THE COMPARISON OF CHEMICAL AND BIOLOGICAL SUPPRESSION ON PYRITE SURFACES DURING COAL FLOTATION

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ABSTRACT

Two types of high sulfur British coals were subjected to desulfurization tests involving both chemical and bio-oxidation treatments prior to coal flotation experimentation. The efficiency of the chemical oxidation of pyrite particle surfaces was compared with the bio-oxidation pre-treatment of coal as a means of pyrite suppression during coal flotation.

ÖZET

İki tür yüksek kükürtlü kömür numunesi, kömür flotasyonu öncesi kimyasal ve biyooksidasyon yöntemleri ile kükürtsüzleştirmeye tabi tutulmuş ve her iki yöntemin piritin bastırılmasındaki etkinliği karşılaştırılmıştır.

Key Words: Desulfurization of coal, bio-oxidation of pyrite.

1. INTRODUCTION

Sulfur occurs in coal in the forms of pyrite (FeS_2), organic and sulfate sulfur [1,2]. Between 60-70% of the total sulfur in a typical British coal is in the form of pyrite. In order to remove pyritic sulfur from coal various chemical and physical processing techniques can be applied as shown in Table 1. In addition to these techniques the bio-oxidation of pyrite surfaces prior to coal flotation has been investigated in several studies [3,4,5].

Table 1 . The methods used for coal desulfurization.

1. Physical techniques	(a) Differences in relative density
	- Jig washer
	- Concentrating table
	- Dense media cyclone
	(b) Differences in surface properties
	- Froth flotation
	- Oil agglomeration
	- Electrostatic separation
	(c) Differences in magnetic properties
	- Magnetic separation
2. Chemical techniques	(a) Caustic leaching: NaOH, KOH
	(b) Oxidation leaching

The bio-oxidation of pyrite particles in coal has been achieved in very short time periods (15 minutes) [6]. During such treatment *Thiobacillus ferrooxidans* is used as the iron-oxidizing bacteria. *Thiobacillus ferrooxidans* is a very small (0.2x2 microns), rod shaped bacteria (Figure 1) capable of oxidizing iron and sulfur under the correct process conditions.

The advantages of bio-oxidation of pyrite surfaces for coal desulfurization are (1) selectivity of bacteria in bio-oxidation of pyrite particles over coal, when compared with chemical oxidation techniques, (2) improved desulfurization of coal through the selectivity of the bacteria, (3) the possibility of reuse of the bacteria. This paper describes an experimental process in which bacteria can be used to selectively oxidize pyrite surfaces to achieve the subsequent suppression of the pyrite particles during standard coal flotation tests.

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Figure 1. The photograph of *Thiobacillus ferrooxidans*

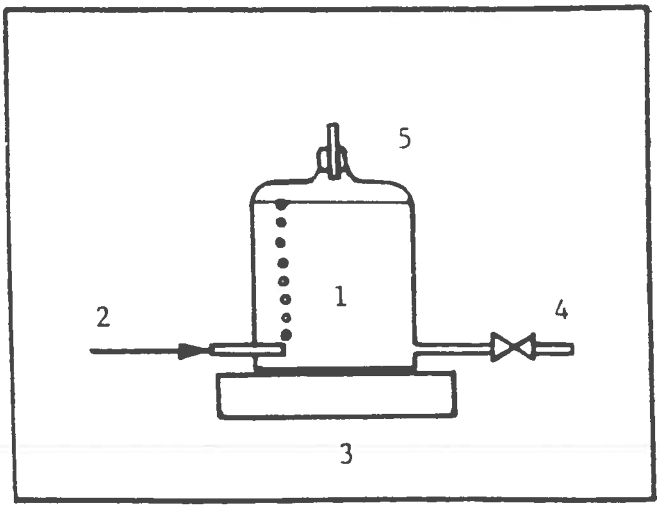
2. MATERIALS AND METHODS

2.1. Adaptation of Bacteria

The cultures of *Thiobacillus ferrooxidans* were adapted over coal flotation tailings with 8% total sulfur content. 50 gram samples of tailings were placed in 1 liter conical flasks and 500 ml of distilled water was added. After adjusting the acidity of the mixture (pH 2.0) it was sterilized in an autoclave at 120 °C for 30 minutes and subsequently inoculated with 10 ml bacterial culture. All the flasks were incubated at 30°C for two months.

2.2. Growth of Bacteria

Adapted cultures were removed from the flasks and the growth of the bacteria was carried out in a 10 liter carboy. The system used to obtain the growth of *Thiobacillus ferrooxidans* is shown in Figure 2. The rate of growth of *T. ferrooxidans* was increased by addition of air at a flow rate of 100 ml/minute. Tuovinen & Kelly Medium[8] was used as nutrient because of its proven efficiency under these operating conditions [6]. The pH of medium was set to 2.0 by addition of sulfuric acid. The carboy containing medium was sterilized in an autoclave at 120°C for 30 minutes and then adapted culture was inoculated. A bacterial growth period of two weeks was used, and the growth of bacteria was observed by monitoring the pH of the mixture. After centrifugation of the bacterial liquor, the adapted *T. ferrooxidans* were bottled in 30 ml vessels and refridgerated at -4°C.



1. 10 liter Carboy, 2. Air inlet at 100 ml/minute, 3. Heater, 4. Sample and bacterial culture outlet, 5. Sterilized cotton wool air exit

Figure 2. The diagram of system used in growth of bacteria.

2.3. Coal Flotation Tests

Initially, chemical oxidation of pyrite surfaces was carried out to provide baseline data to compare with subsequent bio-oxidation test results. The method used for chemical oxidation pre-treatment of pyrite particles is summarized in Figure 3. The method used for bio-oxidation of the surfaces of pyrite in the coal is outlined in Figure 4. Total sulfur, pyritic sulfur and ash contents of coals used in the experiments are given in Table 2. In this report 10% ash content of Type 1 coal can be regarded as an high ash content for bio-oxidation of pyrite particles in coal.

Table 2. Chemical analysis of two types of British coal.

Coal	Ash, %	Total Sulfur, %	Pyritic Sulfur, %
Type 1 Coal	10.00	4.20	1.50
Type 2 Coal	5.00	3.00	1.25

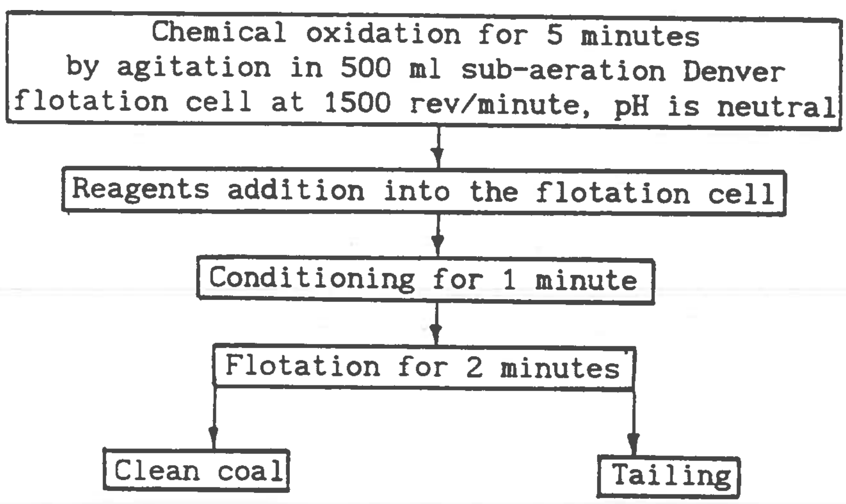


Figure 3. The procedure followed in chemical oxidation of surfaces of pyrite particles during standard coal flotation test.

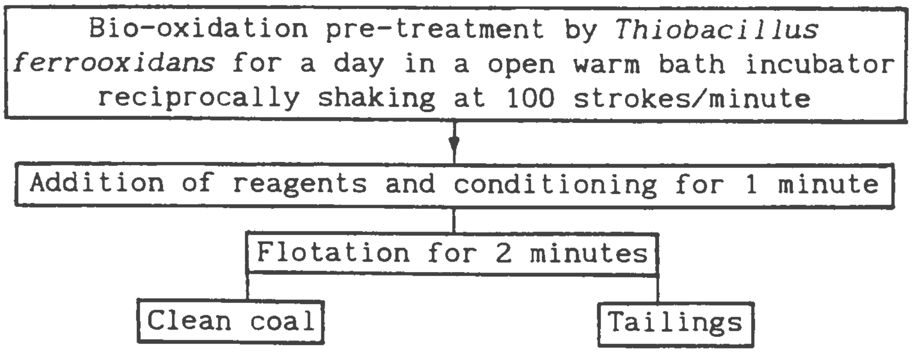


Figure 4. The procedure followed by bio-oxidation of surfaces of pyrite particles during standard coal flotation tests

3. RESULTS AND DISCUSSION

The two types of British coal used in this work were treated by chemical pyrite oxidants and the iron-oxidizing bacteria, *Thiobacillus ferrooxidans.* The results showed that the bio-oxidation of the surface of pyrite particles in Type 1 coal was not as effective as chemical oxidation. This was possibly due to the high ash content of Type 1 Coal (10% ash) (Figure 5). The bio-oxidation pre-treatment of Type 2 Coal improved the depression of pyritic sulfur in coal flotation tests in comparison with the chemical oxidation of pyrite particles. It is suggested that the basic ash content of Type 1 Coal destroyed the bacterial activity in the bio-oxidation treatment.

Different types of nutrient medium for growth of *T.ferrooxidans* were examined. These nutrient media are given in Table 3. The growth of bacteria over Tuovinen & Kelly Medium was found to be best.

As seen from Figure 6 the depression of pyrite from Type 1 Coal did not occur in the flasks with Modified Tuovinen & Kelly or 9K medium. This might be due to the high basic ash content of Type 1 Coal (10% ash) and increased precipitation of *jarosite* type sulfohyroxides which was observed.

The effect of bacterial cell density was also investigated.

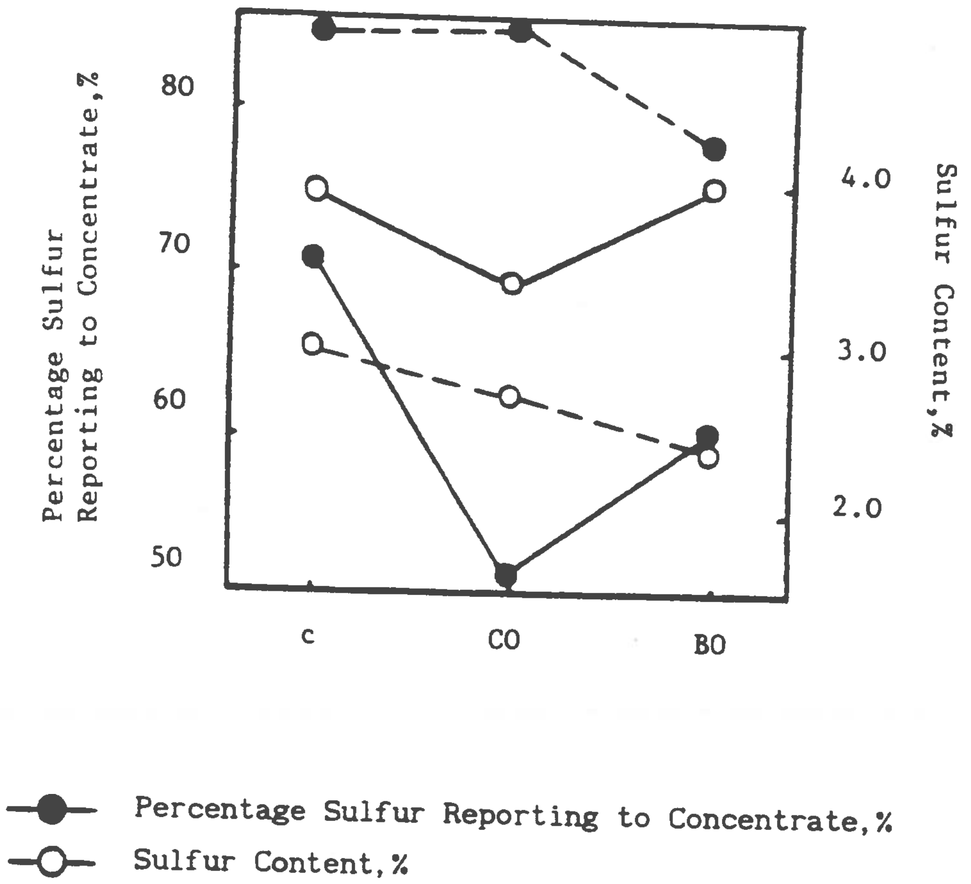


Figure 5. Effect of chemical oxidation and bio-oxidation of surfaces of pyrite particles in coal on coal desulfurization. c: Control test, CO: Standard coal flotation test with chemical oxidation of surfaces of pyrite particles in coal, BO: Standard coal flotation test with bio-oxidation of surfaces of pyrite particles in coal, ___ Type 1 Coal, ---- Type 2 Coal.

It can be seen from Figure 7 that the depression of pyritic sulfur during flotation was not affected by increasing the cell density by a factor of ten.

The pH value of the bio-oxidation pre-treatment was varied between 1.3 and 2.0. In Figure 8, it can be seen that at pH 1.5, the percentage of total sulfur reporting to the clean coal concentrate decreased, but, the sulfur content of clean coal after bio-oxidation treatment did not change significantly.

Table 3. Nutrient medium compositions used in bio-oxidation pre-treatment tests.

Nutrient medium	Composition
Tuovinen & Kelly Medium (1973)[8]	4 parts of solution A + 1 part of solution B Solution A: 0.5 g K_2HPO_4 0.5 g $MgSO_4$ 0.5 g $(NH_4)_2SO_4$, dissolved in 1 l of 0.01 N H_2SO_4 Solution B: 167 g $FeSO_4$ dissolved in 1 l of 0.05 N H_2SO_4
Modified Tuovinen & Kelly Medium [9]	0.05 g KH_2PO_4 0.05 g $MgSO_4.7H_2O$ 0.4 g NH_4NO_3 33.3 g $FeSO_4.7H_2O$, dissolved in 1 l distilled water
9K Medium (1959)[10]	3.0 g $(NH_4)_2SO_4$ 0.1 g KCl 0.5 g K_2HPO_4 0.5 g $MgSO_4.7H_2O$ 0.01 g $Ca(NO_3)_2$ 700 ml distilled water 300 ml of a 14.74 %(w/v) solution of $FeSO_4.7H_2O$

Acid leaching of the Type 2 Coal prior to the bio-oxidation of pyrite particles was investigated. The objective was to remove calcium and sodium salts from the coal by use of acid leaching. It can be seen from Figure 9 that acid leaching reduced both the ash and sulfur contents of the coal and the subsequent bio-oxidation

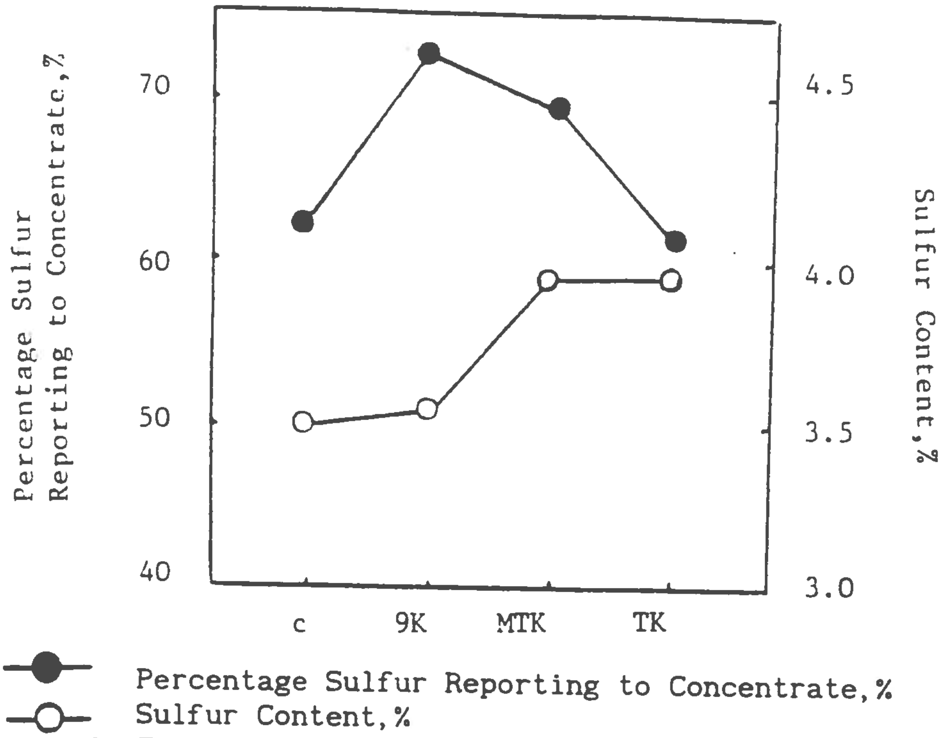


Figure 6. Effect of nutrient medium on coal desulfurization (Type 1 Coal), c. Control, 9K. 9K Nutrient Medium, MTK. Modified Tuovinen & Kelly Medium, TK. Tuovinen & Kelly Medium.

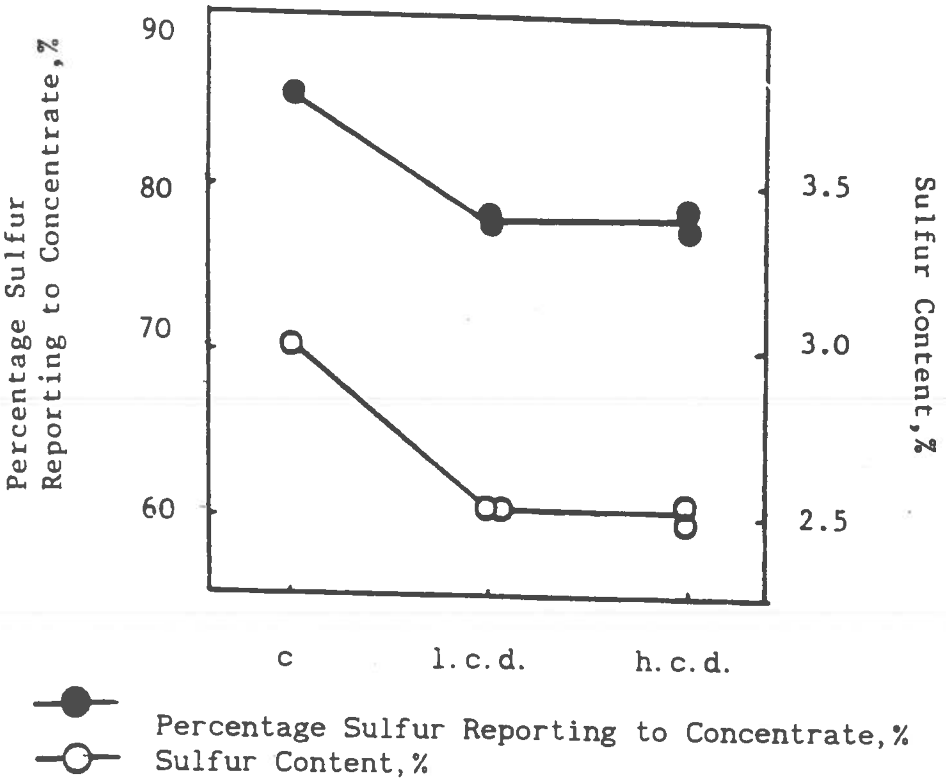
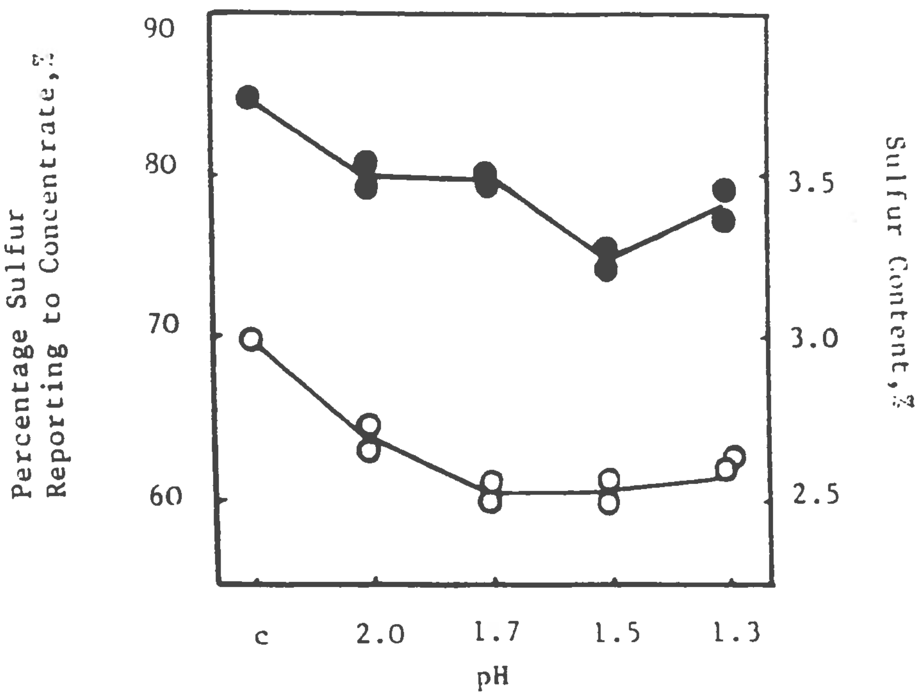
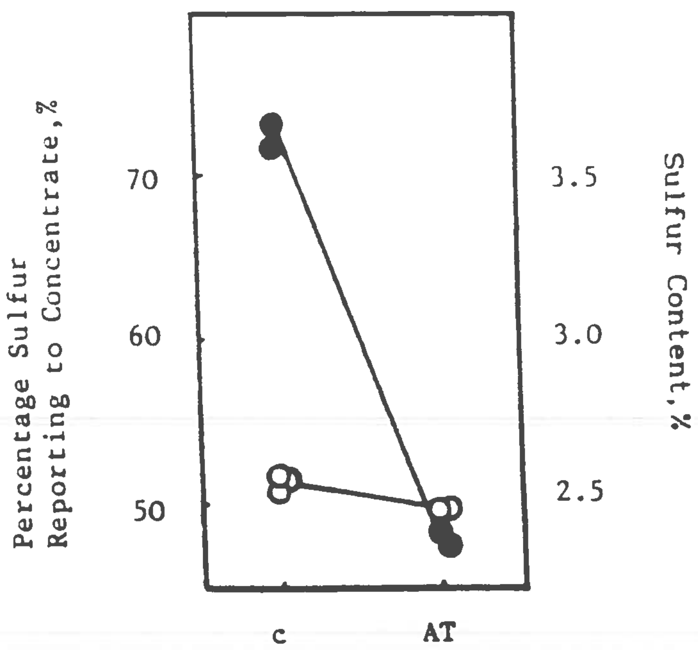


Figure 7. Effect of cell density on coal desulfurization (Type 2 Coal), c. Control, l.c.d. low cell density, h.c.d. high cell density.



Percentage Sulfur Reporting to Concentrate,%
Sulfur Content,%

Figure 8. Effect of pH on coal desulfurization (Type 2 **Coal**), c. Control.



Percentage Sulfur Reporting to Concentrate,%
Sulfur Content,%

Figure 9. Effect of acid leaching of coal prior to standard coal flotation tests on coal desulfurization (Type 2 Coal).
c: Control test, AT: Test with Acid Treatment

pre-treatment was found to be more effective. This was possibly due to increased activity of bacteria after removal of basic components of the ash content of the coal.

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