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The effect of storage in an inert atmosphere on the release of inorganic constituents during intermittent wetting of a cement-based material

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Abstract

Monolithic waste materials (e.g. Portland cement treated wastes) in many field scenarios do not remain continuously saturated, but experience intermittent wetting interspersed with periods of storage in an unsaturated environment. During storage, the matrix may loss moisture to the environment, promoting precipitation or redistribution of species. In addition, the matrix may react with the surrounding atmosphere through carbonation or oxidation. Upon subsequent leaching, changes in the chemical and physical composition incurred over the storage interval can influence the release of inorganic species. Current assessment approaches, which use continuous leaching data to project release over some assessment interval, do not allow for changes in leachability resulting from intermittent wetting and storage. Thus, this study evaluates the effect of storage intervals in an inert atmosphere on subsequent release of inorganic species from a synthetic Portland cement matrix. Tank leaching in deionized water was interspersed with storage at three relative humidity (RH) levels (nominally 0, 50 and 100% RH) in a 100% nitrogen atmosphere. Leaching data from the three intermittent wetting cases were compared to continuous leaching for the release of structural species (Ca, OH), highly soluble species (Na, K, Cl) and pH-dependent species (As, Cd, Pb).

The RH of storage environment, which acted as a boundary condition for the drying process, influenced the precipitation of species within dried pores and relaxation of pH and concentration gradients within water-filled regions. Gradient relaxation resulted from continued mass transport within saturated pores over the storage interval and was most evident when storage was conducted at 98% RH. However, when storage RH promoted drying of the matrix, the effect of gradient relaxation

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was balanced by precipitation. When release was normalized to total leaching time, relaxation of concentration gradients of highly soluble species resulted in greater cumulative release for the intermittently wetted cases than in the case of continuous leaching. The release of pH-dependent constituents was controlled by relaxation of the pH gradient and species solubility as a function of local pore water pH. Application of a current assessment protocol to estimate intermittent wetting release resulted in either over or underestimation of actual cumulative release, depending on the nature of the constituent of interest. These results imply that long-term constituent release from Portland cement-based waste forms should not be made by simple correction of saturated release assessments because alterations to the matrix leachability induced by the storage environment need to be considered.

Keywords: Wet/dry cycles; Relative humidity; Storage; Leaching; Long-term release

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1. Introduction

Industrial waste management and remediation of contaminated sites frequently requires evaluation and assessment of soils or industrial wastes contaminated with heavy metals and other inorganic pollutants. Characterization of release rates and leaching potentials from these materials is often used to predict the impact of contaminant release on the surrounding environment or to evaluate the efficacy of treatment processes such as solidification/stabilization. The solidification/stabilization treatment represents an important class of waste management alternatives in which untreated process wastes or contaminated soils are mixed with a binder, often Portland cement, and other additives to form a cementitious matrix with improved handling and leaching properties. Typically, solidified/stabilized (S/S) materials are formed into monoliths that may be disposed in regulated landfills. However, recent focus on reuse options, such as use in roadbeds or backfill, has intensified the need for a risk-based acceptance approach founded in leachability characterization and assessment.

The reliance on characterization as a basis for decision-making, as well as the need for improved knowledge of the long-term leaching behavior and eco-compatibility of wastes, has resulted in the development of new evaluation tools. In this framework, research programs have been ongoing in Europe and the United States to define a methodology for evaluating the release of inorganic constituents from a broad spectrum of solid wastes types. This methodology is comprised of leaching tests and interpretation protocols, which emphasize the integrated use of fundamental leaching parameters to estimate constituent release [1–3]. Thus, the release of “constituents of potential concern” (COPC) from monolithic materials is evaluated from data provided by tank leaching of the matrix under continuously water-saturated conditions. Projected long-term field performance is currently evaluated using the semi-infinite diffusion model or shrinking core models [4–8] to describe cumulative COPC release and flux. The coupled dissolution–diffusion model [8] incorporates dissolution kinetics between solid phase and aqueous species into a Fickian diffusion process. This model has been adapted to project saturated inorganic release from soils and cement-based materials over extended assessment intervals [2,3]. In general, the current characterization and assessment approaches assume a continuously saturated matrix and account for only relatively minor changes in leaching chemistry.

Materials in many field scenarios do not remain fully saturated over the assessment interval due to cyclic weather patterns. The materials are often exposed to intermittent wetting defined as cycles of saturation followed by storage in an environment below saturation. Thus, estimates based on a continuously saturated matrix cannot adequately simulate field scenarios unless adjusted to account for cyclic periods of leaching and "non-leaching". In the current, diffusion-based approach, this is accomplished by multiplying the release estimate under continuously saturated conditions by a wetting frequency term, which is related to the fraction of the total assessment interval that the matrix is saturated. This approach assumes that there are no significant changes to the chemical or physical composition of the solid matrix.

However, alteration of cement-based materials during storage is expected to influence the leaching potential and release rate of inorganic contaminants by changing the chemical and physical properties of the treated material that control constituent release. For example, it is the highly alkaline nature of the Portland cement matrix that renders the pore water susceptible to reaction with the carbon dioxide from the storage atmosphere resulting in carbonation and neutralization of the solid matrix [9–12]. Another potential consequence of storage in an unsaturated environment is the drying of the matrix caused by gradients in relative humidity (RH) between the saturated matrix and the surrounding atmosphere. Moisture loss during storage may be expected to influence precipitation and redistribution of contaminants within the pore structure. Much of the recent literature on drying of cementitious materials, however, has focused on the drying process on durability of structural cements and concretes [13–24]. These studies indicate that moisture transport within cement-based materials promotes changes in the pore structure that lead to sparing, micro-cracking, creep or shrinkage. Little information exists regarding the influence of drying on the chemical properties of cement-based materials with respect to the release of inorganic constituents.

Thus, the specific objective of this paper was to examine the effect of intermittent wetting and RH during storage on constituent leaching from a synthetic cement-based material. These effects were shown by comparing the release of structural components, highly soluble species, and pH-dependent species from samples that were exposed to continuous leaching or intermittently wetting and storage. In this study, storage was conducted in an inert atmosphere to minimize the potential for chemical reaction between the matrix and the storage environment through carbonation or oxidation.

2. Experimental

The general approach used to study intermittent wetting phenomena was to expose monolithic samples of a solidified matrix to cycles of leaching in deionized water interspersed with storage under nitrogen at three levels of RH (0, 50 and 100% RH). Since the storage atmosphere was considered inert to the matrix, alteration due to carbonation or other chemical changes was not considered. Continuous leaching of the solid matrix was conducted in parallel to provide a basis of comparison for release. All experiments were conducted in duplicate at room temperature ($20 \pm 2\,^{\circ}\mathrm{C}$).

2.1. Materials

A synthetic waste matrix was created by adding metal oxide powders to a mixture of ordinary Portland cement (36.0 wt.%), sand (49.1 wt.%), and water (12.7 wt.%). The principal "contaminants" in the S/S metal oxide (S/S MeO) matrix were arsenic, cadmium, copper, lead and zinc at approximately 0.30 wt.% of each cation. These elements were selected to cover a wide range of solubility behavior with minima obtained at different pH values. The level of contamination was chosen such that diffusion through the matrix would control constituent release due to depletion near the surface. Sodium chloride (0.29 wt.%) was added as a of source tracer ions (Na, 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 COPCs 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 [25]. These analytical techniques provide a true total assay of the waste material in a manner that is non-destructive to the solid matrix.

The S/S MeO waste was cast in sealed, rectangular molds of approximately 24 cm × 19 cm × 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 not monitored. However, the air space was purged with 100% N_2 prior to curing and an aqueous solution of 0.5 N NaOH was used as a CO_2 scavenger within the chamber to minimize absorption of CO_2 by the matrix. At the end of the curing period, cubic monoliths of the S/S MeO material with sides of 4 ± 0.3 cm were cut from the bulk mold with a diamond-edged paver saw using dry cutting techniques.

Table 1
Total elemental content of the synthetic S/S MeO matrix[a]

Element		Total content (mg/kg)	
Aluminum	Al	13700	±300
Arsenic	As	3050	±60
Calcium	Ca	217000	±40000
Cadmium	Cd	3100	±100
Chloride	Cl	1880	±66
Copper	Cu	2920	±6
Iron	Fe	9100	±300
Potassium	K	3400	±100
Magnesium	Mg	1150	±300
Sodium	Na	1610	±25
Lead	Pb	2700	±7
Sulfur	S	10700	±110
Strontium	Sr	892	±76
Titanium	Ti	2470	±490
Zinc	Zn	3220	±6

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

Table 2
Leaching and non-leaching intervals for intermittent wetting and continuous leaching cases[a]

Cycle	Continuous leaching (Schedule 0)					Intermittent leaching (Schedule 1)				
	Leaching intervals (h)[b]					Leaching intervals (h)[c]				Storage intervals (days)[d]
1	3	3	6	12	24	3	3	6	12	1
2	6	6	12	24	48	6	6	12	24	2
3	12	12	24	48	96	12	12	24	48	4
4	24	24	48	96	192	24	24	48	96	8
5	48	48	96	192	384	48	48	96	192	16
6	48	48	96	192	384	48	48	96	192	16

[a] Cumulative time: 94 days.
[b] Extracts: 30 per replicate; 94 days (30 intervals).
[c] Extracts: 24 per replicate; 47 days (24 intervals).
[d] Extracts: 47 days (24 intervals).

2.2. Leaching and non-leaching schedules

Table 2 shows the two schedules used in this study as intervals of leaching and storage. The continuous leaching Schedule 0 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 intermittent wetting cases. For each of two replicates, 30 extracts were collected for chemical analysis from six cycles of five extracts each, over a total cumulative leaching time of 94 days (2256 h).

The intermittent wetting Schedule 1 was carried out for three RH cases (0, 50 and 100% RH) and was used to determine the influence of storage conditions and intermittent wetting on constituent release. In this schedule, an intermittent wetting cycle consisted of four consecutive leaching intervals followed by a storage interval equivalent in duration to the cumulative leaching time of that cycle. For instance, cycle 1 consisted of 24 h of leaching (intervals of 3, 3, 6 and 12 h) and one 24 h storage interval. A pattern of six intermittent wetting cycles of leaching and storage was used to complete the 94 day schedule. For each of two replicates, four extracts were collected for chemical analysis from each of six cycles, totaling 24 extracts over 47 days (1128 h) of cumulative leaching time.

2.3. Dynamic leaching protocol

A dynamic leaching protocol similar to ANSI 16.1 [26] was carried out on monolithic S/S MeO samples to determine the rate of constituent release under intermittent wetting and continuous leaching conditions. Cubic samples, having a side dimension of 4 cm, were contacted with a volume of deionized water corresponding to a liquid-to-surface-area ratio of $10\ \mathrm{cm}^3/\mathrm{cm}^2$. At the end of the leaching interval, the leachate pH and conductivity of the leachate were measured and the sample was then immersed in fresh leachant. The remaining leachate volume was filtered under vacuum through a $0.45\ \mu\mathrm{m}$ polypropylene membrane.

Analytical samples from each leaching interval were collected and preserved for subsequent chemical analysis.

2.4. Storage intervals

During non-leaching intervals, samples of the S/S MeO material were stored in desiccation chambers under positive pressure. Pure nitrogen gas was passed through the storage chamber to minimize the reaction of the matrix with atmospheric carbon dioxide or oxygen. At the beginning of a storage interval, each chamber atmosphere was purged for approximately 1 h at a high flow rate (300 ml/min). For the duration of the storage interval, the flow of incoming gas was reduced to 20–50 ml/min. The CO_2 content of each chamber was monitored periodically by injecting of a vapor sample of storage atmosphere onto a HP 6890 gas chromatograph (Hewlett-Packard, Wilmington, DE) equipped with a TCD detector.

Reservoirs of silica oxide desiccant and deionized water were used to control RH for the target levels of 0 and 100% RH, respectively. An intermediate humidity level was maintained by storing samples over a saturated solution of K_2CO_3 and deionized water. The activity of water vapor over this hygroscopic salt solution is modified to yield a RH of approximately 44% [27]. The RH in each storage chamber was monitored using dedicated hygrometers and recorded periodically during the storage intervals.

2.5. Analytical methods

Leachate samples were analyzed for concentrations of structural matrix components (Ca, OH), highly soluble species (Na, K, Cl) and pH-dependent species (As, Cd, Cu, Pb, Zn). 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 Corporation, Sunnyvale, CA). Voltimetric probes were used to measure leachate pH and conductivity on an Accumet 20 meter (Fisher Scientific, Springfield, NJ).

3. Results and discussion

The effects of intermittent wetting and storage environment RH on the release of COPCs were evaluated by comparing cumulative release and interval flux between samples representing the three intermittent wetting cases (0, 50 and 100% RH) and the continuous leaching case. For interpretation of cumulative release, it was necessary to normalize the comparison to the cumulative leaching time rather than the overall assessment time in order to obtain an equivalent comparison to the continuous leaching case. Thus, the duration of the storage intervals in the intermittent wetting Schedule 1 were subtracted from the elapsed time. For these cumulative release comparisons, data was presented as the average of duplicates with error bar symbols used to indicate the spread in measurement. In the case of COPC flux, however, interpretation could be based on the total assessment time including the duration of the storage interval.

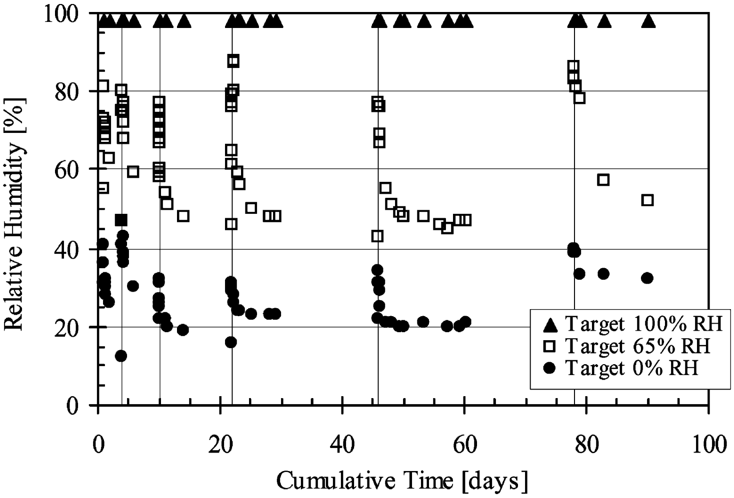

Fig. 1. Relative humidity of the nitrogen storage environments for intermittently wetted S/S MeO samples shown as a function of cumulative storage time.

3.1. Storage interval conditions

A record of the RH in each storage chamber for each of six cycles is presented in Fig. 1. Although the values of RH in the storage chambers at the low and mid-range levels of RH were targeted to be 0 and 50% RH, the figure shows that these levels could not be easily achieved or maintained using desiccants and saturated salt solutions. In both of these cases, the humidity of the atmosphere in the chamber increased sharply, to 50% RH (low-level case) and 90% RH (mid-level case), at the beginning of each storage period due to the release of moisture from the saturated samples. As the samples dried, the RH in the storage chamber decreased and stabilized at approximately 23 and 48% RH for the low and mid-range humidity levels, respectively. For the target level of 100% RH, the upper limit of the digital hygrometer (98% RH) was maintained throughout each storage interval. Due to the disparity between target and achieved RH, the three levels of RH will be referred to by the respective experimental values (i.e. “23”, “48” and “98% RH”) in the following discussion.

3.2. Effect of storage intervals on sample moisture content

The moisture content of the S/S MeO matrix after each leaching and storage interval was estimated from the change in mass over the leaching or drying phase of each cycle. This estimate was made under the assumption that the total mass of the constituents released during the leaching intervals did not significantly alter the dry sample mass. The change in moisture content over each storage interval was then determined by subtracting the moisture content after storage from that before the storage. Fig. 2 presents the average loss in moisture content as a function of storage environment RH in each of the six storage intervals.

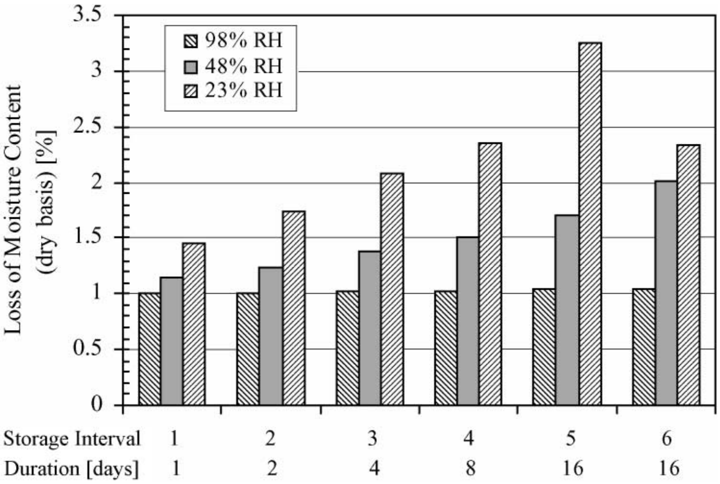

Fig. 2. Estimated loss in S/S MeO moisture content over each storage interval presented as a function of storage environment relative humidity. The duration of each storage interval also is indicated.

The reduction in moisture content with storage was dependent on the duration of the storage interval for 23 and 48% RH. However, the reduction in moisture content in the 98% RH case was constant at approximately 1% (dry basis) indicating that some moisture loss had occurred. This loss was most likely due to the removal of surface water from saturated samples during the storage environment purge. Under this assumption and considering the consistency of the data, it is not likely that significant pore drying occurred in the 98% RH case. In general, the moisture content data was consistent with a moisture transport mechanism dominated by the diffusion of water vapor with a boundary condition represented by the RH of the ambient environment. Further investigation and modeling of the moisture transport phenomena for this system are ongoing.

3.3. *Effect of intermittent wetting on leachate pH and conductivity*

Values of leachate pH for intermittent wetting samples of the S/S MeO matrix at each level of RH (23, 48 and 98% RH) are shown in Fig. 3a and 3b in comparison to leachate pH data for the continuous leaching case. In general, the pH of the leachate collected during the six leaching cycles varied from 11.0 to 11.8 with the value controlled by the release of hydroxides over the duration of the leaching period. The leachate pH was greater in the first leaching interval of each cycle than in the second interval and increased for the remainder of the leaching cycle. The first leachate of each intermittent wetting case was generally higher than that of the corresponding leachate in the continuous leaching case. This behavior suggested that some pH gradient relaxation occurred within the pore water over the storage period, resulting in an increase in hydroxide release, seen as elevated leachate pH, in the first leachate of the subsequent leaching cycle. Comparison between leachate pH values from samples stored at 23, 48 and 98% RH showed little influence of storage RH.

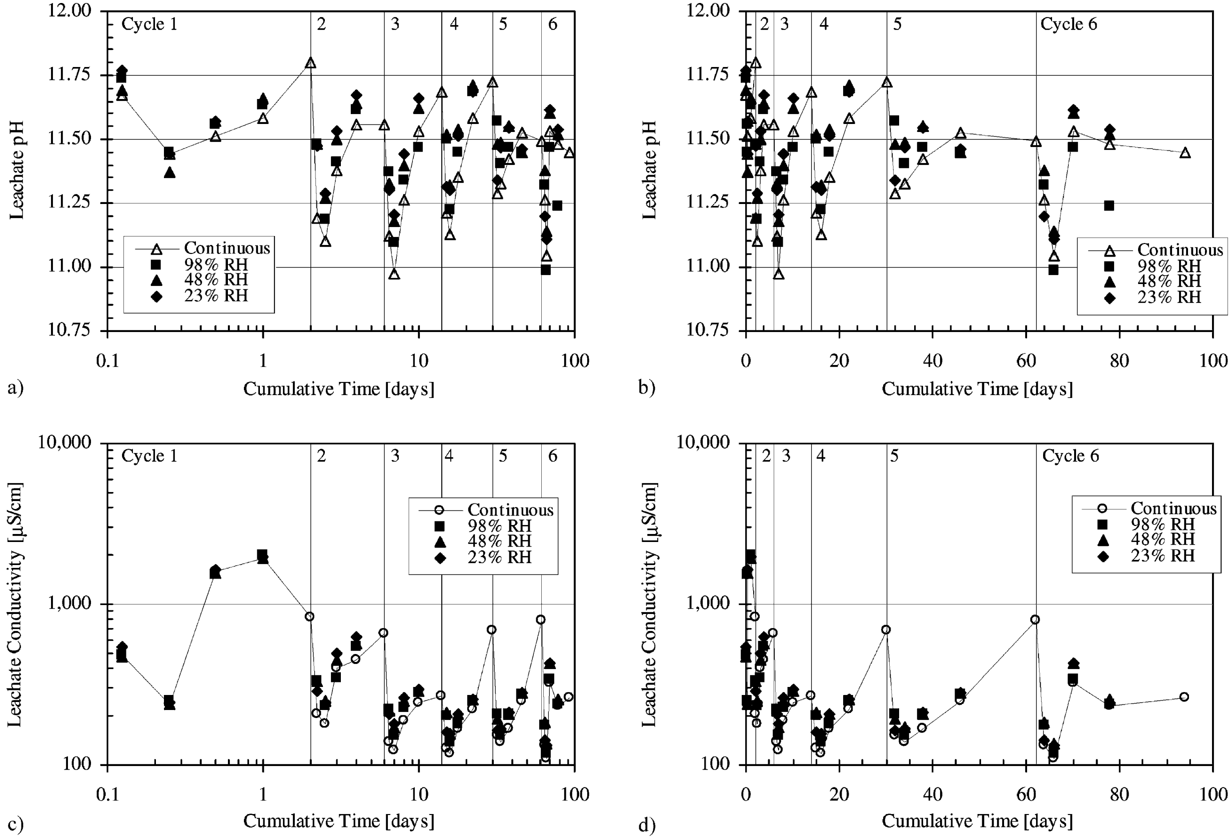

Fig. 3. Physical characterization of leachates from intermittently wetted S/S MeO samples compared to continuously leached samples shown as a function of time (log(s) and (s)): (a) and (b) leachate pH (–); (c) and (d) leachate conductivity (μS/cm).

Leachate conductivity values for each of the three intermittent wetting cases and the continuous leaching case are shown in Fig. 3c and 3d. The conductivity during the first leaching interval of each cycle (e.g. 2000 μS/cm for cycle 1) was much greater than all subsequent intervals (200–500 μS/cm) regardless of the RH of the storage environment or whether the sample was exposed to intermittent wetting or continuous leaching. This observation supports the concept of gradient relaxation in that the first leaching interval following storage behaved as wash-off period until a concentration gradient of highly soluble species was formed.

3.4. Effect of intermittent wetting on the release of structural components

Calcium and hydroxide ions were considered 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 [28]. The release and eventual depletion of calcium hydroxide is largely responsible for the chemical properties of the pore solution and the efficacy of the S/S treatment process. The flux and cumulative release of hydroxide ion and calcium from the S/S MeO matrix obtained for the three intermittent wetting conditions (23, 48 and 98% RH) are compared to flux and release from the continuous leaching case in Figs. 4 and 5, respectively. In all cases, hydroxide ion release was derived from leachate pH data.

3.4.1. Leaching behavior of hydroxide

Fig. 4a indicates that no significant influence of intermittent wetting or storage humidity level on the release of hydroxide was observed on the basis of cumulative release. However, when the comparison was based on hydroxide flux, as shown in Fig. 4b, a slight influence of the duration of the storage intervals was seen. In the intermittent wetting cases, the flux of hydroxide during the first leaching interval of each cycle was much greater than in subsequent intervals. The flux of hydroxide 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 would be an expected result of continued mass transport in water-filled pores during the storage intervals when no continuous liquid phase is present outside of the matrix.

In addition, it was observed that the hydroxide flux during the first leaching interval was greatest for samples stored at the highest level of RH during storage. Samples stored at 23 or 48% RH showed correspondingly lower hydroxide ion flux. These observations support the occurrence of gradient relaxation because the least amount of drying and, consequently, the greatest degree of continued mass transport would be expected in the 98% RH case. Thus, relaxation of the hydroxide gradient over the storage intervals appeared to be logically related to the extent of drying in the pore structure.

3.4.2. Leaching behavior of calcium

Comparison of the cumulative release of calcium between intermittent wetting and continuous leaching cases, showed no significant effect of cyclic leaching and non-leaching (Fig. 5a). In addition, no significant effect of RH could be observed on either the cumulative release or the flux of calcium amongst the intermittent wetting cases. For both intermittent

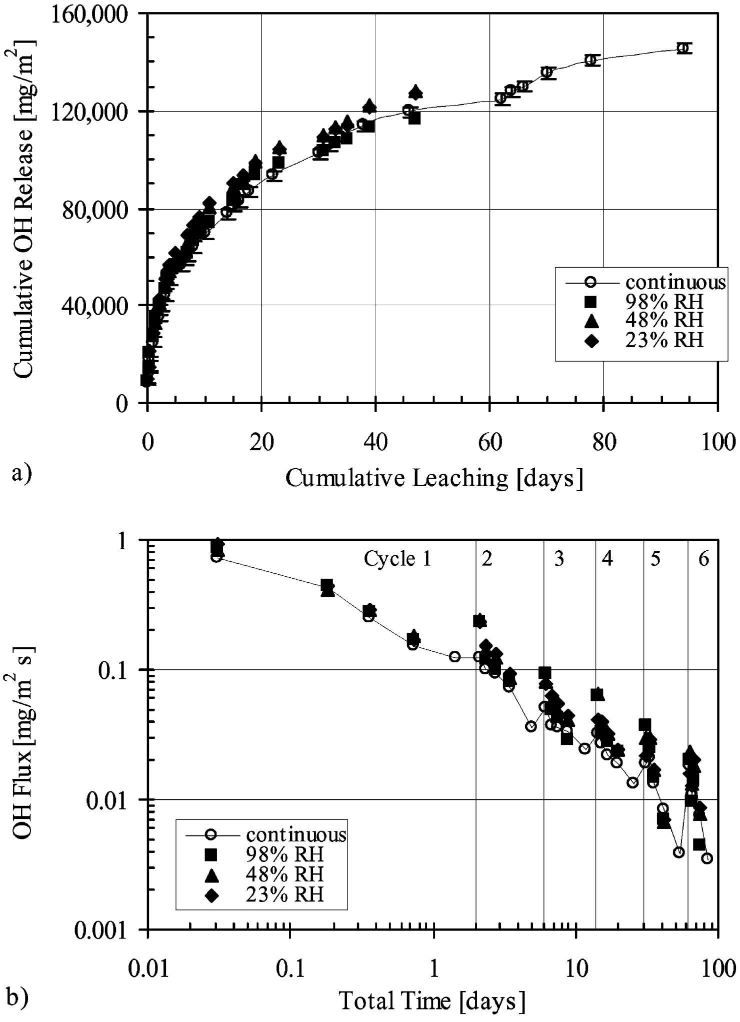

Fig. 4. Release of hydroxide ion determined from leachate pH (average of duplicates) for intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2); (b) flux (mg/m^{2}s).

wetting and continuous leaching cases, 2.0% of the total calcium content (217,000 mg/kg Ca) was released after 47 days of total leaching time.

The flux of calcium under continuous leaching conditions, as shown in Fig. 5b, was greater over the shorter intervals of each cycle than over longer intervals. The flux was higher despite the fact that the concentrations of calcium in the leachates collected from the shorter leaching intervals were lower than the concentrations of calcium in the long leaching intervals of the preceding cycle. Within each leaching cycle, the resultant effect was that calcium flux decreased with a decrease in the duration of the leaching interval.

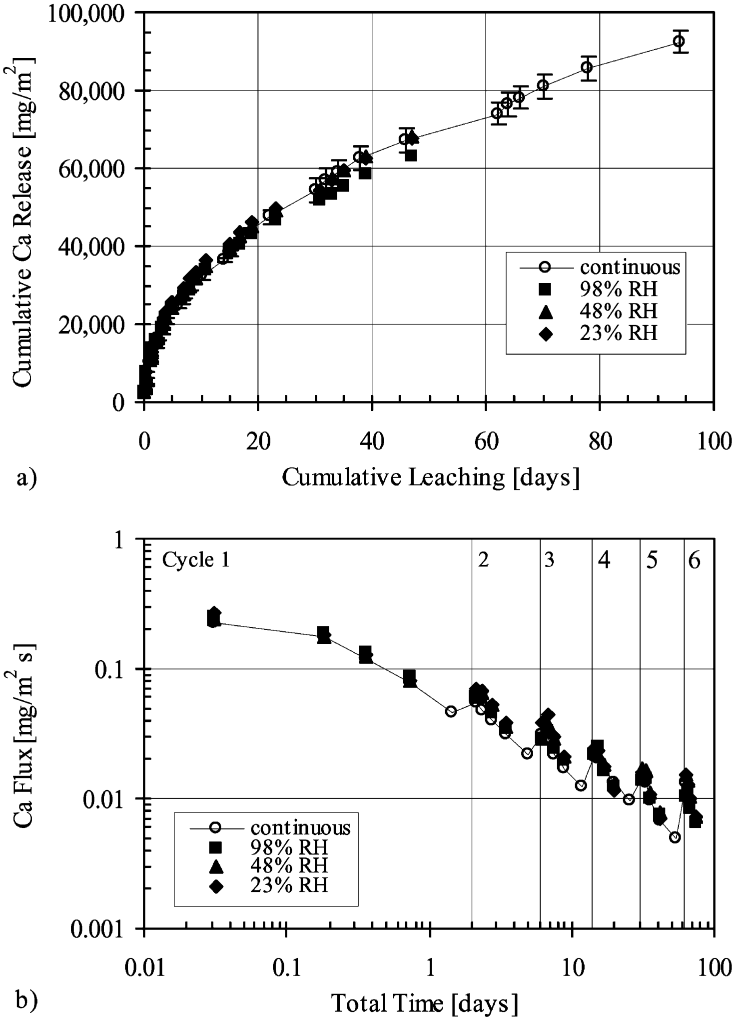

Fig. 5. Release of calcium (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2); (b) flux (mg/m^{2}s).

This flux behavior might indicate that the infinite bath assumption was not valid for this system in the case of continuous leaching of calcium and that the driving force of calcium release was not constant with leaching time. In this context, the average driving force for calcium release over the longer leaching intervals was less than that for shorter intervals, resulting in a lower average flux over longer leaching intervals.

3.4.3. Leaching of structural components—summary

Based on total leaching time, the observed release of structural components from the S/S MeO matrix was a strong function neither of intermittent wetting nor of the RH of the storage environment. Only a minor increase in hydroxide ion flux from intermittently wetted materials over that of continuously leached samples was observed when the comparison was based on release flux. This increase corresponds to the previously noted increase in leachate pH at the beginning of the leaching phase of each cycle. However, when the cumulative release of the S/S MeO matrix structural components is compared over the entire assessment interval, the effect of the non-leaching period itself will be more significant to the total amount of constituent released than the effects of gradient relaxation during periods of non-leaching under intermittent wetting conditions.

3.5. Effect of intermittent wetting on the release of highly soluble species

Sodium, potassium and chloride ions are common cement-based waste constituents, which exhibit a high-level of solubility that is relatively independent of pH. The release of these highly soluble species is not influenced by the pH gradients within the pore water. Typically, the semi-infinite diffusion model is used to model the release of these constituents, however, the assumptions of this model are considered valid as long as no more than 20% of the leachable concentration has been released [6,29]. If greater than 20% of the total concentration is released, depletion occurs and the release would be no longer proportional to $t^{1/2}$ [30]. For the S/S MeO matrix, the flux and cumulative release of the highly soluble species for the three intermittent wetting conditions (23, 48 and 98% RH) are compared as a function of time to flux and release of these species in the continuous leaching case in Fig. 6 through Fig. 8.

3.5.1. Leaching behavior of sodium

In the case of continuous leaching, cumulative sodium release appeared to be initially diffusion-controlled with depletion occurring in later intervals (Fig. 6a). A diffusion-controlled release mechanism was supported by the initially linearity of the flux curve, shown in Fig. 6b, with the expected slope of $-1/2$ typical of a diffusion-controlled process. Depletion of sodium from the matrix in later intervals is most clearly seen by a flattening of the cumulative release in cycles 5 and 6. However, since more than 26% of the total sodium content was released after the first leaching cycle of Schedule 0, depletion most likely occurred after only 2 days of continuous leaching. The limit for cumulative release after 94 days of leaching time was approximately 70% of the total sodium (1,610 mg/kg Na) in the continuous leaching case. This value represents 99% of the sodium added to the treatment recipe (1141 mg/kg Na).

The cumulative release curve (Fig. 6a) indicated that, based on total leaching time, samples exposed to intermittent wetting released more sodium than did the continuous leaching samples. After 47 days of total leaching time, the fraction of total sodium released was approximately 70% for the three intermittent wetting cases and 63% for continuous leaching samples, representing respectively 99 and 89% of the sodium added to the matrix. No significant effect of storage RH was observed for the cumulative release of sodium. When the same comparison was based on the sodium flux, however, a greater flux in the first interval of each leaching phase was consistently recorded for samples intermittently stored at 98% RH. The difference in the release flux became more defined in cycles 5 and 6 of Schedule 1, where the duration of the storage intervals was increased. Thus, the flux

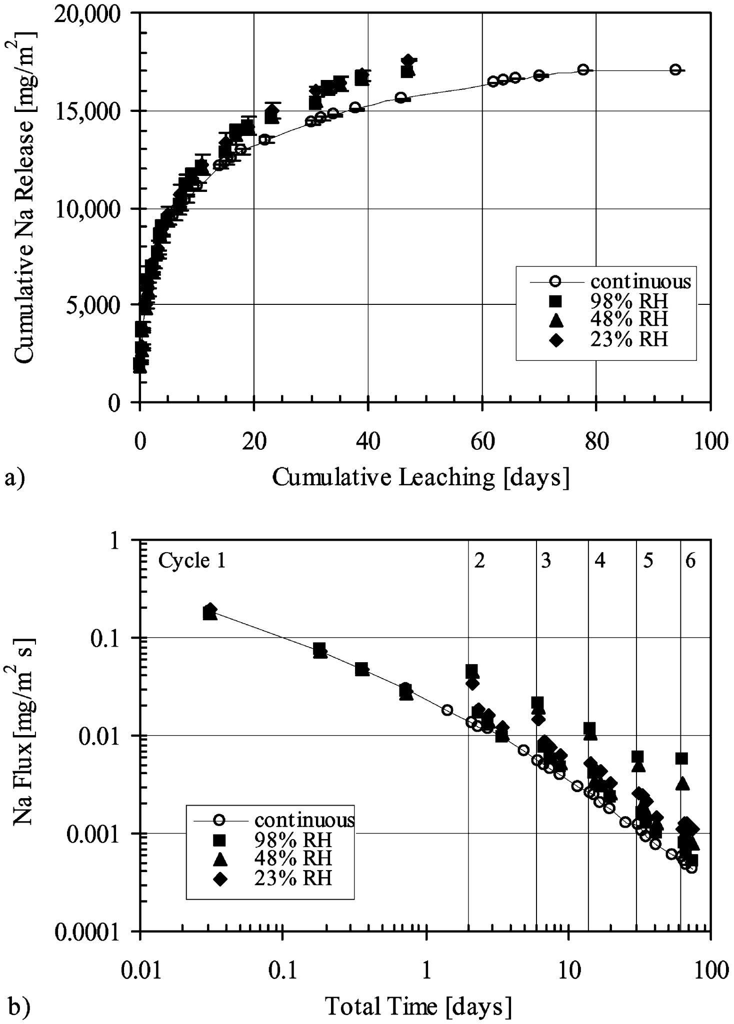

Fig. 6. Release of sodium (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2); (b) flux (mg/m^{2}s).

of sodium was observed to be dependent on the duration of the drying interval and, consequently, the extent of drying within the matrix. This implies that relaxation of the sodium gradient resulted in a redistribution of sodium concentration in the pore water of the S/S MeO matrix during the storage interval.

3.5.2. Leaching behavior of potassium

The cumulative release of potassium from continuous leaching and intermittently wetted samples is presented in Fig. 7a. In a similar manner to the release of sodium, the

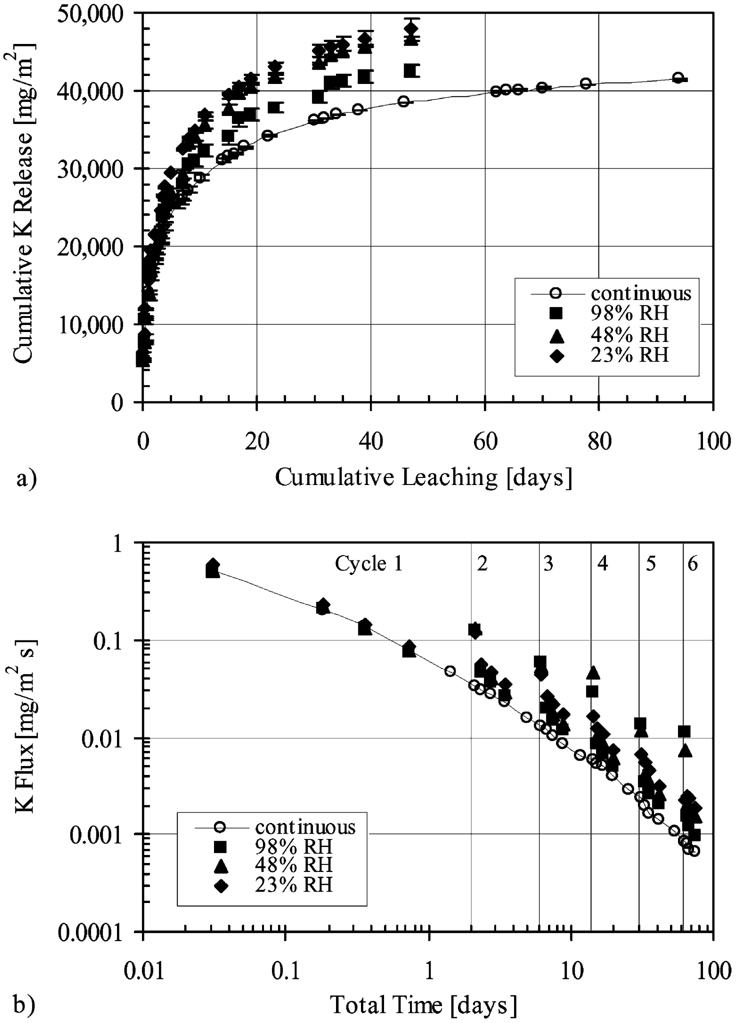

Fig. 7. Release of potassium (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2); (b) flux (mg/m^{2}s).

cumulative release of potassium from the continuous leaching material appeared to be initially diffusion-controlled with depletion in the later intervals. Depletion seems to begin during the first leaching cycle where 34% of the total potassium content was released after 2 days of continuous leaching. The limit for cumulative potassium release after 94 days of continuous leaching was approximately 80% of the total potassium content (3,400 mg/kg K). No potassium was specifically added to the recipe during preparation of the matrix.

Fig. 7b showed a pattern of potassium flux similar to that of sodium with increased flux during the first interval of each leaching cycle. Unlike sodium, however, the effect of storage RH on the flux of potassium was not consistent amongst the leaching cycles. Whereas the sodium flux showed a clear hierarchy of intermittent wetting cases (98% RH $>$ 48% RH $>$ 23% RH) for all leaching cycles, the flux of potassium showed this hierarchy only in the intermittent wetting cycles 5 and 6. Samples stored at lower RH underwent a higher degree of drying and tended to have a higher cumulative release of potassium. Thus, in cases where the matrix was expected to dry during the storage interval, potassium could have been precipitated from the liquid boundary layer onto the pore walls. These potassium precipitates were easily dissolved during rewetting of the matrix providing a wash-off effect observed as an initial increase in potassium release in each leaching phase. Potential changes in speciation due to precipitation could explain the different levels and degrees of separation in the cumulative release after 47 days of total leaching time.

3.5.3. Leaching behavior of chloride

Although the cumulative release curve for chloride shown in Fig. 8a indicated depletion had occurred in the continuous leaching case, only 17% of the total elemental chloride (1,880 mg/kg Cl) was released after 94 days. This value represents 18% of the chloride added into the recipe. From these observations, it was assumed that only a small fraction of the total chloride content (approximately 20%) was available for leaching. Under this assumption, the release of chloride from continuously leached samples appeared to be diffusion-controlled with depletion occurring during later leaching intervals. The cumulative release after 94 days of continuous leaching could be considered to comprise approximately 85% of the assumed leachable content.

The cumulative release of chloride from samples exposed to intermittent wetting showed that 20, 18 and 16% of the total chloride was released after 47 days of total leaching time from samples stored under 23, 48 and 98% RH, respectively. After the same amount of leaching time, 15% of total chloride was released in the continuous leaching case. Thus, the release of chloride from the S/S MeO matrix was not significantly influenced by relaxation of the chloride gradient during the storage interval as shown by the similarity between cumulative chloride release from the intermittent wetting case at 98% RH and the continuous leaching case. Conversely, the elevated cumulative release observed for the intermittent wetting cases at 48 and 23% RH indicated that the release of chloride was affected by precipitation of chloride species in the pore structure.

3.5.4. Leaching behavior of highly soluble species—summary

Gradient relaxation resulted in an increased release of sodium and potassium from intermittent wetting samples over the continuous leaching case. Within the intermittent wetting cases, samples exposed to storage at 98% RH were more significantly influenced by gradient relaxation than samples exposed to lower levels of storage environment RH. The increase in release due to gradient relaxation was dependent on the duration of the storage interval indicating that gradients may not have relaxed to equilibrium over shorter storage intervals. The release of chloride was influenced by solubilization of precipitates formed during the drying phase. A minor effect of precipitation also could be seen on the release of potassium indicating that there may be a balance between these mechanisms in the drying matrix. Since precipitation was associated with the drying process, the effect of

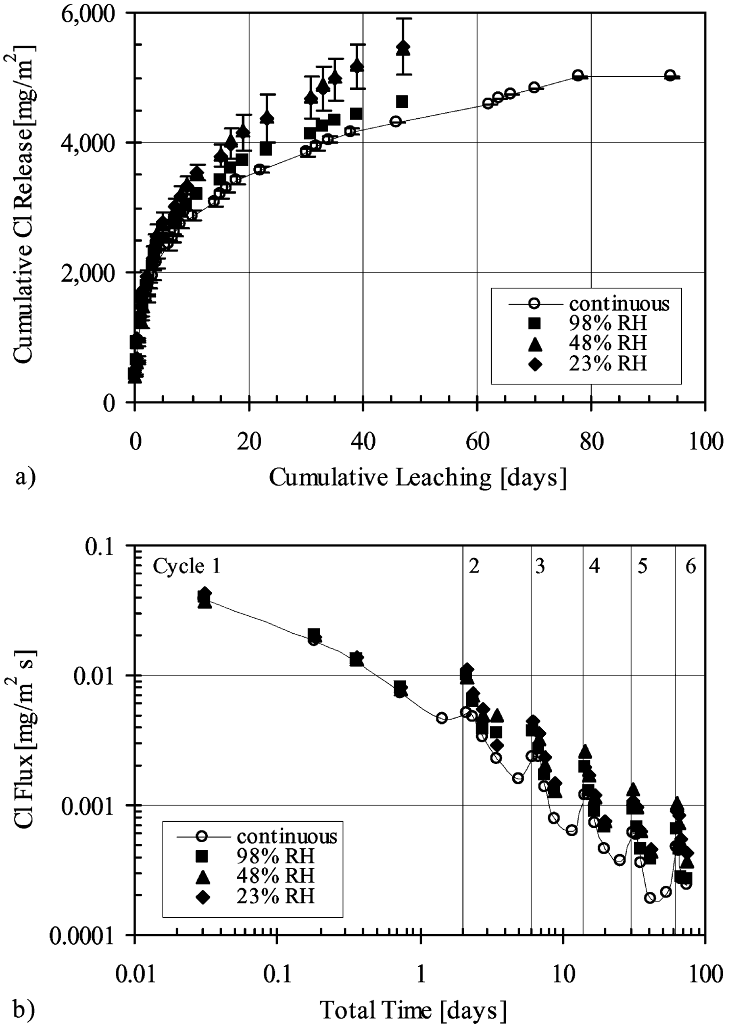

Fig. 8. Release of chloride (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2); (b) flux (mg/m^{2}s).

precipitation was observed to be stronger in intermittent wetting cases with storage at 23 and 48% RH.

In general, the effect of intermittent wetting on the S/S MeO matrix was to promote alteration of the matrix chemistry and an increase in the cumulative release of highly soluble species when the comparison was based on total leaching time. Due to the delay in leaching from the matrix caused by the storage interval, the overall effect of intermittent wetting, however, would be a lower cumulative release of highly soluble species from the cementitious material than from a continuously saturated matrix.

3.6. Effect of intermittent wetting on the release of pH-dependent COPCs

The release of many regulated inorganic pollutants (e.g. heavy metals) from S/S treated wastes is not controlled by diffusion alone. The aqueous solubility of these species is often a strong function of pH. Thus, diffusional mass transport processes are coupled with equilibrium phenomena at the solid–liquid interface. In the pore water of the cement material, local aqueous concentrations are dependent on the pH of the pore water and relaxation of pH gradients would be expected to significantly influence the species release.

For the S/S MeO matrix, the cumulative release and flux curves for arsenic, cadmium and lead for both the continuous leaching and intermittent wetting intermittent wetting cases at three levels of RH (23, 48 and 98% RH) are presented in Fig. 9 through Fig. 11. Copper and zinc concentrations measured in the leachates of both continuously leached and intermittently wetted S/S MeO were near or below the analytical detection limits of 0.07 μg/l Cu and 0.008 μg/l Zn. Therefore, confident interpretation of the data for copper and zinc was not possible.

3.6.1. Leaching behavior of arsenic

The arsenic flux for the continuous leaching case, shown in Fig. 9b, was similar in behavior to the fluxes of hydroxide and calcium. The flux of arsenic under continuous leaching conditions was dependent on the duration of the leaching interval and resulted in a greater flux over the shorter intervals at the beginning of each leaching cycle. This was followed by a decreasing arsenic flux over subsequent longer leaching intervals. In general, the flux of arsenic from the S/S MeO matrix was consistent with arsenic solubility in the range of measured leachate pH values, which decreases with increasing pH between 10 and 12. Therefore, both the local solubility of arsenic and arsenic release are dependent on the flux of hydroxide shown in Fig. 4b.

Intermittent wetting of the S/S MeO material tended to lower the observed cumulative release of arsenic. Under intermittent wetting conditions, the release of arsenic was dependent on the RH of the storage environment with the lowest arsenic release obtained for samples stored at 98% RH. After 47 days of total leaching, the release of arsenic from intermittent wetting samples stored at 23% RH was very similar to the arsenic release under continuous leaching conditions at approximately 30 mg/kg. This value is approximately 1% of the total arsenic content of the S/S MeO matrix (3050 mg/kg As). After the same duration of leaching, 25 and 22 mg/kg of arsenic were release from intermittently wetted samples with storage conducted at 48 and 98% RH, respectively.

In a similar manner as the continuous leaching case, arsenic flux in intermittent wetting cases was consistent with the solubility of arsenic as a function of leachate pH. This implied that the local solubility and consequent release of arsenic was dependent on the degree of relaxation in the pH gradient during storage. For example, the greatest degree of pH gradient relaxation over the storage interval was observed for the intermittent wetting case with storage at 98% RH. Due to the behavior of the arsenic solubility in this range of leachate pH values, a low arsenic flux was noted in the first leachate of each cycle for samples stored at 98% RH. In the cases of intermittent wetting with storage at 23 and 48% RH, the flux of arsenic during the first leaching interval of each cycle was significantly greater than for the 98% RH case because the relaxation of the pH gradient was minimized by drying of the pore water.

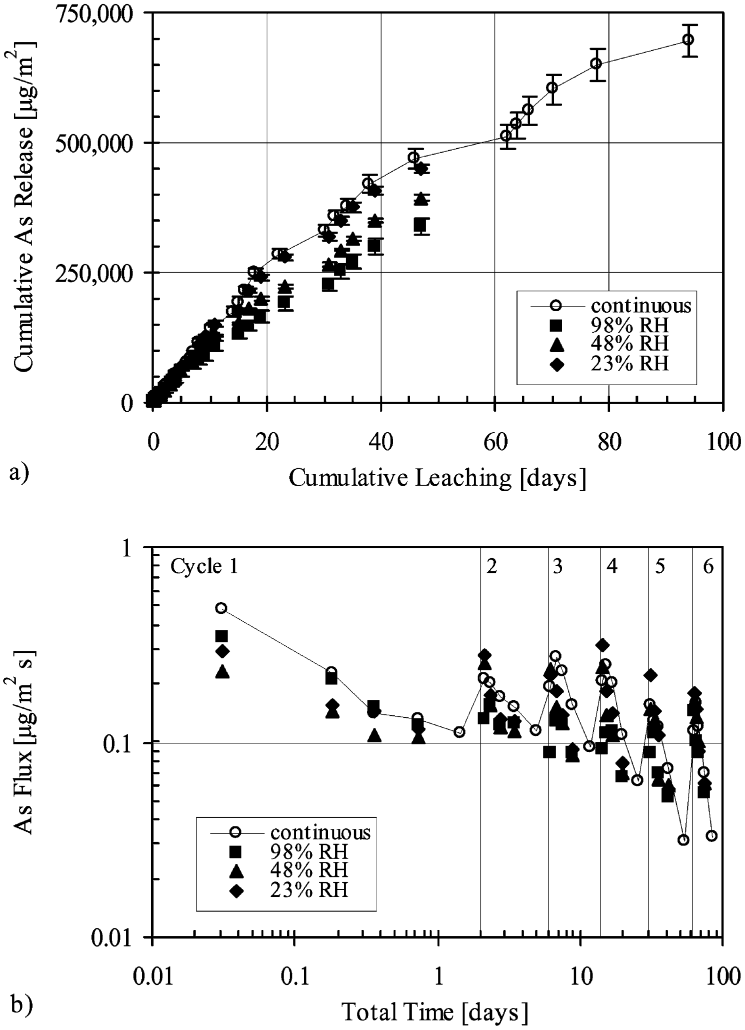

Fig. 9. Release of arsenic (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2); (b) flux (mg/m^{2}s).

3.6.2. Leaching behavior of cadmium

For the case of continuous leaching of cadmium, a decrease in the duration of the leaching interval resulted in significantly greater cadmium flux at the beginning of each leaching cycle (Fig. 10b). As each cycle continued and the leaching interval increased, the flux decreased during subsequent longer leaching intervals in a manner similar to the behaviors of hydroxide and calcium fluxes. Cadmium flux from continuous leaching samples followed the release flux of hydroxide shown in Fig. 4b and was consistent with the general behavior of cadmium solubility in this range of leachate pH values where solubility decreases with

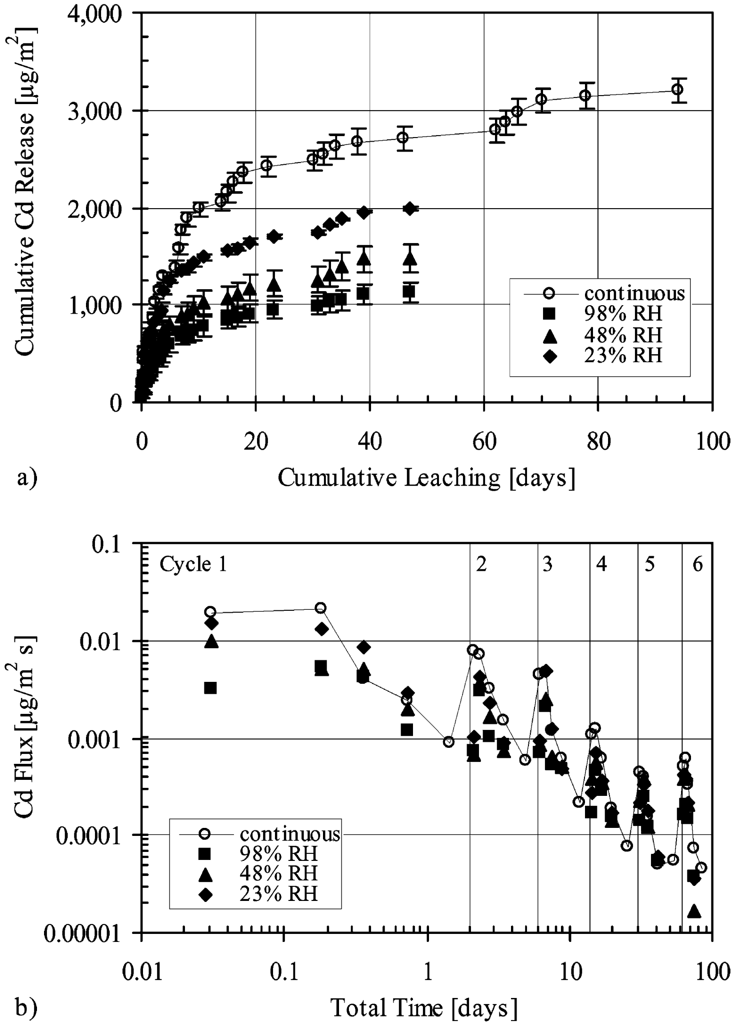

Fig. 10. Release of cadmium (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2); (b) flux (mg/m^{2}s).

increasing pH. Thus, the observed lower pH in the leachates collected for the short leaching intervals (Fig. 10a) resulted in increased solubility of cadmium.

In general, intermittent wetting resulted in a significantly lower release of cadmium. The effect was more pronounced for intermittent wetting cases stored at higher levels of RH and less evident for lower RH cases. After 47 days of total leaching time, approximately 175 μg/kg of cadmium was released from the continuous leaching samples compared to 130, 96 and 74 μg/kg of cadmium from intermittent wetting samples stored at 23, 48 and 98% RH, respectively. These releases represent less than 0.005% of the total cadmium in the matrix (3,100 mg/kg Cd). Although the highest flux for other COPCs under intermittent wetting conditions was observed during the first leaching interval of each cycle, cadmium flux was greatest during the second leaching interval and decreased in subsequent intervals within each leaching cycle. However, this behavior was still consistent with cadmium solubility as a function of leachate pH since the second leachate pH of each cycle is lower than the other leachates, resulting in a higher cadmium release.

3.6.3. Leaching behavior of lead

Under continuous leaching conditions, the coupled dissolution–diffusion model [8] indicated that the main phenomenon controlling mass transfer of lead from the S/S MeO matrix over the time scale of the laboratory testing ($\sim$3 months) was dissolution of precipitated lead at the interface between the cement matrix and the leachant. This result was mainly a result of the pH gradient formed between the dissolution front of $Ca(OH)_2$ (s) and the matrix surface and was consistent with the primary release mechanisms found for a similar synthetic material [8] and for S/S treated soil [2]. The dissolution release mechanism was also indicated by the lower flux over the shorter intervals of each leaching cycle as shown by the lead flux curve in Fig. 11b. The flux of lead was dependent on the duration of the leaching interval and the pH of the pore water at the solid-leachate interface.

The curve of lead cumulative release (Fig. 11a) from intermittent wetting samples indicated that no significant effect of intermittent wetting for samples stored at 23 and 48% RH in comparison to the continuous leaching case. For example, after 47 days of total leaching time, approximately 2,700 mg/kg was released from continuous leaching samples as well as intermittent wetting samples stored at 23 and 48% RH. This release value represents approximately 0.1% of the total lead (2,700 mg/kg). When leaching was interspersed with storage at 98% RH, however, a significantly lower cumulative release (2,300 μg/kg of lead), representing less than 0.09% of the total lead in the S/S MeO material, was observed.

These results indicated that the effect of intermittent wetting on lead release was consistent with lead solubility as a function of pH controlled by relaxation of the pH gradient. In the range of leachate pH values shown in Fig. 3a, the solubility of lead increases with increasing pH and relaxation of the pH gradient during storage would result in an increase in local lead solubility near the surface. Gradient relaxation would also promote dissolution of precipitated lead described by the coupled dissolution–diffusion model as the controlling phase for lead transport. Thus, during subsequent leaching, the flux of lead would be diminished due to a reduction in the source of lead at the bulk solid–liquid interface. In this context, the lowest cumulative lead release was observed for the intermittent wetting case with storage at 98% RH because of the high degree of pH gradient relaxation.

3.6.4. Leaching behavior of pH-dependent COPCs—summary

When the comparison was based on total leaching time, the cumulative release of pH-dependent species under the influence of intermittent wetting conditions was lower than cumulative release in the continuous leaching case. The effect of RH of the storage environment on the release and flux of pH-dependent COPC was consistent with the behavior of COPC solubility with leachate pH and relaxation of the pH gradient over the storage interval. The release of pH-dependent COPCs from Portland cement-based materials highlights the necessity to understand both the mechanisms of mass transfer as well as the equilibrium between the solid and liquid phases in order to estimate release of these species. Coupling

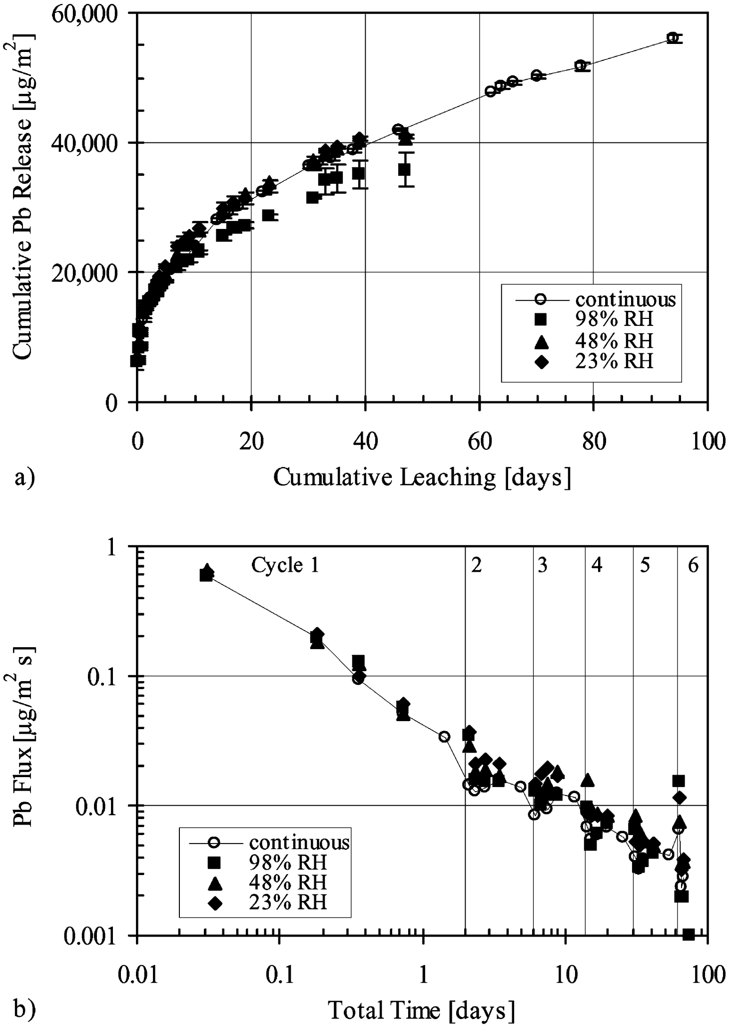

Fig. 11. Release of lead (average of duplicates) from intermittently wetted and continuously leached samples of S/S MeO: (a) cumulative release (mg/m^2); (b) flux (mg/m^{2}s).

of transport and chemistry is especially important when gradient relaxation or precipitation may be expected to alter the leaching properties of the matrix under intermittent wetting conditions.

3.7. Estimating intermittent wetting release using the current assessment approach

The current approach for estimating COPC release under intermittent wetting conditions is to project saturated release over the assessment interval *t* (s) and then to correct this estimate by application of a wetting frequency term $F_{\mathrm{w/d}}$ (−), which is related to the time that the matrix is wetted $t_{\mathrm{w/d}}$ (s) within an interval. Thus, a predicted release under intermittent wetting conditions $M_{\mathrm{a,w/d}}$ (mg/m^2) may be determined correcting saturated release M_{a} (mg/m^2) to reflect only that portion of the total assessment time that the matrix is saturated [31].

$$M_{\mathrm{a,w/d}} = M_{\mathrm{a}} F_{\mathrm{w/d}} = M_{\mathrm{a}} \left(\frac{t}{t_{\mathrm{w/d}}} \right)^{-1/2} \tag{1}$$

This assessment approach was applied to cumulative COPC release from the continuous leaching case of the S/S MeO matrix in order to obtain release predictions under intermittent wetting conditions. The wetting frequency term over a 94 day assessment interval was determined from the intermittent wetting Schedule 1 presented in Table 2. Estimates of COPC cumulative release under intermittent wetting conditions are shown in Table 3 in comparison to measured cumulative release data for the continuous leaching and intermittent

Table 3
Cumulative release of COPCs over an assessment interval of 94 days[a]

COPC	Continuous leaching release, Schedule 0 (mg/m^2)	Estimated intermittent wetting release (mg/m^2)	Storage relative humidity (%)	Intermittent wetting release, Schedule 1 (mg/m^2)	Difference in intermittent wetting release (%)*
Hydroxide	146000	103000	98	116000	−12
			48	128000	−19
			23	127000	−19
Calcium	92500	65400	98	63000	4
			48	68200	−4
			23	68000	−3
Sodium	17000	12000	98	17000	−29
			48	17100	−30
			23	17600	−31
Potassium	41400	29300	98	42500	−31
			48	46800	−37
			23	48000	−39
Chloride	5000	3530	98	4610	−23
			48	5450	−35
			23	5470	−35
Arsenic	700	490	98	338	45
			48	390	25
			23	450	9
Cadmium	3.2	2.3	98	1.1	101
			48	1.5	53
			23	2.0	14
Lead	56	40	98	36	11
			48	41	−3
			23	41	−3

[a] Comparison is shown for continuous release under saturated conditions (Schedule 0), estimated intermittent wetting release, and actual intermittent wetting release (Schedule 1) for three values of relative humidity.

* Calculated on the basis of measured release with a difference less than 0% representing under-estimation $\mathrm{Diff_{IW}} = (\text{estimated} - \text{measured})/\text{measured} \times 100\%$.

wetting cases at three levels of RH. The difference between estimated and measured release values was normalized to measure cumulative release so that underestimation was indicated by a difference value less that 0%. This comparison is used only to illustrate that misuse of the current assessment approach for intermittent wetting scenarios may result in erroneous estimates of contaminant release.

In general, the estimated release of many constituents differed from measured release by greater than 20% over a relatively short interval, implying that the current approach cannot accurately estimate release due to intermittent wetting over much longer periods (e.g. years or decades). This approach was most appropriate for estimating the release of structural components of the matrix (Ca, OH) because the assumption of diffusion-controlled leaching without significant matrix alteration is most valid for these species. Conversely, the release of highly soluble species (Na, K, Cl) was underestimated by greater than 30% because correction of the saturated release using the current approach does not take into account relaxation of the concentration gradients or precipitation of species upon matrix drying. In addition, the use of a simple wetting frequency term does not allow for the incorporation of the effects of field conditions (i.e. RH) during periods of storage on overall COPC release. In the present study, the RH of the storage environment was found to have a significant influence on the release of many COPCs through control of the drying process and the distribution of water-filled pores.

When COPC release cannot be adequately described by diffusion alone, the diffusional model correction really cannot be used to estimate release because it is not appropriate to describe release under saturated conditions. In this context, any similarity between estimate and actual release for arsenic, cadmium and lead was coincidental since the release for these pH-dependent species was partially controlled the pH of the pore water. Depending on the storage RH, misuse of the current approach applied to the intermittent release of pH-dependent species could result in overestimations of up to 45, 100 and 11% for arsenic, cadmium and lead, respectively. Because of the high costs associated with waste management and treatment, gross overestimation of the leachability of regulated contaminants must be minimized and an approach must be developed to provide more accurate estimate constituent release under realistic field scenarios such as intermittent wetting.

4. Conclusions

Typically, the release of inorganic contaminants from monolithic materials, such as Portland cement treated wastes, is evaluated by tank leaching under continuously saturated conditions. Currently, most models used to evaluate laboratory leaching data and project long-term field performance assume a continuously saturated matrix and only relatively minor changes in leaching chemistry. In many field scenarios, however, porous materials cannot be assumed continuously wetted but will experience cyclic wetting and drying under varied environmental conditions including variable RH or changes in carbon dioxide concentration. Within this framework, the effect of intermittent wetting interspersed with storage in an inert atmosphere on the cumulative release and flux of constituents from a synthetic Portland cement-based material was evaluated and compared to the case of continuous leaching.

When the comparison was based on total leaching time, the difference in cumulative release between continuously leaching and intermittent wetting cases was attributed to chemical and physical alteration of the matrix during intermittent storage. These changes were seen to occur through a balance between relaxation of concentration or pH gradients in water-filled pores and precipitation of species in dried pores of the matrix. Gradient relaxation resulted from continued mass transport within water-filled pores and influenced the release of species differently depending on the nature of the species. For example, relaxation of the concentration gradients for highly soluble species tended to flatten the concentration profile that had been established during the previous the leaching phase, resulting in a “wash-off” effect upon subsequent leaching. Conversely, the reduction in lead release from samples stored at 98% RH was controlled by relaxation of the pH gradient and resulted in dissolution of solid phase precipitates that controlled the rate of lead release during leaching.

The RH of the storage environment during periods of non-leaching was seen to influence the degree of drying and its subsequent influence on precipitation and gradient relaxation within the matrix. For instance, the effect of concentration gradient relaxation was most evident in intermittent wetting samples stored at 98% relatively due to minimal drying whereas precipitation mechanisms were most evident when a significant degree of drying occurred. In general, the RH of the storage environment served as a boundary condition for moisture transport from the matrix. This boundary condition may indicate a moisture transport mechanism dominated by diffusion of water vapor with generation through evaporation of liquid water. Further investigation and modeling of the moisture transport phenomena for this system is required.

Application of current assessment models for materials exposed to intermittent wetting interspersed with storage in an inert atmosphere, led to either over or underestimation of actual release depending on the nature of the species of interest. For instance, application of the current assessment approach to the release of highly soluble species (e.g. sodium, potassium, chloride) resulted in up to 40% underestimation of release under intermittent wetting conditions because relaxation of concentration gradients over storage intervals was not considered. Indeed, the results shown here indicated that gradient relaxation or precipitation during storage of a cementitious matrix might result in more rapid depletion of highly soluble species, when the comparison is based on the same duration of leaching, during intermittent wetting than in continuous leaching cases. The current assessment approach applied to intermittent release of pH-dependent species had a varied effect with a general overestimation of release due to the ignored pH gradient relaxation. The most significant effect was when storage was conducted at high RH resulting in 45, 100 and 10% overestimation for the release of arsenic, cadmium and lead, respectively. In all cases, however, the overall effect of intervals of non-leaching reduced the cumulative release of all species when compared to the same total assessment interval of continuous leaching.

This research showed that the assumption of continuously saturated field scenarios for the estimation of inorganic constituent release from cement-based waste material might result in erroneous long-term field performance assessments. These results also imply that long-term constituent release from Portland cement-based waste forms should not be made by simple correction of saturated release assessments based solely on diffusion mechanisms.

It is therefore necessary to develop a predictive model coupling release phenomena with drying of the porous media as function of environmental conditions.

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