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The effects of carbonation and drying during intermittent leaching on the release of inorganic constituents from a cement-based matrix

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Abstract

A Portland cement mortar was submitted to cycles of intermittent wetting (IW) in which tank leaching was interspersed with periods of storage in either an inert or a reactive atmosphere. Relative humidity (RH) (23%, 48% and 98%) was maintained during storage to control the drying process. The effects of IW were qualified by comparing flux and cumulative release of matrix constituents (Ca, OH, Na, K and Cl) to that of continuous water saturation. The carbonation process was associated with the degree of drying occurring due to storage. Cumulative release of most major constituents was suppressed in samples storage under 100% CO_2 in comparison to the inert atmosphere (100% N_2). Results suggest that accurate long-term performance assessment must account for the potential impact of phenomena associated with IW.

Keywords: Carbonation; Cycles; Transport properties; Portland cement; Intermittent wetting

1. Introduction

Characterization of the leaching behavior of primary matrix constituents in Portland cement mortars is important for understanding the long-term durability of these materials under environmental conditions. In natural leaching environments, cement matrices lose calcium and soluble salts to the environment. When the leaching solution is "acidic" in comparison to the pH of the bulk matrix, two distinct compositional zones are formed within the Portland cement matrix during long-term release [1–7]. The matrix can be described as an unleached core of high pH (i.e., pH ~ 12.5) at initial constituent composition surrounded by a porous leached shell with a significantly lower pH (i.e., pH ~ 9). The neutralized leached zone is essentially void of calcium-bearing mineral phases and has high silica content. The works of Carde et al. [8] and Carde and François [9–11] suggest that progressive decalcification of cement-based materials leads to an increase in matrix porosity and a decrease in compressive strength. Similar zonation has been observed during liquid-phase carbonation of cement matrices [12]. Thus, the literature infers that one measure of cement matrix durability may be obtained through characterization and prediction of inorganic constituent release.

The release of inorganic constituents is typically evaluated by laboratory-scale tank leaching of continuously water-saturated material. The results of these tests are then projected over a longer time interval to assess constituent leaching under saturated release conditions [13–19]. However, materials in many field or management scenarios are not continuously wetted but experience wetting and nonwetting periods under varied environmental conditions (i.e., variable relative humidity [RH] and atmospheric CO_2 or CO_2 from biological activity). During nonwetting periods, release of constituents into the surrounding environment does not occur due to the lack of a continuous liquid phase external to the material. Therefore, the assumption of a continuously saturated environment when evaluating inorganic constituent release from cement-based materials may result in erroneous assessment of long-term field performance.

When cement-based materials are stored in a nonwetted environment, three distinct storage scenarios may be envis-

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aged: (i) storage without drying or carbonation, (ii) drying without carbonation and (iii) drying with carbonation. Sanchez et al. [20] and Garrabrants et al. [21] focused on the first two of these scenarios, respectively. The drying of a subject cement matrix has been simulated using a two-regime moisture transport model [22], and this approach has been incorporated into current mass transport models to describe the release of major and trace constituents of the matrix under the conditions of intermittent wetting (IW) without carbonation [23]. In order to address the third scenario of drying with carbonation, the specific objective of this research was to show how the phenomena of IW and carbonation influence the release potential and release rate of "constituents of potential concern" (COPCs) in the matrix during cyclic wetting and storage. The COPCs for this paper include both structural species (Ca and OH) and highly soluble species (Na, K and Cl) that are common to most Portland cement-based materials. The test matrix of concern was a Portland cement mortar containing a mixture of metal oxides used in previous research, and the release behavior of trace contaminants with pH-dependent solubility (As, Pb and Cd) under the same environmental conditions is examined in a related paper [24].

2. Background

Carbonation is the most common chemical reaction influencing cement-based materials in natural environmental scenarios [25]. The highly alkaline nature of the Portland cement matrix renders the pore water and the surface water film susceptible to reaction with the carbon dioxide from the storage atmosphere, resulting in carbonation and finally in neutralization of the solid matrix. Carbonation can be associated with the drying of the matrix, which is caused by gradients in RH between the saturated matrix and the surrounding atmosphere. Both phenomena may be expected to influence precipitation and redistribution of contaminants within the pore structure. Much of the recent literature on carbonation of cementitious materials, however, has focused upon structural aspects (i.e., compressive strength, permeability, creep and microcracking). Little information exists regarding the influence of carbonation on the chemical properties of cement-based materials with respect to the release of inorganic constituents.

Carbonation is a liquid-phase reaction of carbon dioxide with aqueous hydroxide and cations to produce carbonates. The carbonation process firstly involves gas/liquid transfer of CO_2 followed by the reaction of aqueous CO_2 in the leachant. The gas/liquid transfer is a classic absorption process enhanced in this case by chemical reaction. The absorbed CO_2 flux is controlled by parameters such as the gas/liquid exchange surface and the concentrations in the gas (partial pressure) and liquid phase [26]. Thus, carbonation takes place within a water film that is left when cement matrices undergo drying [27–29]. Partial drying of liquid-filled pore passages facilitates the carbonation process allowing atmospheric carbon dioxide to diffuse into the pore structure and enhances the gas/liquid exchange surface. The carbonation reaction is hindered if CO_2 must diffuse through water-filled pores [28,29] or when pores are completely dried [28]. In Portland cement-based materials, carbonation results primarily in the conversion of portlandite, $Ca(OH)_2$, to calcite, $CaCO_3$, according to the stoichiometry

$$Ca^{+2} + 2OH^- + CO_2(aq) \leftrightarrow CaCO_3(s) + H_2O \tag{1}$$

The rate of this process is controlled physically by the diffusion of carbon dioxide into the pore vapor space and chemically by the availability of aqueous calcium and hydroxide ions in the pore water [27]. Due to diffusion of OH^- from regions of higher to lower pH, the local rate of $Ca(OH)_2(s)$ dissolution may differ from the rate of $Ca(OH)_2(aq)$ consumption due to the carbonation reaction [28]. As the portlandite is depleted, calcium ions are provided by the decalcification and polymerization of CSH gel [28,30,31].

$$x\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O} + y\text{H}_2\text{O} \rightarrow (x-y)\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O} + y\text{Ca(OH)}_2 \tag{2}$$

Long-term attack by carbonic acid decomposes the CSH gel into calcium carbonate, acid-insoluble silica gel and water [12].

$$\text{CSH} + \text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{SiO}_2\ (\text{gel}) + \text{H}_2\text{O} \tag{3}$$

In general, the carbonation reaction leads to the neutralization of the cement matrix by the conversion of alkaline constituents to carbonates. Carbonated matrices exhibit pore water pH of 2–3 units less than the pore water pH of 12.5 normally associated with the dissolution of portlandite in noncarbonated cements [32]. Carbonation of cement matrices has a significant physical effect on mass transport properties of materials through narrowing of the pore structure due to the increase in solid volume (11–12%) expected when portlandite is converted to calcium carbonate [31,32]. This increase has been cited as the primary explanation for reduced pore diameter, porosity and pore surface area in carbonated cementitious materials [33–35]. Consequently, the diminished pore structure resulting from carbonation leads to a decrease in water permeability [33,36] and an increase compressive strength [37,38]. However, complete carbonation results in decalcification of the CSH gel [12] and an overall decrease in strength. CSH is primarily responsible for the pore structure in the microporous region [39–41], and hence, complete decalcification may be associated with increases in mean pore diameter [11]. In IW scenarios, infiltrating liquid upon rewetting is "acidic" in comparison to the pore fluid and promotes rapid dissolution of calcium carbonate. Thus, the resultant matrix has been found to be more porous than the original material prior to rewetting [33,42,43].

Since the carbonation process in natural environments may be very slow, laboratory experimentation has been conducted under a variety of carbon dioxide levels. Many of the studies on carbonation of cement-based materials have used low levels of CO_2 (i.e., 4–5% CO_2) [33,44] or simply the CO_2 level in air (i.e., approximately 0.035%) [31,36]. Accelerated carbonation studies using 100% CO_2 [38,45–53] have allowed for the characterization of carbonation processes in much shorter times. Under atmospheric conditions, the depth of carbonation has been noted to reach a depth of approximately 1 cm per year in structural concretes [54,55]. One week of accelerated carbonation of cement-based matrices using 4% CO_2 has been shown to be equivalent to one year of atmospheric exposure based on carbonate penetration depth [56].

3. Approach

Tank leaching was interspersed with periods of storage at three levels of RH (23%, 48% and 98%) in both an inert atmosphere (100% N_2) and a reactive atmosphere (100% CO_2). In addition, tank leaching was interspersed with periods of storage under laboratory ambient conditions. The impact of IW and carbonation was illustrated through comparison of constituent flux and cumulative release under the seven IW conditions to flux and release under continuously water-saturated conditions. Data from batch equilibrium leaching tests [57] were used to determine the acid neutralization capacity of the solid matrix for noncarbonated and carbonated materials.

4. Materials and methods

4.1. Cement matrix

A Portland cement mortar containing a mixture of five metal oxides (As, Cd, Cu, Pb and Zn) was used for this study. The stabilized/solidified metal oxide (S/S MeO) matrix was prepared by mixing ordinary 36.0 wt.% ordinary Portland cement, 49.1 wt.% sand, 12.7 wt.% water and sufficient metal oxide powders so that the final product contained approximately 0.30 wt.% of cation. These metal species were selected to cover a wide range of sparingly soluble behaviors with minima obtained at different pH values. Leaching results for these metal species are presented in a previous study [24]. Sodium chloride at 0.29 wt.% was added to the cement recipe as a source of trace ions (Na and Cl) with high and non-pH-dependent solubility. The treatment process criterion was to obtain a material of good durability that contained enough quantities of constituents of interest to ensure constituent leaching consistent with analytical capabilities.

Table 1 presents the total elemental content of major constituents as determined by X-ray fluorescence and neutron activation analysis. The S/S MeO material was cast in sealed rectangular moulds of approximately 24 cm by 19 cm by 7.5 cm and cured in bulk form at room temperature in a humid environment for a minimum of 28 days. During the curing process, atmospheric CO_2 content of the curing environment was minimized by purging the air space with N_2 prior to curing and by including an aqueous solution of 0.5 N NaOH as a CO_2 scavenger within the chamber. At the end of the curing period, 4-cm cubes were cut from the bulk mould with a diamond-edged saw using dry cutting techniques. In addition, some fragments of the rectangular blocks were size reduced to a maximum particle size of 300 μm for equilibrium-based tests [57]. Subsamples of the particle size reduced material were carbonated by storing the material in a 100% CO_2 atmosphere at constant RH of 65%. The granular materials were periodically stirred by hand mixing until the material was uniformly carbonated as determined by CO_2 generation and gas chromatography.

4.2. Batch equilibrium leaching tests

Batch equilibrium leaching tests were carried out to determine the acid neutralization capacity of the solid matrix on noncarbonated and carbonated materials. Characterization methods and their applicability as well as results with respect to trace species have been presented in detail elsewhere [57] and therefore will not be discussed here. The test was conducted according to the SR002.1 protocol [16]. Thus, 11 aliquots of finely crushed material (< 300 μm) were contacted with either nitric acid or sodium hydroxide solutions of varying concentrations to cover a range of pH from 3 to 13. The L/S ratio was 5 mL/g dry sample. After a contact time of 24 h under agitation, the leachates were filtrated through 0.45-μm pore size polypro-

Table 1
Total elemental content of the S/S MeO matrix

Element	S/S MeO (mg/kg)
Aluminum	13,700 ± 300
Arsenic	3050 ± 60
Calcium	217,000 ± 40,000
Cadmium	3100 ± 100
Chloride	1880 ± 66
Copper	2920 ± 6
Iron	9100 ± 300
Potassium	3400 ± 100
Magnesium	1150 ± 300
Sodium	1610 ± 25
Lead	2700 ± 7
Sulfur	10,700 ± 110
Strontium	892 ± 76
Titanium	2470 ± 490
Zinc	3220 ± 6

Content as determined by X-ray fluorescence and neutron activation analysis [62].

pylene membranes, and the leachate pH of each extract was measured.

4.3. Dynamic mass transfer leaching tests

Continuous tank leaching and intermittent tank leaching (i.e., leaching with interspersed periods of storage) were carried out on the 4-cm cubic monoliths. Table 2 shows the two schedules used in this study as intervals of leaching and storage. The continuous leaching schedule consisted of uninterrupted leaching of the monolithic sample with leachant exchange at designated intervals. This schedule was used as a basis of comparison to the IW cases. For each of two replicates, 30 extracts were collected for chemical analysis from 6 cycles of 5 extracts each, over a total cumulative leaching time of 94 days.

The IW schedule was used to determine the influence of storage conditions and IW on constituent release. In the IW schedule, a sequence of four consecutive leaching intervals followed by a storage interval was considered to comprise an IW cycle. The duration of the storage interval was equivalent to the cumulative leaching time of the respective IW cycle. For example, IW Cycle 1 consisted of cumulative leaching time of 24 h (leaching intervals of 3, 3, 6 and 12 h) and one 24-h storage interval. A pattern of six IW cycles of leaching and storage was used to complete the 94 days of schedule. For each of two replicates, 4 extracts were collected for chemical analysis from each of 6 cycles, totaling 24 extracts over 47 days of cumulative leaching time.

4.3.1. Leaching intervals

During leaching intervals, samples were immersed in a volume of deionized water corresponding to a liquid-to-surface–area ratio of 10 mL of water for every square centimeter of exposed solid surface area. At the end of the leaching interval, the pH of the leachate was measured and the sample was then immersed in fresh leachant. The remaining leachate volume was filtered under vacuum through a 0.45-μm polypropylene membrane. Analytical samples from each leaching interval were collected and preserved for subsequent chemical analysis.

4.3.2. Environmental conditions during storage periods

Storage during IW was conducted under controlled atmospheres at three RH cases (nominally 23%, 48% and 98%) and in both an inert atmosphere (100% N_2) and a reactive atmosphere (100% CO_2). As a comparison of accelerated carbonation to natural placement environments, a seventh IW case was conducted in which samples were stored at ambient laboratory conditions. For all controlled atmosphere storage intervals, samples were stored in airtight desiccation chambers. Fig. 1 presents a schematic of the controlled atmosphere storage apparatus and a picture of S/S MeO samples in a desiccation chamber.

The carbon dioxide content of the storage atmosphere was maintained by passing either 100% CO_2 or 100% N_2 gas through the chamber at a low flow rate. RH of the storage atmosphere was controlled by inlet gas streams: (i) passed through a column of silica oxide desiccant (23% RH), (ii) bubbled through a column of deionized water (98% RH) or (iii) mixed after conditioning using silica oxide desiccant and deionized water (48% RH). The RH in each storage chamber was recorded periodically depending on the duration of storage intervals. At the beginning of each storage interval, the atmosphere of each storage chamber was purged for a short time (1–2 h) at a high flow rate (approximately 300 mL/min). For the duration of the storage interval, the flow of incoming gas was reduced to 20–50 mL/min.

RH control for mid-level RH in an inert atmosphere additionally was controlled by storing test specimens over a saturated solution of potassium carbonate. This saturated salt solution is known to provide 44% RH at 20 °C when in an enclosed space [58]. However, saturated K_2CO_3 solution could not be used in the reactive atmosphere (high CO_2 partial pressure) due to the precipitation of non-hygroscopic bicarbonates. Thus, the RH in the reactive CO_2 atmosphere at 48% RH was maintained solely by the mixing of gas streams passed over silica oxide desiccant and through deionized water.

Table 2
Leaching and nonleaching intervals for IW and continuous leaching cases

Cycle	Intermittent tank leaching					Continuous tank leaching				
	Leaching intervals (h)				Storage intervals (days)	Leaching intervals (hr)				
1	3	3	6	12	1	3	3	6	12	24
2	6	6	12	24	2	6	6	12	24	48
3	12	12	24	48	4	12	12	24	48	96
4	24	24	48	96	8	24	24	48	96	192
5	48	48	96	192	16	48	48	96	192	384
6	48	48	96	192	16	48	48	96	192	384
Extracts	24 per replicate					30 per replicate				
	47 days (24 intervals)				47 days (6 intervals)	94 days (30 intervals)				
Cumulative time	94 days					94 days				

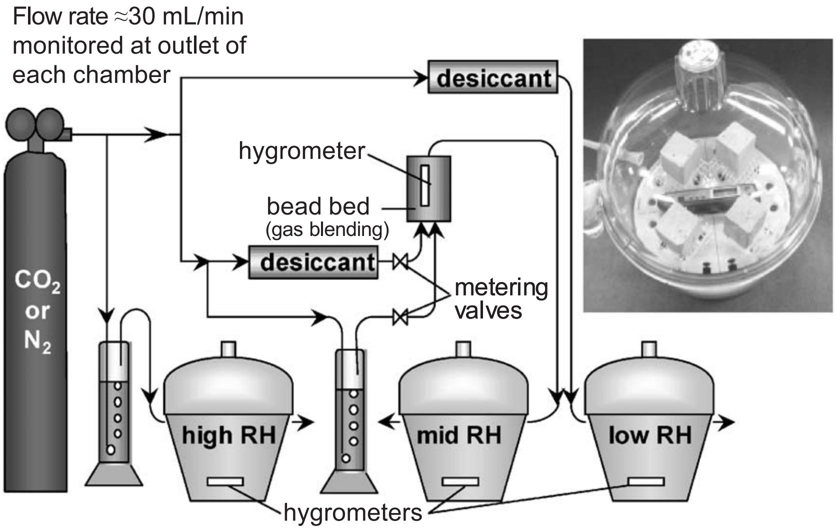

Fig. 1. Apparatus for controlled atmospheric storage at three levels of RH during IW.

4.4. Analytical methods

During storage, the CO_2 content of each storage chamber and the laboratory atmosphere was monitored periodically by gas chromatography analysis of an aliquot of storage atmosphere. Leachate cation concentrations were determined using either a Varian 640 flame atomic absorption spectrophotometer or a Varian 640Z graphite furnace atomic absorption spectrophotometer (Varian Analytical Instruments, Sugarland, TX). Chloride ion concentration was determined by using a Dionex AI-4500 ion chromatograph (Dionex, Sunnyvale, CA). Voltimetric probes were used to measure leachate pH on an Accumet 20 pH/conductivity meter (Fisher Scientific, Springfield, NJ).

5. Results and discussion

5.1. Environmental conditions during storage

Carbon dioxide concentrations in the reactive storage atmospheres varied from 70% to 100% for the storage chamber maintained at low-level RH, 80–100% for the storage chamber maintained at mid-level RH and 90–100% for the storage chamber maintained at high-level RH. The lowest CO_2 concentrations were present at the beginning of the experiments where the storage periods were short. No significant CO_2 concentration was measured for any of the inert atmosphere cases, indicating that the carbonation reaction was not feasible during storage in these chambers.

A record of the RH of the desiccation chambers during the storage period of each IW cycle is presented for both inert and reactive atmospheres at the mid-level RH (Fig. 2a) and low-level RH (Fig. 2b). Ambient RH is shown with the low-level RH cases in order to separate this data from the other mid-level measurements and to improve data presentation. The RH data for the high-level RH chambers are not shown, as these measurements were constant at the highest detectable value of the hygrometers (98% RH) irrespective of inert or reactive gases. Fig. 2 indicates that the level of

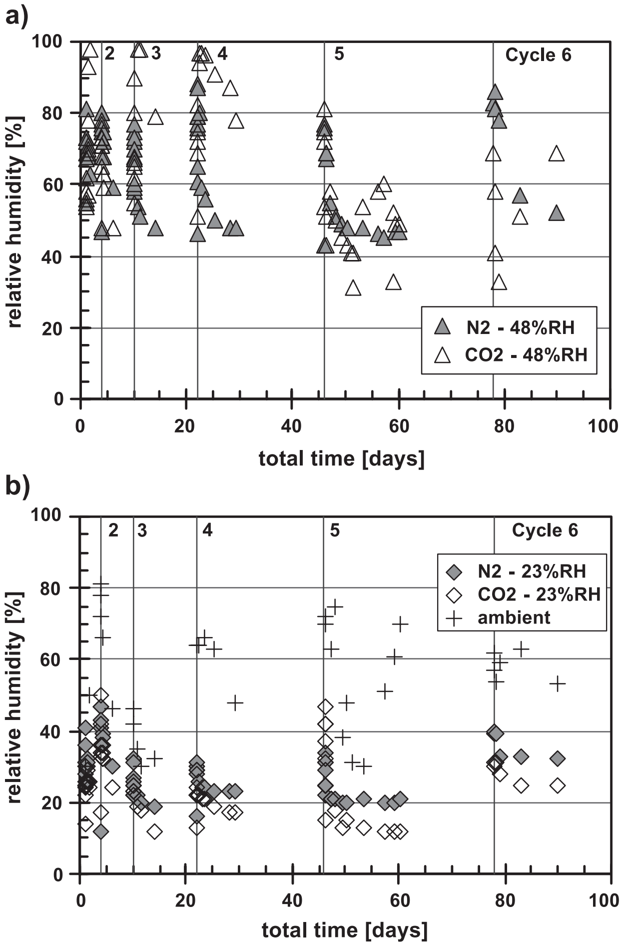

Fig. 2. RH of storage environmental during nonleaching periods: (a) inert atmosphere (100% N_2) and (b) reactive atmosphere (100% CO_2).

RH could not be easily maintained or controlled externally using desiccants and saturated salt solutions.

For the inert storage atmospheres (100% N_2), RH in the chambers increased sharply at the beginning of each storage period due to the release of moisture from the saturated samples. The RH in the low- and mid-level RH chambers under N_2 reached 40% and 80% during the first hour of storage before leveling out at approximately 23% and 48% RH, respectively. A similar initial increase in RH was observed for the CO_2 atmospheres (i.e., initial RH increases to approximately 40% and 80% for low- and mid-level RH, respectively). Ambient RH varied randomly from 30% to 80% during 100 days of the experiment with a mean value of $55 \pm 15\%$ RH. Mid-level RH during storage in a reactive atmosphere was difficult to maintain because the hygroscopic salt solution of K_2CO_3 could not be used. Thus, a constant end-state value could not be determined in this case. Due to the similarity in the initial RH response between levels in inert and reactive atmospheres, the stabilized values of RH observed for the inert storage atmospheres (i.e., 23%, 48% and 98% RH) are used as nominal case names in the remaining discussion.

5.2. Effect of storage environment on carbonation

The greatest apparent extent of carbonation was obtained during the lowest storage humidity (i.e., 23% RH) and the lowest apparent carbonation extent during the storage under ambient conditions. This hierarchy was determined by the measured increase in mass during storage based on the mass change associated with the conversion of portlandite to calcite. Furthermore, the extent of carbonation increased with increasing storage periods (i.e., initial pH of cycle decreased). According to the literature [28,43,59,60], carbonation reaction is optimum when the RH in the pores of the matrix is close to 65% and decreases as the RH in the pores increases while quasi-inhibited when the RH is below ca. 50%. Thus, the storage under 23% RH seemed likely to have led to an RH in the pore water close to or higher than 65%, and the storage under 48% to an RH between 65% and 100%.

5.3. The effects of IW and carbonation on species release

The effect of IW with carbonation during storage periods on the release of the species of interest was evaluated by comparing cumulative release and interval flux from the continuously leached samples to that of the seven IW cases (i.e., different RH and CO_2 content of the storage atmosphere). Although intervals of storage reduced the cumulative release of species when compared to the same time interval of continuous leaching without storage, the influence of IW and carbonation is apparent when equivalent periods of leaching are compared. Therefore, cumulative release of the species of concern was presented as a function of cumulative leaching time (ignoring nonleaching intervals). However, mean release flux was reported as a function of the overall cumulative time including leaching and storage times. In all IW cases, it is assumed that the influx of water during subsequent leaching intervals was relatively rapid and thus insignificant to the overall release process.

The cumulative mass release and release flux for the matrix components and highly soluble species are presented in Figs. 3–9. In these figures, the two levels of carbon dioxide are shown to correspond to a reactive atmosphere of 100% CO_2 (“CO2” in figures) or an inert storage atmosphere of 100% N_2 (“N2” in figures). The three levels of RH are presented according to the steady state RH observations for the inert atmosphere as “98% RH”, “48% RH” and “23% RH”. In addition, data with storage under ambient laboratory conditions are referred to as “ambient” and the continuous leaching test as “continuous”.

5.3.1. Effect of carbonation on the release of structural matrix components

Calcium and hydroxide ions were considered as structural components of the cement-based material since calcium hydroxide has been noted to make up nearly 25 wt.% of Portland cement-based S/S matrices [61]. The release and eventual depletion of calcium hydroxide influences the chemical properties of the pore solution and the durability of the cement matrix. Leachate pH values as a function of time are shown in Fig. 3. The cumulative release and flux of hydroxide ion and calcium from the S/S MeO matrix obtained for intermittently wetted and continuously leached samples are presented in Figs. 4–6. In all cases, hydroxide ion release was derived from leachate pH data (Fig. 3).

5.3.1.1. Leaching behavior of hydroxide (leachate pH). Figs. 3a and 4a indicates that in an inert atmosphere (100% N_2), no significant influence of IW and storage humidity level was observed on the leachate pH or the release of hydroxide when comparison was conducted on the basis of cumulative release. However, in the reactive atmosphere of 100% CO_2, leachate pH (Fig. 3b) decreased significantly in relation to the decrease in RH during storage (e.g., samples stored at low RH showed the most significant decrease in leachate pH). The release of hydroxide subsequent to storage in a reactive atmosphere was suppressed compared to release under continuous leaching conditions because of the carbonation reaction. Thus, after 47 days of leaching, ca. 45,000 mg/m^2 was released compared to 120,000 mg/m^2 for the noncarbonated samples. This release was independent of the storage humidity level. Yet, storage under ambient conditions resulted in a greater cumulative release (ca. 88,000 mg/m^2). This result was consistent with rate limitations of the carbonation reaction and the lower CO_2 content provided by the ambient atmosphere.

Fig. 4b presents the mean release flux of hydroxide ion from the matrix for all eight test cases. In the IW cases stored under inert atmosphere, the flux of hydroxide during

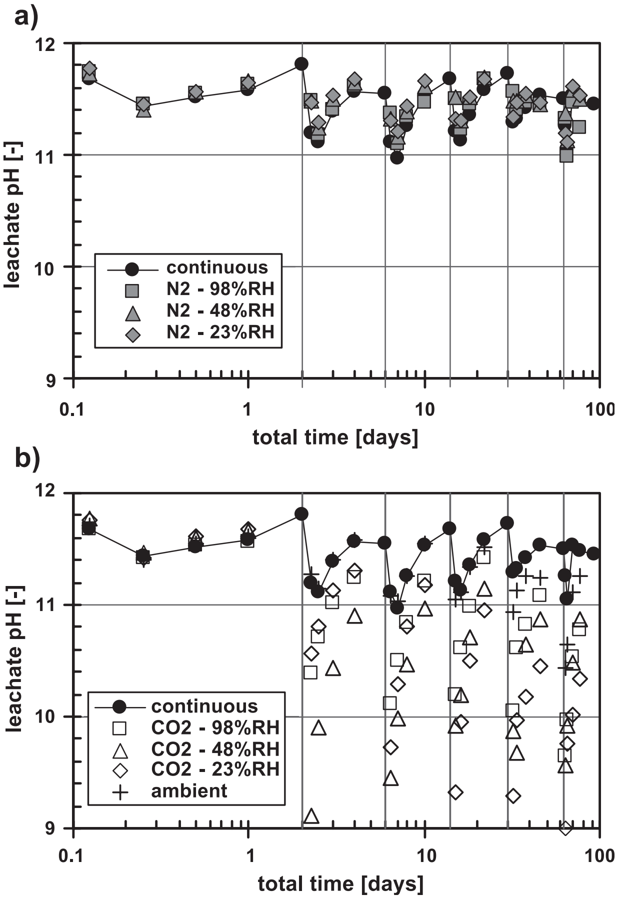

Fig. 3. Leachate pH (average of duplicates) for intermittently wetted and continuously leached samples of S/S MeO: (a) IW under inert storage and (b) IW under reactive storage.

the first leaching interval of each cycle was much greater than in subsequent intervals and then decreased toward that value observed for the continuous leaching case. This pattern of flux was consistent with the reformation of a concentration gradient at the beginning of each leaching cycle and was seen to be indicative of gradient relaxation. The relaxation of the hydroxide gradient resulted from continued mass transport within water-filled pores during the storage intervals when no continuous liquid phase is present outside of the matrix. Additionally, the hydroxide flux during the first leaching interval was greater for samples stored at the highest level of RH. This observation supports the occurrence of the greatest relaxation of the hydroxide gradient to be related to least amount of drying and, consequently, the greatest degree of continued mass transport.

Conversely, when storage is conducted under a reactive atmosphere, the release flux within each leaching period shows a reversal of the behavior measured for either the continuous leaching case or the IW cases with storage in an inert atmosphere. For IW cases stored under CO_2 atmosphere, the release flux of hydroxide during the first leaching interval of each cycle was much lower than in subsequent leaching intervals. The release flux then increased and remained below the release flux obtained for the continuously leached samples. In addition, the release flux during the first leaching interval generally was lower for samples stored under 23% RH than for samples stored under 98% RH. This observation is consistent with a greater extent of carbonation obtained for the lowest storage humidity level. The flux behavior when storage is conducted in a reactive atmosphere indicates the local neutralization of the matrix pore water very near the interface of the bulk matrix.

The increase in hydroxide release caused by the relaxation phenomenon observed under inert atmosphere was overcome by the effect of carbonation, which prevented hydroxide release by fixation through the carbonation reaction. The increased release in the subsequent leaching periods may reflect the dissolution of calcium carbonate due to the infiltrating liquid that was ‘‘acidic’’ in comparison to the pore fluid allowing the release of hydroxide. Finally, the hydroxide release flux for leaching interspersed with storage under ambient conditions was similar to the one obtained during continuous leaching for the first three cycles. The effect of carbonation became evident by a

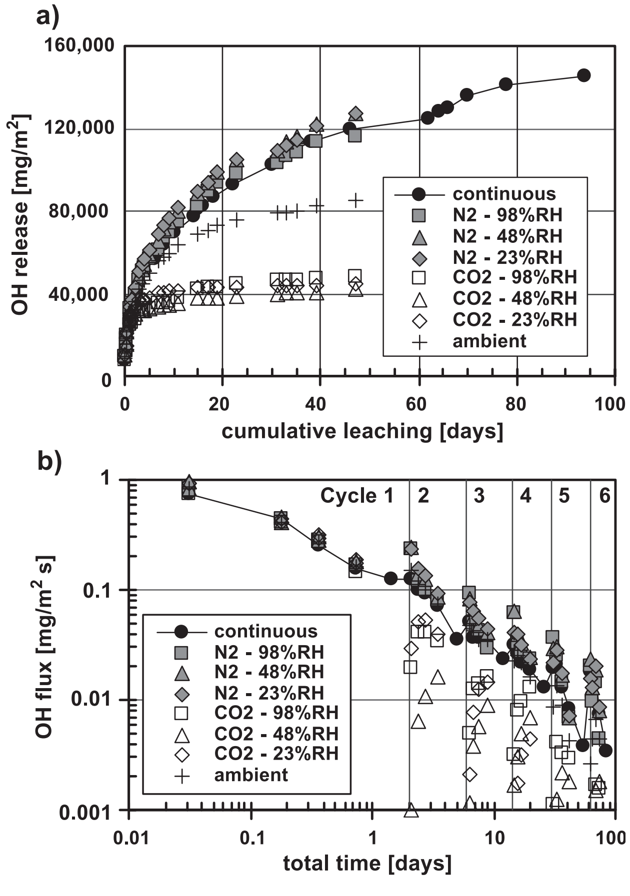

Fig. 4. Release of hydroxide ion determined from leachate pH (average of duplicates) for intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2) and (b) flux (mg/m^2 s).

reduction in flux of the initial leaching interval of each IW cycle. This reduction was due to the consumption of hydroxides in the carbonation reaction, starting at the fourth IW cycle. Indeed, the increase in storage period duration affected the extent of carbonation by allowing increased drying of the matrix and an increase in the gas/liquid interfacial area.

5.3.1.2. Leaching behavior of calcium. Comparison of the cumulative release of calcium between continuously leached samples and intermittently wetted samples stored in 100% N_2 atmosphere (Fig. 5a) showed no significant effect of IW and humidity level during storage. After 47 days of leaching, 2% of the total calcium content was released. However, the cumulative release of calcium from intermittently wetted samples stored in 100% CO_2 atmosphere was substantially less than for the noncarbonated samples. Within the series of carbonated samples, a greater cumulative release of calcium was observed with increasing extent of carbonation. Thus, after 47 days of leaching, 32,000 mg of calcium/m^2 was released when stored in 23% RH in CO_2 atmosphere, while almost the same amount of calcium were released from samples stored under 48% and 98% RH (i.e., respectively, 22,200 mg/m^2 and 24,000 mg/m^2).

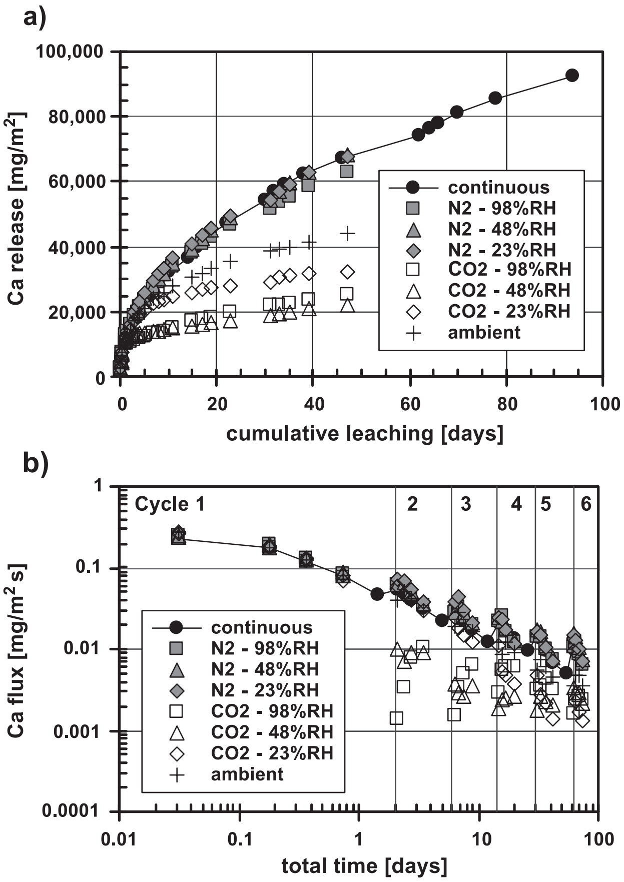

Fig. 5. Release of calcium (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2) and (b) flux (mg/m^2 s).

When comparison is based on the calcium flux (Fig. 5b), no significant effect of the RH was observed between the continuous leaching case and the intermittent leaching cases when storage was conducted in an inert atmosphere. Remarkably, for continuous leaching, greater flux values of calcium were observed each time there was a decrease in the interval duration (i.e., at the beginning of each cycle) followed by decreasing release flux during subsequent, longer leaching intervals. This behavior was most likely an effect of the finite bath reducing the driving force for leaching. A similar pattern was observed for the release of hydroxide. Moreover, for intermittently wetted samples stored in an inert atmosphere (100% N_2), the release flux of calcium during the first leaching interval was lower than in the second interval, followed by a decrease tending towards the release flux of continuously leached samples. This calcium flux pattern was reverse of pH pattern, which is consistent with the decrease of the calcium solubility when pH increases, as shown in Fig. 6.

Conversely, intermittently wetted samples stored in 100% CO_2 atmosphere presented release flux of calcium dependent on the storage RH level and much lower than for the continuously leached samples. For leaching interspersed with periods of storage in 23% RH, for each leaching cycle, the release flux of calcium during the first leaching interval was greater than subsequent intervals and decreased within a cycle remaining below the release flux obtained for the continuously leached samples at longer time intervals. This calcium flux pattern might be the result of the presence of a calcium hydroxide front ahead of the carbonate front due to a fast drying rate (i.e., carbonate front within the matrix and not at the matrix interface). In addition, the calcium flux pattern was identical with that of hydroxide, which is consistent with the previous hypothesis for indicating a release of calcium hydroxide. For leaching interspersed with periods of storage under 98% RH, for each leaching cycle, the release flux during the first leaching interval was much less than subsequent leaching intervals. Within a cycle, the release flux increased with each leaching period and remained less than the release flux obtained for the continuously leached samples. This calcium flux pattern is likely the result of the (i) initial dissolution of calcium carbonate before the release of calcium hydroxide (i.e., carbonate front at the matrix interface) and (ii) significantly lower solubility of calcium carbonate than calcium hydroxide. Furthermore, this calcium flux pattern was reverse of hydroxide flux pattern.

5.3.2. Effect of carbonation and drying on the release of highly soluble species

Unlike sparingly soluble species where local equilibrium is dependent on the pore water composition and pH, the release of highly soluble species is not typically coupled with the release of other matrix constituents. Sodium, potassium and chloride were determined to be present in the matrix at high enough concentrations to suit analytical

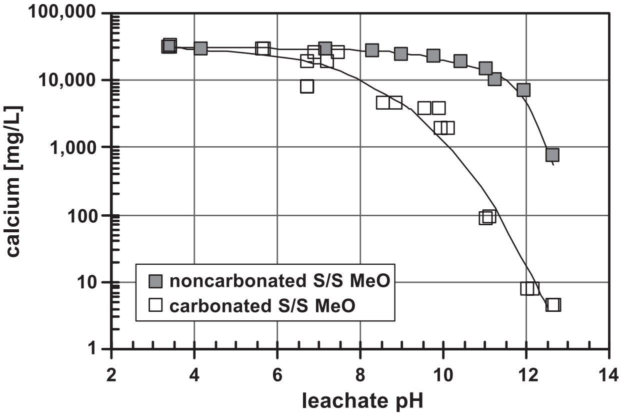

Fig. 6. Solubility of calcium as a function of pH for noncarbonated and carbonated S/S MeO samples determined using a batch equilibrium test [57].

capabilities. The release of these species is evaluated to illustrate the effect of IW with carbonation of the leaching of highly soluble species.

5.3.2.1. Leaching behavior of sodium. The cumulative release curve for sodium (Fig. 7a) showed that carbonation suppressed the release of sodium. After 47 days of leaching interspersed with storage in a reactive atmosphere, 54% of the total sodium was released when stored under 23% RH, 79% of the total sodium for storage under 48% and 98% RH, and 99% of the total sodium content for storage under ambient conditions. These values are significantly less than those measured for sample stored under an inert atmosphere (i.e., 99% of total Na content for all IW cases). The greatest sodium release suppression was observed when storage is conducted at 23% RH (i.e., greatest extent of carbonation). However, storage under ambient conditions had no effect relative to carbonation on the release of sodium. Thus, these results might be explained because carbonation reduced the release of sodium by forming a diffusion barrier (i.e., carbonate front) ahead of the sodium precipitation front.

When the same comparison was based on the sodium flux, Fig. 7b shows that a greater flux was observed for the intermittently wetted samples stored in an inert atmosphere. There was a significant increase in sodium flux during the first leaching interval of each cycle than in subsequent intervals. Then the flux of sodium decreased toward that value observed for the continuously leached samples. In addition, the increase in release flux in the first leaching interval was consistent with the extent of drying associated with the storage atmosphere. Thus, the relaxation of the sodium gradient, which results from a redistribution of sodium concentration in the pore water of the material during the storage intervals, was observed to be dependent on the extent of drying within the matrix.

For the samples stored in 100% CO_2 atmosphere, sodium release flux during the first leaching interval was greater than subsequent leaching intervals of an IW cycle. This flux showed an increase over the continuously leached samples for samples stored at 48% and 98% RH and ambient conditions. A decrease in flux was observed for samples stored at 23% RH. Within an IW cycle, sodium release flux decreased toward the release flux obtained for continuously leached samples for IW samples stored under 48% RH, 98% RH and ambient conditions. The release flux of sodium remained less than that obtained for continuously leached samples when IW was conducted at 23% RH. The reduction in flux was most evident for cases where the degree of carbonation was greatest. This result may be due to increased resistance to sodium diffusion through a carbonate precipitate layer on pore surfaces.

5.3.2.2. Leaching behavior of potassium. Although potassium was not added to the cement recipe, this highly soluble specie was found in high enough concentrations in the matrix. In general, the release of potassium was consistent with the previous analysis for sodium. The cumulative release of potassium presented in Fig. 8a showed that a greater degree of gradient relaxation lead to increased potassium release for IW samples stored in an inert atmosphere in comparison to potassium release after the same

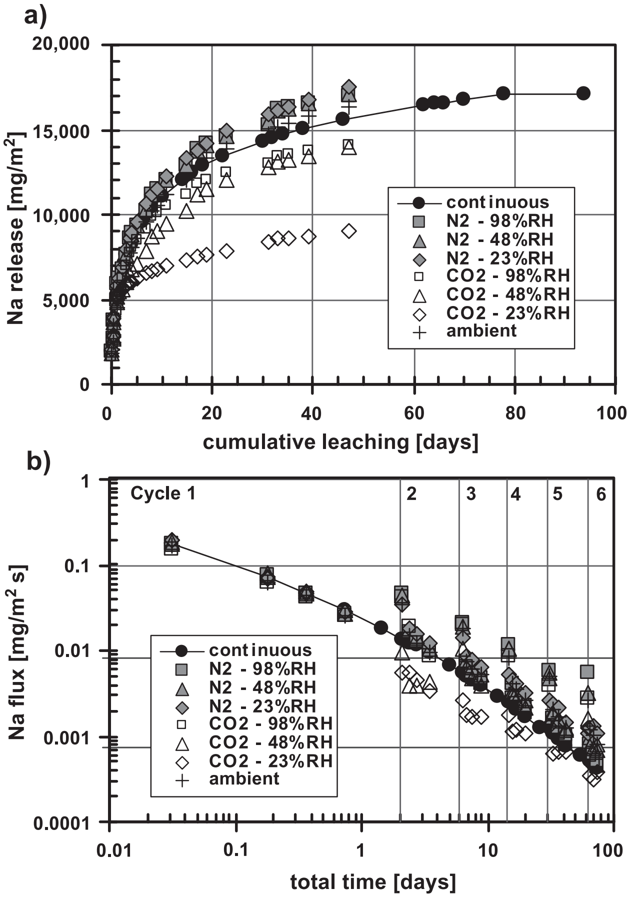

Fig. 7. Release of sodium (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2) and (b) (mg/m^2 s).

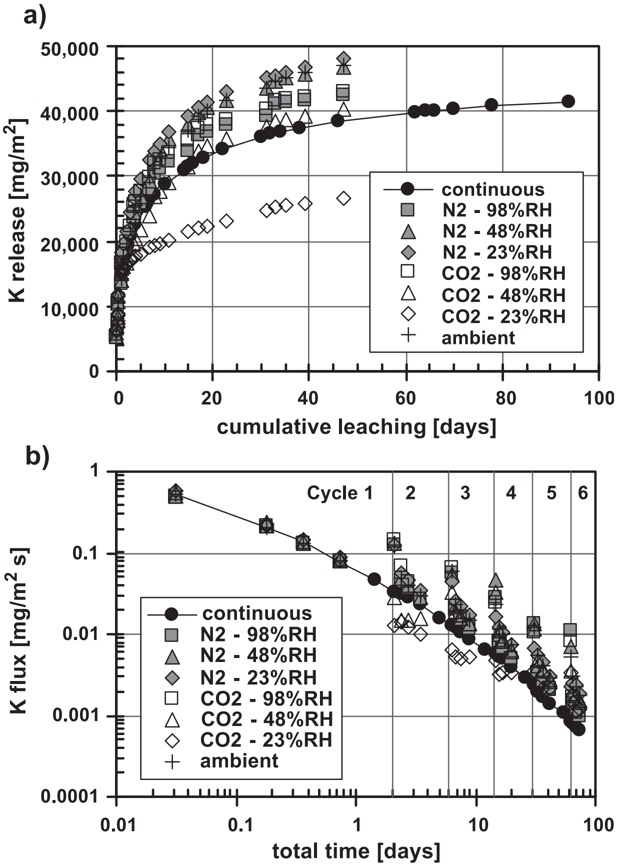

Fig. 8. Release of potassium (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2) and (b) (mg/m^2 s).

cumulative leaching time for the continuously leached samples. After 47 days of continuous leaching, 77% of the total potassium content was released. However, intermittent leaching in an inert atmosphere led to the release of 96%, 94% and 85% of the total potassium when storage was conducted at 23%, 48% and 98% RH, respectively. When storage was conducted under a reactive atmosphere, cumulative release of potassium was found to be 53%, 81% and 86% of the total potassium content for IW cases with storage at 23%, 48% and 98% RH, respectively. Ambient conditions during the storage interval resulted in a cumulative release of 94% of the total potassium after 47 days of leaching time. Thus, significant suppression of potassium release was seen only for the IW case where carbonation was greatest.

The relationship between carbonation and potassium release suppression is reflected in Fig. 8b, which shows the release flux of potassium as a function of total experimental time. A significant decrease in flux is seen in the case of storage in a reactive atmosphere at 23% RH. There is no obvious effect of carbonation on the release of potassium when storage is conducted at 98% RH. This observation is most likely due to the limited carbonation reaction at high RH as found by Papadakis et al. [28].

5.3.2.3. Leaching behavior of chloride. The cumulative release curve for chloride (Fig. 9a) showed that 21%, 20% and 17% of the chloride added in the recipe were released after 47 leaching days from intermittently wetted samples stored in an inert atmosphere at 23%, 48% and 98% RH, respectively. After the same leaching time, 16% of chloride was released in the continuous leaching case. Carbonation reduced the release of chloride for leaching interspersed with periods of storage at 48% and 98% RH, while increasing the release of chloride for leaching interspersed with periods of storage at 23% RH (i.e., for the greatest extent of carbonation). When storage was conducted at 48% and 98% RH in a reactive atmosphere, carbonation of the matrix resulted in a lower cumulative release of chloride than that for the noncarbonated samples. However, when storage was conducted at 23% RH (i.e., fast drying and greatest extent of carbonation), the cumulative release of chloride from carbonated samples was greater than for noncarbonated samples or continuously leached samples. Thus, after 47 days of leaching, 21.2%, 13.6% and 11.5% of chloride were released when stored in CO_2 atmosphere under 23%, 48% and 98% RH, respectively. Chloride cumulative release obtained with storage under ambient

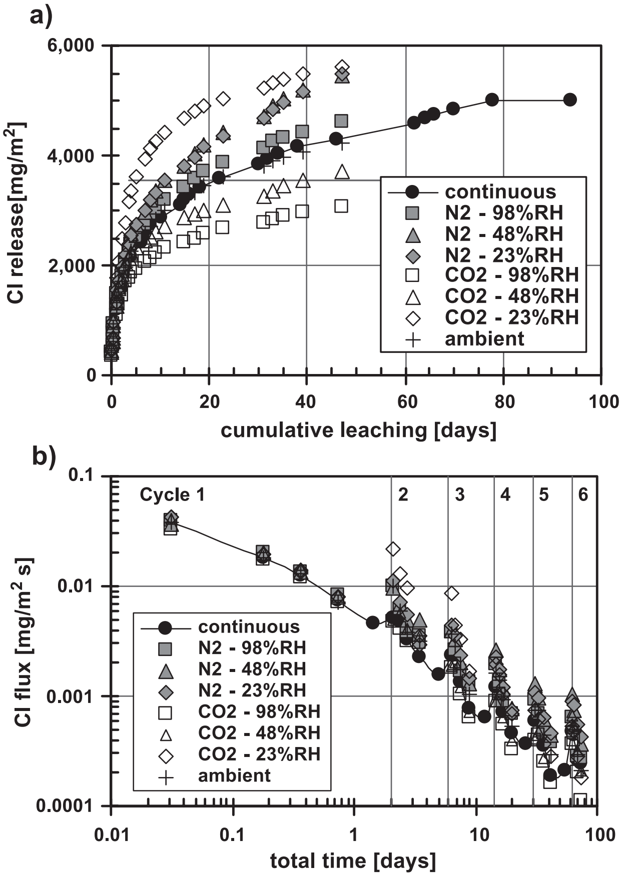

Fig. 9. Release of chloride (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2) and (b) (mg/m^{2}s).

conditions was similar to the release obtained during continuous leaching with ca. 16% of chloride released.

A possible explanation for the observed results may be the relative positions of the carbonation and chloride precipitation fronts. When the drying rate was slow (i.e., case of storage under 48% RH), carbonation reduced the release of chloride by forming a diffusion barrier (i.e., carbonate front) ahead of the chloride precipitation front. Conversely, a chloride precipitation front was separated and ahead of the carbonate front when the drying rate was fast (e.g., in the case of storage under 23% RH). Therefore, the chloride release was not suppressed. This explanation was supported by the release flux of chloride observed for leaching interspersed with periods of storage at 23% RH and ambient conditions (Fig. 9b). For each leaching cycle, the release flux of chloride during the first leaching interval was greater than subsequent intervals and decreased within a cycle tending towards the release flux of continuously leached samples. This behavior of the flux was similar to the one obtained when storage occurred in inert atmosphere.

6. Conclusions

Monolithic samples of a Portland cement matrix were submitted to cyclic patterns of leaching and storage (i.e., IW). During storage, the samples were maintained in either an inert atmosphere (100% N_2) or a reactive atmosphere (100% CO_2) at three values of RH. The effects of matrix drying and carbonation were observed in terms of leaching behavior of the main soluble constituents.

The RH of the storage atmosphere was used to control the degree of drying that occurred over the storage interval. Consequently, the degree of carbonation resulting from the liquid-phase reaction of CO_2 with the hydroxide ions was inversely associated with the level of RH in the storage environment. As a result, samples stored for relatively at the lowest level of RH showed the greatest effects of the carbonation reaction. However, since these samples were stored for relatively short intervals, the RH within the pore structure did not come to hygric equilibrium with the surrounding environment. The RH of the pore space, a controlling factor in the carbonation reaction, for the low- and mid-level RH cases was most likely greater than the atmospheric RH. Therefore, the low-level RH conditions, which yielded a high degree of carbonation effects, were probably close to a pore RH of 65%, shown in the literature to correspond to a maximal carbonation.

Carbonation of the cementitious matrix was seen to suppress leachate pH in each leaching interval by reducing the hydroxide content. Mass transport and release of hydroxide ions were decreased due to the consumption of hydroxide ions during the carbonation reaction (i.e., conversion of hydroxides to carbonate species). In addition, the cumulative release of calcium from the carbonated samples was substantially less than that from the noncarbonated material. Within the series of carbonated samples, a higher cumulative calcium release was observed with increasing extent of carbonation due to the formation of calcium carbonate precipitate during storage and subsequent dissolution during leaching.

IW coupled with carbonation did influence the release of highly soluble species. Two different behaviors were observed. For sodium and potassium, increasing the degree of drying (i.e., decreasing storage atmosphere RH) resulted in a decrease in release and flux in comparison to the continuous leaching case. This was most likely because of the formation of a carbonate front ahead of a sodium precipitation front. For chloride, increasing drying during storage appeared to result in a chloride precipitation front ahead of the carbonate front, and therefore, an increase in chloride release was observed.

The results of this study indicate that both drying and carbonation phenomena, which are natural consequences of IW, influence the release of major soluble constituents in cement-based matrices. The effects of these phenomena on constituent release vary according to (i) intrinsic species characteristics (i.e., diffusion rate and solubility) and (ii) external storage conditions (i.e., level of RH, duration of storage period, inert or reactive atmosphere). Different behaviors were observed depending on (i) the rate of gradient relaxation and therefore the diffusion rate of the species of concern, (ii) the drying rate and precipitation phenomenon and (iii) the carbonation rate. Overall, this work illustrates the importance of accounting for the impact of IW phenomena on constituent release estimates used in the performance assessment process for cementitious materials in both structural and environmental applications.

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