

Retention of As during coal combustion: Devolatilization and char combustion

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ABSTRACT

The retention of arsenic (As) during coal combustion facilitates As emission control. A fixed-bed experimental system was used to conduct devolatilization and char combustion experiments at 1100–1300 °C using three types of coal. Both processes contributed to the As release. As in coal was bound to carbonate, oxide, sulfide, and aluminosilicate (Als-As). During devolatilization, carbonate- and oxide-bound As and Als-As remained stable, while sulfide-bound As was completely decomposed. The gaseous As was partially retained as Char-As. During char combustion, Char-As was oxidized to As₂O₃, which was partially retained by minerals. Carbonate- and oxide-bound As reacted with silicon (Si) and aluminum (Al) to produce Als-As, which was the main As form in ash. As retention was significantly inhibited by the destruction of the lattice structure. As retention by char during devolatilization and minerals during char combustion promoted As enrichment in solid products and its removal.

1. Introduction

Arsenic (As) and its compounds are highly toxic (Rahman and Singh, 2019). As in coal is easily discharged into the atmosphere during combustion and endangers human health and the ecological environment, which has attracted extensive attention (Finkelman, 2004). Coal combustion is a primary emission source of As in the atmosphere (Tian et al., 2015). In some countries worldwide, standards for As emission from coal-fired plants have been set (U.S. Environmental Protection Agency, 2012; European Union, 2016). After coal combustion, most of the As can be captured by the dust collector as well as wet desulfurization devices in the form of coarse particles, while part of the As in the form of fine particle and the gas phase in the flue gas is emitted into the air (Zhao et al., 2017; Wang et al., 2019; Czech et al., 2020). Studying the transformation of As during coal combustion and strengthening the enrichment of As in the solid phase, particularly in coarse particles, should facilitate the coordinated removal of As by air pollution control devices and As emission control.

In a coal-fired system, the transformation of As consists of two stages, and they are the coal combustion stage and the post-combustion stage (Seames and Wendt, 2000). In the coal combustion stage, As is partially

retained in solid products owing to its thermal stability or retention by the inorganic contents in coal (Zhou et al., 2019a; Song et al., 2022); the remaining As is released into the flue gas. During the cooling of the flue gas in the post-combustion stage, gaseous As may be retained in fly ash after reaction with mineral components in the ash or physical adsorption and condensation (Wang et al., 2020a; Xu et al., 2021; Hu et al., 2021). Regulating the As transformation in the coal combustion process through blending coal or injecting sorbents into the furnace can strengthen the retention of As (Zhao et al., 2021; Yu et al., 2021) and help reduce the bioavailability and environmental risk of As in solid products (He et al., 2020; Han et al., 2022).

Previous studies have shown that different methods, coal types, as well as combustion conditions affect the process of As retention in the coal combustion stage and result in significant differences in the As retention characteristics in solid combustion products. Song et al (Song et al., 2022). carried out coal combustion experiments on 25 kinds of coal and found that the ratio of As retained in the solid phase was 21–82% at 1100 °C and 0–20% at 1300 °C. Ji et al (Ji et al., 2019). conducted combustion experiments on three kinds of coal and obtained that the retention ratio of As was 29–47% at 1300 °C. Zou et al (Zou et al., 2017). carried out combustion experiments with 6 types of coal

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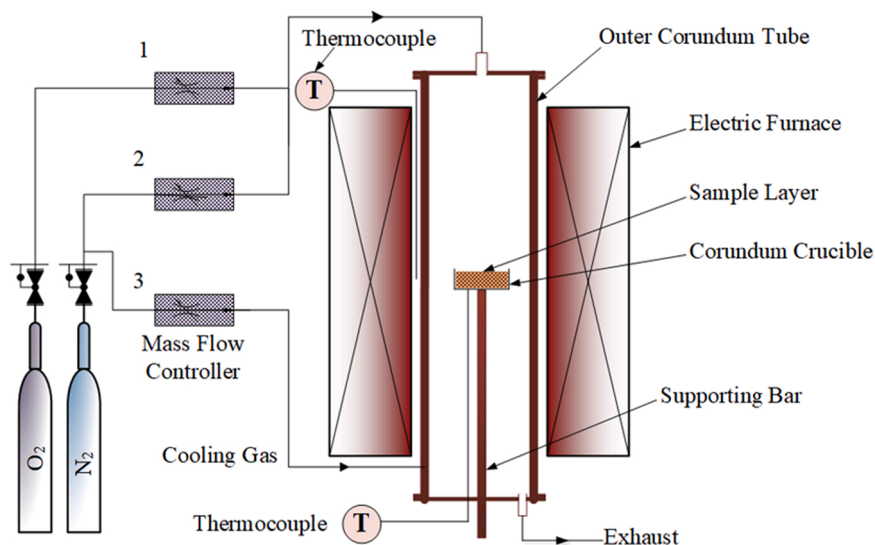


Fig. 1. Schematic diagram of the fixed-bed reactor system (Song et al., 2022).

and found that the retention ratio of As was 10–45% at 1300 °C. Different scholars (Song et al., 2022; Ji et al., 2019; Zou et al., 2017) have performed coal combustion experiments at the same temperature, and the retention ratio of As obtained varied widely, indicating the complexity of the As retention process.

The difference in the retention ratio of As is related to the form of As present in coal (Wierońska-Wisniewska et al., 2022). The main forms of As in coal included carbonate- and oxide-bound (making up 5–35%), sulfide-bound (making up 0–80%), and residual forms (making up 5–45%) (Finkelman et al., 2018). During the high-temperature combustion of coal, some of the As remained in the solid products because it is thermally stable, which varied for different As forms (Song et al., 2022; Liu et al., 2009). Liu et al (Liu et al., 2009), performed pyrolysis experiments on Yima coal at 1000 °C and concluded that the retention ratio of residual As was higher than those of carbonate-, oxide-, and sulfide-bound As. Pyrolysis experiments above 1000 °C on coal have not been conducted before, and thus the thermal stability of As in different forms at higher temperatures remains to be studied. Some unstable As can be transformed into forms with higher stability and hence retained during combustion. Zou et al (Zou et al., 2017), found that a small quantity of exchangeable As occurred in the solid products of coal combustion at 1000 °C. Song et al (Song et al., 2022), discovered that the proportion of residual As in combustion products at 1100–1200 °C was higher than that in raw coal. This indicates the transformation of other forms of As into exchangeable and residual As in the course of combustion.

The transformation of As occurring in different forms is relevant with the inorganic component in coal. Seames et al (Seames and Wendt, 2007), reported that the As content in fly ash particles correlated well with those of calcium (Ca) and iron (Fe), and concluded that Ca and Fe were the main mineral components that retained As. Experiments on the adsorption of As_2O_3 by minerals were performed at 1000–1300 °C (Cao et al., 2020; Fu et al., 2021; He et al., 2021; Song et al., 2020a) and revealed that Ca- and Fe-based minerals, including CaO , CaSiO_3 , CaSO_4 , and Fe_2O_3 , adsorbed As_2O_3 to generate $\text{Ca}_3(\text{AsO}_4)_2$ and FeAsO_4 . Song et al (Song et al., 2022), discovered that the silicon (Si) together with aluminum (Al) components strengthened the retention ability of CaO and Fe_2O_3 on As via coupling effects. The above research indicates that Ca, Fe, Si, as well as Al components present in coal can retain gaseous As during high-temperature combustion. Chen et al (Chen et al., 2015), suggested that SO_2 restrained the retention of As by CaO via a competitive reaction below 900 °C. Fu et al (Fu et al., 2019), found the conversion of As_2O_3 into AsCl_3 under the action of chlorine (Cl)

components, which promoted the release of As as AsCl_3 was unstable when the temperature was above 1000 °C (Zhang et al., 2020). These results indicate that the influence of the non-mineral components on the retention of As in coal at high temperatures is limited.

The As transformation during coal combustion is complex. The retention of As in the solid phase and the change in the forms of As are markedly different due to the various components and combustion conditions of coal. Studying the retention mechanism of As in the course of coal combustion is essential to control As emissions. Previous studies have focused only on the gas-solid and form distributions of As at the end of coal combustion. Nevertheless, the retention paths of As remain unclear, which requires process analysis on the transformation of As in different forms. The process of coal combustion is composed of two stages: the coal devolatilization stage and the char combustion stage (Zhou et al., 2019b). Research on the transformation of other elements (such as alkali metals) during fuel combustion has shown that the transformation mechanism of alkali metals in the devolatilization stage is different from that in the char combustion stage (Zhao et al., 2015a; Viljanen et al., 2018). Both stages contribute significantly to the retention of alkali metals at the end of combustion. After devolatilization, the form distribution of alkali metals affects the transformation during char combustion. For example, char retained part of the volatile KCl as Char-K during devolatilization (Zhao et al., 2015b); thereafter, Char-K reacted with Si to form K-silicates that remained in the ash during combustion and reduced the release of potassium (K) (Zhao et al., 2022). Regulating the retention of As in the two stages is conducive to the control of As emissions; however, no research has been reported on As retention in the two stages.

To reveal the retention characteristics and mechanisms of As in the coal devolatilization and char combustion stages, three types of coal were used to conduct coal devolatilization and char combustion experiments between 1100 and 1300 °C using a fixed-bed experimental system. The retention ratios of As during coal devolatilization and char combustion were obtained via measurement of the content of As in coal and solid products. The form distribution was analyzed for As in coal as well as solid products using a sequential chemical extraction method. The retention characteristics of As were studied in the coal devolatilization and char combustion stages. A co-heating experiment of the char and As model compound was carried out, and the retention effect of char on gaseous As in the devolatilization stage was revealed. The retention mechanism of As in the char combustion stage was explored via a co-heating experiment of char and minerals, combined with the thermodynamic equilibrium calculation of the ash components. The retention

Table 1

Devolatilization time of coals at 1100–1300 °C (min).

Coal	A1	A2	A3
1100 °C	1.2	2.1	2.6
1200 °C	1.0	1.5	2.0
1300 °C	0.5	1.0	1.3

pathways of As in the coal devolatilization and char combustion stages were established.

2. Experimental

2.1. Sample

Three types of thermal coal produced in different regions of China, which were processed into powders (particle size in the 74–96 μm range) and labeled A1–A3, were used. The proximate and ultimate results of the coal are presented in Table S1 and Table S2, respectively. The concentrations of the mineral elements in coal samples are presented in Table S3. Additionally, an atomic fluorescence spectrophotometer (AFS; AFS-9320, Jitian, China) was employed when measuring the As content in coal, the results of which are presented in Table S3.

2.2. Experimental setup

A fixed-bed experimental system (Fig. 1) was used to conduct coal devolatilization and char combustion experiments. The system was introduced in detail in a previous study (Song et al., 2022). The reaction gas used for the coal devolatilization experiments was N₂, and the gas flow rate was 500 mL/min. The reaction gas was introduced from top of the reactor and discharged via the bottom. After continuous heating and introduction of the reaction gas until the stabilization of temperature and atmosphere, a sample (0.8 g), which was contained in a crucible, was put in the constant-temperature area with minimal delay. The reaction time was set as 0.5–2.6 min during the devolatilization experiments and 45 min during the char combustion experiments. After reaching the set time, the crucible was quickly moved to the cooling zone of the reactor; the flow of the reaction gas was turned off, and the cooling gas was turned on. The crucible was purged with N₂ at a rate of 2 L/min for 10 min to guarantee the quick cooling of samples in an inert atmosphere. Subsequently, the solid products were collected for analysis. For the combustion experiments, the devolatilization was first performed on 0.8 g of a coal sample. After reaching the set time, the crucible containing the char was transferred into the cooling area. Simultaneously, the reaction gas was switched to a mixture of N₂ and O₂ gas, where the volume fraction of O₂ was 21%, and the total gas flow was 500 mL/min. When the temperature and atmosphere had stabilized, the crucible was returned to the constant-temperature zone for combustion. After reaching the set time, the crucible was moved to the bottom of the reactor for cooling and sample collection.

2.3. Methods

Three kinds of coal samples were used in the devolatilization experiments at 1100–1300 °C. During devolatilization, numerous gaseous components are formed, including H₂, H₂O, CO₂, CO, and CH₄ (Zhang et al., 2016). The concentrations of CO₂, CO, and CH₄ were analyzed using a Fourier transform infrared spectrometer (FTIR; Thermo Fisher Scientific Nicolet 6700, USA), which was used to determine the time required for coal devolatilization. The concentrations of CO₂, CO, and CH₄ changed synchronously with time and were integrated and added over time. When the total quantity of gases released exceeded 95% of the maximum releasable quantity, the process of coal devolatilization was considered complete (Zhao et al., 2015b). The characteristic time of coal devolatilization was determined (Table 1), which was the set time in

devolatilization experiments.

The CO₂ concentration in the gas discharged at the bottom of the reactor was measured in the char combustion experiments. The char generated by the devolatilization of the three kinds of coal burned out at 1100 °C within 45 min. As a result, the time of the combustion experiments was set to 45 min to obtain the ash.

The As content and form in coal, char, and ash were analyzed. The solid samples were digested in a mixture of HNO₃, H₂O₂, and HF. The detailed digestion process was introduced in a previous study (Song et al., 2019). AFS was employed to determine the concentration of As in the resulting solutions. The retention ratios of As to the total As in coal after devolatilization and char combustion, $R_{As, dev}$ and $R_{As, com}$, respectively, were calculated using Eqs. (1) and (2).

$$R_{As, dev} = \frac{m_{char} \times C_{char}}{m_{coal} \times C_{coal}} \times 100\% \quad (1)$$

$$R_{As, com} = \frac{m_{ash} \times C_{ash}}{m_{coal} \times C_{coal}} \times 100\% \quad (2)$$

where m_{coal} , m_{char} , and m_{ash} are the mass (g) of coal, char, and ash samples, respectively. C_{coal} , C_{char} , and C_{ash} are the concentrations of As (μg/g) in coal, char, and ash, respectively.

A previously reported sequential chemical extraction method was employed when analyzing the forms of As present in coal, char, and ash (Song et al., 2020b). As was classified into five forms: As in F1 form was soluble in water or ion-exchangeable; As in F2 form was bound to carbonate and oxide; As in F3 form was bound to sulfide; As in F4 form was bound to organic material and As not classified in any of the F1–F4 forms was residual As (F5). The extraction solvent and duration for all steps are shown in Table S4. The detailed extraction process was described in a previous study (Song et al., 2020b). The proportion of As present in each form in the solid sample to the total As in coal, P_{s, F_j} , (where s corresponds to coal, char, or ash; $F_{j=1-4}$ corresponds to the As forms in Table S4), was calculated using Eq. (3). The proportion of the residual As in coal, char, and ash, $P_{coal, F5}$, $P_{char, F5}$, and $P_{ash, F5}$ were calculated using Eqs. (4), (5), and (6), respectively.

$$P_{s, F_j} = \frac{M_{s, F_j}}{M_t} \times 100\% \quad (3)$$

$$P_{coal, F5} = 100\% - \sum_{j=1}^4 P_{coal, F_j} \quad (4)$$

$$P_{char, F5} = R_{As, dev} - \sum_{j=1}^4 P_{char, F_j} \quad (5)$$

$$P_{ash, F5} = R_{As, com} - \sum_{j=1}^4 P_{ash, F_j} \quad (6)$$

where M_{s, F_j} is the content of As (μg) of F_j form in coal, char, and ash samples. M_t is the total content of As (μg) present in the coal sample.

For the retention mechanism of gaseous As, the char sample was prepared by the pyrolysis of fulvic acid at 1100–1300 °C for 10 min and thereafter co-heated with 1% p-aminophenylarsenic acid for 5 and 45 min. The content and form distributions of As in the products were analyzed.

To explore the interaction between carbonate- and oxide-bound As and Si/Al minerals, the A2 char produced at 1100–1300 °C was heated with 5% SiO₂ or Al₂O₃ in an N₂ atmosphere for 5 min. Changes in the content and form distribution of As retained in the solid phase were analyzed.

To compare the melting characteristics of the combustion products of different coal samples, the Equilib module of the Factage software (Li et al., 2022; Song et al., 2010) was used to perform thermodynamic equilibrium calculations, and the melting ratios of different ash samples

Table 2

Retention ratios of As in the coal devolatilization stage at 1100–1300 °C (%).

Coal	A1	A2	A3
1100 °C	88 ± 3	85 ± 2	89 ± 2
1200 °C	66 ± 2	78 ± 1	77 ± 3
1300 °C	56 ± 1	55 ± 2	65 ± 2

were obtained. The range of temperature was 1100–1300 °C, and the temperature interval was 100 °C.

3. Results and discussion

3.1. As transformation in the coal devolatilization stage

3.1.1. Distribution of As in coal and devolatilization products

The retention ratios of As in the char to the total As in coal after devolatilization at 1100–1300 °C are listed in Table 2. The retention ratios of As decreased as the temperature increased, with an average value of 87%, 74%, and 59% at 1100, 1200, and 1300 °C, respectively. Most of the As remained in the solid phase after the devolatilization stage.

Fig. 2 illustrates the proportions of different forms of As in the char after the devolatilization of the three types of coal at 1100–1300 °C. As forms in coal mainly included carbonate- and oxide-bound As (25–54%) and sulfide-bound As (43–56%). Residual As accounted for 21% and 12% of the total As in A2 and A3 coal, respectively. After devolatilization, the proportion of carbonate- and oxide-bound As was basically similar to that in raw coal. Organic-bound As was generated, and its proportion to the total As in coal was 12–26% at 1100 °C and decreased with an increase in temperature. The proportions of residual As were higher than those in raw coal, reaching 17–34% at 1100 °C. But the change in the trend when the temperature increased varied with the coal type: in A1 char, the retention ratio continuously decreased, and in A2 and A3 char, the retention ratio first increased and subsequently

decreased.

The As present in coal was mainly associated with carbonate, oxide, and sulfide, and the rest of As was residual As. After devolatilization, the main forms were carbonate- and oxide-bound, organic-bound, and residual forms. Upon comparing the distribution of the As forms in coal and char, it was found that the residual As and the As bound to carbonate and oxide in coal were retained in the char owing to their thermal stability during devolatilization; sulfide-bound As was thermally unstable but was partially retained because it was converted into organic-bound and residual As after reaction with the other components in coal.

3.1.2. Retention of gaseous As by char and characterization of products

The organic-bound As increased during the devolatilization of the three coals, which may be due to the retention of gaseous As by char. Zhao et al (Zhao et al., 2015a; Xu et al., 2019). proposed a reaction mechanism between char and inorganic K to form Char-K during

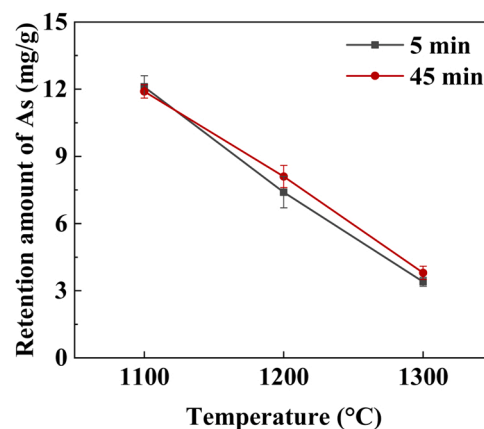


Fig. 3. Retention amount of As by fulvic acid char at 1100–1300 °C.

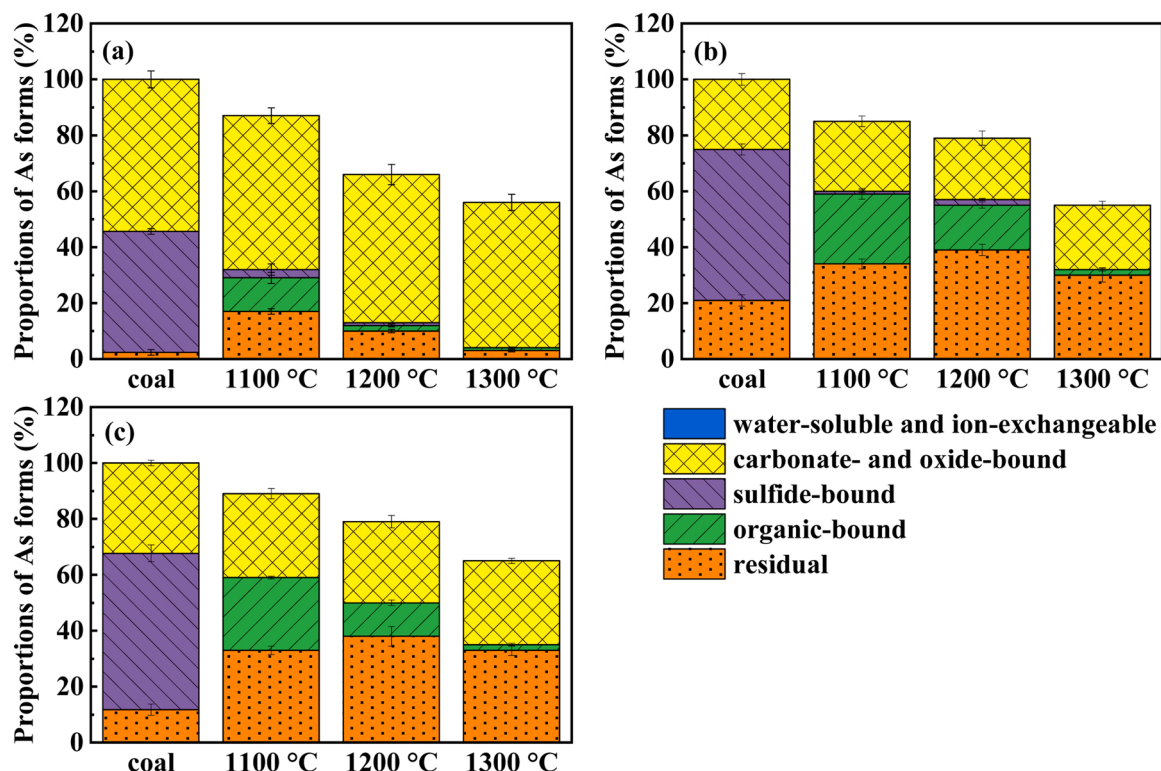


Fig. 2. Proportions of As in different forms in the coal and char: (a)A1; (b)A2; (c)A3.

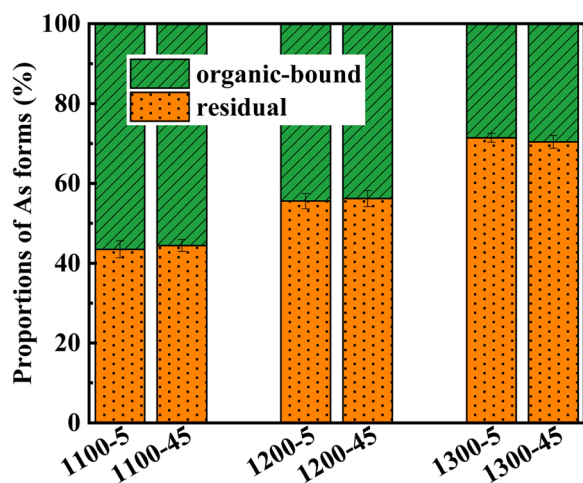


Fig. 4. Form distribution of Char-As generated at 1100–1300 °C for 5 and 45 min.

biomass pyrolysis. A similar reaction may occur with As during coal devolatilization; that is, the gaseous As generated in the course of devolatilization is retained by char and exists in the solid phase in organic-bound form.

To verify the retention of gaseous As on char, char prepared by the pyrolysis of fulvic acid was mixed with 1% p-aminophenyl arsenic acid and heated to 1100–1300 °C in an inert atmosphere for 5 and 45 min the retention amount of As is illustrated in Fig. 3. Char retained As to a marked extent, and the retention amount decreased with an increase in temperature. This may be due to the shorter contact time between the gaseous As and char when the formation of gaseous As by p-aminophenyl arsenic acid was accelerated, and the lower activity of char at higher temperatures. When the heating time was prolonged to 45 min, the retention amount of As was similar, indicating that the As retained by char was thermally stable. In this study, the As retained by the char was denoted as Char-As.

As is shown in Fig. 4, 56% of the Char-As retained at 1100 °C was extracted by $\text{HNO}_3 + \text{H}_2\text{O}_2$ and thus classified as organic-bound As. The remaining 44% of Char-As did not dissolve and was classified as residual As. In this study, insoluble Char-As was termed ins-Char-As. The proportion of organic-bound As in Char-As decreased and the proportion of ins-Char-As increased with increasing temperature, accounting for 29% and 71%, respectively, of the total As at 1300 °C. When the heating time was extended to 45 min, the proportions of the two As forms remained unchanged, indicating that they were thermally stable and did not undergo thermal decomposition or transformation.

Char retained gaseous As into Char-As at 1100–1300 °C, and the retention amount decreased with an increase in temperature. According to the chemical extraction method, 29–56% of the Char-As was organic-bound As, and the proportion decreased with an increase in temperature. The remaining Char-As consisted of insoluble residual As (ins-Char-As). The formation of Char-As may also be the reason for the increase in the proportion of the residual As during coal devolatilization, and further characterization of As forms in char is required to verify this.

3.1.3. Transformation pathways of As during coal devolatilization

Sulfide-bound As in coal was thermally unstable during devolatilization, a part of which was converted into organic-bound and residual As and retained in the solid phase. This occurrence may be because char retained gaseous As, thus forming Char-As, which is divided into soluble organic-bound As and insoluble residual As (ins-Char-As). The residual As in coal was combined with aluminosilicate (Yu et al., 2021), which is designated as Als-As. In addition to ins-Char-As, some of the residual As in char might also be Als-As. The residues of coal and char were treated using different digestion methods after sequential chemical extraction to further identify the existence of ins-Char-As and Als-As in the residual As. Ins-Char-As cannot be extracted at room temperature, but $\text{HNO}_3 + \text{H}_2\text{O}_2$ can be used to dissolve ins-Char-As during microwave digestion to measure its content. The total quantity of residual As in the sample was determined using $\text{HNO}_3 + \text{H}_2\text{O}_2 + \text{HF}$ to digest the extracted residue. The content of Al-As was obtained by subtracting the quantity of ins-Char-As from that of the residual As in the sample.

The proportions of organic-bound As and ins-Char-As to the total As in coal were added to obtain the proportion of Char-As (Fig. 5(a)). The proportion of Char-As to the total As in coal decreased when the temperature increased. The proportion of Char-As was negatively correlated with the content of volatile compounds in coal, as shown in Table S1. The negative correlation occurred because the char generated from coal that contained a lower concentration of volatile compounds had a more complex spatial structure, more micropores, and a larger specific surface area (Wang et al., 2020b), which resulted in the char having a stronger retention ability for gaseous As. Fig. 5(b) illustrates the proportion of organic-bound As and ins-Char-As in the Char-As. The proportion of organic-bound As in Char-As decreased as the temperature increased, and the proportion of ins-Char-As increased. This trend is similar to that exhibited by the char retaining As.

Fig. 6 displays the proportion of Als-As in coal and char at 1100–1300 °C. The original residual As in coal was Als-As. The proportions of Als-As in coal were close to that in char formed at different temperatures, indicating that Als-As was thermally stable.

As exists as carbonate- and oxide-bound, sulfide-bound, and residual forms (Als-As) in coal. Als-As and carbonate- and oxide-bound As in coal were retained in char owing to their thermal stability during

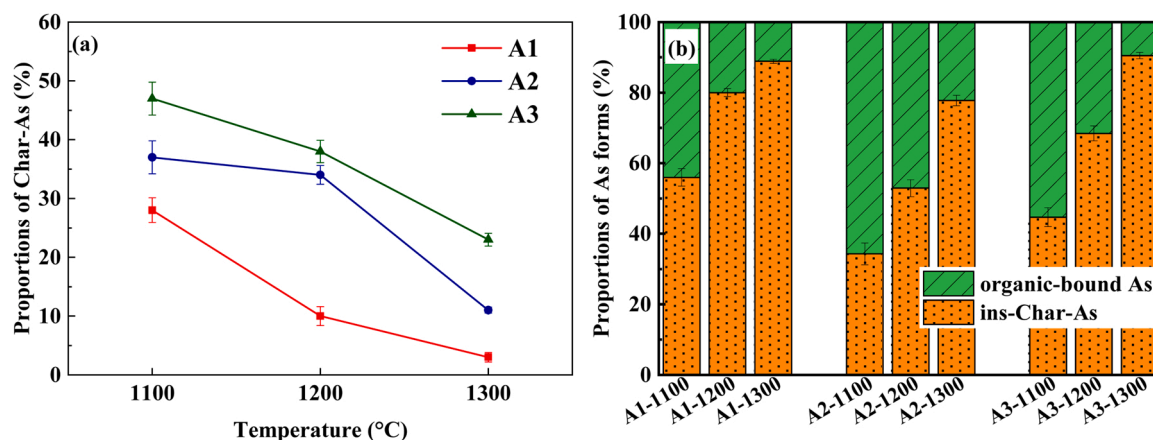


Fig. 5. Distribution of Char-As in devolatilization products: (a) proportions of Char-As to the total As in coal; (b) proportions of organic-bound As and ins-Char-As.

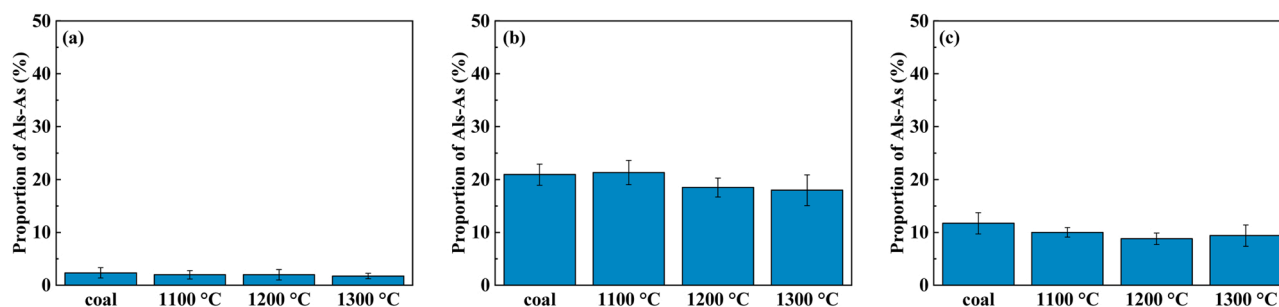


Fig. 6. Proportions of Als-As to the total As in coal and char: (a)A1; (b) A2; (c)A3.

Table 3

Retention ratios of As in the char combustion stage at 1100–1300 °C (%).

Coal	A1	A2	A3
1100 °C	29 ± 1	64 ± 2	75 ± 2
1200 °C	8 ± 1	10 ± 1	45 ± 2
1300 °C	1.2 ± 0.2	1.3 ± 0.1	21 ± 1

devolatilization. Sulfide-bound As was thermally unstable, but the generated gaseous As was partially converted into Char-As by char and was retained. Part of the Char-As was classified as organic-bound As, and the remainder was classified as residual As that was insoluble in $\text{HNO}_3 + \text{H}_2\text{O}_2$.

3.2. As transformation in the char combustion stage

3.2.1. Distribution of As in char and combustion products

The retention ratios of As in ash after char combustion at 1100–1300 °C are listed in Table 3. Comparing the data in Tables 2 and

3, a significant decrease of the As retention ratio during char combustion was observed. The retention ratios decreased with an increase in temperature, which was close to zero for A1 and A2 ash but 21% for A3 ash at 1300 °C.

Fig. 7 illustrates the proportions of different forms of As in the ash produced after char combustion between 1100 and 1300 °C. In char produced at 1100 °C, As was predominantly in carbonate- and oxide-bound, organic-bound and residual forms. After combustion, As retained in ash was mainly in residual form and accounted for 23%–61% of the total As in coal. In addition, a small amount of As in coal was retained as water-soluble and ion-exchangeable As and carbonate- and oxide-bound As. After combustion at 1200 and 1300 °C, only residual As was retained in ash, and its proportion decreased with the increasing temperature. The residual As retained in the ash was Als-As.

Part of the As in char was mainly associated with carbonate, oxide and organic, and the rest of the As was in residual forms (including ins-Char-As and Als-As). After combustion, As was predominantly retained in ash as residual As (Als-As), with a small quantity of water-soluble and ion-exchangeable As as well as carbonate- and oxide-bound As at

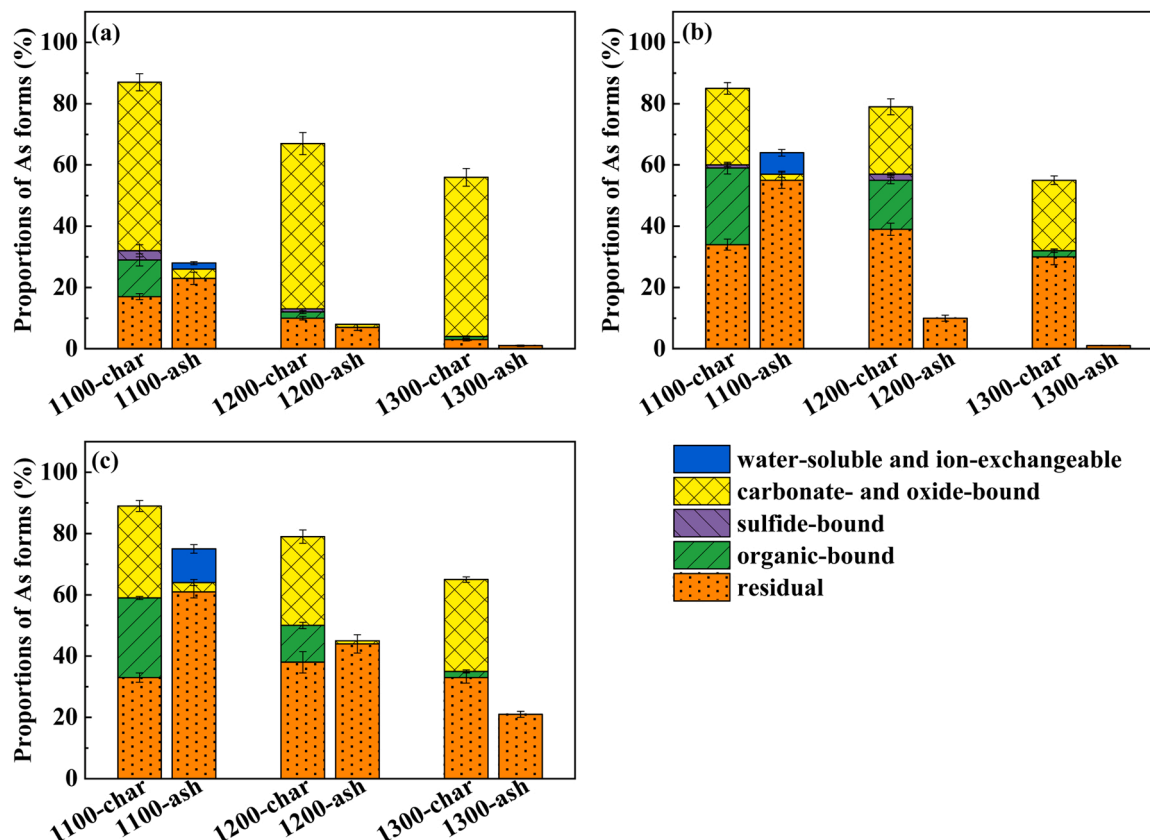


Fig. 7. Proportions of As in different forms in the char and ash: (a)A1; (b)A2; (c)A3.

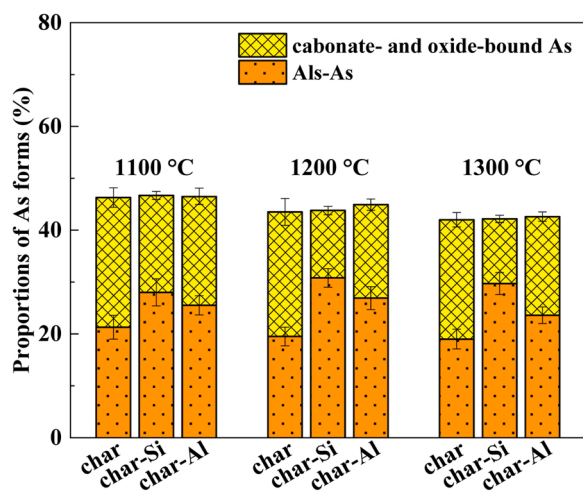


Fig. 8. Effects of SiO_2 and Al_2O_3 on carbonate- and oxide-bound As.

1100 °C. Comparing the forms of As in char and ash, Als-As and a small part of As bound to carbonate and oxide in char were stably retained in the solid phase during combustion. Char-As and most of the carbonate- and oxide-bound As were released or transformed during combustion. Part of them were transformed into water-soluble and ion-exchangeable As or Als-As at 1100 °C in ash but in the form of Als-As above 1200 °C.

3.2.2. Transformation pathways of As during char combustion

Char-As (including organic-bound As and ins-Char-As) was completely converted to gaseous As_2O_3 owing to the oxidation reaction during char combustion (Cao et al., 2020). Some gaseous As_2O_3 was retained by the mineral components in char and then retained in water-soluble and ion-exchangeable form and Als-As in ash. Previous studies have shown that Ca, Fe in coal can retain As (Song et al., 2022; Seames and Wendt, 2007). Minerals including CaO, CaSiO_3 , CaSO_4 , and Fe_2O_3 can adsorb As_2O_3 to form soluble $\text{Ca}_3(\text{AsO}_4)_2$ or FeAsO_4 (Cao et al., 2020; Song et al., 2020a; Sutopo et al., 2021), which was the water-soluble and ion-exchangeable As generated at 1100 °C. The coupling of Ca/Fe and Si/Al in retaining gaseous As_2O_3 resulted in the Ca-Si-Al-As and Fe-Si-Al-As composite salts (Als-As) (Song et al., 2022). Therefore, some As_2O_3 was retained in ash as Als-As during the char combustion stage. When the temperature increased, the reaction between Ca, Fe and Si, Al minerals to form aluminosilicate proceeded more fully (Wang et al., 2015). Therefore, gaseous As was retained only as Als-As when interacting with mineral components.

During char combustion, only a small quantity of carbonate- and oxide-bound As was stably retained in ash at 1100 °C but was absent at 1200 °C. This is assigned to the decomposition and release of As bound to carbonate and oxide or conversion by reacting with the other components in coal. To investigate the thermal stability of carbonate- and oxide-bound As, the char produced by the three types of coal was

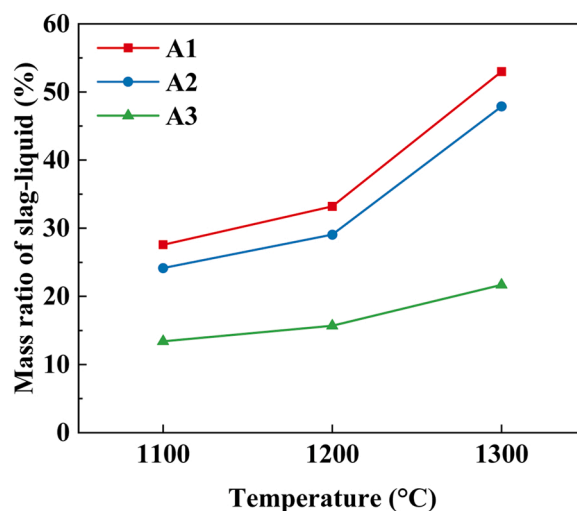


Fig. 10. Mass ratio of slag-liquid in ash produced at 1100–1300 °C in thermodynamic equilibrium.

continuously pyrolyzed at 1100, 1200, and 1300 °C for 45 min. The proportion of carbonate- and oxide-bound As to the total As in coal was similar to that at the end of devolatilization. This phenomenon indicates that the absence of carbonate- and oxide-bound As during char combustion was not due to thermal instability but due to the interaction with the other components in an oxidizing atmosphere. Previous studies have shown that the non-mineral components, SO_2 and HCl, do not promote the release of As during high-temperature combustion (Chen et al., 2015; Fu et al., 2019; Zhang et al., 2020), and the disappearance of carbonate- and oxide-bound As was more likely due to the action of the mineral components. Zhao et al. (2022). found that during biomass combustion, K reacted with Si to form insoluble K-silicates in the char combustion stage. Furthermore, Wang et al. (2021). found that when coal with high contents of Si and Al was co-burned with Zhundong coal, Si and Al promoted the conversion of acid-soluble Na to insoluble Na in the ash. Therefore, it is speculated that the carbonate- and oxide-bound As were transformed into Als-As by a reaction with the Si and Al components. To verify this, the char generated from A2 coal between 1100 and 1300 °C was mixed with 5% SiO_2 and Al_2O_3 in a N_2 atmosphere and heated for 5 min. The products were termed "char-Si" and "char-Al". The analysis results for the As forms are illustrated in Fig. 8. After the addition of SiO_2 and Al_2O_3 , the carbonate- and oxide-bound As decreased, and a similar proportion of Als-As increased concomitantly. This phenomenon confirms that the carbonate- and oxide-bound As can react with the Si and Al components to produce Als-As. During char combustion, the contact between the minerals increased and the reaction proceeded closer toward completion (Wen et al., 2016).

These conversion processes increased the content of Als-As in ash. However, as is shown in Fig. 9, the proportion of Als-As decreased after

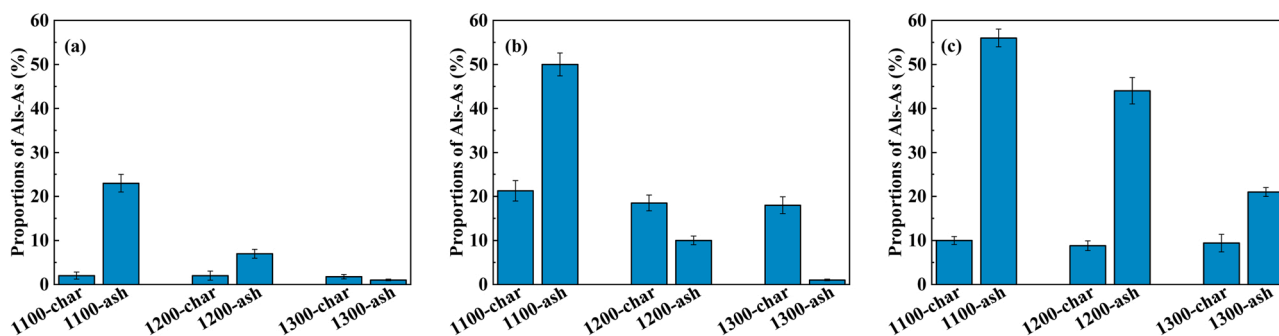


Fig. 9. Proportions of Als-As to the total As in the char and ash: (a) A1; (b) A2; (c) A3.

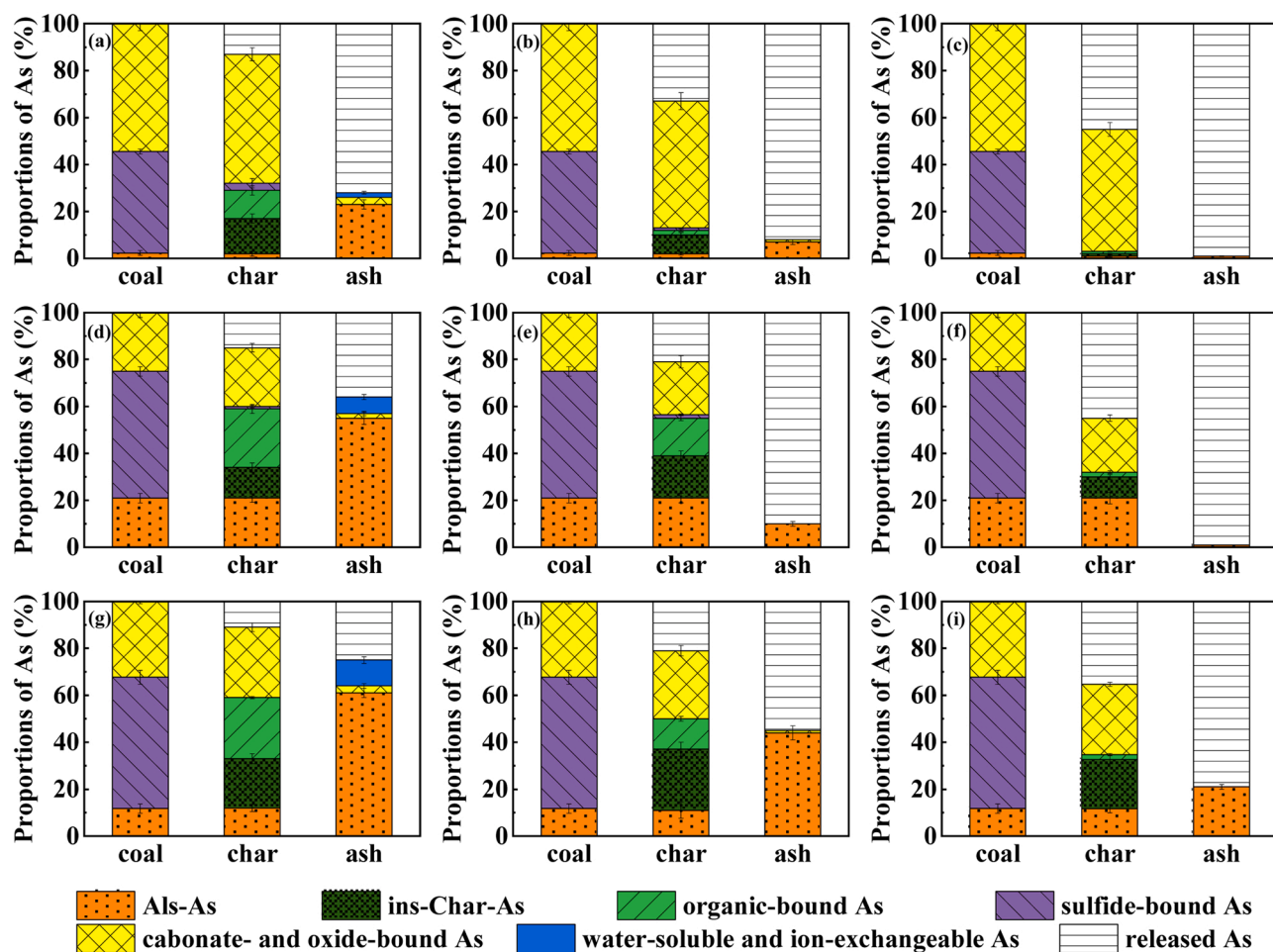


Fig. 11. As distribution in coal, after devolatilization and char combustion: (a)A1, 1100 °C; (b)A1, 1200 °C; (c)A1, 1300 °C; (d)A2, 1100 °C; (e)A2, 1200 °C; (f)A2, 1300 °C; (g)A3, 1100 °C; (h)A3, 1200 °C; (i)A3, 1300 °C.

the combustion of A1 char at 1300 °C and A2 char at 1200–1300 °C. This indicates the release of Als-As at higher temperatures, which might have been caused by the destruction of the mineral lattice structure (Xu et al., 2021). Fig. 10 illustrates the mass ratio of slag-liquid in the thermodynamic equilibrium state of the ash generated by the three types of coal between 1100 and 1300 °C. The mass ratio of the slag-liquid in A3 ash was lower than that in A1 and A2 ash, indicating that the degree of ash melting was lower and the mineral lattice was mostly intact. Therefore, Als-As still exhibited an increasing trend in the course of combustion of A3 char at 1300 °C, while the Als-As in A1 and A2 char decreased due to the destruction of the mineral lattice structure by ash

melting during combustion.

The As in char mainly included carbonate- and oxide-bound As, Char-As (including organic-bound As and ins-Char-As), and Als-As. During char combustion, Char-As generated gaseous As_2O_3 due to oxidation, some of which was retained in water-soluble and ion-exchangeable form and Als-As by the mineral components, including Ca, Fe, Si, and Al present in ash. Carbonate- and oxide-bound As reacted with Si/Al components to produce Als-As, which remained in the solid phase. Als-As was retained owing to its thermal stability. However, with the increase in temperature and the destruction of the mineral lattice structure, Als-As in the ash was also released.

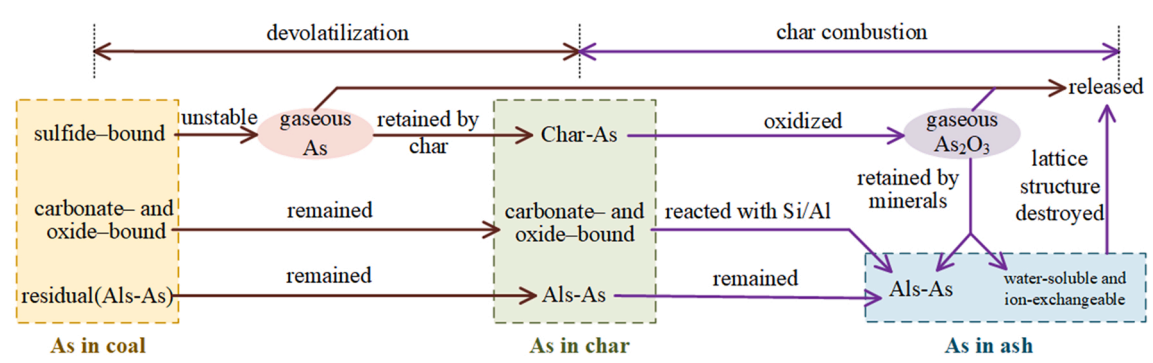


Fig. 12. Transformation paths of As during coal combustion.

3.3. Analysis on As retention during coal combustion

The gas-solid and form distributions of As during combustion of the three coals are illustrated in Fig. 11. As in coal was mainly bound to carbonate and oxide, sulfide and aluminosilicate (Als-As). In the devolatilization stage, sulfide-bound As basically disappeared. Carbonate- and oxide-bound As and Als-As remained unchanged. Char-As was generated, and the proportion decreased with the increase in temperature. In the char combustion stage, more As was released. As was mainly retained in the ash as Als-As, with a small quantity of water-soluble and ion-exchangeable, and carbonate- and oxide-bound As at 1100 °C.

The retention pathways of As during coal combustion are illustrated in Fig. 12. In the devolatilization stage, residual As (Als-As) and carbonate- and oxide-bound As in coal were retained owing to thermal stability; sulfide-bound As was thermally unstable, generating gaseous As, which was partially retained as Char-As. In the char combustion stage, Char-As was oxidized into gaseous As_2O_3 , which was partially retained as Als-As and water-soluble and ion-exchangeable As by mineral components including Ca, Fe, Si, and Al. Carbonate- and oxide-bound As reacted with Si/Al components to produce Als-As. The thermal stability of Als-As decreased owing to the increasing temperature and destruction of the mineral lattice structure.

The As retained in the devolatilization stage consisted of two parts: one was the thermally stable As bound to carbonate, oxide and aluminosilicate in coal, and the other was the gaseous As retained as Char-As. The proportions of thermal stable As in coal were ranked as follows: $\text{A1} > \text{A2} > \text{A3}$. More Char-As was formed in the A2 and A3 chars because of the difference in the char properties, so the retention ratio of As after devolatilization was ranked as $\text{A3} > \text{A2} > \text{A1}$. In the char combustion stage, the gaseous As_2O_3 released by the oxidation of Char-As was partially retained in the ash through the coupling mechanism of Ca, Fe, Si, and Al (Song et al., 2022). The contents of Si and Al in A3 coal was the highest, which was conducive to the retention of As_2O_3 . The retention ratio of As in A1 char was similar to those of A2 and A3. However, because of the inhibition of As retention by ash melting and the destruction of the mineral lattice structure, the retention ratio of As in A1 and A2 ash (close to zero at 1300 °C) was markedly lower than that of A3 ash (21% at 1300 °C).

4. Conclusions

The retention ratios of arsenic (As) in the devolatilization and char combustion stages of three kinds of coal at 1100–1300 °C were obtained, indicating that both stages contribute to the As release.

The main forms of As in coal showed great difference in thermal stability during devolatilization, as the Als-As and carbonate- and oxide-bound As were almost retained and sulfide-bound As was completely decomposed. The generated gaseous As was partially retained as Char-As by char. The char produced by the coal that contained a lower content of volatile compounds exhibited a stronger retention ability for gaseous As. Char-As was composed of organic-bound As and residual As (ins-Char-As), which were significantly different in solubility. The higher the temperature, the higher the proportion of ins-Char-As in Char-As. After devolatilization, the As was predominantly retained in char as carbonate- and oxide-bound As, Char-As (including organic-bound As and ins-Char-As), and Als-As.

In the char combustion stage, Char-As generated gaseous As_2O_3 owing to oxidation; part of the As_2O_3 was retained in Als-As and water-soluble and ion-exchangeable As by the mineral components, including calcium (Ca), iron (Fe), silicon (Si), and aluminum (Al). As was retained as Als-As at temperatures above 1200 °C. Carbonate- and oxide-bound As were thermally stable but reacted with Si and Al mineral components in an oxidizing atmosphere to produce Als-As in ash. Als-As in char was retained in ash owing to thermal stability. After char combustion, As was predominantly retained in ash as Als-As. A small quantity of As was retained as water-soluble and ion-exchangeable As, and carbonate- and

oxide-bound As at 1100 °C. As retention was significantly inhibited by the destruction of the lattice structure.

The results could provide guidance for the regulation of the enrichment of As in solid products during coal combustion and for removing As using air pollution control devices. The quantitative relationship between As retention capacity and char properties or mineral composition is worth exploring.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.psep.2022.09.028.

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