

Article

# Modes of Occurrence of Fluorine by Extraction and SEM Method in a Coal-Fired Power Plant from Inner Mongolia, China

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**Abstract:** In this study, an extraction method and environmental scanning electron microscopy (SEM) are employed to reveal the changes in the occurrence mode of fluorine in a coal-fired power plant in Inner Mongolia, China. The different occurrence states of fluorine during coal combustion and emission show that fluorine in coal mainly assumes insoluble inorganic mineral forms. The results illustrate that the three typical occurrence modes in coal are  $\text{CaF}_2$ ,  $\text{MgF}_2$  and  $\text{AlF}_3$ . The fluorine in fly ash can be captured by an electrostatic precipitator (EPS) or a bag filter. In contrast, the gaseous fluorine content in flue gas is only in the range of several parts per million; thus, it cannot be used in this study. The occurrence mode of fluorine in bottom ash and slag is inorganic villiaumite (e.g., soluble NaF, KF and insoluble  $\text{CaF}_2$ ) which is difficult to break down even at high temperatures. The occurrence mode of fluorine with the highest content in fly ash is physically adsorbed fluorine along the direction of the flue gas flow. The insoluble inorganic mineral fluoride content in fly ash is also high, but the gradually increasing fluorine content in fly ash is mainly caused by physical adsorption. Fluorine in the coal-fired power plant discharges mostly as solid products; however, very little fluorine emitted into the environment as gas products ( $\text{HF}$ ,  $\text{SiF}_4$ ) cannot be captured. The parameters used in this study may provide useful references in developing a monitoring and control system for fluorine in coal-fired power plants.

**Keywords:** extraction; SEM; occurrence mode of fluorine; coal-fired power plant; combustion products

## 1. Introduction

In recent years, the toxic elements in coal have been research highlights in many countries, especially in China, the largest coal-consuming country in the world. The fluorine in coal is a toxic trace element, with a general content of 100–300 ppm. The average fluorine concentration level in coal in China is 130 ppm [1], 48% higher than that in the rest of the world (the average level in the world is 88 ppm [2]). The reason China is higher than the rest of the world is that the amount in the sample determined by researchers in China is limited, or different determination method was used. Although the concentration of fluorine in coal is on a ppm level, the emission needs to be paid special attention as the coal consumption increases. A gas product of coal combustion: HF, poses the most harm to humans and animals.

There have been a number of studies on modes of fluorine in coal. Eskenazy [3] illustrated the occurrence modes of fluorine in coal by examining the relationship of fluorine with ash yield, as well as the oxides in fly ash. Martinez [4] analyzed the modes of fluorine in Austrian coals. Dai [5] studied the correlation between fluorine and minerals to evaluate the occurrence modes of fluorine in different

coal types. He discovered mineralogical and geochemical compositions of the coal in Inner Mongolia, China [6], and made a case study of factors on controlling compositions of coals [7]. He also discussed elements and phosphorus minerals in the middle Jurassic inertinite-rich coals including the existence of trace elements [8]. Wang [9] employed the continuous extraction/density separation method to reveal the occurrence modes of fluorine in Chinese coal. Liu [10] investigated the correlation between fluorine and alkalis to identify the occurrence states of fluorine in Guizhou coal. The conventional analytical method to assess the fluorine occurrence states in coal mainly uses correlation analysis, but a relatively simple and effective extraction method has been adopted in recent years.

The extraction method [11] has been proved suitable for occurrence studies on sulfur, selenium and other elements. Such a method was also used to analyze fluorine in soil and for chemical extraction for trace elements in coal [12–14]. However, this method has been seldom used for analyzing fluorine in coal [15], especially for tracking the changes in fluorine occurrence modes in power plant boilers. In this study, an extraction method and scanning electron microscopy (SEM) are employed to determine the fluorine changes during coal combustion in a coal-fired power plant. During coal combustion, the fluorine in coal remains in slag and bottom ash or adheres to fly ash. This research also provides a reference for the study on the change regularity of the occurrence modes of fluorine in coal-fired power plants.

## 2. Method and Sampling

Several types of samples, including pulverized coal, slag, flue gas desulfurization gypsum and fly ash, in different parts of the boiler were collected from the Shangdu coal-fired power plant in Inner Mongolia, China. All samples were dried and filtered through a 200-mesh sieve. The extraction method means that fluorine from solid samples was leached by solvent. The fluorine content in the extraction solution was determined using the fluoride ion-selective electrode method (GB/T 4633-1997 [16]). SEM was used to analyze the fluorine mineral forms in the samples. Figure 1 shows the experimental procedure. We adopted 4 g coal sample (or 2 g other samples) and 50 mL extraction solution (deionized water, 0.1 mol/L NaOH solution, 1 mol/L HNO<sub>3</sub> solution, 0.1 mol/L KCl solution, 0.05 mol/L CaCl<sub>2</sub> solution, respectively). Additionally, these samples are adopted with 30 min magnetic stirring and 1 h extraction, then filtered and combined with 25 mL liquid supernatant to adjust their pH concentration. Determination of fluoride by the ion-selective electrode should be obtained in the end.

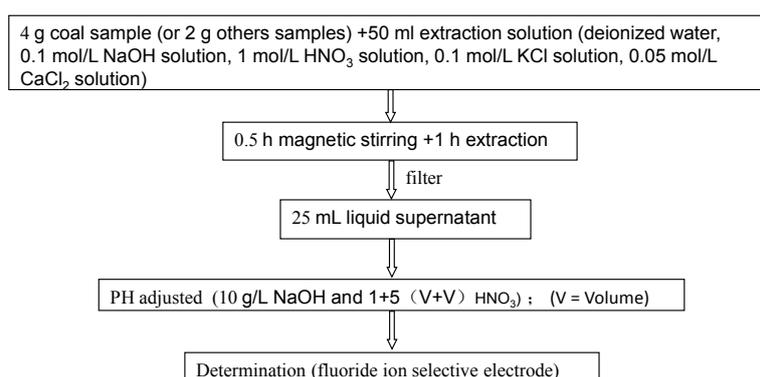


Figure 1. Scheme for extraction of fluorine in the samples (referred to Qi [17]).

## 3. Results and Discussion

### 3.1. Occurrence Modes of Fluorine in Coal

The extraction data are presented in Table 1. The results show that water-soluble fluorine content is 4.51 µg/g with an extraction rate of 1.33%. Extraction rate means that the leaching amount accounted

for the proportion of the total content in the sample. It can be expressed: extraction rate = leaching amount/total amount. The alkali-soluble fluorine content is 9.74 µg/g with an extraction rate of 2.88%. The acid-soluble fluorine content is 39.92 µg/g with an extraction rate of 11.81%. The acid solution has the highest extraction rate among solutions. In salt-soluble fluorine, the calcium chloride is 4.89 µg/g with an extraction rate of 1.45%, and potassium chloride is 4.16 µg/g with an extraction rate of 1.23%. The water-soluble fluorine forms, namely NaF, KF and NH<sub>4</sub>F, mainly come from soluble fluoride and adsorbed fluoride. The extraction rate of water-soluble fluorine indicates that free-state F<sup>-</sup> is adsorbed on mineral particle surfaces, and fluorine is among the mineral particles in pore water; however, water-soluble fluorine is not the main occurrence mode of fluorine in coal. Alkali-soluble fluorine is fluoride adsorbed by the clay minerals in coal, and OH<sup>-</sup> can replace the fluorine adsorbed by the clay minerals, thereby increasing the OH<sup>-</sup> concentration in the solution. OH<sup>-</sup> can also displace a certain amount of fluorine in the mineral lattice [18–20], which is ionic with an isomorphism. This process can be expressed by the following formula:



**Table 1.** Extraction results from the coal-fired power plant.

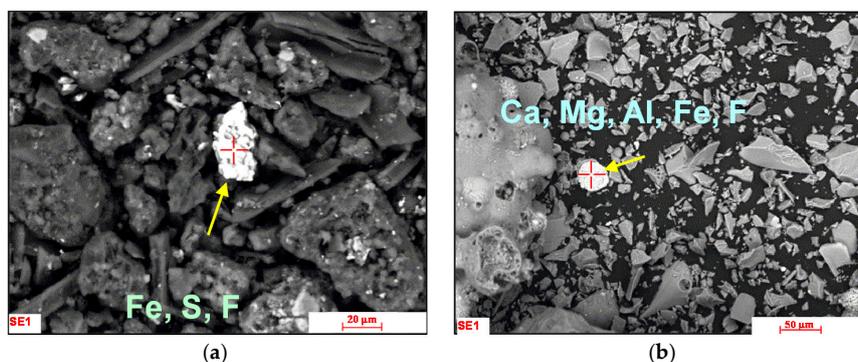
Items	Water-Soluble		Alkali-Soluble		Acid-Soluble		CaCl <sub>2</sub> -Soluble		KCl-Soluble	
	Con (µg/g)	E-Rate (%)	Con (µg/g)	E-Rate (%)	Con (µg/g)	E-Rate (%)	Con (µg/g)	E-Rate (%)	Con (µg/g)	E-Rate (%)
YM	4.51	1.33	9.74	2.88	39.92	11.81	4.16	1.23	4.89	1.45
LZ	2.45	3.03	2.77	3.42	4.33	5.34	2.36	2.91	2.17	2.68
QH	6.36	11.78	6.49	12.02	34.22	63.38	6.06	11.22	6.76	12.52
HHC	57.97	21.08	71.0	25.82	85.21	30.99	48.69	17.71	63.64	23.14
HHX	349.37	42.87	383.52	47.06	426.15	52.29	324.70	39.85	365.30	44.82

Con = Content; E-rate = Extraction rate; YM = coal; LZ = slag; QH = ash of sample before ESP; HHC = sample of ESP ash; HHX = sample of bag filter ash.

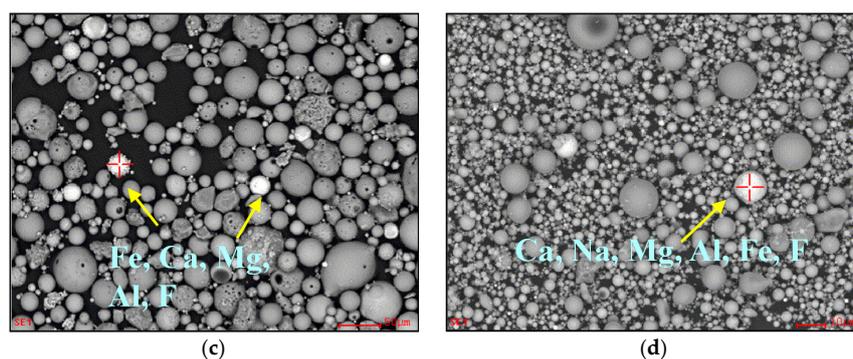
The fluorine in coal is mainly insoluble fluoride. Unlike water and alkali, acid can dissolve insoluble fluoride, including CaF<sub>2</sub>, MgF<sub>2</sub>, AlF<sub>3</sub>, FeF<sub>3</sub> and Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F. Iron and sulfur contents are high in fluorine-containing minerals (Figure 2a). In addition, the fluorine content of calcium chloride solution is slightly below that of potassium, and it is on the ppm level as CaF<sub>2</sub> is in the coal. The proximate and ultimate analysis of the coal are shown in Table 2.

**Table 2.** Proximate and ultimate analysis of coal.

Proximate (wt %)			Ultimate (wt %)				
Moisture	Ash	Volatile	C	H	O	N	S
16.83	13.57	48.65	68.84	5.12	22.73	1.51	1.32



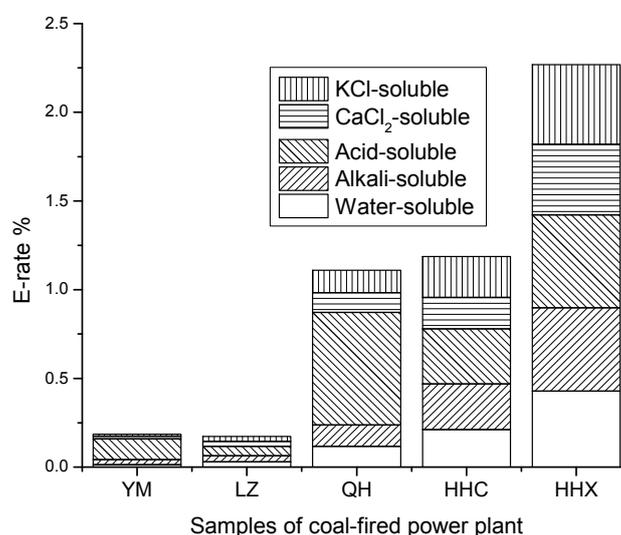
**Figure 2.** Cont.



**Figure 2.** SEM analysis of coal and products of combustion: (a) is the backscattered image of YM; (b) is the backscattered image of LZ; (c) is the backscattered image of QH; (d) is the backscattered image of HHX. YM = coal; LZ = slag; QH = ash of sample before ESP; HHX = sample of bag filter ash.

### 3.2. Occurrence Modes of Fluorine in LZ

As shown in Figure 3, the extraction rate of the fluorine in LZ minimally changed, and only the acid-soluble fluorine content slightly decreased. Adsorbed fluoride, organic fluorides, and some mineral fluorine are released into the flue gas at elevated temperatures during coal combustion. Some fluorides were retained in the LZ, such as soluble fluorine (NaF, KF) and insoluble fluorine (CaF<sub>2</sub>, MgF<sub>2</sub>, FeF<sub>3</sub>, AlF<sub>3</sub>). Water-soluble fluorine and salt-soluble (CaCl<sub>2</sub> and KCl) fluorine mainly came from NaF and KF; alkali-soluble fluorine was derived from NaF, KF and the mineral lattice. Acid-soluble fluorine primarily resulted from soluble (NaF, KF) and insoluble fluorine (CaF<sub>2</sub>, MgF<sub>2</sub>, FeF<sub>3</sub> and AlF<sub>3</sub>). Those fluorides are difficult to break down even at high temperatures. It is obvious that soluble and insoluble fluorine are the dominative occurrence modes in LZ. Figure 2b shows the SEM results of LZ. The outcomes also showed that CaF<sub>2</sub>, MgF<sub>2</sub>, FeF<sub>3</sub> and AlF<sub>3</sub> are the main occurrence states.



**Figure 3.** Different extraction rate of each sample.

### 3.3. Occurrence Modes of Fluorine in QH

As shown in Figure 3, the extraction rate of fluorine in QH, *i.e.*, 63.38%, is significantly higher than those in coal and slag, especially the extraction rate of acid-soluble fluorine. Some minerals are decomposed during coal combustion, and metal oxides (*i.e.*, CaO, MgO and Al<sub>2</sub>O<sub>3</sub>) are subsequently generated. There are some metal oxides (*i.e.*, CaO, MgO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>) in the fly ash [21]. These

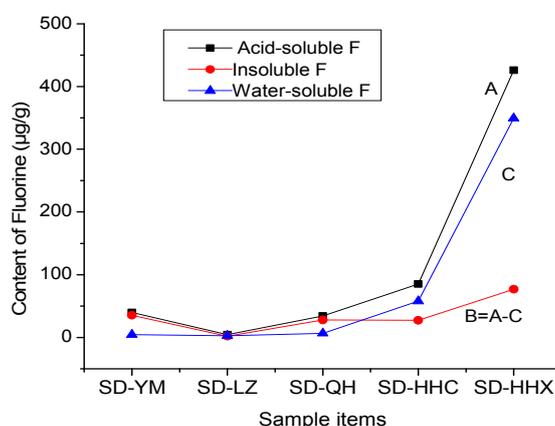
metal oxides react with gaseous fluorine (mostly HF) in flue gas to produce insoluble fluorides ( $\text{CaF}_2$ ,  $\text{MgF}_2$ ,  $\text{FeF}_3$  and  $\text{AlF}_3$ ) and other soluble fluorides (NaF, KF). Figure 2c shows that the Ca, Mg, Al and Fe contents in fluorine-containing minerals are high. Therefore, adsorbed fluorine and insoluble fluoride (*i.e.*,  $\text{CaF}_2$ ,  $\text{MgF}_2$  and  $\text{AlF}_3$ ) are the main occurrence modes in QH.

### 3.4. Occurrence Modes of Fluorine in HHC and HHX

Among QH, HHC and HHX, HHX has the smallest particle diameter, whereas QH has the largest particle diameter. A smaller particle size indicates stronger fluoride absorption. The extraction fluorines in HHC and HHX, which are electrostatic precipitator ash and bag filter ash, respectively, are significantly more than those in YM, LZ and QH. The proportion of acid-soluble fluorine in HHC and HHX is less than that in QH. The fluorine in QH is mainly  $\text{CaF}_2$ ,  $\text{MgF}_2$ ,  $\text{FeF}_3$  and  $\text{AlF}_3$ , while the fluorine in HHC and HHX is physically adsorbed fluorine, and a certain amount of fluorines are soluble fluorine (NaF, KF) in HHC and HHX. As shown in Figure 3, fluorines ordered from the fluorine with the lowest content on the basis of their extraction rates are as follows: acid-soluble, alkali-soluble, KCl-soluble, water-soluble and  $\text{CaCl}_2$ -soluble fluorines. Acid-soluble fluorine accounts for the largest proportion of extraction-soluble fluorine. Thus, physically adsorbed fluorine and insoluble inorganic mineral fluoride ( $\text{CaF}_2$ ,  $\text{MgF}_2$  and  $\text{AlF}_3$ ) are the main occurrence modes of fluorine in HHC and HHX, according to the experimental results. The results are also consistent with Figure 2c,d.

### 3.5. The Changes of Fluorine in the Power Plant

Figure 4 shows that the water-soluble fluorine content rapidly increases along the flue gas flow, and the insoluble fluorine content can be estimated from acid-soluble fluorine and water-soluble fluorine. The change in insoluble fluorine content is represented by curve B in Figure 4, and the insoluble fluorine contents in HHC and HHX are 27.24 and 76.78  $\mu\text{g/g}$ , respectively. The gradually increasing fluorine content in fly ash is caused by physical adsorption.



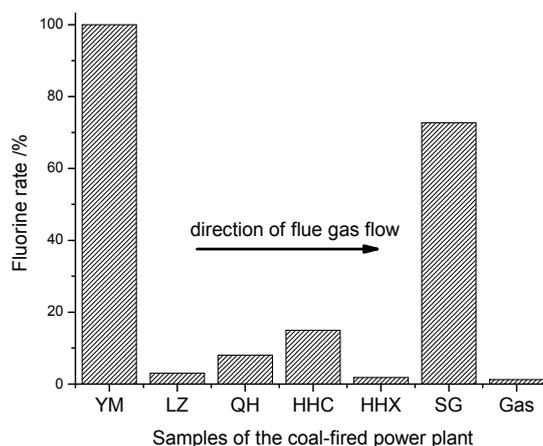
**Figure 4.** Transformation of fluorine during coal combustion in a coal-fired power plant.

Fluorine content in YM is 169 ppm (Table 3), and migration takes place during coal combustion. The fluorine is immigrated into LZ, QH, HHC, HHX, SG and flue gas flow. As shown in Figure 5, only 3.02% of fluorine remains in LZ, and a total of 23% immigrates into QH (8.05%), HHC (14.96%) and HHX (1.84%) during coal combustion. The rest of the fluorine is released into the flue gas flow, and only 1.24% is emitted into the environment, and 72.74% of the fluorine is absorbed by flue gas desulfurization gypsum. Fluorine in the coal-fired power plant discharges mostly as solid products; however, only tiny amounts of fluorine (1.24%) emitted into environment as gas products (HF,  $\text{SiF}_4$ ) cannot be captured.

**Table 3.** Fluorine content of different samples in the coal-fired power plant.

Sample	YM	LZ	QH	HHC	HHX	SG	Gas
P (%)	100	3.02	8.05	14.96	1.84	72.74	1.24
S (ppm)	169	81	54	275	815	2730	-

$P = X_i / X$  ( $X_i$  = total fluorine in a by-product of 1 kg coal,  $X$  = total fluorine in 1 kg coal);  $S$  = fluorine content of a sample; Gas = gaseous fluorine emitted into environment; SG = flue gas desulfurization gypsum.

**Figure 5.** Migration of fluorine during coal combustion in the coal-fired power plant.

#### 4. Conclusions

The different occurrence modes of fluorine during combustion and emission are as follows: (1) the fluorine in YM mainly exists in insoluble inorganic mineral forms, such as  $\text{CaF}_2$ ,  $\text{MgF}_2$  and  $\text{AlF}_3$ ; (2) the fluorine occurrence modes in LZ are inorganic villiaumite, such as soluble NaF, KF, and insoluble  $\text{CaF}_2$ , which are difficult to break down even at high temperatures; and (3) physically adsorbed fluorine and insoluble inorganic mineral fluoride ( $\text{CaF}_2$ ,  $\text{MgF}_2$  and  $\text{AlF}_3$ ) are the main occurrence modes of fluorine in HHC and HHX. The high fluorine content in fly ash is mainly attributed to physically adsorbed fluorine along the direction of the flue gas flow. The insoluble inorganic mineral fluoride content in fly ash is also high, but the gradually increasing fluorine content in fly ash is mainly caused by physical adsorption. Fluorine in the coal-fired power plant discharges mostly as solid products; however, very little fluorine as HF and  $\text{SiF}_4$  released into air cannot be captured.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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