Calculation of Un-Fired Carbon Content of Circulating Fluidized Bed Combustion Ash

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The circulating fluidized bed combustion ash was studied to determine its un-fired carbon content. The differential scanning calorimetry and the thermal reaction process of circulating fluidized bed combustion ash includes 3 main stages: (a) escape of moisture and volatiles; (b) carbon oxidation and mineral decomposition; (c) continuing reaction. The thermal reaction process is greatly affected by the minerals in original ash. The typical loss-on-ignition method can not used for estimating the carbon content in circulating fluidized bed combustion ash because of the interference of mineral transformation in heat treatment. A method comparing the TG, DTG, DSC curve under nitrogen and oxygen atmosphere to determine carbon content of circulating fluidized bed combustion ash is improved.

Key Words: LOI, Unfired-carbon, TG, DTG, DSC, Circulating fluidized bed combustion ash.

INTRODUCTION

The un-fired carbon in fly ash is a product of incomplete combustion of firing boiler. For classic pulverized coal firing boiler, the un-fired carbon has been transferred to hard coke or semi-coke which has a porous structure and strong adsorption capacity. Generally, the content of un-fired carbon is used to evaluate the firing efficiency of boiler and seriously effect the comprehensive utilization of fly ash. For example, more water or additives would be needed when a high un-fired carbon fly ash is used as a blend of concrete. Nowadays, the un-fired carbon content has been accepted worldwide as an important parameter to appraise fly ash quality. The typical standard measuring process is LOI (loss-on-ignition) method which detecting the mass loss of fly ash after burn under 900-1000 ºC[1]. According to Chinese fly ash standard[2], when fly ash used to make concrete and mortar, the LOI of level 1 fly ash has to be lower than 5 %, level, 2 fly ash be lower than 8 % and level 3 fly ash be lower than 15 %. The LOI of fly ash used for cement blend must be lower than 8 %.

Circulating fluidized bed combustion (CFBC) ash is a solid waste coming from CFBC firing boiler (firing temperature from 800-900 ºC) which has a special SO_2 captured device. Compared with classic pulverized coal fly ash, the unfired carbon content should be lower because of longer residence time of coal particles in firing boiler. However, due to the decomposition reaction of calcium minerals (such as $CaCO_3$, $CaSO_3$ and $CaSO_4$) under LOI test process, higher LOI values are usually received and give much difficult to

determine the real un-fired carbon content[3-6]. Many new methods have been improved aiming to receive a more exacter un-fired carbon content in fly ash[7-9] while the study about CFBC ash is few. This paper focuses on using TG (thermogravimetry)-DSC (differential scanning calorimetry) technology to calculate the un-fired carbon content in CFBC ash. The results could improve present understanding of thermo stability of CFBC ash and give an accurate method to determine the un-fired carbon content.

EXPERIMENTAL

The two CFBC ash samples used in this study obtained from a 220 t/h Pyroflow CFBC boiler firing coal and high-sulphur petroleum coke and using limestone as the SO_2 sorbent in Power plant at the Sinopec Jinling Petrochemical Corporation state in Jiangsu province. The ratio of coal to coke was 60:40 (cal %). Nos. 1 and 2 were gained from forth and first electric field of electrostatic precipitator. The chemical composition and XRD patterns were showed in Table-1 and Fig. 1. As Table-1 (Fig. 1), compared with typical F-fly ash, the SiO_2 and Al_2O_3 of CFBC ash are lower when CaO and SO_3 are higher. The main mineral phases in CFBC ash include calcite, anhydrite, lime, portandite (only in No. 2), albite and quartz. Because the burning temperature of CFBC boiler is only 800-900 ºC which is much lower than classic coal firing boiler (1000-1500 ºC), it is difficult to find mullite, one of main minerals in classic F-fly ash, whose firing temperature is relatively higher (higher than 1000 ºC).

TABLE-1
CHEMICAL COMPOSITION OF CFBC ASH (%)

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	LOI [a]
1	14.37	9.42	1.38	19.00	0.90	0.13	0.21	0.57	14.10	30.6
2	22.35	13.86	2.24	31.00	1.84	0.58	0.35	0.61	7.62	16.7

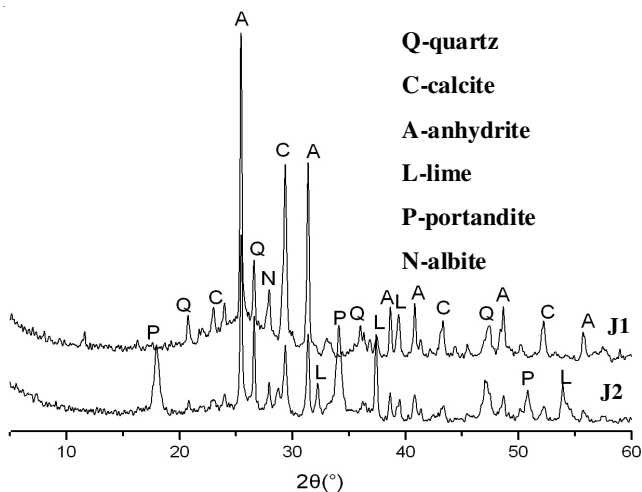[a]LOI loss on ignition at 960 ºC.

Fig. 1. X-Ray diffraction pattern of the CFBC ash, anhydrite (A), quartz (Q), calcite (C), lime (L), albite (N), portlandite (P)

The thermo quality of CFBC ash was test by differential scanning calorimetry equipment (DSC/NETZSCH STA-409). The temperature range is from room temperature to 1000 ºC. Temperature rise speed is 10 ºC/min. The atmospheres were nitrogen and oxygen. X-Ray diffraction patterns for the powder samples were taken on a Shimadzu XD-3A diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54056 Å).

RESULTS AND DISCUSSION

The results of differential scanning calorimetry analysis (TG curves, DTG curves and DSC curves) are shown in Figs. 2-5. It is suggested that there are 3 main reaction phase during the thermo process:
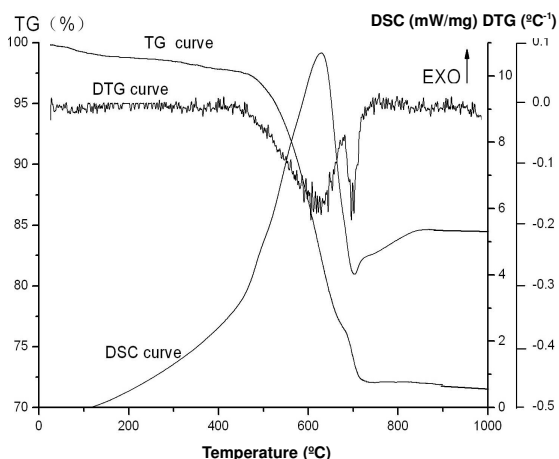

Fig. 2. TG, DTG and DSC curve of CFBC ash (sample No. 1, oxygen atmosphere)

Escape of moisture and volatiles: The temperature range of this stage is from room temperature to 400 ºC. The DTG curve keeps a constant during the stage which implies that the
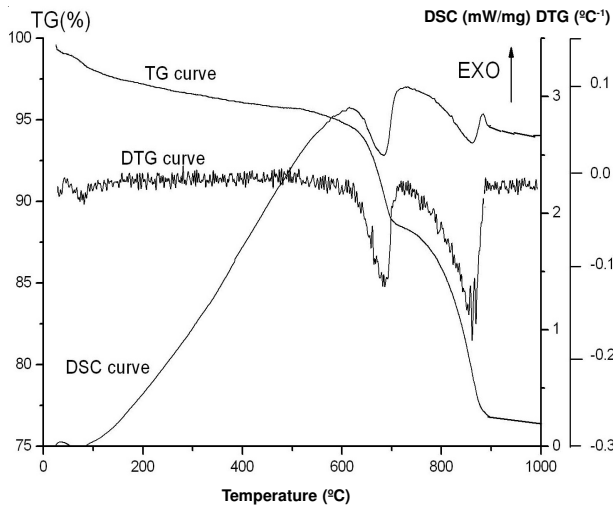

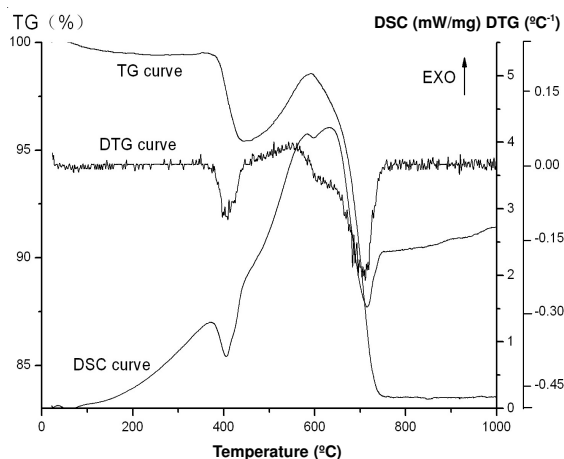Fig 3. TG, DTG and DSC curve of CFBC ash (sample No. 1, nitrogen atmosphere)

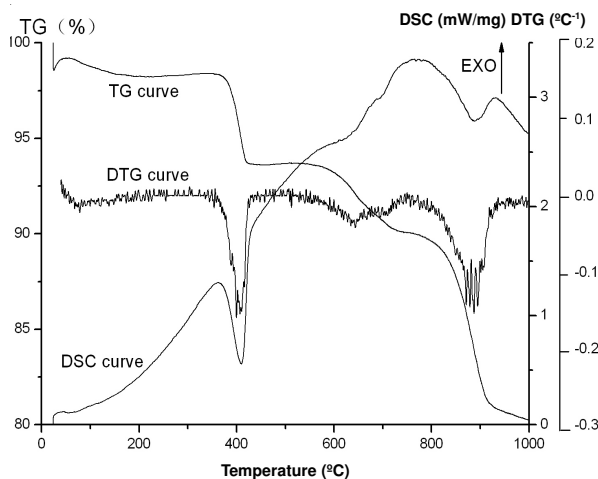Fig 4. TG, DTG and DSC curve of CFBC ash (sample No. 2, oxygen atmosphere)

Fig 5. TG, DTG and DSC curve of CFBC ash (sample No. 2, nitrogen atmosphere)

mass loss speed is relatively stable. There are no apparent heat evolution and adsorption peaks in DSC curves. The total mass loss of this stage is *ca.* 1-2 % because of the escaping of moisture and volatiles in original CFBC ash.

Carbon oxidation and mineral decomposition: The temperature range of this stage is 400-750 ºC. In the stage, obvious difference could be found between two CFBC ash samples. For No. 1 sample (no portandite), under oxygen atmosphere (Fig. 2), apparent mass loss (26.1 %) could be found from 475-700 ºC. Meanwhile, two overlap mass loss peaks appear in DTG curves and DSC curves present one strong heat adsorption peak and one weak heat evolution peak. All of these suggested that the mass loss during the 475-700 ºC devices from a heat evolution reaction (carbon oxidation) and a heat adsorption reaction (calcite decomposition). Under nitrogen atmosphere (Fig. 3), about only 6.4 % mass loss could be found because carbon can not be oxide and only calcite decomposition reaction occurs.

In case of sample No. 2 (contain portandite), under oxygen atmosphere (Fig. 4), the first mass loss (4.1 %) is the decomposition of portandite from 370-425 ºC. After this, a mass improving process is found in TG curve from 420-750 ºC. Meanwhile, a mass improving peak and two mass loss peaks are overlap in DTG curve. DSC curve also shows an overlap of a strong heat evolution peak (carbon oxidation) and two weak heat adsorption peaks (one is calcite decomposition). Because both the carbon oxidation and calcite decomposition reactions lead to the mass loss, it is proved that the reason of mass improving due to a heat adsorption combination reaction. Fig. 6 shows XRD pattern of No. 2 sample after heating at 600 ºC for 1 h. Compared with original sample, the peak of calcite become much stronger and even exceed the quartz and anhydrite which suggests that lots of calcite forms during the heating process. The XRD pattern implied that the reason leading to mass improving of sample No. 2 is the similar reaction as eqn. 1.
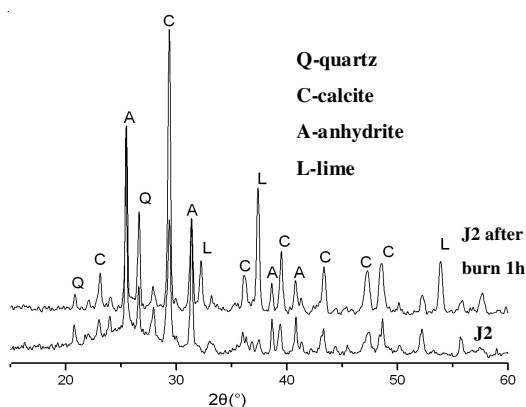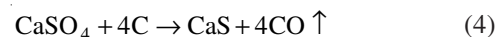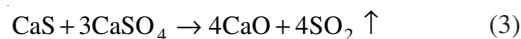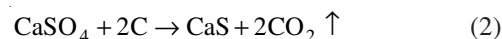

Fig. 6. X-Ray diffraction pattern of the CFBC ash and products after burn 1h under 600 ºC, anhydrite (A), quartz (Q), calcite (C), lime (L)

$$CaO + C + O_2 \rightarrow CaCO_3 \tag{1}$$

According to literatures[10,11], lime with higher porosity and specific surface area could be gained from decomposition reaction of portandite before the temperature reach 800 ºC. After this, the porosity and specific surface area would decrease again because of agglomeration action. As firing temperature

of CFBC is 800-900 ºC, the lime got from this situation could not possess higher porosity and specific surface area, which leading to the reaction as eqn. 1 would not occur in sample No. 1. However, the lime in the sample No. 2 is product from portandite decomposition, whose higher porosity and specific surface area make the reaction as eqn. 1 easy to occur. On the other hand, the mass loss of sample No. 2 from 420-750 ºC could also be explained by the decomposition of original calcite and the oxidation of originals carbon because the new calcite forming from the eqn. 1 would also decompose under 750 ºC. Under nitrogen atmosphere (Fig. 5), besides the portandite decomposition, only the carbon oxidation and mineral decomposition are observed from TG, DTG and DSC curve.

Continuing reaction: The time range of this stage is from 750-1000 ºC. In the stage, the carbon oxidation and calcite decomposition finished. Under oxygen atmosphere, no apparent changes were observed in TG, DTG and DSC curve. Under nitrogen atmosphere, because of the reaction from eqns. 2-5, mass loss results are found from TG and DTG curve meanwhile heat adsorption peak appears in DSC curve.

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \uparrow \tag{2}$$

$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2 \uparrow \tag{3}$$

$$CaSO_4 + 4C \rightarrow CaS + 4CO \uparrow \tag{4}$$

$$3CaS + CaSO_4 \rightarrow 4CaO + 4S \tag{5}$$

According to above analysis, the total loss from 400-750 ºC under oxygen atmosphere means the mass of original carbon and carbon dioxide from calcite decomposition. Under nitrogen atmosphere, the mass loss results only equal to the carbon dioxide from calcite decomposition. So, through calculating the distribution from eqn. 6, the real mass of original carbon could be gained.

$$M_C = M_1 - M_2 \tag{6}$$

Note: M_C means the mass of original carbon in CFBC ash. M_1 means the mass loss of carbon oxidation and calcite decomposition under oxygen atmosphere. M_2 means the mass loss of calcite decomposition under nitrogen atmosphere.

Table-3 shows the calculating result of TG curve by eqn. 6. As Table-2, for CFBC ash, there exits distinct deference between the real carbon content and LOI value. The LOI values are 55.3 and 96.4 % higher than real carbon content. These suggested again that the LOI can not be used for estimating the carbon content of CFBC ash.

Conclusion

Differential scanning calorimetry analysis is used for studying how to determine the unburned carbon content of Circulating fluidized bed combustion ash. There are three thermal stages during reaction process: escape of moisture and volatiles, carbon oxidation and mineral decomposition and continuing reaction stage. Because of the thermo reaction process is more complicated than classic F-fly ash, the LOI method can not be used to estimate the carbon content in circulating fluidized bed combustion ash. The real data of carbon content could be gained from analyzing the TG, DTG and DSC curve of CFBC ash under nitrogen and oxygen atmosphere.

No.	Atmosphere	Temperature range (°C)	Reasons	Mass loss (%)	Carbon content (%)	LOI (%)
		TABLE-2 ANALYSIS RESULTS OF TG-DSC CURVE				
1	Nitrogen	650-700	Calcite decomposition	6.4	19.7	30.6
1	Oxygen	475-700	Carbon oxidation and calcite decomposition	26.1		
2	Nitrogen	625-725	Calcite decomposition	3.5	8.3	16.7
2	Oxygen	475-700	Carbon oxidation and calcite decomposition	11.8		

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