Introduction

The distribution of coal pyrite in coal is relatively complex, and it is therefore impossible to reach ideal separation efficiency by means of a common flotation technique. The key factor affecting the separation between coal and pyrite is that the hydrophilic surface of pyrite became hydrophobic after oxidation, with oxidized products such as polysulphide FeS₅ and free sulphur. The oxidized products on the pyrite surface were reduced by an electrochemical method, returning the surfaces to a hydrophilic state and thus increasing the separating efficiency of coal from pyrite by flotation.

Key words: surface oxidation, pyrite, SEM, XRD pattern, electrochemical modification.

SEM analysis

A JEM-200CX electron microscope with an EM-ASID3D attachment and a TN-5500 spectroscopy analyser was used for the investigation.

Sample preparation

Pulverized coal pyrite from Zhongliangshan mine, Chongqing, was pasted onto a double-faced rubber belt on a special sample disk. The sample powder was distributed evenly onto the tape and fixed. The disk was then injected into a JEE-4X vacuum cladding table and covered with a conductive film of spectroscopically pure gold leptonema. The film was about 12 nm thick, and the size of the gold particles 5 nm.

Results

SEM micrographs of coal pyrite at three different stages of oxidation are shown in Figures 1–3. Figure 1 is of fresh pulverized pyrite, Figure 2 shows pyrite after it had been soaked in water for 72 hours, and the sample in Figure 3 had been oxidized in air for 3 months. The fresh pyrite surface consisted mainly of medium-sized particles (10–50 µm) with a rough granular structure, with a few compact, small blocky particles with straight edges and edge angles. After it had been soaked in water for 72 hours, the surface of pyrite was coated with scaly oxidation products (Figure 2). From XRD pattern analysis, the initial oxidized products were deduced to be free sulphur and FeSₓ (polysulfide lacking metals). The coating was very active. Irradiation by 80 kV electron beam
Analysis of surface modification on coal pyrite

for 20 minutes resulted in radiation damage to the surface, proving that the cover had poor thermal stability. The radiation oxidized the sulphur compounds to $\text{SO}_2$, resulting in the rupture of the gold film. After oxidation in air for 3 months, the pyrite surface presented 'corrosion pits' of deeply oxidized products (Figure 3). Small crystallized minerals (<2 µm) that formed in the pits may be the products of deep oxidation. Some prismatic towers crystallized on the smooth surfaces of a few large particles.

Analysis of XRD patterns

Experimental conditions

- Blowing agent: capryl alcohol
- pH conditioner: HCl, NaOH
- Electrolyte: NaCl
- 120 ml Hallimond flotation tube.

Measurement conditions

A D/Max-IIIB X-ray diffractometer made in Japan was used, with a Cu target, Kα radiation, and a graphite curved crystal monochromator.

- X-ray tube voltage 35 kV
- Current 30 mA
- Diffraction slit 1°
- Receiving slit 0.3 mm
- Prismatical slit 1°
Analysis of surface modification on coal pyrite

Figure 4—XRD patterns of fresh coal-series pyrite powder

Figure 5—XRD pattern of initial oxidized coal-series pyrite

Figure 6—XRD pattern of pyrite after electrolytic reduction
Results and discussion

Figures 4–6 show the diffraction patterns of fresh, initially oxidized, and electrochemically reduced coal pyrite. The patterns show the following features:

- The characteristic of FeS$_2$ is the strong peaks at 0.1634, 0.2710, and 0.2427 nm, with inferior strong peaks at 0.2212, 0.1916, and 0.3125 nm, and other weak peaks.
- The characteristic of FeS is the strong peaks at 0.3135, 0.1916, and 0.1634 nm, with inferior strong peaks at 0.242, 0.1563 nm, and other weak peaks.
- The characteristic of FeS$_x$ is the strong peak at 0.265 nm and other weak peaks.
- Composite peaks of FeS$_2$ plus FeS are at 0.1916 nm, 0.1634 nm, and 0.315 nm.

The initially oxidized pyrite (Figure 5) has a strong peak at 0.2710 nm, inferior strong peaks at 0.313, 0.242, 0.221, 0.191, and 0.163 nm, and weak peaks at 0.156 nm, 0.124 nm, etc. The peak appearing at 0.265 nm is that of FeS$_x$. We can therefore deduce that the surface of pyrite after initial oxidation consists mainly of FeS$_2$ and FeS$_x$.

Figure 6 is the diffraction pattern of pyrite after electrolytic reduction. Comparison with Figure 5 shows that:

- The diffraction peak at 0.2212 nm has weakened 70.2%, which proves that the amount of FeS$_2$ has decreased.
- The peaks of FeS$_2$ and FeS overlap, but can be distinguished by their intensity. In Figure 6 (after electrolytic reduction), the FeS peaks at 0.313, 0.191, 0.163, 0.156, and 0.124 nm are all stronger than those in Figure 4 (initially oxidized). This is the result of overlapping with the peaks for FeS$_2$, which is proof of the existence of S$^{2-}$.
- The intensity of FeS$_2$ at 0.265 nm after electrolytic reduction is obviously weaker than that after oxidation. It decreases 18.8% according to the relative peak heights. The equation is:

$$FeS_2 + ne \rightarrow FeS + FeS_n$$

i.e. $S + 2e \rightarrow S^{2-}$.

The relationship between the oxidation state of pyrite and its floatability can be explained as follows. Fresh pyrite is hydrophilic, and can be separated from coal by flotation. In oxidizing condition (such as in pulp with dissolved oxygen), the iron undergoes preferential dissolution, and crystal lattice defects (iron-deficient areas) appear in the crystal structure of the pyrite. A sulphur-rich coating of polysulphide then forms, which lacks metal and behaves hydrophobically. The consequence of these reactions is a decrease of separation efficiency during flotation.

The oxidation equation is:

$$nFeS_2(S) \rightarrow (n - 2)Fe^{2+} + 2FeS_n + 2ne.$$

Further oxidation produces free sulphur:

$$FeS_n \rightarrow S^0.$$

FeS$_2$ and S$^0$ on the surface of pyrite can be reduced to a hydrophilic state using an electrochemical method:

$$FeS_n + ne \rightarrow FeS + (x - 1)S^{2-}$$

$$S + 2e \rightarrow S^{2-}.$$  

Further oxidation causes the production of the hydrophilic complex ions $S_xO_y^{2-}$ and Fe (OH)$_3$, as mentioned in the literature. Therefore, by optimizing the electrochemical conditions, the surface of pyrite could be modified, thus improving its surface hydrophilicity. We are currently developing an electrochemical controller to be used in coal flotation. This is aimed at encouraging industry to use flotation for the desulphurization of coal, by providing a technique to enhance the process.

Conclusions

The degree of oxidation of coal pyrite directly affects the separation of coal and pyrite by flotation. SEM and XRD examination of coal pyrite showed that the initial products of oxidation, FeS$_x$ and free sulphur, cause the pyrite to become hydrophobic. The fresh pyrite surface and the deeply oxidized surface are both hydrophilic$^4$. This raises the possibility of using electrochemical modification method to enhance coal desulphurization by flotation.

References

What’s green, stands six metres high, is chock full of rocks, and has the potential to save mining companies millions of dollars? Give up?

With funding from a consortium of major international mining companies, known as the International Caving Study, JKMRC Ph.D. student and former geotechnical engineer Gavin Power has embarked on research aimed at adding value to the popular sub-level caving and block mining methods.

With the aid of a six-metre high physical model, which has the appearance of a large storage bin, Gavin is researching how broken rocks—both ore and waste—of different shapes flow towards a mine’s draw points.

JKMRC Mining Research Manager Dr Gideon Chitombo said this is the critical step prior to crushing the ore and hauling it to the surface.

‘Valuable ore can be lost if the drawing is not done properly and this requires a good understanding of how large chunks of broken rock flows.’

The big, green physical 1:50 scale model for sub-level and block caving operations has a 42.5m³ rock holding capacity and is based at the JKMRC’s pilot plant in Brisbane. It is believed to be the largest structure of its type ever used for simulation studies of block cave and sub-level cave mining.

The research project started two years ago when the Newcrest Ridgeway mine—who are part of the consortium—decided to sponsor Gavin Power’s Ph.D. work in granular flow.

The process of sub-level caving involves firing narrow sliced rings of ore, which are surrounded by waste above and behind the ore.

The way this material flows down to the draw point at the bottom of these slices determines how ore is recovered and how much dilution—or waste material—occurs in the mining process.

‘My original work was aimed at developing a numerical model to simulate the flow of granular material,’ Gavin said.

‘Very early on in this work I came to the conclusion that a numerical model is fine but it needs to be validated and calibrated with physical results.’

Gavin came up with two basic solutions—one was full-scale experimentation in real mines, and the other was physical modelling work.

‘We basically came to the conclusion that a physical model was the most efficient way to gain that data.

‘Full-scale experiments are expensive, and have limitations, but also give valuable information. In addition to the physical modelling we are hoping to run full-scale experiments at Ridgeway in the near future to match results against the physical model at the JKMRC,’ Gavin explained.

The model cost about $A200,000 to construct, and as at mid-June 2002, three full experiments had been run through the physical model, two on 18 mm rock and one on 7 mm rock. Rock material is being brought from the Mt Coot-tha quarry in Brisbane for the experiments.

Getting the model up and running has been a team effort between Gavin Power, his Ph.D. supervisor Dr Bob Trueman, Andrew Logan at Newcrest Ridgeway, ICS II sponsors, JKMRC Pilot Plant staff, and Mining Research program manager Dr Gideon Chitombo.

Mining research consortium—ICS II—funded construction of the 3-dimensional physical model.

‘The ICS II work aims to validate a unique simulator called REBOP developed by Itasca in the USA, which like my own, aims to simulate the flow of granular material in caving mines,’ Gavin said.

‘At present there is a real need for a properly validated model to simulate granular flow in caving mines.’

In terms of Gavin’s Ph.D. research for Newcrest Ridgeway’s gold mining operation, he believes he has made significant progress towards clearing up misconceptions about the importance of particle size and its effect on mining operations using the sub-level and block caving methods.

‘Initial indications are that there is a significant size effect in that the flow zone does depend on the size of the particles, which has not been properly understood up until now,’ Gavin said.

‘There has been a lot of confusion because some people were saying that size was important and others said particle size had no effect on flow and draw control behaviour.

‘Enhanced draw control can mean millions of dollars to a mine over its life,’ he said.

‘We feel that this knowledge will go into mine design, but the findings haven’t been finalized yet.’

Nevertheless, the mining industry’s view is that the physical model experiments will lead to significant operational benefits.

Gavin said mining engineers could look forward to designing block and sub-level cave mines with more confidence, while helping to better manage their ore reserves.

Newcrest Mining Limited’s Ridgeway Gold Mine Technical Services Manager, Andrew Logan said sponsorship of Gavin Power’s research is part of the company’s longer term strategy for new mine design.

He added that better control measures put in place resulting from Gavin’s research would impact on the grade of the material drawn relative to the reserve forecast.

‘If you have the right draw design and processes, you can substantially improve your resource recovery and project returns.’

Andrew said improved prediction would also provide for better process control of head grade volatility, helping mine to mill optimization.

‘If we can improve our forecasting from the mine to the mill, then our metal outcomes from the mill should be better.

‘However, it would be difficult to place a dollar value on Gavin’s contribution: ‘In terms of how this work potentially impacts on grade and recovery, the value is quite substantial. The potential leverage of Gavin’s work may be substantially above the investment.’

And while the large green physical model may have potential applications for bulk handling research in other industries, Gavin says there is a big demand for its use in the mining industry.

‘We have many more experiments planned on different aspects of flow, looking at flow mechanisms, the effects of size distributions, interactive draw and different mine geometries,’ he said.

‘Basically we can test almost anything we want with the physical model as long as it is related to granular flow.

Gavin predicts the large-scale 3-D physical model would still be running on mining applications for at least the next ten years.

‘It’s got a lot of life in it.’

* Issued by: Dr Gideon Chitombo, JKMRC Mining Research Manager, Tel: 61 7 5365 5888, E-mail: g.chitombo@mailbox.uq.edu.au
Analysis of surface modification on coal pyrite