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Influence of carbonation and carbonation methods on leaching of metals from mortars

T. Van Gerven[a,*], D. Van Baelen[a], V. Dutré[b], C. Vandecasteele[a]

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

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Abstract

Mortars with varying water-to-cement (w/c) ratio were spiked with heavy metals. After hardening, some samples were carbonated in a CO_2 chamber, others were carbonated using supercritical CO_2 (SCC). Porosity and carbonation depth of treated and untreated samples were compared. Leaching was tested using the diffusion (NEN 7345) and extraction test (based on DIN 38414-S4). The results show that carbonation decreases the porosity of the samples. The decrease is more important with increasing w/c ratio. Carbonation runs deeper into the monolith with increasing w/c ratio. In the supercritical method, not all samples were carbonated to the same extent. The diffusion test shows that carbonation decreases leaching of Na, K, Ca, Ba, Cu, and Pb and increases leaching of Mg. Ni leaching depends on the pH induced by carbonation. Influence of pH and formation of metal carbonates is evaluated with the extraction test and enhances understanding of metal leaching in the diffusion test.

Keywords: Carbonation; Mortar; Heavy metals; Leaching; Waste management

1. Introduction

When waste materials are reused in cementitious matrices, leaching of heavy metals has to be controlled. In order to assess long-term leachability, aging and more specifically carbonation of the cement matrix have to be taken into account [1]. Carbonation has also been investigated to further improve immobilization of solidified/stabilized waste [2].

Carbonation involves the chemical reaction of portlandite, $Ca(OH)_2$, and calcium silicate hydrate, C-S-H, in the cement matrix with carbon dioxide gas leading to calcite, $CaCO_3$ [3]. Carbonation has three major effects: the pH in the pore water is lowered, portlandite reacts to give calcite and other metal hydroxides give carbonates. These three effects influence leaching of heavy metals by changing the solubility of components and the porosity of the matrix.

The pore water in the cement matrix has a typical pH of 12–13. Reaction of portlandite and C-S-H to calcite can lower the pH ultimately to 8.3, depending on the degree of carbonation. While some metals are more soluble at pH 8 than at 12, amphoteric metals typically have a minimum solubility between pH 8 and 10.

The calcite mineral is 17% larger than the portlandite mineral [4], so that reaction of portlandite to calcite induces structural changes in the cement matrix. Research [5] found that the total porosity of hardened cement pastes decreases with carbonation. In addition, these researchers noticed a shift from smaller pores to pores larger than 30 nm because smaller pores grew bigger due to the reaction of C-S-H with CO_2. Whereas in Ref. [3], a reduction in porosity was noted after carbonation, physical retention of highly soluble components in the matrix decreased as well. The explanation may be microcracking due to accelerated carbonation or rearrangement of pores to decrease occluded porosity.

Contradictory leaching results were reported for carbonated samples in the last years so that the situation is rather confusing. In Refs. [6–8], carbonation during curing accelerated hydration and led to enhanced calcite contents, greater strength, and significant reduction in leaching of calcium, mercury, nickel, zinc, copper, lead, chromium, molybdenum, and arsenic. Ref. [9] reports, however, an increase of chromium leaching. Other researchers concluded that through carbonation after curing, some metals, like stron-

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* 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).

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tium, were chemically bound in calcite by formation of a solid solution resulting in a decreased leaching [3], but that leaching of calcium, lead and cobalt [3], cadmium [3,10], copper [11,12], zinc [11,13], chromium [12,13], arsenic [10,11,14], molybdenum [12], nitrate [3,14], sulphate [11–13], and chloride [11,12,14] increased. In Ref. [14], a decrease in leaching was found for strontium as well, but also for calcium, contrary to Ref. [3], and cesium. Lower leaching of lead after carbonation is reported in Ref. [10], and for lead, calcium, sodium, potassium, and fluoride in Ref. [12]. In Ref. [15], a decrease in leaching of Eu and Th after carbonation is reported.

The accompanying pH of the leachates is not always reported, although this is an essential parameter in the understanding of leaching processes. Using extraction tests, Ref. [6] reports 'lower local pH-conditions by 3 units' for carbonated samples, Ref. [8] indicates that pH in the leachate of an extraction test is 12.5 for uncarbonated samples, and 9.5 for carbonated samples and in Ref. [7], the pH decreases from 11.5–12.5 to 8–10. Ref. [11] reports that for leachates of a batch-leaching test, similar pHs of 12 for uncarbonated samples and 8 for carbonated samples were indicated. In Ref. [13], a 'decrease in pH produced by the carbonation' is mentioned, Ref. [14] describes 'lower pHs of the carbonation environment'.

It remains unclear what is the influence of the carbonation method, the type of samples tested, the carbonation degree, and the leachate pH on leaching of metals. Performing carbonation during or after curing also seems to have an effect on leaching, but remains largely uninvestigated as well.

To study carbonation in cement matrices, samples can be stored for a period of time in contact with atmosphere [16] or the carbonation process can be artificially intensified. Several acceleration methods have been described in literature.

Using a high concentration of gaseous CO_2 in a closed chamber is the oldest and most common method. In Refs. [6,8], cementitious waste forms were stored in a CO_2 environment for curing. Other researchers subjected samples to carbonation only after curing. Several conditions were applied: 50% CO_2 atmosphere at 50–75% relative humidity (RH) and a temperature of 50 °C for 26 up to 52 days [3,17], up to 5% CO_2 at 65% RH for 30 min per day during several weeks [5], saturated CO_2 atmosphere at 60% RH for 56 days [13], and saturated CO_2 atmosphere at 65% RH for eight cycles of 8 days each [11].

Another technique is the use of supercritical CO_2 (SCC). The advantage of SCC is the combination of gaslike properties of low viscosity, high diffusivity, and absence of surface tension with fluidlike properties of high density and high solvent power. The critical conditions for CO_2 are 31.1 °C and 73.8 bar. Reported applied conditions are 59 °C and 97 bar for 24 h with up to 100% RH [18], 40 °C and 276 bar for 2 h [2], 35–62 °C and 84–280 bar for 2 h [15], and 40–50 °C and 150–250 bar for 15, 60, and 120 min [12].

Recently, a 'vacuum method' was introduced [14]. This reduced-pressure technique with a desiccant present in the reactor vessel removes the water of reaction as it is produced, thereby maintaining an open pore network to facilitate the transfer of introduced CO_2 into the specimen.

In this study, the influence of carbonation on the porosity of monoliths and on metal leaching is evaluated. Leaching is tested using the diffusion test, which is a semidynamical batch test. Because the spatial presence of metal carbonates and the pH of the leachate are suspected to be essential parameters in the understanding of the leaching behavior, carbonation depth is measured and extraction tests are performed to measure the influence of pH on leachability. The CO_2 chamber and supercritical method are applied to accelerate carbonation and their results are compared.

2. Materials and methods

2.1. Production of mortars

Mortars were produced by mixing ordinary Portland cement (CEM I 42.5 R) with Rhine sand (0/4) and distilled water in which Na, K, Ni, Cu, Ba, and Pb were dissolved as chlorides, in such an amount that the added concentration of the elements in the hydrated mixture is 0.05% (w/w). Three different water-to-cement (w/c) ratios were applied: low (L), medium (M), and high (H). The recipes are given in Table 1.

The mixtures were then poured in moulds of 160 × 40 × 40 mm. After 48 h, the samples were demoulded and stored for 28 days in a humid room (20 °C, >95% RH) for hardening. Finally, the mortars were sawn into cubes of 40 × 40 × 40 mm.

2.2. Carbonation methods

2.2.1. Carbon dioxide chamber

Mortar samples were placed in a closed chamber at a temperature of 37 °C and a RH of over 90%. One set of samples was exposed for 360 h to an atmosphere containing

Table 1
Mix designs for the produced mortars

(kg/m^3)	L (low w/c)	M (medium w/c)	H (high w/c)
Cement	730	658	599
Sand	1440	1298	1182
Water	250	325	359
NaCl	3.5	3.2	2.7
KCl	2.6	2.4	2.1
$NiCl_2 \cdot 6H_2O$	5.6	5.0	4.4
$CuCl_2 \cdot 2H_2O$	3.7	3.3	2.9
$BaCl_2 \cdot 2H_2O$	2.4	2.2	1.9
$PbCl_2$	1.8	1.7	1.4
w/c	0.34	0.49	0.60

5% CO_2 (AC5) and another set for 72 h to 20% CO_2 (AC20).

2.2.2. Supercritical carbonation

A Separex supercritical fluid extraction (SFE) pilot installation was used to carbonate mortars (SCC samples) with SCC. Liquid CO_2 is first put under pressure by means of a high-pressure pump and subsequently heated in a heat exchanger to obtain supercritical conditions. The SCC is then carried from bottom to top through a preheated reactor vessel that has a cylindrical shape with an inner volume of 2 l. After passing through the vessel, the SCC is decompressed in an automatic backpressure regulator and collected in three preheated high-performance cyclonic separators. The gaseous CO_2 is then recycled to a condenser, and the resulting liquid CO_2 is sent back to the CO_2 pump. The reactor vessel can be bypassed to allow introducing or collecting of the samples.

The reactor vessel can contain eight mortar cubes. A nickel wire was wound around the cubes in order to allow CO_2 to reach all sides of the cubes when they are piled up one another in the vessel. The working conditions of the SFE installation were a temperature of 80 °C, a pressure of 400 bar, and a flux of 5 kg CO_2 per hour. The installation was allowed 2 h to reach these conditions with the reactor vessel in bypass. The vessel was then loaded with samples. After 20 min, the samples were at the desired temperature and the bypass was lifted. An additional 7 min were then needed to obtain the desired conditions of pressure and flux in the vessel. For 120 min, the installation was kept at the working conditions. Afterwards, the vessel was bypassed, the pressure was released, and the heating was turned off. About 60 min later, the vessel could be opened.

2.3. Measurement of physical parameters

For the assessment of the degree of carbonation, a sample was cut in two and the inner surfaces were sprayed with a solution of 1 g phenolphthalein in 50 ml ethanol 95% and 50 ml distilled water. Phenolphthalein is a pH indicator with a red color at $pH>10$ [noncarbonated (NC) cement matrix] and no color at $pH<8$ (carbonated cement matrix). The depth of the carbonation front was then estimated by averaging the four measured distances of each of the two surfaces to the edge of the NC core.

The open bulk porosity of the samples is calculated according to Eq. (1).

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

Three samples of each type of the cementitious matrices were therefore dried until constant weight, weighed (dry mass), immersed in water (density = 1 g/cm^3) until constant weight, and weighed again (wet mass).

2.4. Measurement of chemical parameters

Three samples of each mixture and each carbonation technique (CO_2 chamber, SCC, as well as NC samples) were leached in a semidynamical batch test according to the Dutch diffusion test NEN 7345 ([19], hereafter called the diffusion test). The cubes were immersed in distilled water (brought to pH 4 with nitric acid) that was renewed after 6, 24, 54, 96, 216, 384, 864, and 1536 h. The volume of the leachant equals 5 times the volume of the cube. The pH of the leachate of each renewal was measured, and 50 ml of this leachate was acidified with 1 ml of concentrated HNO_3 for analytical measurement. Results of the subsequent renewals are summed and expressed as cumulative mass per sample surface (mg/m^2).

The leachability of metals as a function of pH was measured, based on the DIN 38414-S4 test [20], by milling the cubes and leaching 10 g of the powder (more than 95% <125 μm) in 100 ml of distilled water acidified with different volumes of concentrated HNO_3. After 24 h of agitation, the leachate was filtered through a 0.45-μm membrane, pH of the leachate was measured, and 50 ml of this leachate was acidified with 1 ml of concentrated HNO_3 for analytical measurement. Results are expressed as mass per leachant volume (mg/l). The measured leachability in this test, hereafter called the extraction test, is assumed to equal the solubility of the metals because the sample is milled to a powder, agitation is applied, and the time of leaching should be enough to reach chemical equilibrium. The results of the extraction test are therefore considered to be solubilities and are described as such in this paper.

Acidified leachate samples were analyzed for metal concentrations using a VG PlasmaQuad PQ-2 Plus ICP mass spectrometer.

3. Results and discussion

3.1. Carbonation depth

Table 2 shows that carbonation with SCC occurs much faster than with the CO_2 chamber. The AC20 samples are less carbonated than the AC5 samples because of the

Table 2
Average carbonation depth (mm) of carbonated mortars for which different w/c ratios (low, medium, and high) were applied

	L (w/c = 0.34)	M (w/c = 0.49)	H (w/c = 0.60)
AC20	0.8 (11.5)	1.8 (24.6)	4.0 (48.8)
AC5	1.0 (14.3)	3.0 (38.6)	6.0 (65.7)
SCC	1.1 (15.6)	12.9 (95.5)	12.5 (94.7)

The corresponding carbonation percentage (vol.%) is indicated inside brackets.

difference in exposure time (72 and 360 h, respectively), although the applied partial CO_2 pressure was higher for the AC20 samples than for the AC5 samples (20% and 5% CO_2, respectively).

Carbonation runs deeper with increasing w/c ratio in the AC samples. In the SCC samples, a maximal carbonation depth seems to be reached for the applied conditions from w/c = 0.49 and higher, where a carbonation percentage of about 95% is obtained.

Measurement on some additional samples from the CO_2 chamber gave similar carbonation depths. Samples from the supercritical carbonation method, however, showed a carbonation depth varying as a function of the sample's position in the reactor vessel (Fig. 1): the most carbonated samples were situated in the middle of the reactor vessel. Therefore, it must be specified which supercritically carbonated samples were used in further experiments. For the measurement of carbonation depth and porosity, samples from position 'e' were used. For the leaching experiments, samples from position 'd' were used.

The variation of carbonation depth as a function of the sample's position in the reactor vessel was an unexpected outcome in the supercritical experiments and cannot be explained. This influence of position has never been reported up to now but is an important issue, both in view of preparing representative samples for leaching research as well as in view of using this type of supercritical set up in an additional step during the immobilization process of incorporating waste in cement. Possibly, this drawback can be avoided when using the supercritical installation as a static carbonation method as in Ref. [18] and not dynamic (constant CO_2 flow), as this study does and as reported in Refs. [2,15].

3.2. Influence of carbonation on porosity

The results of the porosity are shown in Table 3. Only the average porosities of the NC w/c sequence are significantly different from each other ($P < .05$). For the NC samples, the porosity increases as the w/c ratio increases. This increase is, however, lowered so much through carbonation that the difference between the average porosities of the w/c ratios of the carbonated samples is not significant.

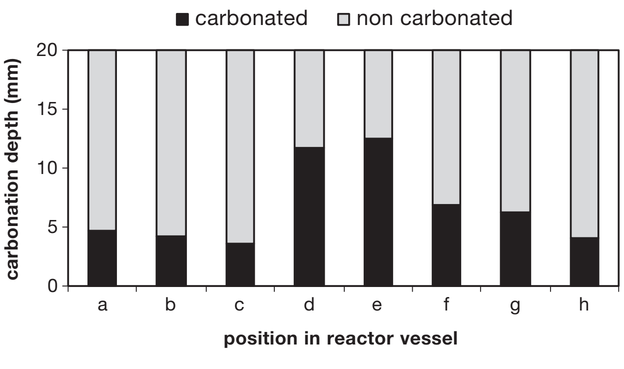

Fig. 1. Influence on carbonation depth of the position of H samples in the reactor vessel of the supercritical pilot installation (position 'a' is below, position 'h' is on top).

Table 3
Open porosity (%) for NC and carbonated samples with S.D. between brackets (average of three samples)

	L (w/c = 0.34)	M (w/c = 0.49)	H (w/c = 0.60)
NC	22.2 (0.4)	24.9 (1.6)	29.9 (1.6)
AC20	19.8 (0.6)	22.9 (0.5)	24.8 (1.1)
AC5	20.4 (0.8)	24.0 (1.2)	25.3 (1.1)
SCC	20.4 (0.5)	20.7 (1.3)	21.9 (2.3)

Three different w/c ratios (low, medium, and high) were applied.

Looking at the carbonation influence, the differences between the average porosities of medium NC and CO_2 chamber and between the average porosities of low CO_2 chamber and SCC are not significant ($P > .05$). The other average porosities of samples with the same w/c are significantly different ($P < .05$) from each other. Carbonation has a clear influence on the porosity: it decreases porosity and this decrease is more important for higher w/c ratios. Within the CO_2 chamber samples, AC20 samples all seem to have a lower porosity than AC5 samples, but this difference is not significant at the .05 level. In most cases—except for the L samples—samples carbonated with supercritically CO_2 have a lower porosity than samples carbonated in the CO_2 chamber. This is congruent with the results of the carbonation depth measurements.

The results of the carbonation depth and the porosity indicate that the degree of carbonation is highest in SCC samples compared to AC samples. The porosity decreases as carbonation proceeds. This is in agreement with findings of other researchers, mentioned in the Introduction section.

3.3. Diffusion test results

From here, we will proceed with the H samples (w/c 0.60). The L and M samples gave roughly the same leaching results as the H samples.

The pH of the leachates of the NC samples remains high throughout the whole period of the diffusion test (Fig. 2). Due to carbonation, the pH of the leachates is lowered from about pH 12 down to pH 9–10.5. The pH of leachates of the carbonated samples increases at first because the leaching periods become longer. To the end of the diffusion test, the pH decreases considerably, indicating exhaustion of portlandite leaching. This is particularly the case for the AC20 and AC5 samples, which are carbonated for about 25% (Table 3). Leachates from SCC samples have a consistently lower pH than leachates from AC samples because of a more carbonated matrix.

The results of the diffusion test (Fig. 3) indicate that carbonation decreases leaching of Na, K, Ca, Ba, Cu, and Pb. Leaching of Mg increases with carbonation. The influence of degree of carbonation is, however, not always clear.

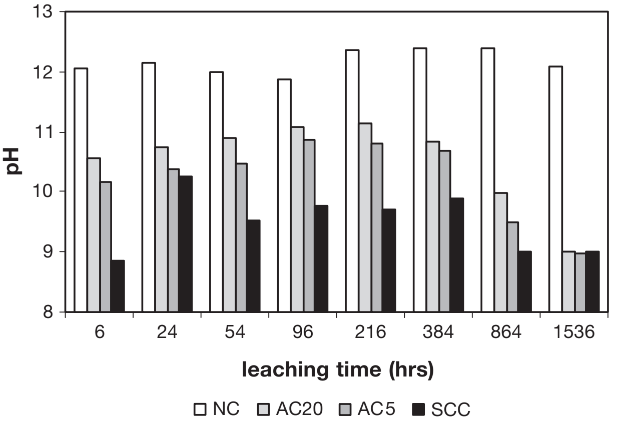

Fig. 2. Measured pH at the end of each leaching period for NC and carbonated H mortars (average of three samples).

AC samples leach less Ca, Ba, Ni, and Pb than NC samples, but SCC samples leach more of these metals than AC samples in spite of a higher carbonation degree. Leaching of Ni from SCC samples even exceeds leaching from NC samples, although this is not significant. In the Introduction section, contradictory leaching results were already noticed in the literature.

Leaching of sodium and potassium is often used to calculate diffusion coefficients and tortuosity values, assuming that their interaction with the cement matrix is minimal. The lower Na and K leaching of carbonated samples in the diffusion test would then be attributed to the decrease in porosity. To confirm this assumption and to understand the leaching results of the other metals in the diffusion test, the influence of pH on solubility is assessed with the extraction test in the following paragraph.

3.4. Extraction test results

Fig. 4 shows the solubilities of eight metals in function of pH for milled NC and carbonated samples. AC20 samples gave the same results as AC5 samples and is not shown in the figure.

Influence of pH on solubility of sodium and potassium from NC samples is indeed negligible for the relevant pH range of 7–13. Carbonated samples, however, show Na and K solubility, which is not only lower than NC samples but also pH dependent. This was also found for weathered bottom ashes [21] cement-stabilized metallurgical slag [12]. It can be concluded that even for Na and K, a combination of porosity, carbonation, and pH is responsible for lower release. Calculation of diffusion coefficients and tortuosity values for carbonated monoliths from Na and K results is questionable.

Leaching of Ca, Mg, Ba, Ni, Cu, and Pb is clearly dependent on pH and metal–carbonate formation. Calcium, magnesium, nickel, and copper show a higher solubility at neutral than at high pH, and this for both NC and carbonated samples. Barium is more soluble at high than at neutral pH. Pb shows its amphoteric character with a minimum solubility between pH 8 and 10. Between pH 7 and 13, all considered metals are less soluble in the carbonated than in uncarbonated samples.

In the extraction test, the sample is milled. The carbonated and uncarbonated phases, which were spatially sepa-

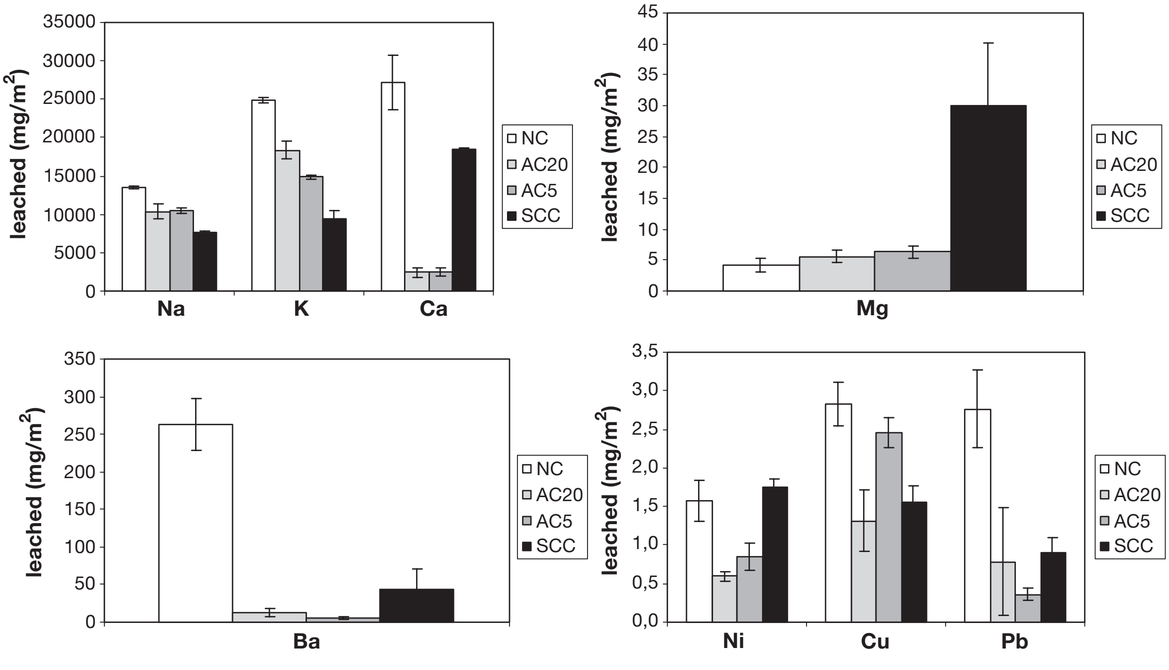

Fig. 3. Cumulative leaching (mg/m^2) for NC and carbonated H mortars (average of three samples, S.D. is indicated).

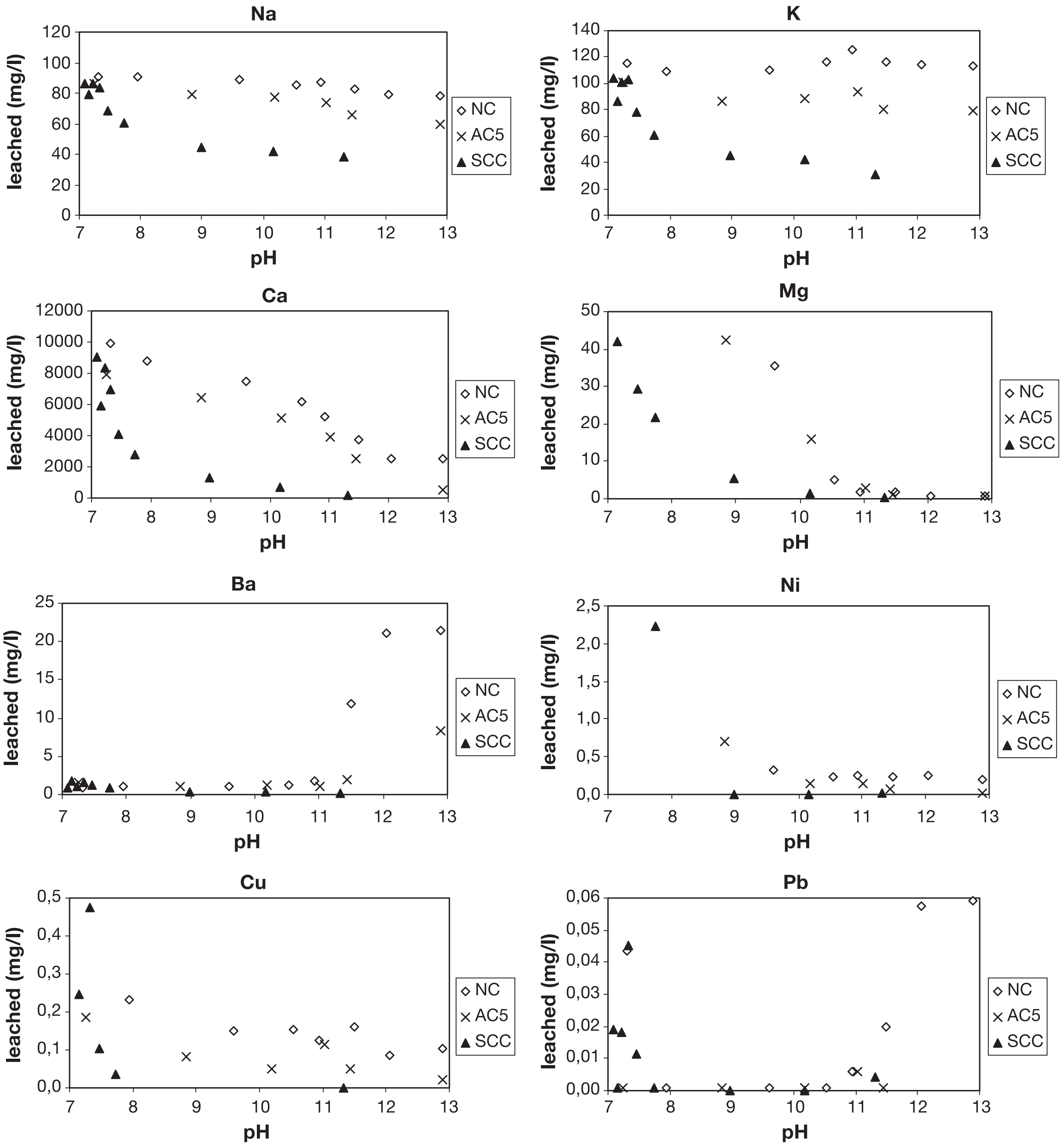

Fig. 4. Solubility (mg/l) as a function of pH for milled NC and carbonated H mortars.

rated in the monolith, now become mixed. All considered metals have a lower solubility in the carbonated samples over the range of pH 7–13. The same results were found for weathered coal fly ashes and bottom ashes [21,22]. Ca, Mg, Ni, and Cu follow the same trend in the pH 7–13 range: increasing solubility with decreasing pH and a consistently lower solubility for carbonated samples. In the NC samples, all these metals are present as hydroxide, which dissolves relatively easy as pH goes down (a simple acid–base reaction). In the milled AC samples, part of the metals are present as carbonates that decrease solubility over the whole considered pH interval. The SCC samples consist mainly of metal carbonates (about 95% of the original monolith is carbonated). Still, some hydroxides are present, enough to bring the pH up to 11.3 when no acid is added in the solubility test. When acid is added to the carbonated samples, carbonate is gradually transformed in bicarbonate, as can be seen in Fig. 5. This transformation enhances solubility of metal carbonates. The solubility of Ba decreases dramatically from pH 12 down to 11 due to precipitation with sulphate released by decomposition of ettringite and other calcium sulphoaluminate hydrates [11,23]. Carbonation decomposes ettringite as well [24], leading to even more precipitation of Ba. In NC samples, the solubility of Pb is controlled by its amphoteric character. In carbonated samples, this amphoteric behavior is decreased due to the formation of $PbCO_3$, and solubility of Pb is decreased over the whole considered pH interval.

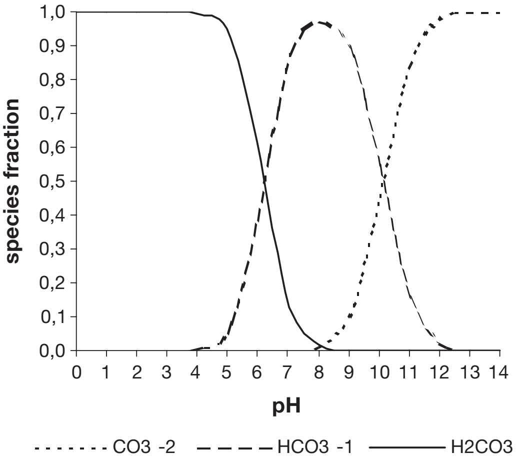

Fig. 5. Speciation of carbonate ion as a function of pH.

The decreased leaching of Ca, Ba, Cu, and Pb from carbonated samples in the diffusion test is in agreement with previously reported results for Ba [11], Ca [12,14], and Pb [10,12], but in contrast with other reported results for Ca and Pb [3] and Cu [11,12].

The lower metal leaching in AC samples, compared to NC samples in the diffusion test, corresponds with the results of the extraction test. Only for Mg, there is no difference in solubility between the AC and the NC samples. This is reflected in the insignificant difference in Mg release in the diffusion test.

The carbonate phases form an outer shell around uncarbonated material in the diffusion test. The metal–carbonate influence is therefore greater than in the extraction test because leached metals originate from the carbonated matrix or because they are carried through the carbonated shell and experience a carbonated environment if they come from within the uncarbonated core. As a consequence, the pH in the leachates of the diffusion test is consistently lower than in the leachates of the corresponding samples in the extraction test without acid addition. While in the AC leachates, carbonate will be mainly present as the carbonate ion; in the SCC leachates, carbonate will be mainly present as the bicarbonate ion due to the lower pH. The equilibrium towards bicarbonate will enhance the solubility of metal carbonates and hence increase metal leaching. This is the reason that leaching of metals from SCC samples in the diffusion test is consistently higher than from AC samples. This apparent contradiction with the extraction test is due to the spatial presence of hydroxides/carbonates and the pH influence on carbonate/bicarbonate equilibrium.

4. Conclusion

The following conclusions can be made:

- carbonation with SCC occurs much faster than with the CO_2 chamber;
- carbonation decreases the porosity of monolithic samples and this decrease is more important for higher w/c ratios;
- while Na and K solubility in NC samples is pH independent, their solubility in carbonated samples is lower than in NC samples and also pH dependent; and
- leaching of Ca, Ba, Cu, and Pb is reduced in carbonated monolithic samples. Ni leaching is decreased by chamber carbonation but reaches the original leaching with samples carbonated using SCC. Mg leaching is increased through SCC.

Important parameters in the understanding of leaching and carbonation are the spatial presence of the carbonated/uncarbonated phases and the pH of the leachate. The carbonation influence on leaching will be higher when a carbonated shell covers an uncarbonated core, which is the case in a diffusion test of monolith samples, than when the two phases are mixed, which is the case when leaching milled material in the extraction test. Decreasing pH will turn carbonate into bicarbonate, which is much more soluble. Samples that undergo stronger carbonation in the supercritical method may therefore show higher leaching values than the less carbonated samples in the chamber method.

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