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RESEARCH

# The release and migration mechanism of arsenic during pyrolysis process of Chinese coals

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## Abstract

Special attention was drawn to the heavy metals contained in coal, due to it will cause harm to the environment during coal processing and utilization. The sequential chemical extraction of Shanxi coal (SX coal) and Wulanchabu coal (WLCB coal) was carried out to investigate the distribution of arsenic (As) in coals. Two raw coals were pyrolyzed at 300–900 °C in horizontal tubular furnace to investigate release behavior of As during pyrolysis process. The results showed that As in SX coal mainly existed in aluminosilicate-bound state (40.25%) and disulfide-bound state (32.51%), followed by carbonate-bound state and organic-bound state. The As in WLCB coal mainly existed in aluminosilicate-bound state (62.50%), followed by disulfide-bound state (19.10%). The As contents of water-soluble, ion-exchange and residue states in the two coals were less than others. The modes of occurrence of As had great influence on its volatilization behavior. As in organic part was easy to volatilize at low temperature. Sulfide-bound state would escape with the decomposition of pyrite. Because SX coal contained higher organic state and sulfide-bound state, the volatilization rate of As was higher than WLCB coal at any temperature, and the difference was more obvious at low temperature. In addition, FactSage simulation value was basically consistent with the experimental value.

**Keywords** Pyrolysis · Heavy metal elements · Release behavior · Low-rank coal

## 1 Introduction

Although China needs to achieve the goal of "Carbon Neutrality", the demand for coal in China for economic and social development has been high for a long time. According to preliminary calculations, in 2022, raw coal output in China reached to $4.56\times10^9$ t, a year-on-year increase of 10.5%. The total energy consumption in China is $5.41\times10^9$ tce, and coal consumption accounts for more than half (56.2%) (National bureau of statistics 2022). In order to reduce carbon emissions, coal chemical industry, which can transform coal from fuel into raw material, has been receiving widespread attention in recent years. Pyrolysis is an important technology to realize the clean and efficient utilization of coal (Deng and Tan 2021; Sun et al. 2022; Chi et al. 2022; Kuznetsov et al. 2023), and it is crucial to gasification and combustion process as the initial reaction (Zhou et al. 2018). Pyrolysis technology has been industrialized to varying degrees in China at present (Guo et al. 2004; Lu et al. 2004). However, the extensive utilization and transformation of coal will release harmful elements, which will cause harm to the environment and human health (Wang et al. 2004, 2022; Zhang, 2004; Liu, 2009).

Arsenic (As) is one of the main harmful elements in coal (Finkelman et al. 2002), and belongs to the five most toxic heavy metal elements (HMEs) (Swaine 1992). As released in coal processing and utilization is the main source of As pollution in the atmosphere (Cai and Jiang 2008). Especially in the process of combustion, gasification and pyrolysis, almost all forms of As in coal will generate highly toxic $As_2O_3$ (commonly known as As). Many studies have shown that the release behavior of As in coal mainly depends on its mode of occurrence in coal (Guo et al. 2003; Hu et al. 2021; Xie and Nie 2010; Zhou et al. 2015; Jiang et al. 2021; Luo et al. 2020). Zhang (2004) found that the content of As in coal determined the release capacity of As. As in low As coal hardly migrated. The migration characteristics of As in high As coal were similar to that of mercury, but the mobility

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was smaller than that of mercury. Wang et al. (2022) used some high-precision technologies, such as SEM–EDS and EPMA (electron microprobe analyzer) to investigate mode of occurrence in high As coal, and found that As in coal mainly occurred in pyrite, which migrated and transformed with pyrite during coal pyrolysis. Liu (2009) found that the thermal stability of organic matter-bound As in coal was the weakest, and it was almost completely released at 800 °C. The thermal stability of aluminosilicate-bound As was strong, and almost no release occurred during the pyrolysis process at 1000 °C. The thermal stability of other bound state of As was related to the thermal stability of related minerals. In previous studies carried out extensive research in release behaviors of HMEs during coal pyrolysis in recent years, and found that the release behavior of HMEs was significantly affected by their modes of occurrence in coal (Zhou et al. 2019a, 2021, 2019b; Wang et al. 2021).

To study the modes of occurrence of HMEs in coal, this paper not only used sequential chemical extraction (SCE), and prepared single-components samples (only containing one group of similar minerals). The release behaviors of As in raw and single-components samples were study to reveal the release mechanism during pyrolysis process, which was also crucial for study the release of heavy metals in coal during high temperature process, such as combustion and gasification process.

## 2 Materials and methods

In the present study, Chinese low-rank coals from Shanxi and Neimeng province were selected. Modes of occurrence of As were studied by the method of sequential chemical extraction (SCE), and to obtain three single-components (SC). Raw coal and SC samples were pyrolyzed in a fixed-bed reactor during 300–900 °C and the interval of 100 °C, with heating rate of 5 °C/min, to investigate the release behaviors of As. In addition, thermodynamic software FactSage 7.3 was used to simulate the release behaviors of As and transformation of minerals during pyrolysis process.

### 2.1 Preparation and characterization of coal samples

This study collected and used two low-rank coals in China, named SX coal (Shanxi Province) and WLCB coal (Wulanchabu). The materials were crushed and screened to obtain a particle size less than 2 mm. All samples were vacuum dried at 80 °C for 24 h to remove moisture and sealed for storage for experimental use. Proximate and ultimate analysis of the two samples were conducted according to the Chinese Standard Method GB/T 212-2008 and the Vario MACRO Cube, respectively.

The ashes of SX coal and WLCB coal were prepared at 815 °C according to GB/T 212-2008. Then, X-Ray Fluorescence Spectroscopy (XRF) analysis was conducted on ashes to determine the ash components, including $SiO_2$, $Al_2O_3$, $Fe_2O_3$, CaO, MgO, $K_2O$ and $SO_3$.

X-Ray Diffraction (XRD) analysis was used to analyze the mineralogical characteristics of the SX coal and WLCB coal. Prior to the XRD analysis, the coal samples were burned at 250 °C in a muffle furnace for 60 h to obtain the low-temperature ash of the coal samples. The low-temperature ash was analyzed using a Japanese Rigaku D/max-2500PC X-Ray diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a copper tube. The XRD pattern was recorded within the 2θ range of 5°-70° with a step size of 0.02°, the scan speed was 2°/minute. The accelerating voltage and tube current of the X-Ray diffractometer were 40 kV and 150 mA, respectively.

### 2.2 Determination of As in coal

The samples including raw coal, three single-component samples and all semi-cokes, were needed to be dissolved before measuring As. A coal sample of 0.1 g was placed in a Teflon tank, and 6 ml $HNO_3$, 3 ml $H_2O_2$, and 3 ml HF are added as reagents, then placed in a microwave digestion instrument (CEM MARS 5) for three-step dissolution. The solid coal sample was pre-treated by microwave digestion to transfer elements to the solution. Then, the solution and liquid samples obtained by sequential chemical extraction (SCE) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, NexlON300X). The ultra-pure water made by Milli-Q™ A10 system-produced was used in the microwave digestion process to reduce background values. The elemental concentration data used above were the average of three determination data.

### 2.3 Sequential chemical extraction experiment

In order to study the mode of occurrence of As in coal, SCE (Sequential Chemical Extraction) experiments were carried out on SX coal and WLCB coal. In this study, four-step SCE was adopted and the mode of occurrence of As in coal were determined, including carbonate (containing monosulfide, sulfate, phosphate and oxide)-bound state, aluminosilicate-bound state, disulfide-bound state and organic-bound state. The specific extraction conditions and procedures refer to other literature (Zhou et al. 2019b) as shown in Fig. 1. The extraction rate ($E_r$) of organic matter, mineral, and mode of occurrence of As in SX-coal and WLCB-coal can be calculated using the following formula:

$$E_r = C_{extracts} + C_{rawcoal} * 100\% \quad (1)$$

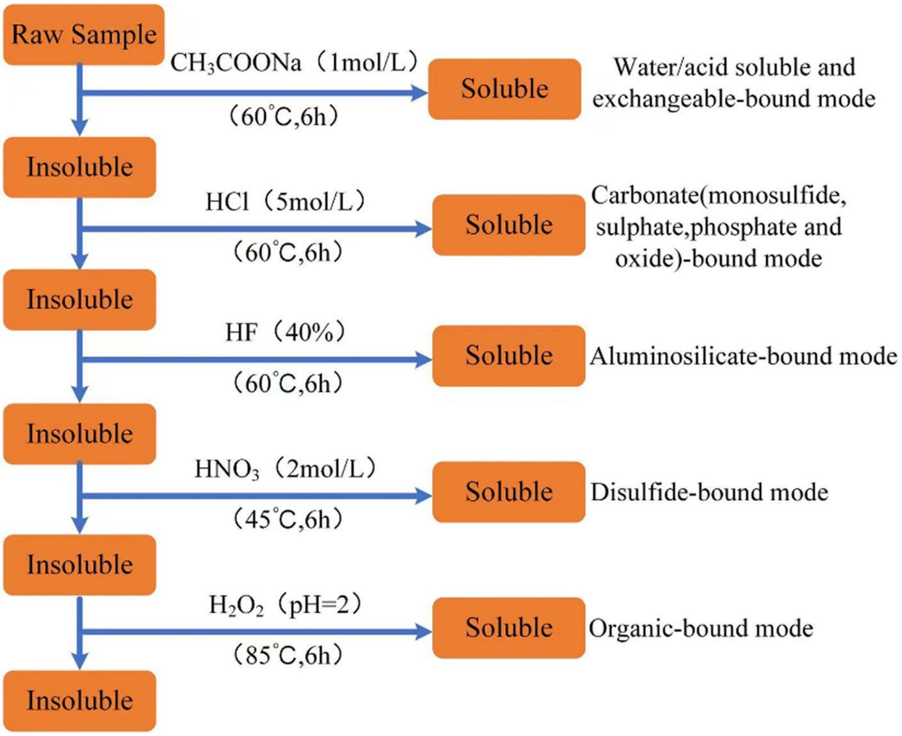

**Fig. 1** Flow chart of sequential chemical extraction

where $E_r$ was the extraction ratio of the As, organic matter or minerals; $C_{extracts}$ was the content of As, organic matter or minerals in the extracts; $C_{rawcoal}$ was the content of As, organic matter or minerals in raw coal.

## 2.4 Preparation of single-component samples

SX coal and WLCB coal were extracted with $CH_3COONa/HCl/HF/HNO_3$, $CH_3COONa/HCl/HF/H_2O_2$ and $CH_3COONa/HCl/HNO_3/H_2O_2$, respectively. As a result, three samples were obtained, each containing a single occurrence state of As (aluminosilicate-bound state, disulfide-bound state, organic-bound state). Studies (Steel and Patrick 2001) has shown that HCl can dissolve carbonates, sulfates, phosphates, and oxides. HF can remove aluminum silicates with its strong reactivity. Both HCl and HF solvents have no effect on pyrite in coal, while $HNO_3$ can remove pyrite. However, due to the addition of HCl, it is not possible to obtain a carbonate (containing a single sulfide, sulfate, phosphate, and oxide) binding state sample of As through this method. In order to understand the release behavior of As from carbonate-bound state sample, $CH_3COONa$ washed sample and $CH_3COONa/HCl$ washed sample were pyrolyzed, and the release behavior of carbonate-bound state sample can be obtained by comparison.

## 2.5 TG analysis

In order to study the release behavior of As during pyrolysis, the pyrolysis behavior of SX coal and WLCB coal (10 mg) was studied using a thermal analyzer (Mettler-Toledo TGA/DSC 1) at a heating rate of 10 °C /min from room temperature to 900 °C under atmospheric pressure by analyzing mass loss (TG) and reaction rate (DTG) graphs. Nitrogen was used as the carrier gas (50 mL/min) to ensure an oxygen-free environment.

## 2.6 Pyrolysis experiment in fixed-bed reactor

All pyrolysis experiments, including the raw coal and the single-component samples (SC), were carried out in a fixed bed with a heating rate of 5 °C/min to the desired final temperature (300, 400, 500, 600, 700, 800 and 900 °C), using a horizontal quartz tube and a programmable electric furnace as shown in Fig. 2. The reactor was maintained at the final temperature for 60 mins. After cooling, the semi-coke was weighed and digested to determine the concentrations of As. To evaluate the volatility of As in the raw coal and SC samples, the concept of volatilization rate ($V_r$) was introduced, defined as

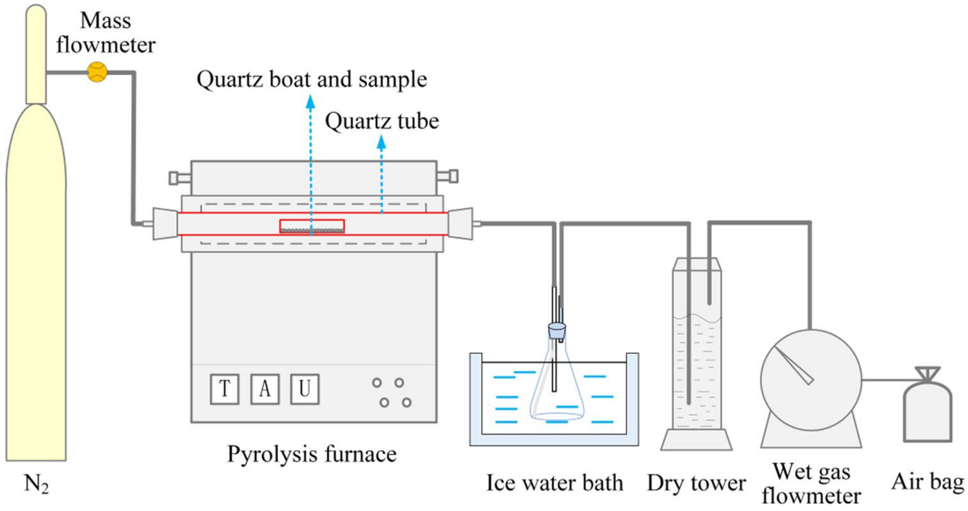

**Fig. 2** Schematic diagram of fixed-bed reactor

**Table 1** Input values for thermochemical equilibrium calculation

| Element | Mass (g) | | Ash composition | Mass (g) | |
|---|---|---|---|---|---|
| | SX | WLCB | | SX | WLCB |
| C | 817.700 | 828.4 | $SiO_2$ | 148.44 | 180.030 |
| H | 40.000 | 38.1 | $Al_2O_3$ | 64.30 | 122.910 |
| O | 73.800 | 113.8 | CaO | 88.38 | 14.540 |
| N | 11.300 | 15.4 | $SO_3$ | 53.48 | 11.940 |
| S | 57.200 | 4.3 | MgO | 14.85 | 0.035 |
| As | 0.022 | 0.1218 | $K_2O$ | 58.14 | 0.043 |
| | | | $Fe_2O_3$ | 56.15 | 16.610 |

**Table 2** Basic properties of SX and WLCB raw coal

| Sample | SX | WLCB |
|---|---|---|
| Proximate analysis (wt%) | | |
| $M_{ad}$ | 0.36 | 1.46 |
| $A_d$ | 35.64 | 24.51 |
| $V_{daf}$ | 18.23 | 39.93 |
| $FC_{daf}$ | 81.77 | 60.07 |
| Ultimate analysis (wt%) | | |
| $C_{daf}$ | 81.77 | 82.84 |
| $H_{daf}$ | 4.00 | 3.81 |
| $O_{daf}$ (calculated by dirrerence) | 7.38 | 11.38 |
| $N_{daf}$ | 1.13 | 1.54 |
| $S_{t,d}$ | 5.72 | 0.43 |
| Ash composition (wt%, d) | | |
| $SiO_2$ | 50.60 | 60.60 |
| $Al_2O_3$ | 34.49 | 26.23 |
| $Fe_2O_3$ | 4.66 | 2.29 |
| CaO | 4.08 | 3.61 |
| Cl | 0.02 | 0 |
| MgO | 0.35 | 0.57 |
| $K_2O$ | 0.43 | 2.37 |
| $SO_3$ | 3.35 | 2.18 |
| Others | 0.36 | 0.55 |
| Concentration of As (μg/g) | 21.95 | 106.87 |

$$V_{\mathrm{r}} = \left(1 - \frac{C_{\text{semi-coke}}}{C_{\text{rawcoal}}}\right) * 100\% \tag{2}$$

where $V_r$ was the volatilization ratio of As, $C_{\text{rawcoal}}$ was the content of As in raw coal, $C_{\text{semi-coke}}$ was the content of As in semi-coke. The content of As in coal or semi-coke was obtained by multiplying the measured element content by the mass of raw coal or semi-coke.

## 2.7 Thermodynamic equilibrium calculation

Modeling of the release and migration behavior of As during pyrolysis can be performed to understand the characteristics of elements and their compounds related to the actual process (Wang 2020). In this study, the thermodynamic calculation was carried out using the FactSage 7.3 software package. To calculate the ash transformation, FactPS and FToxide databases were applied in a specific order. The calculation assumes the use of 1000 g of coal sample, represented by the content of C, H, O, N, S, As and ash components. The gas value is 210 g, the pressure is 1 atm, and the temperature input value is "300, 1000, 100", representing the pyrolysis process from 300 to 1000 °C with a temperature interval of 100 °C. The specific input values of elements and oxides in the coal are listed in Table 1.

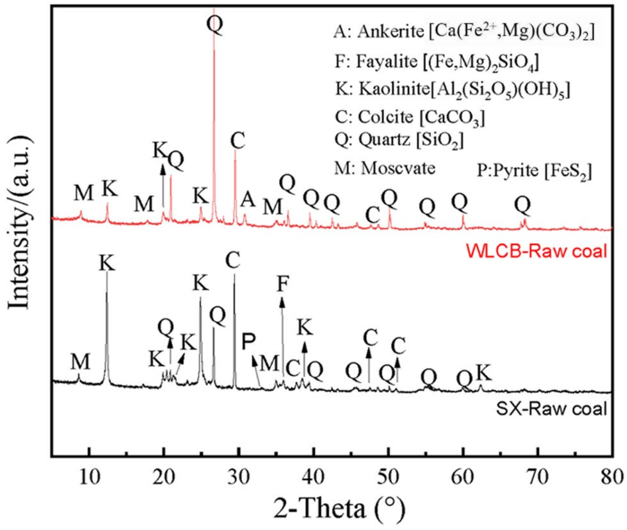

**Fig. 3** XRD analysis of low-temperature ash of SX and WLCB coal

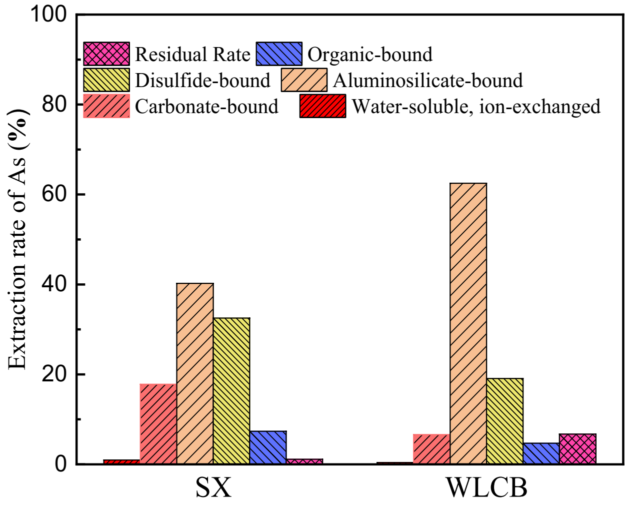

**Fig. 4** Extraction rate of As of SX and WLCB coal after chemical extraction

## 3 Results and discussion

### 3.1 Basic characteristics of coal samples

Proximate, ultimate, XRF and XRD analysis of SX coal and WLCB coal were performed, and the results were shown in Table 2 and Fig. 3. The volatile matter was 18.23% for SX coal and 39.93% for WLCB coal, showing its low-rank characteristic. XRF showed that $SiO_2$ and $Al_2O_3$ were the main ash composition in both coals. The content of ash and sulfur of SX coal was much higher than that of WLCB coal. The XRD analysis in Fig. 3 indicated that the major minerals in both types of raw coals were quartz, kaolinite, and calcite, which was consistent with the results of XRF analysis. It was worth noting that pyrite was detected only in SX coal due to its high sulfur content (5.72%). The content of As in raw coals was measured and the results were listed in Table 2. Determination results indicated that the content of As in two coals (21.95 μg/g for SX coal and 106.87 μg/g for WLCB coal) were much higher than the average (6.4 μg/g) in Chinese coal (Dai et al. 2012), which can cause serious environmental issue.

### 3.2 Occurrence modes of As in raw coals

Figure 4 shows the extraction ratio ($E_r$) of As from SX coal and WLCB coal after sequential chemical extraction by $CH_3COONa/HCl/HF/HNO_3/H_2O_2$. As in SX coal mainly existed in the form of aluminosilicate-bound (40.25%) and disulfide-bound (32.51%), followed by carbonate-bound and organic-bound As (less than 20%). As in water-soluble state, ion-exchange state and residue state were little (around 1%). As in WLCB coal mainly existed in aluminosilicate-bound state (62.50%), followed by As in disulfide-bound state (19.10%). The total content of As as carbonate, water-soluble, ion-exchanged, and residual states were just 13.50%. As is an element with strong sulphophilicity and usually existed in pyrite as orpiment, arsenopyrite and realgar (Xie and Nie 2010). The main occurrence forms of As in the two coals were similar, and both are dominated by aluminosilicate and disulfide. Table 2 shows that sulfur content of SX coal was much higher than that of WLCB coal. Therefore, disulfide-bound As contained in SX coal was higher than that in WLCB coal.

### 3.3 Pyrolysis in TGA

In order to study the release behavior of As, the thermal decomposition behavior of SX and WLCB coals was studied by TG analysis. As shown in Fig. 5a, the maximum mass losses of SX and WLCB coals were approximately 82.6 wt% and 73.4 wt%, respectively. Throughout the TG analysis process, the mass loss of WLCB coal was higher than that of SX coal, due to the high volatile matter content in WLCB coal (Table 2). By comparison, it can be found that the weight loss of SX coal was larger before 200 °C, which may be caused by the more content of water or adsorbed gas. However, due to different coal ranks, the weight loss curve of WLCB coal was gradually far below that of SX coal after 200 °C. When the temperature was between 350 and 600 °C, weight loss rate of WLCB coal was much higher than that of SX coal, and went to highest at around 500 °C. In secondary pyrolysis stage of coal (600–900 °C), the weight loss rate of SX coal was higher than that of WLCB coal, which might was due to minerals decomposition at high temperatures. At this stage, some

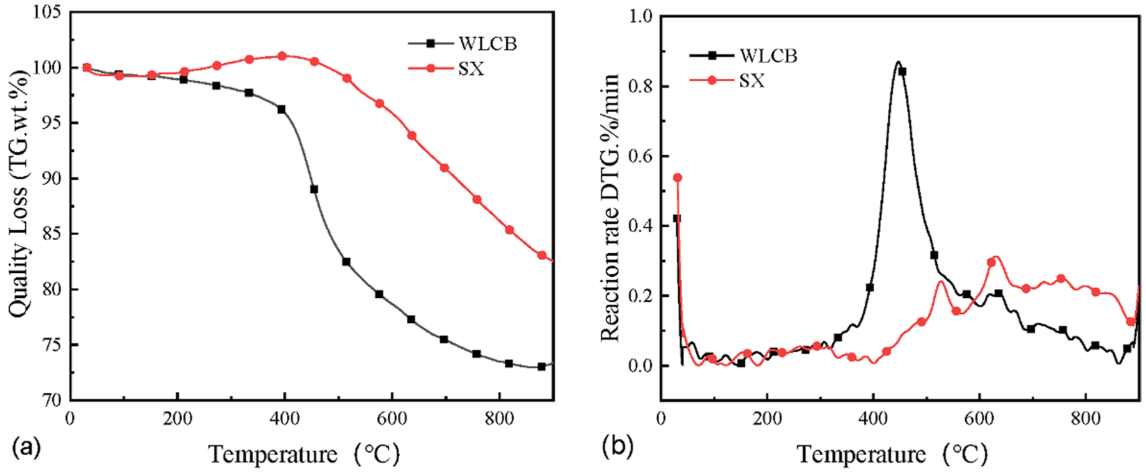

**Fig. 5** TG **a** and DTG **b** Analysis of SX and WLCB coal

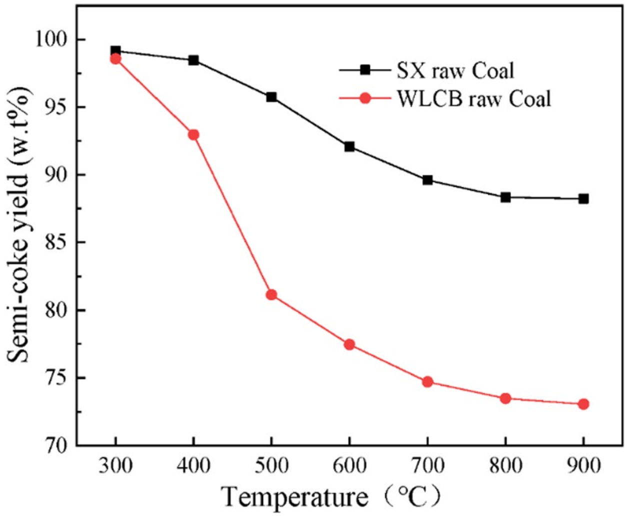

**Fig.6** Semi-coke yield of SX and WLCB raw coals at different pyrolysis final temperatures

minerals begin to decompose and transform. For example, pyrite loses a sulfur atom to form ferrous sulfide between 490 and 690 °C, and iron dolomite decomposes at 780 °C (Jiang et al. 2021). As in Table 2, the ash content of SX coal was very high (35.64%) and content of sulfur, $Fe_2O_3$ and was also higher that WLCB coal.

It is hereby stated that the thermogravimetric curve of SX coal in Fig. 5a has an increasing tendency between 200 and 450 °C. To avoid experimental error, repeat experiments were conducted several times, the increasing tendency of SX coal showed every time. The main reason might be caused by substances contained Mg in SX coal. Under inert atmosphere, a series of reactions would occur at 200 °C to generate $Mg_2N_3$, leading to weight increase.

**Table 3** Reaction of As-containing minerals under atmospheric pressure pyrolysis

| Order | Reaction equation | Temperature (°C) |
|---|---|---|
| 1 | $As_2(g)+3H_2(g)=2AsH_3(g)$ | 170 |
| 2 | $As_2S_3(s)+6H_2(g)=2AsH_3(g)+3H_2S(g)$ | 282 |
| 3 | $2As_2S_3(s)+6H_2(g)=2As_4(g)+6H_2S(g)$ | 551 |

### 3.4 Semi-coke yields of raw coal during pyrolysis

Figure 6 shows the semi-coke yields of SX coal and WLCB coal in fixed bed reactor under different pyrolysis final temperatures. As the final temperature of pyrolysis increased, the yield of semi-coke gradually decreased due to the continuous release of gases and tar, such as $CO_2$, CO, $CH_4$, $H_2$, and unsaturated hydrocarbons, during the pyrolysis process. The semi-coke yield of SX coal dropped by 11% from 300 to 900 °C. The semi-coke yield of WLCB coal dropped by 25%, due to its low rank and high volatile content, from 98.56% at 300 °C to 73.06% at 900 °C.

### 3.5 Volatilization behavior of As in raw coal pyrolysis

As is an extremely volatile thiophilic element, and its elemental melting point was around 817 °C. As and its compounds were easy to react with hydrogen, and the specific reaction equations were shown in Table 3. It can be seen from Fig. 7 that the As volatility of SX coal was higher than that of WLCB coal in the whole pyrolysis temperature range. The release of As from SX coal increased from 68% at 300 °C to 97% at 900 °C. The release of As from WLCB coal increased from 11% at 300 °C to 81% at 900 °C. Before

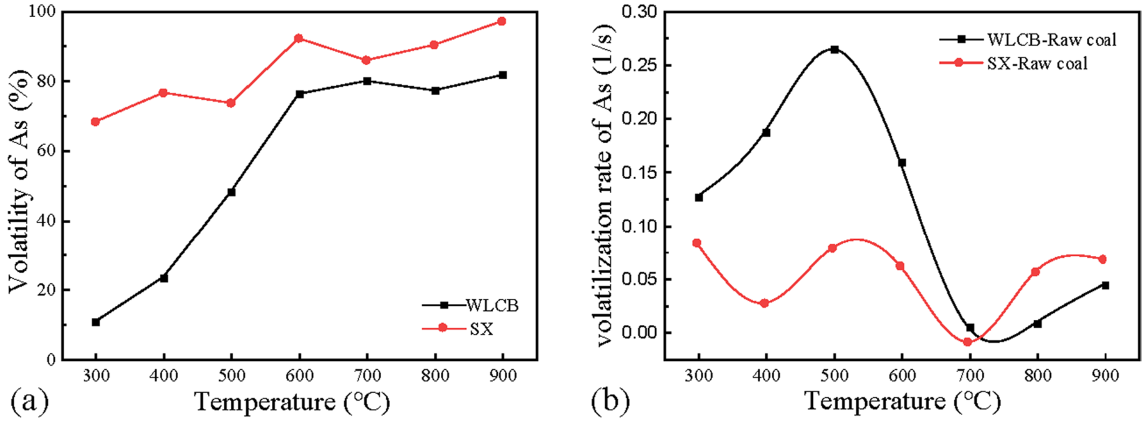

**Fig. 7** **a** The volatility curve and **b** Volatilization rate curve of As in SX and WLCB coals at different pyrolysis final temperatures

400 °C, the difference in volatility of As between the two coals was the most obvious. Combined with the occurrence of As, SX coal contained more organic-bound As, which will be released more along with organic matter decomposition during pyrolysis process. From Table 3, it can be seen that hydrogen can promote the release of As, it can react with some sulfides of As, which can be reduced and released. When the temperature was higher than 500 °C, the continuous generation of hydrogen gas during the pyrolysis process can promote the release of As. In addition, Table 2 shows that the sulfur content in SX coal (5.72 wt%) was obviously higher than that in WLCB coal (0.43 wt%). When the pyrite was thermally decomposed (500–600 °C), the As contained in both coals was released rapidly, resulting in a sharp increase in the As release rate at 500 °C, as show in Fig. 7b. However, the release rate of As in the two coals decreased at 500–600 °C, which may be because the pores in the coals became larger with the progress of the pyrolysis process, and a part of the volatilized As was adsorbed. In addition, after 600 °C, the volatility of As in the two coals did not change significantly, indicating that the volatile As element had been released in large quantities, while some non-volatile As mainly remained. For volatilization rate, the rate of WLCB coal was obvious higher during 300–700 °C, due to its rank. The volatile matter content of WLCB coal was 39.93%, which was much higher than that of SX coal (18.23%). Much As would be released with the decomposition of coal itself.

### 3.6 Occurrence modes of As in semi-cokes

In order to further study the release mechanism of As during the pyrolysis process, the extraction ratio ($E_r$) of As in semi-coke pyrolyzed at 600 °C was measured, as shown in Fig. 8. The As in SX semi coke was mainly composed of carbonate-bound, disulfide-bound and aluminosilicate-bound states, accounting for 28.56%, 27.17%, and 26.91%, respectively, followed by residual As, accounting for 13.10%. While in WLCB semi coke, As was mainly in aluminosilicate-bound state and carbonate-bound state, accounting for 56.0% and 23.05%, respectively, followed by residual As, accounting for 10.86%.

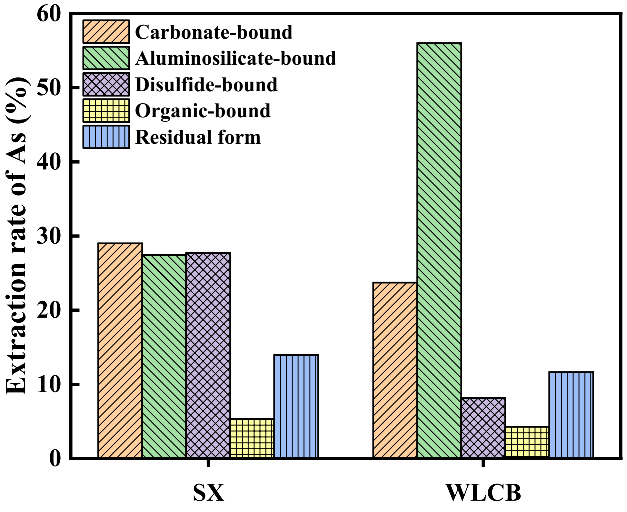

**Fig. 8** Extraction rate of As of SX and WLCB semi-cokes pyrolyzed at 600 °C

Comparing the distribution of As in raw coal, the extraction ratio ($E_r$) of As in the form of disulfide, aluminosilicate, and organic-bound As in SX semi coke and WLCB semi coke decreased with the increasing pyrolysis temperature, while the $E_r$ of As in the residual and carbonate state increased with the increasing temperature. Compared with other occurrence states, almost all the organic-bound As in SX coal and WLCB coal volatilized, indicating that most of the organic-bound heavy metals were released in large quantities during the pyrolysis process, which is consistent with the conclusions of Guo et al. (2004, 2003). However, with the increase of pyrolysis temperature, the content of

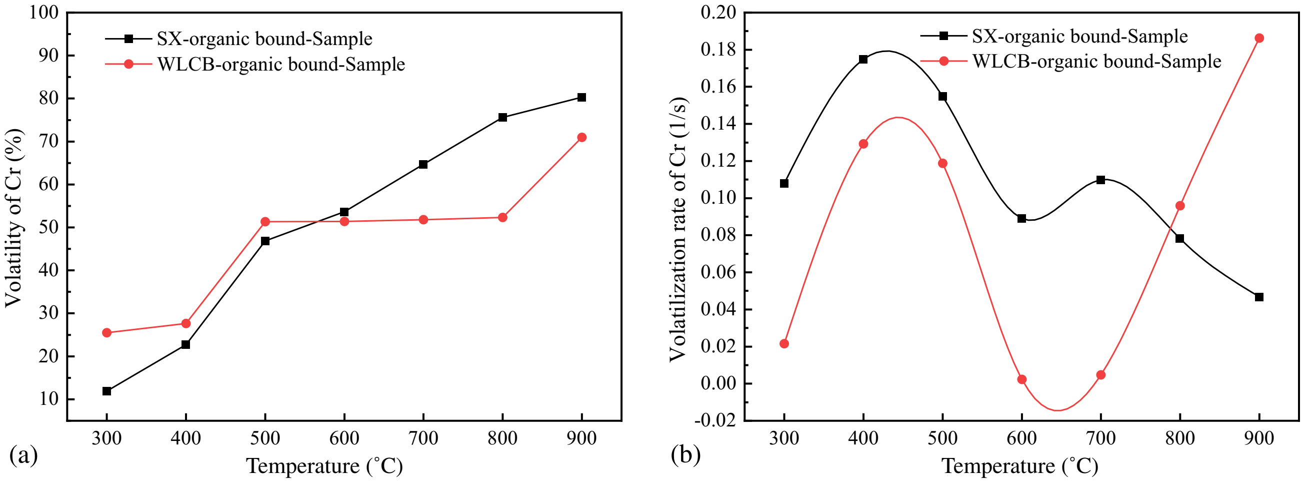

**Fig. 9** **a** The volatility curve and **b** Volatilization rate curve of organic bound As at different final pyrolysis temperatures

aluminosilicate-bound As in semi-cokes did not change much, indicating that the aluminosilicate-bound As were relatively stable and not easily volatile, similar results were concluded by Liu (2009).

## 3.7 Volatilization behavior of As in single-component samples pyrolysis

To investigate the impact of mode of occurrence of As on its release behavior, pyrolysis experiments was adopted for three single-component (SC) samples obtained by SCE (organic-bound state, disulfide-bound state, aluminosilicate-bound state) in fixed-bed reactor and shown in Fig. 9. The volatilization ratio ($V_r$) of As was calculated based on their content in each SC sample. It can be found that the release behavior of As in single-component (SC) samples in the two coals was basically the same with the increasing temperature, that is, with the increase of temperature, the release rate of As gradually increased, and the organic-bound As was more volatile than As in other occurrence modes.

### 3.7.1 Volatilization behavior of organic-bound As

Figure 9 compares the volatilization behavior of organic-bound As in the two coals as a function of temperature. From Fig. 9a, it can be found that the volatility of organic-bound As gradually increased as the temperature increased. The volatility of organic-bound As in SX coal increased from 27.64% at 300 °C to 94.90% at 900 °C, which increased by about 67%. The volatility of organic-bound As in WLCB coal increased from 60.54% at 300 °C to 86.16% at 900 °C, which increased by about 26%. By comparison, it was found that the volatility of organic-bound As in SX coal changed more obviously with temperature than that in WLCB coal. From Fig. 9b, the volatilization rate of WLCB coal was greater than that of SX coal before 700 °C. After 700 °C, the volatilization rate of SX coal was greater than that of WLCB coal. Combining the occurrence mode, it can be seen that the content of organic-bound As in SX coal was greater than that in WLCB coal (17.10% in SX coal and 7.36% in WLCB coal). Therefore, the volatility of organic-bound As in SX coal at 900 °C was greater. However, since WLCB coal was a low-rank coal, owned poor thermal stability, so the volatilization rate in early stage was large.

### 3.7.2 Volatilization behavior of disulfide-bound As

Figure 10 compares the volatilization behavior of disulfide-bound As in the two coals as a function of temperature. The volatility of disulfide-bound As from SX coal increased from 19.67% at 300 °C to 79.61% at 900 °C, which increased by about 60%. For WLCB coal, it increased from 19.95% at 300 °C to 66.47% at 900 °C, which increased by about 46%. By comparison, it was found that before 600 °C, the volatility of disulfide-bound As of WLCB coal was higher than that of SX coal, and the volatilization rate of the two decreased as the temperature increased. After 600 °C, the volatility of SX coal gradually increased, which was equal to that of WLCB coal at around 650 °C and beyond it at higher temperatures. Combining the occurrence mode, it can be seen that the content of disulfide-bound As in SX coal was greater than that in WLCB coal (32.51% in SX coal and 19.10% in WLCB coal). Therefore, the volatility of disulfide-bound As in SX coal was beyond WLCB at temperatures higher 600 °C, when sulfides began to decompose. However, since WLCB coal was a low-rank coal, owned poor thermal stability, so the volatilization rate in early stage was large.

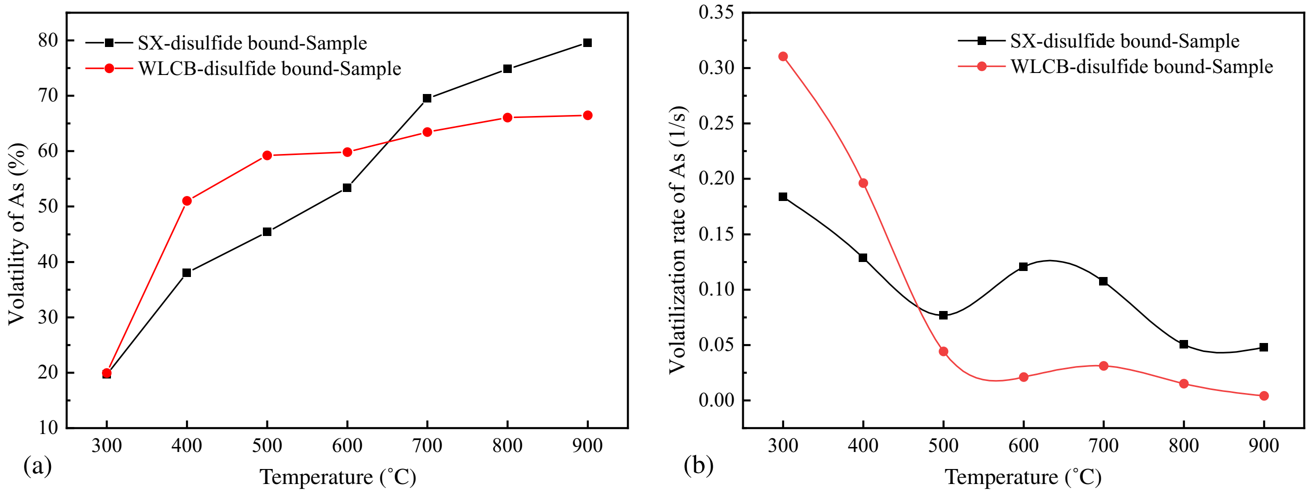

**Fig.10** **a** The volatility curve and **b** Volatilization rate curve of disulfide bound As at different final pyrolysis temperatures

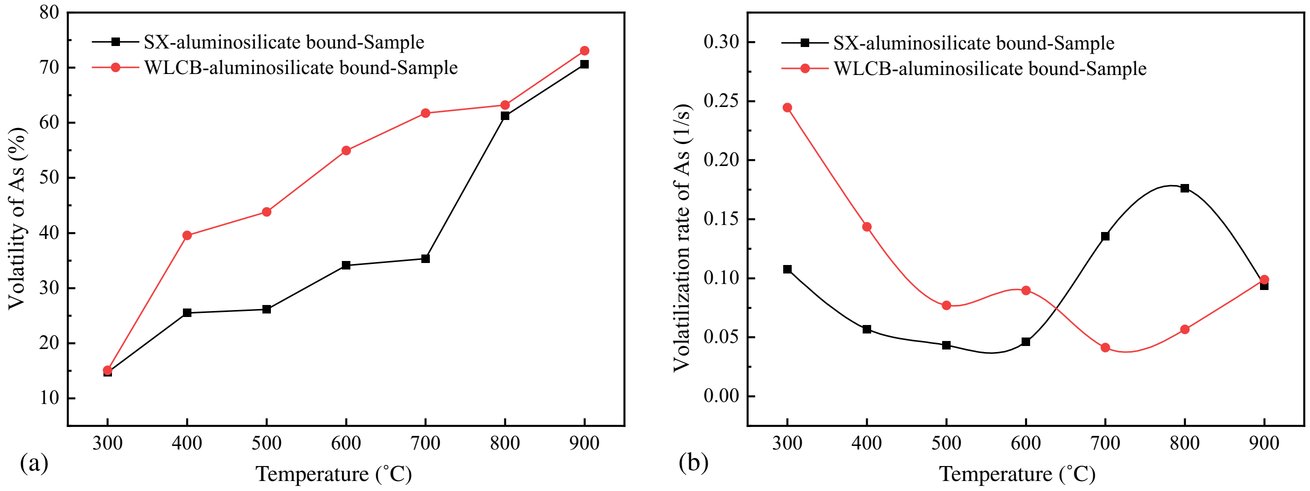

**Fig. 11** **a** The volatility curve and **a** Volatilization rate curve of aluminosilicate bound As at different final pyrolysis temperatures

### 3.7.3 Volatilization behavior of aluminosilicate-bound As

Figure 11 compares the volatilization behavior of aluminosilicate-bound As in the two coals withing increasing temperature. As shown in Fig. 11a, the volatility of aluminosilicate-bound As gradually increased as the temperature increased. The volatility of aluminosilicate-bound As from SX coal increased from 14.72% at 300 °C to 79.61% at 900 °C, which increased by about 56%. For WLCB coal, it increased from 15.05% at 300 °C to 73.08% at 900 °C, which increased by about 48%. Combining the occurrence mode, it can be seen that the content of aluminosilicate-bound As in WLCB coal was greater than that in SX coal (62.50% in WLCB coal and 40.25% in SX coal). Therefore, the volatility of disulfide-bound As in WLCB coal at 900 °C was greater, with a higher volatilization rate.

### 3.7.4 Volatilization behavior of carbonate-bound As

In the single-component preparation process, carbonate-bound state sample can never be obtained. In order to investigate the release behavior of carbonate-bound As, raw coal samples and the samples after HCl extraction were pyrolyzed respectively, and the difference subtraction method was used to obtain the release behavior of carbonate-bound As. Figure 12 compares the volatilization behavior of carbonate-bound As in the two coals withing increasing temperature. As shown in Fig. 12a, the volatility of carbonate-bound As

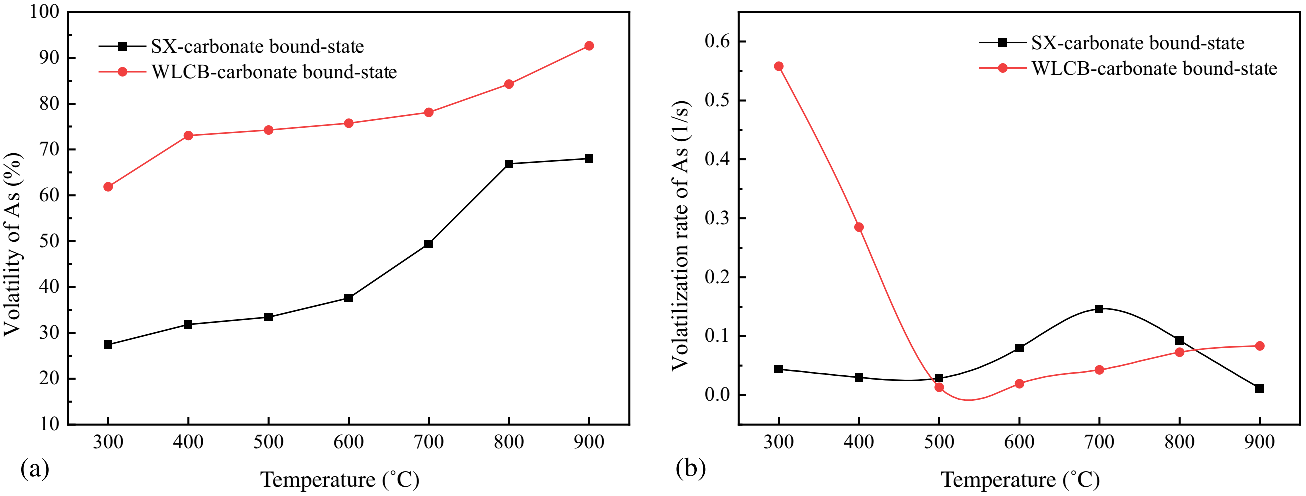

**Fig. 12** **a** The volatility curve and **b** Volatilization rate curve of carbonate bound As at different final pyrolysis temperatures

gradually increased as the temperature increased. The volatility of carbonate-bound As from SX coal increased from 27.42% at 300 °C to 68.05% at 900 °C, which increased by about 41%. For WLCB coal, it increased from 61.85% at 300 °C to 92.64% at 900 °C, which increased by about 31%. Combining the occurrence mode, it can be seen that the content of carbonate-bound As in SX coal was greater than that in WLCB coal. Therefore, the volatility of disulfide-bound As in WLCB coal at 900 °C was greater, with a higher volatilization rate.

Figure 13 compares the volatility behaviors of all single component samples. It can be found that the organic matter in coals was mainly volatilized, and the organic-bound As was decomposed and released along with it before 400 °C. Between 400 and 800 °C, with the increasing pyrolysis temperature, hydrogen was produced and to react with As sulfide, leading to the release of disulfide-bound As. During the period, pyrite was mainly decomposed into ferrous sulfide and hydrogen sulfide in the presence of hydrogen. With the continuous increase of the final temperature of pyrolysis, a large amount of pyrite in coal was decomposed, resulting in the growing release rate of disulfide-bound As. The carbonate-bound As in coal began to release after 600 °C. When the pyrolysis temperature reached 800 °C, the release rate of As tended to be flat, and the rest was mostly non-volatile aluminosilicate-bound As. At 600–800 °C, aluminosilicate minerals had strong physical adsorption capacity, and generate new condensed states under heating conditions, such as $AlAsO_4$ and other substances, reducing the volatilization rate of As.

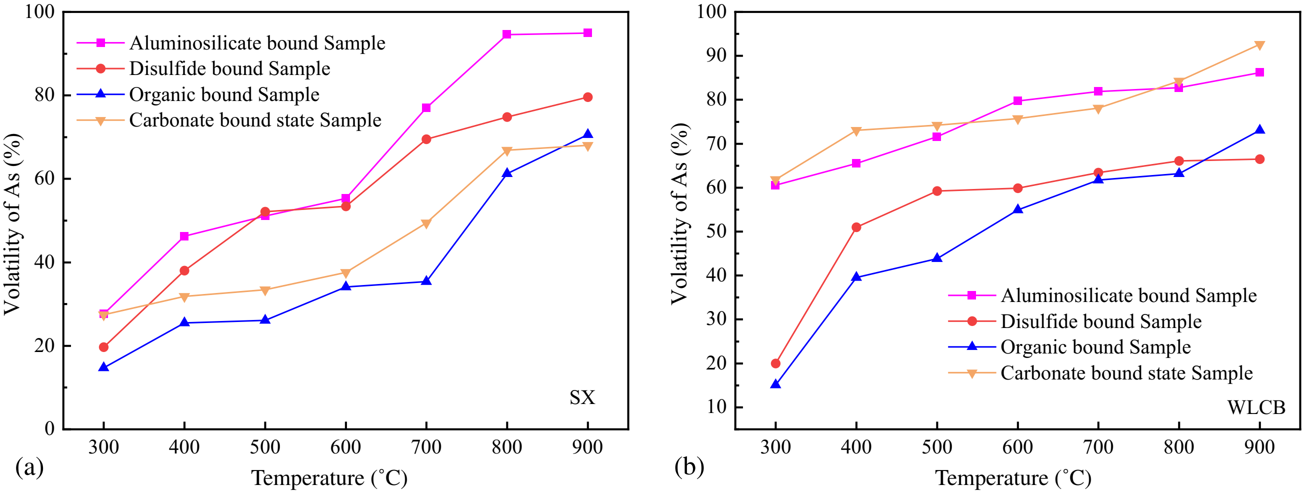

**Fig. 13** The volatility curve of As in **a** SX and **b** WLCB Coal samples with pyrolysis temperature

To sum up, the main release behavior of As in single components was that at low temperature (< 400 °C), organic-bound As was mainly released along with the pyrolysis decomposition reaction. At medium temperature (400–600 °C), the disulfide-bound As was released with the decomposition of pyrite in coal, and a part of As reacted with $H_2$ generated by pyrolysis and was released in the form of $AsH_3$ and As. At high temperature (800–900 °C), a part of calcite and clay minerals were decomposed, and the As occurred with them were also released.

### 3.8 FactSage equilibrium calculation

In order to study the release and migration behavior of As more deeply, a thermodynamic equilibrium calculation was carried out using the FactSage 7.3 to calculate the transformation behavior of As at 300–1000 °C under the ideal conditions. As shown in the Fig. 14, before 700 °C, the As in SX coal and WLCB coal mainly existed in the form of gaseous $As_4$, and a small amount of solid $As_2S_3$ and $As_2O_3$ also existed during this period. The difference was that there was a small amount of $As_2S_3$ solid in SX coal, but WLCB coal did not have it, which may be related to different sulphur content. After 700 ℃, As in SX coal and WLCB coal mainly existed in the form of gaseous $As_2$ and $As_4$. Combining simulation and experimental results, it can be found that As was very volatile, and the solid oxide of As was almost completely converted at about 700 °C, and almost completely volatilized in the form of gaseous $As_4$ after 900 °C, and hydrogen can promote the release of As.

## 4 Conclusions

The volatilization behaviors of As in the two coals were mainly determined by the pyrolysis temperature, occurrence mode of As and their coal ranks.

(1) As in SX coal mainly exists in the form of aluminosilicate-bound (40.25%) and disulfide-bound (32.51%), followed by carbonate-bound and organic-bound As. The As in WLCB coal mainly existed in aluminosilicate-bound state (62.50%), followed by disulfide-bound state (19.10%). The content of As existed in water-sol-

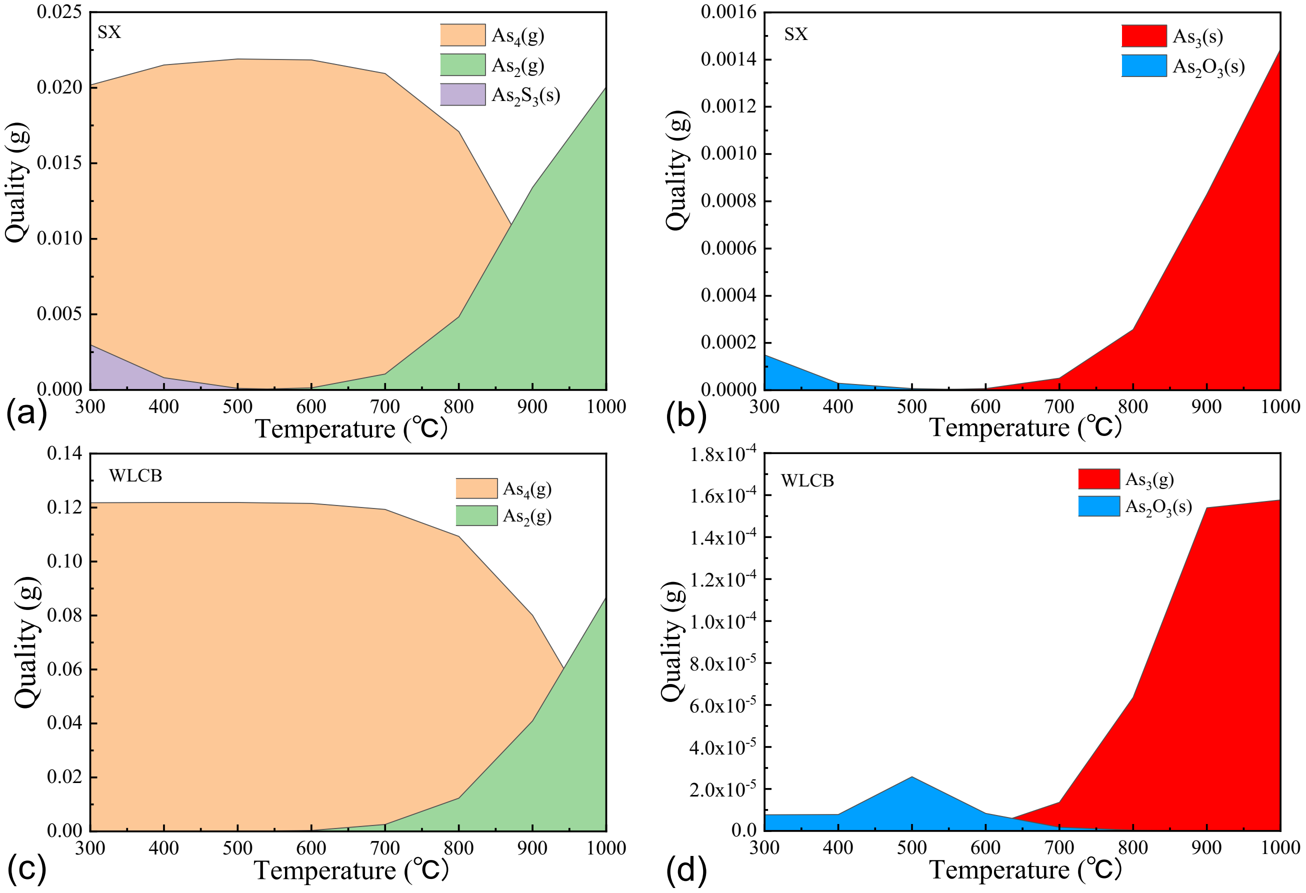

**Fig.14** FactSage calculation of As in **a**, **b** SX and **c**, **d** WLCB Coal

uble state, ion-exchange state and residue state in the two coals was less.

(2) During pyrolysis, the volatility of As in SX coal during 300–900 °C was 68% to 97%, which is significantly lower than that in low-grade WLCB coal, which was 11% to 81%. The occurrence modes of As had serious impacts on its volatilization behavior. The difference thermal stability of the two coal samples in single components provided the possibility for the different release rules of heavy metals. The content of organic-bound As in SX coal was higher than that of WLCB coal, which can be volatilized at low temperature, leading to higher volatility at 300 °C. As in the disulfide and aluminosilicate-bound states were released as the minerals decompose at high temperatures, which also attributed high volatility for SX coal at 900 °C. Higher volatilization rate for WLCB coal during 300–700 °C was due to its low rank. Much As would be released with the decomposition of coal itself.

(3) FactSage thermodynamic calculations show that before 700 °C, As in SX coal and WLCB coal mainly existed in the form of gaseous $As_4$, and a small amount of solid $As_2S_2$ and $As_2O_3$ exists. The solid oxide of As at about 700 °C was almost completely converted, and it was almost completely volatilized in the form of gaseous $As_4$ at 900 °C, and hydrogen can promote the release of As.

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## Declarations

**Conflict of 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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