

# Effect of H<sub>2</sub>O on the volatilization characteristics of arsenic during isothermal O<sub>2</sub>/CO<sub>2</sub> combustion

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**Abstract:** The effect of H<sub>2</sub>O on the volatilization behavior of arsenic in coal was studied under O<sub>2</sub>/CO<sub>2</sub> 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 H<sub>2</sub>O under O<sub>2</sub>/CO<sub>2</sub> combustion conditions. The effect of CO<sub>2</sub> on As volatilization was first investigated and it was found that increasing CO<sub>2</sub> concentrations inhibits the volatilization of As, with this effect decreasing with increasing temperature. When a fraction of the CO<sub>2</sub> was replaced with H<sub>2</sub>O, the volatilization of As increased, but the positive effect of H<sub>2</sub>O also decreased with increasing temperature. The volatilization percentage of As with 30% H<sub>2</sub>O was 6.1% higher than that without H<sub>2</sub>O at 800 °C, while it was only 2.7% higher at 1300 °C. When the concentration of H<sub>2</sub>O 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 H<sub>2</sub>O was not limited to only one specific coal.

**Keywords:** O<sub>2</sub>/CO<sub>2</sub> combustion; arsenic; volatilization characteristics; H<sub>2</sub>O

## 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 O<sub>2</sub>/CO<sub>2</sub> combustion, the CO<sub>2</sub> 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 O<sub>2</sub>/CO<sub>2</sub> combustion, and found that the concentration of As in fly ash was lower than that in O<sub>2</sub>/N<sub>2</sub> 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 O<sub>2</sub>/CO<sub>2</sub> combustion and O<sub>2</sub>/N<sub>2</sub> combustion at 21% oxygen. However, Liu et al. [8] conducted combustion experiments in a customized isothermal thermogravimetric system, and concluded that high concentrations of CO<sub>2</sub> 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 O<sub>2</sub>/CO<sub>2</sub> combustion than that observed in O<sub>2</sub>/N<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> on As volatilization during O<sub>2</sub>/CO<sub>2</sub> combustion.

In addition, H<sub>2</sub>O is known as one of the main components of the flue gas in oxy-fuel combustion, and the concentration of H<sub>2</sub>O may be up to 25%~35% as a result of flue gas recycle [18]. Roy et al. [17] studied the effect of H<sub>2</sub>O on the volatilization of As during O<sub>2</sub>/CO<sub>2</sub> combustion, and their experimental results indicated that the addition of H<sub>2</sub>O inhibited the volatilization of As. Wang et al. [19] found that the As concentration in particulate matter (PM) decreased with more H<sub>2</sub>O in the inlet gas of O<sub>2</sub>/CO<sub>2</sub> combustion experiments in a drop furnace at 1500 °C. Wang et al. [20] simulated the speciation of arsenic under O<sub>2</sub>/CO<sub>2</sub> combustion with FactSage 5.2 software, and showed that the effect of H<sub>2</sub>O on arsenic distribution was dependent on the concentration of H<sub>2</sub>O. However, these studies focused on the effect of H<sub>2</sub>O 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 H<sub>2</sub>O on the volatilization characteristics of As during O<sub>2</sub>/CO<sub>2</sub> combustion. Combustion experiments were carried out with three coals in a customized isothermal thermogravimetric reactor. The influence of temperature, CO<sub>2</sub>, and especially H<sub>2</sub>O concentration were explored. Both scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses were employed to further understand the effect of H<sub>2</sub>O 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  $\mu\text{m}$ . 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 <sup>a</sup>	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 <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	TiO <sub>2</sub>	SO <sub>3</sub>	K <sub>2</sub> 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		

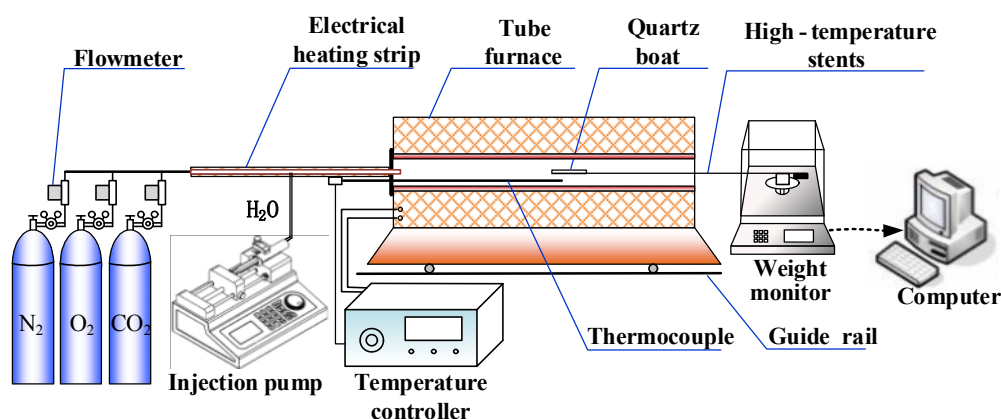
<sub>ad</sub>: air dry

<sup>a</sup>: 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 N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O. The individual gas flowrates

were controlled by flowmeters. H<sub>2</sub>O 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 H<sub>2</sub>O 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

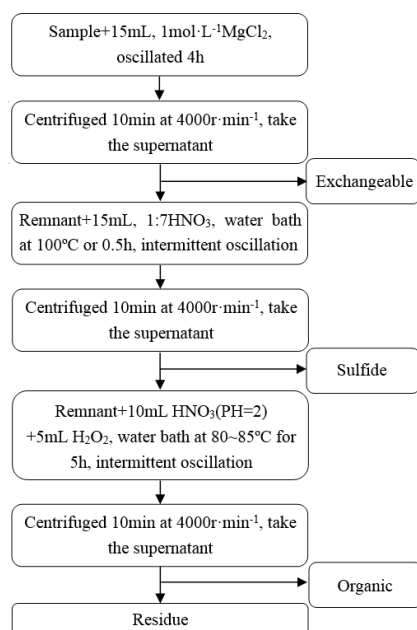
The volatilization characteristics of As were determined by measuring the As concentration in ash at specified combustion residence times (30, 60, 90, 120, 150, 180, 210, 240, 300, 360, 420, 480, and 540 s). All experiments followed the same procedure: the coal samples ( $0.50 \pm 0.01$  g) were placed 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 N<sub>2</sub> 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 H<sub>2</sub>O on As volatilization.

## 2.4 Data analysis

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

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

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

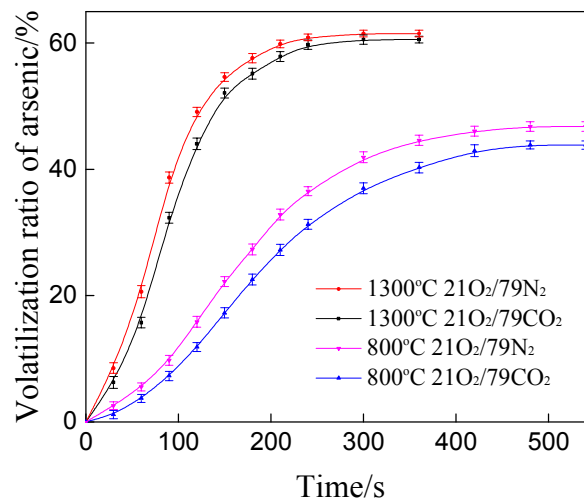
$$\text{volatilization rate of As at } i \text{ s, } v_i = dX_i / di , \% / \text{s} \quad (3)$$

where  $\eta_i$  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 $\text{O}_2/\text{CO}_2$ combustion

The volatilization characteristics of As in 21%  $\text{O}_2/79\%$   $\text{N}_2$  and 21%  $\text{O}_2/79\%$   $\text{CO}_2$  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 21O<sub>2</sub>/79N<sub>2</sub> and 21O<sub>2</sub>/79CO<sub>2</sub> at 800 and 1300 °C for ST coal

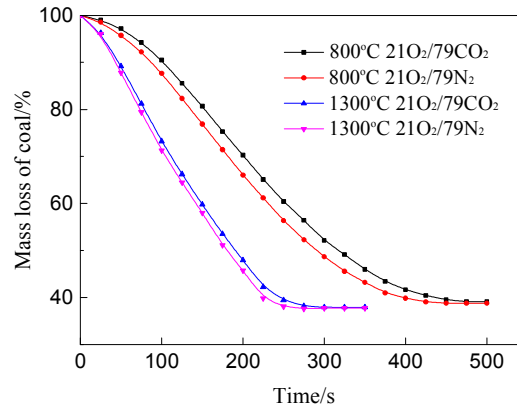
Fig. 3 shows that for both 21O<sub>2</sub>/79N<sub>2</sub> and 21O<sub>2</sub>/79CO<sub>2</sub> atmospheres, the volatilization percentage of As becomes larger and then tends to stabilize as the combustion time increases. At both temperatures, compared to 21O<sub>2</sub>/79N<sub>2</sub>, the volatilization proportion of As was reduced in 21O<sub>2</sub>/79CO<sub>2</sub>, and these results are consistent with the results of Wang et al. [19]. Here, the

21O<sub>2</sub>/79CO<sub>2</sub> 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 O<sub>2</sub>/CO<sub>2</sub> combustion, the high CO<sub>2</sub> 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 21O<sub>2</sub>/79N<sub>2</sub> is 3% higher than that in 21O<sub>2</sub>/79CO<sub>2</sub> at 800 °C, while the value is less than 1% higher at 1300 °C. This indicates that the negative effect of CO<sub>2</sub> on As volatilization is reduced with increasing temperature. To examine the effects of CO<sub>2</sub> further, the combustion reaction kinetics of ST coal at 800 and 1300 °C in 21O<sub>2</sub>/79N<sub>2</sub> and 21O<sub>2</sub>/79CO<sub>2</sub> were studied, and results are shown in Fig. 4.



**Fig. 4.** Combustion reaction kinetics of ST coal at 800 and 1300 °C in 21O<sub>2</sub>/79N<sub>2</sub> and 21O<sub>2</sub>/79CO<sub>2</sub>

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



**Table 2.** Burnout time and corresponding ash yield of ST coal combustion in 21O<sub>2</sub>/79N<sub>2</sub> and 21O<sub>2</sub>/79CO<sub>2</sub> atmosphere

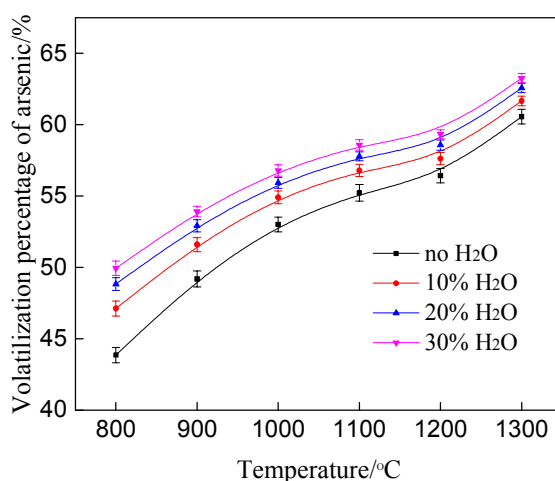
Parameters	800°C		1300°C	
	21O <sub>2</sub> /79N <sub>2</sub>	21O <sub>2</sub> /79CO <sub>2</sub>	21O <sub>2</sub> /79N <sub>2</sub>	21O <sub>2</sub> /79CO <sub>2</sub>
Burnout time, s	440	475	280	290
Ash yield, %	38.77	38.91	37.74	37.82

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

#### 3.2.1 Effect of H<sub>2</sub>O on final volatilization percentage of As

To elucidate the role of H<sub>2</sub>O, the final volatilization percentage of As at various reaction temperatures (800~1300 °C) with different H<sub>2</sub>O concentrations (0, 10%, 20%, and 30%) was investigated in a 21O<sub>2</sub>/79CO<sub>2</sub> atmosphere, as shown in Fig. 5.



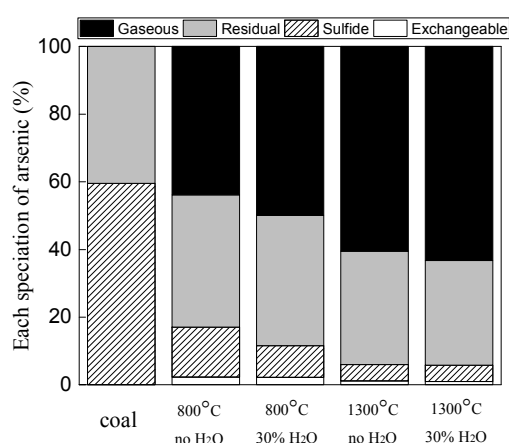
**Fig. 5.** Volatilization percentage of As at different temperatures during isothermal O<sub>2</sub>/CO<sub>2</sub> combustion for ST coal

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 H<sub>2</sub>O, the volatilization percentage of As becomes larger than that without H<sub>2</sub>O, indicating that H<sub>2</sub>O has a positive effect on As volatilization. The reason for this seems to be that the gasification reaction between H<sub>2</sub>O and char can enhance coal combustion [28, 29], and consequently promote the release of arsenic. In addition, the reaction between H<sub>2</sub>O 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 H<sub>2</sub>O 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 H<sub>2</sub>O, while those micropores grow into mesopores and macropores at a higher concentration of H<sub>2</sub>O [33], which leads to a decrease of the pore area

of the char. Thus, the positive effect of H<sub>2</sub>O on the volatilization of As declines with the increase of H<sub>2</sub>O concentration.

From Fig. 5, it also can be seen that H<sub>2</sub>O has a greater impact on As volatilization at 800 °C than at 1300 °C. To clarify how H<sub>2</sub>O 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

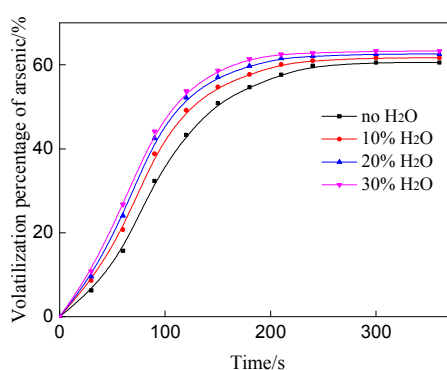
	Mode of occurrence of arsenic in coal or ash (%)			Gaseous (%)
	Exchangeable	Sulfide	Residue	
Coal	nd <sup>a</sup>	59.5	40.5	0
Ash (800 °C, no H <sub>2</sub> O)	2.3	14.7	39.1	43.9
Ash (800 °C, 30% H <sub>2</sub> O)	2.1	9.4	38.5	50.0
Ash (1300 °C, no H <sub>2</sub> O)	1.1	4.9	33.5	60.5
Ash (1300 °C, 30%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

<sup>a</sup>nd=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% H<sub>2</sub>O is 6.1% higher than that without H<sub>2</sub>O at 800 °C, while only a 2.7% increase is obtained at 1300 °C. This indicates that H<sub>2</sub>O has a greater impact on As volatilization at 800 °C than at 1300 °C. At 800 °C, the percentage of sulfide-bound arsenic without H<sub>2</sub>O (14.7%) is larger than that with 30% H<sub>2</sub>O (9.4%). This illustrates that the increase of gaseous arsenic with 30% H<sub>2</sub>O 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% H<sub>2</sub>O 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% H<sub>2</sub>O declines by 2.4% compared to that without H<sub>2</sub>O at 1300 °C, indicating that the percentage increment of gaseous arsenic with 30% H<sub>2</sub>O 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 H<sub>2</sub>O at 1300 °C.

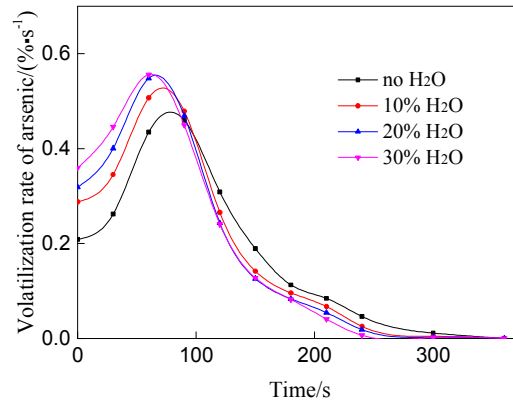
### 3.2.2 Effect of H<sub>2</sub>O on volatilization rate of As

The effect of H<sub>2</sub>O 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 O<sub>2</sub>/CO<sub>2</sub> combustion

Fig. 7 shows the volatilization percentage of As increases with time and then levels off, with or without steam. However, higher H<sub>2</sub>O 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 O<sub>2</sub>/CO<sub>2</sub> combustion

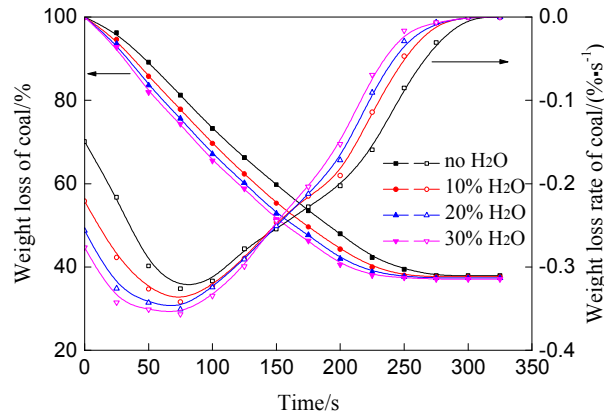
As can be seen in Fig. 8, the volatilization rates of As first increased and then decreased, and the curves had peak values at 70-90 s. The volatilization characteristics of As in different combustion atmospheres are shown in Table 4.

**Table 4.** As volatilization rate peak in different combustion atmospheres

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

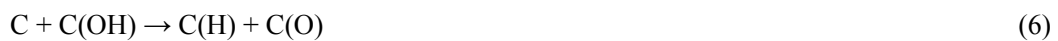
From Table 4, it can be seen that when the concentration of H<sub>2</sub>O increased from 0 to 30%, the peak value for the As volatilization rate increased from 0.47%·s<sup>-1</sup> to 0.56%·s<sup>-1</sup>, and the time to reach the peak value shortened. To clarify the effect of H<sub>2</sub>O on the volatilization behavior of As, the combustion reaction kinetics of ST coal at different H<sub>2</sub>O concentrations were measured and

the results are shown in Fig. 9.



**Fig. 9.** Combustion reaction kinetics of ST coal during O<sub>2</sub>/CO<sub>2</sub> combustion at 1300 °C

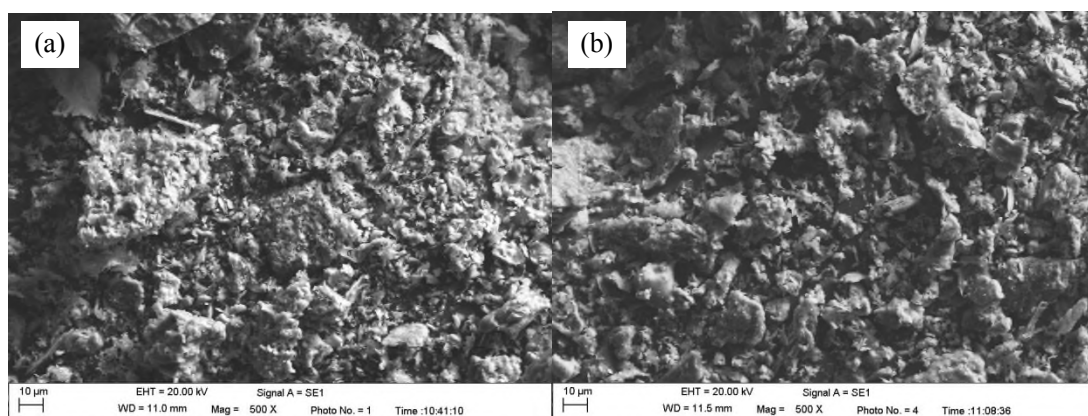
Comparing Fig. 8 to Fig. 9, it can be seen that the volatilization characteristics of As are related to the isothermal mass loss characteristics of ST coal during the combustion process. The isothermal weight loss rate and As volatilization rate of ST coal are relatively high in the initial combustion 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 H<sub>2</sub>O concentration, the isothermal weight loss rate of ST coal increased gradually, similarly to the volatilization rate of As. First, the diffusion rate of O<sub>2</sub> in H<sub>2</sub>O is higher than that in CO<sub>2</sub> during coal combustion [19], which would increase the combustion rate. Second, the gasification reaction between H<sub>2</sub>O and char can produce hydrogen atoms and hydroxyl radicals by means of the following elementary reactions [39]:



The dissociation of H<sub>2</sub>O 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  $H_2O$  on As volatilization, morphological characterizations of ST combustion ashes without  $H_2O$  and with 30%  $H_2O$  at 1300 °C were performed by SEM. The qualitative SEM examinations are shown in Fig. 10.

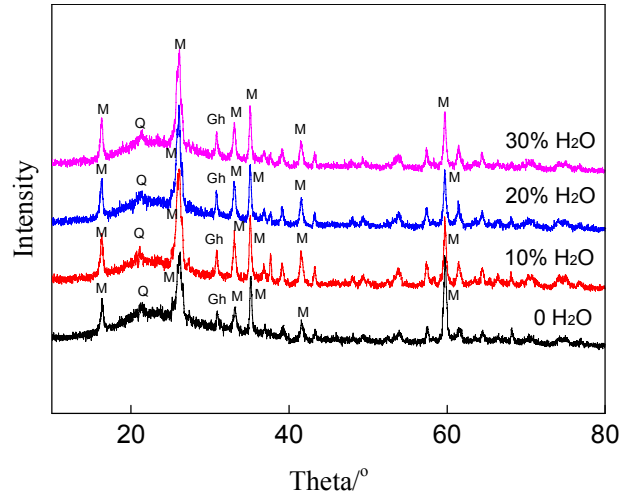


**Fig. 10.** SEM micrographs of ST combustion ash at 1300 °C

(a) without  $H_2O$ ; (b) 30%  $H_2O$

As can be seen in Fig. 10, ash samples without  $H_2O$  mainly occur in a granular form (Fig. 10 (a)); ash samples with 30%  $H_2O$  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  $H_2O$  and char. As mentioned in section 3.2, the gasification reaction between char and  $H_2O$  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  $H_2O$  is different from that without  $H_2O$ . To examine this further, the mineralogical characterization of ST ashes under different  $H_2O$  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  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaO}$  (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  $\text{CaO}$ .



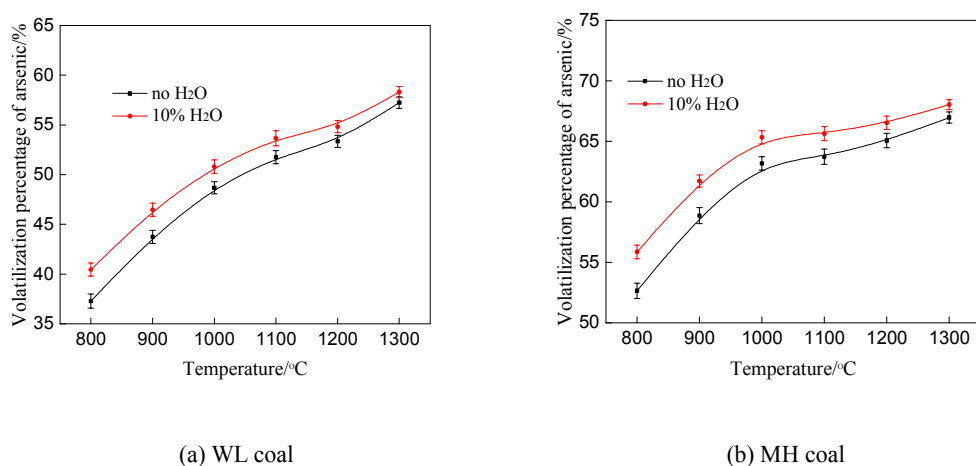
When the concentration of  $\text{H}_2\text{O}$  was increased from 0 to 30%, the mineral types remained the same, but the content of each given type changed. By comparison of the spectra under different  $\text{H}_2\text{O}$  concentrations, it can be seen that combustion atmospheres with more  $\text{H}_2\text{O}$  produce a



stronger peak intensity for gehlenite than those without H<sub>2</sub>O. This is mainly due to the fact that the diffusion rate of O<sub>2</sub> in coal particles became larger and, hence, the transformation of minerals was enhanced [45]. As a result, the interaction between minerals (CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) was promoted and more gehlenite was generated. Thus, the presence of H<sub>2</sub>O 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% H<sub>2</sub>O.



**Fig. 12.** Volatilization percentage of As during isothermal O<sub>2</sub>/CO<sub>2</sub> 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 H<sub>2</sub>O, the volatilization percentage of As is larger than that without H<sub>2</sub>O. In addition, H<sub>2</sub>O 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 H<sub>2</sub>O 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 21O<sub>2</sub>/79N<sub>2</sub>, the final volatilization percentage of As is reduced by 3% in 21O<sub>2</sub>/79CO<sub>2</sub> at 800 °C, and by only 1% at 1300 °C. This indicates that CO<sub>2</sub> has a negative effect on the volatilization of As and this inhibitory effect decreases with higher temperature. The volatilization of As is promoted by H<sub>2</sub>O, and the positive effect is enhanced with more H<sub>2</sub>O (0-30%). The final volatilization percentage of As at 30% H<sub>2</sub>O is 6.1% higher than that without H<sub>2</sub>O at 800 °C, while only a 2.7% increase is obtained at 1300 °C. This shows that H<sub>2</sub>O plays a more important role at lower temperatures, nonetheless it can be concluded that H<sub>2</sub>O 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 O<sub>2</sub> in a atmosphere with H<sub>2</sub>O is higher than that with CO<sub>2</sub> during coal combustion, which can promote the isothermal weight loss rate and As volatilization. Qualitative phase analysis confirmed the positive effect of H<sub>2</sub>O on the volatilization of As.

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