On–Line Analysis and Kinetic Behavior of Arsenic Release during Coal Combustion and Pyrolysis

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On-Line Analysis and Kinetic Behavior of Arsenic Release during Coal Combustion and Pyrolysis

Fenghua Shen, Jing Liu,* Zhen Zhang, and Jinxin Dai

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

ABSTRACT: The kinetic behavior of arsenic (As) release during coal combustion and pyrolysis in a fluidized bed was investigated by applying an on-line analysis system of trace elements in flue gas. This system, based on inductively coupled plasma optical emission spectroscopy (ICP-OES), was developed to measure trace elements concentrations in flue gas quantitatively and continuously. Obvious variations of arsenic concentration in flue gas were observed during coal combustion and pyrolysis, indicating strong influences of atmosphere and temperature on arsenic release behavior.

Kinetic laws governing the arsenic release during coal combustion and pyrolysis were determined based on the results of instantaneous arsenic concentration in flue gas. A second-order kinetic law was determined for arsenic release during coal combustion, and the arsenic release during coal pyrolysis followed a fourth-order kinetic law. The results showed that the arsenic release rate during coal pyrolysis was faster than that during coal combustion. Thermodynamic calculations were carried out to identify the forms of arsenic in vapor and solid phases during coal combustion and pyrolysis, respectively. $Ca_3(AsO_4)_2$ and $Ca(AsO_2)_2$ are the possible species resulting from As−Ca interaction during coal combustion. $Ca(AsO_2)_2$ is the most probable species during coal pyrolysis.
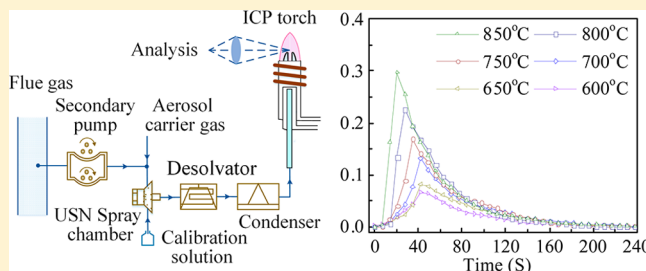
1. INTRODUCTION

Arsenic (As) is regarded as one of the most volatile hazardous elements. Arsenic is not only carcinogenic and potentially mutagenic, but also imposes a long-term burden on biogeochemical cycling in the ecosystem.[1] The emission of arsenic from coal utilization has been identified as one of the main sources of anthropogenic arsenic contamination.[2,3] To better control the emission of arsenic from coal utilization, it is of great importance to understand its release behaviors during coal combustion and pyrolysis.

The release behaviors of arsenic during coal combustion and pyrolysis have been investigated previously by sampling and analyzing residues under different conditions. Seames et al.[4] investigated the partitioning of arsenic between the vapor and solid phases in coal combustion processes. They suggested that the reaction of arsenic vapor with ash particle was essential for the transformation of arsenic from the vapor phase to the solid phase. Zhou et al.[5] studied the influence of mode of occurrence of arsenic in coal on the release behavior of arsenic during combustion. They found that arsenic was mainly associated with Fe−Mn oxides and residual fractions in coal, and transformed to exchangeable and organic fractions after coal combustion. Lu et al.[6] reported that the mineral matters can retard the release of arsenic during coal pyrolysis. However, the release behaviors of arsenic during coal combustion and pyrolysis cannot be satisfactorily interpreted because the methods for sampling and analyzing residues give only the arsenic emission integrated over a long period, thus disregarding the possible peaks of arsenic release.

There is as yet no detailed understanding of the temporal evolution of arsenic during coal combustion and pyrolysis, and the effects of atmosphere on arsenic release kinetics are unclear. Kinetic studies indeed need to be conducted to clarify the dynamic characteristics of arsenic release during coal combustion and pyrolysis. Yu et al.[7] investigated the release behaviors of Cd, Pb, Zn, and Cu from impregnated mineral matrices (Al_2O_3 particles) by aspirating and analyzing the samples directly at given times. They aspirated the Al_2O_3 particles in intervals of 10 min by using a vacuum pump since Al_2O_3 particles will not break during the process of incineration. However, when dealing with coal samples, it is difficult to obtain the release kinetics of trace elements because of the difficulty of sampling a burning solid. The concentration of trace elements in flue gas is the only measurable temporal data. Therefore, the ability to continuously measure the arsenic concentration in flue gas is one of the key points of a kinetic study about arsenic release during coal combustion and pyrolysis.

So far, many efforts have been made to develop reliable technologies for on-line measurement of the concentrations of trace elements in flue gas.[8] The on-line analysis system based on inductively coupled plasma optical emission spectroscopy (ICP-OES) has been identified as a reliable technique, which is able to measure the temporal concentrations of trace elements
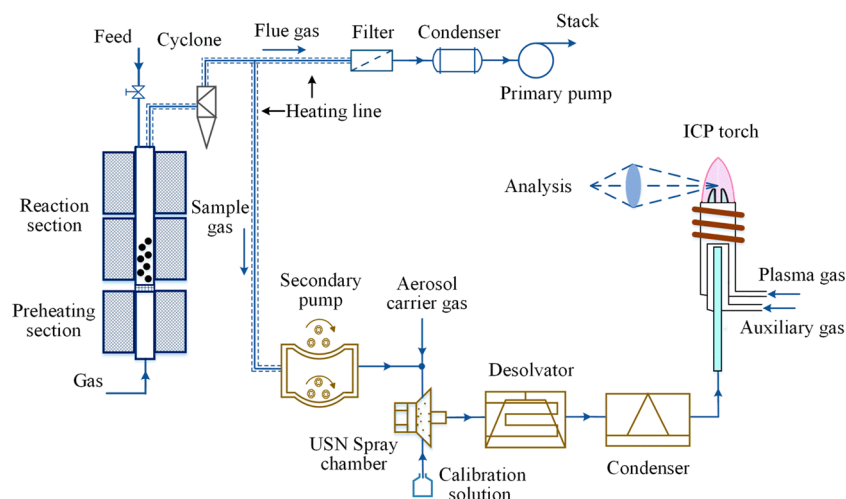
Figure 1. Schematic diagram of experimental setup.

in flue gas quantitatively and continuously during waste incineration.[9−11] It is thus helpful for understanding the industrial processes and monitoring of trace elements emissions for legislative purposes.[9,12] Nevertheless, to the best of the authors' knowledge, quantitative data about on-line analysis of arsenic release during coal combustion and pyrolysis is lacking.

The objective of this study was to develop an on-line analysis system for quantitatively measuring the concentration profiles of arsenic in flue gas under different conditions, and to identify the kinetic behavior of arsenic release from coal. Both coal combustion and pyrolysis have been considered as they are important processes of coal utilization. The kinetic laws of arsenic release during coal combustion and pyrolysis were determined based on the results of on-line analysis and the inverse method.

2. EXPERIMENTAL SECTION

2.1. Fluidized Bed Reactor. The experimental setup scheme is illustrated in Figure 1. A bubbling fluidized bed made of $Cr_{25}Ni_{20}$ stainless steel was employed as reactor. The reactor was a 1500-mm high chamber with inner diameter of 40 mm. The upper section (1100 mm) of the reactor was designed for reaction, and the lower section (400 mm) was designed for preheating. A three-section electric furnace was used to heat the reactor and maintain its temperature. Thermocouples were immersed into the reactor to monitor and measure the temperature of the reactor. Batch feeding was used in the experiments. For each experiment, a given mass of coal sample (2 g) was loaded once the reactor was in stable condition. The fluidization gases (5 L·min⁻¹) were introduced into the reactor from the bottom and preheated by the lower section of the reactor. Air was employed for combustion, and argon was used for pyrolysis. The bed material was composed of quartz sand with particle diameter of 0.55−0.83 mm (initial bed height 35 mm).

2.2. On-Line Arsenic Analysis System. An on-line analysis system based on ICP-OES (Spectro Arcos Sop, Germany) was developed to measure arsenic concentration in flue gas, as shown in Figure 1. This system can measure multielements (wavelength coverage 125−770 nm) concentrations in flue gas continuously and quantitatively, with one measurement being made per 7 seconds. The torch employed for measurement was a quartz demountable torch with an

injector i.d. of 1.8 mm. This torch can realize a higher coolant gas flow, which is needed for a higher power to maintain the stability of plasma under atmospheric conditions.[13] The emission signal intensity of arsenic was measured at 189.042 nm.

An ultrasonic nebulizer (USN, Cetac U5000AT⁺) was used to prepare standard aerosols for calibrations. This ultrasonic nebulizer was able to improve the nebulizing efficiency significantly, and thus could enhance the signal sensitivity of elements.[14] Calibration solutions of arsenic were produced with concentrations of 0.1, 0.2, 1, and 2 μg·L⁻¹. These solutions were nebulized by the ultrasonic nebulizer and fed to the plasma for determining the calibration curves. The water load in the standard aerosol and sample gas was diminished by the evaporation and condensation loop of the ultrasonic nebulizer. The evaporation loop was set to 140 °C, and the condensation loop was set to 3 °C. Part of the fluidization gas flow was used as blank gas, in order to keep the gas composition of standard aerosol constant with the sample aerosol. CO_2 and H_2 were in small amount in flue gas since only 2 g of coal sample was used for each experiment. Therefore, the effects of other gases including CO_2/H_2 on the calibration curves of arsenic are very small in this study. The operating parameters of the on-line analysis system are shown in Table 1.

3. RESULTS AND DISCUSSION

3.1. Comparison of Calibration Curves for Arsenic in Flue Gas. Calibration curves for arsenic in flue gas of coal

Table 1. Operating Parameters of On-Line Analysis System

parameter (unit)	value
generator frequency (MHz)	27.15
power RF (kW)	1.42
plasma gas flow rate (L·min⁻¹)	13
auxiliary gas flow rate (L·min⁻¹)	0.8
aerosol carrier gas flow rate (L·min⁻¹)	0.8
sample gas flow rate, combustion (L·min⁻¹)	0.14
sample gas flow rate, pyrolysis (L·min⁻¹)	0.2
injector tube diameter (mm)	1.8
integration time (s)	3
nebulizer desolvator temperature (°C)	140
nebulizer condenser temperature (°C)	3

combustion and pyrolysis are shown in Figure 2. The relative standard deviation (RSD) of the arsenic calibration curves is
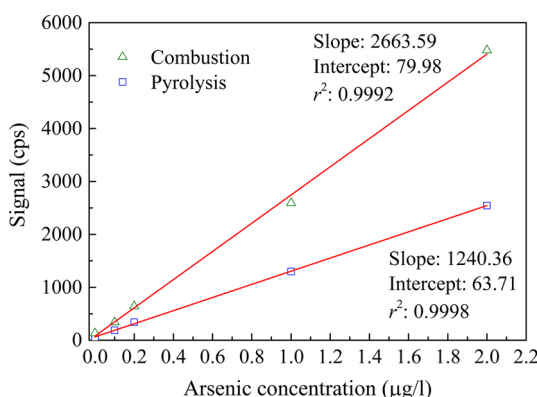

Figure 2. Calibration curves for arsenic in flue gas of coal combustion and pyrolysis.

lower than 1%. The linearity has been obtained over a wide calibration range. The change of the blank gas affects the calibration as indicated in the slopes and intercepts of the calibration curves. The sensitivity (slope value) of arsenic of using air as blank gas is higher than that of using argon as blank gas. The limit of detection (LOD) and background equivalent concentration (BEC) of arsenic under different blank gas are thus different. When using air as blank gas, the LOD of arsenic in flue gas of combustion is 0.0044 mg·m^{-3}, and the BEC is 0.0022 mg·m^{-3}. When using argon as blank gas, the LOD of arsenic in flue gas of pyrolysis is 0.0097 mg·m^{-3}, and the BEC is 0.0049 mg·m^{-3}. The feature of calibration curves is related to the effects of molecular gases on the plasma. The mix of molecular gases (air) in standard aerosol leads to the formations of ionic species in plasma. These ionic species can improve the ionizations of elements with lower ionization energies.[13] The signal of arsenic in standard aerosol is thus enhanced when using air as blank gas, and the LOD of arsenic in flue gas from coal combustion is lower than that from coal pyrolysis. Thus, the calibrations for combustion and pyrolysis should be conducted separately.

3.2. Sampling Optimization. The sampling system is able to sample gaseous arsenic and arsenic in ultrafine particles. A cyclone was used to remove larger particulates from the outlet gas of the fluidized bed. The primary isokinetic sampling stage allowed the flue gas to be carried from the outlet of the reactor to the on-line analysis system. The secondary sampling stage controlled the high flow rate of the primary stage to the relatively lower flow rate to the plasma. The sample line was maintained at 200 °C to avoid water condensation.

To realize a more precise measurement, the flow rate of sample gas was optimized by using a background element. Osmium was selected as the background element because its emission line (189.863 nm) is close to the emission line of arsenic (189.042 nm). When the conditions of detection (plasma power and gas flow rate) are the same, the signal intensity of osmium (189.863 nm) is close to that of arsenic (189.042 nm). Thus, it is reasonable to use the signal intensity of osmium (189.863 nm) to represent the signal intensity of arsenic (189.042 nm). A solution of arsenic (2 μg·L^{-1}) was employed for the optimization tests. The signal intensities of arsenic and osmium in the nebulized solution were measured simultaneously at different flow rates of sample gas. The sample

gas flow rate was adjusted by setting the revolutions per minute (rpm) of the peristaltic pump. The relationship of signal intensity and equal background noise at each sample gas flow rate was then clarified, as shown in Figure 3.
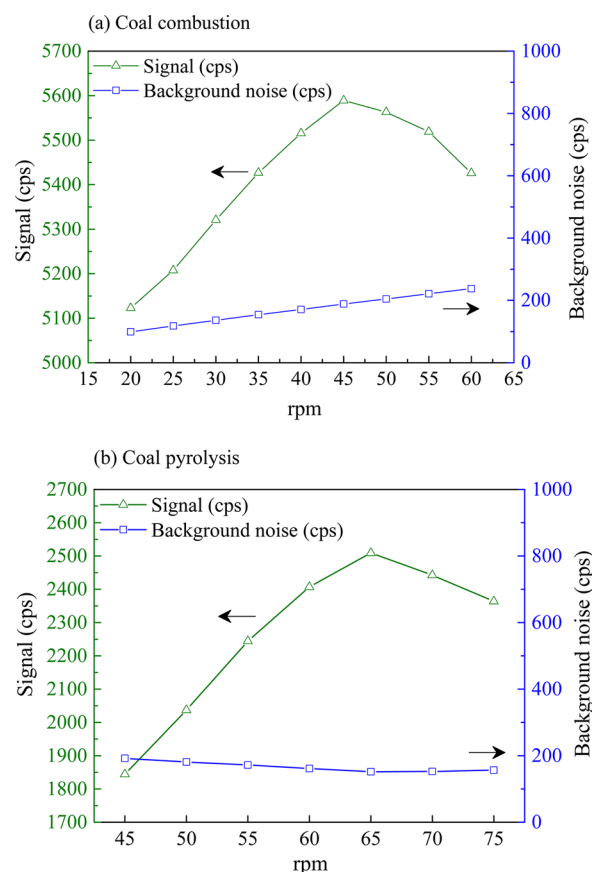

Figure 3. Sample gas flow rates optimization: (a) coal combustion, (b) coal pyrolysis.

It appears from Figure 3a that the signal intensity of arsenic reaches a maximum when the rpm of peristaltic pump is 45 r·min^{-1}. The change of background noise is very small relative to that of signal intensity during the process of changing rpm. Thus, the optimum rpm of peristaltic pump for measuring arsenic in flue gas during coal combustion is 45 r·min^{-1}, and the corresponding sample gas flow rate is measured to be 0.14 L·min^{-1}. In the same manner, for measuring arsenic during coal pyrolysis, the optimum rpm of peristaltic pump is 65 r·min^{-1}, and the sample gas flow rate is 0.2 L·min^{-1}.

3.3. Temporal Concentrations of Arsenic in Flue Gas. Experiments were conducted at several temperatures: 600, 650, 700, 750, 800, and 850 °C. The concentration profiles of arsenic in flue gas at different conditions were measured by the on-line analysis system. Each experiment was repeated three times in order to ensure the accuracy of the temporal concentration curves of arsenic. The concentrations of arsenic in flue gas for each temperature during coal combustion and pyrolysis are presented in Figure 4.

The concentration of arsenic in flue gas exhibits a peak almost instantaneously after the injection of coal sample. It is clear that the temperature has a significant influence on arsenic release during coal combustion and pyrolysis. The required time for arsenic concentration in flue gas reaching the peak decreases with increasing of temperature during coal
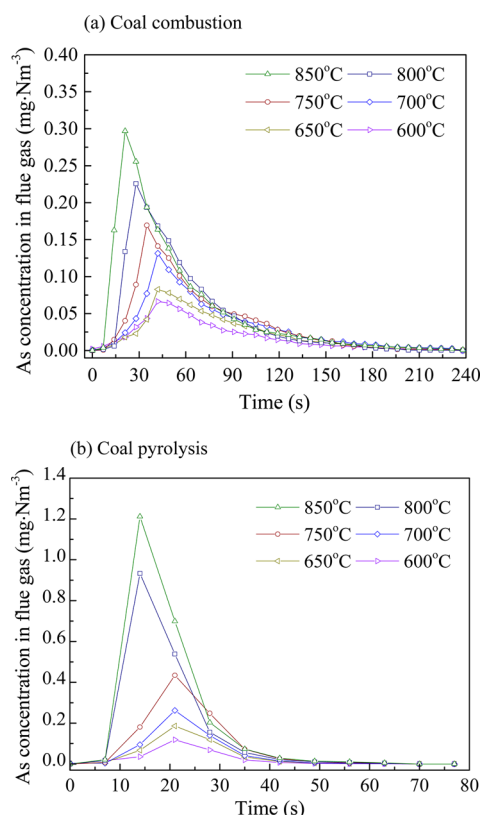
Figure 4. Temporal concentrations of arsenic in flue gas: (a) coal combustion, (b) coal pyrolysis.

combustion and pyrolysis. For example, the arsenic concentration in flue gas reaches a maximum at about 20 s during coal combustion at 850 °C, which is significantly faster than that at 600 °C. In all cases, the area under the curve increases with increasing temperature. This indicates that the total amount of arsenic released from coal particles increases with a rise of temperature. A higher reaction temperature facilitates the decomposition of the coal particle,[15] and thus arsenic in coal could release into flue gas easily. It appears from Figure 4 that the duration time of arsenic release during coal pyrolysis is shorter than that during coal combustion. The arsenic concentration in flue gas from coal pyrolysis reaches the peak faster than that from coal combustion. The arsenic concentration in flue gas during coal pyrolysis is higher than that during coal combustion. For example, the maximum of arsenic concentration in flue gas is found to be 1.2 mg·Nm^{3-} at 850 °C during coal pyrolysis, which is about four times higher than that during coal combustion. This phenomenon suggests that the atmosphere has a strong influence on arsenic release from coal. The results of on-line analysis indicate that the release characteristics of arsenic during coal combustion and pyrolysis cannot be described by the same kinetic law. The on-line analysis system developed in this study gave a unique insight into the temporal concentration of arsenic in flue gas during coal combustion and pyrolysis. This system detected the minor variations in arsenic concentration in flue gas successfully, and obtained quantitative data on arsenic release during coal combustion and pyrolysis.

3.4. Kinetic Laws of Arsenic Release during Coal Combustion and Pyrolysis.
From the above analyses of temporal concentrations of arsenic in flue gas, two different mechanisms may be involved in the release of arsenic during

coal combustion and pyrolysis, respectively. To examine the mechanisms, kinetic studies were conducted. The difference of dynamic characteristics of arsenic release between coal combustion and coal pyrolysis was examined by a comparison. The release rates (r) of arsenic during coal combustion and pyrolysis were determined by applying inverse method,[16,17] which was developed and validated previously. The modified Kunii and Levenspiel model was adapted in the inverse method. The bed is assumed to be isothermal. This macroscopic approach utilizes only the global flux of generation of species at the external surface of the particles. Global release flux is related to the release rate in the inverse method. Thereby, the inverse method can predict the release rate of arsenic from coal particles based on on-line arsenic concentration profiles in flue gas. The detailed description of the inverse model can be found in our previous paper.[17] The release rate profiles of arsenic during coal combustion and pyrolysis are presented in Figure 5.
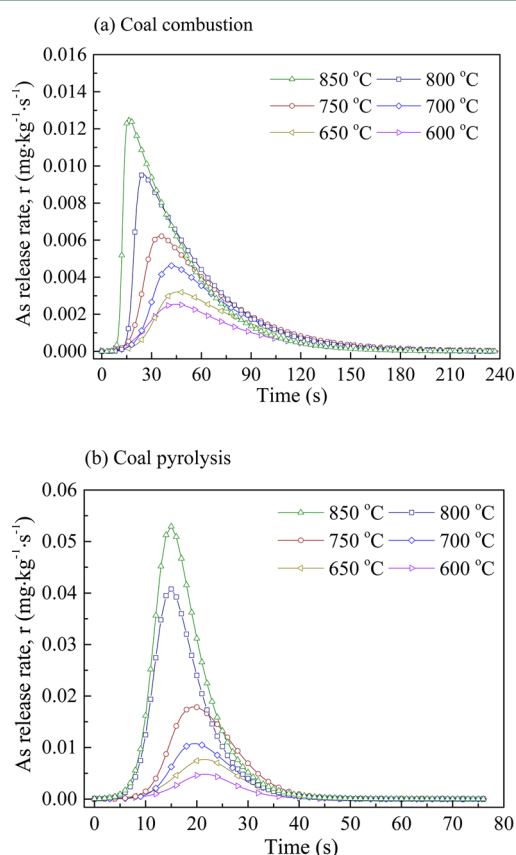

Figure 5. Temporal release rates (r) of arsenic from coal: (a) coal combustion, (b) coal pyrolysis.

In all cases, the release rate of arsenic increases with increasing temperature. The required time for arsenic release rate reaching the peak decreases with increasing of temperature during coal combustion and pyrolysis. The release rate of arsenic during coal pyrolysis is faster than that during coal combustion. Results of release rate indicate that the atmosphere has strong influence on arsenic release kinetics.

The formal kinetic parameters of arsenic release were calculated based on the results of the release rate. The release rate constant (k) was expressed by Arrhenius equation

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

where A, E_a, R, and T are the pre-exponential factor, activation energy, ideal gas constant, and temperature, respectively. The influence of initial particle size on the experimental kinetics was integrated into the theoretical laws by defining the release rate with respect to the external surface (unit $mg\cdot kg^{-1}\cdot s^{-1}\cdot m^{-2}$).[18]

By fitting r_{max} into eq 1, plotting $\ln(r_{max})$ versus $1/T$ at the experimental temperature range, and fitting a linear regression equation to the data points, eq 1 can be calculated, and the activation energy and pre-exponential factor can be obtained. The calculated activation energy is 53.7 $kJ\cdot mol^{-1}$ for arsenic release during coal combustion, and 80.9 $kJ\cdot mol^{-1}$ for arsenic release during coal pyrolysis. The pre-exponential factor is 3.7 $mg\cdot kg^{-1}\cdot s^{-1}\cdot m^{-2}$ for arsenic release during coal combustion, and 290.3 $mg\cdot kg^{-1}\cdot s^{-1}\cdot m^{-2}$ for arsenic release during coal pyrolysis.

The mechanism function $f(x)$ is used to describe the relationship of release rate and release degree (x). Release degree of arsenic from coal during combustion and pyrolysis is defined by the expression

$$x = \frac{q_0 - q}{q_0 - q_f} \tag{2}$$

where q is the instantaneous arsenic concentration in the coal, and q_f is the final concentration of arsenic in the coal. Values of q and q_f are calculated based on the results of on-line analysis. Variable q_0 is the arsenic concentration in the coal sample (1.06 $mg\cdot kg^{-1}$), which was measured by ICP-OES coupled with ultrasonic nebulizer after acid digestion of particles.

The mechanism functions $f(x)$ were further determined by plotting the normalized experimental curves r/r_{max} versus x for each temperature, as shown in Figure 6. These curves were fitted into n-order polynomials. The $f(x)$ was obtained from the mean values of both increasing and decreasing points of the polynomials.

The mechanism function of arsenic release during coal combustion is expressed as follows.

$$\text{If } x < x_a, \text{ then } f(x) = -46.34x^2 + 13.7x + 0.01$$

$$\text{If } x \geq x_a, \text{ then } f(x) = -0.76x^2 - 0.28x + 1.04 \tag{3}$$

The mechanism function of arsenic release during coal pyrolysis is expressed as

$$f(x) = -5.86x^4 + 16.02x^3 - 17.43x^2 + 7.26x + 0.01 \tag{4}$$

When $x_a = 0.1$, the release rate of arsenic during coal combustion starts decreasing in this study. The release process of arsenic during coal combustion can be divided to two parts: $x < 0.1$ and $0.1 \leq x \leq 1$. Two second-order polynomials of mechanism function of arsenic release during coal combustion were then obtained. The mechanism function of arsenic release during coal pyrolysis was mathematically expressed by a four-order polynomial.

The kinetic law governing arsenic release during coal combustion is expressed as

$$\text{If } x < 0.1, \text{ then } r(x)$$
$$= 3.7e^{-53.7/RT}(-46.34x^2 + 13.7x + 0.01)$$
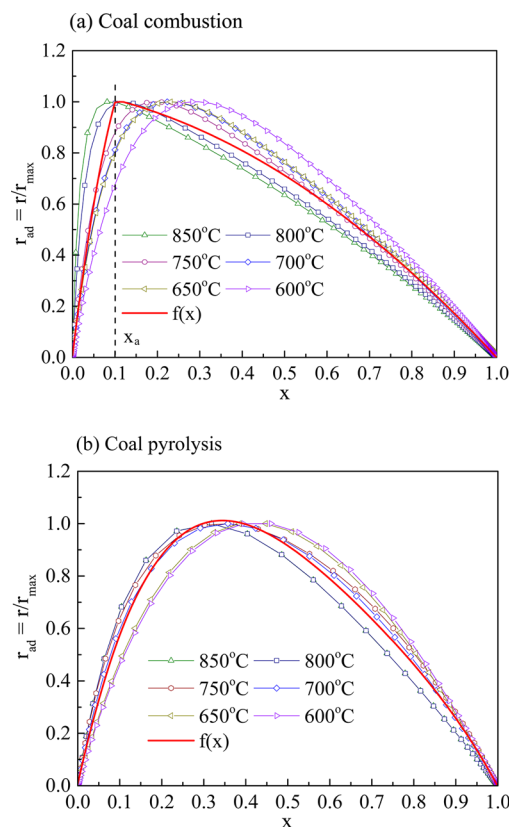

(a) Coal combustion

(b) Coal pyrolysis

Figure 6. Normalized mechanism functions fitted by $f(x)$ for all temperatures: (a) coal combustion, (b) coal pyrolysis.

$$\text{If } x \geq 0.1, \text{ then } r(x)$$
$$= 3.7e^{-53.7/RT}(-0.76x^2 - 0.28x + 1.04) \tag{5}$$

The kinetic law governing arsenic release during coal pyrolysis is expressed as

$$r(x) = 290.3e^{-80.9/RT}(-5.86x^4 + 16.02x^3 - 17.43x^2 + 7.26x + 0.01) \tag{6}$$

The kinetic equations 5 and 6 take into account the influence of temperature. This is beneficial for them to be used in the complex combustion and pyrolysis model. Comparisons between kinetic laws and the experimental kinetics are shown in Figure 7. The red lines were calculated by kinetic laws. It can be seen that these red curves of kinetic equations 5 and 6 are in good agreement with the experimental data. This indicates that the kinetic equations 5 and 6 successfully predict the dynamic characteristics of arsenic release during coal combustion and pyrolysis, respectively.

Considering the start of arsenic release has only insignificant physical meaning, and represents a lesser part of the total arsenic vaporized, the initial part $(x < 0.1)$ of arsenic release during coal combustion can be neglected in order to simplify the final mathematical equation of the kinetic law. However, a similar method could not realize a simplification of the kinetic law for pyrolysis.

The simplified kinetic law governing arsenic release during coal combustion is expressed as follows.

$$r(x) = 3.7e^{-53.7/RT}(-0.76x^2 - 0.28x + 1.04),$$
$$0.1 \leq x \leq 1 \tag{7}$$
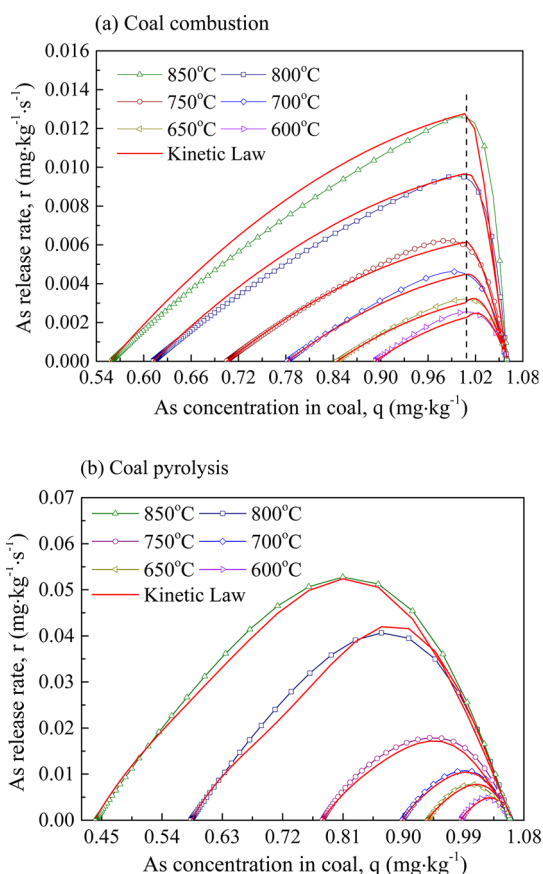
Figure 7. Validation of the kinetic laws at each temperature: (a) coal combustion, (b) coal pyrolysis.

Figure 8. Comparison between the kinetic laws predicted and the experimental concentration profiles in coal: (a) coal combustion, (b) coal pyrolysis.

It appears from Figure 7 that the dynamic characteristics of arsenic release during coal combustion and pyrolysis are markedly different. The release rate of arsenic during coal pyrolysis is much faster than that during coal combustion. The arsenic release kinetics during coal pyrolysis is more concentration-sensitive than that during coal combustion. The effects of reaction conditions on release rate of arsenic should be considered in the determination of kinetic law. It can be concluded that the kinetic laws proposed in this study describe correctly the strong influences of temperature and atmosphere on the arsenic release dynamics. The on-line analysis technique will be useful for both laboratory studies and industrial processes. Further work will consist of integrating the kinetic law into a global model of coal combustion, in order to simulate the effects of operating parameters on trace element behavior.

3.5. Temporal Evolutions of Arsenic in Coal and Thermal Equilibrium Analysis. The total amount of arsenic remaining in coal particles for each temperature is presented in Figure 8. The red lines were calculated by the kinetic equations 5 and 6. The arsenic release process during coal combustion continued for about 120 s, whereas the arsenic release process during coal pyrolysis lasted only about 40 s. The results of arsenic concentration predicted by the kinetic laws are in good agreement with the experimental results, indicating that these two kinetic laws are very useful to predict the arsenic concentration evolution in coal particles during combustion and pyrolysis, respectively. The release ratio of arsenic during coal combustion and pyrolysis increased drastically with a rise of temperature. The release ratio of arsenic increased from 15.4% to 46.3% as the combustion temperature increased from
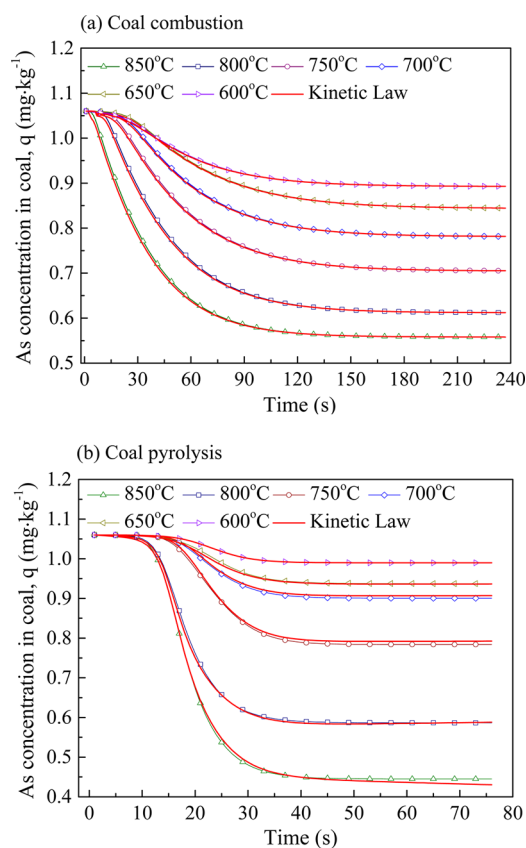
600 to 850 °C. The release ratio of arsenic increased from 6.7% to 59.1% as the pyrolysis temperature increased from 600 to 850 °C.

The mode of occurrence of arsenic in coal is mainly mineral pyrite.[19,20] Upon coal combustion and pyrolysis, a large amount of arsenic is released from the coal matrix, and it is distributed between the vapor and solid phases in different proportions. Understanding the interactions of trace elements with solid adsorbents,[21,22] and the influences of flue gas,[23,24] are important for clarifying their fate during coal utilization. To discuss theoretical interpretations of emission and partitioning of arsenic during coal combustion and pyrolysis, thermal equilibrium calculations were conducted for simulated coal combustion and pyrolysis atmospheres including ash and arsenic based on the minimization of the free Gibbs energy. The input parameters for equilibrium calculation are listed in Table 2. Figure 9 shows the mole fractions of arsenic chemical species derived from thermal equilibrium calculations for coal (a) combustion and (b) pyrolysis conditions. Arsenic oxides are found to be the dominant arsenic species in the oxidizing flue gas environment of coal combustion. As_4, AsH_3, As_2, As, and AsS are found to be the dominant arsenic species in the reducing flue gas environment of coal pyrolysis. In addition, the proportions of different arsenic species in flue gas of coal combustion and pyrolysis vary with temperature. Volatilized arsenic species may be condensed and enriched in fine particles, and released into the atmosphere as various species and particles finally. Interactions of gaseous arsenic species with fly ash have significant influence on the partitioning of arsenic between the vapor and solid phases.[19,25] Calcium oxide (CaO)

Table 2. Parameters for Equilibrium Calculation

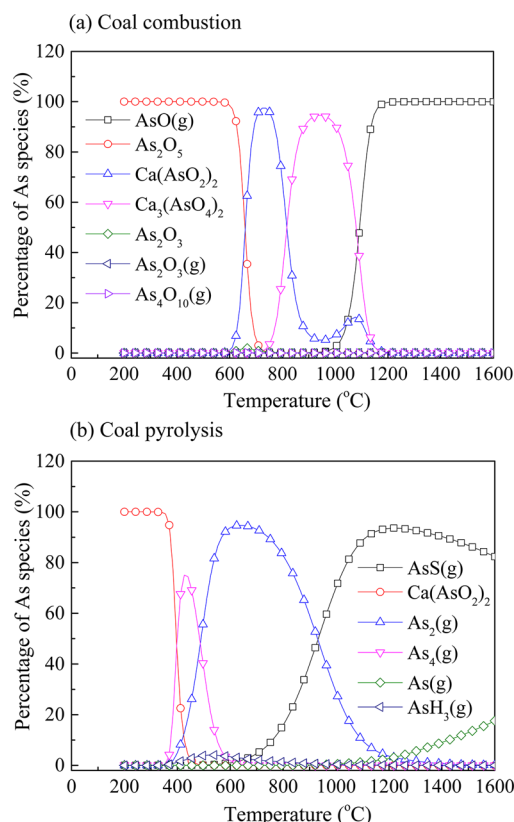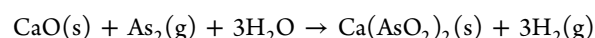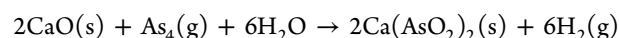| element	combustion (mol)	pyrolysis (mol)
C	61.69	61.69
H	48.00	48.00
O	176.33	9.40
N	628.60	0.64
S	0.19	0.19
As	1.4×10^{-5}	1.4×10^{-5}
Ca	0.18	0.18
Fe	0.11	0.11
Si	0.38	0.38
Ar		331.21

Figure 9. Equilibrium distribution of arsenic: (a) coal combustion, (b) coal pyrolysis.

is a catalyst in fly ash and arsenic has a strong affinity for Ca; arsenic is thus likely to react with Ca in fly ash and lead to the formation of As−Ca complexes.[26,27] As indicated in Figure 9, $Ca_3(AsO_4)_2$ and $Ca(AsO_2)_2$ are the possible forms of arsenic in fly ash during coal combustion. $Ca(AsO_2)_2$ is the dominant form of arsenic in fly ash during coal pyrolysis. The different arsenic species in flue gas and the reaction of arsenic with Ca in fly ash account for the differences in arsenic release mechanisms from coal.

The following reaction paths are suggested for the formation of As−Ca complexes during coal combustion:[28,29]

$$3CaO(s) + As_2O_3(g) + O_2 \rightarrow Ca_3(AsO_4)_2(s)$$

$$6CaO(s) + As_4O_{10}(g) \rightarrow 2Ca_3(AsO_4)_2(s)$$
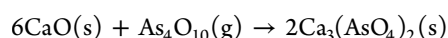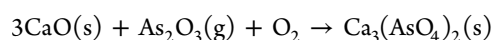
The reaction paths for the formation of As−Ca complexes during coal pyrolysis can be written as follows:[29,30]

$$2CaO(s) + As_4(g) + 6H_2O \rightarrow 2Ca(AsO_2)_2(s) + 6H_2(g)$$

$$CaO(s) + As_2(g) + 3H_2O \rightarrow Ca(AsO_2)_2(s) + 3H_2(g)$$

It is clear that arsenic species present in flue gas of coal combustion is different from that of pyrolysis. Parallel reactions of gaseous arsenic species with Ca in fly ash lead to the formation of arsenates. During coal combustion, both As^{5+} and As^{3+} are possible forms of arsenic present in fly ash, whereas during coal pyrolysis As^{3+} is the dominant form of arsenic present in fly ash. In addition, the release rates of arsenic in different conditions may affect the reactions of gaseous arsenic species with Ca in fly ash.

■ AUTHOR INFORMATION

Corresponding Author
*Tel: +86 27 87545526; fax: +86 27 87545526; e-mail: liujing27@mail.hust.edu.cn.

Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Kitchin, K. T. Recent advances in arsenic carcinogenesis: modes of action, animal model systems, and methylated arsenic metabolites. *Toxicol. Appl. Pharmacol.* **2001**, *172* (3), 249−261.

(2) Chen, J.; Liu, G.; Kang, Y.; Wu, B.; Sun, R.; Zhou, C.; Wu, D. Atmospheric emissions of F, As, Se, Hg, and Sb from coal-fired power and heat generation in China. *Chemosphere* **2013**, *90* (6), 1925−1932.

(3) Zhao, Y.; Zhang, J.; Huang, W.; Wang, Z.; Li, Y.; Song, D.; Zhao, F.; Zheng, C. Arsenic emission during combustion of high arsenic coals from Southwestern Guizhou, China. *Energy Convers. Manage.* **2008**, *49* (4), 615−624.

(4) Seames, W. S.; Wendt, J. O. Partitioning of arsenic, selenium, and cadmium during the combustion of Pittsburgh and Illinois# 6 coals in a self-sustained combustor. *Fuel Process. Technol.* **2000**, *63* (2), 179−196.

(5) Zhou, C.; Liu, G.; Fang, T.; Wu, D.; Lam, P. K. S. Partitioning and transformation behavior of toxic elements during circulated fluidized bed combustion of coal gangue. *Fuel* **2014**, *135*, 1−8.

(6) Lu, H.; Chen, H.; Li, W.; Li, B. Transformation of arsenic in Yima coal during fluidized-bed pyrolysis. *Fuel* **2004**, *83* (6), 645−650.

(7) Yu, J.; Sun, L.; Xiang, J.; Hu, S.; Su, S. Kinetic vaporization of heavy metals during fluidized bed thermal treatment of municipal solid waste. *Waste Manage.* **2013**, *33* (2), 340−346.

(8) Liu, J.; Falcoz, Q.; Gauthier, D.; Flamant, G.; Zheng, C. Volatilization behavior of Cd and Zn based on continuous emission measurement of flue gas from laboratory-scale coal combustion. *Chemosphere* **2010**, *80* (3), 241−247.

(9) Poole, D.; Sharifi, V.; Swithenbank, J.; Argent, B.; Ardelt, D. On-line detection of metal pollutant spikes in MSW incinerator flue gases prior to clean-up. *Waste Manage.* **2007**, *27* (4), 519−532.

(10) Poole, D. J.; Nasserzadeh Sharifi, V.; Swithenbank, J.; Ardelt, D. Identification of metal concentration fluctuations in waste-to-energy plant flue gases—a novel application for ICP-OES. *J. Anal. At. Spectrom.* **2005**, *20* (9), 932−938.

(11) Clarkson, P.; Poole, D.; Sharifi, V.; Swithenbank, J.; Waarlo, H.-J.; Ardelt, D.; Falk, H. Continuous measurement of mercury in flue gas using ICP-OES. *J. Anal. At. Spectrom.* **2004**, *19* (5), 652−653.

(12) Liu, J.; Liu, X.; Gauthier, D.; Abanades, S.; Flamant, G.; Qiu, J.; Zheng, C. Kinetics of heavy metal vaporization from coal in a fluidized bed by an inverse model. *Asia-Pac. J. Chem. Eng.* **2010**, *5* (2), 266−273.

(13) Clarkson, P.; Poole, D.; Ryu, C.; Sharifi, V.; Swithenbank, J.; Waarlo, H.-J.; Ardelt, D.; Falk, H. Continuous measurement of metals in flue gas using ICP-OES. *Anal. Bioanal. Chem.* **2003**, *377* (1), 39−47.

(14) Wellinger, M.; Biollaz, S.; Wochele, J. r.; Ludwig, C. Sampling and online analysis of alkalis in thermal process gases with a novel surface ionization detector. *Energy Fuels* **2011**, *25* (9), 4163−4171.

(15) Zhou, C.; Liu, G.; Yan, Z.; Fang, T.; Wang, R. Transformation behavior of mineral composition and trace elements during coal gangue combustion. *Fuel* **2012**, *97*, 644−650.

(16) Abanades, S.; Flamant, G.; Gauthier, D. The kinetics of vaporization of a heavy metal from a fluidized waste by an inverse method. *Combust. Flame* **2003**, *134* (4), 315−326.

(17) Liu, J.; Abanades, S.; Gauthier, D.; Flamant, G.; Zheng, C.; Lu, J. Determination of kinetic law for toxic metals release during thermal treatment of model waste in a fluid-bed reactor. *Environ. Sci. Technol.* **2005**, *39* (23), 9331−9336.

(18) Falcoz, Q.; Gauthier, D.; Abanades, S.; Flamant, G.; Patisson, F. Kinetic rate laws of Cd, Pb, and Zn vaporization during municipal solid waste incineration. *Environ. Sci. Technol.* **2009**, *43* (6), 2184−2189.

(19) Sterling, R.; Helble, J. Reaction of arsenic vapor species with fly ash compounds: kinetics and speciation of the reaction with calcium silicates. *Chemosphere* **2003**, *51* (10), 1111−1119.

(20) Liu, R.; Yang, J.; Xiao, Y.; Liu, Z. Fate of Forms of arsenic in Yima coal during pyrolysis. *Energy Fuels* **2009**, *23* (4), 2013−2017.

(21) Zhang, B.; Liu, J.; Dai, G.; Chang, M.; Zheng, C. Insights into the mechanism of heterogeneous mercury oxidation by HCl over V_2O_5/TiO_2 catalyst: Periodic density functional theory study. *Proc. Combust. Inst.* **2015**, *35* (3), 2855−2865.

(22) Xiang, W.; Liu, J.; Chang, M.; Zheng, C. The adsorption mechanism of elemental mercury on CuO(110) surface. *Chem. Eng. J.* **2012**, *200-202*, 91−96.

(23) Liu, J.; Qu, W.; Joo, S. W.; Zheng, C. Effect of SO_2 on mercury binding on carbonaceous surfaces. *Chem. Eng. J.* **2012**, *184*, 163−167.

(24) Liu, J.; Qu, W.; Yuan, J.; Wang, S.; Qiu, J.; Zheng, C. Theoretical studies of properties and reactions involving mercury species present in combustion flue gases. *Energy Fuels* **2010**, *24* (1), 117−122.

(25) Shah, P.; Strezov, V.; Prince, K.; Nelson, P. F. Speciation of As, Cr, Se and Hg under coal fired power station conditions. *Fuel* **2008**, *87* (10), 1859−1869.

(26) Liu, H.; Zhang, Q.; Hu, H.; Liu, P.; Hu, X.; Li, A.; Yao, H. Catalytic role of conditioner CaO in nitrogen transformation during sewage sludge pyrolysis. *Proc. Combust. Inst.* **2015**, *35* (3), 2759−2766.

(27) Hu, H.; Liu, H.; Chen, J.; Li, A.; Yao, H.; Low, F.; Zhang, L. Speciation transformation of arsenic during municipal solid waste incineration. *Proc. Combust. Inst.* **2015**, *35* (3), 2883−2890.

(28) Li, Y.; Tong, H.; Zhuo, Y.; Li, Y.; Xu, X. Simultaneous removal of SO_2 and trace As_2O_3 from flue gas: mechanism, kinetics study, and effect of main gases on arsenic capture. *Environ. Sci. Technol.* **2007**, *41* (8), 2894−2900.

(29) López-Antón, M. A.; Díaz-Somoano, M.; Fierro, J.; Martínez-Tarazona, M. Retention of arsenic and selenium compounds present in coal combustion and gasification flue gases using activated carbons. *Fuel Process. Technol.* **2007**, *88* (8), 799−805.

(30) Díaz-Somoano, M.; Martínez-Tarazona, M. Retention of trace elements using fly ash in a coal gasification flue gas. *J. Chem. Technol. Biotechnol.* **2002**, *77* (3), 396−402.