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Chemical characteristics and risk assessment of typical municipal solid waste incineration (MSWI) fly ash in China

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HIGHLIGHTS

- Fly ashes from 15 MSWI plants were collected all over China.
- Excessive leaching of Zn, Pb and Cd were observed in over 40% of samples.
- The mobility of heavy metal was strongly relative to their acid soluble fraction.
- Cd and Pb posed a very high risk to the environment.

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ABSTRACT

The release of heavy metals in municipal solid waste incineration (MSWI) fly ash has become a worrying issue while fly ash is utilized or landfilled. This work investigated the potential mobility of heavy metals in the fly ashes from 15 typical MSWI plants in Chinese mainland by the characterization of distribution, chemical speciation and leaching behavior of heavy metals. The results showed that total content of heavy metals decreased in the order Zn > Pb > Cu > Cr > Ni > Cd in samples. The toxicity characteristics leaching procedure (TCLP) of fly ash indicated that the amount of leached Cd in 67% of samples exceeded the regulated limit. Also, the excess amount of leached Zn and Pb was observed in 40% and 53% of samples, respectively. The chemical speciation analysis revealed that this excess of heavy metal leached in TCLP was contributed to the high content of acid soluble fraction (F1) and reducible fraction (F2) of heavy metal. Moreover, the great positive relevance between leaching behavior of heavy metals and F1 fraction was supported by principal component analysis (PCA). Risk assessment code (RAC) results suggested that Cd and Pb showed a very high risk class to the environment.

1. Introduction

Incineration as one of the municipal solid wastes (MSWs) disposal methods developed vastly in recent years because of its superiority in reducing the mass and volume of MSWs and producing heat to generate electricity or steam [1,2]. In some countries, Japan, Denmark, Sweden, etc., the incineration has been one of the dominant treatments for MSWs [3]. In Shanghai, only 20% of MSWs were disposed by incineration in 2009 [3] and it will treat over 60% of MSWs in the next few years. This will result in more than 100 thousand tons of fly ash per year produced in future.

Municipal solid waste incineration (MSWI) fly ash is characteristic of fine particles with the size < 10–50 μm [4], providing sufficient specific surface area to enrich toxic heavy metals Zn, Pb, Hg, Cu, Cr, Cd and Ni, etc. [5–8]. The concentration of Zn, Pb, Cu, Cr, Cd and Ni in MSWI fly ash in China ranged 4136.0–19311.0, 1473.0–5670.0, 370.0–1061.0, 240.0–361.4, 40.1–412.5 and 60.8–185.2 mg/kg, respectively [5–10]. The heavy metals in MSWI fly ash, such as Cd [4] and Pb [11], can easily leach out and contaminate soil and groundwater, posing high potential risks to environment and human health [4,7,9]. Therefore, it is the main reason why MSWI fly ash is categorized as a hazardous waste.

A series of work tried to evaluate the risk of heavy metals by its total concentration in fly ash, but the conclusions are usually ambiguous [6,12]. The characterization of the total concentration of heavy metals in MSWI fly ash may indicate the enrichment of elements, but cannot well predict the availability and toxicity behavior of heavy metals in the environment. Moreover, chemical speciation of heavy metal demonstrates that the soluble and exchangeable fractions of heavy metals are quite mobile and the residual fraction is relatively stable even under weathering conditions

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[13]. Therefore, it can be reasonably proposed that the environmental risk of heavy metals has a close relationship with its chemical speciation instead of the total amount of heavy metal in fly ash.

Usually, Tessier and BCR extraction methods were used to find relevance between chemical speciation and extraction of heavy metals. Tessier et al. [14], Basta et al. [15] and Semple et al. [16] reported that, in Tessier method, the sum of the first two fractions of heavy metals was significantly correlated with bioavailability by gastrointestinal simulation experiment and produced harmful interaction for organisms. Moreover, Perin et al. [17] proposed an index named risk assessment code (RAC) for environmental toxicity determination of heavy metals. RAC assesses the availability of metals by using the percentage of metals in acid soluble fraction in BCR method, which is widely used to estimate the environmental risk of heavy metals in various media such as oil and sediment [18,19]. However, the currently research information about relations among total concentration, chemical speciation, leaching behavior and environment risk of heavy metals in MSWI fly ash was scarcely reported.

The objective of this study was to assess the chemical characteristic and risk of heavy metals in MSWI fly ash in Chinese mainland through the following work: (i) the total content of Zn, Pb, Cu, Cr, Cd and Ni in fly ashes sampled from 15 different MSWI plants in China; (ii) TCLP leaching characteristics of heavy metals, and a modified four-step chemical extraction of heavy metal fractions with statistics frequency analysis; (iii) the principal component analysis (PCA) method to establish the correlations between speciation and leaching characteristic of heavy metals; (iv) the risk assessment index (RAC) to assess potential environmental risks of fly ashes.

2. Materials and methods

2.1. Sample collection and preparation

Fly ash samples were collected from 15 MSWI plants in different cities all over China. These plants are equipped with typical grate-type or fluidized bed incinerator that has the treatment capacity over 300-ton MSW/d. The samples were dried in an oven at 105 °C for 24 h. The final dried fly ash samples were stored in a sealed jar at room temperature. These fly ashes were designated by notations indicating the respective sample of origin (S1, S2 . . . and S15).

2.2. Chemical analysis

Total content of heavy metal was determined by treating 0.2 g sample with $HNO_3/HClO_4/HF$ acid mixture digestion method at about 120 °C until the digested solution was clear [20].

A modified four-step procedure sequential extraction method (see Table 1) was adopted to fractionate heavy metals in acid soluble fraction, reducible fraction, oxidizable fraction and residual fraction [21]. After each extraction, the separation was achieved by centrifuging at 3000 rpm for 30 min and the supernatant was filtered through 0.45 μm membranes. The residual was also analyzed by the digest method [20]. The recovery of the metal was calculated by follows formula:

$$\text{Recovery} = \frac{F1 + F2 + F3 + F4}{\text{Total concentration}} \times 100\% \quad (1)$$

Zinc, Pb, Cu, Cr, Cd and Ni concentration in digested solutions and extracts was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-AES). The samples were performed in triplicate throughout all the analysis and the results reported were the average values.

Table 1
Detailed information of the modified four-step sequential extraction method.

Step	Target phase	Extraction agent and conditions
F1	Acid soluble fraction	40 mL acetic acid, 16 h
F2	Reducible fraction	40 mL hydroxyl ammonium chloride, 16 h
F3	Oxidizable fraction	10 mL hydrogen peroxide (30%), digested at room temperature for 1 h; A second 10 mL hydrogen peroxide, digested at 85 °C (water bath) for 1 h; 50 mL of ammonium acetate, pH = 2, 16 h
F4	Residual fraction	10 mL of HNO_3, 5 mL of H_4ClO_4, 10 mL of HF, digested

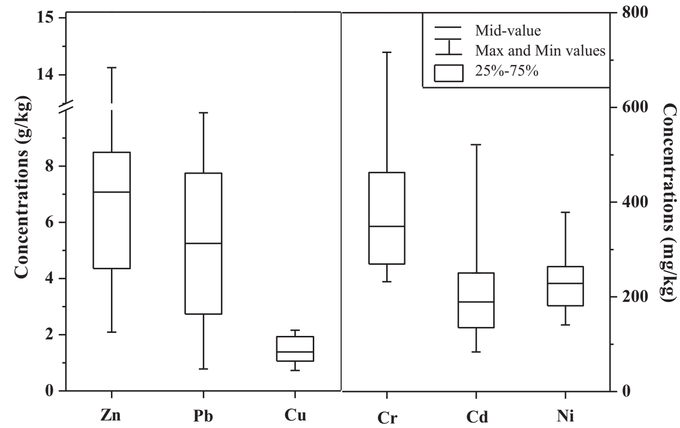

Fig. 1. Total concentrations of heavy metals (Zn, Pb, Cu, Cr, Cd and Ni) in MSWI fly ash samples.

2.3. Leaching behavior

The fly ash samples were characterized for heavy metal leachability according to US EPA SW 846 Method 1311 toxicity characteristics leaching procedure (TCLP) [22]. The leaching procedure was as followed: 1 g (dry weight) of fly ash samples were extracted using acetic acid (pH = 2.88) at an L/S ratio of 20 for 18 h with rotary tumbler at 30 ± 2 rpm. The eluates were filtered using a 0.45 μm membrane filter. Heavy metal contents were tested by ICP-AES. The samples were also performed in triplicate and the results reported were the average values.

2.4. Statistical analysis

The frequency distribution was applied to describe the percentage distribution of heavy metal in each speciation. Principal components analysis (PCA) was carried out to find out the relationship of the leaching and various speciations. The statistical analyses above were all preceded using the software Statistical Product and Service Solutions.

The risk index RAC was used to assess the level of risk of heavy metals in MSWI fly ash. The design formula is as follows:

$$\text{RAC} = \frac{\text{The amount of F1}}{\text{The total concentrations}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Total concentration of heavy metals

The total concentration of six main heavy metals Zn, Pb, Cu, Cr, Cd and Ni in 15 MSWI fly ash samples are shown in Fig. 1. There were widely undulatory concentrations of heavy metals. The ranges of