Occurrence Characteristics of Fine-Grained Pyrite in Coal and Its Scaling Effect on Flotation Desulfurization

Mengya Ma, Wenfeng Wang,* and Kun Zhang

ABSTRACT: To explore the occurrence and distribution characteristics of fine-grained pyrites in coal and the effect of pyrite particle size on flotation efficiency, coal samples from Guizhou province and Shanxi province, China, were selected for pyrite morphology observation and sulfur content test before and after flotation desulfurization experiments with different coal particle sizes. Experimental results showed that the fine-grained pyrites in coal have various occurrence forms and complex connections with the coal matrix. The fragmentation process can change the distribution of pyrite content in coal. Flotation desulfurization experiments showed that the sum of pyrite content in the cleaned coal and middlings gradually became significantly higher in coal particles with size 15−37 μm compared with particle sizes 37−44 and 44−75 μm. The complex occurrence morphology and crystal structure of fine-grained pyrite make it difficult to be removed from the coal matrix by ore grinding during flotation. Fine-grained pyrite mainly occurs in the form of framboidal pyrite, disseminated pyrite, and monomer pyrite with a size of 0.69−33.94 μm in the middlings and cleaned coal. Therefore, 37 μm is considered as the critical dimension for ore grinding to improve the effective flotation desulfurization efficiency in this study, and some more effective methods should be used to increase the desulfurization efficiency of fine-grained pyrite.

1. INTRODUCTION

Sulfur is one of the main harmful elements in coal, which affects the quality of industrial products, corrodes equipment, and endangers human health and ecological environment during coal combustion. Sulfur in coal is mainly controlled by the sedimentary environment of coal, especially by the seawater factor. The formation environment of coal seams in China includes offshore and continental deposits, and the content and distribution of sulfur in coal vary in different regions. Most of the coal seams in Northeast, Northwest, and North China, such as the Shanxi Province, are formed by continental and marine-continental deposits with a low sulfur content. However, coal seams in South and East China, e.g., the Guizhou Province and Yunnan Province, are mainly formed by offshore deposits, which have a high sulfur content. Pyrite is the main carrier of the sulfur element in Chinese coal seams. Therefore, identifying the distribution characteristics of pyrite in coal is a prerequisite for effective desulfurization and clean utilization of coal resources.

The occurrence and size distribution of pyrite are determined by the depositional environment of coal. The particle size of pyrite in different occurrence modes varies greatly, ranging from centimeters to submicrons. Coarse-particle pyrite is mainly enriched in agglomerated, nodular, and fracture-filling forms, and fine-grained pyrite has a relatively complex occurrence state, including framboidal, euhedral crystalline, spherical, caviar-like, fine-grained agglomerated, etc. Flotation is a common desulfurization method of coal before combustion, which has the advantages of cost savings and environmental protection. Generally, pyrite with coarse particles larger than 60 μm in diameter can be removed by conventional flotation methods.

However, fine-grained pyrites (smaller than 60 μm) are difficult to separate by the flotation method. On the one hand, the formed foam of the mixture of fine-grained pyrite and coal particles during the flotation process has strong stability and low fluidity, making the pyrite difficult to separate from coal. On the other hand, the fine-grained pyrite can form a complex symbiotic relationship with the coal matrix, resulting in a flotation behavior similar to that of coal particles. In addition, the sulfur atoms on the crystal surface of fine-grained pyrite are easily replaced by carbon atoms, reducing the physical adsorption ability of pyrite toward water molecules and increasing the difficulty of separation. Wang et al. analyzed the influence of the coal particle size on flotation recovery and...
concluded that the optimum coal particle size ranges from 50 to 250 μm (recent advances in the beneficiation of ultrafine coal particles). Peng et al. found that ultrafine coal particles have strong adsorption toward collectors, which hinders the recovery of coal particles. Wang et al. obtained better flotation recovery of fine pyrite (<26 μm) using a mixed coco-acyl-amine-acetate/\textit{N}’-bis (2-hydroxyphenyl) acetic acid (1:1) reagent scheme at pH 8.5. Research on the flotation desulfurization of fine-grained pyrite mainly focuses on the minimum pyrite particle size of effective movement (called the scaling effect in this study). Generally, a grinding particle size distortion smaller than 20 μm can gradually affect the flotation recovery, and the smallest pyrite particle size with desulfurization effect in conventional flotation experiments is about 10 μm. Zhang et al. suggested that 10–120 μm is the optimal particle size for the separation of pyrite in a flotation experiment. Besides, scholars have carried out much research on the growth mechanism, crystal structure, and occurrence state of pyrite crystals. However, there are few reports regarding the occurrence and morphology of fine-grained pyrite in coal and the comprehensive effects of fine-grained pyrite size and occurrence state on flotation desulfurization.

Accordingly, coal samples from the Xingyi coalfield in Guizhou Province (formed by offshore deposits) and the Datong coalfield in Shanxi Province (formed by marine-continental deposits) in different coal-forming environments were selected in this study, and the micromorphological observation experiment of fine-grained pyrite and the flotation desulfurization experiment with different particle sizes were carried out. The research results can help identify the occurrence characteristics of fine-grained pyrite and its scaling effect on flotation desulfurization.

2. MATERIALS AND METHODS

2.1. Coal-Forming Environment and Geological Conditions. Coal samples from North China (Shanxi Province) and Southwest China (Guizhou Province) were selected in this study. As shown in Figure 1, the Guizhou coal samples were collected from the Aozichong, Chaoyang, Xiongwuxin, Jiashun, and Erwan coal mines in the Xingyi coalfield, and the Shanxi coal samples were collected from the Tongxin, Nanyangpo, Baidong, and Tashan coal mines in the Datong coalfield. These coal samples have different formation environments and properties, as shown in Table 1.

The Guizhou coal samples were collected from the coal-bearing formation of the upper Permian, belonging to the coastal tidal flat-lagoon sedimentary facies. The influence of river and ocean tides results in a higher sulfur content in most of the coal seams. In addition, Emeishan basalt and subvolcanic diabase were formed in the coal seam due to magmatic erosion. Some faults developed in the sampling location (Figure 2).

The Shanxi coal samples were obtained from the upper Carboniferous Taiyuan Formation, formed in a swampy environment with transitional sedimentary facies dominated by continental sediments. The sampled coal seams were formed from flood basin sediments mainly in the peat bog delta plain and were affected by fluvial action. The sulfur content in coal is relatively lower. Magmatic rocks such as lamprophyre, basaltic andesite, and diabase are developed in the sampling location.

2.2. Sample Preparations and Experimental Procedures. 2.2.1. Sample Preparations. The ore-grinding method
can promote the separation of minerals and the coal matrix and is widely used to improve the flotation desulfurization efficiency. The coal samples were dried at 70 °C and crushed by a multifunctional crusher. Then, the coal particles were sieved according to the Chinese National Standards (GB/T 477-2008). The grinding and sieving process was repeated until all samples completely passed through a sieve with a pore size of 250 μm. Pulverized coal smaller than 125 μm did not exceed 10%, and the remaining coal was incorporated in the subsequent screening to minimize errors. Coal samples (10.00 g) of 125−250 μm diameter were weighed to prepare the polished grain mounts using the coning and quartering method, according to the American standard ASTM C702. The polished grain mounts were prepared following the Chinese National Standard (GB/T 16773-2008). The remaining coal was further crushed to 44−75 and <44 μm in diameter for the subsequent tests. In addition, a TJC-450 planetary ball mill was used to further break up the coal particles to smaller than 44 to 37−44 μm, 15−37, and <15 μm in diameter for the flotation experiments of fine-grained coal. The grinding treatment was repeated until the coal particle diameter and weight met the experimental requirements.

In addition, two types of coal-pyrite samples and one type of hydrothermal-pyrite sample were selected for X-ray photoelectron spectroscopy (XPS) analysis after grinding to explore the structural differences of pyrite in coal. The coal-pyrite samples were patiently and carefully picked out from Guizhou coal particles with tweezers and then sonicated in deionized water. The hydrothermal-pyrite samples collected from the Yaogangxian Mine, Hunan Province, were used as the experimental control. These pyrite samples were crushed to 75 μm using a multifunctional crusher and washed with absolute ethanol for the X-ray photoelectron spectroscopy (XPS) analysis.

2.2.2. Flotation Experiment. Fine-grained pulverized coal particles smaller than 75 μm were selected for flotation experiments using an XFD-63 1.5L single-slot flotation machine (purchased from Shicheng Guobang Mining Machinery Co. Ltd.) based on the Chinese National Standard GB/T 477-2013. Distilled water and the coal samples were mixed evenly in a flotation machine. n-Dodecane was used as the collector, and the foaming agent was methyl isobutyl methanol (MIBC) in the flotation experiment. The experimental process is shown in Figure 3. After that, the obtained flotation products (cleaned coal, middlings, and tailings) were filtered, dried at 70 °C, and then sealed for storage. The yield errors for cleaned coal and ash are 0.6−1.3 and 0.3−0.5%, respectively.

2.3. Analytical Methods. Mineral morphology and species of coal samples were analyzed by optical microscopy, electron probe microanalysis (EPMA), and scanning electron microscopy (SEM). A Zeiss Axioscope A1 optical microscope was used to identify and photograph the mineral of the oil-immersed polished grain mounts through 20-fold and 50-fold eyepieces under reflected light conditions, according to GB/T 8899-2013 and GB/T 6948-2008 standards in the China University of Mining and Technology (CUMT).

The surface of the coal sample was treated with gold spray to enhance the conductivity during the EPMA and scanning electron microscopy—energy dispersive spectroscopy (SEM-EDS) observations. An EPMA-8050G was used for the microanalysis of pyrite in the Advanced Analysis and Computation Center (AACC) of CUMT. The analysis conditions for the EPMA instrument are as follows: acceleration...
Figure 3. Process of the flotation experiment.

Table 2. Distribution of Total Sulfur and Form Sulfur in Coal Samples\(^a\)

| Sample ID | S\(_{t.d}\) | S\(_{p,d}\) | S\(_{o.d}\) | S\(_{P}\) | S\(_{O}\) | Classification |
|-----------|-------------|-------------|-------------|-------------|-------------|----------------|
| Aozichong G1 | 8.82        | 7.55       | 1.17        | 13.27       | 0.1        | high sulfur (S\(_{t.d}\) > 3.00%) |
| Zhaoyang G2 | 5.99        | 5.35       | 0.6        | 10.02       | 0.04       | 0.67 |
| Xiongxin G3 | 5.3         | 4.72       | 0.51        | 9.62        | 0.07       | 1.32 |
| Jiashun G5 | 5.73        | 3.94       | 1.66        | 28.97       | 0.13       | 2.27 |
| Erwan G7 | 3.2         | 2.29       | 0.52       | 16.35       | 0.38       | 11.86 |
| Erwan G8 | 2.69        | 2.18       | 0.49       | 18.22       | 0.02       | 0.74 |
| Jiashun G6 | 1.88        | 0.3        | 1.51       | 80.11       | 0.07       | 3.76 |
| Xiongxin G4 | 0.97        | 0.21       | 0.56       | 57.89       | 0.19       | 20 |
| Tongxin S1 | 8.15        | 4.77       | 2.93       | 36          | 0.45       | 5.5 |
| Nayangpo S3 | 3.02        | 1.75       | 1.11       | 36.73       | 0.16       | 5.44 |
| Baidong S4 | 1.2         | 0.69       | 0.49       | 40.68       | 0.02       | 1.69 |
| Tongxin S2 | 0.87        | 0.33       | 0.53       | 60.47       | 0.01       | 1.16 |
| Baidong S5 | 0.7         | 0.33       | 0.36       | 50.72       | 0.02       | 2.9 |
| Tashan S6 | 0.35        | 0.02       | 0.32       | 91.18       | 0.01       | 2.94 |

\(^a\)S\(_{t.d}\), total sulfur; S\(_{p,d}\), pyritic sulfur; S\(_{o.d}\), organic sulfur; S\(_{P}\), sulfide sulfur; S\(_{O}\), content of sulfur, %; and P, proportion of sulfur in different forms to total sulfur, %.

The enrichment of sulfur is mainly controlled by transgression during peat accumulation, diagenesis, and magmatism after sedimentation.\(^4\) The sulfur content of coal samples from different regions varies greatly. As listed in Table 2, the main carrier of sulfur in coal is pyrite, and the proportion of sulfur in pyrite gradually increases as the total sulfur content increases. Meanwhile, even in the same sedimentary environment, differences in the sulfur sources (seawater, coal-forming plants, and magmatic-hydrothermal fluids)\(^4,32\) can also result in different proportions of pyrite sulfur, organic sulfur, and sulfate sulfur. For example, coal samples G2 and G5 have similar sedimentary environments and total sulfur contents, but the proportion of pyrite sulfur content in the G2 sample is obviously higher than that in the G5 sample.

3. EXPERIMENTAL RESULTS AND ANALYSES

3.1. Sulfur Content in Coal. The sulfur contents in coal samples were tested by industrial analysis methods according to the Chinese Nation standards (GB/T 215-2003 and GB/T 214-2007). As shown in Table 2, the sulfur content of Guizhou coal is in the range of 0.97–8.82% and that of Shanxi coal is between 0.34 and 8.14%. The coal samples were classified based on the sulfur classification of the Chinese National Standard (GB/T 15224.2-2021).

3.2. Microscopic Morphology of Pyrites in Coal. Aggregates of pyrites with different forms present various macroscopic and microscopic morphologies. As pyrites smaller than 60 \(\mu\)m are difficult to remove directly, 60 \(\mu\)m is the boundary between fine-grained particles and coarse particles of pyrite according to the classification standard of Yang.\(^17\) The microscopic morphology of pyrites in Guizhou and Shanxi coal samples was observed by SEM, and the particle sizes of pyrites with different microscopic morphologies were measured and are shown in Table 3. Among them, the aggregated massive pyrite has a larger particle size, while the particle sizes of the frameboidal, euhedral crystalline, and agglomerated pyrites are generally less than 60 \(\mu\)m, and the morphology of the filled pyrite (fracture-filling pyrite and biostuctured pyrite) is controlled by the filling location.

3.2.1. Coarse-Particle Pyrites.

(1) Aggregated massive pyrites...
Agglomerated massive pyrite is often associated with vitrinite, whose diameter is generally greater than 60 μm. As shown in Figure 4, the surface of the agglomerated massive pyrite is porous and contains organic matter or minerals (Figure 4a), and some are formed by the bonding of fine-grained pyrite particles (Figure 4b). They are distributed in both Guizhou coal and Shanxi coal, whose particle sizes are in the range of 100−600 μm (Figure 4c,d).

(2) Fracture-filling and biostuctured pyrites

Filled pyrite is the most common type in coals, including fracture-filling pyrite and biostuctured pyrite. Depending on the shape and size of the filling space, fracture-filling pyrites are normally banded, dendritic, and reticulated, and the filling width is 1−160 μm (Figure 5). Filled pyrites in Shanxi coal are filled with fine-striped fissures (Figure 5b) and massive cell cavities (Figure 5d), and the filling widths are 1−10 μm. However, the pyrites in Guizhou coal are mostly filled with wide-striped fissures (Figure 5a) and fine-grained aggregate cell cavities with a diameter of 3−160 μm.

The biostuctured pyrite can be divided into two subtypes: one is characterized by cell wall pyritization of pyrofusinite (Figure 5c) and the other is filled in the fusinite and semi-fusinite of cell cavities (Figure 5d). The shape of biostuctured pyrite depends on the plant remains, with a diameter of approximately 10−120 μm.

3.2.2. Fine-Grained Pyrite.

(1) Framboidal pyrites

Framboidal pyrites are aggregates of pyrite spheres resembling raspberries, which mainly occur in groups and along the bedding (Figure 6) in the vitrinite, especially in colloidetrinite, and a few filled in the fissures between components or the cellularity of other components. Framboidal pyrites can be agglomerated into spherical or massive pyrites, disseminated along with other fine-grained pyrites, and form lamellar or banded pyrite aggregates with euhedral crystalline pyrite particles. The content of framboi dal pyrites in Guizhou coal is higher than that in Shanxi coal, which can be observed in the polished grain mounts of G1 to G8 with a particle size of 2−20 μm. In addition, there are hundreds of fine-grained pyrites inside the framboidal pyrites, which are equicrystalline, with diameters ranging from 0.5 to 5 μm. The cross-sectional morphology of framboidal particles is dominated by inequivalent hexagons or inequivalent pentagons.

(2) Euhedral crystalline pyrites

Euhedral crystalline pyrites are normally associated with clay minerals and distributed in the colloidetrinite in the form of lamellar aggregates, linear aggregates, and disseminated content. As shown in Figure 7, the intact crystal facets of euhedral crystalline pyrites are triangular, square, rhombic, pentagonal, hexagonal, etc. (Figure 7a). The euhedral crystalline pyrites have a larger diameter in Shanxi coal, usually 4−40 μm, and their surface is uniform, smooth, and complete (Figure 7b,c). The euhedral crystalline pyrites in Guizhou coal have a relatively incomplete crystal structure, which is distributed in the colloidetrinite, with the particle size ranging from 2 to 15 μm (Figure 7d−f). In addition, some euhedral crystalline pyrites with a diameter of less than 1 μm are observed under the microscope; they appear in dense clusters or are distributed

| pyrite types | microscopic morphology | Guizhou coal sample (μm) | Shanxi coal sample (μm) |
|--------------|------------------------|---------------------------|-------------------------|
| coarse-particles pyrites | aggregated massive pyrite | 100−600 | 1−10 |
|          | fracture-filling pyrite (width) | 3−160 | 1−10 |
|          | biostuctured pyrite | 3−70 | 3−90 |
|          | frambooidal pyrite | 2−20 | 2−33 |
|          | euhedral crystalline pyrite | 2−15 | 4−40 |
| fine-grained pyrites | fine-grained agglomerated pyrites | 3−20 | 3−20 |

Figure 4. Aggregated massive pyrites in coal samples: (a) G3 sample, Xiongwuxin coal mine, Guizhou; (b) S6 sample, Tashan coal mine, Shanxi; (c) G5 sample, Jiashun coal mine, Guizhou; (d) S2 sample, Tongxin coal mine, Shanxi; (a), (c), and (d) are reflected-light and oil-immersion images obtained using a stereomicroscope; (b) is the secondary electronic image by SEM.
intermittently in moniliform shapes and often coexist with framboidal pyrites (Figure 7e,f).

(3) Fine-grained agglomerated pyrites
Fine-grained agglomerated pyrite does not have a complete crystal form, but it has an irregular shape with uneven edges, is semi-colloidal, and has a porous clay-filled surface. As shown in Figure 8, the particle size of fine-grained agglomerated pyrite is generally small, ranging from 3 to 20 μm. The fine-grained agglomerated pyrite is scattered and embedded in the collodetrinite in Guizhou and Shanxi coals and coexists with kaolinites and quartz.

In summary, it can be seen from the morphological observations that the pyrites in the Guizhou coal are predominantly disseminated in the coal matrix in the form of frambooidal, fine-grained euhedral crystalline, and fine-grained agglomerated pyrites filled with wide-striped fissures and fine-grained aggregate cell cavities. However, pyrites in Shanxi coal are primarily disseminated in the form of fine-grained euhedral crystalline and agglomerated pyrites, embedded in coarse-grained euhedral crystalline pyrites filled with fine-grained fractures and cell cavities.

3.2.3. Interaction with Organic Matter. Freshly denuded aggregates of massive pyrite in coal were tested by SEM-EDX to analyze their microstructure and elemental content. Figure 9 shows that the carbon content on the fresh surface of pyrite is 16.40%. Shao et al. revealed the complex morphology of carbon

![Figure 8](https://example.com/image8) Fine-grained agglomerated pyrite in coal samples: (a) G8 sample, Erwan coal mine, Guizhou; reflected-light and oil-immersion images obtained using a stereomicroscope; (b) S2 sample, Tongxin coal mine, Shanxi; secondary electron image by SEM.

![Figure 9](https://example.com/image9) Pyrite in freshly denuded S3 coal sample.

![Figure 10](https://example.com/image10) Statistics of organic sulfur and sulfate sulfur in pyrite samples based on XPS. (a) Organic sulfur in pyrites based on XPS. (b) Sulfate in pyrites based on XPS.
in pyrite using spectral analysis. Wang et al. believed that the carbon atoms in pyrite may cause crystal defects in pyrite. To confirm whether carbon is involved in the chemical structure of pyrite, two coal-pyrite samples from Guizhou Province and hydrothermal-pyrite from the Yaogangxian Mine, Hunan Province, were crushed and analyzed by XPS. Spike-fitting analysis of the sulfur showed that some organic sulfur occurs in the coal-pyrite and hydrothermal-pyrite samples, including sulfones, sulfoxides, thiophenes, thiols, and thioethers. It can be seen in Figure 10a that the total organic sulfur content in coal-pyrite samples is significantly higher than that in hydrothermal-pyrite samples. In addition, sulfate is a product formed by the oxidation of pyrite, and its content can be used to some extent to characterize the oxidation degree of pyrite. As shown in Figure 10b, the higher sulfate content in the coal-pyrite indicates that it is more susceptible to oxidation by strong chemical activity.

3.3. Flotation Experiment. 3.3.1. Flotation Products. Coal samples G3 and S1, which have similar pyrite sulfur contents (Table 1), were selected for flotation experiments. The coal samples were crushed into different particle sizes (75−44, 44−37, and 37−15 μm) before the flotation experiment, and the products were collected and weighed after the experiment according to the Chinese National Standard (GB/T 4757-2013). The flotation yield and the ash yield of the flotation product were calculated according to eqs 1 and 2, respectively. Among them, the flotation yield ($Y_{ad}$) is the mass ratio of each flotation product to the total flotation product after air-drying.

$$Y_{ad} = \frac{m_1}{m} \times 100\%$$

(1)

where $Y_{ad}$ is the yield of each flotation product after air-drying (including cleaned coal, middling, and tailings), %; $m_1$ is the mass of each flotation product after air-drying, g; and $m$ is the total mass of flotation product, g.

The ash yield ($A_{ad}$) is the mass ratio of the residue to the pulverized raw coal sample and can be calculated using eq 2. When the ash content was less than 15%, the samples were burned for 20 min each time until the mass change of two consecutive burnings did not exceed 0.01 g, and the weight of the sample after the last burning was used for calculation.

$$A_{ad} = \frac{m_2}{m_1} \times 100\%$$

(2)

where $A_{ad}$ is the ash yield of the pulverized coal sample after air-drying, %; $m_2$ is the weight of the residue, g; and $m_1$ is the weight of the pulverized raw coal sample, g.
The sulfur content of the flotation production was tested based on the Chinese National Standards GB/T 215-2003 and GB/T 214-2007. The proportion of pyrite sulfur in each flotation product to the raw coal before flotation \( D_{\text{ad}} \) can be calculated by the product of the pyrite sulfur content in each flotation product and the corresponding yield, as shown in eq 3.

\[
D_{\text{ad}} = S_{p,d} \times Y_{\text{ad}}
\]  

where \( D_{\text{ad}} \) is the proportion of pyrite sulfur in each flotation product to the raw coal before flotation, %; and \( S_{p,d} \) is the pyrite sulfur content in the flotation product.

Based on the flotation experimental results, the yield, ash yield, and pyritic sulfur content of flotation products of G3 and S1 samples are shown in Table 4.

The yield distribution of each flotation product (cleaned coal, middlings, and tailings) with different particle sizes is shown in Figure 11. It can be seen that the yield of cleaned coal gradually decreases as the particle size decreases while the proportion of tailings gradually increases. When the particle size is 15−37 μm, the cleaned coal yields of the G3 and S1 samples are only 2.45 and 4.31%, respectively. Besides, as shown in Figure 12, the ash yield increased with a decrease in the coal particle size, and the ash yield of cleaned coal of particle size 37−15 μm is much

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![Figure 13. Pyrite content distribution and proportion in flotation products with different particle sizes: (a, b) pyrite content; (c, d) pyrite proportion.](image-url)

![Figure 14. Morphological characteristics of fine-grained pyrites in coals in flotation products: (a) irregular pyrite disseminated in coal, middlings from G3; (b) irregular pyrite, tailings from G3; (c) irregular pyrite, cleaned coal from G3; (d) fracture-filling pyrite, middlings from S1; (e) framboidal pyrite, middlings from G3; (f) euhedral crystalline pyrite, tailings from S1.](image-url)
higher than that of 75−44 and 44−37 μm, which means that the coal with smaller particles has a higher mineral content.

3.3.2. Occurrence Changes of Pyrite.

(1) Changes in pyrite content

Flotation desulfurization is the process of separating sulfur from coal samples into tailing products based on the differences in the physical and chemical properties of the mineral surfaces without changing the original sulfur content of the entire coal. Thus, the higher the yield of cleaned coal and middlings and the higher the sulfur content in tailings, the better the desulfurization effect of flotation. As shown in Table 4, based on the yields of different flotation products and their pyrite sulfur content, the pyrite sulfur content and proportion in the flotation products were calculated using eq 3, as shown in Figure 13. It can be seen from Figure 13a,b that the fragmentation process can change the distribution of pyrite content in coal. Particle sizes of 44−37 μm had a relatively lower pyrite content than other particle sizes in these two samples. Meanwhile, the sum of pyrite content in the cleaned coal and middlings gradually increased with a decrease in the particle diameter, which was significantly higher in coal particle sizes of 15−37 μm. In addition, it can be seen in Figure 13c,d that the pyrite proportion in tailings gradually decreased with a decrease in the pyrite particle size, indicating that when the coal particle is broken to a certain extent (less than 37 μm), the flotation desulfurization effect instead decreases as the crushing degree increases.

(2) Pyrite morphology in flotation products

The morphology of pyrite in flotation products with different particle sizes was observed by SEM. As shown in Figure 14, the crushing process of the coal samples destroys the surface morphology of the fine-grained pyrite, resulting in irregular pyrite crystal morphology (Figure 14a−c). There are a few pyrites that retain the original morphological features, such as fracture-filling pyrite (Figure 14d), Framboidal pyrite (Figure 14e), and euhedral crystalline pyrite (Figure 14f).

The pyrite in coal mostly coexists with the coal matrix, called coal-pyrite in this study, and some monomer pyrite. Among them, frambooidal pyrite, smaller euhedral crystalline pyrite, and fine-grained agglomerate pyrite can maintain their morphological characteristics. They are abundant and disseminated in coal (Figure 14a), while a small part is broken to form the monomer pyrite (Figure 14e). As the degree of coal fragmentation increases (the coal particle sizes are 44−37 and 37−15 μm), the proportion of monomer pyrite increases slightly and mainly comprises fragments of agglomerated pyrite, but the content is still much lower than that of the coal-pyrite intergrowth. In addition, it can be seen in Figure 14 that the pyrites in the middlings and tailings have relatively larger particles (e.g., microcrystalline aggregates of frambooidal pyrite; Figure 14a) and a higher content (e.g., disseminated fine-grained pyrite; Figure 14e), while a small amount of fine-grained monomers, small encapsulated particles, or pyrite with low disseminated content are present in the cleaned coal.

The pyrite distribution in each flotation product is shown in Figures 15 and 16. Monomer pyrite and the pyrite symbiotic with minerals mainly occur in tailings (Figure 15c), and the filled pyrites (e.g., fracture-filling, fibroblast-filled pyrite) are mainly

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Figure 15. SEM backscattered images of middlings (a, b) and tailings (c); (a) middlings from the G3 sample, 75−44 μm; (b) middlings from the S1 sample, 75−44 μm; (c) tailings from the G3 sample, 75−44 μm.

Figure 16. SEM backscattered images of cleaned coal with 75−44 μm size; (a) cleaned coal from the Guizhou G3 sample with 75−44 μm particle size, Xiongwuxin coal mine; (b) cleaned coal from the Shanxi S1 sample with 75−44 μm particle size, Tongxin coal mine.

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Distribution of pyrites with different morphologies and sizes. Therefore, flotation experiments can change the coal particles decreases, the size range of pyrite particles with small-particle-size pyrite. In addition, as the particle size of tailings after flotation, and the cleaned coal is mainly enriched be seen that the coarse-grained pyrite tends to concentrate in the flotation products of different coal samples is slightly.

**DISCUSSION**

In the flotation products of different coal samples is slightly different. The frambooidal pyrite and euhedral crystalline pyrite can be seen in the cleaned coal of G3, whereas fracture-filling pyrite is more common in the cleaned coal of S1. According to the observation results of pyrite morphology (Figures 4-6), the main particle size distribution of pyrite in coal particles with different particle sizes (75-44, 44-37, and 37-15 μm) was determined and is presented in Table 5. It can be seen that the coarse-grained pyrite tends to concentrate in the tailings after flotation, and the cleaned coal is mainly enriched with small-particle-size pyrite. In addition, as the particle size of coal particles decreases, the size range of pyrite particles decreases. Therefore, flotation experiments can change the distribution of pyrites with different morphologies and sizes.

**4. DISCUSSION**

**4.1. Enrichment of Fine-Grained Pyrites in Coals.**

**4.1.1. Occurrence and Genetic Environment of Pyrite.** The occurrence and distribution of pyrite in coal are mainly controlled by the depositional environment of the coal seams. Generally, the formation of pyrite undergoes a transition process from monosulfide to mackinawite (FeS₄) to melnikovite (FeS₃).²³ The evolution process is summarized in Figure 17 according to microscopic observation results in this study and the Dai et al. study.³⁸ The Guizhou coal samples were deposited in coastal tidal flat-lagoon facies, resulting in a higher pyrite content (Table 1). Seawater sulfur and magmatic-hydrothermal sulfur are the main sulfur sources of pyrite in coal. The Shanxi coal samples were accumulated on the delta plains, which have a lower sulfur content. Part of the coal samples is affected by magmatic-hydrothermal fluids or brackish water to yield an abnormally high pyrite content.³⁹

Fine-grained pyrites in coal are generally formed in the sedimentary period in the early peat accumulation stage. These pyrites are typically smaller than 20 μm in size and have a low content of coal. The atomic ratio of sulfur to iron (N(S)/N(Fe)) is less than 2 but rich in associated elements.³⁹ Fine-grained pyrite is usually in the frambooidal, fine-grained euhedral crystalline, caviar-like, and fine-grained agglomerated forms. Among them, frambooidal pyrite is formed by metasomatism or filling of organic matter spherules with the participation of bacteria or other organisms.³⁹ Fine-grained agglomerated pyrite is often associated with kaolinite and quartz and is disseminated in the collodetrinite, which may be formed by the reaction of iron on the clay mineral lattice with H₂S (Figure 8a). Therefore, organic matter and other minerals may be directly involved in the formation of pyrite and limit the growth space of pyrite.

In addition, the crystal morphology of pyrite is affected by the depositional environment. According to the microscopic observation and statistics, the average size of frambooidal pyrite is more than 6 μm, and the diameter varies widely: the diameter range of frambooidal pyrite in the Guizhou coal is 2-20 μm, the diameter range of frambooidal pyrite in the Shanxi coal is 5-22 μm, and the maximum diameter is higher than 18 μm. This means that the redox conditions of the depositional environment have changed during the formation of frambooidal pyrite, resulting in two kinds of pyrite formation conditions: anoxic (pyrite with small particle size) and aerobic (pyrite with large particle size).³⁹,⁴⁰

Guizhou coal samples were deposited in the coastal tidal flat-lagoon facies, where the seawater intrusion and the input of basalt terrigenous clastic during the peat accumulation stage provide a stable source supply. Changes in the sea level make the anaerobic reduction environment below the surface have the

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**Table 5. Pyrite size distribution in flotation products with different coal sizes**

| flotation product | coal particle size of G3 (μm) | coal particle size of S1 (μm) |
|-------------------|-------------------------------|-------------------------------|
|                   | particle size of pyrite (μm)  | particle size of pyrite (μm)  |
| cleaned coal      | 75-44                         | 75-44                         |
|                   | 44-37                         | 44-37                         |
|                   | 37-15                         | 37-15                         |
| middlings         | 8.28–11.82                    | 6.98–10.82                    |
|                   | 7.58–30.3                     | 1.52–33.94                    |
|                   | 3.03–72.00                    | 2.59–70.30                    |
| tailings          | 2.35–11.05                    | 0.69–10.69                    |
|                   | 1.67–14.39                    | 1.67–16.92                    |
|                   | 4.71–35.2                     | 2.55–34.41                    |

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**Figure 17. Formation conditions and evolution process of pyrite in coal.**
characteristics of a micro-oxidation environment, which affects the sulfate reduction and inhibits the growth of pyrite particles. Therefore, the fine-grained pyrite in Guizhou coal samples has crystal defects, and its grains are relatively small with a size range of \(2-20 \mu m\) (Figure 7d–f). However, the relatively higher content of fine-grained pyrite with good crystal shape in the Shanxi samples may be authigenic after the sedimentary period, and their particle size ranges from 4 to 40 \(\mu m\) (Figure 7b,c). In addition, a small part of the fine-grained and large-grained pyrites can be formed in the hydrothermal precipitation during the later stage of coal formation. Among them, the fine-grained pyrite fills the interior and gaps of the cell cavity (Figure 5), resulting in a relatively higher sulfur content and an atomic ratio of sulfur to iron (N(S)/N(Fe) > 2). Some fracture-filling pyrites also lead to a high content of sulfur and ash in coal.

### 4.1.2. Crystal Evolution of Pyrite

Generally speaking, the pyrite crystals at the early and late stages of mineralization are mainly cubes \((a \{100\})\), and the pyrite crystals are dominated by pentagonal dodecahedrons \((e \{210\})\) and their aggregations in the intermediate stages.\(^{[11,41]}\) The sulfur fugacity required for the formation of pentagonal dodecahedral pyrites and octahedral pyrites is larger than that of cubic pyrite.\(^{[41]}\) When the medium state is saturated, the simple crystal form of a cube has a higher crystal face energy and can be formed easily, while the formation of pentagonal dodecahedral and octahedral crystals from the cubic crystal is relatively difficult because of the complex crystal structure and lower face energy.\(^{[42,43]}\) In addition, Meng et al. found that pyrite was more prone to form a combination of pentagonal dodecahedrons \((210)\) and octahedrons \((111)\) at medium-high temperatures \((210-220 \, ^{@}C)\) and in a sulfur-rich environment \((S/Fe \text{ molar ratio of } 4/1)\).\(^{[43]}\)

According to the observation results of SEM, the pyrite crystals in Shanxi coal samples mostly appear in the form of cubic pentagonal dodecahedrons and cubic octahedrons, as shown in Figure 18a–c, indicating the abundant material supply for pyrite formation in the middle stage of mineralization; the metallogenic environment is continuous and stable, with a relative higher temperature \((>200 \, ^{@}C)\). Compared with the Guizhou coal sample, the Shanxi coal samples have more types of pyrite crystals, and their crystal structure is relatively complete. Therefore, taking the crystal morphology observation of pyrite in Shanxi coal as an example, and combined with the previous research,\(^{[42,43]}\) we summarize three types of evolution sequences of pyrite formation and crystal morphology, as shown in Figure 18.

Note: I, Cube \((a \{100\})\); II, cube + pentagonal dodecahedron \((a + e)\); III, pentagonal dodecahedron \((e \{210\})\); IV, pentagonal dodecahedron + cube \((e + a)\); V, cube + octahedron \((a + o)\); VI, octahedron + pentagonal dodecahedron \((o + e)\); VII, octahedron + cube \((o + a)\); VIII, octahedron \((o \{111\})\). (a) S6 sample, Tashan coal Mine, Shanxi; (b) S6 sample, Tashan coal mine, Shanxi; (c) S6 sample, Tashan coal mine, Shanxi.

In addition, the physical and chemical conditions of the ore-bearing fluids can affect the crystal morphology of pyrite. When the temperature of ore-bearing fluids decreases or the molar concentration of S/Fe decreases, the morphologies of the formed pyrite will change from a combination of pentagonal dodecahedrons \((e \{210\})\) and octahedrons \((o \{111\})\) to a combination of octahedrons \((o \{111\})\) and cubes \((a \{100\})\) or a single form such as cubes \((a \{100\})\).\(^{[43]}\) There are many crystal types of pyrite in the Shanxi coal, in which the crystals of type VII \((o + a)\) and type V \((a + o)\) are present in higher content, indicating the changes in temperature conditions and the concentration of S/Fe during the pyrite formation.

### 4.1.3. Interaction with Organic Matter

Previous studies have shown that a part of the fine-grained pyrite can be formed by metasomatism or the filling of organic matter spherulites,\(^{[19,20]}\) and the sulfur atoms in pyrite can be replaced by carbon atoms. Meanwhile, defects in fine-grained pyrite crystals can also form surface groups with strong chemical activity, such as surface hydroxyl functional groups \((>SOH)\), Lewis acid sites (or Bronsted acid sites), and sulfur groups of sulfides,\(^{[44]}\) which can form various complexes with carboxyl, carbonyl, amino, sulfo, and hydroxyl groups in the organic matter.\(^{[44]}\) Analytical results of

![Figure 18. Crystal morphology and evolution model of pyrite crystals in coal.](https://doi.org/10.1021/acsomega.2c05698)
SEM and XPS (Figures 9 and 10) indicate that the fine-grained pyrite would be embedded in the organic components of coal by chemical bonding. Fine-grained pyrite with a sufficiently small particle size can be linked by S=O bonds with inorganic sulfur, thiophenes, and heterocyclic compounds or be combined with organic compounds through Fe−S bonds of other molecules except for pyrite.

In addition, Xie et al. and Zhao et al. confirmed that the pyritic sulfur in coal can be partially converted into organic sulfur during pyrolysis experiments of coal in a reducing atmosphere, including relatively stable thiophene sulfur. The specific conditions for the conversion of pyrite and organic sulfur are still very complex due to the particle size effect of fine pyrite and need to be further studied. However, what is certain is that the smaller particles of pyrite have a closer interaction with the organic matter, which makes it difficult to effectively remove the fine-grained pyrite from coal.

4.2. Scale Effect of Fine-Grained Pyrite. 4.2.1. Size Distribution of Fine-Grained Pyrite. The removal efficiencies of pyrite with different particle sizes and occurrence states are different in the flotation experiments. As shown in Figure 12, when the particle size of pulverized coal is larger than 37 μm (Figure 12), the yield of cleaned coal is relatively high and the ash yield is lower than 8%. The frambooidal pyrite, agglomerate pyrite, and pyrite coexisting with other minerals with a particle size larger than 37 μm can be easily precipitated in tailings, indicating that ore grinding is helpful for flotation separation of large-particle pyrite.

For coal particle sizes of 37–15 μm, the total pyrite content in cleaned coal and middlings increases significantly (Figure 13a,b), and the yield of cleaned coal is the lowest and the ash yield is the highest (Figure 12). The particle size of pyrite in middlings is relatively small, mostly in the form of microcrystalline aggregates such as raspberry pyrite (<16.92 μm) or a high content of disseminated distribution (0.5–15 μm) (Figures 14a,b and 15a,b). This is because the particle hydration film formed by small-particle coal is difficult to rupture during the flotation process, which makes it difficult to distinguish pyrite from coal particles. At the same time, the ore-grinding process can break up the agglomerated pyrite, thus increasing the hydration degree and reducing the floatability. Pyrites with a small particle size (<15 μm) in pulverized coal can form a complex symbiotic relationship with organic matter (Figure 10a), making it difficult to remove them during flotation experiments. In addition, the main enrichment forms of pyrite in cleaned coal of small-particle coal include disseminated distribution (0.69–11.05 μm) (Figure 14a,d) and broken monomer pyrite (8.28–11.82 μm), as shown in Figure 16.

4.2.2. Occurrence Distribution of Pyrite in the Flotation Product. The morphological observation of pyrite in the flotation product showed that the aggregated massive pyrite, filled pyrite, and frambooidal pyrite with a large grain size could be removed by the flotation method (Figure 14, Table 5). The fine-grained frambooidal pyrite and disseminated pyrite can be transferred to the middlings during flotation experiments. The fine-grained monomer pyrite and disseminated pyrites smaller than 15 μm occur in cleaned coal (Figure 14c). Besides, some fine-grained pyrite associated with the coal matrix can also be transferred into the cleaned coal due to a flotation behavior similar to that of coal particles.

In summary, frambooidal pyrite, disseminated pyrite, and monomer pyrite are the main forms of pyrite occurrence in the middlings and cleaned coal with different coal particle sizes (75–44, 44–37, and 37–15 μm), and their size is between 0.69 and 33.94 μm (Table 5). Fine-grained pyrite is difficult to effectively separate from the coal matrix through further ore-grinding treatment (even broken to 37–15 μm). Therefore, 37 μm was considered as the critical dimension for ore grinding to improve the effective flotation efficiency in this study. Some other methods except ore grinding should be selected to increase the flotation desulfurization recovery for the smaller pyrite in coal, such as changing the composition of the flocculant.

5. CONCLUSIONS

Coal samples from the Xingyi coalfield in Guizhou Province and the Datong coalfield in Shansi Province were selected for the pyrite morphology observations, crystal structure evolution analysis, and flotation desulfurization experiments with different coal particle sizes, and the following conclusions were drawn.

1. The fine-grained pyrite in coal is mostly formed in the peat accumulation stage in the early sedimentary period with various occurrence forms and has complex connections with organic matter.

2. The flotation desulfurization experiments showed that the yield of cleaned coal gradually decreases as the particle size decreases while the proportion of tailings gradually increases. The sum of pyrite content in the cleaned coal and middlings gradually became significantly higher in coal particles with sizes of 15–37 μm.

3. Frambooidal pyrite, disseminated pyrite, and monomer pyrite are the main occurrence forms of pyrite in the middlings and cleaned coals with a size range of 0.69–33.94 μm.

4. The complex occurrence morphology and crystal structure of fine-grained pyrite make it difficult to be removed from the coal matrix by ore grinding during flotation, and some other methods should be used to increase the flotation desulfurization recovery when the pyrite is smaller than 37 μm.

APPENDIX A

Figure 19

![Figure 19](https://doi.org/10.1021/acsomega.0c05698)
AUTHOR INFORMATION

Corresponding Author
Wenfeng Wang — Key Laboratory of Coalbed Methane Resources & Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008 Jiangsu, China; School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116 Jiangsu, China; orcid.org/0000-0002-2200-0250; Email: wangwenfeng@cumt.edu.cn, wenfwang@vip.163.com

Authors
Mengya Ma — Key Laboratory of Coalbed Methane Resources & Reservoir Formation Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008 Jiangsu, China; School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116 Jiangsu, China; orcid.org/0000-0003-2673-1007
Kun Zhang — State Key Laboratory of Mining Response and Disaster Prevention and Control in Deep Coal Mines, Anhui University of Science and Technology, Huainan 232001 Anhui, China; orcid.org/0000-0002-0076-1139

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c05698

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was supported by the National Natural Science Foundation of China (Nos. U1903207, 41972176, 42072192, 42002184, and 42202200) and A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). The authors thank the anonymous reviewers for their constructive and detailed comments on this manuscript.

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