# Distribution Characteristics of Valuable Elements, Al, Li, and Ga, and Rare Earth Elements in Feed Coal, Fly Ash, and Bottom Ash from a 300 MW Circulating Fluidized Bed Boiler

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ABSTRACT: Feed coal, fly ash (FA), and bottom ash (BA) were collected from a 300 MW circulating fluidized bed boiler. A mechanical screen classifier was used to separate and obtain particles with different sizes. The distribution of valuable elements, including aluminum (Al), lithium (Li), and gallium (Ga), and rare earth elements (REE) in the samples was investigated. Results indicate that the contents of SiO_2 and Al_2O_3 in sized ash particles decreased as the particle size decreased; meanwhile, the contents of CaO, SO_3, and Fe_2O_3 apparently increased. The sulfur-fixing product anhydrite tended to be distributed in the fine ash particles. The valuable elements were more enriched in FA than in BA. The Li, Ga, and REE were evenly distributed in FA particles with different sizes. Separating ash particles with a superhigh concentration of these rare elements was difficult using the mechanical screen, but a part of the anhydrite or CaO in circulating fluidized bed ash could be removed easily. The Li and REE in the feed coal were highly associated with quartz, kaolinite, and other fractions containing SiO_2 and Al_2O_3. No definitive relationship between the Ga concentration and Al_2O_3 content in the feed coal and ash samples was observed.
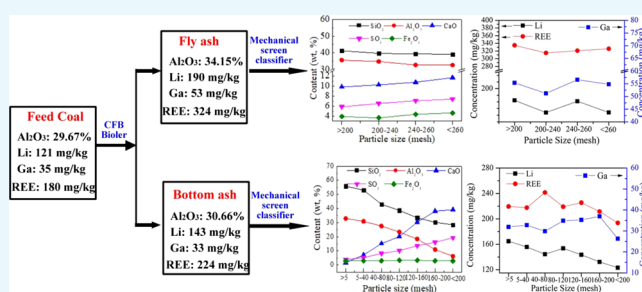
1. INTRODUCTION

Coal is the primary fossil energy resource in China, and the yield of coal production in the country reached 3.41 Gt in 2016.[1] Coal gangue and coal sludge produced from coal mining and washing processes are regarded as industrial solid wastes, and their average production is approximately 15−25% of the raw coal production in China.[2,3] Circulating fluidized bed (CFB) combustion technology has great fuel flexibility, and CFB boilers can burn the worst grade of available fuels.[4] Electric power generation via coal gangue combustion in a CFB boiler is a potential method for heavily consuming these wastes. In recent years, the amount of CFB boilers has been increasing in China, especially in the Shanxi Province. Combustion in these CFB boilers generates large amounts of fly ash (FA) and bottom ash (BA) solid wastes, which are presently underutilized. With low economic benefits, CFB FA and BA have been mainly used in the building material industry as fillers in brick manufacturing and additives in cement and concrete.[5] Large amounts of CFB ash could not be consumed and are still dumped into ponds or piled on land. The irregular accumulation and inappropriate disposal of ashes endanger human health and the environment.

Many coalfields with high content of valuable elements, such as aluminum (Al), lithium (Li), gallium (Ga), and rare earth elements (REE) have been discovered in Northwest China, especially in Inner Mongolia and Shanxi Province.[6,7]

Compared with common Chinese and worldwide coals, the coals from Jungar, Inner Mongolia are more highly enriched with Al, Li, Ga, and REE.[8,9] Sun et al.[10] found that the Li, Ga, and Al contents of the coals from the Pingshuo Mining District, Ningwu Coalfield, Shanxi Province in China have reached an economically valuable level. In addition, the contents of these valuable elements in coal gangue from these districts are evidently higher than those in coal because these valuable elements are mainly found in the inorganic matter of coals.[11] Most of these inorganic valuable elements in coal gangue or coal are moved to FA and BA during combustion in the CFB boilers.[12,13] The recycling of these valuable metals from coal ash not only conserves natural resources and reduces environmental impacts but also utilizes ash with high economic benefit.[14] Generally, the selection of recovery technology and recovery cost is considerably influenced by the concentration of valuable elements in coal ash. Understanding the distribution of valuable elements in FA and BA is essential for the improvement of recovery technology. Furthermore, coal ash is a complex mixture and is assumed to be composed of various particles. The particle size and distribution of elements are uneven due to the

different formation conditions of coal ash. Ke et al.[15] corroborated that the larger CFB ash particles were composed of some hard materials such as quartz, mullite, and glass particles with different sizes have different chemical composition and mineral matter. Li et al.[16] investigated the distribution characteristics of heavy metals in different sizes of FA from a sewage sludge circulating fluidized bed incinerator and corroborated that the heavy metal contents of small-sized FA were higher than those of large-sized FA. Raclavská et al.[17] studied the enrichment and distribution of 24 elements within the subsieve particle size distribution ranges of FA from waste incinerator plants and affirmed that a great enrichment of the majority of elements was observed for a particle size range of <100 μm and was attributed to the vaporization and condensation mechanisms. López-Antón et al.[18] investigated the behavior of thallium in a 50 MW industrial circulating fluidized bed combustion plant and the distribution of thallium among BA and FA. They contended that thallium is relatively homogeneously distributed in all of the ash samples regardless of their composition but is slightly related to surface area, which in turn is dependent on particle size and unburned carbon content. Most studies on element distribution in coal ash are focused on deleterious elements.[19−22] However, the distribution characteristics of valuable elements, including Al, Li, Ga, and REE, in different sizes of FA and BA from industrial CFB boilers are unclear to date. In addition, extracting the rare elements from coal ash is difficult due to the relatively low concentration of rare elements in coal ash. The difficulty in extraction will be reduced, and the economics of valuable element extraction will be enhanced if certain size fractions are more enriched in these valuable elements. Furthermore, whether the simplest mechanical screening can be used to increase the concentration of rare elements in coal ash with specific particle size is still unclear.

In this work, the mineral matter, chemical composition, and rare element (Li, Ga, and REE) content in feed coal, FA, and BA from a 300 MW circulating fluidized bed in a coal gangue power plant are investigated. A mechanical screen classifier is used to separate particles in different sizes of FA and BA. The distribution characteristics of mineral matter, oxides, and rare elements in the sized particles are investigated systematically. This study mainly aims to clarify the distribution and enrichment of valuable elements in the differently sized feed coal, FA, and BA from the industrial CFB boiler.

2. RESULTS AND DISCUSSION

2.1. Characteristics of Feed Coal. *2.1.1. Particle Size Distribution.* Figure 1 depicts the particle size distribution of feed coal. The percentage of 5−40 mesh coal particles is the highest (reaches up to 67%), and the percentage of other particle sizes is less than 10%. Compared with the particle size of feed coal in a pulverized coal furnace, the size of feed coal in the CFB furnace is relatively bigger (0.4−3 mm).

2.1.2. Proximate Analysis. Table 1 exhibits the proximate analysis of sized feed coal samples. The ash contents of coal particles with different sizes vary. As the particle size decreases, the ash content in coal particles gradually decreases, indicating that more inorganic matter exists in coarse coal particles. In contrast, the content of fixed carbon in coal particles increases with the decrease in particle size.

2.1.3. Mineral Matter. Figure 2 illustrates the mineral matter and their contents in coal samples with different particle
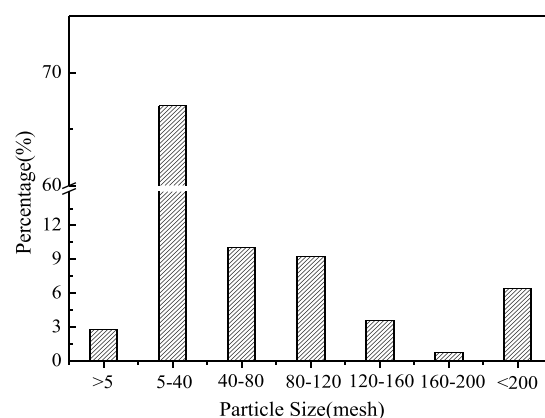

Figure 1. Particle size distribution of feed coal.

Table 1. Proximate Analysis of Feed Coal Samples with Different Sizes[a]

particle size (mesh)	proximate analysis (wt %, d)			
	M	A	V	FC
>5	1.45	74.28	14.26	10.01
5−40	1.52	73.45	15.11	9.92
40−80	1.61	72.19	15.27	10.93
80−120	1.70	70.56	15.68	12.06
120−160	1.73	68.37	16.21	13.69
160−200	1.67	65.26	15.51	17.56
<200	1.58	62.79	15.99	19.64

[a]M, moisture; A, ash; V, volatile matter; FC, fixed carbon.

sizes. The X-ray diffraction (XRD) patterns of coal particles with sizes of 5−40, 40−80, 80−120, and 160−200 mesh are not given because they are similar to the patterns illustrated in Figure 2. The major minerals in feed coal are kaolinite ($2SiO_2$·Al_2O_3·$2H_2O$) and quartz (SiO_2). The feed coal also contains a small amount of boehmite (AlOOH) and gypsum ($CaSO_4$·$2H_2O$). The mineral matter content in coal varies with the size of coal particle. The content of kaolinite in coal particles bigger than 80 mesh decreases slightly as the particle size decreases and then decreases dramatically when the coal particle size is smaller than 120 mesh. The content of quartz in coal particles decreases with the decrease in particle size. The boehmite is mainly distributed in the coarse coal particles (>160 mesh), whereas the gypsum is mainly distributed in the fine coal particles (<80 mesh). In addition to crystalline minerals, coal also contains noncrystallized inorganic matter, which is usually referred to as amorphous matter.[23] The main chemical composition of amorphous matter in coal should be SiO_2 and Al_2O_3 based on the chemical composition of inorganic matter and mineral content in coal. The content of amorphous matter in coal particles increases gradually with the decrease in particle size.

2.1.4. Chemical Composition. Table 2 presents the major chemical composition and rare element content in raw feed coal and sized coal particles. The distribution of mineral matter in coal particles with different sizes causes the chemical composition variation of coal particles. Overall, the contents of SiO_2 and Al_2O_3 decrease gradually as the coal particle size decreases, whereas the contents of Fe_2O_3, CaO, and SO_3 show an increasing trend with the decrease in coal particle size. The decrease of kaolinite and quartz with a decrease in feed coal particle size results in the decrease in SiO_2 and Al_2O_3 contents
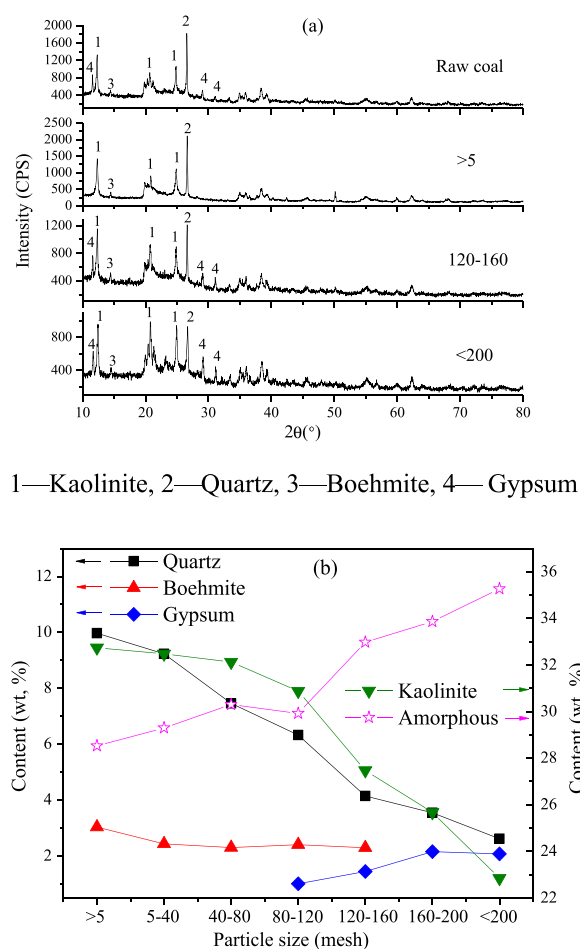
1—Kaolinite, 2—Quartz, 3—Boehmite, 4—Gypsum

Figure 2. Mineral matter (a) and their contents (b) in feed coal particles with different sizes.

in the fine coal particles. The variation of CaO and SO_3 content in the coal particles with different sizes is caused by the distribution of gypsum in feed coal particles. The concentration variation trend of Li and REE with coal particle size is consistent with that of SiO_2 and Al_2O_3. Unlike Li and REE, Ga is evenly distributed in coal particles.

Figure 3 shows the concentration of Li and REE as a function of the contents of quartz and kaolinite. The Li and REE concentrations in feed coal particles are highly correlated with the content of quartz. A clear relationship is found between the concentration of Li/REE and the content of kaolinite, although r^2 is lower than that of quartz. Figure 4 shows that the Li and REE concentrations in feed coal particles are highly correlated with the contents of SiO_2 and Al_2O_3 and their sum. These results confirm that the occurrence of Li and REE in coals is related to minerals and amorphous fractions. Karayigit et al.[24] found that Li is closely related to the aluminosilicates in coal. Lewińska-Preis et al.[25] proved that Li in the Kaffioyra coal was bound to minerals and that 72% of Li was associated with organic matter in Longyearbyen coal. Sun et al.[26] claimed that the content of Li was much higher in inorganic matter than that in organic matter. This result implies that the occurrence of Li in coal deeply depends on the type, origin, and characteristics of coal. Coal gangue containing abundant kaolinite accounts for approximately 60% of the feed coal. Hence, the Li and REE in the feed coal are associated with quartz, kaolinite, and other fractions containing SiO_2 and Al_2O_3.

Gallium is generally related to clay minerals, boehmite or other aluminum-containing fractions, and probably as substitute for Al in the framework structure of minerals.[8] In addition, Ga may occur in organic matter in some coals.[27] However, no definitive relationship between the concentration

Table 2. Chemical Composition of Inorganic Matter in Feed Coal Particles with Different Sizes

| chemical composition		feed coal particles with different sizes							
		raw	>5	5−40	40−80	80−120	120−160	160−200	<200
major composition (wt %, coal basis)	SiO_2	34.23	37.26	35.19	32.49	30.55	28.67	27.28	26.14
	Al_2O_3	29.67	31.18	29.34	27.52	26.01	24.37	23.21	21.46
	Fe_2O_3	2.36	1.27	1.98	3.04	3.48	3.58	3.69	3.94
	CaO	1.98	0.41	1.32	2.15	2.67	3.02	3.22	3.75
	SO_3	2.49	0.38	1.67	2.44	2.83	3.17	4.38	5.21
rare elements (mg/kg, coal basis)	Li	121	134	108	85	77	63	49	37
	Ga	35	35	33	37	32	37	29	32
	REE	180	211	185	170	153	135	141	114
	La	3.10	4.75	4.57	3.44	3.89	3.01	3.91	2.56
	Ce	21.58	21.58	17.15	14.44	11.36	13.16	11.16	8.60
	Pr	15.58	21.97	18.76	14.29	11.02	11.58	10.15	7.41
	Nd	54.43	62.81	54.47	55.14	45.62	40.82	49.64	36.72
	Sm	5.64	7.48	5.95	4.39	4.66	5.59	4.76	4.77
	Eu	1.31	1.55	1.43	1.35	1.17	0.75	1.14	0.22
	Gd	5.21	6.87	5.45	5.08	5.29	5.76	6.87	5.30
	Tb	3.94	7.32	5.75	4.23	2.05	1.64	1.44	0.71
	Dy	5.40	5.56	5.20	4.85	4.69	3.46	4.72	2.27
	Ho	0.56	0.96	0.65	0.35	0.69	0.13	0.38	0.05
	Er	27.43	28.32	27.31	26.36	22.84	17.31	16.32	14.84
	Tm	2.94	4.28	3.06	2.68	2.93	2.30	3.67	1.51
	Yb	2.74	2.47	2.25	2.18	1.98	1.53	1.62	1.33
	Lu	5.26	5.42	6.16	5.49	6.19	4.81	3.81	3.86
	Y	25.00	29.98	27.10	26.16	28.56	23.22	21.72	23.78
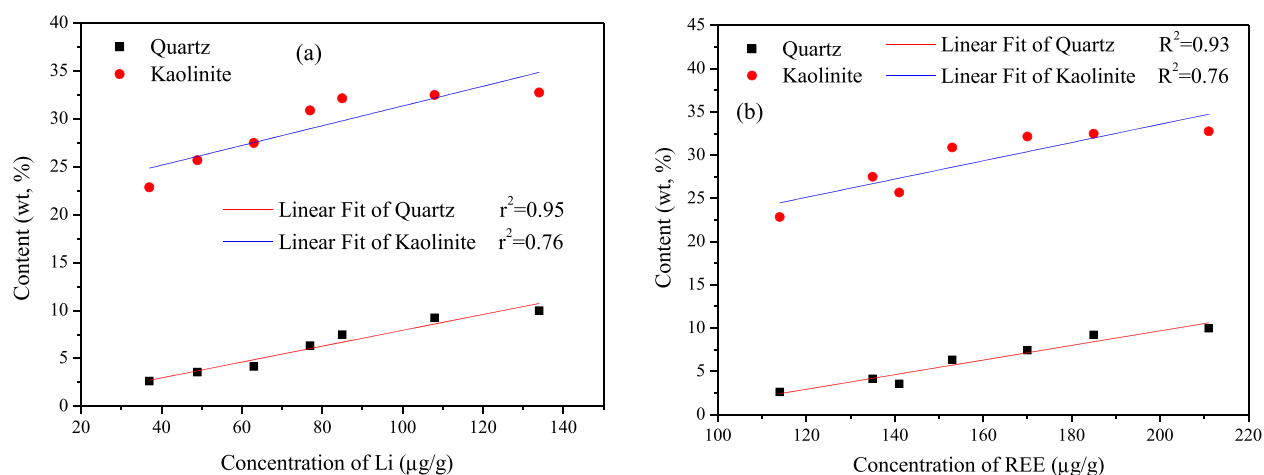
Figure 3. Relationship between the concentration of (a) Li and (b) REE and contents of quartz and kaolinite.
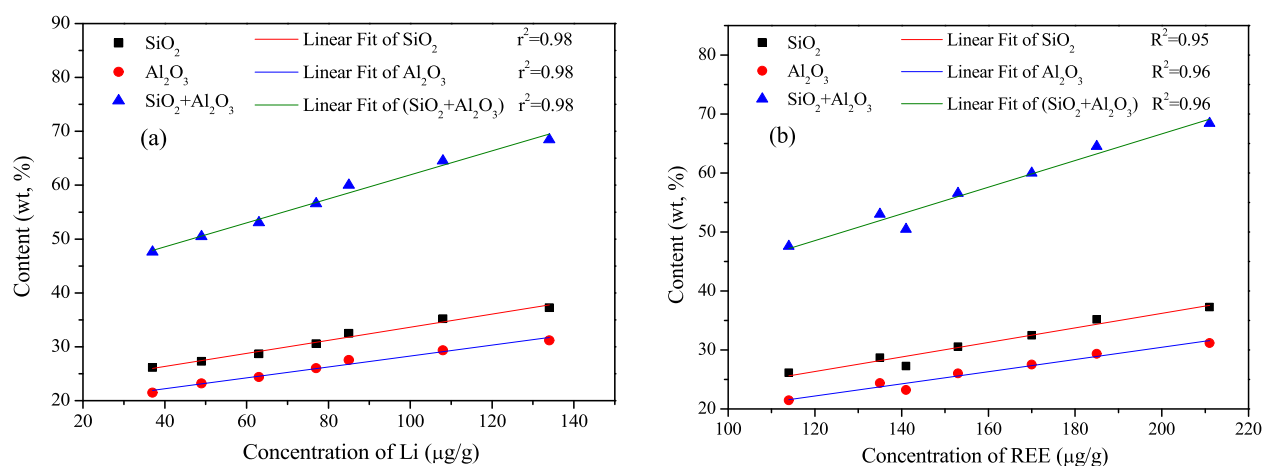

Figure 4. Relationship between the concentration of (a) Li and (b) REE and contents of SiO_2, Al_2O_3, and their sum.

of Ga and the contents of kaolinite, boehmite, organic matter, and Al_2O_3 in the feed coal is observed in this work.

2.2. Comparison of Chemical Composition between FA and BA. Table 3 shows the chemical composition of FA and BA.

The loss of ignition (LOI) of BA is higher than that of FA due to the high content of unburned carbon or unreacted limestone in BA. The content of SiO_2 in FA is lower than that in BA, whereas the contents of Al_2O_3, Fe_2O_3, and MgO in FA are higher than those in BA. These results indicate that the inorganic matter rich in SiO_2 tends to be distributed in coarse BA particles and that the inorganic matter rich in Al_2O_3 is more likely to enter the fine FA particles. Table 2 affirms that the contents of CaO and SO_3 are enriched in the fine particles. However, the contents of CaO and SO_3 in FA are similar to those in BA caused by the addition of limestone ($CaCO_3$), which is used for catching sulfur oxide in the flue gas in this plant. The particle size range of limestone is 0.08–2.5 mm, and the content of the 0.63–2.5 mm particle is the highest in the feed limestone.[28] Compared with the FA, the feed limestone is coarser. Therefore, the sulfur-fixing product anhydrite ($CaSO_4$) and unreacted limestone/lime enter the BA easily.[29] The particle size of limestone can decrease dramatically due to the decomposition of limestone at high temperatures. A part of fine limestone and its derivative particles enter the FA, leading to similar contents of CaO and SO_3 in the FA and BA.

Table 3 shows that the concentration of rare elements in the FA particle is higher than that in the BA particle, indicating that the Li, Ga, and REE are more abundant in fine FA particles during coal combustion. Elements, such as Al, Li, Ga, and REE, in ash are widely considered to be valuable elements, which can be extracted for recycling. They can also be concentrated from coal to FA during coal combustion. The content of alumina in FA is approximately 15% higher than that in coal. Compared to those in coal, the concentrations of Li, Ga, and REE in FA increase by approximately 57, 51, and 80%, respectively.

2.3. Composition of Ash Particles with Different Sizes. *2.3.1. Particle Size Distribution.* Figure 5 shows the particle size distribution of the ash samples. The weights of particles with the sizes of >160 mesh and <300 mesh are extremely low. The particle size distribution of FA is narrow, ranging from 160 to 300 mesh. Particles in the range of 200–240 mesh account for approximately half of the FA particles. Unique working conditions, including coarse feed coal and the relatively low combustion temperature, cause the FA collected from the CFB boiler to be distinctly coarser than the FA collected from the pulverized coal plant.[30]

In contrast, the particle size distribution of BA is wide, ranging from 5 to 200 mesh, and the particles with sizes between 5 and 40 mesh hold the largest proportion of BA.

Table 3. Chemical Composition of FA and BA

| chemical composition		FA samples					BA samples				
		FA1	FA2	FA3	FA4	average	BA1	BA2	BA3	BA4	average
major composition (wt %, ash basis)	SiO_2	39.27	38.21	39.64	40.03	39.29	44.97	44.17	44.41	45.49	44.76
	Al_2O_3	33.46	34.95	33.98	34.21	34.15	30.49	30.22	31.25	30.67	30.66
	CaO	10.07	9.20	9.65	9.44	9.59	10.62	11.02	10.69	10.14	10.62
	Fe_2O_3	4.48	3.96	4.01	4.20	4.16	3.29	2.62	2.42	2.40	2.68
	SO_3	5.65	6.17	5.81	6.17	5.95	5.23	5.17	4.55	5.37	5.08
	MgO	1.93	2.32	2.05	2.33	2.16	0.70	0.89	0.87	0.76	0.81
	LOI	2.51	2.65	2.81	2.25	2.55	3.36	3.48	3.50	3.82	3.54
rare elements (mg/kg, ash basis)	Li	204	180	183	192	190	146	144	139	141	143
	Ga	54	53	51	55	53	34	32	31	35	33
	REE	331	332	314	318	324	211	226	233	224	224
	La	9.37	8.45	7.74	9.22	8.69	5.62	6.04	6.67	4.99	5.83
	Ce	29.88	31.80	31.47	32.29	31.36	19.75	23.64	22.85	21.18	21.86
	Pr	26.06	25.07	22.42	23.32	24.22	12.41	13.07	11.08	15.46	13.01
	Nd	172	173	167	173	171	111	121	124	122	120
	Sm	7.64	7.61	7.56	7.76	7.64	5.06	5.03	4.94	4.99	5.00
	Eu	5.51	5.98	5.01	6.19	5.67	3.41	2.80	2.32	2.31	2.71
	Gd	2.95	3.47	3.30	2.18	2.98	2.47	2.14	3.31	1.68	2.40
	Tb	6.02	5.30	5.54	5.16	5.51	3.34	2.99	3.52	2.95	3.20
	Dy	4.03	3.90	3.65	2.52	3.53	2.39	2.19	3.21	2.08	2.47
	Ho	0.76	0.70	0.62	0.46	0.63	0.38	0.37	0.49	0.38	0.41
	Er	23.69	23.26	20.30	17.46	21.18	11.51	11.69	16.03	13.05	13.07
	Tm	3.63	3.63	3.20	2.41	2.34	1.50	1.90	2.15	2.32	1.97
	Yb	2.37	2.47	2.11	2.41	2.34	1.27	1.14	1.43	1.31	1.29
	Lu	3.30	3.60	2.73	2.49	3.03	1.52	1.53	2.06	2.20	1.83
	Y	33.74	33.65	30.87	31.20	32.36	28.84	31.02	28.46	27.22	28.89
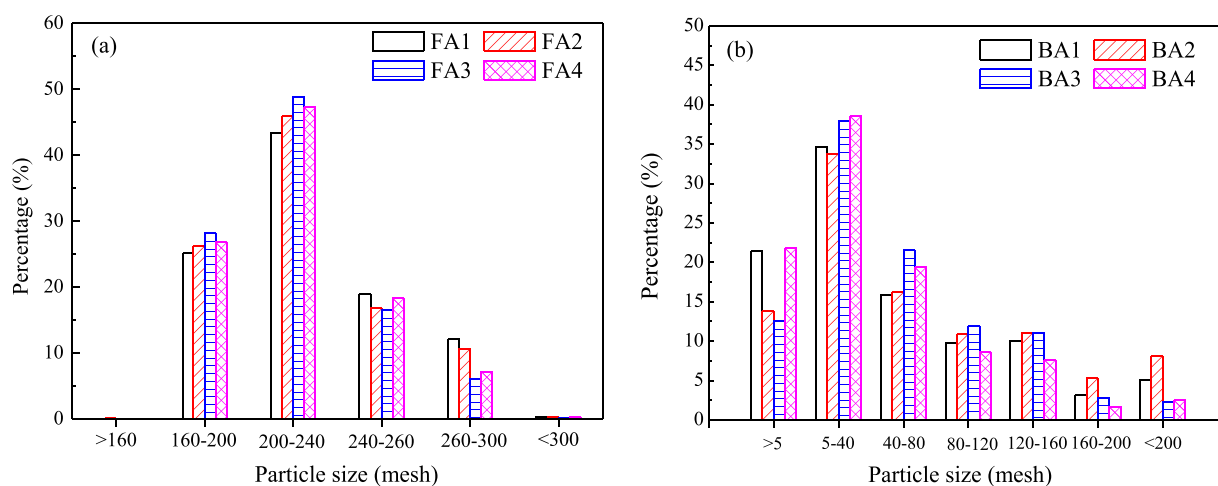
Figure 5. Particle size distribution of (a) FA and (b) BA.

2.3.2. Composition of FA Particles with Different Sizes. The main chemical composition and mineral content in FA particles with different sizes are determined by X-ray fluorescence (XRF) and XRD, respectively. The results of the FA1−FA4 samples are similar. Therefore, only the results of FA1 are illustrated in Figure 6 to avoid redundancy. The contents of SiO_2 and Al_2O_3 in FA decrease slightly as the particle size decreases; meanwhile, the contents of CaO, SO_3, and Fe_2O_3 increase. The mineral matter in FA comprises quartz, anhydrite, and hematite (Fe_2O_3). The amount of crystalline minerals accounts for ∼20% of FA quality and the other is the amorphous component. The kaolinite in feed coal decomposes above 600 °C and transforms into amorphous matter including metakaolin and amorphous Al and Si oxides,

which would transform to mullite or other crystalline aluminosilicates above 1000 °C.[31,32] However, the operation temperature of CFB boilers is 800−900 °C. The amorphous metakaolin, Al, and Si oxides cannot transform to crystalline mineral and still exist in the ash. Similar to the content variation of quartz in feed coal particles, the quartz content decreases with the decrease in FA particle size. Limestone ($CaCO_3$) powder is used for capturing sulfur oxide in the flue gas in this plant, and it transforms into anhydrite during coal combustion. The content of anhydrite in fine FA particles is higher than that in coarse FA particles. Iron oxide in FA mainly exists in the form of hematite according to their similar contents in FA.
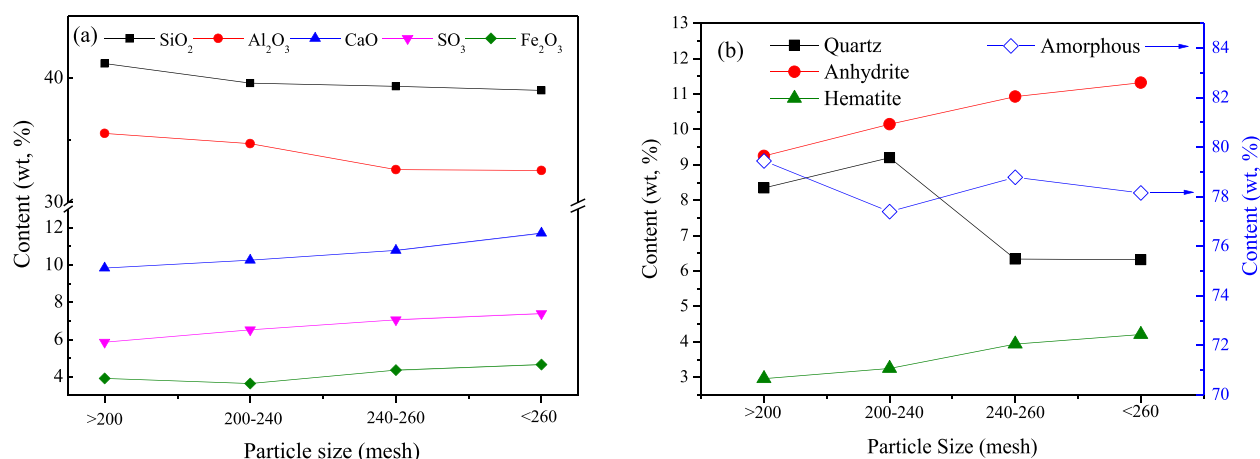
Figure 6. Content variation of (a) main components and (b) minerals in FA1 with particle size.
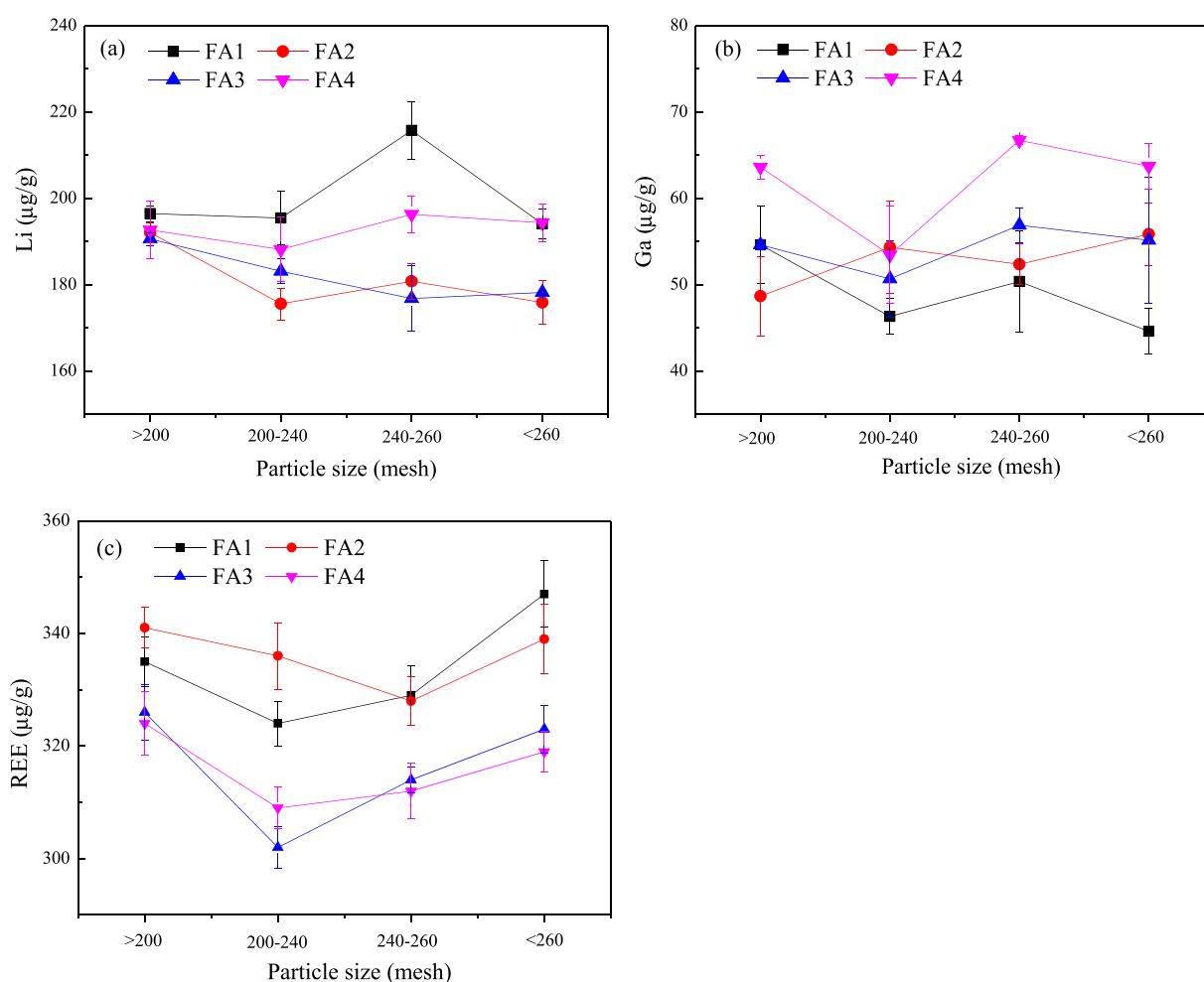

Figure 7. Content variation of (a) Li, (b) Ga, and (c) REE in FA with particle size.

Figure 7 depicts the content variation of Li, Ga, and REE in FA with particle size. Results demonstrate that the distribution of Li, Ga, and REE in FA particles with 200−260 mesh is basically homogeneous. Previous studies[20,33] have noted that the heavy metals or some trace elements were more abundant in the small-sized FA particles. However, no definitive trend in variation of Li, Ga, and REE was observed between the FA particles with different sizes. Generally, the volatile elements tend to be enriched in fine FA particles. These indicate that the

Li, Ga, and REE in the coal are nonvolatile or weak-volatile elements under CFB conditions.

Figures 3 and 4 show that the Li and REE in the feed coal are associated with quartz, kaolinite, and other fractions containing SiO_2 and Al_2O_3. However, the relationship is not observed in the FA particles. The inorganic matter, including minerals in feed coal, underwent a series of complex changes during the combustion process. The chemical structure of inorganic matter and the environment of rare elements have
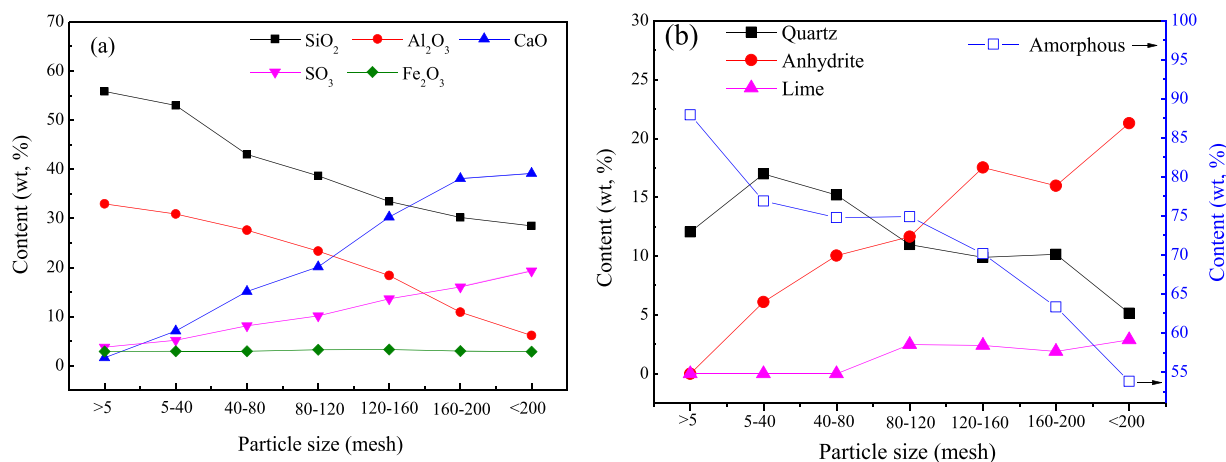
Figure 8. Content variation of (a) main components and (b) minerals in BA1 with particle size.
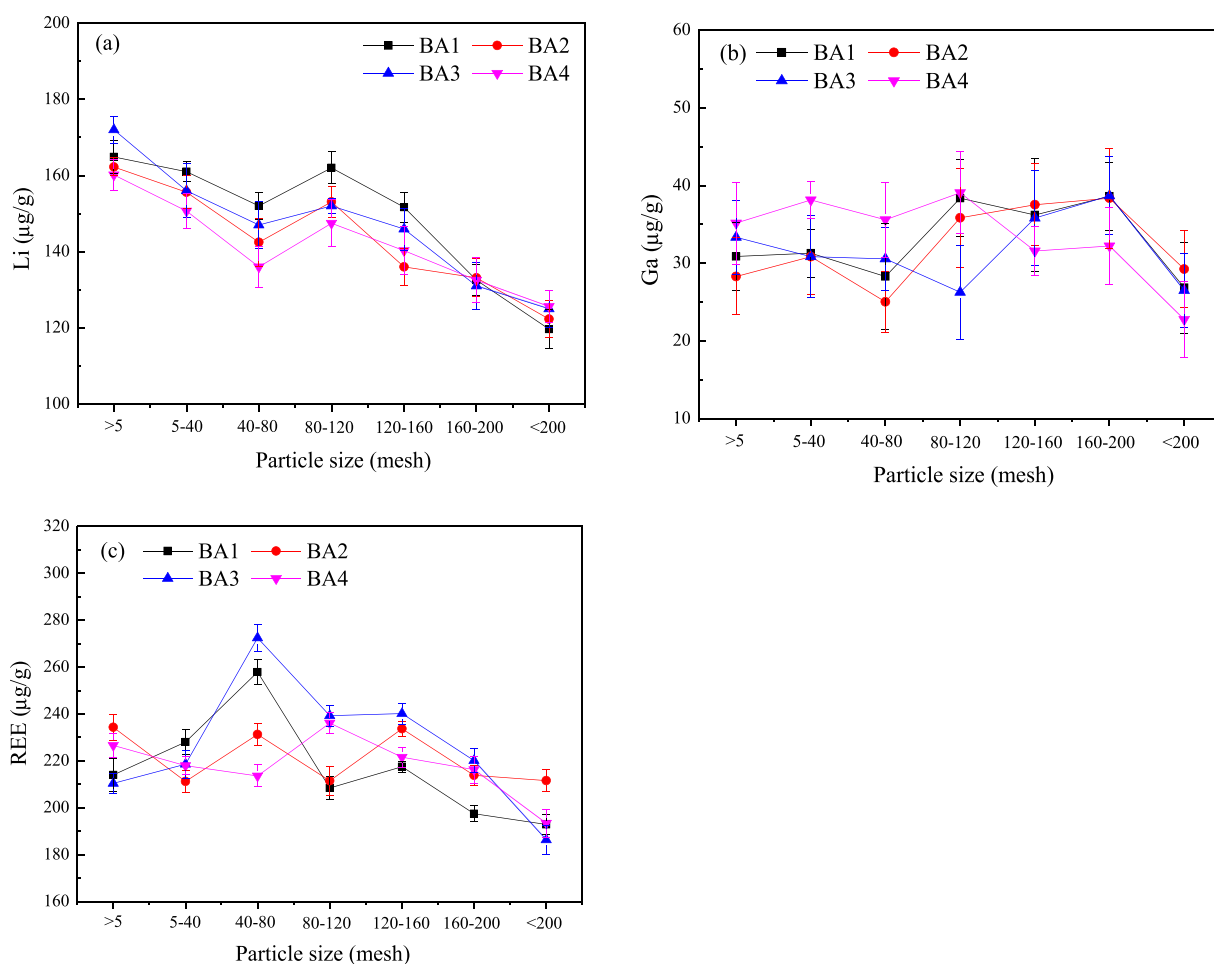

Figure 9. Variation of (a) Li, (b) Ga, and (c) REE concentration in BA with particle size.

changed, which may lead to the scattered distribution of these rare elements in FA.

Figure 8 illustrates the content variation of the main chemical components and mineral matter in BA1 particles with different sizes. Similar to the element distribution in the FA particles, the contents of SiO_2 and Al_2O_3 in BA decrease as the particle size decreases; meanwhile, the contents of CaO and SO_3 increase. The mineral matter in BA comprises quartz, anhydrite, and lime (CaO). Limestone decomposes to form lime at high temperatures. A small amount of lime cannot react with sulfur oxide to form anhydrite and remains in the BA. Hematite is not found in BA. Figure 8b shows that the quartz tends to be distributed in coarse BA particles and anhydrite and lime tend to be distributed in fine BA particles. Minerals containing Al_2O_3 are not detected in FA and BA. Hence, all of the Al_2O_3 exist in CFB coal ash in the form of amorphous matter. The content of amorphous matter in the BA particles decreases with the decrease in particle size.
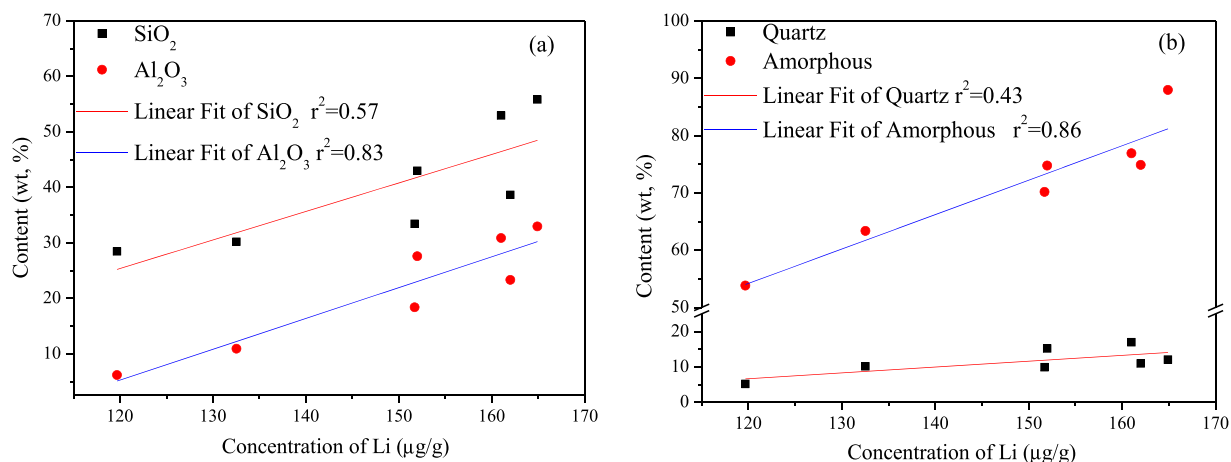
Figure 10. Relationship between Li concentration and major chemical composition (a) and mineral contents (b).

Figure 9 illustrates the variation of Li, Ga, and REE concentrations in BA with particle size. Overall, the concentration of Li in BA decreases with the decrease in particle size. Figure 9b shows that Ga is evenly distributed in the BA particles of 5−200 mesh size. Figure 9c demonstrates that the concentration of REE in the 40−80 mesh sized BA particles is slightly higher than that in other sizes of BA particles. The concentration of REE in BA particles decreases when the particle size is smaller than 160 mesh.

Figure 10 indicates that the Li concentration in BA is poorly correlated with the content of SiO_2 and quartz compared with the relationship in feed coal. In contrast, the Li concentration in the BA is positively correlated with the contents of Al_2O_3 and amorphous fractions. However, no definitive relationship is observed between the concentration of Ga/REE and the contents of minerals or other oxides in the BA.

3. CONCLUSIONS

Al is mainly found in feed coal in kaolinite and boehmite. A small amount of Al exists in the amorphous matter of feed coal. The average contents of Li, Ga, and REE are concentrated at 121, 35, and 180 mg/kg in the feed coal, respectively. The contents of Al, Li, and REE in the feed coal decrease gradually with the decrease in coal particle size. Ga is evenly distributed in sized coal particles.

These valuable elements are more enriched in FA than in BA. The average contents of Al_2O_3 and Li, Ga, and REE are concentrated at 34.15% and 190, 53, and 324 mg/kg in FA, respectively. The content of Al_2O_3 in FA is approximately 15% higher than that in coal. Compared to those in coal, the concentrations of Li, Ga, and REE in FA increase by approximately 57, 51, and 80%, respectively.

For the FA and BA, the contents of SiO_2 and Al_2O_3 decrease as the particle size decreases; meanwhile, the contents of CaO, SO_3, and Fe_2O_3 increase. The sulfur-fixing mineral anhydrite is enriched in the fine particles, whereas Al_2O_3 is enriched in the coarse particles. However, no significant variation is found in the concentrations of Li, Ga, and REE in the FA particles with different sizes. The concentration of Li in BA decreases with the decrease in particle size.

These rare elements are not enriched in a certain size particle and are evenly distributed in the sized FA particles. Enrichment of these rare elements in FA particles with a certain size using the mechanical screen is difficult, but a part

of anhydrite or CaO in FA and BA can possibly be removed using this method.

The Li and REE in the feed coal are highly associated with quartz, kaolinite, and other fractions containing SiO_2 and Al_2O_3. The Li concentration in the BA is positively correlated with the contents of Al_2O_3 and amorphous fractions. However, no definitive relationship between the Ga concentration and contents of minerals containing Al_2O_3, organic matter, and other fractions in the feed coal and ash samples is observed. A thorough understanding of the physical and chemical nature of FA and BA from an industrial CFB boiler is invaluable in the proper utilization of this important resource. Data in this study can be helpful in the development of an efficient utilization technology of CFB FA.

4. MATERIALS AND METHODS

4.1. Materials and Preparation. Feed coal, FA, and BA were collected in Pingshuo Coal Gangue Power Plant in the north of Shanxi Province in China, which generates electricity using mixtures of coal gangue and weathered coal as raw materials. Feed coal (5 kg) was collected on the conveyer belt. To investigate the distribution of valuable elements in coal with different particle sizes, the feed coal was sieved using a stack of nested sieves with the following meshes: 5, 40, 80, 120, 160, and 200 (about 3080, 385, 193, 128, 96, and 77 μm, respectively). The coal particles after sieving were ground to less than 77 μm using a grinder for 20 min.

FA and BA were collected from the outlet of the precipitator and slag separator, respectively. First, the FA was collected each day at 5:00 am, 10:00 am, 17:00 pm, and 22:00 pm, respectively. These ash samples were mixed evenly to guarantee representative ash samples. The BA samples were collected using the same method. The FA and BA samples were collected at the same time. The fly ash samples collected in four days were denoted as FA1, FA2, FA3, and FA4, respectively. The BA samples collected in four days were denoted as BA1, BA2, BA3, and BA4, respectively.

The FA samples were sieved using a stack of nested sieves with the following meshes: 160, 200, 240, 260, and 300 (about 96, 77, 64, 59, and 51 μm, respectively). The BA samples were sieved using a stack of nested sieves with the following meshes: 5, 40, 80, 120, 160, and 200 (about 3080, 385, 193, 128, 96, and 77 μm, respectively). The sieving operation generally lasted 30−60 min depending on the particle size and the

amount of sample loaded. The weight of particles with different sizes was recorded, and the mass fraction of these particles was calculated.

4.2. Analytical Methods. *4.2.1. Proximate Analysis of Coal Sample.* The proximate analysis of coal sample was conducted according to the Chinese National Standards GT/T 212-2008.

4.2.2. Measurement of Chemical Composition. The main chemical compositions of all samples were measured by X-ray fluorescence (XRF, Bruker, S8 Tiger).

To analyze the chemical composition of inorganic matters and mineral matter in coal samples accurately, the organic matter in the coal was removed by oxygen plasma oxidation in a K1050X plasma furnace (Quorum Technologies Ltd.). The acquired ash sample was referred to as low-temperature ash (denoted LTA).

The LTA, FA, and BA samples (0.1g) were digested using a mixture of 4 mL of aqua regia (V_{HCl}/V_{HNO_3} = 3:1) and 2 mL of n hydrofluoric acid (HF) at 180 °C for 60 min in a microwave digestion system (Anton Paar, 3000). Then, the contents of Li, Ga, and REE in digestion solution were determined by an inductively coupled plasma emission spectrometer (Thermo Scientific, ICAP6000).

4.2.3. Determination of Mineral Matter. X-ray powder diffractometer (XRD, D2, Bruker) with Cu Kα radiation was used to determine the mineral matter in specimens, which were scanned with a 2θ step size of 0.02° from 10 to 80°. The mineral matter in ash samples was quantified by TOPAS software (Version 4.2, Bruker). Zinc oxide was added into ash samples to determine the content of minerals and amorphous matter.[34] The detailed method was given in other literature data.[35]

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Notes
The authors declare no competing financial interest.

■ ABBREVIATIONS

CFB, circulating fluidized bed
LTA, low-temperature ash
FA, fly ash
BA, bottom ash
XRD, X-ray diffraction
XRF, X-ray fluorescence

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