# Influence of Coal Properties and Combustion Conditions on Specific Surface Area of Fly Ash

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## 1. INTRODUCTION

In the utilization of fly ash as an admixture to concrete, it is important to know an adsorption amount for added surfactant such as air entraining agent beforehand. Generally, the surfactant adsorption amount is in proportion to a specific surface area, for example measured by B.E.T. method with nitrogen, and t is known that the specific surface area of fly ash depends on unburned carbon concentration in fly ash. However, it is shown that the specific surface area is different among coals with a strictly comparison, even if the unburned carbon concentration in fly ash is the same. In this study, a cause for its difference was clarified.

## 2. MEASURMENT ITEM

In this study, Methylene-Blue (for short, MB) adsorption amount, which correlates closely with the specific surface area, is always measured to judge the adaptability for the utilization of fly ash, since its measurement is very simple. Then, we evaluated MB data for many kinds of coal as an index which expresses the specific surface area. Unburned carbon concentration in fly ash and B.E.T specific surface area were used as related items with MB adsorption amount. Measuring methods are described as follows.

(1)MB adsorption amount

MB is pure blue stain. If the solution which dissolved MB is added to fly ash, a part of MB will be adsorbed by fly ash and the color of solution will be weak. The amount of MB adsorption is determined from the difference of color between the color of added solution and the color of the solution after adsorption. An absorption photometer is used to determine the quantity of color. MB concentration in solution is obtained from the calibration curve between MB concentration and the absorbance.

(2)Unburned carbon concentration in fly ash

Based on the JIS method, loss in quantity after burning at 815 degrees C in a muffle furnace for 1 hour is made into the weight of unburned carbon.

(3)B.E.T specific surface area

The specific surface area is measured by B.E.T method with Nitrogen gas. The weight of fly ash sample is about 0.3g.

## 3. INFLUENCE OF COAL PROPERTIES ON SPECIFIC SURFACE AREA OF FLY ASH

### 3.1 Relation between specific surface area and unburned carbon in fly ash

The adsorption of MB to fly ash is assumed to be a physical adsorption. Fig. 1 shows the relation between MB adsorption amount and B.E.T specific surface area with nine kinds of coal used at three power plant units. This shows an excellent proportion regardless of power plant unit or coal kind. Thus, it can be said that the MB adsorption amount will express the surface area of fly ash. The surface area of fly ash is a sum total of the surface area which is possessed by both the unburned carbon and the mineral matter in fly ash. Therefore, MB adsorption amount is thought to be a sum total of the adsorption amount to both the unburned carbon and the mineral matter as follows.

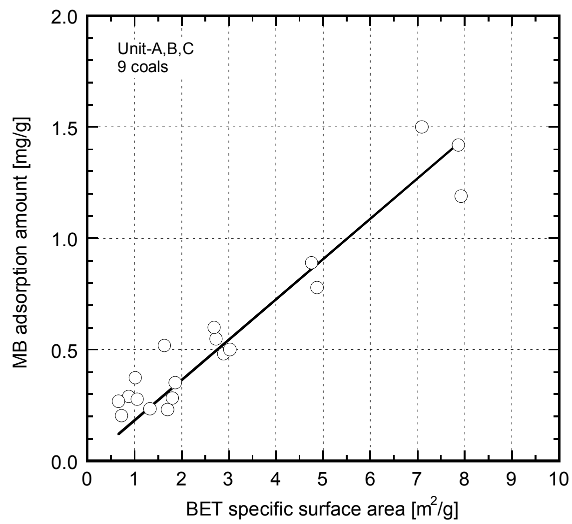



Fig.1 Relation between MB adsorption amount and BET specific surface area

MB = MBc x (Uc/100) + MBm x (100-Uc)/100 (Eq.1)

MB: MB adsorption amount to fly ash [mg/g-fly ash]
MBc: MB adsorption amount to unburned carbon [mg/g-unburned carbon]
MBm: MB adsorption amount to mineral matter [mg/g-mineral matter]
Uc: Unburned carbon concentration in fly ash [%]

In this study, the adsorption amount to unburned carbon and the adsorption amount to mineral matter were evaluated individually.

First, the fly ash was heated in a muffle furnace and the unburned carbon was removed. The fly ash except unburned carbon was considered to be a mineral matter. MB adsorption amount to unburned carbon was calculated by subtracting MB adsorption amount to mineral matter from MB adsorption amount to fly ash. We considered that the surface area of unburned carbon was influenced by combustion efficiency of combustible matter. By using coal ashes with different unburned carbon concentration in fly ash at the same kind of coal, the result of

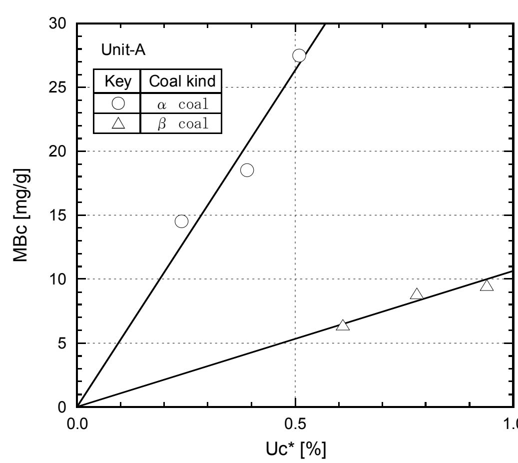



Fig.2 Relation between MBc and Uc*

examining the relation between MB adsorption amount to unburned carbon (MBc) and the unburned fraction of combustible matter (Uc*) is shown in Fig. 2. It was clarified that MBc was almost directly proportional to Uc*, and the proportion coefficient was different according to the coal kind.

MBc = a x Uc*  (Eq. 2)
a: Proportion coefficient [mg/(g-unburned carbon)•%]
Uc*: Unburned fraction of combustible matter [%]
Uc*= 100 x Uc/(100-Uc) x Mm/(100-Mm)
Mm: Mineral matter content in coal [%]

MB adsorption amount is expressed as a function of the unburned carbon concentration in fly ash (Uc) by substituting Eq. 2 to Eq. 1.

$$MB = a \times Uc^2 /(100-Uc) \times Mm / (100-Mm) + MBm \times (100-Uc)/100 \quad \text{(Eq. 3)}$$

Fig. 3 shows relations between MB adsorption amount and Uc. Solid lines obtained by using Eq. 3 expressed the actual increasing tendency of MB adsorption amount according the increase of Uc.

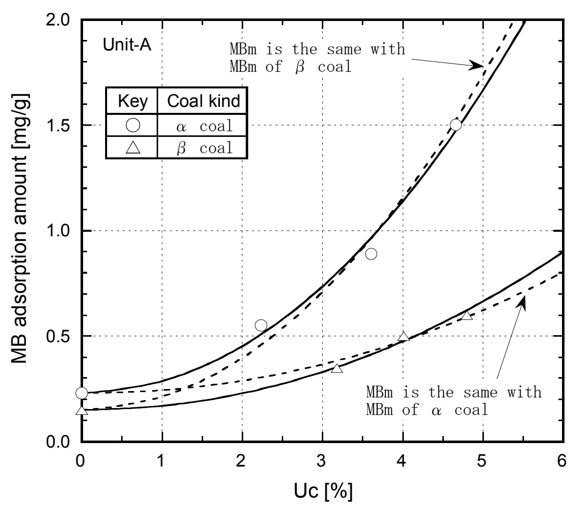


Fig.3 Relation between MB adsorption amount and Uc

3.2 Influence of coal properties on MB adsorption amount

Broken lines in Fig. 3 mean the tendency in case of shifting MB adsorption amount to the mineral matter (MBm). Values of MBm for alpha coal and beta coal were mutually replaced. Although there was some difference of MBm between alpha coal and beta coal, it was shown that the influence of MBm on the relation between MB adsorption amount and Uc was little. Then, MBm was considered to be constant.

MBm = b (const.)    (Eq. 4)

The dependency of proportion coefficient [a] on the coal kind was investigated with seven coals data of unit-D. MBm was assumed 0.12 for any kinds of coal. The proportion coefficient [a] was calculated by the similar method in Fig. 2. We used the fuel ratio (FR), which is the ratio of fixed carbon to volatile matter, as an index that shows the difference of coal kind. Fig.4 shows the relation between the calculated proportion coefficient [a] and the fuel ratio. It was clarified that the proportion coefficient [a] grew responding to a decrease of the fuel ratio. This means that the surface area of low fuel ratio coal is easier to become large than high fuel ratio coal.

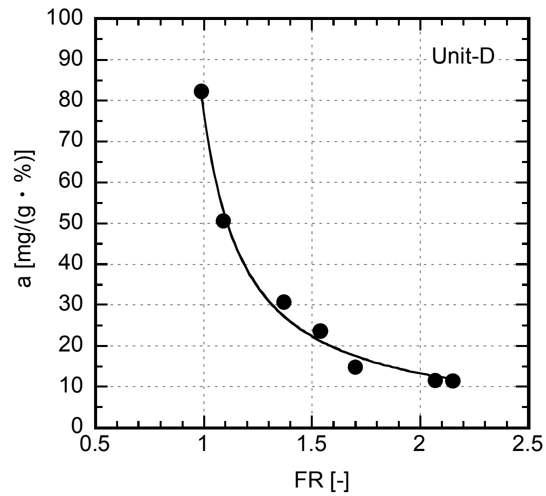


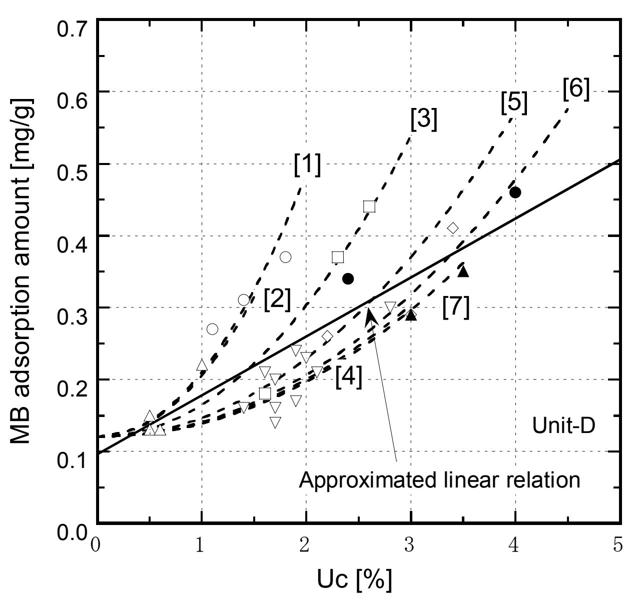
Fig.4 Relation between a and FR

$a = f(FR)$ (Eq. 5)
FR: Fuel ratio (Volatile matter content / Fixed carbon content)

In the case of unit-D, Eq.3 is turned to Eq. 6.

$$MB = f(FR) \times Uc^2 /(100-Uc) \times Mm /(100-Mm) + 0.12 \times (100-Uc)/100 \quad \text{(Eq. 6)}$$

Fig.5 shows the prediction result for seven kinds of coal with Eq. 6. The predicted line expressed the actual increasing tendency of MB adsorption amount according the increase of unburned carbon in fly ash accurately. This method improved the dispersion of predicting results caused by the difference of coal properties as compared with the method that the relation between MB adsorption amount and Uc was approximated to be linear. The adaptability of this method to actual utility boilers was verified by the investigation for four unit's data. The adaptability was confirmed for thirty kinds of coal.



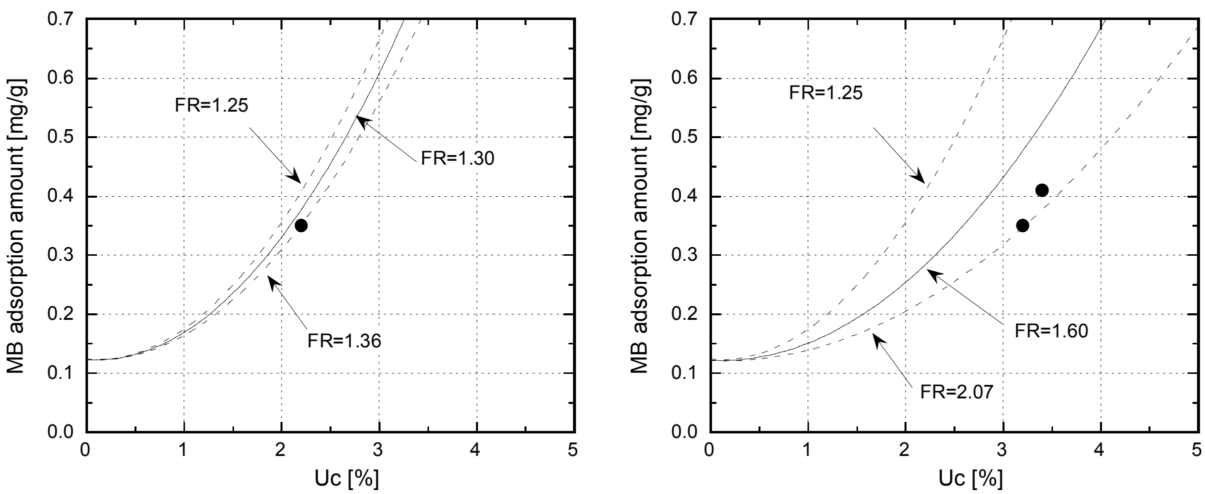

| Key | FR[-] | Mm[%] | Line No. |
|---|---|---|---|
| ○ | 0.99 | 10.0 | [1] |
| △ | 1.09 | 13.9 | [2] |
| □ | 1.37 | 14.3 | [3] |
| ▽ | 1.54 | 8.7 | [4] |
| ◇ | 1.70 | 13.5 | [5] |
| ● | 2.07 | 14.7 | [6] |
| ▲ | 2.15 | 14.0 | [7] |

Fig.5 Prediction results of relation between MB adsorption amount and Uc

## 4. INFLUENCE OF COMBUSTION CONDITION ON SPECIFIC SURFACE AREA

### 4.1 Blended coal combustion

In order to investigate the influence of coal blending on MB adsorption amount of fly ash, measurement data were compared with above-mentioned predicted line as shown in Fig.6. Broken lines show predicted relations at single coal comparison. A solid line shows the predicted line at blended coal combustion. FR and Mm at blended coal combustion were apparent values calculated by weighted average according to the blending rate. When the difference of FR between the two coals was small, data almost agreed with the predicted line. On the other hand, when the difference of fuel ratio between the two coals was large, data was close to the predicted line in higher fuel ratio coal. This indicates that the ratio of the unburned carbon originated from higher fuel ratio coal was increased at blended coal combustion.




(a) Difference of FR is small (b) Difference of FR is large

Fig.6 Influence of blending coal on MB adsorption amount

At blended coal combustion with coal 1 and coal 2, MBc was given in Eq. 7. It is thought that the generating ratio of unburned carbon from coal 1 and coal 2 was depended on the combustibility of coal. We considered a method which gave added weight to the generating ratio of unburned carbon. This method was on the basis of the relation that the unburned fraction of combustible matter increased in proportion to the fuel ratio at single coal combustion.

$$MBc = a_1 \times Uc^*_1 \times Uc_1/100 + a_2 \times Uc^*_2 \times Uc_2/100 \quad \text{(Eq. 7)}$$

$a_1$: proportion coefficient for coal 1 [mg/(g-unburned carbon)•%]
$a_2$: proportion coefficient for coal 2 [mg/(g-unburned carbon)•%]
$Uc^*_1$: Unburned fraction of combustible matter for coal 1 [%]
$Uc^*_2$: Unburned fraction of combustible matter for coal 2 [%]
$Uc_1$: Unburned carbon concentration in fly ash originated from coal 1 [%]
$Uc_2$: Unburned carbon concentration in fly ash originated from coal 2 [%]

$$Uc = Uc_1 + Uc_2 \quad \text{(Eq. 8)}$$

$$Uc^*_1 / Uc^*_2 = Uc_0{}^*_1 / Uc_0{}^*_2 = \text{const.} \quad \text{(Eq. 9)}$$

$Uc_0{}^*_1$: Standard unburned fraction of combustible matter for coal 1 [%]
$Uc_0{}^*_2$: Standard unburned fraction of combustible matter for coal 2 [%]

Standard unburned fractions of combustible matter for coal 1 and coal 2, which were expressed as $Uc_0{}^*_1$ and $Uc_0{}^*_2$, were determined from FR individually as shown in Fig. 7. It was assumed that the ratio of $Uc_0{}^*_1$ and $Uc_0{}^*_2$ was kept constant at blended coal combustion as shown in Eq.9. With this idea, unburned fractions of combustible matter at blended coal combustion, $Uc^*_1$ and $Uc^*_2$, for arbitrary unburned carbon concentration in fly ash was determined. By the determination of $Uc^*_1$ and $Uc^*_2$, it was possible to calculate $Uc_1$ and $Uc_2$. As results, Uc was obtained with Eq.8 and MB adsorption amount was calculated with Eq. 1, 4 and 9. Fig.8 shows the prediction results by using this idea. Under this improvement, the prediction accuracy in blended coal combustion became similar to that in single coal combustion at rated load.

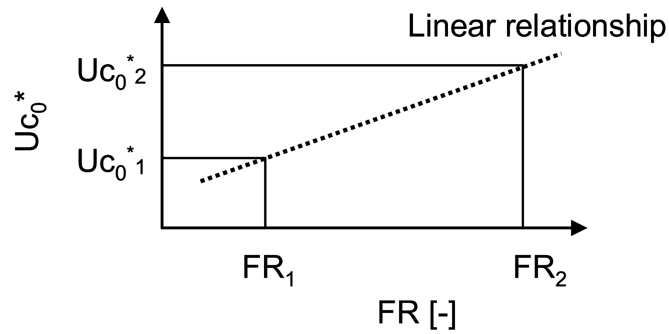



Fig.7 Determination method of $Uc_0^*$

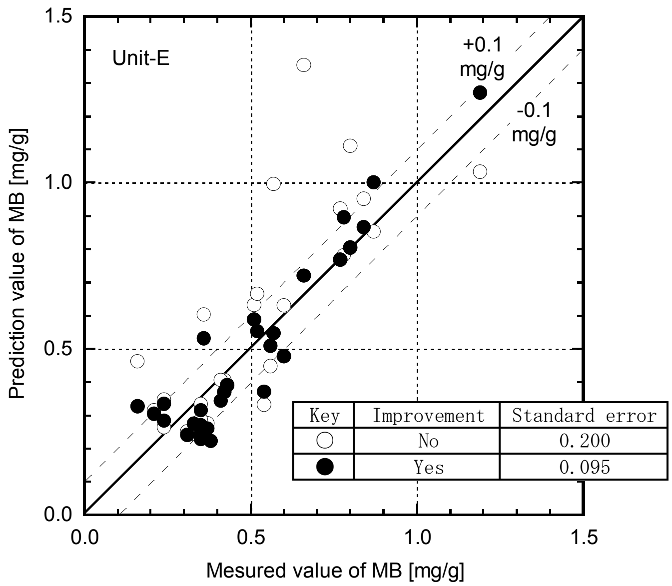



Fig.8 Comparison of prediction accuracy

4.2 Partial load combustion

MB adsorption amount at partial load combustion, which was every load condition, was almost the same with MB adsorption amount at rated load, as shown in Fig. 9. Therefore, the above-mentioned prediction method of MB adsorption amount could be applied to the evaluation of MB adsorption amount at partial load combustion.

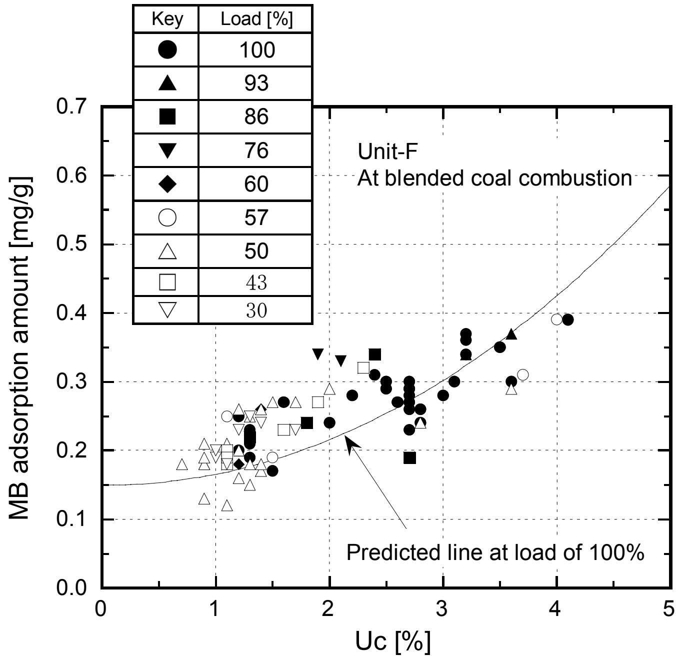



Fig.9 Relation between MB adsorption amount and Uc at partial load combustion

## 5. CONCLUSIONS

In this study, influences of coal properties and combustion conditions on the specific surface area of fly ash were evaluated by Methylene-Blue adsorption amount which correlates closely with the specific surface area. It was confirmed that the difference for MB adsorption amount to mineral matter among coals was not much. On the other hand, it was cleared that MB adsorption amount to unburned carbon increased with the decrease of the fuel ratio, which was defined as a ratio of the fixed carbon content to the volatile matter content. At the blended combustion of two coals, MB adsorption amount was close to that in higher fuel ratio coal, because the unburned carbon in higher fuel ratio coal generated more than that in lower fuel ratio coal. MB adsorption amount in partial load condition was almost the same with MB in rated load condition. On a basis of these result, the prediction method of MB adsorption amount to fly ash which could be applied to single coal combustion, blended coal combustion and partial load combustion, was established.

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