Characterization of Fly Ashes from Circulating Fluidized Bed Combustion (CFBC) Boilers Cofiring Coal and Petroleum Coke

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Received November 15, 2005. Revised Manuscript Received March 22, 2006

The chemistry, mineralogy, morphology, and particle size distribution were investigated in fly ashes from the burning of Datong (ShanXi, China) bituminous coal and the cofiring of Mideast high-sulfur petroleum coke (PC) with 30:70 (cal %) and 50:50 (cal %) blends of Datong bituminous coal in two commercial CFBC boilers. With the exception of CaO, the amounts of major oxides in the fly ashes from cofiring PC and coal were close to those of the common coal fly ashes. The PC−coal fly ashes were enriched in Ni, V, and Mo, implying these trace elements were mainly derived from PC. Ni and V, along with several other elements, such as Cr, Cu, Se, Pb, U, Th, and possibly As and Cd, increased in content with a decrease in temperature of the electrostatic precipitator (ESP). The results of chemistry, mineralogy, and morphology studies suggested that the desulfurization rate of the CFBC boilers at current conditions was low, and the PC tends to coarsen the fly ash particles and increase the loss on ignition (LOI) values, making these fly ashes unsuitable for use as a cement additive or a mineral admixture in concrete. Further studies on the combustion status of the CFBC boilers are needed if we want to be able to increase the desulfurization rate and produce high-quality fly ashes for broader and full utilization.

Introduction

Circulating fluidized bed combustion (CFBC) technology has so many advantages, such as wide fuel flexibility, low combustion temperatures (typically in the range 800−900 °C), low NO_x emissions, high combustion efficiency, and significant desulfurization rate (typically 90%), and so on,[1−3] that it has been installed and operated by more and more Chinese power plants.

It has been proved that CFBC boilers are ideally suited to combust fuels such as high-sulfur coal or other sulfur-bearing fuels. In a CFBC boiler, the resulting SO_2 is captured by limestone added in situ, which reacts via the following two-step process:

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

$$CaO + SO_2 + {}^1/_2O_2 = CaSO_4 \quad (2)$$

A particularly important example of high-sulfur fuel used in CFBC boilers is petroleum coke (PC) that is derived from petroleum refining and may have 5−8 wt % sulfur content. There are more and more such commercial units operating worldwide because the properties of PC, such as low volatility, low ash, a higher calorific value generated from higher carbon contents than that from bituminous coal, a lower price than coal, and so on, make it attractive to use.[4−6] In addition, when it is cofired with coal, PC can also provide flame stability and lower the operating cost of combustion units. The resulting ashes, however, require handling procedures radically different from those for a pulverized coal combustor because of a fair amount of residual sorbents (mainly unreacted CaO) and residual carbon generated from PC in the ashes.[6−8]

Recently, there have been several publications on properties or utilizations of CFBC fly ashes[9−12] and fly ashes from cofiring PC and coal[5−7,13] but few on fly ashes originating from cofiring PC and coal in a CFBC boiler. Only Anthony and his co-researchers have presented some investigations on such fly ashes, but they mostly focused on fouling and agglomeration in boilers[3,8,14] and on vanadium compounds in the fly ashes.[15] Data are still scarce for describing the full properties of such fly ashes, and thus, further studies are necessary if we wish to provide more data and then improve these special fly ash applications.

The present study attempted to characterize three groups of fly ashes, which were produced and collected at different PC: coal thermal ratios (cal %), 0:100, 30:70, and 50:50, in two commercial CFBC boilers. Comparative studies of the three

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10.1021/ef050377w CCC: $33.50
Published on Web 05/03/2006

Table 1. Composition of Feed Coal, Petroleum Coke, and Limestone

	C	H	N	S	O	Ash
Datong bituminous coal (wt % coal, dry basis)	59.97	3.96	1.07	1.10	9.05	24.85
Mideast PC (wt % PC, dry basis)	87.82	3.56	1.30	5.28	0.94	1.10

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	LOI
limestone (oxide form, wt %, Nanjing)	2.86	0.31	0.31	53.25	0.40	0.3	0.02	0.07	42.21

Table 2. Fly Ash Sources

group	sample	sampling position	fuel (cal %)
1	FA1	1st row ESP ash-hopper	100% coal
	FA2	2nd row ESP ash-hopper	100% coal
	FA3	3rd row ESP ash-hopper	100% coal
	FA4	4th row ESP ash-hopper	100% coal
2	FA301	1st row ESP ash-hopper	30:70 PC:coal
	FA302	2nd row ESP ash-hopper	30:70 PC:coal
	FA303	3rd row ESP ash-hopper	30:70 PC:coal
	FA304	4th row ESP ash-hopper	30:70 PC:coal
3	FA501	1st row ESP ash-hopper	50:50 PC:coal
	FA502	2nd row ESP ash-hopper	50:50 PC:coal
	FA503	3rd row ESP ash-hopper	50:50 PC:coal
	FA504	4th row ESP ash-hopper	50:50 PC:coal

groups of fly ashes in chemistry, mineralogy, morphology, and particle size distribution were expected to show the influences of PC addition to the coal blend on the qualities of fly ashes in a CFBC condition and examine whether the PC−coal fly ashes were suitable for utilization as a cement additive. These fly ashes were characterized in detail by XRF, XRD, SEM, and size distribution.

Experimental

Samples. Fuel feed, a combination of bituminous coal and petroleum coke (PC), and fly ash samples were obtained from Sinopec Jinling Petrochemical Power Plant boiler units 5 and 6, both Pyroflow CFBC (Alhstrom, Finland) boiler units rated at 50 MW on May 17, 2002. The feed bituminous coal originated in Datong (Shanxi, China), whereas the PC derived from the Mideast area. Some composition analytical data of both fuels and limestone are summarized in Table 1. The origins of these fly ashes are given in Table 2. The following notation was used to describe these ashes:

Group 1 fly ash samples, including FA1, FA2, FA3, and FA4 collected from the 1st to 4th rows, respectively, of the electrostatic precipitator (ESP) ash-hopper, were generated in CFBC unit 6 burning 100% coal.

Group 2 fly ash samples, including FA301, FA302, FA303, and FA304 collected from the 1st to 4th rows, respectively, of the ESP ash-hopper, were generated in CFBC unit 5 burning a blending fuel composed of 30% PC (cal %) and 70% coal (cal %).

Group 3 fly ash samples, including FA501, FA502, FA503, and FA504 collected from the 1st to 4th rows, respectively, of the ESP ash-hopper, were generated in CFBC unit 5 burning a blending fuel composed of 50% PC (cal %) and 50% coal (cal %).

Characterization Tests for Fly Ashes. Sample preparation was conducted at the State Key Laboratory of Pollution Control & Resource Reuse (SKLPCRR), Nanjing University. Before analyses, all fly ash samples except those for size distribution analysis were screened at 20 mesh (0.9 mm) to exclude the abnormal coarse particles especially emerging in the ash samples from the 1st and 2nd rows of the ESP ash-hopper. All tests of the screened fly ashes were performed at the Center of Modern Analysis (CMA), Nanjing University.

Chemistry analyses of major oxides and trace elements were conducted on a model ARL 9800 X-ray fluorescence spectrometer (XRF) (Thermo Electron, Switzerland) by the fused and pressed disk methods, respectively. For the fused disk method procedure, approximately 0.7 g of the LOI-determined fly ash was weighed into a platinum crucible and thoroughly mixed with 7.7 g of flux (a mixture of 67% $Li_2B_4O_7$ and 33% $LiBO_2$, to enhance the fluxing process); 1 mL of LiBr (40 mg/mL) solution was then added in the mixture to enhance the fluxing process. The solution was next heated at 1100 °C for 13.5 min to melt the mixtures completely and then poured into a platinum cup to form a glasslike penny-shaped disk that was now ready for major oxide analysis by XRF. For the pressed disk method, a plastic cylinder (inner diameter 32 mm, height 4 mm) filled with fly ashes was pressed to form a disk at ∼354 MPa pressure, getting ready for trace element analysis by XRF.

Mineralogical characterization of the fly ashes was determined by a model ARL X'TRA high-performance powder X-ray diffractometer (XRD) (Thermo Electron, Switzerland) with Cu Kα radiation. Step scans were performed over the range of 15−60° 2θ with stepping intervals of 0.04° and a count time of 0.12 s (scanning rate 10.00°/min, 50 kV, 40 mA). The mineralogy results of these fly ashes are presented in Figure 2.

The instrument used for morphology was a Hitachi scanning electron microanalyzer (SEM, model X650) equipped with a model PV900 energy-dispersive X-ray (EDX) system. Gold coatings were applied on the ash samples, and photomicrographs were taken with secondary electrons that could give a better three-dimensional feeling. Various magnifications were used, and the magnification and scale are given at the bottom of the photomicrographs.

Particle size distribution analyses were performed by a model Mastersizer 2000 particle size analyzer (Malvern, U.K.) equipped with a model Hydro 2000MU (A) sample dispersion unit at the Nanjing Institute of Geography & Limnology (NIGL), CAS. The original fly ashes were wet-dispersed in a beaker (capacity 1000 mL) by the sample dispersion unit, using water as dispersant. Continuously variable pump/stirrer and ultrasonics were used to optimize the suspension before analysis. The results of particle size distribution analyses of selected fly ashes are shown in Figure 4.

Results and Discussion

Fuel Chemistry. The feed coal has a moderate ash content and a very low sulfur content (Table 1). In contrast, the feed petroleum coke has a very low ash content and a relatively high sulfur content, in the range of 5−8 wt %. Both fuels have a high carbon content, and especially PC has more carbon than the coal. The hydrogen and nitrogen contents in both fuels are of similar magnitude, but the oxygen content in the coal is higher than that in the PC. Furthermore, both fuels have various trace elements such as As, Cr, Cu, Mo, Pb, Ni, V, U, and Th (Table 4), most of which are typical of heavy metals found in the environment. As shown in Table 4, the amounts of these trace elements except Cr, Mo, Ni, and V are higher in the coal, and the amounts of Cr, Mo, Ni, and V are higher in the PC, suggesting that the PC−coal fly ashes have more Cr, Mo, Ni, and V than the coal fly ashes.

Besides the coal and the PC, the limestone that originated in Longwang Mountain, Nanjing, was added into the boilers simultaneously to capture the SO_2 in situ. As summarized in Table 1, the limestone is rich in CaO content, implying a high potential for combining with SO_2. A high LOI value of the limestone means a large amount of CO_2 loss when igniting the limestone at 960 °C in a furnace. Additionally, the limestone has a low content of other oxides such as SiO_2, Al_2O_3, Fe_2O_3, MgO, TiO_2, Na_2O, and K_2O; undoubtedly, these oxides will remain in the ashes.

Ash Chemistry. In the investigated fly ash samples, the most abundant major oxides are SiO_2, Al_2O_3, Fe_2O_3, CaO, TiO_2,

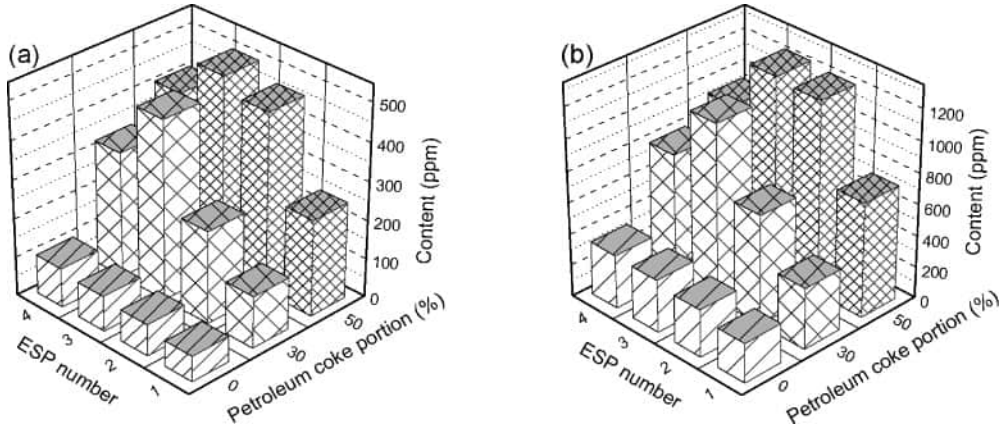

Figure 1. (a) Content of Ni by ESP (ash-hopper) number for fly ashes from CFBC boiler cofiring different portions of petroleum coke. (b) Content of V by ESP (ash-hopper) number for fly ashes from CFBC boiler cofiring different portions of petroleum coke.

MgO, K_2O, and Na_2O, all of which are mainly derived from the coal and the added limestone (Table 3). As shown in Table 3, for the fly ashes sampled at the same position (e.g., FA1, FA301, and FA501 all sampled at the 1st row of the ESP ash-hopper), the SiO_2 content of each fly ash sample of group 1 is higher than that of each sample of group 2. Similarly, the SiO_2 content of each fly ash sample of group 2 is higher than that of each sample of group 3. This observation is due to the increase in the PC:coal ratio of the fuel blend from group 1 to group 3 and the fact that SiO_2 mainly originates from the coal. Other major oxides such as Al_2O_3, Fe_2O_3, and TiO_2 all have the same tendency.

CaO, most of which is derived from the added limestone, shows a reverse trend; the more high-sulfur a PC feed, the more limestone added to capture the resulting SO_2 in situ and the more unreacted CaO retained in the fly ash. For the rest of the major oxides, such as MgO, Na_2O, K_2O, and P_2O_5, their trends are not so evident because of their low amounts. The SO_3 content of group 1 samples was undetected by XRF, probably because of the low sulfur content of the feed coal. Fly ashes of the other two groups of samples have measurable SO_3 contents, but in both groups of samples, the amount of SO_3 (about 0.09−0.55 wt %) is far less than that specified in the ASTM C618-00 standard (4.0 wt % for class N fly ash, 5.0 wt % for both class F and class C fly ash). However, several publications[3,15,16] have reported that the SO_3 content of the fly ashes from a CFBC boiler firing high-sulfur fuels was very high (about 19.25−27.45 wt %), far higher than that in both groups of samples. These data suggest that the desulfurization rate in both cases is very low, and further studies are necessary before we are able to increase the desulfurization rate in the CFBC boilers.

The LOI values of each group of samples have a trend similar to that for CaO, i.e., the LOI values decrease with the addition of PC to the coal blend. This trend is in a good agreement with the fact that the addition of PC to the coal blend results in adding carbon to the fly ashes, as reported by several earlier studies.[5−7,17] Most of these fly ash samples, however, have high LOI values >6 wt %, out of the range defined in ASTM C618-00 on class F/C fly ash, indicating that we may have to be cautious in allowing utilization of these fly ashes as a cement additive or a mineral admixture in concrete.

The trace element contents of the fly ash samples on a dry ash basis are shown in Table 4. It is well-known that going from the 1st to 4th row of the ESP ash-hopper represents a decrease in flue gas temperature. Among the trace elements that increase in content with a decrease in temperature are Cr, Cu, Se, Pb, Ni, V, U, Th, and possibly As and Cd (Table 4). We should note that the contents in certain elements are especially low, making it difficult to clearly distinguish trends. However, the Mo content is likely to decrease with temperature, but the reason for this phenomenon is not understood yet. In addition, the As contents of each group of ash samples evidently decrease with the addition of PC to the coal blend, suggesting that As is mainly derived from the feed coal. Other elements, such as Cu, Cd, Se, and Pb, have the same trends, too. We can therefore conclude that most of these trace elements originate from the coal. On the contrary, Ni, V, and Mo in these fly ashes all increase with the addition of PC (Figure 1), indicating that these trace elements are mainly associated with the PC, a conclusion that is in good agreement with the work of Hower et al.[7] and the chemical analysis results of the feed fuels. But Cr, U, and Th have a special trend that is quite different from that of the other trace elements noted above. They decrease with an increase in the PC portion of the fuel blend from 0 to 30 cal % but increase with an increase in the PC portion from 30 to 50 cal %. This case may arise from the difference in combustion conditions between CFBC unit 5 and 6. Moreover, most of these trace elements are toxic heavy metals and will have a potentially negative impact on the environment, human health, and groundwater as well as on surface water resources if such fly ashes are inadvertently discharged during storage and utilization.

Ash Mineralogy. Mineralogy is one of the important methods for understanding the coalescence status of elements in the fly ashes. Toxicity of fly ashes is dependent not only on the polluting element contents but also on the speciation of the pollutant elements and the nature of the host phases.[18] Furthermore, the combustion conditions of the CFBC boilers can be indirectly reflected by mineralogical study of the resulting fly ashes. Therefore, a detailed mineralogical study of these fly ashes is necessarily required.

Results obtained by XRD (Figure 2) suggest that these fly ashes are basically constituted of a major noncrystalline amorphous phase (halo registered between $2\theta \approx 20°$ and $2\theta \approx 30°$) and some minor crystalline phases (quartz, anhydrite, calcite, hematite, and lime presented in most of these fly ashes, and some portlandite and albite presented in a small part of these fly ashes). All the fly ashes investigated have a similar mineralogical composition. The respective quantities of the different minerals identified by XRD analysis can probably be

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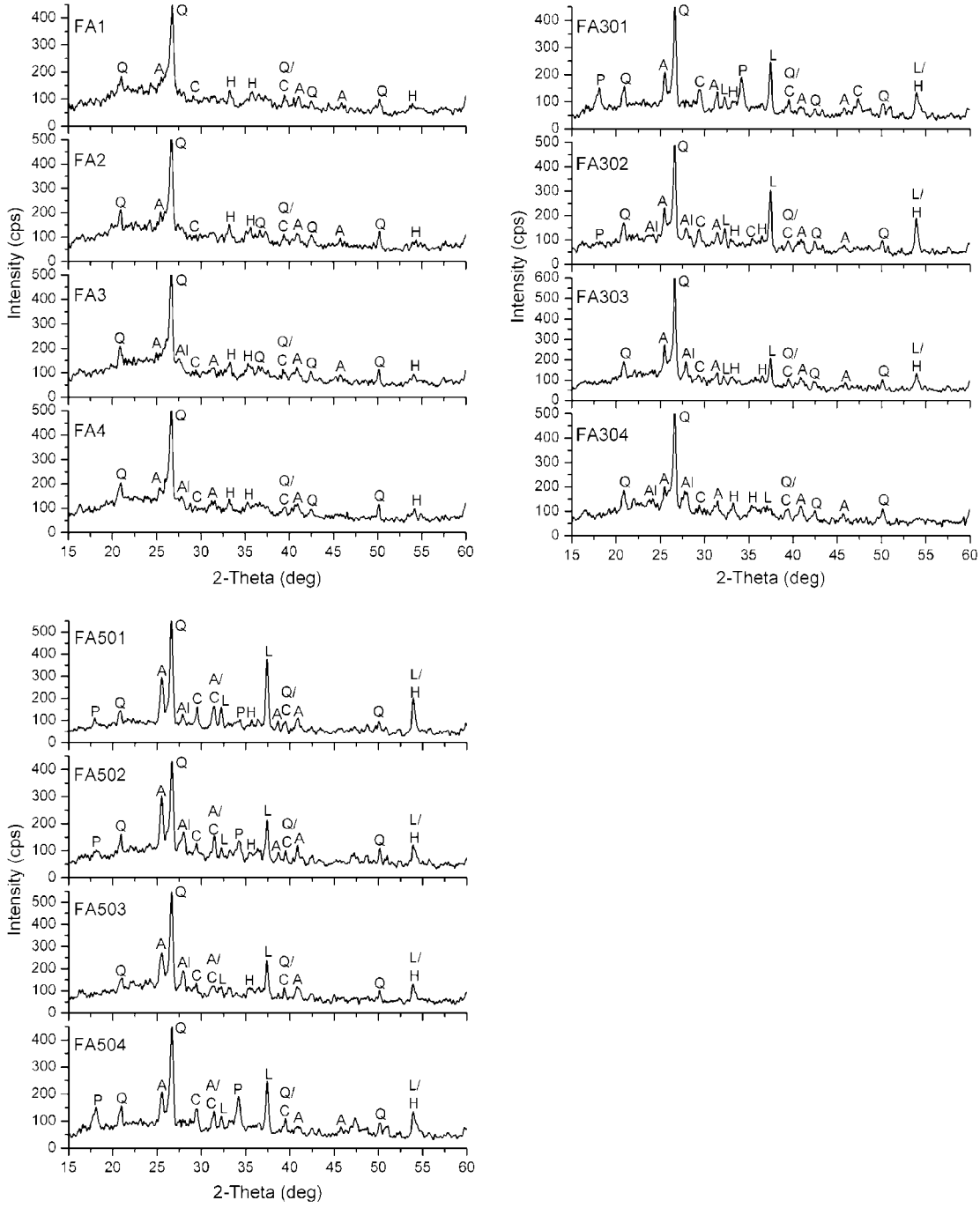

Figure 2. XRD patterns of fly ashes showing the presence of Q, quartz (α-SiO_2); A, anhydrite ($CaSO_4$); C, calcite ($CaCO_3$); L, lime (CaO); H, hematite (Fe_2O_3); P, portlandite ($Ca(OH)_2$); Al, albite ($NaAlSi_3O_8$).

estimated from the corresponding peak intensities (counts per second) in the XRD patterns. The group 1 fly ash samples (FA1 to FA4) present a very low anhydrite intensity and never a lime peak compared with the other two groups of samples (group 2 and 3), suggesting that the group 1 fly ash samples have a very low anhydrite content and none of the lime. This conclusion is in good agreement with the fact that the feed coal has a very low sulfur content and the limestone was not used in this case. Moreover, with the addition of PC to the coal blend, the anhydrite and lime show an increase in intensity as the more high-sulfur PC feed, the more limestone added, thus the more anhydrite produced and the more unreacted lime retained in these fly ashes. However, with the addition of PC to the coal blend, the hematite tends to decrease slightly and the quartz shows a slight fluctuation in intensity. All tendencies are in good agreement with the chemical analysis results of these fly ashes.

Previous publications[11,14,15] reported that the anhydrite dominated in the fly ashes from CFBC boilers firing high-sulfur fuels, but it seems that we cannot draw a similar conclusion on the basis of the XRD results coupled with the chemical analysis results, i.e., the XRD results confirm the fact that the desulfurization rate of the CFBC boilers was at a low level. According to several previous publications,[1,3,19,20] the desulfurization rate can be optimum with a Ca:S molar ratio of 2.4−4; other parameters also thought to affect the desulfurization level include

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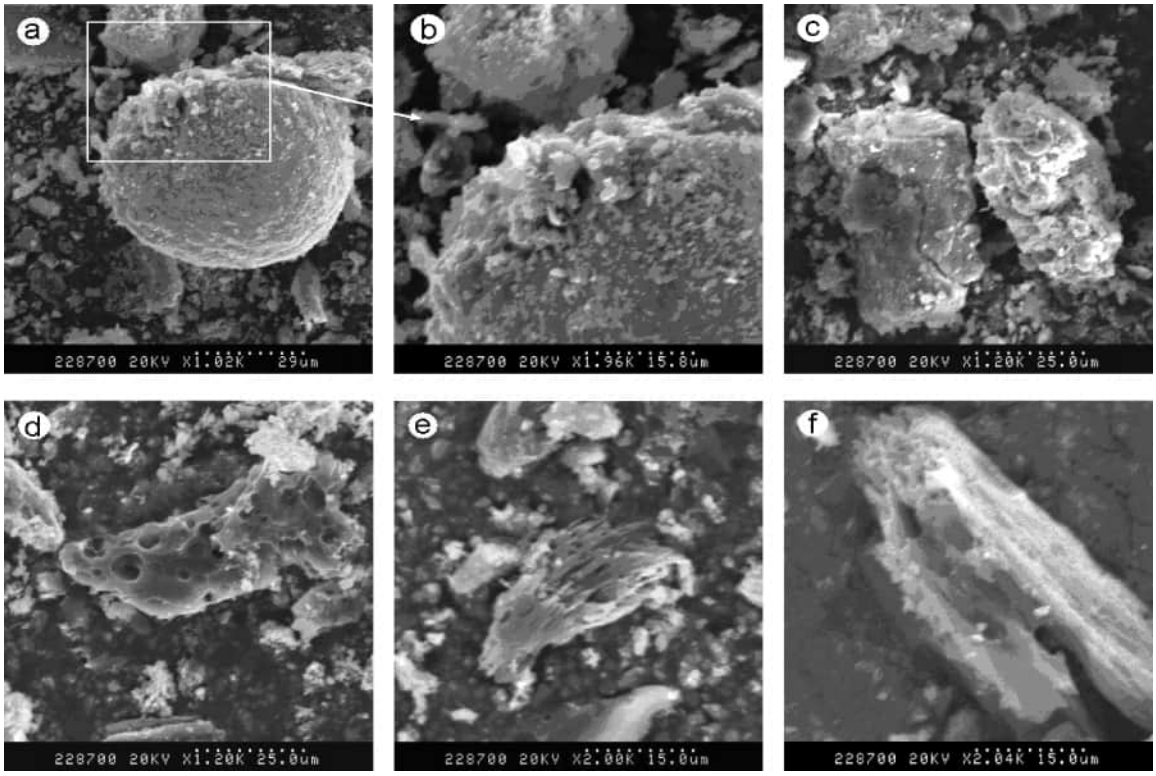

Figure 3. Selected SEM photomicrographs of some typical fly ash particle individuals: (a) FA301, ×1020; (b) FA301, ×1960; and (c) FA301, ×1200; (d) FA302, ×1200; (e) FA303, ×2000; and (f) FA303, ×2040.

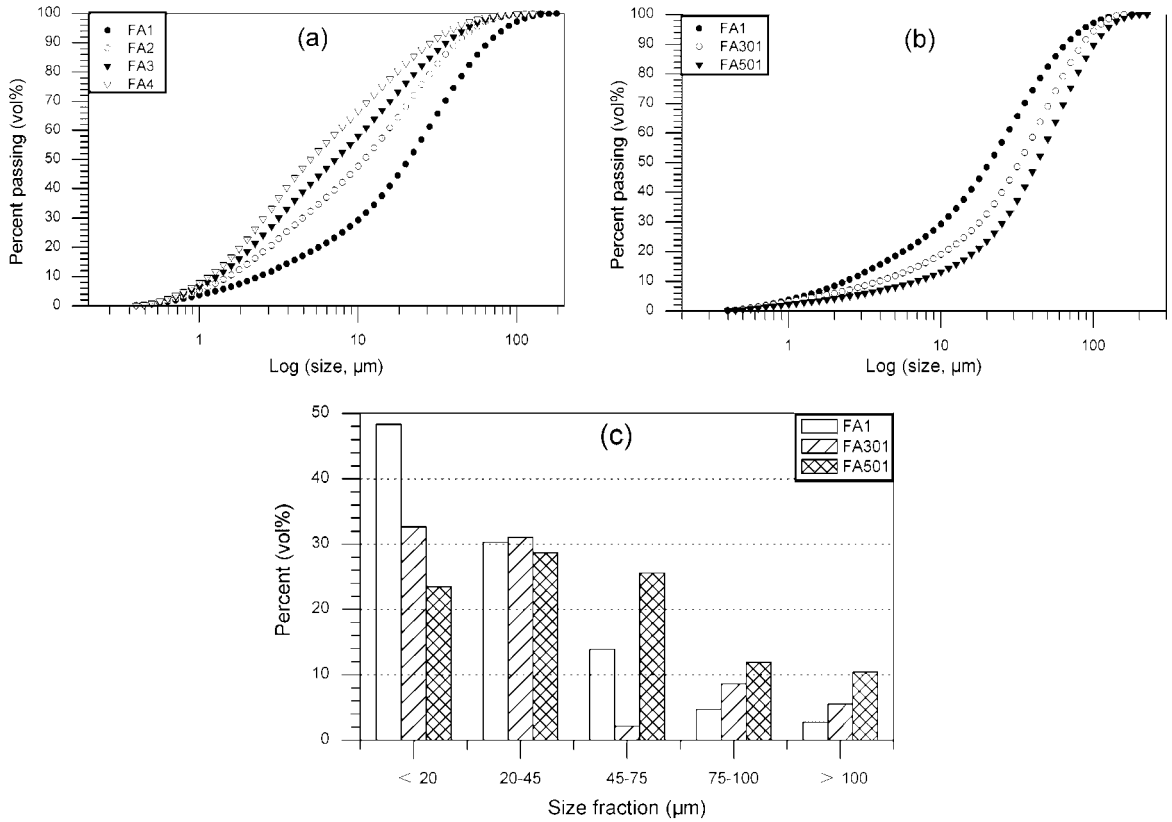

Figure 4. (a) Size distribution of fly ashes from pure bituminous coal combustion; (b) size distribution of fly ashes from the 1st row of the ESP ash-hopper burning different fuel blends; (c) size distribution in different size fractions of fly ashes from the 1st row of the ESP ash-hopper burning different fuel blends.

the in-bed resident time (of the lime), temperature, and particle size (of the lime). The low desulfurization level may be due to the Ca:S molar ratio (2.1 used in both cofiring cases). A detailed discussion of desulfurization seems to be beyond the scope of this paper, but the subject should be further investigated to increase the desulfurization rate.

Ash Morphology. Morphology is of interest as it relates to the influences not only of the shape and size of the particles

Table 3. Composition of These Fly Ashes (oxide form, wt %)

group	sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	P_2O_5	SO_3	LOI
1	FA1	48.71	32.19	3.80	1.96	0.57	1.30	0.44	0.63	0.17	Und[a]	8.72
	FA2	49.86	33.52	3.45	1.97	0.60	1.62	0.48	0.72	0.19	Und[a]	6.95
	FA3	49.80	33.84	3.41	1.93	0.59	1.80	0.51	0.75	0.19	Und[a]	6.12
	FA4	50.25	34.16	3.25	1.99	0.60	1.90	0.50	0.80	0.19	Und[a]	4.83
2	FA301	40.37	23.22	3.02	18.41	0.53	0.84	0.31	0.48	0.11	0.40	9.91
	FA302	43.23	26.16	3.09	14.29	0.56	1.12	0.34	0.53	0.14	0.30	7.52
	FA303	44.00	27.56	2.98	8.98	0.54	1.33	0.41	0.56	0.14	0.09	10.05
	FA304	49.55	32.10	3.27	5.42	0.66	1.76	0.51	0.71	0.16	0.55	4.93
3	FA501	43.08	24.13	3.53	20.79	0.55	0.86	0.30	0.53	0.09	0.38	7.38
	FA502	40.20	24.70	2.94	15.22	0.53	1.16	0.35	0.46	0.12	0.17	12.45
	FA503	42.80	26.82	2.88	10.24	0.55	1.30	0.38	0.53	0.13	0.09	11.21
	FA504	48.93	31.23	3.22	5.23	0.61	1.63	0.46	0.67	0.15	0.29	5.96

[a] Und= undetected.

Table 4. Trace Element Content of Feed Fuels and Fly Ashes (ppm, dry basis)

group	sample	As	Cr	Cu	Cd	Se	Mo	Pb	Ni	V	U	Th
	Coal	8.4	12.9	19.6	N/A	N/A	0.6	12.2	17.7	30.6	1.9	6.6
	PC	2.3	35.4	18.9	N/A	N/A	2.3	10.3	160.8	329.7	1.5	4.9
1	FA1	16.0	92.1	99.1	3.2	33.0	7.1	52.1	66.3	251.7	9.9	30.2
	FA2	17.5	107.1	110.6	4.4	37.6	6.7	64.2	81.9	302.6	11.9	36.1
	FA3	19.3	112.8	118.2	3.7	42.8	7.8	69.7	91.1	334.6	14.0	38.4
	FA4	17.9	111.3	117.8	3.0	39.3	5.7	75.0	101.9	339.9	13.0	38.6
2	FA301	9.1	71.0	58.3	1.0	16.0	9.8	33.8	134.9	391.5	3.8	15.9
	FA302	9.7	88.1	79.6	3.2	29.0	10.6	52.3	239.6	697.6	7.8	20.1
	FA303	3.2	110.3	92.7	3.2	29.9	9.2	75.7	465.5	1125.5	10.0	25.0
	FA304	7.8	117.9	101.3	3.8	44.4	6.4	95.6	326.2	794.7	13.1	35.7
3	FA501	3.9	92.4	52.4	1.0	10.2	11.9	44.3	249.7	728.5	6.0	18.6
	FA502	6.9	92.6	73.0	0.7	19.7	11.4	53.2	466.9	1223.5	9.3	19.7
	FA503	7.1	110.9	89.7	2.7	29.9	8.7	67.6	504.1	1243.4	11.5	32.0
	FA504	4.7	113.1	109.0	3.6	39.1	7.4	90.8	409.1	934.6	11.9	36.5

(and conglomerates) upon workability and particle packing efficiency but also of the leaching behavior of the fly ashes, especially the heavy-metal leachability from the ashes. Moreover, the morphology of fly ashes, along with the mineralogy, could also indicate the operational condition of the boiler, e.g., temperature, and in-bed resident time of the feed fuels.[21,22]

Figure 3 shows the selected SEM photomicrographs of some typical individual fly ash particles. The dominant particles of these fly ash samples comprise mainly coarse and angular, flaky, drossy, and irregular particles with a broad particle size range. Smooth, spherical, and uniform particles were not observed easily, although few spheroidic particles with various spherical or drossy surface precipitates could be detected occasionally (Figure 3a). We also found that the fly ash particles from the same ESP ash-hopper (e.g., FA1, FA301, and FA501) tend to coarsen with the addition of PC and that the ash particle size gets finer gradually with the ash-hopper number, which suggests that the ESP is screening the fly ashes.

Several typical particle features can be distinguished in Figure 3. They include: spheroidic particle with various surface precipitates (Figure 3a,b); monolithic irregular particle with spherical or drossy surface precipitates (Figure 3c, left); fused amorphous agglomeration (Figure 3c, right); and unburnt carbon particle (Figure 3d−f). According to the work of Yu et al.,[6] the unburnt porous carbon particle with isotropic texture (Figure 3c) may derive from the coal and the unburnt, sharp-edged, grooved carbon particle with pronounced optical anisotropy (Figure 3e,f) may derive from the petroleum coke.

The absence of glazed spherical glass particles and the presence of numerous irregular particles indicates that the CFBC boiler combustion temperature is not high enough to melt the crystals in the ashes to form uniform, regular, and spherical glass particles. The presence of unburnt carbon, especially derived from the petroleum coke, further suggests that the boiler conditions are not optimized for even the initial combustion and that the addition of petroleum coke to the feed coal that is possibly exceeding the appropriate amount should be further investigated.

Ash Particle Size Distribution. As mentioned above, the ESP has a function of segregating fly ashes emitting with the heated smokes by the turn of ESP number. This fact has been proved again by the results of particle size distribution of ash samples FA1, FA2, FA3, and FA4, which are shown in Figure 4a. As we can see in Figure 4a, the higher the ESP number, the higher the cumulative distribution curves are located, indicating that the fly ashes are getting finer. Also, both of the other two groups of ash samples (group 2 and 3) have the same trends in particle size distribution whether or not they are derived from cofiring of coal and petroleum coke.

Figure 4b shows the result of the particle size distribution of ash samples FA1, FA301, and FA501, which are all derived from the 1st row of the ESP ash-hopper. Similarly to Figure 4a, the curves are smooth and without any overlaps. The particle size in the coal ash (FA1) is significantly lower than those in both PC−coal ashes (FA301, FA501), i.e., with the addition of PC to the feed coal, the particles have a marked tendency to get coarse gradually, as reported by others.[6] Moreover, the trend can also be explained as shown in Figure 4c by using the particle size distribution of the three ash samples in different size fractions, >100, 100−75, 75−45, 45−20, and <20 μm. In the size fraction <20 μm, sample FA1 has the largest proportion of finer particles among these selected three samples. They have a similar proportion of particles in size fraction 20−45 μm, but in the size fraction >75 μm, sample FA501 has the largest

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proportion of coarser particles among the three samples. Surprisingly, sample FA301 has the lowest proportion of particles in size fraction 45−75 μm. Notwithstanding, the cumulative content of each fly ash in all size fractions is evidently consistent with the result shown in Figure 4b.

Conclusions

Three groups of fly ashes from two commercial CFBC boilers were characterized and evaluated in this work. We confirmed that the addition of petroleum coke to the feed coal added more unburnt carbon to the fly ashes and coarsened the fly ash particles, which made such PC−coal fly ashes unsuitable for use as a cement additive or a mineral admixture in concrete.

Chemical analyses showed that the major oxides such as SiO_2, Al_2O_3, and Fe_2O_3 were mainly derived from the bituminous coal except for CaO, most of which originated from the limestone. In addition, most of the trace elements, which were from the coal with the exception of Ni, V, and Mo derived from the PC, tended to condense on the finer fly ash particles. The LOI values of most of fly ashes exceeded the limit defined in ASTM C618-00 on class F/C fly ash, which made them difficult to use in cement and concrete. XRD analyses indicated that the noncrystalline amorphous phase content is high for all the fly ashes, and the common crystalline constituents are quartz, anhydrite, calcite, hematite, and lime. These findings are in good agreement with the chemical analysis results. From the SEM, we observed that coarse, flaky, drossy, and irregular particles predominated in all the fly ashes because of the lower combustion temperature. Also, unburnt porous carbon particles with isotropic texture derived from the coal were observed, and they were evidently distinguishable from the unburnt, sharp-edged, grooved carbon particle with optical anisotropic walls that resulted from the PC. Moreover, morphological analyses of these fly ashes also revealed that the ESP functions are screening tool for fly ashes and that the fly ash particles coarsened with the addition of PC to the coal blend, both of which were demonstrated by the results of particle size distribution analysis. Therefore, to improve the quality and utilization of these fly ashes and to increase the desulfurization rate of the CFBC boilers, it is necessary to perform further studies.

Acknowledgment. The authors gratefully acknowledge the financial support of this work by the Sinopec Jinling Petrochemical Power Plant. We would particularly like to acknowledge the support provided by CMA.

EF050377W