Original Research Paper

Analysis of Dynamic Leaching Test About Heavy Metals in Solidification Body of Municipal Solid Waste Incineration Fly Ash

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ABSTRACT

A new method, Dynamic Leaching Test (DLT), was put forward to analyse the leaching behaviour and leaching mechanism of heavy metals in solidification body of municipal solid waste incineration (MSWI) fly Ash. In this study, two groups of solidification materials were used, one with ordinary Portland cement (C), and the other with slag-and-clinker (SC). In each solidification body, solidification material/ (solidification material + MSWI fly ash) weight ratio was 25% and water/solid weight ratio was 0.3. After a 60-day curing period, DLT was applied to analyse the leaching behaviours and leaching mechanisms of lead and chromium in solidification body with a mathematical model based on Fick's first law. The test results showed that most of lead and chromium were leached out during the initial stage (0~7d), and their leachability decreased greatly later. In the cement-based solidification body, the leaching behaviour of chromium is approximately consistent with Fick's first law. The leaching of lead is a combination of diffusion and acid erosion mechanisms. In the slag and clinker-based solidification body, the leaching of lead is approximately consistent with Fick's First law. The leaching of chromium is more complicated than simple diffusion or acid erosion, which indicated the need for further research.

INTRODUCTION

Municipal solid waste incineration (MSWI) fly ash is especially classified as hazardous waste, because it usually contains concentrated, highly leachable heavy metals (Li & Li 2015, Pan & Yang 2013). If not treated properly, the heavy metals in MSWI fly ash will release into external environment, causing secondary pollution (Kubonova et al. 2013, Chen et al. 2012).

Studies around the world have proven the feasibility of immobilizing waste fly ash with cement, coal ash and slag-based materials, which have good-immobilization effect and low leaching ratio of heavy metals (Liu & Hou 2009, Park 2000, Chrysochoou & Dermatas 2006). Heavy metal ions may be solidified and stabilized in the structure of cement hydration products such as tobermorite and zeolites in the following ways: physical encapsulation (Sun et al. 2015), isomorphous substitution (Thevenin & Pera 1999), precipitation (Xu & Sarkar 1991), and adsorption (Lin et al. 1994).

Actually, the stabilization/immobilization of toxic, hazardous wastes ca not reduce the total amount of them, but can reduce the leachability of the wastes, which in turn can minimize the pollution risk of them to their final disposal sites (Yang & Cao 2013). Among the factors that determine the success of the stabilization/immobilization process, an important parameter is the resistance capability of the toxic, hazardous wastes processed against the natural physical or chemical reactions that may cause their release, namely the leachability of stabilized/immobilized pollutants (Shi et al. 2013). Leaching tests can be used to evaluate the durability of stabilized/immobilized wastes and simulate their short-term and long-term leaching behaviours after final disposal under a specific environmental condition (Al-Abed et al. 2006), which can be used in research and development of various stabilization/immobilization methods for different environmental conditions.

On the basis of physical and chemical research of stabilization/immobilization, mathematical models can be used to simulate leaching mechanisms as an effective way to predict the long-term effects of immobilization (Lee et al. 2002). Up to now, the mathematic models built for researching leaching mechanism of immobilization/stabilization systems can be divided into the following categories: (1) the diffusion model: heavy metals in immobilized or stabilized samples can permeate into an external solution because they diffuse from high-concentration samples to the low-concentration solution (Batchelor 1990, Poon & Chen 1999, Catalan & Merliere 2002); (2) the dissolution model: an acid solution is used to dissolve immobilized/stabilized sample, so that the immobilized/stabilized heavy metals are dissolved in the solution (Bama & Moszkowicz 1994, Kersten 1996), (3) the dissolution and diffusion model: the leached heavy metals are composed of diffused heavy metals due to concentration difference and dissolved heavy metals from immobilized/ stabilized sample due to acid erosion (Moszkowicz & Pousin 1996). Based on the existing hypothesis and the diffusion

theory, cement and slag are used as solidification materials for dynamic leaching tests (DLT) and the measurement of leaching behaviour of heavy metals in solidification body, to speculate on the leaching mechanism of heavy metals.

MATERIALS AND METHODS

Materials

Slag and clinker: Made at Wuhan Iron and Steel (Group) Corp (Fineness after grinding: 1.9%);

Cement: Commercially available grade 32.5 Portland cement.

MSWI fly ash: From Waste Incineration Power Plant in Pudong New Area of Shanghai.

The main components of the above materials are given in Table 1 and Table 2.

Methods

Test of content of heavy metals in the MSWI fly ash: In order to test the content of heavy metals in the fly ash, 2.0g fly ash sample was firstly dissolved in concentrated nitric acid solution in the course of heating. When most of the sample was dissolved in the acid solution, some distilled water was added into the container to fix the dimension as 100mL. The concentration of heavy metals in the filtrate was analysed with Inductively Coupled Plasma Emission Spectroscopy (ICP-ES), and the contents of heavy metals in fly ash were calculated.

Test of leaching toxicity of MSWI fly ash: The leaching toxicity of MSWI fly ash was determined according to extraction toxicity identification standard of China (China EPA 1996), and the method is as described below: for 100g MSWI fly ash, 900 mL water is added, and the pH is adjusted with NaOH or HCl in the range of 5.8-6.3. Then the solution is diluted to 1000 mL, with the pH value kept in this range. If the pH deviates outside this range, NaOH or HCl solutions should be added during the leaching operation. The sample is leached by rotating in a mechanical shaker with an oscillating frequency of 110 ± 10 min^{-1} for 8 h at 25°C. The sample was allowed to settle for 16 h and filtered. The filtrate is analysed by ICP-ES.

Preparation of solidification materials: 1. Solidification material (C): cement (100%)

2. Solidification material (SC): slag (83%) and clinker (17%)

Preparation of MSWI fly ash solidification body: This test used the two solidification materials above. In the tested solidification body, solidification material/(solidification material+ MSWI fly ash) weight ratio was 25% and water/solid weight ratio was 0.3. The prepared paste was poured

Table 1: Main chemical components of MSWI fly ash (%).

Sample MSWI	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	(Na,K)Cl
Fly Ash	23.0	7.3	36.9	2.1	3.3	14.8	12.6

Table 2: Main chemical components of the materials (%).

Material	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	R_2O	L.O.I
Slag	32.91	4.28	9.72	46.87	4.41	/	0.74	1.07
Cement	25.30	3.40	8.80	52.88	4.52	3.60	0.46	1.04
Clinker	20.33	3.36	4.96	64.98	3.65	0.62	0.68	1.42

Table 3: The schedule of replacing extraction solution.

Permeation Interval (N)	Cumulative Time (s)	Interval Time (s)
0	0	0
1	43200	43200
2	86400	43200
3	259200	172800
4	604800	345600
5	864000	259200
6	1209600	345600
7	1728000	518400

into ø40×90mm PVC bottles and stirred with a plastic rod until bubbles disappeared. After a 60-day curing period, the mixture was demolded and the resulting solidification bodies were named as C (25) and SC (25) respectively.

Steps of Dynamic Leaching Test (U.S. EPA.1993)

1. The undamaged samples C (25) and SC (25) were hung inside two beakers respectively, and leaching solutions (pH=2.88, adjusted with NaOH or HCl) were added. The ratio of solution volume to sample volume is 8:1.
2. Samples were placed inside an insulated box at 20°C for the leaching test.
3. The extraction solution was replaced according to the schedule as given in Table 3. Each time, a solution of required amount was poured into a new beaker, and the samples were moved into it from the old extraction solution.
4. Each new round of leaching test was still done in the insulated box at 20°C. 90mL old extract was poured into a 100mL flask after proper stirring, and acidized with 0.2mL heavy nitric acid. Deionized distilled water was then added to the full scale. And the solution was mixed well.
5. 30mL extraction solution was taken for measuring heavy metal content with ICP-ES.

RESULTS AND DISCUSSION

Table 4: Heavy metal content and leaching concentration in MSWI fly wash.

Heavy Metal	Percentage of heavy metal in fly ash (%)	Leaching concentration of MSWI fly ash/(mg·L⁻¹)	Leaching toxicity identification standard of solid waste(mg·L⁻¹)[a]
Pb	42.7	159	≤ 3
C r	20	4.64	≤ 1.5
Zn	4.6	14.3	≤ 50
Cu	0.9	0.394	≤ 50
Cd	4.0	0.082	≤ 0.3
Hg	-	not detected	≤ 0.05

[a]Dangerouse waste discriminate criterion in China (GB5085.3-1996)

Test Results of Heavy Metal Content and Leaching Concentration in MSWI Fly Ash

From Table 4, it is found that the concentrations of lead and chromium in the leaching solutions of MSWI fly ash exceed the identification standards of leaching toxicity for solid wastes. This is why MSWI fly ash is generally considered as a hazardous waste and must be subjected to solidification treatment. In this study, we used two types of solidification materials to immobilize MSWI fly ash: one was ordinary Portland cement (C), the other was slag and clinker (SC). Because the leaching concentrations of three other metals (Zn, Cu, Cd) were much lower than the toxicity identification standard, this research focuses on the leaching behaviour and leaching mechanisms of lead and chromium in MSWI fly ash solidification bodies.

Dynamic Leaching Test Results

Test results of cumulative leaching amount of Pb and Cr in each phase: According to Fig. 1 and Fig. 2 above, it can be seen that the cumulative leaching amount of heavy metals increased with the passage of leaching time. In the SC(25) solidification body, the increase of lead and chromium concentrations slowed down greatly after 168 hours of leaching. During the initial stage (0~3d), the leached chromium accounted for more than 60% of the total leached chromium and the leached lead accounted for more than 50% of the total leached lead in SC(25). During 0~7d, the leached chromium accounted for more than 85% of the total leached chromium and the leached lead also accounted for more than 85% of the total leached lead. In the C(25) solidification body, the cumulative amount of leached heavy metals also increased with the passage of time. After 240 hours of leaching, the increase of lead and chromium concentrations slowed down greatly. During the initial stage (0~7d), the leached chromium accounted for 85% and the leached lead accounted for 60% of the total leached amount. The majority of leached lead and chromium were leached out in the initial stage in SC (25) and C (25). This was because the mechanical immobilization effect was weaker on the surface layer of solidifi-
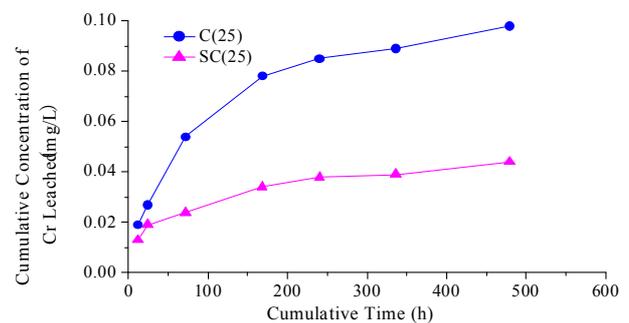
Fig. 1: The relationship between cumulative concentration and leaching time of leached chromium in samples SC (25) and C (25) in DLT.
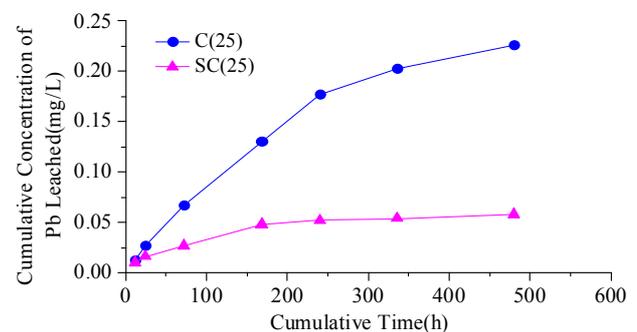
Fig. 2: The relationship between cumulative concentration and leaching time of leached lead in samples SC (25) and C(25) in DLT.

cation body. The surface heavy metals diffused gradually due to the effects of water molecules. As a result, the diffusion started with high leaching rates during 0~7d. However, in the later stage, with most surface layer heavy metals dissolved, the leaching process shifted to the interior layers of the solidification body, and the metals diffused through capillaries. Due to the good compactibility of the solidification bodies, water molecules permeated deeper at a very slow rate and were unable to permeate further after reaching a certain depth, and as a result, the leaching velocity dropped and leachability declined drastically.

It can also be seen from Fig. 1 and Fig. 2 that the leached amounts of both lead and chromium in SC(25) were smaller
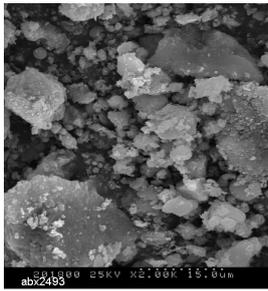
Fig. 3: SEM photograph of C(25) (60d)
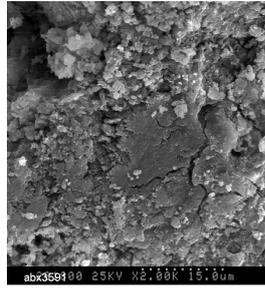
Fig. 4: SEM photograph of SC(25) (60d)

than in C(25) throughout the test, which can be explained by the scanning electron microscopy (SEM) photograph of the two solidification bodies (Fig. 3 and Fig. 4)

It can be seen from Fig. 3 that through hydration reaction, flake and acicular hydration products appeared in the C(25) samples, which might be hydrated calcium silicate gel (C-S-H) and ettringite, and the hydration products are not much, the sample structure is loose. Fig. 4 showed that the hydrates in SC(25) have been cemented together due to the high degree of hydration reaction, so that unable to distinguish one phase alone, and SC(25) is denser than C(25) which results in lower leaching of the heavy metals in SC(25) than in C(25).

In addition, relevant researches have shown that the slag-based cement materials have many advantages comparing ordinary Portland cement. Hardened slag-cement paste has a low porosity and smaller pore size, which are conducive to reduce the leachability of water-soluble ions of heavy metals (Lu Linchao 1999, Kim & Jung 2011). The hardened slag-cement paste has high early-strength and high long-term strength, which are favourable to long-term immobilization of heavy metal ions in hardened cement pastes (Zhang et al. 2007). The hydration products of hardened slag-cement paste mainly consist of low alkalinity minerals such as tobermorite and zeolites, which have good capabilities of absorbing metal ions, and may benefit the solidification of heavy metal ions (Chen & Yan 2012). Hydration products of hardened slag-cement paste have low solubility, which is approximately 1/15~1/25 of that of ordinary Portland cements, and favourable to long-term stability of solidification bodies in adverse environments (Kolani & Buffo-Lacarriere 2012).

A mathematical model for leaching based on Fick's first law: Diffusion can be recognized as the statistical outcome of molecule displacement resulting from random motion of molecules. A concentration difference causes a mass flow in the macroscopic sense. The basic equation for Fick's first law of diffusion is given as follows (Caio & Edson 2013):

$$J = Aj = -AD\frac{\partial C}{\partial X} \qquad ...(1)$$

Where, J is the "diffusion flux" within the diffusion area; A is the "diffusion area"; j is the "diffusion flux" per unit area; C is the "solute concentration", X is the "distance", $\frac{\partial C}{\partial X}$ is the "concentration gradient"; D is the "diffusion coefficient", a kinetic parameter indicating the velocity of diffusing particles.

Suppose that the sectional area of the sample is shown in Fig. 5 is A. The mass balance equation within the area $A \Delta X$ is as following:

Change rate of solute mass within = (out-diffusion velocity at location) – (in-diffusion velocity at location). It can be expressed in a mathematic formula as follows:

$$\frac{\partial(A\Delta XC)}{\partial t} = A(j\big|_x - j\big|_{x+\Delta x})]$$

Dividing the equation above by $A\Delta X$, resulting in:

$$\frac{\partial C}{\partial t} = -\left(\frac{j\big|_{x+\Delta x} - j\big|_x}{(X+\Delta X) - X}\right)$$

Let $\Delta X \rightarrow 0$, using the definition of derivative, we get:

$$\frac{\partial C}{\partial t} = -\frac{\partial j}{\partial X} \qquad ...(2)$$

Introduce Eq. 1 into Eq. 2, then we get

Let $\xi = \frac{X}{\sqrt{4Dt}}$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} \qquad ...(3)$$

So $\frac{dC}{d\xi}\left(\frac{\partial \xi}{\partial t}\right) = D\frac{d^2C}{d\xi^2}\left(\frac{\partial \xi}{\partial X}\right)^2$

i.e. $\frac{d^2C}{d\xi^2} + 2\xi\frac{dC}{d\xi} = 0 \qquad ...(4)$
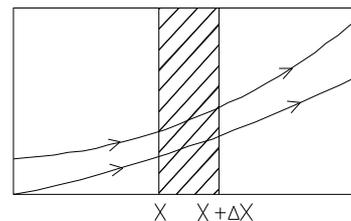
Fig. 5: The permeation behaviours inside the sample within the area.

Finally, we get

$$j = -D\frac{\partial C}{\partial X} = \sqrt{\frac{D}{4t}} \cdot e^{-x^2/4Dt}(C_1 - C_0) \qquad ...(5)$$

Where C_1, C_0 are control constants for border conditions (>0)

The flux at the solid-liquid interface, i.e. at the location where $X = 0$ is:

$$j\big|_{x=0} = \sqrt{\frac{D}{4t}}(C_1 - C_0)$$

Through integration of time t, we get a specific time period $0 \sim t$. Therefore the solute mass at the solid-liquid interface per unit area is given as follows:

$$j = \int_{t_0}^{t} \sqrt{\frac{D}{4t}}(C_1 - C_0)dt = \sqrt{Dt}(C_1 - C_0) \qquad ...(6)$$

$$J = Aj = A\int_{t_0}^{t} \sqrt{\frac{D}{4t}}(C_1 - C_0)dt = A\sqrt{Dt}(C_1 - C_0)$$

Using the logarithm of both sides of the formula, we get:

$$\lg J = \frac{1}{2}\lg t + \lg A\sqrt{D}(C_1 - C_0) \qquad ...(7)$$

It can be seen from Eq.7 that the logarithm of leaching amount at the solid-liquid interface is linear to the logarithm of cumulative leaching time under the action of diffusion, with a slope of 0.5.

Logarithmic relationship between cumulative leaching amount and leaching time of Pb and Cr in samples: From Fig. 6 and Fig. 7, it can be seen that the logarithmic slopes of different heavy metals, or the same metal in different solidification systems differ from each other: for example, the calculated slopes of chromium in C(25) and lead in SC(25) are both close to 0.5, but the calculated slopes of lead in C(25) is as high as 0.82, and that of chromium in SC(25) is as low as 0.33. It can be seen from Eq.7 that more the permeation mechanism of a kind of metal is close to full diffusion, the more the corresponding calculated slope is close to 0.5. Given the results, we know that the permeation of chromium in C(25) and lead in SC(25) both are approximately a diffusion process. According to Poon & Lio (2001) and Cote & Constable (1987), when the calculated slope is between 0.5 and 1.0, the permeation mechanism of heavy metals is a process combining diffusion and erosion. Thus, the permeation of lead in C(25) is a combination of diffusion with erosion. However, the calculated slope of chromium in SC(25) is much lower than 0.5, showing that the permeation mechanisms of heavy metals in the samples are much more complicated than simple diffusion or erosion. The permeation mechanisms of different heavy metals in
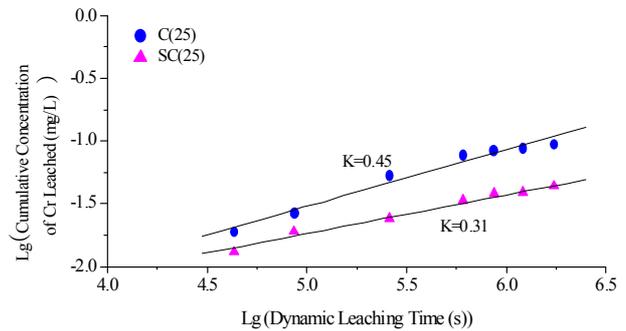
Fig. 6: The logarithmic relationship between cumulative concentration and leaching time of leached chromium in samples C (25) and SC (25).
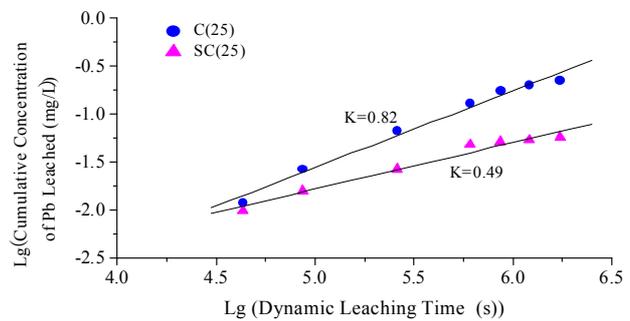
Fig. 7: The logarithmic relationship between cumulative concentration and leaching time of leached lead in samples C (25) and SC (25).

the same solidification system, or the same metal in different solidification systems are all different from each other.

CONCLUSIONS

This study focused on analysis of two types of heavy metals, lead and chromium in solidification bodies with DLT method. It shows that leaching behaviours take place mainly during the initial stage. After that, the leaching rate decreases drastically with the passage of time. Throughout the leaching tests, the leached amounts of lead and chromium in SC(25) solidification body are smaller than those in C(25), which can be mainly attributed to the properties of hydration products of solidification bodies. It also indicates that slag-based solidification materials are better than ordinary Portland cement in immobilizing MSWI fly ash. The permeation mechanisms of heavy metals vary among heavy metal types. Even the same heavy metal exhibits different permeation mechanisms depending on the types of solidification materials. The permeation of chromium in C (25) and lead in SC (25) both are approximately a diffusion process. The permeation of lead in C (25) is a combination of diffusion with erosion. The permeation mechanisms of chromium in SC (25) are much more complicated than simple diffusion or erosion.

Further tests are needed for other heavy metals such as zinc, copper, cadmium and mercury in MSWI fly ash. Comprehensive considerations should be given regarding the contents of major heavy metals in MSWI fly ash and permeation mechanisms of heavy metals in the corresponding solidification bodies. The most effective solidification materials should be chosen for the treatment of MSWI fly ash in order to minimize the pollution risk at landfill or waste disposal sites.

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