

# The leachability of heavy metals in hardened fly ash cement and cement-solidified fly ash

Qijun Yu<sup>a,\*</sup>, S. Nagataki<sup>b</sup>, Jinmei Lin<sup>c</sup>, T. Saeki<sup>c</sup>, M. Hisada<sup>d</sup>

<sup>a</sup>College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, PR China

<sup>b</sup>Research Institute for Industrial Technology, Aichi Institute of Technology, Toyota-shi 470-0392, Japan

<sup>c</sup>Department of Civil Engineering and Architecture, Niigata University, Niigata 950-2181, Japan

<sup>d</sup>Public Works Research Institute, Minamihara, Tsukuba-shi 305-8516, Japan

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## Abstract

The effect of mix proportion, leachant pH, curing age, carbonation and specimen making method etc. on the leaching of heavy metals and Cr(VI) in fly ash cement mortars and cement-solidified fly ashes has been investigated. In addition, a method for reducing the leaching of Cr(VI) from cement-solidified fly ashes is proposed. The results mainly indicate that: (1) either Portland cement or fly ash contains a certain amount of heavy and toxic metals, and the leaching of them from hardened fly ash incorporated specimens exists and is increased with fly ash addition and water to cement ratio; (2) the leachability of some heavy metals is greatly dependent on leachant pH; (3) when carbonation of cement mortars occurs the leaching of chromium ions is increased; (4) the amount of heavy metals leached from cement-solidified fly ashes depends more on the kind of fly ash than their contents in fly ash; and (5) with ground granulated blast furnace slag addition, the leaching of Cr(VI) from solidified fly ashes is decreased.

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## 1. Introduction

There is a growing interest in the environmental impacts of cement-based materials, especially for the materials in which industrial by-products are contained. Organic components in cement and in concrete admixtures, such as fly ash, slag and silica fume, are at a very low level because they have been burned away during their formation processes. The main aspect in respect of the environmental impacts of cement-based materials, therefore, is the leaching of inorganic compounds when they are contact with environmental waters, e.g. rain or groundwater. Refs. [1–4] shows that both cement and fly ash contain trace amounts of heavy metals and other toxic inorganic components, hence, will pollution occur due to the release of the metals

or components to environment, from construction works in which cement and fly ashes or fly ash containing materials are used? And another raising concern is how to prevent or reduce the release of them to environment. In this study, therefore, the leachability and leaching behavior of heavy metals and toxic Cr(VI) in fly ash cement mortars and cement-solidified fly ashes have been investigated. In addition, a method for reducing the leaching of Cr(VI) from cement-solidified fly ashes is proposed.

For assessing the leachability, leach rate and leaching mechanisms of environmentally relevant components, a number of leaching test methods are used in the world, such as the German DEV S4, Dutch NEN 7341, 7343, 7345 and 7349, French X31-210, USA's TCLP, Swiss TVA, Notification 13 and 46 specified by the Environmental Agency of Japan and British repetitive shaker test and so on. For the characterization of samples and determination of totally leachable components, an extraction test such as the method specified in Ref. [5] or the Dutch NEN 7341 availability

\* Corresponding author. Tel./fax: +86 20 8711 4233.

E-mail address: [concyuq@scut.edu.cn](mailto:concyuq@scut.edu.cn) (Q. Yu).

test—an extraction test for assessment of maximum leachability [6], is often applied. But for concrete samples, an appropriate leaching procedure should at least include a diffusion test, such as tank leaching test, because the leaching of environmentally relevant components from them is often a diffusion-dominated process [7]. In this study, therefore, the leaching of heavy metals from fly ash cement mortars was investigated by both tank leaching test and a shaken extraction test method in accordance with Ref. [5]. In addition, a modified shaken extraction test method with the advantage of leachant pH stable at  $6.6 \pm 0.3$  is proposed.

## 2. Experiments

### 2.1. Raw materials

Commercial ordinary Portland cement (JIS R 5210, OPC for short in the following), Toyoura sand, fly ash M and pure water with electric resistance over  $18.0 \text{ M}\Omega \cdot \text{cm}$  and pH of about 6.8 were used for preparing  $40 \times 40 \times 160 \text{ mm}$  mortar specimens. Toyoura sand was the standard sand used for cement mortar strength test in Japan before 1997, it is a natural silicon sand produced in Yamaguchi-ken of Japan, with residue  $<1\%$  on  $300 \mu\text{m}$  sieve,  $50 \pm 10\%$  on  $212 \mu\text{m}$  sieve and  $>95\%$  on  $106 \mu\text{m}$  sieve. In another experiment, two other fly ashes N and L, commercial B type Portland blast-furnace slag cement (JIS R 5211, BSC for short) and ground granulated blast-furnace slag (GGBFS) were used to make solidified fly ash specimens. The chemical compositions of the materials used are shown in Table 1, and trace amounts of toxic elements, such as Pb, Cr, Zn, Se and As, were observed in them (Table 2). Metals and toxic elements extracted from the cements and fly ashes by a shaken extraction test as described below are given in Table 3. From Tables 2 and 3, it can be seen that both cements and fly ashes contain a certain amount of heavy metals and toxic elements, and in some cases environmental elements

Table 1  
Chemical compositions of the materials used (%)

Oxide	OPC	BSC	GGBFS	Ash M	Ash N	Ash L
SiO <sub>2</sub>	21.26	26.10	33.90	67.70	48.50	63.10
Fe <sub>2</sub> O <sub>3</sub>	2.77	1.70	0.30	4.10	7.59	4.28
Al <sub>2</sub> O <sub>3</sub>	4.98	8.80	14.80	17.40	28.20	23.21
CaO	64.57	60.90	48.40	0.90	3.27	1.09
MgO	1.03	4.10	7.20	0.70	1.17	0.53
SO <sub>3</sub>	2.14	2.10	0.10	0.17	0.49	0.25
P <sub>2</sub> O <sub>5</sub>	— <sup>a</sup>	0.09	0.01	0.17	0.43	0.11
MnO	—	0.18	0.21	0.04	0.03	0.02
TiO <sub>2</sub>	—	0.72	1.00	0.78	1.37	1.14
Na <sub>2</sub> O	0.24	0.35	0.23	0.66	1.41	0.69
K <sub>2</sub> O	0.47	0.35	0.24	0.90	1.56	0.96
LOI <sup>b</sup>	2.04	1.00	0.0	6.10	7.10	3.90

<sup>a</sup> Undetected.

<sup>b</sup> Loss on ignition.

Table 2

Amount of heavy metals in the materials used (mg/kg)<sup>a</sup>

Metal	Cd	Pb	Cr	Mn	Cu	Zn	As	Se
OPC	0.60	240	80	150	51	60	15	1.5
BSC	0.50	150	60	1410	76	290	13.8	1.4
Ash M	0.10	50	90	150	51	60	15	1.5
Ash N	0.12	45	60	270	60	60	18	5.1
Ash L	0.10	24	58	160	25	30	5.2	5.2

<sup>a</sup> Decomposed with HNO<sub>3</sub>/HCl=1:2 (v/v) solution at 200 °C for 20 h, then analyses were done by ICP-AES.

leached from them, such as Cr, Cr(VI), Pb, Se and As, are with high concentration.

### 2.2. Specimen preparation

In the preparation of cement mortar prisms of  $40 \times 40 \times 160 \text{ mm}$ , one kind of water reducing agent was used to regulate the flow of all the mortars within  $200 \pm 10 \text{ mm}$ . After demoulding, the specimens were cured in an air chamber at  $22 \pm 2 \text{ °C}$  at relative humidity (R.H.)  $>90\%$  to definite ages (28, 91, 180 and 360 days). Table 4 gives the mixture proportions and compressive strength of cement mortars at the age of 28 days. Besides, some specimens, after cured for 28 days under the same condition, were subjected to carbonation at  $5 \pm 0.2\%$  CO<sub>2</sub> concentration,  $20 \pm 1 \text{ °C}$  and R.H. of about 50% until wholly carbonated.

According to Table 5, fly ash N and L, BSC and GGBFS were weighed and mixed, then according to JIS A 1210 the mixtures were consolidated into cylinders of  $\phi 100 \times 127 \text{ mm}$  (Fig. 1) at the optimum moisture content (OMC for short in the following) and demoulded after 24 h. Besides, the mixtures were made to slurry with flow of about 240 mm. All the specimens were wet cured for 3, 7, 28 and 91 days at  $22 \pm 2 \text{ °C}$ .

Table 3

Metals in shaken extraction leachates of OPC, BSC and fly ash ( $\mu\text{g/L}$ ) and leached fractions (%)

Metal	OPC	BSC	Ash M	Ash N	Ash L	Metal	OPC	Ash M
Cr	1611 (5111) <sup>b</sup> 20.1% <sup>c</sup>	— <sup>a</sup> — —	18 (6) 0.2%	197 — 3.3%	100 — 1.7%	V	9 (251)	256 (333)
Cr(VI)	1240	0.89	16	180	79	Co	9 (11)	3 (19)
Cd	2 (6) 3.3%	N <sup>d</sup> — 0%	3 (2) 30%	N — 0%	N — 0%	Ni	8 (12)	15 (83)
Pb	41 (71) 0.17%	2 — 0.01%	19 (18) 0.4%	N — 0%	N — 0%	Cu	24 (16)	N (13)
As	— — —	N 0% —	— 8 —	8 10 0.4%	10 1.9%	Mn	20 (41)	34 (114)
Se	— — —	9 6.4% —	— — —	84 16.5% 20.4%	106 — —	Zn	10 (15)	N (12)

<sup>a</sup> —: undetected.

<sup>b</sup> Data in brackets are concentrations of the leachants with CO<sub>2</sub> bubbling.

<sup>c</sup> Leached fraction by mass percentage.

<sup>d</sup> N: below analytical detection limit.

Table 4

Proportions and properties of cement mortars with fly ash M replacement

Specimen	A	B	C	D	E	F
w/b (water/OPC+fly ash)	0.50	0.60	0.50	0.60	0.50	0.60
s/b (sand/OPC+fly ash)	1.60	2.00	1.60	2.00	1.60	2.00
Fly ash M (%)	0	0	25	25	40	40
Flow (mm)	193	200	201	207	203	210
Compressive strength (MPa)	51.5	43.7	26.3	22.6	19.2	12.8

Specimens used for shaken extraction test were previously size reduced to 1–5 mm for cement mortar specimens and less than 2 mm for solidified fly ash specimens, and dried at  $60 \pm 2$  °C for 24 h, then evacuated for 2 h.

### 2.3. Leaching tests and analysis of heavy metals

#### 2.3.1. Tank leaching test

Tank leaching test was performed at  $22 \pm 1$  °C, using pure water as leachant. Three  $40 \times 40 \times 160$  mm mortar prisms aged for 28 days were placed in a tank in which leachant was filled to achieve  $V_L/V_S=3.00$  (Fig. 2). The leachate was removed and replaced every 3 days for the first 21 days, every 7 days for the next 14 days, then every 14 days. After 100 days, the leachate was renewed every 28 days. The same volume of leachant was used for each renewal.

#### 2.3.2. Shaken extraction test

In this test, crushed cement mortar specimens and solidified fly ashes with size as shown above were used. Pure water, adjusted to pH 6.2 with dilute HCl solution, was served as leachant with leachant volume (mL) to sample mass (g) ratio of 10.0 [5]. Shaking was commenced continuously for 6 h at 250 cycles per minute with amplitude of 50 mm (Fig. 3). For preventing leachant pH from increasing, Glasser et al. applied a method of continuously bubbling CO<sub>2</sub> into leachant in a long-term leach test of cement-stabilized MSWAF paste [8]. This method, as shown in Fig. 3, was also used in this experiment. CO<sub>2</sub> at 0.1 N/mm<sup>2</sup> was bubbled into the shaken leachants of cement mortars at a rate of about 0.04 L/min in respect to 100 ml of leachant; as a result, the pH of all leachants were kept at  $6.6 \pm 0.3$  throughout the extraction process. The other conditions were the same as before.

Table 5

Proportions of fly ash specimens

Specimen	Mixture proportion	Water to binder ratio (%)			
		OMC		Slurry	
		FA-N	FA-L	FA-N	FA-L
K1	100%FA <sup>a</sup>	27.5	31.3	55.5	60.5
K2	94%FA+6%BSC	27.1	30.7	54.7	60.2
K3	88%FA+6%BSC+6%GGBFS	26.8	30.5	53.6	59.6
K4	82%FA+6%BSC+12%GGBFS	26.6	29.6	52.7	58.6

<sup>a</sup> FA: fly ash.



Fig. 1. Soil consolidation device (JIS A 1210).

#### 2.3.3. Analysis of heavy metals in leachates

The leachates obtained both from the tank leaching and shaken extraction tests were filtered to remove particulates and larger colloids using 0.45-μm membrane filter and, after measurement of pH, acidified with HNO<sub>3</sub> solution to pH 0.9–1.1. Cr, Mn, Cu, Zn, Cd and Pb were analyzed by means of an ICP-AES, to which an ultrasonic nebulizer was attached. 0.1 mg/L yttrium solution was used as an internal standard. Each leachate was analyzed at least two times; data without large deviation from means were averaged. The concentration of Cr(VI) in leachate was measured with a Hach DR/4000 Spectrophotometer.

## 3. Results and discussions

### 3.1. Tank leaching test

In the tank leaching test, the pH of each leachate, varying with proportion of cement mortars and the interval of leachant renewal, was between 10 and 12 when using pure water as leachant. The cumulative leached heavy metals during a leaching period of 132 days, expressed as mg per m<sup>2</sup> of specimen surface and against the logarithmic leaching time (hour), is shown in Fig. 4, and the total amount and fraction of heavy metals leached from the tested specimens are given in Figs. 5 and 6. The amount of leached Mn, Zn



Fig. 2. Tank leaching test.

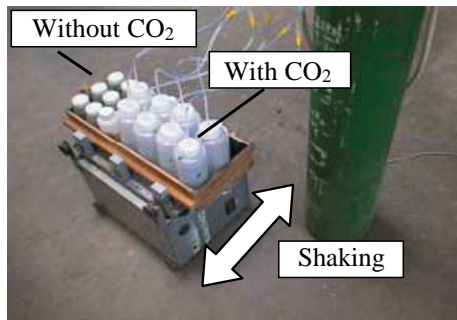


Fig. 3. Shaken extraction test.

and Cd from the specimens immersed in water was very low, sometimes not exceeding the analytical detection limit of the ICP instrument used. It can be seen that: (1) heavy metals do leach out both from OPC mortars and fly ash cement mortars; (2) leached heavy metals is increased with fly ash replacement and water to binder (OPC+fly ash) ratio (w/b); (3) cumulative leached amount is proportional to logarithmic leaching time although there are irregularities, which means that the leaching of heavy metals from cement mortars is a diffusion controlled process; (4) the slope of the leach curve varies greatly with the kind of metal, that is to say different metals have different leachabilities; and (5) the leaching of Pb in pure water from mortar A and B seems to be a delayed diffusion controlled process.

Nagataki et al. observed that the leaching of some heavy metals in mortar specimens mainly occurred during the first 30 days of immersion; thereafter the leaching rate is greatly reduced [9]. Data in Fig. 6 show that except for cadmium, up to 132 days cumulative leached metals only account for a small fraction of metals originally contained in the binders (OPC+fly ash), with most of heavy metals being retained in specimens. These results indicate that in the course of testing, leaching of heavy metals only occurs from the surface layers of specimens, as shown in Fig. 7. For the release of metals in the inner part of specimen to outer environment, much more time is required because of the difficulty in diffusion, the fixation effect of cement hydrates and the reduced leachability of most heavy metals under the high pH condition in the inner part of specimen [10–17].

### 3.2. Shaken extraction tests

#### 3.2.1. Effect of CO<sub>2</sub> access on the leaching of heavy metals in fly ash cement mortars

In the shaken extraction test, the leachability of heavy metals also varies with the kind of metals, w/b, fly ash replacement and leachant pH. The results of cement mortars with age of 28 days are given in Table 6. Without the intrusion of CO<sub>2</sub> to shaken leachants, the pH of all the obtained leachates were greater than 12 and the concentrations of Mn in the leachates fell below the analytical detection limit of the instrument used. After introducing CO<sub>2</sub> to the shaken leachant, leachate pH decreased to

$6.6 \pm 0.3$ ; at the same time the leaching of heavy metals, particularly that of Mn and Zn, was much increased. An advantage of this method is that leachant pH is kept constant and close to 7; hence the influence of leachant pH variation on the leachability of heavy metals is reduced. Another advantage is that the pH is close to the pH in nature. The leaching of heavy metals in the presence of CO<sub>2</sub> is realistically encountered on site as rain and groundwater often contain CO<sub>2</sub>. In shallow burial in temperate soils, high  $P_{CO_2}$  may exist due to biogenic production of CO<sub>2</sub> [8].

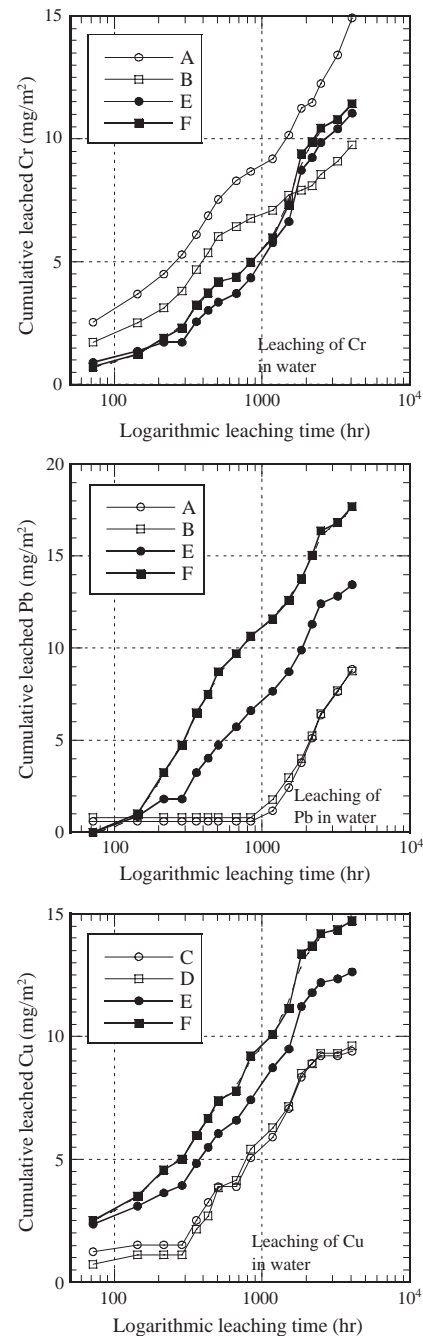


Fig. 4. Leached Cr, Pb and Cu from cement mortars independence on leaching time in tank leaching test.



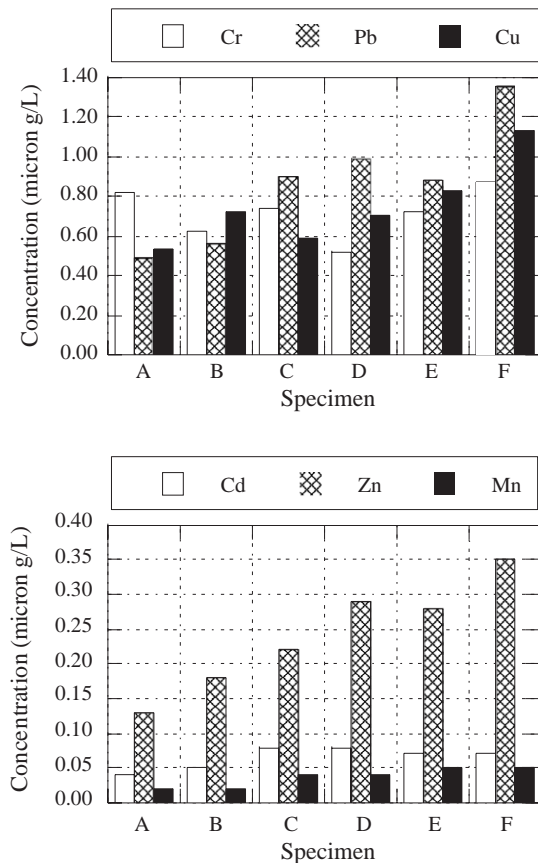


Fig. 5. Total leached heavy metals up to 132 days from cement mortar specimens (mg/kg-OPC+fly ash).

### 3.2.2. Leaching behaviors of heavy metals in long-term cured and carbonated cement mortars

Generally speaking, in shaken extraction test the leaching of heavy metals from fly ash cement mortar also increases with fly ash replacement and w/b (Table 6). Even though a considerable amount of leachable Cr and Cr(VI) exists in the OPC (Table 3), chromium leaching is much reduced

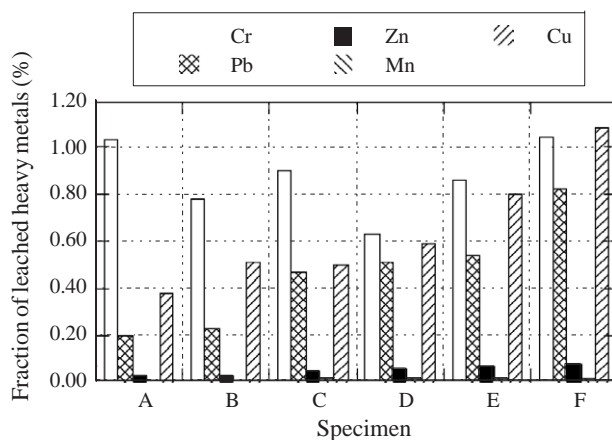


Fig. 6. Fraction of cumulatively leached heavy metals from cement mortar specimens up to 132 days (%).

after hardening and furthermore, especially for Cr(VI), leaching is decreased with curing time.

Table 6 also shows that after carbonation, leached Cr and Cr(VI) are much increased. It has been found that C–S–H gel and AFt have a large capacity to fix and adsorb Cr ions [10–15]. Therefore, the increased leaching of Cr and Cr(VI) seems to be related to the decomposition of C–S–H gel and AFt in mortars caused by carbonation.

### 3.2.3. Leaching behaviors of heavy metals in solidified fly ashes

The amount of heavy metals leached from solidified fly ashes is mainly dependent on the kind of fly ash in spite of their original contents in fly ash, for example, leached Cr from solidified fly ash L was much lower than that from solidified fly ash N even though N and L are nearly equivalent in Cr content (Table 2). This shows that the leachability of heavy metals in fly ash is a complicated matter. The source of coal, combustion condition of coal in furnace and capturing method of fly ash have great influence on the chemical, mineral compositions, content of crystalline phase, particle size, surface structure and reactivity of fly ash and result in different leachability of the same heavy metal but in different fly ashes.

In general, fly ash slurry specimens are with a higher leachability of heavy metals than the specimens solidified at OMC. Compared to slurry specimens, specimens consolidated under OMC condition are more compact and with higher strength, which are helpful to reduce leaching. But contrary to this, in the presence of cement addition less Cr is extracted from slurry specimens than from OMC specimens (Tables 7 and 8). The possible reasons for this are: (1) presence of cement is effective in immobilizing chromium ions due to the following effects: adsorbing Cr in C–S–H gel; precipitating with calcium or silicate compounds and forming chromium containing calcium sulfoaluminate hydrates [10–12]. Compared to OMC specimen, more cement particles will hydrate in slurry specimen due to the high water content, thus leading to reduced leaching of chromium; and (2) chromium containing compounds existing in the surface layer of fly ash particles become easy to separate from fly ash particles

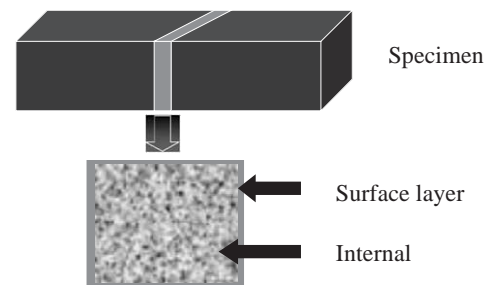


Fig. 7. Schematic drawing of the leaching of heavy metal from concrete specimen.

Table 6  
Heavy metals in shaken leachates<sup>a</sup> of fly ash cement mortars (μg/L)

Sample	Cd			Pb			Co			Cr			Cr(VI)			Zn			Cu			Mn		
	28 days	91 days	180 days	Carbonated	28 days	91 days	180 days	Carbonated	91 days	28 days	91 days	180 days	Carbonated	91 days	180 days	Carbonated	28 days	91 days	180 days	Carbonated	28 days	91 days	180 days	
A Without CO <sub>2</sub>	3	N <sup>b</sup>	N	N	36	28	23	24	32	4	4	4	4	64	78	87	67	245	55	30	32	178	9	5
B	4	N	N	N	38	25	25	28	27	4	4	5	4	59	92	115	89	390	58	66	43	238	8	4
C	— <sup>c</sup>	N	N	N	—	22	19	16	29	33	20	15	9	—	78	61	73	323	60	40	17	296	—	—
D	—	N	N	N	—	21	19	15	27	35	24	17	9	—	95	86	55	444	76	50	17	436	—	—
E	3	N	N	N	33	17	18	14	57	41	28	16	11	92	84	78	82	480	61	45	43	448	6	20
F	3	N	N	N	33	21	17	14	30	45	3	21	12	99	84	83	125	480	67	60	49	455	7	14
A With CO <sub>2</sub>	4	4	4	2	61	33	35	33	45	5	5	4	9	117	94	73	54	201	88	68	56	164	85	8
B	5	4	4	2	70	39	36	39	41	6	5	5	10	150	105	91	96	295	91	88	57	226	124	35
C	—	4	4	2	—	37	39	41	43	8	8	9	9	—	119	74	72	327	151	92	43	299	—	—
D	—	4	4	3	—	41	39	35	44	9	8	8	13	—	154	103	119	433	—	94	60	420	—	—
E	3	4	4	3	61	38	38	39	11	9	10	15	16	130	103	101	109	499	158	90	70	472	109	49
F	3	4	4	4	55	36	38	40	52	9	10	12	15	171	147	154	157	458	135	106	90	401	142	38

<sup>a</sup> In the presence of CO<sub>2</sub> bubbling, pH of leachates was kept at 6.3–6.7, while without CO<sub>2</sub> bubbling pH was over 12.5.

<sup>b</sup> N: below analytical detection limit.

<sup>c</sup> Undetected.

Table 7

Concentrations of metals in the shaken leachants of solidified fly ash N<sup>a</sup> (μg/L)

Sample	CO <sub>2</sub>	pH	Zn	Cr	Cu	Mn	Cd	Pb
K1-O <sup>b</sup>	Without	9.9	4	325	N <sup>c</sup>	1	N	14
K2-O	Without	11.3	7	84	N	1	N	14
K3-O	Without	11.6	6	65	N	1	N	16
K4-O	Without	11.8	8	29	N	1	N	16
K1-O	With	6.9	42	366	7	280	7	42
K2-O	With	6.3	69	11	17	1766	6	62
K3-O	With	6.4	35	10	23	1623	5	54
K4-O	With	6.3	44	8	40	1919	5	58
K1-S <sup>d</sup>	Without	9.9	3	269	N	1	2	20
K2-S	Without	11.0	4	72	N	1	N	16
K3-S	Without	11.4	5	44	N	1	N	16
K4-S	Without	11.6	6	24	N	1	N	14
K1-S	With	6.9	36	270	7	228	6	37
K2-S	With	6.6	45	70	13	1160	6	57
K3-S	With	6.4	47	3	10	11 <sup>e</sup>	4	40
K4-S	With	6.4	31	3	11	11 <sup>e</sup>	4	39

<sup>a</sup> Aged for 28 days.

<sup>b</sup> OMC specimen.

<sup>c</sup> N: below analytical detection limit.

<sup>d</sup> Slurry specimen.

<sup>e</sup> Abnormal data, possibly caused by the failure in the pretreatment of the solution for Mn detection.

by the force exerted on fly ash particles during the OMC consolidation procedure.

After the intrusion of CO<sub>2</sub> to leachant, leachant pH was decreased; at the same time more leaching of metals, especially for that of Mn, much more occurred (Tables 7 and 8).

The leaching of heavy metals, especially for that of Cr, from solidified fly ashes, was reduced by BSC addition, and it was further decreased when both BSC and GGBFS were added.

### 3.2.4. Environmental considerations

Zn, Cu, Mn and Cd concentrations of all the shaken leachates are below the permissible concentration limits for waters (ground water, surface water and tap water) and farmland soil specified by the Chinese Standards and Notifications No. 10, 1997 and No. 46, 1991 of the Environmental Agency of Japan (Table 9). Cr, Cr(VI) and Pb concentrations can meet the requirement of the standards and notifications for industrial wastewater discharge. After 1-year curing, leached Cr(VI) from fly ash cement mortars is below 0.05 mg/L, being in conformity to the standards for waters protection of the both countries. However, Pb concentration of all the leachates exceeds the critical limit of 0.01 mg/L for waters specified by the both countries. Attention should be paid to it and further studies are needed.

Due to the uncertain and varying application purposes of cement-based products, the authors consider that the following leaching procedures should be contained in the evaluation of their environmental impacts: (1) a test procedure to observe the leaching of heavy metals in cement-based products under acidic conditions because

Table 8

Concentrations of metals in the shaken leachants of solidified fly ash L<sup>a</sup> (μg/L)

Sample	CO <sub>2</sub>	pH	Zn	Cr	Cu	Mn	Cd	Pb
K1-O <sup>b</sup>	Without	9.6	3	14	N	1	N <sup>c</sup>	10
K2-O	Without	11.0	3	28	N	1	N	14
K3-O	Without	11.5	6	25	N	1	N	15
K4-O	Without	11.5	6	14	N	1	N	16
K1-O	With	6.3	53	8	5	88	5	37
K2-O	With	6.3	130	12	13	1584	5	63
K3-O	With	6.3	46	11	12	1642	4	59
K4-O	With	6.3	50	12	13	2023	5	64
K1-S <sup>d</sup>	Without	9.7	3	43	N	1	N	12
K2-S	Without	10.9	4	22	N	1	N	16
K3-S	Without	11.2	3	18	N	1	N	15
K4-S	Without	11.6	6	6	N	1	N	15
K1-S	With	6.9	52	6	4	115	6	30
K2-S	With	6.6	132	13	13	1809	5	69
K3-S	With	6.4	50	31	7	1834	3	35
K4-S	With	6.4	45	12	15	1440	4	60

<sup>a</sup> Aged for 28 days.<sup>b</sup> OMC specimens.<sup>c</sup> N: below analytical detection limit.<sup>d</sup> Slurry specimens.

sometimes or in some cases they are exposed to acidic environments, e.g. acidic rains or acidic soils; (2) a comprehensive method to investigate the leaching of heavy metals and toxic components accompanied by degradation, aging and the leaching of cementing components, such as Ca, Al and Si, etc. The latter is helpful to understand the leaching mechanism of heavy metals under varying conditions, and to make a comprehensive judgment of the environmental impact of cement-based products during their service life or any secondary service life.

#### 4. Conclusions

The following remarks are commonly applied to the leaching of heavy metals both in cement mortars and

cement-solidified fly ashes: heavy metals do leach from cement mortars and solidified fly ashes; the leachability of the tested heavy metals in this study bears largely on leachant pH and leaching test method; at lower pH enhanced leaching of heavy metals occurs, but the influence degree of leachant pH on leachability is dependent on particular metal; concentrations of Zn, Cu and Cd in the leachates, either of cement mortars or of solidified fly ashes, can meet the relevant standards of Japan and China, leached Cr(VI) from cement mortars with age of 1 year, being below 0.05 mg/L, is in conformity to the standards for waters protection of the two countries. Some other observations and remarks of this study are listed below:

- (1) Amount of heavy metals leached from cement mortars is increased with fly ash addition and w/b. Increased leaching of Cr will take place in carbonated mortars. Compared with tank leaching method, shaking test method can extract more toxic heavy metals from hardened mortars.
- (2) The amount of heavy metals leached from cement-solidified fly ashes depends more on the kind of fly ash than their contents in fly ash. Generally speaking, leached heavy metals from solidified fly ash slurry specimens are more than those from the specimens solidified at OMC. But the leaching of Cr is an exception of it.
- (3) With BSC and GGBFS addition, the leaching of Cr from solidified fly ashes is decreased.
- (4) Continuously bubbling CO<sub>2</sub> into leachant in shaken extraction test makes leachant pH remain constant at 6.6±0.3, leading to diminished interference of leachant pH variation on the leachability of heavy metals, especially the metals contained in the materials with cement addition. Compared with the shaken extraction test methods, currently used in Japan and China, it gives a more severe and reliable estimation of the

Table 9

Permissible metal concentrations in waters and in soils specified in Chinese and Japanese relevant standards (mg/L)

Element		Total Cr	Cr(VI)	Mn	Fe	Cu	Zn	As	Se	Cd	Total Hg	Pb
China <sup>a</sup>	Ground water (Type III)	— <sup>b</sup>	≤0.05	≤0.1	≤0.3	≤1.0	≤1.0	≤0.05	≤0.01	≤0.01	≤0.001	≤0.05
	Surface water (Type III)			—	—					≤0.005	≤0.0001	
	Soil (mg/kg)	≤90	—	—	—	≤35	≤100	≤15	—	≤0.2	≤0.15	≤35
	Discharged waste water	≤1.5	≤0.5	≤2.0	—	≤0.5	≤2.0	≤0.5	—	≤0.1	≤0.05	≤1.0
Japan <sup>c</sup>	Ground water	—	<0.05	—	—	—	—	<0.01	<0.01	<0.01	<0.0005	<0.01
	Tap water			<sup>d</sup>								
	Soil			<0.05	<0.3	<1.0	<1.0	<0.01 <sup>e</sup>		<0.01 <sup>f</sup>		<0.05
	Discharged waste water	<2.0	<0.5	<10.0	<10.0	<3.0	<5.0	<0.1	<0.1	<0.1	<0.005	<0.1

<sup>a</sup> Refs.: The Chinese Standards: GB 14848-1993, GB 3838-2002, GB 8978-1996 and GB 15618-1995.<sup>b</sup> Unspecified.<sup>c</sup> Refs.: The Environmental Agency of Japan, Specification for Groundwater Preservation (Notification No. 10, 1997) and Specification for Soil Preservation (Notification No. 46, 1991).<sup>d</sup> <125 mg per 1 kg of farmland soil.<sup>e</sup> Coherently <15 mg in 1 kg of farmland soil.<sup>f</sup> Coherently <1 mg in 1 kg of farmland soil.

environmental impact of heavy metals in cement-based materials.

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