Abstract

High-efficiency separation of hard-to-float high-ash fine coals has been a research hotspot in some countries, especially in China. Separation of hard-to-float high-ash fine coals by froth flotation, although considered to be the most effective, remains some challenges to be overcome. In this paper, the mineralogical/petrologic, physical and chemical characteristics of the of a hard-to-float high-ash fine coal collected in Kailuan mining area were studied. The floatability and liberation characteristics of this coal sample and potential separation processes were investigated experimentally. According to the coal characteristics, four separation processes were put forward and evaluated. Experimental results indicated that classified floatation couldn’t effectively improve the fine coal quality, while the processes of fine grinding-recleaning to roughing cleaning coal and selective agglomeration-floatation were suitable for the Kailuan coal. Compared with the original coal flotation process, the processes of fine grinding-recleaning to roughing cleaning coal increased the cumulative yield from 50.87% up to 55.53% while reduced the product ash content from 11.76% down to 10.74%. In the processes of selective agglomeration-floatation, the lowest ash of clean coal is 10.69%, with 58.72% yield, 7.85% higher in yield and 1.07% lower in ash content. The ash contents of the products from the two processes are lower than 11%, which meets the clean coal requirement.

Keywords: hard-to-float high-ash fine coal; separation process; liberation analysis; selective agglomeration-floatation

1. Introduction

The separation of hard-to-float high-ash fine coals is gaining greater and greater significance. This is because the proportion of fine coal in raw coal increases consistently with mechanization in mining, deprivation of geological conditions, and application of dense medium cyclone. Froth flotation has been a dominant separation technology employed for the production of coal concentrate from high-ash coal slurries, particularly in the coal size range below 0.5 mm. The flotation feed particle size affects the float yield and grade and thus the separation efficiency. The best coal flotation efficiency usually is achieved at a feed particle size of 0.5-0.074 mm. The selectivity is lower for <0.074 mm particles. The separation of fine coal slime becomes more and more difficult, due to: 1) micronization of original coal slime decreases the separation particle size, thus flotation selectivity and efficiency; 2) high content of...
ash and coal with low floatability; 3) high concentration of slime exacerbates floatability; and 4) application of heavy medium cyclone separator declines lower limit.

The increasing proportion of hard-to-float high-ash fine coal slime exposes limitation of traditional processes in coal preparation plant. Because of high-ash-content clean coal, low separation recovery and efficiency, fine coal separation becomes the bottle-neck problem that restricts the quality of clean coal [1-2].

Coking coal and fat coal are rare resources in China, accounting for less than 10% of coal reverse. According to a several surveys of fine coal separation, the poor washability and low recovery cause great loss of these valuable resources. For example, in Kailuan and Qitai coal areas, clean coal recoveries of coking coal and fat coal are less than 40%, and in Panjiang coal area, mainly composed by fat coal, the recovery is 43%. Hence, the advanced fine coking and fat coal separation technology is greatly needed.

Coking and fat slimes in Kailuan coal area are typical hard-to-float high-ash coal slimes. In this paper, we focus on seeking suitable floatation processes for the hard-to-float high-ash coal slime according to the coal characteristics, mineral compositions, floatability and liberation characteristics.

2. Analysis of coal characteristics, mineral compositions and floatability

The coal characteristics, mineral compositions, and floatability of the fine coal slime collected from a coal preparation plant in Kailuan coal area were studied. Table 1 shows the coal particle size distribution. It can be seen from the Table 1 that the +0.45 mm size range accounts only 6.69%. The ash content of +0.45 mm coal is slightly higher than that of 0.45-0.05 mm coal. This is probably because coarser coal particles have the relatively lower degree of liberation of mineral matter from coal. The coal particles are fairly evenly distributed within particle fraction of 0.45-0.28, 0.28-0.154 and 0.154-0.09 mm, with percentage from 15% to 19%. However, the minus 0.05 mm fraction accounts for 36.62%, with ash content as high as 29.34%. That indicates the clay content of the minus 0.05 mm fraction is high. There exists a certain pelitization during the coal separation, which may pollute clean coal.

Table 1. Particle size composition

| Samples (mm) | Yield (%) | Ash (%) | Cumulative oversize | Cumulative undersize |
|--------------|-----------|---------|---------------------|----------------------|
|              |           |         | Yield (%) | Ash (%) | Yield (%) | Ash (%) |
| >0.45        | 6.69      | 23.36   | 6.69       | 23.36   | 100.00    | 23.62   |
| 0.45-0.28    | 13.79     | 18.46   | 20.48      | 20.06   | 93.31     | 23.64   |
| 0.28-0.154   | 17.95     | 19.80   | 38.40      | 19.94   | 79.52     | 24.54   |
| 0.154-0.09   | 15.21     | 19.94   | 53.64      | 19.94   | 61.57     | 25.92   |
| 0.09-0.05    | 9.74      | 22.43   | 63.38      | 20.32   | 46.36     | 27.89   |
| <0.05        | 36.62     | 29.34   | 100.00     | 23.62   | 36.62     | 29.34   |
| Total        | 100.00    |         | 23.62      |         |           |         |

Table 2. Fine coal float-sink test

| Density (g/cm³) | Yield (%) | Ash (%) | Accumulation of floating | Accumulated sediments | δ+0.1 |
|-----------------|-----------|---------|--------------------------|-----------------------|-------|
|                 |           |         | Yield (%) | Ash (%) | Yield (%) | Ash (%) | Yield (%) | Ash (%) | Density (g/cm³) | Yield (%) |
| -1.3            | 7.85      | 4.17    | 7.85       | 4.17    | 100.00    | 24.61   | 1.30      | 30.20   | 1.30             | 30.20   |
| 1.3-1.4         | 22.35     | 9.14    | 30.20      | 7.85    | 92.15     | 26.35   | 1.40      | 48.81   | 1.40             | 48.81   |
| 1.4-1.5         | 26.45     | 17.24   | 56.66      | 12.23   | 69.80     | 31.87   | 1.50      | 49.49   | 1.50             | 49.49   |
| 1.5-1.6         | 23.04     | 24.49   | 79.69      | 15.77   | 43.34     | 40.79   | 1.60      | 27.82   | 1.60             | 27.82   |
| 1.6-1.7         | 4.78      | 31.87   | 84.47      | 16.68   | 20.31     | 59.29   | 1.70      | 7.34    | 1.70             | 7.34    |
| 1.7-1.8         | 2.56      | 40.20   | 87.03      | 17.38   | 15.53     | 67.72   | 1.80      | 3.75    | 1.80             | 3.75    |
| 1.8-2.0         | 2.39      | 52.25   | 89.42      | 18.31   | 12.97     | 73.16   | 1.90      | 2.39    | 1.90             | 2.39    |
| +2.0            | 10.58     | 77.88   | 100.00     | 24.61   | 10.58     | 77.88   |           |         |                 |         |
| total           | 100.00    | 24.61   |            |          |           |         |           |         |                 |         |
The fine coal float-and-sink test result shown in Table 2 reveals that the low mass contents are low in both low density fraction (-1.3 g/cm³) and high density fraction (+1.8 g/cm³). The high mass content of middle density fraction means low washability. High ash content of the middle density fraction (about 25%) indicates the low degree of liberation of coal from minerals. Relatively low ash content of 1.8-2.0 g/cm³ density fraction depicts a certain gangue mixture. This makes it difficult to yield high ash tailings. In the coal preparation plant, the tailing ash content is about 40%.

Floatability curves (see Fig. 1) indicate that when the clean coal ash contents are 11.0%, 12.0% and 13.0%, the corresponding yields will be 12.79%, 35.15% and 57.52%, and E vaules will be 14.88%, 30.93% and 50.04%, respectively. According to classification index in floatability curves, if the ash content of the clean coal is lower than 13%, the coal belongs to difficult floatable coal or great difficult floatable coal [3-4].

Fourier transform infrared spectrometer was used to analyze coal, and organic structures were speculated according to absorbance. Red infrared spectrum (See Fig. 3) show great absorbtance in 3400 cm⁻¹ (non-hydrocarbon hydrogen), which indicated Kailuan coal has low metamorphic degree. Meanwhile, the higher non-hydrocarbon hydrogen, the higher oxygen, which shows the coal slime may be oxidized in certain degree. Absorbance in 2910 cm⁻¹ (stretching of C-H in methyl) shows methyl in slime is small. Strong absorbance of O-Ar in 1610 cm⁻¹ presents vibration of oxygen substitutional aromatic hydrocarbon, and absorbsines from 1000 cm⁻¹ to 700 cm⁻¹ are contributed to out-of-plane bending of substitutional aromatic hydrocarbon. These groups have little connection with coal etamorphic degree [5].

3. Grinding and liberation

According to the above analysis, there may be some fine mineral particles disseminated within the coal particles. Fine grinding of the coal particles is needed to remove the mineral and reduce the ash content [6]. Therefore, grinding conditions were studied as follows.

Grinding time: with the grinding time going, the mass content of -0.074 mm fraction increases gradually. At 40 min, it reaches 90.57%. The grinding time vs the -0.074 mm yield curve (see Fig. 4) illuminates that the curve slope is great within 20 min and the yield of -0.074 mm increased significantly. This indicates grinding efficiency is high in this period. After 20 min, the grinding efficiency decreases. Moreover the yield of -0.074 mm increases only 3.72% from 30 to 40 min, which shows it is difficult to further reduce the particle size. The relationship curve of grinding time and the ash content (see Fig. 5) shows the frangible gangue was crushed into the -0.074 mm fraction, which makes the increase of ash in the beginning 10 min. While from 10 to 40 min, ash of product -0.074 mm decreases, indicating some minerals in coal has been separated.

Grinding coal cumulative yield - ash curve (see Fig. 6) shows that for a given clean coal ash, the clean coal yield increases with time and at the time of 40 min, the yield reaches the highest. That means the liberation degree increases as the particle size decreases. According to the study of coal and rock constituent, different structure and mechanical properties will result in different grinding characteristics. In general, grindability index and micro
The frangibility of fusain is greater than that of vitrain [7]. Thus, fusain is more frangible in the same grinding condition, which results in vitrain usually enriches in coarse coal, and inertinites are easily enriches in fine coal.

Fig. 3. FTIR analysis of coal

The yields of different density fractions (see Fig. 7) show the greatest yield in 1.40 g/cm³ and the enrichment of vitrains in lower density grades, accounting for 35% of float. While the float yield decreases with increasing of density, however, it increases again after density reaches 1.60 g/cm³, which indicates that weak separation of coal rock in 1.40-1.60 g/cm³ and enrichment of fusain in +1.60 g/cm³.

Fig. 4. Relation between grinding time & material yield

4. Separation process of hard-to-float high-ash fine coal

Fine coal slime in Kailuan coal area usually belongs to great difficult floatable slime, and traditional slime separation processes are hard to decrease ash while ensuring the certain clean coal yield. By exploring characteristics of slime and comparing of different separation processes, optimized process for Kailuan coal were designed.

4.1. Grinding-one roughing process

According to selective test of flotation reagent, the best flotation reagent are kerosene associated with GF [8-9]. The regulator sodium hexametaphosphate is capable to disperse and restrain separation. In this study, kerosene was used as collector, GF as frother and sodium hexametaphosphate as regulator to explore the effect of reagent dosage. Other conditions are: 40% concentration of grinding coal, grinding for 30 min, and -0.074 mm material accounting for 86.85%. Results are listed in Tables 3 and 4. Fig. 8 shows the different separations of direct floatation, grinding plus floatation and grinding plus floatation and dispersion inhibitor.
Table 3. Experimentation data of Process 1

| Reagent Dosage (g/t) | Clean coal | Tailing | Ash of feed (%) |
|---------------------|------------|---------|-----------------|
|                     | Kerosene  | GF      | Yield (%) | Ash (%) | Yield (%) | Ash (%) | Ash (%) |
| 265                 | 50        | 49.41   | 11.77     | 50.59   | 35.49     | 23.77   |
| 265                 | 100       | 57.81   | 12.32     | 42.19   | 39.73     | 23.89   |
| 370                 | 150       | 62.64   | 12.55     | 37.36   | 42.41     | 23.71   |
| 530                 | 200       | 72.22   | 13.21     | 27.78   | 50.53     | 23.58   |

Table 4. Experimentation data of Process 2

| Sodium Hexametaphosphate (g/t) | Clean coal | Tailing | Ash of feed (%) |
|-------------------------------|------------|---------|-----------------|
|                               | Yield (%)  | Ash (%) | Yield (%) | Ash (%) | Ash (%) |
| 1000                          | 51.36      | 11.79   | 48.64     | 35.73   | 23.43   |
| 1500                          | 48.47      | 11.37   | 51.53     | 34.53   | 23.30   |
| 1800                          | 44.30      | 10.71   | 55.70     | 33.96   | 23.66   |
| 2000                          | 44.47      | 11.04   | 55.53     | 33.25   | 23.37   |

According to the tests, in direct floatation, when kerosene dosage is 265 g/t and GF dosage is 100 g/t, the yield and the ash content of the clean coal are 50.87% and 11.76%, respectively. Being grinded, the yield increases by 6.94%, however, the ash content increases to 12.32% simultaneously. Keeping the dosages of kerosene and GF, adding 1000 g/t sodium hexametaphosphate decreases the ash content of clean coal and increases yield up to 51.36%. The ash content of clean coal is almost the same as that of direct floatation clean coal, while yield increases 0.49%. Other three data were abandoned for more sodium hexametaphosphate’s restraint, causing low yields.

Separation grade of coal rock increases, surface area increases simultaneously, causing the exposing of hydrophobic groups. Hence, yield of clean coal increases even in the same dosage. Sodium hexametaphosphate was added as dispersant, ash of clean coal didn’t decrease obviously. The reason of which may lie on the frangible kaolinite enhancing the mudding degree of slime, which causes great entrainment of high ash fine clay into clean coal in floatation process. One roughing flotation process could not reach an ideal separation effect.

4.2. Grinding-One roughing and one cleaning process

In fine coal separation process, it is hard to prevent the pollution of clean coal by minerals. However, adjusting separation time could decrease the pollution in some degree because in cleaning process, concentrations of mineral slurry and reagent decreases, which benefits to enhance separation selection and lighten the contamination of
minerals. Thus, process of grinding-one roughing and one cleaning process was designed with fine particle accounting for 86.85%. Fig. 9 shows the flow sheet and test conditions.

![Flow sheet and test conditions](image)

Fig. 9. Grinding-one roughing and one cleaning process

Compared with one rouging process, this process yields the same clean coal and the ash content decreases in limited scope. Process of batch adding sodium hexametaphosphate is better than one roughing floatation process.

4.3. Roughing and cleaning-grinding process

Poor separation effect of direct floatation after grinding lies on contamination of friable kaolinite even abundance dispersing agent was added. Roughing and cleaning-grinding process (See Fig. 10) was put forward for solving this problem. One roughing floatation process was taken firstly to control higher clean coal yield. High ash tailing could throw away directly while clean coal was transported in ball mill. This process enhances the separation of coarse coal, and decreases the contamination of high ash clay by abandoning high ash tailing in roughing floatation process. Selective middle coal and clean coal were yielded by one cleaning process.

Results show that when clean coal ash is 10.74%, cumulative clean coal yield is 55.53% and recovery of combustible materials is 64.75%. While ash rises to 11.68%, yield rises to 65.55% and recovery is 75.63% respectively. Compared with one roughing and one cleaning processing, this process enhances about 20.0% yield by keeping the same ash or, ash decreases by 1.05% by keeping the same yield.

4.4. Classifications- grinding of coarse grade slime process

Classification floatation [10] is floatation in different facilities of processes according to different characteristics of coarse and fine slimes. We focus on classifications- grinding of coarse grade slime process. According to integrated accumulative curves of classified clean coal (See Fig. 11), grinding after classification process is better than that of all particles floatation. When ash of clean coal is about 11%, its yield is 55%.

![Integrated accumulative curves of classified clean coal](image)

Fig. 11. Integrated accumulative curves of classified clean coal

![Stirring speed on the effect of refine coal recovery and ash](image)

Fig. 12. Stirring speed on the effect of refine coal recovery and ash
4.5. Selective agglomeration-floatation process

Selective agglomeration-floatation process [11] is a separation way of forming agglomeration in stirred tank and separating from bubble. Kerosene was used as agglomeration reagent and collector, sodium hexametaphosphate as dispersant, GF as foaming agent, agitation intensity, dosages of agglomeration reagent and dispersant were studied to see the effect of agglomeration-floatation. XHF-D high speed deconcentrator was utilized, and dosages of kerosene and GF are 265 g/t and 100 g/t respectively. Firstly confirm the agitation speed and then agitation time. According to effect of stirring speed (See Fig. 12), with the increase of speed, clean coal ash decreases. Inflexion of clean coal yield curve is on 8000 r/min.

At the speed of 8000 r/min for 30min, yield of clean coal is 52.37% and ash is 10.99%. Compared with those processes without stirring by high speed deconcentrator, yield enhances 1.5% and ash decreases by 0.77%.

Effect of stirring time on separation (See Fig. 13) shows that short time stirring leading to high ash and low yield clean coal. While prolong stirring time, flotation indexes are improved and ash decreases sharply and yield increases evidently. An inflexion appears at 15 min and yield increases slow and ash decreases unconspicuously. At the time of 20 min, yield of clean coal is 52.38% and the ash is 11%. From then on, that is 20 min to 30 min, yield and ash are almost kept the same. The time is called critical stirring time, that is, increase of hydrophobic groups reaches equilibrium.

Conclusively, stirring speed of 8000 r/min for 20 min is the optimized condition for XHF-D high speed deconcentrator to separate Kailuan slime.

In order to reduce effect of clay to agglomeration, and avoid cover of clay on coal surface, dosage of sodium hexametaphosphate was studied. Test conditions are: XHF-D deconcentrator speed is 8000 r/min, stirring time is 20 min, GF is 100 g/t, and kerosene is 265 g/t. Results (See Table 5) indicate sodium hexametaphosphate is efficient to decrease clean coal ash. At dosage of 1500 g/t, clean coal yield is 10.80%, decreasing by 0.2% compared with that without sodium hexametaphosphate. However, continue to increase the dosage, ash decreasing scope becomes low.

Table 5. Effect of sodium hexametaphosphate on the flotation

| Sodium Hexametaphosphate (g/t) | Clean coal | Tailing | Ash of raw coal (%) |
|-------------------------------|------------|---------|--------------------|
|                               | Yield (%)  | Ash (%) | Yield (%)          |
| 500                           | 52.32      | 11.08   | 47.68              |
| 1000                          | 52.18      | 10.86   | 47.82              |
| 1500                          | 51.95      | 10.80   | 48.45              |
| 2000                          | 48.74      | 10.77   | 51.26              |
| 2500                          | 45.20      | 10.78   | 54.80              |

Fig. 13. Stirring time on the effect of refine coal recovery and ash

Fig. 14. Kerosene dosage on the effect of refine coal recovery and ash
In selective agglomeration-floatation process, non-polar oil enhances behaviors of hydrophobic agglomerates and changes the size and structure of agglomerates. Dosage of kerosene on floatation shows in Fig. 14, with condition of stirring 8000 r/min for 20 min, GF 100 g/t and sodium hexametaphosphate 1500 g/t.

5. Conclusions

1) Fine coal slime in Kailuan coal area belongs to typical hard-to-float high-ash slime according to its characteristics, mineral compositions, floatability. Fine slime has a certain pelitization. Kaolinite is the main minerals.

2) The liberation degree of coal and mineral increases and the particle size decreases significantly within the 20 min grinding time. The particle size and liberation degree changes slightly as the grinding time increases from 20 min to 40 min. When concentration of coal is 40%, the best grinding time is 30min and the minus 0.074 mm fraction accounts 86.85%.

3) Based on the analysis of coal and rock constituent, slime with density grade from 1.40 to 1.60 g/cm$^3$, has low separation degree. Fusain is enriched in high density fraction.

4) Grindig-floatation process and classification floatation process are effective to decrease ash of clean coal. The yield of grinding-one roughing one cleaning process is 52.87% while the ash content is 11.27%. The separation efficiency can be improved by grinding coarse particles into -0.074 mm, accounting for more than 40%.

5) Rough floatation-grinding process and selective agglomeration-floatation process are suitable for separating slime from Kailuan coal area. In rough floatation-grinding process, when accumulative yield of clean coal is 55.53%, its ash could be reduced to 10.74%. In selective agglomeration-floatation process, the best separation conditions are: stirring 8000 r/min for 20 min, GF 100 g/t, sodium hexametaphosphate 1500 g/t, and kerosene 790 g/t. The lowest ash of clean coal is 10.69%, with yield 58.72%. With compared with direct floatation, yield increases by 7.85% and ash decreases by 1.07%. Both processes reach the requirement of ash lower than 11%.

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