Fluorine emission from combustion of steam coal of North China Plate and Northwest China

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Abstract **To study the amount of fluorine emission from the combustion of the steam coal (mainly Permo-Carboniferous coal) from the North China Plate and Northwest China, the fluorine contents of the coal, the fly ash and the cinder in high-temperature power stations as well as mid-low temperature power stations have been analyzed. This note provides a rough estimate of the total annual amount of fluorine emission as well as emission ratio from steam coal combustion in China. Our results show that by combustion of 1 t of Permo-Carboniferous coal (containing roughly 100 g fluorine), high-temperature power stations emit roughly 90 g fluorine into the atmosphere. The fluorine emission ratio of coal combustion in high-temperature power stations is about 96% and that in mid-low temperature power stations is about 78%. A total of 800 million tons of coal is burnt in China every year, and the coal comes mainly from Permo-Carboniferous deposite in the North China Plate and Northwest China coal mines. Taking the average fluorine content of the coal used at a low value of 100 mg/kg, the total annual fluorine emission from steam coal combustion into the atmosphere is estimated to be 66398 t.**

Keywords: coal, fluorine, annual emission.

Coal is the basic power source in China and about 84% (800 million t per year) is consumed directly as fuel[1—4]. Steam coal burnt in power stations accounts for about 500 million t per year, 60% of the total consumption[1—12]. Fluorine is a nocuous trace element in coal. While coal is burning, most of the fluoride content is decomposed into HF and other gases such as SiF_4, CF_4, etc., resulting in contamination of the atmosphere[13—19]. Toxicity of HF is 10—100 times higher than that of SO_2 and is one of the most hazardous pollutants to animals and plants. China has begun to supervise fluorine contamination of the atmosphere and has established a environmental criterion for fluorine emission. Fluorine from coal combustion has received increasing attention and a few important studies have been reported[14, 15].

Scientists in China have done a lot of work and made much progress in fluorine emission patterns from coal combustion, especially from mid-high fluorine coal[14,15]. They have carried out innovative studies including fluorine dissipation patterns in the process of coal incineration[20]; fluorine pollution, its control and countermeasure in coal burning power plants[21]; household fluorine pollution from burning of high-fluorine coal[22] and study on emission and retention of fluorine during coal combustion in the chain-grate furnace[23].

But integrated research on fluorine emission and pollution from steam coal of the North China Plate and Northwest China, which accounts for 84% of China's coal reserves, is lacking at present. There is practically no study on fluorine emission from coal-powder furnace at high temperature in power stations and no report on fluorine distribution patterns of different kinds of coal in different combustion conditions.

Generally speaking, steam coals include lignite, anthracite, non-coking coal of bituminous coal which include long-flame coal, non-caking coal, weakly caking coal, meager coal, lean coal, meager lean coal, etc.

Most of steam coal in China comes from non-coking coal of Permo-Carboniferous bituminous coal in the North China Plate and Northwest China[5]. The fluorine content of this coal is low, varying from 50 to 200 g/t[13,16], and about 100 g/t on the average[13,16]. Coal in the southwest of China only accounts for 10% of coal reserves in China[5], while stone coal in the South Qinling Mountain and the Daba Mountain accounts for about 0.5%[1)]. But most of these coals have high fluorine contents, which results in fluorosis in southwestern China and the southern part of Shaanxi Province [13,16, 24—26].

In order to study the amount of fluorine emission from steam coal (mainly Permo-Carboniferous coal) combustion in North China and Northwest China at high temperature (coal-powder furnace, 1200—1500℃) and at mid-low temperature (800—1200℃) respectively, we collected coal samples from Hancheng Mine, Chenghe Mine and #2, #3, #5, #10 and #11 coal from Tongchuan Mine in Shaanxi Province[13]. Samples also came from Datong Mine, Yangshuo Mine and Xishan Mine in Shanxi Province, and from #4, #5, #8, #9 and #11 coal of Pingyin Mine in Shandong Province[5]. The fluorine contents of these coal samples, their fly ash and cinder in high-temperature as well as mid-low temperature power stations were analyzed, and the total fluorine emission and the emission ratios from steam coal combustion were evaluated. A quantitative method for the evaluation of fluorine emission and a formula for its calculation are proposed.

1 Sampling and analyses

(ⅰ) Getting representative samples. Coal in China

1) Geology Research Institute of Geology Prospecting Department, Academy of Coal Sciences, The general report on stone coal resource in the south of China, 1982.

is classified in two ways: one is classified as anthracite, bituminous coal and lignite by V_{daf}% (volatile matter), and the other by the caking index G and the plastometer index Y [4].

Steam coal includes lignite, anthracite, and non-coking coal of bituminous coal, among which long-flame coal, non-caking coal, weakly-caking coal, lean coal, etc. account for 60% of all steam coal resource[5].

The Permo-Carboniferous coal is widely distributed and constitutes the largest reserve in China. It includes mainly bituminous coal and a small quantity of anthracite, and it is the main power coal[4—7].

In China, coal distribution concentrates in the north and the west, while it is less in the south and the east. Coal depositions to the north of the Kunlun-Qinling Mountains account for about 90% of all coal reserves, within which, coal in the North China Plate and Northwest China accounts for 84%, and Mesozoic lignite in Northeast China accounts for only about 4%, while coal in southern China only amounts to 9%. Coal deposition in Guizhou Province accounts for about 80% of coal reserves in southern China[4—7].

Coal in the same tectonic unit has similar paleostructure, paleogeography, paleoclimate, tectonism and metamorphism during and after the coal-forming process and has the similar fluorine content. For example, the lowest bed of Carboniferous coal has a similar fluorine content in Shaanxi, Shanxi and Shandong provinces. Based on our pilot study, the fluorine content of coal is related to the coal-forming age. The fluorine content of low metamorphic grade coal is a little more than that of high metamorphic grade coal and the fluorine content of coal formed in older ages is a little more than that formed in younger ages[13]. The fluorine content of Permo-Carboniferous anthracite in Shaanxi and Shanxi is about 50 mg/kg, a little lower than that of bituminous coal (70 mg/kg); and the fluorine content of Jurassic and Permian coal is about 50 mg/kg, a little lower than that of Carboniferous coal (80 mg/kg). But the difference in the fluorine content between coals of different ages is little. However, the fluorine content of Chinese coal is closely related to the structure position of coal basins. For example, although the Early Paleozoic stone coal in southern Shaanxi is mainly anthracite and has a higher metamorphic grade, its fluorine content is very high (400—3000 mg/kg) because it is situated in the Qinling-Daba Mountain tectonic belt. The fluorine content of Permo-Carboniferous anthracite in the North China Plate is low, about 50 mg/kg. There is a great difference in fluorine content of Permian bituminous coal between deposits in northern China (50—100 mg/kg) and western Guizhou (up to 500 mg/kg)[4,13].

So it is more reasonable to collect coal samples and analyze their fluorine content according to their structure positions and forming ages than according to their classifications.

Moreover, most of Jurassic low-ash and low-sulfur coal in China is exported to foreign countries, because of its high volatile components it is unfit to use in Chinese power stations. So, non-coking coal of Permo-Carboniferous bituminous coal is the main steam coal in big power stations and anthracite of Permo-Carboniferous coal is the main coal for household use in China. Therefore, it is reasonable to select non-coking coal and anthracite of Permo-Carboniferous coal as representative samples to study the amount of fluorine emission from steam coal combustion in China.

(ii) Selection of power stations. Large-sized high-temperature power stations such as the Baqiao Power Station in Xi'an, the Pucheng Power Station in Shaanxi, the Taiyuan 2nd Power Station in Shanxi and the Shiheng Power Station in Shandong were selected in this study. At the same time, a small power plant, the Wangcun Power Station was also included in this study, where coal combustion temperature is low (about 900℃). The anthracite and coal cinder samples were also collected from the hot water boilers (4 t/h) in Xi'an City.

(iii) Sample analyses. Some of the samples were analyzed by the Northwest Geological Testing Center which has been accredited by the China National Metrology Bureau and CNNC, and is a first-class analytical laboratory of the CNNC. The samples were analyzed by the alkali fusion/fluorine ion-selective electrode method (GB4633-84). Most of the coal samples and all the fly ash and cinder samples were analyzed in the Geological Testing Center of the Academy of Coal Sciences and the Coal Testing Center of the Shanxi Quality Testing Center, and the high alkali-fusion/fluorine ion-selective electrode method was used. The reporting limit is 10^{-7} mg/kg and the relative error is 10%. The proximate analysis and ultimate analysis of the coal and ash were performed by the Lab of the Chenghe Mining Bureau of Shaanxi. The reporting limit is 10^{-3} mg/kg and the relative error is 10%.

2 Physical and chemical characterestics of Permo-Carboniferous coal in North China and Northwest China

The coal evolved from higher plants in the Permo-Carboniferous system is named humic coal, which has the largest reserves and is most widely distributed both in China and in the world. Permo-Carboniferous coal, mainly including bituminous coal and a little anthracite, is the main resource of steam coal and coal for household use in China.

A lot of industrial and elemental studies on Permo-Carboniferous coal in North China and Northwest China has been carried out by many coalfield teams and mining bureaus of the former Ministry of Coal Industrial of

Table 1 Proximate analysis and ultimate analysis of #10 coal in Chenghe Coal Mine

Mad (%)	Ad(%)	Vd (%)	St, d (%)	Qgr, d/MJ • kg^{-1}	Cad (%)	Had (%)	Nad (%)	Oad (%)
2. 25	21. 55	34. 06	2. 04	26. 75	62. 04	4. 29	1. 02	6. 01

Mad, moisture in the air dried sample; Ad, ash in the air dried sample; Vd, volatile matter of dry basis; St, d, total sulfur of dry basis; Qgr,d, gross calorific value of dry basis; Cad, Had, Nad and Oad, content of C, H, N and O in the air dried sample respectively.

Table 2 Proximate analysis and ultimate analysis of #5 coal in Chenghe Coal Mine

Mad /%	Ad (%)	Vd (%)	St,d (%)	Qgr, v/MJ • kg^{-1}	Cad (%)	Had (%)	Nad (%)	Oad (%)
$\frac{0.32–1.56}{0.71}$	$\frac{10.60–30.31}{19.79}$	$\frac{16.69–25.54}{19.04}$	$\frac{1.74–7.46}{3.44}$	$\frac{33.92–36.60}{35.27}$	79.10	4.20	0.68	3.05

Qgr, v, Gross calorific value at constant volume.

China. The ash content of most Permo-Carboniferous coal in North China and Northwest China varies from 15% to 30% (~20% on average), and the carbon content varies from 50% to 80% (~60% on average). Tables 1 and 2 show the results of industrial and elemental analyses of Permo-Carboniferous coal from the Chenghe Coal Mine.

3 Evaluation of fluorine emission from steam coal combustion

Fluorine in coal is apt to vaporize. When the coal is burnt, a part of fluorine remains in coal cinder and the other part is released along with coal dust, among which, only a small part is trapped with the fly ash by the dust catcher, while the majority of fluorine goes directly into the atmosphere. Suppose that the fluorine in the fly ash and cinder is of less importance to the atmosphere, so, only the fluorine that goes directly into the atmosphere is considered later in this note.

The quantity of fly ash and cinder and their fluorine content are closely related to coal burning temperature and other combustion conditions. For example, the Pucheng Power Station with high-temperature boiler and well controlled combustion conditions produced fly ash which was off-white in color. The fly ash and cinder had the similar compositions (mainly SiO_2 and Al_2O_3) and when burnt completely, their carbon content was very low. Their fluorine contents were very low too. The fly ash and the cinder accounted for 90% and 10% of all ashes produced respectively.

There is little difference between the quantities of fly ash and cinder when coal is burnt at low temperature and combustion condition is poor. The fly ash and the cinder generally account for 60% and 40% of all ashes respectively. But their fluorine contents make a great difference, higher in fly ash and lower in cinder.

For example, the same kind of coal (lean coal from the Chenghe and the Pubai Mining Bureau), which had the same fluorine content of 85 mg/kg, was used in both the Wangcun Power Station and the Pucheng Power Station. But in the Pucheng Power Station, the carbon content and fluorine content in fly ash (about 0 and 16 mg/kg respectively) were much lower than those of the Wangcun Power Station. Such differences are attributed to the high-temperature boilers and more complete combustion.

In better coal combustion conditions, there is less carbon residue in the coal ash and also less fluorine remaining in fly ash and cinder. There is only a little difference in the fluorine content between fly ash and cinder but there is a great difference in their relative amounts. If coal combustion condition is less favorable, the carbon content in coal ash tends to be high and there is a great difference in the fluorine content between fly ash and cinder. The fluorine content in fly ash is higher than that in cinder, but their total quantities vary very little.

All the above conclusions are based on our analyses of fly ash and the amount of cinder emission.

(ⅰ) Fluorine emission from coal combustion in high-temperature boilers of large-midium sized power stations. To estimate the emission of trace elements from coal combustion, we used to calculate by multiplying a coefficient or directly subtract a trace element content in each ton of coal ash from that in each ton of coal.

In fact, the ash content of coal is defined as the amount of residuals after complete combustion. For example, suppose that the ash content of the coal is 20%, which means that 0.2 t of residuals remain after 1 t of coal is completely burnt. Therefore, if we evaluate the amount of fluorine emission from 1 t of coal combustion, we should subtract the amount of fluorine in fly ash and cinder, namely the fluorine content in 0.2 t of residuals after coal combustion, from the fluorine content of 1 t of coal before its combustion. Fluorine emission from coal combustion (D) can be expressed as $D = A - (B + C) \times E$, where A, B and C are the fluorine concentrations of the coal, the cinder and the fly ash, respectively, and E is the ash content in coal.

The Baqiao Power Station and the Pucheng Power Station are about 10 and 150 km away from Xi’an City respectively, the Shiheng Power Station is about 120 km away from Ji’nan City, and the Taiyuan 2nd Power Station is about 10 km away from Taiyuan City. Like most of the large-sized power stations in China, coal-powder furnaces were used in these power stations, whose hearth temperature reach 1200—1500℃. Their coal came mainly from non-coking coal of the bituminous coal from Permo-

Carboniferous in the North China Plate and Northwest China. These bituminous coal are formed in steady platforms, including #2, #3, #5, #8, #9, #10 and #11 of Permo-Carboniferous coal seams. Their fluorine contents are low, 50—200 g/t, about 100 g/t on average. The fluorine contents of coal, fly ash, cinder of these power stations are analyzed in this study. In addition, the carbon content of fly ash and cinder from both the Pucheng Power Station and the Baqiao Power Station are 0 and 0.04% respectively.

The furnace hearth temperature is high in the large-sized power station, so coal is burnt more completely and the fly ash plus cinder quantity is approximately equal to the ash content of coal.

For the large-sized power station with good combustion condition and high-temperature furnace hearth, we can get fluorine emission amount from coal combustion (D) based on the following formula:

$$D = A - (B \times 10\% + C \times 90\%) \times E.$$

The fluorine emission ratio (V) can be expressed as

$$V = D/A \times 100\%.$$

(ii) Fluorine emission from coal combustion in mid-low temperature boiler of power station and in hot water boilers. The same coal as used in the Pucheng Power Station is burnt in both the Wangcun Power Station of Chengcheng County in Shaanxi and the hot water boilers in Chenghe Mining Bureau (chain-grate furnace ~20 t/h), which is the #5 lean coal from Chenghe and Pubai Mine Bureau and its fluorine content is about 85 mg/kg.

Generally speaking, the hearth temperature of the mid-low temperature power station and boiler for hot water supply varies from 800 to 1200℃. As a result, coal is burnt incompletely and about 5—20% of coal remain in fly ash and cinder. Our analyses show that the carbon content of fly ash and cinder are 5% and 20% respectively in mid-low temperature power stations. Therefore, for mid-low temperature power stations and hot water boilers, the total amount of fly ash and cinder is more than the ash content in coal, which should be equal to the ash content in coal plus the coal remaining in the fly ash and cinder.

For mid-low temperature power stations and hot water boilers, we can calculate the fluorine emission from coal combustion (D) based on the following formula:

$$D = A - (B \times 40\% + C \times 60\%) \times E - A \times L,$$

where L is used to express the percent of coal remaining in the fly ash and cinder and it is 7% for mid-low temperature power stations and large-midium sized (20 t/h) hot water boilers.

The temperature in the most of small hot water boilers is very low, the coal combustion residual is mainly cinder, and there are more un-burnt coal remaining in coal cinder. The carbon content in cinder is about 9.89% in small boilers, where the hearth temperature is about 700—850℃ and L is around 15%.

Tables 3 and 4 show that the average fluorine emission into the atmosphere per ton of coal combustion, with 70—100 g (~100 g on average) of fluorine content, is 90 g at high-temperature power stations and 78 g at mid-low temperature power stations. The fluorine emission rate from coal combustion is about 96% in high-temperature

Table 3 Fluorine emission per ton of coal combustion in high-temperature power stations ($g \cdot t^{-1}$)

Sampling spot	Sample No.	Ash content (%)	Fluorine in coal			Fluorine in fly ash			Fluorine in cinder			Fluorine to atmosphere /g	Fluorine emission rate (%)
			min.	aver.	max.	min.	ave.	max.	min.	ave.	max.		
Baqiao Power Station	12	20.01	51.01	70.03	98.60	14.26	19.89	22.19	8.30	11.12	15.63	66.23	94.57
Pucheng Power Station	9	22.23	48.13	85.21	134.30	11.53	15.90	19.32	8.21	12.01	16.21	81.76	95.95
Shiheng Power Station	6	23.12	50.09	98.91	129.60	11.10	14.85	18.01	12.10	18.13	22.09	95.40	96.45
Taiyuan Power Station	8	20.16	50.10	120.10	149.20	11.01	19.10	24.78	18.03	20.98	25.32	116.21	96.76
Average												89.90	95.93

Table 4 Fluorine emission per ton of coal combustion in mid-low temperature power stations and small hot water boilers ($g \cdot t^{-1}$)

Sampling spot	Sample No.	Ash content (%)	Coal remains in cinder (%)	Fluorine in coal			Fluorine in fly ash			Fluorine in cinder			Fluorine to atmosphere /g	Fluorine emission rate (%)
				min.	ave.	max.	min.	ave.	max.	min.	ave.	max.		
Chengcheng in Shaanxi	6	22. 12	7	46. 14	104. 90	151. 01	54. 21	71. 26	83. 05	14. 89	21. 03	25. 03	86. 24	82. 21
Wangcun in Shaanxi	6	22. 05	7	51. 23	86. 18	104. 36	71. 32	77. 83	80. 13	12. 11	17. 98	21. 61	68. 27	79. 22
Hot water boilers	8	20. 13	15	58. 12	114. 79	130. 03				46. 03	56. 35	72. 06	86. 23	75. 12
Hot water boilers	7	20. 56	15	64. 98	94. 68	121. 21				38. 26	52. 01	75. 05	69. 78	73. 70
Average													77. 63	77. 56

power stations and 78% in mid-low temperature power stations. The fluorine emission rate from coal combustion in high-temperature power stations is higher than that in mid-low temperature power stations, which results from different hearth temperatures and coal combustion conditions. Whether high fluorine coal or low fluorine coal is burnt, there is little difference in fluorine content of fly ash and cinder, which is very low, in high-temperature power stations with good combustion conditions. So we can conclude that the higher the hearth temperature, the more complete the coal combustion, and the more fluorine in coal is released.

4 Conclusion

The higher the hearth temperature in coal combustion is, the higher the fluorine emission ratio is. About 800 million t of coal is burnt directly every year in China, among which 500 million t is burnt for power generation, within which about 30% is burnt in mid-low temperature power stations[2—6]. The average fluorine content of the coal is 100 mg/kg in China, so the annual fluorine emission from power stations to the atmosphere is about 90 g/t $\times$ 3.5 $\times$ 10^8 t + 78 g/t $\times$ 1.5 $\times$ 10^8 t, namely about 4.3×10^4 t. About 300 million t of coal is burnt in hot water boilers in China annually, so the fluorine emission of these boilers into the atmosphere is about 78 g/t $\times$ 3$\times$ 10^8 t, namely about 2.3×10^4 t. So, the total fluorine emission from steam coal combustion into the atmosphere is about 6.6×10^4 t/a in China, which is not a negligible fact.

The fluorine content of the North China Plate and Northwest China coal, which accounts for 84% of coal reserves in China, is much lower than that of the stone coal in South of Shaanxi and the Permian Xiaolongtan Formation coal in Southwest of China, but it is widely used for power generation nationwide. So, a great amount of fluorine emission from the combustion of coal should not be overlooked.

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