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Facile Route for Effective Separation and Full-Scale Recycling of Fly Ash and Unburned Carbon

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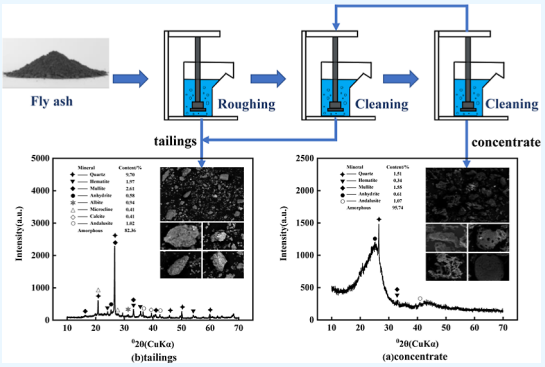
ABSTRACT: The synchronous production of high-quality unburned carbon concentrate and cleaned ash from high LOI (loss on ignition) fly ash without yielding secondary solid waste is a dilemma issue. In this study, a viable flotation process with one rougher and two cleaners is developed for simultaneously obtaining carbon concentrate with a yield of 18.00% and an ash content of 17.49% and cleaned ash with a yield of 82.00% and a LOI of 4.63% from fly ash, reaching 84.72% of combustible substance recovery and 80.66% of flotation perfection index. The characteristic analyses of the stage by stage releasing products using laser particle size analysis, XRF, XRD, and SEM−EDS demonstrate that the inevitable factors that lead to a remaining higher ash content in the one-step flotation carbon concentrate are the random entrainment of mineral particles in the size range of 0−20 μm, especially the quasi-colloidal parts within 0−12.5 μm and the weak selective collection of fine-grained conjoined granules in the size range of 0−40 μm. Consequently, at least two cleaning steps are required for the effective separation of unburned carbon and ash. Furthermore, batch flotation test results show that diesel is superior to kerosene in the collection of unburned carbon, with an optimum dosage of 800 g/t; no. 2 oil acts more positively than MIBC for the separation of unburned carbon and ash, with an optimal dosing amount of 600 g/t; the optimum pulp concentration and flotation time are as follows: 100 g/L and 3.5 min for the rougher, 45 g/L and 2 min for the first cleaning, and 30 g/L and 3 min for the second cleaning. This study provides an economically feasible technological solution for the full-scale recovery of high-LOI fly ash in one step and avoids the problem of secondary solid waste that would have been generated in previous studies.



1. INTRODUCTION

Fly ash is the side product collected from the fumes of burned coal and consists of inorganic minerals (ash) and unburned carbon. As one of the main industrial solid wastes, the utilization of fly ash resources has attracted the attention of many investigators.[1] Normally, fly ash can be utilized as a cement mixture,[2,3] concrete admixture,[4,5] paste filling material,[6,7] road base material,[8,9] low-cost adsorbent,[10,11] and zeolite raw material.[12] The carbon content, which is always characterized by the loss-on-ignition (LOI), is critical for the utilization of fly ash in the construction industry; therefore, there is a strict standard for the carbon content in fly ash, and the lower the LOI value, the better the quality of the fly ash.[13,14] The standard specification for first-grade fly ash in China limits the LOI values to less than 5%, which limits the utilization of fly ash with high LOI.[14] To date, the quantity of unqualified fly ash has reached up to 4 billion in China, which occupies land, causes pollution, and wastes resources.[15] Therefore, removing unburned carbon from fly ash is an important method for increasing the quality of fly ash and utilizing it.[16] There are several technologies for reducing the LOI value of fly ash, such as fluidized bed reactors,[17] oil agglomeration,[18,19] electrostatic separation,[20−24] and froth flotation.[25−32] Flotation is one of the most promising methods for removing unburned carbon from fly ash with high efficiency, effectiveness, and easy commercialization.[33,34] Some studies carried out for the removal of unburned carbon from fly ash by flotation are summarized in Table 1, which shows that the LOI value for different kinds of fly ash can be obviously decreased by flotation and meets the industrial standard. However, when considering the LOI of fly ash as the kernel problem, the recovery of unburned carbon and the quality of carbon concentrate were often neglected. As shown in Table 1, almost all the cleaned ash can meet the LOI requirement; nevertheless, the ash content of most corresponding carbon concentrate is more than 40%, which cannot be utilized without further processing.

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Table 1. Summary of the Indicators for Flotation Separation of Unburned Carbon and Fly Ash[a]

reference number	authors	fly ash	carbon concentrate (%)			cleaned ash		RUC
		LOI (%)	yield	LOI	A_d	yield	LOI	
23	Tao et al.	14.70	*21.15*	*21.09*	*78.91**	35.99	14.06	*30.49**
24	Yang et al.	12.72	*25.74**	*40.63**	*59.37**	74.26	3.59	82.22
26	Yang et al.	11.26	*29.01**	*32.06**	*67.94**	*70.99**	2.76	82.60
27	Hu et al.	24.60	*39.36**	*61.53**	*38.47**	*60.64*	0.63	*98.45**
28	Li et al.	13.60	*15.60**	59.65	*40.35**	*84.40**	*5.09**	68.42
30	Lv et al.	8.32	18.51	41.80	*58.20**	81.49	1.73	*93.00**
32	Xu et al.	22.96	*31.39**	67.18	*32.82**	*68.61**	*2.73**	91.85

[a]* calculated value based on reported data in corresponding reference, $A_d \approx 100 - \mathrm{LOI}$.

Table 2. Technical Related Index for the Fly Ash

proximate analysis (%)					ultimate analysis (%)					LOI (%)
M_{ad}	A_{ad}	V_{ad}	FC_{ad}	$Q_{net,d}$ (kcal/kg)	C_d	H_d	O_d	N_d	$S_{t,d}$	
0.69	82.47	2.53	14.31	1045	15.37	0.20	0.25	0.64	0.50	18.33

From another point of view, the recycling of unburned carbon is another vital issue for the comprehensive utilization of fly ash. It has been reported that unburned carbon collected from fly ash can be used as raw materials for auxiliary fuel,[35] adsorption materials,[36] metallurgical coke,[37] activated carbon,[38,39] graphite substrate,[40,41] etc. Many studies have been carried out to improve the carbon recovery in fly ash floatation, such as optimizing the flotation reagent,[28,29] ultrasonic pretreatment,[30] collector emulsification,[42] strong mixing,[26] conditioning slurry with saline water[43,44] or surfactant,[31,32] using a novel bubble generator[45] or a original flotation column,[46] multistage separation, etc. These above-mentioned technologies work well in improving the unburned carbon recovery and reducing the flotation cost, but the tricky problem of high ash content in the carbon concentrate is not solved; moreover, the LOI value of cleaned ash was not paid the required attention. Consequently, both the produced carbon concentrates and the cleaned ash are poorly qualified, which restricts the market acceptance and the comprehensive utilization of fly ash.

In this study, both the carbon concentrate and ash products were taken into account. The aim of this study is to simultaneously produce carbon concentrates of low ash content (A_d < 20%) as well as cleaned ash of low LOI (<5%), realizing the full-scale recycling of high-carbon fly ash and no secondary solid waste generated. The influence of kerosene, diesel, MIBC, no. 2 oil, flotation time, pulp concentration, and flotation stage on the separation effectiveness of unburned carbon and ash was explored. First, the optimum floatation parameters for ash cleaning were determined by batch floatation test, obtaining the first-grade fly ash and the maximum decarbon rate. Second, the step-by-step flotation test was carried out to explore the kernel factors which hinder the effective separation of unburned carbon and ash. Subsequently, combining the characteristic analyses of stepped products and closed-circuit floatation experiment, the reasonable separation flowsheet and operation conditions were founded, synchronously producing the market-acceptable cleaned ash and refined carbon of high quality.

2. MATERIALS AND METHODS

2.1. Materials. The fly ash used in this study was obtained from a fluidized bed boiler dust collector in a gangue thermal power plant in Shanxi Province, China. The parameters of the fly ash are listed in Table 2, and Table 3 shows the chemical composition of the fly ash, as determined by X-ray fluorescence (XRF) analysis. The distribution of LOI in fly ash with different sizes is shown in Table 4. Figure 1 shows X-ray diffraction (XRD), laser particle size analysis, scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS) of the fly ash. The results show that the ash content of fly ash is as high as 82.47%, and the calories are as low as 1045 kcal/kg; consequently, the fuel property of FA is very poor. Carbon is the main combustible element component with a proportion of 90.64%, and unburned carbon is the main combustible matter in fly ash. According to the XRF results, the fly ash belongs to the F category (CaO < 10%). For the fly ash, the total SiO_2, Al_2O_3, and Fe_2O_3 content is 73.11% (>50%), and the SO_3 content is less than 3.0%, which meets the standard of GB/T 1596-2017 for the inorganic mineral composition, but the LOI value is much higher than the standard (>10%), which hinders the building industrial utilization of fly ash. As a result, the release of unburned carbon from fly ash is critical for reducing the LOI.

Table 3. Chemical Composition of Fly Ash Determined by XRF Analysis (wt %)

component	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O
content (%)	41.96	24.58	6.57	3.44	1.34	1.25
component	SO_3	Na_2O	MgO	P_2O_5	ZrO_2	SrO
content (%)	1.48	0.24	0.51	0.15	0.08	0.07

It can be observed from the XRD results that the main crystalline minerals in the fly ash are quartz and mullite with a small amount of hemeatite, andalusite, and feldspar, and the amount of anhydrite and calcite is small. In addition, the quantity of amorphous substances is very large, including unburned carbon and amorphous minerals. The SEM−EDS results show that most of the unburned carbon particles in fly ash form a loose spatial network or honeycomb structure, and a few particles are spherical or quasi-spherical, while the

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Table 4. Distribution of the LOI in Fly Ash with Different Particle Size Ranges

size (mm)	yield (%)	LOI (%)	LOI distribution rate (%)	undersize accumulation		
				yield (%)	LOI (%)	LOI distribution rate (%)
0.25−0.5	0.53	10.76	0.31	100.00	18.13	100.00
0.125−0.25	10.41	12.34	7.09	99.47	18.17	99.69
0.074−0.125	14.75	18.24	14.84	89.06	18.85	92.60
0.045−0.074	15.16	25.77	21.55	74.31	18.97	77.76
−0.045	59.15	17.23	56.21	59.15	17.23	56.21
sum	100.00	18.13	100.00			

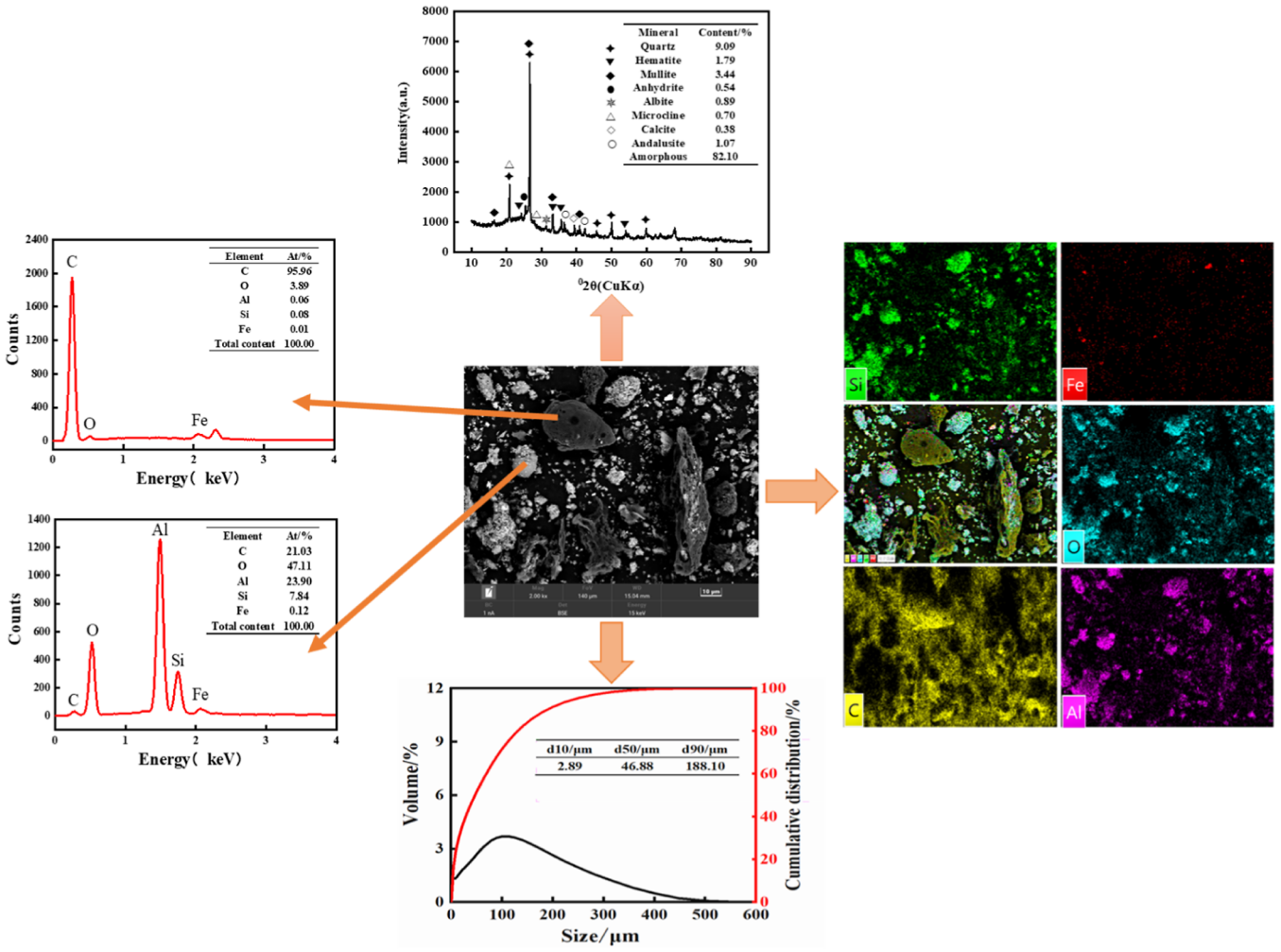

Figure 1. Mineral phase and microscopic characteristics of fly ash.

inorganic mineral particles are irregular in shape. Some of the particles exist as monomers with fine particle sizes, some of them coexist densely with unburned carbon particles, and some fine particles are distributed in the pores or cavities of unburned carbon particles. Since most of the mineral particles in fly ash are fine and a considerable amount of minerals coexist closely with unburned carbon, separation is difficult.

The particle size of the fly ash is relatively fine, with an average particle size of 46.88 μm. The results given in Table 4 show that 92.60% of the combustibles (i.e., LOI) in the fly ash are concentrated in the size range of 0−0.125 mm, among which the highest LOI of 25.77% is found in the particle size range of 0.075−0.045 mm. However, the difference of combustible content between particle size range is very smaller; therefore, it is impossible to obtain qualified fly ash or refined carbon through classification. Considering that the −0.045 mm particle content in the fly ash has reached 60%, to avoid deterioration of the flotation process with a larger amount of fine mud, the fly ash was directly separated by flotation without grinding in this study, which is undoubtedly beneficial to the subsequent dewatering.

2.2. Flotation Experiment. With reference to the National Standard of the People's Republic of China GB/T 4757-2001 (method for batch flotation testing of fine coal), the flotation was conducted in an XFD-1L batch flotation machine. In order to ensure the accuracy and repeatability of the test results, three parallel tests were carried out for each flotation. The test results of the three flotation tests were within the error range, and the average values of the three tests were the final data. When the test was complete, the concentrate (Con)

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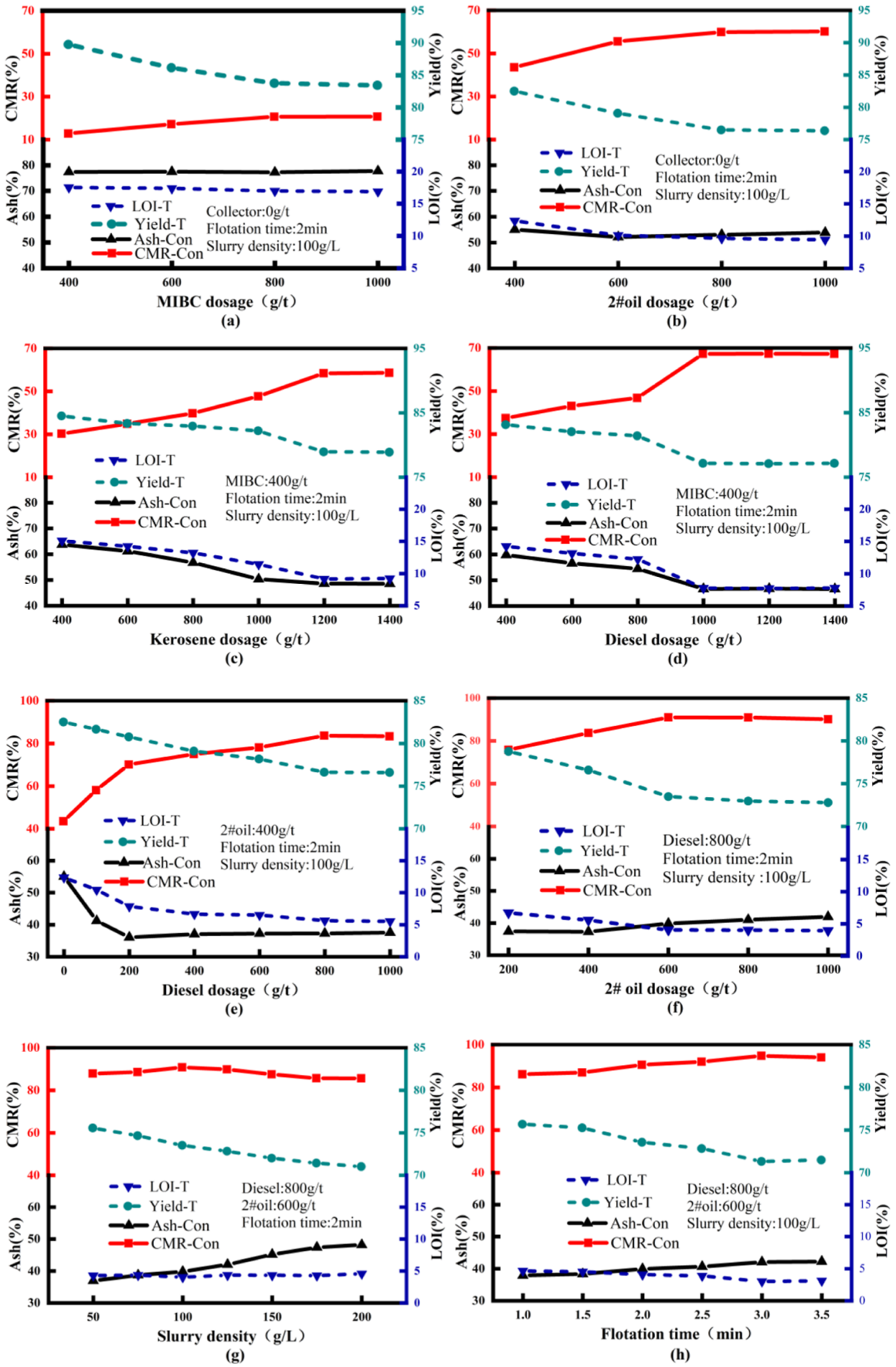

Figure 2. Primary flotation experimental results: (a,b) no collector; (c,d) different collector; (e) diesel dosage; (f) no. 2 oil dosage; (g) slurry density; and (h) flotation time.

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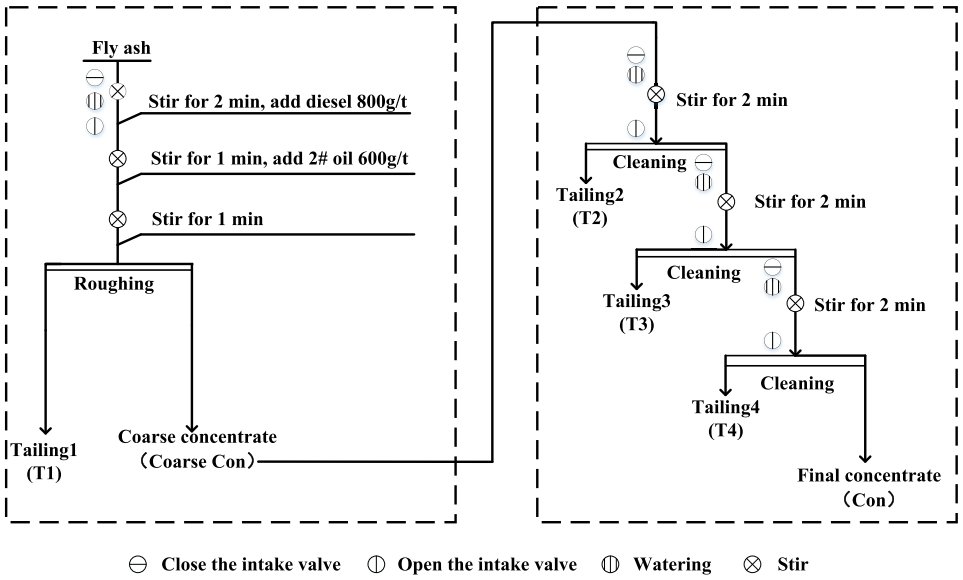

Figure 3. Stage-by-stage release flotation flow diagram.

and tailings (T) were filtered, dried, and weighed separately, and the yield of product was determined. Then, the ash content (Ash) of the concentrate and the loss-on-ignition (LOI) of the tailings were analyzed, and the recovery rate for the combustible material (CMR) of the concentrate was calculated. The muffle furnace combustion method (combusting at 815 °C for 1 h) specified in the national standard of the People's Republic of China GB/T 212-2008 (Methods for Industrial Analysis of Coal) was applied to determine the ash content. The LOI was also measured by the muffle furnace combustion method, but combustion was performed at 950 °C for 20 min according to the National Standard of the People's Republic of China GB/T 176-2017 (Methods for Chemical Analysis of Cement). The following equations were used for the calculations

$$A = \frac{M_1}{M_0} \times 100 \tag{1}$$

$$\mathrm{CMR} = \frac{\gamma_C \times (100 - A_C)}{100 - A_F} \tag{2}$$

$$\mathrm{LOI} = 1 - \frac{M_1'}{M_0'} \times 100 \tag{3}$$

where A represents the ash content (%), CMR represents the recovery rate of the combustible material (%), LOI represents the loss on ignition (%), M_0 is the sample weight before burning at 815 °C (g), M_1 is the sample weight after burning at 815 °C (g), γ_C is the product yield (%), A_C is the ash content of the product (%), and A_F is the ash content of the feed (%). M_0' and M_1' represent the sample weight before and after burning at 950 °C (g). Three duplicate tests were performed under the same conditions. The standard deviations for ash, LOI, and γ were within ±0.3, ±0.3, and ±0.5%, respectively. The CMR of the concentrate is approximately equal to the carbon recovery rate of the concentrate and the removal rate of unburned carbon (RUC) from the tailings.

2.3. Characteristic Analysis. The chemical components were tested by using an X-ray fluorescence spectrometer (XRF-1800, Shimadzu Corporation, Japan), which was operated at a voltage and current of 60 kV and 140 mA, respectively, with a scanning speed of 300°/min. Carbon was removed in advance using a combustion method according to the GB/T 176-2017 standard. The residual ash was then analyzed by XRF.

The main mineral phases were quantitatively determined by using the internal standard method (Si was used as the internal standard substance) using XRD. The measurements were performed using a D8 Advance at 40 mA and 40 kV using a Cu anode and Kα radiation with a wavelength of 1.5406 Å in the 2θ range of 10−70° with an angular speed of 4°/min.

The micromorphology was characterized by scanning electron microscopy (SEM, TESCAN MIRA LMS) equipped with an energy-dispersive spectroscopy (EDS) detector. During each measurement, a trace sample was directly glued to the conductive adhesive, and the Oxford Quorum SC7620 sputtering coater was used to spray gold for 45 s and 10 mA; then, a scanning electron microscope was used for sample morphology, energy spectrum mapping, and other tests.

The British Malvern Mastersizer 2000 was used for the laser particle size analysis of the original fly ash, the step-by-step release of each product, and the final flotation product. The samples were dispersed with water before the particle size measurement, and then ultrasonic treatment was conducted for 5 min. The particle size test range was 0.01−2000 μm.

3. RESULTS AND DISCUSSION

3.1. Batch Floatation Test. Different results have been obtained for the different investigation about the effect of kerosene[27] and diesel[28] on the collection of unburned carbon. In addition, different studies of the effect of alcohol foaming reagents, including MIBC,[25] *sec*-octanol,[27] no. 2 oil,[47] etc., on the flotation of unburned carbon have also led to different conclusions. Therefore, in this study, the influences of MIBC and no. 2 oil, diesel oil, and kerosene on the separation of unburned carbon and ash by flotation were compared and analyzed first. The effects of the pulp concentration and flotation time were also studied. The results are shown in Figure 2.

The results shown in Figure 2a depict that a foam concentrate of 10−15% can be yielded by adding the foaming

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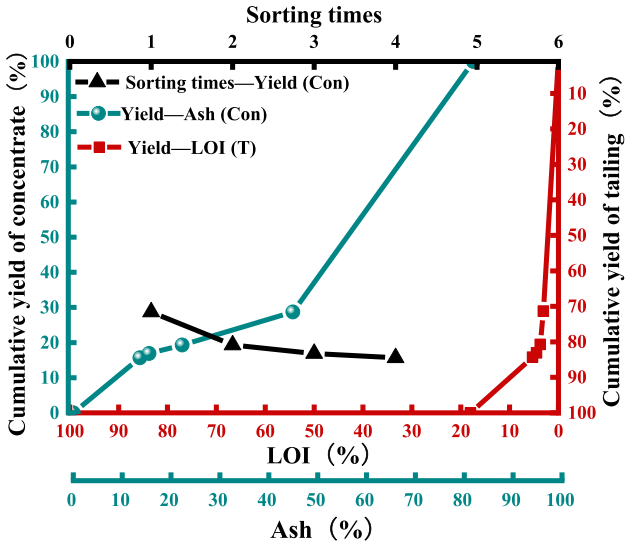

Figure 4. Results of stage-by-stage release flotation.

Table 5. XRF Analysis Results for Step Products of Stage-by-Stage Release Flotation (wt %)

component	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O
T1	50.07	30.93	7.08	3.88	1.79	1.30
T2	47.53	29.95	6.01	3.31	1.89	1.23
T3	36.27	23.52	4.01	2.34	1.59	0.95
T4	20.61	14.53	1.66	1.05	0.94	0.49
Con	6.95	5.22	0.40	0.30	0.40	0.16
component	SO_3	Na_2O	MgO	P_2O_5	ZrO_2	SrO
T1	0.98	0.32	0.36	0.15	0.07	0.05
T2	0.63	0.28	0.33	0.17	0.07	0.06
T3	0.45	0.18	0.25	0.13	0.07	0.05
T4	0.23	0.14	0.13	0.09	0.04	0.03
Con	0.02	0.06	0.05	0.04	0.02	0.02

reagent MIBC, and the ash content of the concentrate and the LOI of tailings can be slightly reduced, indicating the weak enrichment of unburned carbon in the concentrate. However, the LOI of tailings is stable at about 16.5%, and the ash content of the concentrate is between 77.2 and 77.7%, which shows that the selectivity of the flotation process is very poor when only MIBC is used, and the generation of foam concentrate mainly involves nonselective foam entrainment and mechanical entrainment. Compared with MIBC, the no. 2 oil exhibits a positive effect on the separation of unburned carbon and ash. As shown in Figure 2b, when oil no. 2 is used, the ash content of the concentrate is reduced to 52.15%, while the CMR is increased to 60.19%, and the LOI of synchronous tailings is decreased to less than 10%. Obviously, oil no. 2 appears not only excellent foaming performance but also certain selectivity of unburned carbon.

From Figure 2c,d, it is not difficult to find that under the same dosage diesel has a better sorting effect than kerosene. When diesel is used, a lower LOI tailing and a lower ash content concentrate can be obtained. That is, the selective collecting on unburned carbon of diesel is better than kerosene, which is related to the higher degree of crystallinity of unburned carbon in the fly ash.[48,49] However, when MIBC is used, regardless of whether the collector is diesel or kerosene, the LOI for the tailings is greater than 5%, and the ash content of the concentrate is more than 45%. The separation is not satisfying.

As shown in Figure 2e,f, the combination of diesel and no. 2 oil leads to the achievement of a relatively ideal separation results. Sufficient collector is a prerequisite for the full interaction between the unburned carbon and collector, and the adequacy of the frother is favorable for flotation since enough small and stable bubbles can be generated.[50] However, the use of a large amount of no. 2 oil deteriorates the selectivity and causes an increase in concentrate ash and a decrease in the combustible recovery rate.[24] When dosage of diesel oil and no. 2 oil is 800 and 600 g/t, respectively, the LOI of the tailings is reduced to 4.04%, which meets the first-class fly ash standard (LOI < 5%) based on the "National Standard of the People's Republic of China (GB/T 1596-20179) for fly ash used in cement and concrete", with an RUC for concentrate of 90.93%.

As demonstrated in Figure 2g, with the pulp concentration increasing, the LOI for tailings remained less than 5% with little change, but the ash content for the concentrate gradually raised, while the CMR of the concentrate increased at first and then decreased, reaching its largest value at a concentration of 100 g/L. Figure 2h plots that with increasing flotation time, the ash content of the concentrate is increased, and the LOI for the tailings gradually decreases. For a flotation time of 3 min, the tailings' LOI is the lowest, while the ash and CMR of the concentrate are maintained at a good level.

In summary, the optimal conditions for rougher flotation are determined as follows: diesel oil dosage of 800 g/t, no. 2 oil dosage of 600 g/t, pulp concentration of 100 g/L, and flotation time of 3 min. The corresponding product indicators are as follows: concentrate yield of 28.68%, concentrate ash content of 42.06%, concentrate CMR of 94.79%, yield of tailings 71.32%, and LOI for tailings of 3.02%. After one stage of flotation, the LOI for cleaned ash meets the national first-class standard, but the carbon concentrate needs further processing to upgrade its quality.

3.2. Stage-by-Stage Release Flotation. To explore the kernel for the mismatching of ash substances in the coarse concentrate, stage-by-stage release flotation was carried out. The floatation flowsheet is shown in Figure 3. The concentration of the rougher pulp was fixed at 100 g/L, while the cleaner pulp concentration depended on the quantity of flotation foam products in the previous section. The reagent used in the rougher stage was according to the optimal conditions determined in 3.1, and no chemicals were added in the cleaner step. The flotation ended when no foaming product was generated in either the rougher or cleaner. When the flotation finished, all the products were filtrated, dried, weighed, and tested for their ash content and LOI, and the yield and CMR of the concentrate were calculated. The stage-by-stage release experiment results are shown in Figure 4. The XRF analysis, laser particle size analysis, XRD quantitative analysis, and SEM−EDS analysis for each tailings and final concentrate are shown in Table 5 and Figure 5, respectively.

As shown in Figure 4, cleaning is an effective way to obtain a low-ash concentrate, and the ash content of the concentrate decreased to 13.63% after one rougher and three cleaners. Nevertheless, the cumulative LOI of the four tailings is 5.23%, which only meets the national standard of class II fly ash.

According to the particle size distribution results of products at each stage (Figure 5), it can be seen that among the four kinds of tailings, tailings 1 has the coarsest particle size distribution, most particles of which are distributed in the size

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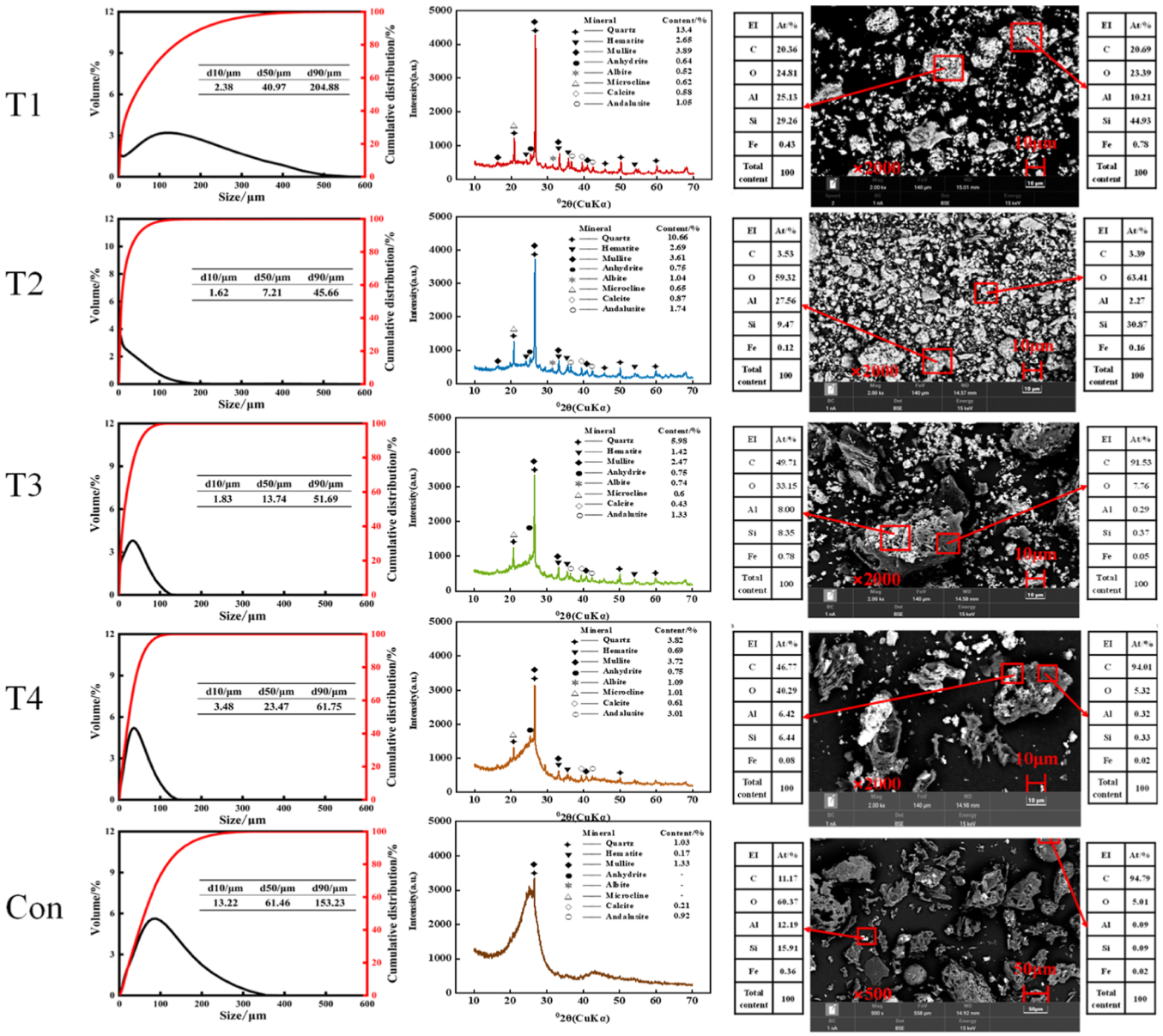

Figure 5. Comprehensive characterization of stage release flotation products.

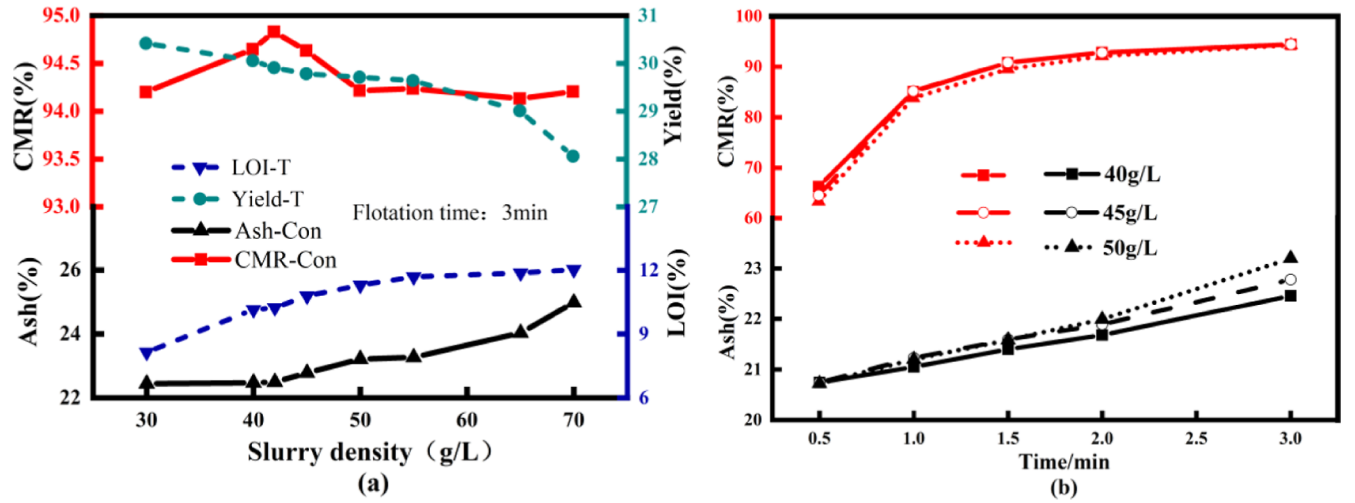

Figure 6. Effect of slurry density (a) and flotation time (b) on primary cleaning.

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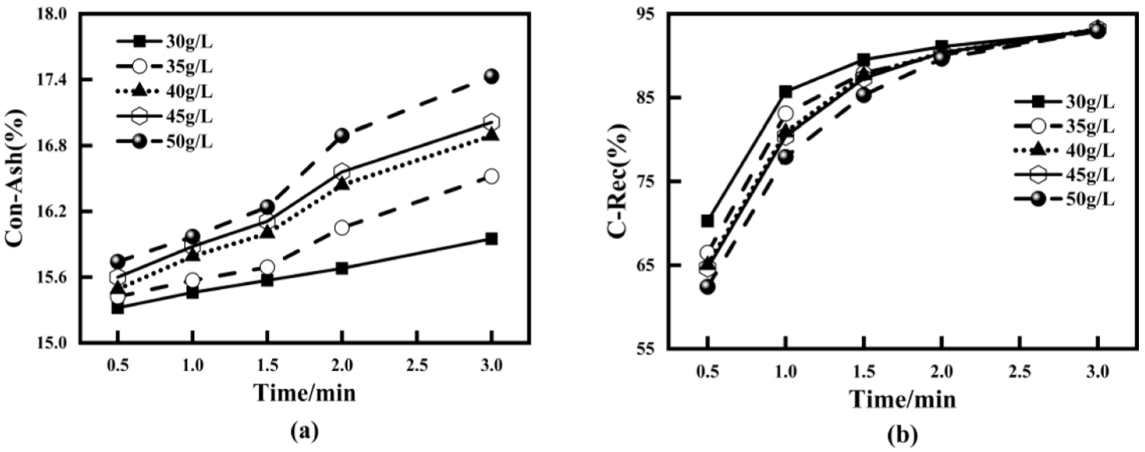

Figure 7. Effect of slurry density and flotation time on secondary cleaning: (a) ash of concentrate and (b) recovery of combustibles from concentrates.

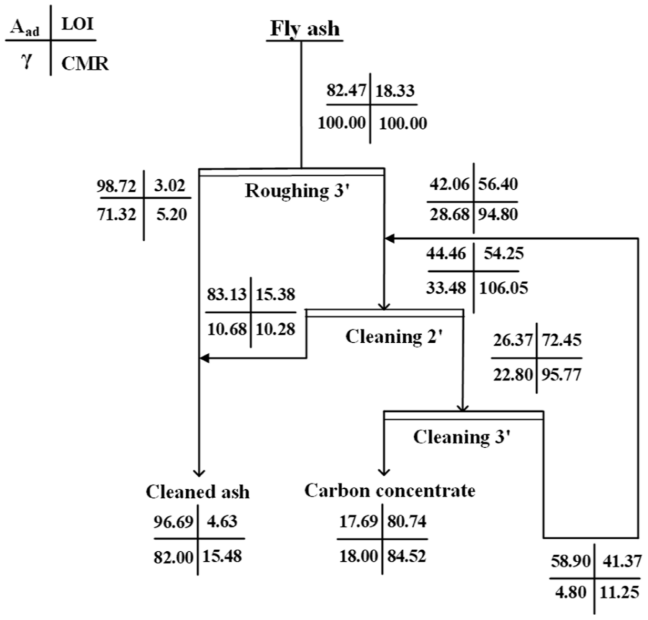

Figure 8. Flowchart of quantity and quality for closed-circuit flotation.

Table 6. Quality Indices for the Closed-Circuit Flotation Products

item	M_{ad} (%)	A_{ad} (%)	V_{ad} (%)	FC_{ad} (%)	$Q_{net,d}$ (kcal/kg)	LOI (%)
carbon concentrate	0.88	17.69	2.75	78.68	6476	80.74
cleaned ash	0.26	96.69	1.56	1.49	269	4.63
item	C_d (%)	H_d (%)	$O_{d,diff}$ (%)	N_d (%)	$S_{t,d}$ (%)	CMR (%)
carbon concentrate	77.53	0.52	1.90	1.19	1.01	84.52
cleaned ash	2.47	0.06	0.34	0.04	0.15	15.48

range between 20 and 250 μm, among the effective flotation size. On the contrary, fineness is a prominent feature of tailings 2, of which −20 μm fine particles account for 74.33%, and −12.5 μm quasi-colloidal particles reach 64.07%, namely, the majority of the particles in tailing 2 are beyond the effective size range for flotation, while particles in tailing 3, tailing 4, and the final concentrate are mainly within the effective size range for flotation, showing a nearly symmetrical particle size distribution centered at 33.59, 35.10, and 100 μm separately.

According to the XRF (Table 5), XRD, and SEM−EDS analysis results (Figure 5) of different stage products, it can be concluded that the inorganic mineral content in tailing 1 is the highest (96.98%), mainly composed of silicic acid salt and aluminosilicate minerals. There are trace interlocked unburned carbon and rare single unburned carbon particles in tailing 1. According to the higher hydrophilicity, tailing 1 is easy to be released from fly ash by floatation. The chemical composition and mineral phase of tailing 2 are very close to that of tailing 1, tailing 2 was entrained into the rougher froth products due to its finer size, which directly leads to an increase in the ash content of coarse concentrates. However, because of the higher mineral content and poor hydrophobicity, tailing 2 can be easily removed by one stage cleaning. Different from tailings 1 and 2, the mineral content of tailings 3 is greatly reduced. It can be clearly observed from the SEM−EDS images of tailing 3 that a considerable amount of unburned carbon and minerals is present as lean mesoconjoined particles except for a small amount of monomeric mineral particles, which delicately affects the ash content of the concentrate. Tailing 3 can be isolated after two cleaning steps. In tailing 4, the content of unburned carbon (60.07%) is more than that for inorganic minerals (39.93%), most appearing as underliberated interlocked body. The main composition of the final concentrate is unburned carbon in addition to a few aluminosilicate and silicate minerals, some of which disperse in the pores or cavities of unburned carbon in the form of fine particles, the others intergrowing with unburned carbon, while monomer mineral particles are rare; consequently, these minerals cannot be further separated from the concentrate by the conventional sorting method.

The stage-by-stage release flotation results further confirmed that owing to a considerable amount of easily separated mineral particles in the fly ash, cleaned ash with a qualified LOI can be simply obtained after one flotation step, as long as under suitable operation condition. However, due to the misplacing of fine mineral particles and interlocked particles in froth products, it is extremely hard to get qualified carbon concentrates via one-stage flotation. Exploring an applicable multistage flotation process is an inevitable choice to reach the standard simultaneously of qualified cleaned ash and unburned carbon. The process details of the multistage flotation depend

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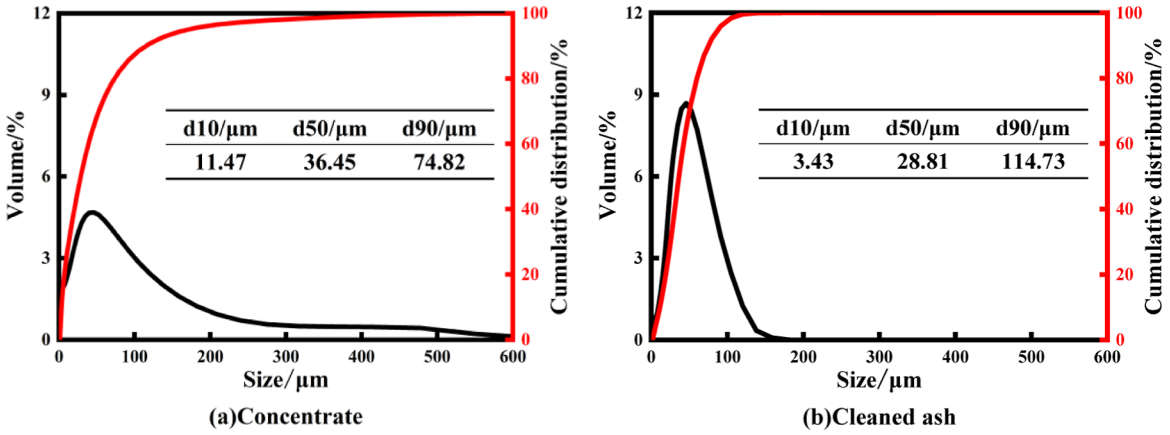

Figure 9. Laser particle size analysis results for closed-circuit flotation products.

Table 7. XRF Analysis Results for Closed-Circuit Flotation Products (wt %)

component	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O
concentrate	10.21	6.80	0.66	0.44	0.51	0.20
cleaned ash	52.14	27.29	7.56	3.58	1.80	1.21
component	SO_3	Na_2O	MgO	P_2O_5	ZrO_2	SrO
concentrate	0.18	0.08	0.06	0.06	0.03	0.03
cleaned ash	0.96	0.21	0.34	0.15	0.08	0.05

not only on the occurrence of unburned carbon and minerals but also on the quality requirements of the products. As mentioned above, the nonselective mechanical entrainment of ultrafine mineral particles in the first concentrate is unavoidable; consequently, at least one cleaning step is required to release fine-grained ash and greatly reduce the ash content of carbon concentrate. The goal of this study was to obtain carbon concentrates with an ash content of less than 20% and simultaneous tailings with a LOI of less than 5%. According to Figure 4, the theoretical flotation times should be no less than 2.3 times, which means that at least three flotation stages (one rougher and two cleaners) are needed. Correspondingly, the theoretical ash content and the CMR of the carbon concentrate are 15.51 and 81.36%, respectively, the theoretical yield for the synchronous tailings is 83.12%, and the LOI is 4.49%.

3.3. Detailed Experiment for Multistage Flotation.

The detailed experiments for the cleaning stage were carried out to determine reasonable parameters for industrially acceptable implementation. The results are shown in Figures 6 and 7. It should be noted that a suitable prestirring time in the cleaning stage is 2 min, which has been identified by previous experiments.

The results of the first cleaning in Figure 6a show that for a pulp concentration of below 55 g/L, the carbon concentrate ash is relatively less affected by an increase in pulp concentration; however, when the pulp concentration exceeds 55 g/L, the concentrate ash content increases rapidly with increasing pulp concentration. There exists an optimal slurry concentration to obtain the optimal CMR. The increase in slurry concentration has a relatively prominent effect on the LOI for the tailings. The tailings' LOI continues to increase with increasing concentration in the range of 30−55 g/L. Considering the ash content, CMR, and LOI together, a slurry concentration of approximately 45 g/L is more favorable. The flotation time test (Figure 6b) further confirms that a pulp concentration of 45 g/L is more beneficial for the isolation and that 2 min is preferable for the first cleaning.

Figure 7 shows that increasing the concentration of the second cleaning pulp is not beneficial for the reduction of the concentrate ash content or recovery of combustibles. The best carbon concentrate outcome is obtained on a slurry concentration of 30 g/L. As shown in Figure 7b, an extension

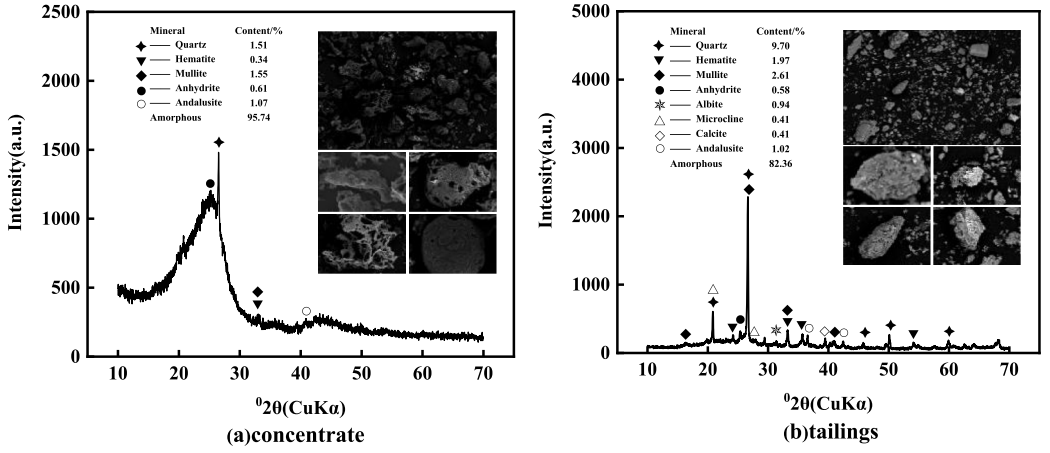

Figure 10. XRD and SEM analysis results of closed-circuit flotation products.

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of the flotation time results in a slow increase in the concentrate ash content and a rapid improvement in the CMR. The concentrate CMR reaches 93.00% for a flotation time of 3 min, which is increased by 1.91% compared to a floatation of 2 min, while the concentrate ash content is increased by only 0.27%. Therefore, the second cleaning time was designated as 3 min.

3.4. Closed-Circuit Flotation Test. The open-circuit flotation test was first carried out using the above optimum flotation conditions, and the flotation indicators were found to be stable. Based on the open-circuit experiment, a final flotation process was recommended, as shown in Figure 8. Then, a continuous closed-circuit flotation test was performed, and the sorting indicators obtained after process balancing are listed in Figure 8. The main quality indices for the concentrate and tailings are shown in Table 6. The laser particle size and XRF analysis results for the concentrate and tailings are shown in Figure 9 and Table 7. The results of XRD and SEM analyses of concentrate and tailings are shown in Figure 10.

Using the recommended process and parameters, carbon concentrate with 82% yield and cleaned ash with 18% yield were obtained by conventional flotation of fly ash, and the flotation perfection index reached 80.66%.[51] The ash content of the concentrate is reduced to 17.69%, and the calorific value is close to 6500 kcal, which manifests that the carbon concentrate possesses the higher quality fuel properties and could be directly used as a raw material for coal water slurry according to its fine particle size (d_{90} = 74.82 μm). Furthermore, as indicated by Figure 10, the concentrate is composed predominantly of loose and porous unburned carbon, with a small quantity of inorganic minerals. Its low ash content, along with well-developed pores and cavities, renders it an ideal precursor for the preparation of activated carbon.[52] Carbon has versatile applications, and for further broadening its scope and enhancing its application value, subsequent research is required to conduct a more comprehensive analysis of the properties of the concentrate.

Meanwhile, the LOI of the cleaned ash is only 4.63%, which meets the first-grade fly ash standard requirements in China. The content of active components (SiO_2 + Al_2O_3 + Fe_2O_3) in the ash product is increased to 86.99%, which is significantly better than the standard requirements of GB/T 1596-2017 for "Fly Ash for Cement and Concrete". Although the content of 0−45 μm particle is high (>40%), the cleaned ash can still be used as a high-quality raw material for cement, concrete, and other building materials.[37]

4. CONCLUSIONS

This study produced refined carbon and cleaned ash simultaneously, and no secondary solid waste was generated, which provides a feasible technical approach for full-component recovery and full-scale utilization of high-carbon fly ash.

(1) The batch flotation experiment shows that the selective capture of unburned carbon by diesel is better than kerosene, and foaming reagent no. 2 oil is more favorable for the separation of unburned carbon and ash mineral. Pulp concentration and separation time are also found to be important factors that affect the effectiveness of the separation. The optimum flotation parameters are given as follows: ① Roughing: feed concentration 100 g/L, flotation time 3 min, diesel oil 800 g/t, and no. 2 oil 600 g/t; ② first cleaning: pulp concentration 45 g/L, flotation time 2 min, and no reagent used; and ③ second cleaning: pulp concentration 30 g/L, flotation time 3 min, and no chemicals added.

(2) The stage-by-stage release flotation test depict that the nonselective entrainment of 0−20 μm fine mineral particles and the weak selective capture of lean conjoined particles contribute to the poor selection and the higher ash content in the rougher concentrate. A multistage flotation is the key to solving the dilemma. The industrially scalable floatation process is a partial closed-circuit process consisting of one roughing and two cleaning steps.

(3) Cleaned ash with a yield of 82.00% and a LOI of 4.63% and a carbon concentrate with a yield of 18.00% and an ash content of 17.49% are simultaneously obtained. The recovery rate for the combustible material reaches up to 84.72%. This study provides a feasible technology for the full-scale utilization of high carbon fly ash.

(4) There is a need to identify a more efficient collector, enabling the achievement of the desired separation effect at a higher pulp concentration. The mineralization mechanism of unburned carbon remains unexplored. The aforementioned areas constitute the primary focus and direction for further research on the separation and comprehensive utilization of fly ash.

■ ASSOCIATED CONTENT

Data Availability Statement

The authors do not have permission to share data.

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Notes

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