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## Partitioning behavior of Arsenic in circulating fluidized bed boilers co-firing petroleum coke and coal

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### ABSTRACT

The emission of Arsenic from coal-fired power plants has generated widespread environmental and human health concerns. This paper discusses Arsenic partitioning from three 440 t/h circulating fluidized bed (CFB) boilers co-firing petroleum coke and coal. All the boilers were equipped with electrostatic precipitator (ESP) or fabric filter (FF), and wet flue gas desulfurization (WFGD). Flue gas was sampled simultaneously both up- and down-stream of the ESP/FF and at the outlet of the WFGD based on EPA Method 29. Concurrent with flue gas sampling, feed fuel, bottom ash, ESP/FF ash, WFGD gypsum, WFGD wastewater, limestone slurry and flush water were also collected. The results show that, for three tested CFB boilers, the overall mass balance ratios of As ranged from 80.0%–114.2%, which can be considered to be acceptable and reliable. Most of the As was distributed in the bottom ash and ESP/FF ash with the values of 17.4%–37.5% and 55.6%–77.5%, respectively. Speciation analysis suggests that  $\text{As}^{5+}$  was the major water-soluble species in the feed fuel, bottom ash and fly ash, while  $\text{As}^{3+}$  was found to be the dominant species in WFGD wastewater. For three CFB boilers, the concentrations of total As in the stack emission were 0.97, 0.32 and 0.31  $\mu\text{g}/\text{m}^3$ , respectively. The CFB boiler equipped with ESP/FF + WFGD was shown to be able to provide good control of the emission of As emitted into the atmosphere.

### 1. Introduction

Arsenic (As) is a hazardous metalloid elements, and can be released to the environment during coal combustion, municipal solid waste incineration and metal smelting [1]. Coal combustion is the major source of power generation in China. It has been reported that in China, nearly 50% of coal consumption was for electric power and heat generation [2]. Despite low As concentration in the majority of coals, the total amount of As released during coal combustion is considerable because of the substantial amounts of coal consumed annually [3,4]. Presently, coal-fired power plants are recognized as the major anthropogenic As emission source [5,6].

When As is introduced into the environment during the coal combustion process, it poses serious pollution problems for environment, as well as a danger to human health. It is reported that for people who live in endemic areas with high As concentrations in drinking water or in regions where coal burning is important, long term exposure to As causes acute and chronic adverse effects including cancer [7,8]. The toxicity of As is highly dependent on its chemical form [9,10]. In general, inorganic arsenite ( $\text{As}^{3+}$ ) is a more potent toxicity than the inorganic arsenate ( $\text{As}^{5+}$ ) [7,11]. Numerous studies have investigated the As

speciation including ( $\text{As}^{3+}$  and  $\text{As}^{5+}$ ) in fly ash [9,12,13]. However, information on the speciation of As in combustion byproducts such as bottom ash, gypsum and wastewater from power plants is scarce.

In the combustion zone, As and its compounds that are associated with coal's mineral matter and organic matter will mostly volatilize, but some of it will be retained in bottom ash. As the flue gas cools down, a portion of gaseous As and its compounds will condense on the surface of particles and recombine with particulates through physical absorption and chemical reaction [14–16]. The As fraction absorbed on the fine particles may be removed by conventional air pollution control devices (APCDs) such as electrostatic precipitators (ESP) or fabric filters (FF), and wet flue gas desulfurization (WFGD), etc. In general, As will be emitted into the atmosphere in both in gaseous form and particulate bound. In recent years, extensive field tests on the partitioning behavior of As across APCDs in coal-fired power plants have been conducted by many researchers [14,17,18]. Cheng et al. [19] carried out a field test on a coal fired power plant to investigation the distribution of As for selective catalytic reduction (SCR), ESP, and WFGD. Swanson et al. [20] determine the partitioning of As in combustion by products including bottom ash, economizer ash and fly ash from two US power plants. However, there is a dearth of studies on As partitioning behavior across APCDs in circulating fluidized bed (CFB) boilers.

Petroleum coke is a byproduct from the oil refining process, which possesses high heating value, high fixed carbon content, high sulfur

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content, and low volatiles content [21]. Due to its excellent fuel flexibility and combustion efficiency, the use of CFB combustion technology for co-firing petroleum coke and coal has been steadily increasing [22,23]. Currently, studies concerning As emission characteristics in CFB boilers have focused mainly on burning or gasifying fuels like biomass and municipal solid waste, and there is little published research on As emission from petroleum coke and coal co-firing [24–26]. Given that petroleum coke is considered to be a significant alternative energy source, it is essential to study As partitioning behavior and environmental effects in CFB boilers co-firing petroleum coke and coal.

The application of APCDs in the power plant can increase the amount of coal combustion byproduct (e.g., fly ash, gypsum) and affect the redistribution behavior of As in some of these combustion byproducts. Furthermore, the disposal (e.g., landfilling and storage) and utilization (e.g., construction) of fly ash and WFGD gypsum, as well as discharge of WFGD wastewater, potentially pose a threat to humans, both in the soil and groundwater [27,28]. To study the partitioning behavior and environmental impacts of As, onsite tests were conducted at three CFB boilers equipped with ESP/FF and WFGD. Flue gas sampling for As was carried out at three points simultaneously, based on the U.S. Environmental Protection Agency (EPA) method 29. The main objectives of this study were to determine: (1) the concentration and enrichment of As in feed fuel and combustion byproducts; (2) mass balance ratio and distribution of As in the entire system; (3) removal efficiency of As by APCDs; and (4) environmental impact of As.

## 2. Materials and methods

### 2.1. Boiler description

The study was conducted at three CFB boilers (unit #1, unit #2, unit #3) co-firing petroleum coke and coal in Guangdong province, China. Each boiler had a rated capacity of 440 t/h. The detailed configurations of these boilers are provided in Table 1. Selective non-catalytic reduction (SNCR) units were employed to reduce nitrogen oxide emissions and the ESP and FF were used for particulate matter (PM) removal. The WFGD unit was operated using limestone as reagent. In addition to WFGD, limestone powder was used as furnace desulphurization agent during the combustion process. Powdered limestone was added to the furnace from limestone bin by means of pneumatic conveying. The additional use of limestone powder is necessary in order to meet stringent SO<sub>2</sub> emission limit and it further has a potential to provide the co-benefit effect of As capture. The Ca/S mole ratios for three units are given in Table 1. Unit #1 was fueled with 100% bituminous coal, while both unit #2 and unit #3 were fueled with the same coal used in unit #1 and petroleum coke with a blending ratio of 2:1. Boiler conditions were maintained as stable as possible during the sampling process. Proximate and ultimate analyses of the fuels are given in Table 2, are based on the National Coal Classification Standard of China (GB/T 5751-2009). The analysis methods used for each test are given in Table 3.

### 2.2. Sampling procedure

For the flue gas sampling, a sampling run was simultaneously begun at all sampling locations. Detailed simultaneous sampling locations in

the tested boilers are presented in Fig. 1. The emission of As from flue gas was determined by EPA method 29 [29]. This method has been historically the most commonly used method for determining mercury and other trace metal elements including As. Gas samples were collected from three sampling points along the flue gas path, at the inlets/outlets of ESP/FF, WFGD. For a given sampling location, gas samples were withdrawn isokinetically from the flue gas through a probe with a quartz fiber filter, maintaining the temperature at 120 ± 20 °C. The gaseous form of As was absorbed and retained by 5% (v/v) nitric acid (HNO<sub>3</sub>)/10% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in two ice-bath-chilled impingers. The particulate bound As can be captured by means of a quartz fiber filter. Samples in both the quartz fiber filter and the HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> solutions were collected and recovered immediately after collection. The whole sampling process lasted for 2 h using a U.S. Apex mercury instrument (Apex Instruments, Fuquay-Varina, NC, USA).

For solid and liquid materials, feed fuel, bottom ash, ESP/FF ash and WFGD samples were collected simultaneously in step with flue gas sampling every hour. The configuration of the WFGD system and locations of the WFGD samples are shown in Fig. 2. The WFGD samples which consisted of input streams such as limestone slurry and flush water, and output streams such as WFGD gypsum and WFGD wastewater were collected from the appropriate locations from WFGD system. The WFGD gypsum samples were collected during the test period when the dewatering system was in operation. Solid samples were stored in zip-lock bags and liquid samples were preserved in high boron silicon bottles and transported to the chemical laboratory immediately after sampling for immediate As analysis. In addition, the temperature at furnace and flue gas locations are given in Table 4. All sampling tests were carried out twice to obtain duplicate results and reduce experimental uncertainties. The results presented in this paper are average values.

### 2.3. Elemental analysis

The solid samples including feed fuel, bottom ash, ESP/FF ash, particulate matter in the flue gas and WFGD gypsum were firstly dried in the oven at 50 °C for 8 h, and then milled and sieved to 200 meshes. The pulverized samples were digested using an acid mixture (HNO<sub>3</sub>:HCl:HF = 3:1:1) in a microwave oven. Then the As concentration in the digestion solutions was determined by inductively-coupled plasma mass spectrometry (ICP-MS). For WFGD limestone slurry and WFGD wastewater, which are not clear or transparent, the solid and liquid portions were separated through filtration and drying, and then the total As content in them was obtained by calculating the content in solid and liquid portion. As content in WFGD flush water, which is clear, can be determined by ICP-MS directly. The detection limits of As in solid and liquid samples by ICP-MS are 0.1 mg/kg and 0.05 µg/L, respectively.

All measurements of As concentration were carried out in third times to obtain parallel results and the relative standard deviation of parallel results is <3%.

### 2.4. Speciation analysis

Water-soluble As<sup>3+</sup> and As<sup>5+</sup> content in bottom ash, ESP/FF ash, WFGD wastewater and WFGD gypsum were determined using ultrasonic microwave-assisted extraction followed by high-performance liquid chromatography coupled with ICP-MS (HPLC-ICP-MS). This method has been used successfully in several previous studies [30,31]. Here, 10-mg solid samples were weighed into HDPE bottles and then 10 mL 1% (v/v) HNO<sub>3</sub> was added. After ultrasonic microwave-assisted extraction for 40 min with constant agitation during the extraction process, samples were centrifuged at 7000 rpm for 10 min and then filtered through 0.25 µm PVDF filter. For liquid samples, As<sup>3+</sup> and As<sup>5+</sup> content in clear samples can be directly determined by HPLC-ICP-MS after filtration. The accuracy of As<sup>3+</sup> and As<sup>5+</sup> content in samples was determined using a blending solution of GBW08667 and GBW08666 as standard reference

**Table 1**  
Configuration of tested boilers.

Item	Rated capacity (t/h)	APCDs	Fuel type	[Ca/S] <sup>a</sup>
Unit #1	440	SNCR + ESP + WFGD	100% coal	2.8
Unit #2	440	SNCR + FF + WFGD	66.7% coal + 33.3% PC	4.8
Unit #3	440	SNCR + FF + WFGD	66.7% coal + 33.3% PC	4.8

<sup>a</sup> Ca/S mole ratio used in the fluidized bed (added limestone to fuel sulfur).

**Table 2**  
Proximate and ultimate analyses of fuels.<sup>a</sup>

Item	Proximate analysis $\omega_{ar}/\%$				$Q_{net,ar}/(MJ/kg)$	Ultimate analysis $\omega_{ar}/\%$				
	M	A	V	FC		C	H	O	N	S
Unit #1	11.18	16.80	22.40	49.62	23.40	59.39	3.55	6.59	1.38	1.11
Unit #2	10.14	11.41	18.07	60.38	26.15	66.48	3.48	4.99	1.37	2.12
Unit #3	10.14	11.41	18.07	60.38	26.15	66.48	3.48	4.99	1.37	2.12

<sup>a</sup> Based on as received basis.

**Table 3**  
Analysis methods used in tests.

Sample	Method
Proximate analysis of fuel	GB/T <sup>a</sup> 212–2008
Carbon/hydrogen/oxygen/nitrogen content in fuel	GB/T <sup>a</sup> 476–2001
Total water content in fuel	GB/T <sup>a</sup> 211–2007
Total sulfur content in fuel	GB/T <sup>a</sup> 214–2007
nitrogen content in fuel	GB/T <sup>a</sup> 19,227–2008
heating value analysis of fuel	GB/T <sup>a</sup> 213–2008
As in solution/slurry/WFGD wastewater	EPA method 6020a
As in fuel/ash/WFGD gypsum	EPA method 6020a

<sup>a</sup> National standard of China.

material. The chromatogram of  $As^{3+}$  and  $As^{5+}$  obtained from the GBW08667 and GBW08666 is shown in Fig. 3. All measurements of As speciation were conducted in six times to obtain parallel results and the relative standard deviation of these parallel results is <5%.

### 3. Results and discussion

#### 3.1. Concentration and enrichment of As in feed fuel and combustion byproducts

##### 3.1.1. Concentration of as in feed fuel and combustion products

The total As concentrations in feed fuel, bottom ash, ESP/FF ash, and WFGD gypsum are provided in Table 5. The emission limits for As in soils and groundwater proposed by the State Bureau of Environmental Protection of China is also provided in Table 5 and Table 6, respectively. In this study, the concentration of As in the feed fuels are generally lower

than most other coals used commercially worldwide [32,33]. The concentrations of As in bottom ash and ESP/FF ash are somewhat higher than those in the feed fuel. The As concentrations in ESP/FF ash and WFGD gypsum are lower than limit value in China, while those in the bottom ash (#2, #3) are above limit value. The results showed that the landfill disposal of ESP/FF ash and WFGD gypsum may have little effect on soils with respect to As contamination. However, care should be taken in the disposal of bottom ash.

The data on the total As concentrations in limestone slurry, flush water and WFGD wastewater are summarized in Table 6. As is shown in Table 6, for three units, limestone slurry is the major As source entering the WFGD system, as compared with flush water. The concentrations of As in WFGD wastewater from three units are under the limit value (GB/T14848–1993). This indicates desulfurization WFGD wastewater has no effect on groundwater in terms of As contamination.

##### 3.1.2. Enrichment factors of As in combustion products

The relative enrichment factor (REF) is used to evaluate the enrichment characteristics of trace elements in bottom ash and fly ash [14, 34,35]. The relative enrichment factor is calculated by following formula (1):

$$REF = \frac{C_{i,Ba/Fa} \times A_f}{C_{i,f}} \quad (1)$$

where  $C_{i,Ba/Fa}$  and  $C_{i,f}$  represent the concentration of element  $i$  in bottom or ESP/FF ash, and feed fuel, respectively.  $A_f$  represents the ash content in fuel.

If the  $REF > 0.7$ , the element  $i$  is considered to be enriched in ashes, and if  $REF < 0.7$ , the element  $i$  is considered to be diluted or depleted

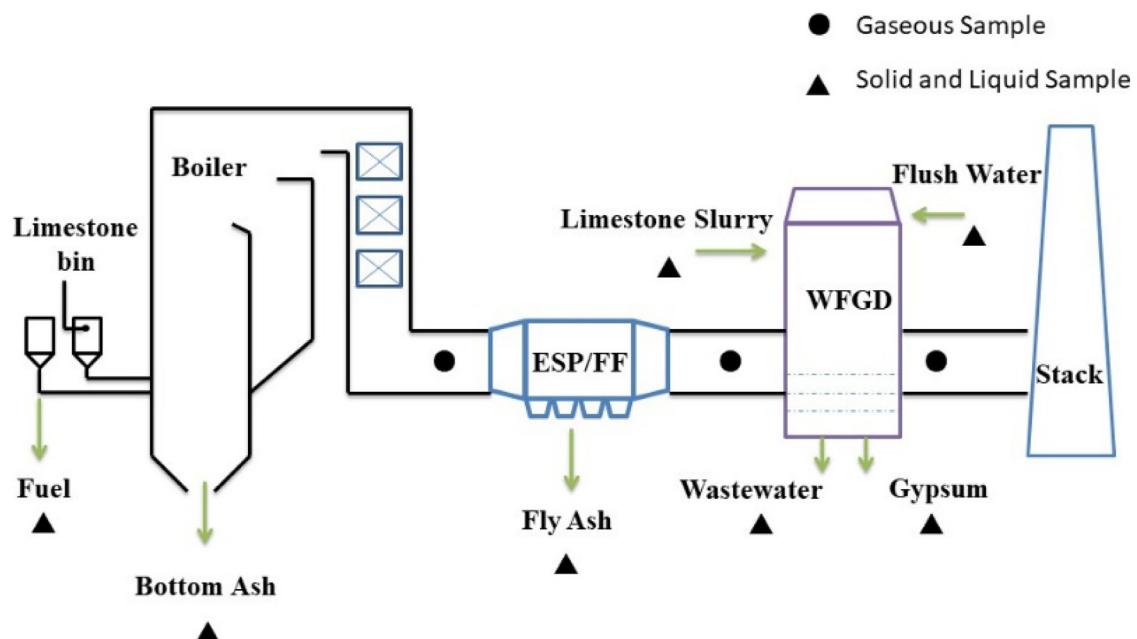


Fig. 1. Schematic configuration of the APCDs and the sampling locations.

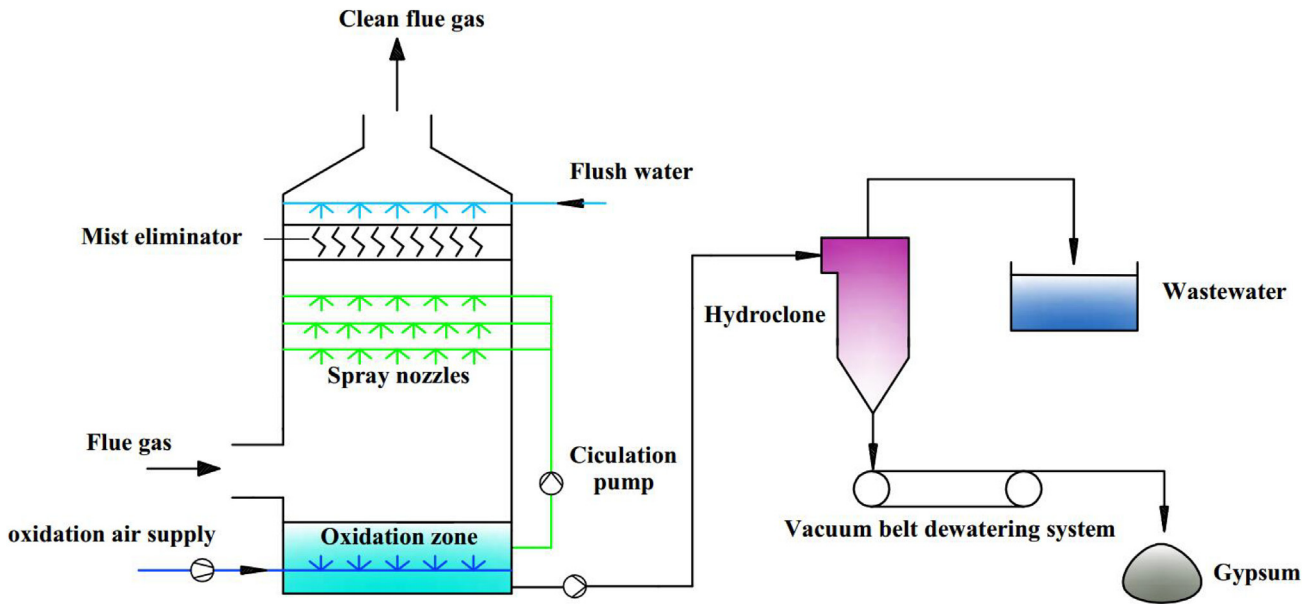


Fig. 2. Schematic configuration of WFGD system and locations of the WFGD samples.

in ashes, while for unit #2 and #3, As tends to be enriched in bottom ash but diluted in FF ash. The relative enrichment factors for As in bottom and ESP/FF ash are presented in Fig. 4. The results indicate that for unit #1, As tends to be enriched in ESP ash and bottom ash to some extent, while for unit #2 and #3, As tends to be enriched in bottom ash but diluted in FF ash. Several studies revealed that the formation of  $\text{Ca}_3(\text{AsO}_4)_2$ , rather than physical absorption, has a great influence on the retention of As in fly ash [36–38]. For unit #2 and unit #3 (co-firing petroleum coke and coal), the relative enrichment factors for As in bottom ash (1.08–1.37) are higher than those in ESP/FF ash (0.51–0.65), indicating that more As will be retained in the bottom ash when coal is co-fired with petroleum coke. This phenomenon can be explained by the relative higher Ca/S mole ratios for unit #2 and unit #3, as compared with that for unit #1 (as shown in Table 1). The following reactions during combustion process are important in helping to retain As in bottom ash [38–40]:



### 3.2. Mass balance ratio and distribution of As in the entire system

#### 3.2.1. Mass balance ratio of As in the entire system

The mass balance ratio is usually used to assess data credibility and reliability for onsite trace elements testing in coal-fired power plants. The overall mass balance ratio can be calculated by the following formula (4):

$$R_{\text{overall}} = \frac{M_{\text{out}}}{M_{\text{in}}} \quad (4)$$

Table 4  
temperature at furnace and sampling locations (°C).

Item/locations	Furnace	Outlet of air preheater/Inlet of ESP/FF	Outlet of ESP/FF	Outlet of WFGD
Unit #1	852.1	150.2	146.3	60.2
Unit #2	891.2	144.2	135.3	56.3
Unit #3	881.2	150.3	144.3	55.9

where  $R_{\text{overall}}$  represents the mass balance ratio for the entire system.  $M_{\text{in}}$  is the total amount of As introduced into the overall system during the sampling process, g/h. In this study, feed fuel, limestone slurry and flush water are the input sources.  $M_{\text{out}}$  is the total output of As, including that in the bottom ash, ESP/FF ash, WFGD gypsum, WFGD wastewater and the amount in the flue gas emitted from the stack, g/h. Taking all components into consideration, formula (4) can be converted to the following formula (5):

$$R_{\text{overall}} = \frac{(C_b * m_{ba} + C_{fa} * m_{fa} + C_g * m_g + C_{ef} * m_{ef} + C_s * m_s)}{(C_f * m_f + C_{ls} * m_{ls} + C_{fw} * m_{fw})} \quad (5)$$

where  $C_{ba}$ ,  $C_{fa}$ ,  $C_g$ ,  $C_{ef}$ ,  $C_s$ ,  $C_f$ ,  $C_{ls}$ ,  $C_{fw}$  represent the concentration of As in the bottom ash, ESP/FF ash, WFGD gypsum, WFGD wastewater, flue gas emitted from the stack, feed fuel, limestone slurry and flush water, respectively (presented in Tables 4, 5 and 7). The parameters  $m_{ba}$ ,  $m_{fa}$ ,  $m_g$ ,  $m_{ef}$ ,  $m_s$ ,  $m_f$ ,  $m_{ls}$  and  $m_{fw}$  represent the output/input amount per hour for bottom ash, ESP/FF ash, WFGD gypsum, WFGD wastewater, flue gas emitted from the stack, feed fuel, limestone slurry and flush water, respectively. Using the operation information of boilers and ASME PTC-1998 [41], the values of these parameters are provided in Table 7.

The overall mass balance ratios of As and relative deviation of the mass balances are presented in Table 8. Here the ratios are in the range of 80.0% ~ 114.2%, and the relative deviations of the mass balance are in the range of 6.2% ~ 8.1%. Because of the slight variation of boiler operating conditions, the fluctuation of components in solid and liquid samples and the complexity and uncertainty in sampling and analysis process, values in the range of 70% ~ 130% are acceptable [42–44]. An analysis of these data suggests the current study can be considered reliable and satisfactory.

#### 3.2.2. Distribution of As in the combustion process

The mass distribution of As in the bottom ash, ESP/FF ash, WFGD gypsum, WFGD wastewater and flue gas emitted from the stack is shown in Fig. 5. Here, the majority of As is distributed in bottom ash and ESP/FF ash, and accounts for 17.4%–37.5% and 55.6%–77.5%, respectively. The differences between the distribution in bottom ash and ESP/FF ash can be explained due to the different forms of As in the fuel. During the coal combustion process, As bonded with sulfur minerals in coal will first vaporize, and then condense on the surface of fly ash as the flue



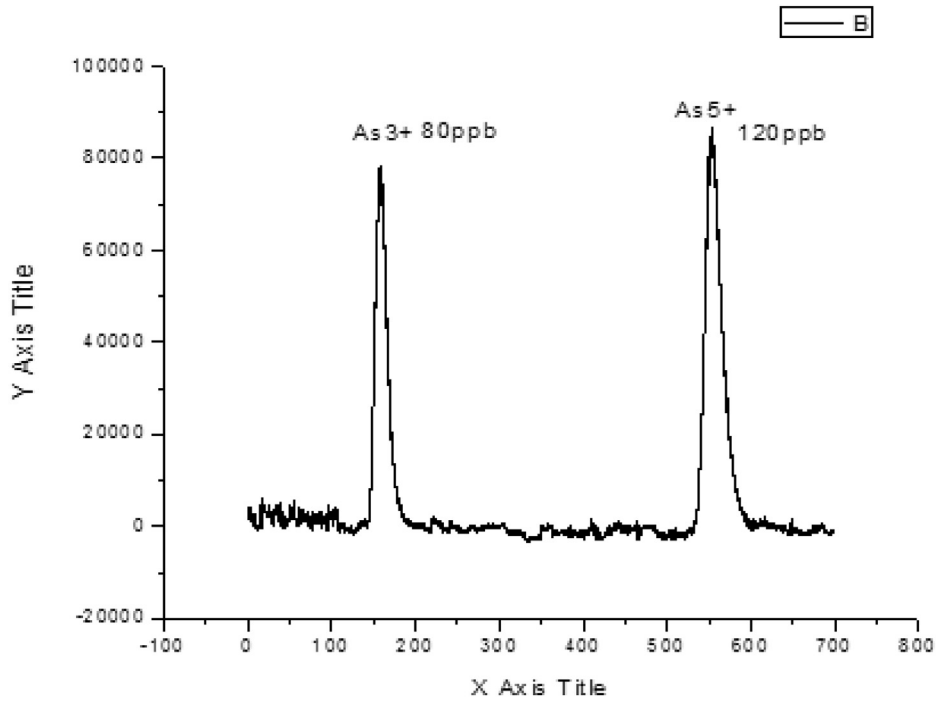


Fig. 3. Chromatogram of  $As^{3+}$  and  $As^{5+}$  based on blending solution of GBW08667 and GBW08666.

gas cools down, while As bonded with discrete mineral will be retained in the ash matrix [44–46]. Comparatively small amounts of As are distributed into WFGD gypsum and WFGD wastewater, and are found with the proportions of 4.9%–9.7% and 0.02%–0.14%, respectively.

### 3.3. Removal efficiency of As by APCDs

The concentrations of As along the flue gas path are summarized in Table 9, which presents data on the two forms of gaseous As and particulate-bound As. The results indicate that particulate-bound As is the

Table 5

As concentrations in feed fuel and solid products.

Unit	Solid samples (mg/kg) <sup>a</sup>				Regulatory standard Soils(mg/kg)
	Fuel	Bottom ash	ESP/FF ash	WFGD gypsum	
#1	3.79	21.80	23.30	1.70	25 <sup>b</sup>
#2	3.05	36.60	13.64	1.81	
#3	3.05	29.00	17.25	2.26	

<sup>a</sup> The concentration of As in solid samples (mg/kg) was calculated based on wet basis.

<sup>b</sup> Values according to National Environmental Quality Standard for soils of China (GB15618-1995).

Table 6

As concentrations in liquid samples.

Unit	Liquid samples (μg/L)			Regulatory standard Groundwater (μg/L)
	Limestone slurry	WFGD wastewater	Flush water	
Unit #1	8.9	6.6	na <sup>b</sup>	50 <sup>a</sup>
Unit #2	4.6	8.5	na <sup>b</sup>	
Unit #3	4.1	2.0	na <sup>b</sup>	

<sup>a</sup> values according to National Environmental Quality Standard for groundwater of China (GB/T14848-1993).

<sup>b</sup> Not available by means of ICP-MS.

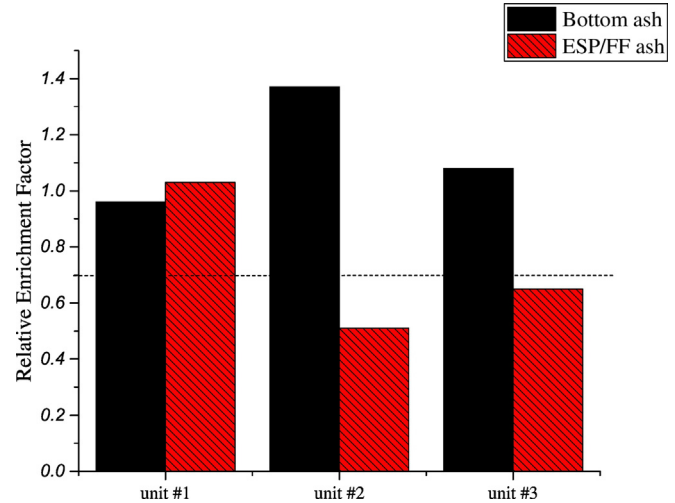


Fig. 4. Relative enrichment factors for As in bottom ash and ESP/FF ash.

predominant existing form in the flue gas at the three sampling points. The removal efficiencies of As in the flue gas by ESP/FF system and

Table 7

Parameters used for the calculation of overall mass balance ratio.

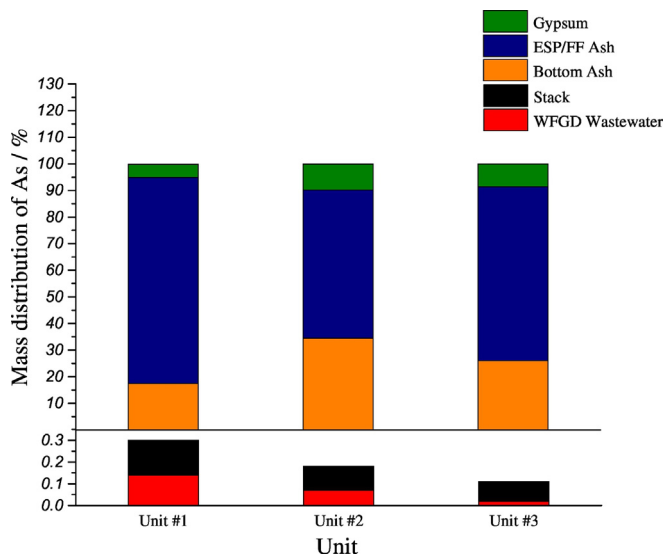
Parameters/unit	Unit #1	Unit #2	Unit #3
$m_f$ (kg/h)	33,180	25,850	36,490
$m_{ba}$ (kg/h)	1138.33	588.95	852.11
$m_{fa}$ (kg/h)	4733.12	2545.30	3594.25
$m_g$ (kg/h)	4130	3360	3580
$m_{ls}$ (kg/h)	810	1340	1980
$m_{fw}$ (kg/h)	7080	5070	4840
$m_{ef}$ (kg/h)	3760	3050	3250
$m_s^a$ (m <sup>3</sup> /h)	229,175	212,601	274,208

<sup>a</sup> Calculated dry flue gas volume at stack.

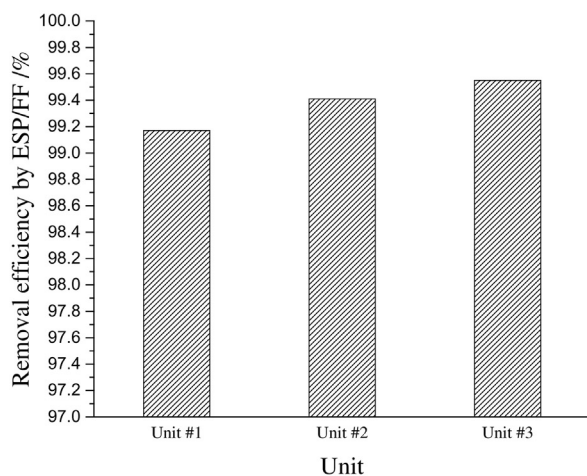
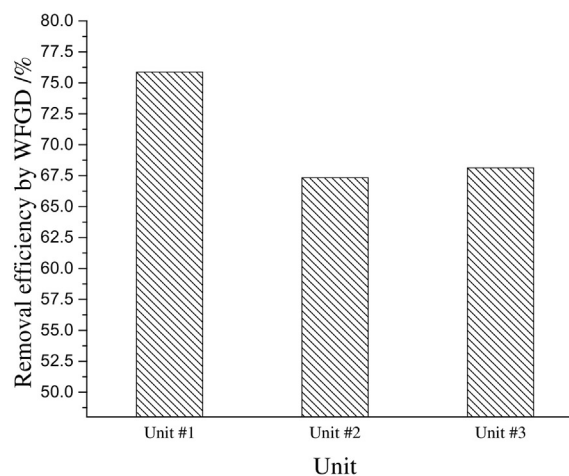
**Table 8**

The overall mass balance ratios of As and the relative deviation of mass balances.

Item	Unit #1	Unit #2	Unit #3
Mass balance (%)	114.2	80.0	86.0
Relative deviation (%)	8.1	7.9	6.2

**Fig. 5.** Mass distribution of As in the combustion process.**Table 9**The concentrations of As along the flue gas path (based on 6% O<sub>2</sub>).

Item	mg/dscm <sup>a</sup>					
	Before ESP/FF		After ESP/FF (before WFGD)		After WFGD	
	As <sub>g</sub> <sup>b</sup>	As <sub>p</sub> <sup>c</sup>	As <sub>g</sub> <sup>b</sup>	As <sub>p</sub> <sup>c</sup>	As <sub>g</sub> <sup>b</sup>	As <sub>p</sub> <sup>c</sup>
Unit #1	0.31	447.4	0.15	3.58	0.12	0.85
Unit #2	0.24	166.7	0.15	0.83	0.11	0.21
Unit #3	0.14	213.2	0.12	0.85	0.11	0.20

<sup>a</sup> mg/dscm: microgram per dry standard cubic meter.<sup>b</sup> As<sub>g</sub>: gaseous As.<sup>c</sup> As<sub>p</sub>: particulate bound As.**a.** Removal efficiency of As by ESP/FF**b.** Removal efficiency of As by WFGD**Fig. 6.** a. Removal efficiency of As by ESP/FF b. Removal efficiency of As by WFGD.

WFGD system are shown in Fig. 6a and b, respectively. The average removal efficiencies by ESP/FF are in the range of 99.2%–99.6%, which is consistent with the high particulate matter (PM) removal efficiency of the ESP/FF system. About 67.3%–75.9% of total As in the flue gas is removed by the WFGD system. A comparatively higher As removal efficiency (82%) was reported by Cheng [19], which is consistent with a comparatively higher As concentration at the inlet of WFGD (7.18 mg/m<sup>3</sup>) in that study. The As retention mechanism in the WFGD process can be explained as follows: on the one hand, particulate-bound As and gaseous As can be removed by the WFGD system by means of the limestone slurry, consistent with the formation of Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>. On the other hand, gaseous As can condense on the surface of particulate matter and become available to be captured by limestone slurry during the FGD process [18,47]. It should also be mentioned that PM can be removed by the WFGD system, and contributes to As abatement capacity [48,49].

### 3.4. Environmental impact

#### 3.4.1. Arsenic speciation analysis

The As speciation analysis was conducted because the toxicity of As is highly dependent on its chemical form for inorganic arsenic (e.g., arsenite and arsenate) [9]. Results of the speciation analysis of samples are presented in Table 10.

As shown, As<sup>5+</sup> is the major water-soluble species in fuel, bottom ash and ESP/FF ash, while As<sup>3+</sup> is under the detection limit in those samples. Arsenic in coal-fired power plant fly ash samples was found to be mainly in the form of arsenate (As<sup>5+</sup>), with little present as arsenite (As<sup>3+</sup>) [12]. It is known that when the temperature is over 500 °C, the following two reactions shown below and Eq. (3) are responsible for the retention of As in bottom ash and the absorption of As on the surface of fly ash during coal combustion process [45,50,51]:



For gypsum samples, neither As<sup>3+</sup> nor As<sup>5+</sup> was detected in this speciation analysis (<1 mg/kg), which indicates that almost no water soluble As was present in gypsum. Previous studies have found that Ca<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> was the dominant and stable species in the WFGD system [52,53]. As<sup>3+</sup> was the major species in WFGD wastewater, while As<sup>5+</sup> was under the detection limit (1 µg/kg). Due to the high toxicity

**Table 10**  
Concentrations of As<sup>3+</sup> and As<sup>5+</sup> in samples (wet basis, mg/kg).

	Unit #1		Unit #2		Unit #3	
	As <sup>3+</sup>	As <sup>5+</sup>	As <sup>3+</sup>	As <sup>5+</sup>	As <sup>3+</sup>	As <sup>5+</sup>
Fuel	—	2.73	—	1.82	—	1.82
Bottom ash	—	23.83	—	18.72	0.85	15.83
ESP/FF ash	—	24.16	—	8.86	—	10.21
Gypsum	—	—	—	—	—	—
Wastewater	0.0066	—	0.0084	—	0.0020	—

Below the detection limit.

of As<sup>3+</sup>, great care is required to ensure the proper treatment of WFGD wastewater.

#### 3.4.2. Atmospheric emission of As

For unit #1, unit #2 and unit #3, the concentrations of total As in the stack emission were 0.97, 0.32 and 0.31 µg/m<sup>3</sup> (presented in Table 9), respectively; the emission ratios of As into the atmosphere were 0.16%, 0.11% and 0.09%, respectively (presented in Fig. 5), which is extremely low. It is clear from these results that the CFB boiler equipped with ESP/FF + WFGD provides good control of the emission of As emitted into the atmosphere.

## 4. Conclusion

Partitioning behavior of Arsenic in circulating fluidized bed boilers co-firing petroleum coke and coal was carefully examined by analyzing the concentration and speciation through various solid, liquid and gas streams. Results show that:

1. The majority of the As is distributed into bottom ash and ESP/FF ash, which accounts for 17.4%–37.5% and 55.6%–77.5%, respectively;
2. Particulate-bound As is the main existing form of As in the flue gas;
3. Both ESP/FF and WFGD demonstrate significant As abatement capacities, which are in the range of 99.2%–99.6% and 67.3%–75.9%, respectively;
4. As<sup>5+</sup> was the major water-soluble species for feed fuel, bottom ash and fly ash, while As<sup>3+</sup> was found to be the dominant species in WFGD wastewater.
5. For three CFB boilers, the concentrations of total As in the stack emission were 0.97, 0.32 and 0.31 µg/m<sup>3</sup>, respectively.

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