



# Thermochemical reaction mechanism of lead oxide with poly(vinyl chloride) in waste thermal treatment



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## HIGHLIGHTS

- The thermochemical reaction mechanism of PVC with PbO was investigated.
- HCl decomposed from PVC reacted with PbO via an exothermal gas–solid reaction.
- Chlorination effect of PVC on Pb was apt to lower-temperature and rapid.
- The product PbCl<sub>2</sub> melted, volatilized and transferred into flue gas at >501 °C.

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## ABSTRACT

Poly(vinyl chloride) (PVC) as a widely used plastic that can promote the volatilization of heavy metals during the thermal treatment of solid waste, thus leading to environmental problems of heavy metal contamination. In this study, thermogravimetric analysis (TGA) coupled with differential scanning calorimeter, TGA coupled with Fourier transform infrared spectroscopy and lab-scale tube furnace experiments were carried out with standard PVC and PbO to explicate the thermochemical reaction mechanism of PVC with semi-volatile lead. The results showed that PVC lost weight from 225 to 230 °C under both air and nitrogen with an endothermic peak, and HCl and benzene release were also detected. When PbO was present, HCl that decomposed from PVC instantly reacted with PbO via an exothermal gas–solid reaction. The product was solid-state PbCl<sub>2</sub> at <501 °C, which was the most volatile lead-containing compound with a low melting point and high vapor pressure. At >501 °C, PbCl<sub>2</sub> melted, volatilized and transferred into flue gas or condensed into fly ash. Almost all PbCl<sub>2</sub> volatilized above 900 °C, while PbO just started to volatilize slowly at this temperature. Therefore, the chlorination effect of PVC on lead was apt to lower-temperature and rapid. Without oxygen, Pb<sub>2</sub>O was generated due to the deoxidizing by carbon, with oxygen, the amount of residual Pb in the bottom ash was significantly decreased.

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## 1. Introduction

Incineration, with the advantages of volume reduction, sanitation, and energy recovery, has been an important treatment alternatives for municipal solid waste (MSW) or combustible hazardous waste. Though waste can be greatly reduced during thermal treatment, heavy metals contained in the waste will be concentrated in

the byproducts of incineration (i.e., flue gas, air pollution control residues and bottom ash) via physicochemical processes (Zhang et al., 2008). The occurrence of heavy metals in flue gas and fly ash (FA) can lead to environmental contamination, which is problematic in secondary pollution control for waste incineration (Belevi and Moench, 2000). Lead as an important semi-volatile heavy metal with environmental toxicity and it is universal in combustible wastes, hence its migration and transformation in thermochemical condition have attracted great concerns.

Chlorination reactions are key for distribution of heavy metals into gas or solid phases. Previous studies have demonstrated that the incineration temperature, content of chlorine atom and species of chloride impact the distribution of lead in incineration

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byproducts. Increasing the temperature (650 to 900 °C) can promote the movement of lead into FA and fuel gas in the presence of chlorine, and the increasing content of chlorine atom and chloride (poly(vinyl chloride) (PVC),  $C_2Cl_4$  and NaCl) can lead to more volatilization of lead (finally condensing on FA or being emitted with flue gas), among which, more lead distribution in flue gas was observed when  $C_2Cl_4$  was present (Wang et al., 1997; Chiang et al., 2007). As a result of this behavior, the lead content in the FA from medical waste (which has more chlorinated compounds) incineration was significantly higher than that from MSW incineration (Zhao et al., 2009). Yu et al. (2012) found that adding HCl to nitrogen, synthetic gas (5%  $O_2$  and 95%  $N_2$ ) and air also increased the volatilization ratio of lead. In the light of this information, chlorinated compounds can be used to remove lead in MSW incineration FA (Jakob et al., 1996; Rio et al., 2007; Nowak et al., 2012), sewage sludge ash (SSA) (Vogel and Adam, 2011; Vogel et al., 2012) and other residues (Lee and Song, 2007) by means of thermal treatment. It has been reported that the volatilization ratio of lead increased by 10–15% during thermal treatment of MSW incineration FA and dredged sediment (treated with phosphoric acid) by adding PVC (5% by weight) (Rio et al., 2007), and the ratio increased by 90% when the temperature changed from 600 °C to 1000 °C when PVC was added into electric arc furnace (EAF) (Lee and Song, 2007). Others (Vogel and Adam, 2011; Vogel et al., 2012) found that the increased temperature, PVC content in the ash and HCl concentration in the inlet gas could all enhance the removal ratios of lead in SSA.  $CaCl_2$  and  $MgCl_2$  can also be used as Cl-donors to remove lead in SSA (Adam et al., 2009).

The increase of lead volatilization and mobility by chlorine during thermal treatment mainly results from the formation of more volatile heavy metal chlorides. Nowak et al. (2012) proposed that chloride can react with heavy metal oxides by direct chlorination, or through indirect reactions with HCl or  $Cl_2$ , which are reaction products of chloride with  $H_2O$  or  $O_2$ . Jakob et al. (1996) and Yoo et al. (2005) proposed that the chlorination reaction of lead with NaCl occurs when a mineral matrix ( $SiO_2$  or  $Al_2O_3$ ) is present, and this resulted in the formation of  $PbCl_2$  in the evaporation products of FA and EAF. Although many researches have reported the promotion effect of chlorine on lead volatilization and migration into the gas phase, the reaction mechanism and variation patterns of chlorine with lead have not been clearly revealed. Therefore, the objective of this study is to investigate the mechanism of PVC reacting with lead compounds, including how and when they react, and how the temperature, and atmosphere influence both their reaction and lead volatilization.

## 2. Materials and methods

### 2.1. Materials

According to the thermochemical handbook of pure substances (Cheng et al., 2003), most lead-containing compounds decompose or transform to PbO during thermal treatment (>400 °C), therefore PbO was chosen to represent lead compounds. The thermal experiments were carried out with standard PVC powder (molecular weight = 48000, particle size = 75–150  $\mu m$ ) purchased from Sigma–Aldrich. PbO powder (analytical reagent grade) was purchased from Sinopharm Chemical Reagent. PbO was dried at 105 °C and then mixed with PVC at a molar ratio of Cl/Pb = 3 (referred to as PVC–PbO hereafter) to ensure the excessiveness of chlorine atom.

### 2.2. Thermogravimetric analysis experiments

Thermogravimetric analysis (TGA) conducted on pure PVC and PVC–PbO using a TGA (Q600 SDT, TA Instrument, USA) instrument

equipped with a differential scanning calorimeter (DSC) as well as with a TGA instrument (SDTA851e, Mettler-Toledo, USA) equipped with a Fourier transform infrared spectroscopy (FTIR) (Netxus 670, Nicolet, USA). In the previous experiments, it was observed that the appropriate heating rate was  $10\text{ }^\circ\text{C min}^{-1}$ , at which hysteresis caused by heat diffusion did not occur, therefore,  $10\text{ }^\circ\text{C min}^{-1}$  was adopted in the TGA experiments. 10 mg of PVC or PVC–PbO samples were heated in air or under nitrogen at a flow rate of  $100\text{ mL min}^{-1}$ , with the temperature increasing from 50 °C to 350 °C, 450 °C, 600 °C or 900 °C, and then the temperature was maintained for 60 min. The FTIR spectral region was set as  $4000\text{--}400\text{ cm}^{-1}$ , with a scanning velocity of  $0.6329\text{ cm s}^{-1}$  and a resolution of  $8\text{ cm}^{-1}$ . In order to reduce the gas condensation along the transfer line, the temperature in the gas cell and transfer line was set to 180 °C (Zhu et al., 2008).

### 2.3. Tube furnace experiments

Fig. 1 shows the tube furnace system, equipped with a quartz tube that was 95 cm in length and 3.5 cm in diameter. According to the modified US EPA Method 5 (Chiang et al., 2007), the absorption system was equipped with six impingers, where the first one was empty, the second to the fifth ones were filled with 100 mL solutions (5%  $HNO_3$  and 20%  $H_2O_2$ , v/v), and the last one was filled with silica gel. The connection between the quartz tube and impingers was maintained above 120 °C with a heating belt to prevent flue gas condensing. The tube was washed thoroughly with 100 mL of the above-mentioned solution after the tube was cooled down to room temperature. Each sample ( $2.00\text{ g} \pm 0.05\text{ g}$ ) was filled in a corundum boat and heated. Based on the TGA results, the heating programs in the tube furnace experiments were set as follows: increase the temperature from 50 °C to 350 °C, 450 °C, 600 °C or 900 °C with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ , and then maintain the temperature for 60 min (for 350 and 450 °C) or 30 min (for 600 and 900 °C). The residues in the corundum boat and condensates on the surface of the glass ring at the end of the quartz tube were bottom ash (BA) and FA, respectively. The chemical species in the BA and FA samples were tested by X-ray powder diffraction (XRD) (D8 Advance X diffractometer with  $Cu\text{ K}\alpha$  radiation, Bruker, Germany) operated at 40 mA, 40 kV, with a step size of  $0.02^\circ$  and a step time of 0.1 s. Triplicate samples were taken from BA and respectively measured by ICP-OES after digestion using HCl,  $HNO_3$ ,  $HClO_4$  and HF.

## 3. Results

### 3.1. Thermal transformation of PVC

According to the derivative thermogravimetry (DTG)–DSC (Fig. 2a) and TGA curve (Fig. 3a) of PVC from 50 °C to 900 °C under air flow, the thermal decomposition of PVC can be divided into two stages. In the first stage (230 to 350 °C), the weight loss of PVC reached 64% (if all the chlorine atoms formed HCl and was released, the weight loss should be 58%), and there was an endothermic peak at around 277 °C on the DSC curve. According to the FTIR result (Table 1 and Fig. 4a), the gaseous products were HCl that decomposed from PVC and benzene generated by carbon-chain polycondensation, which was approximately in agreement with the investigations of Levchik and Weil (2005) and Zhu et al. (2008) on PVC decomposition. Moreover, a small amount of naphthalene, methylbenzene and other ethyl benzenes other than HCl and benzene was detected by Matuschek et al. (2000). As shown in Fig. 4a, HCl started to be generated at 229 °C ( $T_g$ ) and reached a maximum value at 285 °C ( $T_{max}$ ), then its generation decreased as the temperature continued to increase. In the second stage

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