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Desulfurization of Pittsburgh Coal by Microbial Column Flotation

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ABSTRACT

Microbial column flotation using *Thiobacillus ferrooxidans* was applied for desulfurization of Pittsburgh coal of CWM (Coal-Water Mixture) size between 38 μm and 75 μm. The coal contained ferrous ion which would interfere separation of pyrite from coal by microbial flotation. The wash-out of ferrous ion with 0.5N HCl solution enabled pyrite removal from coal. The coal was divided into two parts, the small-size coal between 38 μm and 53 μm, and the large-size coal between 53 μm and 75 μm. The pyritic sulfur content was decreased from 2.88% of the feed coal to 0.98% of the product coal for the large-size coal and from 2.77% of the feed coal to 1.12% of the product coal for the small-size coal by microbial flotation. The decrease was based on removal of liberated pyrite particles (between 20 μm and 70 μm). However, the fine particles (less than 20 μm) could not be removed even though the pyrite particles were liberated from coal particles. The microbial column flotation was more effective for desulfurization of the large liberated pyrite particle than that of the small. It was not effective for desulfurization of the locked pyrite particles that were buried in coal particles. Both the pyrite liberation from coal and its particle size are important factors for the pyrite removal by microbial column flotation.

Index Entries: *Thiobacillus ferrooxidans*; flotation; coal; pyrite; desulfurization.

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INTRODUCTION

Coal has been expected to be an alternative energy source for oil. However, coal has some disadvantages when compared with oil. One is the handling problem, as it is a solid. In recent years, CWM (Coal Water Mixture) technology has been developed to improve coal's handling. The other problem is the sulfur contained in coal. Its combustion releases sulfur dioxide which causes the formation of acid rain (*1*). The sulfur dioxide from coal can be removed by gas desulfurization system. As this system is expensive, a cheaper desulfurization technology is desired (*2*). Microbial desulfurization is one of the cheaper sulfur removal technology for CWM (*3*).

In microbial flotation, pyrite loses its floatability and sinks to the bottom of the flotation machine within a few minutes (*4*). Our previous reports showed that bacterial adhesion to the pyrite surface induced the supression of pyrite floatability by changing the pyrite's surface property from hydrophobic to hydrophilic (*5*) and that bacterial adhesion to pyrite occurred selectively based on the bacterial recognition of reduced iron in pyrite (*6*).

Pyrite removal by microbial flotation had already been reported by some researchers (*7,8,9*) and us (*10*). In these reports, a mixture of pyrite and coal was used for desulfurization experiments as a model of high-sulfur coal. Pyrite removal from actual coal was also reported by Zeky and Attia (*11*), but has not been investigated further. In this study, pyrite removal from pulverized Pittsburgh coal was investigated by microbial column flotation.

MATERIALS AND METHODS

Microorganisms, Medium and Culture

Thiobacillus ferrooxidans T-9 strain was used in this study, which was isolated from the acidic soil of a coal storage site in Takehara in Hiroshima Prefecture in Japan (*10*). The strain was cultured in 9K medium (*12*), consisting of 3 g of $(NH_4)_2SO_4$, 0.5 g of $MgSO_4 \cdot 7H_2O$, 0.1 g of KC1, 0.5 g of K_2HPO_4, 0.01 g of $Ca(NO_3)_2$, and 42.2 g of $FeSO_4 \cdot 7H_2O$ in 1 L of distilled water, adjusted to pH 2.5 by 6*N* H_2SO_4. The subculture was carried out on in 350 mL of the 9K medium with 1-L flask under shaking at 30°C for 1 wk. This was used as a seed culture. The large scale cultivation was carried out in 7 L of the 9K medium with 10 L carboy under aeration (500 mL/min) at 30°C for 3 d.

The culture was filtrated through filter paper (No. 2, Toyo, Sizuoka, Japan), and then the filtrate was centrifuged at 15,000*g* for 15 min to harvest cells. The cells were washed three times with sulfuric acid solution (pH 2.0). The washed cells were resuspended into the solution for following experiments.

Table 1
Sulfur Content of Pittsburgh Coals

	Without wash	With wash by HCl		
	38–75 μm	38–75 μm	53–75 μm	38–53 μm
Total sulfur (%)	5.91	5.20	5.06	5.00
Pyritic sulfur (%)	2.51	2.79	2.88	2.77
Sulfate sulfur (%)	1.63	0.63	0.46	0.45
Ash (%)	—	—	8.13	8.15

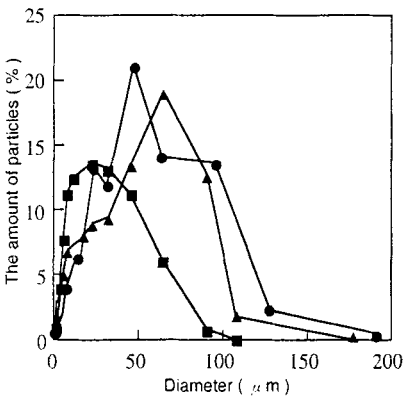

Fig. 1. The size distribution of coals; the symbols expressed the coal size; (●): 38 μm- 75 μm, (■): 53 μm-75 μm, (▲): 38 μm-53 μm.

Preparation of Coal

Pittsburgh coal was purchased from Energy and Fuel Research Center, Pennsylvania State University, University Park, PA. The coal was pulverized into fine particles, and then sieved. Three types of particles size were adopted, 38–75 μm, 53–75 μm, and 38–53 μm. Exactly 100 g of each size coals were soaked in 1000 mL of 0.5*N* NC1 solution. The slurries were stirred and stood for 30 min. Coals were filtrated on membrane filter (10-μm pore size, Millipore, Tokyo, Japan) by suction. The collected coals were washed and distilled water 10 times. The washed coals were dried at 80°C for 4 h. Sulfur and ash analysis of all coals used in this study are shown in Table 1 and their size distributions measured with ELZONE particle counter (model 8XY, Particle Data, Elmhurst, IL), as shown in Fig. 1.

Analysis of Elements in Effluent Solution

One gram of the coal between 200 and 400 mesh was exactly measured with a balance, and then poured into 20 mL of 0.5*N* HC1 solution to make

a slurry. The slurry stood for 30 min. The coal in the slurry was filtrated on membrane filter (10 μm pore size, Millipore) by suction. The collected coal was washed with 30 mL of 0.5*N* HCl and then with 100 mL of distilled water. These filtrates were combined and were made up to 200 mL with distilled water. Twenty-one elements (K, Ca, Mg, Na, P, S, Mn, Fe, Zn, Cu, B, Mo, Al, Be, Cd, Co, Cr, Ni, Pb, Sr, V) in this solution were measured by inductively coupled plasma analysis with JY48P (Seiko Instruments, Tokyo, Japan). Ferrous ion in the solution was measured by titration with cerium sulfate after *o*-phenanthroline addition. The washed coals were dried at 80°C to a constant weight to determine the decrease in weight.

Flotation Experiment

Flotation experiments were carried out with a micro flotation column which was reported in our previous report (*10*). The column size was 38 cm height, 3 cm diameter, and 270 cm^3 working vol. The sulfuric acid solution (pH 2.0) containing methyl isobutyl carbinol (MIBC) at the concentration of 25 μL/L was used as flotation liquor.

Four grams of the washed Pittsburgh coals were soaked in 20 mL of cell suspension (1.0–2.0 × 10^9 cells/mL). Then, the coal slurries mixed with bacteria stood for 2 min, and 250 mL of flotation liquor was poured into the column and aerated at the rate of 350 mL/min. The slurries with bacteria were fed from the middle of the column by pump at the rate of 10 mL/min. The coals that flowed out from the top of the column were taken as froth and the coals remained at the bottom as tail. Each was collected and filtrated on membrane filter (10 μm pore size, Millipore) by suction, and dried at 80°C for 3 h and weighed.

Measurement of Pyrite Liberation

Around 0.5 g of froth was mixed into a few grams of Epoxside Resin (Bucher, Evanston, IL). The mixtures were poured into the plastic cups (2.5-cm diameter). The cup was stood at room temperature overnight to solidify resin. The solidified resin was taken out from the cup. The resin was polished with the slurry, which consisted of alumina powder (5 μm diameter) and distilled water, until coal and pyrite particles appeared on the surface. It was polished with 0.5 μm and 0.25 μm alumina slurry successively to get a mirror surrface. After each polishment, the resin was ultrasonicated for more than 10 min in distilled water to remove any alumina powder. Pyrite liberation was measured visually by observing the mirror surface of the resin under polarized light microscope with 200 × magnification. If pyrite particles were completely liberated from coal particles, liberation ratio is expressed as 100%. If pyrite particles was buried in the coal particle, liberation ratio is expressed as the ratio of pyrite area to total area of the coal particle. The densities of particles in the resin was counted for each liberation ratio. The proportion of each particle to

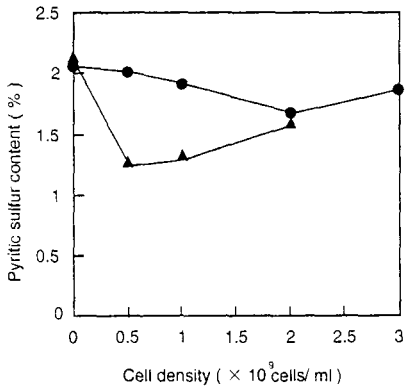

Fig. 2. The effect of HC1 wash on pyrite removal; (●): without wash, (▲): with wash.

all particles was calculated by dividing the particle density at each liberation ratio by the total density of observed particles.

Measurement of Bacterial Density

Bacterial density was measured by counting cells with a bacterial counting chamber (Kayagaki irika kogyo, Tokyo, Japan) under phase-contrast microscope with 600 × magnification.

Analysis of Sulfur

The total sulfur in the coals was measured by a sulfur analyzer (EMIA-512, Horiba, Kyoto, Japan). Pyritic sulfur and sulfate sulfur were measured by the International Organization for Standardization (ISO) 157 (hard coal—determination of forms of sulpher). Ash was measured by ISO 1171 (solid mineral fuels—determination of ash). All analysis data were indicated as a dry basis. The amount of the pyrite in the coal was calculated by multiplying the coal weight by its pyritic sulfur content. The pyrite removal ratio by microbial flotation was calculated by subtracting the pyrite in product coal (froth) from that in feed coal.

RESULTS AND DISCUSSION

Effect of HC1 Wash of Coal on Pyrite Removal

Pulverized Pittsburgh coal (size between 38 μm and 75 μm) was subjected to column flotation, which was in the size of CWM. Pyritic sulfur content of the coal was reduced from 2.51% (feed coal) to 2.03% (froth) by column flotation without bacteria addition. When bacteria were added at the density of 2.0 × 10^9 cell/mL, pyritic sulfur content was reduced to 1.74% (froth) as shown in Fig. 2. In this condition, the pyrite removal by

bacterial addition was 31%, and was less than the reported values (80–90%) that were obtained with coal-pyrite mixture (*7,8,9,10*).

To clarify the reason for low removal of pyrite by microbial flotation, the coal was washed by 0.5*N* HC1 solution and 21 elements in 0.5*N* HC1 effluent solution were analyzed. The main elements in the solution were iron and sulfur, which corresponded 23.1 (± 2.9) mg/g coal and 16.6 (± 0.8) mg/g coal, respectively. From titration of ferrous ion with *o*-phenanthroline method, all the iron in the solution was ferrous ion. In this condition, 63.6 mg of coal weight was lost from 1 g coal with the wash. If the effluent iron and sulfur existed as ferrous sulfate in the coal, the weight of ferrous sulfate was calculated to be 62.4 mg/g coal from the amount of iron in the effluent solution. As the value obtained was almost the same as the value calculated, the largest part of the iron and sulfur seemed to be the ferrous sulfate in the coal. In these experiments, the decrease of the sulfur content in the coal, 16.8 mg/g coal, agreed with the sulfur in the effluent solution.

The coal used in this study was stored at the coal bank for more than 10 yr. During the storage, the pyrite in the coal oxidizes to ferrous sulfate. The pyritic sulfur content of the coal analyzed by us was lower than the content which was given from the coal bank.

Microbial column flotation was applied to Pittsburgh coal washed with 0.5*N* HC1 solution. Pyritic sulfur content of the froth was reduced from 2.79% (feed coal) to 1.19% (froth) by the bacterial addition at the density of 0.5×10^9 cells/mL, as shown in Figure 2. Pyrite removal ratio was improved from 31% (without wash) to 57% by the HC1 wash. Our previous report showed that the addition of ferrous ion quenches the adhesion of *T. ferrooxidans* to pyrite (*6*). Without adhesion of the bacteria to pyrite particles, the pyrite surface property did not change, therefore the separation of pyrite from coal does not occur in the flotation column. The HC1 wash was an indispensable process for microbial column flotation of the coal that contains ferrous salt. Thereafter, all experiments were done with washed Pittsburgh coals.

Effect of Coal Particle Size on Pyrite Removal

The coal was divided into large and small sizes to investigate size factor which would influence on pyrite removal. The large size was between 53 μm and 75 μm, and the small size was between 38 μm and 53 μm (Table 1). For the large-size coal, bacterial addition reduced pyritic sulfur content of froth until bacterial density of 0.5×10^9 cells/mL, but further additions increase the sulfur contents as shown in Fig. 3A. Coal recovery was decreased with increase of the bacteria addition as shown in Fig. 3B. The best result in these experiments for pyrite removal and coal recovery was obtained at a cell density of 0.5×10^9 cells/mL. In this condition, the pyritic sulfur content was reduced from 2.88% (feed coal) to 0.98% (froth) and 71% of feed coal was recovered. At this point, 25% of total pyrite in the feed coal remained in the froth and 75% was removed in the tail.

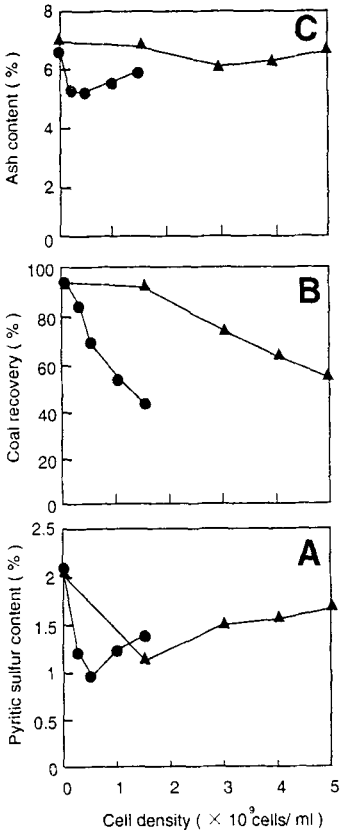

Fig. 3. The effect of coal particle size on pyrite removal: the symbols expressed the coal size; (●): 53 μm–75 μm, (▲): 38 μm–53 μm. (**A**) pyritic sulfur content; (**B**) coal recovery; (**C**) ash content.

For the small-size coal, more bacterial addition was required for pyrite removal than for the large-size coal as shown in Fig. 3A. The bacterial addition of 1.5×10^9 cells/mL was the best condition in these experiments for pyrite removal. In this condition, pyritic sulfur content was reduced from 2.77% (feed coal) to 1.12% (froth). At the same cell density, 95% of feed coal was recovered as shown in Fig 3B, and 62% of total pyrite in feed coal was removed as a tail.

Ash was also removed from both coals by the microbial column flotation as shown in Fig. 3C. More ash was removed from the large-size coal than from the small-size coal. Ash content of the large-size coal was reduced from 8.13% (feed coal) to 5.10% (froth) by bacterial addition of 5×10^8 cells/mL.

Bacterial addition into the column flotation removed pyrite from both size coals, but the excess addition decreased not only pyrite removal but also coal recovery. This tendency for pyrite removal and coal recovery agreed well with the previous report on microbial column flotation with the coal-pyrite mixture (*10*). The microbial flotation removes pyrite particles in pulverized coal by changing the surface property through bac-

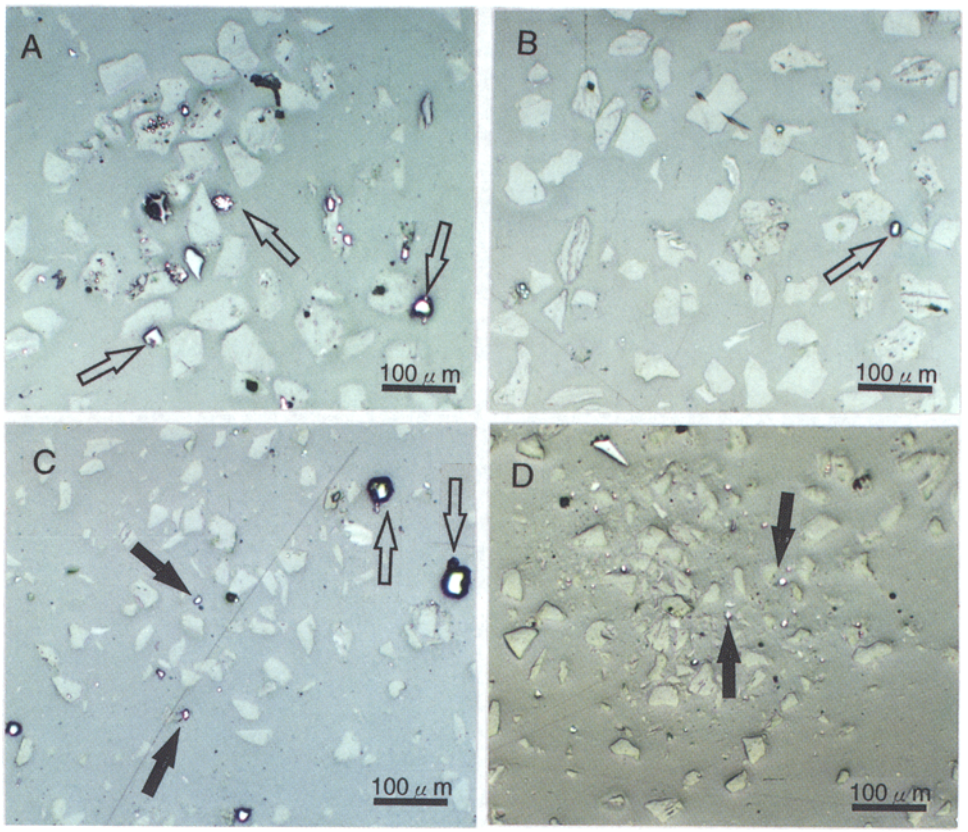

Fig. 4. The pyrite particles in froth: (**A**): without bacteria on coal size 53 μm–75 μm; (**B**): with bacteria on coal size 53 μm–75 μm; (**C**): without bacteria on coal size 38 μm–53 μm; (**D**): with bacteria on coal size 38 μm–53 μm. The open arrow indicated the large pyrite particles (20 μm–70 μm). The closed arrow indicated fine pyrite particles (less than 20 μm). Microbial flotation experiments were carried out at the cell density of 0.5×10^9 cells/mL for the coal (53 μm–75 μm) and that of 1.5×10^9 cells/mL for the coal (38 μm–53 μm).

terial adhesion (*5*). The bacteria can adhere to pyrite particles selectively, but a part of bacteria would adhere to coal particles. The excess addition of the bacteria induce not only the adhesion to pyrite particles but also the adhesion to coal particles, so that the surface property of coal particles would be changed to the same as that of pyrite particles. Therefore, coal floatability was suppressed and coal recovery was reduced. Tiny pyrite particles would not sink down by bacterial addition as shown in the next paragraph (Fig. 4). This means that there is a critical bacteria amount for pyrite depression. If the excess bacterial cells were added to the flotation, only coal particles would be depressed while tiny pyrite particles would still be floating. This would result in the increase of pyrite contents in the froth.

In this study, collector reagents such as kerosene, which ensure enough coal recovery, were not employed to investigate the effect of bacterial

Table 2
Pyrite Liberation Ratio of the Feed Coals

	Pyrite liberation ratio (%)[b]									
Feed coal[a]	10	20	30	40	50	60	70	80	90	100
Large-size coal (%)	47.1	11.3	7.7	2.1	1.2	0	0.3	0	0	30.3
Small-size coal (%)	26.4	5.6	2.9	0.6	0	0	0	0	0.1	64.4

[a]Large-size coal was the feed coal between 53 μm and 75 μm and small-size coal was the feed coal between 38 μm and 53 μm.
[b]Pyrite liberation ratio was determined by the proportion of pyrite area to the total area of particles mentioned in Materials and Methods section.

density on coal and pyrite floatabilities. Therefore, coal recovery became relatively low. As kerosene addition can increase coal recovery in the microbial column flotation (*10*), the flotation collector reagents should be used to get sufficient coal recovery in actual plants.

Pyrite Liberation

Pyrite liberation ratio was measured to investigate the relationship between pyrite removal and its liberation state in coals. Most pyrites in the feed coals existed in two forms, completely liberated particles from coal (liberation ratio 100%, i.e., the particles were completely separated from coal particles and existed as pyrite particles in pulverized coal) and locked particles in coal (liberation ratio 10%, i.e., pyrite particles were buried in coal particles). The liberated particles were 30% of all pyrite particles in the large-size coal and 64% in the small-size coal. The locked particles were 47% of all pyrite particles in the large-size coal and 26% in the small-size coal as shown in Table 2. The small-size coal contained more liberated pyrite particles than the large-size coal, since locked particles buried in the coat particles came out as the liberated pyrite particles by crushing the coal particles into small size.

The photographs of the froth produced by microbial column flotation are shown in Fig 4. Bright particles are pyrite and dark particles are coal. For the large-size coal, a lot of large liberated pyrite particles between 20 μm and 70 μm were observed in the froth of the flotation without bacterial addition (Fig. 4A). On the other hand, few large liberated pyrite particles were observed in the froth of the flotation with bacterial addition (Fig. 4B). The column flotation mainly removed the liberated pyrite particles. In these conditions, the ratio of the liberated and locked particles of all pyrite particles in the froth was measured (Fig. 5A). The ratio of the liberated pyrite particles was reduced from 30% (feed coal) to 22% (froth) by flotation without the bacteria. By flotation with bacteria, it was reduced to 16%. The ratio of locked particles was increased from 47% (feed coal) to 58% (froth) by flotation without the bacteria. By flotation with the bac-

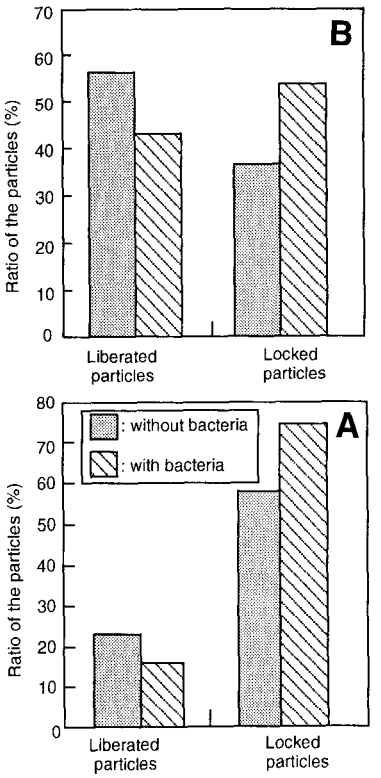

Fig. 5. The comparison of pyrite liberation in froth of microbial flotation. (**A**): Ratio of liberated particles and locked particles in the coal size 53 μm–75 μm. (**B**): Ratio of liberated particles and locked particles in the coal size 38 μm–53 μm. Microbial flotation experiments were carried out at the cell density of 0.5×10^9 cells/mL for the coal (53 μm–75 μm) and that of 1.5×10^9 cells/mL for the coal (38 μm–53 μm).

teria, it was increased to 75%. For small-sized coal, a lot of large pyrite particles and fine pyrite particles (less than 20 μm) were observed in the froth on the flotation without the bacteria (Fig 4C). Few of the large particles were observed on the flotation with bacteria, but the fine particles were still in froth (Fig 4D). The ratios of the liberated and locked particles of all pyrite particles in froth in these conditions were shown in Fig. 5B. The ratio of liberated pyrite particles was reduced from 64% (feed coal) to 56% (froth) by the flotation without bacteria. By flotation with the bacteria, it was reduced to 43%. The ratio of locked particles were increased from 26% (feed coal) to 37% (froth) by flotation with the bacteria addition. By flotation with bacteria, it was increased to 54%.

The reduction of the liberated particle ratio in the froth for both small- and large-size coals showed that the liberated particles were easily removed by microbial column flotation if the particle size is large enough (more than 20 μm). The increase of the locked particle ratio in the froth also showed that the locked particles were not removed by microbial column

flotation. The increase of locked particle ratio was explained as a result of the concentration in froth induced by removal of the liberated particles. Microbial flotation can reduce pyritic sulfur content by removing fully liberated pyrite particles. However, fine liberated pyrite particles were not removed in this condition. These results mean that the pyrite liberation and its particle size are important factors for pyrite removal by microbial column flotation.

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