



Research article

Study on the mechanism of lead release from ash under the action of high-temperature flue gas

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ABSTRACT

The interaction between flue gas and ash causes the redistribution of heavy metals and affect their emission characteristics. In this study, a double-layer fixed-bed reactor was used to investigate the effect of this interaction on Pb distribution at 800–1000 °C. Obvious gaseous Pb adsorption by ash just occurred in the case of high-Pb flue gas and less ash melting. In other cases, significant Pb release from ash occurred under the action of the high-temperature flue gas. The occurrences of Pb in ash was found to be thermally stable. Ash melting is the main reason for the Pb release. Gaseous Na in the combustion flue gas and reducing components in the pyrolysis flue gas promote the Pb release via promoting the ash melting. H₂S and HCl in the pyrolysis flue gas also promote the Pb release by forming PbS and PbCl₂, which are more volatile.

1. Introduction

Pb, a heavy metal element, is neurotoxic and nonbiodegradable with a biological half-life of 1–2 months or longer [1]. Coal-fired power plants are a major source of Pb in the atmosphere. For example, in China, coal-fired units emitted as much as 8600 t of Pb into the atmosphere in 2012 [2]. The mass concentration and distribution patterns of Pb in the flue gas determine the extent of damage it does to the environment. Pb emission can be reduced by transforming gaseous Pb into particulate Pb, which can be captured by a dust removal device [3–5]. Furthermore, understanding the transformation of Pb in the coal-fired unit is meaningful to develop Pb emission control techniques.

Pb is a sulfurphilic element; Pb-containing sulfides such as galena (PbS) are the most common forms of Pb in coal. Pb can also bind to aluminosilicates, carbonates, phosphates, and clay minerals [6,7]. According to the solubility of Pb in different extracts, the binding state of Pb in coal can be classified into water-soluble and ion-exchange state, carbonate-bound state, organic-bound state, sulfide-bound state, and residual form, among which the sulfide-bound state and residual forms are the most dominant. Studies have found that the water-soluble and ion-exchangeable Pb and carbonate-bound Pb are completely released after pyrolysis at high temperature, whereas sulfide-bound and residual Pb are partially released. The different binding states of Pb can be transformed into one another [8,9].

The transformation of Pb in coal-fired systems occurs in two stages: high-temperature combustion and post-combustion [10–12]. The transformation of Pb in the high-temperature combustion stage is influenced by the combustion conditions and coal properties. Xue et al. [13] performed coal combustion experiments at 900–1300 °C and found that the release ratio of Pb increased with an increase in the temperature. Wang et al. [14] also conducted combustion experiments on four types of coal at 1150 °C and found that the release ratio of Pb in coal was 25–60%, indicating that the distribution ratio of Pb in the flue gas and fly ash is different for different types of coal. Gaseous Pb released into the high-temperature flue gas mainly exists in the form of PbO. When the Cl content in coal is high, gaseous Pb exists in the form of PbCl₂, which is easier to release [15,16]. The results showed that the mineral components adsorbed gaseous Pb in the flue gas and promoted its conversion into particulate form. Various adsorbents were used to adsorb PbO and PbCl₂. SiO₂, Al₂O₃, bauxite, kaolin, emathlite, and limestone were found to effectively adsorb PbCl₂ in a simulated flue gas [17–19]. SiO₂, Al₂O₃, CaO, MgO, Fe₂O₃, and kaolin were found to effectively adsorb PbO [20–22]. Whether it was PbO or PbCl₂, Kaolin had the highest adsorption capacity. In the adsorption products of Ca-based adsorbents, Pb mainly exists as CaPbO₃ and CaPbO₄, while in the adsorption products of aluminosilicate, it mainly exists as PbO·Al₂O₃·2SiO₂. Through DFT calculation, Zhang et al. [22] found the unsaturated Al atoms on the α-Al₂O₃ (110) surface were the active sites for Pb adsorption. Due to the

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high volatility of PbCl_2 , PbO was easier to be adsorbed than PbCl_2 [21,22]. In addition to minerals such as aluminosilicate, which can adsorb gaseous Pb in the flue gas, other components in the flue gas influence the Pb distribution. Jiao et al. [23] found that SO_2 and H_2O in the flue gas promoted the solidification of Pb by facilitating the conversion of its gaseous Pb to PbSO_4 .

Fly ash contains mineral components such as Si and Al, and it is also possible to adsorb gaseous Pb in the flue gas through chemical adsorption. Laboratory studies found that Pb in coal was mostly released into the gas after high-temperature combustion. However, field tests at coal-fired plants showed that the mass of Pb in the flue gas after the operation of the dust collector only accounted for 4–10% of the total Pb, and Pb was concentrated in fine particles [24–26]. Therefore, the transformation of Pb should occur during the cooling process of the high-temperature flue gas. Theoretically analyze the possible pathways of Pb transformation, including chemical transformation in the intermediate- and high-temperature ranges, and physical adsorption or condensation in the low-temperature range. When the concentration of gaseous Pb in the low-temperature flue gas is relatively high, the possibility of gaseous Pb physically condensing is greater. However, the influence of chemical conversion on the Pb distribution in the intermediate- and high-temperature ranges lacks direct research evidence.

Therefore, this study focuses on the effect of the interaction between high-temperature flue gas and ash on the Pb distribution. The changes in Pb content in the ash under the action of different flue gases were analyzed. The effects of flue gas constituents on the stability of Pb in ash were discussed. The mechanism of Pb release from ash under the action of the high-temperature flue gas was revealed, which is helpful to understand the transformation of Pb in coal-fired units and develop Pb emission control techniques.

2. Experimental

2.1. Sample

In this study, two types of coal with high Pb contents (35.9 and 32.2 $\mu\text{g/g}$) and different mineral compositions were selected. The results of proximate and ultimate analysis of the two types of coal are shown in Tables 1 and 2. Before the experiment, the pulverized coal was ground and screened to 74–96 μm , dried at 105 $^\circ\text{C}$, and sealed for preservation.

A slow ash program using the muffle furnace at 815 $^\circ\text{C}$ was used to prepare the ash samples in advance. Coal #1 and coal #2 combust to produce ash #1 and ash #2, respectively. Based on the national standard of China (GB/T 219–2008), the melting points of the two ash samples were determined by using the ash melting point tester (BYTHR-9F, Boyuntian, China). The deformation temperatures of the two ash samples were 1296 $^\circ\text{C}$ and 1435 $^\circ\text{C}$, respectively. X-ray fluorescence spectroscopy (XRF; ARL PERFORM X, Thermo Fisher Scientific, USA) was used to analyze the component of the two ash samples and the results are summarized in Table 3.

The chemicals including: Na_2CO_3 (CAS: 497–19–8, purity >99.8%) and cellulose (CAS: 9004–34–6; average diameter = 50 μm) were acquired from Sinopharm Chemical Reagent Co. Ltd. and Sigma-Aldrich, respectively. Cellulose with a Na concentration of 0.13–0.22% was prepared by impregnating, drying and grinding.

Table 1
Proximate analysis results for the coal samples.

Coal sample	Proximate analysis, wt% ad			
	Moisture	Volatile	Ash	Fixed carbon
#1	2.34	32.8	25.9	39.0
#2	1.17	28.5	20.3	50.1

Table 2
Ultimate analysis of the coal samples.

Coal sample	Ultimate analysis, wt% daf						
	C	H	N	O	S	Cl	Pb ($\mu\text{g/g}$)
#1	51.6	3.89	1.03	43.5	1.61	0.02	35.9
#2	61.9	4.01	1.39	32.7	0.410	0.03	32.2

Table 3
Component analysis of the ash samples (%).

	#1	#2
SiO_2	51.7	23.0
Al_2O_3	21.7	53.0
Fe_2O_3	11.7	3.09
CaO	5.17	11.5
MgO	1.47	0.363
Na_2O	0.644	0.185
K_2O	2.23	0.439
The rest	6.42	8.46
Pb ($\mu\text{g/g}$)	168	155

2.2. Experimental method

Fig. 1 presents the schematic of the double-layer fixed-bed experimental system. The detailed parameters, working principles, and experimental procedures can be found in reference [27, 28]. During the experiment, 0.5 NL/min fed gas (N_2 for pyrolysis and 79% N_2 + 21% O_2 for combustion) entered the reactor from the top and flowed through two sample layers to the exit of the reactor. 1 g of coal was loaded into the upper layer to generate flue gas. 0.3 g of ash was loaded into the lower layer to interact with the flue gas. After 40 min of interaction, the residues in the upper layer and the ash in the lower layer were collected for testing and analysis. The contents of Pb and other minerals in the above samples were measured by using inductively coupled plasma atomic emission spectrometer (ICP-AES; Prodigy 7, Teledyne Leeman Laboratories, US) after digestion using HNO_3 -HF- H_2O_2 method. The detailed experimental procedure is similar to reference [28]. The experiment under each condition was repeated at least thrice for accuracy.

For each experiment, the amount of gaseous Pb released into the flue gas from coal layer ($m_{\text{Pb,g}}$, μg) was determined by Eq. (1).

$$m_{\text{Pb,g}} = m_{\text{coal}} \times C_{\text{Pb,coal}} - m_{\text{S}} \times C_{\text{Pb,S}} \quad (1)$$

where m_{coal} and m_{S} are the mass of coal and the residue after pyrolysis/combustion (g), respectively; $C_{\text{Pb, coal}}$ and $C_{\text{Pb, S}}$ are the Pb contents of the coal and residue ($\mu\text{g/g}$), respectively.

After interacting with the flue gas, the Pb content of the ash changed and a Pb release ratio R was determined by Eq. (2).

$$R = 1 - \frac{m_{\text{ash,p}} \times C_{\text{Pb,p}}}{m_{\text{ash,o}} \times C_{\text{Pb,o}}} \quad (2)$$

where $m_{\text{ash, o}}$ and $m_{\text{ash, p}}$ represent the mass of ash before and after the reaction (g), respectively, and $C_{\text{Pb, o}}$ and $C_{\text{Pb, p}}$ represent the Pb contents of the ash before and after the reaction ($\mu\text{g/g}$), respectively.

The thermal stability of Pb in ash was investigated by performing constant-temperature experiments on ash in N_2 and air atmospheres at 800–1000 $^\circ\text{C}$. To explore the effect of flue-gas components on the stability of Pb in ash, 1 g of pure cellulose was used to replace C and H in coal to generate the flue gas containing C_xH_y , CO_x and H_2O , and cellulose loaded with Na_2CO_3 was used to produce the flue gas containing gaseous Na. Besides, 2000 ppm SO_2 + N_2 , 200 ppm HCl + N_2 , 2000 ppm NO + N_2 , 2000 ppm NO_2 + N_2 , and 2000 ppm H_2S + N_2 were used as the simulated flue gas, respectively. The effect of the flue-gas components on the stability of Pb in ash was analyzed by examining the change in the Pb content of ash in the lower layer.

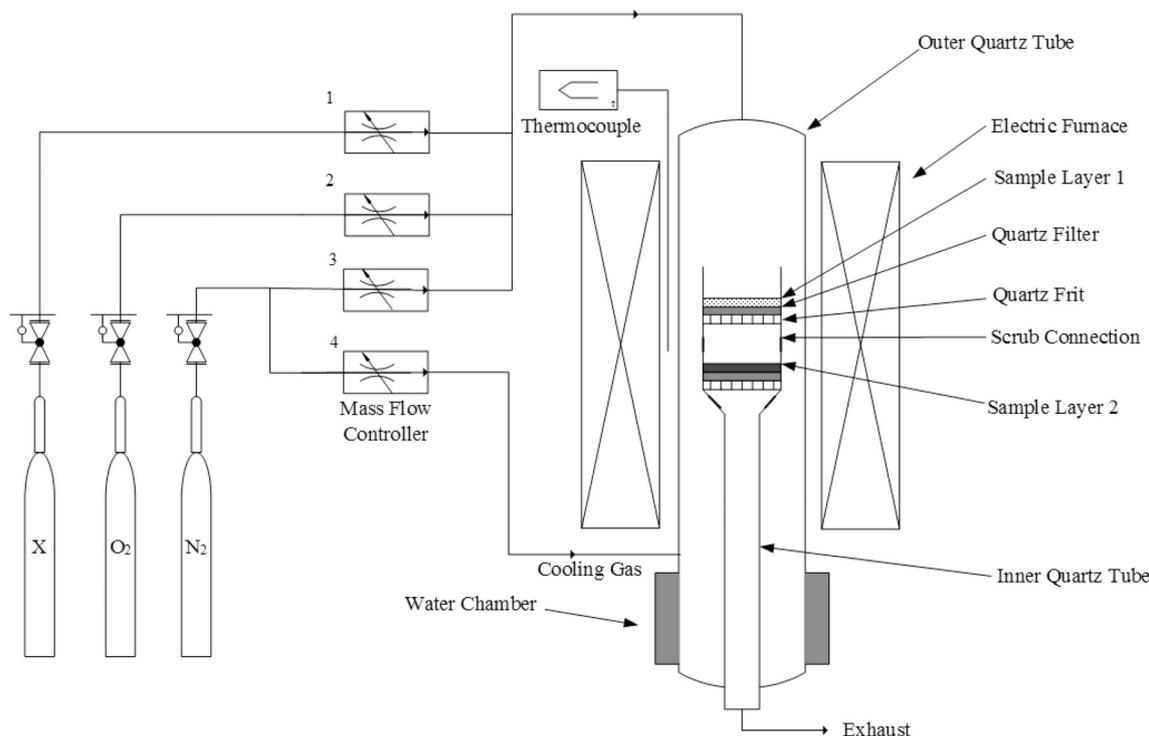


Fig. 1. Schematic of the double-layer fixed-bed experimental system. (X represents SO_2 , NO , NO_2 , HCl , or H_2S , used to investigate the effects of the main flue gas components on the stability of Pb in ash).

The melting characteristics of ash may affect the release of Pb. To analyze the melting of ash under various flue-gas conditions, the liquid phase ratio and crystallization ratio of the ash-slag system was calculated using the Equilib module of FactSage. Table 4 shows the composition of the reactant input. Among them, “#1, #2” were used to calculate the ash-slag system composed of an initial ash composition. “#1 + Na” and “#2 + Na” were used to calculate the influence of increasing the Na content on the ash-slag system. Furthermore, the Na content selected was consistent with that in ash under the action of the flue gas generated by coal #1 combustion. “#1 + Py” and “#2 + Py” were used to calculate the influence of pyrolysis products of organic matter on the ash-slag system. The quantity of CO and CO_2 was the same as that generated by pyrolyzing 1 g of cellulose at 1000 °C. Studies showed that the main gas constituents generated by the pyrolysis of 1 g of cellulose were 0.35 g of CO and 0.052 g of CO_2 [29].

3. Results and discussion

3.1. Transformation of Pb under the action of the combustion flue gas

3.1.1. Redistribution of Pb under the action of the combustion flue gas

Fig. 2 (a) and (b) show the amount of Pb released into the flue gas by coal combustion and the release ratio of Pb in ash under the action of the

Table 4
Composition of the reactant input.

	#1	#2	#1 + Na	#2 + Na	#1 + Py	#2 + Py
SiO_2	51.7	23.0	51.7	23	51.7	23.0
Al_2O_3	21.7	53.0	21.7	53	21.7	53.0
Fe_2O_3	11.7	3.09	11.7	3.09	11.7	3.09
CaO	5.17	11.5	5.17	11.5	5.17	11.5
MgO	1.47	0.363	1.47	0.363	1.47	0.363
Na_2O	0.644	0.185	0.789	0.24	0.644	0.185
K_2O	2.23	0.439	2.23	0.439	2.23	0.439
CO	/	/	/	/	94.6	91.6
CO_2	/	/	/	/	15.8	15.3

combustion flue gas, respectively.

Fig. 2(a) illustrates the amount of Pb released into the flue gas by coal combustion at 800–1000 °C. It can be seen that the amount of gaseous Pb released by coal combustion increased with the increase of temperature and coal #1 released a greater amount of gaseous Pb than coal #2. Under the action of the combustion flue gas, the release ratio of Pb in ash was shown in Fig. 2(b). The Pb content in ash changed little in most conditions, but under the action of the flue gas generated by coal #1 burned at 1000 °C, a significant reduction in the Pb content in ash #1 occurred (85%).

3.1.2. Influence of combustion flue gas components on Pb release

Pb may be released from ash due to its thermal instability, or due to the action of the flue gas. To investigate whether Pb in ash was stable in the thermal environment, we performed the experiments at 800–1000 °C in air atmosphere, without coal in the upper layer. The proportion of Pb released into the gas phase was less than 4.0%. Pb showed a good thermal stability in both ash types in the temperature range of 800–1000 °C. This suggests that the liberation of Pb from ash was not caused by its thermal instability, but rather by the action of the flue gas.

The action of the flue gas caused the release of Pb from ash, which may be due to the certain components in the flue gas. The main constituents of the flue gas generated by coal combustion are inorganic gases, including CO_2 , H_2O , SO_2 , NO , and NO_2 . Because the Pb content in ash under the action of the combustion flue gas decreased significantly only at 1000 °C, the experiment to investigate the influence of the main components was performed at 1000 °C. The flue gas generated by cellulose combustion was used to simulate the atmosphere of $\text{CO}_2 + \text{H}_2\text{O}$, and the atmosphere containing 2000 ppm $\text{SO}_2/\text{NO}/\text{NO}_2$ was formed by gas distribution, respectively. The change in the Pb content was investigated when the ash was maintained at 1000 °C for 40 min in these atmospheres. Table 5 lists the release ratio.

As observed in Table 5, under the action of the flue gas generated by cellulose combustion at 1000 °C, the release ratios of Pb in two types of

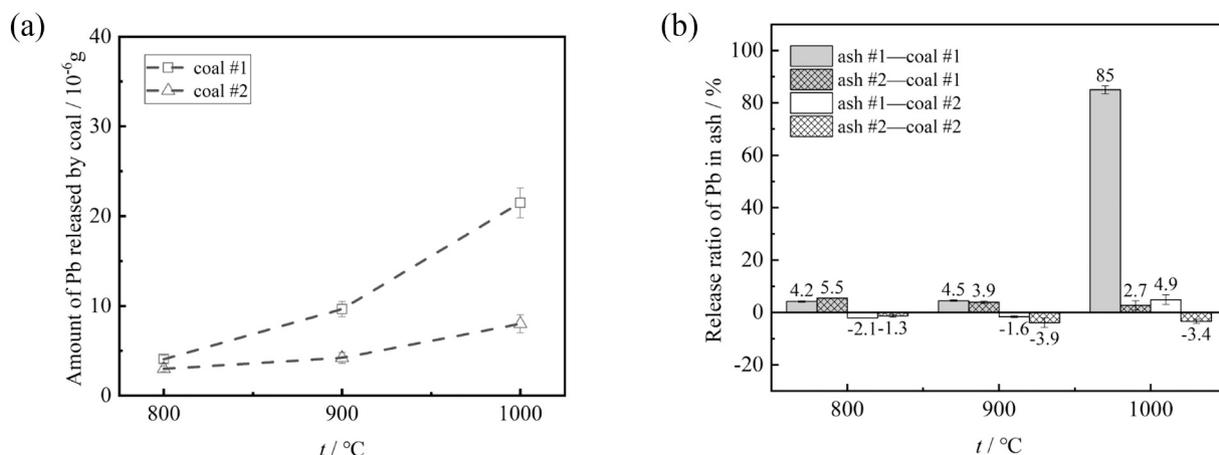


Fig. 2. Transformation of Pb in combustion atmosphere: (a) amount of Pb released by coal combustion; (b) release ratio of Pb in ash.

Table 5

Release ratio of Pb in ash under the action of main components of the combustion flue gas at 1000 °C.

Gas	Concentration	Ash #1	Ash #2
CO ₂ + H ₂ O	Flue gas generated by cellulose combustion	9.6%	1.7%
SO ₂	2000 ppm	2.2%	3.5%
NO	2000 ppm	0.95%	0.27%
NO ₂	2000 ppm	1.7%	0.71%

ash were 9.6% and 1.7%, respectively. With the addition of SO₂, NO, and NO₂, the release ratio of Pb in two types of ash was less than 3.5%, which was significantly less than that of ash #1 under the action of the flue gas generated by coal #1 combustion (85%). Therefore, CO₂, H₂O, SO₂, NO, and NO₂ in the combustion flue gas did not cause the massive release of Pb from ash #1.

3.1.3. Influence of gaseous Na on Pb release

Besides these inorganic gases, the combustion flue gas also contains trace amounts of gaseous mineral elements, such as gaseous Na [30]. In a previous study, we found that gaseous Na, especially in the forms of gaseous Na₂O and NaOH, can promote the release of As in ash by reacting with silicate aluminate in ash [28]. Similarly, 1 g of cellulose with a certain concentration of Na₂CO₃ was loaded in the upper layer and burned at 1000 °C to equalize the Na concentration to that in coal #1. A comparison of the change in the Pb content in two types of ash is shown in Table 6.

As shown in Table 6, Pb was liberated from ash under the action of the flue gas generated by cellulose with a certain concentration of Na₂CO₃ burned at 1000 °C. With an increase in the Na₂CO₃ concentration, the release ratio would also increase, and the effect of this increase on ash #1 was stronger than that on ash #2. In particular, when the concentration of Na₂CO₃ in cellulose was 0.50% (the equivalent concentration of Na was 0.22%), the content of Na in ash #1 increased to 0.59%, and the release ratio of Pb was as high as 80%. This trend was similar to the one under the action of the coal #1 combustion flue gas, where the Na content in ash #1 was 0.60% and the Pb decrease ratio 85%. This also applies to the trend observed for ash #2. The Na content in ash #2 was 0.20%, while the Pb decrease ratio was only 14%. Under

Table 6

Release ratio of Pb in ash under the action of the flue gas generated by combustion of cellulose with Na₂CO₃ at 1000 °C.

Concentration of Na loaded in cellulose	Ash #1	Ash #2
0.13%	19%	0.81%
0.22%	80%	14%

the action of the coal #1 combustion flue gas, the Na content in ash #2 was 0.18% and the Pb decrease ratio was 11%.

At 1000 °C, the effect of gaseous Na on ash #1 was significantly stronger than that on ash #2, which may be due to the high content of Al in ash #2. Entering into the macromolecular structure and crystal lattice of clay minerals by isomorphous substitution is an important form of Pb in ash [1]. Therefore, the destruction of the lattice structure by the melting of ash is not conducive to the stable existence of Pb in ash. Ash #2 has a high Al content and ash melting point. Despite a high content of gaseous Na in the flue gas, ash #2 almost does not melt at 1000 °C, and therefore liberate little Pb.

To analyze the melting phenomenon in two types of ash, we calculated their liquid phase ratios at 800–1500 °C using FactSage (Fig. 3).

As observed in Fig. 3, in the range of 800–1500 °C, the liquid phase ratio of ash #1 was significantly higher than that of ash #2. Ash #2 barely began to melt until 1400 °C, whereas the liquid phase ratio of ash #1 reached 12% at 900 °C. With the addition of 0.145% Na₂O, the ratio of liquid phase in ash #1 increased from 900 °C, whereas the effect on ash #2 did not appear until 1500 °C. Therefore, at 1000 °C gaseous Na significantly promoted the release of Pb from ash #1, whereas the effect on ash #2 was not noticeable.

From this analysis, we concluded that under the action of the high-temperature combustion flue gas, ash liberated Pb from ash by promoting the melting of ash through gaseous Na and breaking its lattice structure. Meanwhile, CO₂, H₂O, SO₂, NO, and NO₂ did not play a role in this process. This explains the results illustrated in Fig. 2. Under the action of the combustion flue gas, the content of Pb in the ash

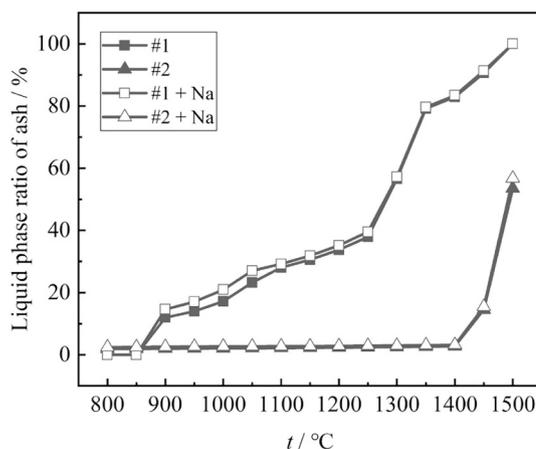


Fig. 3. Effect of Na on the liquid phase ratios of two types of ash at 800–1500 °C.

significantly reduced at 1000 °C because more gaseous Na was released by coal #1 burned at 1000 °C than other conditions [30–32]. The high Al content in ash #2 prevented it from melting in the combustion flue gas; therefore, the release ratio of Pb in ash #2 was much less than that in ash #1.

3.2. Transformation of Pb under the action of the pyrolysis flue gas

3.2.1. Redistribution of Pb under the action of the pyrolysis flue gas

In addition to the combustion atmosphere, we also studied the transformation of Pb in the pyrolysis atmosphere. The amount of Pb released into the flue gas by coal pyrolysis and the corresponding release ratio of Pb in ash were shown in Fig. 4.

Fig. 4(a) shows the amount of Pb released into the flue gas by coal pyrolysis at 800–1000 °C. Similar to combustion, the amount of gaseous Pb released by coal #1 was greater than that of coal #2. Moreover, the amount of Pb released by coal pyrolysis was much more than by its combustion.

Under the action of the pyrolysis flue gas, the release ratio of Pb in ash was shown in Fig. 4(b). Ash #1 lost some of its Pb content under all experimental conditions, and the reduction ratio can reach 76% at 800 °C and as high as 99% at 1000 °C. As for ash #2, the Pb content also decreased significantly at 900–1000 °C, and the reduction ratio was 65%–74% at 900 °C and up to 79%–83% at 1000 °C. But at 800 °C, the Pb content decreased by only 1.7%, and under the action of the flue gas generated by coal 1# pyrolysis even increased by 14%.

The adsorption of gaseous Pb by ash is explained as the presence of elements such as Si and Al in the ash [21,22]. However, the Pb content in both two types of ash decreased for most flue gases studied herein, albeit at different decrease ratios. In N₂ atmosphere without coal in the upper layer, the proportion of Pb released into the gas phase was less than 6.5%. Pb showed a good thermal stability in both ash types in the temperature range of 800–1000 °C. This suggests that the liberation of Pb from ash was not caused by its thermal instability, but rather by the action of the pyrolysis flue gas.

3.2.2. Influence of pyrolysis flue gas components on Pb release

The main constituents of the flue gas generated by coal pyrolysis included CO, H₂, CO₂, H₂O, HCl, and H₂S. Under the action of the pyrolysis flue gas, the Pb content in ash significantly decreased at 800–1000 °C. Therefore, the experiment was carried out to explore the influence of the main constituents of the pyrolysis flue gas on Pb release from ash at 800–1000 °C. The flue gas generated from cellulose pyrolysis was used to simulate the atmosphere of CO + H₂ + CO₂ + H₂O, and the atmosphere containing 200 ppm HCl or 2000 ppm H₂S was formed by gas distribution, respectively. The changes in the Pb content of ash #1 and #2 were investigated after heating them for 40 min in the above

atmospheres. We found two types of ash liberated different amounts of Pb and the release ratios were listed in Table 7.

As shown in Table 7, under the action of the flue gas generated by the pyrolysis of 1 g of cellulose, both types of ash released a significant amount of Pb. The release ratio varied with temperature, which was consistent with that under the action of the coal-pyrolysis-generated flue gas and reached its maximum at 1000 °C. The release ratio of Pb in ash #1 reached 62% at 800 °C, and further increased to 100% at 900–1000 °C. However, the release ratio of Pb in ash #2 was only 5.2% at 800 °C, which rapidly increased to 65% at 900 °C and up to 80% at 1000 °C. This indicates that the reducing constituents in the organic-pyrolysis-generated flue gas can cause a large amount of Pb release from ash.

3.2.3. Mechanism of Pb release under the action of the pyrolysis flue gas

Previous studies showed that the reducing atmosphere decreased the melting point of ash by influencing the valence state of Fe in it. In a weakly reducing atmosphere, a few Fe³⁺ ions can be reduced to Fe²⁺, which can bond with the unsaturated O²⁻ in ash and destroy the network structure, thus lowering the melting point. Meanwhile, Fe²⁺ easily interacts with Al₂O₃ to generate numerous low-melting-point Fe spinel (FeAl₂O₄), further reducing the melting point [33,34]. Therefore, we calculated the influence of pyrolysis products of organic matter on the ash-slag system by FactSage. Fig. 5 displays the results.

As shown in Fig. 5, the reducing gas significantly promoted the melting of two types of ash, which not only increased the proportion of the liquid phase in ash at the same temperature but also decreased the melting point of ash. The initial melting temperature of ash #1 decreased by 50 °C, and that of ash #2 by 100 °C. This also indicates that CO and other reducing gases generated by the pyrolysis of the organic structure caused a massive Pb release from ash via promoting the

Table 7

Release ratio of Pb in ash under the action of the main constituents of the pyrolysis flue gas at 800–1000 °C.

Atmosphere	Temperature/°C	Release ratio of Pb	
		Ash #1	Ash #2
Cellulose pyrolysis	800	62%	5.2%
	900	100%	65%
	1000	100%	80%
200 ppm HCl + N ₂	800	57%	2.5%
	900	56%	1.0%
	1000	65%	43%
2000 ppm H ₂ S + N ₂	800	53%	9.2%
	900	95%	71%
	1000	98%	73%

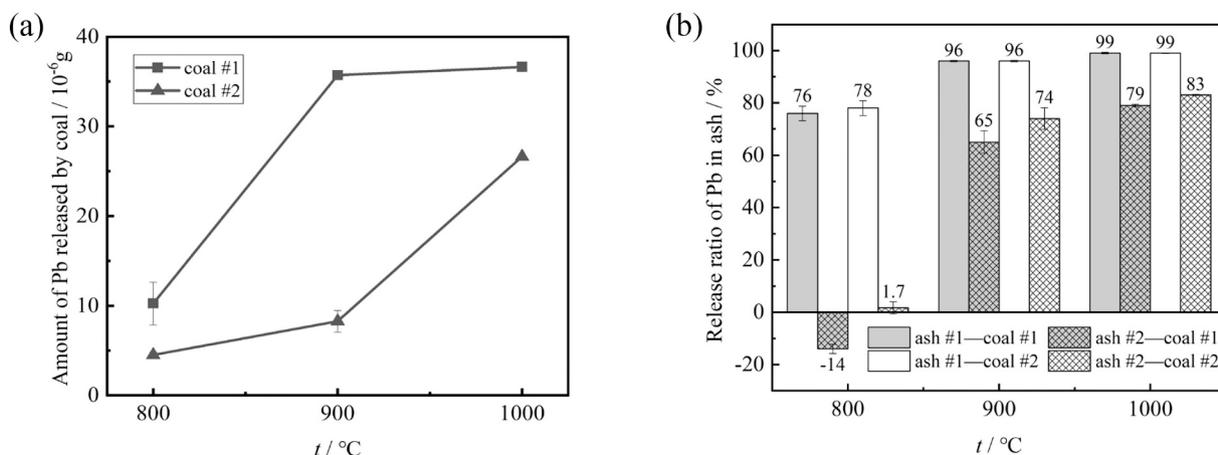


Fig. 4. Transformation of Pb in pyrolysis atmosphere: (a) amount of Pb released by coal pyrolysis; (b) release ratio of Pb in ash.

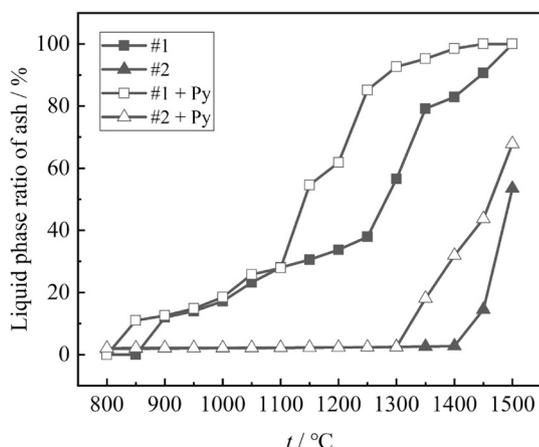


Fig. 5. Effect of reducing gases on the liquid phase ratios of two types of ash at 800–1500 °C.

melting of ash.

In addition, as shown in Table 7, HCl and H₂S also promoted the release of Pb from ash. In the presence of 200 ppm HCl, both types of ash liberated a certain amount of Pb. However, the release ratio of ash #1 was 56–65%, while that of ash #2 was only 1.0–43%, which was significantly less than that under the action of the flue gas generated by the pyrolysis of coal and cellulose. In the presence of 2000 ppm H₂S, the release ratios of both types of ash were similar to those in the flue gas generated by the pyrolysis of coal and cellulose. At 1000 °C, the release ratios of Pb in ash #1 and ash #2 reached 98% and 73%, respectively. Related studies showed that HCl and H₂S promoted Pb release from ash by forming PbCl₂ and PbS, which were more volatile [35,36].

Irrespective of the flue gas generation method (coal/cellulose or H₂S), each type of ash had the same maximum release ratios. However, the maximum release ratios of Pb in two types of ash were different. The release ratio of Pb in ash #1 was 98–100% at 1000 °C, whereas that of ash #2 was 73–79%. This indicates that in a pyrolysis atmosphere, the release ratio of Pb in two types of ash depended on the form of Pb in ash. Pb in the ash is mainly embedded in the macromolecular structure and the clay mineral lattice by isomorphous substitution. There are two primary modes of action of the high-temperature pyrolysis flue gas that can cause the liberation of Pb. One is to reduce the melting point of ash through the reducing gas generated by the pyrolysis of organic matter, destroying the crystal lattice and causing the release of Pb. The other is the reaction between acidic gases (HCl and H₂S) and Pb in the crystal lattice to generate PbCl₂ and PbS with lower boiling points. The effect of H₂S is more pronounced.

The above reasoning can well explain the results in Fig. 4. The pyrolysis flue gases of two types of coal contain reductive components that can promote the melting of ash, and thus significantly promote the release of Pb. Under the action of the same pyrolysis flue gas, ash #1 liberated a significant amount of Pb at a lower temperature than ash #2 owing to the high Al content in the latter. That is, ash with high Al content is difficult to melt and therefore cannot liberate much Pb. Under the action of the flue gas generated by the pyrolysis of coal #1 at 800 °C, ash #2 gained more Pb. This was because the amount of gaseous Pb released by coal was relatively high, and ash #2 adsorbed a certain amount of gaseous Pb. Meanwhile, ash #2 mostly remained unmolten and retained most of the Pb content. We emphasize that although the pyrolysis constituents of two types of coal were different, the decrease ratio of Pb in ash at 1000 °C did not change with the flue gas generation method. This was mainly because the pyrolysis-generated flue gas for two types of coal provided an adequate reducing atmosphere for the release of Pb from the crystal lattice into the gas phase.

4. Conclusions

In the combustion flue gas, the changes of Pb content in ash were less than 5.5% in most conditions, but the Pb in one kind of ash was reduced by 85% at 1000 °C. The constant temperature experiments demonstrated the high thermal stability of Pb in ash. Moreover, CO₂, H₂O, SO₂, NO, and NO₂ cannot liberate Pb from ash. Under the action of the flue gas generated by Na₂CO₃-loaded cellulose combustion at 1000 °C, Pb significantly released from ash. The melting phenomenon analysis by FactSage revealed that gaseous Na in the combustion flue gas was an important constituent to promote the melting of ash and thus cause Pb release from ash.

In the pyrolysis flue gas, gaseous Pb adsorption by ash was also prominent only when the flue gas contained a high concentration of gaseous Pb and the ash was nearly non molten. In other cases, significant Pb release from ash occurred. The reduction ratios of Pb in both types of ash were as high as 99% and 83%, respectively. The reducing atmosphere was found to significantly promote the release of Pb from ash by promoting the melting of ash. In addition, H₂S and HCl in the pyrolysis flue gas also significantly promoted the release by generating more volatile compounds (PbS and PbCl₂), with H₂S having a more significant effect. Irrespective of the pyrolysis flue gas generation method, each type of ash had the same maximum release ratio, and the maximum release ratios of Pb depended on the form of Pb in ash.

The mechanism of Pb release from ash under the action of the high-temperature flue gas is meaningful to understand the transformation pathways of Pb in coal-fired systems and develop Pb emission control techniques, such as low Pb emission by combustion of blended coals.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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