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ScienceDirect

Cement and Concrete Research 38 (2008) 675 – 680

Comparison of the fixation of heavy metals in raw material, clinker and mortar using a BCR sequential extraction procedure and NEN7341 test

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Received 28 May 2007; accepted 3 September 2007

Abstract

The release potential and leaching behavior of five heavy metals (As, Cd, Cr, Cu and Pb) in raw material, clinker and mortar were studied by the three-step sequential extraction procedure proposed by the commission of the European Communities Bureau of Reference (BCR) and NEN7341 leaching test. The results of two experimental methods were compared to show the fixation difference of heavy metals among three kinds of samples. The results of NEN7341 leaching test show that the maximum leached concentration of cement products is low and the leached fraction of five heavy metals represents less than 15% of the total heavy metal content of the cement product. To refer to the bulk content as a criterion of environmental impact is not appropriate. The results of sequential extraction procedures show that the bonding forms of heavy metals change a lot in three samples. The contamination factor (Cf) and the leached fraction of each element in three samples indicate that all the elements are better fixed in cement products than in raw material due to calcination and hydration. To most elements, the relative metal retention is higher in mortar than in clinker. Compared within the five analyzed elements, Cd is better retained and Cu is worse retained in the same kind of sample.

Keywords: Raw material; Clinker; Mortar; Heavy metals; Sequential extraction; NEN7341

1. Introduction

The use of industrial by-products in replacement of natural materials and fuels is now widely encouraged in cement production: this practice enables the residual materials to be recycled and valorized, and at the same time the natural resources and energy are saved effectively. Some of the alternative fuels and raw materials may have a significant content of heavy metals. Gradually, the question of leaching of heavy metals from the cement-based construction products which might be a potential risk of contamination of ground water has been raised as a matter of concern. Many researchers have studied the release of heavy metals in natural circumstances yet the retention mechanism and leaching behavior of heavy metals from cement-based products are not fully clearly explained in existing literatures.

Since the release of heavy metals to the environment is the property of concern and it is controlled by transport through the water phase, leaching test is an appropriate mean to assess environmental impact from cement-based products [1]. In addition, the release potential is also an important factor to environmental impact which strongly depends on the retention mechanism such as chemical species or bonding involved of heavy metals. However, the determination of specific chemical species or bonding forms is difficult and the equipment needed often is not accessible to many researchers. For this reason, sequential extraction procedures are commonly applied because they provide information about the fractions of metals in the different lattices of solid sample, which makes sequential extraction a good compromise method that giving information on the evaluations of environmental contamination risk [2–4]. A large number of sequential extraction procedures have been developed over the years. Sequential extraction procedures have been primarily developed to give valuable information on the mobility and availability of elements in sediments [5,6]. However, these procedures have also been applied to other materials such as contaminated soils [7,8], wastewater sludge [9], municipal solid wastes incineration fly ash and bottom ash [10,11], coal and its combustion wastes [12]. In the present

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doi:10.1016/j.cemconres.2007.09.004

study, the sequential extract procedure was applied to raw material of cement production, clinker and mortar.

The release potentials of As, Cd, Cr, Cu, Pb from raw material, clinker and mortar were compared using a sequential extraction procedure mentioned in this paper. The leaching fractions of several heavy metals from the three solid samples were examined in NEN7341 leaching test. During the formation of clinker, raw materials are heated up to 1450 °C in cement kiln. Heavy metals contained in raw material would transfer into clinker and be fixed in crystallized structures. In the hydration course during which the cement turns to hardened cement paste, heavy metals could form metal hydroxides, adsorb to hydrated compounds, or get into the hydrated cement system in other ways. From raw material to hydrated cement product, heavy metals experience two times of fixation. The objective of this work was to study the fixation of heavy metals by the formation of clinker and the hydration of cement.

2. Experimental

2.1. Sample preparation

Raw material and clinker: Raw material and clinker from a Chinese cement plant, raw material had been homogenized as powder clinker was then crushed in a ball-mill to obtain a homogenized powder (grain size <125 μm).

Mortar power: 95% clinker power and with 5% gypsum was mixed together to obtain cement. Mortars were prepared with the usual cement/sand/water ratio (1/3/0.5), and were moulded in cubical bars(16×4×4 cm); after 28 days of maturation at 20 °C and 98% relative humidity, they were grounded to <125 μm.

All the power samples were dried at 100 °C in an oven until two consecutive mass were identical. They were stored in polyethylene bottles until required. Before each study, the sample was re-homogenized by shaking the bottle.

2.2. Reagent and apparatus

The extractant solution was prepared from analytical grade reagents and was checked for possible trace metal contamination. Sulfuric acid, nitric acid and hydrogen peroxide were analytical reagent grade. Standard solutions of arsenic, cadmium, chromium, copper and lead were prepared by dilution of certified standard solutions (1000 ppm) of corresponding metal ions. All dilutions were performed with deionized water. To calibration solutions, Correlation coefficients of 0.999 or better were obtained for all calibration curves.

Glassware used for the experiments was cleaned beforehand with 10% nitric acid for several days and rinsed three times with deionized water.

The elements concentrations in all extracts were analyzed by inductively coupled plasma atomic emission spectrometry (ICP–AES, IRIS intrepid, Thermo Electron, USA). Wavelengths were fixed at 189.0 nm (As), 226.5 nm (Cd), 267.7 nm (Cr), 324.7 nm (Cu), 221.6 nm (Ni), 220.3 nm (Pb) and 206.2 nm (Zn).

2.3. Experimental methods

2.3.1. Aqua regia/hydrofluoric acid digestion

Approximately 0.5000 g of the sample was accurately weighed into a 100 mL Teflon beaker. 20 mL of aqua regia (HNO_3: HCl = 1:3) and 20 mL of concentrated hydrofluoric acid were added to the beaker. Then, the beaker was placed on a hot plate that had been adjusted to 130–150 °C. After the solution was evaporated to near dryness, the beaker walls were rinsed with deionized water and this solution was heated to dryness. One millilitre of concentrated nitric acid and a further 20 mL of deionized water were added after the beaker was removed from the hot plate and cooled to room temperature. The beaker was heated again on a hot plate at 90–100 °C, most of the sample being digested into solution after 1 h. Cooled to room temperature, the solution was filtered through a 0.45 μm cellulose nitrate filter and then diluted to volume with deionized water in a 100 mL volumetric flask. The element concentrations in the solutions were determined by inductively coupled plasma atomic emission spectrometry (ICP–AES, IRIS intrepid, Thermo Electron, USA). Blank extractions (without sample) were carried out throughout the complete procedure.

2.3.2. Availability test (NEN7341)

For further characterisation of the samples and in order to assess long-term leaching behavior, it is necessary to determine the amount that is available for leaching. Leaching test according to Dutch NEN-7341 [13]: The sample was ground to <125 mm and extracted in two steps of L/S = 50 l/kg each with deionized water at pH = 7 (first extraction) and pH = 4 (second extraction), respectively. pH was kept constant by feedback control and addition of HNO_3 or NaOH. The contact time in each extraction was 3 h. The two extracts were combined prior to analysis.

2.3.3. Sequential extraction procedure

Step 1(*exchangeable fraction, water and acid-soluble*): an aliquot of 40 ml of acetic acid (0.11 mol l^{-1}) was added to 1 g of dry sample in a 100 ml glass container. The mixture was shaken for 16 h (overnight) with a magnetic stirrer at room temperature at a speed of 30 rpm. The extract was separated from the solid residue by centrifuging at 3000 rpm for 20 min and the supernatant was filtered through 0.45 μm cellulose nitrate filter. The supernatant was analyzed immediately or stored at 4 °C. The solid residue was washed with deionized water and underwent step 2.

Step 2(*reducing conditions):* in a 100 ml glass container, an aliquot of 40 ml of hydroxylammonium chloride (0.1 mol l^{-1}, adjusted to pH = 2 with nitric acid) was added to the residue obtained in step 1. The extraction procedure was then performed as described above. After washing with deionized water, the solid residue underwent step 3.

Step 3(*oxidizing conditions):* an aliquot of 10 ml of hydrogen peroxide (8.8 mol l^{-1}) was carefully added in small aliquots to the residue obtained in step 2 in a 100 ml glass container. The container was covered with a watch glass and left at room temperature for 1 h with occasional manual shaking. The

Table 1
Total elementary content in raw material, clinker and mortar (mg/kg)

Elements	Raw Material	Clinker	Mortar	Detection limit (μg/kg)
As	29.60	40.52	12.64	5
Cd	2.90	1.82	0.42	1
Cr	115.30	146.80	41.88	2
Cu	32.80	39.16	10.96	2
Pb	16.8	11.62	3.48	5

procedure was continued for another hour at 85 °C and the volume reduced to a few milliliter by further heating of the uncovered glass container. A further aliquot of 10 ml of hydrogen peroxide (8.8 mol l^{-1}) was added to the residue. The container was covered again and heated at 85 °C for 1 h. The cover was removed and the volume reduced almost to dryness. After cooling, 50 ml of ammonium acetate (1 mol l^{-1} adjusted to pH 2 with nitric acid) were added to the residue. The extraction procedure was then continued as described in the previous steps. After washing with deionized water, the solid residue was digested with strong acids (step 4).

Step 4 *(remaining residue):* the residual solid obtained after the first three extraction steps contains minerals, which may hold elements within their crystal structure. In order to evaluate the content in this residual fraction and to compared total contents, a digestion of this fraction has been carried out using aqua regia and concentrated hydrofluoric acid, according to the procedure described in Section 2.3.1.

After each extraction, the trace element concentrations in the supernatant were finally determined by ICP–AES.

3. Results and discussion

3.1. Characterization of samples

The average content of As, Cd, Cr, Cu and Pb measured in raw material, clinker and mortar are shown in Table 1. From raw material to clinker, carbonate is degraded, organic matter is burnt and partial loss by volatilization will occur. The ignition loss leads to concentrated effect. Thus, the contents of refractory metals (such as arsenic, chromium and copper) [14] are generally higher in clinker than in raw material. Cadmium and lead, as semi-volatile metals [15], probably have smaller content in clinker through calcinations. The data in Table 1 show the trend. From clinker to mortar, no heavy metals are imported and the concentrations of several heavy metals in mortar are about a quarter of that in clinker. This reflects the dilute effect brought by sand added to make mortar.

3.2. Availability test

The purpose of the availability test is to indicate the quantity of a particular component that may leach out from a granular material exposed to extreme conditions (for example, in the very long term, after disintegration of the material, full oxidation and/or loss of acid neutralizing capacity), in an aerobic environment. The test conditions present a worst case leaching scenario rather than the conditions that might be expected to prevail in a landfill, and thus the test provides an upper limit to the leaching potential in environment condition.

Table 2
Leached concentrations and fractions of NEN7341 test[a]

Elements	Leached concentrations (mg/l)			Parametric values[b] (mg/l)	Leached fractions (%)		
	Raw materials	Clinker	Mortar		Raw material	Clinker	Mortar
As	0.031	0.013	0.005	0.01	12.69	3.34	3.96
Cd	0.002	0.001	n.d.	0.001	12.90	5.36	0
Cr	0.300	0.083	0.012	0.01[c]	31.19	6.58	2.79
Cu	0.180	0.047	0.007	0.05	80.59	14.12	6.42
Pb	0.012	0.009	n.d.	0.01	11.61	7.76	0

[a] n.d.: not detected.
[b] Limit for II groundwater quality standards (GB/T14848-93).
[c] Standard for Cr^{6+}.

The NEN7341 test was applied to assess the behavior of As, Cd, Cr, Cu and Pb in terms of mobility, and therefore the potential environmental impact. The concentrations and leached fractions of heavy metals in the leachates of availability tests are shown in Table 2.

The leached heavy metal concentrations of clinker and mortar were near or below the content required by II groundwater quality standards of China (GB/T 14848-93) in NEN7341 test. The fractions of heavy metals leached from clinker and mortar represented less than 15% of the total heavy metal content of the samples. Therefore, it is not appropriate to refer to the bulk content as a criterion to assess the environmental impact from cement products. From raw material, clinker to mortar, the leached heavy metal concentrations gradually decreased. The leached fraction also decreased in turn. Because of concentrated and dilute effects, more attention should be focused on leached fractions to indicate mobility of heavy metals in materials. The results show that the mobility of heavy metals decreases in turn after incineration and hydration. Among the five analyzed elements, copper had a relatively higher leached ratio than other elements no matter in raw material, clinker or mortar.

3.3. Sequential extractions

The procedure performance could have been assessed by the analysis of a certified reference material. In our case, no suitable

Table 3
Summary of the results obtained by sequential extraction for three kinds of samples (mg/kg)

Sample	Step	As	Cd	Cr	Cu	Pb
Raw material	Step 1	4.36	0.1	16.62	12.45	5.88
	Step 2	0	0.14	27.14	6.76	5.36
	Step 3	6.16	1.28	27.44	12.74	2.14
	Step 4	18.99	1.2	41.01	1.3	3.19
Clinker	Step 1	1.5	0.03	10.15	5.46	0
	Step 2	1.48	0.19	10.99	7.92	7.71
	Step 3	0.14	0.02	32.38	11.48	0
	Step 4	35.53	1.36	81.3	15.39	4.95
Mortar	Step 1	0.49	0	1.46	1.4	0
	Step 2	0	0.12	9.28	4.16	0.4
	Step 3	0.26	0	3.7	2.58	0
	Step 4	10.94	0.26	28.05	2.15	2.98

Table 4
Comparison of the direct aqua regia digestion and the sequential extraction procedure and contamination factor

Element	Sample	Sum of the four steps (mg/kg)	Aqua regia digestion (mg/kg)	Recovery (%)	Contamination factor (Cf)
As	Raw material	29.51	29.6	99	0.55
	Clinker	38.65	4.52	95	0.09
	Mortar	11.69	12.64	92	0.07
Cd	Raw material	2.72	2.9	94	1.27
	Clinker	1.6	1.82	88	0.18
	Mortar	0.38	0.42	90	0.46
Cr	Raw material	112.21	115.3	97	1.74
	Clinker	134.82	146.8	92	0.66
	Mortar	42.49	41.88	101	0.51
Cu	Raw material	33.25	32.8	101	24.58
	Clinker	40.25	39.16	103	1.62
	Mortar	10.29	10.96	94	3.79
Pb	Raw material	16.57	16.8	99	4.19
	Clinker	12.66	11.62	109	1.56
	Mortar	3.38	3.48	97	0.13

certified reference material was available for sequential extraction procedure. The sediment CRM 601 which had been studied elsewhere [16] could not be used because its composition and its matrix are to different from the cement products.

The contents of As, Cd, Cr, Cu and Pb in each extract were determined by ICP–AES. The results are presented in Table 3. Since filtration generated loss of particulate material in the sequential extractions, an internal check of the results was performed by comparing the total amount of the metal removed at each step of the procedure with the results from the total amount of aqua regia digestion. The recovery for the sequential extraction procedure was calculated as follows: Recovery (%)=(sum of four steps/total)× 100.

A comparison between the sum of the metal concentrations in the sequential extraction steps and the result from aqua regia digestion was carried out (see Table 4). No significant differences were observed between the two results. Low relative errors (<10%) for all samples and all elements except of cadmium indicate the high quality of the results obtained.

Sequential extraction procedures provide useful information for risk assessment, since the amount of metals mobilized under different environmental conditions can be estimated (weakly acidic condition: step 1, reducing conditions: step 2, oxidizing conditions: step 3). The residual metals are retained within the crystal lattices or inside crystallized oxides and can not release under environment conditions [17]. The mobility and bioavailability of metals decrease approximately in the order of the extraction sequence.

Fig. 1 shows the extracted percentages of evaluated elements in all steps of the sequential extraction procedure of raw material, clinker and mortar. The metal contents in four fractions are evaluated in percentages comparing to the sum of four steps, which presents 100%. In the Fig. 1 presents raw material. 2 presents clinker. 3 presents mortar.

Arsenic: The most arsenic is divided into residual fraction in three kinds of samples. The residual fractions gradually increase (raw material: 64.4%, clinker: 91.9%, mortar: 93.6%) and the acid-soluble fractions decrease after calcination and hydration (raw material: 14.77%, clinker: 3.91%, mortar: 4.19%).

Cadmium: In raw material, the most cadmium is extracted in step 3. Fraction 1and 2 contain relatively little Cd. In clinker and mortar, cadmium is mainly bound to residual phase. The residual fraction in mortar is higher than in clinker. Weisweiler [18] and Kirchner [19] found cadmium was mainly trapped by alite and belite in clinker. After hydration, cadmium species which are released by the clinker are immobilized by physical entrapment of $Cd(OH)_2$ into C–S–H [20].

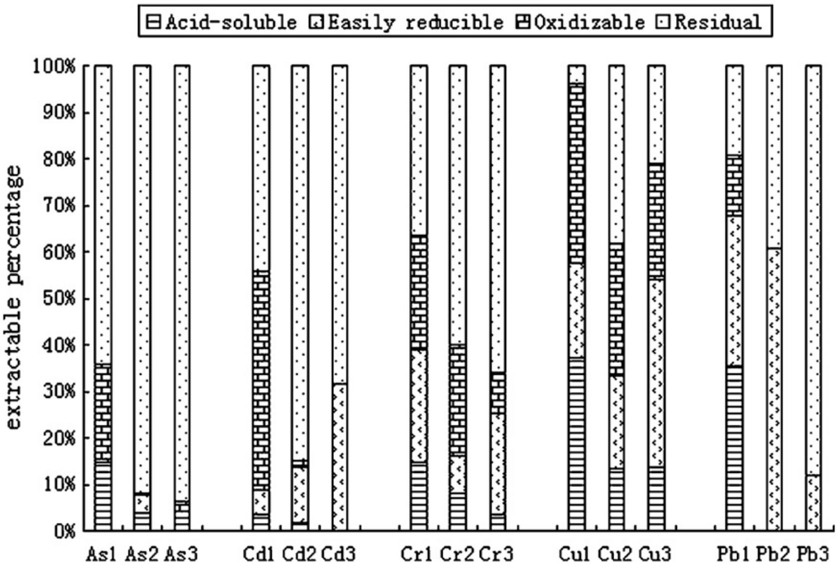

Fig. 1. Distribution of heavy metals among the four fractions in raw material, clinker, mortar.

Chromium: The most chromium is divided into residual fraction in three kinds of samples. The residual fractions gradually increase (raw material: 36.5%, clinker: 60.3%, mortar: 66.0%) and the fractions extracted by weakly acid decrease in turn (raw material: 14.8%, clinker: 7.5%, mortar: 3.4%).

Copper: The highest content of copper is found in the third fraction (38.3%) in raw material, in residual phase (38.2%) in clinker and in the second fraction (40.4%) in mortar. The fractions extracted by weakly acid obviously decrease from raw material to clinker and mortar. The discrepancy of the fractions is small in clinker and mortar.

Lead: Fraction 1 and 3 do not either occur in clinker and mortar. The highest content of lead is found in the first fraction (35.5%) in raw material, in the second fraction (60.9%) in clinker and in residual phase (88.2%) in mortar.

From the figure, it is obvious that the distribution patterns of the five fractions differ from element to element. To an element, the distribution patterns differ in three kinds of samples. From raw material to clinker and mortar, the fractions of more mobile species (extracted by step 1) of all elements obviously decrease, the fractions of immobile species (extracted by step 4) of all elements significantly increase. From clinker to mortar, the fractions of immobile species of most elements increase except of Cd and Cu.

After calcination in cement rotary kiln, heavy metals could be fixed in a crystallized structure of the clinker and the mobility accordingly decreases. In contact with water during the hydration reaction, those heavy metals released by the clinkers could exit as metal hydrated phases, metal hydroxides and calcium–metal compounds, or be immobilized by physical entrapment into the C–S–H [21]. Calcination in cement rotary kiln and hydration could effectively fix heavy metals and decrease the mobility [20]. Fig. 1 also indicated that the mobility of heavy metals gradually decreased from raw material to clinker. From clinker to mortar, the same trend was observed for most elements.

3.4. Comparison of BCR sequential extraction and availability tests for evaluating heavy metals' mobility

One of the aims of this study was to compare the results from the BCR sequential extraction scheme to those from the NEN7341 leaching test, since both of them could be applied in order to assess the behavior of heavy metals in terms of mobility and environmental impact.

The individual contamination factors (Cf) for each analyzed element in three samples were calculated (see Table 4). These factors are defined as the sum of the heavy metal concentrations in the mobile phases (no-residual phases) of the sample divided by the residual phase content. The lower the Cf value, the higher the relative metal retention [22]. For most analyzed elements, the Cf values of samples decrease in the order: raw material > clinker > mortar, which means that the fixation of heavy metals improves. In NEN7341 tests, the leached ratio of each element also showes the same trend, decreasing from raw material to clinker, to mortar. The results mean that the mobility of the five heavy metals decreases due to calcination in cement rotary kiln and hydration with water.

No matter in raw material, in clinker or in mortar, the Cfs of analyzed elements increase in the order: Cd < Cr < Cu, In availability test, the leached ratios of elements show the same order. Especially in clinker, the Cfs and leached fractions of five elements increase in the same order: As < Cd < Cr < Pb < Cu. The results mean that Cd is better retained and Cu is worse retained in the same kind of sample compared within the five elements.

4. Conclusion

The NEN7341 leaching test show that the maximum leached concentration of cement products is near or below the content required by II groundwater quality standards of China (GB/T 14848-93) under extreme environmental conditions. The leached fractions of five heavy metals represent less than 15% of the total heavy metal content of the cement product. To refer to the bulk content as a criterion of environmental impact is therefore unjustified and unduly restrictive.

Leached concentration and fraction of each analyzed element gradually decrease from raw material to clinker, then to mortar except of As in availability test. Going from raw material to clinker, concentrated effect occurs because of ignition loss. Going from clinker to mortar, dilute effect exists due to sand added as aggregate. Thus, the difference of leached fractions could indicate more about the mobility of heavy metals in three types of solid materials.

In sequential extraction procedures, the chemical species or bonding forms of heavy metals change a lot in three samples. The Cf of each element in three samples indicates that all the elements are better fixed in cement products than in raw material due to calcination and hydration. To most elements, the relative metal retention is higher in mortar than in clinker. The experimental results show that incineration in cement rotary kiln and hydration with water could effectively decrease the mobility of heavy metals and then decrease the environmental impact.

Compared within the five analyzed elements, Cd is better retained and Cu is worse retained in the same kind of sample.

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