Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Study on the transformation of gaseous selenium during the cooling process of coal-fired flue gas

Wenting Xu^a, Guochang Song^a, Xingyu Yang^a, Qiang Song^{a,1,2,*}, Qiang Yao^{a,b}

^a Key Laboratory of Thermal Science and Power Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China ^b School of Electric Engineering, Xinjiang University, Urumqi 830047, China

of Se

dsorbed by ash.

ABSTRACT

HIGHLIGHTS

GRAPHICAL ABSTRACT

500 600 700 80

- Thermal stability analysis of Se in ash clarifies main paths of transformation.
- The dynamic curves of SeO₂ adsorption by ash at 200-900 °C were obtained.
- · Se adsorption varies with temperature due to the change in dominating mechanism.
- Both CaO and CaSO₄ in ash contribute to the chemical adsorption of SeO₂.
- · The unburned carbon in ash is the main component to physically adsorb SeO2.

A R T L C L E I N F O

Editor: John D Atkinson

Keywords: Selenium Transformation Flue gas Adsorption Ash



Understanding the transformation of Se during the flue-gas cooling process is important for controlling Se emissions. By analyzing the thermal stability of Se in ash collected from power plant dust collectors, physical migration was found to be the main pathway by which gaseous Se transformed into ash during the flue-gas cooling process. The dynamic curves were obtained for SeO₂ adsorption by ash at 200-900 °C. The adsorbed Se amount first decreased, increased, and then decreased with increasing adsorption temperature (400 °C and 600 °C were the two turning points). By comparing the adsorption characteristics of different ash and minerals and performing a speciation analysis of Se and an elemental distribution characterization after adsorption, the adsorption mechanism of gaseous Se was proposed. In the medium-high temperature range (above 500 °C), SeO₂ was chemically adsorbed by ash through CaO and CaSO₄, generating CaSeO₃ and CaSeO₄, respectively; the thermal stability of CaSeO₄ was weaker than that of CaSeO₃. In the low temperature range (below 500 °C), SeO₂ was adsorbed by ash mainly through physical adsorption of unburned carbon, accompanied by a small amount of chemical adsorption of CaO.

The active components in ash

* Correspondence to: Department of Energy and Power Engineering, Tsinghua University, Haidian District, Beijing 100084, China.

² ORCID: 0000-0002-5484-3594

https://doi.org/10.1016/j.jhazmat.2022.130362

Received 11 May 2022; Received in revised form 13 September 2022; Accepted 7 November 2022 Available online 9 November 2022 0304-3894/© 2022 Elsevier B.V. All rights reserved.



Research Paper





E-mail address: qsong@tsinghua.edu.cn (Q. Song). ¹ Researcher ID: U-4938-2019

1. Introduction

Coal will remain an important aspect of the world's energy structure, and its burning results in a series of pollution emissions. With the widespread implementation of emission control technologies for conventional pollutants such as particulate matter, sulfur dioxide and nitrogen oxides in the thermal power industry (Fu et al., 2014; Wang et al., 2015; Tu et al., 2016; He et al., 2019), trace elements have become important coal-fired pollutants after SO_X, NO_X, and particulate matter. This is because of their strong toxicity and large total emissions; consequently, they have received increasing attention (Xu et al., 2004, Zhao et al., 2017, Duan et al., 2017). Selenium (Se) is an essential trace element in the human body, but excessive consumption of Se can lead to Se poisoning, damage the skin and nervous system, and even cause death (Dai et al., 2017). Coal-fired installations are one of the main sources of atmospheric Se emissions. For example, in China, Se emissions from coal-fired installations accounted for 64.6% of total emissions (Tian et al., 2015). Se emitted from coal combustion is mainly in the inorganic form, which is more toxic. High concentrations of Se in local areas not only have strong teratogenic, carcinogenic and mutagenic effects on the human body, but also destroy ecological balance. Se poisoning caused by the burning of high-Se coal has been observed in Hubei, China (Dai et al., 2017). The United States, the European Union, and other countries and regions have implemented emission limits for toxic trace elements, such as Se from coal-fired power plants, in their air pollutant emission standards (U.S. Environmental Protection Agency, 2012; European Union, 2016). The mass concentration and distribution of Se in coal-fired flue gas determine its effect on the environment, and the emission characteristics of Se depend on its transformation in the coal-fired system. Understanding the transformation process is important in guiding the development of control technologies.

Field test results of the characteristics of Se emissions from coal-fired power plants show that only 0.57–13% of Se is distributed in the bottom ash, and more than 90% of Se is released into high-temperature flue gas after combustion (Otero-Rey et al., 2003; Córdoba et al., 2012; Wang et al., 2019; Chang et al., 2019). There are two forms of Se in flue gas (gaseous Se and particulate Se which is attached to fly ash). Most particulate Se can be removed by the dust collector, and the emission reduction efficiency of Se is 53–91.8%. Gaseous Se can be synergistically removed by the wet flue gas desulfurization device, and Se in the flue gas discharged from chimneys is mainly gaseous (Otero-Rey et al., 2003; Córdoba et al., 2012; Wang et al., 2019; Chang et al., 2019; Cheng et al., 2009; Senior et al., 2015).

Transformation of Se in coal-fired systems can be divided into two stages: high-temperature combustion and post-combustion (Swanson et al., 2013; Vejahati et al., 2010). Laboratory studies showed that majority of the Se content in coal is released into high-temperature flue gas after high-temperature combustion (Seames, 2003; Song et al., 2020; Frandsen et al., 1994; Bool and Helble, 1995). In high-temperature flue gas, gaseous Se exists mainly in the form of SeO₂ (Contreras et al., 2013; Yan et al., 2001). During the flue-gas cooling process, gaseous Se in flue gas transforms probably through the adsorption of minerals in the ash (Itskos et al., 2010). Scholars have carried out a series of studies on the adsorption of gaseous SeO₂ by minerals and found that the adsorption capacity of kaolin and alumina is weak, while Ca-based adsorbents such as CaO, Ca(OH)₂, CaCO₃, and Fe-based adsorbents exhibit a strong adsorption capacity (Ghosh-Dastidar et al., 1996; Li et al., 2006; Huang et al., 2021). Ghosh-Dastidar et al. (1996) used slaked lime, kaolin, Al₂O₃ and CaCO₃ as adsorbents, performed adsorption experiments of SeO₂ at 500 °C and 900 °C, and found that the adsorption effect of slaked lime was the greatest; the adsorption amount of minerals at 500 °C was greater than that at 900 °C. Huang et al. (2021) studied the adsorption of SeO₂ by Fe₃O₄, γ-Fe₂O₃, and α-Fe₂O₃ at 300–900 °C, and found that the three iron-based adsorbents all had a certain adsorption capacity; the variation trends of adsorption capacity differed with temperature. However, when the adsorption temperature increased to 900 °C, the

three kinds of iron-based adsorbents had no adsorption capacity. Yuan et al. (2022) studied the adsorption of SeO₂ by SiO₂, mullite, CaO, CaSO₄, Fe₂O₃, and Fe₃O₄ at 90–200 °C. It was found that mullite had the strongest adsorption capacity at low temperatures, and that the adsorption capacity decreased slightly with the increase of temperature (indicating physical adsorption). The adsorption of SeO₂ by CaO, Fe₂O₃, and Fe₃O₄ was chemical, and the adsorption capacity increased with the increase of temperature. The adsorption capacities of CaSO₄ and SiO₂ were weak.

Ash contains mineral components, such as CaO and Fe₂O₃, which may have certain adsorption capacities for gaseous Se. Seames (2003) carried out combustion experiments on four types of coal using a sedimentation furnace experimental system and performed a correlation analysis on the relationship between the Se and Ca contents in fly ash. A strong linear relationship was found between the Se and Ca contents in fly ash. Huggins et al. (2007) used X-ray absorption fine structure spectroscopy to analyze the forms of Se found in fly ash collected from 10 coal-fired power plants and found that Se in fly ash mainly existed in the form of selenite. Shah et al. (2007) found that in addition to selenite, the Se in fly ash also contained a small amount of selenate. Ma et al. (2020) used different digestive methods to analyze the valence state of Se in fly ash collected from four power plants; they found that more than 90% of the Se in the ash had a valency of + 4, and that only the ash of individual power plants contained 40% of + 6 valent Se. After heating at 350 °C for 1 h, 1-61.73% of Se in the ash was desorbed and considered to be physically-bound. Yuan et al. (2022) analyzed fly ash from five power plants using the same method and found that more than 20% of Se in pulverized coal furnace fly ash was physically bound; the chemically bound Se was mainly selenite, with approximately 10% being selenate. These studies indirectly indicate that gaseous Se transforms into fly ash through chemical adsorption and physical migration during the cooling process of flue gas; however, direct studies on the adsorption of gaseous Se by coal-fired fly ash are very limited. López-Antón et al. (2006) studied the adsorption of SeO₂ by two ash samples at 120 °C and found that there was no correlation between the amount of Se adsorbed by ash and the content of Ca and Fe in the ash. When heated at 120 °C, 90% of the absorbed Se was released, indicating that the adsorption of SeO₂ by ash at 120 °C was physical.

Se exists mainly as gaseous SeO₂ in high-temperature flue gas after combustion. During the cooling process of flue gas, gaseous Se is partially adsorbed by fly ash and transformed into a particulate state; however, the adsorption characteristics and mechanisms are still unclear. Therefore, this study investigated the transformation of Se during the cooling process of coal-fired flue gas. First, the thermal stability of Se in fly ash collected from power plant dust collectors was investigated to clarify the main route of gaseous Se transformation into ash during the coal-fired flue gas cooling process. The adsorption experiments of gaseous SeO₂ by ash were carried out at 200–900 °C, and dynamic adsorption curves at various temperatures were obtained. By comparing the adsorption characteristics of four types of ash, CaO, CaSO₄, and Fe₂O₃, the Se morphology, and the correlation of element distributions in the adsorption products, the mechanisms of SeO₂ adsorption by ash at different temperatures were revealed.

2. Experimental procedure

2.1. Sample preparation

In this study, six types of ash collected from dust collectors of six different power plants were used. The ash samples were screened in the size range of 74–96 μ m using a vibrating screen, placed in an oven at 105 °C for 10 h, sealed, and stored. Two types of ash with high Se contents were selected for the thermal stability experiment: S1 and S2 ash. Four types of ash with relatively low Se contents and significant differences in mineral content were selected for the original Se in ash due to the

thermal instability at high temperatures, the four types of ash were heated at 1000 $^{\circ}$ C in advance, and four types of ash samples (A1–A4) were obtained for adsorption experiments. The components of the six samples were analyzed using X-ray fluorescence (XRF; ARL PERFORM' X, Thermo Fisher Scientific, USA), and the results are summarized in Table 1.

The particle size of the A1–A4 ash was analyzed using laser particle size analyzer (Mastersizer 2000, Malvern, UK), and the specific surface area and pore structure of the A1–A4 ash were determined using nitrogen adsorption apparatus (ASAP 2020, Micrometrics, USA). The results are shown in Table 2.

Solid SeO₂ (CAS: 7446–08–4, purity >99.9%) used to generate gaseous SeO₂ was acquired from Shanghai Macklin Biochemical Technology Co. Ltd. CaO (CAS: 1305–78–8), Fe₂O₃ (CAS: 1309–37–1), CaSO₄ (CAS: 7778–18–9), and SiO₂ (14808–60–7) used for the adsorption experiments were also acquired from Shanghai Macklin Biochemical Technology Co., LTD, and they were analytically pure.

2.2. Experimental setup

The adsorption experiments of SeO_2 by ash and minerals were conducted in a two-stage furnace experimental system as shown in Fig. 1. The two-stage furnace experimental system consisted of a horizontal furnace and a vertical furnace, used for the generation and adsorption of gaseous SeO_2 , respectively. The two furnaces were controlled independently.

Gaseous SeO₂ was generated in the horizontal electric furnace, and the reactor was composed of an outer quartz tube and an inner quartz tube, which were connected and sealed using a rubber plug. A quartz crucible was placed at the end of the inner quartz tube, which was located in the constant-temperature zone and was used to cover the SeO2 powder. The carrier gas was fed into the reactor from the other hole of the rubber plug, and blown horizontally from left to right across the surface of the crucible containing SeO₂, thereby removing the evaporated SeO₂ from the generating device. The temperature measured by thermocouple was the temperature of the outer quartz tube near the crucible. At a constant temperature, the evaporation rate of the sample layer covered with a crucible can remain constant for a certain period (Gückel et al., 1982). To accurately regulate the concentration of gaseous SeO₂ in the generated flue gas, several constant temperature evaporation experiments were conducted. Finally, SeO₂ was evaporated at 120 °C to ensure that the concentration of gaseous SeO₂ generated in the simulated flue gas generated was 1.36 ppm.

The adsorption of gaseous SeO_2 was performed in a vertical electric furnace. The reactor was composed of an outer quartz tube and an inner quartz tube sealed with a rubber plug. A movable quartz basket was placed at the end of the inner quartz tube and sealed by frosting. The inner diameter of the outer quartz tube was 25 mm and the inner diameter of the basket was 15 mm. The quartz basket was located in the constant-temperature region of the furnace. The bottom of the basket was equipped with a quartz screen plate and high-purity quartz filter (MK360, Munktell, Sweden) for the stacking materials. To prevent the gaseous SeO_2 in the experimental pipeline from condensing before

Table I				
The component	analysis	of the	ash	samples

Tabla 1

	S1 ash	S2 ash	A1 ash	A2 ash	A3 ash	A4 ash
SiO ₂	31.9	51.4	49.5	50.3	43.4	48.0
Al_2O_3	19.9	32.2	26.9	21.0	42.1	35.5
Fe ₂ O ₃	5.43	8.08	11.1	11.3	3.95	7.07
CaO	2.71	2.55	5.66	9.52	5.09	3.29
MgO	0.437	0.966	1.33	1.21	0.644	0.915
Na ₂ O	0.328	0.240	0.519	1.37	0.091	0.168
K ₂ O	0.934	1.67	1.98	2.67	0.757	1.48
SO_3	1.60	0.327	0.397	0.532	0.581	0.518
The rest	36.8	2.57	2.61	2.10	3.39	3.06

(%).

Table 2

Physical structure cha	aracterization of ash
------------------------	-----------------------

	A1 ash	A2 ash	A3 ash	A4 ash
D[3,4](µm)	102.8	97.7	93.6	89.0
BET Area(m ² /g)	2.23	1.09	1.37	1.77
Total Pore Volume (cm ³ /g)	0.0031	0.0021	0.0032	0.0035
Average Pore Size (Å)	58.8	73.9	94.0	80.1

reaching the adsorbent layer, heat tracing was performed during the entire process from the outlet of the generation device to the entrance of the adsorption experiment, and the heat tracing temperature was 140 $^{\circ}$ C.

2.3. Method

The adsorption experiments were conducted at 200–900 °C with 200 mL/min of N₂ carrier gas. When the temperature in the constant-temperature zone of the horizontal electric furnace used to generate gaseous SeO₂ rose to the set temperature, the crucible containing SeO₂ powder with the recorded mass was placed into the reactor, and the time was started. After 10 min, when the conditions in the reactor were stable and the temperature of the constant-temperature zone of the adsorbent layer in the vertical electric furnace has rose to the set temperature, quickly put into the inner tube and the quartz basket equipped with 0.2 g ash or mineral, keep for 15, 30, 45, 60, or 75 min, and then quickly remove. The samples were cooled to room temperature, weighed, collected, and sealed for subsequent analyses. Each operating point was repeated at least 3 times.

The thermal stability analysis of Se in the ash was carried out at 120–1000 °C. 200 mL/min of N₂ was directly fed from the upper part of the vertical electric furnace without passing through the horizontal electric furnace. When the reactor temperature increased to the set temperature, the samples were placed into the furnace and kept for 1 h.

Prior to measuring the Se content in the solid samples, the samples were pretreated. Owing to the strong volatility of Se, it was easy to volatilize in the conventional microwave digestion process, resulting in sample loss. Therefore, heating on an electric plate was used to pretreat the solid samples at low temperatures. About 100 mg of each solid sample was weighed and digested with 9 mL HCl and 1 mL HNO₃ for 1 h at 100 °C. After digestion, the solution was cooled to room temperature and reduced to 50 mL using deionized water. After reaching a constant volume, the filtrate was filtered using a 0.225 μ m needle filter, and the filtrate was collected for subsequent analysis. Atomic fluorescence spectroscopy (AFS; Jitian AFS-9320, China) was used to measure the Se concentration in the liquid.

X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi, Thermo Fisher, UK) was used to analyze the binding energies of Se in the adsorbed products. Electron probe microanalysis (EPMA; JXA8230, JEOL, Japan) was used to observe the elemental distributions of the adsorbed products. Observations were done at an acceleration voltage of 20 kV and current of 1×10^{-8} A. The resolution in the X-and Y-directions was 0.28 μm , and the interval between the analysis points was 10 ms. In the fixed-point qualitative analysis experiment, the acceleration voltage was 20 kV, the acceleration current was 1×10^{-8} A, and the spot diameter was 1 μm .

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

$$R = 1 - \frac{m_{\rm a} \times c_{\rm a}}{m_{\rm b} \times c_{\rm b}} \tag{1}$$

where m_b and m_a represent the mass of ash before and after heating (g), respectively; c_b and c_a represent the Se content of the ash before and after heating (μ g/g), respectively.



Fig. 1. The experimental system of SeO₂ adsorption.

3. Results and discussion

3.1. Adsorption characteristics of gaseous SeO₂ by ash

During the cooling process of the flue gas, gaseous Se can transform into ash via chemical adsorption or physical migration. Se migrates to ash in different ways and has different thermal stabilities (Ma et al., 2020). The Se transformed to ash via condensation or physical adsorption had a poor thermal stability and was easy to release when heated at a lower temperature, whereas the Se transformed to ash via chemical adsorption had a good thermal stability and could only be decomposed and released when heated to a higher temperature. To determine the main path of Se transformation during the cooling process, thermal stability experiments were conducted on the fly ash collected from the dust collectors of the two power plants. The release ratios of Se in the two ashes at 120–1000 °C are shown in Fig. 2.

As shown in Fig. 2, the thermal stabilities of Se in the ash collected



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

from the two power plants were similar. The Se in the ash was unstable and was easily released into the gas phase, with varying degrees of release at different temperatures. In the range of 120–500 °C, the release ratio increased gradually with an increase in temperature. When the temperature reached 500 °C, approximately 70% of Se in the ash was released. At 500–800 °C, the Se in S2 ash continued to be released, and 15% of the Se in S2 ash was released in this temperature range. However, the Se in S1 ash was not further released and the release ratio remained unchanged. From 800 °C to 1000 °C, Se in the two types of ash continued to be released, and the release ratios in the ash reached more than 90% at 1000 °C.

Se, which can be released from ash when heated at 120–500 °C, can only transform to ash through physical adsorption or condensation (Ma et al., 2020), which accounted for more than 70% in the present study. However, as the temperature rose to 500–800 °C, another 15% of the Se in S2 ash was released in the gas phase. This part of the Se should be transformed into ash through chemical adsorption, but the adsorption products formed were unstable. However, Se that continued to be released at temperatures above 800 °C should also be transformed into ash through chemical adsorption products, which may be selenite and other substances, were more stable (Huang et al., 2021; Yuan et al., 2022).

The results of the thermal stability experiments showed that the physical adsorption or condensation of Se at low temperatures was the main mechanism by which Se transformed to ash during the cooling process of coal-fired flue gas, accounting for 70% of the ash. The proportion of Se cured by chemical adsorption was approximately 30%, and various forms of Se with different thermal stabilities were obtained. Therefore, the chemical and physical adsorption of SeO₂ by ash were studied, respectively, and adsorption experiments were carried out within a wide temperature range of 200–900 °C.

In the high-temperature flue gas, gaseous Se exists mainly in the form of SeO₂ (Contreras et al., 2013; Yan et al., 2001). Adsorption of gaseous SeO₂ by A1 ash was carried out in the temperature range of 200–900 °C, and dynamic adsorption curves were obtained, as shown in Fig. 3.

As shown in Fig. 3, for the same adsorption temperature and with an increase in adsorption time, the amount of Se adsorbed by A1 ash



Fig. 3. Dynamic processes of gaseous SeO₂ adsorption by A1 ash.

increased rapidly at first, and then slowly. For the same adsorption time and with an increase in adsorption temperature, the amount of Se adsorbed by A1 ash first decreased, increased, and then decreased. The two turning points were 400 °C and 600 °C, as shown in Fig. 4.

Combined with the results shown in Fig. 2, the thermal stability of Se in the ash collected from the dust collector also had 500 °C as its turning point. Therefore, the subsequent studies on the adsorption mechanism of gaseous SeO₂ adsorbed by ash were divided into two sections: the medium-high temperature range above 500 °C and the low-temperature range below 500 °C.

3.2. Mechanism of gaseous SeO_2 adsorbed by ash in the medium-high temperature range

In this section, the adsorption of gaseous SeO₂ by ash in the mediumhigh temperature range of 500–900 °C was studied. To analyze the mechanism of gaseous SeO₂ adsorption by ash, the adsorption characteristics of four ash samples with different mineral compositions were compared. Each adsorption experiment was carried out at 500–900 °C for 45 min. The amounts of Se adsorbed by the four types of ash at different temperatures are shown in Fig. 5.

As shown in Fig. 5, the adsorption behaviors of the different ash samples were similar, and the trend of the change in adsorption amount with temperature was consistent. At 500–600 °C, the adsorption



Fig. 4. The amount of Se adsorbed by A1 ash at different temperatures (adsorbed for 45 min).



Fig. 5. Amount of Se adsorbed by different ash samples at different temperatures (adsorbed for 45 min).

amounts of all four types of ash increased with an increase in temperature. At 600 °C, the order of the adsorption amounts of the four types of ash was A2 >A3 ≈A1 >A4. At 600–900 °C, the adsorption amounts of all four types of ash decreased rapidly with an increase in temperature. The amount of Se adsorbed by A3 ash decreased to 0 at 800 °C, and the adsorption capacities of A2 and A4 ash also reached 0 at 900 °C. However, A1 ash still exhibited a certain adsorption at 900 °C, and this adsorption amount was 25.3 µg/g. This indicates that the adsorption of gaseous SeO₂ by the four types of ash was affected by the ash composition, and there were many kinds of adsorption products with different thermal stabilities.

The adsorption of gaseous SeO₂ by ash occurs mainly through the action of minerals in the ash. Relevant studies have shown that Ca and Fe minerals have adsorption effects on Se. Considering that SiO₂ and Al₂O₃ are the main components in ash, five typical minerals, CaO, CaSO₄, Fe₂O₃, SiO₂, and Al₂O₃ were selected for the adsorption experiment, to further analyze the main mechanism of gaseous SeO₂ adsorption by ash. In the temperature range of 500–900 °C, after 45 min of adsorption, changes in the Se content in the mineral were compared, as shown in Fig. 6.

As shown in Fig. 6, there were significant differences in the adsorption characteristics of the different minerals. In the temperature range of 500–900 °C, the adsorption capacity of SiO₂ and Al₂O₃ was significantly weaker than that of CaO, CaSO₄, and Fe₂O₃. With an



Fig. 6. Amount of Se adsorbed by minerals at medium-high temperature range (adsorbed for 45 min).

increase in temperature, the adsorption amounts of CaO and CaSO₄ first increased and then decreased. The amount of Se adsorbed by CaO reached its maximum at 800 °C and still had a strong adsorption capacity at 900 °C. The amount of Se adsorbed by CaSO₄ reached its maximum at 600 °C, decreased rapidly, and almost reached 0 at 900 °C. The amount of Se adsorbed by Fe₂O₃ continued to decrease, almost reaching 0 at 900 °C.

Combined with the results in Fig. 5, the trend of the adsorption amount of the four types of ash with temperature was consistent with that of CaSO₄, but it may also be the result of the joint action of various minerals, such as CaO, CaSO₄, and Fe₂O₃. To further clarify the main mechanism of gaseous SeO₂ adsorption by ash at various temperatures, the binding energies of Se in the products generated by the adsorption of A1 ash, CaO, CaSO₄, and Fe₂O₃ were analyzed. In the temperature range of 500–900 °C, since the adsorption amount of ash was largest at 600 °C, the adsorption product at 600 °C was used as the reference for analysis. Fig. 7 shows the binding energy of Se in the product after adsorption.

From the results in Fig. 7, for the adsorption product of A1 ash at 600 °C, the peaks of the binding energy of Se were distributed at 56.0 eV and 59.2 eV of the Se 3*d* orbital. As a reference, the binding energies of Se in the products of CaO, CaSO₄, and Fe₂O₃ were also analyzed. The peaks of the binding energy of Se in the products of CaO were distributed at 55.8 eV and 59.1 eV of the Se 3*d* orbital, those in the products of CaSO₄ were distributed at 61.1 eV of the Se 3*d* orbital, and those in the

products of Fe_2O_3 were distributed at 55.4, 56.6, and 58.8 eV. The binding energy of Se in the CaO adsorption product was mainly 59.1 eV, corresponding to the peak of SeO_3^{2-} , while that of Se in the CaSO₄ adsorption product was mainly 61.1 eV, corresponding to the peak of SeO_4^{2-} (Weser et al., 1977; Wagner et al., 1979). This shows that the reaction in Eq. (2) occurs when SeO_2 is adsorbed by CaO and CaSeO₃ is generated, while the reaction in Eq. (3) occurs when SeO_2 is adsorbed by CaSO₄ and CaSeO₄ is generated.

$$CaO + SeO_2 \rightarrow CaSeO_3$$
 (2)

$$CaSO_4 + SeO_2 \rightarrow CaSeO_4 + SO_2 \tag{3}$$

Comparing the binding energies of Se in the products of A1 ash, CaO, CaSO₄, and Fe₂O₃, we found that the binding energy of Se in the A1 ash adsorption product was similar to that in the CaO adsorption product, whereas no peaks corresponding to those in the adsorption products of Fe₂O₃ and CaSO₄ were observed. This may be due to the subjectivity of peak splitting and the low resolution of XPS detection, which may result in errors in the analysis.

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 adsorption of gaseous SeO_2 by ash, the elemental distribution on the surface of the adsorption product of A1 ash at 600 °C was analyzed using EPMA, and the results are shown in Fig. 8.



Fig. 7. XPS results of Se in the adsorption products of (a) A1 ash, (b) CaO, (c) CaSO₄, and (d) Fe₂O₃ at 600 °C.



Fig. 8. Electron probe microanalysis of the adsorption products of A1 Ash at 600 °C.

In the adsorption product of A1 ash at 600 °C, the Se-enriched region coincided with the Ca- and S-enriched regions and had nothing to do with the Fe-, Al-, and Si-enriched regions. This shows that the enrichment of Se in the ash was related to Ca and S, but not to Fe, Al and Si.

To further clarify the elemental distribution in the Se-enriched region, quantitative analyses of the elements were carried out at two points in the Se-enriched region, and the results are shown in Table 3.

It can be seen from the data in Table 3 that the elemental composition of the two points was mainly Ca, O, S, and Se. The mass ratio of Ca and O at point 1 was close to that of $CaSO_4$, and the mass ratio of Ca and O at point 2 was between that of CaO and CaSO₄. This indicates that the enrichment of Se in the A1 ash was mainly related to CaO and CaSO₄, but not to Fe₂O₃.

To further clarify the universality of the Se adsorption mechanism, EPMA analyses were performed on the adsorption products of the A2, A3, and A4 ashes at 600 °C, and the results are shown in Fig. SM-1, Fig. SM-2, and Fig. SM-3. Similar to the A1 ash, the Se-enriched regions in the other three ash samples were Ca- and S-enriched regions, while the signals of Fe, Al, and Si were weak. Therefore, the chemical adsorption of gaseous SeO₂ by ash was related only to CaO and CaSO₄ in the ash.

The analysis of the form of Se found using XPS on the adsorption product and correlation of the elemental distribution found using EMPA clearly show that, in the medium-high temperature range, the chemical adsorption of gaseous SeO₂ by ash had two main paths: adsorption by CaO forming CaSeO₃ and adsorption by CaSO₄ forming CaSeO₄. In the temperature range of 500–900 °C, with an increase in the adsorption temperature, the Se amount adsorbed by the four types of ash first increased and then decreased. The decrease above 600 °C may be related to the instability of the CaSO₄ adsorption product, CaSeO₄. CaSO₄ had no adsorption capacity when it reached 900 °C, whereas the ash still had a certain adsorption capacity, which may be because the

Table 3 The elemental quantitative analysis results of points in the Se-enriched region (wt%).

	Ca	S	0	Se
1	31	1.3	47	12
2	48	1.3	22	24

CaO in the ash still had an adsorption capacity at this temperature.

The thermal stability analysis of Se in the ash collected from the power plant dust collector in Fig. 2 shows that at 500–800 °C, Se in the S2 ash continued to be released and 15% of the Se in the ash was released in this temperature range. However, Se in the S1 ash was not further released and the release ratio did not increase. When the temperature was increased from 800 °C to 1000 °C, Se in both types of ash continued to be released. The Se released at 500–800 °C may be CaSeO₄, whereas that released at 900 °C was CaSeO₃.

To further clarify the reasons for the thermal instability of Se in ash adsorption products, the thermal stability of Se in products formed by adsorption at 600 °C was analyzed. The results are shown in Fig. 9. As shown in Fig. 9, CaSeO₃ produced by CaO was very stable below 800 °C and was not released. When the temperature reached 900 °C, the Se release ratio increased to 70%. The CaSeO₄ formed by CaSO₄ was stable below 500 °C. The release ratio of Se was only 2.1%, which increased to 11% at 600 °C, and the release ratio was 76% at 700 °C. The Se in the products generated by the A1 ash was stable below 500 °C, and the release ratio in the A1 ash adsorption product



Fig. 9. Thermal stability of Se in products formed by adsorption at 600 °C.

was between those of CaO and CaSO₄.

This proves that the chemical adsorption of SeO₂ by ash is a joint action of CaO and CaSO₄ in the medium-high temperature range. Among them, CaO adsorbed SeO₂ to generate CaSeO₃, which began to decompose and release at 900 °C, and CaSO₄ adsorbed SeO₂ to generate CaSeO₄, which began to release at 600 °C. At 500–600 °C, the amount of Se adsorbed by ash increased with rise in temperature; after 600 °C, it began to decrease owing to the reduction in the adsorption capacity of CaSO₄. At 900 °C, CaSO₄ had no adsorption capacity, and the adsorption of SeO₂ by ash depended on the adsorption by CaO. In the thermal stability analysis, the Se desorbed at 500–800 °C was CaSeO₄ generated by CaSO₄ adsorption, and the Se released at 900 °C was CaSeO₃ generated by CaO adsorption.

3.3. Mechanism of gaseous SeO_2 adsorbed by ash in the low temperature range

This section discusses the adsorption characteristics of SeO₂ by ash in the low-temperature range below 500 °C. Because the amount of Se adsorbed by ash was low at 300–400 °C, this section considered 200 °C as reference to conduct the experiments. Similarly, to analyze the mechanism of gaseous SeO₂ adsorbed by ash, the adsorption characteristics of four types of ash with different mineral compositions were compared. Each adsorption experiment was performed at 200 °C for 45 min, and the amount of Se adsorbed by the four types of ash is shown in Fig. 10.

The results in Fig. 10 show that the four types of ash could effectively adsorb gaseous SeO_2 at 200 °C, but there were significant differences in the amount of Se adsorbed. The order of the amounts adsorbed was as follows: A1 ash>A4 ash>A2 ash> A3 ash, which was different from that at 600 °C. This indicates that the adsorption mechanism at 200 °C is likely different from that at 600 °C.

The adsorption of SeO₂ by ash occurs mainly through its internal components. As discussed in Section 3.2, CaO is an important component of ash required for the chemical adsorption of SeO₂. On the other hand, ash contains a large amount of SiO₂, and it may also have a certain physical adsorption effect on SeO₂, although its chemical reaction is inert. To further analyze the main mechanism of SeO₂ adsorption by ash at low temperatures, adsorption experiments of gaseous SeO₂ at 200–400 °C were carried out for two mineral components, CaO and SiO₂, and the results are shown in Fig. 11.

As shown in Fig. 11, there were significant differences in the adsorption characteristics of gaseous SeO_2 for the different minerals. CaO had a strong ability to adsorb gaseous SeO_2 , which was significantly higher than that of SiO₂. In the temperature range of 200–400 °C, with an increase in the adsorption temperature, the amount of Se adsorbed by



Fig. 10. Amount of Se adsorbed by different ash at 200 $^\circ\!C$ (adsorbed for 45 min).



Fig. 11. Amount of Se adsorbed by minerals in the low temperature range (adsorbed for 45 min).

CaO gradually increased, while the amount of Se adsorbed by SiO₂ gradually decreased. Fig. 4 shows that in the temperature range of 200–400 °C, the adsorption amount of ash decreased with an increase in temperature, which was the opposite to that observed for CaO. Therefore, the adsorption of the ash at 200–400 °C was likely to be mainly physical, which was affected by components other than CaO, but the specific adsorption mechanism needs to be further studied.

Fig. 12 shows the XPS spectra of SeO₂ and Se in the adsorption products generated by A1 ash and CaO at 200 °C. The peaks associated with the binding energy of Se in SeO₂ were mainly distributed in the Se 3*d* orbital, with the corresponding peaks being located at 59.5 eV and 55.9 eV. The binding energy peak of Se in the product generated by CaO adsorption at 200 °C was mainly distributed at 59.1 eV of the Se 3*d* orbital, which corresponded with the peak of CaSeO₃, indicating that the adsorption of SeO₂ by CaO at 200 °C was still chemical adsorption. The binding energy peaks of Se in the products generated by A1 ash adsorption at 200 °C were mainly distributed at 59.6 eV and 56.0 eV of the Se 3*d* orbital, and the peak area accounted for 84%, corresponding to the binding energy of SeO₂. At the same time, the binding energy of Se in the product generated by A1 ash adsorption at 200 °C also had a peak at 50.6 eV, corresponding to the adsorption product of CaO.

The binding energy analysis of Se in SeO₂, ash, and mineral adsorption products showed that the adsorption of SeO₂ by ash at 200 °C was mainly physical, and Se in the adsorption products still existed in the form of SeO₂; however, there was also a small amount of CaSeO₃ generated via chemical adsorption by CaO.

To more intuitively see the correlation of the distribution of various elements on the surface of the adsorption product, and to further clarify the main mechanism of gaseous SeO_2 adsorbed by ash at low temperatures, the elemental distribution on the surface of the adsorption product of A1–A4 ash at 200 °C was analyzed using EPMA. Because no obvious Se-enriched region was found in A2 ash, only the results for A1, A3, and A4 ash are shown. The results for A1 ash are shown in Fig. 13, and the results for A3 and A4 ash are shown in Fig. SM-4 and Fig. SM-5. The Se-enriched regions in the three ash adsorption products were black macroparticles, as well as the case in the C-enriched regions, while the signals of Ca, Fe, Al, and Si were weak. This shows that the enrichment of Se in the ash was related to C but not to Ca, Fe, Al, and Si. Therefore, the physical adsorption of SeO₂ by ash at 200 °C was likely mainly related to the unburned carbon in the ash.

Table 4 shows the comparison of the amount of Se adsorbed by the four types of ash at 200 $^{\circ}$ C and the unburned carbon content in the ash. The adsorption amount of the four types of ash at 200 $^{\circ}$ C was positively correlated with the unburned carbon content in the ash, which again

59.6 eV

observed

XPS intensity

50.6

48

50

52

54

56 58

Binding energy (eV)

(b) A1-200

60

62 64

curve fitted

56.0

Se 3d



Fig. 12. XPS results for Se in the (a) SeO₂ and adsorption products of (b) A1 ash, and (c) CaO, at 200 °C.

confirmed that the physical adsorption of SeO_2 by the ash at 200 °C occurred mainly through the adsorption of unburned carbon in the ash.

The analysis of the Se form found using XPS in the adsorption product and correlation of the elemental distribution using EMPA clearly show that the adsorption of SeO₂ by ash at low temperatures was mainly physical, which was related to the unburned carbon in the ash. The thermal stability experiment of Se in the ash collected from the power plant dust collector in Fig. 2 shows that the release of Se in the ash occurred from 120 °C, and the release ratio gradually increased with an increase in temperature in the range of 120–500 °C. To further clarify the reasons for the release of Se in the ash adsorption products in the low-temperature range below 500 °C in the thermal stability experiment, a thermal stability analysis of Se in the products generated by the adsorption of A1 ash and CaO at 200 °C was performed, and the results are shown in Fig. 14.

As shown in Fig. 14, heated below 800 °C, the products generated by the adsorption of CaO at 200 °C were very stable and were not releases. When heated at 900 °C, the release ratio of Se in the adsorption products of CaO increased to 60%, which was the same as the adsorption product of CaO at 600 °C. This confirmed that the adsorption of SeO₂ by CaO was still chemical at 200 °C. When heated at 200 °C in an inert atmosphere, the release ratio of Se from the products generated by A1 ash adsorption at 200 °C reached 36%. With an increase in temperature, the release ratio of Se in the ash continued to increase, reaching 95%.

Based on the above analysis, we found that, in the low-temperature range below 500 °C, the adsorption of gaseous SeO_2 by ash was mainly physical, and a small amount was chemical. Among these, physical adsorption of ash mainly occurred through the adsorption of unburned carbon, whereas the chemical adsorption occurred through the adsorption of CaO.

Therefore, the transformation of Se during the flue gas cooling process included chemical adsorption in the medium-high temperature range and physical adsorption in the low-temperature range. At medium-high temperatures above 500 °C, the ash chemically adsorbed SeO₂ through the intrinsic mineral components CaO and CaSO₄ to generate CaSeO3 and CaSeO4, respectively, which decomposed and were released at high temperatures. CaSeO₄ began to decompose at 600 °C, whereas CaSeO₃ began to decompose at 900 °C. At low-temperatures below 500 °C, the adsorption of SeO₂ by ash mainly occurred through physical adsorption of unburned carbon, accompanied by a small amount of chemical adsorption of CaO, and the physically adsorbed Se was released when heated at 200 °C. This can well explain the results in Fig. 4. At 200–400 °C, the adsorption of SeO₂ by ash is mainly through physical adsorption, and the amount of adsorbed Se decreases with the increase of temperature. At 500-900 °C, the adsorption of SeO₂ by ash is through chemical adsorption, and the amount of adsorbed Se increases



Fig. 13. Electron probe microanalysis of adsorption products of A1 Ash at 200 °C.

Table 4

A comparison of the amount of Se adsorbed by four types of ash at 200 $^\circ\!C$ and the unburned carbon content in the ash.

	A1	A2	A3	A4
unburned carbon content (wt%)	2.7	0.80	0.63	2.1
Amount of Se adsorbed(µg/g)	79.7	60.2	59.1	75.9



Fig. 14. The thermal stability of Se in products formed by adsorption at 200 °C.

with the increase of temperature. However, with the large amount of CaSeO₄ decomposition above 600 °C, the amount of Se adsorbed by ash decreases significantly. And with the decomposition of CaSeO₃ at 900 °C, the amount of Se adsorbed by ash decreases further. In the thermal stability experiment of Se in ash, Se desorbed below 500 °C was physically adsorbed Se, Se desorbed at 500–800 °C was mainly CaSeO₄ generated via chemical adsorption of CaSO₄, and Se released continuously at 900 °C was mainly CaSeO₃ generated via chemical adsorption of CaSO.

4. Conclusions

In this study, by analyzing the thermal stability of Se in ash collected from different power plants, it was found that Se in ash was released in the temperature range of low to high. It is clear that the migration of gaseous Se into ash included two parts: chemical adsorption that mainly occurred in the medium-high temperature range and physical migration that occurred in the low-temperature range. Among them, physical migration was the main way by which gaseous Se transformed into ash, accounting for approximately 70% of the total. Chemical adsorptioncured Se existed in various forms with different thermal stabilities in ash.

Based on the established SeO₂-adsorption experimental system, an adsorption experiment of gaseous SeO₂ by ash was outperformed, and dynamic curves of SeO₂ adsorption by ash at 200–900 °C were obtained. The amount of adsorbed Se increased first rapidly and then slowly with time; it first decreased, increased, and then decreased with increasing adsorption temperature (400 °C and 600 °C were the two turning points).

By comparing the adsorption characteristics of different ash and minerals, combined with speciation analysis and elemental distribution characterization of Se in the adsorption products, a transformation pathway of gaseous Se during the flue gas cooling process was proposed. In the medium-high temperature range above 500 °C, the ash chemically adsorbed SeO₂ through the internal mineral components CaO and CaSO₄ to generate CaSeO₃ and CaSeO₄, respectively, which decomposed and were released at higher temperatures. CaSeO₄ began to decompose at 600 °C, whereas CaSeO₃ began to decompose at 900 °C. In the low-temperature range below 500 °C, the adsorption of SeO₂ by ash mainly occurred through physical adsorption of unburned carbon, accompanied by a small amount of chemical adsorption of CaO, and the physically adsorbed Se began to release when heated at 200 °C.

Therefore, increasing the Ca content in fly ash by blending coal or adding Ca-containing minerals to enhance the chemical adsorption of SeO₂ by ash, or adding activated carbon in the low temperature range to enhance the physical adsorption of gaseous SeO₂, results in more gaseous SeO₂ being absorbed. Once Se is converted into particles, it can be removed cooperatively by the dust collector, thereby controlling Se emissions.

Environmental implication

Selenium (Se) is an essential trace element in the human body, but excessive consumption of Se can lead to Se poisoning, damage the skin and nervous system, and even cause death. Coal-fired units are among the main sources of Se emissions in the atmosphere, and the emitted Se is in the inorganic form, which is more toxic. The mechanism of Se adsorbed by ash during the flue gas cooling process revealed in this work is helpful to understand the transformation pathways of Se in coal-fired systems and provide theoretical support for the development of Se emission control techniques.

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.

Data Availability

The data that has been used is confidential.

Acknowledgments

This work was financially supported by the Fundamental Research Funds for the Central Universities of China (2022ZFJH004).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.130362.

References

- Bool, L., Helble, J., 1995. A laboratory study of the partitioning of trace elements during pulverized coal combustion. Energy Fuels 9, 880–887. https://doi.org/10.1016/ 0140-6701(96)87873-8.
- Chang, L., Yang, J., Zhao, Y., Liu, H., Zhang, J., Zheng, C., 2019. Behavior and fate of As, Se, and Cd in an ultra-low emission coal-fired power plant. J. Clean. Prod. 209, 722–730. https://doi.org/10.1016/j.jclepro.2018.10.270.
- Cheng, C., Hack, P., Chu, P., Chang, Y., Liu, T., Ko, C., Chiang, P., He, C., Lai, Y., Pan, W., 2009. Partitioning of mercury, arsenic, selenium, boron, and chloride in a full-scale coal combustion process equipped with selective catalytic reduction, electrostatic precipitation, and flue gas desulfurization systems. Energy Fuels 23 (10), 4805–4816. https://doi.org/10.1021/ef900293u.
- Contreras, M., García-Frutos, F., Bahillo, A., 2013. Oxy-fuel combustion effects on trace metals behaviour by equilibrium calculations. Fuel 108, 474–483. https://doi.org/ 10.1016/j.fuel.2013.02.029.
- Córdoba, P., Ochoa-Gonzalez, R., Font, O., Izquierdo, M., Querola, X., Leiva, C., López-Antón, M., Díaz-Somoano, M., Martinez-Tarazona, M., Fernandez, C., Tomás, A., 2012. Partitioning of trace inorganic elements in a coal-fired power plant equipped with a wet Flue Gas Desulphurization system. Fuel 92, 145–157. https://doi.org/ 10.1016/j.fuel.2011.07.025.
- Dai, S., Zheng, X., Wang, X., Finkelman, R., Jiang, Y., Ren, D., Yan, X., Zhou, Y., 2017. Stone coal in China: a review. Int. Geol. Rev. 60 (2), 1–18. https://doi.org/10.1080/ 00206814.2017.1378131.
- Duan, L., Li, X., Jiang, Y., Lei, M., Dong, Z., Longhurst, P., 2017. Arsenic transformation behavior during thermal decomposition of P. vittata, an arsenic hyperaccumulator. J. Anal. Appl. Pyrolysis 124, 584–591. https://doi.org/10.1016/j.jaap.2017.01.013.
- European Union, 2016. Directive (EU) 2016/2284 of the European Parliament and of the Council of 14 December 2016 on the reduction of national emissions of certain atmospheric pollutants, amending Directive 2003/35/EC and repealing Directive 2001/81/EC. J. Eur. Union. 344, 1–31.

- Frandsen, F., Dam-Johansen, K., Rasmussen, L., 1994. Trace elements from combustion and gasification of coal-an equilibrium approach. Prog. Energy Combust. Sci. 20, 115–138. https://doi.org/10.1016/0360-1285(94)90007-8.
- Fu, S., Song, Q., Tang, J., Yao, Q., 2014. Effect of CaO on the selective non-catalytic reduction deNOx process: experimental and kinetic study. Chem. Eng. J. 249, 252–259. https://doi.org/10.1016/j.cej.2014.03.102.
- Ghosh-Dastidar, A., Mahuli, S., Agnihotri, R., Fan, S., 1996. Selenium capture using sorbent powders: mechanism of sorption by hydrated lime. Environ. Sci. Technol. 30 (2), 447–452. https://doi.org/10.1021/es950129m.
- Gückel, W., Kastel, R., Lewerenz, J., Synnatschke, G., 1982. A method for determining the volatility of active ingredients used in plant protection. Part III: The temperature relationship between vapor pressure and evaporation rate. Pest. Sci. 13 (2), 161–168. https://doi.org/10.1002/ps.2780130208.
- He, K., Song, Q., Yan, Z., Yao, Q., 2019. Study on competitive absorption of SO3 and SO2 by calcium hydroxide. Fuel 242, 355–361. https://doi.org/10.1016/j. fuel.2019.01.046.
- Huang, Y., Hu, H., Gong, H., Xing, H., Yuan, B., Fu, B., Li, A., Yao, H., 2021. Mechanism study of selenium retention by iron minerals during coal combustion. Proc. Combust. Inst. 38, 4189–4197. https://doi.org/10.1016/j.proci.2020.08.006.
- Huggins, F., Senior, C., Chu, P., Ladwig, K., Huffman, G., 2007. Selenium and arsenic speciation in fly ash from full-scale coal-burning utility plants. Environ. Sci. Technol. 41 (9), 3284–3289. https://doi.org/10.1021/es062069y.
- Itskos, G., Koukouzas, N., Vasilatos, C., Megremi, I., Moutsatsou, A., 2010. Comparative uptake study of toxic elements from aqueous media by the different particle-sizefractions of fly ash. J. Hazard. Mater. 183 (1–3), 787–792. https://doi.org/10.1016/ j.jhazmat.2010.07.095.
- Li, Y., Tong, H., Zhuo, Y., Chen, C., Xu, X., 2006. Simultaneous removal of SO2 and trace SeO2 from flue gas: effect of product layer on mass transfer. Environ. Sci. Technol. 40 (13), 4306–4311. https://doi.org/10.1016/j.combustflame.2011.05.005.
- López-Antón, M., Díaz-Somoano, M., Spears, D., Martínez-Tarazona, M., 2006. Arsenic and selenium capture by fly ashes at low temperature. Environ. Sci. Technol. 40 (12), 3947–3951. https://doi.org/10.1021/es0522027.
- Ma, T., Huang, Y., Deng, S., Fu, B., Luo, G., Wang, J., Hu, H., Yuan, C., Yao, H., 2020. The relationship between selenium retention and fine particles removal during coal combustion. Fuel 265, 116859. https://doi.org/10.1016/j.fuel.2019.116859.
- Otero-Rey, J., López-Vilariño, J., Moreda-Piñeiro, J., Alonso-Rodríguez, E., Muniategui-Lorenzo, S., López-Mahía, P., Prada-Rodríguez, D., 2003. As, Hg, and Se flue gas sampling in a coal-fired power plant and their fate during coal combustion. Environ. Sci. Technol. 37 (22), 5262–5267. https://doi.org/10.1021/es020949g.
- Seames, W., 2003. An initial study of the fine fragmentation fly ash particle mode generated during pulverized coal combustion. Fuel Process. Technol. 81 (2), 109–125. https://doi.org/10.1016/S0378-3820(03)00006-7.
- Senior, C., Tyree, C., Meeks, N., Acharya, C., McCain, J., Cushing, K., 2015. Selenium partitioning and removal across a wet FGD scrubber at a coal-fired power plant. Environ. Sci. Technol. 49 (24), 14376–14382. https://doi.org/10.1021/acs. est.5b03722.
- Shah, P., Strezov, V., Stevanov, C., Nelson, P., 2007. Speciation of Arsenic and Selenium in coal combustion products. Energy Fuels 21 (2), 506–512. https://doi.org/ 10.1021/ef0604083.
- Song, G., Xu, W., Liu, K., Song, Q., 2020. Transformation of selenium during coal thermal conversion: effects of atmosphere and inorganic content. Fuel Process. Technol. 205, 106446 https://doi.org/10.1016/j.fuproc.2020.106446.
- Swanson, S., Engle, M., Ruppert, L., Affolter, R., Jones, K., 2013. Partitioning of selected trace elements in coal combustion products from two coal-burning power plants in the United States. Int. J. Coal Geol. 113, 116–126. https://doi.org/10.1016/j. coal.2012.08.010.
- Tian, H., Zhu, C., Gao, J., Cheng, K., Hao, J., Wang, K., Hua, S., Wang, Y., Zhou, J., 2015. Quantitative assessment of atmospheric emissions of toxic heavy metals from anthropogenic sources in China: historical trend, spatial distribution, uncertainties, and control policies. Atmos. Chem. Phys. 15 (8), 10127–10147. https://doi.org/ 10.5194/acp-15-10127-2015,2015.
- Tu, G., Song, Q., Yao, Q., 2016. Relationship between particle charge and electrostatic enhancement of filter performance. Powder Technol. 301, 665–673. https://doi.org/ 10.1016/j.powtec.2016.06.044.

U.S. Environmental Protection Agency, 2012. National emission standards for hazardous air pollutants from coal and oil-fired electric utility steam generating units and standards of performance for fossil-fuel-fired electric utility, industrial-commercial-institutional, and small industrial-commercial-institutional

- steam generating units. Fed. Regist. 77, 9487–9488.
 Vejahati, F., Xu, Z., Gupta, R., 2010. Trace elements in coal: associations with coal and minerals and their behavior during coal utilization-a review. Fuel 89, 904–911. https://doi.org/10.1016/j.fuel.2009.06.013.
- Wagner, C., Gale, L., Raymond, R., 1979. 2-dimensional chemical state plots: a standardized data set for use in identifying chemical states by x-ray photoelectron spectroscopy. Anal. Chem. 51 (4), 466–482. https://doi.org/10.1021/ac50040a005.
- Wang, A., Song, Q., Ji, B., Yao, Q., 2015. Thermophoretic motion behavior of submicron particles in boundary-layer-separation flow around a droplet. Phys. Rev. E 92 (6), 063031. https://doi.org/10.1103/PhysRevE.92.063031.
- Wang, J., Zhang, Y., Liu, Z., Gu, Y., Norris, P., Xu, H., Pan, W., 2019. Coeffect of air pollution control devices on trace element emissions in an ultralow emission coalfired power plant. Energy Fuels 33 (1), 248–256. https://doi.org/10.1021/acs. energyfuels.8b03549.
- Weser, U., Sokolowski, G., Pilz, W., 1977. Reaction of selenite with biochemically active thiols: an x-ray photoelectron spectroscopic study. J. Electron Spectros. Relat. Phenom. 10 (4), 429–439. https://doi.org/10.1016/0368-2048(77)85039-1.

- Xu, M., Yan, R., Zhen, C., Qiao, Y., Han, J., Sheng, C., 2004. Status of trace element emission in a coal combustion process: a review. Fuel Process. Technol. 85, 215–237. https://doi.org/10.1016/S0378-3820(03)00174-7.
 Yan, R., Gauthier, D., Flamant, G., Peraudeau, G., Lu, J., Zheng, C., 2001. Fate of
- Yan, R., Gauthier, D., Flamant, G., Peraudeau, G., Lu, J., Zheng, C., 2001. Fate of selenium in coal combustion: volatilization and speciation in the flue gas. Environ. Sci. Technol. 35, 1406–1410. https://doi.org/10.1021/es0001005.
- Yuan, B., Hu, H., Huang, Y., Fu, B., Liu, H., Luo, G., Zhao, Y., Yao, H., 2022. Condensation and adsorption characteristics of gaseous selenium on coal-fired fly

ash at low temperatures. Chemo 287, 132127. https://doi.org/10.1016/j. chemosphere.2021.132127.

Zhao, Y., Yang, J., Ma, S., Zhang, S., Liu, H., Gong, B., Zhang, J., Zheng, C., 2017. Emission controls of mercury and other trace elements during coal combustion in China: a review. Int. Geol. Rev. 60 (5/6), 638–670. https://doi.org/10.1080/ 00206814.2017.1362671.