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Physical and Chemical Prosperities Difference Between Pulverized Coal Boiler Fly Ash and Circulating Fluidized Bed Combustion Ash

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This paper focuses on different prosperities of PC fly ash and CFBC ash. The XRD and SEM/EDX have been applied. The results show that: CFBC ash contains more CaO and SO_3 than PC fly ash while the concentration of SiO_2 and Al_2O_3 is lower. CaO of CFBC ash and C-fly ash concentrate in crystalline phase and amorphous phase separately. The main mineralogy phases of CFBC ash is quartz, anhydrite, calcite, portlandite and albite but no mullite. No spherical microspheres could be observed in CFBC ash by SEM and these micro particles appear porous and irregular. Some crystalline particles including anhydrite and lime could also be found in CFBC ash by SEM.

Key Words: F-Fly ash, C-Fly ash, CFBC ash.

INTRODUCTION

Fly ash is the main solid waste coming from thermal power plant. Over 50 million tons of fly ash is generated annually in USA[1]. China produces about 45 million tons of fly ash in 2009, of which approximately 30 % is recycled and the remaining 70 % is landfilled or surface-impounded[2]. Disposal of such a huge quantity of fly ash poses a significant environmental problem all over the world. According to the type of boiler, fly ash could be classed into two types: PC (pulverized coal boiler) fly ash and CFBC (circulating fluidized bed combustion) ash. The technology of pulverized coal boiler has a long history and the typical property is high firing temperature (1000-1500 ºC). The comprehensive utilization field of pulverized coal fly ash is very extensive and significant quantities are being used in a range of applications and particularly as a substitute for cement in concrete[3], advanced geopolymer material[4], agricultural application[5]. Circulating fluidized bed (CFB) boiler is a new cleaning combustion technology, of which the combustion situation is different from pulverized coal boiler. Firstly, the combustion temperature of CFB boiler is only between 800-900 ºC. Secondly, in order to control the SO_2 emission, calcite is added to boiler as sorbent. The reaction process is following eqns. 1 and 2[6].

$$CaCO_3 = CaO + CO_2 \quad (1)$$

$$CaO + SO_3 = CaSO_4 \quad (2)$$

Thirdly, many low-quality fuels as garbage or petroleum coke could be fired in it. Hence, the physical and chemical property of CFBC ash is much different from classic PC fly ash and generally unsuitable for recycling in the traditional fields for PC fly ash. With the development of CFBC technology, CFBC ash has become another Chinese environmental problem. Utilization, technological and environmental impacts of CFBC ash of this kind requires a detailed knowledge of its physical and chemical properties including chemical composition, mineralogy and morphology. Although many literatures about characteristic and utilization of CFBC ash from boilers have been reported[7,8], related scientific literature concerning the difference between CFBC ash and typical PC fly ash is rare. This study aimed at an analysis of physical and chemical difference between PC fly ash and CFBC ash, the results could improve our understanding of CFBC ash properties and expand its recycle fields.

EXPERIMENTAL

Two samples of fly ash from PC boilers firing anthracite (F1 and F2), two samples of fly ash from PC boilers firing lignite (C1 and C2) and two samples from CFBC boilers co-firing coal and high-sulphur petroleumcoke (CF1 and CF2) are examined in this study. These samples are generated in 3 power plants located in 3 provinces of China PR (F1 and F2 from ShanDong, C1 and C2 from ShangHai, CF1 and CF2 from Jiangsu).

The mineral composition of the samples is determined by X-ray diffraction (XRD) using a X'TRA powder diffractometer with a graphite monochromator. The XRD patterns are collected at 4-60º 2θ using CuK_α radiation and scan velocity is 10º/min. Most SEM and EDX analysis is done using scanning electron microscope Mode LEO-1530VP Electron Microscopy equipped with an Oxford InCAX-300 Energy Dispersive X-ray analyzer. Other analysis is done using Scanning Electron Microscope Mode JEOL JSM6300.

RESULTS AND DISCUSSION

The results of chemical compositions are given in Table-1. All of PC fly ash samples contain 47-51 % SiO_2 and 27-32 % Al_2O_3. The Fe_2O_3 and CaO concentrations of C1 and C2 are about 2 to 3 times higher than F1 and F2 because of the different firing coal. CaO and SO_3 content of CF1 and CF_2 are much higher than F1 to C2 while SiO_2 and Al_2O_3 content (14-22 %, 9-13 %) are lower. CaO is one of important elements for fly ash utilization, which directly affect the properties of fly ash added cement and concrete[9]. Based on CaO content, PC fly ash could be classified into type C (high-calcium) fly ash (CaO > 10 %) and type F (low-calcium) fly ash (CaO < 10 %)[10]. More mineralogy phases could be observed when CaO content improving. As typical F-fly ash, main mineralogy phases of F1 and F2 are only quartz and mullite while C1 and C2 (C-fly ash) contain lime (f-CaO) besides these two (Fig. 1 and Table-2). Compared with CaO content in Table-1 (8.24 and 9 %), the f-CaO content of C1 and C2 are only 1.33 and 0.84 % (Fig. 2). These suggest that most of CaO exist in the amorphous phase of C1 and C2 which can not be observed in XRD patterns. On the other hand, the mineralogy of CF1 and CF2 are more abundant than PC fly ash, which including anhydrite, calcite, portlandite (only in CF2) and albite but no mullite (Fig. 1 and Table-2). It implies that all of CaO in CF1 and CF2 is obtained from crystalline phases, which is different from C1 and C2.

Scanning electron microscopic images of F2, C2 are given in Fig. 3. To be a typical F-fly ash, lots of spherical microspheres have been observed. More details about microsphere under a higher magnitude could be found in Fig. 3c. According to EDX results (Fig. 3d), the micro-composition of microspheres is 16.6 % Si, 13.3 % Al, 68.9 % O. Meanwhile, some smaller microsphere could be observed in the hole

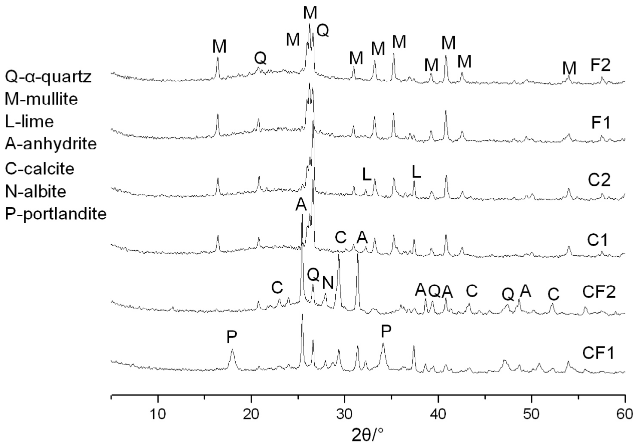

Fig. 1. XRD patterns of PC fly ash and CFBC ash

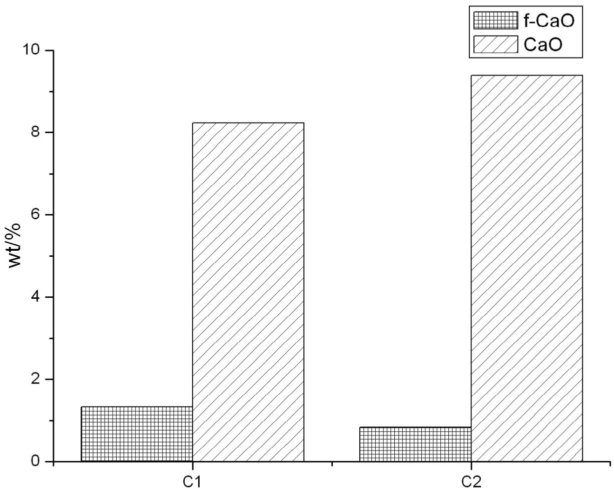

Fig. 2. Concentration of CaO and f-CaO in C1 and C2 samples

of bigger one. Compared with F2 sample, C2 also contain some spherical microspheres but with a coarse surface (Fig. 3b and e). With the magnification of the microscope being larger, there are lots of smaller nodules staying on the surface of

TABLE-1
CHEMICAL COMPOSITION OF FLY ASH SAMPLES (wt. %)

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	LOI [a]
F1	51.06	32.36	4.68	2.91	0.9	1	0.45	1.17	0.42	5
F2	50.97	30.65	4.68	3.09	0.95	1.06	0.47	1.13	0.3	6.6
C1	50.16	28.15	7.6	8.24	1.27	1.07	0.66	1.05	0.81	0.73
C2	47.98	27.2	8.01	9.4	1.35	1.05	0.74	1.03	0.68	0.8
CF1	22.35	13.86	2.24	31	1.84	0.58	0.35	0.61	7.62	18.73
CF2	14.37	9.42	1.38	19	0.9	0.13	0.21	0.57	14.1	39.52

[a]Loss on ignition (950 ºC).

TABLE-2
PEAK INTENSITIES OF MAJOR CRYSTALLINE PHASES IN XRD PATTERNS

Samples	Quartz	Mullite	Lime	Anhydrite	Calcite	Albite	Portlandite
	2θ = 26.6º	2θ = 26.2º	2θ = 37.4º	2θ = 25.5º	2θ = 29.4º	2θ = 27.9º	2θ = 34.1º
F1	1275	1575	–	–	–	–	–
F2	1242	1525	–	–	–	–	–
C1	2200	1192	150	–	–	–	–
C2	2075	1100	550	–	–	–	–
CF1	–	961	803	1664	593	653	898
CF2	–	783	213	3047	1813	339	–

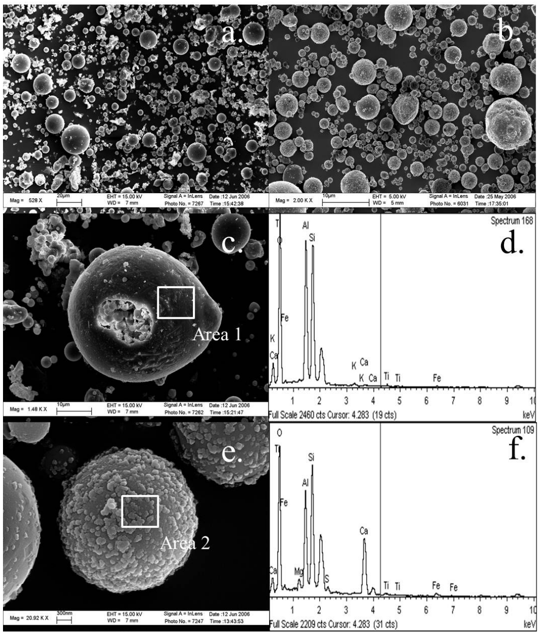

Fig. 3. SEM micrographs of PC fly ash (a and c. F2 sample, b and e. C2 sample, d. EDX results of areas 1, f. EDX results of areas 2)

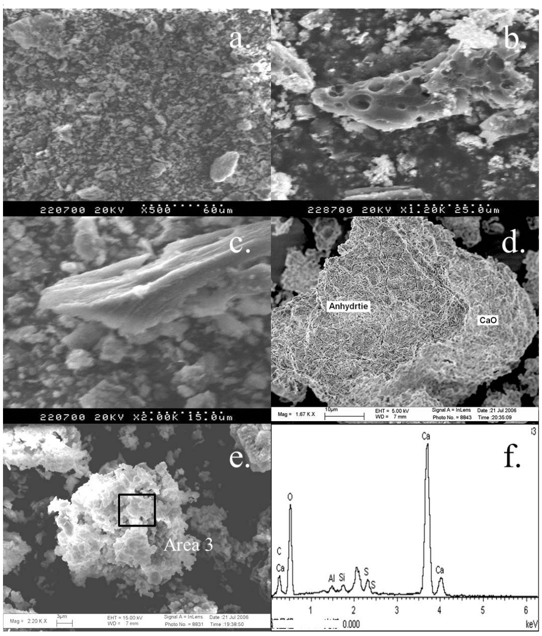

Fig. 4. SEM micrographs of CFBC ash (a, b and c. CF2 sample, d. anhydrite and lime, e. lime, f. EDX results of areas 3)

microspheres. Based on EDX (Fig. 3f), the calcium concentration (13.9 %) is much higher than F2 sample. It could affirm that the majority mineral of the nodules is amorphous phase containing calcium. For PC firing boiler, it is generally thought that the aluminum-silica clay material will melt to glass liquid drop and surface tension would make it to spherical shape after carbon is consumed[11]. In the stage, if the mineral containing much calcium, the calcium would make the liquid drop smaller. And then, the smaller drops would transfer to nodules with higher calcium concentration lying in the surface of microspheres. These should be the reason why most of CaO in C1 and C2 exist in the amorphous phase. Compared with PC fly ash, the CFBC ash contains little spherical microsphere and most of the particles appear porous and irregular. The main reason leading to these should be the lower firing temperature. For CFBC boiler, the firing temperature is only 800-900 ºC. The lower temperature can not make aluminum-silica clay material totally melt. So, the liquid drop can not form and the micro-particles still stay in the porous and irregular shape (Fig. 4a-c). By the utilizing of EDX analysis, some crystalline particles could be found. Fig. 4d shows an admixture with lime and anhydrite, the boundary between anhydrite and lime could be apparently observed. Fig. 4e and f show a lime crystalline with the composition as 49.1 % Ca and 50 % O. These are all the reaction products origin from calcite being added to adsorb SO_2. Because calcite is spurt into tail gas treating unit of CFBC firing boiler, the short residence time and lower temperature can not make calcium containing minerals to melt and react with aluminum-silica clay material as what happens in PC firing boiler. The calcium retains as crystalline phase which is identical with the results of XRD patterns.

Conclusion

The physical and chemical differences between PC fly ash and CFBC ash have been studied. The main composition of PC fly ash is SiO_2, Al_2O_3, Fe_2O_3 and CaO. Type C-fly ash contain higher Fe_2O_3 and CaO than F-fly ash. CFBC ash has a higher CaO and SO_3 concentration while SiO_2 and Al_2O_3 is lower. The main mineralogy phases of PC fly ash are quartz, mullite and f-CaO (only in type C) while the ones of CFBC ash contain quartz, anhydrite, calcite, portlandite and albite but no mullite. The micro particle of PC fly ash is aluminum-silica spherical microspheres. The C-fly ash microsphere has a coarse surface with small calcium-aluminum-silica nodules. The CFBC ash particles appear porous and irregular and some crystalline particles could be found. Most of CaO in C-fly ash exist in the amorphous phase while the one of CFBC ash in crystalline phase.

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