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Partial Removal of PCDD/Fs, Coplanar PCBs, and PCBs from Municipal Solid Waste Incineration Fly Ash by a Column Flotation Process

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Municipal solid waste incineration (MSWI) fly ash has recently attracted much attention because of its large quantity and enrichment of high toxic combustion generating organohalogen contaminants such as polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), coplanar polychlorinated biphenyls (coplanar PCBs), and polychlorinated biphenyls (PCBs). Since the organohalogen contaminants in MSWI fly ash are known to be enriched in the unburnt carbon (UC) fraction, the organohalogen contaminants can therefore be removed by the removal of UC. In this research, we used a modified column flotation technique to remove the organic contaminants from MSWI fly ash. UC was removed for 27.7% under the flotation condition without chemical flotation aids. The removal efficiencies of UC, PCDD/Fs, coplanar PCBs, and PCBs are further improved by adding flotation aids during the flotation process. UC was removed for 49.0% by adding a collector assistant with a HLB value of 13.5 and a concentration in the kerosene of 3% during the flotation process. In addition, the UC removal efficiencies are increased with the decrease of the diameter of the micropores in the gas spargers. By optimizing the flotation condition, 41.9% total PCDD/Fs, 40.8% coplanar PCBs, and 44.1% PCBs with 64.0% UC have been successfully removed from MSWI fly ash. The total toxic equivalent (TEQ) of the fly ash was decreased from 6.2 ng/g to 4.2 ng/g in the residue.

Introduction

Municipal solid waste incineration (MSWI) fly ash has recently attracted much attention because of its large quantity and enrichment of heavy metals with low boiling point and some persistent organic pollutants (POPs) which have high toxicity level and inverse impact on the environment. These POPs include polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and coplanar PCBs, etc. (1–3). The environmental protection agencies of many countries have classified MSWI fly ash as hazardous material and required further treatment of MSWI fly ash before its disposal in landfills (4). Up to date,

intermediate treatments such as ash-melting processes (5), thermal dechlorination processes (6), supercritical fluid extraction (SFE) (7), supercritical water oxidation (SWO) (8), base-catalyzed decomposition (BCD) (9), and bioremediation utilized bacteria (10) or fungus (11) have been studied and developed to decompose the toxic organic micropollutants in MSWI fly ash. However, there are many problems in these techniques, such as the possibility of PCDD/Fs regeneration in the low-temperature zone of thermal dechlorination equipment, the high-energy consumption of melting, the high cost, and the chemical residue problem in physical/chemical remediation technology. Bioremediation techniques are still in the development stage. It is hence urgently required to develop an efficient, low-energy consuming and low cost remediation technology to clean up MSWI fly ash.

Unburnt carbon (UC) is the major source of PCDD/Fs, coplanar PCBs, and PCBs in MSWI fly ash due to its large adsorptive surface area and its role as the origin of the *de novo* synthesis (12, 13). For this reason, it is supposed that most PCDD/Fs, coplanar PCBs, and PCBs can be effectively removed with the removal of UC from fly ash. Column flotation is a low-energy consumption technique widely used in the solids separation of primary mineral and chemical industries, such as coal cleaning (14, 15). By use of this technique, some researchers have successfully removed UC from power plant fly ashes (16, 17). In this research we use this technique to remove UC and so remove PCDD/Fs, coplanar PCBs, and PCBs from MSWI fly ashes.

The aerator is “the heart” of the flotation equipment (18). The characters of the aerator can influence the flotation performance by changing the bubble size, gas hold up, etc. It was also found that the use of nonionic surfactants, which acted on the surface of the oxidized coal particles, could increase the coal recovery (19, 20). The objectives of this study were therefore (1) to investigate the influence of the flotation collector aids and of the gas generators (the most common kind of aerator) with different micropore diameters on the removal efficiencies of UC, PCDD/Fs, coplanar PCBs, and PCBs; (2) to determine the optimum column flotation parameters; and (3) to discuss the kinetic and chemical mechanisms in the flotation removal process.

Experimental Section

MSWI Fly Ash Sample. Fly ash was sampled from an electrostatic precipitator (ESP) of a stoker type municipal solid waste incinerator. There was neither slaked lime nor activated carbon injection in the gas treatment system. The fly ash was divided into five size ranges by sieves. The weight distribution, UC distribution, and UC concentration in each fraction of the fly ash were analyzed. The UC concentration was analyzed by TOC measurement (21). The surface morphologies of the fly ash and UC were performed by JSM-5600T scanning electron microscope (SEM) (JEOL Ltd.). The backscattered electron imaging (BEI) was taken after the fly ash, and UC samples were mounted on graphite paint and rendered conductive by platinum coating. For analyzing the elements in a specified spot of the particle surface, JED 2110 energy dispersive X-ray spectroscopy (EDX) (JEOL Ltd.) was used accompanied by SEM.

Column Flotation with Collector Aids. Two kinds of surfactants, sorbitan mono-oleate (HLB = 4.3) and polyoxyethylene (20) sorbitan mono-oleate (HLB = 15.0), were mixed in different ratios to obtain surfactant mixtures with different hydrophile lipophile balance values (HLB): 7, 9, 12, 13.5, and 15. These surfactant mixtures were added into the kerosene at concentrations of 0, 1.5, 3, 5, 7, and 10 volume

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% to obtain kerosene mixtures with different surfactant concentrations. The kerosene emulsion was obtained by mixing the kerosene mixture (the dosage of kerosene added into the water was fixed at 3 mL) with 350 mL of distilled water for 10 min by jar-tester. After 10 g of fly ash sample was mixed with 400 mL of distilled water for 5 min, the kerosene emulsion was added into the slurry and mixed for a further 5 min. The pH values of the original fly ash slurry (pH = 6.9) were adjusted to the optimum pH value of 5.9 for the UC flotation by using HCl (21). The slurry with surfactant mixtures was used to determine the optimum HLB value and the optimum surfactant-mixture concentration for the highest removal efficiency of UC.

The column flotation system (glass column) and the flotation procedure were the same as described in a former paper (21). The prepared slurry and 0.08 mL/L of methyl isobutylcarbinol (MIBC) were fed from the top of the glass column after starting the air compressor. The flow rate J_g of the compressed air with a pressure of 6.86 N/cm² was 0.0187 m/s. A 2# porous plate was used as the gas sparger. The flotation time was 30 min. After flotation, the froth, residue, and solution samples were collected and analyzed for the UC concentrations and PCDD/Fs, Co-PCBs, PCBs concentrations.

Column Flotation with Different Micropore Size Gas Spargers. The column flotation experiments were performed with different micropore size gas spargers. The porous plate type spargers are made of sintered glass. The sizes of the micropores of these plate spargers are 40–50 μm for the 2# plate, 20–30 μm for the 3# plate, and 5–10 μm for the 4# plate. Since the pore size of 4# porous plate is very small, the pressure of the combining part will be very high when compressed air is passed through the sparger part of the column apparatus. To avoid cracks in the combining part, an acrylic plastic column was used instead of the glass column. The kerosene mixture used in the preparation of the slurry was prepared by adding the surfactant mixtures (HLB = 13.5) into the kerosene at the concentration of 3 volume %.

Analysis of PCDD, PCDF, Coplanar PCBs, and PCBs. The sample preparation procedure for the analysis of PCDD/Fs, coplanar PCBs, and PCBs was based on the Japanese Industry Standard JIS K 0311. The fly ash, froth, and residue samples were extracted by refluxing with 300 mL of toluene for 16 h; the solution sample (approximately 1 L) was extracted three times with 100 mL of dichloromethane and dried over anhydrous sodium sulfate. The extracts were then concentrated by rotary evaporation and divided into two parts for PCBs and PCDD/Fs analysis. After the addition of the internal standards of $^{13}\text{C}_{12}$ -PCBs mix, a part for the PCBs analysis was cleaned up by hexane in a multilayer silica column. The part for PCDD/Fs analysis was cleaned up by hexane in a multilayer silica column and then cleaned up with an aluminum column by 50%-dichloromethane/hexane after the addition of the internal standards of $^{13}\text{C}_{12}$ -2378-TeCDD~OCDD and $^{13}\text{C}_{12}$ -2378-TeCDF~OCDF. Both the PCBs and PCDD/Fs extracts were concentrated to 50 μL prior to GC/MS analysis.

The identification and quantification of PCDD/Fs, coplanar PCBs, and PCBs in these extracts was conducted using HRGC/HRMS (HP6890, Hewlett-Packard and Autospec-Ultima, Micromass). For the measurement of PCDD/Fs, the GC conditions were as follows: SP-2331 capillary column (Supelco, 60 m \times 0.32 mm i.d., 0.20 μm film thickness); the column oven temperature programming, 160 $^{\circ}\text{C}$, 1 min, 6 $^{\circ}\text{C}$ /min to 200 $^{\circ}\text{C}$, 3 $^{\circ}\text{C}$ /min to 260 $^{\circ}\text{C}$, held for 30 min. For the analysis of PCBs and coplanar PCBs, DB-5MS fused silica capillary column (J&W, 60 m \times 0.32 mm i.d., 0.25 μm film thickness) was used. The column oven temperature was programmed: 150 $^{\circ}\text{C}$ held for 1 min, 20 $^{\circ}\text{C}$ /min to 185 $^{\circ}\text{C}$,

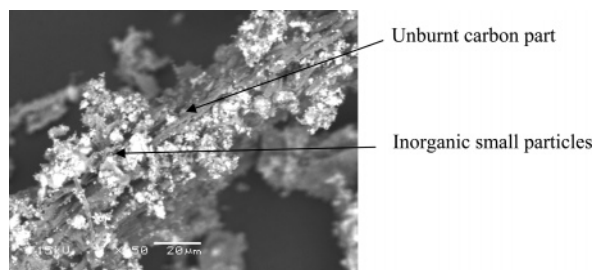


FIGURE 1. SEM picture of unburnt carbon with white inorganic parts.

held for 1 min, 3 $^{\circ}\text{C}$ /min to 245 $^{\circ}\text{C}$, 6 $^{\circ}\text{C}$ /min to 290 $^{\circ}\text{C}$, and finally held for 15 min. The injector temperature was 270 $^{\circ}\text{C}$. The injection volume was 1 μL . Helium was used as the carrier gas. The mass spectrometer was operated in the electron impact ionization mode (EI) with the electron energy at 40 eV. The source temperature was set at 290 $^{\circ}\text{C}$ for PCDD/Fs and set at 270 $^{\circ}\text{C}$ for PCBs and coplanar PCBs. The mass resolution was over 10 000.

Results and Discussion

The data set containing the weight distribution, UC distribution, and UC concentration in each fraction of the fly ash is provided as Supporting Information (Table S1). Most fly ash particles are in the small and middle size fractions of $d < 44 \mu\text{m}$, $44 \mu\text{m} < d < 106 \mu\text{m}$, and $106 \mu\text{m} < d < 250 \mu\text{m}$. However most UC is in the fraction of $d > 500 \mu\text{m}$, where the UC percentage is 55.4%. The total unburnt carbon of the fly ash was 5.24%. There are many organic oxygen functional groups, most commonly, carboxyl, phenolic, and carbonyl functionalities in the carbon part of the UC surface. These oxygen functional groups are hydrophilic. After the MSWI fly ash is stored in ambient air for a long time, the weathering process of the UC results in the formation of more organic oxygen functional groups on the UC surface which decreases the UC floatability (22, 23). There are also a lot of smaller white inorganic particles attached on the black unburnt carbon surface as shown in Figure 1, which is a rodlike UC particle of the $106 \mu\text{m} < d < 250 \mu\text{m}$ fraction. The EDX result reveals that there are high contents of Ca, Al, Si, and O in the white inorganic particles. Fermo (24) reported that gehlenite, gismondine, calcite, anhydrite, etc., are abundant in MSWI fly ash as compounds of, e.g., CaO, Al_2O_3 , and SiO_2 . Al_2O_3 and SiO_2 cannot dilute in the flotation process, CaO has low solution ability, and they are hydrophilic. The existence of these organic oxygen functional groups and inorganic oxides can heavily decrease the hydrophobicity of the UC particles and so decrease the UC removal efficiency in flotation (17).

In order to improve the UC removal efficiency, we added the surfactant mixture of sorbitan mono-oleate (HLB = 4.3) and polyoxyethylene (20) sorbitan mono-oleate (HLB = 15.0) as collector aids to the kerosene. The removal efficiency R is defined by

$$R = \frac{m_f C_f}{m_0 C_0} \times 100\% \quad (1)$$

where m_f and m_0 are the weights of the froth and the original fly ash sample used in the flotation experiment, and C_f and C_0 are the concentrations of UC or PCDD/Fs, coplanar PCBs, and PCBs in the froth and the fly ash.

Figure 2 shows the UC removal efficiency of surfactant mixtures with different HLB values. A material with a higher HLB value has a higher hydrophilicity. Seeing Figure 2, we can find that, in general, higher UC removal efficiencies can be obtained by using surfactant mixtures with a higher HLB value. The highest UC removal efficiency was obtained by

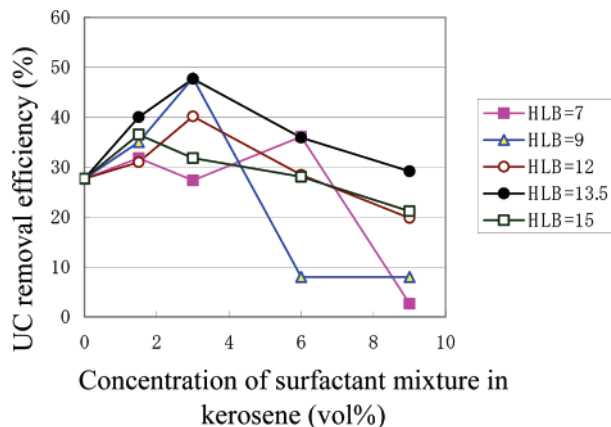


FIGURE 2. UC removal efficiency of the flotation conditions using collector aids with different HLB values.

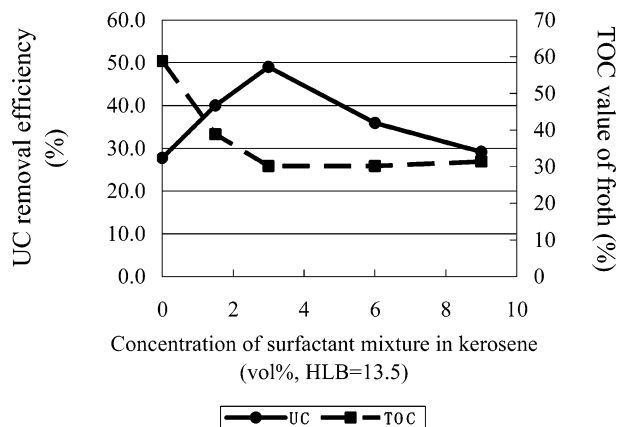


FIGURE 3. The influence of the concentration of the surfactant mixture (HLB = 13.5) in kerosene on the UC removal efficiency and the TOC value of froth.

using surfactant mixture HLB = 13.5. But the UC removal efficiency decreases when the surfactant mixture's HLB equals 15.0. Figure 3 represents the influence of the concentration of the surfactant mixture (HLB = 13.5) on the UC removal efficiency. When the concentration of the surfactant in kerosene is 3%, the maximum UC removal efficiency of 49.0% is obtained, whereas the UC removal efficiency by flotation without the assistance of the surfactant mixture is only 27.7%.

The assistance of the surfactant mixture (the collector aid) to the UC removal efficiencies in the column flotation can be understood from the chemical structures of these two kinds of surfactants (polyoxyethylene (20) sorbitan mono-oleate and sorbitan mono-oleate). The structures of these two surfactants were shown in a previous paper (25). These two kinds of nonionic surfactants are bifunctional. They possess oxygenated functional groups of carboxyl, hydroxyl, esters of sorbitol, and its mono- and dianhydrides groups and a hydrocarbon chain—the oleic acid moiety. The surface of UC inherently contains hydrophobic areas (carbonaceous sites) and also sites containing oxygenated moieties such as carboxyl, carbonyl, phenolic, and ester groups. Therefore, the attachment of the collector aid to the UC particle surface can take place by either hydrogen bonding of polar oxygenated functional groups of the surfactant mixture (collect assistant) with the oxygenated functional groups on the UC surface or van der Waals interaction (hydrophobic bonding) of the nonpolar hydrocarbon chain of the surfactant mixture with the carbonaceous sites on the UC surface.

The hydrogen bonding interaction is much stronger than the van der Waals interaction. For the UC particle that

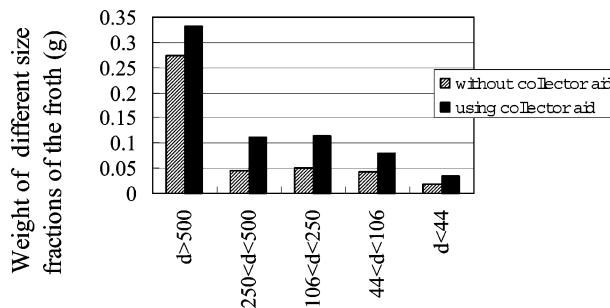


FIGURE 4. Improvement of the froth recoveries of different size fractions under different flotation conditions.

contains a large fraction of oxygen functional groups, attachment of the collector is mainly through hydrogen bonding with the polar oxygen atoms of the collector. Since there are almost no oxygenated functional groups on the molecule of kerosene, kerosene has a limited affinity for a UC particle surface. The attachment and collection efficiency of the UC by kerosene is thereby lower than those of the kerosene mixture with collector aid which contains oxygenated functional groups. Especially because the collector aid with a high HLB value has more oxygenated functional groups, the UC removal efficiency can be considerably improved during the flotation by using the collector aid with the high HLB value at a suitable concentration. However, the UC removal efficiency decreases when the HLB value of the surfactant mixture becomes larger than 13.5 or when the concentration of the surfactant mixture is above 3%. This is because there is an optimum in the balance between the hydrophilic part and hydrophobic part of the surfactant mixture for the UC particle surface. When the HLB value of the surfactant mixture is larger than the optimum value or the surfactant mixture concentration is above the optimum value, excess hydrophilic parts of the surfactant mixture will lead to an improvement in the UC particle hydrophilicity and a decrease in the removal efficiency of UC by flotation. For the UC removal by column flotation, the optimum HLB value of the surfactant mixture is 13.5, and the optimum surfactant mixture concentration is 3% in kerosene.

At the same time, the UC concentration in the froth (TOC value) decreases with the concentration of the surfactant mixture used in flotation as shown in Figure 3. This indicates that the surfactant mixture can collect and float some inorganic oxidic materials, which pack the UC particles or attach on their surface, such as CaCO_3 , Al_2O_3 , and SiO_2 (24). The removal efficiency of the inorganic materials packed UC can thus be improved.

Figure 4 shows the froth recoveries of different size fractions using flotation without and with collector aid. The recovery efficiencies of all size fractions of the froth were increased by adding a collector aid. Especially, the recovery efficiencies increased much for the middle and small size particles (most were UC particles) of $250 \mu\text{m} < d < 500 \mu\text{m}$, $106 \mu\text{m} < d < 250 \mu\text{m}$, $44 \mu\text{m} < d < 106 \mu\text{m}$, and $d < 44 \mu\text{m}$, and the weights of these particle fractions in the froth almost doubled. But the increase of the recoveries of $d > 500 \mu\text{m}$ particles was not so obvious. This is due to the fact that the surfactant mixture could emulsify the kerosene and reduce the kerosene drop size, and the smaller size kerosene drops were more fit for the collection of middle and small size UC particles than big size UC particles. Therefore the recovery of the middle size and small size UC was significantly increased.

The effect of the different gas spargers with different micropore sizes on the UC removal efficiency was investigated. The results are shown in Figure 5 and indicate that the UC removal efficiency of a porous plate sparger with a

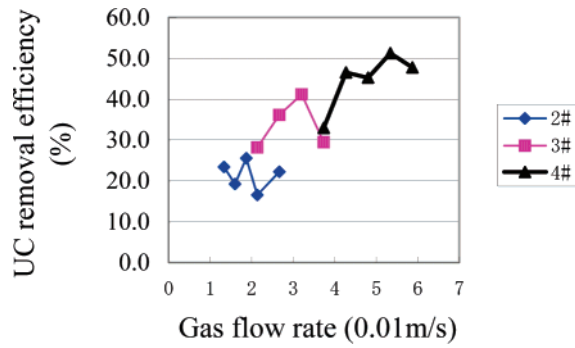


FIGURE 5. Effect of different gas spargers on the UC removal efficiency.

small pore size (4# plate) is higher than those of spargers with larger pore size (2# and 3#).

The diameters of these spargers were the same. The sparger with the smaller pore size had a larger surface area A_s . Therefore, the surface area (A_s) of spargers is $2\# < 3\# < 4\#$. The effect of the sparger surface area on the UC removal efficiency can be explained by hydrodynamic and kinetic theories (15).

Because the removal efficiency of the UC particles is given by (15)

$$R_c = 1 - \exp(-k_c t_p) \quad (2)$$

where t_p is the residence time of the particle in the collection zone (the part under the froth zone) (s), and k_c is the collection rate constant (s^{-1}).

The recovery efficiency R_c is hence determined by the collection rate constant k_c . The relationship between the collection rate k_c and the bubble diameter d_b has been given by (15)

$$k_c = 1.5J_g E_k d_b^{-1} \quad (3)$$

where E_k is the collection efficiency, the fraction of particles swept out by a bubble that collide with, attach to, and remain attached to the bubble (%), J_g is the volumetric gas flow rate Q_g per unit cross-section (ms^{-1}) and equals Q_g/A_c , and A_c is the column cross-sectional area.

The bubble diameter d_b was found to depend on $R_s J_g$ (27)

$$d_b = C_1 (R_s J_g)^n \quad (4)$$

where the ratio R_s is defined in eq 4

$$R_s = A_c / A_s \quad (5)$$

where C_1 and n are constants.

Therefore

$$d_b = C_1 \left(\frac{Q_g}{A_s} \right)^n \quad (6)$$

According to eq 6, the increase of the surface area A_s of the sparger will decrease the bubble diameter d_b . And the decrease of d_b will increase the collection efficiency E_k , which has been explained by the collection model of the column flotation (15). For a given flotation system, at a fixed volumetric gas flow rate Q_g , the gas flow rate J_g will be fixed. Therefore the increase of the surface area A_s of the sparger ($2\# < 3\# < 4\#$) will lead to the increase of $E_k d_b^{-1}$ and the increase of the collection rate k_c and the UC removal efficiency R_c (eqs 2 and 3). The results of R. D. Gehle and K. Schugerl (28) indicated that the volume flow of the froth foam (V_s , $mL \cdot min^{-1}$) increased when the pore size of the aerator was

TABLE 1. Experiments Parameters of Optimum Flotation Condition B and Comparative Flotation Condition A

experiment parameter	A	B
slurry concn (g-fly ash/750 mL-slurry)	10	10
kerosene concn (mL/750 mL-slurry)	3	3.09
collector assistant concn in kerosene (wt %)		3%
porous plate gas sparger	4#	4#
gas flow rate (m/s)	0.0481	0.0534
flotation time (min)	60	60

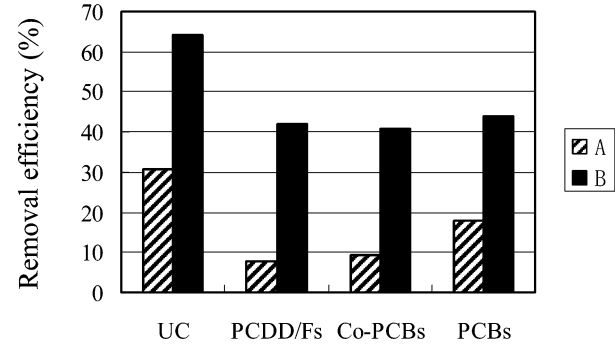


FIGURE 6. The removal efficiencies of UC, total PCDD/Fs, total coplanar PCBs, and total PCBs under different flotation conditions (A: comparative flotation condition and B: optimum flotation condition).

reduced, while the flotation object concentration in the froth foam (C_s , $mg \cdot L^{-1}$) remained constant, which lead to the increase of the flotation removal efficiency.

For every porous plate sparger, the UC removal efficiency increases with the increase of the volumetric gas flow rate (Q_g) at first and then achieves a maximum UC removal efficiency at the optimum Q_g value; above the optimum Q_g value, the UC removal efficiency decreased (21). For 4# porous plate sparger, the maximum UC recovery efficiency of 51.3% was achieved at the point of $Q_g = 0.0534$ m/s. The experiment results of 2# are not stable. This is because the pore size of 2# porous plate is larger than other plates, which leads to the easier logging of fly ash particles in the pores (15). Similar flotation models can be found in the research of S. Liers. (29).

Integrating the results of different flotation conditions, the optimum flotation condition B for UC removal was obtained as shown in Table 1 (21, 25, 26). The collector aid concentration in the kerosene was 3%, and the 4# porous plate was used in flotation B. Flotation A was explored for comparison. A full data set containing the quantity of PCDD/Fs, coplanar PCBs, and PCBs congeners in fly ash, froth, residue, and solution of flotation A and B is provided as Supporting Information (Table S2). The quantity of the original fly ash sample was 10 g, the volume of the solution sample was 0.75 L, and the froth and residue samples were obtained by the flotation A and B with 10 g of fly ash sample, respectively. There are 5100 ng of total PCDD/Fs and 670 ng of total PCBs in 10 g of fly ash. The PCBs quantity is approximately 10% of the total PCDD/Fs. Coplanar PCBs contributes to about 10% of the total PCBs quantity. The quantities of #77, #126, #169, #118, #105, and #156 are 8.1, 8.9, 6.5, 6.3, 5.1, and 5.3 ng, respectively. The high toxic isomer #126 (I-TEF: 0.5) has the highest quantity in these coplanar PCBs.

The UC removal efficiency of the optimum flotation B enhanced by collector aid is 64.0%, whereas the UC removal efficiency of the comparative flotation A without using collector aid is only 30.7% (Figure 6). The removal efficiencies of total PCDD/Fs, coplanar PCBs, and PCBs of optimum flotation B are also increased in line with the increase of UC

removal efficiency. The removal efficiencies of total PCDD/Fs, coplanar PCBs, and PCBs under optimum flotation condition B are 41.9%, 40.8%, and 44.1%, respectively. However, the removal efficiencies of comparative flotation A are only 7.8%, 9.5%, and 17.8%. In the optimum flotation B, the total PCDD/Fs was decreased from 510 ng/g in the fly ash to 380 ng/g in the residue, and the total PCBs was decreased from 67 ng/g to 32 ng/g. The total toxic equivalent (TEQ) of the fly ash was decreased from 6.2 ng/g to 4.2 ng/g in the residue under the optimum flotation condition B.

The removal efficiencies of each homologue of PCDD/Fs, coplanar PCBs, and PCBs under flotation A and B are given in the Supporting Information (Figure S1). We found that the removal efficiencies of lower chlorinated PCBs congeners (i.e., MCBs, DiCBs, TrCBs, and TeCBs) are higher than higher chlorinated PCBs congeners (i.e., PeCBs, HxCBs, HpCBs, OCBs, NCBs, and DeCBs) under flotation condition A. There are more lower chlorinated PCBs in the big size fraction $d > 500 \mu\text{m}$ (26), which corresponds with the magnification of the UC particle size in the froth of the flotation A without using a collector aid (Figure 4). Therefore more lower chlorinated PCBs are concentrated in the froth of flotation A. Under the optimum flotation condition B, more fine UC particles, which contain more higher chlorinated PCB homologues than the lower chlorinated PCBs homologues, are floated and removed by the addition of surfactants. Therefore the removal efficiencies of higher chlorinated PCBs increased quicker than those of lower chlorinated PCBs, and the removal efficiencies of different PCBs homologues become more homogeneous in flotation B, see Figure S1 (26). However there is no significant difference tendency in PCDD/Fs homologues as that in the figure of PCBs under flotation A. But the removal efficiencies of PCDD/Fs homologues decrease with the increase of the chlorination (except TeCDDs) under flotation, in which more fine UC particles are floated in the froth compared with flotation A. This may indicate there are more lower chlorinated PCDD/Fs than higher chlorinated PCDD/Fs concentrated onto fine UC particles.

The leaching ratio is the partition ratio of PCDD/Fs, coplanar PCBs, and PCBs, which are dissolved from the fly ash into the aqueous phase of the slurry during the flotation process. In general, the ratios of PCDD/Fs, coplanar PCBs congeners, and PCBs dissolved in the aqueous phase are much lower than those in the froth and residue. There are 0.04% PCDD/Fs, 0.4% coplanar PCBs, and 0.4% PCBs dissolved in the solution under condition A; 3.2% PCDD/Fs, 11.1% coplanar PCBs, and 10.4% PCBs are dissolved in solution in flotation B. More PCDD/Fs, coplanar PCBs, and PCBs leached to the aqueous phase under condition B than condition A. This is because the collector aid used in condition B enhanced the affinity between the UC and the kerosene, which results in more PCDD/Fs, coplanar PCBs congeners, and PCBs to dissolve in the kerosene and then in the aqueous phase.

From these results presented above, the optimum column flotation conditions are 4 mL/L-slurry of collector kerosene, 3% collector aid in kerosene, pH 5.9, 4# porous plate, gas flow rate of 0.0534 m/s, and flotation time of 60 min. Under these conditions, 41.9% total PCDD/Fs, 40.8% coplanar PCBs, and 44.1% PCBs with 64.0% UC have been successfully removed from MSWI fly ash to the froth. It is worth mentioning that this flotation technique has mere "split-function", i.e. splits the fly ash into three parts: froth, residue, and aqueous phase, which should be treated after the flotation for the final decomposition of the organohalogen contaminants in the fly ash. The generated froth will be further incinerated with high temperature to thoroughly decompose PCDD/Fs, PCBs, etc. The residue left which contains 380 ng/g of PCDD/Fs and 32 ng/g of PCBs must be landfilled as

hazardous materials. The environmental impact caused by the disposal of MSWI fly ash can be decreased because the total toxic equivalent (TEQ) of the fly ash was decreased from 6.2 ng/g to 4.2 ng/g in the residue. The left aqueous phase of the slurry containing the organohalogen contaminants leached from MSWI fly ash should be decomposed by techniques such as photodegradation (30) and catalytic degradation (31). The removal efficiencies of UC, PCDD/Fs, and PCBs from MSWI fly ash by column flotation will be further improved with the improvement of flotation equipment and flotation chemicals.

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Supporting Information Available

Removal efficiencies of PCDD/Fs, coplanar PCBs, and PCBs congeners under different flotation conditions (Figure S1); weight percentage, UC percentage, and UC concentration in each fraction of the fly ash (Table S1); quantity of PCDD/Fs, coplanar PCBs, PCBs congeners in fly ash, froth, residue, solution of optimum flotation B, and comparative flotation A (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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