

# Study on the Distribution of Dioxins with Density in MSWI Fly Ash

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**Abstract:** In this paper, the relationship between dioxin content and density in MSWI fly ash was studied. The MSWI fly ash was leached with ammonium chloride, eliminating  $\text{Ca}(\text{OH})_2$  as well as chlorides, and then separated into different densities using sodium polytungstate solutions as heavy liquids. Carbon content, chemical composition, mineral composition, particle size distribution and concentration and absolute I-TEQ of dioxins in each density fraction were studied. It was found that carbon content is well related to density. With the increase of density, carbon content decreases from 58.47% in the  $<1.8 \text{ g/cm}^3$  fraction to 0.29% in the  $>2.7 \text{ g/cm}^3$  fraction. Chemical compositions have certain degree of differentiation among density. The particle sizes of the two  $>2.5 \text{ g/cm}^3$  fractions were found significantly smaller than the three  $<2.5 \text{ g/cm}^3$  fractions as a whole. The dioxin concentration in each fraction was found to decrease with density, except the  $<1.8 \text{ g/cm}^3$  fraction, indicating that much more dioxins exist in residual carbon than injected activated carbon. The absolute I-TEQ of dioxins was found far exceeding the permit content in the fraction even with lowest carbon content, which indicates that froth flotation alone cannot attain the permit content of dioxins in the tailing. Prospective measures were discussed.

**Keywords:** MSWI Fly Ash; Dioxin; Carbon Content; Density separation

## 1. Introduction

China was the second largest generator of municipal solid waste (MSW) since the year 2016, behind only the United States [1]. In the past decades, incineration has become an increasingly important component of MSW management in China [2]. In 2019 alone, China disposed of 240 million tons of municipal solid waste, of which 121 million tons were incinerated, accounting for more than 50% of the total disposal [3].

At present, the main concern of municipal solid waste incineration (MSWI) is the emission of toxic pollutants. MSWI is considered as a most important source of toxic Persistent Organic Pollutants (POPs), such as the notorious polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) [4]. The removal of PCDD/Fs in flue gases is necessary to reduce the emissions of PCDD/Fs to the environment. During MSWI process, powdered activated carbon is injected before the bag filter and carried by the flue gas to the filter where it builds up a carbon layer which removes PCDD/Fs from the flowing gas. The spent active carbon is cleaned off the bag together with other particulate matter

at certain time intervals. Typically, filter cake from MSW incineration has a dioxin content of 6 ng TEQ/g [5]. As the solid residues, MSWI fly ash, from MSW incineration contain dioxins as well as heavy metals, the environmental protection agencies of many countries, including China, have classified MSWI fly ash as hazardous material.

Presently, landfill is still the dominant method used for processing MSWI fly ash in China. Sanitary landfill has the advantages of mature technology and low treatment cost, but there are hidden dangers which will cause secondary pollution of groundwater resources. A number of other treatment methods for destruction of PCDD/Fs in fly ash has been reported in the literature, including co-processing in a cement kiln, plasma technology degradation, mechanochemical degradation, hydrothermal degradation, etc [6]. However, there are still many problems in these techniques, the high processing cost, high-energy consumption, secondary pollution, etc. It is hence urgently required to develop an efficient, low-energy consuming and low-cost remediation technology to clean up MSWI fly ash.

Carbon is the major source of PCDD/Fs in MSWI fly ash. The injected powered activated carbon (AC) has large adsorptive surface area and can effectively adsorb most of the PCDD/Fs in the flue gas. Residual carbon (RC), or unburn carbon, is the origin of PCDD/Fs through de novo synthesis [7]. For this reason, it was supposed that most PCDD/Fs can be effectively removed with the removal of carbon from MSWI fly ash. Besides, the final usage of MSWI fly ash may be in construction materials, especially as a raw material for concrete production. As there are strict regulations on its carbon content in fly ash as supplementary cementitious material, removing carbon from MSWI fly ash is the key index to determine the suitable utilization [8].

Generally speaking, froth flotation is a low-energy consumption technique widely used in the solids separation of primary mineral and chemical industries, and successfully used for separating RC from coal fly ash [8]. Firstly, Atsushi et al [9] found that column flotation can clean up and reduce the PCDD/Fs-contaminated soil by removing selectively RC including a high PCDD/Fs concentration of incineration fly ash. Huang et al [10] studied an MSWI fly ash without injected AC and found that 41.9% total PCDD/Fs, 40.8% coplanar PCBs, and 44.1% PCBs with 64.0% unburnt carbon have been successfully removed from MSWI fly ash. And the total toxic equivalent (TEQ) of the fly ash was decreased from 6.2 ng/g to 4.2 ng/g in the residue. Liu et al [11] studied hospital solid waste incineration (HSWI) fly ash, which contains powdered AC and RC. They found that 92.7% of the carbon constituents were removed from the HSWI fly ash by optimizing the flotation parameters, and the TEQ of PCDD/Fs decreased from 5.61 ng TEQ/g in the raw fly ash to 1.47 ng TEQ/g in the tailings.

Although froth flotation or column flotation can effectively separate most carbon from MSWI fly ash, the TEQ of PCDD/Fs in the tailing is still exceeding the permit content of the environmental protection agencies. In China, the permitted I-TEQ of PCDD/Fs in MSWI fly ash is 0.1 ng I-TEQ/Nm<sup>3</sup> [6]. If this standard is not reached, the tailing still need to be processed with other techniques.

In this paper, MSWI fly ash was separated into different density fractions. As carbon is much lighter than other inorganic materials, the lightest fraction has highest carbon content, and the heaviest fraction contains pure inorganic minerals, while the intermediate fractions are carbon interwind with or wrapped in inorganic minerals. By classifying the distribution of dioxins with density in MSWI fly ash, further technical measures can be taken to improve the recovery rate of carbon, thus, PCDD/Fs with froth flotation. This will provide a sound foundation and reference for developing new technology to effectively remove dioxins in fly ash with froth flotation so as to reach the permitted I-TEQ of PCDD/Fs in the tailings.

## 2. Materials and Methods

### 2.1 MSWI Fly Ash

Fly ash (FA) was sampled from an MSWI installation in Beijing, China, during steady-state operation. The installation comprises four grate furnace incinerators, with a combined capacity of approximately 3000 tons per day. The flue gas purification process consists of slaked lime suspension spray, SCR denitration, activated carbon injection and bag dust removal. The ash from the deacidification tower and the bag filters is collected together as FA. It was air-dried and kept in glass bottles in the dark.

### 2.2 Density Separation

Float-sink method has been widely adopted for the separation of fine coal particles with different densities in laboratory [12]. Solution of benzene, carbon tetrachloride and benzene are often used to regulate the density of the heavy-media so as to separate coal samples with particle size less than 0.5 mm. But they cannot be used in this study, as PCDD/Fs can be dissolved in the organic solution. Instead, sodium polytungstate (SPT) was selected. SPT,  $3\text{Na}_2\text{WO}_4 \cdot 9\text{WO}_3 \cdot \text{H}_2\text{O}$ , has a molecular weight of 2986 g/mol. It is highly soluble in water. The density of aqueous sodium polytungstate solutions can be adjusted from 1.10 to 3.10 g/cm<sup>3</sup>, depending on its concentration. It has been successfully used in the separation of fine minerals in many studies [13].

The problem with the use of SPT as heavy-media in this study is that it can react with  $\text{Ca}^{2+}$  to form insoluble calcium tungstate. As there are high content of soluble calcium in MSWI fly ash, the formation of calcium tungstate will affect the composition of the density fractions. Water washing process is often used as a pretreatment step to remove chlorides like sodium chloride (NaCl), potassium chloride (KCl) and calcium chloride ( $\text{CaCl}_2$ ) [14]. But high content of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is left in the residue, from which calcium ion dissolved will reach with SPT. In this study,  $\text{NH}_4\text{Cl}$  solution was selected to dissolve calcium hydroxide as well as chlorides.

All the leaching tests were performed in duplicate. 100 g of the FA sample was leached with 2.49 mol/L ammonium chloride solution at a liquid/solid ratio (L/S) of 3/1 for 40 mins in a water bath at 25°C with a stirring rate at 300 rpm. The leachate was filtered through paper filter. The residue was then washed with deionized water till there was no  $\text{Cl}^-$  ion in the liquid out. Finally, the residue was dried at 105°C.

Sodium tungstate was mixed with deionized water to provide solutions with densities from 1.8 to 2.7 g/cm<sup>3</sup>. About 40 g of ammonium leached residual ash for each test were density fractionated using the float-sink method. The procedure is detailed in the reference [12].

### 2.3 Characterizations

X-ray diffractometer (XRD) (D8 ADVANCE, Bruker) was used to analyze the mineral phases. The test conditions were Cu target, tube pressure 40 kV, tube flow 40 mA, scanning speed 5°/min, scanning range 5-70°. An X-ray fluorescence spectrometer (XRF) (9900 X-ray, Thermo Fisher Scientific) was used to analyze the chemical composition. The measurement conditions were Rh target, the accelerating voltage was 40 kV, and the current was 67 mA.

A particle-size analyzer (LS100Q, Beckman Coulter) was employed to analyze particle size distributions. Before the measurement, the samples were subjected to an ultrasonic treatment to destroy the aggregation of the fine particles.

## 2.4 Carbon Content Analysis

Loss of ignition (LOI) is often used as the measure of carbon content in coal fly ash [8], as there is no constituent other than carbon that contributes to LOI. In MSWI fly ash, besides carbon there are many other constituents having LOI, including calcium hydroxide, calcium carbonate etc. In this study, the samples were leached with hydrochloric acid, dissolving carbonates, such as  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  as well as  $\text{Ca(OH)}_2$ . The carbon content in the residue were then analyzed with the classic three-section furnace method widely used in coal analysis [15].

5 g of each sample was mixed with 5 mol/L HCl solution with liquid/solid (L/S) at 7/1. It was stirred at 300 rpm for 20 min at 50°C in a water bath. It was then filtrated and washed with deionized water until the solution reached pH 7. Finally, the sample was dried at 105°C for 2 h and then placed in the air to reach moisture balance.

0.2 g of the leached and air-dried sample was weighed and put into a ceramic boat. It was placed in the furnace of the three-section furnace. Carbon in the sample will be fully converted into  $\text{CO}_2$  after combustion and catalyzation in the oxygen stream. Carbon content can be calculated from the weight gain of soda-lime.

## 2.5 Dioxins Analysis

The sample was firstly treated with a dilute HCl solution, 2 mol/L, for 4 h, followed by filtration and washing using deionized water. The filtrate was then extracted using dichloromethane. The separated solid part was spiked with a mixture of  $^{13}\text{C}$ -labeled PCDD/Fs internal standards for quantification and subject to Soxhlet extraction using toluene. The mixture of the dried dichloromethane layer and the separated solid part were mixed and then concentrated to 10 mL by evaporation. The concentrated solution was purified stepwise by a multistage silica gel column and an alumina column. High-resolution gas chromatographymass spectrometry (DFS, Thermo Fisher, Ger.) was used to determine the PCDD/Fs concentration.

## 3. Results and Analyses

### 3.1 Composition of MSWI fly Ash Leached with $\text{NH}_4\text{Cl}$ Solution

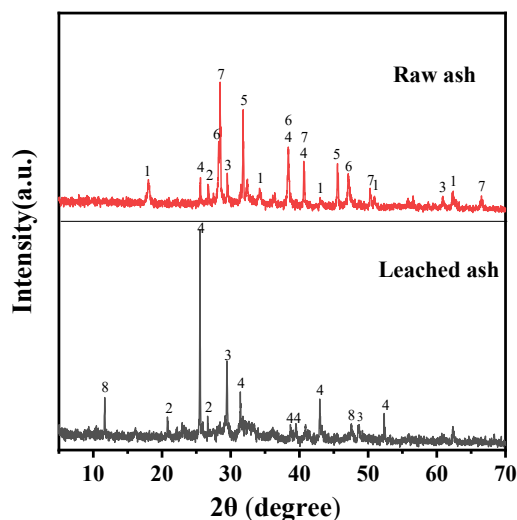
To exclude the interference of calcium ion during the float-sink test with SPT solution, the MSWI fly ash sample was pretreated with  $\text{NH}_4\text{Cl}$  solution. The leached ash (LA) lost 61.86% in weight as compared with the raw ash (RA). The chemical compositions of RA and LA are shown in Table 1.

**Table 1:** Chemical Composition of Raw Ash and Leached Ash (wt, %).

Sample	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Cl <sup>-</sup>	K <sub>2</sub> O	Na <sub>2</sub> O	LOI
RA	42.81	6.78	2.96	0.96	4.57	5.01	14.83	6.41	6.19	7.86
LA	40.26	16.62	5.92	2.32	8.56	12.3	3.83	1.04	1.47	4.63

The results in Table 1 indicate that the contents of Cl<sup>-</sup>, K<sub>2</sub>O and Na<sub>2</sub>O in LA were greatly decreased and those of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO and SO<sub>3</sub> greatly increased after leaching. There is still 3.83% Cl<sup>-</sup> in the leached sample, due to some Cl<sup>-</sup> existing in the form of insoluble chloroaluminate [16]. It should be noted that the content of CaO shows only a slight decrease. By taking the leaching weight loss into account, 64.13% of CaO was actually dissolved.

RA and the LA were analyzed with XRD. The results are shown in Figure 1.



**Figure 1:** XRD Patterns of Raw Ash and Leached Ash (1- $\text{Ca}(\text{OH})_2$ ; 2-Quartz; 3-Calcite; 4-Anhydrite; 5- $\text{NaCl}$ ; 6- $\text{CaClOH}$ ; 7- $\text{KCl}$ ; 8-Gypsum).

In Figure 1 drastic difference in mineral composition between LA and RA can be found. In RA, strong diffraction peaks of  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{CaClOH}$  can be found, which is consistent with many other authors[14,16]. In LA,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{CaClOH}$  disappear, while the diffraction intensity of calcite ( $\text{CaCO}_3$ ), quartz ( $\text{SiO}_2$ ) and anhydrate ( $\text{CaSO}_4$ ) were greatly increased. Apparently, the leaching agent,  $\text{NH}_4\text{Cl}$  solution, can dissolve  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaClOH}$  and  $\text{Ca}(\text{OH})_2$ . After leaching, the contents of the insolvable minerals are relatively increased.

PCDD/Fs in RA and LA were analyzed and the results are shown in Table 2.

**Table 2:** Mass Concentration of Dioxins (pg/g) in RA and LA.

PCDD/PCDFs	RA	LA
2,3,7,8-T4CDF	94.04	270.00
1,2,3,7,8-P5CDF	132.96	400.00
2,3,4,7,8-P5CDF	140.01	380.00
1,2,3,4,7,8-H6CDF	143.81	370.00
1,2,3,6,7,8-H6CDF	174.10	470.00
2,3,4,6,7,8-H6CDF	230.87	570.00
1,2,3,7,8,9-H6CDF	13.19	44.00
1,2,3,4,6,7,8- H7CDF	571.37	1400.00
1,2,3,4,7,8,9- H7CDF	96.57	240.00
O8CDF	286.37	1100.00
2,3,7,8-T4CDD	15.16	63.00
1,2,3,7,8-P5CDD	53.76	150.00
1,2,3,4,7,8- H6CDD	49.11	130.00
1,2,3,6,7,8-H6CDD	118.34	300.00
1,2,3,7,8,9-H6CDD	71.87	210.00
1,2,3,4,6,7,8-H7CDD	978.11	2400.00
O8CDD	1455.31	5100.00
$\Sigma$ PCDFs	1883.28	5244.00
$\Sigma$ PCDDs	2741.66	8353.00
$\Sigma$ PCDFs+ $\Sigma$ PCDDs	4624.93	13597.00

The results in Table 2 show that the total mass concentration of dioxins ( $\Sigma$ PCDFs+ $\Sigma$ PCDDs) in RA is 4624.93 pg/g, and its toxic equivalent concentration of dioxins is 226.42 pg I-TEQ/g, which is similar to other authors [17]. The mass concentration of dioxin in LA is 13597 pg/g, and corresponding toxic equivalent concentration is 631.00 pg I-TEQ/g. As lipophilic substances, PCDD/Fs are difficult to dissolve in water or inorganic solution. The mass concentration of dioxins in LA should be 2.94 times that of RA, apparently due to the weight loss during leaching.

According to three-section furnace method, the total carbon contents in RA and LA were also analyzed, increasing from 1.48% in RA to 4.42% in LA.

### 3.2 Density Composition of Leached MSWI Fly Ash and Their Characterizations

LA was separated into density fractions between 1.8-2.7 g/cm<sup>3</sup>. The yield and corresponding carbon content of each fraction were determined and are shown in Figure 2.

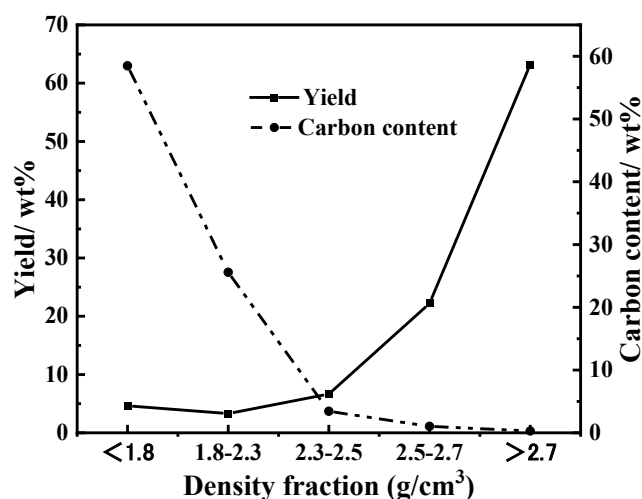


Figure 2: The Yield and Carbon Content of Each Density in LA.

Figure 2 indicates that carbon content is well related to density in LA. The lightest fraction, <1.8 g/cm<sup>3</sup>, has a carbon content 58.47%. Apparently, it is a mixture of AC and RC, as AC usually has an ash content lower than 20% [18]. The 1.8-2.3 g/cm<sup>3</sup> fraction has a carbon content 25.59%, which indicates that they are inorganic particles with RC. The three highest density fractions, >2.7, 2.5-2.7 and 2.3-2.5 g/cm<sup>3</sup>, have carbon contents 0.29%, 1.02% and 3.44%, respectively. They are particles in which carbon is interwind with or wrapped in mineral matters.

The results of XRF and XRD analysis of the density fractions in LA are shown in Table 3 and Figure 3, respectively. It should be noted that the chemical compositions were normalized by leaving out LOI.

Table 3: Chemical Composition of Each Density in LA (wt, %).

g/cm <sup>3</sup>	CaO	Cl	SiO <sub>2</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
<1.8	24.37	1.22	31.85	2.69	2.76	7.34	5.59	11.50	5.52	2.80
1.8-2.3	21.63	0.79	39.60	2.89	1.62	3.07	5.09	10.60	5.32	2.25
2.3-2.5	24.41	0.59	37.58	2.06	1.57	4.40	6.78	11.53	3.92	1.99
2.5-2.7	27.64	0.63	35.85	1.94	2.01	2.32	6.71	9.94	3.85	2.68
>	36.77	0.63	18.58	0.65	1.91	6.74	9.54	7.95	4.51	5.60

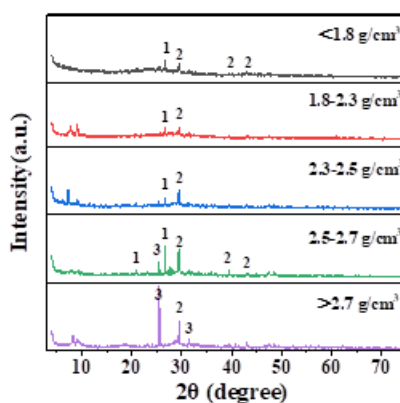


Figure 3: XRD Pattern of Each Density Fraction in LA 1-Quartz; 2-Calcite; 3-Anhydrite.



From Table 3, it can be found that the chemical compositions of the density fractions in LA have certain degree of differentiation. The chemical composition on  $>2.7 \text{ g/cm}^3$  is obviously different from the other fractions. The contents of CaO, MgO, SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub> in  $>2.7 \text{ g/cm}^3$  fractions are significantly higher, while those of SiO<sub>2</sub>, K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> are significantly lower. From Figure 3, the XRD results show that three minerals, quartz (SiO<sub>2</sub>), calcite (CaCO<sub>3</sub>) and anhydrate (CaSO<sub>4</sub>), can be identified. Quartz can hardly be found in the  $>2.7 \text{ g/cm}^3$  fraction. Calcite can be clearly identified in all the five density fractions, and the content of calcite can be found increasing with density below  $2.7 \text{ g/cm}^3$ . The content of anhydrate can be found increasing drastically with density, and highest CaSO<sub>4</sub> diffraction intensity can be found in the highest-density fraction.

The particle size of MSWI fly ash also affects the adsorption of dioxin [19]. Even observed with naked eyes, large ash particles can be clearly found in the lowest density fraction, while the particle sizes of higher density fractions are much smaller. With a laser particle size analyzer, the particle size distributions of five density samples were quantitatively analyzed, and the results are shown in Figure 4.

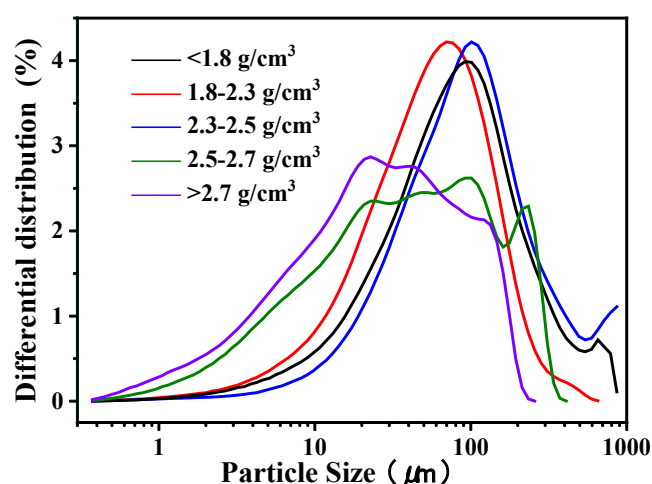


Figure 4: The Particle Size Distributions of Different Density Samples.

Figure 4 shows that the particle sizes of two  $>2.5 \text{ g/cm}^3$  fractions are found significantly smaller than those of the  $<2.5 \text{ g/cm}^3$  fractions as a whole. Attention should be paid to particles with diameter less than  $10 \mu\text{m}$  as they are liable to absorb dioxins [19]. In particle size range between  $0\text{-}10 \mu\text{m}$ , the proportions in the two  $>2.5 \text{ g/cm}^3$  fractions are significantly higher than the rest.

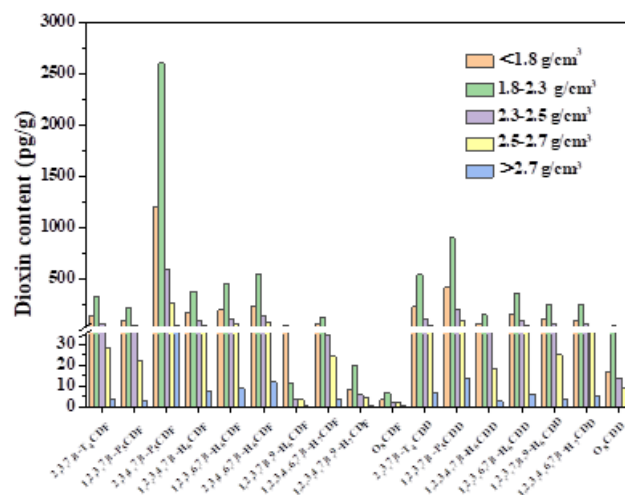
### 3.3 The Distribution of Dioxins with Density in Leached MSWI Fly Ash

The dioxin composition and equivalent toxicity of all the density fractions in LA are shown in Table 4 and Figure 5, respectively.



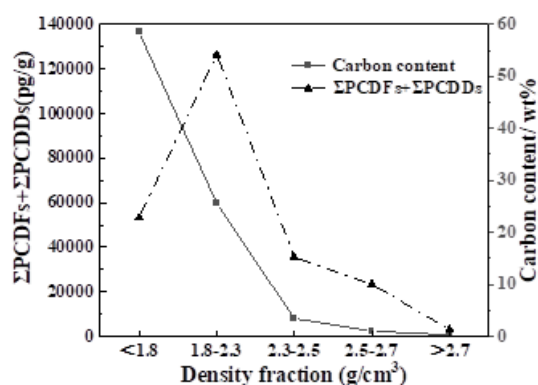
**Table 4:** The Mass Concentration of Dioxins in Each Density Fraction in LA (pg/g).

Comparison items	<1.8 g/cm <sup>3</sup>	1.8-2.3 g/cm <sup>3</sup>	2.3-2.5 g/cm <sup>3</sup>	2.5-2.7 g/cm <sup>3</sup>	>2.7 g/cm <sup>3</sup>
2,3,7,8-T4CDF	1400.00	3300.00	680.00	280.00	38.00
1,2,3,7,8-P5CDF	1900.00	4400.00	950.00	450.00	62.00
2,3,4,7,8-P5CDF	2300.00	5200.00	1200.00	540.00	80.00
1,2,3,4,7,8-H6CDF	1700.00	3800.00	930.00	510.00	76.00
1,2,3,6,7,8-H6CDF	2000.00	4600.00	1100.00	610.00	90.00
2,3,4,6,7,8-H6CDF	2400.00	5400.00	1400.00	840.00	120.00
1,2,3,7,8,9-H6CDF	540.00	110.00	35.00	35.00	3.60
1,2,3,4,6,7,8- H7CDF	5500.00	12000.00	3400.00	2400.00	370.00
1,2,3,4,7,8,9- H7CDF	840.00	2000.00	570.00	440.00	58.00
O8CDF	3400.00	6700.00	2200.00	2400.00	310.00
2,3,7,8-T4CDD	230.00	540.00	110.00	49.00	6.90
1,2,3,7,8-P5CDD	830.00	1800.00	410.00	200.00	27.00
1,2,3,4,7,8- H6CDD	660.00	1500.00	370.00	180.00	28.00
1,2,3,6,7,8-H6CDD	1500.00	3600.00	900.00	410.00	61.00
1,2,3,7,8,9-H6CDD	1100.00	2500.00	620.00	250.00	36.00
1,2,3,4,6,7,8-H7CDD	10000.00	25000.00	6800.00	3900.00	520.00
O8CDD	17000.00	44000.00	14000.00	9900.00	1200.00
ΣPCDFs	21980.00	47510.00	12465.00	8505.00	1207.60
ΣPCDDs	31320.00	78940.00	23210.00	14889.00	1878.90
ΣPCDFs+ΣPCDDs	53300.00	126450.00	35675.00	23394.00	3086.50

**Figure 5:** Equivalent Toxicity of Dioxins in each Density Fraction in LA (pg I-TEQ/g).

From Table 4 and Figure 5, it can be found that the composition and concentration of dioxins in each density is highly different. The highest density fraction has lowest concentration. Highest concentration of dioxins is found in the 1.8-2.3 g/cm<sup>3</sup> fraction, not in <1.8 g/cm<sup>3</sup> fraction. Except 1.8 g/cm<sup>3</sup>, the concentration of dioxins is decreasing drastically with density.

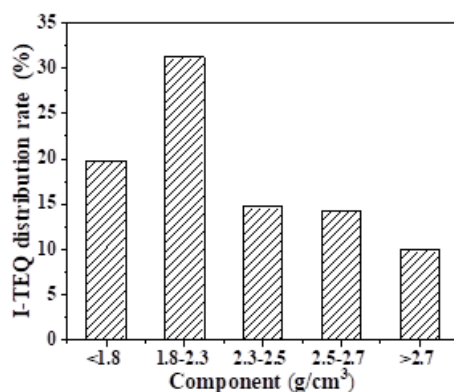
The changes of the concentration of dioxin and carbon content with density are shown in Figure 6.



**Figure 6:** Relationship Between Carbon Content and ( $\Sigma$ PCDFs+ $\Sigma$ PCDDs) with Density.

As is shown in Part 3.2, the 1.8-2.3 g/cm<sup>3</sup> fraction contains only 25.59% carbon while <1.8 g/cm<sup>3</sup> fraction contains 58.47% carbon. Carbon in MSWI fly ash consists of injected powdered activated carbon (AC) and residual carbon (RC). RC usually interwinds with or is wrapped in mineral matter [7], while AC contains little ash. The 1.8-2.3 g/cm<sup>3</sup> fraction contains only RC while the <1.8 g/cm<sup>3</sup> fraction contains both AC and RC. This result indicates that much more dioxins exist in RC than AC. AC adsorbs dioxins from the flue gas [20].

Taking into account of the yield, the absolute contribution of each fraction to the toxicity of LA is shown in Figure 7.



**Figure 7:** The Distribution Absolute I-TEQ of Dioxins Among Density Fractions in LA.

This is a very interesting result. From Figure 7, it can be found that the difference in the absolute amounts of dioxins among density fractions is much less than their concentration per unit weight. The 1.8-2.3 g/cm<sup>3</sup> fraction contributes largest dioxins toxicity, 31.22%; The <1.8 g/cm<sup>3</sup> is the second, 19.82%; and the fractions between 2.3->2.7 g/cm<sup>3</sup> contribute 9%-15%. Obviously, the difference between the total toxicity of fractions of different densities and the toxicity equivalent per unit weight is greatly reduced, which is mainly caused by their yields. Furthermore, the >2.7 g/cm<sup>3</sup> fraction with neglectable carbon content still has the I-TEQ of dioxins exceeding the permit content of the national standard, which indicates that fine inorganic ash particles also absorb dioxins. Similar results were found by other authors [21].

### 3.4 Discussions

Generally speaking, two methods, gravity separation and froth flotation, are widely used for separating target and non-target mineral particles in the mineral processing and coal preparation industry. Gravity separation takes advantage of density differences. Up to date, traditional equipment of gravity separation in mineral processing such as shallow cell, heavy media cyclone, shaking table, spiral separator, Knelson concentrator, Falcon concentrator and air dense medium fluidized bed have not been applied commercially in the separation of fine minerals [8]. Lower density particles could be effectively separated from higher density ash particles by density separation only for particles larger than 0.5 mm. The froth flotation technique is based on the differences in surface hydrophobicity between organic matter and inorganic matter. The organic particles can be attached onto the oily bubble surface and separated with rising bubbles from the sinking inorganic particles. It is a widely used separation technique for fine minerals, such as unburned carbon from coal fly ash [8].

In the MSWI fly ash, carbon, including AC and RC, is wettable to oil and the inorganic minerals to water. As is shown in Figure 2, the carbon content in the  $<1.8$  g/cm<sup>3</sup> density fraction attains as high as 58%, which can be easily separated with flotation. For the 1.8-2.3 g/cm<sup>3</sup> fraction, it will be a little difficult to separate as it has a carbon content only 25%. In this case highly efficient flotation column or highly efficient agents will be needed [22]. As for the  $>2.3$  g/cm<sup>3</sup> fraction with carbon content below 4%, it is unable to separate with direct flotation.

From Figure 7, the I-TEQ of dioxins in the tailing is 2637.85 pg/g assuming full separation of the  $<1.8$  g/cm<sup>3</sup> and 1.8-2.3 g/cm<sup>3</sup> fractions. Similar results were found by Huang et al [10] and Liu et al [11]. Further technical measures need to be taken to decrease the content of dioxins in the tailing, so as to meet the standards, 0.1 ng I-TEQ/Nm<sup>3</sup>. Grinding is an effective measure. It can break the intertwinement between RC and minerals, or break the shell of ash particles so as to liberate the carbon. Besides carbon, fine inorganic particles also have a certain adsorption effect on dioxins [21]. The second measure is to develop special organic admixtures to drag dioxins from the surface of mineral particles into water. Then they will adhere on the oily bubbles, float up, and be separated by flotation.

With the two technical measures combined together, the overall dioxins content in the tailing is expected to be decreased below the limit required by the standards.

### 4. Conclusion

In this paper, the relationship between dioxin content and density in MSWI fly ash was studied. The MSWI fly ash was pretreated with ammonium chloride, eliminating Ca(OH)<sub>2</sub> as well as chlorides, and then separated into different densities using sodium polytungstate. It was found that carbon content decreases with the increase of density. The toxic equivalent concentration of dioxins decreases with the increase of density too, except the 1.8 g/cm<sup>3</sup> fraction. This result indicates that higher concentration of dioxins exist in RC than AC, as AC enriched in the 1.8 g/cm<sup>3</sup> fraction adsorbs dioxins only from flue gas.

The relationship between absolute amounts of dioxins with density were also calculated. It was found 1.8-2.3 g/cm<sup>3</sup> fraction has the highest toxic equivalent of dioxin apparently due to its high concentration. But unneglectable amounts of dioxins exist in other density fractions, especially the  $>2.3$  g/cm<sup>3</sup> fraction with little carbon content. It is proved that dioxins are not only distributed on carbon, but also distributed in inorganic particles.

New measures were proposed to eliminate dioxins so as to meet the requirement of the standards.

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