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Journal of Hazardous Materials 40 (1995) 321–335

**JOURNAL OF
HAZARDOUS
MATERIALS**

The effects of simulated environmental attack on immobilization of heavy metals doped in cement-based materials[☆]

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Received 5 May 1994; accepted in revised form 12 September 1994

Abstract

Environmental corrosion as is manifested in the form of CO₂ attack has been found to have a profound effect on the leaching characteristics of heavy metals and the microstructure of the cement binder. An external peripheral leached zone was formed, followed by a calcium carbonate-rich layer, and an intact unleached core. The heavy metals did not substitute for calcium in the calcium silicate hydrate gel, rather nickel and cadmium gradually reacted to form hydroxides. This reaction is diffusion controlled, and depends on the initial grain size distribution of the heavy metal compounds. The incorporation of metals results in a decrease of the Ca(OH)₂ content of the cement paste and increases its vulnerability to carbonation and resistance against acidic corrosion. A pH decrease to about 9 in the leached zone can account for the cadmium and nickel concentration in the leachates.

1. Introduction

The growing number of papers and conferences devoted to waste immobilization reflects a genuine need for economic solutions for restoring a safe, clean, green environment. Waste stabilization has been specified by the US Environmental Protection Agency as the best demonstrated available technology for a number of wastes regulated under the Resource Conservation and Recovery Act (RCRA). Portland cement is probably the most common binder for waste immobilization as it has been proven to be an effective, safe, easily controlled, and a relatively inexpensive material. The retention of heavy metals in portland cement, as evaluated on the basis of leach

[☆] Presented at the 73rd TRB Annual Meeting, Washington, DC, January 9–13, 1994.

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tests (e.g., TCLP), has been usually found to meet the regulatory guidelines [1]. However, these tests are usually carried out on fresh stabilized/solidified samples in an assumption that limited physical and/or chemical changes take place post stabilization. Apart from other possible chemical reactions between the binder and the waste, such an assumption overlooks the long-term deterioration of cement-based materials due to environmental corrosion. It may be postulated that the performance of corroded specimens is inferior to that of a fresh one. Thus, leaching tests on fresh specimens may turn out to be insufficient, or even erroneous indicators.

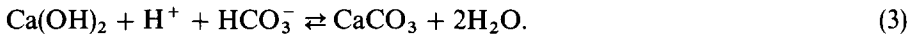
Portland cement-based materials are prone to various types of chemical attack, including corrosion by soft water and groundwater [2, 3]. Carbon dioxide-bearing water is more deleterious as the calcium silicate hydrate (C–S–H)¹ gel of ordinary portland cement paste is readily dissolved in an acidic environment, thus affecting the leachability characteristics of waste-based cement over time.

Aggressive solution attack on cement-based materials results in a considerable amount of dissolution and precipitation. In all of these reactions, Ca²⁺ is an essential ingredient, since it is needed for the formation of secondary minerals such as calcium carbonates, ettringite (Ca₆Al₂S₃O₁₈ · 32H₂O), and gypsum. The immediately available sources for the Ca²⁺ ions are the pore solution, and the calcium hydroxide (CH) present in the cement paste. Thereafter, additional Ca²⁺ is supplied by the decalcification process of the C–S–H.

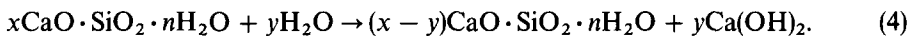
Cement-based monoliths are usually exposed to percolating groundwater or infiltrated rainwater, and are, therefore, subjected to carbonic acid attack. The carbonic acid is formed through a natural process in which carbon dioxide is dissolved in water according to:



In the presence of carbonic acid, the calcium from the pore solution leaches out. Calcium hydroxide dissolves, and provided the pH pore solution is not too low calcium carbonate precipitates:



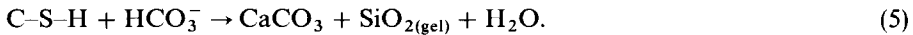
Following the consumption of CH, more Ca²⁺ for carbonate precipitation becomes available through the decalcification of the C–S–H gel according to [4]:



It should be noted that due to the low permeability of the hardened cement paste the latter two reactions are diffusion controlled and reaction (4) follows the consumption of the CH on a micron scale. Thus, while at the outer surface the C–S–H may be strongly decalcified, abundance of CH may still be in its interior [5]. Nevertheless, the

¹ The customary cement chemical notation is used: C = CaO; S = SiO₂; A = Al₂O₃; F = Fe₂O₃; \bar{S} = SO₃; H = H₂O; thus, CH = Ca(OH)₂; C₃S = Ca₃SiO₅, etc.

long-term CO₂ attack alters and softens the C–S–H gel, which eventually is decomposed to calcium carbonate, acid-insoluble silica gel, and water:



Heavy metal immobilization in cement-based materials can be related to either physical containment or chemical fixation. However, if the heavy metals are introduced as nitrates they are readily dissolved in the mixing water, thus they cannot be detected by a microscopical examination. In contrast, heavy metal oxides have lower solubilities in the alkaline pore solution of the cement paste. It was anticipated therefore that for recording the interaction of the heavy metals with the cement constituents and delineating heavy metal depleted zones by microscopical examination addition of heavy metals in the form of oxides is more suitable. Indeed, under these conditions, except for lead the fate of all the other elements could be directly found.

The objectives of the research reported here were threefold: (a) to evaluate the effects of a long-term simulated corrosive environmental condition on the leaching characteristics of selected heavy metal oxides stabilized in portland cement, (b) to portray the specimens' microstructure and the fate of the heavy metals, and (c) to compare the leaching from paste and mortar.

2. Experimental

Pastes and mortar bars prepared from an ASTM Type I portland cement and doped with cadmium, nickel, lead, and mercury oxides were subjected to aggressive CO₂ attack for up to 180 days.

2.1. Materials

The cement used was an ASTM Type I portland cement having a chemical composition of: CaO = 65.54, SiO₂ = 21.64, Al₂O₃ = 3.75, Fe₂O₃ = 3.74, TiO₂ = 0.27, Na₂O = 0.10, K₂O = 0.72, SO₃ = 3.55, and LOI = 0.29%, and a corresponding Bogue composition of C₃S = 62.1, C₂S = 15.6, C₃A = 3.6, and C₄AF = 11.7. According to its low C₃A content, this cement can also be regarded as an ASTM Type V. The fine aggregate was composed of graded quartz Ottawa sand Type C-109, and the heavy metals were analytical grade cadmium, nickel, lead, and mercury oxide powders with a mean particle size of 1, 10, 7, and 5 μm, respectively. Deionized water was used throughout.

2.2. Mixture proportioning, casting, and curing

Pastes and mortars were prepared at a water:cement ratio of 0.5. For mortar, the aggregate-to-cement ratio was 2. Two metal loads of 1 and 4% of the cement content by mass were used, each consisting of a mixture of 0.25 and 1% by mass of the above four oxides, respectively, in addition to control specimens.

The materials were prepared according to the ASTM C109 mixing procedure. Prior to the mixing, the metals were mixed with the water for 30 s at a low speed, followed by an additional 30 s mixing period at a medium speed. Then, the mixtures were cast in thin brass molds, $164 \times 34 \times 7$ mm in internal dimensions, covered and moist cured for 3 days at room temperature. Following demolding, the hardened bars produced were immersed in lime-saturated water for 4 additional days of curing. At the end of this 7-day curing period, the bars were placed in glass vessels filled with deionized water through which CO_2 gas bubbled continuously throughout the experimental period. The water-to-solid ratio in the vessels was 20:1. In order to study the effects of early to late age corrosion upon leaching, the bars were subjected to this kind of attack for 7, 50, and 180 days. The pH of the water was monitored periodically and set to 6.25 ± 0.25 by controlling the CO_2 flow rate (a low bubbling rate followed by pH increase).

At the end of the corrosion periods, following the removal of the bars, the leachates were acidified and any deposits on the bottom and walls of the glass vessels were dissolved by adding concentrated HCl so the final concentration of the HCl in the leachate was 5%. All of the following analyses were carried out on duplicates. The leachates were analyzed for heavy metals content by ARL model 3560 AES ICP (simultaneous inductively coupled plasma spectrophotometry). The analytical error as expressed in terms of relative standard deviation for nickel, cadmium, and lead was less than 7%. The results for mercury, however, were not reproducible and are not reported here. The calcium carbonate and calcium hydroxide contents of the pastes were calculated from thermal gravimetric analysis (TGA) carried out on a Seiko SSC/5200 thermal analysis system.

Specimens for microstructural examination were prepared by slicing the specimens with a diamond saw, impregnating the sliced portions with an epoxy mixture, and polishing them with successively finer grades of diamond pastes down to $1 \mu\text{m}$. The flat, polished surfaces so produced were sputter-coated with a Pd–Au layer and examined under a JEOL JSM 840A SEM coupled with a Link EDX system mainly in a backscatter mode. Further details about the latter technique is given elsewhere [6, 7].

3. Results

As a result of this simulated environmental attack, a considerable amount of calcium was leached out and deposited both at the bottom of the vessels as a finely divided powder (Fig. 1), and on the bars' surfaces (Fig. 2). In addition, in accord with both, the microstructural observation and TGA, a substantial amount of CaCO_3 was deposited within the pastes. In the former, CaCO_3 is distinguished from CH by its lower gray level and relatively larger crystals. Fig. 3 shows a characteristic secondary electron image micrograph across the full width of the bar subjected to CO_2 attack for 180 days. Three distinct zones were generated. Along the outer surfaces, a gray spotted rim about $600\text{--}1200 \mu\text{m}$ wide was formed. This rim, which is referred to as a leached zone, is followed by a bright 300 to $600 \mu\text{m}$ wide calcium carbonate-rich layer, and an

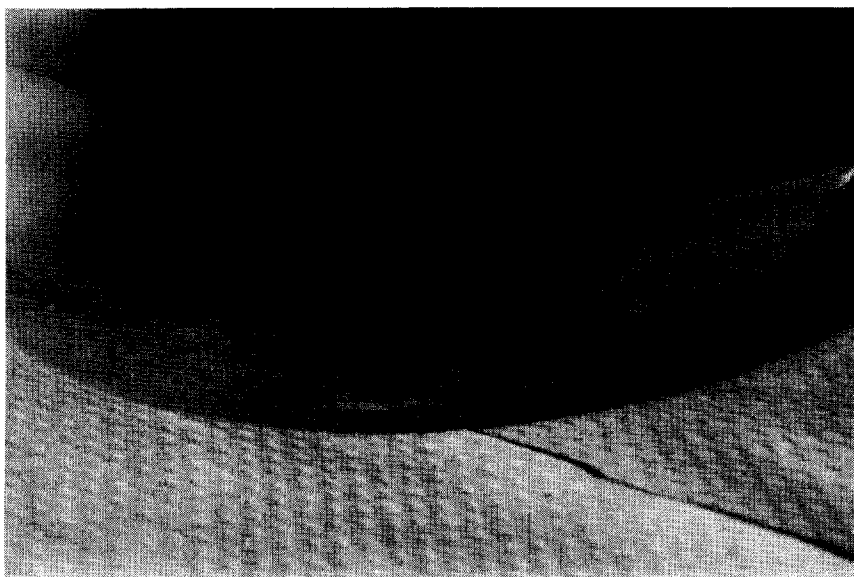


Fig. 1. Deposition of calcium carbonate in the form of finely divided powder on the bottom of the beaker.



Fig. 2. Secondary electron image micrograph showing deposition of euhedral calcium carbonate crystals about 10 to 15 μm long on the bar's surface.

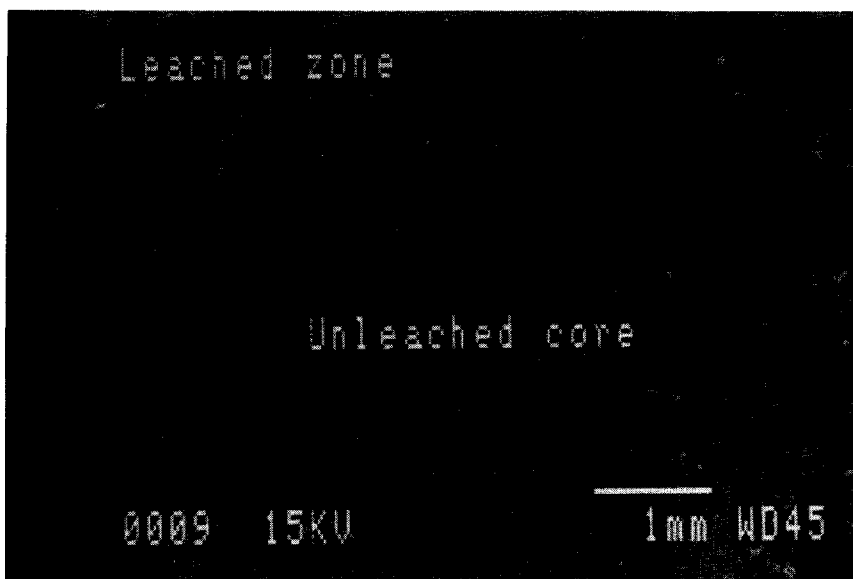


Fig. 3. Secondary electron image micrograph across the full width of the bar. The CO_2 attack resulted in the formation of three zones: a peripheral spotted rim which is referred to as a leached zone, a bright 200 to 500 μm wide zone, and at the center, an apparently homogenous zone which is referred to as an unleached core.

apparently homogeneous zone at the interior designated as an unleached core. The unleached core presumably comprises the internal intact portion of the paste as is interpreted from its microstructure that is similar to that of uncorroded hardened cement paste (HCP) [8].

Nearly the same area that is presented in Fig. 3 is viewed in Fig. 4 in a backscatter mode. The leached zone is characterized by a darker gray level due to the decalcification of the C–S–H gel (Eq. (4)). The gray level of the HCP progressively becomes brighter inward as the unleached core is approached. To be noted is the formation of several thin inner veins parallel to the bar's outer surfaces that appear in the leached zone. These veins closely resemble morphologically the formation of inner gypsum layers which were observed in pastes subjected to magnesium sulfate attack [9]. Recently, Cheng and Bishop noted similar zonation in small spheres of cement containing waste after immersing in acid solutions, and a pH change from 6 at the specimen surface to about 12 in the interior [10, 11]. Of interest is the distribution of the heavy metals in the HCP. These metallic compounds are characterized by their relatively high backscatter coefficients and appear in Fig. 4 as bright spots. Evidently, a majority of them are present in the unleached core, whereas only a few are located in the leached zone.

The microstructure of the leached zone is presented in Fig. 5. The only phase that survived this kind of attack is ferrite (C_4AF). The C–S–H gel was severely decalcified and altered. X-ray spot analyses have shown that the dark grains (probably

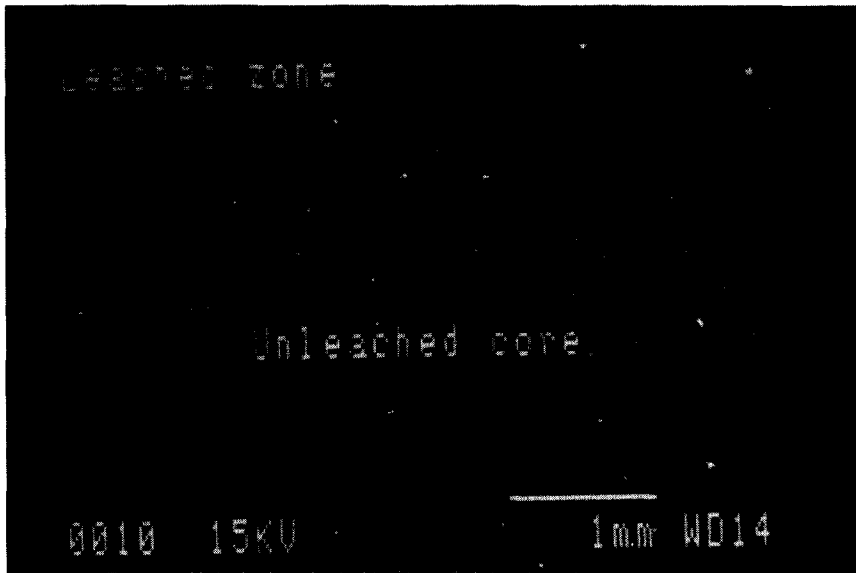


Fig. 4. Backscatter electron image (BEI) micrograph across the full width of the bar. The leached zone is characterized by a lower gray level than the unleached core due to decalcification of the C–S–H there. Note the distribution of the heavy metal compounds that appear as bright spots. Most of them are located within the unleached core, whereas only a few are located in the leached zone.

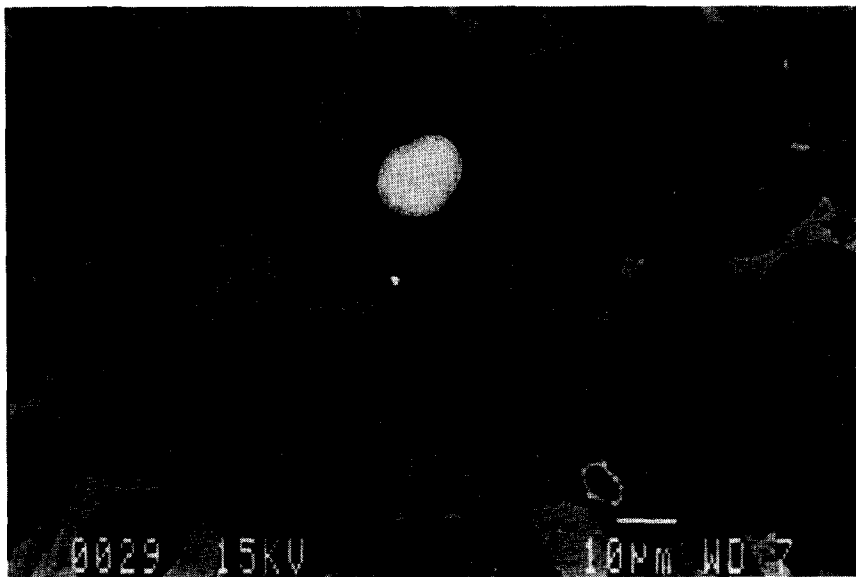


Fig. 5. BEI micrograph showing the microstructure of the leached zone. The C–S–H gel was decalcified and altered. The dark grains are composed of silicon dioxide probably in the form of amorphous silica gel. The bright sphere is a zoned Ni particle. Note the substantial porosity that has developed.

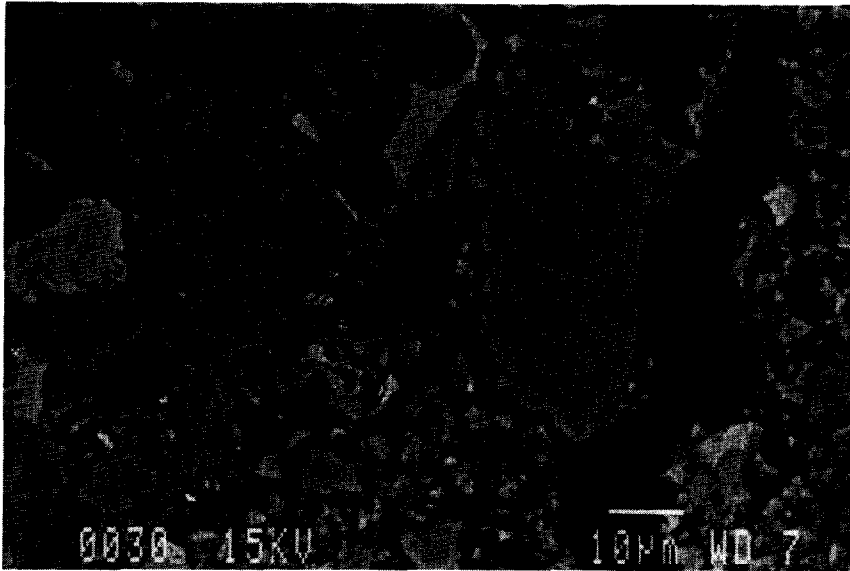


Fig. 6. BEI micrograph presenting two elongated CaCO_3 grains in the calcium carbonate-rich zone. A wide crack is associated with these grains.

pseudomorph of incompletely hydrated phenograins [8]) are composed of silicon, most likely in the form of amorphous silica gel. In addition, substantial porosity is seen to have developed. Inward, in the calcium carbonate-rich layer, large dispersed crystals of calcium carbonate were deposited (Fig. 6). In places, the calcium carbonate precipitation is associated with cracking.

At the interior, in the unleached core, the HCP microstructure is similar to that of an intact paste. Fig. 7 shows distinct heavy metal compounds embedded in the unleached core displaying smooth clear contacts with the surrounding C–S–H gel. This indicates absence of any chemical reaction between the heavy metals and the C–S–H gel. Conversely, the monosulfate grains ($\text{Ca}_4\text{Al}_2\text{SO}_{10} \cdot 12\text{H}_2\text{O}$) designated as AFm are characterized by a relatively higher gray level than their usual one in plain paste [7], suggesting incorporation of heavy metals into their structure. X-ray spot analyses of the AFm phase gave minor peaks for nickel and cadmium, but due to the small AFm grain size, inadvertent contamination from the surrounding paste cannot be ruled out. Another type of chemical fixation is presented in Fig. 8. The large nickel grain at the center possesses two gray levels: a gray rim and a brighter core. In turn, the small nickel grain at the bottom displays only one gray level corresponding to that of the rim of the large grain. According to these gray level differences and X-ray spot analyses calculated by differences, it is interpreted that the brighter core of the large grain is composed of the original NiO that was introduced into the cement, whereas its rim and the small Ni grain at the bottom reacted with the pore solution to form

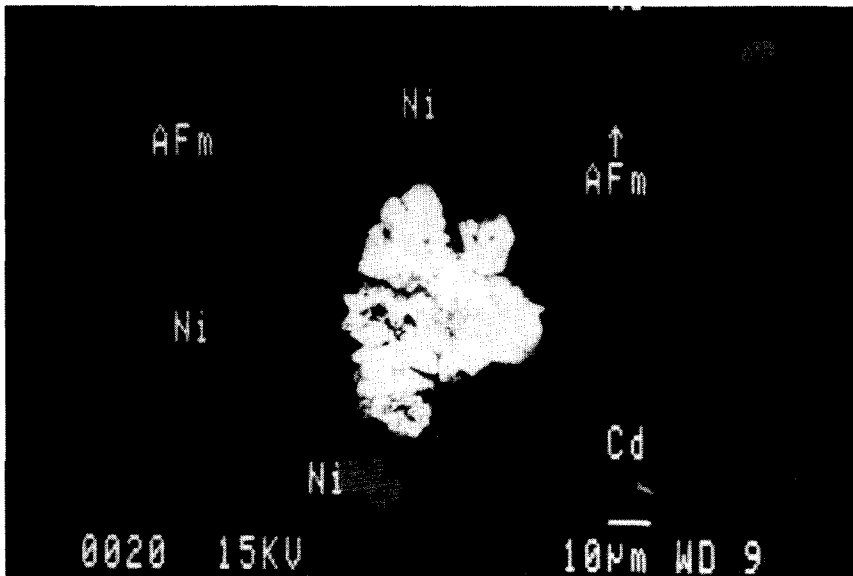


Fig. 7. BEI micrograph showing distinct heavy metal compounds designated by their metallic symbols embedded in the unleached core. The bright cluster at the center is composed of HgO. The monosulfate particles designated as AFm are characterized by a relatively higher gray level than in plain paste, indicating incorporation of heavy metals into their structure.

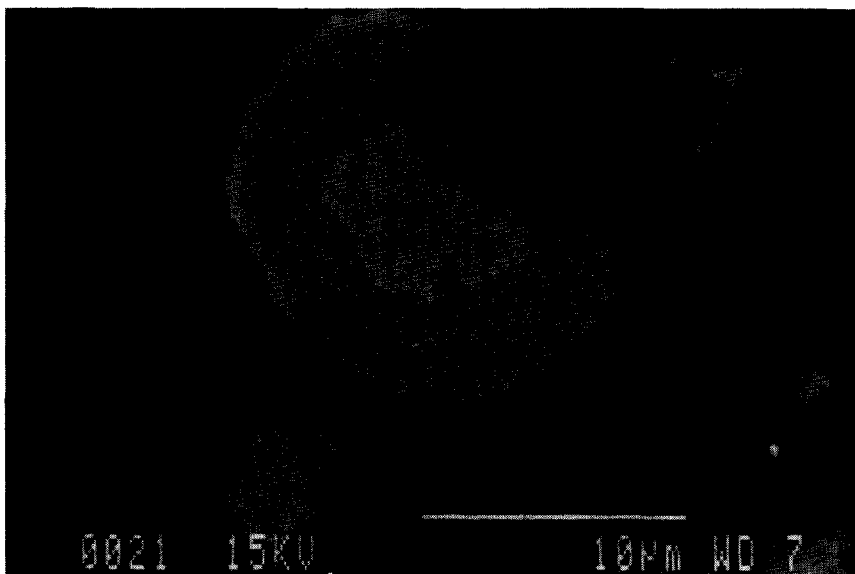


Fig. 8. BEI micrograph displaying two nickel grains. At the center, the larger grain is composed of two phases, unreacted NiO in the brighter core, and Ni(OH)₂ in the rim. The small grain at the bottom was completely reacted to form Ni(OH)₂.

$\text{Ni}(\text{OH})_2$ or another hydrated phase. This illustrates that respeciation of insoluble compounds is a diffusion controlled process which depends on the grain size distribution.

Cadmium grains are disseminated all across the unleached core and characterized by a uniform gray level in backscatter mode and fuzzy outlines that indicates chemical reaction. It is assumed therefore that as with nickel, cadmium was stabilized as hydroxide [12, 13], but due to its fine grain size of about 0.5 to 2 μm , all of the original cadmium oxide was converted to $\text{Cd}(\text{OH})_2$. On the other hand, the mercury crystals have preserved their euhedral structure displaying no sign of chemical fixation. This is in agreement with the suggestion of McWhinney et al. [14] that HgO is a stable phase and does not react with the cement constituents. Interestingly, distinct lead grains were not found, rather weak Pb X-ray signals were detected in existing calcium carbonate grains within the paste, and the lead state needs further investigation.

The variations of the CH and CaCO_3 contents within the pastes are given in Table 1. The CH content of the pastes decreased with time, and for equal time, more CH was found in the control sample (metals load 0%) than in those that contained 1 and 4% metal oxides.

Nevertheless, increasing the metal load did not bring about a decrease of the CH content. Calcium carbonate content followed a reverse trend. All the pastes gained more CaCO_3 through time, and for an equal period, more CaCO_3 was deposited in the pastes containing heavy metals than in the control. Again, an increase in metals load did not increase the CaCO_3 content, and as a matter of fact even a slight decrease was recorded. Regardless of the metal load, these results demonstrate that heavy metal doping increases the vulnerability of the pastes to carbonation, and decreases their CH alkaline buffering capacity. The adverse effect on augmenting carbonation rate may be related to the increase in permeability and pore size distribution that is associated with heavy metal doping [15]. The CaCO_3 was partly deposited at the expense of CH, and additional calcium was supplied by the decalcification of the C–S–H.

Fig. 9 shows the leaching characteristics of the paste and mortar specimens subjected to the CO_2 attack. The concentration of the metals in the leachates is

Table 1

CH and CaCO_3 contents in portland cement pastes doped with cadmium, nickel, lead and mercury oxides subjected to aggressive CO_2 attack

Days/ metal load	CH (wt%)			CaCO ₃ (wt%)		
	0%	1%	4%	0%	1%	4%
7		15.6	16.8		10.2	4.4
50	16.0	15.5	15.6	9.0	10.4	9.7
180	15.4	13.1	13.5	10.4	14.5	13.2

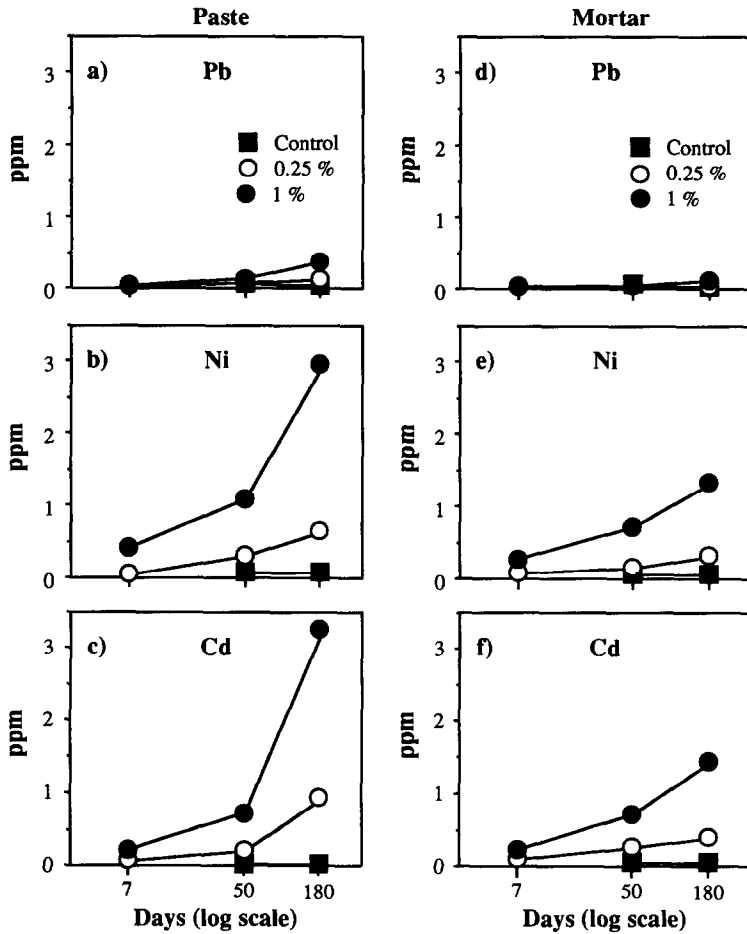


Fig. 9. Leachate composition of 25 cm³ of plain paste and mortar bars placed in 1000 ml water.

calculated on the metals released from 25 cm³ of cement-based materials per 1000 ml water. Evidently, the attack had a profound effect on the leachability and it is obvious that:

- (a) Increasing the metals load augments the metal concentration in the leachates.
- (b) For equal volumes of cementitious materials more metals are released from pastes than mortars. However, if the concentrations of the elements are expressed in terms of equal cement weights, the reverse trend applies. This can be related to the greater permeability of mortar than paste.
- (c) Lead is best retained, nickel and cadmium are mobilized, and the cadmium concentration in the leachates goes well above the 1.0 mg/l guideline.

4. Discussion

The high pH environment characterizing plain HCP favors the precipitation of many heavy metals as hydroxides or hydrous oxides. Other potential precipitates can be in the form of sulfate and carbonate [16, 17]. Another mechanism of fixation can be by ion substitution or sorption.

By adding soluble heavy metal nitrates, Komarneni and his coworkers have shown that almost all of the calcium in tobermorite ($C_5S_6H_5$) and xonotlite (C_5S_5H) (natural crystalline phases of calcium silicate hydrate) can be replaced with either cobalt or nickel at 25 °C. Lead, cadmium, and zinc, however form hydroxy carbonate or carbonate, and deposit on the calcium silicate minerals. It was suggested that the latter elements probably substitute for surface Ca^{2+} , but the extent of such substitution could not be evaluated [18, 19]. Ivey et al. [20] have proposed that chromium substitutes for silicon and chemically incorporates into the C–S–H.

Scanning electron microscope studies on the microstructure of waste-based cement have been carried out for a number of years by several researchers (e.g. [19–21]), primarily using fracture specimens in secondary electron mode. More recently, the functional utility of examining plane polished surface mounts in backscatter electron mode have been established (e.g. [5, 8, 22]). Backscatter SEM provides representative, unbiased surfaces and a much more revealing image of the intricate textural details. It therefore permits a much greater appreciation of the spatial relationships and juxtapositions of the viewed features. Figs. 7 and 8 clearly illustrate that the heavy metals are not incorporated into the C–S–H structure; rather the heavy metal compounds are physically encapsulated by the C–S–H. In contrast, some heavy metals did incorporate into the AFm phase, demonstrating the greater capacity of this phase for ion substitution [23]. Nickel and cadmium reacted with the high pH pore solution to form hydroxides. However, if waste is added in the form of insoluble compounds, the fixation of waste due to chemical reaction is governed by its particle size distribution (Fig. 8).

The distribution of the heavy metals in the HCP, as viewed in Fig. 4, indicates that the heavy metals primarily dissolved out from the leached zone. This microscopic observation substantiates the Hinsenveld and Bishop view that the shrinking core model is more suitable for evaluating the leach rate of cement-based waste than the bulk diffusion model [24, 25].

The leaching characteristics of heavy metals stabilized in cement are quite controversial. In many studies, cadmium has been reported to be better retained than lead, e.g. [26–28]. On the other hand, Bishop recorded a better immobilization for lead than cadmium [29]. Cartledge et al. [26] attributed the greater retention of cadmium to a rapid deposition of $Cd(OH)_2$ at the beginning of the hydration process, so that these precipitates served as nucleation sites for $Ca(OH)_2$ and C–S–H gel. Herrera et al. [27] related the greater mobility of lead either to the formation of the relatively soluble species $Pb(OH)_3^-$ or formation of soluble Al and Si polymers.

Trussell and Batchelor investigated the pore solution compositions of cement doped with heavy metals. They reported better immobilization of cadmium and lead than chromium and mercury. They also noted a dependence between the pH and the

leaching rate: the lower the pH, the greater the leaching. However, the impact of lowering the pH on the leachability was not the same. Cadmium and mercury were found to be highly leachable at low pH, whereas a moderate mobilization was recorded for lead and chromium [30]. Jones et al. [31] also concluded that leaching is primarily related to the final pH of the leachant. Accordingly, nitrate addition increased leaching, whereas NaOH suppressed it.

Obviously, leachability is directly affected by the test setup. Thus, a number of the above discrepancies can be attributed to differences in sample preparation and test procedure. However, to a large extent, leachability is governed by the waste form (nitrates, sulfates, oxides, etc.) and the particle size distribution. For example, if cadmium is added as an oxide rather than nitrate, it would gradually be transformed to hydroxide, and not preferably encapsulated as suggested by Cartledge et al. [26]. Based on the above data, the greater mobility of nickel and cadmium as recorded in this study can be attributed to a single mechanism. Assuming the outer surfaces of the cadmium and nickel oxide grains were converted to hydroxides, and the solubility product constants (K_{sp}) of their hydroxides at 25 °C are 5.3×10^{-15} and 5.5×10^{-16} , respectively [32], their measured concentrations in the leachates of the pastes at 180 days can be explained by the lowering of the pH of the pore solution in the leached zone to about 9.15 for cadmium and 8.5 for nickel. Such pH values conform with the pH of the leached zone that was recently reported by Cheng and Bishop [10, 11].

Fig. 9 also shows that the lead level in the leachates is substantially lower than that of nickel and cadmium. For the 7- and 50-day corrosion periods, lead was practically immobilized, and only at 180 days did a small amount of it leach out. Although no discrete lead phase was found in the microscopical analysis, we suggest that it was stabilized as lead carbonate, which may also account for its low solubility in the mild pH environment that was formed [33]. This interpretation points to the ambivalent role of low level carbonic acid that, on one hand, has adverse effects by lowering the pH, and, on the other hand, through inorganic carbon supply is capable of stabilizing metal carbonate precipitates.

5. Conclusions

Portland cement-based materials doped with heavy metal oxides were found to be susceptible to aggressive CO₂ attack. The attack resulted in formation of a peripheral decalcified zone which is referred to as a leached zone, and an apparent intact unleached core. This research led to the following results:

(1) A layered structure composed of a leached zone, a calcium carbonate-rich layer, and an unleached core was formed by subjecting cement-based materials doped with heavy metals to mild carbonic acid attack. The leached zone is characterized by its decalcified C–S–H and depleted heavy metal content. Thus, leaching can be more appropriately modelling by a shrinking core concept, rather than in terms of bulk distribution coefficients.

(2) The heavy metals did not incorporate into the C–S–H structure. Rather, nickel and cadmium were converted into hydroxides and mercury remained in its original oxide form. The former reaction is a diffusion controlled one.

(3) Incorporation of heavy metals reduced the CH alkaline buffering capacity of the cement paste and increased its susceptibility to carbonation.

(4) The leaching rates of the metals increased in the order: $Pb \ll Ni \leq Cd$.

(5) Increasing the metal load increases the amount of metals leached at any time.

(6) The concentration of cadmium and nickel in the leachates can be explained by a pH decrease to about 9 in the leached zone.

(7) For an equal volume of cement-based materials and equal metals load/cementitious materials ratio, the heavy metals retention in mortar was found to be better than that in paste.

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