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23 which volatilizes more easily than CdO at high temperatures. In fact, in the reducing atmosphere,
24 the volatilization of Cd far outweighs the volatilization of Pb at 700°C~800°C. On the other hand,
25 adding Na₂SO₄ almost has no influence on the volatilization of lead and cadmium below 900°C.

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

27 1. Introduction

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

41 Heavy metals emissions are influenced by many factors including the waste composition such as
42 the contents of chlorine (Cl), sulfur (S), H₂O, combustion temperature [7-9], and the composition
43 of the gas stream such as HCl, SO₂ and H₂O [10-13]. What's more, some sorbents in the furnace or
44 in the flue gas can reduce the emissions of heavy metals [14, 15]. Because of the low heating value

45 and high moisture content of MSW, mixing MSW with some coal, especially high sulfur coals, is a
46 common operational practice in China's MSW incineration plants. The sulfur in the coal is
47 transformed to various forms of sulfur compounds during the combustion process which may impact
48 on the heavy metals emissions of the MSW plant. There have been a number of previous studies
49 focusing on the effects of sulfur compounds on heavy metals emissions from MSW incineration [9,
50 16-19]. For example, lead and cadmium partitioning in a simulated MSW incinerator was found to
51 be influenced by the presence of sulfur compounds which contribute to fix cadmium in the bottom
52 ash and prompt the lead into the fly ash [16]. The effect of sulfur on the volatilization of cadmium
53 was found to be completely opposite in the oxidizing atmosphere to that in the reducing atmosphere
54 as sulfur could stabilize cadmium in CdS in the reducing atmosphere while in the oxidizing
55 atmosphere sulfur slightly enhanced the volatilization of Cd [17]. The results of thermodynamic
56 equilibrium calculations showed that many heavy metals such as Cd, Zn, Pb and Cu could be
57 immobilized in sulfate phases below 800°C [18]. The volatilization of Pb is both temperature
58 dependent and fuel specific [19]. The influences of sulfur compounds on the volatilization and
59 distribution of cadmium and lead were also investigated during sewage sludge incineration [20-22].
60 The effect of sulfur on the volatilization of Cd during sludge incineration was found to be the same
61 as that of MSW incineration for both the reducing environment and the oxidizing environment [20,
62 21]. There are two steps in volatilizations of Pb and Cd: the first step of volatilizations are mainly
63 controlled by the decomposition of their exchangeable, carbonate bound, iron-manganese bound
64 fractions, and the second step of volatilizations originates from their complexed and residual
65 fractions [22]. Almost all of these previous studies, however, have only focused on the effects of
66 sulfur compounds on the partitioning of heavy metals in the incinerator, whereas the mechanisms

67 responsible for the effects of sulfur compounds on the heavy metals emissions have not been fully
68 explored.

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

76 **2. Materials and methods**

77 **2.1 Dynamic experimental investigation on the volatilization of Pb and Cd during the** 78 **incineration of simulated MSW**

79 **2.1.1 Experimental samples**

80 Real MSW is inhomogeneous in nature due to its complexity and variability in composition,
81 shapes and sizes and this makes it extremely difficult to obtain consistent results with gram-scale
82 real MSW samples as used in this study. Therefore, simulated MSW samples are used in the
83 experiment of this study so that stable waste components, controllable heavy metal components and
84 uniform mixing can be ensured. Carbon particles are used to represent the combustible components
85 of MSW, whereas SiO₂ and Al₂O₃ powders are used to substitute the non-combustible components
86 of MSW. Table 1 shows the components of the simulated MSW. Pb and Cd are added to the
87 simulated MSW in the forms of PbO and CdO with the same concentration of 1500 mg Pb/kg or
88 Cd/kg (dry weight). The contents of PbO and CdO used in the simulated waste represent the

89 maximum levels of both heavy metals expected to be in real MSW. The use of the maximum levels
90 of both heavy metals in the simulated MSW makes it easy to detect and more accurate to measure
91 the volatilizations of heavy metals.

92 **2.1.2 Experimental apparatus**

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

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

102 **2.1.3 Experimental procedure**

103 The samples used in this study are listed in Table 2. After a sample is placed in the alumina
104 boat, the boat is carefully pushed into the center of the combustion chamber. The air flow rate
105 controlled by the flowmeter is maintained at 3 L/min. The temperature of the combustion chamber
106 controlled by the thermocontroller rises from the room temperature to 900° with the heating rate
107 of $10^\circ/\text{min}$, and stays at 900° for 60 min. Starting from 300° , the fly ash carried by the gas flow
108 from the incinerator is collected by the glass fiber membrane filter as a sample for every 10min until
109 the temperature reaches 900°C and then a sample is collected for every 15min when the temperature
110 remains at 900°C . The heating of the furnace is terminated at the end of sampling and the alumina

111 boat is withdrawn away from the high temperature zone for natural cooling. In order to continuously
112 collect volatile heavy metals in different periods, when a sample is collected, the air supply to the
113 combustion chamber is suspended, and a new set of membrane filter is replaced immediately before
114 resuming the air supply with the whole process being completed in 5 seconds in order to minimize
115 the escape of the volatized heavy metals. The inner side of the membrane filter clamp is cleaned by
116 a solution of 5% HNO₃ after sampling, and then the cleaning solution and glass fiber membrane
117 filters are digested in the same beaker. The residue in the alumina boat is also collected and is
118 digested. For each of the dynamic experiments reported in this paper, at least three repeated runs
119 have been completed.

120 **2.1.4 Detection of Pb and Cd concentrations and data analysis**

121 All samples collected in each period are digested in a solution of 10 ml HCl and 2.5 ml HNO₃
122 at 95 °C ± 5 °C without boiling for 8 h according to the modified U.S. EPA method 3050b [23].
123 Then, the acid solution is filtered with constant volume and analyzed by Atomic Absorption
124 Spectroscopy (AAS) to detect the concentrations of Pb and Cd.

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

$$130 \quad m_{ir} = m_i \times (m_a - m_b) / \sum_{i=1}^n m_i \quad (1)$$

131 m_i indicates the weight of the heavy metal in the flue gas collected in the i^{th} period; m_a is the
132 weight of the heavy metal in the simulated waste; m_b is the weight of the heavy metal in the bottom

133 ash; the average volatilization rate in the i^{th} period (v_i) is calculated by Equation (2), the cumulative
134 volatilization rate in the i^{th} period (k_i) is calculated by Equation (3).

$$135 \quad v_i = m_{ir} / (\Delta t \times m_a) \quad (2)$$

$$136 \quad k_i = (\sum_{j=1}^n m_{ir}) / m_a \quad (3)$$

137 **2.2 Flue gas analysis**

138 Concentrations of CO and CO₂ in the flue gas are continuously analyzed by a gas analyzer
139 (VARIOplus for Syngas-Analysis made by MRU Company in Germany) during the incineration of
140 the simulated MSW. The results are used to confirm whether the volatilization of heavy metals
141 occurs in the oxidizing or reducing atmosphere. This is especially important as previous studies
142 have shown that the effect of sulfur on the volatilization of Pb and Cd in the reducing atmosphere
143 is different from that in the oxidizing atmosphere [17].

144 **2.3 Thermal gravimetric analysis of PbO and CdO**

145 In order to understand the characteristics of the related heavy metal oxides investigated by this
146 study, the thermal gravimetric analyses of PbO and CdO are carried out with a NETZSCH STA
147 449C Thermogravimetric Analyzer. The weight losses (TG signals) of the samples are recorded
148 continuously under non-isothermal conditions within the temperature range from room temperature
149 to 1200 °C at a linear heating rate of 20°C /min. The original mass of each sample is kept at ca.
150 10mg, and the gas flow rates of the air and CO under two different conditions are fixed at 100
151 ml/min.

152 **2.4 Crystalline phase analysis**

153 In order to identify the crystalline phases and heavy metal speciation of the residue after the
154 interactions between the heavy metals and the sulfur compounds, the heavy metal oxides and sulfur

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

162 **3 Results and discussion**

163 **3.1 Effects of sulfur compounds on the volatilization of Pb and Cd**

164 3.1.1 Average volatilization rate

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

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

180 3.1.2 Cumulative volatilization rate

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

193 **3.2 Analysis on the influence mechanisms of the added sulfur compounds on the** 194 **volatilizations of Pb and Cd during the incineration of the simulated MSW**

195 **3.2.1 Concentrations of CO and CO₂ in flue gas**

196 Figure 4 shows the concentration profiles of CO and CO₂ in the flue gas during the incineration
197 process of the simulated MSW. The simulated MSW begins to burn and release CO₂ at about 400°C
198 (Figure 4(a)). The concentration of CO₂ in the flue gas reaches the maximum level at about 600°C,

199 stays at the high level until about 750°C, reduces gradually when the temperature is increased to
200 900°C and then is further decreased to less than 1% after the temperature remaining at 900°C for
201 20mins, which indicates the end of the simulated MSW combustion. Figure 4(b) shows that CO
202 begins to appear in the flue gas at about 460°C and its concentration increases rapidly after this
203 point. The concentration of CO reaches the maximum value of about 5800 ppm at about 550°C,
204 stays at this value until the temperature is about 610°C and then decreases rapidly to almost zero
205 ppm at 740°C. The concentration profiles of CO and CO₂ in the flue gas shown in Figure 4 indicate
206 that the simulated MSW undergoes pyrolysis, gasification and combustion reactions and
207 experiences both reducing and oxidizing atmospheres during the incineration process in the tube
208 furnace. When the pyrolysis and gasification reactions are fast, more CO is generated than it can be
209 burned by the combustion reactions, hence resulting in the simulated MSW experiencing a period
210 of a reducing atmosphere in the tube furnace. At the later stage of the incineration (after 75th min),
211 there is no CO detected in the flue gas (Figure 4(b)), indicating the simulated MSW is further
212 incinerated under oxidizing conditions.

213 **3.2.2 Thermal gravimetric characteristics of PbO and CdO**

214 In order to understand the thermal gravimetric characteristics of PbO and CdO under oxidizing
215 and reducing conditions, TGA analyses of PbO and CdO have been carried out in the atmospheres
216 of air and CO, respectively and the results are presented in Figure 5. Figure 5(a) shows the weight
217 loss of PbO in the gas flow of air begins at about 900°C, whereas in the gas flow of CO, it begins
218 at about 300°C. Similarly, Figure 5(b) shows the weight loss of CdO does not begin until the
219 temperature reaches about 1000°C in the gas flow of air, however, in the gas flow of CO, the weight
220 loss of CdO begins at a much lower temperature, about 300°C. These results indicate there is no

221 volatilization of PbO and CdO before 900°C under the oxidizing condition. However, there are
222 significant weight losses for both PbO and CdO before 900°C under the reducing condition. Under
223 the reducing condition, both PbO and CdO can react with CO to generate CO₂ and the elemental
224 heavy metals according to (R1-R2). The generated CO₂ and the subsequent volatilizations of Pb and
225 Cd lead to the observed reductions in the remaining sample weights before 900°C (Figure 5(a)-(b)).
226 Comparing Figure 5(a) with Figure 5(b), it can be seen that CdO is reduced more easily than PbO
227 under the same reducing condition. At 900°C, more than 97% of CdO has been lost whereas the
228 weight loss of PbO is less than 14%.



231 3.2.3 XRD analysis

232 The crystalline phases and heavy metal speciation of the residue in the alumina boat after the
233 interactions between the heavy metal oxides and the sulfur compounds (Section 2.4) are identified
234 by the X-ray powder diffraction (XRD) analysis. As shown in Figure 6 (a), for the mixture of PbO
235 and S at 700°C, the bottom residue contains PbS, PbSO₄ and PbO and this indicates that some PbO
236 has reacted with S and O₂ to generate PbS and PbSO₄. At 800°C, PbO is no longer in the bottom
237 residue and only PbS and Pb₂(SO₄)O can be found (Fig.6 (a)). This indicates that when the
238 temperature reaches 800°C, all PbO has reacted with S and O₂ to generate PbS and PbSO₄ and all
239 Pb is fixed in the bottom residue in the form of PbS and condensed sulfate phase. Figure 6(b) shows
240 that at 700°C some CdO has reacted with S and O₂ to generate CdS and Cd₃O₂SO₄ but at 800°C the
241 bottom residue only contains a large amount of CdO (both larger diffraction peak intensity and peak
242 area) and a small amount of CdS. This indicates at 800°C Cd is largely remaining in the bottom

243 residue in the form of CdO, rather than is fixed as CdS in the bottom residue, contrasting to what is
244 observed with Pb in Figure 6(a). Results in Figure 6 (c) and 6 (d) show that PbO and CdO do not
245 react with Na₂SO₄ even the temperature reaches 900°C, indicating that adding Na₂SO₄ to MSW will
246 have little influence on the volatilization of lead and cadmium below 900°C.

247 **3.2.4 Discussion on the influence mechanisms of the added sulfur compounds on the** 248 **volatilizations of Pb and Cd during the simulated MSW incineration**

249 The experimental results and analysis described in the above subsections (Subsections
250 3.2.1~3.2.3) can be used to deduce the influence mechanisms of sulfur compounds on the
251 volatilizations of Pb and Cd during the incineration of the simulated MSW (Section 3.1). Adding S
252 inhibits the volatilization of Pb from the incineration of the simulated MSW (Figure 2(a) and Figure
253 3(a)) and this is partly due to fact that the oxygen in the air combines with sulfur to produce sulfur
254 dioxide which is propitious to the formation of condensed sulfate phase [19, 21, 24]. The presence
255 of S also leads to Pb fixation in the form of PbS which will more likely stay in the bottom residue
256 as the melting point and boiling point of PbS are higher than those of heavy metal oxides and sulfates
257 and the vapor pressure of PbS is lower than that of heavy metal oxides and sulfates [16, 17, 20, 25].

258 The reasons for the promotional influence of the added S on the volatilization of Cd during the
259 incineration of the simulated MSW (Figure 2(b) and Figure 3(b)) can be deduced as follows: S start
260 to burn in air at about 300°C, but CO appears in the incinerator at about 460°C; therefore, oxygen
261 in the air combines with sulfur to produce sulfur dioxide firstly; the reduced oxygen available for
262 the incineration of the simulated MSW leads to more CO in the tube furnace comparing with the
263 case without the addition of S. Figure 5 has already showed that at 900°C, in the gas flow of CO the
264 weight loss of CdO is more than 97%, while the weight loss of PbO is less than 14%. The large

265 difference of the weight loss between CdO and PbO indicates that the volatilization of Cd far
266 outweighs the volatilization of Pb in the reducing atmosphere and this is one of the reasons why S
267 promotes the volatilization of Cd but inhibits the volatilization of Pb in the dynamic tests shown in
268 Figures 2-3. In addition, CdO can be reduced by CO according to R2 to Cd which has much lower
269 melting point and boiling point than those of CdO, and this also leads to more volatilization of Cd
270 from the simulated MSW.

271 Figures 6 (c) and (d) have already showed that Na₂SO₄ does not react with PbO and CdO even
272 at 900°C and therefore, adding Na₂SO₄ to the simulated MSW should have no influence on the
273 volatilization of the heavy metals (lead and cadmium) in the simulated MSW. However, as the
274 Na₂SO₄ in the incineration system can absorb heat when being melted, which can slightly inhibit
275 the volatilizations of Pb and Cd as shown in Figures 2-3.

276 **4 Conclusions**

277 The dynamic volatilization processes of Pb and Cd during the simulated MSW incineration
278 with and without the addition of sulfur compounds (S and Na₂SO₄) have been investigated with a
279 tube furnace. Adding sulfur compounds to the simulated MSW have no effect on the volatilizations
280 of Pb and Cd below 700°C but the influences increase with temperature once it is above 700°C.
281 Adding elemental S to the simulated MSW inhibits the volatilization of Pb but also promotes the
282 volatilization of Cd. On the other hand, adding Na₂SO₄ to the simulated MSW has little influence
283 on the volatilization behaviors of Pb and Cd during the incineration process.

284 In order to elucidate the influence mechanisms of the added sulfur compounds on the
285 volatilizations of heavy metals (Pb and Cd) during the incineration process, additional tests have
286 been carried out. Considering the existence of both oxidizing and reducing atmospheres during the

287 incineration process of the simulated MSW, the TGA tests of PbO and CdO have been carried out
288 under both oxidizing (in the gas flow of air) and reducing (in the gas flow of CO) conditions. The
289 interactions between the heavy metal oxides and the sulfur compounds have also been studied by
290 using the same tube furnace and the same temperature-programmed incineration process as the
291 dynamic volatilization tests of the simulated MSW and XRD analyses have been carried to identify
292 heavy metal species left in the solid residue.

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

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308 **References**

309 [1] Chinese Statistics Yearbook Compiling Committee. Chinese statistics yearbook 2004; Chinese
310 Statistics Press: Beijing, 2004.

311 [2] Chinese Statistics Yearbook Compiling Committee. Chinese statistics yearbook 2014; Chinese
312 Statistics Press: Beijing, 2014.

313 [3] Yu, J.; Sun, L.; Xiang, J.; Hu, S.; Su, S.; Qiu, J., Vaporization of heavy metals during thermal
314 treatment of model solid waste in a fluidized bed incinerator. *Chemosphere* **2012**, 86, (11), 1122-
315 1126.

316 [4] Dong, J.; Chi, Y.; Tang, Y.; Ni, M.; Nzihou, A.; Weiss-Hortala, E.; Huang, Q., Partitioning of
317 Heavy Metals in Municipal Solid Waste Pyrolysis, Gasification, and Incineration. *Energy & Fuels*
318 **2015**, 29, (11), 7516-7525.

319 [5] Ji, L.; Lu, S.; Yang, J.; Du, C.; Chen, Z.; Buekens, A.; Yan, J., Municipal solid waste incineration
320 in China and the issue of acidification: A review. *Waste Management & Research* **2016**, 34, (4),
321 280-297.

322 [6] Hu, H.; Liu, H.; Shen, W.; Luo, G.; Li, A.; Lu, Z.; Yao, H., Comparison of CaO's effect on the
323 fate of heavy metals during thermal treatment of two typical types of MSWI fly ashes in China.
324 *Chemosphere* **2013**, 93, (4), 590-596.

325 [7] Rio, S.; Verwilghen, C.; Ramarosan, J.; Nzihou, A.; Sharrock, P., Heavy metal vaporization and
326 abatement during thermal treatment of modified wastes. *Journal of Hazardous Materials* **2007**, 148,
327 (3), 521-528.

328 [8] Morf L S, Brunner P H, Spaun S. Effect of operating conditions and input variations on the
329 partitioning of metals in a municipal solid waste incinerator. *Waste Management and Research*, **2000**,
330 18, (1), 4-15.

331 [9] Zhang, Y.; Meng, H.; Chen, Y.; Zhou, Q.; Chen H., Effects of Sulfur Compounds on Cd
332 Partitioning in a Simulated Municipal Solid Waste Incinerator. *Chinese Journal of Chemical*
333 *Engineering* **2007**, 15, (6), 889-894.

334 [10] Zhang Y, Li Q, Jia J, et al. Thermodynamic analysis on heavy metals partitioning impacted by
335 moisture during the MSW incineration. *Waste management*, **2012**, 32(12): 2278-2286.

336 [11] Li Q, Meng A, Jia J, et al. Investigation of heavy metal partitioning influenced by flue gas
337 moisture and chlorine content during waste incineration. *Journal of Environmental Sciences*, **2010**,
338 22, (5), 760-768.

339 [12] Jiao F, Zhang L, Yamada N, et al. Effect of HCl, SO₂ and H₂O on the condensation of heavy
340 metal vapors in flue gas cooling section. *Fuel processing technology*, **2013**, 105, 181-187.

341 [13] Jiao F, Cheng Y, Zhang L, et al. Effects of HCl, SO₂ and H₂O in flue gas on the condensation
342 behavior of Pb and Cd vapors in the cooling section of municipal solid waste incineration.
343 *Proceedings of the Combustion Institute*, **2011**, 33, (2), 2787-2793.

344 [14] Tang Y T, Ma X Q, Zhang C, et al. Effects of sorbents on the heavy metals control during tire
345 rubber and polyethylene combustion in CO₂/O₂ and N₂/O₂ atmospheres. *Fuel*, **2016**, 165, 272-278.

346 [15] Ma L, Mao Y, JiantaoChen H Z. Removal of Cd-Pb-Hg Heavy Metal Ion from Simulation
347 MSW Incineration Flue Gas by Modified Mineral Adsorbents. *Frontier of Environmental Science*,
348 2014, 3, (3), 109-118.

349 [16] Chen, Y.; Zhang, Y.; Li, H.; Zhou, Q.; Chen H., Effects of sulfur compounds on Cd and Pb
350 partitioning in a simulated MSW incinerator. *J Tsinghua Univ (Sci & Tech)* 2008, 48, (2), 232-
351 235. (In Chinese)

352 [17] Zhang, Y.; Chen, Y.; Meng, A.; Li, Q.; Cheng, H., Experimental and thermodynamic

353 investigation on transfer of cadmium influenced by sulfur and chlorine during municipal solid waste
354 (MSW) incineration. *Journal of Hazardous Materials* **2008**, 153, (1-2), 309-319.

355 [18] Verhulst, D.; Buekens, A., Thermodynamic Behavior of Metal Chlorides and Sulfates under
356 the Conditions of Incineration Furnaces. *Environ. Sci. Technol* **1996**, 30, (1), 50-56.

357 [19] Pedersen A J, Van Lith S C, Frandsen F J, et al. Release to the gas phase of metals, S and Cl
358 during combustion of dedicated waste fractions. *Fuel Processing Technology*, **2010**, 91, (9), 1062-
359 1072.

360 [20] Liu, J.; Fu, J.; Sun, S.; Ning, X.; Wang, Y.; Chen, T.; Luo, G.; Xie, W.; Yang, Z.; Zhuo, Z.,
361 Effect of different sulfides on cadmium distribution during sludge combustion based on
362 experimental and thermodynamic calculation approaches. *Environmental Science and Pollution*
363 *Research* **2015**, 22, (2), 1113-1126.

364 [21] Luan, J.; Li, R.; Zhang, Z.; Li, Y.; Zhao, Y., Influence of chlorine, sulfur and phosphorus on the
365 volatilization behavior of heavy metals during sewage sludge thermal treatment. *Waste Management*
366 *& Research* **2013**, 31, (10), 1012-1018.

367 [22] Luan, J.; Li, R.; Zhang, Z.; Li, Y.; Zhao, Y., Speciation evolutions of target metals (Cd, Pb)
368 influenced by chlorine and sulfur during sewage sludge incineration. *Frontiers of Environmental*
369 *Science & Engineering* **2014**, 8, (6), 871-876.

370 [23] Wang X, Huang Y, Zhong Z, et al. Control of inhalable particulate lead emission from
371 incinerator using kaolin in two addition modes. *Fuel Processing Technology*, **2014**, 119, 228-235.

372 [24] Mkilaha, I.; Yao, H.; Naruse, I., Thermodynamic analysis of the role of chlorine and sulfur
373 environments during combustion and incineration processes. *Journal of Material Cycles & Waste*
374 *Management* **2002**, 4, 143-149.

375 [25] Wu, F.; Su, Y.; Wang, H.; Hu, H.; Zhao, Q., Effect of atmospheres on transfer characteristic of
376 heavy metals during municipal solid waste incineration process. *Chinese Journal of Environmental*
377 *Engineering*, **2011**, 5, (07), 1623-1626.

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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 ₂ O ₃	10%	1.5g
Heavy metal component	PbO	1500 mg /kg	24.2mg
	CdO	1500 mg /kg	25.6mg

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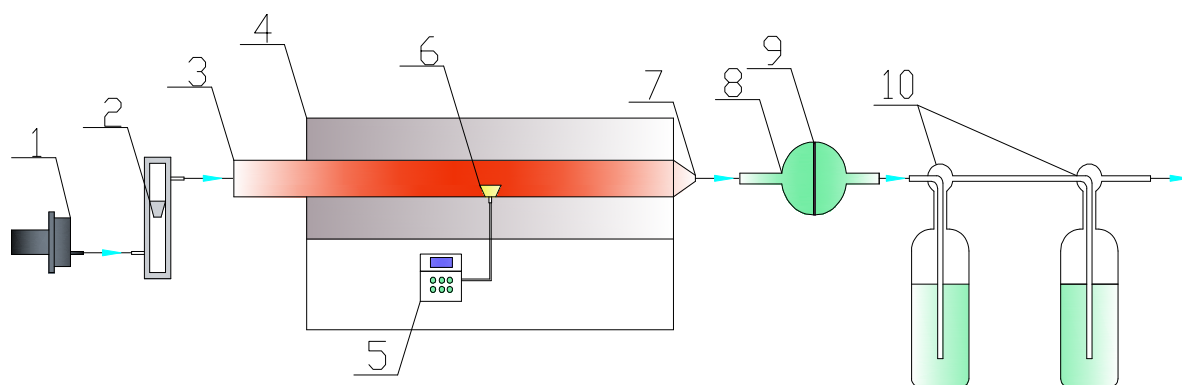
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Table 2 Components of the samples

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% Na₂SO₄	15.0489g simulated MSW and 0.675g Na₂SO₄
3% Na₂SO₄	15.0489g simulated MSW and 2.995g Na₂SO₄

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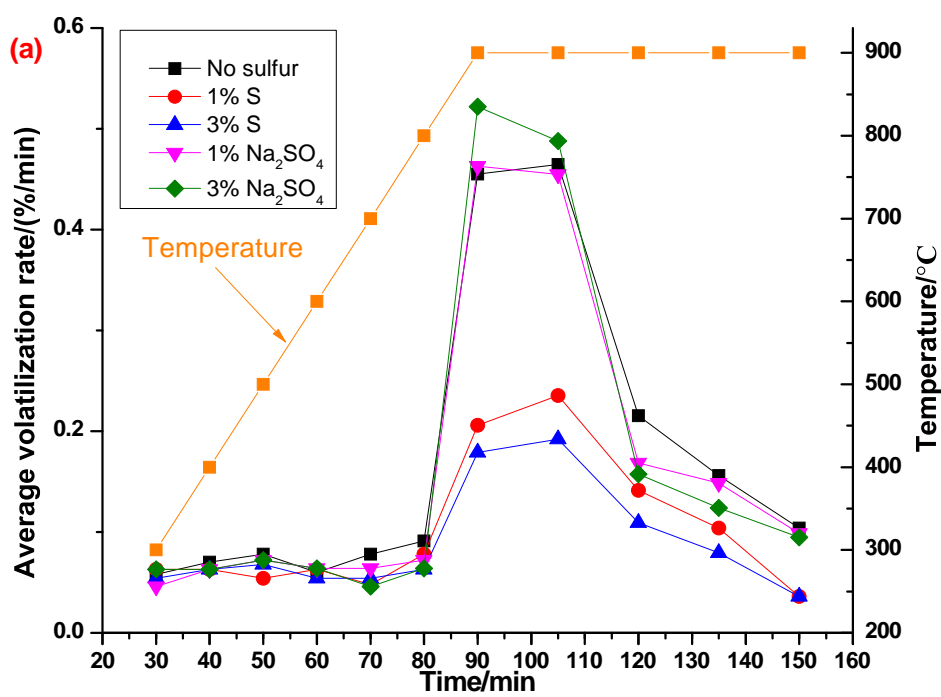


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Fig. 1 Schematic diagram of the laboratory incinerator

**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% HNO₃)**

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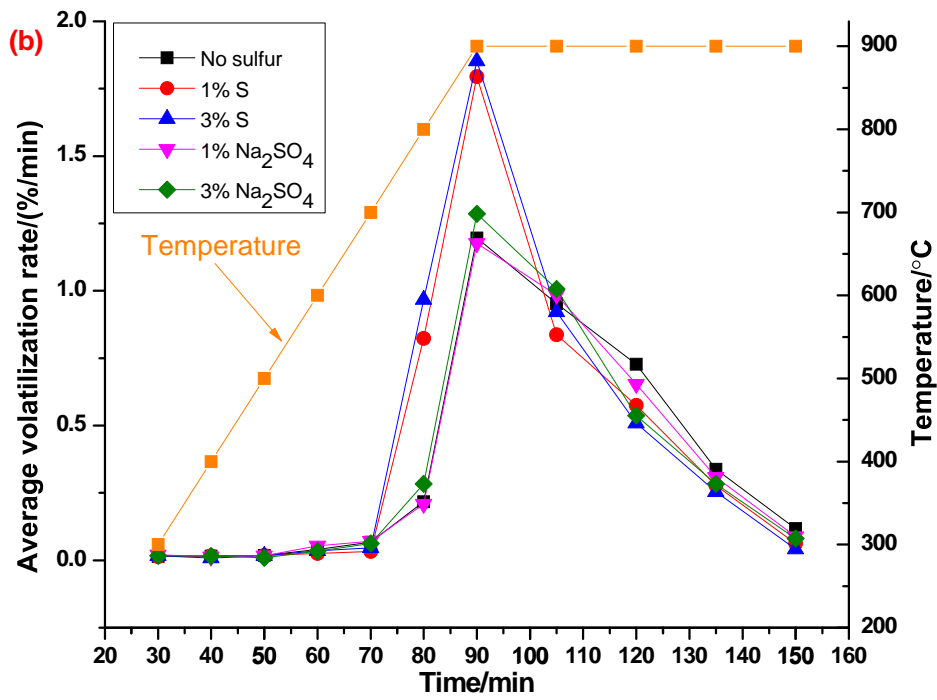
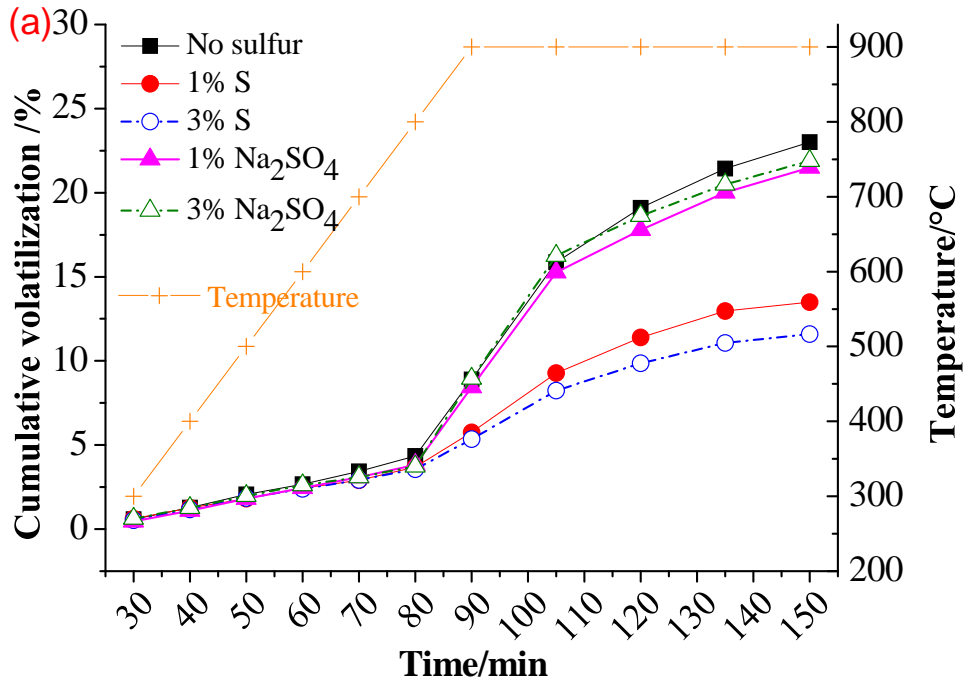
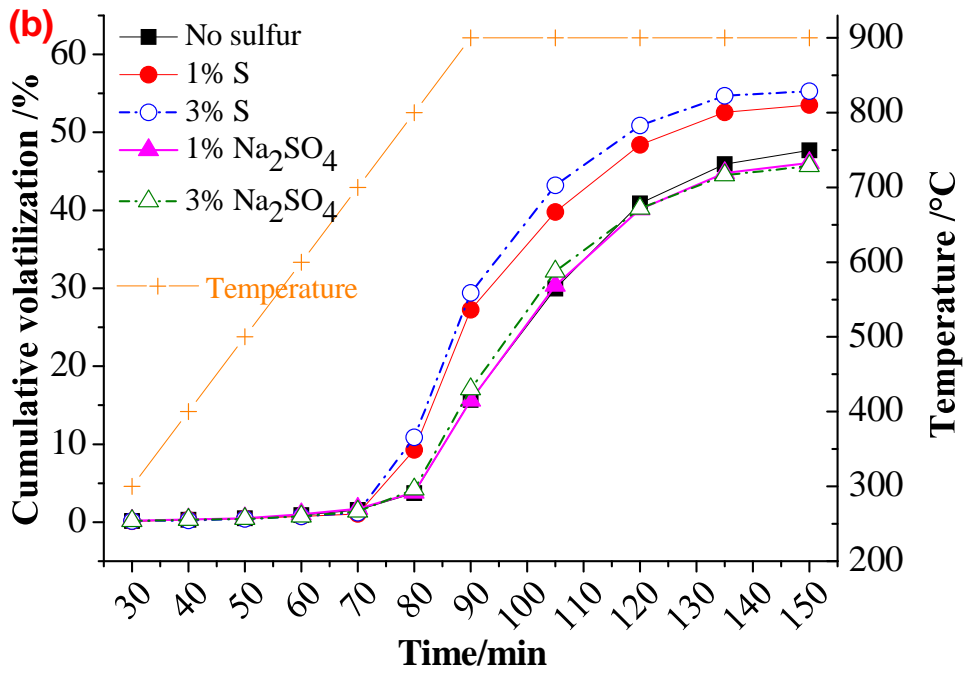


Fig. 2 Effects of sulfur compounds on the average volatilization rates of Pb (a) and Cd (b)

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

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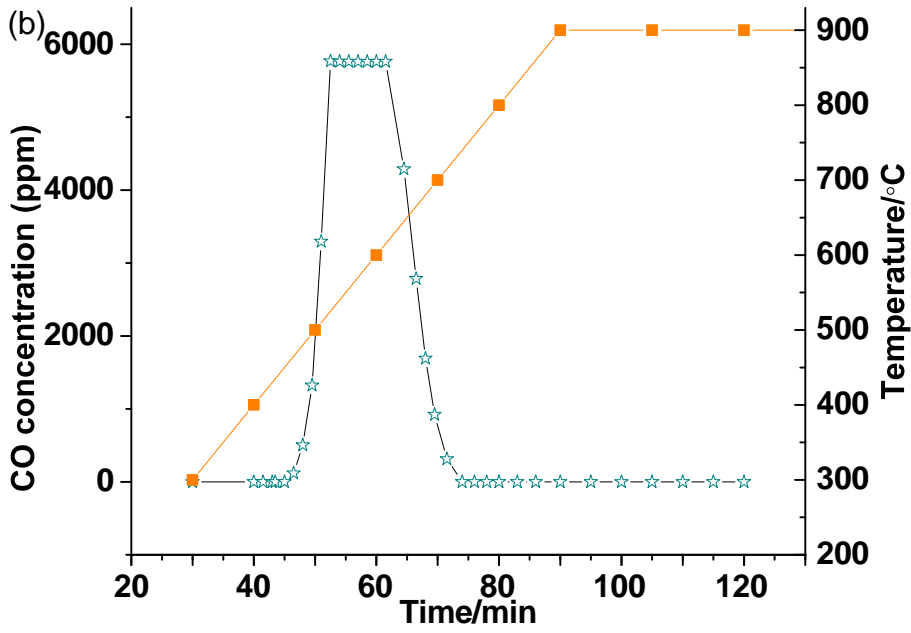
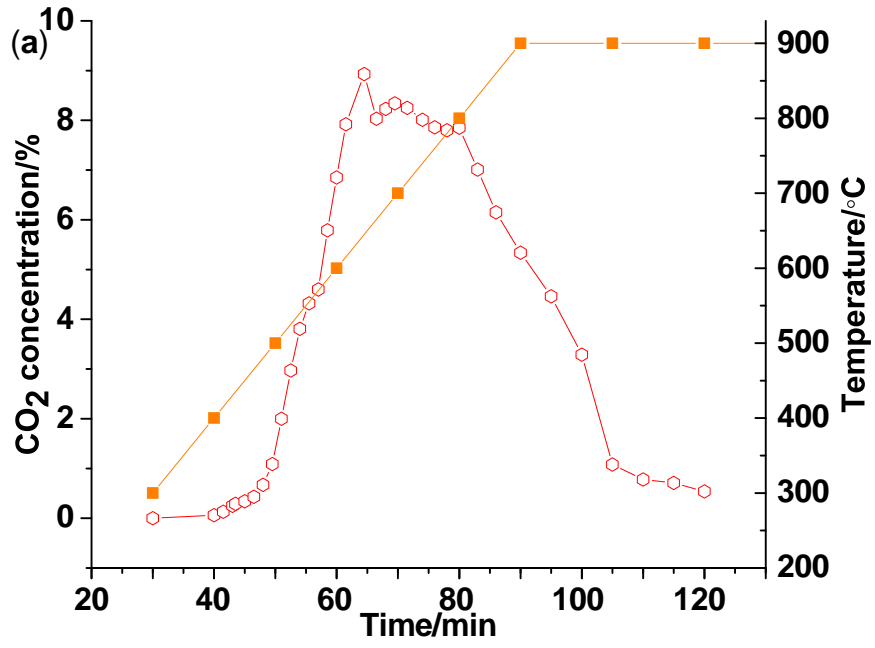


Fig.4 Concentrations of CO₂ (a) and CO (b) in the flue gas

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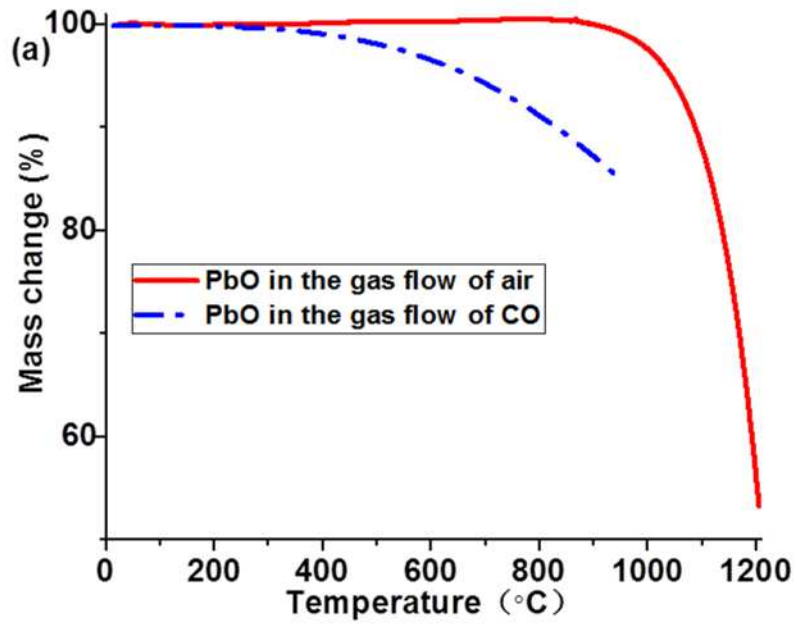
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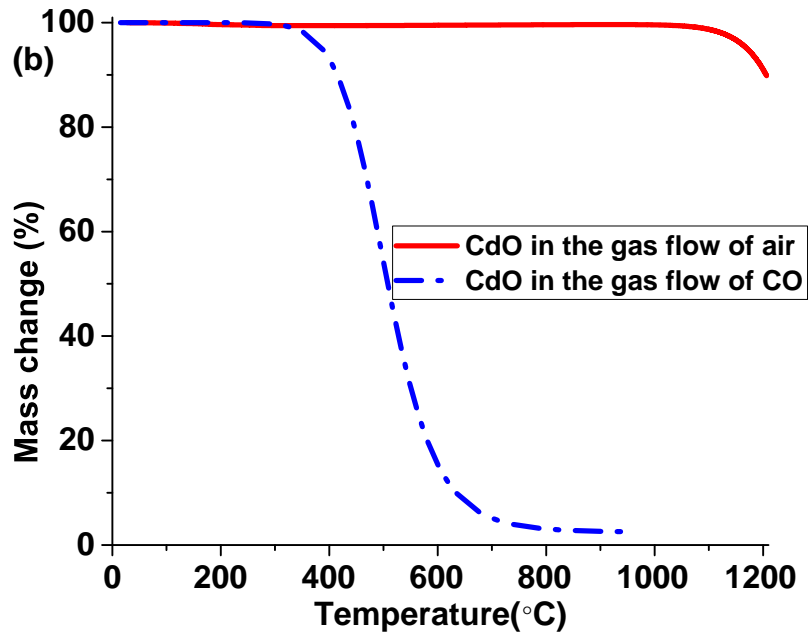
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Fig.5 Thermogravimetric (TG) curves of PbO (a) and CdO (b)

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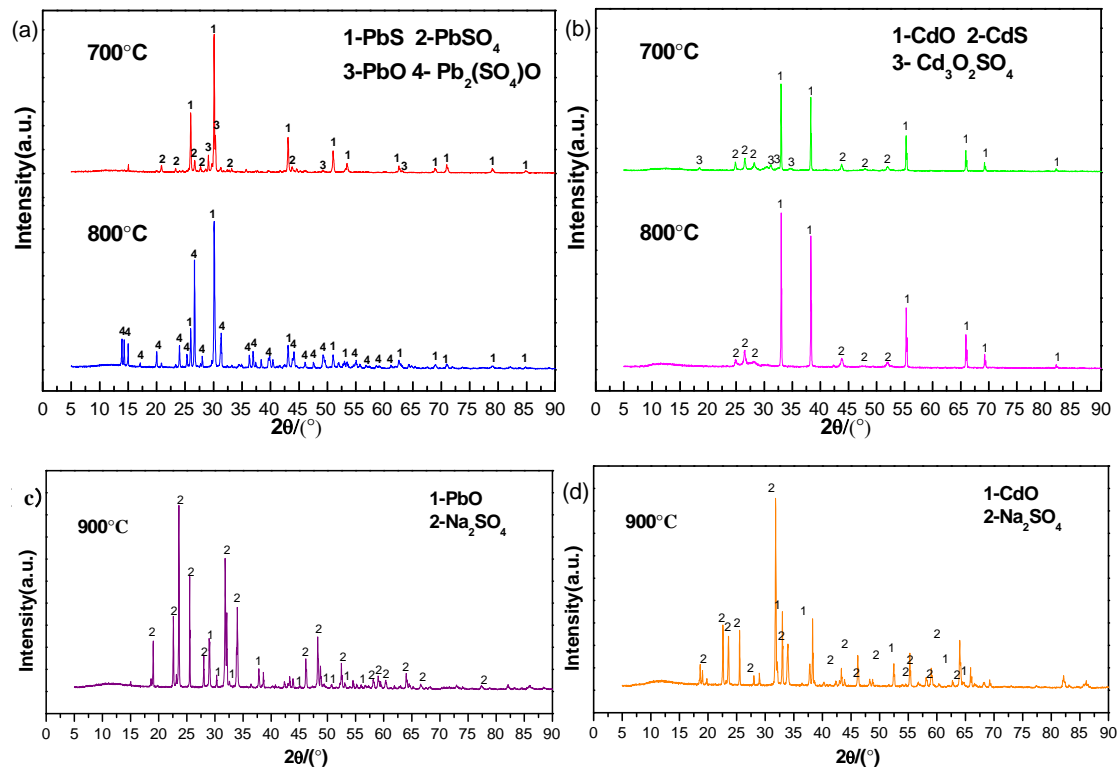
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Fig. 6 XRD patterns of mixture of heavy metal oxides and sulfur compounds
(a)PbO + S, (b) CdO + S, (c) PbO + Na₂SO₄, (d) CdO + Na₂SO₄