STUDY ON BORON BEHAVIOR IN PULVERIZED COAL FIRED PROCESS

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ABSTRACT

The partitioning behavior of boron in pulverized coal combustion is investigated to estimate boron concentration in waste water from power station. To clear the partitioning behavior of boron, it is important to understand the origin, chemical form of boron in coal and reaction of boron compound during combustion. Fundamental tests: specific gravity separation test, combustion test and leaching test were performed to determine property of boron in coal and control process of boron behavior during combustion. According to these results, boron in coal has a high affinity for organic matter in coal and exists in two forms: water-soluble and water-insoluble and the transfer of boron to fly ash during combustion is influenced by Ca and Mg in coal and boron compounds in fly ash also exist in two forms: water-soluble and water-insoluble.

KEY WORDS: Boron in coal, Maceral, Specific gravity separation test, Leaching test

INTRODUCTION

Recently, trace elements emission in waste water from a coal fired power plant, fluorine, boron and selenium, are regulated in Japan. The trouble is that some coals are over the regulation even if their species content is low in a coal. Many research have been published for the behavior of trace elements during combustion[1], however, the knowledge of boron behavior during combustion is very few. Goodarzi and Swaine described that boron in coal is released during combustion[2], and boron in coal is associated with organic matter and its content is influenced on environment of coal deposition[3]. In the combustion tests using simple drop tube furnace, Kambara et al.[4,5] reported that boron in coal is not released during early stage combustion, but almost all boron is released during final stage combustion. However, the partitioning of boron and coal quality impacts on it is unknown.

In this study, we focused on boron, one of the trace elements in coal, and conducted specific gravity separation tests, burning tests, and leaching tests to investigate how boron behaves during combustion. This paper reports the analysis of test results in terms of the distribution and chemical form of boron in coal as well as the transfer characteristics of boron onto fly ash and leaching characteristics of boron during the pulverized coal fired process.

COAL PROPERTIES AND BORON CONTENT

To examine the correlation between the boron content of coal and the coal properties, a total of 32 coal types used at coal fired power plants in Japan, including 18 types of Australian coal, 4 types of American coal, 4 types of Chinese coal, 4 types of South African coal, and 2 types of Indonesian coal were analyzed. The test results showed that the boron content ranged from 7 mg/kg to 245 mg/kg, with an average at 48 mg/kg. The average values for coal mining areas were 23 mg/kg for Australian coal, 73 mg/kg for American coal, 137 mg/kg for Chinese coal, 37 mg/kg for South African coal, and 90 mg/kg for Indonesian coal. American, Chinese, and Indonesian coals had relatively high boron content while Australian and South African coals had low boron content.

As a result of analysis on the correlation between the boron content and the coal properties, the former was found to have a negative correlation with the carbon content, fuel ratio, O/C, etc. that show the characteristics of organic matter in coal. As a result of analysis concerning inorganic matter, on the other hand, the boron content was found to have a negative correlation with the ash content except for some coal types. These facts are considered to indicate that the boron content has a relation with the coal rank and organic matter in coal.

EXPERIMENTAL

Coal Samples

Specific gravity separation tests and leaching tests were conducted to examine the distribution and chemical form of boron in coal. As the test samples for the specific gravity separation and leaching tests, ten coal types A to J were selected out of the aforementioned 32 coal types. Table 1 lists coal samples with their proximate analysis, ultimate analysis, boron contents, and maceral analysis. Coal types A and B were mined in Indonesia; C, D, and E in China; F and G in South Africa; and H, I, and J in Australia. The four of them, A, B, F, and H, were used as test samples for specific gravity separation tests and all of them as test samples for leaching tests.

Table1: Proximate, ultimate and boron analysis for 10 sample coals

Coal	Proximate Analysis[wt%,db]			Fuel ratio	Ultimate Analysis [wt%,daf]					B	Maceral Analysis [vol%]		
	Ash	V.M	F.C	[-]	C	H	N	S	O	[mg/kg,db]	Exinite	Vitrinite	Inertinite
A	3.3	49.4	47.4	0.96	74.17	5.43	1.16	0.18	19.02	128	3.2	92.6	4.2
B	2.2	49.1	48.7	0.99	72.66	5.45	1.04	0.12	20.71	78	1.2	96.0	2.8
C	19.8	36.9	43.3	1.17	74.77	5.37	1.75	0.66	17.15	245	1.2	97.0	1.8
D	7.7	34.8	57.5	1.65	83.13	5.18	1.50	0.47	9.72	92	3.2	59.6	37.2
E	10.3	32.5	57.3	1.76	82.89	5.16	1.48	0.57	9.90	65	5.6	48.0	46.4
F	14.4	28.5	57.0	2.00	83.13	5.50	2.13	0.45	8.79	21	0.8	42.4	56.8
G	13.5	27.6	58.9	2.14	83.26	4.60	2.03	0.58	9.52	31	1.0	34.6	64.4
H	15.1	32.9	51.9	1.58	83.13	5.50	2.13	0.45	8.79	30	2.4	80.4	17.2
I	11.5	28.0	60.5	2.16	83.62	4.88	1.77	0.94	8.79	13	1.2	52.4	46.4
J	14.7	31.4	53.9	1.72	83.40	5.14	2.04	0.63	8.79	17	2.4	58.4	39.2

Specific Gravity Separation Tests and Leaching Tests

About 10kg of a coal sample was coarsely ground into 5 mm or smaller particles and, as a representative sample for analysis, about 500 g was taken out and prepared. The remaining samples were sifted through 0.5 mm sieves and prepared into samples consisting of below-0.55 mm particles and 0.5-to-5 mm particles. For elution tests, representative samples were ground into below-150 mm particles and then prepared. To prepare specific gravity liquid, high-grade organic reagents were used in order to prevent the leaching of boron from coal. Toluene (0.868 g/ml in density) and carbon tetrachloride (1.598 g/ml in density) were used to prepare five fractions of specific gravity liquid: 1.2, 1.3, 1.4, 1.5, and 1.6. The below-0.5 mm samples and 0.5-to-5 mm samples were gravity-separated each using a specific gravity liquid. Then,

samples in the same specific gravity fraction were mixed together to prepare a sample for each of the specific gravity fractions. We calculated the recovery rate for each of these samples and analyzed each of the samples for specific gravity fractions. The analysis items included proximate analysis, ultimate analysis, boron contents, maceral analysis, ash composition analysis, and X-ray analysis of low-temperature ash.
In the leaching test, samples were ground into below-150 mm particles and mixed with pure water to attain a slurry concentration of 0.5% and then the mixture was stirred for four hours to conduct leaching. After leaching, the boron content of coal was measured to obtain the leaching rate of boron.

RESULT AND DISCUSSIN

Coal Recovery Rate

Figure 1 shows the relationships between specific gravity classes and coal recovery rates. Coal A had the highest coal recovery rate in a specific gravity fraction from 1.3 -1.4, marking about 70%. The coal recovery rate in a specific gravity fraction from 1.2 -1.4 was 98% or more, indicating that the coal was concentrated in a low specific gravity range. Coal C had the highest coal recovery rate in a specific gravity fraction from 1.3 -1.4, marking 58%. Like Coal A, the coal was concentrated in a low specific gravity range but a little higher in specific gravity fraction +1.6. Coal F had the highest coal recovery rate in a specific gravity fraction from 1.4 -1.5, indicating that the coal was concentrated in the highest specific gravity range of all the four coal types. Coal H had the highest coal recovery rate in a specific gravity fraction from 1.3 -1.4, indicating that the coal was concentrated at a relatively low specific gravity range. All the four coal types had a coal recovery rate of 1% or less in a specific gravity fraction -1.2. Particularly, Coals F and H indicated low values.

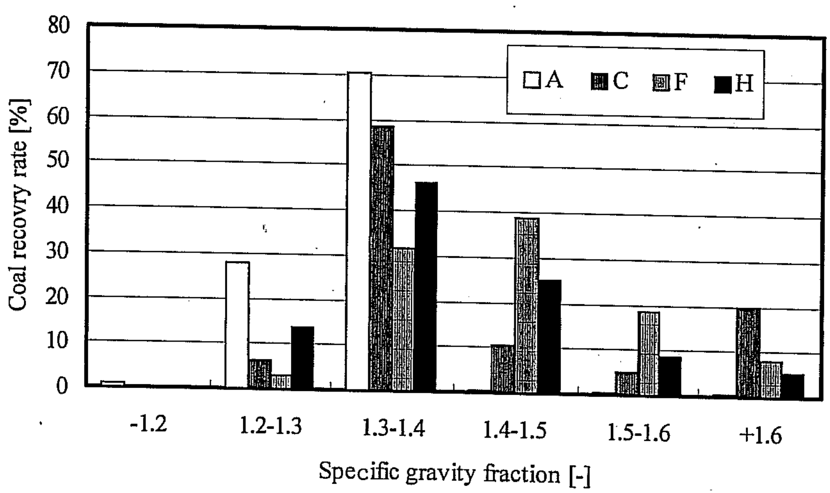

Fig.1: Relationship between specific gravity fraction and coal recovery rate

Boron Content

Figure 2 shows the relationships between specific gravity fractions and boron contents. Coal A has a higher boron content at a higher specific gravity, marking the highest value of 134 mg/kg in a specific gravity fraction from 1.3 -1.4 and lower values at higher specific gravities. The boron content is 33 mg/kg, an extremely low value, in a specific gravity fraction -1.2. Coal C has the highest boron content in a specific gravity fraction from 1.3 -1.4, marking 310 mg/kg and, like Coal A, has an extremely low boron content in a specific gravity fraction -1.2. Up to a specific gravity fraction from 1.4 -1.6, the boron content tends to decrease as the specific gravity increases, marking 161 mg/kg in specific gravity fraction +1.6. Coal F has the highest boron content of 37 mg/kg in a specific gravity fraction from 1.2 - 1.3 but has a lower boron content at higher specific gravity fractions. The boron content in a specific gravity fraction -1.2, unlike Coals A and B was not an extremely low value. Coal H has approximately the same tendency as Coal F.

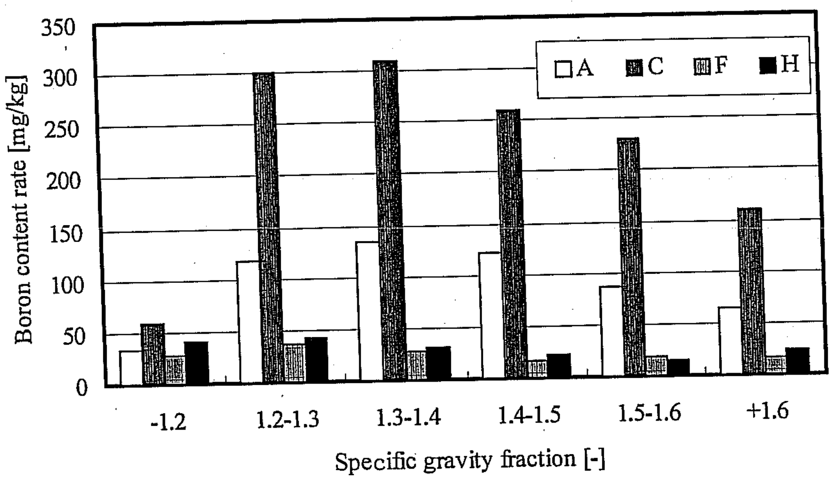

Figure 2: Relationship between specific gravity fraction and boron content

Relationship Between Boron Content and Coal Properties

To find out which property of coal boron has an affinity for, we examined the correlations between boron contents and analysis values/resultant parameters in each specific gravity class. Figure 3 shows the relationship between boron contents and atomic ratios H/C, in which H and C are the structural parameters of organic matter in coal, obtained from ultimate analysis.

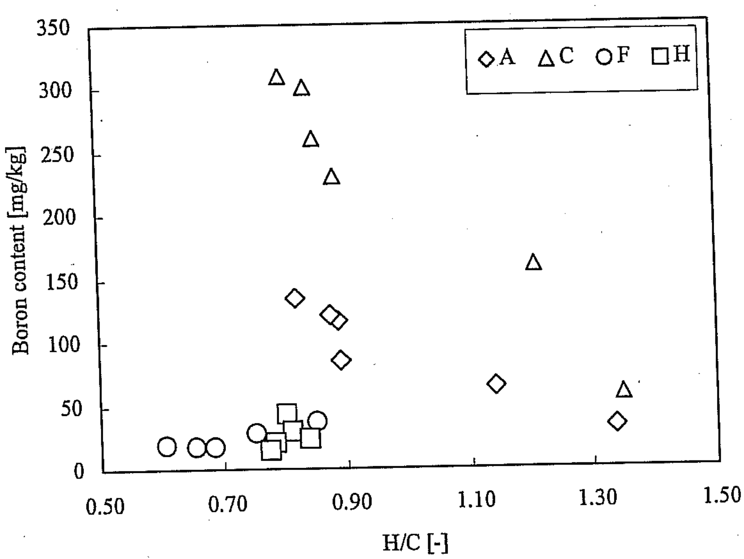

Figure 3:Relationship between boron content and H/C

It was found that the boron content of Coals A and C decreases as H/C increases, having a negative correlation. In contrast, the boron content of Coal F tends to increase somewhat as H/C increases, demonstrating a different tendency than Coals A and C. Coal H does not demonstrate a definite correlation. Coals A and C have a characteristic of an exceedingly low boron content in a specific gravity fraction -1.2 but indicate a fairly high H/C value for coal. Coals A and C with a low coal rank are considered to suggest some kind of a relationship between the organic matter in coal and the boron content. However, the sources of C and H may be carbonate minerals, hydrated minerals, etc. in coal. Therefore, H/C values in high specific gravity fractions with high ash contents may be influenced by these parameters.

In order to examine the correlation between boron content and maceral analysis value, the latter of which is used to selectively analyze coal organic matter. Maceral analysis, conducted by distinguishing coal organic matter from mineral matter through oil immersion observation by optical microscope, allows us to obtain an analysis value based only on coal organic matter, totally free from the influence of mineral matter. Coals A and C had a high vitrinite content of 88% or higher and low exinite and inertinite contents in a specific gravity fraction from 1.2 -1.6. Exinite is found to exist as sporinite in this fraction but exist in large quantity as resinite isolated from the coal component in a specific gravity fraction -1.2. These macerals were analyzed using a fluorescent filter under mercury light because they could not be distinguished from resins surrounding coal, in oil immersion observation under halogen light.

To examine the correlation between maceral and boron content, we needed to convert a maceral analysis value based on coal organic matter to a coal-based value to make it conform to the basis of boron content. Using low-temperature oxygen plasma at 200 degrees centigrade, we oxidized the gravity-separated coal and obtained the mineral matter content. All the four coal types were found to have a common tendency of higher mineral matter content at higher specific gravity, which is the same as for the mineral matter distribution of ordinary gravity-separated coals. Using this result, we converted the maceral analysis values to coal-based values and obtained the correlations between vitrinite contents and boron content. Figure 4 shows the result. As shown in the figure, all the four coal types were found to have a high positive correlation between vitrinite and boron content.

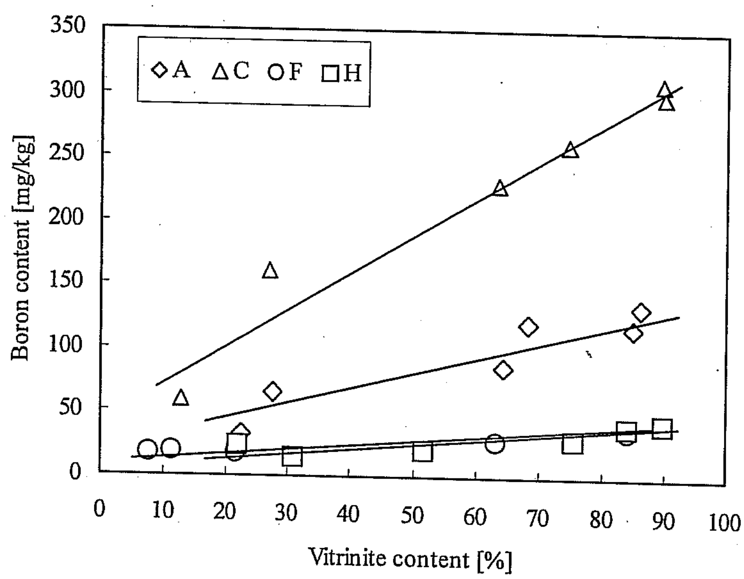

Figure4 :Relationship between boron content and vitrinite content

This indicates that boron has a high affinity for vitrinite. Therefore, vitrinite is presumed to have high concentration of boron. Coals A and C in a specific gravity fraction -1.2 have low mineral matter content and high resinite content, consequently low vitrinite content. Although the boron content of resinite cannot be identified, the extremely low boron content in this specific gravity fraction is assumed to indicate low boron content of resinite. In high specific gravity fractions, on the other hand, the mineral matter content increases and the vitrinite content decreases. The boron content also decreases in the same way, demonstrating that an increase in mineral matter gives influence to a decrease in the boron content. This is considered to indicate that the boron content of mineral matter is lower than that of vitrinite.

Boron, known as an essential element of plants, mostly exists in cell walls of plants in the present world and has a function of stabilizing cell walls, being ester-bonded with polysaccharide(6). This function has been confirmed for ferns. In consideration of these facts, it is highly likely that a high concentration of boron exists in vitrinite deriving from the woody parts of plants.

On the other hand, boron derived from mineral matter exists as tourmaline in illite, a clay mineral. It has been reported that the percentage of tourmaline in boron concentration in coal is as low as a few percent(7). The principal constituents of coal are silicate, ferric sulfide, and carbonate and the calculated boron contents of these minerals are only a few mg/kg. Therefore, the ratio of boron derived from mineral matter to the boron content of coal is considered to be significantly low.

Leaching Test

X-ray diffraction of low-temperature-ash may be a method to identify the chemical form of boron but cannot be easily adopted because the mineral matter has as low boron content as around 1%.

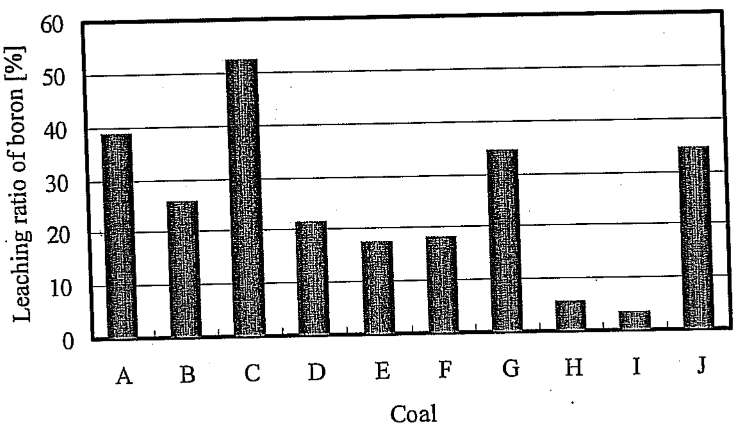

Figure5: Results of leaching test

Therefore, we examined the chemical form through leaching test. Figure 5 shows the boron leaching rates by coal type. All the coal types were found to undergo elution of boron, which ranged from 3% to 52%. Water-soluble boron compounds include sassolite and borate minerals, which are expected to be included in coals in these chemical forms.

Boron Recovery Rate and Leaching Characteristics of Fly Ash

To research the behavior of boron in pulverized coal fired process, combustion tests were conducted using coal types shown in Table 1 as test samples(8). According to this result, it was found that the boron recovery rate of fly ash is influenced not only by the Ca and Mg contents but also by their dispersions and forms. And then, by conducting leaching test on fly ash to research the boron leaching rates, it was found that the boron in coal ash consists of two forms: water-soluble and water-insoluble.

CONCLUSION

Boron in coal has a high affinity for organic matter in coal and exists in two forms: water-soluble and water-insoluble.

The transition of boron to fly ash during combustion is influenced by Ca and Mg in coal and boron compounds in fly ash also exist in two forms: water-soluble and water-insoluble.

In the future, we are going to identify boron compounds in coal and fly ash and investigate the transition mechanism of boron during combustion.

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