THE BEHAVIOR OF HEAVY METAL Cr, Pb AND Cd DURING WASTE INCINERATION IN FLUIDIZED BED UNDER VARIOUS CHLORINE ADDITIVES

MING-YEN WEY, JIANN-HARNG HWANG,
JYH-CHERNG CHEN
Dep. of Environmental Engineering, Chung-Hsing University,
Taichung, Taiwan, R. O. C.

Key Words: Metal Partitioning, Fluidized-Bed Incineration, Operating Temperature, Chlorine Additives

Previous theoretical studies have demonstrated that chlorine-containing materials significantly affected heavy metals behavior during incineration. In this study, we examine the effects of operating temperature in both primary and second combustion chambers along with those of various chlorine-containing materials (organic or inorganic) on metal partitioning in sand-bed sorbents, fly ash, waste water, and flue gas.

A bubbling fluidized bed made from 310 stainless steel (100 cm bed height; 10 cm ID; and 100 cm freeboard; 25 cm ID) was used, in addition to two cyclones and a wet scrubber. The synthetic solid wastes used were plastics, sawdust and water. These results indicated that the fluidized medium (silica sands) can absorb a high proportion of metals in the incineration process; in addition, the extent of absorption ability follows the sequence: Pb > Cr > Cd. The effect of organic and inorganic chlorine on metal partitioning were very different; organic chlorine (P.V.C.) caused a more serious metal emission than inorganic chlorine (NaCl). The operating temperature and chemical reaction influenced absorption by the fluidized media. Within the operating temperature ranges, 500–600 °C for the main combustion chamber, 600–800 °C for the second combustion chamber, the effect of freeboard temperature on the metal partitioning is insignificant.

Introduction

Trace heavy metals in plastics, rubber, newspapers, ink and waste batteries inevitably enter an incinerator since the separation of waste can not be completely achieved. The heavy metals in bottom ash, fly ash and flue gas produced by incineration treatment cause Environment pollution. Therefore, the safe design and operation of incineration system that handle metal bearing wastes are dependent on an understanding of the heavy metal behavior in the incineration process (Eddings and Lihty, 1992).

Previous work (Braun et al., 1986; Clark and Seeker, 1990; Law and Gordon, 1979; Vancil et al., 1991; Linak and Wendt, 1993) on heavy metal pollution produced by incineration indicated that metals with higher saturated vapor pressures (e.g., Hg, Cd and Pb) entered the atmosphere easily after combusting and evaporating, subsequently making their amount in the fly ash high than in the bottom ash. However, metals with higher boiling points (such as Cr, Mg and Cu), remained primarily in the bottom ash. Reimann (1989) and Fournier et al. (1991) investigated the proportion of metal in the bottom ash, fly ash, scrubber waste water and stack flue gas. However, they neglected the effects of operating conditions on metal distribution.

To more thoroughly understand the effects of operating temperature, amount of chlorine, the amount of oxygen on metal partitioning, Lee (1988) proposed a preliminary equilibrium model for analyzing metal partitioning during incineration. Those simulations revealed that all of the lead and mercury in the waste vaporizes under all the conditions examined; however, the behavior of chromium is influenced by the operating conditions. The term "partitioning" is defined as the distribution of an element between the various materials leaving an incinerator. In addition, "partitioning" refers to the chemical and physical forms of an element. More detailed thermodynamic equilibrium analyses (Fernandez et al., 1992; Rizeq et al., 1992; Wu and Biswas, 1993) were performed; however predictions from those thermodynamic equilibrium models conflicted with each other, as well as with the operating data.

Heavy metals can react with chlorine, sulfur and oxygen during incineration, subsequently producing various compounds. Chlorine of the element has the most significant impact on the behavior of metals. Formatting of heavy metal chlorides is a conventional process in metallurgical engineering, in addition to being one of the most well known processes for eliminating heavy metals from iron ore (Habanis, 1986). Owing to this reason, the previous studies have examined the thermodynamics of the formatting chlorides from oxides and chlorine gas. Greenberg et al. (1978) indicated that the possible effects of high concentrations of HCl in the gas stream may have in the volatilizing heavy metals. The HCl concentration in the combustion gases from burning is $10^2$ –
10^3 mg/m^3, i.e., sufficiently high to facilitate the formation of metal chlorides in the combustion chamber. Fournier et al. (1991) indicated increasing the chlorine in the feed (tetrachloro-ethylene, chlorobenzene) would increase the volatility of some volatile metals (cadmium, lead and bismuth) and of copper (less volatile); chlorine also appeared to decrease the particles size. Therefore, the content and form of chlorine in wastes is important. Among the species in municipal solid waste, one source of organic chlorine is poly vinyl chloride (P.V.C.). Previous studies indicated PVC can give rise to gaseous hydrogen chloride (Palma et al., 1964). Inorganic chlorides, such as NaCl, present in food trash or refuse, have been suggested to give rise to the formation of HCl during combustion. PVC (organic chlorine) and NaCl (inorganic chlorine) are the primary sources of chlorine-containing materials (Peterson et al., 1990).

A fluidized-bed incinerator, owing to its lower operating temperature, has the capability of reducing the volatility of the trace and minor elements, thereby retaining a higher concentration of the elements in the ash, while simultaneously reducing stack-gas emissions. Previous works (Ho et al., 1992) demonstrated that a fluidized bed incinerator is suitable for using sorbents to capture metals and thereby control metal emissions. Incinerating municipal solid waste (M.S.W.) in a fluidized bed has been practiced in Japan for many years due to the advantages of high mixing, heat conduction, low SOx emissions by the directly adding Ca(OH)2 and low NOx emissions.

This study examines the effect of operating parameters on metal partitioning between sand, bed sorbents, fly ash, waste water and waste gas in a fluidized bed incinerator. The operating parameters evaluated include: (1) bed temperature, (2) freeboard temperature, (3) the organic waste feed, (4) the inorganic feed. To compare the differences in metal partitioning between organic and inorganic wastes during incineration. PVC and NaCl were added to the waste to represent organic and inorganic wastes.

### Table 1 The operating parameters and compositions of synthetic wastes

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature</th>
<th>Chlorine content</th>
<th>Sawdust</th>
<th>PP</th>
<th>PVC</th>
<th>NaCl</th>
<th>Water</th>
<th>PE bag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>T1 = 600, T2 = 600</td>
<td>0%</td>
<td>1.0</td>
<td>0.70</td>
<td>0.00</td>
<td>0.00</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Run 2</td>
<td>T1 = 600, T2 = 700</td>
<td>0%</td>
<td>1.0</td>
<td>0.70</td>
<td>0.00</td>
<td>0.00</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Run 3</td>
<td>T1 = 600, T2 = 800</td>
<td>0%</td>
<td>1.0</td>
<td>0.70</td>
<td>0.00</td>
<td>0.00</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Run 4</td>
<td>T1 = 500, T2 = 700</td>
<td>0%</td>
<td>1.0</td>
<td>0.70</td>
<td>0.00</td>
<td>0.00</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Run 5</td>
<td>T1 = 600, T2 = 700</td>
<td>5% PVC</td>
<td>1.0</td>
<td>0.55</td>
<td>0.15</td>
<td>0.00</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Run 6</td>
<td>T1 = 600, T2 = 700</td>
<td>10% PVC</td>
<td>1.0</td>
<td>0.40</td>
<td>0.30</td>
<td>0.00</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Run 7</td>
<td>T1 = 600, T2 = 700</td>
<td>5% NaCl</td>
<td>1.0</td>
<td>0.55</td>
<td>0.00</td>
<td>0.15</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>Run 8</td>
<td>T1 = 600, T2 = 700</td>
<td>10% NaCl</td>
<td>1.0</td>
<td>0.40</td>
<td>0.00</td>
<td>0.30</td>
<td>1.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

a) 0.015 g Cr, Pb, Cd dissolved in water. Using: g T1: bed temperature (°C). T2: Freeboard temperature (°C).

2. Experimental

#### 2.1 Preparation of synthetic feed wastes

The synthetic solid wastes fired during the tests were composed of sawdust, plastics, water (simulated ordinary municipal solid waste) and three investigated metals (with nitrate) of 0.5%wt, and then dissolved in water. The samples were enclosed in a polyethylene (P.E.) bag of 0.3 g. The compositions of the various artificial composed feedstocks and operating parameters are shown in Table 1. The P.V.C. and P.P. plastics used were obtained from commercially available rigid plastic raw material grains for manufacturing purpose. The grain size is about 0.5 cm in diameter.

#### 2.2 Apparatus

Figure 1 illustrates the incineration system. The reactor is a fluidized bed, consisting primarily of a feeder, a preheated chamber (50 cm long), main combustion chamber (100 cm height; i.d. 10 cm), and a secondary combustion chamber (100 cm height; i.d. 25 cm). The chambers were constructed of stainless steel (AISI 310) with 3 mm walls. The incinerator was fitted with a perforated stainless steel gas distributor. The static bed height was 70 cm and the expanded bed height was about 90 cm. Six thermocouples were used to determine the temperature profile in a preheated chamber, sand bed and in freeboard. The combustion gas was treated by two consecutive cyclones and a wet scrubber, and then output into the atmosphere.

#### 2.3 Experimental procedures

The general case of excess air of 30% was used, i.e. ~40 liter/min at room temperature. When comparing the effects of the temperature, the main combustion chamber is controlled at 500°C and 600°C, and freeboard zone from 600°C to 800°C for every continuous feed rate of 3 bags/min. When investigating the effects of chlorine-containing materials, the main combustion chamber was controlled at 600°C, and freeboard zone at 700°C.

First, when the main combustion chamber was
heated to the desired temperature by the electrical heaters, the gas burner was started to raise the freeboard temperature. Next the synthetic waste without metals was fed into the incinerator. After the temperature reaching the steady state, the fly ash in the cyclones was cleared out, the pump of the wet scrubber was turned on and metal containing synthetic wastes were added. The experiment was performed continuously for 50 min continuously.

The ashes produced are all fly ashes and without bottom ashes due to the synthetic wastes being combustible. Therefore, the accumulated samples were sand from the bed, fly ashes, scrubber blowdown water and flue gas from the scrubber. Isokinetic sampling (Reist, 1993) of flue gas was in a steady state after 50 min; acetate cellulose filters (0.8 μm) with low metal interference was also used. After the experiment and the bed had cooled to an ambient temperature, the silica sand (5.0 kg) in the bed was removed. Two cyclones were of special demountable design; the fly ashes absorbed in the walls could be taken out. 30 liter of wastewater in the wet scrubber was mixed completely by an air compressor; 0.5 liter then was taken out and filtered into two kinds of samples of liquid and solid. Analysis was performed to yield the total amount of inorganic metals in the sample. First, pre-treatment was made by microwave digestion, and the metal concentration was then measured by atomic absorption spectroscopy (A.A.S.).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Elemental</th>
<th>Oxide</th>
<th>Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1857/2672*</td>
<td>2266/4000*</td>
<td>824/1200−1500* (Cl₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>−96/118* (O₂Cl₂)</td>
</tr>
<tr>
<td>Pb</td>
<td>328/1745*</td>
<td>886/−</td>
<td>501/950* (Cl₂)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>−15/105* (Cl₄)</td>
</tr>
<tr>
<td>Cd</td>
<td>321/765*</td>
<td>1550/−</td>
<td>568/960*</td>
</tr>
</tbody>
</table>

After completely mixing silica sand and fly ashes individually, three representative samples were taken out, then digested and measured. The metals concentration was determined by averaging value of three measurements.

3. Results and Discussion

The melting and boiling points of various metallic species can be used as an indication of their relative volatilities. Table 2 displays the melting and boiling points for different species of Cr, Pb and Cd. This table clearly reveals that the different species of the same metal exhibit different volatilities and reactivates. With current analytical methods, however, distinguishing between different species of the same metal is extremely difficult. More sophisticated analytical methods need to be developed to
distinguish between those species (Eddings and Lihty, 1992). The following results were therefore obtained in terms of the total metal concentration. The mass balance of Cr, Pb and Cd is summarized in Tables 3, 4, 5. The range of loss (may be from the absorption on the inner wall of sand bed, freeboard and flue duct), Cr was about 18–53 wt.%, Pb was about 3%–26%, Cd was about 18–50%. Possibly, the stronger absorption on the wall occurred on Cr and Cd. The amounts in the fly ash were Cr 6–12%, Pb 7–15% and Cd 8–16%. Uptakes in the scrubber were Cr 3%, Pb 3–5% and Cd 3–15%. Values for the flue gas were Cr 1%, Pb 5% and Cd 3–10%. A study involving the capturing of metal by various sorbents during fluidized bed incineration of test wood, containing lead chloride indicated that the capturing process is highly promising. The capture efficiency ranges from 20% to over 90%, depending on the operating conditions (Ho, Chen, Hopper and Oberacker, 1992). An optimum incinerator temperature exists for metal capture. Metal capturing by a sorbent includes melted ash deposition, vapor condensation and/or chemisorption, and particulate collection.

The absorption capacity of silica sands for three metals in 8 runs appears to be extremely high and in the sequence of Pb>Cr>Cd. Cr was 33.1–73.2% of total feedstocks, Pb 57.6–81.8% and Cd 22.2–54.8%. Pb was up to 81.8% and the high volatile metal Cd, was also up to 54.8%. Since boiling points follow the sequence: Cr>Pb>Cd, the proportion of metal remaining in the sand seemed to not only depend on the metals' volatility. Another primary factor was chemical absorption with reaction between a metal and the silica sand in the high temperature atmosphere. The distribution of those three metals
at different operating conditions is considered again in the following.

3.1 The effect of chlorine on metal partitioning

Because the chloride of the heavy metals concerned are relatively volatile, a reaction with gaseous HCl to form metal chlorides was expected to increase the vaporization of the metals relative to an atmosphere without HCl. The formation of HCl is not only from PVC, but also from inorganic chlorides such as NaCl and KCl. The source of hydrogen may exert an influential role in increasing the formation of HCl when burned in air. Wey and Fang (1994) indicated that with different sources of hydrogen element contained (e.g., H2O, sawdust, PE), and various sources of chlorine (organic chlorides (e.g., PVC), inorganic chlorides (e.g., NaCl), the HCl emitted will change significantly. In this study, experiments involving three metals demonstrated the effects of different sources of chlorine (without, with PVC, or NaCl) on the partitioning of the metal during incineration.

Figures 2 - 4 summarize the effects of different chlorine additives on the Cr, Pb, Cd partitioning during incineration. Compared with the case without organic chlorine PVC, the proportion of three metals remaining in sands was lower by 10% in the presence of organic chlorine PVC. The primary reason for this occurrence was that metals react with the chlorine from PVC or with of HCl produced by PVC and subsequently produce volatile metal chlorides. The proportion of metals remaining in the sand is reduced owing to the increase of metal chloride volatility. Compared with the case without inorganic chlorine NaCl, the proportion of metal Cr and Cd in silica sand increased 10~15% in the presence of inorganic chlorine NaCl. However, for Pb, there are no significant changes occurred for its partitioning with or without inorganic chlorine (NaCl). This phenomenon indicated that the effect of organic and inorganic chlorine on metal partitioning is quite different. The metals not captured by the sand, enters the combustion gases, leaves the second combustion chamber and become distributed in the control units after cooling. The proportion of the three metals remaining in fly ash increased by 5~15% in the presence of organic chlorine. However, the proportion of the three metals in fly ash reduced in the presence of inorganic chlorine. The proportion of Pb and Cd compounds remaining in wet scrubber increased in the presence of inorganic chlorine NaCl. However, in the presence of organic chlorine PVC, Pb and Cd metal compounds easily passed through the wet scrubber and, subsequently, entered into waste flue gas. Metal Cd distribution in the wet scrubber reduced by 14% in the presence of PVC and increased 15~38% in the presence of NaCl. Metal Cd distribution in the flue gas increased 4~9% in the presence of PVC and reduced 15% in the presence of NaCl.

3.2 The effects of operating temperature on metal partitioning

Many factors are involved in volatilizing of a metal and its reaction during incineration, e.g., thermodynamics, reaction kinetics, and mass and heat transfer operations. Incineration temperature, in most cases, has a significant effect on the above described phenomena, and further effect on the metal partitioning during incineration. Experiments were performed in various operating temperatures for both
The effect of temperature on Cr metal distribution. (T1=snad-bed temperature, T2=freeboard temperature)

The effect of temperature on Pb metal distribution. (T1=snad-bed temperature, T2=freeboard temperature)

The effect of temperature on Cd metal distribution. (T1=snad-bed temperature, T2=freeboard temperature)

sand bed temperature and freeboard temperature.

Figures 5 - 7 summarize the effects of operating temperature on Cr, Pb, Cd partitioning during incineration. For 600°C sand-bed temperature, the fraction of Cd in silica sands is lower, as compared to 500°C sand-bed temperature. However, the fraction of Cr and Pb in 600°C sand-bed temperature was higher than the fraction of Cr and Pb in 500°C sand-bed temperature. Those results indicate that the metal contents of remaining silica sands depend not only on metal volatility, but also on chemical and physical reactions between metals and silica sands. Within the operating temperature at 600 – 800°C for the second combustion chamber, the effect of temperature on metal partitioning is insignificant.

Conclusion

This study presented a fluidized bed incinerator along with an air pollution apparatus, capable of performing metal partitioning experiments in a well controlled operating temperature, and reactive environments were set up. Experimental results are summarized as follows:

1. The fluidized media (silica sands) of fluidized bed incinerator absorbs high proportions of the three metals studied, following the sequence of Pb > Cr > Cd. Therefore, fluidized bed incinerators seem to be quite suitable for retaining metals during incineration.

2. Organic chlorine PVC not only reduces the absorption capacity of Pb, Cr and Cd on silica sands but, also increases the volatility of those metals. Reducing the solubility of the metals Cd and Pb causes a lower scrubbing efficiency for the wet scrubber and, ultimately, more air pollution.

3. In the presence of inorganic chlorine, NaCl, the metal retained in the sand increases but reduces in the flue gas. The high proportion of Cd and Pb remaining in the wet scrubber causes in low emissions of Cd and Pb.

4. Within the operating temperature ranges, (500 – 600°C for the main combustion chamber, and 600 – 800°C for the second combustion chamber), the effect of temperature on metal partitioning is insignificant.

Literature Cited


