



Leaching behavior of heavy metals from municipal solid wastes incineration (MSWI) fly ash used in concrete

Hui-Sheng Shi^{a,b,*}, Li-Li Kan^b

^a Key Laboratory of Advanced Civil Engineering Materials of Education Ministry, Tongji University, Shanghai 200092, China

^b Institute of Environmental Materials, Tongji University, Shanghai 200092, China

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ABSTRACT

The characteristics of municipal solid waste incineration (MSWI) fly ash, surface leaching toxicity and successive leaching concentration of heavy metals from MSWI fly ash–cement hardened pastes were studied. And, the relationships between leaching concentrations of heavy metals and leaching time were also discussed. Experimental results showed that immobilization effect of cement on MSWI fly ash is good. Even if MSWI fly ash–cement hardened pastes were damaged, the leaching toxicity is still in a safety range. In early leaching stage, the surface leaching rate is relatively a little high, up to 10^{-5} – 10^{-4} cm d⁻¹ order of magnitude, in the later time of leaching, its rate rapidly declined, down to 10^{-7} . Most of leached heavy metals are produced at early ages. The leaching concentration of heavy metals and leaching time has strong positive relationships. In factual utilizing circumstances, heavy metals' leaching from MSWI fly ash–cement hardened pastes is a very slow and gradually diluting process. The leaching toxicity of heavy metals is far lower than that of the National Standard of China, and minimum harmful matters can be contained and released in the environment. Reusing of MSWI fly ash as partial replacement for cement in concrete mixes is potentially feasible.

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1. Introduction

With the rapid development of municipal construction, management and treatment of municipal solid waste (MSW) has taken more and more importance. In China, it is estimated that 200 million tons of MSW is generated annually, accounting for 29% of the total world MSW production [1]. Landfills are known to be the more expedient, inexpensive method to dispose of MSW. However, this simple method has caused various problems such as groundwater pollution from landfill leachate, odor emission and soil contamination [2]. Moreover, spaces for landfills have becoming increasingly limited, especially in countries with a large population. Thus, in recent years, municipal solid waste incineration (MSWI) has become a popular method to treat MSW in places such as Japan and several European countries as the method has the merits of volume reduction up to 90% [3,4] and recovery of much of the energy in the waste [5,6]. During the incineration, most MSW is converted to combustion residues such as fly and bottom

ash. Based on composition, incineration temperature and time, the residue varies from 5% to 30% of the weight before incineration. The fly ash and scrubber ash from the MSW incinerator contain various hazardous element such as easily leachable heavy metals, soluble salts and organic compounds, so it is regarded as a serious threat against surrounding [7,8]. Since these elements in fly ash are present in more soluble forms than in bottom ash, the latter is less likely to leach these elements [9], so the treatment and disposal of fly ash is more urgent and necessary.

At present, various methods of treating MSWI fly ash such as melting, solidification/stabilization (S/S), acid extraction, vitrification and sintering have been used to treat MSWI fly ash [10–15]. Among them, the most frequently applied approach to minimize the environmental impact of MSWI fly ash is the S/S technology that gives also the possibility of reusing the final materials [16–18]. S/S treatment often involves the addition of some additives to fix or encapsulate hazardous materials inside agglomerate. In the past few decades, the most widely used S/S systems are the cement-based materials [19]. A major factor is that cement is easy to form a durable, monolithic material that will not easily leach hazardous components under the disposal conditions [20,21]. American State Bureau of Environmental Protection refers to cement immobilization as the best technology to dispose the poisonous and harmful wastes [22].

* Corresponding author at: Key Laboratory of Advanced Civil Engineering Materials of Education Ministry, Tongji University, Shanghai 200092, China.

Tel.: +86 21 65982939; fax: +86 21 65985385.

E-mail address: shs@mail.tongji.edu.cn (H.-S. Shi).

Table 1
Main chemical composition of MSWI fly ash and OPC (wt.% by weight)

Sample	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	SO ₃	Cl ⁻	f-CaO	Loss
OPC ^a	20.60	3.33	5.37	0.23	0.61	1.53	64.20	2.19	0.50	0.20	1.85
MSWI ^b fly ash	24.50	4.01	7.42	4.00	4.60	2.72	23.37	12.03	10.00	1.50	22.04

^a Ordinary Portland Cement.

^b Municipal solid waste incineration.

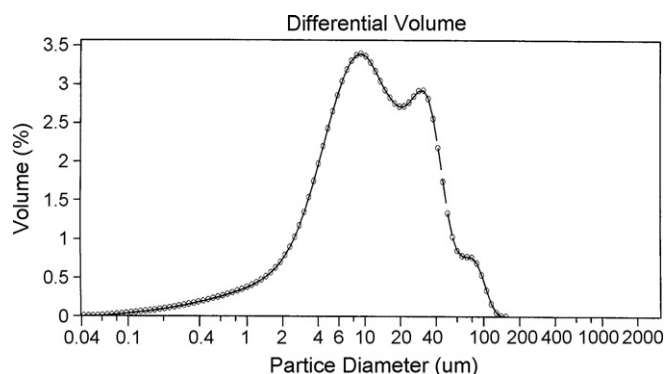


Fig. 1. Particle size distribution of MSWI fly ash.

Although cement S/S is a technology applied for MSWI fly ash treatment, it can also be oriented to promote its reuse. The potential for MSWI fly ash application in concrete is a replacement of cement. Our previous study [23] confirms that the MSWI fly ash contains some quantities of typical cement minerals and has certain cementitious activity. The incorporation of MSWI fly ash slightly retards cement hydration, but the ettringite can be found during the hydration process which is beneficial to strength development.

Therefore, in view of recycling of MSWI fly ash as a replacement for cement in concrete mixes, the characteristics and heavy metals content of MSWI fly ash, leaching toxicity and surface leaching behavior of heavy metals from MSWI fly ash-cement hardened pastes were investigated in this research.

2. Experimental

2.1. Raw materials and preparation

MSWI fly ash was originated from Shanghai Yuqiao Wastes Incineration Plant. Prior to mixing with cement, the MSWI fly ash was ball-milled to specific surface of 360 m²/kg. A class P II 52.5 Ordinary Portland Cement (OPC) from Anhui (province in PR China) Conch Cement Co., Ltd. is used in this study. The chemical compositions of MSWI fly ash and OPC are given in Table 1. The particle size distribution of MSWI fly ash is given in Fig. 1. As shown in Fig. 1, more than 90% of particles have a smaller size of 40 μm, and the average particle size attains 11.25 μm.

Table 2
Leaching toxicity of MSWI fly ash

Element	Leaching concentration in the leachate (mg/L)	Content of heavy metals in MSWI fly ash (mg/kg)	Leaching ratio (%)	Leaching limit concentration of solid wastes in China Standard (mg/L) [25]
Zn	56.11	3269	17.2	50
Pb	26.47	1515	17.5	3.0
Cu	8.17	563.2	14.5	50
Cd	1.62	36.71	44.1	0.3
Cr	2.47	157.0	15.7	1.5

2.2. Experimental

2.2.1. Surface leaching toxicity of heavy metals in MSWI fly ash-cement hardened pastes

The leachability of matrices is an important index to evaluate the adsorption behavior and immobilizing effect. The leaching rates of immobilizing matrices were carried out by using the method recommended by the Chinese National Standard GB 7023-86 (national standard for long-term leach testing of solidified radioactive waste forms). According to the standard method, the specimens containing 40% MSWI fly ash and 60% OPC were made into the cylinder of 70 mm in diameter × 30 mm in height and cast and remained in molds for 24 h, then, demoulded and kept in a curing room at a temperature of 20 ± 2 °C and relative humidity at 90 ± 5% for 28 d. Then, the specimens hung by a thread were immersed into the distilled water solution in a 1000-mL-columned Teflon container at 25 °C for different duration times of 3, 7, 28 and 60 d (the ratio of surface area of specimen to volume of distilled water is 1:10). The leachability of matrices is expressed by the leaching rate R (cm d⁻¹) in the following equation.

$$R_n^i = \frac{A_n^i/A_0^i}{(F/V)t_n} \quad (1)$$

Where i is the heavy metals ion in MSWI fly ash-cement matrices, A_n^i is the mass of leached heavy metals ion at certain period (g), A_0^i is the mass of initial addition for heavy metals ion in the specimen (g), F is the surface area of the specimen (cm²), V is the volume of the specimen (cm³) and t_n is the leaching time.

Diffusion coefficient D_a (cm²/s) was calculated by the following equation.

$$D_a = \pi \left[\frac{A_n^i V}{A_0^i F \Delta t_i} \right]^2 t_n \quad (2)$$

Where D_a is the apparent diffusion coefficient (cm²/s); V is the volume (cm³); Δt_i is the total leaching time (s) and t_n is the duration leaching time.

2.2.2. Leaching toxicity test of heavy metals in MSWI fly ash-cement hardened pastes

20 mm × 20 mm × 20 mm cube specimens with 40% MSWI fly ash are made in accordance with Chinese National Standard GB/T 1346-2001. Casting under sealed condition for 28 d, then successive leaching concentrations of heavy metals in cement hardened pastes of 4–72 h were tested. The leachate was prepared based on Chinese National Standard GB 5086.2-1997 (solid

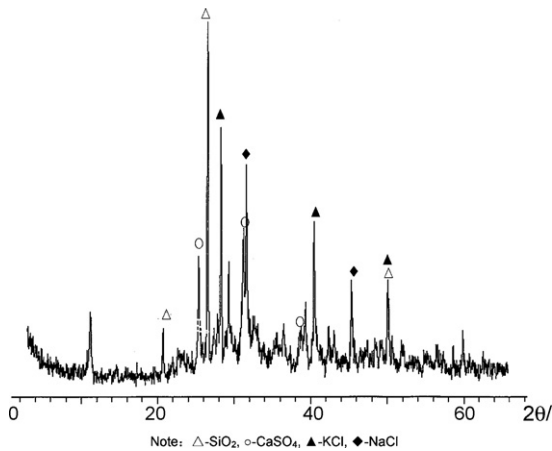


Fig. 2. XRD diffraction pattern of MSWI fly ash.

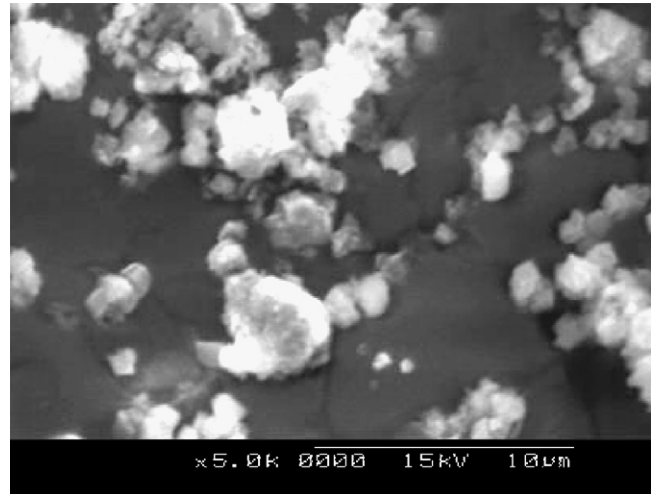


Fig. 3. SEM figure of MSWI fly ash.

waste-extraction procedure for toxicity of solid waste-horizontal vibration method). 100 g coarse grains below 5 mm were placed into a 2000-mL-lidded polythene bottle containing 1000 mL of distilled water. The suspension was fixed onto a horizontal vibrator and shook at the frequency of 110 ± 10 times per min and with an amplitude of 40 mm. Then, the solution was filtrated with a medium-speed quantitative filter paper. The concentrations in the filtrate (pH adjusted to 5.8–6.3 with sodium hydroxide or hydrochloric acid) were determined by inductively coupled plasma (ICP).

3. Results and discussion

3.1. Characteristics of MSWI fly ash

3.1.1. Analysis of chemical properties and components

In this study, MSWI fly ash is from scrubber after incineration of MSW. As shown in Table 1, it is evident that its main chemical compositions are CaO, SiO₂, Al₂O₃ and Fe₂O₃, which is quite similar to those of complementary cementitious materials presently commonly used such as granulated blast-furnace slag and fly ash produced by burning pulverized coal in power stations. As presented in Table 2, MSWI fly ash includes such harmful high content heavy metal as Zn, Pb, Cu, Cd and Cr.

XRD diffraction pattern of MSWI fly ash was shown in Fig. 2. We can find that the main minerals of MSWI fly ash include: SiO₂, NaCl, KCl, CaSO₄, etc., which is consistent with other research [24]. Fig. 3 is a picture of MSWI fly ash by scanning electron microscope. From it, we can know that MSWI fly ash has various shapes, but is not mainly made up of spherical particles like coal fly ash and quite a few MSWI fly ash are amorphous. The MSWI fly ash seems to have same micrograph as silicon fume or calcined clay.

3.1.2. Leaching toxicity of the heavy metals in the MSWI fly ash

Table 2 also provides an experimental result regarding leaching toxicity of heavy metals in MSWI fly ash. As reported in Table 2, it contains a certain amount of harmful heavy metals that can be leached by water. The concentrations of Zn, Pb, Cd and Cr in the leachate greatly exceed the allowable regulatory limit based on the Chinese National Standard GB 5085.3-1996 (identification standard for hazardous wastes-identification for extraction procedure toxicity). Accordingly, the MSWI fly ash is considered to be a hazardous waste and must be solidified/stabilized.

3.2. Surface leaching of heavy metals in MSWI fly ash-cement hardened pastes

The leaching rate is a useful index to assess the security of hardened pastes. Lower leaching rate value indicates higher safety. The experimental test results are reported in Table 3. As shown in Table 3, leaching rates attain 10^{-4} cm d⁻¹ order of magnitude at early leaching age of 0–3 d. The ratio of leaching rate is between 60% and 80% for 0–3 d, and between 18% and 36% for 3–7 d, which the ratio of leaching rate at 0–7 d accounts for above 97% of total leaching quantities. It reveals that most of leached heavy metals are produced at early ages, which is caused by the weak mechanical solidification in the surface of matrices. Under water molecule immersing, the leaching behavior is mainly controlled by the leaching rate of surface heavy metals ion of matrices. As the diffusion of surface heavy metals, the leaching rate is increased rapidly, which rather results in a high ratio of leaching rate at an early stage. In the later course of leaching, with the dissolving of surface heavy metals, together with the good compactness of pastes caused by cement hydration, deep penetration of water molecules becomes very slow. When the penetration of water molecules attains certain

Table 3
Surface leaching of heavy metals from MSWI fly ash-cement solidification body

Element	Leaching concentration (mg/L)				Leaching rate ($\times 10^{-5}$ (cm d ⁻¹))				Ratio of leaching rate (%)			
	0–3 d	3–7 d	7–28 d	28–60 d	0–3 d	3–7 d	7–28 d	28–60 d	0–3 d	3–7 d	7–28 d	28–60 d
Zn	0.085	0.063	0.012	0.002	5.3	3.0	0.11	0.012	62.93	35.62	1.31	0.14
Pb	0.068	0.040	0.008	0.002	9.2	4.1	0.15	0.025	68.27	30.42	1.11	0.19
Cu	0.039	0.012	0.003	0.001	14.2	3.3	0.16	0.034	80.25	18.65	0.90	0.19
Cd	0.005	0.003	0.001	ND ^a	27.9	12.5	0.80	ND ^a	67.70	30.30	1.94	–
Cr	0.012	0.009	0.003	0.001	15.6	8.8	0.56	0.120	62.20	35.10	2.23	0.48

^a Not detected.

Table 4
Diffusion coefficient of heavy metals in different leaching periods

Element	D_a (m ² /s)			
	0–3 d	3–7 d	7–28 d	28–60 d
Zn	8.95×10^{-14}	6.57×10^{-14}	2.16×10^{-15}	5.29×10^{-16}
Pb	2.67×10^{-13}	1.23×10^{-13}	2.58×10^{-14}	5.56×10^{-15}
Cu	6.35×10^{-13}	8.03×10^{-14}	2.62×10^{-14}	4.45×10^{-15}
Cd	2.46×10^{-12}	1.18×10^{-12}	6.86×10^{-13}	–
Cr	7.74×10^{-13}	5.81×10^{-13}	3.38×10^{-13}	5.73×10^{-14}

depth, they cannot penetrate any more. This causes the leaching rate is slow and the ratio of leaching rate is significantly decreased. After the balance is obtained, the increase of leaching concentration of heavy metals becomes flat. Combined with Table 4, the diffusion coefficient of different types of heavy metals is decreased with prolonging of cement pastes hydration, which also indicates that it is difficult for heavy metals to diffuse into surface in the later stage.

Therefore, the experimental results indicate that the long-term resistance to heavy metals leaching capability of MSWI fly ash-cement hardened pastes is better except early leaching quantity is relatively higher. Additionally, in the later stage, calcium hydroxide of hardened pastes surface gradually reacts with carbon dioxide dissolving in the water, which leads to the decrease of surface leaching rate of hardened pastes. The neonatal calcium carbonate can form a membrane in the pastes surface, which further prevents heavy metals in the pore migrating, thus resulting in the decreasing or delaying of heavy metals leaching from pastes [26].

3.3. Successive leaching toxicity of heavy metals in MSWI fly ash-cement hardened pastes

The relationships between leaching concentration of different types of heavy metals and leaching time are illustrated in Fig. 4(a–e). As displayed in Fig. 4, it appears that the leaching concentration of heavy metals in the pastes is increased as leaching

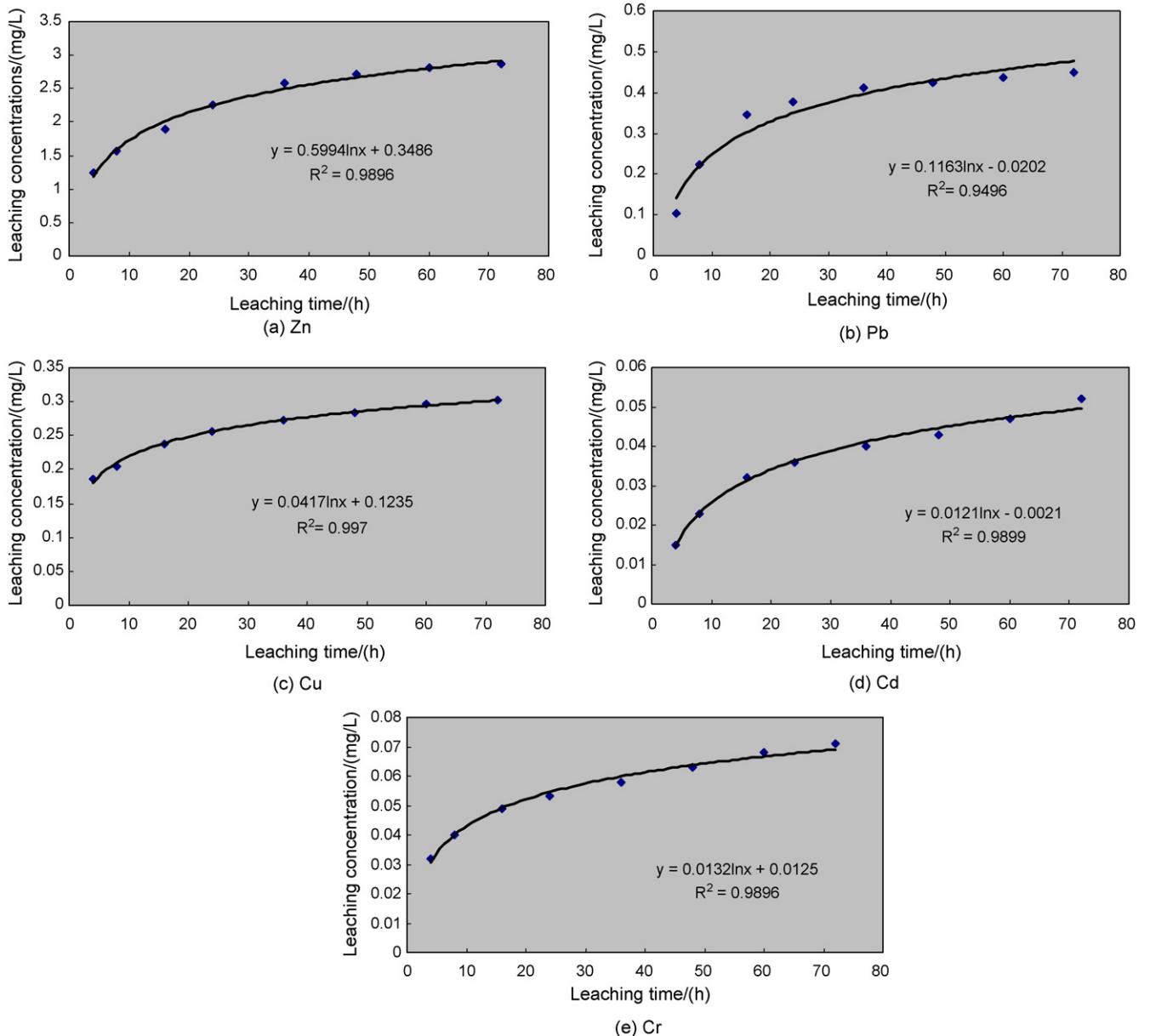


Fig. 4. Relationships between different types of heavy metals leaching concentration and leaching time.

Table 5
Required leaching time reaching limit concentration

Element	Leaching time reaching limit concentration (year)
Zn	1.08×10^{32}
Pb	2.17×10^7
Cu	∞^a
Cd	7.95×10^6
Cr	9.95×10^{44}

^a Infinite.

time delays. In the beginning stage, the increasing extent is relatively rapid, but it becomes slow in the later ages. The reason mainly is that the leaching is controlled by surface heavy metals of pastes in the beginning age, which results in significant increased leaching rate. As dissolving of surface heavy metals, leaching process was mainly controlled by the diffusion of capillary, which causes the decreasing of leaching rate. In addition, the correlation coefficient of each equation is rather high, which further confirms that leaching concentration is well correlated to leaching time.

Based on Fig. 4 and the allowable regulatory limit data reported in Table 2, leaching time reaching limit concentration was calculated in Table 5. As presented in Table 5, under experimental condition (pH 5.8–6.3, the vibration frequency of 110 ± 10 times per min), if heavy metals leaching from MSWI fly ash-cement hardened matrices at this rate, the required time reaching the allowable threshold is significantly long. As a matter of fact, compared with the experimental condition, hardened pastes leaching in situ is a slow and gradually diluting process and only few grains are below 5 mm, so the heavy metals immobilizing of MSWI fly ash-cement matrices could be more reliable in the practical environment. Therefore, the solidification capability of cement on heavy metals in MSWI fly ash is better. Further investigation of the immobilization/stabilization mechanism of cement on various types of heavy metals in MSWI fly ash was needed.

4. Conclusions

Surface leaching rates of heavy metals from MSWI fly ash-cement hardened pastes at early stage attain 10^{-5} – 10^{-4} cm d^{-1} order of magnitude, for 10^{-7} at later ages. The ratio of leaching rate at 0–7 d accounts for above 97% of total leaching quantities. The diffusion coefficient of different types of heavy metals is decreasing with delaying of ages. The correlation of leaching concentration and leaching time is better. Immobilization effect of cement on MSWI fly ash is good. Even if MSWI fly ash-cement hardened pastes were damaged, the leaching toxicity is still in a safety range. The long-term resistance to heavy metals leaching capability of MSWI fly ash-cement hardened pastes is better. It is likely to be used as partial replacement for cementitious material in concrete mixes.

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