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Progress in Mineral Processing Technology, Demirel & Ersayın (eds) © 1994 Balkema, Rotterdam, ISBN 90 5410 513 5

Bio-column flotation of coal for desulfurization and comparison with conventional and column flotation

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ABSTRACT: Coal desulfurization of a type of British coal, containing 3% total sulfur, by bio-oxidation of surfaces of pyrite particles in the coal during column flotation was investigated. Growth of bacteria occurred in Tuovinen&Kelly Medium (1973). Sulfur depressions in conventional, column and bio-column flotation were compared. Bio-column flotation was more effective than column and conventional coal flotation techniques.

1 INTRODUCTION

Sulfur occurs in coal in the forms of pyrite (FeS2), organic, elemental and sulfate sulfur (Aplan 1976). 60-70 % of the total sulfur in a typical British coal is in the form of sulfide sulfur or pyritic sulfur (Atkins et al 1987). In order to remove sulfide sulfur from coal various flotation techniques have been developed as given in Table 1. Bio-oxidation of pyrite particles in coal during coal flotation was an efficient process in them and has improved coal desulfurization (Atkins et al 1987, Attia 1985, Tosun et al 1992).

Bio-column flotation of coal has been a new improved process in column flotation technique. Pyrite particles in coal has been oxidized in a very short time period of 15 minutes by Thiobacillus ferrooxidans (Attia 1990). Surface modification of pyrite minerals prior to flotation has been applied to the removal of pyritic sulfur from coal (Atkins et al 1987). Bio-modification of surfaces of pyrite particles in coal takes place with the reactions given as follows;

Table 1. The methods used for coal desulfurization.

1. Conventional coal flotation
    - (a) Coal flotation for high native hydrophobic coal types
    - (b) Reverse coal flotation or Sulfide flotation
    - (c) Coal flotation with basic reagents
    - (d) Coal flotation with bio-oxidation
2. Column flotation of coal
    - (a) Column flotation of coal with basic reagents
    - (b) Column flotation of coal with bio- oxidation treatment (Bio-column flotation of coal)

(1) direct oxidation of the surfaces of pyrite mineral particles in coal with the bacterial medium (Silver 1978, Silverman 1967):

$$FeS_2 + 7/2\ O_2 + H_2O \text{ ----> } FeSO_4 + H_2SO_4 \quad (1)$$

$2FeSO_4 + 1/2O_2 + H_2SO_4$-bacteria> $Fe_2(SO_4)_3 + H_2O$ (2)

$FeS_2 + Fe_2(SO_4)_3$ -----> $3FeSO_4 + 2S^o$ (3)

$2S^o + O_2 + 2H_2O$ --bacteria--> H_2SO_4 (4)

Firstly, on surfaces of pyrite, ferrous sulfate forms in oxygen rich water solutions (Equation 1) and then ferrous iron is oxidized to ferric iron by means of bacteria. This reaction produces the required ferric ion in the solution so as to increase the kinetic rate of the reaction in Equation 3. In Equation 4, elemental sulfur is converted to sulfate anion by means of bacteria.

(2) Indirect oxidation of pyrite:

$Fe_2(SO_4)_3 + FeS_2$ --bacteria--> $3FeSO_4 + 2S^o$ (5)

Chemical species in solution such as ferric iron reacts with pyrite surface and bacteria catalyze this reaction (Equation 5).

The oxidation may also occur chemically, however, the kinetic rate of the chemical oxidation reactions of sulfide minerals is relatively slow. The types of iron and sulfur oxidizing bacteria are given in Table 2. Thiobacillus ferrooxidans is the most useful one in them regarding to iron oxidation of pyrite surfaces in coal. Combination of column flotation and bacterial treatment of coal for pyrite depression during column flotation of coal was investigated in this research. Comparison of bio-column flotation of coal with column flotation and conventional flotation techniques were made.

2 COLUMN FLOTATION AND BIO-COLUMN FLOTATION OF COAL

Column flotation of coal fine may improve both ash and sulfur depression during flotation without reducing combustible material recovery and, in general, it is more efficient for cleaning

Table 2. The types of bacteria providing energy from oxidizing iron and sulfur.

Type of Bacteria	**Energy**
Thiobacillus ferrooxidans	ferrous iron and sulfur in mine waters and hot springs
Thiobacillus thiooxidans	sulfur in mine waters and hot springs
Sulfolobus acidocalderius	ferrous iron and sulfur in hot springs
Acidianus brierleyi	ferrous iron and sulfur oxidation in hot springs
Leptospirillum ferrooxidans	ferrous iron and sulfur in mine waters and hot springs

of fine coal samples as fine as -20 microns. The advantages of column flotation are as follows:

(1) production of higher grade concentrates without influencing recovery,

(2) less power consumption than conventional flotation techniques and

(3) more efficient flotation of ultrafine coal (-0.1 mm).

In the literature, it has been stated that column flotation is more efficient at treating fine particle size range materials. The main differences from a conventional flotation cell are the length and use of microbubbles. The column length can range between 1 and 5 metres in laboratory type models, and from 5 to 20 metres in plant scale units. In addition, the cross-section of column may be circular or square in design. On plant scale, the column length/column diameter ratio (H_{col}/D_{col}) is between 10 and 50. For laboratory scale units it ranges from 40 to 100. Increasing this ratio may reduce the capacity of the column, but it improves retention time of feed in the column. Another advantage of column flotation is the absence of a mechanical agitation system which is employed in conventional flotation cells to suspend mineral particles in the slurry. In column flotation, a sparger mechanism, such as a glass frit or a cloth filter, generates microbubbles which catch the descending particles in a counter current column flotation system. therefore increased feed particle size and also particle density may significantly reduce the recovery in a column. James reported that at recoveries in the 96-97% range, column cells achieved far superior grades to conventional flotation cells and the residence time of particles in the column was approximately half that of conventional flotation cells. Variables affecting column flotation are as follows;

(1) Air flow rate,
(2) Hydrophobicity,
(3) Solid/liquid ratio,
(4) Bubble diameter,
(5) Sparger area,
(6) Specific gravity of floating particles,
(7) Particle size,
(8) Bias water,
(9) Column diameter and height,
(10) Wash water flow rate,
(11) Feed rate,
(12) Viscosity,
(13) Froth depth,
(14) Frother concentration.

Column flotation of coal has been found to be much more efficient than conventional coal flotation techniques for desulfurization of coal. Columns used for coal flotation are different from the columns used for ore flotation. The reason for this fact is the difference between the densities of coal and ore minerals. Hence the columns used in coal flotation may be smaller than the columns used in ore flotation. H_{col}/D_{col} ratio accepted theoretically as 10 in column design for ore flotation may be less than 10 even half of it for the column flotation of coal. The main variables affecting sellectivity in column flotation of coal are

(1) froth depth and
(2) wash water rate.

An increase in either froth depth and wash water velocity has been found to improve the product obtained from the column (Finch & Dobby 1990). These two variables mainly influence the optimum operation of the column. Bio-column flotation of coal is a combination of bio-oxidation of pyrite particles in coal during column flotation and flotation of coal in column. Thus, this process involves two cleaning effects on coal desulfurization. Firstly, bio-oxidized pyrite surfaces resulting in depression of pyrite particles during column flotation of coal improves the efficiency of coal desulfurization more than that in column flotation. Secondly, the flotation of minerals or coal particles in the column takes places slower than in conventional flotation units. The main reasons for this are ;

(1) the effect of wash water, inhibiting the attachment of hydrophilic particles on to the rising bubbles, and
(2) restricted air sparging.

Coal flotation rate mainly increased with a corresponding increase in water recovery rate in float (Yoon & Lutrell 1986). It is clearly seen that wash water rate is a significant variable affecting quality of froth in column flotation of coal.

3 MATERIALS AND METHODS

The type of British coal was defined by proximate analysis of coal. British coal used in column flotation tests comprimised 3% total sulfur and 1.25 % pyritic sulfur.

In this study, coal flotation tests were carried out in a standardized procedure as shown in Figure 1. Chemical or bacterial oxidation of pyrite particles during coal flotation practiced in this procedure as seen from Figure 1. However, bio-oxidation period was higher than conditioning time of chemical depressants. While conditioning time of chemical pyrite depressants was 5 minutes, bio-oxidation pre-conditioning time was an

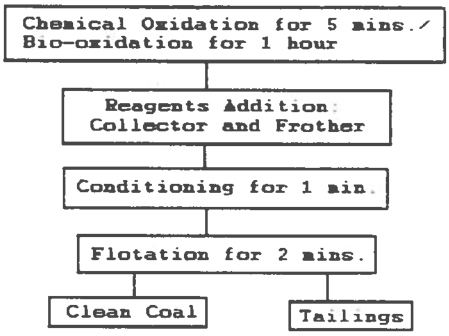


Figure 1. Flowsheet of conventional coal flotation tests for desulfurization.

hour in the conventional coal flotation tests and column flotation tests. The standard conditions in conventional coal flotation tests are given in Table 3. Column flotation tests were carried out in a Canadian column.

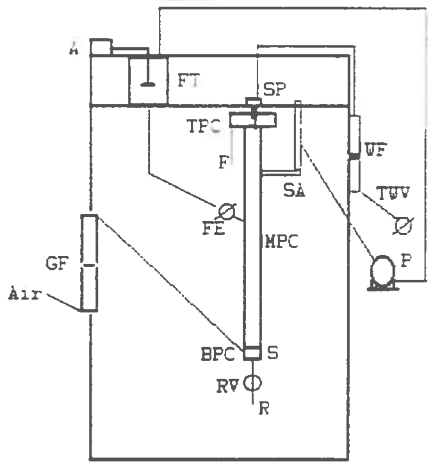
The column apparatus was installed in a box frame with a height of 2 m and width of 50 cm and clipped to the frame at two points . The frame supported the column apparatus in a vertical position and also acted as a base for other ancilliary equipment. The column was made from a glass tube with a thickness of 2 mm. As can be seen from Figure 2 the column consisted of 4 main glass parts. These component parts were as follows;

(1) top part of the column,
(2) main body part of the column,
(3) side arm part ofthe column and
(4) bottom part of the column.

The top and bottom parts of column were used for recovery of froth and tailings, respectively. The side arm part of the column was designed to provide a means producing a constant froth level. This modification was succesfully operated on the column apparatus and different from the other types of Canadian columns. The main body part of the column was a glass tube (Figure 2). This part was 140cm long with a diameter of 2.5 cm. The main function of this part of the apparatus was to allow the slurry and bubbles to achieve

Table 3. The conditions and reagents used in conventional coal flotation tests.

Conditions	
Feed	100 g
Wetting time of coal	15 mins.
Chemical depressants	NaCl, $CaCO_3$
Dosages of chemical depr.	50 g/t
Conditioning time of ch. depr.	5 mins.
Type of bacteria	Thiobacilllus ferrooxidans
Bacterial cell density	10^7 and 10^9
Conditioning time of bacteria	1 hour
Collector (Diesel oil)	1250 g/t
Frother (Non-toxol 300)	250 g/t
Conditioning time	2 mins.
Floating time	3 mins.
Flotation machine	Leeds cell (2000 cl)
Agitation speed	1200 rpm



A. Agitator, FT. Feed tank, SP. Shower part, TPC. Top part of column, F. Froth, WF. Water flowmeter, SA. Side arm of column, FE. Feed entrance and valve, MPC. Mainart of column, GF. Gas flowmeter, P. Pump, TWV. Tap wter valve, BPC. Bottom part of column, S. Sparger, RV. Reject valve, R. Reject

Figure 2. Diagram of column apparatus for coal desulfurization.

countercurrent contact. Conditioning with chemical depressants or bacteria was carried out in a 5000 cl feed tank and agitated at a speed of 1200 rpm same as that in conventional flotation cell.

Duplicated column flotation tests were carried out. Firstly, standard column flotation tests were performed on coal samples under optimum conditions given in Table 4. Chemical oxidation of pyrite particles for depression of sulfur and bio-column flotation of coal were practiced in the conditions related with bio-oxidation as given in Table 4.

In the conventional coal flotation tests and column flotation tests, 100 g coal samples were used. The samples were put into the feed conditioning tank and wetted by mechanical stirring in this vessel (5000 cl) for 15 minutes. The solid/liquid ratio of slurry was 10% in the feed tank and in the column. When the column apparatus was put into action, a feed rate of 100 ml/min was employed through a calibrated valve system. The procedure that was adopted was similar to the standard coal flotation tests, but frother dosage and flotation time were different.

In column flotation tests of coal samples, stable conditions were achieved in 3 minutes after feed was introduced, and once this condition was established the flotation tests were carried out. froth and reject of the column apparatus were collected. A flotation time of 10 minutes was used as standard for all tests.

4 RESULTS AND DISCUSSION

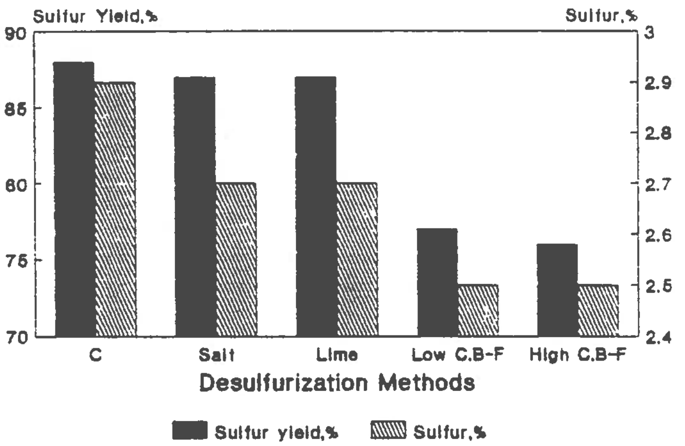
The results of conventional coal flotation tests were shown in Figure 3. Regarding to the sulfur contents and yields of clean coal products, efficiency of desulfurization of every test was determined. As seen from Figure 3, salt (NaCl) and lime ($CaCO_3$) decreased sulfur content from a head of 3% total sulfur to 2.6% and 2.7% with 87% sulfur yield, respectively. This high

Table 4.The operation conditions of laboratory type column apparatus for coal desulfurization with bio-flotation.

Fixed Operating Parameters	
Height of Column	140 cm
Diameter of Column	2.50 cm
Frother Composition	Non-Toxol 300
Frother concentration	0.5 ml/l
Collector composition	Diesel Oil
Collector concentration	1.25 kg/t
Slurry agitation time	15 mins.
Pulp density	10%
Feed slurry flowrate	100 ml/min
Wash water flowrate	800 ml/min
Microbubble flowrate	100 ml/min
Operating time	13 mins.
Formation of stable froth	3 mins.
Flotation time	10 mins.
Particle size of feed	-250 microns

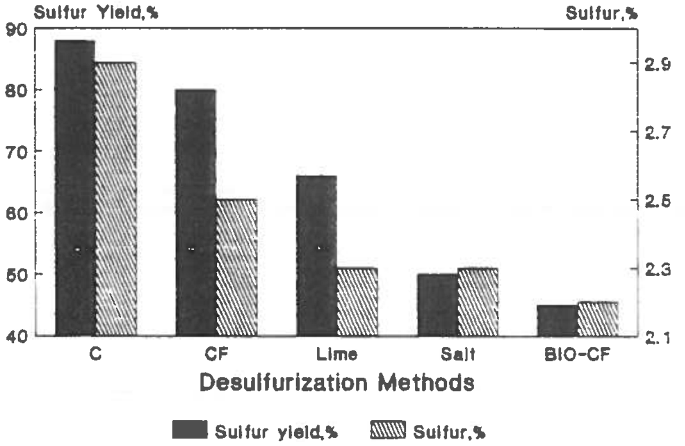
sulfur yield of clean coal product showed that conventional coal flotation technique using chemical pyrite depressants could not be efficient in desulfurization of coal.

Bio-oxidation treatment during conventional coal flotation decreased sulfur contents and yields of clean coal products more. Cell density of bacteria grown in Tuovinen & Kelly medium (Tuovinen & Kelly 1973) did not significantly affect desulfurization efficiency as seen from Figure 3. At low and high cell densities sulfur content of clean coal decreased to 2.5% and sulfur yield to 76%. It is certainly understood that bio-oxidation of coal during conventional coal flotation was more efficient in desulfurization of coal.



C. Conventional coal flotation without using pyrite depressant or bacteria. Salt: Conventional coal flotation with using salt (NaCl) as pyrite depressant. Lime: Conventional coal flotation with using lime (CaCO3) as pyrite depressant.
Low C.B-F: Bio-flotation of coal at low cell density.
High C.B-F: Bio-flotation of coal at high cell density.

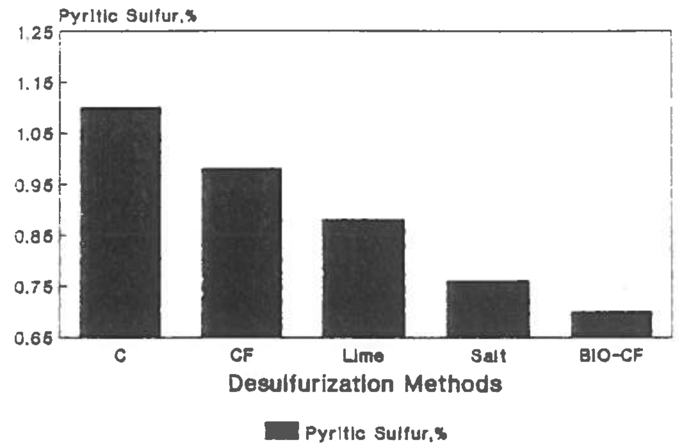
Figure 3. Effect of conventional coal flotation and bio-flotation of coal on desulfurization.



C. Conventional coal flotation without using pyrite depressant or bacteria.
CF. Column flotation of coal without using pyrite depressant or bacteria,
Salt: Column flotation of coal with using salt (NaCl) as pyrite depressant. Lime: Column flotation of coal with using lime (CaCO3) as pyrite depressant.
BIO-CF. Bio-column flotation of coal.

Figure 4. Effect of column flotation and bio-column flotation of coal on desulfurization.

The results of column flotation tests of coal samples were seen from Figure 4. Column flotation of coal without any chemical depressants
and bio-treatment of coal was more efficient than conventional coal flotation techniques. Column flotation of coal reduced sulfur content of clean coal to 2.4% and sulfur yield to 80%. Column flotation methods using chemical pyrite depressants, salt (NaCl) and lime ($CaCO_3$), decreased sulfur contents of clean coal products to 2.3% and 2.2% at sulfur yields of 65% and 50%, respectively (Figure 4). The column flotation methods using NaCl and CaCO3 depressed significantly high amount of sulfur. NaCl was more efficient than CaCO3 in desulfurization of coal with column flotation. Bio-oxidation treatment of coal suppressed more sulfur, and particularly pyritic



C. Conventional coal flotation without using pyrite depressant or bacteria.
CF. Column flotation of coal without using pyrite depressant or bacteria.
Salt. Column flotation of coal with using salt (NaCl) as pyrite depressant. Lime. Column flotation of coal with using lime (CaCO3) as pyrite depressant.
BIO-CF. Bio-column flotation of coal.

Figure 5. Effect of column flotation and bio-column flotation of coal on desulfurization with respect to pyritic sulfur content.

sulfur. Sulfur content of clean coal decreased to 2.2% in bio-column flotation of coal at a sulfur yield of 45%. Pyritic sulfur content of clean coal reduced to 0.70 % from a sulfur content of 1.25% of feed (Figure 5).

It is clearly seen that total sulfur and pyritic sulfur contents of coal greatly removed in bio-column flotation of coal and ,thus, it has been found that bio-column flotation of coal was the most efficient method for desulfurization of coal among various flotation techniques.

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3 Ağustos 1994

Sayın Dr. Yıldırım İsmail Tosun,

5. Uluslararası Cevher Hazırlama Sempozyumunun programı ekte verilmiştir. "**Bio-column Flotation of Coal for Desulfurization and Comparison with Conventional and Column Flotation**" başlıklı bildirinizin 8 Eylül 1994 günü sempozyumun Ihlara Salonundaki 6.Oturumunda saat 11:50-12:10 arasında sunulmasına karar verilmiştir.

Herbir bildiri için 20 dakikalık süre verilmiş olup, bu sürenin 15 dakikası sunum, 5 dakikası tartışma olarak ayrılmıştır. Sempozyum salonunda slayt projektörü ve tepegöz olanakları bulunmaktadır.

Kapadokya'da görüşmek dileğiyle.

Saygılarımla

Prof. Dr. Halim DEMİREL
Yürütme ve Yayın Kurulu Başkanı