the concentration of alkalis in the pore solution for the cement/fly ash combination and the denser microstructure produced by fly ash. Since storage in a foil provides good reaction conditions for fly ash, most of the fly ash will have reacted after 90 d producing capillary pore systems equivalent to the w/b ratios in Table 2 rather than the equivalent ratio 0.6. In Fig. 3b, the pH of the eluate at the end of each elution step of the tank leach test results mainly from released alkalis where the particular value is determined by the duration of the elution step and the alkali concentration in the concrete pore solution, i.e. the concentration gradient for diffusion flux. Alkali release should therefore affect the release of elements whose solubility depends strongly on pH, e.g. Al and V.

Carbonation has a pronounced effect on the availability of Si in dependence of pH, Fig. 4a. The availability of Si for non-carbonated specimens increases towards lower pH as more Si in C–S–H dissolves. Decalcification of C–S–H during carbonation lowers its Ca/Si ratio resulting in a highly porous, hydrous form of silica [14]. Thus the availability of Si at pH > 10 increases for carbonated samples owing to higher solubility of the amorphous silica phase in comparison to Si bound in C–S–H.

The release of Si from non-carbonated fly ash concrete, Fig. 4b, exhibits no systematic dependence on fly ash content which indicates that the release of Si in the tank leach test is primarily controlled by C–S–H dissolution in the surface region rather than diffusion from inside the concrete. In contrast, larger quantities of fly ash systematically reduce the amount of Si released from carbonated concrete despite the larger Si content of the fly ash. This suggests that diffusion of Si from inside carbonated concrete also contributes to Si release. Moreover, the increase in Si solubility at high pH produced by carbonation, Fig. 4a, will also enhance the surface dissolution of Si explaining why Si release is similar for natural and accelerated carbonation, Fig. 4b.

The pH dependence of Al in Fig. 5a is characteristic of its amphoteric solubility behaviour and solubility control by, in general, AFt and AFm at high pH, and the hydroxide towards low pH. For carbonated specimens an increase in the availability of Al at pH > 9.8 was observed. However, in the tank leach test a distinct

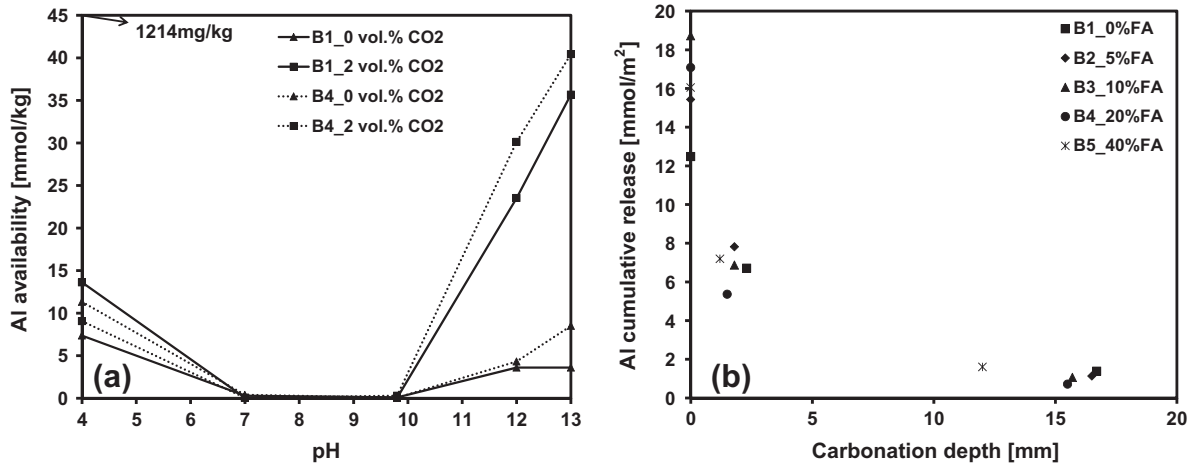


Fig. 5. Effect of carbonation and fly ash content on (a) availability and (b) cumulative release of aluminium.

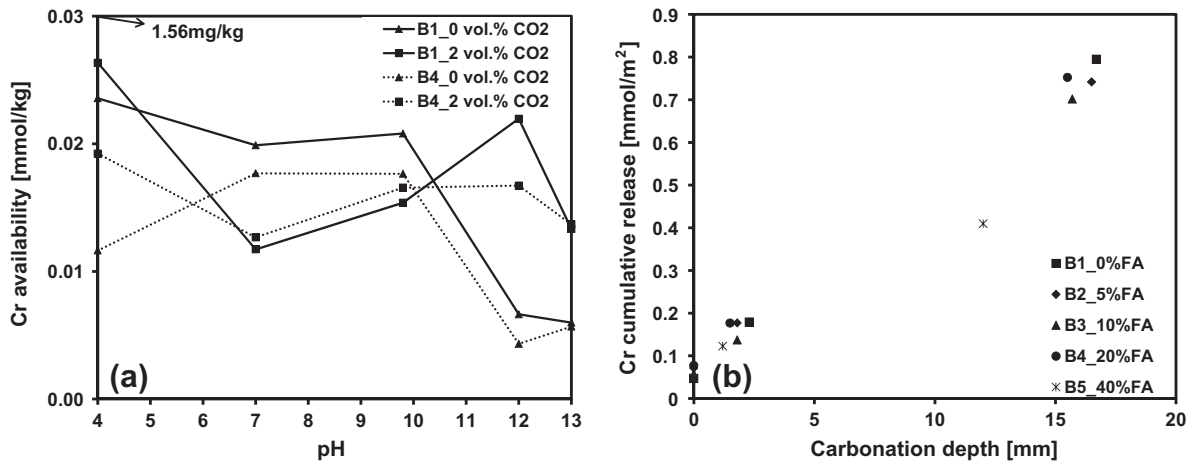


Fig. 6. Effect of carbonation and fly ash content on (a) availability and (b) cumulative release of chromium.

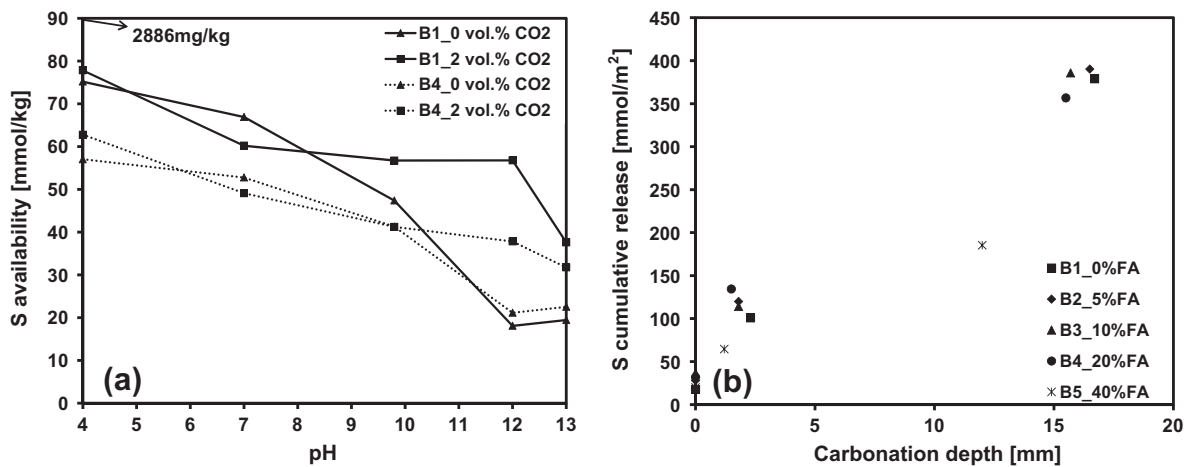


Fig. 7. Effect of carbonation and fly ash content on (a) availability and (b) cumulative release of sulphate as sulphur.

decrease in Al release occurred for larger carbonation depths, Fig. 5b. This is presumably due to the reduction of the pH of the

pore solution which lowers the solubility of Al in the eluate and, most likely, the exertion of solubility control by Al(OH)₃ derived

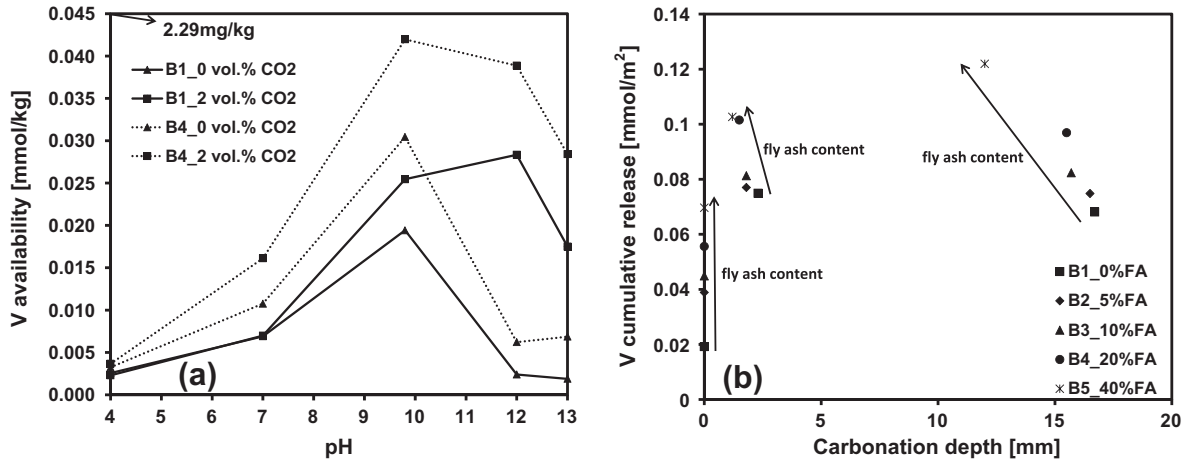


Fig. 8. Effect of carbonation and fly ash content on (a) availability and (b) cumulative release of vanadium.

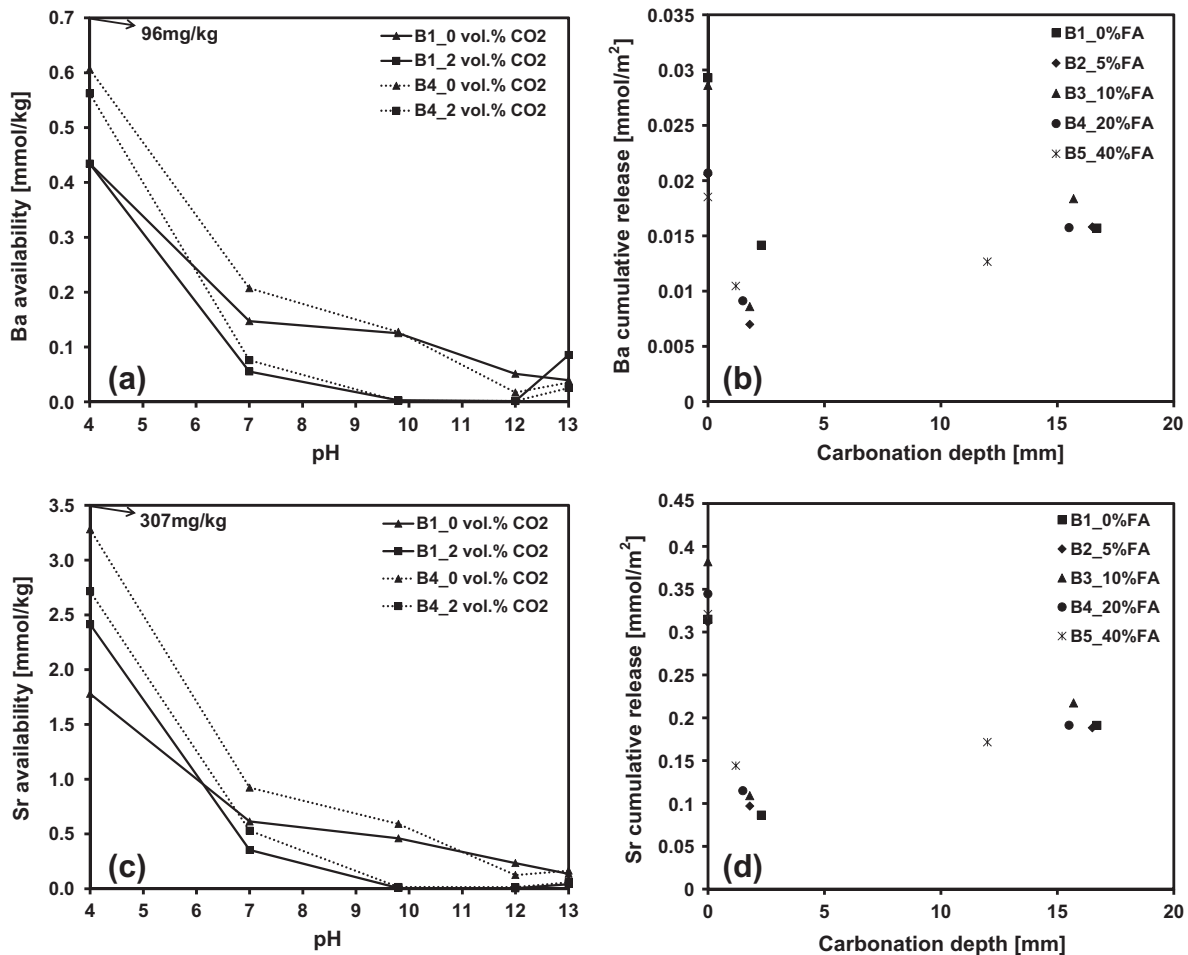


Fig. 9. Effect of carbonation and fly ash content on availability of (a) barium, (c) strontium and cumulative release of (b) barium and (d) strontium.

from AFt and AFm dissolution. A systematic dependence of Al release on fly ash content was observed neither for non-carbonated nor for carbonated concrete.

The availability of Cr as a function of pH and the cumulative release of Cr in dependence of carbonation depth are shown in Fig. 6. The availability of Cr at pH > 10 is increased by carbonation. A well-defined correlation between the cumulative release of Cr and carbonation depth is apparent where, for all concretes, carbon-

ation increases the release of Cr by as much as a factor of 8. There is much evidence [8,15,16] supporting the substitution of SO_4^{2-} by CrO_4^{2-} in AFt and AFm at high pH. Thus the decomposition of these phases explains the observed effect of carbonation on Cr availability and leaching. Based on the data in Table 1, replacement of 20% cement by fly ash increases the total amount of Cr in concrete B4 by 50%. It is apparent that this does not increase the availability of Cr in either carbonated or non-carbonated concrete, Fig. 6a.

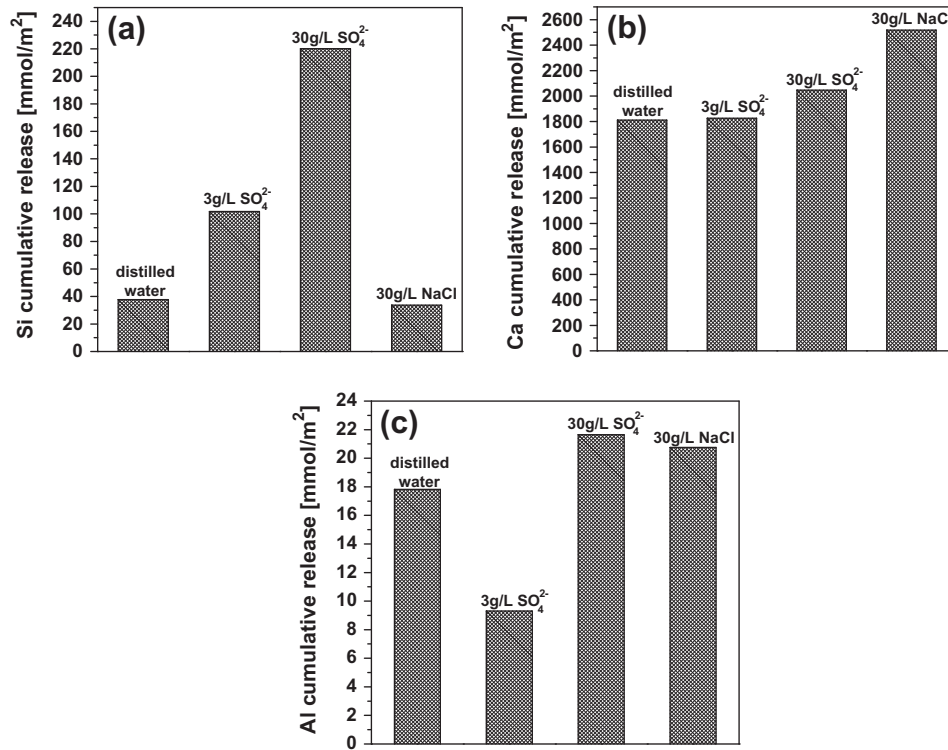


Fig. 10. Cumulative release of (a) silicon, (b) calcium and (c) aluminium from concrete B1 (OPC without fly ash) exposed to sulphate and chloride solutions.

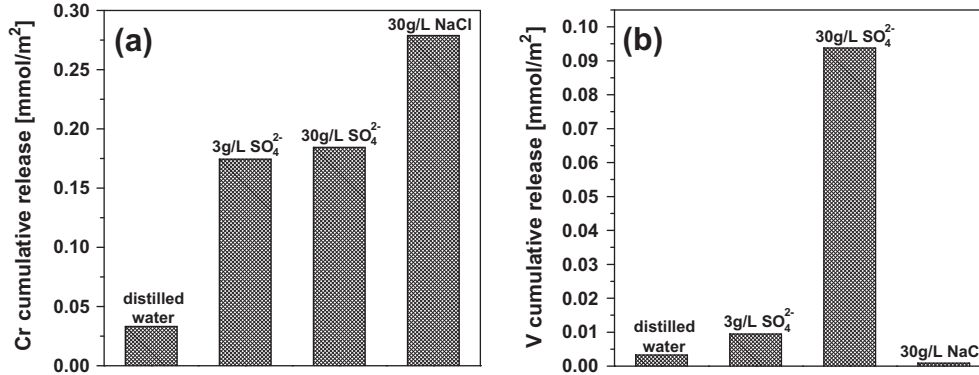


Fig. 11. Cumulative release of (a) chromium and (b) vanadium from concrete B1 (OPC without fly ash) exposed to sulphate and chloride solutions.

Correspondingly, fly ash content has no significant effect on the release of Cr, Fig. 6b.

The effect of carbonation on the availability and release of sulphate as S, Fig. 7, is very similar to that of Cr indicating that their release is controlled by common mechanisms and phases.

As already known from earlier studies with concrete [17] and mortar [1], the availability of V is pH-dependent with a maximum near pH 9, Fig. 8a, suggesting solubility control by different calcium vanadates in dependence of the predominant aqueous V complex. However, low availability of V is expected at pH 11 while ettringite is still present because VO_4^{3-} may well substitute SO_4^{2-} in ettringite, see Kumarathasan et al. [16] and Gougar et al. [18]. Thus the large increase in V availability produced by carbonation at pH 11 in Fig. 8a is explained by the decomposition of VO_4^{3-} substituted ettringite. This is supported by the results of availability tests performed by Engelsen et al. [19] with recycled concrete aggregates in different states of natural carbonation where a similar increase in V

availability at high pH was observed. Based on the data in Table 1, replacement of 20% cement by fly ash increased the total amount of V in concrete B4 by a factor of 2.4. The additional V from the fly ash raised the overall availability of V observed for both carbonated and non-carbonated concretes, Fig. 8a.

The release of V in the tank leach test is enhanced by both carbonation and, irrespective of carbonation depth, replacement of cement by fly ash, Fig. 8b. Thus higher levels of cement replacement by fly ash increase the amount of leachable V. Carbonation reduces the pH of the pore solution promoting ettringite dissolution and higher V solubility. V release does not increase strongly with carbonation depth which points to V leaching by surface dissolution processes rather than diffusion.

The dependence of Ba and Sr availability on pH is very similar, whether for carbonated, non-carbonated concrete or concrete with or without fly ash, Fig. 9a and c. Such behaviour is expected if Ba and Sr carbonates control Ba and Sr dissolution in carbonated con-

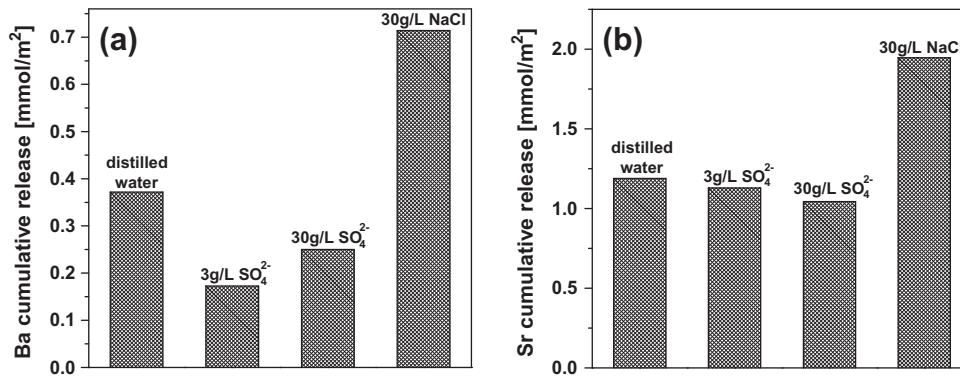


Fig. 12. Cumulative release of (a) barium and (b) strontium from concrete B1 (OPC without fly ash) exposed to sulphate and chloride solutions.

crete since the carbonates are less soluble than the corresponding sulphates, the latter probably determining Ba and Sr solubility in non-carbonated concrete. The dependence of Ba and Sr release in the tank leach test on the degree of carbonation is also very similar and, moreover, is also similar to Ca, Fig. 2b. This provides further evidence that carbonates controls the release of Ba and Sr from carbonated concrete.

3.2. Chloride and external sulphate

The cumulative release of Ca, Ba and Sr in distilled water measured in this series of experiments (Figs. 10b, 12a and b, respectively) is generally above that for the equivalent specimens stored in argon in the above carbonation investigations (Figs. 2a, 9b and d, respectively). The opposite is true for V (Figs. 8b and 11b). In addition, the pH of eluate was about 0.5 above the value measured for the argon-stored specimens. These differences are probably due to higher age of the argon-stored specimens and thus their denser microstructure as well as a small degree of surface carbonation not registered by the phenolphthalein test.

Fig. 10 shows the cumulative release of Si, Ca and Al during exposure of concrete B1 to NaCl and Na₂SO₄ solutions in the tank leach test. The presence of Na₂SO₄ in the eluent enhances the release of Si markedly; by up to 5 times compared with storage in distilled water. Now, when external sulphate ions penetrate concrete AFm is converted into ettringite, see for example Müllauer et al. [10,11], the reaction requiring additional Ca which is supplied by portlandite and, at pH 12.6, C–S–H dissolution. This reaction tends to increase pH (for distilled water: pH_{i=6} = 12.04; for 30 g SO₄²⁻/L: pH_{i=6} = 12.11) as observed, by Müllauer et al. [11] in experiments with powdered hardened cement paste in sulphate solutions. The observed increase in Si release cannot be explained by the equilibrium solubility behaviour of C–S–H with regard to pH and the total amounts of dissolved Si and Ca [20,21]. Thus it is unlikely that ettringite precipitation affects Si release. It is suggested that by supplying Ca from C–S–H for ettringite and gypsum formation in the surface regions of the concretes C–S–H is decalcified, decomposing towards hydrous silica. Thus as considered above for carbonated concrete, more Si is available for surface dissolution which increases Si leaching as shown in Fig. 10a. Addition of NaCl to the eluate had no discernible effect on Si release.

Apart from a reduction in the cumulative release of Al from specimens leached in 3 g SO₄²⁻/L, the effect of sulphate or chloride in the eluent on Ca and Al release is not large, Fig. 10b and c. An increase in Ca and Al leaching on addition of NaCl to the eluent may be due to the decrease in pH of the eluate (for distilled water: pH_{i=6} = 12.04; 30 g/L NaCl: pH_{i=6} = 11.58).

Exposure of the concretes to sulphate or chloride solutions was found to increase the release of Cr to a large extent, Fig. 11a. Appar-

ently, high sulphate concentrations disturb the solubility equilibrium of CrO₄²⁻ substituted ettringite and AFm. SO₄²⁻ replaces CrO₄²⁻ which then enters the pore solution. XRD measurements revealed the presence of Friedel's salt in the specimens eluted in the chloride solutions. This phase is known to form at the expense of the AFt and AFm phases and is frequently observed in concrete structures subjected to chloride ingress. It is concluded that more Cr is released from concrete exposed to NaCl solutions because CrO₄²⁻ incorporated in AFt and AFm dissolves in the pore solution when Friedel's salt forms. Moreover, the lower pH of the eluate with NaCl also favours Cr dissolution. Although evidence exists for the fixation of CrO₄²⁻ in AFm as 3CaO · Al₂O₃ · CaCrO₄ · 10H₂O at 4 < pH < 10 as observed by Dai et al. [9], the present results indicate that this phase is less stable at the higher pH values of the eluate in these investigations.

Whereas NaCl had no discernable effect on the release of V, high sulphate concentrations increased V leaching considerably; the addition of 30 g SO₄²⁻/L to the eluent increased the cumulative release of V by a factor of about 30, Fig. 11b. In this case, the introduction of more SO₄²⁻ into the pore solution causes VO₄³⁻ in ettringite to be displaced by SO₄²⁻ thus enhancing the release of V.

Exposure to external sulphate was observed to lower Ba release in the tank leach test, Fig. 12a. This is explained by the precipitation of SO₄²⁻ as scarcely soluble barium sulphate which removes Ba from the pore solution. This effect will be less for strontium sulphate which is more soluble than barium sulphate, Fig. 12b. Opposed to this behaviour, more Ba and Sr are released in the presence of NaCl. This may be due to the reduction in pH of the eluate mentioned above which tends to enhance the solubility of Ba and Sr, Fig. 9a and c, and thus their cumulative release.

4. Conclusions

Tank leach tests (56 d: duration, ratio of eluent volume to concrete surface: 90 L/m²) were performed to determine the effect of carbonation depth and NaCl or Na₂SO₄ in the eluent on the release of Al, Ca, K, Na, S, Si, Ba, Sr, Cr and V from concretes made with OPC and fly ash. The availability of the elements was determined between pH 4 and 13 following the Dutch standard test NEN 7341. The results show that the leaching behaviour of major and trace elements from concrete depends significantly on the environmental factors carbonation, exposure to deicing salt (sodium chloride) or external sulphates. This is not taken into account by contemporary tank leach tests used to assess the environmental impact of concrete.

The cumulative release of Cr increased proportionally to carbonation depth from about 0.05 to 0.8 mmol/m² for a carbonation depth of 16 mm. Replacement of the cement by fly ash with a high-

er Cr content had no discernible effect on Cr release. The leaching behaviour of SO_4^{2-} (as S) was analogous to Cr suggesting that CrO_4^{2-} partly substituted for SO_4^{2-} in AFt and/or AFm dissolves when these phases decompose during carbonation.

More V was released from carbonated concrete, the amount increasing from 0.02 to 0.07 mmol/m² for carbonation depths of 3 mm and above. Replacement of the cement by fly ash with a higher V content resulted in additional release of V in proportion to replacement level (0.05 mmol/m² for 40% fly ash). It is suggested that V release is mainly due to surface dissolution processes involving VO_4^{3-} substituted ettringite.

Like Ca, smaller amounts of Ba and Sr were released from carbonated concrete. This is explained by the formation of the corresponding low-solubility carbonates.

Elution of the concrete specimens in 30 g/L NaCl increased the release of Cr from 0.03 to 0.28 mmol/m². This is attributed to the dissolution of CrO_4^{2-} predominantly incorporated in AFt/AFm which forms Friedel's salt thus enhancing Cr release. V release was not significantly affected by penetrating chloride. Exposure to chloride increased both Ba and Sr release (0.38–0.71 mmol/m² and 1.4–1.9 mmol/m², respectively).

Elution in 3 g SO_4^{2-} /L (external sulphates) increased both Cr and V release considerably (0.03–0.17 mmol/m² and 0.004–0.01 mmol/m², respectively). This is attributed to CrO_4^{2-} or VO_4^{3-} mainly in AFt and AFm which are displaced by SO_4^{2-} thus becoming mobile for leaching. In contrast, Ba and, to some extent, Sr leaching was reduced by sulphates in the eluent. BaSO_4 precipitation is expected to remove Ba from the concrete pore solution.

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References

- [1] van der Sloot HA. Characterization of the leaching behaviour of concrete mortars and of cement-stabilized wastes with different waste loading for long term environmental assessment. *Waste Manage* 2002;22:181–6.
- [2] NEN 7341. Leaching characteristics of solid (earthy and stoney) building and waste materials, leaching tests, determination of the availability of inorganic components for leaching. Delft, Netherlands; 1995.
- [3] Andac M, Glasser FP. Long-term leaching mechanisms of Portland cement-stabilized municipal solid waste fly ash in carbonated water. *Cem Concr Res* 1999;29:179–86.
- [4] Van Gerven T, Moors J, Dutré V, Vandecasteele C. Effect of CO_2 on leaching from a cement-stabilized MSWI fly ash. *Cem Concr Res* 2004;34:1103–9.
- [5] Van Gerven T, Van Baelen D, Dutré V, Vandecasteele C. Influence of carbonation and carbonation methods on leaching of metals from mortars. *Cem Concr Res* 2004;34:149–56.
- [6] Van Gerven T, Cornelis G, Vandoren E, Vandecasteele C, Garrabrants AC, Sanchez F, et al. Effect of progressive carbonation on heavy metal leaching from cement-bound waste. *Am Inst Chem Eng* 2006;52(2):826–37.
- [7] Gervais C, Garrabrants AC, Sanchez F, Barna R, Moszkowicz P, Kosson DS. The effect of carbonation and drying during intermittent leaching on the release of inorganic constituents from a cement-based matrix. *Cem Concr Res* 2004;34:119–31.
- [8] You KS, Ahn JW, Cho HC, Han GC, Han DY, Cho KH. Competing ion effect of stabilization by Cr(III) & Cr(VI) in ettringite crystal structure. *Solid State Phenom* 2007;124–126:1629–32.
- [9] Dai Y, Qian G, Cao Y, Chi Y, Xu Y, Zhou J, et al. Effective removal and fixation of Cr(VI) from aqueous solution with Friedel's salt. *J Hazard Mater* 2009;170:1086–92.
- [10] Müllauer W, Beddoe RE, Hilbig H, Heinz D. Effect of phases and microstructural development on expansion and damage by sulfate attack. In: *International congress on the chemistry of cement, Madrid*; 2011. p. 435.
- [11] Müllauer W, Beddoe RE, Heinz D. Sulfate attack on concrete – solution concentration and phase stability. In: *Proc intern RILEM TC 211-PAE final conference, Toulouse*; 2009. p. 18–27.
- [12] DAfStB-Richtlinie. Bestimmung der Freisetzung anorganischer Stoffe durch Auslaugung aus zementgebundenen, Baustoffen; 2005.
- [13] DIN 1045-2. Concrete, reinforced and prestressed concrete structures – part 2: concrete – specification, properties, production and conformity – application rules for DIN EN 206-1; 2008.
- [14] Taylor HFW. *Cement chemistry*. Academic Press; 1990.
- [15] Schiopu N, Tiruta-Barna L, Jayr E, Méhu J, Moszkowicz P. Modelling and simulation of concrete leaching under outdoor exposure conditions. *Sci Total Environ* 2009;407:1613–30.
- [16] Kumarathasan P, McCarthy GJ, Hassett DJ, Pflughoeft-Hassett DF. Oxyanion substituted ettringites: synthesis and characterization and their potential role in immobilization of As, B, Cr, Se and V. *Mater Res Soc Symp Proc* 1990;178:83–104.
- [17] Jungermann W, Hecht M, Beddoe RE. Elutionsverhalten von betonbauteilen – szenarien und mechanismen. 16. ibausil, Weimar; 2006. p. 1/1337–45.
- [18] Gougard MLD, Scheetz BE, Roy DM. Ettringite and C-S-H Portland cement phases for waste ion immobilization: a review. *Waste Manage* 1996;16:295–303.
- [19] Engelsens CJ, van der Sloot HA, Wibetoe G, Justnes H, Lund W, Stoltenberg-Hansson E. Leaching characterisation and geochemical modelling of minor and trace elements released from recycled concrete aggregates. *Cem Concr Res* 2010;40:1639–49.
- [20] Greenberg SA, Chang TN. Investigation of the colloidal hydrated calcium silicates. II. Solubility relationships in the calcium oxide–silica–water system at 25°. *J Phys Chem* 1965;69:182–8.
- [21] Chen JJ, Thomas JJ, Taylor HFW, Jennings HM. Solubility and structure of calcium silicate hydrate. *Cem Concr Res* 2004;34:1499–519.