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

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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.

Keywords: Toxic metal; Leaching; Heavy metals; Cement; Fly ash

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

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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±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 M$\Omega \cdot$cm and pH of about 6.8 were used for preparing 40×40×160 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 μm sieve, 50±10% on 212 μm sieve and >95% on 106 μm 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 been seen that both cements and fly ashes contain a certain amount of heavy metals and toxic elements, and in some cases environmental elements leached from them, such as Cr, Cr(VI), Pb, Se and As, are with high concentration.

Table 1
Chemical compositions of the materials used (%)

Oxide	OPC	BSC	GGBFS	Ash M	Ash N	Ash L
SiO_2	21.26	26.10	33.90	67.70	48.50	63.10
Fe_2O_3	2.77	1.70	0.30	4.10	7.59	4.28
Al_2O_3	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_3	2.14	2.10	0.10	0.17	0.49	0.25
P_2O_5	–[a]	0.09	0.01	0.17	0.43	0.11
MnO	–	0.18	0.21	0.04	0.03	0.02
TiO_2	–	0.72	1.00	0.78	1.37	1.14
Na_2O	0.24	0.35	0.23	0.66	1.41	0.69
K_2O	0.47	0.35	0.24	0.90	1.56	0.96
LOI[b]	2.04	1.00	0.0	6.10	7.10	3.90

[a] Undetected.
[b] Loss on ignition.

Table 2
Amount of heavy metals in the materials used (mg/kg)[a]

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

[a] Decomposed with HNO_3/HCl=1:2 (v/v) solution at 200 °C for 20 h, then analyses were done by ICP-AES.

2.2. Specimen preparation

In the preparation of cement mortar prisms of 40×40×160 mm, one kind of water reducing agent was used to regulate the flow of all the mortars within 200±10 mm. After demoulding, the specimens were cured in an air chamber at 22±2 °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±0.2% CO_2 concentration, 20±1 °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 ϕ 100×127 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±2 °C.

Table 3
Metals in shaken extraction leachates of OPC, BSC and fly ash (μg/L) and leached fractions (%)

Metal	OPC	BSC	Ash M	Ash N	Ash L	Metal	OPC	Ash M
Cr	1611	–[a]	18	197	100	V	9	256
	(5111)[b]	–	(6)	–	–		(251)	(333)
	20.1%[c]	–	0.2%	3.3%	1.7%	Co	9	3
Cr(VI)	1240	0.89	16	180	79		(11)	(19)
Cd	2	N[d]	3	N	N	Ni	8	15
	(6)	–	(2)	–	–		(12)	(83)
	3.3%	0%	30%	0%	0%	Cu	24	N
Pb	41	2	19	N	N		(16)	(13)
	(71)	–	(18)	–	–	Mn	N	10
	0.17%	0.01%	0.4%	0%	0%		(14)	(208)
As	–	N	–	8	10	Zn	20	34
	–	0%	–	0.4%	1.9%		(41)	(114)
Se	–	9	–	84	106	Ti	10	N
	–	6.4%	–	16.5%	20.4%		(15)	(12)

[a] –: undetected.
[b] Data in brackets are concentrations of the leachants with CO_2 bubbling.
[c] Leached fraction by mass percentage.
[d] N: below analytical detection limit.