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Dynamic volatilization behavior of Pb and Cd during fixed bed waste incineration: Effect of chlorine and calcium oxide

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HIGHLIGHTS

- The dynamic volatilization data were obtained by continuous interval sampling.
- Fixed bed generated reducing atmosphere which affected volatilization greatly.
- PVC chlorinated PbO and CdO indirectly while NaCl chlorinated them directly.
- CaO adsorbed HCl from PVC at low temperature but released back at high temperature.

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ABSTRACT

Simulated solid waste was incinerated in a fixed bed, while continuously collecting volatized Pb and Cd to investigate the dynamic volatilization behavior. The dynamic data revealed the reducing atmosphere generated by the fixed bed as the main reason for the lower initial volatilization temperatures of Pb and Cd compared to PbO and CdO melting points during chlorine-free incineration. CdO was easier to reduce than PbO; consequently, Cd volatilized stronger than Pb in the chlorine-free fixed bed. However, CdO volatilization was expected to be weaker than PbO volatilization in an air atmosphere. In contrast to the reduction in a fixed bed, the addition of PVC led to *indirect* chlorination of Pb and Cd at 300–400 °C and 400–500 °C, respectively and their volatilization was significantly enhanced via chlorination. NaCl *directly* chlorinated Pb and Cd at comparatively high temperatures of 800–900 °C and 700–800 °C, respectively via involvement of SiO_2 and Al_2O_3. Moreover, CaO absorbed HCl from PVC, resulting in volatilization inhibition of Pb and Cd at a temperature below 700 °C. However, chlorine was released at a higher temperature. Furthermore, CaO had no effect on NaCl-induced volatilization enhancement of Pb and Cd.

1. Introduction

Lead (Pb) and cadmium (Cd) within solid waste have been raising severe concern due to their high toxicity and elevated concentrations of 200–2000 mg/kg and 10–1000 mg/kg, respectively [1–3]. During solid waste incineration, the combustion temperature is typically above the melting points of $PbCl_2$ and $CdCl_2$ (~500 °C), but close to the boiling points of PbO and CdO (~900 °C) [4–6]. Consequently, due to evaporation-condensation, the semi-volatile heavy metals Pb and Cd migrate from solid fuel to bottom ash, fly ash, and even submicron aerosol, which cannot be effectively captured by conventional dedusting equipments such as electrostatic precipitators and bag filters [7–10]. Submicron Pb and Cd can directly be inhaled into the lungs and subsequently permeate into the blood stream, therefore making submicron aerosol the most harmful form of both metals [11–14].

To ultimately control the emission of submicron Pb and Cd, the volatilization properties of both elements were investigated during incineration. Typically, Pb and Cd are both investigated concurrently because these two elements possess common characteristics. In a high-temperature oxidizing furnace, Pb and Cd both exist as divalent compounds such as monoxides and dichlorides [15,16]. The corresponding compounds and elementary substances of Pb and Cd have similar melting and boiling points. Compared to Zn, Cu, and other heavy metals, Pb and Cd have far lower tolerable intake levels, resulting in similar toxicity to human [17,18].

Heavy metal volatilization and evaporation during incineration are typically investigated via fluidized bed or fixed bed. In fluidized

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bed, unevaporated metals are entrained as fly ash via flue gas resulting in a difficulty to evaluate the volatilities. Here, volatilization is in fact a form of migration. In contrast, in fixed bed only little ash is entrained from the solid fuel and all metals that do not remain in the bottom ash can be considered evaporated. Consequently, fixed bed is more suitable to investigate metal volatilization during incineration. Furthermore, deeply studying as a main incinerator technique will further guide industrial operation. During incineration, chlorine (Cl) can bond with Pb and Cd, forming $PbCl_2$ and $CdCl_2$, which have much lower melting points compared to PbO and CdO. Therefore, the presence of Cl enhances the volatilities of Pb and Cd [19–21]. The most abundant forms of Cl in solid waste are PVC and NaCl supplying organic Cl and inorganic Cl, respectively. Although Pb and Cd have many similarities, their volatilities are different whether Cl is present during waste incineration. The traditional research method is the collection of the evaporated metal from flue gas or detecting the leftover metal in the residue subsequent to incineration. Several typical studies are listed in Table 1 [21–24]. The solid waste in these studies can be divided into combustible waste (such as SMMW and sewage sludge) and incombustible waste (such as fly ash). In sewage sludge incineration investigation, chlorine source is usually conditioning agents [22]. In waste incineration investigation, chlorine source is usually PVC and NaCl [25]. In fly ash thermal treatment investigation, chlorine comes from inorganic chlorinating agents [21,26]. A comparison of the data of the studies listed in Table 1 reveals several interesting phenomena: Firstly, during combustible waste incineration, Cd has a stronger volatility than Pb; however, this is not the case during incombustible waste thermal treatment. Secondly, PVC has a higher capability to enhance metal volatilization than NaCl. In previous research, solid waste components were usually constant except for Cl; therefore, the effect of combustible matters on metal volatilization has not been investigated yet [21–24]. Consequently, the first phenomenon has not been discussed in previous studies. The second phenomenon has been reported by previous studies which extensively compared the effect of different Cl containing materials [21–24]. However, few investigations were performed on the mechanisms causing these differences or similarities.

This study investigated the volatilization of Pb and Cd during solid waste incineration in a fixed bed in three conditions: without Cl, with Cl, and with a combination of Cl and CaO. Compared to previous experiments, the SMSW components were further simplified to analyze the effects of these components on metal volatilization. Furthermore, a different sampling method was adopted to acquire the dynamic volatilization data that revealed the change of volatilization rate with incineration temperature and time. Combined with auxiliary experiments, several novel findings were revealed including a satisfying explanation of the first and second phenomenon mentioned above. These results enhance our understanding of the volatilization behaviors of Pb and Cd during incineration.

2. Experimental

2.1. Solid waste incineration in fixed bed

Incineration was performed in a horizontal tube furnace with an electrical heating zone of 500 mm in length and 70 mm in diameter. The tube was made of 310S stainless steel instead of corundum and quartz to avoid possible reaction with Pb and Cd vapor [27]. The tube outlet was cone-shaped to lessen condensed metal deposition. The heating procedure started at room temperature, increased to 900 °C with a rate of 10 °C/min, then retaining 900 °C for 60 min. The simulated solid waste was composed of both combustible matter and incombustible matter. Both were presented by charcoal particles and a SiO_2/Al_2O_3 powder mixture, respectively with mass proportions of 7:2:1, which is similar to the that of MSW and sewage sludge [2,5,28,29]. The simulated object is MSW in this study. This extremely simplified simulation maximally eliminated otherwise uncontrollable components in the waste. Most Pb/Cd containing compounds in solid waste transform to monoxides during thermal treatment above 400 °C, therefore PbO and CdO were chosen for this experiment and added to the incineration mixture to ensure Pb and Cd concentrations in waste of 1500 mg/kg each [19]. 15 g waste was used per trial. Air-flow was 3 L/min during incineration.

The incineration conditions were divided into: without Cl, with Cl, and with Cl and CaO combined. Cl sources were PVC and NaCl, which are two typical Cl sources in municipal solid waste and represent organic Cl and inorganic Cl, respectively. During incineration conditions with Cl present, addition levels of Cl were 1% and 3% (mass percentage) of simulated solid waste. During incineration conditions with Cl and CaO combined, addition levels of Cl and CaO were 3% and 6%, respectively (mass percentage) of simulated solid waste.

The exhaust was monitored online via infrared gas analyzer. CO_2 emission indicated complete combustion of carbon, while CO emission indicated incomplete combustion. Both were detected at ~400 °C and reached maximal concentrations at ~600 °C (Fig. 1). The presence of CO for long durations revealed that the fuel bed was under a reducing atmosphere, which is an identical condition with industrial stoke grate [30].

The dynamic volatilization data collection of metals was achieved via interval sampling. The outlet flue gas passed through a glass fiber filter, which was nipped by two semi-spherical glass tubes. During the stage of temperature increase (room temperature to 900 °C) and the stage of constant temperature (900 °C),

Table 1
The comparison of Pb and Cd on volatilization fraction during incineration in fixed bed.

Solid waste	Furnace temperature (°C)	Volatilization fraction (%)		Reference
		Pb	Cd	
Sludge without additives	600–900	10–21	42–53	[22]
Sludge with CaO/$FeCl_3$	600–900	3–24	40–57	[22]
SMSW[a] without Cl	700–950	3–11	69–87	[23]
SMSW with PVC	950	30	97	[23]
SMSW without Cl	850	3	98	[24]
SMSW with PVC	650–900	10–53	85–100	[24]
SMSW with NaCl	650–900	3–30	80–100	[24]
Fly ash without Cl	800–1000	85–98	50–98	[21]
Fly ash with $CaCl_2$	800–1000	91–98	81–99	[21]
Fly ash with NaCl	800–1000	90–98	47–95	[21]

[a] SMSW here means simulated municipal solid waste.