

## Volatilization of heavy metals during incineration of municipal solid wastes

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**Abstract:** Incineration experiments with MSW, which had been impregnated with heavy metals, were presented to obtain information on the volatilization behavior of the elements cadmium (Cd), lead (Pb), and zinc (Zn) under different conditions. Experiments were carried out in a bubbling fluid bed system connected to a customized inductively coupled plasma optical emission spectroscopy (ICP-OES) for analyzing metals in the flue gas. The results indicated that the combustion temperature, the gas atmosphere, and the chlorine content in the flue gas could affect the volatilization behavior of heavy metals. In the fluidized bed combustion, a large surface area was provided by the bed sand particles, and they may act as absorbents for the gaseous ash-forming compound. Comparer with the metals Cd and Pb, the vaporization of Zn was low. The formation of stable compounds such as  $\text{ZnO} \cdot \text{Al}_2\text{O}_3$  could greatly decrease the metals volatilization. The presence of chlorine would enhance the volatilization of heavy metals by increasing the formation of metal chlorides. However, when the oxygen content was high, the chlorinating reaction was kinetically hindered, which heavy metals release would be delayed.

**Keywords:** municipal solid waste; incineration; heavy metal emission; fluidized bed

### Introduction

Thermal treatment has been considered as a more effective approach to handle growing municipal solid waste (MSW) quantities because of the advantages of minimization, sanitation, stabilization, and resource recovery by incineration or pyrolysis. However, almost all of the components of MSW contain some quantity of the heavy metals, which are categorized as toxic at certain concentrations: lead (Pb), cadmium (Cd), chromium (Cr), mercury (Hg), and nickel (Ni) (Chandler, 1997). Once these solid refuse are burned in the furnace, the heavy metals are released from the fuel and transformed into inorganic residues as bottom ash, fly ash, residues from the emission control system and gaseous emissions ash. It was estimated that in Europe, 3.0%, 0.7% and 7.0% of the emissions of Cd, Pb and Zn, respectively, originated from refuse incineration (Pacyna, 1984). Potential emissions of heavy metals from these municipal solid waste incinerators (MSWI) have caused much public concerns.

In recent years, many investigations focus on the behavior of heavy metals in the combustion processes of MSW (Jakob, 1995; Durlak, 1997; Vssailiev, 1999; Hasan, 2000a). Previous studies indicated that the degree of heavy metal volatilization from refuse incinerators is a complex function of many factors, including metal species and concentration in the waste feed, combustion temperature,

treatment duration, composition of the gas stream, and the performance of the air pollution control devices (Brunner, 1986; Greenberg, 1978; Hasan, 2000b). Furthermore, high chlorine contents of MSW may cause the formation of the volatile heavy metal compounds, thus increase metal partition to the fly ash and the flue gas (Chiang, 1997; Verhulst, 1996).

In fluidized bed combustors, the temperature is lower (750–900 °C) and the particle size is much greater than that in pulverized coal combustion (PCC) system. The lower temperature is expected to decrease the metal emissions, but the longer residence time at a high temperature can cause increased volatilization. According to Clarke (Clarke, 1993), addition of limestone to the bed to control emissions of sulphur dioxide may increase emissions of As, Co, Cr, Cu, Ni, Pb, V, Zn and Cd. He explained this by increased fine particulate loading when limestone was added.

Recently, many experimental efforts have been made to investigate the mechanisms of metal behavior using laboratory-scale apparatus and mathematic models (Masseron, 1999; Sukrut, 2001; Wang, 2001; Ho, 1995). Abanades studied the kinetics of heavy metal vaporization during the incineration of model waste samples in a fluidized bed reactor (Abanades, 2002). The results indicated that the parameters (solid residence time, temperature, gas composition and matrix of model samples) had strong influence on the HM volatilization. The previous paper (Abanades, 2001) also

developed a mathematical model to predict the fate of metallic species according to the main phenomena controlling the vaporization process: heat and mass transfer (transport phenomena) and chemical reactions involving HM (by a thermodynamical analysis).

In this study, laboratory experiments with synthetic MSW samples, which had been impregnated with heavy metals, were presented to obtain information on the volatilization behavior of the elements Cd, Pb, and Zn under different conditions of incineration. The objective of this study is to evaluate the effects of operating parameters of waste incinerators on metal vaporization with the process.

Experiments were carried out in a bubbling fluid bed connected to a customized ICP-OES for analyzing metals in flue gas. The release of three metals (Cd, Pb, Zn) from MSW were studied under different atmosphere (air, gas mixture simulating that in the incinerators, N<sub>2</sub>).

1 Experimental section

1.1 Experimental system

Metal volatilization experiments were carried out in a fluidized bed combustion system. A schematic diagram of the experimental apparatus is shown in Fig. 1. It included a

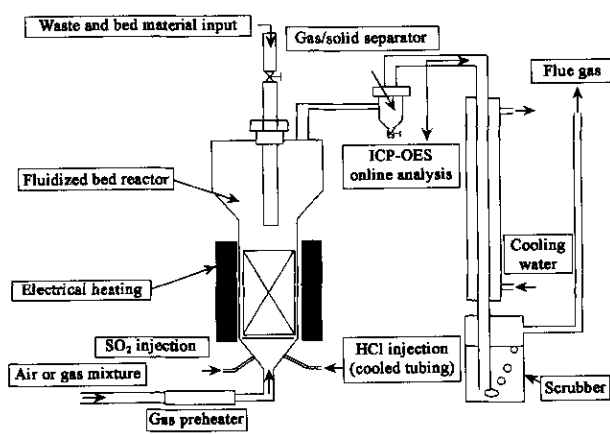


Fig. 1 Schematic illustration of the experimental set-up

fluidized bed reactor, a gas preheater, a gas/solid separator, and an on-line ICP-OES analyzer.

The fluidized bed reactor was made of AISI 316L stainless steel,  $4.5 \times 10^{-3}$  m thick. It was a 0.105 m ID and 0.6 m high cylinder. By means of a device based on compressed air and a tubing (0.041 m ID) plunging in the bed, reactive particles were injected when the bed was at steady-state, and solid samples were aspired at given times. The fluidizing gas, which could be air or a mixture N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, was preheated through an electrical resistance, and the preheater temperature was set to 900 °C. In order to simulate the composition of fluidizing gas in incinerator, SO<sub>2</sub> and HCl diluted in water could be added into the gas mixture. The synthetic gas composition in the experiments (by volume) was: 70.8% N<sub>2</sub>, 4.8% O<sub>2</sub>, 8.8% CO<sub>2</sub>, 15.6% H<sub>2</sub>O, 400 mg/Nm<sup>3</sup> SO<sub>2</sub>. HCl was titrated in the feed solution to obtain the desired mass ratio HCl/H<sub>2</sub>O in the fluidizing gas.

1.2 Characteristics and preparation of the MSW samples

Both MSW sample and alumina model waste were chosen in the present experimental research.

The initial MSW samples used in this study were offered by TIRU (Traitement Industriel des Residus Urbains) and the ultimate and proximate analysis data of these samples are shown in Table 1. From Table 1, it can be found that the contents of sulfur and nitrogen in MSW were very low and the volatile content was high. Furthermore, results of the analysis indicated that the chlorine content in MSW samples was about 8 mg/g: 15.6% of inorganic and 84.8% of organic.

According to experimental analysis and thermodynamic calculations, the most preferential reaction for cadmium and lead during the incineration process is to produce metal chloride. In the combustion chamber, zinc can either be transformed into an oxide or a chloride (Chiang, 1997; Verhulst, 1996; Frandsen, 1994). In this study, metal chlorides were used as typical examples of HM in the combustion system.

Table 1 Ultimate analysis and proximate analysis of MSW samples(dry basis, wt. %)

Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Chlorine	Volatile matter	Moisture	Ash	Heating value, kcal/kg
35.4—39	4.9	31.9—33.8	0.02—0.07	< 0.01	0.8	69—72	6—7	23—25	~ 3600

Due to the low concentration of the heavy metals in the initial MSW, metal chlorides (CdCl<sub>2</sub>, PbCl<sub>2</sub> and ZnCl<sub>2</sub>, respectively) were added into the waste samples firstly. On the other hand, since the original MSW sample was unsuitable for fluidized bed system directly, it is important to make the sample into shapen material with higher density. Hence, the first step of the preparation of sample was to mix the waste, the heavy metal solution, the sand(diameter  $0.5 \times 10^{-3}$  m) and the glue together equably and thoroughly. Then the sample was shredded and pressed into column form particle using a hydraulic compressor. The weight rate of

MSW/sand was 2:1. Where after, the samples were dried at 50 °C during at least 24 h. The diameter of the made-up samples was 10 mm, and the length was  $6—12 \times 10^{-3}$  m, and the density was about 600 kg/m<sup>3</sup>. This technique ensured MSW samples with metal concentration ranging between 2000 and 15000 µg/g.

In the present experiment, a kind of mineral matrix was also used as model waste. The matrix was a porous spherical alumina substrate ( $1.6—2 \times 10^{-3}$  m ID) which was chosen because Al<sub>2</sub>O<sub>3</sub> was one of the main ash compounds together with SiO<sub>2</sub>, and it enabled reliable analysis (it is not

destroyed during the heat treatment). The alumina matrix was impregnated with metal by mixing with the appropriate volume of metal chlorides solutions ( $\text{CdCl}_2$ ,  $\text{PbCl}_2$  and  $\text{ZnCl}_2$ , respectively) during 5 h. Then the sample was dried at  $80^\circ\text{C}$  for at least 24 h. This technique lead to model wastes with metal concentration ranging between 700 and  $4000\ \mu\text{g/g}$ . Previous to impregnation, mineral matrices were calcined for 4 h at  $850^\circ\text{C}$  in order to eliminate volatile substances and to stabilize their properties (mass, porosity). The initial metal concentration of alumina samples was measured by ICP-OES after microwave-assisted digestion ( $\text{H}_3\text{PO}_4$  was used to dissolve  $\text{Al}_2\text{O}_3$ ). The metal distribution inside the particle was analyzed using WDS microprobe (CAMECA Microbeam), and homogeneous distribution of metal inside the porous structure of alumina particle was observed.

### 1.3 Experimental procedure and method

For each experimental run, the fluidized bed reactor was first loaded with silica sand (1.6 kg) of mean diameter  $0.7 \times 10^{-3}\text{ m}$  ( $0.6 \times 10^{-3}\text{ m} < d < 0.8 \times 10^{-3}\text{ m}$ ). When at thermal steady state at desired temperature, a given amount of sample particles (0.13 kg) was injected into the reactor.

In the experiments with MSW samples, the HM concentration in exhaust gases was measured on-line by ICP-OES according to the method developed by Hassaine *et al.* (Verhulst, 1996). In order to do so, the gas outlet was connected to the nearby ICP by a heated tubing ( $T = 400^\circ\text{C}$ ). The gas to analyze was aspirated through a set including a primary sampler (membrane pump) and a secondary sampler (peristaltic pump), and the ICP was previously adapted for analyzing heavy metals in gas. The on-line analysis of gases was implemented dealing with the MSW samples, impregnated with respectively Cd, Pb and Zn chlorides. In each run, after injecting the particles, the evolution of the net emission intensity  $I_{\text{net}}$  (background intensity deduced; units of counts per second) of the metallic spectral lines was measured continuously by the customized ICP-OES system. The intensity was proportional to the metal concentration since both the gas composition and the sampling flow were constant with time in each run. Therefore, this method could give a good qualitative overview of the transient metal concentration in the outlet gas (Hassaine, 2001). A calibration method is required to obtain absolute metal concentrations, and it will be implemented in the next step.

With regard to the alumina model waste, the solid particles were left in the bed for predestined period of time, and then were aspirated from the bed for chemical analysis. The metallic concentration in the residual was measured using ICP-OES after manual sorting and microwave-assisted acid digestion. This led to the concentration versus time profile  $q(t)$  (vaporization kinetics) for given conditions. Then, the vaporization percentage of HM [defined as  $1 - q(t) / q_0$ ]

could be obtained (Hassaine, 2001).

## 2 Results and discussion

### 2.1 Kinetics of heavy metals volatilization

The values of volatilization percentage of metals during the incineration process were carried out in the cases of alumina model samples. The results, as shown in Fig. 2–3 indicated that the rate of volatilization was relatively fast at the initial stage of the treatment, and then it slowed down and leveled off later. The final percentage of vaporization obtained for Cd was around 50% (47%–54% under different atmosphere conditions, Fig. 2), and for Pb was about 20% (18%–22%, Fig. 3) after nearly 80 min. However, the maximum percentage of volatilization for Zn was less than 3%. Consequently, for the three metals with alumina, the volatility in increasing order was Cd, Pb, Zn. The X-ray observation and thermodynamic equilibrium calculation had both validated the occurrence of the chemical reactions between metals and alumina under high temperature (Verhulst, 1996; Abanades, 2001). The chemical sorption inside the pores, coupled with the internal diffusion of gases metal species, controls the volatilization process (Hassaine, 2001). The formation of stable compounds such as  $\text{CdO} \cdot \text{Al}_2\text{O}_3$  and  $\text{ZnO} \cdot \text{Al}_2\text{O}_3$  could greatly decrease the metals volatilization. The effects of chlorides on the volatilization of heavy metals were investigated by varying the HCl content in the fluidized gas. However, increasing the chlorine concentration ( $C_{\text{HCl}}$ ) had little influence on the vaporization kinetics of Cd and Pb with alumina. The reactions of metals with clay ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ) were found to be thermodynamically preferable to other metal reaction at a temperature below  $950^\circ\text{C}$  (Ho, 1995).

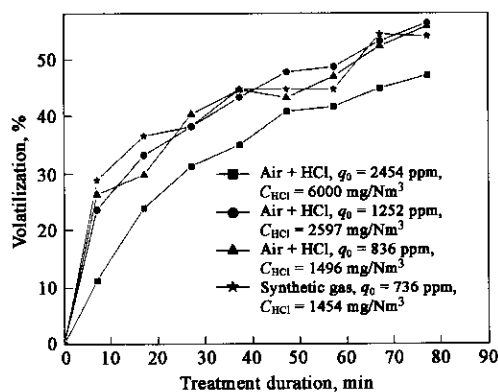


Fig. 2 Percentage volatilization of Cd vs. treatment duration ( $\text{Al}_2\text{O}_3$ ,  $865^\circ\text{C}$ )

### 2.2 Effects of combustion temperature on heavy metals volatilization

Temperature is a significant factor for metal vaporization. The alumina model samples were treated for about 80 min at various temperatures. As expected, increasing the temperature enhanced the volatilization of the

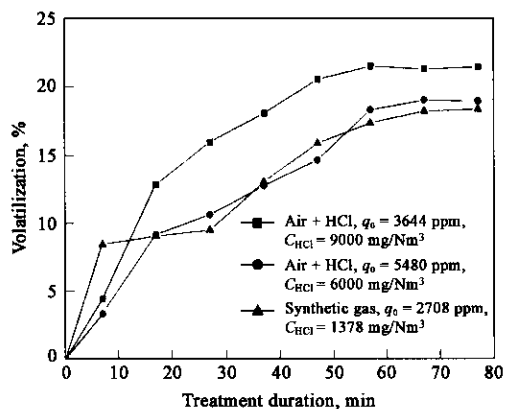


Fig. 3 Percentage volatilization of Pb vs. treatment duration ( $\text{Al}_2\text{O}_3$ ,  $855^\circ\text{C}$ )

heavy metals in each case. As shown in Fig. 4, about 35% Cd was volatilized at  $755^\circ\text{C}$ , and about 54% was volatilized at  $865^\circ\text{C}$ . In general, increasing the temperature could enhance vaporization by raising the vapor pressure of the heavy metal chlorides, by improving the rates of diffusion, and result in a higher percentage of volatilization.

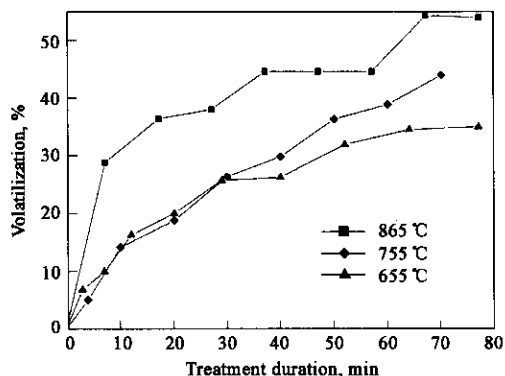


Fig. 4 Percentage volatilization of Cd under different combustion temperature (synthetic gas,  $q_0 = 836$  ppm)

### 2.3 Effects of the gas composition on heavy metals volatilization

When the MSW samples were burned in the furnace, the particles shrunk rapidly, the heavy metals were released from the fuel and transformed into the gas stream. Then, absorption and chemical reactions of heavy metals with absorbent particles would happen. However, in the fluidized bed combustion, a large surface area is provided by the bed sand particles, and they may act as absorbents for the gaseous ash-forming compound, including heavy metals (Uberoi, 1991). Chlorides could react with heavy metals to form more volatile metal chlorides during waste incineration. Indeed, the chlorides were the mainly evaporated compound of heavy metals in the temperature range of  $300\text{--}1000^\circ\text{C}$  (Jakob, 1995; Lind, 1999). In the present work, the on-line analysis of gases was implemented when dealing with MSW, impregnated with respectively Cd, Pb and Zn chlorides. The volatilization tendencies of the three metals in

MSW under different atmospheres are shown in Fig. 5—7.

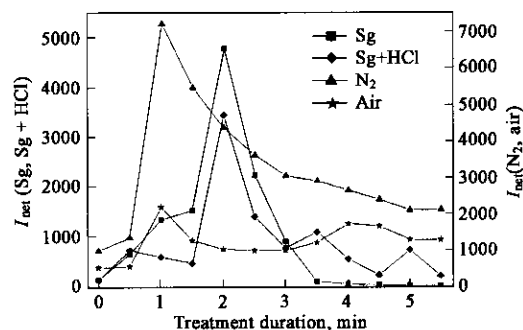


Fig. 5 On-line gases emission intensity of Cd vs. treatment duration (MSW,  $865^\circ\text{C}$ ,  $q_0 = 3682$  ppm)

**Cadmium:** The emission intensities of Cd vs. time in the flue gas under different atmosphere at  $865^\circ\text{C}$  are shown in Fig. 5. It could be found that the gaseous metal concentration exhibited a peak almost instantaneously after injecting the samples into the fluidized bed. The volatilization of Cd had the same tendency under various gas atmospheres, whereas the intensity was different ( $\text{N}_2 > \text{Sg} \approx \text{SgHCl} > \text{Air}$ ). In a reducing gas atmosphere, cadmium was found entirely in the gas phase as  $\text{Cd}(\text{g})$  at about  $850^\circ\text{C}$ . In contrast to reductive environment, it was found in the condensed phase as  $\text{CdSiO}_3$  in the oxidizing atmosphere (Abanades, 2001). When HCl was added, metallic chlorides with high volatility were rapidly formed, thus could increase Cd volatilization during a long time.

**Lead:** As shown in Fig. 6, the vaporization of Pb kept the same trend under various conditions. The following order of intensity was observed:  $\text{N}_2 > \text{Sg} + \text{HCl} > \text{Sg} \gg \text{Air}$ . This suggested that the gas composition affects the vaporization behavior intensively. The oxygen content had played a major role of Pb vaporization. When the oxygen content was high (in the case of air), the chlorinating reaction was kinetically hindered, which would delay Pb release. When the synthetic gas was used as fluidizing gas, the volatilization of lead increased. Furthermore, the vaporization was slight higher if chlorine was added. Pilot tests showed that increasing HCl from 400 ppm to 1000 ppm increased the quantity of lead vaporized from 2 units to 10 units at  $1000^\circ\text{C}$ , and from 1 unit to 4 units at  $900^\circ\text{C}$  (Chan, 1996).

**Zinc:** According to Fig. 7, Zn volatilization was rather high in both synthetic gas with HCl and  $\text{N}_2$ . Nevertheless, the vaporization processes in air and synthetic gas were short and rapid. When the fluidized gas contained high oxygen content, the chlorination reaction was hampered, and the zinc release was delayed. It was an effective means of increasing zinc volatilization by adding chlorine into the gas or retaining reducing conditions. Due to the reaction with bed sand in the bed and the fly ash particles and formation of stable compound such as silicates and silicoaluminates, zinc was found entirely in the coarse fly ash particles, and was

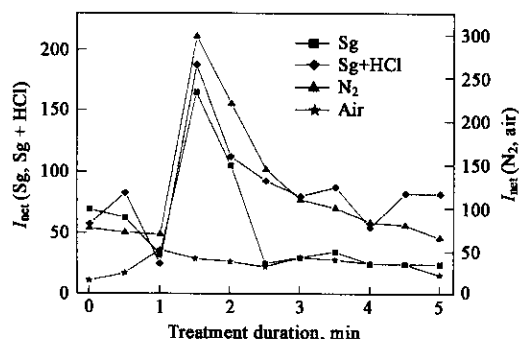


Fig. 6 On-line gaseous emission intensity of Pb vs. treatment (MSW, 855 °C,  $q_0 = 17160$  ppm)

enriched in the bottom ash(Uberoi, 1991).

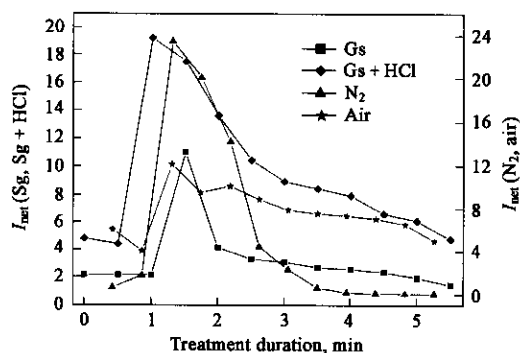


Fig. 7 On-line gaseous emission intensity of Zn vs. treatment duration (MSW, 850 °C,  $q_0 = 2720$  ppm)

### 3 Conclusions

The volatilization of selected heavy metals from MSW incinerator had been investigated on a laboratory fluidized bed system under various conditions. The following conclusions could be summarized from this study:

The combustion temperature, the gas atmosphere, and the chlorine content in the flue gas could affect the volatilization behavior of heavy metals.

In the fluidized bed combustion, a large surface area is provided by the bed sand particles, and they may act as absorbents for the gaseous ash-forming compound. Compare with the metals Cd and Pb, the vaporization of Zn was low. The formation of stable compounds such as  $ZnO \cdot Al_2O_3$  could greatly decrease the metals volatilization.

The presence of chlorine would enhance the volatilization of heavy metals by increasing the formation of metal chlorides. However, when the oxygen content was high, the chlorinating reaction was kinetically hindered, thus heavy metals release would be delayed.

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