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Research article

Leaching of metals from cement under simulated environmental conditions

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ABSTRACT

Leaching of metals from cement under various environmental conditions was measured to evaluate their environmental safety. A cement product containing clinker, which was produced from cement kiln co-processing of hazardous wastes, was solidified and leaching of metals was characterized using the 8-period test. Concentrations and speciation of metals in cements were determined. Effects of ambient environment and particle size on leachability of metals and mineralogical phases of cement mortars were evaluated by use of XRD and SEM. Results indicated that metals in cements were leachable in various media in descending order of: sea water, groundwater and acid rain. Cr, Ni, As, Co and V were leached by simulated sea water, while Cu, Cd, Pb, Zn, Mn, Sb and Tl were not leached in simulated sea water, groundwater or acid rain. When exposed to simulated acid rain or groundwater, amounts of Cr, Ni, As and V leached was inversely proportional to particle size of cement mortar. According to the one-dimensional diffusion equation, Cr was most leachable and the cumulative leached mass was predicted to be 9.6 mg kg^{-1} after 20 years. Results of this study are useful in predicting releases of metals from cement products containing ash and clinkers cement kiln co-processing of hazardous wastes, so that they can be safely applied in the environment.

1. Introduction

Co-processing of hazardous waste in cement kilns offers an alternative to disposal or incineration of certain waste streams. It has been widely and successfully employed in the United States, Europe, Japan and other developed countries for several decades. Compared to other treatment technologies, cement kiln co-processing of hazardous waste has many advantages such as complete and effective disposal, lower cost and lesser secondary pollution, and thus is increasingly being adopted by developing countries (Stafforda et al., 2015; Yan et al., 2010). As the first product line for cement kiln co-processing of hazardous waste in China, Beijing Cement Company produces Portland cement in a rotary kiln in which hazardous waste, both solid and semisolid, is used as part of the raw materials or cement ingredients according to its state and chemical properties after appropriate pretreatment (Fig. S). Currently, this technology can treat 33 of 49 hazardous wastes listed in the national hazardous waste inventory of China, and thus is recognized as one of the solutions to reduce volumes of waste. About 10–15 thousand tons hazardous wastes were co-processed per year by the Beijing Cement Company. These solid and semisolid hazardous wastes being co-processed were mainly derived from soil contaminated with heavy metals or organic matters, water treatment sludge and industrial wastes.

However, metals in wastes might be discharged through different streams during co-processing of hazardous wastes in cement kilns. Based on mass balance of metals, during burning of cement in the kiln, most metals in waste materials were transported into clinkers in cement (Trezza and Scian, 2007). Accordingly, releases of metals into the environment has become an increasing important issue when cement or concrete products are exposed to water, soil and air, which may result in a threat to

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environmental safety and human health (Van der Sloot, 2002). It is necessary to evaluate and analyze leaching of metals from cement products in different environments.

Sequential extraction of metals from cement with determination of metal speciation is valuable for forecasting mobility and leaching of metals from cement or concrete products when they are placed into various environments (Hullebusch et al., 2005). Speciation of metals usually includes characterization by fractionation of total concentrations into exchangeable (ES), acidic sodium acetate extractable (ASA), acidic hydroxylamine hydrochloride extractable (AHH), sulfide bound (SB) and residual (R) forms according to modified Tessier sequential extraction procedures. Metals in exchangeable forms are most leachable, whereas those in residual forms are more recalcitrant. Therefore, investigation of metal speciation and leaching behavior is an important way to determine risks to the environment (Song et al., 2013).

In this study, concentrations of metals in cement clinker, produced during co-processing of hazardous waste procedure in the cement kiln of the Beijing Cement Company, were analyzed. Chemical speciations of twelve metals were investigated by use of modified sequential extraction procedures. Effects of exposed environments such as groundwater, sea water and acid rain, as well as particle size on the leachability of metals in cement mortar were analyzed in detail. Microstructural analysis including X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to investigate changes of mineral phases of cement paste during leaching. Finally, leaching behaviors of metals were discussed, and cumulative masses of metals leached were predicted.

2. Materials and methods

2.1. Preparation of samples of cement mortar

Cement clinkers were obtained from different batches of product of cement kiln co-processing of hazardous wastes by the Beijing Cement Company, China, and then mixed for experiments. Desulfurized gypsum and testing sand were obtained from China Resources Cement Holdings Limited and Tianjin Bohai Chemical Industry Group Supply and Sales Co. Ltd, respectively. Cement clinkers were ground to fine particles with 5% desulfurization gypsum. Measured amounts of cement clinkers and testing sand were mixed with distilled water in a concrete mixer, and then shaped using a jolting table for compacting cement samples. Shaped samples were first cured in cement curing boxes for 2 d and further cured in water for 28 d according to the standard method (GBT17671-1999, 1999). Finally, Cement mortar was crushed and screened into three different particle sizes; fine particle (CS1), coarse particle (CS2) and block (CS3) with particle size d ≈ 1.0 mm, d ≈ 10.0 mm and 40 mm × 40 mm × 10 mm, respectively to test the influence of particle size on metals leaching behavior.

2.2. Simulation of leaching environment

Three different exposure environments, including groundwater, sea water and acid rain, were simulated for investigating leachability of metals from cement products in different environments. Groundwater was simulated by dissolving defined amounts of $MgSO_4$, $CaCl_2$, $NaHCO_3$ and Na_2SO_4 in pure water according to the statistical result of chemical components of groundwater in Handan city in north China (Chen et al., 2004). Because SO_4^{2-} and NO_3^- were the primary acid radical ions of acid rain, to simulate acid rain, H_2SO_4 and HNO_3 were mixed with a mass ratio of 2:1, and pH was adjusted to 3.2 using pure water to (Duan, 2006). Simulated sea water was prepared according to the nation standard GB8650-88 (GB8650-88, 1988). Compositions of simulated groundwater and sea water are shown (Table 1).

2.3. Experimental procedure

2.3.1. Digestion of samples of cement

Samples of cement were digested by use of microwave-assisted digestion. Approximately 0.5 g of sample was digested with 5.0 ml HF and 10 ml concentrated HNO_3 in a microwave with an polytetrafluoroethylene (PTFE) vessel at 120 °C for 15 min, and then at 150 °C for 15 min, finally, at 180 °C for 30 min. After cooling, the solution was heated to nearly dry at 150 °C, and 1% HNO_3 added to the solution to dissolve the residue, and then cooled to room temperature and then transferred to a 25 ml test-tube (Das et al., 2001).

2.4. Sequential chemical extraction

Speciation of metals in cement was determined by using modified sequential extraction procedures. In this modified method of Tessier, metals were divided into five fractions: ES, ASA, AHH, SB and R (Li et al., 2001). After each extraction, the solution was centrifuged for 15 min with centrifugal force of 1509.3 g. The supernatant was collected and filtered through a 0.45 μm membrane filter, and then diluted to 100 ml for metal concentration determination.

2.5. Continuous leaching test

EA NEN, 2004, 2004 “tank leaching test” is a dynamic test for assessing diffusion-controlled leaching and is commonly used to assess leaching characteristics of metals from porous monoliths (EA NEN, 2004, 2004; Menéndez et al., 2014). The tank test involves leaching of cement mortar specimens (after curing for 28 days) with fine particle size in sealed polyethylene beakers, using simulated sea water as the leachant, to assess leaching characteristics of metals from cement mortar when exposed to sea water. The leachant is renewed at eight specific times (0.25, 1, 2.25, 4, 9, 16, 36 and 64 days). After the period indicated, all the leachate was drained off and the beaker was filled again with the same quantity of simulated sea water (1 L) to keep liquid–solid mass ratio at 20. An aliquot of leachate was filtered through a 0.45 μm cellulose nitrate membrane filters and was acidified with (1 + 1) nitric acid immediately following filtration to $pH < 2$. A fixed volume of 50 mL of each sample was stored at 4 °C for further analysis of the concentration of the leached components by “ICP-MS” by use of US EPA method 200.8. (EPA 200.8, 1994) .

2.6. Analytical method

2.6.1. Quantification of metals

After digestion or extraction the solution was filtered with a nylon membrane of 0.45 μm of pore size and analyzed using a Elan DRC-e inductive coupled plasma mass spectrometry (ICP-

Table 1
Compositions of simulated groundwater and sea water.

Simulated groundwater					
Component	$MgSO_4$	$CaCl_2$	$NaHCO_3$	Na_2SO_4	
Concentration ($mmol \cdot L^{-1}$)	5.3	16.7	16.1	8.0	
Simulated sea water					
Component	NaCl	$MgCl_2$	Na_2SO_4	$CaCl_2$	KCl
Concentration ($mmol \cdot L^{-1}$)	24.5	5.2	4.1	1.2	0.69
Component	KBr	H_3BO_3	$SrCl_2$	NaF	$NaHCO_3$
Concentration ($mmol \cdot L^{-1}$)	0.10	0.03	0.02	0.003	0.20

MS) (Perkin Elmer, Waltham, USA) (EPA 2008, 2008).

2.7. Microstructural observation

XRD analysis was also used for evaluating effects of ambient environment on mineralogical phases of cement mortar. Cement mortar of fine particle diameter (≈ 1.0 mm), including before and after leaching the three aqueous media, were air dried and ground for XRD analysis. Equipment used for the XRD was a D/Max 2500v/pc X-ray diffractometer (Rigaku Corporation, Japan) operating at 40 kV and 40 mA. The XRD data were analyzed using Jade 5.0 software and the mineralogical composition of the tested cement mortar was determined based on the database of Joint Committee on Powder Diffraction Standards. Surfaces of samples were coated with gold to be conductive for SEM analyses by a QUANTA 200 SEM (FEI Corporation, Oregon, USA). These SEM investigations were performed at voltage of 15 kV, working distance of 9.8–10.8 mm and magnification of 20000X.

2.8. Statistics analysis

Each test was performed in triplicate, and average results were corrected by subtracting the results of the equivalent control experiment. Analytical precision, which was determined as the percentage relative standard deviation for the triplicate tests using ANOVA, was on the order of 5.0%.

2.9. Prediction of long-term cumulative mass of metals leached

Cumulative masses of metals predicted to be leached during long-term exposure, were estimated according to the one-dimensional diffusion equation derived from Fick diffusion law (Kosson et al., 2002). Cumulative leaching massM_{mass}^{t}, of Cr, Ni, As and Co was calculated (Equations (1)–(3)).

$$M_{mass}^{t} = 2 \cdot \rho \cdot C_0 \cdot \frac{S}{V} \left[\frac{D^{obs} \cdot t}{\pi} \right]^{1/2} \tag{1}$$

Where: M_{mass}^{t} is cumulative released mass per unit of surface area at time t (mg m^{-2}); ρ is the sample density (kg m^{-3}); C_0 is initial leachable concentration (mg kg^{-1}); D^{obs} is observed diffusivity of the concerned specie (m^2 s) and t is time interval (s).

$$D_i^{obs} = \pi \left[\frac{M_i}{2\rho C_0 \left(\sqrt{t_i} - \sqrt{t_{i-1}} \right)} \right] \tag{2}$$

Where: D_i^{obs} is observed diffusivity of the concerned specie at the ith extraction (m^2 s); M_i is measured cumulative leached mass of the concerned specie at the ith extraction (mg m^{-2}); t_i is replenishing time of extraction i (s) and t_{i-1} is replenishing time of fraction extraction i-1(s).

$$D^{obs} = \frac{1}{n} \sum_{i=1}^{n} D_i^{obs} \tag{3}$$

Where: D^{obs} is average diffusivity of the concerned specie (m$^2 \cdot$s) and n is number of extraction.

Since the useful life of cement and concrete products in China is estimated to be 20–30 years, cumulative mass of constituents released was predicted by using the available concentration as the reference value of C_0, in this study, leaching time, t, was set to 20 years.

3. Results and discussion

3.1. Metal concentration and speciation in cement

Concentrations of metals in cement clinker are presented (Table 2). Concentrations of Mn and As, which were as great as 320.0 and 196.7 mg kg^{-1}, respectively, were greater than those of the other ten metals. Concentrations of Cd and Sb were relatively small. On the basis of the specifications for design of cement plants (GB50295-2008, 2008) (Table S), concentrations of metals in cement clinkers must satisfy certain criteria during operation of a cement kiln co-processing of hazardous wastes. Metal concentrations in cement clinkers were all less than standard values except Cd, Tl and As with concentrations of 3.1, 67.3 and 196.7 mg kg^{-1}, respectively.

Percentages of each of 12 metals extracted during each step of the sequential extraction before and after cement was exposed to sea water are presented (Fig. 1). Before leaching Cr, Ni, Pb, Zn and Mn were extracted primarily into the AHH fraction, with proportions leached ranging from 55.2% to 80.2%. Considering the alkaline conditions of the cement matrix, these metals might exist as metal oxides, metal hydroxides or metallic calcium silicate compounds. Cu, V and Co was mostly distributed in the R and AHH fractions. However, more than 90% of As, Sb, Cd and Tl existed in cement as R, especially for Tl, which approximately 99%. These four metals were bond into crystal lattices of crystalline silicate minerals during the cement kiln co-processing of hazardous waste. Therefore, As, Sb, Cd and Tl were stable and not leached into the ambient environment.

However, speciation differed significantly among the 12 metals tested before and after leached in simulated sea water. Metals in the R fraction were more recalcitrant and less likely to be leached into the environment. Therefore, according to the change of the percentage in fraction R after leaching, the 12 metals tested could be classified into three types: those for which the proportion in R increased, decreased or did not change. For Cr, Ni, Pb and Zn, the percentage in the R fraction increased, which could be attributed the fact that Cr, Ni, Pb and Zn existed in other four fractions, such as ES, ASA, AHH and SB, were easily leached out after leached in the simulated sea water, and thus resulted in increased relative percentage in the R fraction (Fig. 1(a) and b). However, for Co, Cu, Cd and As, the percentage in fraction R decreased. This result implied that stable structures of Co, Cu, Cd and As were readily eroded and or even damaged, and thus the more stable form of R was converted into less stable forms during leaching. For Sb, Tl, Mn and V, the percentage of R changed slightly because they existed as stable forms in cement. Although concentrations of Tl in cement clinkers were greater than the required standard (Table S1), more than 90% of Tl remained stable as R in cement, even after a long-term leaching in sea water.

3.2. Effect of leaching conditions on leachability of metals

The leaching test plays a vital role in assessing potential effects of disposal of waste into the environment. Results of a number of studies have demonstrated that leachability of metals in waste materials is intimately associated with the ambient environment and particle size of cement mortar (Nosrati et al., 2014). An experiment was conducted with different particle size under three different simulated ambient environments in order to investigate the leachability of metals in cement under several conditions of ambient aquatic environment. The results indicated that ambient environment has an important influence on kind and concentration of leachable metals (Fig. 2). In general, metals in cement were leachable in descending order of sea water, groundwater and acid

Table 2
Total concentration of metals in cement clinkers.

Concentration	Mn	Cr	V	Zn	Ni	Pb
$(\mathrm{mg \cdot kg^{-1}})$	320.0 ± 12.4	17.1 ± 0.7	36.8 ± 1.5	66.3 ± 2.6	20.6 ± 0.8	16.8 ± 0.7
Concentration	Cu	Co	As	Cd	Sb	Tl
$(\mathrm{mg \cdot kg^{-1}})$	25.0 ± 0.9	6.9 ± 0.3	196.7 ± 7.0	3.1 ± 0.1	2.8 ± 0.1	67.3 ± 2.7

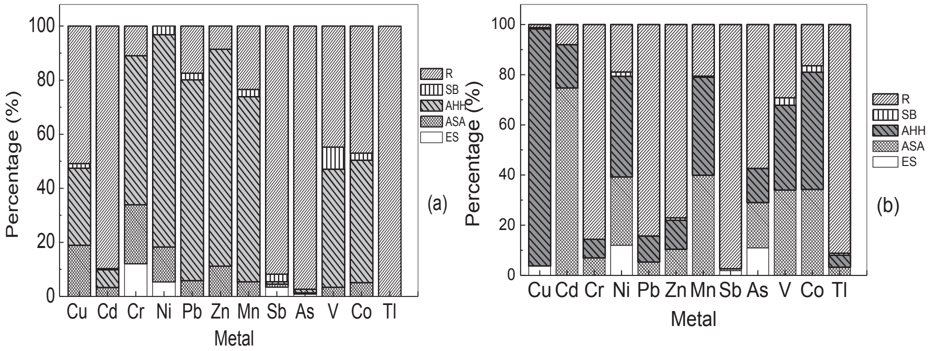

Fig. 1. Relative proportions of metals in exchangeable (ES), acidic sodium acetate extractable (ASA), acidic hydroxylamine hydrochloride extractable (AHH), sulfide bound (SB) and residual (R) fractions before (a), and after (b) leaching in simulated sea water.

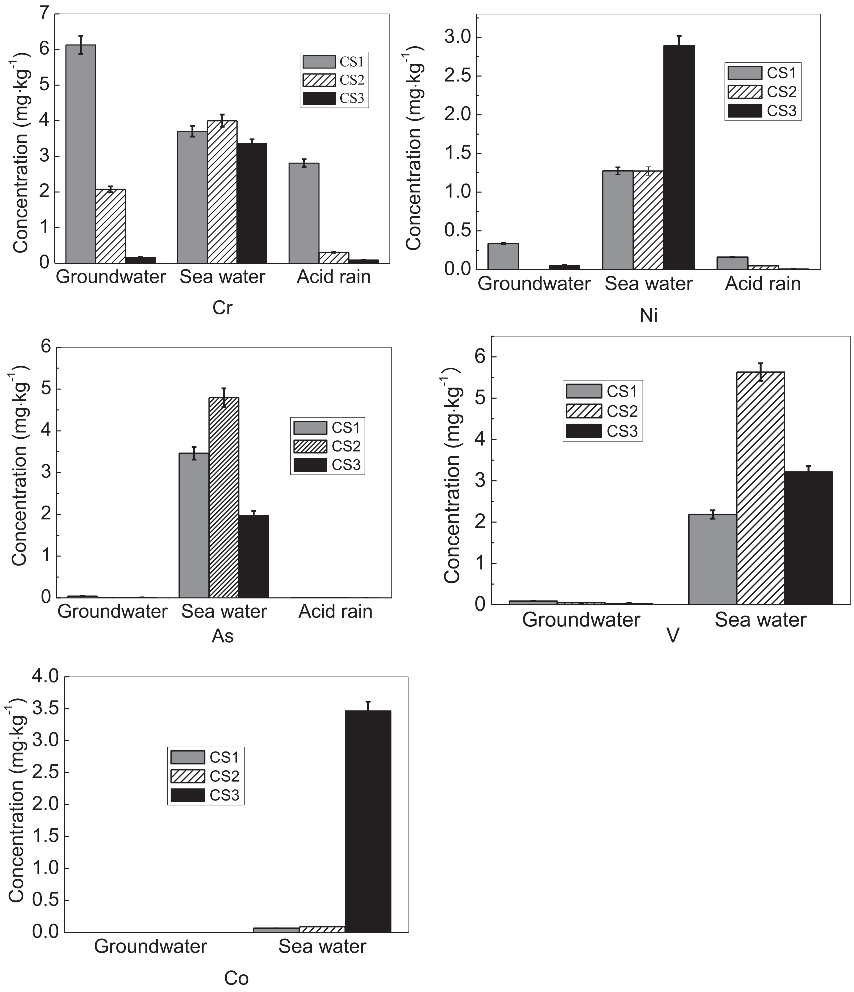

Fig. 2. Total concentrations of metals leached in the three particle sizes of cement mortars under different conditions. CS1, fine particle (d ≈ 1.0 mm); CS2, coarse particle (d ≈ 10.0 mm); CS3, block (40 mm × 40 mm × 10 mm).

rain. Only Cr, Ni and As were leached from cement in simulated acid rain, whereas V also could be leached out in groundwater. For Co, it could be leached out only in sea water. However, Cu, Cd, Pb, Zn, Mn, Sb and Tl were not detected (less than 0.01 mg/L) in all the leachates, which means that the above seven metals were almost totally encapsulated in solidified cements because of formation of more stable chemical forms by two processes, cement hydration and calcination. Cd, Pb and Zn were more likely to form stable chemical forms after calcination at higher temperatures and subsequent hydration, and thus reducing the leachability and subsequent release to the environment (Zhang et al., 2009).

Amounts and kinds of metals were both least in simulated acid rain. This might be attributed to oxides in cement, such as CaO, Al_2O_3 and Fe_2O_3. Although the initial pH of the simulated acid rain was adjusted to 3.2, the pH of leachate increased rapidly to 8.0–9.0 within a few hours because of the hydration of the above-mentioned basic oxide in cement. It has been previously reported the amount of metals inversely proportional to pH under mildly acidic conditions (Du et al., 2014). The weakly basic characteristic of cement hindered leaching of metals from cement. However, metals in cement were more leachable in sea water because of the concentration of Mg^{2+} and Cl^- ions (Table 1). Mechanisms that affect leachability of metal from cement are complex and have been described in previous literature (Yang et al., 2012). After being leached in simulated sea water, a large amount of white floccule occurred on the surface of cement, which indicated the erosive effect of sea water.

The amount of metals leached was associated with the particle size of cement mortar (Fig. 2). When exposed to the simulated acid rain and groundwater, the leached amounts of Cr, Ni, As and V increased with the decrease of particle size of the cement mortars. For Cr, the trend was most obvious when exposed to groundwater. The amount of Cr leached from a cement block (CS3, 40 mm × 40 mm × 10 mm) was 0.17 mg kg^{-1}, while that leached amount increased remarkable up to 6.1 mg kg^{-1} when the particle size of cement mortar reduced to 1.0 mm (CS1, $d \approx 1.0$ mm). The phenomena could be ascribed to the larger surface area of CS1. Leaching of metal was affected by sizes of particles of solid waste, with more rapid dissolution occurring for that with larger surface areas per mass or volume (Mizutani et al., 2006). Additionally, 12% of Cr in cement clinker was distributed in the ES fraction (Fig. 1) and might exist free or only attached to the surface of cement minerals, which makes it be more leachable and more easily released to the environment.

When exposed to sea water, however, the correlation between the leached amount of metals and the particle size of cement mortar was not obvious. It was interesting that the leached amount of Co and Ni from CS3 reached 3.5 and 2.9 mg kg^{-1}, respectively, which were much higher than those from cement mortar of CS1 or CS2. This result could be explained by the chemical forms of Co and Ni in cement clinker and their leaching mechanism. From a chemical point of view, Co and Ni exist as trivalent ions, Co^{3+} and Ni^{3+} in cement clinker. Besides, the ionic radii of Co^{3+} and Ni^{3+} are 61 and 60 pm, respectively, which is very close to the ionic radii of Fe^{3+} of 65.4 pm. Therefore, Co^{3+} and Ni^{3+} ions can replace Fe^{3+} ions in the crystal structure of ettringite (Kolovos et al., 2002; Lan, 2008). Under the erosive effect of sea water, Co and Ni entered into the crystal lattices of cement would gradually release to the leachate. For cement mortar of CS1, the concentration of Co and Ni in the leachate would rapidly reach equilibrium with that of the solution in the pores of cement, and thus concentration gradient of Co and Ni approached zero, which inhibited diffusion of Co and Ni from the solution in the pores of cement to leachate, and then hampered the leaching of Co and Ni from the cement mortar to the ambient environment (Yang et al., 2011). This phenomenon is in accordance with that reported by Yang et al. They also observed that concentrations of metals would come into equilibrium with that of the water in the pores of cement, and thus concentration gradient of heavy metal approached zero, which inhibited diffusion of heavy metal from the water in the pores of cement to leachate, and then hampered the dissolution of heavy metal form the solid surface into the water in the pores of cement sample.

As and V were more leachable from CS2 in sea water, which might be because the chemical forms and properties of As and V in cement. As exists as arsenic oxide or calcium arsenate, and V exists as calcium vanadate or calcium silicon vanadate in cement clinker. Such two metallic salts were more leachable in the simulated sea water due to both the basic characteristic of cement and erosive effect of Mg^{2+} and Cl^- ions in sea water. Compared to CS3, leaching of As and V was more leachable from CS2 because of erosion by sea water. On the contrary, amounts of As and V leached was directly proportional to size of particles between 10 mm and 1.0 mm, which is probably a result of maximum adsorption of arsenate or vanadate on surfaces of cement mortar of CS1. This result is consistent with those of a number of studies reporting significant sorption of arsenate on minerals, such as goethite, alumina oxides, and iron oxides, occur at neutral pH (Komonweeraket et al., 2015).

3.3. *Effect of exposure environment on mineralogical composition and surface appearance of cement*

Patterns of composite XRD in cement prior to leaching and after leaching in sea water, groundwater and acid rain are illustrated (Fig. 3). By comparing composite XRD patterns of cement before and after leaching in different aqueous environments, it was observed that the mineralogical composition of cement changed appreciably during leaching. Before leaching, there were various crystalline compounds on surfaces of cement. Silicate and gypsum were the main minerals and C_3S was predominant (Fig. 3(a)). However, these cement mortars exhibited different diffraction peaks after leached (Fig. 3(b), (c) and 3(d)). The three different ambient environments affected mineralogical phases of cement differently. For instance, SiO_2 was the main crystalline compound on the surface of cement prior to leaching but after leaching, the mineralogical phase composition became more simple. This result suggested that the mineralogical phase of calcium silicate had been destroyed during leaching. Changes in mineralogical phases of cement also depended on ambient environment. Composite XRD patterns of cements after leaching in groundwater or simulated acid rain were similar, which indicated that the amount of erosion of the surface of cements were also similar. However, the degree of erosion of cement was most serious and the mineralogical phase was simplest after leaching in sea water, which is believed to have significant effects on mechanical properties of cement. This result is consistent with that of metals leaching, which implies that metals in cements are more leachable due to the damage of mineral structure when exposed to sea water.

SEM is a well-established method that can offer useful information concerning structures of materials. SEM micrographs of surfaces of cement before and after leached are shown (Fig. 4). As expected, amorphous calcium silicate hydrate, plates of calcium hydroxide, needle-like forms of ettringite and crystalline rods of gypsum particles were observed on surfaces of cement before leaching (Fig. 4(a)). After leaching, however, large crystalline rods, plates of calcium hydroxide and amorphous calcium silicate hydrate were observed, but needle-like forms of ettringite were not observed (Fig. 4(b)). According to the XRD composite patterns (Fig. 3(b)), the large crystal rods were not gypsum. These crystal rods might be crystallized substances resulting from salt with high concentrations in simulated sea water. Leaching in sea water

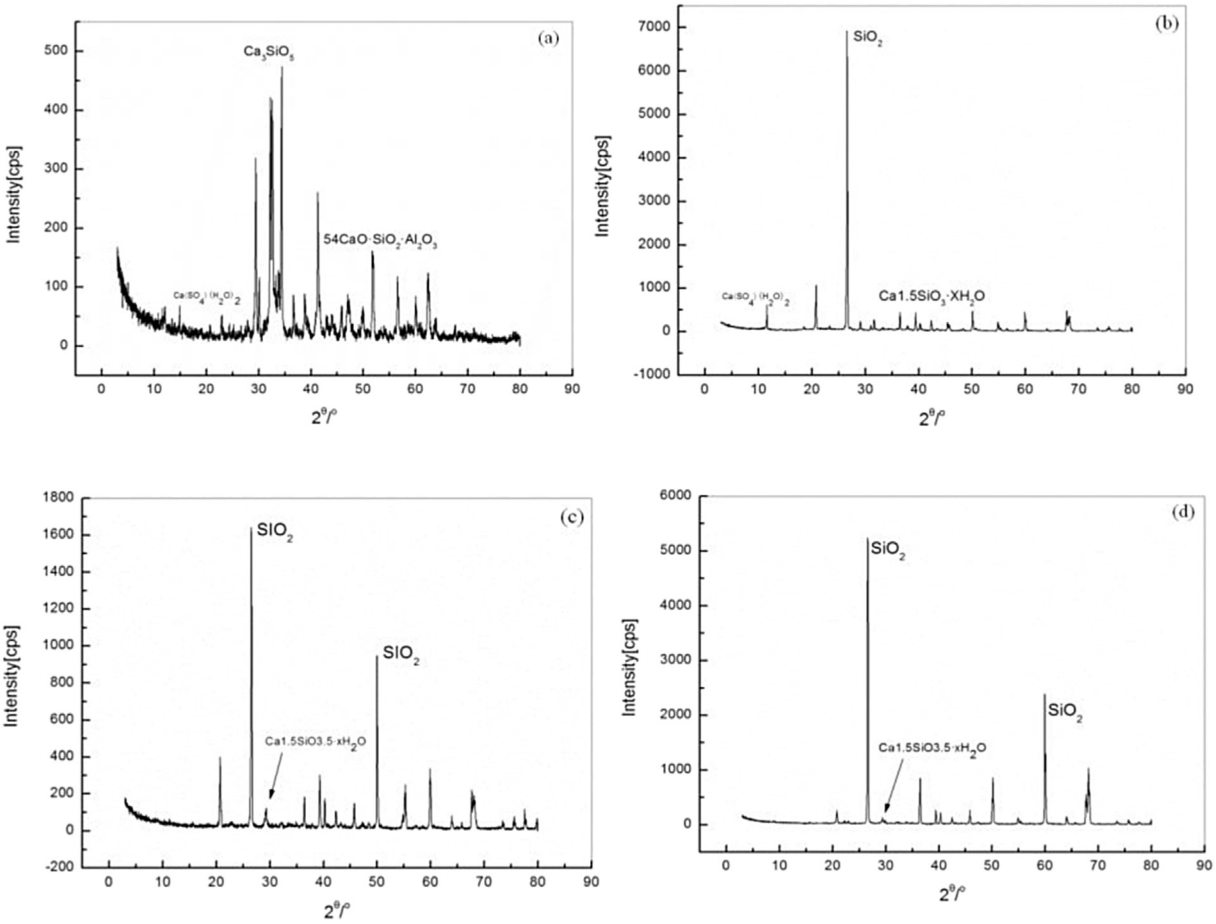

Fig. 3. XRD patterns of cement mortars before leached (a), after leached in sea water (b), in groundwater (c) and in acid rain (d).

changed mineralogical phases of cement products. After leaching in ground water or acid rain few regular crystals were observed, which indicated that some crystals found in natural cement had been destroyed after a long duration of leaching.

3.4. *Simulation of leaching behavior of metals from cement mortar*

The gradient of a log–log plot of cumulative derived leaching vs. time indicates the predominant leaching mechanism (EA NEN, 2004, 2004). Gradients less than 0.35 denoted surface wash-off for durations from 0.25 to 4 d, or depletion for the rest of time increments, but since values ranged from 0.35 to 0.65, diffusion was indicated as the most likely mechanism. However, the mechanism was indicated to be delayed diffusion for increments from 0.25 to 4 d or dissolution for the rest of the time increments since the gradient was greater than 0.65. A gradient of 0.5 indicated standard diffusion control. Therefore, mechanism of leaching of metals from cement mortar of CS1 in sea water was discussed according to NEN 7375 norm.

Cumulative, (log–log) plots of leaching of Cr, Ni, As and Co as a function of time as well as the fitting of lines with a slope of 0.5 (Fig. 5) were used to determine likely mechanisms of leaching. The maximum cumulative amount leached over 64 d were 3.7, 1.3, 3.5 and 0.07 mg kg^{-1} for Cr, Ni, As and Co, respectively. Accordingly, retentions observed for Cr Ni, As and Co were 78.3%, 93.8%, 98.2% and 99.0%. The retention of Cr was less than those of the other three metals. This could be attributed to poor immobilization of Cr. Lasheras-Zubiate et al. reported that metals were immobilized in assayed cement matrices, and retentions of Pb and Zn were 99.6% and 99.9%, but that of Cr was only 70–75% after 64 d (Lasheras-Zubiate et al., 2012). Different leaching behaviors of Cr Ni, As and Co might be due to different solid-state matrices among cements. For example, Cr exists predominantly as chromate (CrO_4^{2-}) under high temperature and strongly oxidizing conditions during cement kiln co-processing of hazardous waste procedure (Sinyoung et al., 2011). However, Ni and Co were mainly layered in double hydroxide phases or hydroxide-like phases, and then became immobilized in the cement mortars. The result is consistent with that of a previous study, in which it was demonstrated that binding mechanism for Ni in cement was the existence of Ni- and Al-containing hydrotalcite-like layered double hydroxides (Sheidegger et al., 2000). The process of immobilization could reduce mobilities of Co and Ni in cement mortar.

The slope of the cumulative log–log plot of leaching was calculated by linear regression analysis and the result is shown in Table 3. As for Cr, a slope close to 0.5 was found, according to the interpretation of the EA NEN, 2004, which suggested that the mechanism of leaching for Cr in cement was diffusion. However, leaching behaviors of Ni and Co in cement were governed by a combination of diffusion and depletion during early stages (Lampris et al., 2011). For As, the slope was 0.64 (time increment 1–4 in Table 3), but was less than 0.35 at later stages, indicating that leaching of As was near delayed diffusion-controlled mechanism during initial stages. Chemical immobilization of As was better and resulted in a sluggish leaching diffusion for early stages and depletion for later stages.

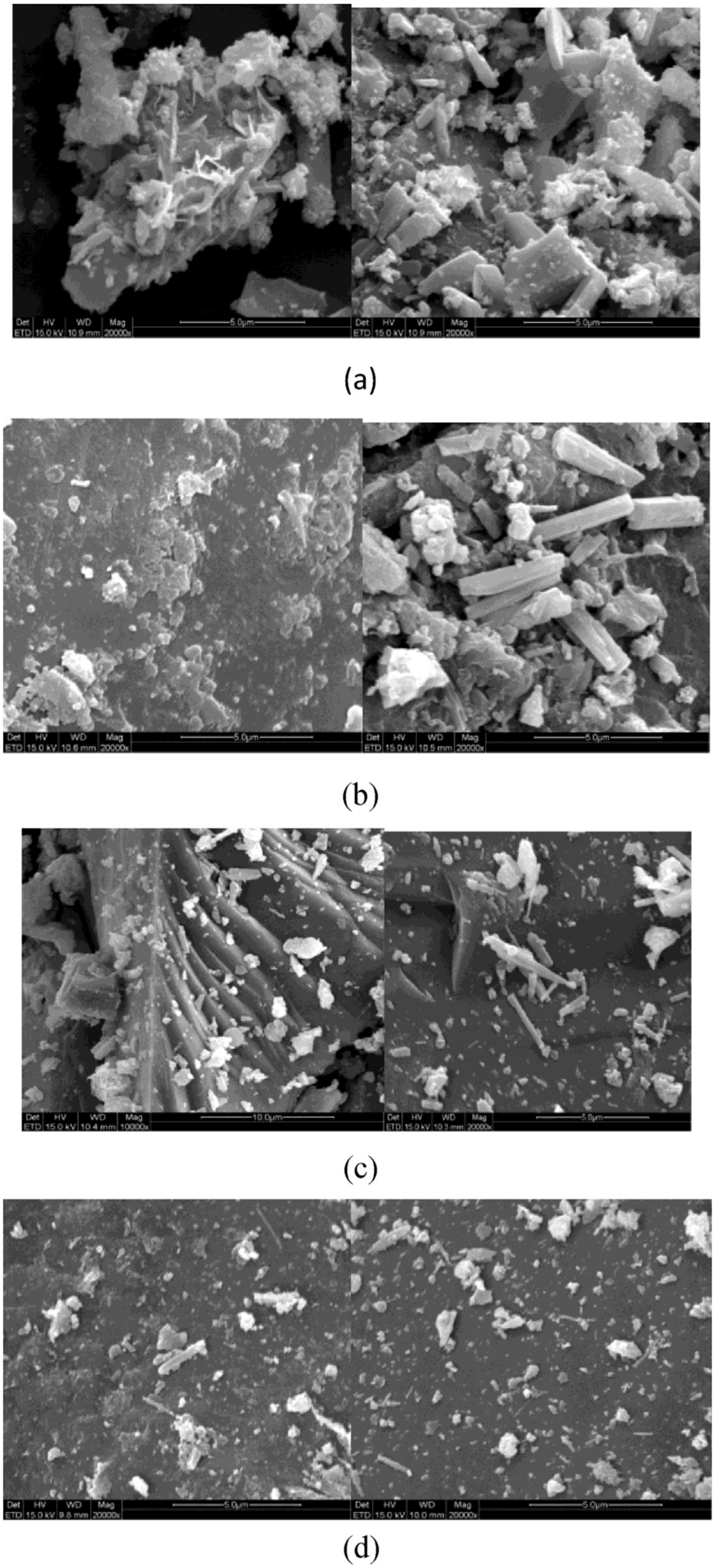

Fig. 4. SEM micrographs of cement mortars before leached (a), after leached in sea water(b), in groundwater(c) and after leaching in acid rain (d).

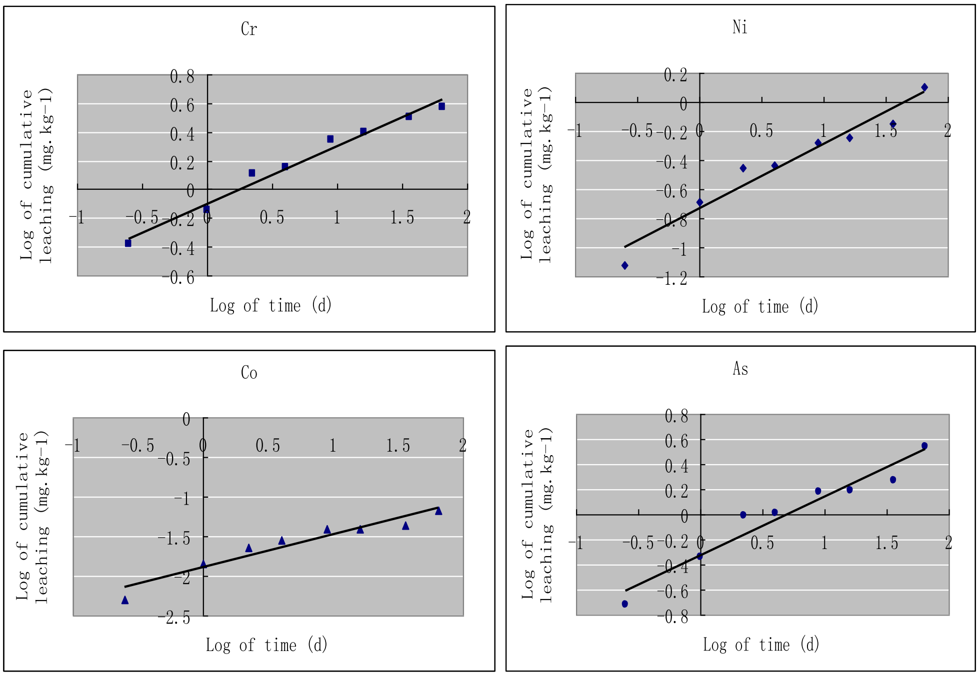

Fig. 5. Log–log plots of cumulative leaching vs. time for Cr (a), Ni (b), Co (c) and As (d) over 64 d.

Table 3
Slopes of log–log plots of derived cumulative leaching vs.time for different time increments.

Step	Slope			
	Cr	Ni	Co	As
2-7 Increment	0.40	0.33	0.28	0.36
5-8 Increment	0.26	0.42	0.24	0.39
4-7 Increment	0.36	0.29	0.15	0.25
3-6 Increment	0.37	0.27	0.25	0.27
2-5 Increment	0.49	0.40	0.44	0.52
1-4 Increment	0.47	0.60	0.64	0.64

Increment 1–4: from 0.25 to 4 d; increment 2–5: from 1 to 9 d; increment 3–6: from 2.25 to 16 d; increment 4–7: from 4 to 36 d; increment 5–8: from 9 to 64 d; increment 2–7: from 1 to 36 d.

A significant correlation was observed between D^{obs} and M^t_{mass} (Table 4). Also, values of D^{obs} and the percent of M^t_{mass} to C_0 were all Cr > Ni > As > Co. This result indicated that D^{obs} was the main factor influencing leaching, while the effect C_0 on cumulative mass leached was not significant.

4. Conclusions

Influences of ambient environment and particle size of cement mortar on leachability of metals were evaluated. Cu, Cd, Pb, Zn, Mn, Sb and Tl were not leached out when exposed to simulated sea water, groundwater or acid rain, while Cr, Ni, As, V and Co could be leached in sea water. The amount of metals leached was associated with particle size of cement mortar. The amount of Cr leached out of cement was the greatest in the CS1 fraction. Erosion of cement mortar was the most serious in seawater, and composition of the mineralogical phase determined by use of XRD and SEM analysis was the simplest after leaching in sea water. Based on the one-dimensional diffusion equation, cumulative masses of metals leached over 20 years were predicted to be 9.6, 6.1, 0.42 and 0.04 mg kg^{-1} for Cr, Ni, As and Co, respectively. Cr was the most unstable metal. Therefore, production of cement during cement kiln co-processing of hazardous wastes, Cr should be controlled to avoid its potential environmental risk.

Table 4
Predicted cumulative masses of Cr, Ni, As and Co leached.

Metal	Cr	Ni	Co	As
C_0 $(\mathrm{mg\cdot kg^{-1}})$	12.9	20.6	3.2	0.2
$D^{obs}(\mathrm{m^2\cdot s})$	5.4 E−14	8.8 E−15	1.7 E−15	2.5 E−15
t (a)	20	20	20	20
$M^t_{mass}(\mathrm{mg\cdot kg^{-1}})$	9.6	6.1	0.42	0.04
Percent of M^t_{mass} to C_0	73.9	29.8	13.2	15.8

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2015.12.008.

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Supplementary materials

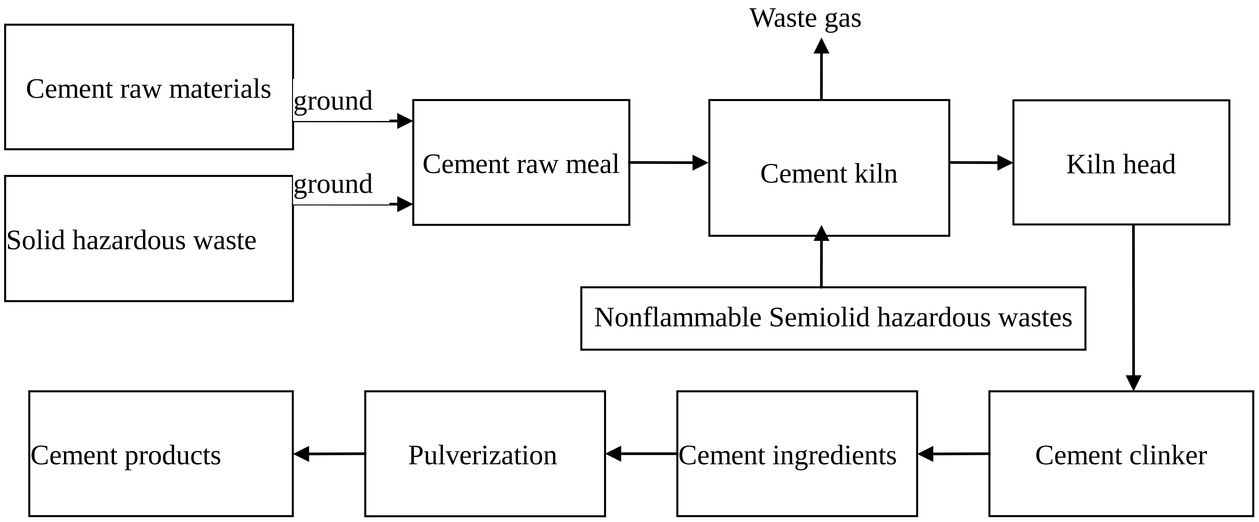

Fig.S Simplified process diagram of cement kiln co-processing of hazardous wastes in Beijing Cement Company.

Table S Regulatory requirements for concentrations of metals in cement clinker and products.

Elements	Cement clinker (mg·kg^{-1})	Cement products (mg·kg^{-1})
Sb	5	--
As	40	--
Be	5	--
Cd	1.5	1.5
Cr	150	--
Co	50	--
Cu	100	--
Sn	25	--
Hg	Not checked out	0.5
Ni	100	--
Pb	100	--
Se	5	--
Tl	2	2
Zn	500	--

--: not provided