Chemosphere 134 (2015) 346–354

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Detoxification of ashes from a fluidized bed waste incinerator

Jie Yu, Yu Qiao *, Lushi Sun *, Limei Jin, Wenxia Wang, Chuan Ma

*State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, 430074 Wuhan, Hubei, China*

## HIGHLIGHTS

- Bottom and fly ashes were subject to TCLP test.
- Leachates of finer bottom ash and fly ash may exceed the regulatory limit.
- Thermal treatment of fly ash for removal of heavy metals were carried out.
- Almost all Cd, Pb and more than 90% of Cu and 95% of Zn could be removed.
- A maximum 20% of Cr was removed due to formation of stable Cr compounds.

## ARTICLE INFO

*Article history:*
Received 26 December 2014
Received in revised form 8 April 2015
Accepted 19 April 2015

*Keywords:*
Municipal solid waste
Heavy metal
TCLP
Thermal treatment
Fluidized bed incinerator

## ABSTRACT

This paper was to test and control the toxicity of bottom and fly ashes from a circulated fluidized bed (CFB) incinerator. Bottom and fly ashes were firstly subject to TCLP test. Even though leachates of most particle size of bottom ash were below regulatory limit, the leachates of finer bottom ash may exceed the regulatory limit. Therefore, finer bottom ash should be separated and treated before landfilled directly or used as cement replacement. Due to high amounts of leached heavy metals, thermal treatment of fly ash was carried out to remove heavy metals. The influence of temperature, residence time, metal chloride and gas velocity were studied. In all conditions, Cd can be well removed. Pb can be almost completely removed with $MgCl_2$ addition at 1000 °C in 1 h. The removal of Zn and Cu was accelerated significantly by $MgCl_2$ and higher temperature separately. At optimum conditions, more than 90% of Cu and 95% of Zn could be removed, while a maximum 20% of Cr was removed due to the existence or formation of $CaCr_2O_4$, $MgCr_2O_4$ and $K_2Cr_2O_4$ in raw or treated fly ashes.



## 1. Introduction

Up to 2009, the amount of municipal solid waste (MSW) disposal in China was 112.32 million tones, of which 79.22% was landfilled, 1.59% composted and 18% incinerated (Yu, 2013). Due to increasing cost and scarcity of landfill sites, thermal treatment technology has been developed as an attractive method of disposing municipal solid waste. Up to 2010, the number of incinerator has increased up to 104 (Yu, 2013). Chinese government is now building more incinerators to treat continuously growing MSW. Nevertheless, in terms of the environment consideration, MSW incineration faces many serious restrictions. During an incineration process, various solid residues, such as bottom ash, fly ash and particulate are produced. For a typical moving grate incinerator, 250–300 kg bottom ash and 25–50 kg fly ash are produced for 1000 kg municipal solid waste (Jakob et al., 1995). Bottom ash is mainly used as construction materials, such as for coffering road and making brick, or used as material for landfill (Banks and Lo, 2003). Although bottom ash has been used for road construction, it is expected that in the near future this will no long be tolerated since more and more stringer regulations regarding reutilization of residues will be put forward (Jakob et al., 1995). Nevertheless, MSW fly ash is generally classified as a hazardous material because it contains higher amount of heavy metals and soluble salts. In order to evaluate possible environmental effects related to the release of contaminants from bottom and fly ashes, the toxicity characteristic leaching procedure (TCLP) was used comprehensively to evaluate the hazardous properties of the ashes (Feng et al., 2007; Yu et al., 2013). Song et al. (2004) carried out TCLP test of different particle size of bottom ash and fly ash from different locations at the MSW incinerator. It was found that the leachates from most sizes of bottom ash were below their national regulatory limit values, while that of fly ash failed to meet regulatory limit values. Sukandar et al. (2006) performed TCLP tests of

* Corresponding authors.
*E-mail addresses:* yuqiao@mail.hust.edu.cn (Y. Qiao), sunlushi@hust.edu.cn (L. Sun).

http://dx.doi.org/10.1016/j.chemosphere.2015.04.045
0045-6535/

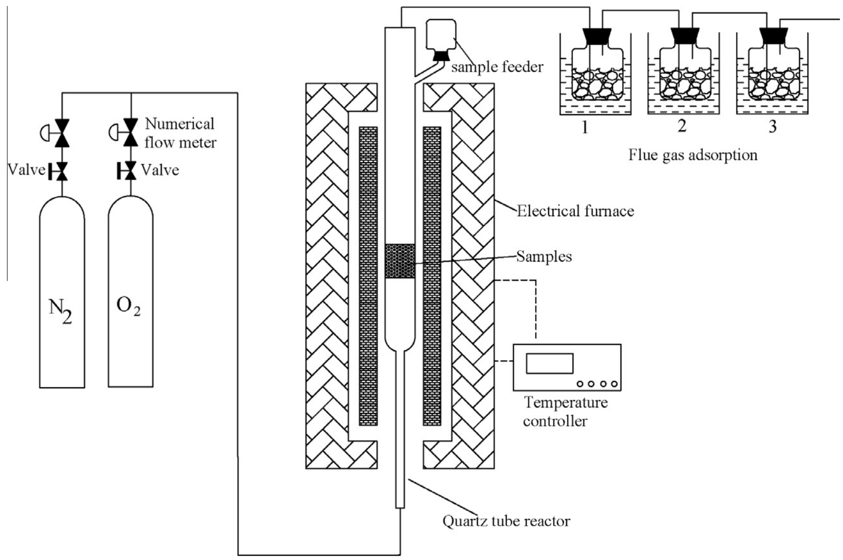


**Fig. 1.** Scheme of experimental setup.

different particle size of fly ash and found that leachates from some particle size fractions did not meet national TCLP standard. Therefore, treatment methods must be developed to make fly ash safe for landfill or construction use.

The different types of treatment may be grouped into three categories: separation processes, solidification/stabilization, and thermal methods (Quina et al., 2008). A wet process of extracting the metals from the fly ash with acids has been used in some places (Bipp et al., 1998; Chang et al., 2001). The drawbacks of this process are the difficulties of filtering the leachate due to the formation of the gelatinous silicate and aluminum compounds, and in recovering the individual metals from the leachate due to its complex matrix (Chan, 1997). Comparatively, thermal treatment is potentially attractive. Thermal treatment of MSW fly ash causes both the evaporation and the stabilization of heavy metals depending on the treatment temperature. At relatively moderate temperature, thermal treatment in combination with chlorination is a promising way to remove heavy metals (Fraissler et al., 2009). Many researchers studied the heavy metal removal from fly ash by thermal treatment method (Jakob et al., 1995; Chan et al., 1996; Jakob et al., 1996; Nowak et al., 2010; Nowak et al., 2012; Nowak et al., 2013). Heavy metal removal was found to increase with the increase of treatment temperature (Jakob et al., 1996) and favored by solid chlorides (Nowak et al., 2010; Nowak et al., 2012). Jakob et al. (1995) studied the heavy metal removal from fly ash from MSW incinerator and synthetic powder mixtures. It was found that Zn and Cu were the less volatile heavy metals and chloride can promote Zn and Cu removal. Fraissler et al. (2009) performed thermodynamic equilibrium calculations to determine the heavy metals removal from sewage sludge ash. With regard to their calculated removal results, the heavy metals investigated can be classed into three fractions, namely "easily volatile" (Cd and Pb), "semi-volatile" (Cu and Zn) and "low-volatile" heavy metals (Cr and Ni). For the "semi-volatile" heavy metals, high amounts of Cl were required for the removal. Among Cl-donor ($Cl_2$, HCl, $CCl_4$ and metal chlorides, especially alkali or alkaline earth chlorides), metal chlorides offer the advantages of low costs, easy availability, low toxicity and unproblematic handling of the chlorination process. Among metal chlorides, Nowak et al. (2012) reported that $CaCl_2$ and $MgCl_2$ were more effective than NaCl in the removal of heavy metals. Chan et al. (1996) found that heavy metal removal was dependent on time and temperature and $CaCl_2$, $MgCl_2$ and $FeCl_2$ were more effective than NaCl and $AlCl_3$. Li et al. (2015) also pointed that $MgCl_2$ was the most effective agent for most heavy metals. This may be because compared with other alkali/alkaline earth metals, the formation of $Cl_2$ or HCl through the reaction of $MgCl_2$ with $O_2$ or $SiO_2$ was favored.

The evaporated metal chlorides can be captured in the flue gas cleaning system (e.g. scrubber) and be recovered in an ensuing treatment step, leaving a less contaminated fly ash for cement or landfilled. Moreover, during thermal treatment, unburned particles and organic materials will be destroyed because of high temperature. Nowak et al. (2010) reported a process, "CT-Fluapur-process", to recovery heavy metal from fly ash. In this system, Cd, Cu, Pb and Zn were nearly completely removed within 2 h. However, the evaporation of Cr and Ni was incomplete. Further work should be done to separating heavy metals from fly ash and lower the costs of treatment process.

This work focuses on the detoxification of ashes from a CFB waste incinerator. Firstly, the chemical, physical and mineralogical of ashes were characterized. Toxicity of different particle sizes of bottom and fly ashes were tested by TCLP. For the fly ash, heavy metal removal at 800, 900 and 1000 °C in a laboratory-scale fixed reactor, were performed to get a less contaminated ash and recover heavy metals. Moreover, the influence of $MgCl_2$, residence time, silica and gas velocity was also investigated to establish optimum working conditions for removal and recovery of these heavy metals.

## 2. Experimental procedures

### 2.1. Materials

The ashes used in this study were sampled from a fluidized bed incinerator in Wuhan, which can handle 600 tons MSW per day. Before the discharge of bottom ashes in this incinerator, the coarse bottom ashes were screened. To get homogeneous samples, bottom ash samples were mixed thoroughly and dried in the oven at 105 °C. After cooling, the samples were kept in desiccators. Specifically, the fly ash samples collected from the bag house filter