Effects of Progressive Carbonation on Heavy Metal Leaching from Cement-Bound Waste

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Contradictory leaching results from carbonated cement-bound wastes have been reported in various investigations. However, the degree of carbonation of the examined samples is rarely considered as an important parameter in leaching results. This article focuses on the effect of progressive carbonation on leaching properties of cement-bound waste (bottom ash or flue gas cleaning residue), including uncarbonated, partially carbonated, and almost completely carbonated samples. Leaching is investigated after carbonation by means of semi-dynamic leaching of monoliths, supported by batch solubility and release measurements on particle-size reduced material. For partially carbonated samples, leaching of metals is in most cases less than observed from uncarbonated samples, resulting from the conversion of hydroxides to carbonates. For completely carbonated samples, increased leaching of most metals was observed in comparison to partially carbonated samples, resulting from leachate induced transformation of carbonate into more soluble bicarbonate speciation. © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 826–837, 2006
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Introduction

Leaching of heavy metals from wastes is a major concern for waste management. Depending on the heavy metal concentration and the physico-chemical characteristics of the waste, landfill disposal or reuse as construction material may be viable management options.[1,2] In both treatment options, addition of cement and water in order to form a monolithic product is a well-known technique.[1,3] For landfill disposal, the goal is to decrease heavy metal solubility and decrease permeability and geometric surface area to limit transport of contaminants to the environment. Increasing material strength is an additional requirement when recycling materials.

Use of portland cement as a treatment technique results in the formation of an alkaline matrix, which is subject to reaction with carbon dioxide, either gaseous or dissolved in water, and is referred to as carbonation. Once a monolith has been produced, aging, and more specifically carbonation, starts changing the original characteristics of the material. Carbonation involves the chemical reaction of cement hydration products (e.g., portlandite, $Ca(OH)_2$, and calcium silicate hydrate) with carbon dioxide from the atmosphere in the presence of sufficient moisture, leading to formation of calcite, $CaCO_3$.[4-6] This reaction lowers the pH in the pore water of the monolith from pH 13 to ultimately about pH 8. Heavy metals, originally present as hydroxides in the matrix, are progressively converted to carbonates, thus changing their solubility.[5-7] In addition, matrix porosity may change due to precipitation of products with higher molar volume than reactants. Precipitates may clog pores, leading to lower porosity, or may induce expansive stress, leading to microcracking and an increase in porosity.[4]

The carbonation reaction involves a transfer of CO_2 from the

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gas phase into water, and reaction of CO_2 with water to carbonic acid, which dissociates into protons and bicarbonate (HCO_3^-) or carbonate (CO_3^{2-}) ions, depending on the pH of the solution. The dissolution of gaseous CO_2 then can be followed by precipitation of carbonate ions with cations present in the solution, provided the solubility of the corresponding metal carbonate has been exceeded.[7,8] When bicarbonate is present, precipitation of metal bicarbonate is theoretically possible but in practice saturation is seldom achieved, as these minerals are highly soluble. The process described above implies that carbonation is slow in water-saturated monoliths because CO_2-diffusion is hindered when the pores are filled with water.[9] Completely dry pores will also slow down carbonation because the formation of metal carbonate occurs in the liquid phase, often in water films within pores.

In cement-based monoliths, carbonation will slowly progress from the outer surface into the matrix.[6,10] After a sufficiently long time, three zones can be distinguished: a carbonated zone close to the surface, where the degree of carbonation is maximal and constant; a transition zone, also called the carbonation front, where the degree of carbonation decreases to zero; and the uncarbonated matrix.[10] In highly porous monoliths, these zones will occur as shells, with the uncarbonated zone as the core. When the porosity of the bulk material is low, carbonation may be observed only on external surfaces and in spots around damaged zones or cracks.

Carbonation has been studied as a process to further improve immobilization of solidified/stabilized waste[11] and granular waste.[12] Carbonation also must be considered to assess long-term leachability of naturally aging alkali monoliths.[2,13] In nature, carbonation and leaching occur intermittently during the life cycle of a monolith. Research has been performed on carbonation taking place at different moments in the life cycle:

- Carbonation *during the curing process* of a solidified/stabilized waste seems to increase matrix strength through accelerated hydration of tricalcium silicate and reduce leaching of most heavy metals (e.g., calcium, arsenic, nickel, lead, and zinc).[14-18]
- Carbonation *after curing* decreases strength because of decalcification and eventual decomposition of the calcium silicate hydrate gel, this mineral being the primary strength-provider in cement-based monoliths.[13,18] The influence on metal leaching is less clear than in the case of carbonation during curing. Some investigations on carbonation after curing report increased leaching of metals, while others report decreased leaching of the same metals (e.g., calcium, antimony, cadmium, lead, and zinc). A detailed overview is given in a previous article.[6]
- Carbonation has also been studied *during leaching*[19,20]; but in this water-saturated scenario, transport of atmospheric CO_2 will be slow. Bubbling of pure CO_2 through the leachant also has been included in experimental evaluations, which decreases leachate pH to about 6 and converts carbonate ions into bicarbonate ions that do not form insoluble precipitates.[20]
- The most realistic scenario, but also the most complicated one, is *intermittent leaching*, where leaching periods are interspersed with storage/drying/carbonation periods.[7,21,22]

All previously cited references compare uncarbonated samples to carbonated samples; in some instances fully carbonated, in others only partially carbonated. Apart from the limited results in previous research,[6,7] the question of a progressive carbonation effect has not been addressed. Specifically, do aging effects increase with progressive penetration of the carbonate front, or is there an optimal degree of carbonation after which no additional effect or even contrary effects are observed? The decreasing pH is associated with the progressive carbonation reaction, which in conjunction with mildly acidic leachants, may convert relatively insoluble carbonates to more soluble bicarbonates. Thus, while some degree of carbonation decreases leaching due to metal carbonate precipitation, subsequent conversion of carbonates to bicarbonates in response to material characteristics and external conditions could result in increased leaching.

This article focuses on potential increases in leaching due to bicarbonate production at low pH during progression of the carbonation front into monoliths of solidified wastes. Two cement-based materials were produced using typical residues from the municipal solid waste incineration industry: (i) a bottom ash replacing the sand fraction in mortar, and (ii) a flue gas cleaning residue substituting for a portion of the cement in cement paste. Samples from the two sample sets were carbonated for 14, 30, or 60 days, and were compared to samples that were not carbonated. Leaching was investigated by means of a semi-dynamic monolith leach test and equilibrium-based experiments. The effects of progressive carbonation and leaching on monolith porosity are discussed in a related article[23] that also addresses the influence of porosity change by carbonation on the leaching properties.

Experimental

Production of monoliths

Residues from a municipal solid waste incinerator (MSWI) were incorporated in cement matrices. One residue was a 0-2 mm fraction of a bottom ash that underwent a wet-sieving treatment as described in a previous article,[12] while the other was a flue gas cleaning residue originating from a scrubber with semi-dry injection of lime.[24] These waste residues were chosen because they represent two waste streams with distinctly different properties, but both contain heavy metals.[2] Bottom ash is a coarse material consisting of mainly silica, alumina, iron, and calcium oxides, as well as unburned organic matter. Flue gas cleaning residue is finer material, including the reaction products and excess reagent of the air pollution control process, thus often containing a high proportion of calcium (hydr)oxide and chloride salts.

Mortars were produced by mixing 548 kg/m^3 (28 wt %) of ordinary portland cement (CEM I 42.5 R HES, Holcim), 1096 kg/m^3 (57 wt %) dried bottom ash, and 281 kg/m^3 (15 wt %) distilled water, giving a $w/c = 0.5$ (B-samples). Cement pastes were produced by mixing 900 kg/m^3 (48 wt %) of ordinary portland cement, 385 kg/m^3 (21 wt %) flue gas cleaning residue, and 578 kg/m^3 (31 wt %) distilled water (F-samples). The flue gas cleaning residue has pozzolanic properties and acts as a 30 wt % substitution of the cement. The resulting $w/c = 0.45$ (including the waste as cement).

The mixtures were poured in molds of 150 × 150 × 150 mm and vibrated. After 24 hours of setting time, the samples were demolded and cured for 28 days in a humid room (20°C, >95% RH, 0.035% CO_2). At the end of the curing period, approximately 1.5 cm of material was cut from the edges of the monoliths to obtain a fresh uncarbonated surface, and the remaining cubes were cut into samples of 40 × 40 × 40 mm using a dry cutting technique.

Carbonation

One set of samples was dried in a vacuum oven at 40°C and subsequently stored in a bag filled with nitrogen gas, awaiting further treatment (uncarbonated samples: B0 and F0). Another set was placed in a closed chamber with the atmosphere at a temperature of 37°C, RH over 90%, and containing 20% of CO_2. Some B-samples were carbonated for 14 days (B14), others for 30 days (B30), and yet another set for 60 days (B60). F-samples were carbonated for 30 days (F30) and 60 days (F60). The duration of carbonation was based on the progressive carbonation front in the B-samples. This front was qualitatively assessed by regularly cutting a sample in two and spraying the inner surfaces with a solution of 1 g phenolphthalein in 50 ml ethanol 95% and 50 ml distilled water. Phenolphtalein is a pH indicator with a red color at pH > 10 (noncarbonated cement matrix) and colorless at pH < 9 (carbonated cement matrix). After 60 days of carbonation, phenolphthalein gave no color to the inner surfaces of a B-sample, indicating that carbonation was complete.

Total concentration

The total concentration of metals in the samples was determined by digesting 0.1 g of dried and particle-size reduced material with concentrated HNO_3, $HClO_4$, and HF, consecutively. The resulting liquid sample was diluted to 100 ml with distilled water and acidified with 2 ml of concentrated HNO_3 for analytical measurement.

Mass transfer from monoliths

Three samples of each mixture and each period of carbonation were leached in a semi-dynamic monolith leaching procedure modified from the Dutch diffusion test NEN 7345[25] or the similar mass transfer test for monolithic materials MT001.1.[26] The test procedure was modified by prolonging exposure to a cumulative 225 leaching days and the use of acidified leachant. Each cube was immersed in 320 ml of distilled water (initially adjusted to pH 4 with concentrated HNO_3) that was collected and renewed with fresh leachant 17 times after cumulative leaching times of 6, 24, 54, and 96 hours and 9, 16, 25, 36, 49, 64, 81, 100, 121, 144, 169, 196, and 225 days. The volume of the leachant equals 5 times the volume of the cube. A lid was loosely placed on top of each leaching vessel. The pH and the electrical conductivity of each collected leachate were measured, and 50 ml of the leachate was saved for anion analysis. Then the remaining leachate was acidified with 5 ml of concentrated HNO_3 and the walls of each leaching tank were scrubbed to include precipitation in the leaching results, as recommended in a previous article.[20] This acidified sample was conserved for analytical measurement of cations. Results of the subsequent renewals are summed and expressed as cumulative mass per sample surface (mg/m^2). The above test will from now on be called the "diffusion test."

Equilibrium-Based leaching

The release of metals into a fixed bath as a function of pH was measured based on the EN12457 test[27] or the similar SR002.1 protocol used in the U.S.[26] The equilibrium-based leaching test is conducted on 10 g of particle-size reduced material (95 + wt % < 125 μm diameter) in 100 ml of distilled water acidified with different volumes of concentrated HNO_3. After 24 hours of agitation, the leachate was filtered through a 0.45 μm membrane filter (Chromafil PET) and the pH of the leachate was measured prior to preservation of a 50 ml aliquot for cation analysis with concentrated HNO_3 (final 2% acid). Results are assumed to equal the solubility of the metal at the measured pH. Concentrations of constituents in each leachate are plotted as a function of leachate pH and a curve is fitted on the solubility results so that the solubility concentration can be deduced at any given pH. By converting added volumes of acid to molar equivalents, the acid neutralization capacity (ANC) of the particle-size reduced material is obtained.

Inter-Test comparison (quality control)

The results of equilibrium-based leach tests also can be compared with the leachate concentrations from the diffusion test to assess whether or not release in the diffusion test was limited by saturation in the bulk leachate.[26] The solubility is calculated using the equilibrium-based results for each leachate final pH from the mass transfer test and compared to leachate concentration measured from the mass transfer test. The solubility estimated from the equilibrium-based tests should be much greater than the measured concentration from the mass transfer-based test to ensure that a sufficient gradient is maintained between the solid and bulk leachate as the driving force for diffusion. If this concentration difference is not maintained, then the necessary condition of an infinite bath in the diffusion test is not fulfilled.

Analytical techniques

Chloride and sulfate concentrations in 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 analyzed for cation concentrations using a VG PlasmaQuad PQ-2 Plus ICP-mass spectrometer.

Results and Discussion

Degree of carbonation and acid neutralization capacity

Inner surfaces of specimens that were sprayed with phenolphthalein are shown in Figure 1. The results show that B60 is nearly completely carbonated, whereas B14 and B30 are partially carbonated. F30 and F60 are both only slightly carbonated: the carbonated shell is only 1 mm thick in F60 and even less in F30. B-samples are more carbonated than F-samples because the latter contain mainly small pores,[23] which hinder CO_2 diffusion into the monolith.

Sanchez[28] described a technique to estimate the amount of free portlandite in cementitious samples from the results of the equilibrium-based leaching test on particle-size reduced samples, assuming that all acid needed to reach pH 11.9 is used to neutralize free portlandite. For the B-samples, this approach provides estimates of portlandite content of 61, 11, and 1 mg/g of dry sample for samples B0, B14, and B30, respectively. No free portlandite is present in the carbonated B60 sample. In the F-samples, portlandite content of 85, 72, and 71 mg/g were estimated for F0, F30, and F60 samples, respectively. These

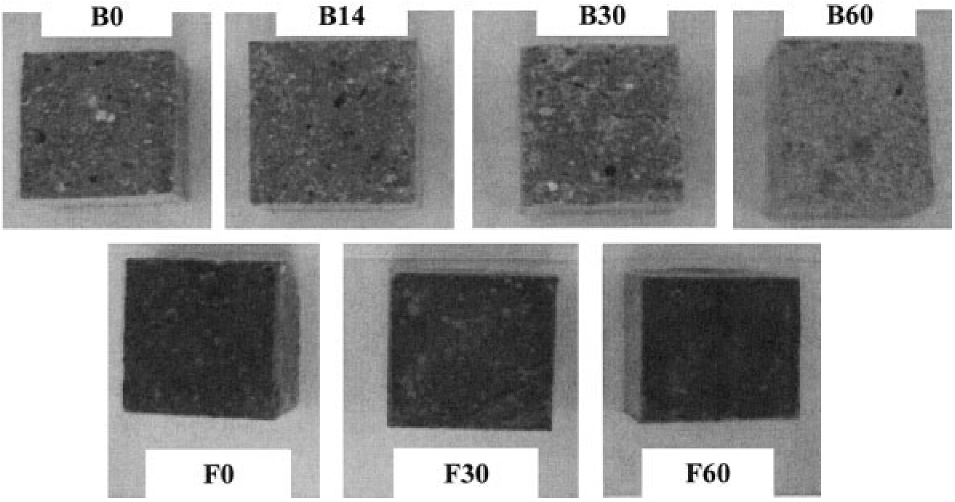

Figure 1. Photographs of the inner surface of B- and F-samples that were sprayed with phenolphthalein.

results represent the average portlandite content for the whole sample. It can be assumed that in the carbonated monoliths more portlandite than the average is present in the core and less portlandite than the average is present in the carbonated shell.

Assuming that free portlandite is transformed into calcite by the carbonation reaction, the calcite content can be deduced from the difference between the free portlandite in uncarbonated and carbonated material. B14 and B30 contain, respectively, 68 mg and 81 calcite/g of dry matter. Because it was estimated that B60 contained no free portlandite, at least 82 mg calcite/g of dry sample is produced directly from portlandite; however, more calcite can be produced from decalcification of calcium silicate hydrate gels. In the F-samples, calculations result in a calcite content of 18 mg/g for F30 and 19 mg/g for the F60. This relatively high content of calcite is situated in the thin carbonated shell, resulting in a very dense zone with low porosity, whereas carbonation in the B-samples induces a much thicker carbonated zone that is less dense.

The ANC curves, determined on the monolith as a whole after particle-size reduction, provide insight into the transformations occurring during progressive carbonation (Figure 2). The B0 curve is typical for a material with a high buffering capacity at alkaline pH due to the presence of portlandite and calcium silicate hydrate, while that of B60 shows a high buffering capacity at pH 7 due to calcite presence.[5] The B14 and B30 curves are slowly transforming from one shape to the other, indicating that these specimens contain a mix of portlandite, calcite, and calcium silicate hydrate. The uncarbonated samples show a considerable ANC: 8 meq H^+/g dry material is needed to reach pH 7 for B0, and even 13 meq H^+/g dry material is needed for F0. After 60 days of carbonation, the B-samples need only 2 meq H^+/g dry material to reach pH 7, where the ANC stabilizes. The carbonated F-samples show a slight decrease in ANC, but the curve shape of F60 is still far from the typical curve of a thoroughly carbonated sample.

Influence of atmospheric carbon dioxide on leaching in the diffusion test

During the study it was observed that carbon dioxide from the atmosphere interfered with leaching of uncarbonated samples in the diffusion test by a decrease of pH and precipitation of carbonates. Although this phenomenon renders interpretation of leaching results more complex, it is a realistic leaching situation in nature.

As appears from Figure 3a, the pH of the uncarbonated B0 decreases to the same level as that of the carbonated B-samples, indicating either depletion of the major hydroxides or an

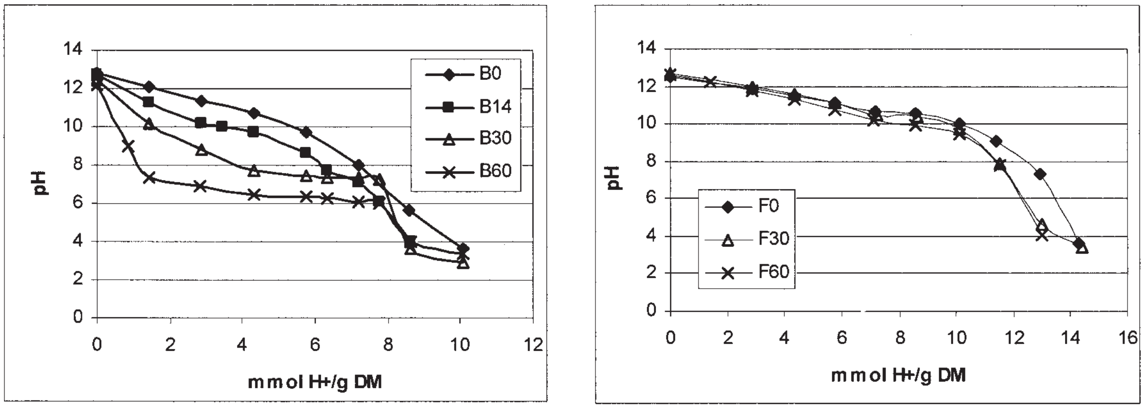

Figure 2. ANC of particle-size reduced B- and F-samples with progressive carbonation.

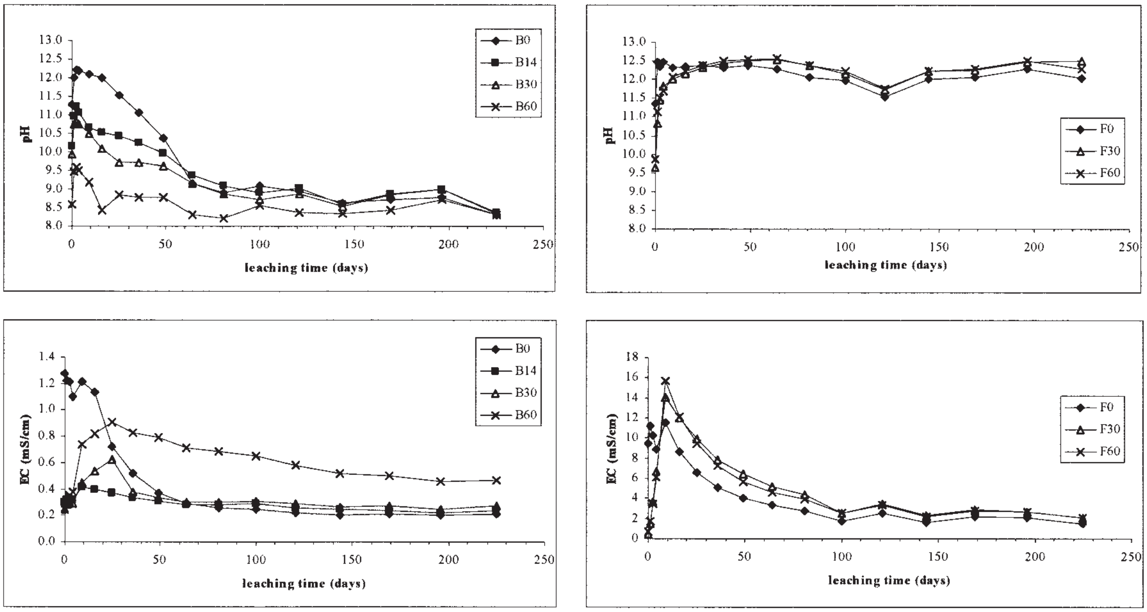

Figure 3. Measured pH and electrical conductivity at the end of each leaching period for B- and F-samples (average of three measurements).

external acidifying source. Comparing the amount of calcium leached from B0 at the end of the experiment with the portlandite content of 61 mg/g of dry sample shows that only 5% at most of this portlandite has been leached, assuming that all leached calcium is originating from portlandite. When calcium is also present as, e.g., chlorides, this proportion would even be lower. By analogy, assuming sodium and potassium are present as hydroxides, only 34% and 57%, respectively, of the total concentration at most has leached. These low proportions indicate that depletion at the end of the diffusion test has not occurred.

Furthermore, when the uncarbonated samples that were leached for 225 days were subsequently leached for an additional 24 hours in a tightly closed leaching vessel, the pH was around 10.7. This result indicates that the considerably lower leachate pH observed in the later stages of the diffusion test was influenced by atmospheric carbon dioxide, which dissolved into the leachant and lowered its pH. Previous tests had nevertheless shown that in the standard NEN7345 diffusion test (total leaching time of 64 days), the influence of atmospheric carbon dioxide on leaching was negligible.[20] However, in the prolonged diffusion test (total leaching time of 225 days), leaching periods become longer, release rates from the monoliths are decreased as the leaching front within the matrix progresses, and external carbon dioxide effects on leaching become significant.

The carbon dioxide from the atmosphere affected in particular leaching of calcium. Figure 4a shows that the cumulative calcium release from B0 indeed has a peculiar curve shape. After the eighth renewal, almost no additional calcium is released from the matrix. This can be explained by comparing the leachate concentrations of calcium from the monolith samples in the diffusion test with the solubility at that pH to assess whether saturation occurred (Figure 5a). It appears that the leachate concentration of calcium at the ninth renewal in the diffusion test suddenly is a factor of 10 less than the previous renewal. The solubility, however, does not show this decrease. This implies a reaction with calcium during the long leaching

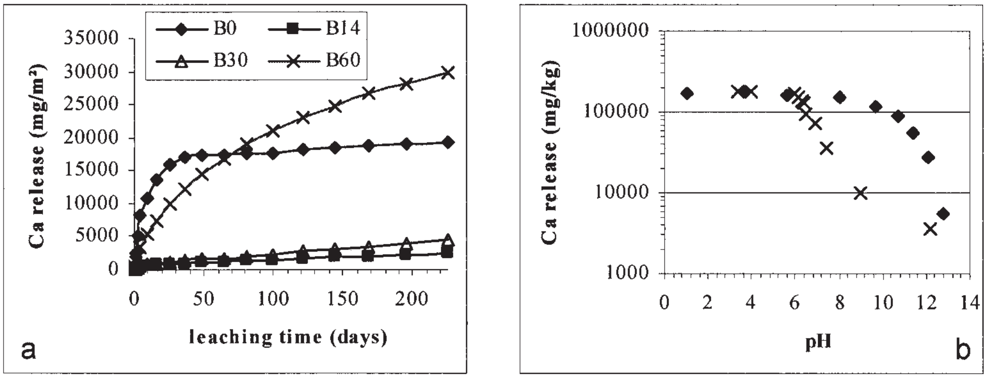

Figure 4. (a) Cumulative release (average of three measurements) and (b) solubility of calcium from uncarbonated and carbonated B-samples.

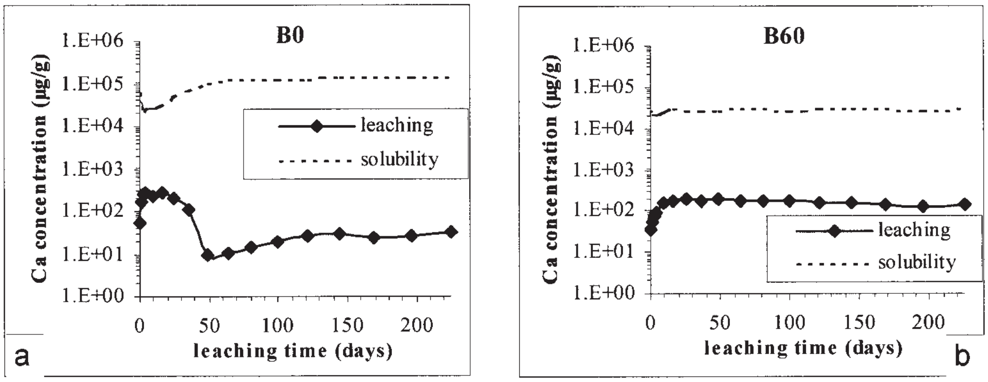

Figure 5. (a) Comparison of leachate calcium concentration in the diffusion test (average of three measurements) and (b) calcium solubility for B0 and B60.

periods in the diffusion test, which does not take place in the short-term period (24 hours) in which the equilibrium-based test is performed. This reaction is again the dissolution of atmospheric carbon dioxide into the alkaline leachate, followed by formation of carbonate and precipitation of carbonate with calcium as calcite on the surface of the monolith samples, on the walls of the leaching vessel, and on the upper surface of the leaching water. While before each renewal the leachate was acidified and the vessel walls were scrubbed to dissolve precipitated calcite, the formation of a calcite layer on the sample itself could not be avoided. When phenolphthalein was sprayed on a leached uncarbonated sample, colorless spots were indeed visible, indicating that carbonation must have taken place during leaching.

In Figure 5b no decrease in leaching of calcium is observed around the ninth renewal of B60; the effect of dissolving atmospheric carbon dioxide appears to be negligible in the case of carbonated B-samples because of the reduced hydroxide flux from the solid matrix into the leachate.

In F0 atmospheric carbon dioxide causes a slight decrease of calcium leaching at the ninth renewal (Figure 6b), resulting in similar cumulative release of calcium from the carbonated and uncarbonated samples from subsequent renewals. For the carbonated F-samples no effect is observed, as appears from Figures 6a and 6c.

Effect of degree of carbonation on leaching

Leachate pH and Electrical Conductivity in the Diffusion Test. Figure 3 shows the pH and electrical conductivity of the leachates from the diffusion test. The pH at first increases to its maximum: 12.5 for the F-samples and slightly lower for the B-samples. This is due to the fact that bottom ash contains less alkaline components than the flue gas cleaning residue. Subsequently, the pH decreases due to progressive depletion.

During the first days of the diffusion test, the more carbonated the samples are, the lower the leachate pH is. This is more pronounced in the B-samples than in the F-samples. Towards the end of the test, the pH's become more similar, due in part to the influence of the atmospheric carbon dioxide.

From the measurements of the leachate electrical conductivity, it appears that salt leaching from the carbonated samples is slower than that from the uncarbonated samples. This retardation is probably due to the formation of a less porous carbonated shell. The leachates of F-samples give much higher conductivity results than the B-samples, indicating that the F-samples contain much more soluble components. Flue gas cleaning residues indeed contain a much higher amount of sodium, potassium, and calcium hydroxides and chlorides than bottom ash.[1]

Leaching Results for Sodium and Potassium. Leaching of sodium and potassium is considered to be pH-dependent, but only to a limited extent.[4,5] This is confirmed by results in Figures 7 and 8, which show that solubility of sodium and potassium increases with lower pH.

Cumulative leaching of sodium and potassium in the diffusion test decreases as the degree of carbonation of the samples progresses (Figure 7). After 225 days of leaching, 23% less sodium and 70% less potassium has leached from B60 than

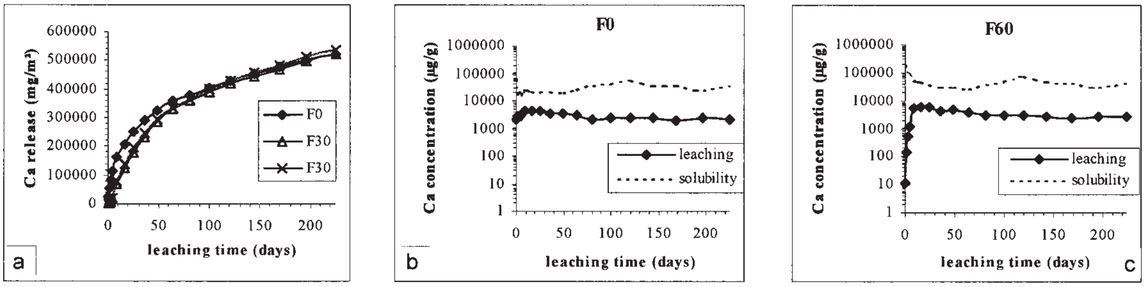

Figure 6. (a) Cumulative release (average of three measurements) for calcium from uncarbonated and carbonated F-samples and comparison of leachate calcium concentration in the diffusion test (average of three measurements); and solubility for (b) F0 and (c) F60.

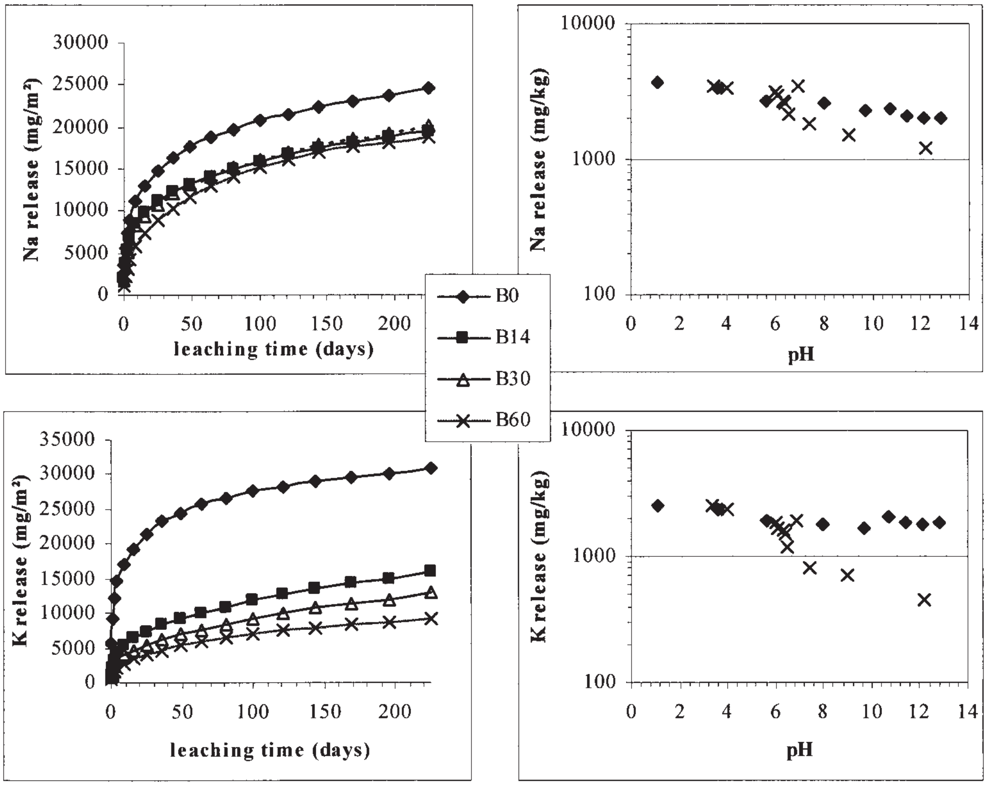

Figure 7. Cumulative release (average of three measurements) and solubility of sodium and potassium for uncarbonated and carbonated B-samples.

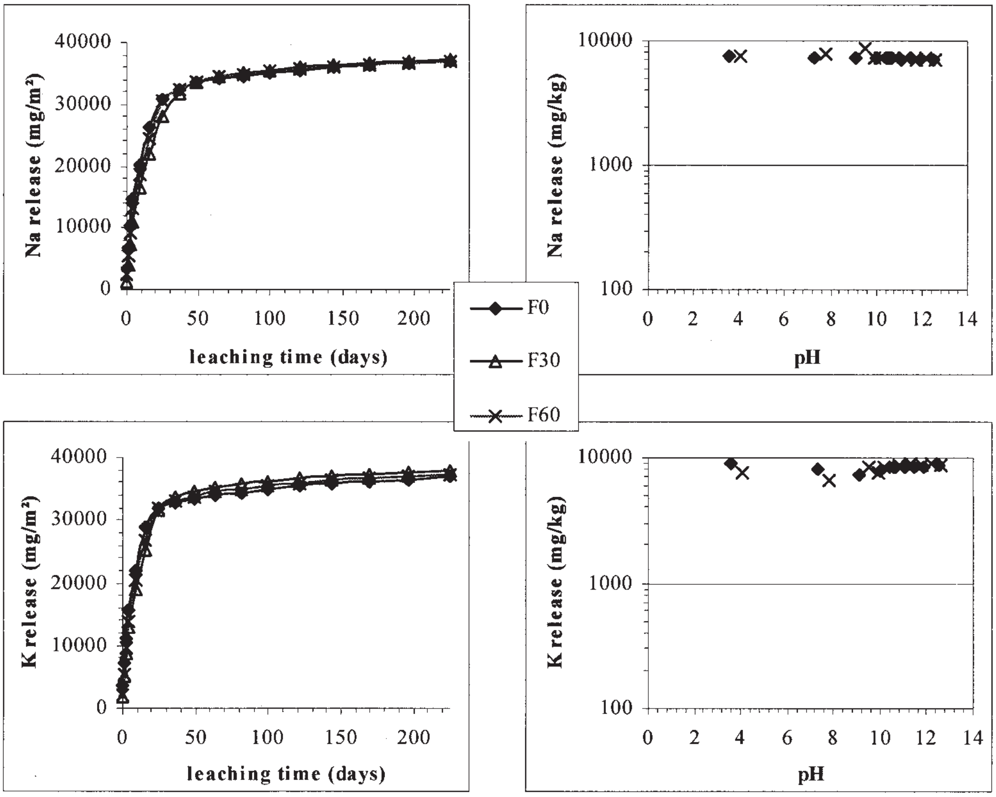

Figure 8. Cumulative release (average of three measurements) and solubility of sodium and potassium for uncarbonated and carbonated F-samples.

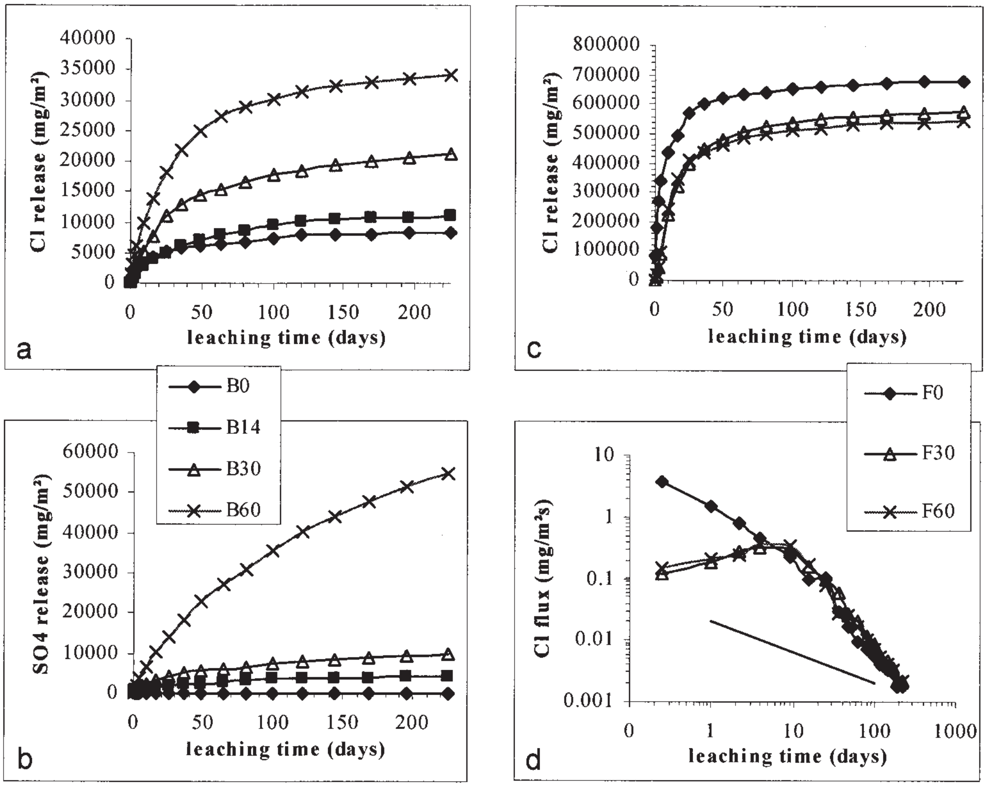

Figure 9. Cumulative release (average of three measurements) for chloride and sulfate from B-samples (a and b) and F-samples (c), as well as release flux of chloride during the diffusion test of F-samples (d, the full line giving the theoretical flux in case of diffusion).

from B0. For B14 and B30, the decrease in leaching is less important. Decrease of porosity by 12% (for B60) due to carbonation accounts for this decrease, although it is in part counteracted by the decrease of the pH, which increases leaching.[23]

For the F-samples there is no significant decrease of sodium and potassium leaching (Figure 8), because only slight carbonation occurred.

Leaching Results for Chloride and Sulfate. Leaching results for chloride and sulfate during the diffusion test are shown in Figure 9. Sulfate leaching from B0 and from all F-samples was below the detection limit of CZE (that is, 1 ppm). Anion leaching as a function of pH could not be measured because of the large nitrate peak from the added nitric acid.

In the B-samples, cumulative release of chloride and sulfate increased with progressive carbonation from B0 to B60 (Figures 9a and 9b). Increase of anion leaching due to carbonation has already been described for both cement-based material and plain bottom ash in previous articles.[5,6,20] Carbonation induces the formation of carbonates in the pore water that compete with other anions, such as hydroxides, sulfates, and to a lesser extent chlorides, for precipitation with cations. In addition, carbonation dissolves the sulfate-containing mineral ettringite, a typical species in cement matrices.

The F-samples, however, show a decrease of the cumulative release of chloride as carbonation proceeds from F0 to F60 (Figure 9c). The decrease in chloride release is most likely the result of the presence of the thin but dense carbonated shell slowing diffusion.

Leaching Results for Calcium. The decrease in calcium leaching from partly carbonated monoliths compared to that from uncarbonated monoliths and the increase in calcium leaching from almost completely carbonated monoliths compared to that from partly carbonated monoliths (Figure 4) results from the combined effects of pore-water pH and the presence of hydroxides, carbonates, or bicarbonates as a function of the extent of matrix carbonation.[6] In the partly carbonated monoliths, pore water and leachate pH are still relatively alkaline ($pH > 10$) so that carbonate is present as the carbonate ion, which can form insoluble precipitates, such as calcite. In almost completely carbonated samples, the pH of the pore water and, hence, of the leachate is more neutral ($6 < pH < 10$), so that the presence of bicarbonate dominates over the presence of carbonates. Bicarbonate salts are highly soluble, leading to increased leaching of calcium.

Leaching Results for Trace Metals. In the B-samples, leachate concentrations for cobalt, copper, manganese, and lead are above the detection limits. In the F-samples, this is the case for chromium, nickel, and lead. Results of the diffusion and equilibrium-based tests are shown in Figure 10 for B-samples and in Figure 11 for F-samples.

Cobalt behaves the same way as calcium, both in the equilibrium-based test and in the diffusion test (Figure 10): carbonation decreases solubility, and B14 as well as B30 exhibit lower leaching than B0 and B60 in the diffusion test.

Copper leaching from B-samples in the diffusion test decreases with progressive carbonation. In the equilibrium-based leaching test, copper release in the interval of interest (pH

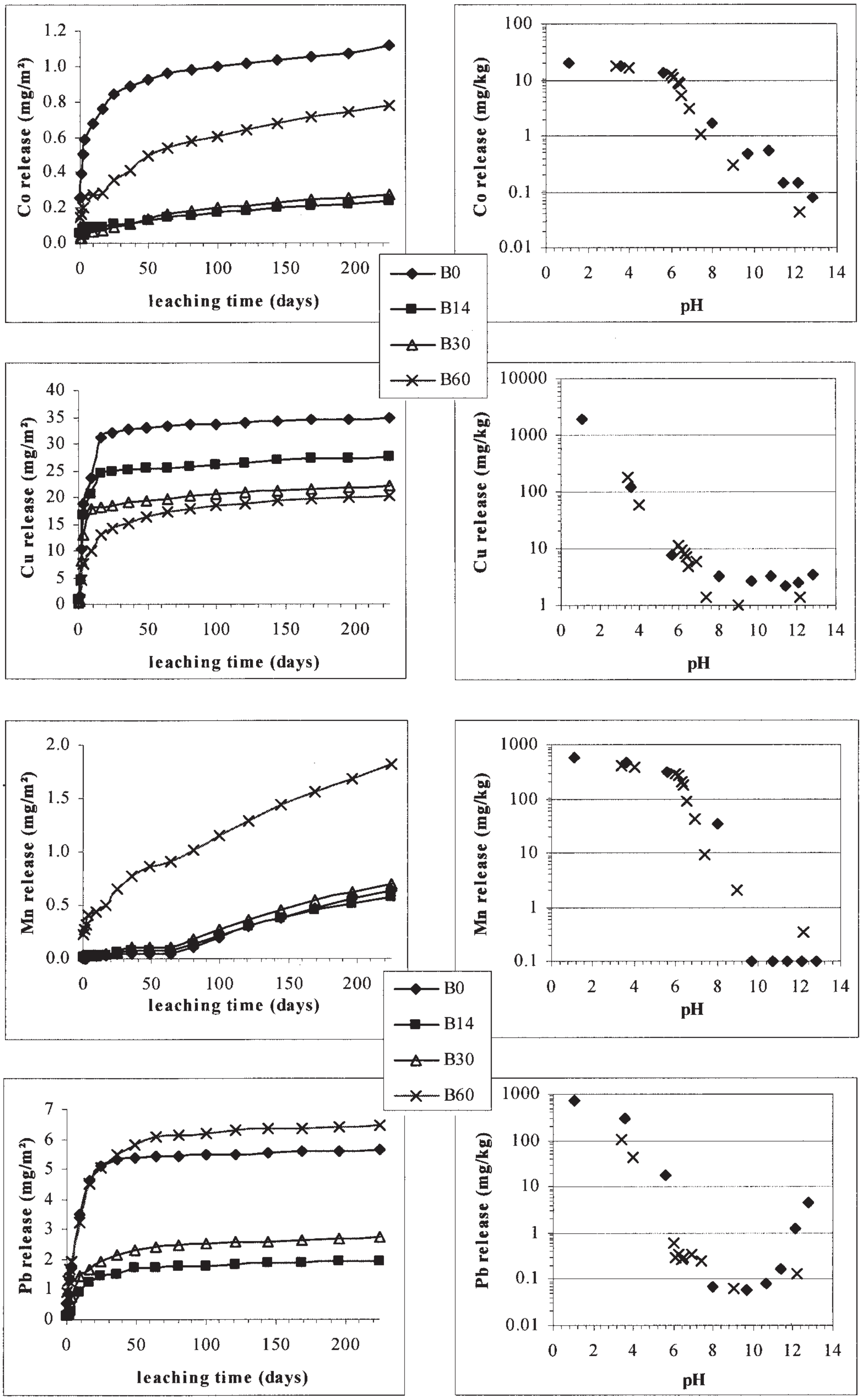

Figure 10. Cumulative release (average of three measurements) and solubility of cobalt, copper, manganese, and lead from uncarbonated and carbonated B-samples.

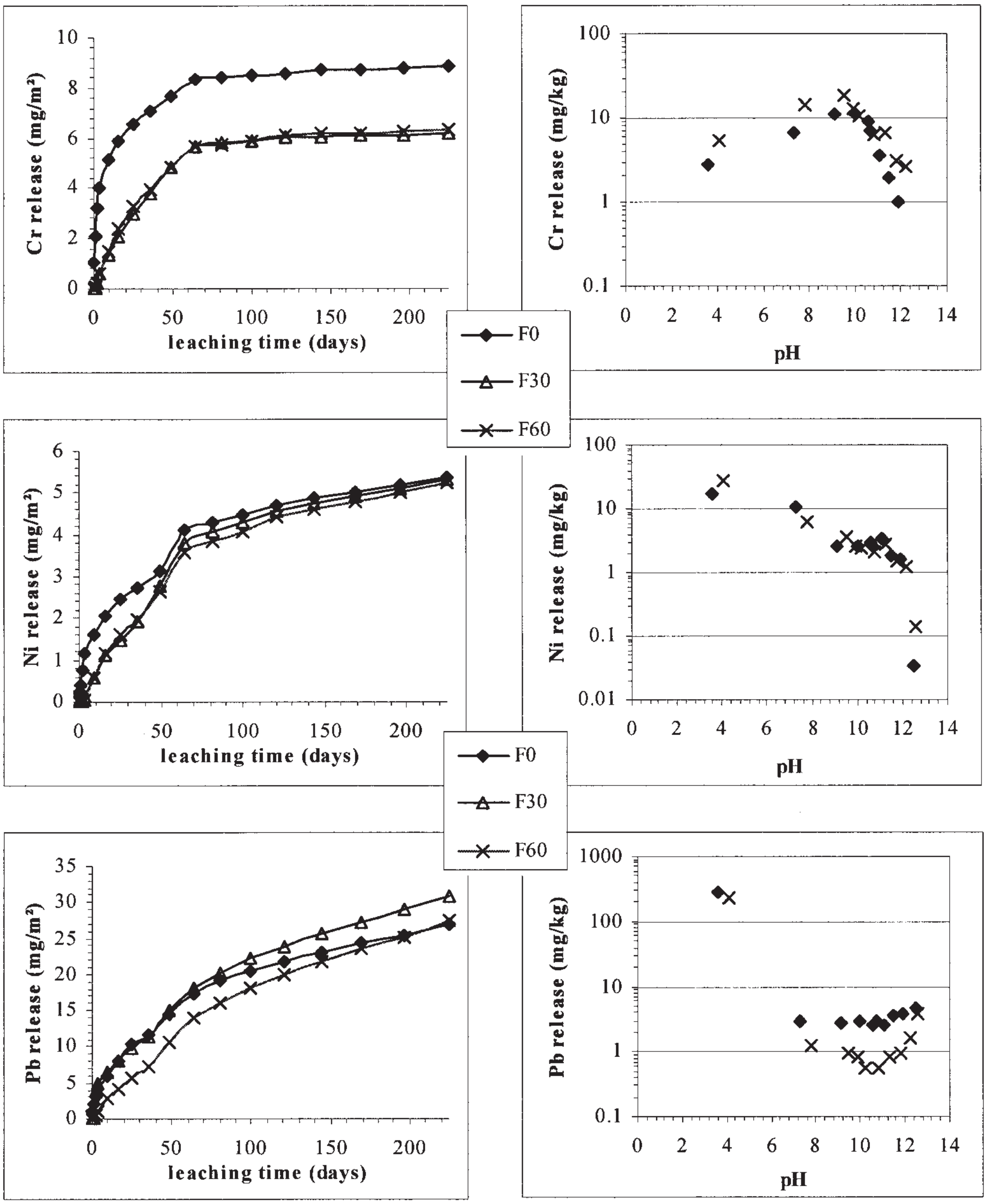

Figure 11. Cumulative release (average of three measurements) and solubility of chromium, nickel, and lead from uncarbonated and carbonated F-samples.

8-12) is lower from B60 than from B0. This is in agreement with previously reported results[5,6,12] and is consistent with lower copper leaching in the diffusion test from B14 and B30 compared to B0. B60 gives the lowest cumulative release in the diffusion test, indicating that the formation of bicarbonate plays a minor role in the case of copper. Bottom ash contains organic matter and amorphous alumina and iron oxides, which complicate leaching processes. The amorphous oxides, e.g., are known to decrease leaching of copper at more neutral pH.[12,29,30]

Leaching of manganese from B0 is low in the diffusion test and similar to that of B14 and B30. From the equilibrium-based test, it can be seen that manganese (hydr)oxide has indeed a very low solubility, with results falling below detection limits from pH 9.5 and higher. From samples carbonated to a higher extent, more manganese is released. The results of the equilibrium test also show that solubility of manganese increases with decreasing pH. In addition, formation of bicarbonate in the case of B60 also limits precipitation as carbonates.

The behavior of lead in the diffusion test of B-samples is similar to that of calcium and cobalt. Leaching from B14 and B30 is lower than from B0 and B60. Lead shows its amphoteric character in the results of the equilibrium-based leaching test, with a solubility minimum between pH 8 and 10. These results agree with previous results[6] and other research.[5] At pH > 10, higher solubility is observed than at neutral pH, in contrast to calcium and cobalt, but in the diffusion test this high pH is only attained in the early renewal periods of B0. In the later leaching periods, the leachate pH of B0 in the diffusion test falls well within the solubility minimum interval, whereas that of B60 is close to pH 8, leading to higher leaching of lead from B60.

Leaching of chromium from F0 is significantly higher than that from F30 and F60 (Figure 11). The pH equilibrium results, however, do not support this observation. Similar to chloride in Figure 6d, chromium fluxes in the first four renewals are much lower for the carbonated samples than for F0, implying leaching is retarded. Again, the presence of the dense carbonated shell accounts for this.

Cumulative release of nickel is barely influenced by the slight progressive carbonation in the F-samples. Results in the equilibrium test are equally unaffected due to negligible carbonation.

The results of lead for the F-samples are less clear than for the B-samples, due to the negligible degree of carbonation of the carbonated samples.

Conclusions

Cement samples with different degree of carbonation were produced in order to examine the influence of progressive carbonation on leaching.

Carbonation of a monolith decreases the leachate pH and introduces the carbonate/bicarbonate-ion in the leachate and, thus, in the pore water, affecting leaching of constituents. Carbonates compete with other anions, such as hydroxides, chlorides, and sulfates, for precipitation with cations. Leaching of anions other than carbonate mainly increases; leaching of most cations decreases. A higher degree of carbonation, however, decreases pH to the level where carbonates are transformed into bicarbonates, the salts of which are highly soluble. Therefore, leaching from almost completely carbonated samples in conjunction with mildly acidic leachant is higher than leaching from partially carbonated samples: progressive carbonation eventually decreases the pore water pH below the pH interval where dissolved carbon dioxide is mainly present as carbonates ($pH > 10$), to the pH interval where mainly bicarbonate is present ($6 < pH < 10$).

The leaching results in this article have shown that the degree of carbonation is very important when assessing the influence of carbonation on leaching. When reporting leaching results from carbonated samples, the degree of carbonation should be determined and clearly stated. In order to compare results from various investigations, the degree of carbonation of samples should, ideally, be the same.

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