

Effect of H₂O on the volatilization characteristics of arsenic during isothermal O₂/CO₂ combustion

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Abstract: The effect of H₂O on the volatilization behavior of arsenic in coal was studied under O₂/CO₂ combustion conditions at 800-1300 °C, which covers the effective range of coal combustion temperatures appropriate for conventional coal combustion technologies. By controlling the combustion time of coal, the volatilization percentage and rate of As versus time were obtained. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses were used to study the evolution of minerals with and without H₂O under O₂/CO₂ combustion conditions. The effect of CO₂ on As volatilization was first investigated and it was found that increasing CO₂ concentrations inhibits the volatilization of As, with this effect decreasing with increasing temperature. When a fraction of the CO₂ was replaced with H₂O, the volatilization of As increased, but the positive effect of H₂O also decreased with increasing temperature. The volatilization percentage of As with 30% H₂O was 6.1% higher than that without H₂O at 800 °C, while it was only 2.7% higher at 1300 °C. When the concentration of H₂O increased from 0 to 30%, the peak value of the As volatilization rate increased and the time needed to reach the peak value decreased. The volatilization characteristics of As for three coals were very similar, which demonstrates that the effect of H₂O was not limited to only one specific coal.

Keywords: O₂/CO₂ combustion; arsenic; volatilization characteristics; H₂O

1 Introduction

Coal combustion accounts for about 70% of Chinese power generation and this situation is unlikely to change in the near future [1]. Pollutants from coal combustion are responsible for numerous environmental problems [2, 3]. Given its nature as a semi-volatile toxic metal, most of the arsenic (As) in coal will volatilize during combustion and be found in fly ash, bottom ash and the gas phase as the flue gas cools down, and some of it will finally be emitted into the atmosphere [4, 5]. The release of As is attracting increasing attention because it not only affects several human organs, but also interferes with the immune system [6].

The volatilization and partitioning behavior of As is influenced by several factors, including the combustion temperature and combustion atmosphere [7-11]. In O₂/CO₂ combustion, the CO₂ concentration in the furnace can reach 60%~80% or more [12-15], which is significantly higher than that in air fired combustion. Zhuang and Pavlish [16] studied the fate of As in a pilot-scale furnace during O₂/CO₂ combustion, and found that the concentration of As in fly ash was lower than that in O₂/N₂ combustion. While for a bench-scale fluidized bed study, Roy et al. [17] found that there was little difference in the volatilization of As between O₂/CO₂ combustion and O₂/N₂ combustion at 21% oxygen. However, Liu et al. [8] conducted combustion experiments in a customized isothermal thermogravimetric system, and concluded that high concentrations of CO₂ in oxy-fuel atmosphere inhibited the volatilization of As as compared to air at a low temperature, but that the volatilization ratio of As was larger in O₂/CO₂ combustion than that observed in O₂/N₂ combustion above 1300 °C. This work hypothesized that the differences in As volatilization can be partially ascribed to the physical properties (e.g., radiant characteristics and heat capacity) in a

boiler experienced with these two atmospheres. Moreover, few studies have investigated the effect of CO₂ on As volatilization at different temperatures. Thus, more work needs to be conducted to study the volatilization characteristics of As, in order to better understand the effect of CO₂ on As volatilization during O₂/CO₂ combustion.

In addition, H₂O is known as one of the main components of the flue gas in oxy-fuel combustion, and the concentration of H₂O may be up to 25%~35% as a result of flue gas recycle [18]. Roy et al. [17] studied the effect of H₂O on the volatilization of As during O₂/CO₂ combustion, and their experimental results indicated that the addition of H₂O inhibited the volatilization of As. Wang et al. [19] found that the As concentration in particulate matter (PM) decreased with more H₂O in the inlet gas of O₂/CO₂ combustion experiments in a drop furnace at 1500 °C. Wang et al. [20] simulated the speciation of arsenic under O₂/CO₂ combustion with FactSage 5.2 software, and showed that the effect of H₂O on arsenic distribution was dependent on the concentration of H₂O. However, these studies focused on the effect of H₂O on the final volatilization percentage of As, and hence cannot completely describe the release kinetics of As in the combustion process. In addition, determination of the volatilization rate of As is probably a more useful parameter in helping understand the release behavior of As and provide insights for As volatilization in coal-fired boilers.

The aim of this work is to determine the effects of H₂O on the volatilization characteristics of As during O₂/CO₂ combustion. Combustion experiments were carried out with three coals in a customized isothermal thermogravimetric reactor. The influence of temperature, CO₂, and especially H₂O concentration were explored. Both scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses were employed to further understand the effect of H₂O on As

volatilization.

2 Samples and Analytical Procedures

2.1 Coal samples

Three Chinese coals, Shitan (ST), Wuli (WL) and Meihua (MH), were used for testing. The coal samples were air-dried, crushed and sieved to a diameter range of 100-150 μm . Table 1 gives the ultimate/proximate analysis, and major ash composition of the coals. The ash composition was determined by X-ray fluorescence (XRF)

Table 1. Properties of coal samples

Coal	Ultimate analysis, $w_{\text{ad}}/\%$					Proximate analysis, $w_{\text{ad}}/\%$				As, $\mu\text{g}\cdot\text{g}^{-1}$
	C	H	O ^a	N	S	M	A	V	FC	
ST	51.02	2.70	5.81	0.83	0.38	0.55	38.71	11.39	49.35	4.99
WL	70.92	3.28	0.42	1.20	0.30	1.92	21.96	11.69	64.43	3.83
MH	57.70	4.18	16.17	0.80	0.32	2.74	18.09	35.58	43.59	4.42
Ash composition, %										
	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	MgO	TiO ₂	SO ₃	K ₂ O		
ST	42.70	50.93	1.70	1.99	0.06	1.47	0.60	0.55		
WL	42.03	53.32	0.50	1.03	0.14	1.54	0.93	0.51		
MH	25.66	50.24	6.27	9.2	0.15	0.83	6.32	1.33		

_{ad}: air dry

^a: by difference

2.2 Combustion facility

Combustion experiments were conducted in a customized isothermal thermogravimetric system, as shown in Fig. 1. After heating to a set temperature and maintaining this for 30 min, the furnace was quickly moved to the set position, and coal samples rapidly burned at a specific temperature. The mixed gas flow rate was maintained at 2.33 L/min throughout the test. Preliminary experiments have verified that the flow rate used eliminate the influence of external diffusion [7, 8]. The combustion atmosphere was composed of N₂, CO₂, O₂ and H₂O. The individual gas flowrates

were controlled by flowmeters. H₂O was injected into a pre-heated tube and evaporated by means of a heating band. The temperature of the heated tube was controlled by a temperature controller, and the flow of H₂O was controlled by an injection pump. More details about this testing can be found in our previous work [7, 8, 21, 22].

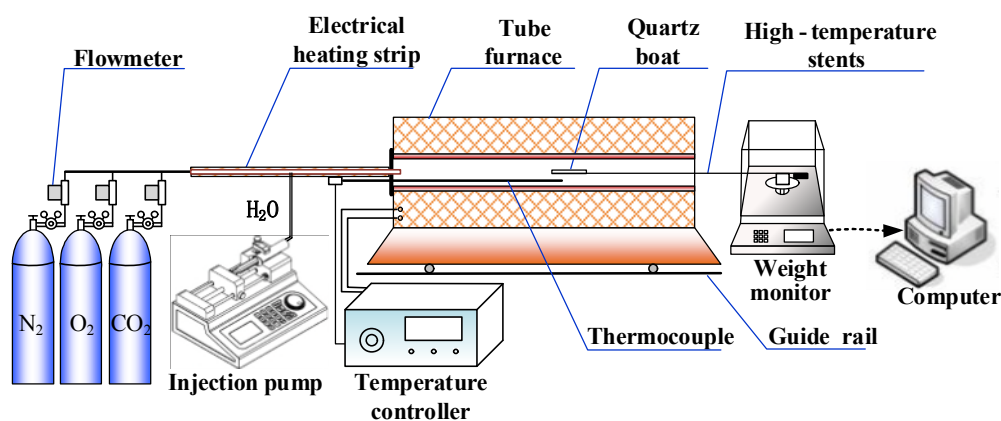


Fig. 1. Isothermal thermogravimetric experimental system for coal combustion

The volatilization characteristics of As were determined by measuring the As concentration in ash at specified combustion residence times (30, 60, 90, 120, 150, 180, 210, 240, 300, 360, 420, 480, and 540 s). All experiments followed the same procedure: the coal samples (0.50 ± 0.01 g) were placed in a corundum boat, and the furnace was quickly pushed along the guide rail to ensure that the coal sample burned in the constant temperature zone of the furnace. After combustion, the sample was rapidly transferred to a pure N₂ atmosphere to cool down. Then, the sample was weighed and collected for subsequent measurements. Each combustion case was repeated at least three times, in order to confirm the experimental results and obtain sufficient ash samples for subsequent analyses. To deal with the buoyancy effect and negate its influence on the experimental accuracy, blank curves were drawn for every tested condition.

2.3 Sample analysis method

Solid samples were weighed and then put into polytetrafluoroethylene (PTFE) containers

together with 4 mL of nitric acid and 1 mL of hydrofluoric acid (both acids were trace metal grade) for preliminary digestion. As hydrofluoric acid is very dangerous, extreme care was taken when hydrofluoric acid was transferred to the PTFE containers. After 12 h, 1 mL of hydrogen peroxide was added, and then the containers were put into a thermostat (160 °C) for 8 h. More details on the experimental procedures can be found elsewhere [23]. After digestion, the concentration of As was analyzed using an atomic fluorescence spectrometer (AFS).

The mode of occurrence of As in coal and ash was determined using a sequential chemical extraction method described by Liu et al. [24]. The schematic of a sequential chemical extraction analysis is presented in Fig. 2, and the detailed analysis procedures also can be found elsewhere [23].

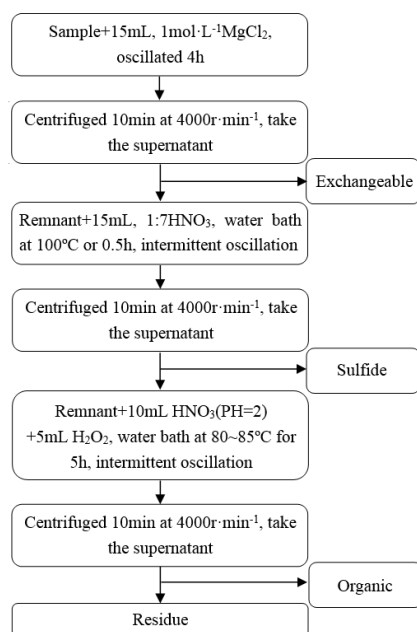


Fig. 2. Schematic of a sequential chemical extraction analysis

The mineral compositions of ashes were determined by XRD analysis. Also, photo-micrographs of ashes were obtained using SEM to help elucidate the effect of H₂O on As volatilization.

2.4 Data analysis

The following relationships were used to characterize the volatilization of arsenic:

$$\text{retention percentage of As in ash at } i \text{ s, } \omega_i = \eta_i m_i / m_o \times 100\% , \% \quad (1)$$

$$\text{volatilization percentage of As at } i \text{ s, } X_i = (1 - \omega_i) \times 100\% = (1 - \eta_i m_i / m_o) \times 100\% , \% \quad (2)$$

$$\text{volatilization rate of As at } i \text{ s, } v_i = dX_i / di , \% / \text{s} \quad (3)$$

where η_i is the percentage of ash yield at i s; m_o is the As content of the raw coal, $\mu\text{g/g}$; and m_i is the As content of the ash at i s, $\mu\text{g/g}$.

3 Results and Discussion

3.1 Volatilization characteristics of As in O_2/CO_2 combustion

The volatilization characteristics of As in 21% $\text{O}_2/79\%$ N_2 and 21% $\text{O}_2/79\%$ CO_2 combustion are compared at 800 and 1300 °C. ST coal was used for the test, and the volatilization percentage of As at different combustion times is shown in Fig. 3.

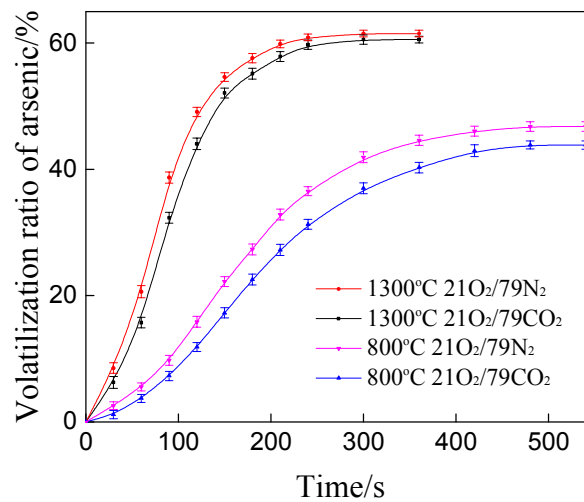


Fig. 3. Volatilization percentage of As in 21O₂/79N₂ and 21O₂/79CO₂ at 800 and 1300 °C for ST coal

Fig. 3 shows that for both 21O₂/79N₂ and 21O₂/79CO₂ atmospheres, the volatilization percentage of As becomes larger and then tends to stabilize as the combustion time increases. At both temperatures, compared to 21O₂/79N₂, the volatilization proportion of As was reduced in 21O₂/79CO₂, and these results are consistent with the results of Wang et al. [19]. Here, the

21O₂/79CO₂ combustion condition reduced the temperature of the coal particle surface, which inhibits As volatilization [19]. Furthermore, given the reduction mechanism [25], the refractory arsenic oxide in coal would be reduced to the sub-oxides by the following process:



Under O₂/CO₂ combustion, the high CO₂ concentration can be expected to inhibit the forward reaction, and thereby suppresses the volatilization of As [26].

In addition, as shown in Fig. 3 that the final volatilization percentage of As in 21O₂/79N₂ is 3% higher than that in 21O₂/79CO₂ at 800 °C, while the value is less than 1% higher at 1300 °C. This indicates that the negative effect of CO₂ on As volatilization is reduced with increasing temperature. To examine the effects of CO₂ further, the combustion reaction kinetics of ST coal at 800 and 1300 °C in 21O₂/79N₂ and 21O₂/79CO₂ were studied, and results are shown in Fig. 4.

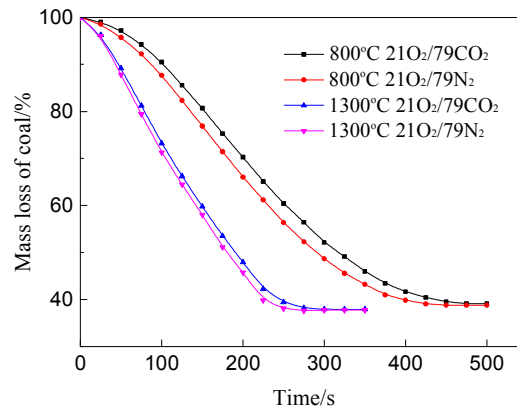


Fig. 4. Combustion reaction kinetics of ST coal at 800 and 1300 °C in 21O₂/79N₂ and 21O₂/79CO₂

In Fig. 4, it can be seen that compared with the 21O₂/79N₂ combustion, 21O₂/79CO₂ combustion leads to a shift to the right of the isothermal weight loss curves at 800 or 1300 °C, suggesting that CO₂ has a negative influence on the combustion rate of coal. The burnout time and corresponding ash yield of ST coal in 21O₂/79N₂ and 21O₂/79CO₂ at 800 and 1300 °C are given in Table 2.

Table 2. Burnout time and corresponding ash yield of ST coal combustion in 21O₂/79N₂ and 21O₂/79CO₂ atmosphere

Parameters	800°C		1300°C	
	21O ₂ /79N ₂	21O ₂ /79CO ₂	21O ₂ /79N ₂	21O ₂ /79CO ₂
Burnout time, s	440	475	280	290
Ash yield, %	38.77	38.91	37.74	37.82

Based on the results in Fig. 4 and Table 2, it can be seen that the burnout time of ST coal in 21O₂/79CO₂ is longer than that in 21O₂/79N₂, which is consistent with the research of Liu et al. [8]. Compared to 21O₂/79CO₂, the burnout time is shortened by 35 s in 21O₂/79N₂ at 800 °C, but only by 10 s at 1300 °C. The reason for this behavior is that the diffusivity of O₂ in N₂ is higher than that in CO₂, which accelerates the combustion rate. However, the negative effect of CO₂ on the combustion rate of coal decreases with increasing temperature. This may be caused by the gasification reaction between CO₂ and char, which contributes to the conversion rate of char and decreases the burnout time [27]. Given a similar negative effects of CO₂ on the mass loss rate of coal as on the volatilization of arsenic, one can hypothesize that the volatilization characteristics of As may be largely related to the combustion characteristics of coal.

3.2 Effect of H₂O on As volatilization under O₂/CO₂ combustion

3.2.1 Effect of H₂O on final volatilization percentage of As

To elucidate the role of H₂O, the final volatilization percentage of As at various reaction temperatures (800~1300 °C) with different H₂O concentrations (0, 10%, 20%, and 30%) was investigated in a 21O₂/79CO₂ atmosphere, as shown in Fig. 5.

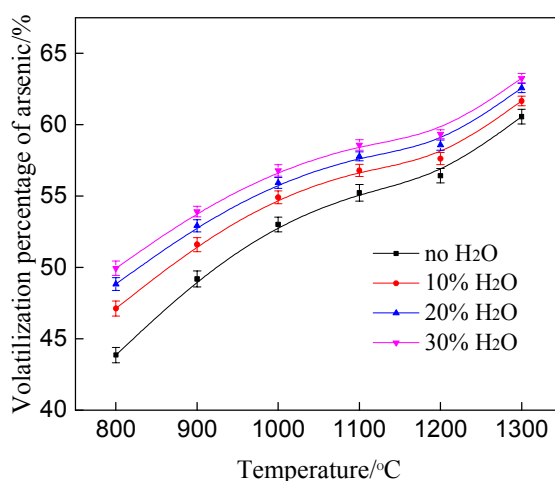


Fig. 5. Volatilization percentage of As at different temperatures during isothermal O₂/CO₂ combustion for ST coal

It can be seen in Fig. 5 that the volatilization percentage of As becomes larger with increasing temperature. The reason for this behavior is that the coal combustion rate will be accelerated at a higher temperature, so a larger proportion of As is volatilized [8].

When the combustion atmosphere contains H₂O, the volatilization percentage of As becomes larger than that without H₂O, indicating that H₂O has a positive effect on As volatilization. The reason for this seems to be that the gasification reaction between H₂O and char can enhance coal combustion [28, 29], and consequently promote the release of arsenic. In addition, the reaction between H₂O and char tends to generate more micropore and mesopore structures [30, 31], which can improve the transport of molecules/atoms through the pores of the char to the atmosphere, thereby accelerating the evaporation of As [32]. From Fig. 5, it can also be seen that the promotional effect of H₂O on the volatilization of As becomes less with more steam (0-30%). A probable reason for this phenomenon is that more micropores are generated as a result of the gasification reaction at a low concentration of H₂O, while those micropores grow into mesopores and macropores at a higher concentration of H₂O [33], which leads to a decrease of the pore area

of the char. Thus, the positive effect of H₂O on the volatilization of As declines with the increase of H₂O concentration.

From Fig. 5, it also can be seen that H₂O has a greater impact on As volatilization at 800 °C than at 1300 °C. To clarify how H₂O affects As volatilization, the mode of occurrence of As in coal and ash was analyzed, as shown in Fig. 6.

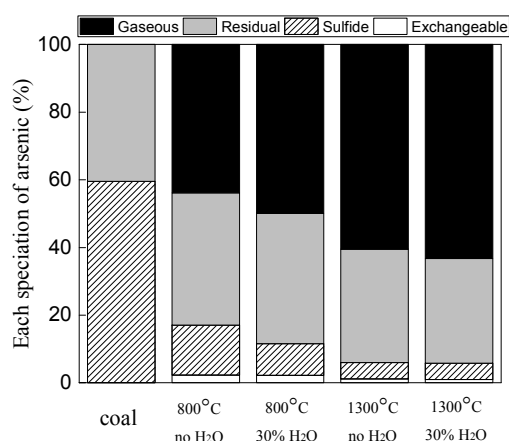


Fig. 6. Mode of occurrence of As in ST coal and its ash

It can be seen from Fig. 6, that for ST coal, about 60% of the total As is sulfide-bound, which is consistent with previous work [34-36]. Compared to the raw coal, the content of sulfide-bound As in ashes decreased greatly, with higher temperatures as sulfide-bound As is relatively unstable and more likely to oxidize and decompose [37]. The percent for the As speciation in coal or ash is given in Table 3.

Table 3. Percent for the speciation of As in coal or ash

	Mode of occurrence of arsenic in coal or ash (%)			Gaseous (%)
	Exchangeable	Sulfide	Residue	
Coal	nd ^a	59.5	40.5	0
Ash (800 °C, no H ₂ O)	2.3	14.7	39.1	43.9
Ash (800 °C, 30% H ₂ O)	2.1	9.4	38.5	50.0
Ash (1300 °C, no H ₂ O)	1.1	4.9	33.5	60.5
Ash (1300 °C, 30% H ₂ O)	0.9	4.8	31.1	63.2

^and=not detected. Organic arsenic was not detected in coal or ash

From Table 3, it can be seen that the percent of gaseous arsenic with 30% H₂O is 6.1% higher than that without H₂O at 800 °C, while only a 2.7% increase is obtained at 1300 °C. This indicates that H₂O has a greater impact on As volatilization at 800 °C than at 1300 °C. At 800 °C, the percentage of sulfide-bound arsenic without H₂O (14.7%) is larger than that with 30% H₂O (9.4%). This illustrates that the increase of gaseous arsenic with 30% H₂O is mainly a result of enhancing the decomposition of sulfide-bound As at 800 °C. However, the percentage of sulfide-bound arsenic is almost the same without or with 30% H₂O at 1300 °C. This shows that sulfide-bound arsenic was almost completely evaporated at 1300 °C, and made little contribution to the volatilization of As. The percent of residual arsenic with 30% H₂O declines by 2.4% compared to that without H₂O at 1300 °C, indicating that the percentage increment of gaseous arsenic with 30% H₂O is mainly a result of enhanced decomposition of stable arsenate and minerals [38]. Arsenate has a high thermal stability and is difficult to evaporate as a result of its high melting point. Thus, only a small increase of the volatilization percentage of As was observed in the presence of H₂O at 1300 °C.

3.2.2 Effect of H₂O on volatilization rate of As

The effect of H₂O on the volatilization kinetics of As was explored for ST coal at 1300 °C, as shown in Fig. 7. The combustion atmosphere was the same as for the tests in Fig. 5.

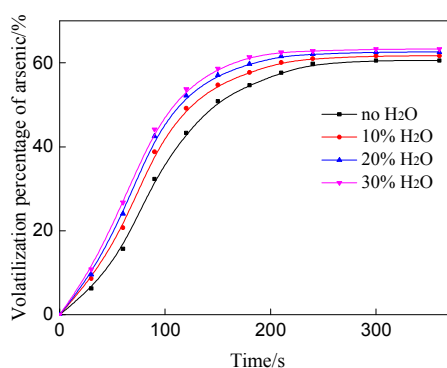


Fig. 7. Volatilization percentage of As at different specified residence times during isothermal O₂/CO₂ combustion

Fig. 7 shows the volatilization percentage of As increases with time and then levels off, with or without steam. However, higher H₂O concentration is helpful in accelerating the volatilization of As. To better understand the volatilization behavior of As, volatilization rates were calculated by taking the derivatives of the volatilization percentage curves in Fig. 7, as shown in Fig. 8.

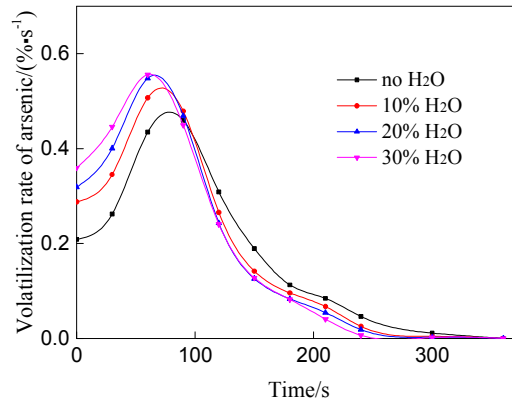


Fig. 8. Volatilization rate of As during isothermal O₂/CO₂ combustion

As can be seen in Fig. 8, the volatilization rates of As first increased and then decreased, and the curves had peak values at 70-90 s. The volatilization characteristics of As in different combustion atmospheres are shown in Table 4.

Table 4. As volatilization rate peak in different combustion atmospheres

Atmosphere	Peak time/s	Peak value of volatilization rate /%·s ⁻¹
21%O ₂ /79%CO ₂	90	0.47
21%O ₂ /10%H ₂ O/69%CO ₂	80	0.53
21%O ₂ /20%H ₂ O/59%CO ₂	76	0.55
21%O ₂ /30%H ₂ O/49%CO ₂	73	0.56

From Table 4, it can be seen that when the concentration of H₂O increased from 0 to 30%, the peak value for the As volatilization rate increased from 0.47%·s⁻¹ to 0.56%·s⁻¹, and the time to reach the peak value shortened. To clarify the effect of H₂O on the volatilization behavior of As, the combustion reaction kinetics of ST coal at different H₂O concentrations were measured and

the results are shown in Fig. 9.

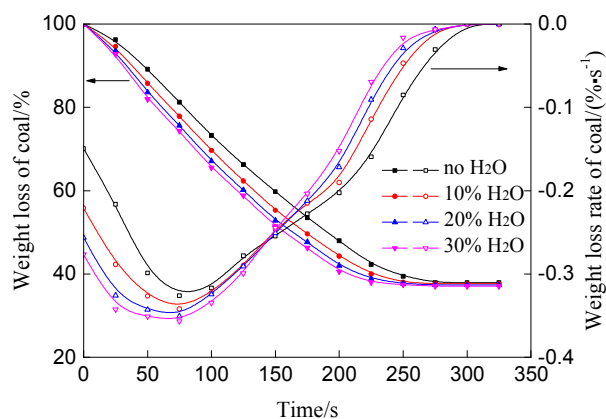


Fig. 9. Combustion reaction kinetics of ST coal during O₂/CO₂ combustion at 1300 °C

Comparing Fig. 8 to Fig. 9, it can be seen that the volatilization characteristics of As are related to the isothermal mass loss characteristics of ST coal during the combustion process. The isothermal weight loss rate and As volatilization rate of ST coal are relatively high in the initial combustion stage (0~90 s). During this period, moisture and volatiles in coal were first released and volatile combustion releases a great deal of heat, which promotes an isothermal weight loss rate and As volatilization rate. With the increase of H₂O concentration, the isothermal weight loss rate of ST coal increased gradually, similarly to the volatilization rate of As. First, the diffusion rate of O₂ in H₂O is higher than that in CO₂ during coal combustion [19], which would increase the combustion rate. Second, the gasification reaction between H₂O and char can produce hydrogen atoms and hydroxyl radicals by means of the following elementary reactions [39]:



The dissociation of H₂O can significantly accelerate the isothermal carbon weight loss rate and As volatilization rate [21].

3.3 Morphological characterization and mineral compositions

To analyze the effect of H₂O on As volatilization, morphological characterizations of ST combustion ashes without H₂O and with 30% H₂O at 1300 °C were performed by SEM. The qualitative SEM examinations are shown in Fig. 10.

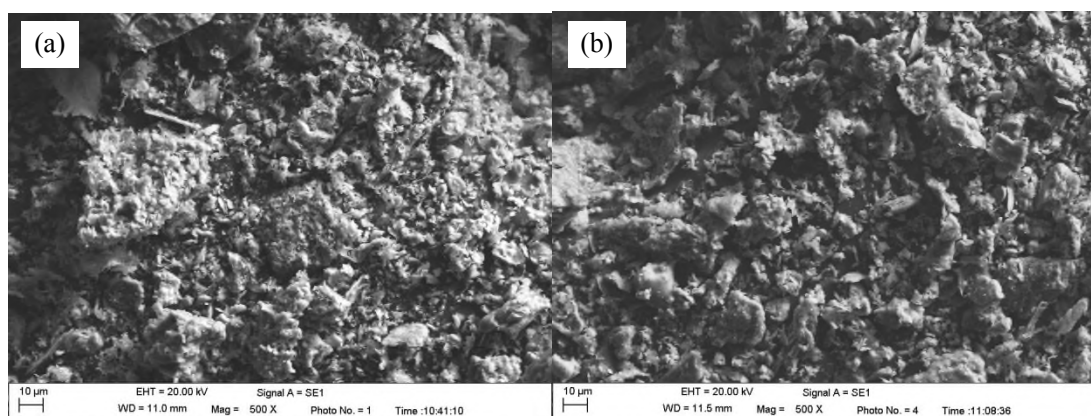


Fig. 10. SEM micrographs of ST combustion ash at 1300 °C

(a) without H₂O; (b) 30% H₂O

As can be seen in Fig. 10, ash samples without H₂O mainly occur in a granular form (Fig. 10 (a)); ash samples with 30% H₂O are mainly in the form of flakes (Fig. 10 (b)). Compared with Fig. 10 (a), the ash particles are smaller and have a plentiful formation of cavities, as can be seen in Fig. 10 (b). The change of pore structure characteristics is primarily caused by the gasification reaction between H₂O and char. As mentioned in section 3.2, the gasification reaction between char and H₂O tends to generate more micropores and mesopores [30, 31], which can enhance coal combustion and improve As volatilization simultaneously.

There are some differences in microstructure in Fig. 10 (a) and (b), suggesting that the mineral composition of ash with H₂O is different from that without H₂O. To examine this further, the mineralogical characterization of ST ashes under different H₂O concentrations (0, 10%, 20%, and 30%) at 1300 °C was analyzed by XRD, and the results are shown in Fig. 11.

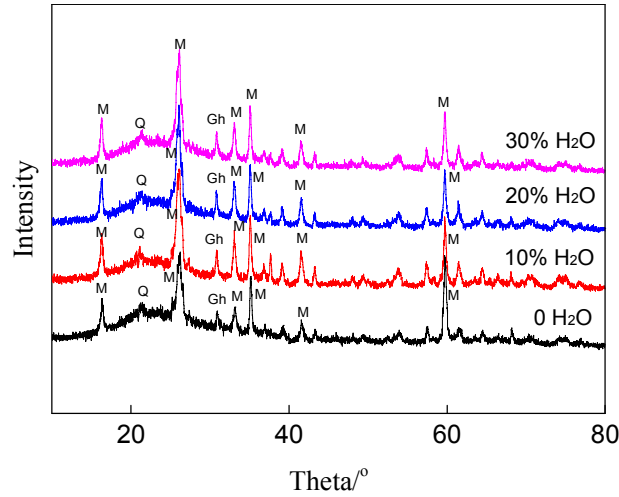


Fig. 11. X-ray diffraction of ST ash in different combustion atmospheres
The minerals identified are: Gh, Gehlenite; M, mullite; Q, quartz

From Fig. 11, it can be seen that the mineral composition of ST ash consists of mullite and a small amount of quartz and gehlenite. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and Eq. 7) is primarily produced from the decomposition of kaolinite (Eq. 8) in the feed coal [40], while gehlenite ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), which is very stable, is likely the reaction product of SiO_2 , Al_2O_3 , and CaO (Eq. 9). Arsenic is likely to adhere to highly reactive cationic compounds during combustion [41], and some researchers [42-44] have confirmed that calcium-based minerals are the common active sites and react easily with As to form calcium arsenate (Eq. 10). It can be expected that reactions (9) and (10) compete for CaO .



When the concentration of H_2O was increased from 0 to 30%, the mineral types remained the same, but the content of each given type changed. By comparison of the spectra under different H_2O concentrations, it can be seen that combustion atmospheres with more H_2O produce a

stronger peak intensity for gehlenite than those without H₂O. This is mainly due to the fact that the diffusion rate of O₂ in coal particles became larger and, hence, the transformation of minerals was enhanced [45]. As a result, the interaction between minerals (CaO, Al₂O₃ and SiO₂) was promoted and more gehlenite was generated. Thus, the presence of H₂O enhanced the formation of gehlenite, and increased As volatilization.

3.4 Verification testing of other coals

Two other coals, WL and MH, were examined to determine whether the same experimental phenomena with ST coal could be observed. The results are presented in Fig. 12 and tests were carried out at six reaction temperatures (800~1300 °C) with 0 or 10% H₂O.

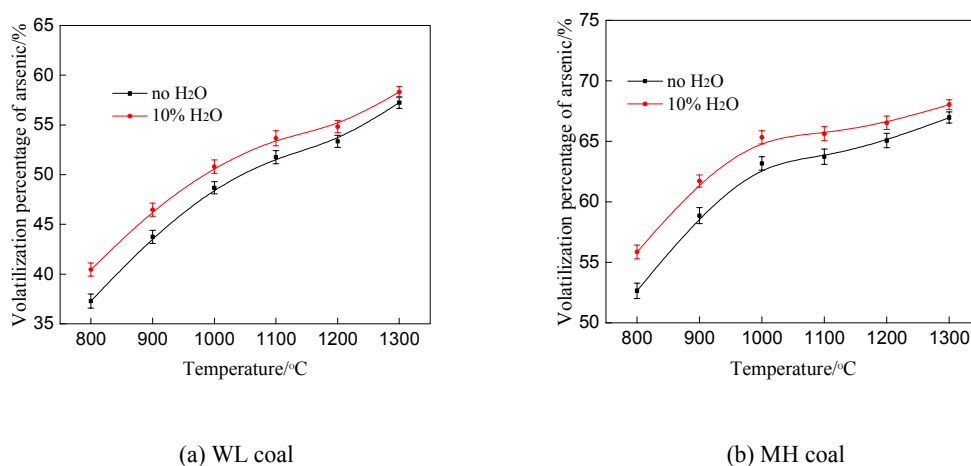


Fig. 12. Volatilization percentage of As during isothermal O₂/CO₂ combustion for WL and MH coal

The curves of arsenic volatilization for WL and MH coal shown in Fig. 12 are very similar to those for ST coal shown in Fig. 5. When the combustion atmosphere contains H₂O, the volatilization percentage of As is larger than that without H₂O. In addition, H₂O has a greater impact on the volatilization percentage of As at 800 °C than at 1300 °C. The similar trends in behavior of the three coals tested during this study indicate that the effect of H₂O is not limited to only one coal.

4 Conclusions

Combustion experiments were conducted in a customized isothermal thermogravimetric reactor to study the volatilization characteristics of As in some typical Chinese coals. Compared to combustion in 21O₂/79N₂, the final volatilization percentage of As is reduced by 3% in 21O₂/79CO₂ at 800 °C, and by only 1% at 1300 °C. This indicates that CO₂ has a negative effect on the volatilization of As and this inhibitory effect decreases with higher temperature. The volatilization of As is promoted by H₂O, and the positive effect is enhanced with more H₂O (0-30%). The final volatilization percentage of As at 30% H₂O is 6.1% higher than that without H₂O at 800 °C, while only a 2.7% increase is obtained at 1300 °C. This shows that H₂O plays a more important role at lower temperatures, nonetheless it can be concluded that H₂O always has a positive impact on As volatilization. This suggests that feeding raw coal with relatively low moisture in coal-fired plants, may be an effective method of reducing As emissions. The volatilization rate of As is accelerated with more steam; and a likely explanation is that the diffusion rate of O₂ in a atmosphere with H₂O is higher than that with CO₂ during coal combustion, which can promote the isothermal weight loss rate and As volatilization. Qualitative phase analysis confirmed the positive effect of H₂O on the volatilization of As.

5 Acknowledgement

The financial support from Fundamental Research Funds for the Central Universities (2018ZD03) and Key Research and Development (R&D) Projects of Shanxi Province (201803D31027) are gratefully acknowledged. The authors would also like to acknowledge the many useful comments and suggestions from Dr David Granatstein.

References:

- [1] Q Tang, G J Liu, C C Zhou, R Y Sun. Distribution of trace elements in feed coal and combustion residues from two coal-fired power plants at Huainan, Anhui, China. *Fuel* 2013; 107: 315-322.
- [2] M A López-Antón, M Díaz-Somoano, J Fierro, M R Martínez-Tarazona. Retention of arsenic and selenium compounds present in coal combustion and gasification flue gases using activated carbons. *Fuel Processing Technology* 2007; 88: 799-805.
- [3] G Liu, L Zheng, N S Duzgoren-Aydin, L Gao, J Liu, Z Peng. Health Effects of Arsenic, Fluorine, and Selenium from Indoor Burning of Chinese Coal. *Reviews of Environmental Contamination and Toxicology* 2007; 189: 89-106.
- [4] J Wang, A Tomita. A Chemistry on the Volatility of Some Trace Elements during Coal Combustion and Pyrolysis. *Energy & Fuels* 2003; 17: 954-960.
- [5] Y Zhao, J Zhang, W Huang, Z Wang, Y Li, D Song, F Zhao, C Zheng. Arsenic emission during combustion of high arsenic coals from Southwestern Guizhou, China. *Energy Conversion and Management* 2008; 49: 615-624.
- [6] A A Duker, E J M Carranza, M Hale. Arsenic geochemistry and health. *Environment International* 2005; 31: 631-641.
- [7] H Liu, W Pan, C Wang, Y Zhang. Volatilization of Arsenic during Coal Combustion Based on Isothermal Thermogravimetric Analysis at 600-1500 °C. *Energy & Fuels* 2016; 30: 6790-6798.
- [8] H Liu, C Wang, X Sun, Y Zhang, C Zou. Volatilization of Arsenic in Coal during Isothermal Oxy-Fuel Combustion. *Energy & Fuels* 2016; 30: 3479-3487.
- [9] F Jiao, Y Ninomiya, L Zhang, N Yamada, A Sato. Effect of coal blending on the leaching characteristics of arsenic in fly ash from fluidized bed coal combustion. *Fuel Processing Technology* 2013; 106: 769-775.
- [10] O Font, P Córdoba, C Leiva, L M Romeo, I Bolea. Fate and abatement of mercury and other trace elements in a coal fluidised bed oxy combustion pilot plant. *Fuel* 2012; 95: 272-281.
- [11] C Wang, H Liu, Y Zhang, C Zou, E J Anthony. Review of arsenic behavior during coal combustion: Volatilization, transformation, emission and removal technologies. *Progress in Energy and Combustion Science* 2018; 64: 1-28.
- [12] R M Cuéllar-Franca, A Azapagic. Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts. *Journal of CO₂ Utilization* 2015; 9: 82-102.
- [13] P Gładysz, A Ziębik. Life cycle assessment of an integrated oxy-fuel combustion power plant with CO₂ capture, transport and storage – Poland case study. *Energy* 2015; 92: 328-340.
- [14] A Gopan, B M Kumfer, J Phillips, D Thimsen, R Smith, R L Axelbaum. Process design and performance analysis of a Staged, Pressurized Oxy-Combustion (SPOC) power plant for carbon capture. *Applied Energy* 2014; 125: 179-188.
- [15] E S Hecht, C R Shaddix, M Geier, A Molina, B S Haynes. Effect of CO₂ and steam gasification reactions on the oxy-combustion of pulverized coal char. *Combustion and Flame* 2012; 159: 3437-3447.
- [16] Y Zhuang, J H Pavlish. Fate of hazardous air pollutants in oxygen-fired coal combustion with different flue gas recycling. *Environmental Science and Technology* 2012; 46: 4657-4665.
- [17] B Roy, S Bhattacharya. Release behavior of Hg, Se, Cr and As during oxy-fuel combustion using Loy Yang brown coal in a bench-scale fluidized bed unit. *Powder Technology* 2016; 302: 328-332.

- [18] E Hecht, C R Shaddix, M Geier, A Molina, B S Haynes. Effect of CO₂ and steam gasification reactions on the oxy-combustion of pulverized coal char. *Combustion and Flame* 2012; 159.
- [19] C Wang, X W Liu, D Li, W C Wu, Y S Xu, J P Si, B Zhao, M H Xu. Effect of H₂O and SO₂ on the distribution characteristics of trace elements in particulate matter at high temperature under oxy-fuel combustion. *International Journal of Greenhouse Gas Control* 2014; 23: 51-60.
- [20] H Wang, Y Duan, Y Li, Y Xue, M Liu. Prediction of Synergic Effects of H₂O, SO₂, and HCl on Mercury and Arsenic Transformation under Oxy-Fuel Combustion Conditions. *Energy & Fuels* 2016; 30: 8463-8468.
- [21] C Wang, H Shao, M Lei, Y Wu, L Jia. Effect of the coupling action between volatiles, char and steam on isothermal combustion of coal char. *Applied Thermal Engineering* 2016; 93: 438-445.
- [22] H Liu, C Wang, Y Zhang, X Huang, Y Guo. Experimental and modeling study on the volatilization of arsenic during co-combustion of high arsenic lignite blends. *Applied Thermal Engineering* 2016; 108: 1336-1343.
- [23] C Zou, C Wang, H Liu, H Wang, Y Zhang. Effect of Volatile and Ash Contents in Coal on the Volatilization of Arsenic during Isothermal Coal Combustion. *Energy & Fuels* 2017; 31: 12831-12838.
- [24] J Liu, Zheng C, Zhang J, Wang M. Study on the Speciation of Most Volatile Trace Elements in Coal. *Journal of Combustion Science and Technology* 2003; 9: 295-299.
- [25] R J Quann, A F Sarofim. Vaporization of refractory oxides during pulverized coal combustion. *Symposium (International) on Combustion* 1982; 19: 1429-1440.
- [26] A Suriyawong, M Gamble, M Lee, R Axelbaum, P Biswas. Submicrometer Particle Formation and Mercury Speciation Under O₂-CO₂ Coal Combustion. *Energy and Fuels* 2006; 20: 2357-2363.
- [27] W Wang, C Bu, A G Barea, B Leckner, X Wang, J Zhang, G Piao. O₂/CO₂ and O₂/N₂ combustion of bituminous char particles in a bubbling fluidized bed under simulated combustor conditions. *Chemical Engineering Journal* 2018; 336: 74-81.
- [28] H Liu, H Zhu, M Kaneko, S K A T Kojima. High-Temperature Gasification Reactivity with Steam of Coal Chars Derived under Various Pyrolysis Conditions in a Fluidized Bed. *Energy and Fuels* 2010; 24: 68-75.
- [29] G Liu, S Niksa. Coal conversion submodels for design applications at elevated pressures. Part II. Char gasification. *Progress in Energy and Combustion Science* 2004; 30: 679-717.
- [30] A Linares-Solano, I Martin-Gullon, C Salinas-Martinez De Lecea, B Serrano-Talavera. Activated carbons from bituminous coal: effect of mineral matter content. *Fuel* 2000; 79: 635-643.
- [31] F Rodriguez-Reinoso, M Molina-Sabio, M T Gonzalez. The use of steam and CO₂ as activating agents in the preparation of activated carbons. *Carbon* 1995; 33: 15-23.
- [32] T Zeng, A F Sarofim, C L Senior. Vaporization of arsenic, selenium and antimony during coal combustion. *Combustion and Flame* 2001; 126: 1714-1724.
- [33] R Tseng. Physical and chemical properties and adsorption type of activated carbon prepared from plum kernels by NaOH activation. *Journal of Hazardous Materials* 2007; 147: 1020-1027.
- [34] V Bouška, J Pešek. Quality parameters of lignite of the North Bohemian Basin in the Czech Republic in comparison with the world average lignite. *International Journal of Coal Geology* 1999; 40: 211-235.
- [35] R A Zielinski, A L Foster, G P Meeker, I K Brownfield. Mode of occurrence of arsenic in feed coal and its derivative fly ash, Black Warrior Basin, Alabama. *Fuel* 2007; 86: 560-572.
- [36] Y Kang, G Liu, C Chou, M H Wong, L Zheng, R Ding. Arsenic in Chinese coals: Distribution,

- modes of occurrence, and environmental effects. *Science of the Total Environment* 2011; 412-413: 1-13.
- [37] R Guo, J Yang, D Liu, Z Liu. Transformation behavior of trace elements during coal pyrolysis. *Fuel Processing Technology* 2002; 2002: 137.
- [38] H Hu, H Liu, J Chen, A Li, H Yao, F Low, L Zhang. Speciation transformation of arsenic during municipal solid waste incineration. *Proceedings of the Combustion Institute* 2015; 35: 2883-2890.
- [39] S Kajitani, H Tay, S Zhang, C Li. Mechanisms and kinetic modelling of steam gasification of brown coal in the presence of volatile - char interactions. *Fuel* 2013; 103: 7-13.
- [40] D A Spears. Role of clay minerals in UK coal combustion. *Applied Clay Science* 2000; 16: 87-95.
- [41] W S Seames. An initial study of the fine fragmentation fly ash particle mode generated during pulverized coal combustion. *Fuel Processing Technology* 2003; 81: 109-125.
- [42] W S Seames, J O L Wendt. Partitioning of arsenic, selenium, and cadmium during the combustion of Pittsburgh and Illinois #6 coals in a self-sustained combustor. *Fuel Processing Technology* 2000; 63: 179-196.
- [43] R A Jadhav, L Fan. Capture of Gas-Phase Arsenic Oxide by Lime: Kinetic and Mechanistic Studies. *Environmental Science & Technology* 2001; 35: 794-799.
- [44] S Mahuli, R Agnihotri, S Chauk, A A Ghoshdastidar, L S Fan. Mechanism of Arsenic Sorption by Hydrated Lime. *Environmental Science and Technology* 1997; 31: 3226-3231.
- [45] F Huang, L Zhang, B Yi, Z Xia, C Zheng. Effect of H₂O on pyrite transformation behavior during oxy-fuel combustion. *Fuel Processing Technology* 2015; 131: 458-465.