Waste Management xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

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

Mechanism on heavy metals vaporization from municipal solid waste fly ash by $MgCl_2 \cdot 6H_2O$

Jie Yu, Lushi Sun *, Chuan Ma, Yu Qiao, Jun Xiang, Song Hu, Hong Yao

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

ARTICLE INFO

Article history:
Received 11 August 2015
Revised 21 November 2015
Accepted 19 December 2015
Available online xxxx

Keywords:
Municipal solid waste
Fly ash
Heavy metal
$MgCl_2 \cdot 6H_2O$
Thermal treatment

ABSTRACT

This work aims to study the mechanism of heavy metals vaporization by $MgCl_2 \cdot 6H_2O$. Firstly, the decomposition mechanism of $MgCl_2 \cdot 6H_2O$ was investigated by thermodynamic equilibrium calculations, XRD and TG. Upon heating, $MgCl_2 \cdot 6H_2O$ went through the processes of dehydration and hydrolysis simultaneously accompanied by the release of HCl between 150 and 500 °C. At temperature higher than 500 °C, Mg(OH)Cl gradually release part of HCl. $MgCl_2 \cdot 6H_2O$ followed the similar processes of decomposition at both oxidative and reductive atmospheres. In oxidative atmosphere, vaporization of Zn and Cu was significantly accelerated by $MgCl_2 \cdot 6H_2O$. However, in inert atmosphere, vaporization of Cu was not promoted since copper chloride was only stable in oxidative atmosphere. Under slow heating condition, vaporization of heavy metals were close to that under fast heating condition. This may be partially attributed to that most heavy metals already reacted with HCl forming metal chlorides below 500 °C, which can be vaporized at higher temperature. Moreover, the Mg(OH)Cl contributed to release HCl up to 800 °C. At such high temperature, the metal chlorides continue to be formed and then vaporized. After treatment, the leaching concentration of heavy metals from treated fly ashes were much lower than that from raw fly ash and met the regulatory limit of leachate. Since a large amount of $MgSiO_3$ were formed during thermal treatment, the fly ash treated with $MgCl_2 \cdot 6H_2O$ can be used as raw materials for glass–ceramics production.

1. Introduction

In China, the amount of (municipal solid waste) MSW generated increases significantly due to booming economy and rapid urbanization. In 2011, more than 25 Mt of MSW was incinerated (Hu et al., 2015), and it is estimated that the total amount of MSW in 2030 will increase to 480 Mt (East Asia and Pacific Urban Development Sector Unit, 2005). Due to limited land, thermal treatment of MSW is taking the place of landfill and becoming the major way of handling MSW. By the end of 2012, there are 142 municipal solid waste incineration (MSWI) power plants in operation (Zheng et al., 2014). However, in terms of environmental issues, MSWI faces many serious restrictions. During the process of incineration, various solid residues, such as bottom ash, fly ash and particulate, were produced. For a typical moving grate incinerator, 250–300 kg bottom ash and 25–50 kg fly ash were produced for 1000 kg municipal solid waste (Jakob et al., 1995). The bottom ash is usually disposed of in landfills or used as construction materials due to low heavy metal concentrations. However, the fly ash must be further treated due to high concentration of heavy metals.

There are two major ways of handling fly ash in terms of heavy metals (Quina et al., 2008): (1) recovery of heavy metals from fly ash; (2) reducing heavy metal leachability by stabilization of heavy metals in fly ash. Considering fly ash also contains large amounts of dioxins and furans, thermal treatment of fly ash seems to be a good option of removing/stabilizing heavy metals and destroying harmful organic compounds simultaneously. Thermal treatment of fly ash causes recovery or stabilization of heavy metals depending on the treatment temperature. Vitrification, fusion/melting, and sintering are three major ways of stabilizing heavy metals in fly ash by thermal treatment method (Quina et al., 2008). The disadvantage of stabilization of heavy metals in fly ash by thermal treatment is energy consuming. Comparatively, vaporization/recovery of heavy metals by thermal treatment method is potentially attractive (Chan and Kirk, 1999). Briefly, heavy metals in fly ash are vaporized at comparatively low temperatures (800–1000 °C), then the vaporized heavy metals can be collected in the cooling system. This method can remove heavy metals and destroy organic compounds simultaneously. At the same time, heavy metals can be recycled and reused.

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* Corresponding author.
E-mail address: sunlushi@hust.edu.cn (L. Sun).

http://dx.doi.org/10.1016/j.wasman.2015.12.015
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Please cite this article in press as: Yu, J., et al. Mechanism on heavy metals vaporization from municipal solid waste fly ash by $MgCl_2 \cdot 6H_2O$. Waste Management (2015), http://dx.doi.org/10.1016/j.wasman.2015.12.015

The volatility of heavy metals depends on their mode of occurrence. Generally, metal chlorides are more volatile than other forms. However, heavy metals in fly ash may not exist in the form of chlorides. Therefore, chlorinating agents, such as gaseous chlorine, hydrochloric acid and metal chlorides, can be used to transform less volatile metals in fly ash into more volatile metal chlorides (Li et al., 2015; Nowak et al., 2013; Nowak et al., 2012a). According to Li et al. (2015), inorganic chloride is more effective than PVC. Among inorganic chlorides, Nowak et al. (2012a) found $CaCl_2$ and $MgCl_2$ were more effective than NaCl for most studied heavy metals. Adam et al. (2009) also found $MgCl_2$ was effective in vaporizing heavy metals from fly ash. They proposed that $CaCl_2$ and $MgCl_2$ can directly react with H_2O and/or O_2 releasing HCl and/or Cl_2, as shown in Eqs. (1) and (2). The released Cl_2 or HCl then reacted with metal oxides forming more volatile metal chlorides.

$$MgCl_2 + O_2 \rightarrow MgO + Cl_2 \tag{1}$$

$$MgCl_2 + H_2O \rightarrow MgO + HCl \tag{2}$$

Mg can be replaced by Ca.

It means $CaCl_2$ and $MgCl_2$ may have negligible effect on heavy metals vaporization in the absence of O_2 and H_2O. Actually, Nowak et al. (2012a) used $MgCl_2{\cdot}6H_2O$ in their work. It is not clear if the mechanism of promoting effect of $MgCl_2{\cdot}6H_2O$ on heavy metals vaporization is different with $MgCl_2$ and $CaCl_2$. Therefore, this study aims to study the mechanism of promoting effect of $MgCl_2{\cdot}6H_2O$ on heavy metals vaporization. Different amount of $MgCl_2{\cdot}6H_2O$ were mixed with fly ash and treated at different temperatures. The mixtures were also treated at different heating rate and atmospheres to deeply understand the effect of $MgCl_2{\cdot}6H_2O$ on heavy metals vaporization. Finally, TCLP analysis was employed on treated fly ashes to test toxicity of treated fly ash.

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 of MSW per day. Before experiment, the fly ash samples, which were collected from the bag house filter and the heat exchanger, were ground and homogenized, then dried at 105 °C for 24 h in an oven and kept in desiccators. $MgCl_2{\cdot}6H_2O$ (technical grade) was chosen to study its effect on the heavy metal vaporization.

2.2. Thermal treatment of fly ash

The thermal treatment experiment was conducted in a quart tube furnace (Yu et al., 2015). The heart of the furnace was a quartz tube (Length: 80 cm; Inner diameter: 6 cm) since steel equipment can be corroded by HCl. A quartz-sinter disk was used to support fly ash and silica wool was above the samples to prevent the take-over of fine fly ash. The heavy metals in the flue gas were adsorbed by passing successively through three impingers immersed in an ice–water bath. The first two impringers contain 5% HNO_3 and 10% H_2O_2, and the third one contains silica gel to remove moisture. When the furnace reached 900 °C, samples were introduced into the reaction zone. After 30 min, the furnace was moved away and quartz tube was air-cooled down until room temperature. In order to study the effect of atmosphere on heavy metal vaporization, air and N_2 were chosen in this study. For each experiment, $MgCl_2{\cdot}6H_2O$ was mixed with fly ash (100 g Cl/kg ash) and homogenized.

The release of single element was quantified assuming that the released fraction of an element applied to the difference between the initial amount of an element in raw ash and the residual amount retained in ash after treatment. The volatilization of heavy metals is defined as:

$$R = \left[1 - \frac{C_1 m_1}{C_0 m_0}\right] \times 100\% \tag{3}$$

C_0: Heavy metal concentration in raw ash (mg kg^{-1});
C_1: Heavy metal concentration in ash after treatment (mg kg^{-1});
m_0: Mass of raw ash (g);
m_1: Mass of ash after treatment (g).

2.3. Chemical analysis

The major components of ash were performed by X-ray fluorescence spectrometry (XRF) in triplicate. Crystalline compounds were identified using a PANalytical B.V. X'Pert Pro multipurpose X-ray diffractometer (XRD). The thermal behavior of $MgCl_2{\cdot}6H_2O$ was obtained by thermogravimetry (TG), STA 449 F3-Netzsch, with a heating rate of 20 °C/min in air or N_2. Total trace elemental compositions of bulk samples were determined using inductively coupled plasma with mass spectrometric detection (ICP–MS) after total acid digestion by HNO_3–HCl–HF. 100 mg of dried ash sample were digested with an acidic solution of 65% nitric acid (2 ml), 35% HCl (6 ml) and 40% hydrogen fluoride (2 ml) in microwave. The solution was then diluted to 100 ml with deionized water and analyzed by ICP–MS.

TCLP analysis was employed on the raw and treated fly ashes in order to analyze metal leachability. The leaching tests were carried out according to a modified TCLP procedure for the ashes (George et al., 2007). The samples and leaching solution (CH_3COOH) were mixed at a weight/volume ratio of 1/20 and agitated in an overhead extractor at a rate of 30 rev/min for 16 h. The leachate was then filtered and heavy metals were analyzed by ICP–MS.

2.4. Thermodynamic equilibrium calculations

Thermodynamic equilibrium calculations are performed by CHEMKIN software based on the Gibbs free enthalpy of possibly occurring reactions. The thermodynamic data of studied species were converted into CHEMKIN-compatible fitting coefficients using the included FITDAT routine (Barin, 1993; Chase, 1998; Knacke et al., 1991).

3. Results and discussion

3.1. Decomposition mechanism of $MgCl_2{\cdot}6H_2O$

Among alkali and alkaline earth chlorides, $MgCl_2{\cdot}6H_2O$ was most effective in promoting heavy metals vaporization from fly ash (Nowak et al., 2012a). Unfortunately, the mechanism is still unclear. In order to understand this mechanism, the thermal decomposition of $MgCl_2{\cdot}6H_2O$ was firstly studied. Thermodynamic equilibrium of thermal decomposition of $MgCl_2{\cdot}6H_2O$ was performed in CHEMKIN and shown in Fig. 1. The simulation results clearly showed that the decomposition of $MgCl_2{\cdot}6H_2O$ went through dehydration and hydrolysis simultaneously from 50 to 500 °C. Between 50 and 150 °C, $MgCl_2{\cdot}4H_2O$ was predicted due to the decomposition of $MgCl_2{\cdot}6H_2O$. At temperature higher than 150 °C, $MgCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}H_2O$, MgOHCl, HCl and $MgCl_2$ were formed, while $MgCl_2{\cdot}4H_2O$ became unstable between 200 and 250 °C, chlorine speciation shifted gradually from $MgCl_2{\cdot}2H_2O$ and $MgCl_2{\cdot}H_2O$ to HCl, Mg(OH)Cl and $MgCl_2$. HCl, Mg(OH)Cl and

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