Coal Quality Impacts on Partitioning of Boron in Coal Fired Power Plants

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ABSTRACT
Boron content in raw coals, fly ash, and waste water from FGD is measured to understand effects of coal quality on partitioning of boron in pulverized coal fired power plant. It is important for coal users to predict accurately boron concentration in waste water from FGD because of severe regulation of boron emission in Japan. Boron recovery in the fly ash and boron concentration in the waste water has changed greatly in combustion for ten different coals.

Boron release behavior during combustion was examined for some different coals by using drop tube furnace. It is found that boron in the coal is almost all released finally. Therefore, it is seemed that gaseous boron is condensed on ash surface after combustion. XPS study on boron functional forms is performed for the fly ash and leached ash. It is clear that there are two types of boron functionality on the fly ash surface, and the boron form of low binding energy is readily soluble in water. The partitioning mechanism of boron is discussed.
KEYWORDS: Boron, Coal Combustion, Fly ash, Partitioning behavior, XPS

1. INTRODUCTION
In the future, coal will be the most important position as an alternative energy resources because of its huge reserves in comparison to the decreasing of petroleum and natural gas energy resources. However, as well known, the pollutant emissions from coal combustion processes may be anxious environmental and health effects. Actually, emission of some trace element from flue gas, fly ash and waste water is the most interest issue in Japanese power stations, because some light elements have also been found to have great impacts on the environment such as boron (B), selenium (Se) and arsenic (As).

In Japanese power station, most of the steaming coal has been imported from various coal producing countries such as Australia, China and Indonesia. Since it is required to burn a wide variety imported coals more than 100 different coals in a single boiler, evaluation of acceptability of such unfamiliar coals is one of the most critical issues.

In studies on trace elements behavior in coal utilization processes, the partitioning behavior of well-know volatiles such as mercury, arsenic and selenium are researched by previous reserchers[1-3]. Unfortunately, studies on boron behavior in coal combustion processes are insufficiency.

This paper describes behavior of boron during combustion, moreover, partitioning behavior to fly ash is discussed in the view of boron functionalities on fly ash surface which measured by X-ray photoelectron spectroscopy (XPS). Boron release is examined for 5 different coals by drop tube furnace.

2. EXPERIMENTAL CONDITION AND SAMPLES

2.1 Coal samples

Twelve coals and there fly ashes from a pulverized coal fired power plant were used for boron partitioning studies. Table1 shows coal properties of sample coals which come from Australia, Indonesia (coal A and G) and China (coal L). Its boron concentrations are 24 - 114 mg/kg-coal on a dry basis. Indonesian coals are rich in boron. These coal samples are used for drop tube furnace (DTF) tests to understand boron release during combustion.

Figure 1 shows boron content for 12 coals and their fly ashes. After combustion, fly ash is enriched boron. Boron recovery of their fly ashes was 10 – 62 %.

Table 1 Coal samples analysis

Coal	Proximate analysis, wt%				FR	B
	Mois.	Ash	VM	FC		mg/kg-coal
A	7.1	7.4	43.2	42.3	0.98	114
B	3.8	15.2	30.8	50.2	1.63	40
C	4.3	10.8	30.4	54.5	1.79	43
D	2.4	14.4	26.8	56.4	2.10	43
E	2.5	14.0	30.6	52.9	1.73	42
F	2.6	15.0	26.4	56.0	2.12	18
G	4.9	7.1	41.8	46.2	1.11	109
H	2.6	17.3	27.0	53.1	1.97	24
I	2.8	12.5	33.9	50.8	1.50	36
J	2.0	12.6	35.0	50.4	1.44	32
K	4.2	11.1	32.4	52.3	1.61	42
L	2.6	15.2	33.1	49.1	1.48	50

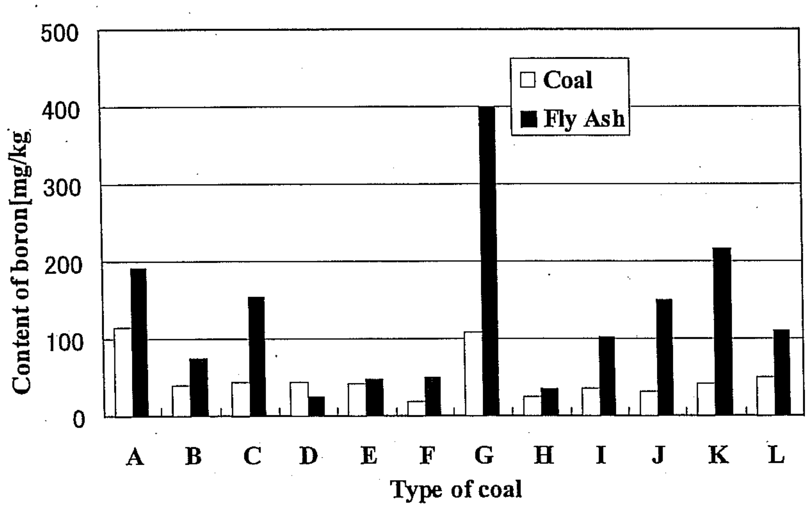

Fig. 1 Boron content of raw coals and their fly ashes

2.2 Combustion test

A drop tube furnace (42mm diameter and 1150mm length) was employed to obtain char burnout and boron conversion during combustion. The pulverized coal feed rates were controlled at 5g/hr and oxygen contents of flue gas were kept at 3.0% at 1500C. This DTF has nine sampling ports, SP1 to SP9, every 125mm along with furnace wall for gas and char sampling during combustion. Collected some char samples were analyzed carbon content, ash content and boron content. Boron release rate was calculated by ash trace method. Combustion tests were performed for typical three coal samples.

2.3 XPS measurements

To determine boron functionalities on fly ash surface, X-ray photoelectron spectroscopy measurements are performed for 16 chemical reagents and fly ashes. Binding energy of boron 1s, 178 – 197 eV, are scanned for fly ash samples under 200 W of MgK_{α} source. Obtained boron spectrum is corrected binding energy of Si 1s.

3. RESULTS AND DISCUSSION

3.1 Boron conversion

Figure 2 shows relation between carbon conversion and boron conversion for coal A, B and C in DTF combustion test. It is found that boron in coal is released rater than carbon conversion for all coals. Finally, more than 90% of boron is released at final stage of combustion. Boron release behavior is expected that boron structure in coal may exist as organic compound. Released boron in combustion will condense on fly ash surface at low temperature zone after combustion.

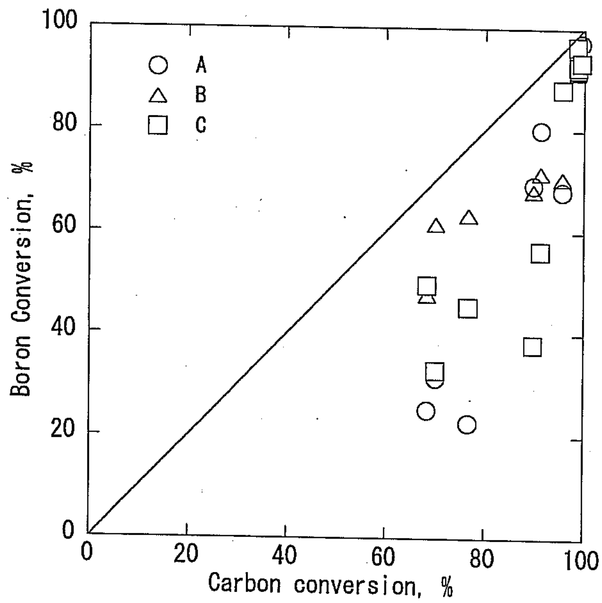

Fig. 2 Variation of boron conversion during combustion for three coals

3.2 Binding energy of various model compounds

Figure 3 shows binding energy of various model compounds in XPS measurement. This analysis was performed to determine boron functionalities on fly ash surface. Binding energy of boron compounds is between 186 eV and 193 eV, and most of the compounds are observed within 190 eV - 192 eV.

3.3 Boron spectra of fly ashes

Figure 4 indicates XPS spectra of boron for two kinds of fly ashes. In both Fig. 4(a) and Fig. 4(b), main peak are observed at near 193.5 eV. However this main peak is not boron, because this peak is always observed even boron poor samples. Peak of 193.5 eV is determined as phosphorus.

Boron functionalities are characterized at 185 eV and 188 eV. The peak of 188 eV is estimate AlB_2 from Figure 3, but another peak position is not found in Figure 3. Therefore, we tried to determine boron functionality at 185 eV by leaching test and thier XPS analysis.

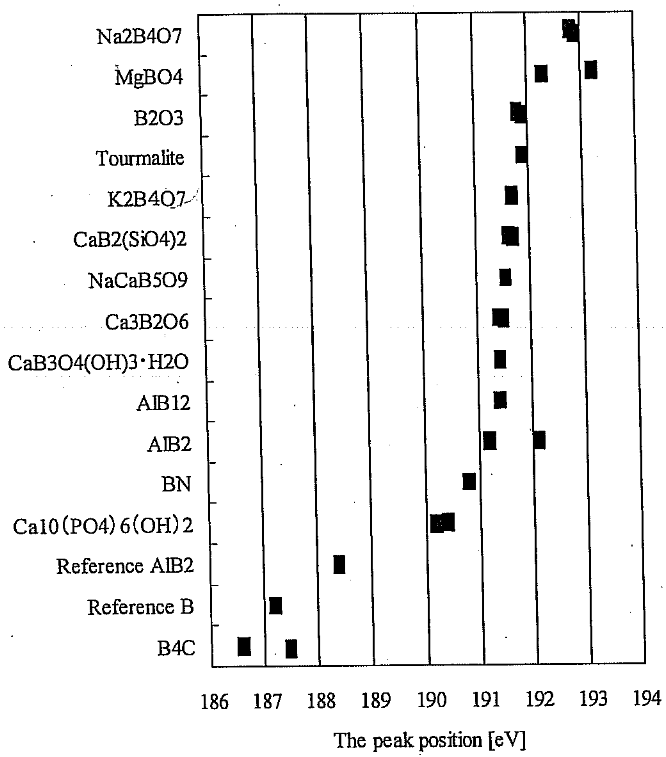

Fig. 3 Binding energy of various model compounds

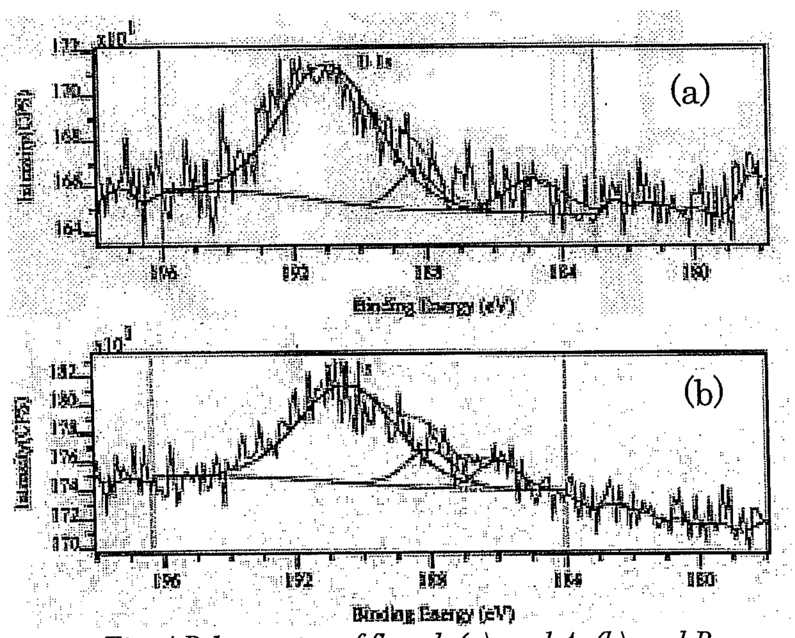

Fig. 4 B 1s spectra of fly ash (a) coal A, (b) coal B

3.4 Boron functionalities

Figure 5 shows leaching test procedure to measure variation of boron functionalities by XPS. 5 samples that leached for 0.5 h, 1.0 h, 2.0 h, 3.0 h and 4.0 h are prepared for fly ash A and B.

Figure 6 shows variation of boron leaching rate with leaching time. It is found that fly ash A is leached almost all boron at 4.0 h, but boron of fly ash B is leached only 40%. It is indicated that boron functionalities on fly ash surface have some types which are water-soluble boron type and wate-insoulble boron type.

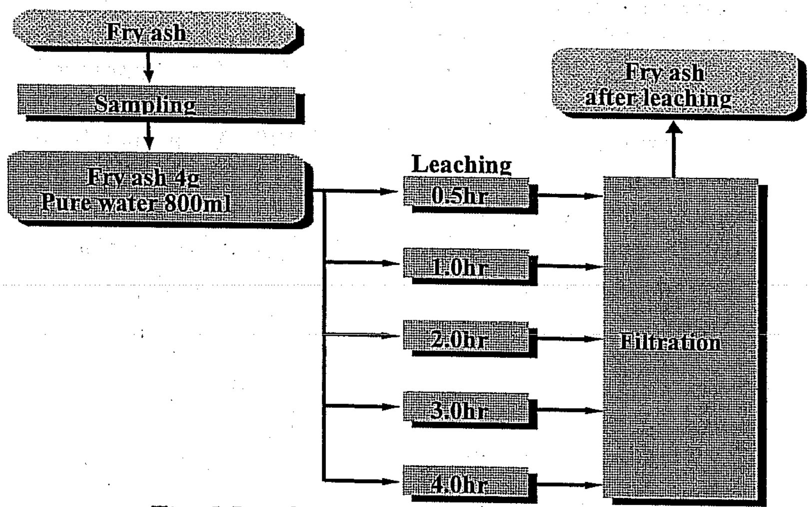

Fig. 5 Leaching test procedure of fly ashes

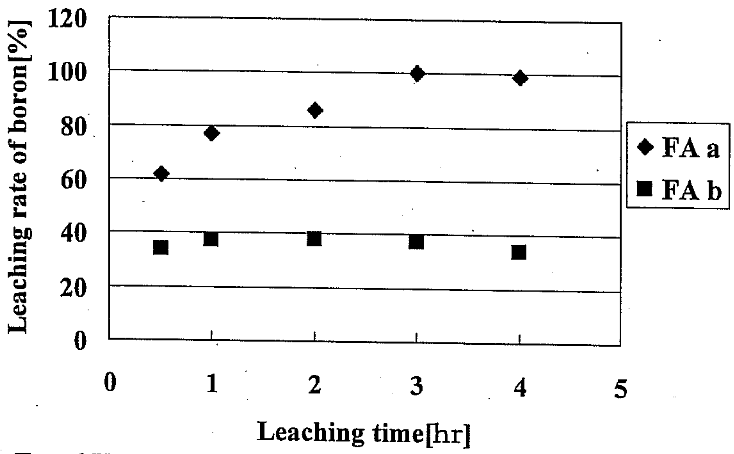

Fig. 6 Variation of boron leaching rate with leaching time

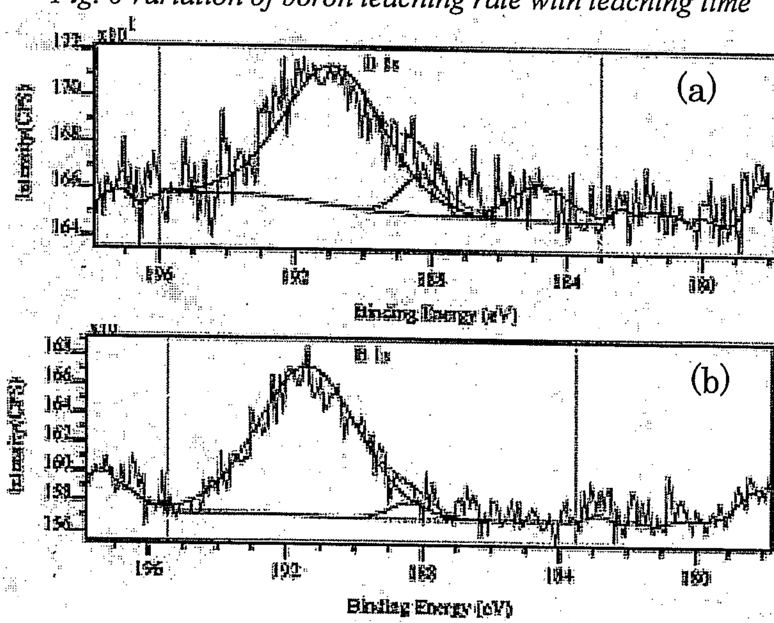

Fig. 7 XPS spectra of (a) before leaching test, and (b) after leaching test

To determine boron functionalities, leaching tested samples were analyzed by XPS. Figure 7(a) and (b) are XPS spectra of fly ash A and after leaching test, respectively. As mentioned above, two boron functionalities are observed in fly ash A (Fig.7a), however, leaching tested fly ash indicates only one peak at 188 eV. The peak of 185 eV is disappeared by leaching test. This means that the peak of 185 eV is soluble boron, on the other hand, the peak of 188 eV is insoluble boron that is estimated AlB_2. The peak of 185 eV can not be decided its boron functionality because model compounds have not that peak as shown in Fig.3.

Typical boron compound in combustion process and soluble compound is estimated boric acid. Boric acid may be formed easily on fly ash surface. We concluded that boron in gas phase during combustion is condensate as AlB_2 and boric acid on fly ash surface after combustion zone.

4. CONCLUSION

Boron release behavior during combustion was examined for some different coals by using drop tube furnace. It is found that boron in the coal is almost all released at final combustion stage. Therefore, it is seemed that boron in gas phase is condensed on fly ash surface after combustion. XPS study on boron functional forms is performed for the fly ash and leaching tested fly ash. It is seemed that there are two types of boron functionality on the fly ash surface. One is AlB2 that have insoluble characteristics, and another is boric acid that has soluble characteristics.

5. REFERENCES

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