Associations of Gangue Minerals in Coal Flotation Tailing and Their Transportation Behaviors in the Flotation Process

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ABSTRACT: The mass production of flotation tailings has become a serious risk to the environment. Re-concentration of tailings is one of the best ways to solve this problem, which requires a better understanding of flotation tailings. In the present work, flotation kinetics, timed-release flotation, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and solid-state nuclear magnetic resonance (SSNMR) were used to analyze the properties of flotation tailings with different particle sizes and densities, the occurrence and binding state of gangue minerals in tailing, and the transportation behaviors in the re-flotation process. Flotation results showed that the flotation yield exhibited little change with the extension of flotation time, while the ash content of the froth concentrates increased. An increase of the flotation time could reduce the ash content of the obtained product. The characterization results confirmed that the main gangue minerals in the tailings were kaolinite and quartz. With the decrease of particle size or the increase of floating and sinking density, the contents of kaolinite and quartz increased. However, due to the different dissemination characteristics of kaolinite and quartz in the tailings, the distributions of kaolinite and quartz in the different particle sizes and densities of tailing had differences. Although both kaolinite and quartz could exist as monomers, kaolinite was more easily associated with coal. Based on the above cognition, a new flotation method is proposed for coal flotation tailing. A part of the concentrates in the early stage of flotation should be scraped out quickly. Then, the concentrates obtained in the later stage of flotation are collected and merged into the concentrates obtained during the early stage of flotation, while the secondary tailing is directly pumped into the raw feed system.

1. INTRODUCTION
Coal is an important energy source in some countries, especially in China, Australia, Poland, and India. The proportion of fine coal in the raw coal significantly increases with the high mechanization of coal mining technology. The separation of fine coal has become a severe challenge for the coal industry. Froth flotation is widely used for processing fine coal, utilizing the difference between the surface hydrophobicities of particles to separate coal from gangue. In the flotation process, hydrophobic particles are expected to attach to the bubble surface and float to form a froth layer, whereas hydrophilic particles tend to sink to the bottom of the cell to form tailings. It has been reported that the annual output of these coal flotation tailings reaches up to 100 million tons. The long-term storage of coal flotation tailings occupies a huge amount of land resources, causing a serious risk to the environment. Recently, the disposal of coal flotation tailings has received more and more attention. Generally, coal flotation tailings can be mixed into raw coal or medium coal for combustion. Besides, coal flotation tailings contain abundant silicon and aluminum components, which can be used to produce brick, cement, and filling material. The presence of large amounts of carbon in these coal tailings can have a negative effect on the material utilization of tailings. On the other hand, the carbon in the coal flotation tailing is also a valuable resource, which can be used to generate electricity and prepare carbon materials. Therefore, the recovery of carbon components from coal flotation tailings is an important stage to rationally dispose of coal flotation tailings, which is conducive to saving resources, protecting the environment, and creating greater economic benefits for coal enterprises.

Extensive research on the recovery of carbon components from coal flotation tailing has been carried out. Yang et al. reported a novel gravity-flotation process to re-separate the coal flotation tailings, including the disposal of tailings via gravity, grinding liberation, and froth flotation. A clean coal product with an ash content of 12.33% and an appreciable yield of 32.34% could be obtained using this process. Yu et
al.\textsuperscript{15} proposed a separation process of coal flotation tailing, namely reverse flotation–grinding–re-separation, to obtain the clean coal product with a yield of 25% and an ash content of 13.96%. It is worth noting that the above re-separation processes of coal flotation tailing all include a grinding stage. The carbon component in the coal flotation tailings is closely connected with the gangue and needs to be ground to achieve further dissociation. Kaolinite (Al\textsubscript{2}O\textsubscript{3}·2SiO\textsubscript{2}·2H\textsubscript{2}O) and quartz (SiO\textsubscript{2}) are two typical minerals in gangue.\textsuperscript{15–18} In the flotation process, these gangue minerals may enter into clean coal products through coating or entrainment. Numerous studies have been carried out to explore the adverse effects of the nonselective flotation behavior of gangue minerals in the flotation process.\textsuperscript{19–23} However, the associations of gangue minerals such as kaolinite and quartz in raw coal are different; especially for coal flotation tailings with high ash content, the irregular inclusion of gangue minerals makes the tailings complex in nature. In addition, based on the different crystal structures and surface physicochemical properties of kaolinite and quartz, their transportation behaviors in the flotation process are quite different. It is necessary to clarify the association behaviors of gangue minerals in coal flotation tailing and their transportation behaviors in the flotation process.

This work aimed to investigate the associations of gangue minerals in coal flotation tailing and their transportation behaviors in the re-flotation process. Flotation kinetic tests and timed-release flotation tests were performed to analyze the re-flotation efficiency of coal flotation tailing. A series of characterization measurements such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and solid-state nuclear magnetic resonance (SSNMR) measurements were carried out to study the associations of gangue minerals such as kaolinite and quartz in coal flotation tailing, clarifying the transportation behavior differences between kaolinite and quartz in the re-flotation process. The results of this work are expected to provide valuable guidance for the separation and utilization of coal flotation tailing.

2. RESULTS

2.1. Flotation Kinetic Results. The results of the flotation kinetic test are shown in Figure 1. As shown in Figure 1, in each flotation period, the concentrates had a low yield, and the cumulative yield of the concentrates was 31.91%. Moreover, the flotation yield exhibited little change with the extension of flotation time. The ash content of the coal concentrates increased with the increasing flotation time, but the ash content of each concentrate product was high, and the lowest ash content reached 13.37%. The results of the flotation kinetic test indicated that the coal flotation tailings were difficult to effectively separate carbon and ash by increasing the flotation time, and low-ash clean coal could only be collected in a short flotation time.

2.2. Timed-Release Flotation Test Results. The results of timed-release flotation test are shown in Figure 2. As observed, after timed-release flotation, the roughing tailing product T\textsubscript{1} occupied the highest yield, which was 73.13%, and the yields of tailing products obtained by the four subsequent re-flotations were all less than 10%. The ash content of the obtained tailing products gradually decreased with the increase of flotation time, indicating that the gangue minerals were gradually separated from coal slime and the grade of the froth concentrate gradually increased. Tailing product T\textsubscript{4}, exhibited the highest ash content of 67.75%, implying that a large number of coal and gangue combinations existed in the coal flotation tailings, which were difficult to separate directly. After two flotation separations, the low-ash products with a yield of 19.28% and an ash content of less than 10% could be recovered. This result was consistent with the density analysis of the coal samples.

2.3. XRD Results. XRD is a crucial method that reflects the distribution of gangue minerals in coal flotation tailing. Figure 3 shows the XRD patterns of coal flotation tailings with various size and density fractions. As shown in Figure 3a, the peaks of kaolinite and quartz could be observed in coal flotation tailings with different size fractions, and the peak intensity increased with decrease in the tailing particle size. This indicated that higher contents of kaolinite and quartz were present in the fine coal tailing, resulting in a high ash content in the fine coal tailing, which was consistent with the size distribution of the coal tailing samples. It is worth noting that the quartz peak intensity of the size fraction of 0.074–0.045 mm was significantly higher than that of the size fraction of 0.045 mm. However, the characteristic peak intensity of kaolinite did not show a proportional change with the quartz peak. This seems to imply that kaolinite and quartz had different distribution characteristics in coal tailings with different size fractions. The XRD patterns of coal flotation tailings with different density fractions are observed in Figure 3b. For a density fraction of −1.6 g/cm\textsuperscript{3}, a broad peak at 2\textdegree angles of
20–30° representing the amorphous carbon could be observed in the XRD pattern, indicating that the carbon was the main component of the coal tailings of this density fraction. However, for a density fraction of +1.6 g/cm$^3$, the amorphous carbon was difficult to be observed in the XRD patterns, especially for the density fraction of +2.0 g/cm$^3$, indicating that these coal samples were mainly gangue minerals. In addition, similar to the XRD patterns of the screening products, the peak intensities of kaolinite and quartz did not show an obvious correlation.

The XRD patterns of the flotation kinetic test products are shown in Figure 4a. As observed, kaolinite and quartz were distributed in all flotation products, and their XRD peak intensities gradually increased with the continuation of the flotation process, indicating that the content of gangue minerals in the concentrate increased with the increase of flotation time. Figure 4b presents the XRD patterns of the timed-release flotation test products. As noted, amorphous carbon could not be observed in the XRD spectrum of $T_{r1}$ products, and the main components were kaolinite and quartz. Amorphous carbon could be gradually observed in the tailing products with the increase of flotation times, and the peak intensities of kaolinite and quartz were low, especially for $T_{r3}$, $T_{r4}$, $T_{r5}$, and $F$ products. It indicated that the main content of these products was carbon, which was consistent with the ash analysis results of the timed-release flotation test products. Furthermore, the intensity of the quartz peak gradually decreased with the increase of flotation times, and it was difficult to observe the quartz peaks in $T_{r5}$ and $F$ products. However, the peak of kaolinite could be observed in each product. This was consistent with the results reported by Yu et al. In the flotation process, the energy barrier between the kaolinite and coal particles is low, resulting in the occurrence of slime coating and the increase of concentrate ash content.

2.4. FTIR Results. The FTIR spectra of the timed-release flotation test products are shown in Figure 5. The peaks at around 3600, 1600, and 1000 cm$^{-1}$ are the OH stretching vibration of kaolinite, OH bending vibration, and Si–O–T ($T$ is Al or Si) asymmetric stretching vibration, respectively. The two peaks at around 700 cm$^{-1}$ represent the Si–O–Al symmetric absorption vibration. As shown in Figure 5, the intensity of these infrared peaks in the products gradually decreased with the continuation of the flotation process. Only a very weak Si–O peak could be observed in the FTIR spectra of $T_{r5}$ and $F$ products, and the OH stretching vibration peak had disappeared. These results indicated that the products obtained by multiple flotation still contained kaolinite, but the relative content was low, which was consistent with the ash analysis results of the timed-release flotation test products.

2.5. SEM-EDS Results. Figure 6 presents the SEM-EDS images of the raw coal sample and partial timed-release flotation test products. As shown in Figure 6a, the raw coal flotation tailing contained C, Si, and Al elements, and the carbon content was found to be relatively low. The particle appearing in the central area of the SEM image of Figure 6a was rich in silicon elements, while the corresponding position was less in aluminum, indicating that this particle may be a quartz particle. This result implied that the quartz could exist in the coal flotation tailing in the form of a monomer. In the surrounding area of the image, the distributions of Si and Al elements almost overlapped, inferring the existence of kaolinite. Additionally, a large amount of carbon elements was present in this area, indicating that kaolinite was associated with coal. Figure 6b presents the SEM-EDS images of the concentrate samples obtained from the timed-release flotation test. The surface of the concentrates mainly contained C elements, and Si and Al elements were distributed in the form of scattered points. The distributions of Si and Al elements almost overlapped, inferring the presence of kaolinite. It indicated...
that the concentrates were mainly composed of carbon, with a small amount of kaolinite and almost no quartz. As noted in Figure 6c,d, the distributions of C, Si, and Al elements had a high degree of coincidence, indicating that much kaolinite might cover the coal particle surface. A part of the Si elements existed almost alone (highlighted by red boxes), confirming the existence of the quartz monomer. SEM-EDS test results suggested that the ash content of the concentrates decreased with the flotation process continuing, and the quartz could be gradually separated. However, part of the kaolinite could cover the coal surface and enter into the concentrates, which affected the grade of the concentrates.

2.6. SSNMR Results. $^{29}$Si solid-state nuclear magnetic resonance can confirm the coordination situation around the Si atoms, which is beneficial to understand the association behavior of Si components. Figure 7 presents the SSNMR results of $T_{r1}$ and $F_r$ products obtained from the timed-release flotation test. The Si in kaolinite is tetracoordinated, and the silicon-oxygen tetrahedron is connected with an aluminum-oxygen octahedron and three other silicon-oxygen tetrahedra. As observed, the peak at around a chemical shift of 97 ppm was $Q^3$, corresponding to the coordination of silicon in kaolinite.26,27 The peak marked by the dotted line on the right was $Q^4$, corresponding to the coordination of silicon in quartz.28 These results were consistent with the XRD analysis. For $F_r$ products, two new peaks (i.e., peak 1 and peak 2) were observed, indicating that the Si in $F_r$ products had other coordination forms besides kaolinite and quartz. Based on the elemental composition analysis, Si might bond with the carbon in coal to form a new coordination form. The chemical shifts that peaks 1 and 2 were located at were high, which could rule out the embedding of single Si atoms in the coal macro-
molecular network. The inorganic phase (gangue) and organic phase (coal) atomic layers could have mutual inclusions, resulting in the substitution of Si atoms on the surface of kaolinite by C atoms to form C–O–Si bonds.20

3. DISCUSSION

According to the analysis of the above characterizations, kaolinite and quartz were found to exist in most concentrate products. Among them, quartz was found to appear in the form of monomers, while kaolinite presented in two forms, i.e., monomer and kaolinite–coal integration. Kaolinite is a 1:1 layered silicate of dioctahedral structure, and its basic structure is composed of a silicon-oxygen tetrahedron and an aluminum-oxygen octahedron layer. The interlayers are connected by hydrogen bonds, which are easily split into small flakes along the 001 surface. Quartz has a shelf-like structure, and its structural unit is a silicon-oxygen tetrahedron.30,31 In the flotation process, kaolinite and quartz have exhibited different partitioning behaviors. The Si\(^{29}\) in kaolinite is easily replaced by Al\(^{3+}\) and Fe\(^{3+}\), resulting in the 001 crystal face being negatively charged. Quartz becomes negatively charged by losing the charged particles. The bubble surface is usually negatively charged, causing its strong electrostatic repulsion with kaolinite and quartz. On the other hand, kaolinite and quartz are hydrophilic particles with a low attachment force to the bubbles, which are difficult to adhere to the bubble surface. Therefore, kaolinite and quartz in monomeric forms contaminate the flotation concentrates due to the water entrainment rather than the capture of bubbles, increasing the ash content of the concentrates. An increase of froth flotation times can effectively slow down the water entrainment to increase the concentrate grade, and it is confirmed by the timed-release flotation test results. Additionally, the surface of coal is usually negatively charged, resulting in the electrostatic repulsion between kaolinite, quartz, and coal particles to hinder the adhesion. However, kaolinite is easy to sludge in the process of coal mining and separation, resulting in a finer particle size, which is reflected from the XRD patterns of the screening products. In the flotation process, the kaolinite particle has an interface polar interaction energy with the coal particle, which is the attraction potential energy, and the value is much larger than the van der Waals potential energy and electrostatic force potential energy. It dominates the total interaction energy between the kaolinite and coal particles, because of which kaolinite particles can coat the coal surface after overcoming the “energy barrier”, which has been confirmed by numerous studies.19–21 The fine kaolinite particle has a lower “energy barrier”, which explains why kaolinite can exist in various products in the form of a continuum, which is difficult to be effectively restrained by increasing the flotation process or time.

Based on the above analysis of the association behaviors of gangue minerals in coal flotation tailing and their transportation behaviors in the re-flotation process, an effective separation method of combustion in the coal flotation tailing is proposed, as shown in Figure 8. Firstly, the froth concentrates with the low ash preferentially separated in the flotation process should be collected, and the entrainment of gangue minerals is weak. For the froth concentrates collected at the later stage of flotation, one or more re-flotation processes may be used for further separation and enrichment to obtain the low-ash products. The concentrates obtained from the above flotation process are mixed to form the final concentrate products. Referring to the experimental process and coal samples of the flotation kinetic test and timed-release flotation test, the laboratory flotation test using the above flotation process showed that the concentrate product with a yield of 24% and an ash content of 11% could be obtained.

4. CONCLUSIONS

To improve the utilization efficiency of coal flotation tailing, achieving the clean production of fine coal, the association behaviors of gangue minerals such as kaolinite and quartz in coal flotation tailing and their transportation behaviors in the re-flotation process were explored. The following conclusions can be drawn:

(1) Results of the flotation kinetic test illustrated that the flotation yield exhibited little change with the extension of flotation time, while the ash content of the froth concentrates increased. A low yield of concentrate products with low ash content could be obtained in the initial flotation time. Furthermore, analysis of the timed-release flotation test showed that the ash content of the obtained tailing products gradually decreased with the increase of flotation time, indicating that the products with high grades could be obtained by the re-flotation.

(2) A series of characterization analyses confirmed that the main gangue minerals in coal flotation tailing were kaolinite and quartz. With the decrease of particle size or the increase of density fraction, the contents of kaolinite and quartz showed an increasing trend. The association behaviors of the kaolinite in the coal flotation tailing were different from quartz, which was found to present in the form of monomers, while kaolinite presented in two forms: monomer and kaolinite–coal complex. In the flotation process, the kaolinite and quartz presented different transportation behaviors. Quartz in monomeric form contaminated the flotation concentrates due to the water entrainment, and it could be relieved by the increase of the flotation time. Kaolinite entered into the froth products by the water entrainment and coating, which was difficult to be effectively restrained.

(3) A separation method of combustion in coal flotation tailing was proposed. Firstly, the froth concentrates with the low ash preferentially separated in the flotation process should be collected. Once or more flotation may be used to further separate the froth concentrates collected at the later stage of flotation to obtain the low-ash products. The concentrates obtained from the above flotation process are mixed to form the final concentrate product. The laboratory flotation test showed that the
concentrate product with a yield of 24% and an ash content of 11% could be obtained using this method.

5. EXPERIMENTS

5.1. Materials. The test coal samples for coal flotation tailing were obtained from the Zaozhuang mining area, Shandong province, China. The size distribution of the coal samples is given in Table 1. As observed, the ash content increased with the decrease of coal particle size. The size fraction of -0.045 mm with a high ash content of 64.42% occupied the highest mass fraction, which was 75.50%. The density analysis of the coal samples is shown in Table 2. As noted, the ash content increased with increase in the coal sample density. The highest mass fraction and ash content located at the density fraction of +2.0 g/cm³ were 51.80 and 71.85%, respectively. It is worth noting that the density fraction of −1.5 g/cm³ with a yield of 19.23% had a low ash content of 9.46%, and these needed to be separated and recovered. The X-ray diffraction analysis of the test samples was conducted using a D8 Advance type X-ray diffractometer (Bruker, Germany), as shown in Figure 9. An initial observation indicated that some peaks of quartz and montmorillonite were present, indicating that the main mineral phases in the test coal samples were quartz and kaolinite. It is also worth noting that kaolinite is a typical gangue mineral with high argillization, which is not conducive to flotation. Furthermore, the collector and frother used in this study were diesel and 2-octanol, respectively.

5.2. Flotation Kinetic Test. In this study, an XFD-1.0 L type lab-scale single mechanical flotation machine was used to carry out the flotation kinetic test. The coal samples were added to the flotation cell containing 1.0 L of water with a concentration of 80 g/L, and premixed at an impeller speed of 1800 rpm for 180 s. After that, the collector was added to the coal slurry at a dosage of 275 g/t coal with a mixing time of 180 s. Subsequently, the frother was added to the slurry at a dose of 115 g/t coal and mixed for another 60 s. Air was then introduced into the flotation cell at a constant air intake of 0.18 m³/h. The total flotation process was 180 s. In the flotation process, five froth concentrate products, namely, F₁, F₂, F₃, F₄, and F₅, were consecutively collected after 20, 40, 80, 120, and 180 s, and the collected tailing product was named Tₖ. The collected products were filtered, dried, and weighed for yield and ash analysis, and the yield (γᵢ, %) of each concentrate was calculated as eq 1

\[
\gamma = \frac{m_f}{m_i} \times 100\%
\]

where \(m_i\) and \(m_f\) are the mass of each concentrate and the flotation feed, respectively (g).

5.3. Timed-Release Flotation Test. The timed-release flotation test was also performed using the above mechanical flotation machine at an impeller speed of 1800 rpm and an air intake of 0.18 m³/h. The amounts of collector and frother added were 500 and 300 g/t coal, respectively. The whole flotation experimental process is shown in Figure 10. As noted, five tailing products and one concentrate product were collected. All six products were filtered, dried, and weighed for the following analysis, and the yield was calculated using eq 1.

5.4. Characterizations. In this study, a D8 Advance type X-ray diffractometer (Bruker, Germany) was used to conduct the XRD measurements of various coal samples. Prior to the XRD measurements, coal samples were ground to obtain 0–45 μm size fractions and pressed to form a coal plate. The XRD patterns (scanning range: 5–70 2θ/degree) were recorded using Cu Ka (40 kV, 40 mA) at a scanning speed of 2° min⁻¹. The FTIR spectra of the coal samples after diluting by KBr were recorded using a Vertex 80v spectrometer with a resolution of 4 cm⁻¹. The surface morphology and elemental composition analyses of the coal samples were carried out.

Table 1. Size Distribution of the Coal Sample

| size (mm) | yield (%) | ash (%) | cumulative floats | cumulative oversize | cumulative undersize |
|----------|-----------|---------|------------------|---------------------|---------------------|
|          | yield (%) | ash (%) | yield (%) | ash (%) | yield (%) | ash (%) |
| +0.5     |           |         |           |         |           |         |
| 0.5–0.25 |           |         |           |         |           |         |
| 0.25–0.125 | 6.08    | 9.02    | 14.71    | 7.87    | 91.57    | 56.20 |
| 0.125–0.074 | 6.10     | 17.32   | 20.81    | 10.50   | 85.29    | 59.67 |
| 0.074–0.045 | 3.70    | 32.63   | 24.50    | 13.83   | 79.19    | 62.93 |
| −0.045   | 75.50     | 64.42   | 100.00   | 52.02   | 75.50    | 64.42 |
| total    | 100.00    | 52.02   |          |         |          |         |

Table 2. Density Analysis of the Coal Sample

| density (g/cm³) | yield (%) | ash (%) | cumulative floats | cumulative oversize | cumulative undersize |
|-----------------|-----------|---------|------------------|---------------------|---------------------|
| −1.3            | 3.50      | 5.29    | 3.50             | 5.29                | 100.00             | 52.32             |
| 1.3–1.4         | 9.51      | 8.43    | 13.01            | 7.59                | 96.50              | 54.03             |
| 1.4–1.5         | 6.22      | 13.37   | 19.23            | 9.46                | 86.99              | 59.01             |
| 1.5–1.6         | 4.87      | 18.23   | 24.09            | 11.23               | 80.77              | 62.53             |
| 1.6–1.8         | 6.76      | 26.80   | 30.85            | 14.64               | 75.91              | 65.37             |
| 1.8–2.0         | 17.35     | 49.09   | 48.20            | 27.04               | 69.15              | 69.14             |
| +2.0            | 51.80     | 75.85   | 100.00           | 52.32               | 51.80              | 75.85             |
| total           | 100.00    | 52.32   |                   |                     |                     |                   |

Figure 9. XRD pattern of the coal flotation tailing.
using a Quanta 250 scanning electron microscope-energy dispersive spectrometer (FEI, USA). Before the experiments, the dried coal samples were adhered to the conductive tape on the sample stage, and gold layers were sputtered on the sample surfaces. The whole test was carried out in a low-vacuum environment. The $^{29}$Si SSNMR (solid-state nuclear magnetic resonance) spectra of the coal samples were measured using an Avance NEO 400 WB solid-state nuclear magnetic resonance spectrometer (Bruker, Switzerland).

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**Notes**

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