

# HEAVY METAL LEACHING BEHAVIOUR OF CEMENT-SOLIDIFIED MUNICIPAL SOLID WASTE INCINERATION FLY ASH IN SANITARY LANDFILL

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## INTRODUCTION

With the increase of municipal solid waste (MSW) discharge and the development of the incineration technology, at least 10 million tons of MSW incineration fly ash (MSWIFA) is discharged annually in China (Wang and Fan, 2020). According to the ‘Directory of National Hazardous Wastes’ of China (Ministry of Ecology and Environment of the People’s Republic of China, 2021), MSWIFA is categorized as a hazardous waste because it contains considerable amounts of heavy metals and toxic organic pollutants (e.g. dioxins). It may cause fatal harm to human health and ecological environment if MSWIFA is not disposed properly (Tong et al., 2020). In the light of the exemption list of ‘National List of Hazardous Waste’, an appropriately pre-treated MSWIFA can be disposed in sanitary landfills as a non-hazardous waste, thus providing an economical and practical scheme for MSWIFA disposal. However, notable, the pre-treated MSWIFA needs to meet the standard limits (e.g. heavy metals and dioxins content) before entering a sanitary landfill. In our pre-experiment, the dioxin content of MSWIFA we used was in a range of 0.23-0.89 ug/kg (data not shown), which is far below the limit set by GB 16889-2008 (i.e. < 3 µg/kg). Therefore, release of heavy metals is the main environmental risk for MSWIFA landfilled. Currently, pre-treatment technologies, especially cement solidification, have been widely used to reduce the mobility of heavy metals in MSWIFA to meet the regulation of sanitary landfill (GB 16889-2008, China) (Yu et al., 2005; Chen et al., 2021). Similar to TCLP, the ‘Solid waste-extraction procedure for leaching toxicity acetic acid buffer solution method’ (HJ/T 300-2007, China) is the standard in evaluating whether the leachable heavy metals in the solid waste can meet the threshold (i.e. GB 16889-2008). As per HJ/T 300, acetic acid (pH = 2.64) can be used as the leaching solvent to simulate the leaching behaviour of the solid waste in MSW sanitary landfill scenarios (i.e. mixed landfill). However, cement-solidified MSWIFA blocks is

commonly transported to a separated area of the landfill (i.e. zoning landfill) in China. In this context, the cement-solidified MSWIFA blocks rarely comes in contact with the leachate generated in the sanitary landfill. Therefore, the reliability of the leaching toxicity and long-term environmental risk assessment of cement-solidified MSWIFA blocks in sanitary landfill following the HJ/T 300 leaching protocol is debatable.

At present, the environmental risk assessment for solid waste is mostly based on leaching tests. Technically, the accuracy of leaching toxicity and long-term environmental risk assessment of the solidified MSWIFA in sanitary landfill is mostly affected by the leaching protocols (including leaching solvents and methods) and evaluation methods. In a zoning landfill scenario, rainwater is the most typical leaching solvent encountered by cement-solidified MSWIFA blocks. Acid rainwater represents the worst condition of solvent leaching. Compared with acetic acid, acid rainwater would be a more appropriate leaching solvent for leaching toxicity and long-term environmental risk assessment. In addition to the leaching solvent, the leaching toxicity assessment results might vary greatly with the leaching method. Techniques for leaching can be divided into three categories according to purpose (Kosson et al., 2019). The first type is ‘availability test’, such as EA NEN7371. In this method, solid waste block is broken into tiny particles (i.e. <125 µm), and nitric acid is used as a leaching solvent to quickly determine (i.e. 6 h) the maximum leaching potential of heavy metals in the solid waste block. This index can provide a conservative estimate for maximum leaching to study the leaching characteristics of heavy metals in the solid waste block (Yang et al., 2011). The second method evaluates whether the solid waste block can meet the specific disposal threshold and determines the effect of influencing factors (e.g. pH (Yan et al., 2004; Quina et al., 2009; Leelarungroj et al., 2018), liquid–solid ratio (Van der Sloot, 2002; Xie et al., 2021) and dissolved organic matter (DOM) (Li et al., 2021). These indices

can determine the leaching of heavy metals in a short time (i.e. 18 h) with different leaching solvents [e.g. H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> (HJ/T 299-2007, China) and acetic acid (TCLP and HJ/T 300-2007)] after crushing the solid waste block to medium particle size (i.e. <9.5 mm). The actual environmental risk evaluation for solid waste block is based on such leaching methods. However, these techniques only consider the short-term leaching behaviour of solid waste block under specific exposure scenarios but neglects the influence of time (Garrabrants et al., 2004; Shi et al., 2019) and therefore are not suitable for the long-term environmental risk evaluation of cement-solidified MSWIFA blocks in zoning landfill. The third method is static or dynamic leaching experiment (e.g. EA NEN7375) based on the principle of mass transfer control (i.e. interface diffusion) to analyse the leaching characteristics of inorganic components in solid waste block (i.e. particle size >4 cm). Under this leaching scenario, the leaching amounts of inorganic components in solid waste block are closely related to the leaching time. The leaching solvent is usually deionised water, and the experimental cycle is 64 days. Compared with those from the previous methods, the experimental results obtained by this leaching experiment are closer to the leaching characteristics of solid waste block in actual exposure scenarios, especially the leaching characteristics of heavy metals in solid waste block (Ogundiran et al., 2013; Taha et al., 2018). However, the use of a single leaching protocol for the environmental risk assessment of solidified MSWIFA in sanitary landfill is no longer adequate due to the diverse properties of the solid waste block and the complexity of disposal scenarios. Therefore, the development of a research framework combining different leaching protocols to investigate the leaching behaviours of cement-solidified MSWIFA blocks in sanitary landfill is the foundation of long-term environmental risk research.

Given the characteristics of these leaching tests (e.g. short-term experiment), their obtained results cannot be used directly for the long-term environmental risk assessment in a specific exposure scenario (Sanchez et al., 2000). Numerical simulations based on short-term leaching test results have been widely developed to describe the temporal-dependent leaching behaviours of contaminants in solid waste block and to obtain accurate reference data for long-term environmental risk assessment. Some of the typical models include first-order reaction kinetics, shrinking core and bulk diffusion (Zhang et al., 2021). The bulk diffusion model (BDM) based on Fick's second diffusion law is the most widely used and is particularly applicable when the heavy metal leaching in solid waste block is controlled by diffusion (Kim et al., 2020). However, this model is not applicable to all heavy metals and does not fit well when the heavy metal leaching is controlled by other mechanisms (Sanchez et al., 2003). Therefore, a BDM on the basis of

the leaching characteristics of cement-solidified MSWIFA blocks under zoning sanitary landfill scenario must be constructed and calibrated for an accurate long-term environmental risk assessment.

Given that most of the studies on the cement-solidified MSWIFA were either focused on the process parameters optimization and the curing mechanism (Wang et al., 2015; Cerbo et al., 2017), or its environmental risk assessment based on the short-term leaching tests and the empirical models, the long-term environmental risk assessment of the cement-solidified MSWIFA in zoning sanitary landfill scenario was still unclear. Therefore, in this study, the heavy metal leaching behaviours of cement-solidified MSWIFA blocks following the EA NEN7375 leaching protocol were firstly investigated by laboratory batch-scale experiments. Acid rain comprising H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (mass ratio of 2:1) was adopted as the leaching solvent to simulate the most severe exposure scenario of the zoning sanitary landfill. At the same time, deionized water was adopted as the leaching solvent to act as a control group. Additionally, the mechanistic model for a specific heavy metal on the basis of its leaching characteristics was developed and calibrated using the data from EA NEN7375 leaching test. Finally, the calibrated model was applied to evaluate the long-term environmental risk of cement-solidified MSWIFA blocks in acid rain scenarios. The obtained results and developed models might lay the foundation for the optimal design of zoning sanitary landfill and provide a scientific basis for further studies.

## MATERIALS AND METHODS

### Sampling and sample preparation

MSWIFA was obtained from a waste incineration plant in Beijing that adopts reciprocating mechanical grate incinerator to incinerate municipal waste. The flue gas purification of incinerator adopts the combined treatment facilities of 'dry deacidification + activated carbon adsorption + bag filter + SCR denitration'. The collected MSWIFA was dried to constant weight at 105 °C and then stored in sealed bags for later use. The basic physical and chemical properties of the MSWIFA are shown in Table 1.

Table 1. Basic properties of the MSWIFA.

Parameters	Value	Parameters	Value
Moisture content (%)	2.4	Na <sub>2</sub> O (%)	7.47
pH (-)	13.84	SiO <sub>2</sub> (%)	3.67
CaO (%)	56.65	SO <sub>3</sub> (%)	2.79
K <sub>2</sub> O (%)	8.51	Cl (%)	12.52

Cement-solidified MSWIFA blocks was prepared using the collected MSWIFA, benchmark cement (i.e.

ordinary Portland 32.5R cement sold in the market) and deionised water as follows. The MSWIFA and benchmark cement were poured into the mixing container according to the mass ratio of 4:1 and mixed evenly. It was well demonstrated that this mass ratio is applicable for MSWIFA solidification before landfilling (Du et al., 2019; Liu et al., 2019). Deionised water was then added according to the liquid–solid ratio of 0.5:1 for uniform mixing. This optimum liquid–solid ratio was determined in our preliminary experiment in terms of the solidification time and the flowability of the mixture. The mixture was then placed in a mould with dimensions of 5 cm × 5 cm × 5 cm and compacted with a vibrating plate. The cement-solidified MSWIFA blocks were cured in the curing box (temperature 20±2°C and relative humidity 95%±1%) for 24 hours (Berra et al., 2019). The hardened paste was demoulded and maintained for 28 days in the above ambience. The prepared cement-solidified MSWIFA blocks was sealed in a bag and stored at room temperature for later use.

### Leaching tests

The total amount of heavy metals, leaching toxicity of heavy metals, available leaching amounts of heavy metals and temporal-dependent leaching behaviours of the heavy metal in the cement-solidified MSWIFA blocks were measured to systematically study the leaching characteristics of heavy metals in the cement-solidified MSWIFA blocks. The total amount of heavy metals in the cement-solidified MSWIFA blocks was tested by using the microwave digestion method in ‘Solid waste–Determination of 22 metal elements–Inductively coupled plasma optical emission spectrometry’, and the obtained digestion solvent was used to determine the heavy metal content. The leaching toxicity of heavy metals in cement-solidified MSWIFA blocks and in cement blocks was determined according to ‘Solid waste–Extraction procedure for leaching toxicity–Sulphuric acid & nitric acid method’ (HJ/T 299-2007) and ‘Solid waste–Extraction procedure for leaching toxicity–Acetic acid buffer solution method’ (HJ/T 300-2007). The available leaching amounts of heavy metals in the cement-solidified MSWIFA blocks was measured according to EA NEN7371. Particularly, a certain amount of broken and ground cement-solidified MSWIFA blocks (diameter <125 µm) was placed in a beaker, added with deionised water with a liquid–solid ratio (L/kg) of 50:1, titrated with 1 mol/L nitric acid at pH=7±0.5 and maintaining for 3 hours. After filtration, a certain amount of filtrate was obtained. The residue was added with deionised water to a liquid–solid ratio (L/kg) at 50:1, titrated with 1 mol/L nitric acid at pH=4±0.5, and maintained for 3 hours. After filtration, the residue was mixed in the same amount of filtrate as before. The mixed solution was used to determine the content of heavy metals.

The temporal-dependent leaching behaviours of the

heavy metals in the cement-solidified MSWIFA blocks was measured by using an improved version of EA NEN7375. The main component of acid rain in some parts of China is  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  (Xie et al., 2009; Yang et al., 2018; Jia et al., 2021), and the pH of acid rain ranges from 3.2 to 5.6 (Zhou et al., 2017). According to the most unfavourable principle,  $\text{HNO}_3/\text{H}_2\text{SO}_4$  (mass ratio is 1:2) with pH value of 3.2±0.05 was selected as the leaching solvent (Yang et al., 2011), known as acid rain group. In addition, the group using deionized water as leaching solvent is designated as the control group. EA NENE7375 stipulated a liquid–solid ratio ( $\text{L}/\text{m}^3$ ) of 2:1-5:1, and the most unfavourable principle stated a liquid–solid ratio ( $\text{L}/\text{m}^3$ ) of 5:1 for this study. After the leaching solvent and liquid–solid ratio in the leaching experiment were set, a certain volume of cement-solidified MSWIFA blocks was continuously immersed in a specific volume of leaching solvent. According to the leaching protocols of EA NEN7375, the leaching solvent was replaced in eight steps, namely, 0.25 days, 1 day, 2.25 days, 4 days, 9 days, 16 days, 36 days and 64 days. At the end of each leaching step, a certain amount of leaching solvent was filtered through a 0.45 µm membrane filter and was immediately acidified with (1+1) nitric acid following filtration to pH <2. This leaching solvent was then stored in a refrigerator at 4 °C. According to the concentration of heavy metals in the leaching solvent obtained in different steps, the cumulative leaching amount (Formula (1) and Formula (2)) and leaching rate of heavy metals (Formula (3)) during the immersion of cement-solidified MSWIFA blocks were calculated.

$$E_i^* = (C_i \times V)/m \quad (1)$$

$$\varepsilon_n^* = \sum_{i=1}^n E_i^* \quad (2)$$

$$F_i = E_i^*/(t_i - t_{i-1}) \quad (3)$$

where  $\varepsilon_n^*$  is cumulative leaching amounts of heavy metals, mg/kg;  $E_i^*$  is the leaching amounts of heavy metals in step  $i$ , mg/kg;  $C_i$  is the concentration of heavy metals in the leaching solvent of step  $i$ , µg/L;  $V$  is Volume of leaching solvent, L;  $m$  is the weight of the MSWIFA, g;  $F_i$  is the leaching rate of heavy metals in step  $i$ , mg/kg/d; and  $t_i$  and  $t_{i-1}$  are the end time and start time of step  $i$  respectively, d.

### Governing equations

When the leaching of heavy metals is controlled by diffusion, the bulk diffusion model (BDM) based on Fick’s second diffusion law developed by Crank in 1975 (Lu et al., 2016) can fit the leaching amounts of heavy metals. The expression of this model is show in Formula (4).

$$M = 2\left(\frac{S}{V}\right)C_0\left[\left(D^{obs}t\right)/\pi\right]^{1/2} \quad (4)$$

When the leaching characteristics of heavy metals

under the control of surface wash-off can be described by first-order reaction model (FRM) (Formula 5), and its analytical solution is shown in Formula 6 (Zhang et al., 2021). Dissolution model (DIM) can be used to describe the leaching characteristics of heavy metals under dissolution, and the derivation process is shown in Formulas 7–9. Therefore, heavy metals controlled by diffusion and surface wash-off can be expressed as Formula 10, and heavy metals controlled by diffusion and dissolution can be expressed as Formula 11.

$$\frac{dQ}{dt} = -kQ \quad Q|_{t=0} = Q_0 \quad (5)$$

$$Q = Q_0 [1 - \exp(-kt)] \quad (6)$$

$$U_{(t)} = U_0 \left( 1 - \frac{C_t^l}{C_{sat}^l} \right) \quad (7)$$

For the simple case,  $C_t^l/C_{sat}^l$  is approximately 0, that is,  $U_{(t)} = U_0$ , then

$$M = C_0 \left( \frac{S}{V} \right) U_0 t \quad (8)$$

Since  $C_0$  and  $U_0$  are constants in Equation (8), let  $K = C_0 U_0$ , then

$$M = K \left( \frac{S}{V} \right) t \quad (9)$$

$$M = Q_0 [1 - \exp(-kt)] + 2 \left( \frac{S}{V} \right) C_0 \left[ (D^{obs} t) / \pi \right]^{1/2} \quad (10)$$

$$M = 2 \left( \frac{S}{V} \right) C_0 \left[ (D^{obs} t) / \pi \right]^{1/2} + K \left( \frac{S}{V} \right) t \quad (11)$$

where  $Q$  is the content of soluble heavy metals in the cement-solidified MSWIFA blocks at time  $t$ , mg/kg;  $Q_0$  is the initial content of soluble heavy metals in the cement-solidified MSWIFA blocks ( $t = 0$ ), mg/kg;  $k$  is the rate constant, 1/d;  $U_{(t)}$  is the dissolution rate of soluble heavy metals in the cement-solidified MSWIFA blocks at leaching time  $t$ , cm/d;  $U_0$  is the maximum dissolution rate of soluble heavy metals in the cement-solidified MSWIFA blocks, cm/d;  $C_t^l$  is the concentration of heavy metals in the leaching solvent at leaching time  $t$ , mg/L;  $C_{sat}^l$  is the saturation concentration of heavy metals in the leaching solvent, mg/L;  $M$  is the cumulative leaching amounts of heavy metals per unit mass in the cement-solidified MSWIFA blocks at time  $t$ , mg/kg;  $C_0$  is the available leaching amount of heavy metals per unit mass in the cement-solidified MSWIFA blocks, mg/kg;  $D^{obs}$  is the observed diffusion coefficient, cm<sup>2</sup>/d;  $t$  is the leaching time, d.  $S$  is the surface area of the cement-solidified MSWIFA blocks, cm<sup>2</sup>;  $V$  is the volume of the cement-solidified MSWIFA blocks, cm<sup>3</sup>.

## Analytical methods

X-ray fluorescence spectroscopy (PANalytical Axios) was used to determine Chemical composition (Zhang et al., 2021). pH was determined by A PHS-3C digital acidity detector (INESA Scientific Instrument Co., Ltd., Shanghai, China). Water content was determined by standard method (GB 7172-1987), and heavy metal concentration in the leaching solvent was determined by ICP-MS (NexLON350X, PerkinElmer, USA), each test was performed in triplicate (Wang et al., 2020).

## RESULT AND DISCUSSION

### Leaching toxicity of the cement-solidified MSWIFA blocks

According to the ‘Standard for pollution control on the landfill site of municipal solid waste’ (GB 16889-2008), solid waste block that can be disposed in a sanitary landfill must meet two basic requirements: (1) the solid waste block buried in the landfill should not be hazardous waste and (2) after pre-treatment, the leaching solvent of MSWIFA must meet the concentration limit of pollutants. Therefore, this study firstly evaluated whether the cement-solidified MSWIFA blocks meet the admission requirements of sanitary landfill according to the standard requirements.

The national standard GB 16889-2008 lists 11 heavy metals in the leaching solvent of solid waste, including Hg, Cu, Pb, As, Ni, Cr and Zn. Owing to its high environmental risk and easy leaching, the concentration limit of Cu, Cr, Pb, As and Ni in the leaching solvent is lower than the standard. Therefore, the five heavy metals mentioned above were selected as the investigation targets. The leaching toxicity of the cement-solidified MSWIFA blocks and cement blocks is shown in Table 2. Heavy metal leaching concentrations in cement blocks were substantially lower than in MSWIFA blocks that have been cement-solidified. As a result, the impact of heavy metals in cement could be overlooked in future studies. For the cement-solidified MSWIFA blocks, the leaching concentration of heavy metal Cu, Cr, Pb, As and Ni is lower than the concentration limit of heavy metal stipulated in GB 5085.3 and GB 16889, indicating that the MSWIFA is no longer classified as a hazardous waste after cement solidification, has met the admission standard of domestic solid waste block landfill and can be disposed in sanitary landfill. The leaching solvent prepared by HJ/T 300-2007 leaching protocol (using acetic acid as leaching solvent) has significantly higher As, Cu and Cr concentration but lower Ni and Pb than the leaching solvent prepared by HJ/T 299-2007 leaching protocol (using sulfuric acid and nitric acid as leaching solvent). Whether the leaching toxicity results of solid waste block prepared with the HJ/T 300-2007 leaching protocol can be used to evaluate the environmental risk of cement-solidified MSWIFA blocks in zonation landfill remains to be clarified. Given the complex and changeable composition of cement-

solidified MSWIFA blocks and landfill environment, further investigation must be conducted to determine whether the results of short-term leaching experiments (e.g. HJ/T 300-2007 and HJ/T 299-2007) can represent the long-term environmental safety of cement-solidified MSWIFA blocks in the zoned landfill.

Table 2. Leaching toxicity of heavy metals in cement-solidified MSWIFA blocks (ug/L).

Items	Leaching test protocol	Heavy metal (ug/L)				
		Cu	Cr	As	Ni	Pb
MSWIFA <sup>a)</sup>	HJ/T 299-2007	1.60 ± 0.45	9.96 ± 2.20	6.67 ± 1.42	56.83 ± 4.46	870.83 ± 89
GB5085.3-2007		100000	15000	5000	5000	5000
MSWIFA <sup>a)</sup>	HJ/T 300-2007	8.67 ± 0.74	62.40 ± 9.30	37.90 ± 0.75	35.67 ± 10.92	91.87 ± 13
GB16889-2008		40000	5500	300	500	250

<sup>a)</sup> represents the mean and standard deviation values of the three parallel samples.

### Heavy metals leaching behaviours of the cement-solidified MSWIFA blocks

#### (1) Total amount and available leaching of heavy metals

To reduce the time for the long-term environmental risk assessment of heavy metals in solid waste block, researchers estimate long-term stability according to the leaching amounts of heavy metals from solid waste block under extreme leaching environment (e.g. high temperature, low pH value, high liquid-solid ratio and small particle size). Particularly, the total amount of heavy metals and available leaching amount are the most common indicators. The total amount of heavy metal and available leaching amount of the cement-solidified MSWIFA blocks are shown in Fig. 1. The total amount of heavy metals in the cement-solidified MSWIFA blocks ranges 36–646 mg/kg, and the available leaching amount ranges 1–37 mg/kg. The total amount of heavy metals in cement-solidified MSWIFA blocks is higher than that their available leaching amount. When cement was used to solidify the MSWIFA, hydration occurred and prompted the heavy metals in MSWIFA to combine with silicate or be wrapped in C-S-H gel, thus preventing leaching (Wang et al., 2020). Although the total amount of Pb in cement-solidified MSWIFA blocks is the largest (i.e. 645.7 mg/kg), its available leaching amount and available leaching rate (i.e. ratio of available leaching amount to total amount of heavy metals) are only 22.8 mg/kg and 3.5%, respectively. The total amount of Ni is the smallest (i.e. 36.6 mg/kg), but its available leaching rate is as high as 22.2%. The above results show that the available leaching rate of different heavy metals in cement-solidified MSWIFA blocks are different. The leaching rate of heavy metals is related to cement solidification process, matrix characteristics, heavy metal species and leaching protocol. In specific exposure scenarios, the available leaching amounts of heavy metals in the cement-solidified MSWIFA blocks can better reflect its actual environmental risk than the total amount. This index will be used as a control parameter to study the leaching characteristics of heavy metals (Yang et al., 2009).

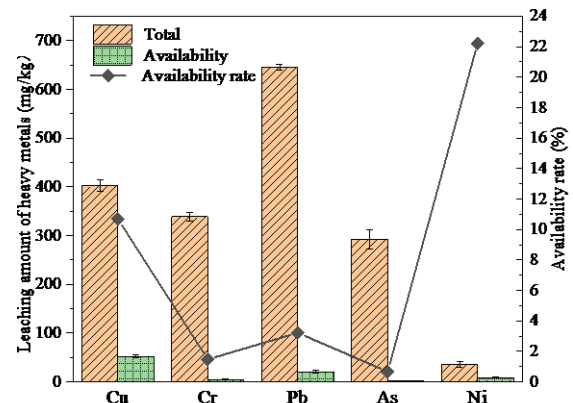


Fig. 1. Total, availability and availability rate of Cu, Cr, Pb, As and Ni in the cement-solidified MSWIFA blocks.

#### (2) Leaching characteristics of the heavy metals:

Heavy metal leaching from solid waste block is an unsteady process that varies with time. The leaching characteristics of heavy metals in the cement-solidified MSWIFA blocks are shown in Fig. 2. In acid rain group, the leaching rates of five heavy metals in the cement-solidified MSWIFA blocks follow the same pattern, with the rate being highest at the start and gradually decreasing. Among the heavy metals, the leaching of Cu, Cr and Ni is similar. The cumulative leaching amounts of heavy metals increase rapidly in the first 16 days of leaching experiment and approach the maximum cumulative leaching amount on the 36th day. However, the cumulative leaching amount of As in the first 16 days of leaching experiment increases rapidly and approaches an equilibrium state. This phenomenon can be explained as follows. Firstly, the leaching control mechanism of As in the cement-solidified MSWIFA blocks is different from that of other heavy metals. Secondly, As has the lowest available leaching rate (i.e. Fig. 1) and thus reaches the leaching equilibrium point faster than other heavy metals. By contrast, the leaching control mechanism of Pb in the cement-solidified MSWIFA blocks is quite different from that of Cu, Cr, As and Ni. The cumulative leaching amount of Pb increases rapidly in the first 16 days of leaching experiment and maintains a high level at 16–64 days when the leaching rate is constant. This finding indicates that the cumulative leaching amount of Pb fails to reach the equilibrium state in this experimental period. On the other hand, the cumulative leaching levels of heavy metals in the control group have a comparable growth trend to those in the acid rain group, showing that each heavy metal has a similar leaching rate. The cumulative leaching levels of heavy metals were lower than in the acid rain group, owing to the fact that the leaching solvent, HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (mass ratio 1:2) with pH value of 3.2±0.05, stimulates heavy metal leaching more than deionized water. In acid rain group, during the 64-day leaching experiment, the cumulative leaching amounts of Cu, Cr, Pb, As and Ni

are 1.3, 1.1, 1.6, 0.3 and 0.5 mg/kg, respectively, which are only a percentage of its available leaching at 2.5%–22.0%. This result reveals that the leaching period of these five heavy metals in the cement-solidified MSWIFA blocks is longer than the experimental period of EA NEN7375 leaching protocol. Therefore, a set of mechanism models based on the leaching control mechanisms of different heavy metals were developed and used to predict the long-term stability of the cement-solidified MSWIFA blocks to effectively shorten the experimental period.

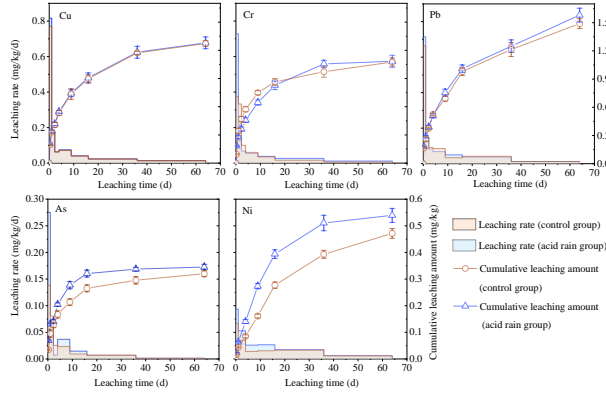


Fig. 2. Cumulative leaching amount and leaching rate of Cu, Cr, Pb, As and Ni in the cement-solidified MSWIFA blocks.

### (3) Leaching mechanism and leaching model of heavy metals:

At present, the most recognised and widely used model to describe the leaching of pollutants from solid waste block is the BDM. In this study, BDM (Formula 4) was firstly used to fit the cumulative leaching amounts of heavy metals in the cement-solidified MSWIFA blocks. The observed diffusion coefficient  $D^{obs}$  in the formula is only related to leaching temperature (Song et al., 2013). At the same temperature, the square of accumulated leaching amounts (i.e.  $M^2$ ) of heavy metals will show a linear relationship with leaching time  $t$ . BDM has the best fitting on Pb ( $R^2 = 0.98$ ), followed by Ni ( $R^2 = 0.92$ ). For the other heavy metals, the fitting effect of BDM is poor (i.e.  $R^2 < 0.9$ ). In the light of the result, BDM has the best fitting on Pb (i.e.  $R^2 = 0.97$ ) and Ni (i.e.  $R^2 = 0.98$ ). The fitting effect of BDM is likewise incorrect for other heavy metals (i.e.  $R^2 \leq 0.9$ ). The above results indicate that the leaching control mechanism of some heavy metals (e.g. Cu, Cr and As) in the cement-solidified MSWIFA blocks is influenced by mechanisms other than diffusion control. Therefore, analysing the leaching control mechanism of different heavy metals is necessary to accurately predict their leaching law in the cement-solidified MSWIFA blocks.

According to the EA NEN7375 leaching protocol, the leaching control mechanism of inorganic components (e.g. heavy metal) in solid waste block

includes surface wash-off, diffusion, dissolution, depletion and delayed diffusion. Surface wash-off refers to the dissolution of inorganic components in the solid–liquid interface when the leaching solvent contacts the block surface. Diffusion refers to the leaching of inorganic components due to molecular motion. Both of which are physical leaching control mechanisms. Dissolution refers to the leaching of inorganic components caused by the dissolution of some oxides in the block, and depletion means that the inorganic components is depleted in the block, these two are chemical leaching control mechanisms (Sun and Vollpracht, 2020). With this leaching protocol, the leaching control mechanism of heavy metals in solid waste block was identified by calculating (Formula 12) the leaching characteristics of different heavy metals at varying leaching intervals [i.e. leaching rate; Fig.2].

$$rc_{a-b} = (\log \varepsilon_a^* - \log \varepsilon_b^*) / (\log t_a - \log t_b) \quad (12)$$

Where  $\varepsilon_a^*$  and  $\varepsilon_b^*$  are the cumulative leaching of heavy metals in the leaching increment 1-a and 1-b, respectively, mg/kg;  $t_a$  and  $t_b$  are the completion time of leaching period a and b, respectively, d.

The heavy metal leaching rate and leaching control mechanism of the cement-solidified MSWIFA blocks at different leaching increments are shown in Table 3. Different heavy metals in the cement-solidified MSWIFA blocks are found to be controlled by varying leaching control mechanisms at different leaching increments. Pb is controlled by diffusion, which is also the reason why BDM can accurately fit its cumulative leaching data in the cement-solidified MSWIFA blocks. The leaching of Cu, Cr and As is controlled by diffusion, surface wash-off and depletion, and that of Ni is controlled by diffusion, dissolution and depletion. In a block solid, the proportion of heavy metal leaching caused by depletion control mechanism is extremely small and can be ignored (Tiruta-Barna et al., 2005). Therefore, the leaching of Cu, Cr and As in the cement-solidified MSWIFA blocks is mainly controlled by diffusion and surface wash-off, and that of Ni is mainly controlled by diffusion and dissolution. However, in the control group, BDM can also well fit the cumulative leaching amounts of Ni, possibly because the amount of Ni released by dissolution is very small.

Therefore, for acid rain group, formulas (10) and (11) were used to fit the accumulative leaching amounts of Cu, Cr, As and Ni (Fig. 2), and the fitting results and parameter values are shown in Table 3. Compared with those of BDM, the fitting results of FRDM and DDIM are closer to the actual test values. The correlation coefficients ( $R^2$ ) of Cu, Cr, As and Ni obtained from BDM are 0.87, 0.89, 0.74 and 0.92, respectively, which increase to 0.98, 0.95, 0.97 and 0.95, respectively. For the control group, the accumulative leaching quantities of Cu, Cr, and As were fitted using formula (10); the fitting results and parameter values are provided in Table



Table 3. Slope of heavy metal Cu, Cr, Pb, As and Ni at different leaching increment and determination of leaching mechanism.

Increment	Cu		Cr		Pb		As		Ni	
a-b	1#	2#	1#	2#	1#	2#	1#	2#	1#	2#
2-7	Dif	Dif	Dif	Sur	Dif	Dif	Sur	Sur	Dif	Dif
5-8	Dep	Dep	Dep	Dep	Dif	Dif	Dep	Dep	Dep	Dif
4-7	Dif	Dif	Dif	Dep	Dif	Dif	Dep	Dep	Dif	Dis
3-6	Dif	Dif	Dif	Dep	Dif	Dif	Dif	Dif	Dis	Dis
2-5	Dif	Dif	Dif	Dif	Dif	Dif	Dep	Dif	Dis	Dif
1-4	Sur	Sur	Sur	Dif	Dif	Dif	Dif	Dif	Dif	Dif

Note: Dif-Diffusion; Dep-Depletion; Dis-Dissolution; Sur-Surface wash-off; 1# represents acid rain group; 2# represents control group

4. The correlation coefficients ( $R^2$ ) of Cu, Cr, and As are enhanced from 0.90, 0.84, and 0.84, respectively, to 0.98, 0.99, and 0.98, respectively, using this formula. Therefore, the above corrected models can be used to predict the long-term leaching characteristics of heavy metals from the cement-solidified MSWIFA blocks during zonal landfill.

Table 4. Nonlinear regression parameters of different leaching models for Cu, Cr, Pb, As and Ni in cement-solidified MSWIFA blocks.

Heavy metals	Sample number	Model	Parameters				$R^2$ (-)
			$D^{obs}$ ( $cm^2/d$ )	$Q_0$ ( $mg/kg$ )	$k$ ( $1/d$ )	$K$ ( $mg \cdot cm/kg \cdot d$ )	
Cu	1#	FRDM	$2.72 \times 10^{-6}$	0.40	0.54	--	0.98
	2#	FRDM	$2.65 \times 10^{-6}$	0.40	0.49	--	0.98
Cr	1#	FRDM	$1.69 \times 10^{-4}$	0.45	0.33	--	0.97
	2#	FRDM	$9.91 \times 10^{-5}$	0.56	0.50	--	0.99
Pb	1#	BDM	$4.40 \times 10^{-5}$	--	--	--	0.98
	2#	BDM	$3.94 \times 10^{-5}$	--	--	--	0.97
As	1#	FRDM	$2.66 \times 10^{-5}$	0.25	0.37	--	0.95
	2#	FRDM	$5.78 \times 10^{-5}$	0.17	0.41	--	0.98
Ni	1#	DDIM	$4.43 \times 10^{-5}$	--	--	$3.31 \times 10^{-7}$	0.95
	2#	BDM	$2.71 \times 10^{-5}$	--	--	--	0.98

Note: 1# represents acid rain group; 2# represents control group

### Long-term stability assessment

At present, GB 16889-2008 is the standard for identifying the environmental risk of solid waste block entering sanitary landfills in China. When the concentration of heavy metals in solid waste block leachate (preparation method: HJ/T 300-2007) is lower than the limit specified in this standard, the environmental risk of solid waste block in the landfill is acceptable. Although the cement-solidified MSWIFA blocks used in this experiment can meet the requirements of entry materials in China's sanitary landfills, the leaching concentration of Pb may exceed the limit specified in GB 16889-2008 under the exposure scenario of partition landfills (Table 2). In addition, the cumulative leaching amounts of heavy metals in cement-solidified MSWIFA blocks using  $HNO_3/H_2SO_4$  (simulated acid rain) as the leaching solvent are greater

than those using deionized water (Fig. 2), indicating that cement-solidified MSWIFA blocks pose a greater environmental risk under acid rain scenarios. Therefore, the corrected pollutant leaching model was used to predict the daily and cumulative leaching amounts of different heavy metals and to judge the long-term environmental risk of the zoned landfill of the cement-solidified MSWIFA blocks in acid rain scenarios (as shown in Fig.3).

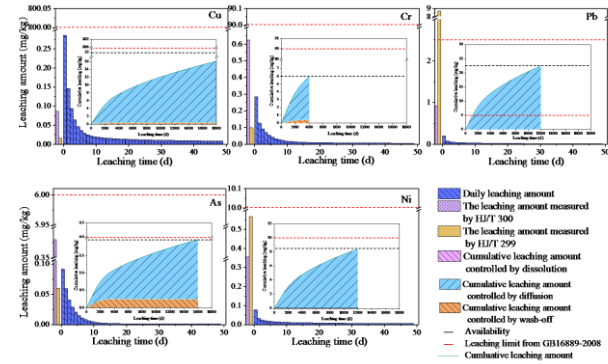


Fig. 3. Prediction of cumulative leaching amounts of heavy metals Cu, Cr, Pb, As and Ni in the cement-solidified MSWIFA blocks in acid rain scenarios.

Figure 3 shows that in the case of zoned landfill exposure, the daily leaching amounts of heavy metals in the cement-solidified MSWIFA blocks are maximised at the 1st day, then gradually decrease, and tend to balance after 10 days. Additionally, the maximum daily leaching of heavy metals in the cement-solidified MSWIFA blocks is lower than the leaching limit set by GB16889-2008, indicating that, in the zoned landfill, the leaching toxicity of the heavy metals in the cement-solidified MSWIFA blocks with high liquid-solid ratio or leaching solvent (i.e. acid rain) under short contact time is below the sanitary landfill environmental risk acceptable level. Moreover, according to the predicted leaching characteristics of heavy metals by the established model under the assumption that the leaching environment (e.g. temperature, pH, liquid-solid ratio and disregarded the bacterial effects) and the physicochemical properties (e.g. mineralogical phase particle size and porosity) of the test blocks remained constant, the cumulative leaching of Cu, Cr, As and Ni for the next 50 years is still lower than the leaching limit specified in GB16889. Therefore, cement solidification treatment has a good fixation effect on these four heavy metals and can significantly reduce the environmental risk of their landfill. Additionally, the leaching of these four heavy metals from surface wash-off control accounts for a low proportion of the total leaching of heavy metals (i.e. between 2.4% and 29%). According to the model prediction, the leaching of Pb is mainly controlled by diffusion, and the cumulative leaching amount in 718 d is higher than the limit in GB16889. When the liquid-solid ratio is low or the

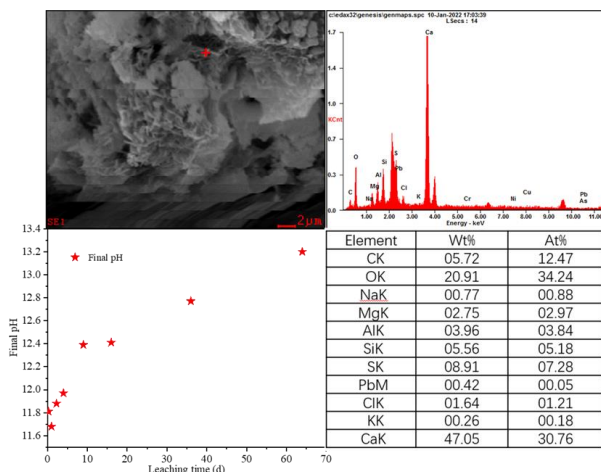


Fig. 4. Final pH of the solvent after each leaching step and SEM-EDS of ettringite in cement-solidified MSWIFA blocks.

leachate discharge is not smooth in landfill (i.e. the cement-solidified MSWIFA blocks is in contact with leachate for a long time), Pb leaching toxicity may exceed the acceptable levels of environmental risk in sanitary landfills. The main reasons for the high environmental risk of Pb in cement-solidified MSWIFA blocks are as follows. Firstly, the content of Pb is high in the cement-solidified MSWIFA blocks (i.e. 645 mg/kg) and GB16889 stipulates a low concentration limit of Pb in the leachate of landfill materials due to the high environmental toxicity of Pb. Secondly, it was documented that the pore solution of cement-solidified MSWIFA blocks was highly alkaline which contained large amount of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$  and  $\text{SO}_4^{2-}$  ions. Under this alkaline condition, Pb is mainly present in the form of  $\text{Pb}(\text{OH})_2$  and  $\text{PbSO}_4$  in the blocks. However, given the Pb is a amphoteric metal, the  $\text{Pb}(\text{OH})_2$  and  $\text{PbSO}_4$  precipitates can exist below a certain pH point (i.e.  $\text{pH} < 12$ ). When the pH of the solution rises above this point, the  $\text{Pb}(\text{OH})_2$  and  $\text{Pb}(\text{SO}_4)_4$  precipitates will gradually dissolves into  $[\text{Pb}(\text{OH})_3]^-$ ,  $[\text{Pb}(\text{OH})_4]^{2-}$  and  $[\text{Pb}(\text{OH})_2\text{SO}_4]^{2-}$ , increasing the solubility of Pb (Zhou et al., 2015; Wang, 2016). Although the hydration products of the cement-solidified MSWIFA blocks (e.g. ettringite; Fig. 4) could prevent partial Pb leaching out, the final pH of the leaching solvent was still mostly higher than 12 (Fig. 4), inducing large amount of Pb leaching out from the blocks. Therefore, the removal of partially soluble salts (e.g. Pb salts) from the freshly made cement-solidified MSWIFA blocks by water or natural rainwater washing in the initial landfilling stage (i.e. in this stage, the landfill is not capped with a final cover system and the leachate drainage system remains functional) is an effective countermeasure to reduce the environmental risk of cement-solidified MSWIFA blocks in zoning sanitary landfill.

## CONCLUSION

This study tends to estimate the long-term environmental risk of cement-solidified MSWIFA in zoning sanitary landfill in terms of the leaching behaviours of five different heavy metals (i.e. Cu, Cr, Pb, As, Ni). The following conclusions was drawn.

(1) Under simulated acid rain scenarios, Pb leaching from cement-solidified MSWIFA was controlled by diffusion, whereas Cu, Cr and As were dominated by wash-off and diffusion. Ni leaching was mostly controlled by diffusion and dissolution. The established BDM, FRDM and DDIM could accurately described the leaching behaviours of the abovementioned heavy metals with different control mechanisms ( $R^2 > 0.95$ ).

(2) The prediction results of the calibrated models indicated that the long-term environmental risk of Pb was high in acid rain scenarios, in terms of the cumulative leaching amount of Pb exceeded the limit issued in GB-16889 after 718 days' leaching. It could be attributed to the strong alkali environment of the cement-solidified MSWIFA ( $\text{pH} > 12$ ) which might stimulate the dissolution of partial Pb salts (e.g.  $\text{Pb}(\text{OH})_2$  and  $\text{PbSO}_4$ ).

(3) Removal of partially soluble Pb salts from freshly made cement-solidified MSWIFA is an effective countermeasure to reduce the environmental risks in zoning sanitary landfill.

## ACKNOWLEDGEMENT

The study was supported by the National Key Research and Development Program of China (2021YFE0112100).

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