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DESULPHURIZATION OF COAL BY CHEMOLITOTHROPHIC BACTERIA

Pyritic sulphur has been removed from hard coal and coal waste by their treating with bacteria. Four strains of *T. ferrooxidans* and one strain of *T. thiooxidans* in pure culture and in the mixture were used. It was possible to remove about 34–49% of sulphur from coal waste and 33–55% from coal in two weeks. The most successful result (about 60% removal of sulphur) was obtained when the mixture of *T. ferrooxidans* and *T. thiooxidans* strains was used.

1. INTRODUCTION

Of undesirable chemical compounds, which are emitted during the combustion of coal, sulphur dioxide is particularly dangerous. It has an extraordinarily harmful effect on people and plants. The distinctly negative action of sulphur dioxide in a concentration as low as 0.25 ppm is observed.

Most coals available in Poland are characterized by high concentrations of sulphur [11] which must be reduced to a minimum level in order to burn these coals without emission of objectionable quantities of sulphur oxides. The sulphur is present in coal mainly in the form of pyrite sulphur, therefore our investigations have been directed to the process of its removal from coal.

It is generally known that pyritic sulphur can be removed from coal by its chemical oxidation to the forms soluble in water. Since these processes require both elevated temperatures and pressures, they are too expensive in removing pyrite from coal.

Microbiological processes of leaching pyrite and other sulfide minerals under normal conditions have been also applied to practice [4], [5], [10].

In the paper we describe the use of *T. ferrooxidans* and *T. thiooxidans* – acidophilic bacteria present in coals, as specific agents removing pyrite from coal.

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2. EXPERIMENTAL

Coal wastes from power plant (W I) and hard coal from the mine "Siersza" (W II) were ground to obtain grains of dimensions smaller than 0.3 mm. The total sulphur contents in coal wastes (W I) and coal samples (W II) amounted to 13.32% and 2.29%, respectively.

Cultures of *T. ferrooxidans* N and *T. thiooxidans* have been separated from acid mine waters. Other strains of *T. ferrooxidans* have been donated to us by the Higher Institute of Mining and Geology, Sofia, Bulgaria. The strains of *T. ferrooxidans* were maintained on the 9 K medium [12], while the culture of *T. thiooxidans* was cultivated on the Waksman medium [8].

The experiments were carried out in 500 cm^3 flasks containing: 10 g of coal material, 95 cm^3 of 9 K medium (pH = 2.5) and 5 cm^3 of inoculum. In the case of the mixtures of *T. ferrooxidans* and *T. thiooxidans* strains, the inoculum comprised 5 cm^3 of suspension of *T. ferrooxidans* cells and 2.5 cm^3 of the culture of *T. thiooxidans*. Cell suspension of *T. ferrooxidans* contained 1.6×10^9 cells/cm^3, whereas that of *T. thiooxidans* – 2.8×10^8 cells/cm^3. The number of cells in the inoculum was established by means of the counting chamber method.

The experiments have been carried out at 28°C, some under stationary conditions, the others in a reciprocal shaker (160 rpm). 5 cm^3 of a methanol solution containing 2% of thymol have been added into sterile control samples instead of the inoculum. In some cases 0.04% Tween 20 solutions have been added. The whole process of leaching has been conducted in three replications (data in tables show the mean of three measurements).

After the experiments, the coal material has been carefully separated on filter paper and washed with 200 cm^3 of distilled water. Then coal samples have been dried to a constant weight and total sulphur content in these samples determined by the BENNEVITZ method [2].

3. RESULTS AND DISCUSSION

A series of experiments have been carried out to estimate the effect of shaking and adding the surfactant on the effeciency of desulphurization of coal materials. Data obtained (table 1) showed that both shaking and adding the surfactant enhanced removal of sulphur from the coal wastes (W I). Removal of sulphur was by 4–6% higher in samples shaken (samples 3 and 4) than in those incubated under stationary conditions. Addition of Tween 20 improved efficiency of desulphurization by 2–4% (samples 2 and 3). The positive effect of shaking on the process can result from better exchange of gases which enhances development of *T. ferrooxidans bacteria*, both obligate aerobes and autotrophs. On the contrary, the surfactant makes easier the adhesion of bacteria to the surface of the grains of pyrite in coal [7]. Taking into account the above mentioned results, further experiments have been carried out with shaking and Tween 20 additives.

Table 1

Effect of shaking and adding of Tween 20 on efficiency of coal waste desulphurization by N *T. ferrooxidans* strain

Sample	Shaking	Tween 20	Content of coal waste after leaching [%]	Efficiency of desulphurization [%]
1	–	–	9.84	26.13
2	–	+	9.58	28.08
control	–	+	12.69	4.73
3	+	–	9.26	30.50
4	+	+	8.78	34.09
control	+	+	12.25	8.14

The next step of our work was testing if *T. ferrooxidans* strains are capable of leaching pyrites in the materials investigated. Results of these experiments are presented in table 2. The most active strain in desulphurization of both W I wastes and W II coals was G 11 *T. ferrooxidans*. During 25 days of leaching this strain caused 49% removal of sulphur from W I, whereas about 55% removal of sulphur from W II coal samples was observed after 14 days of leaching. The other strains: N, V 3, and M, under the same conditions showed lower activity. These results show that proper selection of biological material is essential for efficient coal desulphurization.

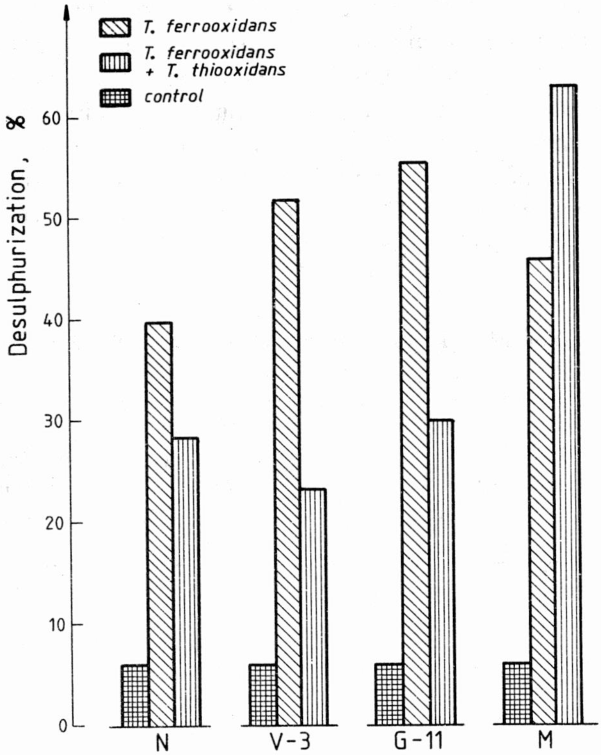
Table 2

Desulphurization of coal wastes (W I) and hard coal (W II) by the various *T. ferrooxidans* strains

Symbol of bacterial strain	Material	Time [days]	Content of sulphur in material after leaching [%]	Efficiency of desulphurization [%]
N	W I	25	8.78	34.09
N	W II	14	1.38	39.74
G 11	W I	25	6.75	49.32
G 11	W II	14	1.02	55.46
V 3	W I	25	7.04	47.08
V 3	W II	14	1.10	51.97
M	W I	25	7.42	44.29
M	W II	14	1.25	45.42
control	W I	25	12.38	7.06
control	W II	14	2.15	6.12

The W II coal samples from the "Siersza" mine were more susceptible to desulphurization than W I coal wastes. It may be caused by specific form of pyrite in the material. The great quantity of alkaline components (e.g., carbonates) in the coal and presence of toxic substances may inhibit growth of *T. ferrooxidans* strains.

The further experiments aimed to explain the role of *T. thiooxidans* in coal pyrite oxidation by *T. ferrooxidans*. Figure shows that *T. thiooxidans* strain decreased efficiency of desulphurization caused by the N, V 3, and G 11 *T. ferrooxidans* strains. For example, addition of *T. thiooxidans* cells to the culture of V 3 *T. ferrooxidans* reduced efficiency of sulphur removal by about 50%. However, in the case of the mixture of *T. thiooxidans* and M *T. ferrooxidans* strains, the increase (by about 18%) in the yield of the process was observed. In this case the simplified balance of the process can be presented as follows: 1 kg of coal (W II), (2.29% of total S) + 14 days *T. ferrooxidans–T. thiooxidans* mixture = 0.986 kg of coal (W II) (0.92% of total S) + 0.014 kg of S.



Desulphurization of coal (W II) by *T. ferrooxidans* strains and mixed *T. ferrooxidans* and *T. thiooxidans* cultures

Obviously *T. thiooxidans*, which is an active sulphur oxidizer, can aid the activity of M *T. ferrooxidans* strain by oxidizing the elemental sulphur formed during oxidation of pyrite. On the other hand, the harmful effect of *T. thiooxidans* on cultures of N, V 3, G 11 *T. ferrooxidans* may be due to its competitive participation in the consumption of oxygen and carbon dioxide, and to its adsorption on the surface of mineral. The problem of coöperation of *T. ferrooxidans* and *T. thiooxidans* strains in the leaching of pyrite from coals was discussed by many investigators. In the available literature there exist some controversial opinions on this subject [6], [7], [9]. Results of our experiments cannot solve this problem either. The data reported in our work are compatible with those reported by other authors [1], [4], [6], [7], [13].

REFERENCES

[1] ANDREWS G. F., MACZUGA J., *Bacterial coal desulphurization*, Biotechnol. Bioeng. Symp., 12 (1982), pp. 337–348.

[2] BENNEVITZ R., *Reproduzierbarkeit der Halbmikrobestimmungen von Chlor, Brom, Schwefel und Phosphor nach der Kolbenmethode von W. Schoniger*, Microchimica Acta, 5, 6 (1963), pp. 1094–1108.

[3] BOS P., HUBER T. F., KOS C. H., RAS C., KUENEN J. G., *A dutch feasibility study on microbial coal desulphurization*, [in:] R. W. Lawrance, R. M. R. Branion, H. G. Ebner (eds.), *Proceedings of the Sixth International Symposium of Biohydrometallurgy*, Vancouver, B. C. Canada, August 21–24, 1985, Elsevier, Amsterdam – Oxford–New York–Tokyo, pp. 129–150.

[4] CAPES C. E., MC ILHINNEY A. E., SIRIANNI A. F., PUDDINGTON I. E., *Bacterial oxidation in upgrading pyritic coals*, Can. Mining. Bull, 68 (1973), pp. 88–91.

[5] DETZ C. M., BARVINCHAK G., *Microbial desulphurization of coal*, Min. Cong. J., 65, 7 (1979), pp. 75–86.

[6] DUGAN R., APEL W. A., *Microbial desulphurization of coal*, [in:] L. E. Murr, A. E. Torma, J. A. Brierley (eds.), *Metallurgical applications of bacterial leaching and related microbiological phenomena*, Academic Press, New York, San Francisco, London 1978, pp. 223–250.

[7] GROUDEV S. N., *Biological removal of pyritic sulphur from different kinds of coal*, The Third Turkish Coal Congress, 10–14th May, 1982, Zonguldak, Turkey.

[8] KARAVAIKO G. I., KUZNECOV S. I., GOLOMZIK A. I., *The bacterial leaching of metals from ores* (in Russian), Moscow 1972.

[9] MCGREGOR R. A., *Uranium devidends from bacterial leaching*, Mining Eng., 21, 3 (1969), pp. 54—59.

[10] MCCREADY R. G. L., ZENTILLI M., *Beneficiation of coal by bacterial leaching*, Can. Metall. Quarterly, 24, 2 (1985), pp. 135–139.

[11] SAKAŁUS E., *Odsiarczanie spalin czy węgla*, Chemik, 5, 30 (1977), pp. 129–135.

[12] SILVERMAN M. P., LUNDGREEN D. S., *Studies on the chemoautotrophic iron bacterium Ferrobacillus ferrooxidans*, J. Bacteriol., 77 (1959), pp. 642–645.

[13] WILCZOK T., BUSZMAN E., CWALINA B., CHROSTOWSKA D., *Bakteryjne odsiarczanie węgla*, Przegląd Górniczy, 11 (1983), pp. 12–17.

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ODSIARCZANIE WĘGLA PRZY UŻYCIU BAKTERII CHEMOLITOTROFICZNYCH

Odsiarczano węgiel i odpady węglowe przy użyciu hodowli bakteryjnych. Zastosowano 4 szczepy *Thiobacillus ferrooxidans* i jeden szczep *Thiobacillus thiooxidans*. W ciągu dwóch tygodni usunięto 34–49% siarki całkowitej z odpadów węglowych i 33–55% z węgla. Najlepsze wyniki, około 60% odsiarczenia, uzyskano w przypadku użycia mieszaniny szczepów *T. ferrooxidans* i *T. thiooxidans*.

ОБЕССЕРЕНИЕ УГЛЯ ПРИ УПОТРЕБЛЕНИИ ХИМИОЛИТОТРОФИЧЕСКИХ БАКТЕРИЙ

Обессеривали уголь и угольные отбросы при употреблении бактериальных култур. Применили 4 штамма *Thiobacillus ferrooxidans* и один штамм *Thiobacillus thiooxidans*. В течение двух недель удалили 34–49% полного содержания серы из угольных отбросов и 33–55% – из угля. Самые лучшие результаты (ок. 60% обессерения) получили в случае употребления смеси штаммов *T. ferrooxidans* и *T. thiooxidans*.