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Microorganisms desulfurization of coal

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Abstract— A culture of *Thiobacillus* ferrooxidans strain T-4, isolated from Song Zao Coal Mining, China, is able to use pyrite from coal as a source of energy. The bacterial culture solution with 10^8 – 10^9 cells/ml, pH 1.55–1.70 was employed in the nine coal samples with −200 mesh have been studied at initial pH 1.7. 30℃, 20–30% coal pulp density. The bacterial removal sulfur from coal in samples 3, 4, 6 and 7 were reduced to 1.05–1.33% and 86.11% of pyritic sulfur can be removed in 4–24 hours.

Keywords: *Thiobacillus* ferrooxidans; microorganisms; desulfurization.

INTRODUCTION

Pollution from coal combustion is the most important problem in the current use of coal and the biggest constraint on the increased use of coal. Both organic and inorganic sulfur contained in coal can be removal prior to combustion by physical, chemical and microbiological means. The microbial desulfurization of coal has been done in many countries (Kargi, 1986; Couh, 1987). The work on pyrite removal has been more extensive. Up to 90% removal of sulfur can be achieved. However, the reaction is too slow.

It is the purpose of this paper to report the removal of pyritic sulfur from coal employing *Thiobacillus* ferrooxidans strain T-4.

MATERIAL AND METHOD

Source of coal and pyrite samples

The nine samples of coal used in all the experiments were obtained from Chongqing area of China, and crushed to −200 mesh. Pyrite samples were separated from coal mine of Song Zao and Nan Tong, and crushed to −200 mesh and −20 mm, respectively. Analysis of sulfuric content of coal samples were shown in Table 1 and Table 2.

Table 1 Analysis of sulfuric content of some coal samples

Locality	No.	Total sulfur, %	Pyritic sulfur, %	Organic sulfur, %	Sulfate sulfur, %
Song Zao	1	2.40	1.85	0.5	0.05
Zhong	3	1.31	0.85	0.46	no
Liangshan	4	2.04	2.04	no	0.03
Nan Tong	5	2.00	0.92	1.07	0.01
	6	1.85	0.72	1.12	no
Tian Fu	7	2.10	1.58	0.51	0.01
Nan Tong	10	2.44	0.64	1.80	no
	11	2.43	0.65	1.80	no
	12	2.45	0.62	1.80	no

Table 2 Chemical analysis of pyrite samples

Locality	Pyrite, %	Pyritic Fe, %	Pyritic S, %
Song Zao	83.38	38.80	44.47
Nan Tong	85.93	40.00	45.93

Bacterial culture

Thiobacillus ferooxidans strain T-4 isolated from the acid soil in Song Zao seam, which was maintained on Leathen medium (Leathen, 1956), at 28－30 ℃, using pyrite as source of energy.

Experimental method

1. Bacterial oxidation of pyrite

(1) Leaching with shake flask: 10 ml active cell suspension (no iron) of strain T-4 was added to 250 ml shake flask with 90 ml medium without iron and 5g pyrite (－200 mesh Song Zao). The initial pH of the medium was adjusted to 2.0－2.3 with 1:1 H_2SO_4. The control was treated with 0.2% Hg_2SO_4. The shake flasks were left to inoculate on a rotary shaker of 150 r/min at 28－30 ℃.

(2) Leaching column

Two columns (150×1000 mm) used in this study containing 20 kg pyrite (－20 mm, Nan Tong), 4.5 L medium without iron, 0.5 L bacterial culture. 10 g Hg_2SO_4 was added to the control column. The leaching solution of pyrite was recycled with a shower. All of the solution collected from the column was used in the coal desulfurization.

Experiment of biodesulfurization

Coal desulfurization studies were carried out in 500 ml shake flasks on a shaker 150 r/min at 28－30 ℃. The samples were withdrawn from the flasks, filtered, washed and the leaching residues were analysed for sulfur.

Assays

Total iron was analysed by titration with potassium dichromate. pH was determined using pH meter (Beckman). Total sulfur in the coal after desulfurizaiton was determined using a auto-measured sulfur meter (Xushou Analysis Meter Factory, China). Cell concentration was estimated by direct counting in a Thoma counting chamber (depth 0.02 mm).

RESULTS

Bacterial oxidation of pyrite separated from coal

The result of bacterial exidation (strain T-4) of pyrite in shake flask and leaching columns are shown in Fig. 1 and Fig. 2. The strain T-4 grew well using pyrite as a

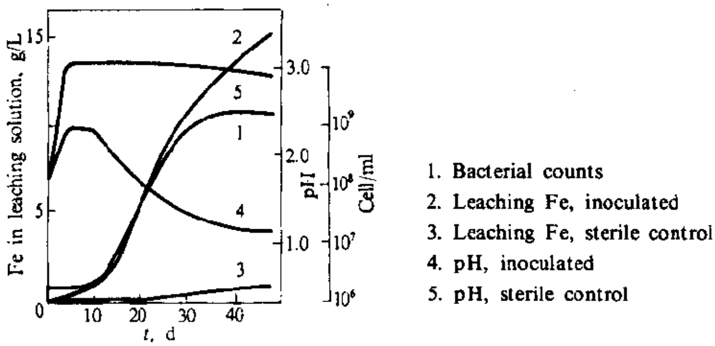

Fig. 1 Oxidation of Song Zao pyrite by strain T-4

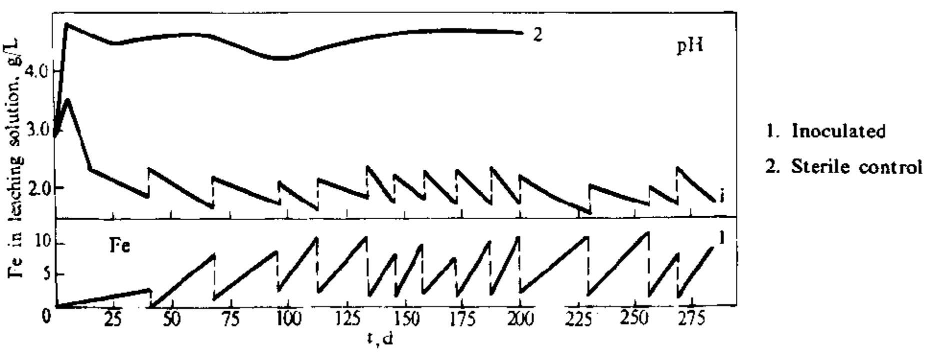

Fig. 2 Continuous leaching efficiency from Nan Tong pyrite by strain T-4 in the shower leaching column

source of energy and produced soluble iron and sulfuric acid. 10^8-10^9 cells/ml in leach solution was obtained. The released iron in inoculation flasks was 100 – 150 times more than the sterile ones. The pH dropped from initial 2.0 – 2.3 to 1.08.

In inoculated column, the released iron and pH maintained at stable level of 8.2 – 12.8 g/L and 1.5 – 1.7, respectively. The cell concentration was 10^8-10^9 cells/ml. There was no any change in sterile column.

Experiment on desulfurization of coal

(1) Effect of inoculation on desulfurization

Inoculation with 10% and 100% of leach solution of pyrite, 10% coal pulp density of sample No. 1 and No. 6 were added to 500 ml shake flasks respectively which containing 100 ml leach solution at an initial pH 1.8 – 2.0. The results are shown in Fig. 3. For sample No. 1, total sulfur reduced from 2.4% to 1.30 – 1.35% in 8 days with 10% inoculation and in 6 days with 100% inoculation. For sample No. 6, total sulfur reduced from 1.85% to 1.5% in 12 days with 10% inoculation and in 1 day with 100% inoculation. The rate of sulfur removal in the control flasks of leach solution of pyrite was very slow.

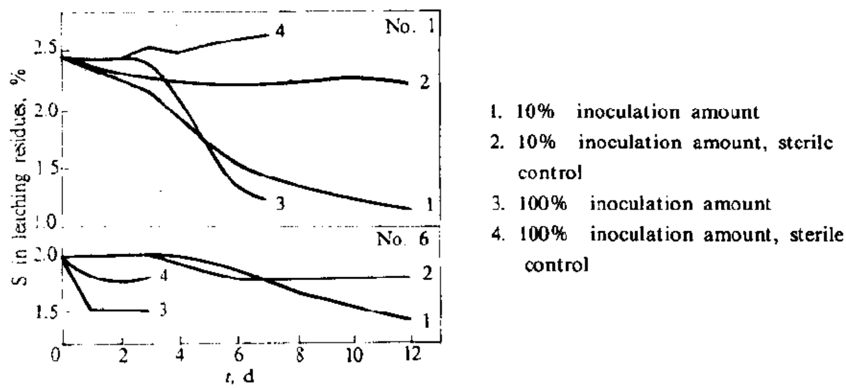

Fig. 3 Effect of inoculation amount on removal sulfur from coal by strain T-4

(2) Effect of coal pulp density on desulfurization

With 10%, 20%, 30% and 40% pulp density of 9 coal samples were used in 500 ml shake flasks. The results are shown in Table 3. Both desulfurization rates and potential economics should be considered 20 – 30% pulp density is probably the most effective concentration.

Table 3 Effect of coal pulp density on removal sulfur from coal by T-4 strain

Coal samples, No.	Total sulfur, %	Time, d	Sulfur amount of leaching Residual, %			
			10	20	30	40
1	2.45	6	1.35	1.58	1.60	–
3	1.31	4h	1.03	1.12	1.27	1.24
		1	1.03	1.05	1.11	1.11
4	2.24	4h	1.15	1.32	1.38	1.72
		1	1.17	1.24	1.38	1.50
5	2.00	3	1.56	1.60	1.58	1.93
6	1.85	3	1.57	1.57	1.63	1.55
7	2.10	1	1.39	1.45	1.52	1.57
10	2.44	3	1.70	1.75	2.26	2.29
11	2.43	3	1.72	1.75	2.25	2.32
12	2.45	3	1.88	1.95	2.38	2.40

(3) Effect of particle size of coal on desulfurization

−100 mesh, −150 mesh, −200 mesh and −300 mesh particle size of samples No. 4 and No. 10 were prepared, 20% coal pulp density, the initial pH 1.6. The desulfurization curves are shown in Fig. 4. In this study, it was found the efficiency of desulfurization was related to the particle size of coal.

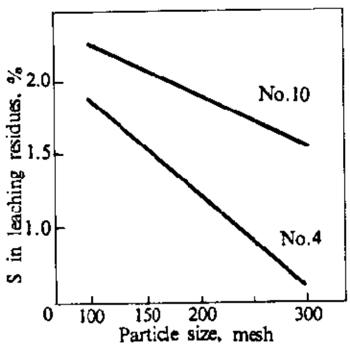

Fig. 4 Effect of particle size on removal sulfur from coal by strain T-4
No. 4 leaching 1 days No. 10 leaching 3 days

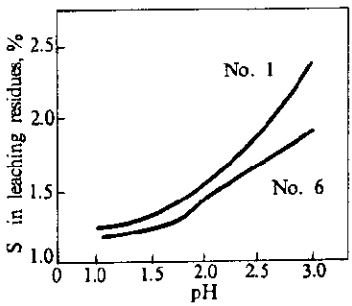

Fig. 5 Effect of pH on removal sulfur from coal strain T-4
No. 1 leaching 6 days No. 6 leaching 2 days

(4) Effect of initial pH on desulfurization

No. 1 and No. 6 coal samples with 20% pulp density were used in the experiment with initial pH of 1.05, 1.53, 1.70, 2.05, 2.52 and 3.0. The results are shown in Fig. 5. It was clear that the optimal pH is below 1.7.

(5) The optimal condition for biodesulfurization of coal

The optimal condition for biodesulfurization of coal in 9 samples were found to be following: the leaching solution of pyrite with 10^8-10^9 cells/ml and pH 1.6–1.7 was employed in desulfurization of pyrite in coal of −200 mesh and 20% pulp density at 28 30 ℃ . The results are shown in Table 4. Total sulfur of samples No. 3, 4, 6 and 7 were reduced to 1.05–1.33%, in 4–24 hours, No. 5, 10, 11 and 12 to 1.58–1.7% in 2–3 days. Bacterial removal of sulfur from coal could reach to 86–95%.

Table 4 Optimal condition efficiency of removal sulfur from coal by T-4 strain

Coal samples, No.	Total sulfur, %	Time, h	Sulfur amount of leaching residual, %	Removal rate of pyritic sulfur, %
1	2.40	8d	1.10	70.27
3	1.31	4–24	1.05	30.59
4	2.04	4–24	1.24	40.0
5	2.00	2d	1.58	45.65
6	1.85	4–24	1.23	86.11
7	2.10	4–24	1.33	48.73
10	2.44	3d	1.88	87.50
11	2.43	3d	1.84	90.77
12	2.45	3d	1.86	95.16

DISCUSSION

Thiobacillus ferrooxidans strain T-4 is able to use pyrite in coal as a source of energy and produce iron sulfate and sulfuric acid containing 10^8-10^9 cells/ml, pH 1.6–1.7, which was employed in biodesulfurization of coal. The reaction involved are represented by following equations:

$$2FeS_2 + 7O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2FeSO_4 + 2H_2SO_4$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \xrightarrow{\text{bacteria}} 2Fe_2(SO_4)_3 + 2H_2O$$

$$FeS_2 + Fe_2(SO_4)_3 \longrightarrow 3FeSO_4 + 2S$$

$$2S + 3O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2H_2SO_4$$

The overall biological oxidation reaction is summarized as:

$$4FeS_2 + 15O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2Fe_2(SO_4)_3 + 2H_2SO_4.$$

2. Both the rate of removal and the total reduction by microbial action are dependent on the available surface area exposed in the media.

3. Microbial removal of inorganic sulfur in coal is an new method in cleaning technique.

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