Two-Step Flotation Treatment for Removal of Toxic Matter from Hospital Solid Waste Incinerator Fly Ash

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ABSTRACT

Application of two-step flotation for removing dioxins and heavy metals from hospital solid waste incinerator (HSWI) fly ash was studied. In the first step, decarburization flotation was executed to remove dioxins from raw fly ash. The second step of precipitation flotation was carried out to recycle the toxic metals in the residual slurry. Finally, an acid leaching-sulphide precipitation-flotation method was proposed. The results showed that carbon removal rate was 90.7%, and the dioxin removal percentage was 91.0% during decarburization flotation. And Zn, Pb and Cu in residual slurry were acid-leached with the removal efficiencies being 91.3%, 79.2% and 85.6%, respectively. The optimum sulphidation condition of heavy metals in the residual slurry were Na_2S molar ratio of 1.4 and sulphidation time of 30 min. Subsequently, precipitation flotation could recover 49.9% of Zn, 42.0% of Pb and 48.7% of Cu from the raw fly ash. After the two-step flotation, the toxicity of the tailings reduced considerably, and the tailings could be disposed in landfill. Therefore, this two-step flotation treatment of HSWI fly ash may result in both detoxification and potential resource recovery.

Keywords: Incinerator fly ash; Two-step flotation; Sulphidation; Dioxins; Heavy metals.

INTRODUCTION

Hospital solid waste incinerator (HSWI) fly ash is categorized as hazardous waste rich in toxic metals and organic pollutants such as chlorobenzenes (CBs), chlorophenols (CPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), etc. (Lee *et al.*, 2003; Wang *et al.*, 2005; Chen *et al.*, 2013; Cheruiyot *et al.*, 2015; Cheruiyot *et al.*, 2016; Lee *et al.*, 2016). Moreover, both unburned and powder-activated carbons are also included in HSWI fly ash, which are the main resources of organic pollutants in the raw fly ash.

Currently, incinerator fly ash can be disposed by four main methods, namely: acid extraction, chemical stabilization, melting treatment and cement solidification, among which cement solidification is widely adopted due to its simple operation and low investment. But it will only reduce the leaching amount of heavy metals and has little effect on organic pollutant removal (Huang *et al.*, 2011). Similarly, traditional chemical stabilization is inappropriate for source recovery from such types of wastes. Even more, this method may produce unexpected wastes (Deliyanni *et al.*, 2017).

Melting treatment could destroy organic substances and produce byproducts, such as glass and slag, which can be used as building materials (Kuo *et al.*, 2012). At the same time, volatile toxic metal chlorides such as $ZnCl_2$ and $PbCl_2$ concentrated in secondary fly ash can serve as feed materials in Zn or Pb smelters. However, melting processes are high energy-consuming and high carbon dioxide-releasing processes and thus are not environmentally friendly. Contrast with the aforementioned methods, acid extraction can leach heavy metals simply by using a suitable acid liquor before the filtration process and the precipitation operation (Bo *et al.*, 2009; Jiao *et al.*, 2016; Tang *et al.*, 2016; Zhang *et al.*, 2016). But the availability of this technique is limited and some bottle necks need to overcome (Hung *et al.*, 2013). Because of the incomplete filtration of heavy metals, a considerable amount of heavy metals in leachates cannot be recycled and must be finally mixed and disposed together with solid residues. Therefore, recycling heavy metals in leachates prior to mixed treatment is necessary (Bo *et al.*, 2011; Zhang *et al.*, 2016).

Flotation technique has a lot of merits, such as flexibility, environmentally benign, and energy savings over conventional filter materials. Based on the lipophilic and hydrophobic nature of PCDD/Fs and PCDD/Fs' characteristic enrichment of carbon constituents, decarburization flotation has been suggested for removing them from HSWI fly ash (Liu *et al.*, 2013). Most dioxins and carbon constituents in ash sample can be effectively removed by transference to

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froths, this can not only achieve the detoxification of dioxins but also the reburning of carbon constituents can provide energy for the incinerator (Wei *et al.*, 2017). After the aforementioned treatment for dioxins in tailings, the toxic equivalent (TEQ) would be reduced to meet the landfill standard value of 3 ng TEQ g⁻¹ for municipal solid waste. However, the contents of toxic metals, particularly Zn, Pb and Cu in the raw fly ash are very high. After decarburization flotation, most heavy metals would be transformed from raw fly ash to the residual slurry and finally to the tailings. From the viewpoint of resource reclamation, these heavy metals contained residual slurry would be served as secondary resources that can be separated and recovered instead of being wasted. Thus, an effective technology for the appropriate treatment and disposal of the residual slurry containing heavy metals is urgently required.

Acid extraction is the most common approach for recovering heavy metals, because most heavy-metal compounds easily dissolve in solution under meta-acid conditions (Fedje *et al.*, 2010). HCl and HNO$_3$ are frequently employed because they can extract almost all metallic elements, and a relatively higher extraction rate can be obtained under a HNO$_3$: HCl ratio of 1:3 (Min *et al.*, 2012). Moreover, in our previous study, the addition of a small quantity of HCl to HSWI fly ash prior to decarburization flotation could be used to leach the toxic metals out of the HSWI fly ash (Liu *et al.*, 2014). However, the performance of decarburization flotation and dioxins removal is inhibited if the slurry pH is very low. Therefore, the acid leaching process of raw fly ash should be performed after the decarburization flotation process.

Sulphidation treatment can transfer metal ions into insoluble metal sulphides that can be removed through precipitation flotation (Amaral Filho *et al.*, 2016). Kuchar demonstrated that sulphidation treatment could transform pure metals into metal sulphides with stable chemical properties and high floatability (Kuchar *et al.*, 2007a). Min found that the sulphidation efficiency of zinc plating sludge with Na$_2$S could reach a maximum of 80.9% at a ratio of liquid: solid = 50 after 48 h (Min *et al.*, 2012). Vanthuyne considered that sulphide pre-treatment could enhance the flotation recovery efficiency of heavy metals in the sediment from 43% to above 90% (Vanthuyne *et al.*, 2003).

The removal of heavy metal sulphides through precipitation flotation has been proposed. This technique is based on an ionic precipitate formation, which is subsequently removed by attaching to air bubbles from suspensions with suitable reagents to form a flotation 'concentrate' because of its hydrophobic surface (Cappponi *et al.*, 2006; Min *et al.*, 2012). Some researchers have successfully employed precipitation flotation to govern metal-concentrated soil, sediment, and wastewater (Peng *et al.*, 2009; Huang *et al.*, 2011; Liang *et al.*, 2012; Min *et al.*, 2012). For example, Liang reported that 33.3%, 58.9% and 68.8% of Zn, Pb and Cu could be

separately removed from sludge by the methods of hydrothermal sulphidation and floatation (Liang *et al.*, 2012). Huang found that the treatment of precipitation flotation after acid leaching could recycle 92.7% of Ti⁴⁺ from the tailings enriched with Ti (Huang *et al.*, 2016). Therefore, as a promising approach, precipitation flotation technology has received increasing attention for its toxic metal recovery ability.

Both heavy metals and organic pollutants including dioxins are present in HSWI fly ash. The purpose of raw fly ash treatment should be not only to positively remove toxic materials such as dioxins, but also to recover valuable materials such as heavy metals. Few technologies can achieve this goal. Furthermore, previous and current research on flotation technologies has focused on both organic constituents and heavy metals, with little focus on mixed wastes. Taking previous results into consideration, this study proposes a two-step flotation process for selectively removing dioxins and heavy metals from raw fly ash. This detoxication process can not only separate out of dioxins through decarburization flotation but also remove and recycle heavy metals through sulphide precipitation flotation to reduce leaching toxicity. The first step of decarburization flotation was provided in our previous study (Liu *et al.*, 2013; Liu *et al.*, 2014). Thus, in this study, we mainly elaborated on the second step of precipitation flotation of heavy metals. We also examined the major factors influencing sulphidation and flotation to sufficiently comprehend the partitioning of toxic metals in flotation products.

MATERIALS AND METHODS

Materials

The raw fly ash (ash sample) received from an HSWI in south China was used as the experimental sample in this study. First, the fresh fly ash obtained from the incinerator was collected with a bag filter after heavy metals and dioxins were absorbed by PAC. Subsequently, it was homogenised and sieved with a 20 meshes of sieve. Finally, it was dried for 24 h at 383 K before the subsequent operation. Table 1 provides the chemical components of ash sample. The PCDD/F concentrations in the ash sample together with four types of flotation products are listed in Table 2. The loss on ignition (LOI), which was defined according to the standard of GB18485-2001 and determined as the weight loss of the subsample in the condition of 3 h and 873 ± 25 K, is also given in Table 2. The concentrations of PCDD/F and its congeners (2,3,7,8-substituted) were analyzed using the isotope dilution high resolution gas chromatography-high resolution mass spectrometry. Moreover, the PCDD/F analytic method was described in detail in our previous study (Wei *et al.*, 2016a). TEQ of dioxin congeners in the sample were calculated on the basis of international toxic equivalency factors.

Table 1. Chemical composition in the raw fly ash (%).

SiO$_2$	CaO	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	K$_2$O	Na$_2$O	SO$_3$	Cl	TiO$_2$	F
14.8	8.3	3.8	4.1	1.0	7.6	19.0	5.0	31.4	1.0	1.0

Table 2. Weight distributions, LOI, concentrations of PCDD/Fs and content of heavy metals in the input and output materials.

		Input	Output				Removal efficiency (%)	Recovery efficiency (%)
		Fly ash	Froths	Concentrate	Tailings	Waste water		
Weight distribution (%)		100	16.2	4.5	12.4	-		
LOI (%)		11.3	63.5	5.3	4.8	-	90.7	
Concentrations of PCDD/Fs	Mass concentrations (ng g^{-1})	81.9	450.9	24.5	24.4	0.2 ng L^{-1}	91.0	
	TEQ concentrations (ng-TEQ g^{-1})	6.1	37.9	1.7	1.7	0.005 ng-TEQ L^{-1}		
Content of heavy metals	Zn (g kg^{-1})	8.2	19.4	9.1	5.0	1.0 mg L^{-1}		49.9
	Pb (g kg^{-1})	1.9	4.1	1.8	2.2	1.0 mg L^{-1}		42.0
	Cu (g kg^{-1})	0.8	1.6	8.2	0.7	0.5 mg L^{-1}		48.7

Experimental Methods

A schematic representation of continuous two-step flotation tests is depicted in Fig. 1. Both stages were operated in a 950-mm long 30-mm I.D. column. First, dioxins and carbonaceous components in ash sample were removed by decarburization flotation. In this step, raw fly ash (30 g), deionized water (600 mL), and a balanced amount of agents including methyl isobutyl carbinol (MIBC) which served as a frother and kerosene which served as a collector were mixed to obtain the slurry, which was then fed from the top of the flotation column. To determine the optimal conditions for decarburization flotation, a series of tests were performed as a function of relevant parameters. Two types of product froths and the residual slurry were obtained. At the end of the flotation test, each batch of the froths was vacuum-filtered by the membrane filter (0.45 μm). Then the froths were dried for 12 h under the temperature of 105°C, and the filtrate was returned to the residual slurry. The froths and the collected residual slurry were analysed for heavy metals through atomic absorption spectroscopy 600.

The residual slurry from decarburization flotation was then disposed by successive acid leaching, sulphidation, and precipitation flotation to remove and recycle heavy metals. During the acid soluble step, HCl was added to the residual slurry to obtain a solution with varying final pH, and then stirred and conditioned for 30 min in a hybrid mixer. The leaching efficiency could be calculated as the ratio of the leachate amount of a given metal over its total amount in the residual slurry. Following acid leaching, $Na_2S \cdot 9H_2O$ was employed for heavy metal sulphidation. The initial pH value of sulphidation reaction usually needs to be adjusted to more than 10.0 to improve the combination of the metal ion with the sulphide ion (Liang *et al.*, 2012). In this study, the pH value after NaOH treatment was determined as 11 according to the result of a preliminary experiment. The molar mass of sulphurated metals after shaking for 10–60 min and the total metal molar mass before sulphidation were also obtained. The sulphidation efficiency was determined according to a previously described method (Kuchar, *et al.*, 2006a). That is, the sulphidation efficiency was calculated as the fraction of the molar mass of the sulphide d-value divided by the molar mass of total heavy metals (Zn, Pb and Cu). Moreover, the sulphide d-value was obtained by subtracting the molar mass of remanent Na_2S in the solution after sulphidation from the total molar mass of Na_2S added during the sulphidation process. The residual sulfide ion concentrations were measured using iodometric method, which is used for the determination of sulfides when evaluating water quality. After sulphidation process, the residual slurry was shifted into the flotation cell; subsequently, the collector, frother and surfactant were added, and the mixture was reconditioned for 5 min. Changes were only made to the reacting condition of kerosene (2–10 g kg^{-1}), the MIBC frother (2–16 g kg^{-1}), the SDS dosage (1–6 g kg^{-1}), the pH values (6–12), the ventilation rate (0.50–1.50 L s^{-1}) and the flotation time (5–30 min). After flotation, the concentrate rich in toxic metals was obtained. And the metal recovery efficiency could be calculated as the ratio of the amount of the heavy metals obtained in the concentrate over the total
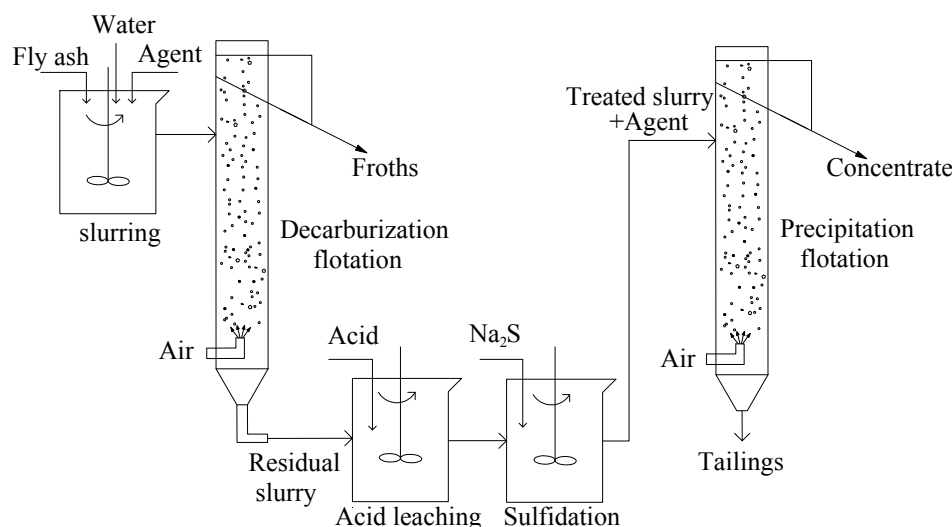
Fig. 1. Flowchart of two-step flotation.

metals in ash sample. The tailings were then dissolved and digested with the mixed liquor of $HNO_3 : HCl = 1 : 3$ (v/v) for 2 h. Acid leaching of the tailings was executed on the basis of the acetic acid buffer solution method, which is a Chinese-formulated solid waste extraction procedure for leaching toxicity.

RESULTS AND DISCUSSION

Decarburization Flotation Results

First, the operating parameters of decarburization flotation were examined to achieve the desired separation performance. According to our previous methods, the optimal parameters indicated below: 0.06 m^3 h^{-1} of air flow rate, 2 kg t^{-1} of frother dosage, 12 kg t^{-1} of kerosene dosage and 0.05 kg L^{-1} of slurry concentration. The frother dosage was lower than that of our present report, which may be attributed to the chloride ions in ash sample used in this study (Liu *et al.*, 2013). A relatively concentrated sodium chloride (NaCl) solution could delay bubble coalescence, thus increasing froth stability (Bournival *et al.*, 2012). Feng reported that heavy metal chloride complexes which were formed and absorbed onto the surface of fly ash could exchange with carbonate ions, which would improve the performance of decarburization flotation (Feng *et al.*, 2015). While, Salmani proved that chloride salts may interfere with the removal of Cr (Salmani *et al.*, 2016). Thus, the effect of chloride salts on toxic matter removal should be further investigated. Weight distribution, LOI and concentrations of dioxins in ash sample and output materials (froths, the concentrate, the tailings and wastewater) were analysed in Table 2. According to experimental results, the weight loss during the water phase was 65.9%, this may be attributed to the dissolution of soluble salts during the flotation process (Liu *et al.*, 2013). The froths, the concentrates and the tailings product had yields of only 16.2%, 4.5% and 12.4% of raw fly ash after flotation, respectively. Thus, removal efficiencies of PCDD/Fs (β_c) and carbon constituents (β_d) could be calculated by the following equations:

$$\beta_c\left(\%\right) = \frac{m}{m_0} \times 16.2\% \times 100 \qquad (1)$$

$$\beta_d\left(\%\right) = \frac{c}{c_0} \times 16.2\% \times 100 \qquad (2)$$

where m and m_0 were the total mass concentrations of PCDD/Fs in the froths and the ash sample, respectively; where c and c_0 were LOI in the froths and the input materials.

As seen in Table 2, LOI of the froth product and fly ash sample were 63.5% and 11.3%, and the carbon removal efficiency in the froths was 90.7% according to the mass distribution. Meanwhile, the PCDD/F content in froths reached 460.9 ng g^{-1}, and 91.0% of PCDD/Fs in ash sample could also enrich the froth product. In addition, the hydrophobicity and structure of dioxins and organic contaminants (such as PAHs, CBs, CPs and PCBs) are similar, thus, their migration laws are also similar. So the froth product also should contain significant amount of these organic contaminant. Considering the high calorific value of froths, the PCDD/F could be effectively destructed by further reburning treatment of froths in the incinerator (Liu *et al.*, 2016). After flotation, the TEQ of PCDD/Fs in the tailings was reduced to 1.7 ng TEQ g^{-1} from an initial level of 6.1 ng TEQ g^{-1} in the input materials. TEQ of the tailings was approximately half of the Chinese content standard value for landfills (3 ng TEQ g^{-1}). Because of the low water solubility of PCDD/Fs, extremely small quantities of PCDD/Fs were detected in waste water. The PCDD/F content in the concentrate product is approximately equivalent to those in the tailings; this portion of PCDD/Fs in the concentrate would be decomposed in metallurgy recovery. Thus, in the first flotation step, dioxins, carbon compounds and chlorides were removed from ash sample.

Results of Acid Leaching

The preliminary analysis showed that the fly ash mainly

contained with Zn, Pb, Cu, Cd and Cr. Among these metals, the content of Zn, Pb and Cu were relative higher and they had the potential of recovery. Therefore, this paper mainly studies the removal and recovery of Zn, Pb and Cu by acid leaching-sulphide precipitation-flotation. Table 3 provides the contents of toxic metals Zn, Pb and Cu in the ash sample which were higher than those reported previously (Liu *et al.*, 2014). Heavy metals in the ash sample will first be allocated between the two products of the froths and residual slurry after decarburization flotation. Then, the residual slurry is subjected to acid leaching, heavy metals are released from the slurry and dissolved. Leaching experiments under different pH values were performed. Results indicate that leaching efficiencies of Zn, Pb and Cu increased as the pH value decreased (Fig. 2). This indicates that the acid soluble fraction is very high for these heavy metals, which bound to the speciation of the carbonate (Wei *et al.*, 2016b). The oxides and hydroxides would be dissolved at a low pH value. At pH = 2, 91.3% of Zn, 79.2% of Pb and 85.6% of Cu were acid-leached. Jiao and Tang accurately indicated that the releasing degree of heavy metal (especially for Cu, Pb, Zn and Cd) showed a plateau at pH = 2 (Jiao *et al.*, 2016; Tang *et al.*, 2016).

The leaching concentrations of Zn, Pb and Cd in ash sample were much higher compared with the limit values; especially Pb is about 70 times higher. Most of those heavy metals leached into the solution were removed through subsequent sulphide precipitation flotation; thus, the leachability of heavy metals from the tailings was significantly reduced. Table 3 also lists the final leaching concentrations of toxic metals in the tailings after the whole treatment process of acid leaching under different pH values and sulphide precipitation flotation. As expected, with a decrease in the pH value from 6 to 2, the leaching concentrations of Zn, Pb, Cu, Cd and Cr in the tailings decreased continuously to 5.8, 0.2, 0.7, 0.08, and 0.03 mg L^{-1}, respectively, which not only meet the permitted limits for the landfill site and enable the tailings to be directly disposed in the landfill, but also reduce the landfill area after dissolution of the soluble salt. Thus, pH values should be adjusted to less than or equal to 2 to ensure complete dissolution of carbonates and oxides of toxic metals.
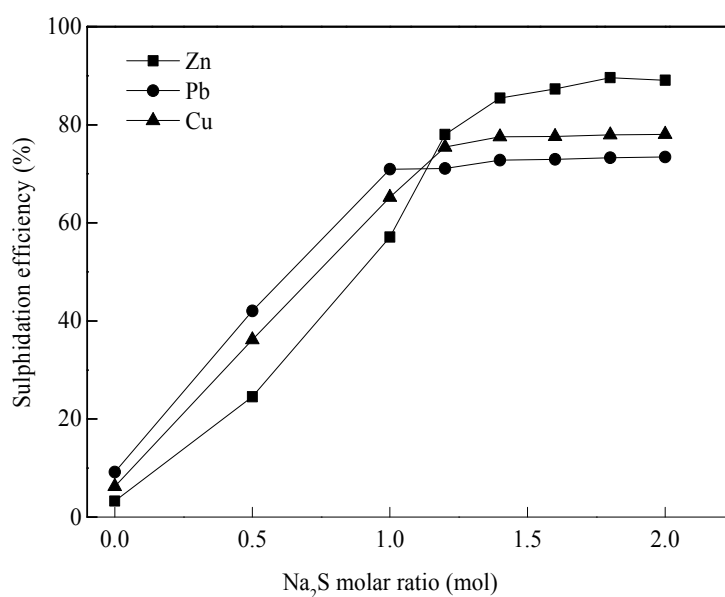
Results of Sulphidation Precipitation

Heavy metals were precipitated and metal sulphides were formed after Na$_2$S was added. The study of Na$_2$S molar ratio versus heavy metal sulphidation efficiency is presented in Fig. 3. With an increase of the molar ratio, the sulphidation efficiency of Pb and Cu reached to the maximum at the molar ratio of 1.2 and then slowed down to attain a stable value of 72.8% and 77.6% at the molar ratio of 1.4, respectively. However, a slight difference was observed for Zn. With the increase of molar ratio for Na$_2$S, the sulphidation efficiency of Zn increased in a large slope first; the sulphidation

Table 3. Leaching concentrations of heavy metals in the tailings at different pH value (mg L^{-1}).

Heavy metals	Raw fly ash	Tailings					Permitted limits of the landfill site
		pH = 6	pH = 5	pH = 4	pH = 3	pH = 2	
Zn	174.2	121.7	82.3	39.0	22.9	5.8	100
Pb	17.9	11.9	7.1	3.3	0.5	0.2	0.25
Cu	9.0	6.2	4.8	2.9	1.4	0.7	40
Cd	3.42	2.36	0.68	0.15	0.11	0.08	0.15
Cr	0.35	0.29	0.17	0.07	0.04	0.03	4.5
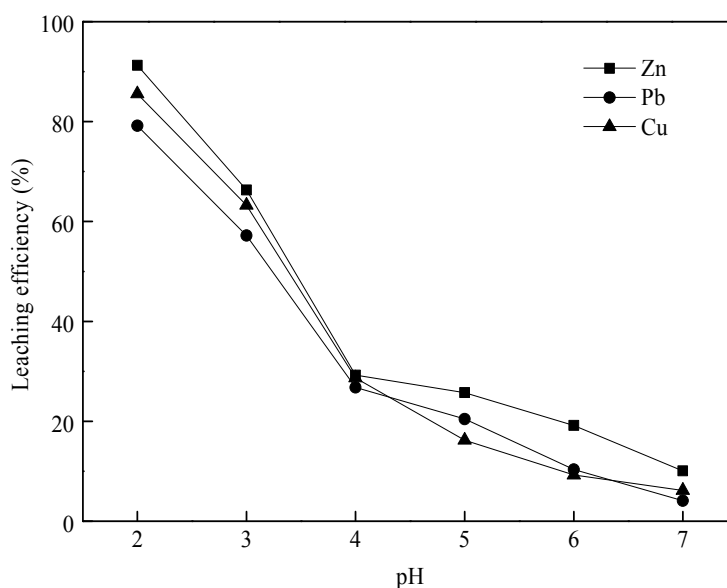
Fig. 2. Effects of pulp pH on leaching efficiency of heavy metals after decarburization flotation.

Fig. 3. Effects of Na$_2$S molar ratio on sulphidation efficiency of heavy metals (sulphidation time = 30 min).

efficiency of Zn reached 85.5% at the Na$_2$S molar ratio of 1.4 and then reached to its maximum (89.6%) at the Na$_2$S molar ratio of 1.8. Precipitation usually follows a sequential order because of different solubility products of heavy metal sulphides. Similar result was observed in a previous study conducted by Kuchar (Kuchar *et al.*, 2006b). Preferable removal efficiency required relatively higher sulphidation efficiency, whereas excessive Na$_2$S consumed more energy and resulted in secondary pollution, especially when it was in an acidic environment. Thus, the molar ratio of 1.4 was selected as an ideal value.

The effect of sulphidation time on the sulphidation extent is shown in Fig. 4. With the extension of time, sulphidation efficiency steeply increased and reached to the maximum within 30 min, in which the conversion extent for Zn, Pb, and Cu were 85.5%, 72.8% and 77.6%, respectively, and it then flattened from 30 min to 1 h. The result was consistent with the literature of Kuchar (Kuchar *et al.*, 2007b). This may be attributed to the rapid reaction of freely soluble metal oxides and hydroxides within 30min. When time was prolonged to 1 h, the insoluble, remnant soluble and sparingly soluble metal oxides and hydroxides were slowly transformed into metal sulphides, a part of which together with the insoluble salts would retain in the slurry to prolong the sulphidation time (Salmani Abyaneh and Fazaelipoor, 2016). Thus, the optimum time was determined as 30 min.

Precipitation Flotation of Heavy Metals in the Residual Slurry

It is expected that various heavy metals would transfer as metal sulphides after sulphidation treatment. Thus, it is necessary to recover metal sulphides from the residual slurry. Fig. 5 draws a conclusion that the employment of collector agent plays an important role in heavy metal recovery. The recovery efficiencies for Zn, Pb, and Cu were enhanced at first, reaching 49.9%, 42.0%, and 48.7%, respectively, at the condition of 6 g kg^{-1} of kerosene; however, they decreased as

the kerosene dosage was further increased. These results are consistent with the literature (Cauwenberg *et al.*, 1998a). As a strong hydrophobic collector, kerosene is more likely to be attached to heavy metals and then the floatation possibility was increased; however, an excessive dosage of it can reduce the floatation efficiency. This was due to the generating of multilevel adsorption reverse layer on the surface of the precipitates, which made precipitates more hydrophilic. Besides, excessive kerosene not only made the external force of the slurry fail to overcome the surface tension of kerosene and then form a stable dispersion system, but also it enhanced the mutual merger role among the oil droplets. Thus, metal sulphides were adsorbed and clustered together to form large precipitate, which were difficult to be floated out and finally formed as sedimentation.

The effect of the frothing agent (MIBC) on the precipitation flotation is illustrated in Fig. 6. The recovery efficiency of heavy metals increased first, reaching the highest level at 6 g kg^{-1} of MIBC, and then dropped off with an increase of the MIBC dosage. In the case of low-concentration MIBC dosage, both the shortage of floating force and the slow floating speed produced a descendant flotation character of the heavy metals or the direct fall-off from the surface of heavy metals for the precipitation, which resulted in the decrease of recovery efficiency (Clift *et al.*, 1978; Kowalczuk *et al.*, 2013). A similar result was reported by Qin, indicating that MIBC has good solubility; impurity entrainment and the mutual merger role among the bubbles could be better restrained in the usage of MIBC; thus, frother volumes and concentrations increased (Polat *et al.*, 2007; Rafiei *et al.*, 2011). When frother concentrations increases, the volume of the membrane containing liquid reduces and brittleness increases; the foams again lose stability. Naik concluded that excessive MIBC increased the microbubble proportion, resulting in a decreased concentrate grade (Cho *et al.*, 2002; Naik *et al.*, 2005).

The surfactant can not only reduce the ascending velocity
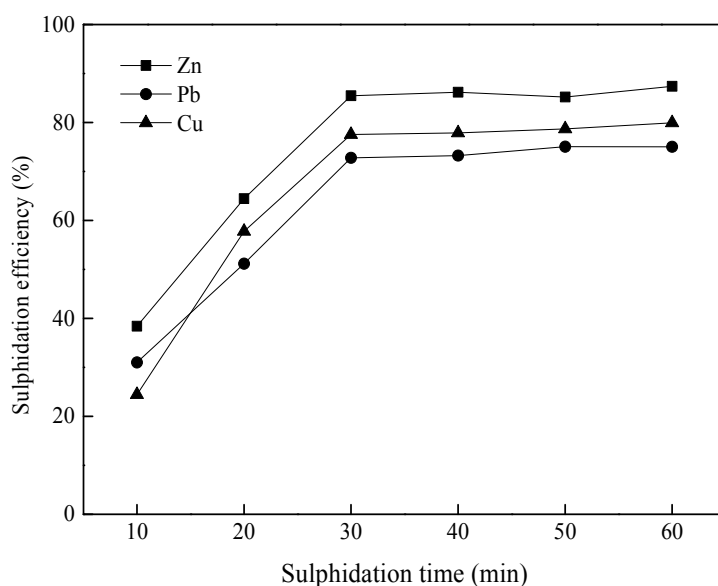
**Fig. 4.** Effects of sulphidation time on sulphidation efficiency of heavy metals (Na_2S molar ratio = 1.4 mol).
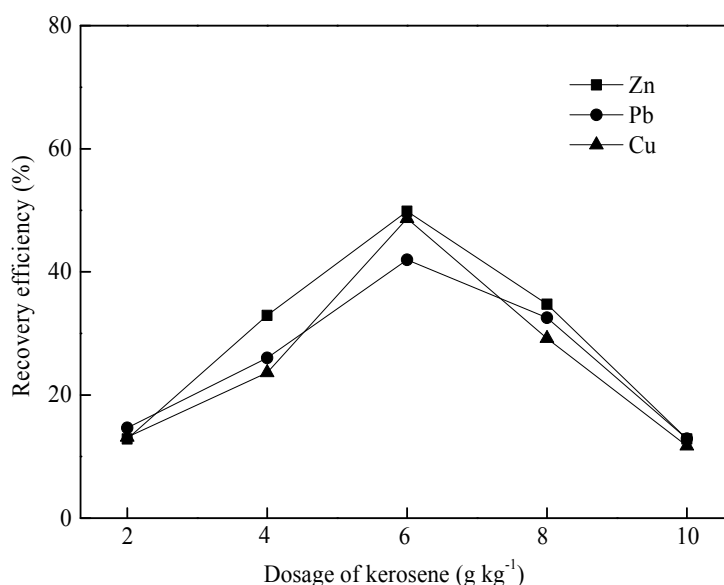
Fig. 5. Effects of dosage of kerosene on heavy metal recovery efficiency (MIBC = 6g kg^{-1}, SDS = 3 g kg^{-1}, pH = 10, V = 1.25 L s^{-1}, t = 15 min).

of foams but also can extend the holdup time of gas in the slurry and increase the bubble collision probability, which are helpful for better usage of surfactants on the bubble surface (Cauwenberg *et al.*, 1998a; Pei *et al.*, 2004; Przemyslaw *et al.*, 2013; Wang *et al.*, 2013; Salmani Abyaneh and Fazaelipoor, 2016). The effects of surfactant dosage (SDS) on the precipitation flotation are displayed in Fig. 7. As the SDS dosage increased, recovery efficiency increased at first until the maximum dosage of 3 g kg^{-1} and then decreased gradually until it flattened. As a negative ionic activator, SDS can improve the hydrophobic performance of positively charged metal cations. With the increase of SDS dosages, the inhibition of particle sizes was enhanced and the formation of large particles was restrained. However, each activator

type has its own critical concentrations to form micellar clusters by itself. When the critical value is exceeded, the molecular structure transforms into dropwise micellar molecules, in which the polar group is outside and the hydrophobic group is inside. Anisotropic ions are attached around the molecular group, and it is difficult to make them float because of the strongly hydrophilic surface. Thus, the recovery efficiency of heavy metals reduces slightly. Besides, Fuerstenau noted that both surfactant dosages and types are resulted to have influence on metal recovery (Fuerstenau *et al.*, 2002; Lee *et al.*, 2002). And the effect of surfactant types is still worthy of further study.

Fig. 8 shows that pulp pH has a prominent effect on metal recovery. With pH increasing from 6 to 12, recovery
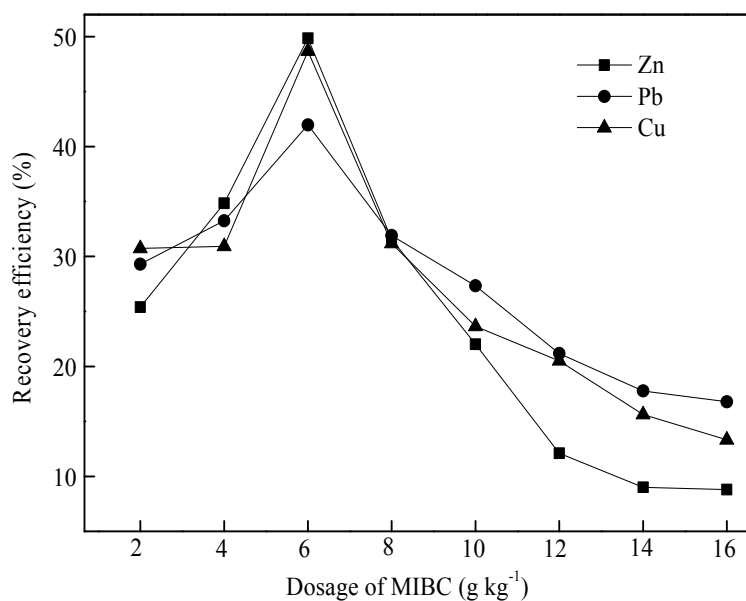
Fig. 6. Effects of dosage of MIBC on heavy metal recovery efficiency (Kerosene = 6 g kg^{-1}, SDS = 3 g kg^{-1}, pH = 10, V = 1.25 L s^{-1}, t = 15 min).
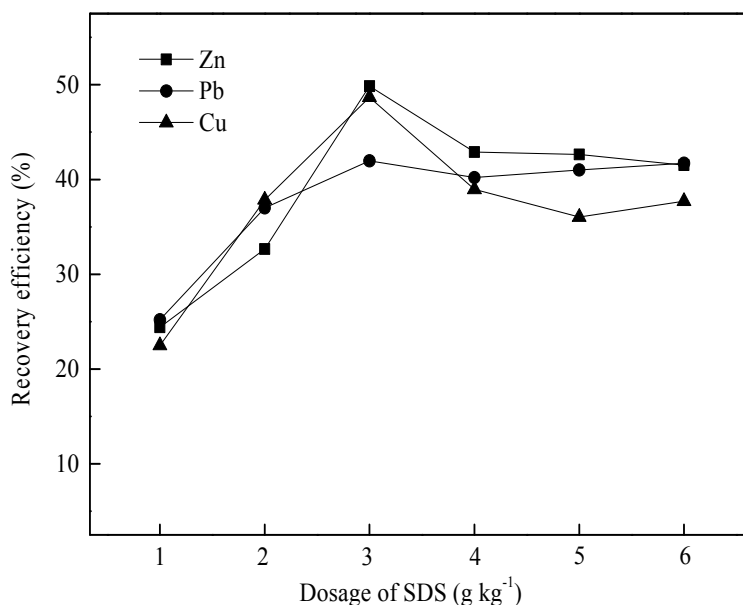

Fig. 7. Effects of dosage of SDS on heavy metal recovery efficiency (Kerosene = 6 g kg^{-1}, MIBC = 6 g kg^{-1}, pH = 10, V = 1.25 L s^{-1}, t = 15 min).

efficiency of heavy metals increased; however, after pH 10, it gradually stabilized. Thus, a pH value of 10 was optimum in this study. Similar results were reported that variations in pulp pH might affect the competence of an anionic activator or MIBC, which indirectly affects heavy metal recovery. According to a previous study (Cauwenberg *et al.*, 1998b), the optimal pH is 8 or 9, which may be related to differences in types and solubilities of heavy metal compounds included in the aforementioned experiments. Furthermore, in the present study, the general order of transition metal recovery with pH was Zn = Cu > Pb. These results are consistent with those reported by Cauwenberg and Dermont (Vanthuyne *et*

al., 2002; Dermont *et al.*, 2010).

The precipitation flotation of heavy metals increased with the enhancement of ventilation velocity (Fig. 9). At an speed of 1.25 L s^{-1}, the recovery efficiency reached to its optimum value. And it then stabilized and decreased slightly. The relation between the ventilation rate and bubble radius can be represented as a linear function; as the ventilation speed increased, the bubble radius also increased, and it was easy for precipitation to stick to the surface of the bubbles. However, an excessive surface area can lead to vigorous agitation for the slurry, and metal sulphides can easily slip off from fragile bubbles. Therefore, it is necessary to keep
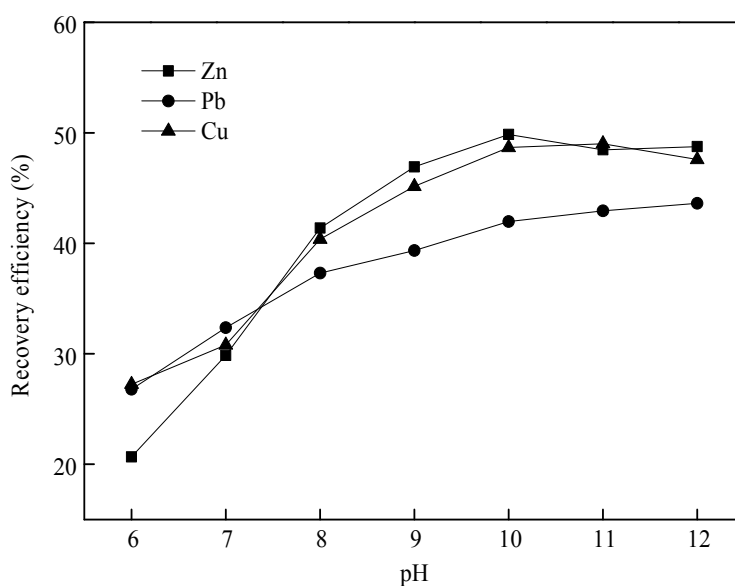
Fig. 8. Effects of pulp pH on heavy metal recovery efficiency (Kerosene = 6 g kg^{-1}, MIBC = 6 g kg^{-1}, SDS = 3 g kg^{-1}, V = 1.25 L s^{-1}, t = 15 min).
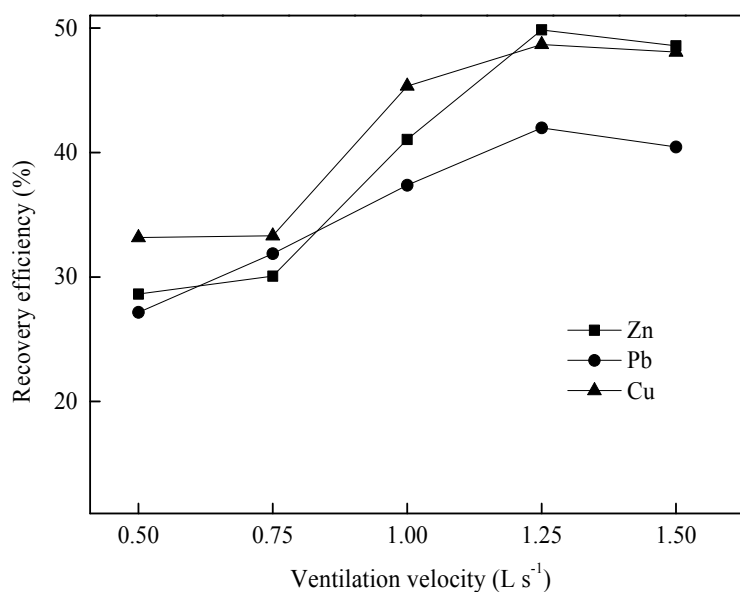
Fig. 9. Effects of ventilation velocity on heavy metal recovery efficiency (Kerosene = 6 g kg^{-1}, MIBC = 6 g kg^{-1}, SDS = 3 g kg^{-1}, pH = 10, t = 15 min).

the bubbles in the right size and evenly distributed during the flotation process.

As shown in Fig. 10, flotation time has a significant effect on metal recovery. The recovery efficiency reached its maximum within 15 min and then slowed to a stable value after 20 min. In the upper course of the experiment, the foams and heavy metals gradually descended. Thus, precipitation compounds that had adhered to the superficies of foams declined substantially, which might have considerably reduced the recovery efficiency. The optimal flotation time was finally determined as 15 min. However, Dermont found that 5 min was an optimal time (Dermont*et al.*, 2010), this might be related to different concentrations of slurry. The

flotation mechanism may change gradually into a mechanical entrained mechanism over time, which may also lead to a slow reaction (Cauwenberg *et al.*, 1998b). When large particles are consumed, the particle spacing is increased and reduces the collision between fine particles, which may further reduce the recovery efficiency (Vanthuyne *et al.*, 2002). Furthermore, in a late reaction process, an insufficiency of the collector can produce a slow reaction; this is consistent with the literature (Dermont *et al.*, 2010).

Migration of Heavy Metals during Two-Step Flotation

Heavy metals might enter into the froths, concentrate, tailings, or remaining waste water. Thus, determining the
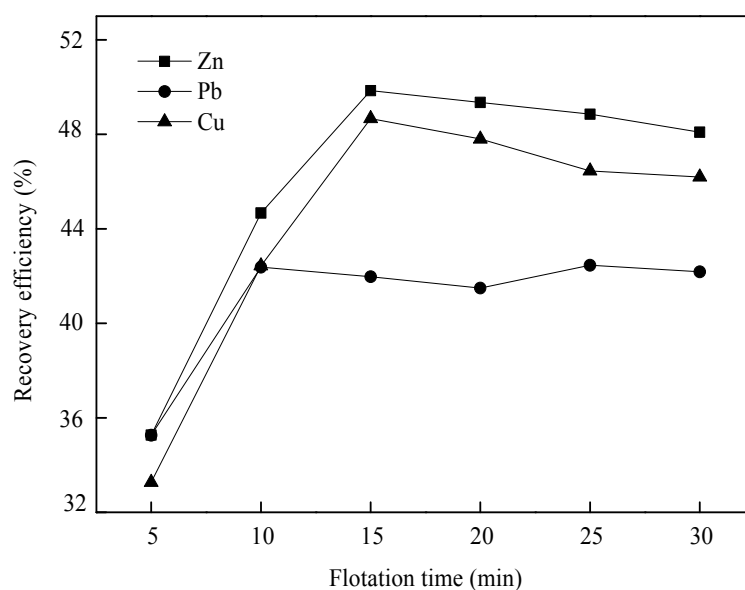
Fig. 10. Effects of flotation time on heavy metal recovery efficiency (Kerosene = 6g kg^{-1}, MIBC = 6 g kg^{-1}, SDS = 3 g kg^{-1}, pH = 10, V = 1.25 L s^{-1})

mass balance of heavy metals from input to output during flotation is necessary. The decarburization flotation process was accompanied by the migration of heavy metals. Analytical results of this step indicated that heavy metal concentrations in the froths were approximately two times higher than that in ash sample. It is possibly due to the adsorption of heavy metals by PAC in froths and the dissolution of water-soluble metal compounds such as chlorine salts. Besides, insoluble heavy metals may also lead to that result (Liu *et al.*, 2014). By calculation, it was found that Zn, Pb and Cu in froths accounted for 38.2%, 34.2% and 35.6% in outputs, respectively. After reburning treatment of froths, these heavy metals would be absorbed by PAC and again captured by the bag filter.

Thus, it was clear that most heavy metals finally migrated from the ash sample to the residual slurry. After acid leaching-sulphide precipitation-flotation of the residual slurry, it was found that heavy metal content in the concentrate product was one order of magnitude higher than that in ash sample. The content of heavy metals in the concentrate reached up to 90.9 g kg^{-1} for Zn, 17.5g kg^{-1} for Pb and 8.2 g kg^{-1} for Cu which correspond to the metal concentrations in natural ores and thus can be recycled as raw ores (Richard *et al.*, 2009; Deliyanni *et al.*, 2017). Kuchar reported that 1%–10% of Zn, 1%–5% of Pb and 0.5%–1.0% of Cu remain in mined natural ores (Kuchar *et al.*, 2007b). The contents of Zn (1.2 mg L^{-1}), Pb (0.3 mg L^{-1}), and Cu (0.3 mg L^{-1}) in waste water were lower than those in the 'Integrated Wastewater Discharge Standard' (Zn ≤ 2.0 mg L^{-1}, Pb ≤ 1.27 mg L^{-1} and Cu ≤ 0.5 mg L^{-1}) and can be directly sent to waste incineration plant wastewater treatment system for centralized treatment. The next stage of the research will consider the whole process, including the recirculation of the effluents produced. After precipitation flotation, leaching concentrations of heavy metals in tailings decreased. Therefore, the stabilisation process of tailings

would be eliminated. After this two-step flotation process, the toxicity and volume of the tailings both decreased considerably and the tailings could be disposed of in a landfill or directly reused. Thus, the goal of separating toxic matter and recovering heavy metals to render HSWI fly ash harmless and resourceful at a low cost is achieved.

CONCLUSION

A new two-step flotation approach for the successive removal of PCDD/Fs and heavy metals from HSWI fly ash has been proposed and its feasibility is demonstrated. The procedure consists of four processes: decarburization flotation to remove dioxins from ash sample, acid leaching to extract heavy metals from the resudal slurry, sulphurisation treatment by Na$_2$S and precipitation flotation to remove and recycle toxic metals. Results show that the carbon and dioxin removal efficiencies reached 90.7% and 91.0%, respectively, during decarburization flotation. Furthermore, Zn (91.3%), Pb (79.2%) and Cu (85.6%) were acid leached from residual slurry at pH = 2, following which the sulphidation percentages of Zn, Pb and Cu reached 85.5%, 72.8% and 77.6%, respectively, at a Na$_2$S molar ratio of 1.4 and sulphidation time of 30 min. The optimum parameters of precipitation flotation were determined as a 6 g kg^{-1} consumption of kerosene and MIBC, a dosage of 3 g kg^{-1} of SDS, a pH value of 10, a ventilation rate of 1.25 L s^{-1} and a flotation time of 15 min, respectively. Under these conditions, 49.9% of Zn, 42.0% of Pb and 48.7% of Cu could be recovered from the ash sample.

After flotation and heavy metal sulphidation, the waste water can be directly concentrated treatment. Therefore, the low PCDD/Fs content and leaching concentrations of toxic metals in tailings were realised successfully by two-step flotation. The combination of decarburization flotation and precipitation flotation appears to be an efficient technology,

through which PCDD/Fs can be removed and heavy metals can be recovered from incinerator fly ash continunously and effectively.

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REFERENCES

Amaral Filho, J., Azevedo, A., Etchepare, R. and Rubio, J. (2016). Removal of sulfate ions by dissolved air flotation (DAF) following precipitation and flocculation. *Int. J. Miner. Process.* 149: 1–8.

Bo, D., Zhang, F.S. and Zhao, L.J. (2009). Influence of supercritical water treatment on heavy metals in medical waste incinerator fly ash. *J. Hazard. Mater.* 170: 66–71.

Bournival, G., Pugh, R.J. and Ata, S. (2012). Examination of NaCl and MIBC as bubble coalescence inhibitor in relation to froth flotation. *Miner. Eng.* 25: 47–53.

Capponi, F., Sartori, M., Souza, M.L. and Rubio, J. (2006). Modified column flotation of adsorbing iron hydroxide colloidal precipitates. *Int. J. Miner. Process.* 79: 167–173.

Cauwenberg, P., Verdonckt, F. and Maes, A. (1998a). Flotation as a remediation technique for heavily polluted dredged material. 1. A feasibility study. *Sci. Total Environ.* 209: 113–119.

Cauwenberg, P., Verdonckt, F. and Maes, A. (1998b). Flotation as a remediaion technique for heavily polluteddredged material. 2. Characterisation of flotated fractions. *Sci. Total Environ.* 209: 121–131.

Chen, Y., Zhao, R.Z., Xue, J. and Li, J.H. (2013). Generation and distribution of PAHs in the process of medical waste incineration. *Waste Manage.* 33: 1165–1173.

Cheruiyot, N.K., Lee, W.J., Mwangi, J.K., Wang, L.C., Lin, N.H., Lin, Y.C., Cao, J.J., Zhang, R.J., Chang-Chien, G.P. (2015). An overview: Polycyclic aromatic hydrocarbon emissions from the stationary and mobile sources and in the ambient. *Aerosol Air Qual. Res.* 15: 2730–2762.

Cheruiyot, N.K., Lee, W.J., Yan, P., Mwangi, J.K., Wang, L.C., Gao, X., Lin, N.H. and Chang-Chien, G.P. (2016). An overview of PCDD/F inventories and emission factors from stationary and mobile sources: What we know and what is missing. *Aerosol Air Qual. Res.* 16: 2965–2988.

Cho, Y.S. and Laskowski, JS. (2002). Effect of flotation frothers on bubble size and foam stability. *Int. J. Miner. Process.* 64: 69–80.

Clift, R., Grace, J.R. and Weber, M.E. (1978). *Bubble, Drops, and Particles*. Academic Press, New York.

Deliyanni, E.A., Kyzas, G.Z. and Matis, K.A. (2017). Various flotation techniques for metal ions removal. *J. Mol. Liq.* 225: 260–264.

Dermont, G., Bergeron, M., Richer-Laflèche, M. and Mercier, G. (2010). Remediation of metal-contaminated urban soil using flotation technique. *Sci. Total Environ.* 408: 1199–1211.

Fedje, K.K., Ekberg, C., Skarnemark, G. and Steenari, B.M. (2010). Removal of hazardous metals from MSW fly ash—An evaluation of ash leaching methods. *J. Hazard. Mater.* 173: 310–317.

Feng, Q.C., Wen, S.M., Zhao, W.J., Wang, Y.J. and Cui, C.F. (2015). Contribution of chloride ions to the sulfidization flotation of cerussite. *Miner. Eng.* 83: 128–135.

Huang, K., Inoue, K., Harada, H. and Kawakita, H. (2011). Leaching of heavy metals by citric acid from fly ash generated in municipal waste incineration plants. *J. Mater. Cycles Waste Manage* 13: 118–126.

Huang, Y.F., Chai, W.C., Han, G.H., Wang, W.J., Yang, S.Z. and Liu, J.T. (2016). A perspective of stepwise utilisation of Bayer red mud: Step two—Extracting and recovering Ti from Ti-enriched tailing with acid leaching and precipitate flotation. *J. Hazard. Mater.* 307: 318–327.

Hung, P.C., Chen, Q.H. and Chang, M.B. (2013). Pyrolysis of MWI fly ash – Effect on dioxin-like congeners. *Chemosphere* 92: 857–863.

Jiao, F.C., Zhang, L., Dong, Z.B., Namioka, T., Yamada, N. and Ninomiya, Y. (2016). Study on the species of heavy metals in MSW incineration fly ash and their leaching behavior. *Fuel Process. Technol.* 152: 108–115.

Kowalczuk, P.B. (2013). Determination of critical coalescence concentration and bubble size for surfactants used as flotation frothers. *Ind. Eng. Chem. Res.* 52: 11752–11757.

Kuchar, D., Kojima, Y., Onyango, M.S. and Matsuda, H. (2006a). Conversion of heavy metals involved in incineration fly ashes to heavy metals sulfide resources by sulfidation treatment with sodium sulfide. *J. Chem. Eng. Jpn.* 39: 241–246.

Kuchar, D., Fukuta, T., Onyango, M.S. and Matsuda, H. (2006b). Sulfidation of zinc plating sludge with Na_2S for zinc resource recovery. *J. Hazard. Mater.* 137: 185–191.

Kuchar, D., Fukuta, T., Onyango, M.S. and Matsuda, H. (2007a). Sulfidation treatment of metal compounds involved in plating sludges. *Desalination* 211: 144–155.

Kuchar, D., Fukuta, T., Onyango, M.S. and Matsuda, H. (2007b). Sulfidation treatment of molten incineration fly ashes with Na_2S for zinc, lead and copper resource recovery. *Chemosphere* 67: 1518–1525.

Kuo, Y.M., Huang, K.L. and Lin, C. (2012) Metal behavior during vitrification of municipal solid waste incinerator fly ash. *Aerosol Air Qual. Res.* 12: 1379–1385.

Lee, K.L., Lee, W.J., Mwangi, J.K., Wang, L.C., Gao, X. and Chang-Chien, G.P. (2016). Atmospheric $PM_{2.5}$ and depositions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in Kaohsiung area, southern Taiwan. *Aerosol Air Qual. Res.*16: 1775–1791.

Lee, T.J., Chung, Y.C. and Chun, B.C. (2002). Efficient separation of mixed ion-exchange resins by the surfactant flotation method and its application to surfactant sensing. *React. Funct. Polym.* 52: 43–51.

Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Tsai, P.J. and Chen, C.K. (2003). Emissions of polychlorinated

dibenzo-*p*-dioxins and dibenzofurans from the incinerations of both medical and municipal solid wastes. *Aerosol Air Qual. Res.* 3: 1–6.

Liang, Y.J., Chai, L.Y., Min, X.B., Tang, C.J., Zhang, H.J., Ke, Y. and Xie, X.D. (2012). Hydrothermal sulfidation and floatation treatment of heavy-metal-containingsludge for recovery and stabilization. *J. Hazard. Mater.* 217–218: 307–314.

Liu, H.Q., Wei, G.X. and Zhang, R. (2013). Removal of carbon constituents from hospital solid waste incinerator fly ash by column flotation. *Waste Manage.* 33: 168–174.

Liu, H.Q., Wei, G.X., Zhang, R. and Liu, F.G. (2014). Simultaneous removal of heavy metals and PCDD/Fs from hospital waste incinerator fly ash by flotation assisted. *Sep. Sci. Technol.* 49: 1019–1028.

Min, X.B., Yuan, C.Y., Liang, Y.J., Chai, L.Y. and Ke, Y. (2012). Metal recovery from sludge through the combination of hydrothermal sulfidation and flotation. *Procedia Environ. Sci.* 16: 401–408.

Naik, P.K., Reddy, P.S.R. and Misra, V.N. (2005). Interpretation of interaction effects and optimization of reagent dosages for fine coal flotation. *Int. J. Miner. Process.* 75: 83–90.

Pei, J., Dong, H.X., Li, Z.S. and Hou, X.Q. (2004). Experimental research on removing lead ion from waste water by floats preconcentration method. *Appl. Sci. Technol.* 31: 63–65.

Peng, J.F., Song, Y.H., Yuan, P., Cui, X.Y. and Qiu, G.L. (2009). The remediation of heavy metals contaminated sediment. *J. Hazard. Mater.* 161: 633–640.

Polat, H. and Erdogan, D. (2007). Heavy metal removal from waste waters by ion flotation. *J. Hazard. Mater.* 148: 267–273.

Rafiei, A.A., Robertze, M. and Finch, J.A. (2011). Gas holdup and single bubble velocity profile. *Int. J. Miner. Process.* 98: 89–93.

Richard, D.A., Naoki, H., Mayumi, I. and Masami, T. (2009). Recovery of heavy metals from MSW molten fly ash by CIP method. *Hydrometallurgy* 97: 8–14.

Salmani Abyaneh, A. and Fazaelipoor, M.H. (2016). Evaluation of rhamnolipid (RL) as a biosurfactant for the removal of chromium from aqueous solutions by precipitate flotation. *J. Environ. Manage.* 165: 184–187.

Tang, J.F. and Steenari, B.M. (2016). Leaching optimization of municipal solid waste incineration ash for resource recovery: A case study of Cu, Zn, Pb and Cd. *Waste Manage.* 48: 315–322.

Vanthuyne, M. and Maes, A. (2002). The removal of heavy metals from contaminated soil by a combination of sulfidisation and flotation. *Sci. Total Environ.* 290: 69–80.

Vanthuyne, M., Maes, A. and Cauwenberg, P. (2003). The use of flotation techniques in the remediation of heavy metal contaminated sediments and soils: An overview of controlling factors. *Miner. Eng.* 16: 1131–1141.

Wang, H.R., Yang, J.J., Lei, S.M. and Wang, X.B. (2013). Comparing the effect of biosurfactant and chemical surfactant on bubble hydrodynamics in a flotation column. *Water Sci. Technol.* 68: 783–790.

Wang, M.S., Wang, L.C., Chang-Chien, G.P. and Lin, L.F. (2005). Characterization of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the stack flue gas of a municipal solid waste incinerator, in the ambient air, and in the banyan leaf. *Aerosol Air Qual. Res.* 5: 171–184.

Wei, G.X., Liu, H.Q., Zhang, R. and Zhu, Y.W. (2016b). Application of microwave energy in the destruction of dioxins in the froth product after flotation of hospital solid waste incinerator fly ash. *J. Hazard. Mater.* 325: 230–238.

Wei, G.X., Liu, H.Q., Zhang, R., Zhu, Y.W. and Xu, X. (2016a). Mass concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and heavy metals in different size fractions of hospital solid waste incinerator fly ash particles. *Aerosol Air Qual. Res.* 16: 1569–1578.

Wei, G.X., Liu, H.Q., Liu, F., Zhang, R. and Gao, S.Y. (2017). Reburning treatment of the froths obtained after the flotation of incinerator fly ash. *Aerosol Air Qual. Res.* 17: 1084–1096.

Zhang, Y., Cetin, B., Likos, W.J. and Edil, T.B. (2016). Impacts of pH on leaching potential of elements from MSW incineration fly ash. *Fuel* 184: 815–825.