# Role of sodium chloride and mineral matrixes in the chlorination and volatilization of lead during waste thermal treatment

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## ARTICLE INFO

## ABSTRACT

Knowledge of the transformation of lead (Pb) to volatile compounds could provide scientific basis for the control of its migration and pollution during waste thermal treatment. The effects and mechanisms of sodium chloride (NaCl) and mineral matrix compounds, which are ubiquitous in waste, on lead volatilization were studied. The results showed that the weight loss of the NaCl + PbO binary system exceeded NaCl mass fraction above its melting point, indicating that NaCl reacted with PbO in the absence of other substances. The reaction product was $PbCl_2$, detected by synchrotron radiation based micro X-ray diffraction. NaCl can also act as a Cl-donor via solid–solid reaction, without $Cl_2$ generation, at about 745 °C in the NaCl + PbO + $Al_2O_3$ system or at 600–611 °C in the NaCl + PbO + $SiO_2$ system, producing $PbCl_2$ in both cases. The minerals ($Al_2O_3$ and $SiO_2$) promoted lead chlorination and volatilization at a lower reaction temperature. In these pure ternary systems below 850 °C, the minerals did not inhibit lead volatilization by limiting diffusion or incorporating lead into the matrixes, which was momentous cognition for emission control. In summary, NaCl plays an important role in lead speciation, fate and transport during thermal treatment.
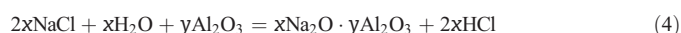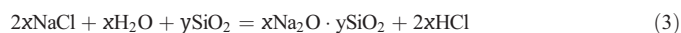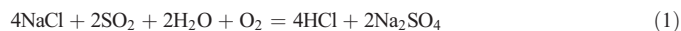
## 1. Introduction

Thermal treatment, with the advantages of volume reduction and energy recovery, is an important waste treatment alternative. One of the key issues is that heavy metals in waste are concentrated in the by-products of thermal treatment via diverse physicochemical processes [1]. The transformation and migration of lead (Pb) under thermal conditions is of particular concern [2–4], because of its semi-volatility, environmental toxicity and ubiquity in combustible wastes.

The coexistence of chloride and Pb in waste is common. Chlorination of Pb with HCl or $Cl_2$ produced by degradation of organic chlorides is known to impact the distribution and speciation of Pb [5–7]. Many studies have shown the influence of the prevalent inorganic chloride, NaCl, on Pb evaporation [3,4,8–10]. When NaCl was added to simulated municipal solid waste (MSW), an increase in the partitioning tendency of Pb into the fly ash or flue gas was found [3]. Similar results were obtained when NaCl was used as a Cl-based additive to remove metals from co-combusted bituminous coal and recovered solid fuel [9], MSW incineration fly ash [4], or electric arc furnace dust [8,10]. Nevertheless, Na has a stronger affinity than Pb for Cl, which may explain why the effect of inorganic chloride on metal volatilization is less significant than that of

organic chloride [3]. Based on this, simulation experiments have suggested that the increased volatilization of lead could be attributed to the formation of $PbCl_2$ by the reaction of PbO with HCl produced by the reaction of NaCl and $H_2O$ [11,12]. It has also been reported that there are thermodynamically favorable mechanisms for the formation of gaseous HCl from reaction of NaCl with $SO_2$, mineral matrixes (e.g., $SiO_2$ and $Al_2O_3$) and $H_2O$, as shown in Eqs. (1)–(5), and subsequent Pb chlorination (Eq. (6)), given that all components are freely available for reaction [8,12].
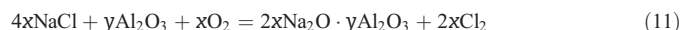
$$4NaCl + 2SO_2 + 2H_2O + O_2 = 4HCl + 2Na_2SO_4 \qquad (1)$$

$$2NaCl + 6SiO_2 + Al_2O_3 + H_2O = 2HCl + 2NaAlSi_3O_8 \qquad (2)$$

$$2xNaCl + xH_2O + ySiO_2 = xNa_2O \cdot ySiO_2 + 2xHCl \qquad (3)$$

$$2xNaCl + xH_2O + yAl_2O_3 = xNa_2O \cdot yAl_2O_3 + 2xHCl \qquad (4)$$

$$\begin{aligned} 2xNaCl + xH_2O + yAl_2O_3 + zSiO_2 \\ = xNa_2O \cdot yAl_2O_3 \cdot zSiO_2 + 2xHCl \end{aligned} \qquad (5)$$

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$$PbO + 2HCl = PbCl_2 + H_2O \tag{6}$$

Other studies have proposed chemical reactions (Eqs. (7)–(8)) to account for the conversion of heavy metal oxides into volatile heavy metal chlorides ($MCl_2$), especially PbO (Eq. (9)) as reported by Yoo et al. [8]. It is possible that the reaction is divided into two steps: the formation of gaseous $Cl_2$ by the reaction of NaCl with mineral matrixes (e.g. $SiO_2$ and $Al_2O_3$), as in Eqs. (10)–(11), followed by the reaction of chlorine with MO (Eq. (12)).

$$xMO + 2xNaCl + ySiO_2 = xMCl_2 + xNa_2O \cdot ySiO_2 \tag{7}$$

$$xMO + 2xNaCl + yAl_2O_3 = xMCl_2 + xNa_2O \cdot yAl_2O_3 \tag{8}$$

$$2NaCl + PbO + 2SiO_2 + Al_2O_3 = PbCl_2(g) + 2NaAlSiO_4 \tag{9}$$

$$4xNaCl + ySiO_2 + xO_2 = 2xNa_2O \cdot ySiO_2 + 2xCl_2 \tag{10}$$

$$4xNaCl + yAl_2O_3 + xO_2 = 2xNa_2O \cdot yAl_2O_3 + 2xCl_2 \tag{11}$$

$$2xMO + 2xCl_2 = xMCl_2 + xO_2 \tag{12}$$
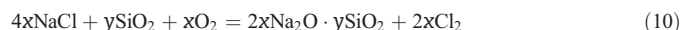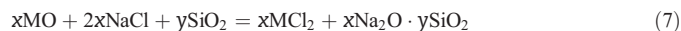
The equations suggest that $SiO_2$ and $Al_2O_3$ are beneficial for Pb chlorination and volatilization, but some studies have shown that the addition of $Al_2O_3$ (Yu et al., 2013) [13] or sand (97.8% $SiO_2$, 2.0% $Al_2O_3$) into simulated MSW reduced Pb volatility. Whether the mineral matrixes are beneficial to Pb evaporation by converting non-volatile lead oxide into volatile lead chloride, or prevent Pb migration by immobilizing lead compounds in the mineral matrix ($Al_2O_3$ and $SiO_2$), is controversial.

These possible mechanisms were proposed based on thermodynamic equilibrium calculations, raising questions such as whether and at what temperature the chemical reaction occurred, and what reactants, intermediates and final products were involved in the actual thermal process. Therefore, the objective of this study was to experimentally investigate the role of NaCl and minerals in lead chlorination.

## 2. Materials and methods

### 2.1. Materials

According to the thermochemical handbook, most lead-containing compounds decompose or transform to PbO during thermal treatment, therefore PbO was chosen to represent non-volatile lead compounds. All the reagents, NaCl, PbO, $Al_2O_3$, $SiO_2$, NaOH, $Na_2S_2O_3 \cdot 5H_2O$, starch, HCl, KI (analytical reagent grade) and $HNO_3$ (guaranteed reagent grade) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The NaCl (ground to <150 μm), PbO, $Al_2O_3$ and $SiO_2$ (originally with the particle size <150 μm) were dried at 105 °C and then mixed at certain molar ratios of Cl/Pb/Al/Si, denoted by CP (NaCl + PbO), CA (NaCl + $Al_2O_3$), CS (NaCl + $SiO_2$), CPA (NaCl + PbO + $Al_2O_3$) and CPS (NaCl + PbO + $SiO_2$). The mass and molar fractions were listed in Table 1.

### 2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) experiments were conducted with 20–40 mg samples (in a platinum crucible to exclude participation of crucible materials such as corundum or quartz) using a TGA instrument (Q600 SDT, TA Instruments, USA) equipped with a differential scanning calorimeter (DSC). The heating rate was 10 °C min$^{-1}$, the air or nitrogen velocity was adjusted to 100 mL min$^{-1}$, the temperature was increased from 50 °C to a specified temperature and then isothermy maintained for 30–180 min. The residues from the crucible after TGA were dissolved in acid solution ($HNO_3$ 15% v/v and HF 15% v/v) and digested to determine Pb concentration by inductively coupled plasma-atomic emission spectrometry (ICP-OES) (7700X, Agilent, Japan) in duplicate. A TGA instrument (STA6000, PerkinElmer, USA) equipped with a Fourier transform infrared (FTIR) spectroscope (Frontier, PerkinElmer, USA) was used to detect HCl. The flow rate was set at 50 mL min$^{-1}$. The FTIR spectral region was set at 4000–900 cm$^{-1}$, with a scanning velocity of 0.2 cm$^{-1}$ s$^{-1}$ and a resolution of 4 cm$^{-1}$. To reduce gas condensation along the transfer line, the temperatures in the gas cell and transfer line were set at 220 °C.

### 2.3. Tube furnace experiments

The tube furnace experiments were carried out with 1 g of samples, which were added to crucibles (made of corundum or quartz) and heated from room temperature to a specified temperature at 10 °C min$^{-1}$ with a flow rate of 1 L min$^{-1}$ (air or nitrogen). Residues remaining in the crucible and condensates on the surface of the glass ring at the end of the quartz tube were collected for analysis.

### 2.4. Micro X-ray diffraction analysis

Lead species in the residues from TGA, crucial to understanding the transformations, were determined using micro X-ray diffraction (μ-XRD) on 15 U beamline at the Shanghai Synchrotron Radiation Facility in China. The beam was $3.0 \times 3.0$ μm, the monochromator was set at 18.0 keV, and multi-point information was collected.

### 2.5. X-ray diffraction analysis

The residues and condensates from the tube furnace experiments were analyzed by XRD (D8 Advance, Bruker, Germany) with Cu Kα radiation, operated at 40 mA, 40 kV, a step size of 0.02° and a step time of 0.1 s.

### 2.6. X-ray photoelectron spectroscopy

The TGA residues were also analyzed by X-ray photoelectron spectroscopy (XPS) (PHI 5000C ESCA System, PHI, USA). An X-ray beam from the Al/Mg target (14.0 kV, 300 W) was focused on the sample surface over an energy range of 0–1200 eV using a step size of 0.02 eV.

### 2.7. Iodometry

Aqueous solutions of NaOH (0.4 wt%), $Na_2S_2O_3 \cdot 5H_2O$ (25 g L$^{-1}$), soluble starch (2 g L$^{-1}$), HCl (1.2 M), and KI (3.567 g L$^{-1}$) were prepared to quantify chlorine. Three impingers were connected in sequence at the outlet of the TGA. The first was empty and the second and third filled with NaOH solution to absorb $Cl_2$. The concentration of $Cl_2$ in the NaOH solution was determined by iodometry.