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## Fuel





# Full Length Article Study on the chemical adsorption of gaseous As<sub>2</sub>O<sub>3</sub> by ash



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### ABSTRACT

Arsenic (As) transformation during flue-gas cooling process determines terminal As emission. In this study, the dominant role of chemical adsorption in gaseous As transformed to ash was confirmed. Dynamic curves of  $As_2O_3$  adsorption by ash at 500–900 °C were obtained. The adsorbed As amount increased linearly with time, far from reaching saturation, and the maximum amount was approximately 10 times the As content in ash collected from power plant dust collectors, indicating that the actual capacity of ash was far higher. Analysis of As form and elemental distribution directly proved that chemical adsorption by ash was mainly through the joint action of Ca and Fe, and its correlation with other components was weak. At 500–900 °C, as temperature increased, the amount of As adsorbed by CaO gradually increased, whereas that of Fe<sub>2</sub>O<sub>3</sub> first increased and then decreased. Therefore, as temperature increased, the amount of As adsorbed by ash with high Fe content first increased and then decreased, reaching a maximum at 800 °C °C, whereas that of ash with higher Ca content kept increasing. The strong adsorption capacity of ash with high Ca and Fe contents helps reduce terminal As emission.

#### 1. Introduction

Coal will still occupy an important position in China's energy structure, and the environmental problems caused by coal combustion cannot be ignored. As conventional pollutants such as SO<sub>2</sub>, NOx, and particulate matter from coal-fired power plants have achieved ultra-low emissions, the emission of unconventional pollutants, such as trace elements, has received more attention [1]. Arsenic (As) is the most toxic trace element in coal [2-4]. It has strong teratogenic, carcinogenic, and mutagenic effects on the human body, and also destroys ecological stability [5]. Coal-fired installations are one of the main sources of atmospheric As emissions, accounting for 74.2% of the total annual emissions in China [6,7]. The United States and other countries have stipulated emission limits for toxic trace elements, such as As in coalfired power plants, in their air pollutant emission standards [8]. The emission characteristics of As from coal-fired flue gas depend on the transformation of As in coal-fired systems. Therefore, understanding the transformation of As plays an important role in guiding the development of control technologies.

Field tests on the distribution of As in coal-fired power plants found that less than 5% of As was distributed in the bottom slag after coal burning, whereas more than 95% of As was released into high-

temperature flue gas [10–13]. There are two forms of As in hightemperature flue gas: gaseous As and particulate As in fly ash. The majority of particulate As can be removed by the dust collector and desulfurization devices, and only a small amount of gaseous As can be removed [9–13]. Therefore, promoting the conversion of gaseous As to particulate As is beneficial for the coordinated removal of As via dust collector and desulfurization devices, thus reducing the emission of As.

The transformation of As in coal-fired systems can be divided into two stages: high-temperature combustion and post-combustion flue-gas cooling. Laboratory studies have shown that the majority of As is released into high-temperature flue gas in the form of gaseous As after high-temperature combustion [14–16]. Gaseous As exists mainly in the form of As<sub>2</sub>O<sub>3</sub> [13,17,18]. Therefore, numerous researchers have attempted to use minerals to adsorb As<sub>2</sub>O<sub>3</sub>. Yu et al. [18] compared the adsorption capacities of CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> for As<sub>2</sub>O<sub>3</sub> at 500–900 °C, and found that CaO had the strongest adsorption capacity, followed by Fe<sub>2</sub>O<sub>3</sub>. Sterling et al. [20] found that CaO, Ca<sub>2</sub>SiO<sub>4</sub>, and CaSiO<sub>3</sub> could effectively adsorb As<sub>2</sub>O<sub>3</sub> at 600–1000 °C. Chen et al. [21] found that the degree of reaction between CaO and As<sub>2</sub>O<sub>3</sub> at medium –high temperatures gradually increased with the increase in temperature until the sintering of CaO at 900 °C when the adsorption of As was significantly inhibited. However, Song et al. [22] found that both CaO

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#### Table 1

The component analysis of the ash samples (%).

-		-		
	S1 ash	S2 ash	A1 ash	A2 ash
SiO <sub>2</sub>	31.9	51.4	49.5	50.3
Al <sub>2</sub> O <sub>3</sub>	19.9	31.2	26.9	21.0
Fe <sub>2</sub> O <sub>3</sub>	5.43	8.08	11.1	11.3
CaO	2.71	2.55	5.66	9.52
MgO	0.437	0.966	1.33	1.21
Na <sub>2</sub> O	0.328	0.240	0.519	1.37
K <sub>2</sub> O	0.934	1.67	1.98	2.67
As(µg/g)	4.13	6.79	4.46	4.36
The rest	38.4	3.89	3.01	2.63

and CaSO<sub>4</sub> could adsorb As<sub>2</sub>O<sub>3</sub> at 1000–1300 °C, and with an increase in temperature, the adsorption amount of CaO gradually increased, whereas that of CaSO<sub>4</sub> gradually decreased. The adsorption products of CaO and CaSO<sub>4</sub> were considered to be Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> [21,22]. Besides,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was also found to significantly adsorb As<sub>2</sub>O<sub>3</sub>, and As in the adsorption product mostly existed in the form of arsenate [23,24]. Zhang et al. [25] found that Fe<sub>2</sub>O<sub>3</sub> and Fe-rich magnets separated from fly ash could significantly adsorb As<sub>2</sub>O<sub>3</sub> at 600–900 °C, and the adsorption capacity of Fe<sub>2</sub>O<sub>3</sub> was significantly stronger than that of CaO and Al<sub>2</sub>O<sub>3</sub>.

The above-mentioned studies show that Ca-based minerals,  $Fe_2O_3$ and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can adsorb As<sub>2</sub>O<sub>3</sub>, and that the ash contains Ca, Fe, Al, and other mineral components, which may have the ability to adsorb gaseous As<sub>2</sub>O<sub>3</sub>. Researchers have also studied the adsorption of gaseous As<sub>2</sub>O<sub>3</sub> by fly ash. Qin et al. [26] separated the Ca- and Fe-rich fly ash by gravity flotation, conducted an adsorption experiment at 300–900 °C, and found that As<sub>2</sub>O<sub>3</sub> could be effectively adsorbed. Zhang et al. [27] analyzed the correlation between the adsorption amount of As<sub>2</sub>O<sub>3</sub> at 400 °C and 600 °C, the physical properties of the fly ash, and the contents of CaO and Fe<sub>2</sub>O<sub>3</sub> in the ash. It was found that the adsorption amount at 400 °C had no correlation with the contents of CaO and Fe<sub>2</sub>O<sub>3</sub>, which means that the adsorption at 400 °C was a physical adsorption. The adsorption amount at 600 °C had a certain correlation with the content of CaO and Fe<sub>2</sub>O<sub>3</sub>, which indicates that the adsorption at 600 °C was a chemical adsorption. However, it was not completely monotonic and may have been affected by other minerals. Li et al. [28] performed valence and binding state analyses of As in the three fly ash adsorption products of As<sub>2</sub>O<sub>3</sub> at 900 °C, and found that the As in the adsorption. The analysis of the binding state of As showed that both Ca-bound and Fe/Al-bound As were present in the ash by sequential chemical extraction.

During the cooling process of flue gas, gaseous As can transform to a particulate state through adsorption by ash or condensation on the ash surface. Ji et al. [29] conducted coal combustion experiments with a sedimentation furnace experimental system and found that more than 60% of the As in the collected submicron fly ash was formed by gas–solid transformation during the cooling process of flue gas.

Previous studies have demonstrated that ash can effectively adsorb gaseous  $As_2O_3$ . The correlation analysis indicated that there was a certain correlation between the adsorption amount and the contents of Ca and Fe, however, it was not completely monotonic and may have been related to other components. The binding state analysis of As in the ash after adsorption by sequential chemical extraction showed that the As generated by ash adsorption had various forms, including Ca-bound and Fe/Al-bound As [28]. The main mechanism of gaseous  $As_2O_3$ adsorption by ash during the cooling process of coal-fired flue gas remains unclear, and the adsorption characteristics require further study. Therefore, this study focuses on the adsorption of gaseous  $As_2O_3$  by ash



Fig. 1. As<sub>2</sub>O<sub>3</sub> adsorption experimental system.



Fig. 2. Thermal stability of As in ash collected from dust collectors.



Fig. 3. Dynamic adsorption process of gaseous As<sub>2</sub>O<sub>3</sub> by A1 ash.

during the cooling process of coal-fired flue gas. First, the thermal stabilities of As in the ash samples collected from the power plant dust collectors were analyzed to clarify the dominance of chemical adsorption in the transformation of gaseous As during the cooling process of coal-fired flue gas. Then, the adsorption experiment of gaseous As<sub>2</sub>O<sub>3</sub> was conducted at 500–900 °C, and the dynamic adsorption curves at each temperature were obtained. The adsorption ratio and capacity of the ash were analyzed. The chemical adsorption mechanism of gaseous As<sub>2</sub>O<sub>3</sub> by ash was revealed by comparing the adsorption characteristics of ash and minerals, combined with the analysis of As speciation and the element distribution in the adsorption product.

#### 2. Experimental procedure

#### 2.1. Sample preparation

In this study, four types of ash collected from dust collectors at four different power plants were used. The ash samples were screened in the size range of 74–96  $\mu$ m using a vibrating screen, placed in an oven at 105 °C for 10 h, sealed, and stored. Two types of ash (S1–S2) with higher



Fig. 4. Amount of As adsorbed by different ash samples at different temperatures (adsorbed for 45 min).



Fig. 5. Amount of As adsorbed by minerals at different temperatures (adsorbed for 45 min).

As content were selected for the thermal stability experiment of As in the ash. Two types of ash with relatively low As contents and significant differences in mineral content were selected for the  $As_2O_3$  adsorption experiment. The ash was pretreated by heating at 1000 °C to avoid the influence of the thermally unstable release of the original As in the ash on the adsorption experiments. Compositional analysis of the four ashes was performed using X-ray fluorescence spectroscopy (XRF; ARL PERFORM' X, Thermo Fisher Scientific, USA), and the results are shown in Table 1. As shown in Table 1, the Fe contents in A1 and A2 ash were similar, however, the Ca content in A2 ash was considerably higher, which was almost twice that of A1 ash.

The specific surface area and pore structure of the A1–A2 ash were determined using a nitrogen adsorption apparatus (ASAP 2020, Micrometrics, USA). The BET specific surface area of A1 ash was larger, which was  $2.23 \text{ m}^2/\text{g}$ , and that of A2 ash was  $1.09 \text{ m}^2/\text{g}$ .

KOH (CAS: 1310–58-3) and KBH<sub>4</sub> (CAS: 13762–51-1) used to generate  $As_2O_3$  were obtained from Sinopharm Chemical Reagent Co., ltd. Among them, KOH was analytically pure, with a purity of  $\geq$  90%,



Fig. 6. XPS results of As in the adsorption products of A1 ash at 700  $^\circ\text{C}.$ 



Fig. 7. XPS results of As in the adsorption products of CaO at 700 °C.

and KBH<sub>4</sub> was of analytical grade, with a purity of 97%. NaAsO<sub>2</sub> (CAS: 7784–46-5) was produced by Sigma-Aldrich Company, and its purity was  $\geq$  90%. To further analyze the main mechanisms by which ash adsorbs gaseous As<sub>2</sub>O<sub>3</sub> at various temperatures, two typical minerals, CaO (CAS: 1305-78-8) and Fe<sub>2</sub>O<sub>3</sub> (CAS: 1309-37-1), were used for the adsorption experiments. The minerals were analytically pure and were produced by Shanghai Macklin Biochemical Technology Co., Ltd.

#### 2.2. Experimental setup

Because  $As_2O_3$  cannot be purchased owing to its high toxicity, gaseous  $As_2O_3$  cannot be directly generated by evaporation. Generating  $AsH_3$  through the reaction of  $NaAsO_2$  solution and  $KBH_4$  solution at room temperature, and then oxidizing  $AsH_3$  to  $As_2O_3$  at a high temperature is a common method to generate gaseous  $As_2O_3$  [25]. This method was used in this work to generate a simulated flue gas containing  $As_2O_3$ . The adsorption experiment for  $As_2O_3$  was performed using the experimental system shown in Fig. 1.

As shown in Fig. 1, the experimental system can be divided into two parts: generation of  $AsH_3$  and generation and adsorption of  $As_2O_3$ . The generation of  $AsH_3$  part includes peristaltic pump, gas–liquid separator, reagent bottle, and pump tube. Three reagent bottles were filled with

0.25% KOH + 0.5% KBH<sub>4</sub>, 1% HCl + 100 ppm NaAsO<sub>2</sub>, and 10% HCl, respectively. The three solutions were stably pumped using a peristaltic pump at a rate of 1 mL/min, and the solutions were mixed and reacted in a 4 m long pump tube to generate AsH<sub>3</sub> and H<sub>2</sub>. The pump pipe led the generated gas and waste liquid after reaction into the gas–liquid separator, and AsH<sub>3</sub> and H<sub>2</sub> were transported into the vertical electric furnace under a carrier gas of 500 mL/min 6% O<sub>2</sub> + 94% N<sub>2</sub>.

The generation and adsorption of As<sub>2</sub>O<sub>3</sub> were performed in a vertical electric furnace. The heating furnace was a three-stage electric furnace with an independent temperature control. A constant-temperature zone of the upper electric furnace was used to oxidize AsH3 and H2 to generate As<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O. The upper constant temperature zone was set at 700 °C because As<sub>2</sub>O<sub>5</sub> could be completely decomposed into As<sub>2</sub>O<sub>3</sub> at this temperature [30]. The constant-temperature zone in the middle was used to adjust the gas temperature, which could be cooled or heated, and was not specially set. The concentration of gaseous As<sub>2</sub>O<sub>3</sub> in the simulated flue gas was 18.84 ppm. A lower constant-temperature zone was used for the adsorption of As<sub>2</sub>O<sub>3</sub>. The reactor consisted of a quartz outer tube and a quartz inner tube, and a rubber stopper was used to seal the inner and outer tubes. A movable quartz basket was placed at the end of the quartz inner tube, and the quartz basket and the inner tube were sealed through a frosted port. The inner diameters of the quartz outer tube and basket were 45 mm and 35 mm, respectively. The quartz basket was located in the constant-temperature zone of the furnace, and the bottom of the basket was equipped with a quartz frit and a high-purity quartz filter (MK360, Munktell, Sweden) to accumulate the material.

#### 2.3. Method

The adsorption experiments were conducted at 500–900 °C with 500 mL/min of 94%  $N_2$  + 6%  $O_2$  carrier gas. When both the upper and lower constant temperature zones in the electric furnace rose to the set temperature, the peristaltic pump was turned on, filling the pump tube with the reaction solution, and  $As_2O_3$  was generated. After 10 min, when the atmosphere in the reactor was stable, quickly put into the quartz basket containing 0.3 g of ash or minerals, holding for 15, 30, 45, 60, or 75 min, quickly removed, cooled to room temperature, and weighed, collected, and sealed for subsequent analysis. Each operating point was repeated at least 3 times.

The thermal stability analysis experiment of As in ash was conducted at 120–1000  $^{\circ}$ C, and 500 mL/min N<sub>2</sub> was fed directly from the upper end of the vertical electric furnace without connecting the peristaltic pump. When the reactor temperature increased to the set temperature, the ash sample was put in and heated for 1 h. The contents of As in the ash before



(b) As 2*p* 

Fig. 8. XPS results of As in the adsorption products of Fe<sub>2</sub>O<sub>3</sub> at 700 °C.

and after heating were compared, and the thermal stability of As in the ash was determined.

Before measuring the As content of the solid samples, the samples were pretreated. The solid samples were pre-treated using a microwave digester (ETHOS UP, Milestone, Italy). Approximately 50 mg of the solid sample was weighed and digested under pressure at 240 °C for 40 min. The acid used for digestion was a mixture of 10 mL of HNO<sub>3</sub>, 1 mL of HF, and 1 mL of H<sub>2</sub>O<sub>2</sub>. After digestion, the digestion solution was heated at 170 °C for 2–3 h to remove acid until the liquid volume reached the size of soybeans. After acid removal, it was cooled to room temperature, and the volume was adjusted to 50 mL with deionized water, which was reserved for subsequent analysis. The As content was measured using atomic fluorescence spectrometry (AFS; AFS-9320, Jitian, China).

The binding energy of As in the adsorption products was analyzed using X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi, Thermo Fisher Scientific, UK). The elemental distributions of the samples were microscopically observed using electron probe microanalysis (EPMA; JXA8230, JEOL, Japan).

In the thermal stability experiment of As in ash, the As release ratio R was determined by comparing the As content in the ash samples before and after heating, which was determined by Eq. (1).

$$R = 1 - \frac{m_a \times c_a}{m_b \times c_b} \tag{1}$$

where  $m_b$  and  $m_a$  represent the mass of the ash before and after heating (g), respectively, and  $c_b$  and  $c_a$  represent the As content of the ash before and after heating ( $\mu g/g$ ), respectively.

#### 3. Results and discussion

#### 3.1. Adsorption characteristics of gaseous As<sub>2</sub>O<sub>3</sub> by ash

During the cooling process of coal-fired flue gas, gaseous As released from coal combustion can be transformed into ash by chemical adsorption or physical migration. As that transforms to ash by condensation or physical adsorption has poor thermal stability and is easily released when heated at a lower temperature, while As that is cured into ash by chemical adsorption has good thermal stability and needs to be heated to a higher temperature for release. Thermal stability experiments were carried out on two ashes collected from two power plants to explore the main pathway of As transformation during the flue gas cooling process. The release ratios of As in the two ashes at 120–1000 °C are shown in Fig. 2.

As shown in Fig. 2, the thermal stability of As in the two ashes was similar, and the change in the release ratio could be divided into two intervals. Below 800 °C, the release ratio of As in the ash was basically unchanged, which was in the range of 5%–8%. More than 90% of As was not released when the heating temperature was below 800 °C. The release ratio of As in S1 ash started to increase significantly after 900 °C, and the release ratio was 15% at 1000 °C. The release ratio of As in S2 ash started to increase at 800 °C, and as the temperature increased to 1000 °C, the release ratio of As in ash increased to 25%.

The As that can be released by heating at 120 °C can only transform from the gas phase to the ash through condensation or physical adsorption, and this part of As accounted for approximately 5%–8%. As







# (b)As 2*p*

Fig. 9. XPS results of As in the adsorption products of A1 ash at 900 °C °C.

the temperature rose above 800 °C, 10%-20% of As in the ash was released into the gas phase. This part of the As should be captured by chemical adsorption, however, the generated adsorption product is unstable at high temperatures. Furthermore, more than 80% of As in the ash had good thermal stability and could not be released even when heated at 1000 °C. This part of As may transform from the gas phase to ash through chemical adsorption during the cooling process or may be retained in the ash during coal combustion. Although it was impossible to determine the specific proportion of As in this part of As that transformed from the gas phase to the ash through chemical adsorption during the cooling process, studies have shown that most of the As in coal can be released into the gas phase after high-temperature combustion [31]. Furthermore, As in the ash was mainly generated by the transformation of gaseous As to the solid phase during the cooling process of coal-fired flue gas [32]. Therefore, it can be considered that most of the As was transformed from the gas phase to the ash by chemical adsorption during the cooling process. This indicates that chemical adsorption was the main route of gaseous As transformation during the cooling process of the coal-fired flue gas, and the As in the adsorption product existed in various forms with different thermal stabilities.

The adsorption experiment of A1 ash on gaseous  $As_2O_3$  was conducted in the 500–900 °C temperature range, and the dynamic adsorption curves were obtained, as shown in Fig. 3.

It can be seen in Fig. 3 that A1 ash had obvious adsorption capacity to gaseous  $As_2O_3$  in the 500–900 °C temperature range. At the same adsorption temperature, during the adsorption process of 75 min, the adsorption amount of A1 ash to gaseous  $As_2O_3$  increased approximately linearly with increasing adsorption time, which indicated that the maximum adsorption capacity of ash to gaseous  $As_2O_3$  was substantially higher than that observed in the experiment (294 µg/g). The adsorption behavior observed in the experiment was in the early stage of adsorption. In addition, it can be seen in Fig. 3 that under the same adsorption time, with an increase in adsorption temperature, the amount of As adsorbed by A1 ash first increased, then decreased, and finally peaked at 800 °C. This shows that some of the adsorption products in the ash were unstable and may decompose above 800 °C; therefore, the amount of As adsorbed by the ash will decrease when the temperature was higher.

In this experiment, the concentration of gaseous As<sub>2</sub>O<sub>3</sub> was 18.85 ppm, the mass of ash was 0.3 g, and the mass ratio of gaseous As<sub>2</sub>O<sub>3</sub> to ash was  $2.54 \times 10^{-4}$ . In the actual coal-fired flue gas, it was assumed that the mass of ash produced by 1 kg of coal was 0.225 kg, and the concentration of As in the coal was  $10 \,\mu g/g$ , all of which were released into the flue gas after combustion. The mass of gaseous As<sub>2</sub>O<sub>3</sub> generated was 0.0132 g, and the mass ratio of gaseous As<sub>2</sub>O<sub>3</sub> to ash was  $5.87 \times 10^{-5}$ . Compared with the experimental conditions, the concentration of ash in the real coal-fired flue gas was higher than that of gaseous As<sub>2</sub>O<sub>3</sub>, and the ash was far in excess. In addition, the maximum amount of As adsorption by ash observed in this experiment was 294  $\mu$ g/g ash, which was more than 10 times the content of As in the ash collected from the dust collector of the power plant. It also showed that the adsorption capacity of gaseous As by the ash in actual coal flue gas was far excess. Therefore, the adsorption of gaseous As<sub>2</sub>O<sub>3</sub> by ash in the actual coalfired flue gas was not limited by the saturated adsorption capacity of ash, and was always in the initial stage of adsorption, and the degree of gaseous As adsorption by ash was limited by the mass transfer and surface reaction kinetics.

#### 3.2. Mechanism of gaseous As<sub>2</sub>O<sub>3</sub> chemical adsorption by ash

#### 3.2.1. Comparison of ash and mineral adsorption characteristics

To analyze the mechanism of gaseous  $As_2O_3$  adsorption by ash, this section compares the adsorption characteristics of two ash samples with different mineral compositions. The Fe contents in the A1 and A2 ash were similar, but the Ca content in A2 ash was significantly higher than that in the A1 ash. After the two types of ash adsorption at 500–900 °C for 45 min, the amounts of As adsorbed by ash at different temperatures were measured, as shown in Fig. 4.

As shown in Fig. 4, there were significant differences between the adsorption characteristics of the two ashes. In the 500–600°C temperature range, the increase in the amounts of As adsorbed by A1 and A2 ash was similar, and the adsorption amount of A1 ash was slightly higher than that of A2 ash. In the 600–800 °C temperature range, with the increase in adsorption temperature, the amount of As adsorbed by both ashes gradually increased, however, the increase in the adsorption amount of A1 ash was significantly higher than that of A2 ash. In the 800–900 °C temperature range, with an increase in the adsorption temperature, the amount of A3 ash was significantly higher than that of A2 ash. In the 800–900 °C temperature range, with an increase in adsorption temperature, the amount of As adsorbed by A1 ash began to decrease, while the amount of As adsorbed by A2 ash began to increase significantly. The difference in the adsorption characteristics of the two types of ash could be related to the different minerals compositions in the ash. Therefore, the adsorption characteristics of the main minerals that adsorb As<sub>2</sub>O<sub>3</sub> in ash will be studied next.



Fig. 10. Electron probe microanalysis of the adsorption products of A1 Ash at 700 °C.

#### Table 2

The elemental quantitative analysis results of points in the As-enriched region (wt%).

	Ca	Fe	0	As	S	The rest
1	39	1.2	5.1	53	-	1.7
2	0.84	23	42	8.5	_	26
3	18	-	45	32	2.1	2.9

The adsorption of  $As_2O_3$  by ash occurs primarily through the action of its intrinsic minerals. Relevant studies have shown that Ca and Fe have adsorption effects on As. To analyze the main mechanism of  $As_2O_3$ adsorption by ash at various temperatures, two typical minerals, CaO and Fe<sub>2</sub>O<sub>3</sub>, were selected for the adsorption experiment. In the temperature range of 500–900 °C, the amounts of As adsorbed by the minerals are shown in Fig. 5. As shown in Fig. 5, both minerals had a strong adsorption capacity for gaseous As<sub>2</sub>O<sub>3</sub>; however, there were significant differences in the adsorption characteristics of different minerals for gaseous As<sub>2</sub>O<sub>3</sub>. In the 500–800 °C temperature range, the amount of As adsorbed by CaO and Fe<sub>2</sub>O<sub>3</sub> increased gradually with adsorption temperature. In the 800–900 °C temperature range, with an increase in adsorption temperature, the amount of As adsorbed by CaO further increased, while the amount of As adsorbed by Fe<sub>2</sub>O<sub>3</sub> began to decrease.

Combined with the results in Fig. 4, it can be seen that the trend of As adsorbed by A1 ash with temperature was consistent with that of Fe<sub>2</sub>O<sub>3</sub>; both increased first, then decreased, and finally peaked at 800 °C, while the adsorption amount by A2 ash increased with temperature, which was consistent with that on CaO. This may be because when the temperature increased from 800 °C to 900 °C, the adsorption capacity of Ca increased, and the adsorption capacity of Fe decreased. The Ca content in the A2 ash was higher, and the increase in the adsorption capacity of



Fig. 11. Electron probe microanalysis of the adsorption products of A2 Ash at 700  $^\circ$ C.

Ca was greater than the decrease in the adsorption capacity of Fe, thus showing that the adsorption capacity of A2 ash increased, whereas the Fe content of A1 ash was high and the Ca content was low. The increase in the adsorption capacity of Ca was less than the decrease in the adsorption capacity of Fe; therefore, the adsorption capacity of A1 ash was reduced.

Therefore, it was speculated that the adsorption of gaseous  $As_2O_3$  by ash may occur through the action of Ca and Fe in the ash. Among them, the adsorption of  $As_2O_3$  by Ca increased with an increase in temperature, while the adsorption of Fe on  $As_2O_3$  began to weaken above 800 °C when the adsorption product was unstable. However, the Fe contents in the two ashes were similar, and the adsorption capacity of A2 ash with higher Ca content in the 500–800 °C temperature range was significantly lower than that of A1 ash. It was unclear whether the adsorption of ash to gaseous  $As_2O_3$  was only related to Ca and Fe or other minerals in the ash.

#### 3.2.2. XPS analysis of As<sub>2</sub>O<sub>3</sub> adsorption products

To further clarify the main mechanism of gaseous  $As_2O_3$  adsorption by ash at various temperatures, XPS was used to analyze the binding energies of As in the products of A1 ash, CaO and Fe\_2O\_3 adsorbing  $As_2O_3$  at 700 °C. Fig. 6 shows the binding energy of As in the A1 ash product.

As shown in Fig. 6, in the products generated by the adsorption of  $As_2O_3$  by A1 ash at 700 °C, the peaks of the binding energy of As were distributed in the As 3*d* and As 2*p* orbitals. The peaks corresponding to the As 3*d* orbital were 45.3 eV and 50.1 eV, and the peaks corresponding to the As 2*p* orbital were 1327 eV and 1364 eV. Owing to the limited data on the binding energy of As, it was not yet possible to directly determine the corresponding As form based on the peak binding energy. For reference, the binding energies of As in the adsorption products of CaO and Fe<sub>2</sub>O<sub>3</sub> were also analyzed, and the results are shown in Fig. 7 and Fig. 8, respectively.

It can be seen in Fig. 7 and Fig. 8 that in the adsorption products of CaO at 700 °C, the binding energy peaks of As were all distributed in the As 3*d* orbital, and the corresponding peaks were 43.5 eV and 49.8 eV. The peaks of the binding energy of As in the adsorption products of Fe<sub>2</sub>O<sub>3</sub> at 700 °C were distributed in the As 3*d* orbital and the As 2*p* orbital. The peak value corresponding to the As 3*d* orbit was 45.6 eV, and the peak values corresponding to the As 2*p* orbit were 1327.6 eV and 1363.9 eV.

Comparisons of the binding energies of As on the adsorption products of A1 ash, CaO, and Fe<sub>2</sub>O<sub>3</sub> at 700 °C showed that the binding energy of the As 3*d* orbital in the adsorption products of A1 ash simultaneously corresponded to the peaks in the adsorption products of CaO and Fe<sub>2</sub>O<sub>3</sub>. The peak at 45.3 eV was consistent with those in the Fe<sub>2</sub>O<sub>3</sub> adsorption products, and the peak at 50.1 eV was consistent with those in the CaO adsorption products. The peaks at 1327 eV and 1364 eV of the As 2*p* orbital in the A1 ash adsorption product were consistent with those in the Fe<sub>2</sub>O<sub>3</sub> adsorption products. This showed that As has two forms in the adsorption products of A1 ash at 700 °C: Ca- and Fe-bound. The adsorption of gaseous As<sub>2</sub>O<sub>3</sub> by ash is related to the Ca and Fe in the ash. To clarify the reason for the decrease in the adsorption product of A1 ash at 900 °C, a binding energy analysis of As in the adsorption product of A1 ash at 900 °C °C was conducted, and the result is shown in Fig. 9.

In the product generated by A1 ash adsorbing  $As_2O_3$  at 900 °C, the binding energy peaks of As were still distributed in the As 3*d* and As 2*p* orbitals. As shown in Fig. 9, the corresponding peak values of the As 3*d* orbital were 45 eV and 50 eV, which were consistent with the adsorption products of A1 ash at 700 °C, corresponding to Ca and Fe adsorption products, respectively. The peak corresponding to the As 2*p* orbital was only 1326.4 eV, and the peak at 1364 eV in the Fe<sub>2</sub>O<sub>3</sub> adsorption product at 700 °C disappeared, which indicates that the Fe<sub>2</sub>O<sub>3</sub> adsorption product corresponding to this binding energy cannot exist stably at 900 °C, which should also be the reason for the decrease in the adsorption capacity of A1 ash at 900 °C. ash and minerals showed that the adsorption of  $As_2O_3$  by A1 ash was affected by the joint action of Ca and Fe in the ash. As in the ash adsorption product has two forms: combined with Ca and combined with Fe. At 900 °C, the adsorption capacity of ash decreased due to some of the unstable Fe adsorption products.

The Fe contents in the two ashes were comparable, and in the 500–800 °C temperature range, the adsorption capacity of A2 ash with higher Ca content was significantly lower than that of A1 ash, which may be due to the significant specific surface area of the A2 ash being less than the A1 ash (Fig. 4). The total pore volume and BET specific surface area of the A1 ash were significantly larger than those of the A2 ash. The total pore volumes of the A1 and A2 ashes were 0.0031 cm<sup>3</sup>/g and 0.0021 cm<sup>3</sup>/g, respectively, and the BET specific surface area strengthened the adsorption capacity of A1 ash.

# 3.2.3. Analysis of element distribution on the surface of $As_2O_3$ adsorption products by EPMA

To more intuitively identify the correlation of the distribution of various elements on the surface of the adsorption product, and to further clarify the main mechanism of gaseous As<sub>2</sub>O<sub>3</sub> adsorption by ash, the elemental distribution on the surface of the adsorption product of A1 ash at 700 °C was analyzed using EPMA, and the results are shown in Fig. 10. As can be seen from Fig. 10, in the adsorption products of the A1 ash at 700 °C, there were two types of As-enriched regions. One was the fine particles distributed in the inter-particle gap or attached to the particles, which coincided with the Ca-enriched region; the other was a relatively regular spherical particle surface, which coincided with the Fe-enriched region. Among them, the As signal in the Ca-enriched region was stronger and the concentration was higher. In addition, the distribution of S had a certain correspondence with the distribution of Ca, while the distribution of As was not strongly correlated with S. The Al and Si signals were relatively weak in the As-enriched region. This shows that the enrichment of As in ash was only related to Ca and Fe, but not to Al and Si.

To further clarify the elemental distribution in the As-enriched region, a quantitative analysis of the elements was performed at three points in the As-enriched region, and the results are shown in Table 2.

Table 2 shows that points 1 and 3 were mainly Ca-bound As, while point 2 was mainly Fe-bound As. No S content was detected in points 1 and 2, and the S content in point 3 was 2.1%. This also proves that the adsorption of  $As_2O_3$  by A1 ash is mainly related to Ca and Fe.

Similarly, EPMA analysis was performed on the adsorption products of A2 ash at 700 °C, and the results are shown in Fig. 11. As shown in Fig. 11, the As-enriched region in the A2 ash coincided with the Caenriched region, while the Fe signal was weaker, and the distribution of As was not correlated with Al and Si. This was because the Ca content in the A2 ash was high, and the adsorption of gaseous  $As_2O_3$  by ash was mainly through CaO; therefore, the As-enriched region in the adsorption product of A2 ash mainly coincided with the Ca-enriched region. This can also explain the results in Fig. 4, where the adsorption capacity of A1 ash decreased as the adsorption capacity of Fe weakened when the temperature increased from 800 °C to 900 °C, while the adsorption capacity of A2 ash continued to increase. The adsorption of gaseous  $As_2O_3$ by A2 ash with relatively high Ca content was mainly caused by Ca. The Ca adsorption product exhibited strong thermal stability and the adsorption capacity continued to increase with temperature.

In summary, at 500–900 °C, the chemical adsorption of  $As_2O_3$  by ash is mainly through the joint action of Ca and Fe, and has nothing to do with other minerals. The adsorption characteristics of ash depend on its active Ca and Fe contents. There are various adsorption products of Ca and Fe in ash, with different thermal stabilities. The adsorption products of Ca are stable in the 500–900 °C temperature range, and certain forms of the adsorption products of Fe begin to decompose and release at 800 °C. The amount of As adsorbed by the ash with high Fe content first increases and then decreases with the adsorption temperature and peaks

Data availability

at 800 °C. The amount of As adsorbed by the ash with higher Ca content increases with increasing adsorption temperature. The results of this study indicate that blending coals or coal with Ca and Fe additives to increase the contents of Ca and Fe in ash can promote the transformation of gaseous  $As_2O_3$  into ash by chemical adsorption, which can effectively be removed by the dust collector, thereby reducing As emissions.

#### 4. Conclusions

The thermal stability analysis of As in ashes collected from dust collectors of different power plants showed that more than 80% of As in the ash had excellent thermal stability and would not be released even when heated at 1000  $^{\circ}$ C. The dominant role of chemical adsorption in gaseous As transformation in the cooling process of coal-fired flue gas was clarified, accounting for more than 90%, and the As solidified by chemical adsorption had various forms in ash with different thermal stabilities.

The dynamic curves of gaseous  $As_2O_3$  adsorption by ash at 500–900 °C were obtained. At the same temperature, the amount of As adsorbed by ash increased approximately linearly with increasing adsorption time, far from reaching saturation. The maximum amount of As adsorbed by the ash observed in the experiments (294 µg As/g ash) was more than 10 times that of the As content in the ash collected from the power plant dust collectors, indicating that the actual capacity of the ash to adsorb gaseous As in the coal-fired flue gas was far higher.

Comparing the adsorption characteristics of different ash and minerals, it was found that in the range of 500–900  $^\circ\text{C},$  with the increase in adsorption temperature, the amount of As adsorbed by A1 ash first increased, then decreased, and peaked at 800 °C, while the adsorption amount of A2 ash with higher Ca content kept increasing. The amount of As adsorbed by CaO increased with the increase of adsorption temperature, while the amount of As adsorbed by Fe<sub>2</sub>O<sub>3</sub> increased first and then decreased, and reached the maximum at 800 °C. The speciation of As in the adsorption product was analyzed using XPS, and the element distribution in the product was analyzed using EPMA, which directly proved that the chemical adsorption of gaseous As<sub>2</sub>O<sub>3</sub> by ash was mainly through the joint action of Ca and Fe, and had nothing to do with other components. There were various Ca and Fe adsorption products in the ash, with different thermal stabilities. The adsorption products of Ca were stable in the 500–900 °C temperature range, and some forms of the adsorption products of Fe began to decompose and release at 800 °C. The amount of As adsorbed by the high Fe ash first increased and then decreased with the adsorption temperature and peaked at 800 °C. The amount of As adsorbed by the ash with higher Ca content monotonically increased with increasing adsorption temperature.

The results of this study indicate that blending coals or coal with Ca and Fe additives to increase the contents of Ca and Fe in ash can promote the transformation of gaseous  $As_2O_3$  into ash by chemical adsorption, which can effectively be removed by the dust collector, thereby reducing As emissions.

#### CRediT authorship contribution statement

Wenting Xu: Methodology, Investigation, Writing – original draft, Writing – review & editing. Guochang Song: Writing – review & editing, Validation. Xingyu Yang: Validation, Writing – review & editing. Qiang Song: Writing – review & editing, Conceptualization, Supervision, Project administration. Qiang Yao: Supervision, Project administration.

#### **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.

The data that has been used is confidential.

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#### Further reading

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