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The concentration of fluorine in coals and gangue of China*

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Abstract A detailed comparison was done between the data about the F in coals published at home and abroad, and associated with the special situation in China. An introduction also was made to illuminate the forming, occurrence and accumulation of the F in coals and its potential hazard to human and environment. Analytical data of coal samples were referred to study the great difference of the F content between coals and gangue. The results show that the average value of the F in the coal samples collected in different coalfields of China is 304×10^{-6}, while that of gangue samples is surprisingly 1 319×10^{-6}, especially the F content of coal ash from Bangmai in Yunnan Province reaches 4 800×10^{-6}. It has been proved in many provinces of China that burning the coal and clay mixture can produce F contamination.

Keywords coal, gangue, fluorine (F) in coals, fluorine (F) contamination

Introduction

As a trace element in coals, fluorine (F) is one of the elements easier tend to accumulate comparatively, and also a major element that could influence the environment and human body seriously. With the development of the utilization of the gangue, scientists also pay attention to the abnormal high content of the F in them, especially the clay minerals such as kaolinite, smectite, and illite. It is found that the abnormal high F content in the mudstone and the shale generating with coals seams in Guizhou, Hubei and Yunnan province of China [1]. There're thousands of people suffered from the F endemic from eating the high F content food, which are usually heat up by burning a kind of mixture made from local coal and claystone. Then, to keep track of the F in coal layer including its origin, motion and accumulation would be very significative.

1 Samples and analytical methods

We collected lots of samples from some big coalfields in China(Table 1), the sampling positions are in Yunnan Province (Xiaolong Tan, Lincang, Bangmai), Shandong Province (Tuocheng, Xiaqiao, Yangcun, Zaozhuang, Taozhuang, Shanjiacun, Tangzhuang, Kongzhuang, Zili), Shanxi Province (Huozhou, Antaibao), Henan Province (Xinmi, Yaomeng), Shenmu in Shanxi Province, the southern area of Anhui Province and so on. 62 samples are studied, including 51 coal samples (including 4 lignite ones), 5 fly ash samples, and 6 gangue (shale) ones. The analytical work is taken by the professional institute of Changchun University of Sciences and Technology. They adopt the method of ion-selective electrode with apparatus of PHS-3C. The following dates are the content of F in these coals and gangue samples.

In general, the method of F for analyzing samples is ion-selective electrode means, but it wouldn't be always accurate owing to the different pretreatment methods. The common pretreatment methods, for example, the oxygenating combustion, the thermal dissolution, the high temperature alkaline fusion(fritting

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law), the wet distillation, low tem-perature cineration and so on, are not always perfect. The F measurement technology has been specially discussed by Mingdong Cheng, Baoshan Cheng and others [2–5]. The first issue discussed on the F in coals, which has been written by Godbeer, Martinez-Tarazona and others, is the inaccuracy caused by the analytical methods. As pointed out by Swaine, it is hard to estimate the scope and the average value of the content of F in coals on the basis of kinds of analytical results owing to the difference generated by diverse methods, which should be noted in the field of studying F element in geochemistry.

Table 1 The F content of samples by region

The description of the samples		The element content $W(F)/(10^{-6})$	The description of the samples		The element content $W(F)/(10^{-6})$
The position	The characteristics of the layer		The position	The characteristics of the layer	
Xiaolongtan	Slag in generating power(light)	105	Tuocheng	Coal in Taiyuan formation 20	135
	Slag in generating power(black)	440	Xiaqiao	Coal in Taiyuan formation 17	65
	Fly ash in generating power(coarse)	255	Yangcun	Coal in Taiyuan formation 17	436
	Fly ash in generating power(fine)	280	Zaozhuang	Coal in Taiyuan formation 16	120
	Coal in stokehole in generating power	230	Taozhuang	Coal in Taiyuan formation 14	102
	Lignite(core)	121	Shanjia county	Coal in Taiyuan formation 14	110
	Lignite(the side of the basin)	135	Tangzhuang	Coal in Taiyuan formation 14	215
Bangmai	Crude coal	184	Kongzhuang	Coal in Shanxi formation 7	92
	Coal ash	4 800	Zili	Coal in Shanxi formation 2	120
	Pure blind coal	185	Zaozhuang	Coal in Shanxi formation 3	92
Shenmu	Lignite in Jura (glance coal)	1 100			
	Lignite in Jura (semilustrous coal)	175	Huozhou	Coal in Shanxi formation	1 050
	Lignite in Jura (durain)	529		Coal in Shanxi formation	995
	Lignite in Jura (semidull coal)	185		Coal in Shanxi formation	576
The southern in Anhui Province	The soleplate in Shanxi Formation	1 080		Coal in Shanxi formation	185
	Coal in Shanxi formation	135		Coal in Shanxi formation	255
	Coal in Shanxi formation	101		Coal in Shanxi formation	110
	Coal in Shanxi formation	148		Coal in Shanxi formation	102
	The coal false roof in the upper Shihezi formation	1 150		Coal in Shanxi formation	252
	Coal in upper Shihezi formation	255		Coal in Shanxi formation	74
	The top plate in Shanxi formation	1 385		Coal in Shanxi formation	128
	Coal in Shanxi formation	141			
The Yaomeng generating power	Coal in Shanxi formation	125	Antaibao	Coal in Shanxi formation	380
	Coal in Shanxi formation	255		Coal in Shanxi formation	349
	Coal in Shanxi formation	155		Coal baulk in Shanxi formation	456
	Coal in Shanxi formation	808		Coal in Shanxi formation	349
	Coal in upper Shihezi formation	285		Coal in Taiyuan formation	320
	Coal in upper Shihezi formation	474		Coal in Taiyuan formation	255
	Coal in upper Shihezi formation	320		Top plate mudstone in Taiyuan formation	1 280
	Coal in Taiyuan formation	325	Xinmi	Coal in Shanxi formation	110
	Coal in Taiyuan formation	1 470		Coal in Taiyuan formation	468
	Coal in Taiyuan formation	285			
	Baulk in Taiyuan formation	2 560			

As indicated by Zheng Baoshan, in the former investigation, there are some coal samples containing high F which are derived from the coal mine in the southwest of China, so the calculated $W_{(F)}$ average content value 248×10^{-6} may be higher based on that samples, the real one is predicted about 200×10^{-6}. In comparison, the arithmetic average value of $W_{(F)}$ in the coal of foreign countries is usually about 100×10^{-6}. The average value in the United States, Australia, and the former soviet is 98×10^{-6}, 110×10^{-6}, 100×10^{-6}. According to the available information at home and abroad, the majority $W_{(F)}$ average content in coals is between 100×10^{-6} and 150×10^{-6} [6, 7]. The F content above 300×10^{-6} belongs to the high F coal, but some samples may exceed 1 000×10^{-6}, the maximum abnormal value had been detected was 4 800×10^{-6} at present [8].

Table 2 shows the mass fraction distribution list of F in Chinese primary coalfields, and it can help us to have a overview about F content of Chinese coalfield.

Table 2 The mass fraction distribution list of F in Chinese primary coalfields

The region	The era of coal succession	The number of samples	Scale	Arithmetic average	Geometric mean	Standard deviation	Data sources
All over the country	C–N	581	20~300	140			Huang Wenhui (2001)
North China	C–P	180	20~300	130			Huang Wenhui (2001)
South China	P	367	20~300	141			Huang Wenhui (2001)
All over the country	J–K	14	20~280	167			Huang Wenhui (2001)
All over the country	E–N	20	20~280	178			Huang Wenhui (2001)
North China	C–P	8	100~3 600	1 200	728.64	1 141.43	Ren Deyi(1999)
North China	C2	5			510.17		Ren Deyi(1999)
North China	P1	3			1 319.82		Ren Deyi(1999)
All over the country		96	17~1 226	202			Qi Qingjie and so on(2000)
All over the country				217			Lu Baihe
All over the country		328	15~2 350	248			Zheng Baoshan and so on (1988)
All over the country		76	53~816	204			Li Wenhua (1986)

2 Data analysis and discussion

(1) The F content of gangue is higher by a factor of always ten than the average content of coals. We found that the F content of the gangue is above 1 000×10^{-6} in the soleplate，top layer and interlayer in the Shanxi formation in the southern Anhui Province, the mudstone in Ningwu Antaibao in Shanxi Province and the Taiyuan formation of Yaomeng generating power in Henan Province. There are many differences of the F contents in the coal of diverse positions of sampling, for example, the average F content of the coal in some ore lands in Shandong Province is 148.7×10^{-6}, whereas the one in Shanxi Province is 364.75×10^{-6}; Even in the same sampling position of the coal seam, the F contents are different. The F content of some coal samples in the Taiyuan formation in Yaomeng generation station in Henan Province amounts to 1 470×10^{-6}, whereas other average value only amount up to 300×10^{-6}, in which the F content in the gangue is up to 2 560×10^{-6}. The reason that the higher F content in gangue is related to the geological conditions forming the coal seams.

F mostly is non-metallic ion in minerals at nature which is the extremely electronegative in all the elements. It forms the electrovalent bond and covalent bond with other elements easily [8]. It also forms some minerals independently like fluorite. The F in rocks can be easily dissolved by the weathering process, part of them would go into the solution, others would be absorbed in and form some new minerals like the clay minerals or proceed isomorphous replacement with the mineral substance in the form of F^- and OH^-. F can be dissolved in the weathering zone in coincidence with the absorption, and then the formative gangue has higher content of the F [9].

Many authors (Francis 1954, correns 1956, Bradford 1957) deem that the F content in coal is associated with apatite. Based on our native studies, we think that there are two main sources of F in coals in normal geochemical conditions. One is the minerals containing the F in the terrigenous debris; the other is some potential sources of F participated in coal seams formation which should be rich in F. For example, the higher quantity of the F content of Longtan formation in the Southwest China may be related with the magma rocks.

Volcanic ash contains lots of the F. The basalt in the Mount Omei could be rich in F. They may be enriched in the assimilation of the coal-forming plant in the form of gaseity, or deposit in the swamp generating the coal bed in coincidence with the dead plant part in solid state. The high F in coal bed in Heshan coalfield in Guangxi Province results in the magma intrusion in stage of Yanshan brought in a large amount of F. The F content is high to 3 275×10^{-6} in the igneous rock in this section. Another example is that the F in the sulfurous iron ore layer enters into the hydrothermal fluid and comes up to the coal seam in the hydro-thermal process underground. The result is that the F content here is higher than the neighborhood coal seam. In conclusion, it would be very hard to form the high content F coal bed except for the other F sources [10, 11].

The potential accumulative state of the F in coals is that the fluorous minerals discovered in the coal seam are fluorite, fluorapatite, mica, illite, kaolinite, smectite, hornblende and so on. Although it is believed that the F in coals could present in different minerals, Finkelman points out it only has half credibility. The abundance of the F in coals is higher, its accumulative state also need further research. Now there are some new evidences showed that the F in coals can incorporate with the organic substance [12].

(2) It is found that the F in the cinder and fly ash is high. The average content of the F in coals of China is near 200×10^{-6}, similar to the coal of the world average value which lies between 100×10^{-6} and 250×10^{-6}. But the F content detected in the Bangmai coal ash is higher to 4 800×10^{-6}, we guesse it may contains fluorous minerals or not enough volatilization in the burning process, and it also could be assumed that the coal ashes absorbed a number of fluorous gas at the end of burning process. But in general, F belongs to the strong volatile elements which should not be upgraded in coal ashes. The intensity of separating out the F in coals is high to 94.5% in the form of gaseity in the burning course in the pulverized fuel fired boiler. The ratio is lower in the grate furnace and 80% F separates out in the gas state. Therefore, it is likely to exceed the value of the F in the cinder before burning. At present, more and more studies indicate that calcium oxide can absorb most of F steam; this technology would be used in practice in the future [13].

(3) Most studies indicate that the difference of the F in coals is huge by region of China, especially the southern China coalfield tends to have more F content, and this is the same outcomes with our studies.

Because of contenting some minerals in coal, the average value of the F in the coal of Shanxi formation of all samples is 297×10^{-6}, in Taiyuan formation is 296×10^{-6}, in upper Shihezi formation is 333×10^{-6}, in lignite is 374×10^{-6}. The Shanxi formation's component concentration is close to the Taiyuan formation's, whereas the upper Shihezi formation's component concentration is much higher than the former two. The F content in lignite is largerthan in other coals. It may be that large amount of solution containing F absorbed in the plant or deposited in the form of mineral, owing to the frequent volcano and hydrothermal activities. The geological activity tends to be slow at the later stage, wherefore, the F content is lower at the later period than at the former one.

The residents exploit the black shale in the Eopaleozoic strata as the fuel which is called "stone coal" in some region of China. "Stone coal" is not "coal" in the exact meaning. The widely prevailing F endemic in China is related with the resident's burning this kind of hazard fuel and the out-of-date life habits. According to the investigation, there are 96.2% residents catch dental F disease and 7.56% has F of bone disease where the F content amounts to 5.0×10^{-4} by process of burning this kind of fuel. In some places of Guizhou Province, this fuel is a mixture of fine clay and coal cinder. Therefore, the specialists suggest that the F content in the coal be out of the level 5.0×10^{-4}, whereas the average content of F in the gangue is high to 13.18×10^{-4}. At present the popular waste disposal scheme of the gangue is the constructional material and used to make the power, but the defluorinating process must be completed before using the gangue materials, to avoid F in the gangue entering into the atmosphere.

The synergy of the gaseous mixture HF and SO_2 imperiling the vegetable is far greater than the super-position of the two independent activities. The F entry into the atmosphere can be decreased by using the wet dust settle in the boiler equipment or using some kind of absorbent. According to the information of the generating station of the Shouyang mountain, about 90% gaseous fluoride in the fume transfers to the buck by water wash using the wet dust settler, part of the fluoride deposits in the transport process, there is about 14 mg/L F quantity when arriving the ash field. The F content in the dry ash is 665.8×10^{-6} after water flashing in the Wei River generating station, the content amounts to the 3 mg/L in the infiltration solution that will pollute the shallow groundwater [14].

3 Conclusions

We can conclude based on our studies and the analysis on the data about the F content in coals at home and abroad. The F concentrations in gangue especially in floor and roof rocks are higher than in coal; but it is found fly ashes from the electricity power plant have the richest F element. The process by coal burning could produce lots of F into the air. The F element in gangue generating in roof and floor bed could be removed away before sending to power plant by washing.

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