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Characterization of heavy metals in fly ash from municipal solid waste incinerators in Shanghai

Zhang Haiying[a,*], *Zhao Youcai*[b], *Qi Jingyu*[c]

[a] *School of Chemical and Environmental Engineering, Shanghai Institute of Technology, 120 Caobao Street, Shanghai, China*
[b] *The State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai, China*
[c] *School of Ocean and Earth, Tongji University, Shanghai, 200092, China*

ABSTRACT

This study aims to develop a methodology for analysis of characteristics of heavy metals in MSWI fly ash. It performed analysis of composition of heavy metals, leaching toxicity, leaching behavior as a function of pH, specification distribution and corresponding mineral components of residue derived from each step of the sequential extraction. It is found that content of heavy metals follows the sequence of Zn > Pb > Cu > Cr > As > Ni > Cd approximately Hg in both plants, and that total heavy metals account for less than 1% by mass of fly ash. Major hazardous heavy metals in fly ash are As, Cd, Hg, Pb and Zn, whose leaching ratios exceed the limit value described in hazardous waste identification standard. Measured leaching results of Cu, Pb and Zn are essentially consistent with the simulated results at pH between 0 and 13. Content of calcium-silicates, alumino-silicates and glass phases in residue derived from sequential extraction procedure increases steadily from the first step to the fifth step of the sequential extraction procedure. Cu, As, Cr, Hg, Cd, and Ni, relatively stable under strong basic conditions, can be leached out under strong acidic conditions, while Zn and Pb tend to be leached out under both strong acidic and basic conditions.

Keywords: MSWI fly ash; Heavy metals; Characterization; Leaching toxicity; Specification analysis; Leaching behavior

1. Introduction

Fly ash is a must by-product of MSW incineration process, which has been classified as a hazardous waste due to its relatively high content of heavy metals all over the world. The presence of heavy metals in municipal solid waste incineration (MSWI) *fly ash* is of environmental concern due to their leaching potential in landfill environments. Hence, its management is becoming a challenge for incineration of MSW, and therefore attracting world attention. Treatment methods of fly ash include solidification with cement-based materials, chemical stabilization with EDTA, sodium sulfide and thiourea (Zhang et al., 2008), hydrometallurgical extraction by dissolution in acidic or alkaline medium, and sintering or vitrification for reuse as a construction material. Safe management of MSWI fly ash depends on a through understanding of its characterization, especially characterization of heavy metals in it.

Wan et al. (2006) of Tsinghua University China performed a sequential chemical extraction on *fly ash* samples from a large-scale municipal solid waste incineration plant in East China, to study the leaching behavior of heavy metals such as zinc, lead, cadmium and copper in MSWI fly ash.

Liu et al. (2009) investigated the composition and morphology of raw *fly ash* and washed *fly ash* at different sintering temperatures, and examined the newly formed minerals during sintering. Toxicity characteristic leaching procedure (TCLP) tests were carried out to investigate the effect of the washing treatment and sintering process on the leaching performance of heavy metals in *fly ash*, to study relationship between leaching toxicity of heavy metals and mineral compositions in the thermal treatment process.

Xue et al. (2008) used HCl as extractant to leach Cd, Cr, Cu, Mn, Ni, Pb and Zn from MSWI fly ash under traditional and microwave acid extraction conditions. The redistributions of heavy metals were determined using the sequential extraction

* *Corresponding author*. Tel.: +86 21 67625727; fax: +86 21 67625727.
E-mail address: juli506@126.com (Z. Haiying).
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procedure before and after extraction. The extraction efficiencies and specification transformation of heavy metals were investigated to study acid extraction efficiencies of heavy metals.

Ye et al. (2007) performed a study on characterization and heavy metals leaching toxicity of fly ash from municipal solid waste incinerators in China. In their study, the characteristics and leaching behavior of heavy metals in fly ash, sampled from 12 MSWI plants in China, were investigated. Component analysis shows that MSWI fly ash in China must be controlled as a hazardous material due to its potential environmental risk. Leaching toxicity of heavy metals, in accordance with TCLP of U.S. EPA and GB 5086.1-1997, was performed, and difference between both standards analyzed.

Lee (2007) studied characterization of bottom and fly ash collected from automobile shredder residue (ASR) incinerator in terms of particle size, compositions, and heavy metal leaching by the standard TCLP method. Two alternative methods were also examined for the treatment of heavy metals in ASR incinerator ash from the aspect of recycling into construction or lightweight aggregate material. It was clearly found in the study that heavy metals could be removed thoroughly or partly from ASR fly ash through acid washing with dilute HCl solution so that the remaining *fly ash* could be landfilled or used as a construction material.

Based on the above studies, analysis of content and leaching toxicity of heavy metals in MSWI fly ash, as well as their specification distribution and leaching behavior as a function of pH, was performed respectively using ICP, a sequential extraction procedure, XRD and MINTEQA2 modeling. Data derived from these methods may help regulators and plant operators to develop methods for handling MSWI fly ash. These data can also be used as a basis for geo-chemical modeling of long-term ash stabilization, which will aid engineers to explore disposal and recycle methods environmentally benign over the long-term.

2. Experiment

2.1. *Sampling and composition analysis of heavy metals*

The ash used in this study came from two biggest municipal solid waste incinerators, Pudong and Jiangqiao MSWI Plant, which handle 1100 tons solid waste per day for the former and 1500 tons per day for the latter. Jiangqiao Plant utilizes German Steinmuller furnace, while Pudong Plant uses French CITY2000 tilted-reversing furnace. Prior to analysis of characteristics of heavy metals, fly ash was dried for 24 h at 105 °C.

Hg detector was used to measure content of Hg, and ICP (IRIS Advantage 5000) used to analyze content of other heavy metals. HNO_3/H_2O_2 digestion method was applied to extract Hg from the ash, and $HNO_3/HF/HClO_4$ method applied for digestion of other heavy metals.

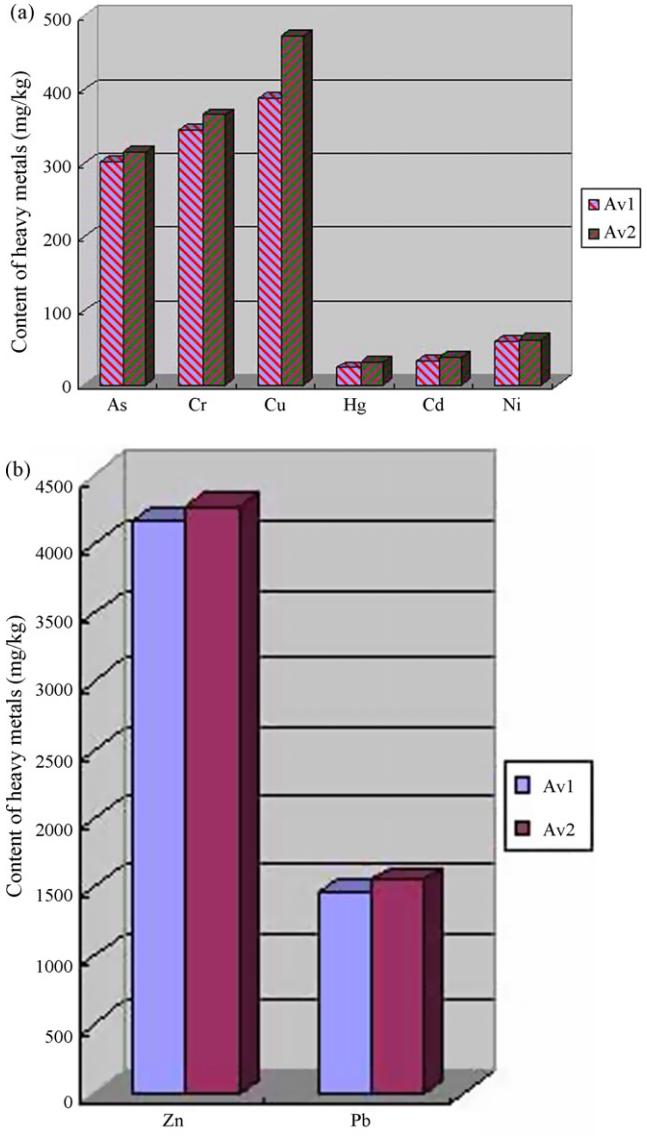

Fig. 1 – Comparison of content of heavy metals in fly ash from two MSWI plants.

2.2. *Leaching toxicity analysis of heavy metals*

Leaching toxicity analysis was performed in accordance with HVEP (GB 5086.2-1997) (Horizontal Vibration Extraction Procedure) and ALT (Kosson et al., 1991) (Available Leaching Toxicity) standards, in which de-ionized water is used as the agent and the liquid to solid ratio registers 10:1 for the former and 100:1 for the latter.

Table 1 – Sequential chemical extraction procedure.

Step	Reagent	Conditions
(1) Water soluble	De-ionized water	3 h continuous agitation
(2) Exchangeable	$MgCl_2$	3 h continuous agitation
(3) Acid soluble	0.5 M CH_3COOH + 0.1 M $Ca(NO_3)_2$	3 h continuous agitation
(4) Organically bound	0.1 M $Na_4P_2O_7$	3 h intermittent agitation
(5) Fe-Zn oxide occluded	0.175 M $(NH_3)_2C_2O_4$ + 0.1 M $H_2C_2O_4$	3 h intermittent agitation
(6) Residual	$HCl/HNO_3/HF/HClO_4$; $HCl/H_2O_2/HNO_3$	Digestion on electric hot plate