THE PARTITIONING BEHAVIOR OF BORON IN A COAL FIRED POWER PLANT

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Introduction

Boron is an environmental harmful element because high boron concentrations give toxic effects on land plants[1]. American Environmental Protection Agency and the Australian National Pollution Inventory have been considered that boron is one of major concern elements. In Japan, boron concentration in waste water discharging to sea, namely, boron concentration in waste water from wet flue gas desulfurzation system in coal fired power plants have been regulated less than 230 ppm since 2002. Japanese power generation companies have accepted boron regulation easily because the regulation seemed a low hurdle. However, in fact, boron concentration in the waste water has been over the regulation for substantial coals used. Therefore, the partitioning behavior of boron in pulverized coal fired processes is an interest issue for Japanese coal users. In addition, in Japanese commercial boilers, most of the thermal coal has been imported from various coal producing countries such as Australia, China and Indonesia. More than 30 different coals have been used in a single boiler. Coal quality impacts on boron partitioning behavior are also required to evaluate acceptability of boron concentration in the waste water as a critical issue.

In pulverized coal combustion processes, boron has the common property of Group II and III[2]. Group II and III elements are not incorporated into the bottom ash. Therefore, it is estimated that a part of volatilized boron during combustion is condensed on fly ash after combustion, and the other boron escape to flue gas and/or are soluble in the water in wet FGD system. Consequently, investigating boron concentration in fly ash and the waste water from commercial plants for various coals is required to understand the boron partitioning behavior in the coal fired plants.

Boyd[3] reviewed previous studies on the boron partitioning behavior during coal combustion, and concluded that boron present in coal as tourmaline is retained in the ash from an original experiment. However, the boron partitioning behavior is not clear quantitatively.

This paper describes the boron partitioning behavior for twelve different coals in a 1000 MWe pulverized coal fired power plant. To explain the behavior and coal quality impacts, boron release behavior and boron functionalities are investigated by DTF combustion tests and X-ray photoelectron spectroscopy (XPS) measurements.

Experimental

Samples Twelve different raw coal samples used in a Japanese pulverized coal fired power plant (1000 MWe), there fly ashes from a electrostatic precipitator, and waste water from wet FGD system when combusted a individual coal are collected. Boron content in all samples is measured by an atomic absorption spectrometry. Table 1 shows coal properties of raw coals that imported from Indonesia (coal A and G), China (coal L), and Australia (other coal). Its boron concentrations indicate 18 - 114 mg/kg-coal on a dry basis. Indonesian coals having low fuel ratio contain high boron content compare to the other coal. As most coals have boron concentrations between 5 and 400 ppm[4], coals used in this research are recognized relatively intermediate concentration.

Table 1. Proximate analysis and boron content for 12 raw coals

Coal	Proximate analysis, wt%, ad				FR	B content
	Mois.	Ash	VM	FC		mg/kg, db
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

DTF tests A drop tube furnace (42mm diameter and 1150mm long) is employed to obtain relation between char burnout and boron release during combustion. Sieved pulverized coal particles (-200+300 mesh) are fed at 5g/hr. Oxygen concentration of combustion air is controlled at 3.0 % under temperature of 900, 1100, and 1300 degree C. The DTF has nine sampling ports every 125 mm along with furnace wall to collect gas and particles during combustion. In this study, carbon content, ash content and boron content in collected char samples are analyzed. Fraction of boron release is calculated by ash trace method. Combustion tests are performed for three coal samples (Coal A, B and C).

XPS measurements To determine boron functionalities on fly ash surface after combustion, X-ray photoelectron spectroscopy measurements are performed for fly ashes and their leaching samples. Binding energy of boron 1s, 178 – 197 eV, is scanned under 200 W of MgKα source. Obtained boron spectrum is corrected binding energy of Si 1s.

Results and Discussion

Boron partitioning behavior Figure 1 shows the boron partitioning behavior on fly ash from ESP No.1 hopper and waste water from wet FGD. It is found that between 9 and 62 % of the boron present in raw coals is distributed to fly ash. All of the rest of boron in raw coals, from 12 % to 83 %, is seemed to detect as soluble boron in waste water, except coal A and G from Indonesia.

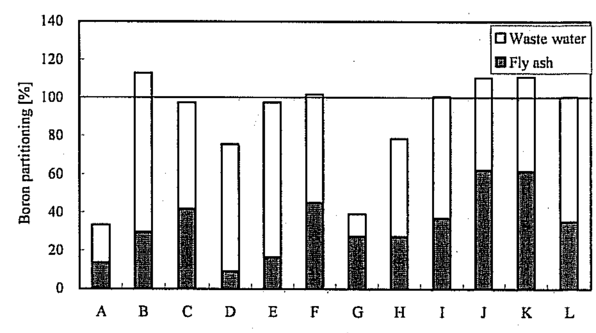

Figure 1. Boron partitioning on fly ash and waste water from a wet FGD system for a 1000 MWe pf. combustion power plant.

Clark et al.[5] indicated that high boron concentrations have been found in fly ash from pulverized coal combustion compared to bottom ash or FGD waste. However, it is clear that waste water contains high concentration of boron in coal combustion processes using wet FGD. It is important for elucidation of the boron partitioning to know boron release behavior during combustion and boron condense behavior on fly ash after combustion to elucidate.

Boron release during combustion Figure 2 shows relation between carbon conversion and boron release for coal A, B and C in DTF combustion tests. It is found that boron present in coal is released later than carbon conversion for all coals. More than 90% of boron is released at final stage of combustion.

Three mode of occurrence for boron in coal are commonly recognized as organically bound, fixed into illite, and in the mineral tourmaline. Ashing experiments[6] indicated that boron is generally retained at temperatures up to 815 degree C. Consequently, all boron species in coals may almost completely release during pulverized coal combustion. Boron species in gas phase during combustion will condense on fly ash surface at low temperature after combustion.

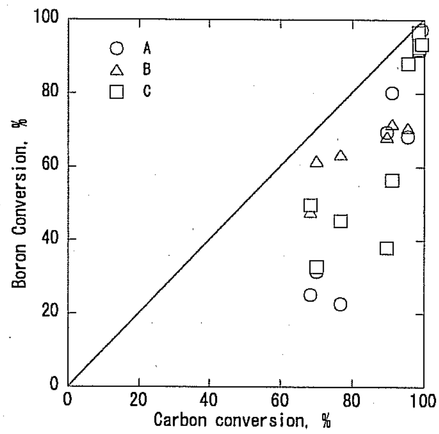

Figure 2. Relation between carbon conversion and boron release during combustion. (O_2=3 %, Tg=900, 1100, 1300 degree C)

XPS measurements Determination of boron functionalities on fly ash surface is important to understand boron partitioning into fly ash as shown Figure 1. Figure 3 shows binding energy of various model compounds of boron 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.

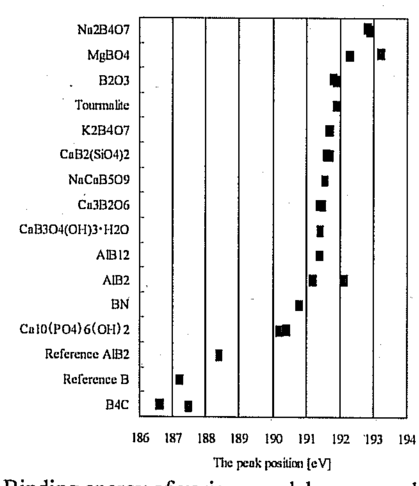

Figure 3. Binding energy of various model compounds of boron.

Figure 4 (a) indicates XPS spectra of boron 1s for fly ash of coal G having high boron content of 400 ppm. Main peak at 193.5 eV observing in the spectrum are not boron functionalities, which is determined as phosphorus by some studies. 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 their XPS analysis.

Figure 4 (b) shows XPS spectrum of fly ash from coal G after leaching test. As well known from comparing of (a) and (b), leached fly ash disappears the peak of 185 eV. This means that the peak of 185 eV is soluble boron. Unfortunately, it can not determine its boron functionality because model compounds have not the peak as shown in Figure 3. However, soluble boron compound can estimate easily as boric acid that is not measured by XPS to be a volatized compound. It is seemed that boron species in gas phase during combustion is condensate as boric acid on fly ash surface after combustion zone.

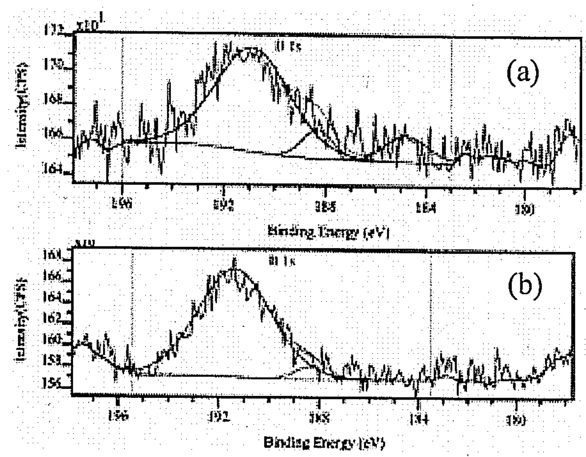

Figure 4. B 1s XPS spectra of (a) fly ash of coal G, and (b) its leaching ash. Binding energy of 193.5 eV is phosphorus.

Conclusions

The partitioning behavior of boron in a pulverized coal fired power plant of 1000 MWe was investigated by analyzed boron content in raw coals, fly ashes from ESP, waste water from wet FGD system. It is clear that waste water contains high concentration of boron in coal combustion processes using wet FGD.

Boron release behavior during combustion was examined for three different coals by drop tube furnace. It is found that boron in coals is almost all released at final stage of combustion.

XPS study on boron functional forms was performed for fly ash and leached fly ash. It is seemed that there are two types of boron functionality on the fly ash surface.

References

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