Dynamic experimental investigation on the volatilization behavior of lead and cadmium in the simulated municipal solid waste (MSW) influenced by sulfur compounds during incineration

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Abstract: In China, Coal, often with high level of sulfur, is always mixed with municipal solid waste (MSW) in waste incineration plants due to the low heating value and high moisture content of MSW. The influence of sulfur compounds on the volatilization of heavy metals in MSW is of great concern for China's waste incineration plants. In this study, the continuous dynamic volatilization process of Pb and Cd is investigated by adding different forms of sulfur compounds, elemental sulfur (S) and sodium sulfate (Na_2SO_4), to the simulated MSW in a laboratory incinerator, both at 1 wt% and 3wt%, respectively. The experimental results show that the added S begins to affect the volatilization of Pb and Cd at about 700°C; adding S can lead up to 49.6% reduction in the volatilization of Pb as the produced sulfur dioxide is promoting the formation of condensed sulfate phase, and part of Pb is fixed in the form of PbS in the bottom ash. But for Cd, adding S causes up to 15.9% increase in its volatilization as S seizes part of O_2 in the air, which is conducive to form the reducing atmosphere. In the reducing atmosphere, CdO can be easily reduced to Cd which volatilizes more easily than CdO at high temperatures. In fact, in the reducing atmosphere, the volatilization of Cd far outweighs the volatilization of Pb at 700°C~800°C. On the other hand, adding Na_2SO_4 almost has no influence on the volatilization of lead and cadmium below 900°C.

Keyword: MSW incineration; Pb; Cd; Volatilization of heavy metals; Sulfur compounds

1. Introduction

With the development of urbanization and industrialization in China, there is a significant increase in the amount of municipal solid waste (MSW) generated annually. According to China's National Bureau of Statistics [1, 2], the amount of MSW generation in China increased from 155.09 million tons in 2004 to 178.60 million tons in 2014. In addition, the annual MSW generation in China is expected to reach over 480 million tons by 2030 [3]. MSW incineration has a number of advantages, especially comparing with landfilling, including considerable waste volume reduction, complete destruction of organic matter, energy recovery, and hence it now plays a significant role in China's MSW management and disposal practices, processing more than a quarter of the total MSW [4, 5]. However, the emissions of fine particulates, heavy metals, trace dioxins and acid gases resulted from MSW incineration are causing major environmental and health concerns and therefore the control and mitigation of these emissions have received a lot of attentions over the recent years. The environmental regulations on the heavy metals emissions from MSW incineration plants in China are also expected to be more stringent in the near future [3, 6].

Heavy metals emissions are influenced by many factors including the waste composition such as the contents of chlorine (Cl), sulfur (S)**,** H_2O, combustion temperature [7-9], and the composition of the gas stream such as HCl, SO_2 and H_2O [10-13]. What's more, some sorbents in the furnace or in the flue gas can reduce the emissions of heavy metals [14, 15]. Because of the low heating value and high moisture content of MSW, mixing MSW with some coal, especially high sulfur coals, is a common operational practice in China's MSW incineration plants. The sulfur in the coal is transformed to various forms of sulfur compounds during the combustion process which may impact on the heavy metals emissions of the MSW plant. There have been a number of previous studies focusing on the effects of sulfur compounds on heavy metals emissions from MSW incineration [9, 16-19]. For example, lead and cadmium partitioning in a simulated MSW incinerator was found to be influenced by the presence of sulfur compounds which contribute to fix cadmium in the bottom ash and prompt the lead into the fly ash [16]. The effect of sulfur on the volatilization of cadmium was found to be completely opposite in the oxidizing atmosphere to that in the reducing atmosphere as sulfur could stabilize cadmium in CdS in the reducing atmosphere while in the oxidizing atmosphere sulfur slightly enhanced the volatilization of Cd [17]. The results of thermodynamic equilibrium calculations showed that many heavy metals such as Cd, Zn, Pb and Cu could be immobilized in sulfate phases below 800°C [18]. The volatilization of Pb is both temperature dependent and fuel specific [19]. The influences of sulfur compounds on the volatilization and distribution of cadmium and lead were also investigated during sewage sludge incineration [20-22]. The effect of sulfur on the volatilization of Cd during sludge incineration was found to be the same as that of MSW incineration for both the reducing environment and the oxidizing environment [20，21]. There are two steps in volatilizations of Pb and Cd: the first step of volatilizations are mainly controlled by the decomposition of their exchangeable, carbonate bound, iron-manganese bound fractions, and the second step of volatilizations originates from their complexed and residual fractions [22]. Almost all of these previous studies, however, have only focused on the effects of sulfur compounds on the partitioning of heavy metals in the incinerator, whereas the mechanisms responsible for the effects of sulfur compounds on the heavy metals emissions have not been fully explored.

This study is carried out to investigate the dynamic volatilizations of lead (Pb) and cadmium (Cd) influenced by sulfur compounds during different periods of simulated MSW incineration. The mechanism of sulfur compounds' influence on the volatilizations of Pb and Cd is further investigated by thermal gravimetric analysis (TGA) and X-ray diffraction (XRD). The results of this study help to better understand the volatilization behaviors of Pb and Cd under the influence of sulfur compounds during MSW incineration and provide useful information for the development of effective heavy metal emission control strategies.

2. Materials and methods

2.1 Dynamic experimental investigation on the volatilization of Pb and Cd during the incineration of simulated MSW

2.1.1 Experimental samples

Real MSW is inhomogeneous in nature due to its complexity and variability in composition, shapes and sizes and this makes it extremely difficult to obtain consistent results with gram-scale real MSW samples as used in this study. Therefore, simulated MSW samples are used in the experiment of this study so that stable waste components, controllable heavy metal components and uniform mixing can be ensured. Carbon particles are used to represent the combustible components of MSW, whereas SiO_2 and Al_2O_3 powders are used to substitute the non-combustible components of MSW. Table 1 shows the components of the simulated MSW. Pb and Cd are added to the simulated MSW in the forms of PbO and CdO with the same concentration of 1500 mg Pb/kg or Cd/kg (dry weight). The contents of PbO and CdO used in the simulated waste represent the maximum levels of both heavy metals expected to be in real MSW. The use of the maximum levels of both heavy metals in the simulated MSW makes it easy to detect and more accurate to measure the volatilizations of heavy metals.

2.1.2 Experimental apparatus

The apparatus used in this study is showed in Fig.1, which mainly consists of the air supply device, a tube incinerator, a quartz-fiber filter and the absorption equipment.

The tube incinerator is made of a 1200mm long horizontal quartz tube with 50mm internal diameter. An alumina boat is placed at the center of the combustion chamber's 500mm long heating zone. The temperature of the electrically heated tubular furnace is controlled by a PID thermocontroller with a precision of ±1℃. The heavy metals in the tail gas are captured by the glass fiber membrane which is fixed in position by the membrane filter clamp. Two bottles of dilute nitric acid absorption liquid (5% v/v) in series are used to detect whether all of the released heavy metals are captured by the membrane filter.

2.1.3 Experimental procedure

The samples used in this study are listed in Table 2. After a sample is placed in the alumina boat, the boat is carefully pushed into the center of the combustion chamber. The air flow rate controlled by the flowmeter is maintained at 3 L/min. The temperature of the combustion chamber controlled by the thermocontroller rises from the room temperature to 900℃ with the heating rate of 10℃/min, and stays at 900℃ for 60 min. Starting from 300℃, the fly ash carried by the gas flow from the incinerator is collected by the glass fiber membrane filter as a sample for every 10min until the temperature reaches 900℃and then a sample is collected for every 15min when the temperature remains at 900℃. The heating of the furnace is terminated at the end of sampling and the alumina boat is withdrawn away from the high temperature zone for natural cooling. In order to continuously collect volatile heavy metals in different periods, when a sample is collected, the air supply to the combustion chamber is suspended, and a new set of membrane filter is replaced immediately before resuming the air supply with the whole process being completed in 5 seconds in order to minimize the escape of the volatized heavy metals. The inner side of the membrane filter clamp is cleaned by a solution of 5% HNO_3 after sampling, and then the cleaning solution and glass fiber membrane filters are digested in the same beaker. The residue in the alumina boat is also collected and is digested. For each of the dynamic experiments reported in this paper, at least three repeated runs have been completed.

2.1.4 Detection of Pb and Cd concentrations and data analysis

All samples collected in each period are digested in a solution of 10 ml HCl and 2.5 ml HNO_3 at 95 °C ± 5 °C without boiling for 8 h according to the modified U.S. EPA method 3050b [23]. Then, the acid solution is filtered with constant volume and analyzed by Atomic Absorption Spectroscopy (AAS) to detect the concentrations of Pb and Cd.

The contents of heavy metals in the flue gas in this study are corrected using the content of heavy metals in the bottom ash remaining in the alumina boat after incineration. The correction takes account of the vaporized heavy metals lost to the walls of the furnace and pipes as well as during the periods of changing filters. The corrected mass of a heavy metal in the flue gas (m_{ir}) in the i^{th} period is calculated by Equation (1):

$$\mathbf{m_{ir} = m_i \times (m_a - m_b) / \sum_{i=1}^{n} m_i} \qquad \mathbf{(1)}$$

m_i indicates the weight of the heavy metal in the flue gas collected in the i^{th} period; m_a is the weight of the heavy metal in the simulated waste; m_b is the weight of the heavy metal in the bottom ash; the average volatilization rate in the i^{th} period (v_i) is calculated by Equation (2), the cumulative volatilization rate in the i^{th} period (k_i) is calculated by Equation (3).

$$\mathbf{v_i = m_{ir}/(\Delta t \times m_a)} \qquad \textbf{(2)}$$

$$\mathbf{k_i = (\textstyle\sum_{i=1}^{n} m_{ir})/m_a} \qquad \textbf{(3)}$$

2.2 Flue gas analysis

Concentrations of CO and CO_2 in the flue gas are continuously analyzed by a gas analyzer (VARIOplus for Syngas-Analysis made by MRU Company in Germany) during the incineration of the simulated MSW. The results are used to confirm whether the volatilization of heavy metals occurs in the oxidizing or reducing atmosphere. This is especially important as previous studies have shown that the effect of sulfur on the volatilization of Pb and Cd in the reducing atmosphere is different from that in the oxidizing atmosphere [17].

2.3 Thermal gravimetric analysis of PbO and CdO

In order to understand the characteristics of the related heavy metal oxides investigated by this study, the thermal gravimetric analyses of PbO and CdO are carried out with a NETZSCH STA 449C Thermogravimetric Analyzer. The weight losses (TG signals) of the samples are recorded continuously under non-isothermal conditions within the temperature range from room temperature to 1200 °C at a linear heating rate of 20°C /min. The original mass of each sample is kept at ca. 10mg, and the gas flow rates of the air and CO under two different conditions are fixed at 100 ml/min.

2.4 Crystalline phase analysis

In order to identify the crystalline phases and heavy metal speciation of the residue after the interactions between the heavy metals and the sulfur compounds, the heavy metal oxides and sulfur compounds are evenly mixed and placed in the alumina boat and incinerated in the tube furnace. The molar ratio of each heavy metal and sulfur (S/M) is fixed at 40, which is similar to that used in the dynamic volatilization tests. Other experimental conditions including the air flow rate and the heating program are also consistent with those of the dynamic volatilization tests (Section 2.1.3). At the end of each test, the solid residue in the alumina boat is removed and turned into powder by mortar and pestle after cooling. The crystalline phases and heavy metal speciation of the residue in the alumina boat are then identified by the X-ray powder diffraction (XRD) analysis.

3 Results and discussion

3.1 Effects of sulfur compounds on the volatilization of Pb and Cd

3.1.1 Average volatilization rate

As shown in Figure 2, the general trends for the average volatilization rates of Pb and Cd against the temperature do not change when the sulfur compounds are added to the simulated MSW. The average volatilization rates are small below 700°C but there are noticeable heavy metals volatilizations. After the temperature reaches 700°C, the average volatilization rates of both Pb and Cd start to increase rapidly and reach the maximum during the 90th-105th min (with the temperature at 900°C), and then decrease with time (with the temperature remaining at 900°C). When no sulfur compounds are added to the simulated MSW, Pb and Cd begin to volatize at 700°C to 800°C, similar to the cases with sulfur compounds additions. When S is the added sulfur compound, the average volatilization rates of Pb in all periods are smaller than those with no sulfur addition (Figure 2(a)) after the temperature reaches 700°C. On the other hand, after the addition of S, the average volatilization rate of Cd has increased during the period of 70th-105th min when the temperature is in the range between 700°C and 900°C and then decreased for the remaining period (Figure 2(b)).

When Na_2SO_4 is the sulfur compound added to the simulated MSW, however, the average volatilization rates of Pb and Cd remain similar to those with no addition of sulfur compounds, indicating Na_2SO_4 has little influence on the volatilizations of Pb or Cd.

3.1.2 Cumulative volatilization rate

The dynamic cumulative volatilization rates of Pb and Cd during the incineration process are shown in Fig. 3. Adding S to the simulated MSW leads to an obvious reduction in the cumulative volatilization rate of Pb. From Figure 3(a), it can be seen that the cumulative volatilization rate of Pb has decreased from 23.0% to 13.5% and 11.6%, respectively, with the additions of 1% S and 3% S. The addition of a larger amount of S (1% vs 3%) has led to a greater reduction in the cumulative volatilization rate of Pb. However, the additions of 1% Na_2SO_4 and 3% Na_2SO_4 have much smaller impact on the cumulative volatilization rate of Pb which is only slightly reduced to 21.5% and 21.9% respectively. These results indicate that S is better than Na_2SO_4 in inhibiting the volatilization of Pb. Results shown in Fig.3 (b) confirm that different sulfur compounds also have different impacts on the volatilization rate of Cd. Adding S promotes the volatilization of Cd with the volatilization rate of Cd increasing with the amount of S added, whereas adding Na_2SO_4 has little influence on the cumulative volatilization rate of Cd.

3.2 Analysis on the influence mechanisms of the added sulfur compounds on the volatilizations of Pb and Cd during the incineration of the simulated MSW

3.2.1 Concentrations of CO and CO_2 in flue gas

Figure 4 shows the concentration profiles of CO and CO_2 in the flue gas during the incineration process of the simulated MSW. The simulated MSW begins to burn and release CO_2 at about 400°C (Figure 4(a)). The concentration of CO_2 in the flue gas reaches the maximum level at about 600°C, stays at the high level until about 750°C, reduces gradually when the temperature is increased to 900°C and then is further decreased to less than 1% after the temperature remaining at 900°C for 20mins, which indicates the end of the simulated MSW combustion. Figure 4(b) shows that CO begins to appear in the flue gas at about 460°C and its concentration increases rapidly after this point. The concentration of CO reaches the maximum value of about 5800 ppm at about 550°C, stays at this value until the temperature is about 610°C and then decreases rapidly to almost zero ppm at 740°C. The concentration profiles of CO and CO_2 in the flue gas shown in Figure 4 indicate that the simulated MSW undergoes pyrolysis, gasification and combustion reactions and experiences both reducing and oxidizing atmospheres during the incineration process in the tube furnace. When the pyrolysis and gasification reactions are fast, more CO is generated than it can be burned by the combustion reactions, hence resulting in the simulated MSW experiencing a period of a reducing atmosphere in the tube furnace. At the later stage of the incineration (after 75th min), there is no CO detected in the flue gas (Figure 4(b)), indicating the simulated MSW is further incinerated under oxidizing conditions.

3.2.2 Thermal gravimetric characteristics of PbO and CdO

In order to understand the thermal gravimetric characteristics of PbO and CdO under oxidizing and reducing conditions, TGA analyses of PbO and CdO have been carried out in the atmospheres of air and CO, respectively and the results are presented in Figure 5. Figure 5(a) shows the weight loss of PbO in the gas flow of air begins at about 900°C, whereas in the gas flow of CO, it begins at about 300°C. Similarly, Figure 5(b) shows the weight loss of CdO does not begin until the temperature reaches about 1000°C in the gas flow of air, however, in the gas flow of CO, the weight loss of CdO begins at a much lower temperature, about 300°C. These results indicate there is no volatilization of PbO and CdO before 900°C under the oxidizing condition. However, there are significant weight losses for both PbO and CdO before 900°C under the reducing condition. Under the reducing condition, both PbO and CdO can react with CO to generate CO_2 and the elemental heavy metals according to (R1-R2). The generated CO_2 and the subsequent volatilizations of Pb and Cd lead to the observed reductions in the remaining sample weights before 900°C (Figure 5(a)-(b)). Comparing Figure 5(a) with Figure 5(b), it can be seen that CdO is reduced more easily than PbO under the same reducing condition. At 900°C, more than 97% of CdO has been lost whereas the weight loss of PbO is less than 14%.

$$\mathbf{PbO + CO \rightarrow Pb + CO_2} \qquad (1)$$

$$\mathbf{CdO + CO \rightarrow Cd + CO_2} \qquad (2)$$

3.2.3 XRD analysis

The crystalline phases and heavy metal speciation of the residue in the alumina boat after the interactions between the heavy metal oxides and the sulfur compounds (Section 2.4) are identified by the X-ray powder diffraction (XRD) analysis. As shown in Figure 6 (a), for the mixture of PbO and S at 700°C, the bottom residue contains PbS, $PbSO_4$ and PbO and this indicates that some PbO has reacted with S and O_2 to generate PbS and $PbSO_4$. At 800°C, PbO is no longer in the bottom residue and only PbS and $Pb_2(SO_4)O$ can be found (Fig.6 (a)). This indicates that when the temperature reaches 800°C, all PbO has reacted with S and O_2 to generate PbS and $PbSO_4$ and all Pb is fixed in the bottom residue in the form of PbS and condensed sulfate phase. Figure 6(b) shows that at 700°C some CdO has reacted with S and O_2 to generate CdS and $Cd_3O_2SO_4$ but at 800°C the bottom residue only contains a large amount of CdO (both larger diffraction peak intensity and peak area) and a small amount of CdS. This indicates at 800°C Cd is largely remaining in the bottom residue in the form of CdO, rather than is fixed as CdS in the bottom residue, contrasting to what is observed with Pb in Figure 6(a). Results in Figure 6 (c) and 6 (d) show that PbO and CdO do not react with Na_2SO_4 even the temperature reaches 900°C, indicating that adding Na_2SO_4 to MSW will have little influence on the volatilization of lead and cadmium below 900°C.

3.2.4 Discussion on the influence mechanisms of the added sulfur compounds on the volatilizations of Pb and Cd during the simulated MSW incineration

The experimental results and analysis described in the above subsections (Subsections 3.2.1~3.2.3) can be used to deduce the influence mechanisms of sulfur compounds on the volatilizations of Pb and Cd during the incineration of the simulated MSW (Section 3.1). Adding S inhibits the volatilization of Pb from the incineration of the simulated MSW (Figure 2(a) and Figure 3(a)) and this is partly due to fact that the oxygen in the air combines with sulfur to produce sulfur dioxide which is propitious to the formation of condensed sulfate phase [19，21, 24]. The presence of S also leads to Pb fixation in the form of PbS which will more likely stay in the bottom residue as the melting point and boiling point of PbS are higher than those of heavy metal oxides and sulfates and the vapor pressure of PbS is lower than that of heavy metal oxides and sulfates [16, 17, 20, 25].

The reasons for the promotional influence of the added S on the volatilization of Cd during the incineration of the simulated MSW (Figure 2(b) and Figure 3(b)) can be deduced as follows: S start to burn in air at about 300°C, but CO appears in the incinerator at about 460°C; therefore, oxygen in the air combines with sulfur to produce sulfur dioxide firstly; the reduced oxygen available for the incineration of the simulated MSW leads to more CO in the tube furnace comparing with the case without the addition of S. Figure 5 has already showed that at 900°C, in the gas flow of CO the weight loss of CdO is more than 97%, while the weight loss of PbO is less than 14%. The large difference of the weight loss between CdO and PbO indicates that the volatilization of Cd far outweighs the volatilization of Pb in the reducing atmosphere and this is one of the reasons why S promotes the volatilization of Cd but inhibits the volatilization of Pb in the dynamic tests shown in Figures 2-3. In addition, CdO can be reduced by CO according to R2 to Cd which has much lower melting point and boiling point than those of CdO, and this also leads to more volatilization of Cd from the simulated MSW.

Figures 6 (c) and (d) have already showed that Na_2SO_4 does not react with PbO and CdO even at 900°C and therefore, adding Na_2SO_4 to the simulated MSW should have no influence on the volatilization of the heavy metals (lead and cadmium) in the simulated MSW. However, as the Na_2SO_4 in the incineration system can absorb heat when being melted, which can slightly inhibit the volatilizations of Pb and Cd as shown in Figures 2-3.

4 Conclusions

The dynamic volatilization processes of Pb and Cd during the simulated MSW incineration with and without the addition of sulfur compounds (S and Na_2SO_4) have been investigated with a tube furnace. Adding sulfur compounds to the simulated MSW have no effect on the volatilizations of Pb and Cd below 700°C but the influences increase with temperature once it is above 700°C. Adding elemental S to the simulated MSW inhibits the volatilization of Pb but also promotes the volatilization of Cd. On the other hand, adding Na_2SO_4 to the simulated MSW has little influence on the volatilization behaviors of Pb and Cd during the incineration process.

In order to elucidate the influence mechanisms of the added sulfur compounds on the volatilizations of heavy metals (Pb and Cd) during the incineration process, additional tests have been carried out. Considering the existence of both oxidizing and reducing atmospheres during the incineration process of the simulated MSW, the TGA tests of PbO and CdO have been carried out under both oxidizing (in the gas flow of air) and reducing (in the gas flow of CO) conditions. The interactions between the heavy metal oxides and the sulfur compounds have also been studied by using the same tube furnace and the same temperature-programmed incineration process as the dynamic volatilization tests of the simulated MSW and XRD analyses have been carried to identify heavy metal species left in the solid residue.

These additional experimental results indicate the added S affects the volatilizations of Pb and Cd in the simulated MSW during incineration through different mechanisms. For Pb, it is mostly fixed in the bottom residue in the form of PbS and condensed sulfate phase and hence the added S inhibits the volatilization of Pb during the incineration process. For Cd, only a small amount of Cd is fixed in the form of CdS in the bottom residue and hence it is either released in the vapor phase or remains in the original form of CdO in the bottom residue. As CdO can be reduced to Cd in the reducing atmosphere experienced by the MSW at 700°C~800°C and the volatilization of Cd occurs more easily than CdO, the added S thus promotes the volatilization of Cd during the incineration process, contrasting to the volatilization of Pb which is inhibited by the added S.

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Table 1 Components of the simulated MSW

Category	Name	Mass ratio	Quantity in each sample
combustible components	Carbon particles	70%	10.5g
non-combustible components	SiO_2	20%	3.0g
	Al_2O_3	10%	1.5g
Heavy metal component	PbO	1500 mg /kg	24.2mg
	CdO	1500 mg /kg	25.6mg

Table 2 Components of the samples

Notations of the Samples	Composition of the samples
No sulfur	15.0489g simulated MSW
1% S	15.0489g simulated MSW and 0.152g S
3% S	15.0489g simulated MSW and 0.465g S
1% Na_2SO_4	15.0489g simulated MSW and 0.675g Na_2SO_4
3% Na_2SO_4	15.0489g simulated MSW and 2.995g Na_2SO_4

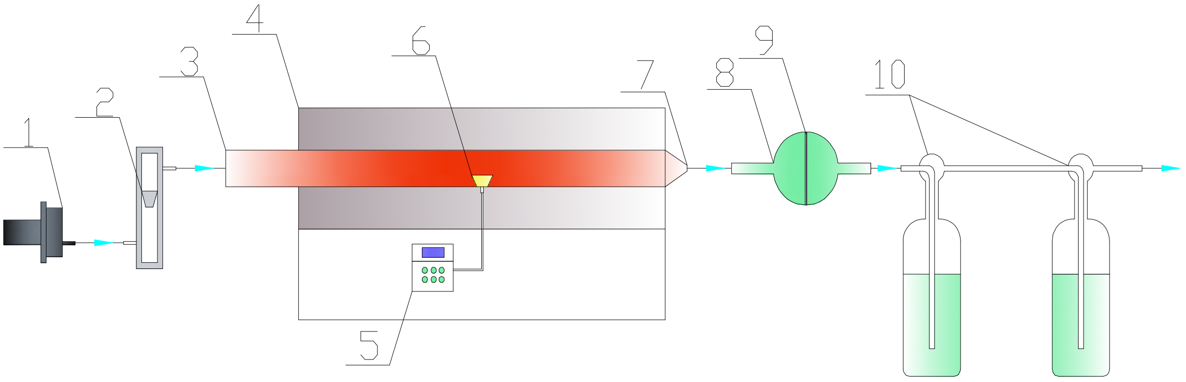
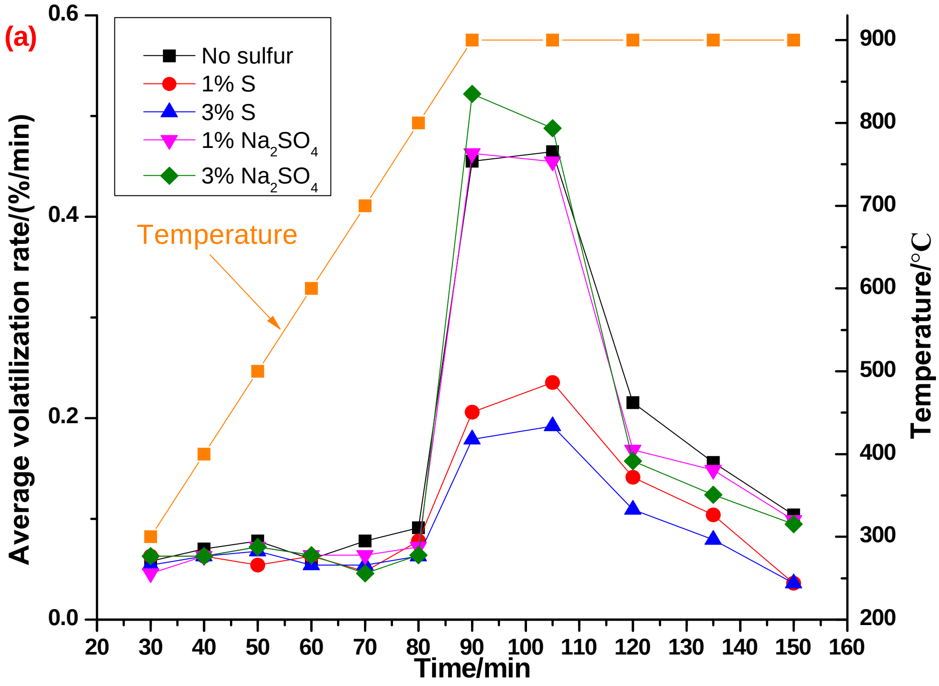


Fig. 1 Schematic diagram of the laboratory incinerator
1-Diaphragm pump, 2- flowmeter, 3- Quartz tube, 4- Tube incinerator, 5- Thermocontroller, 6- Alumina boat, 7-Tapered flange, 8-Membrane filter clamp, 9-Glass fiber membrane, 10-Absorption equipment (5% HNO_3)


(a)
No sulfur
1% S
3% S
1% Na_2SO_4
3% Na_2SO_4
Temperature
Average volatilization rate/(%/min)
0.0
0.2
0.4
0.6
Temperature/°C
200
300
400
500
600
700
800
900
Time/min
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160

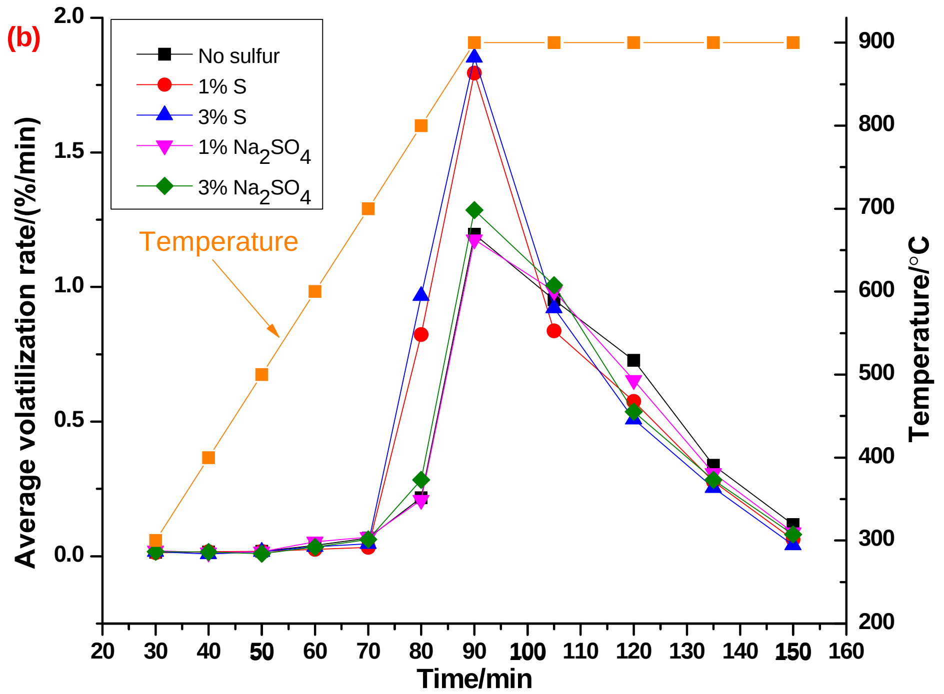


Fig. 2 Effects of sulfur compounds on the average volatilization rates of Pb (a) and Cd (b)

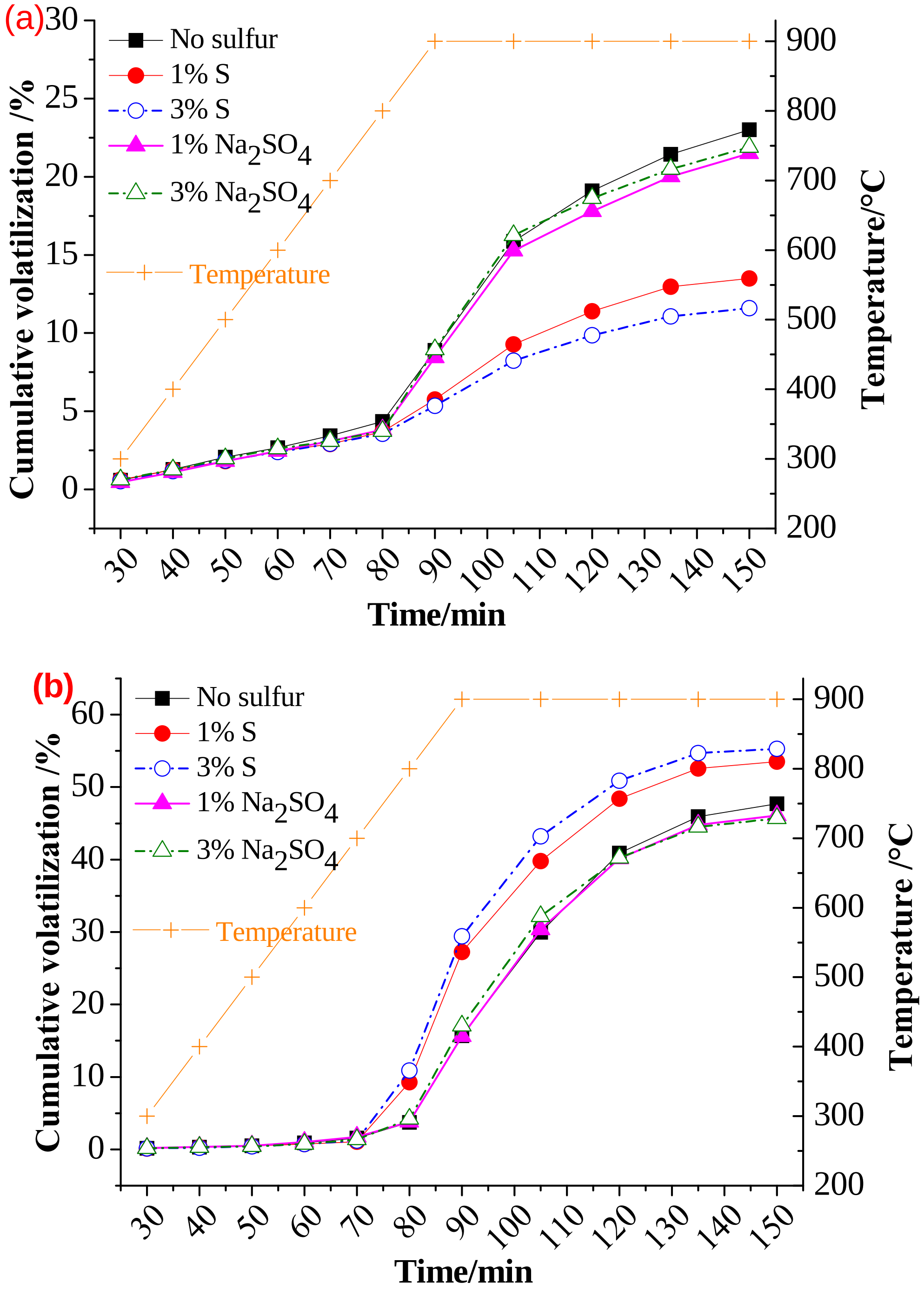


Fig. 3 Effects of sulfur compounds on cumulative volatilizations of Pb (a) and Cd (b)

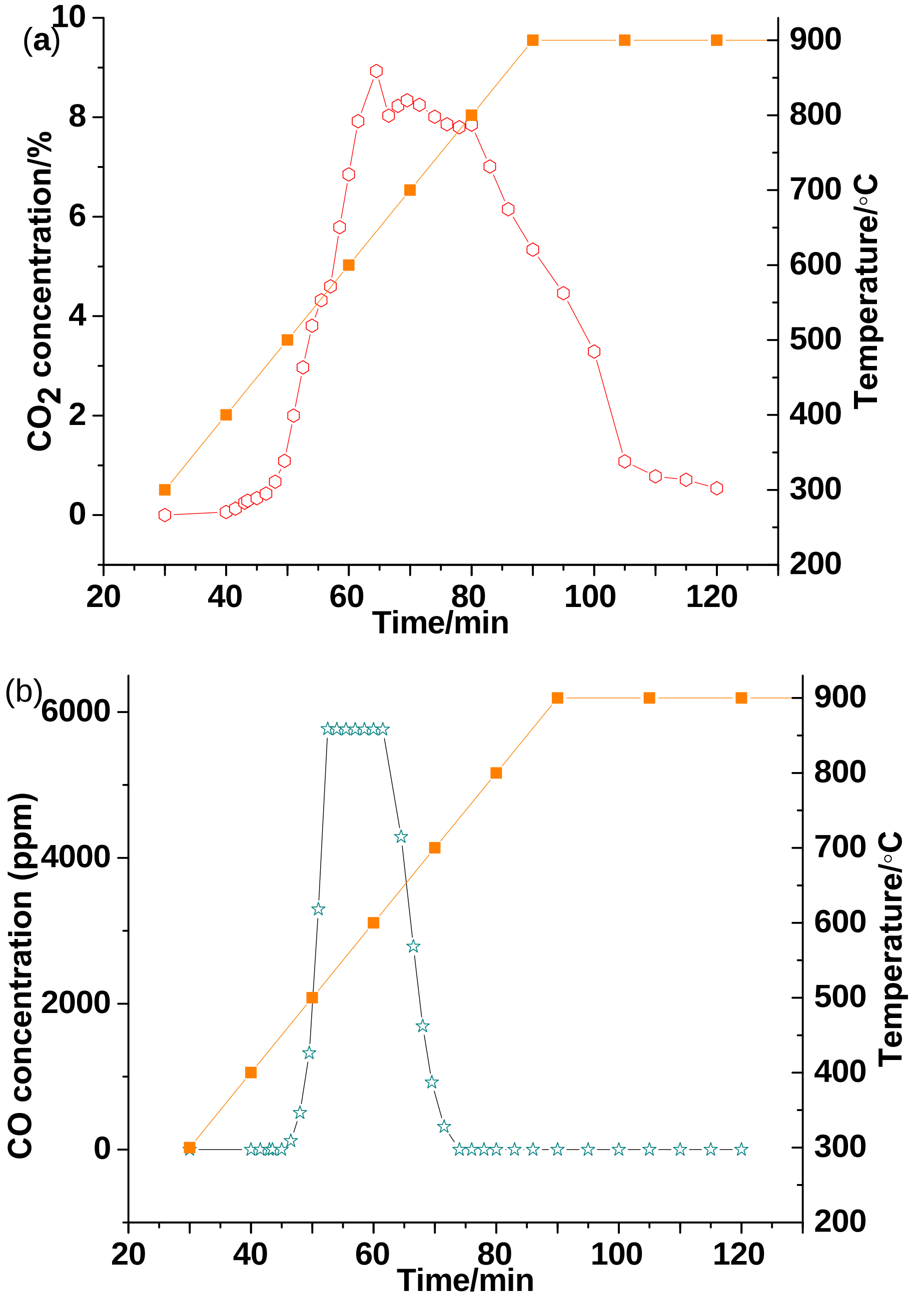


Fig.4 Concentrations of CO$_2$ (a) and CO (b) in the flue gas

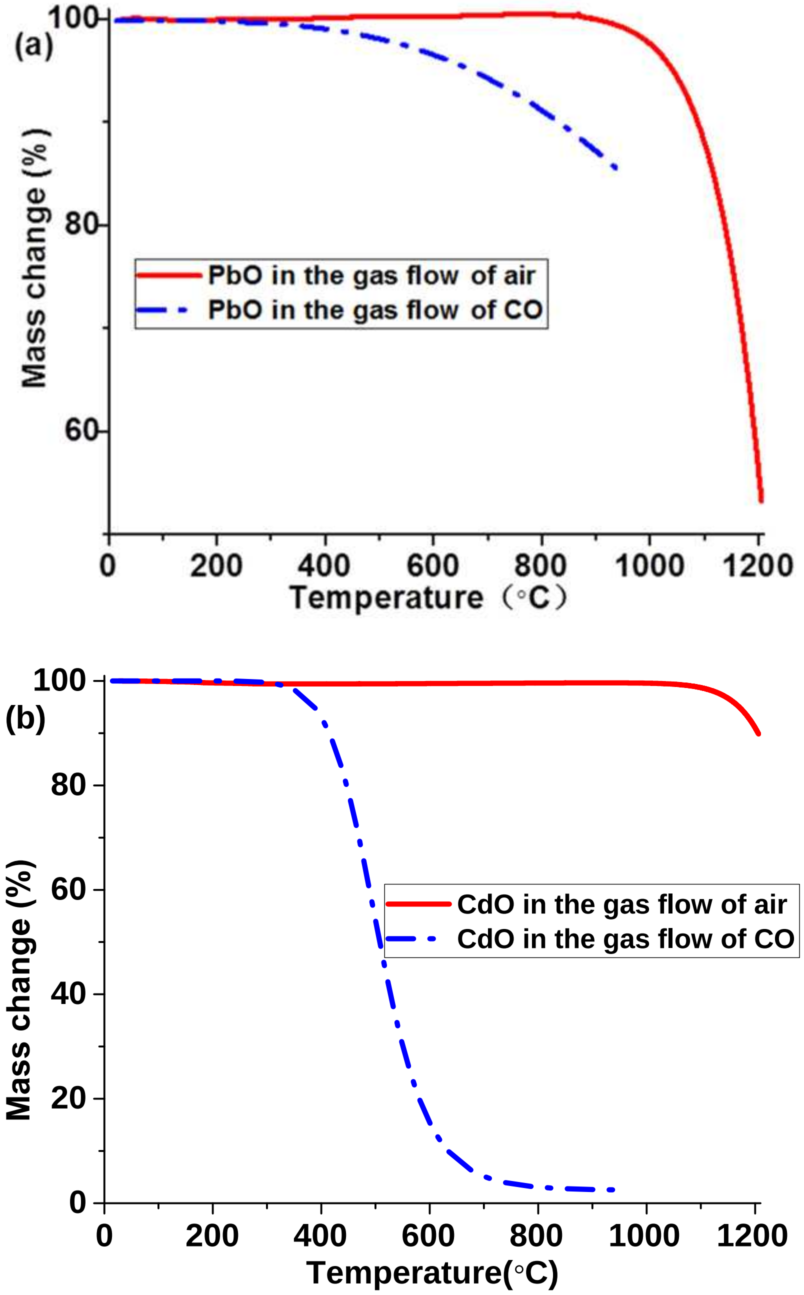


Fig.5 Thermogravimetric (TG) curves of PbO (a) and CdO (b)

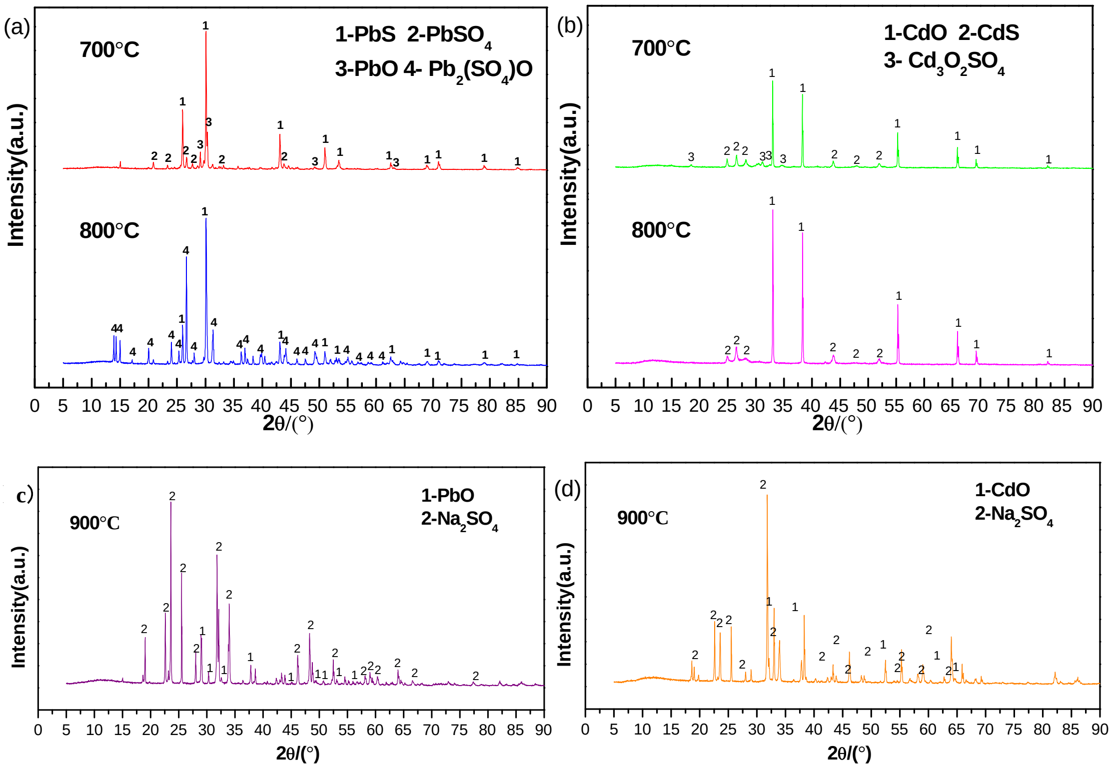


Fig. 6 XRD patterns of mixture of heavy metal oxides and sulfur compounds

(a)PbO + S, (b) CdO + S, (c) PbO + Na_2SO_4, (d) CdO + Na_2SO_4