

BACTERIAL DESULPHURISATION OF COAL

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A b s t r a c t. The aim of this paper was the evaluation of usefulness of bacterial leaching applied to a coal sample from the locality Nastup Tušimice. The results of this work proved that using clean cultures of *Thiobacillus ferrooxidans* was in this case very proper if we evaluated desulphurisation from the pyrite sulphur point of view. After one month of leaching, the pyrite sulphur was almost gone from the sample still containing a lot of organic sulphur amount of which decreased only slightly. The desulphurisation of pyritic sulphur reached about 71% while the total desulphurisation of coal — 42%.

K e y w o r d s : brown coal, bacteria, desulphurisation, Nastup Tumišice Basin.

INTRODUCTION

Desulphurisation of fuels is a problem which even with big effort of humans beings has not been solved yet. It is required to stop SO₂ emission to air. It is well known that the high amount of sulphur in coal has an adverse influence on its utilisation and that it contributes to environment contamination, causing in effect acid rains (Fečko *et al.*, 1991; Fečko *et al.*, 1994; Fečko, 1997). There are evidences that the Czech Republic occupies one of the highest positions in Europe in environment contamination by sulphur oxides, as our main source of energy is the combustion of solids fuels. In the amount of industrial emissions per km², the Czech Republic is the second in the world (25 t/km²), and in the amount of emissions per inhabitant is the third (0.2 t). Combustion is dependent on the concentration of sulphur which reaches somewhere around 12%.

EXPERIMENTAL

Methods of bacterial leaching

For experiment, a 5-litre air-lift glass bioreactor adjusted according to the research of Deutsche Montan Technologie Company, Essen (Beyer, 1988), was used. After sterilisation of reactor, the prepared samples of coal were placed in it together with the medium 9K without FeSO₄. After one hour mixing and homogenising of suspension, bacterial culture *Thiobacillus ferrooxidans* in the amount of 500 ml was introduced into the reactor. For bacterial leaching, clean bacterial cultures of *Thiobacillus ferrooxidans* from the Czechoslovak collection of microorganism in Brno were used.

Concentration of bacteria introduced in the process of bacterial leaching was 10^9 in 1 ml of bacterial solution. Bioreactors were connected to aquarium's water engines, which supplied reactor with air. The air was cleaned in washers in 1 M H₂SO₄ solution to have more moisture and to clean it from air bacteria. Mixing of 5% suspension was done by air. During the whole experiment (28 days), pH was measured by laboratory pH-meter Radelkis and was kept at the optimal value of 1.8-2.0 to prevent the origin of unwanted jarosite. The temperature was kept in the range of $26-30^{\circ}$ C during whole experiment.

During leaching, after 1^{st} , 2^{nd} , 3^{rd} , and 4^{th} week, about 50 ml samples were taken from bioreactor for analyses. From the samples, part of suspension was used for measuring the biomass growth by MPN method, and the rest was filtrated on Buchner funnel from where the filtrate and the filtrate cake were received. In the filtrate, Fe^{2+} was determinated by titration, and in the filtrate cake the content of total sulphur and of its different forms of were determined. Before the analyses, the cake was washed in 100 ml of 1 N HCl and in 200 ml of distilled water.

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Petrographical analyses

Petrographical analyses were done at the Institute of Geological Engineering of the VSB-Technical University in Ostrava. The samples were milled to grains smaller than 1 mm, and from such coal grains, thin sections were prepared in which the macerates compositions were measured on a NUI Carls-Zeiss Jena microscope, under monochromatic light with $\lambda = 546$ nm wavelength using the 25× enlarging objective and an immersion oil with reflection index a = 1.518.

Determination of sulphur and its forms

Sulphur was determined at MUS, a.s. Most on a LECO SC 132 instrument, directed by microprocessor with infrared detection of SO₂. Different forms of sulphur were determined by thermal phase analyses at temperatures of 420°C (organic sulphur), 820°C (pyrite sulphur), and 1370°C (total sulphur), with constant programme conditions. The sulphate sulphur was calculated.

Results

For this sample, high substitution of gelinite with oxidizing edges and desiccant cracks is typical. Character of the sample is shown the on Figure 1. Cells of textinite "impregnated" by fine pyrite are shown in the sample. Pyrite was bound to ulminite and flobafinite. Macerate group of liptinite was supplied firstly by sporinite and rezinite in which cell walls were often mineralised by pyrite. Macerate group of inertinite was created by sporadic presence of fuzinite and sclerotinite that was mineralised by pyrite. The inorganic additive was represented by clay minerals that were formed by fringes in gelinite. Disulphides of iron occurred in all forms.

The results of bacterial leaching are given in the Table 1. The results of bacterial leaching proved that this sample was suitable for application of bacterial leaching, as the desulphurisation degree of total sulphur was 42%, and desulphurisation of pyritic sulphur was 71%.

Results of bacterial leaching

| Duration in leaching days | | Fe ²⁺ [mg/l] | | S _{total} [%] | | Amount of bacteria in 1 ml |
|--|--------------|----------------------------|----------------|---------------------------|---------------------------|--------------------------------------|
| introduction | | - 55.85 | | 5.95 4.92 | | $-17.5 \cdot 10^{8}$ |
| 14 | | 11.17 | | 4.92 | | $60 \cdot 10^8$ |
| 21 28 | | _ | | 3.44 2.98 | | $12.5 \cdot 10^8$ $30 \cdot 10^8$ |
| Sulphur | Before le | 0 | After leaching | | Level of desulphurisation | |
| Stotal | [%] 5.95 | | [%] 2.98 | | [%] 49.92 | |
| S _{pyritic} S _{organic} | 3.52 2.21 | | 1.02 1.79 | | 71.02 19.00 | |
| Sorganic S _{sulphate} | 0.22 | | 0.17 | | 22.73 | |

There is still a problem of the organic sulphur separation. As the bacteria *Thiobacillus ferrooxidans* is not suitable for elimination of organic sulphur, it could be possible to eliminate it by bacteria *Sulfolobulus acidocaldarius*.

Character of sample after one week of leaching

Macerate group of huminite was represented by flobafinite and textinite (Fig. 2). The grains of gelinite were often oxidized. The clay minerals were often bound to ulminite. Macerate group of liptinite were generally created by rezinite and sporinite, occasionally by cutinite. The total amount of this group is small. The macerate groups of inertinite were not identified. The inorganic additive was formed by clay minerals and different forms of pyrite. Framboidal pyrite made up independent grains or was bound to rezinite eventually. Massive pyrite generally filled up the cracks. The occurrence of euhedral pyrite was bound to rezinite. Effect of the sulphur bacteria leaching is clearly shown on Figure 3. From a big pyrite grain remained only small fragments at its edges.

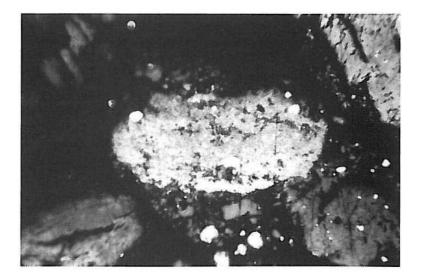


Fig. 1. Character of sample before leaching



Fig. 2. Huminite represented by flobafinite and textinite

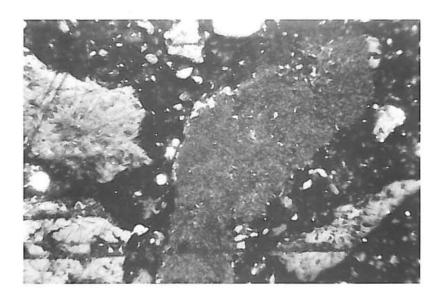


Fig. 3. Sample after one week of leaching — effect of the sulphur bacteria

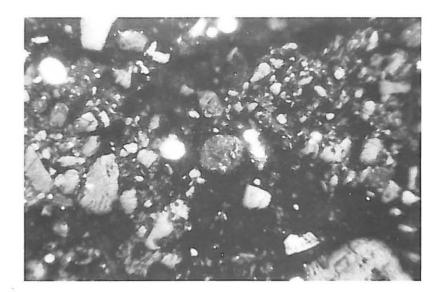


Fig. 4. Sample after 2 weeks of leaching — pyrite influenced by bacteria with slight residues of pyrite

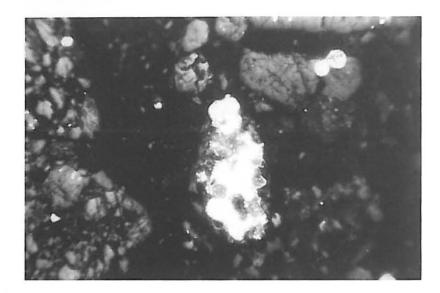


Fig. 5. Sample after 3 weeks of leaching — clusters of pyrite

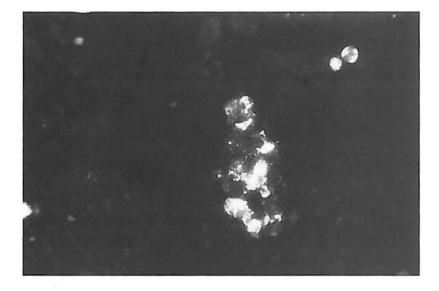


Fig. 6. Effect of bacteria after 3 weeks of leaching (using green filter)

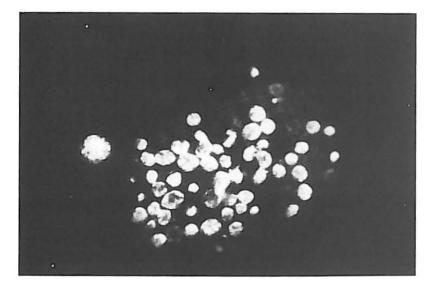


Fig. 7. Effect of bacteria after 3 weeks of leaching (using green filter)

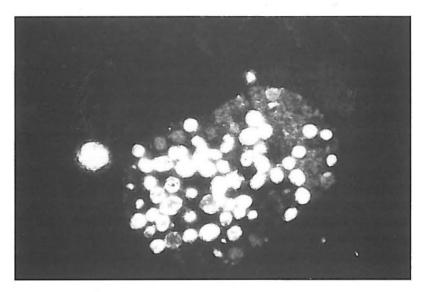


Fig. 8. Effect of bacteria — isolated residues of pyrite in edges

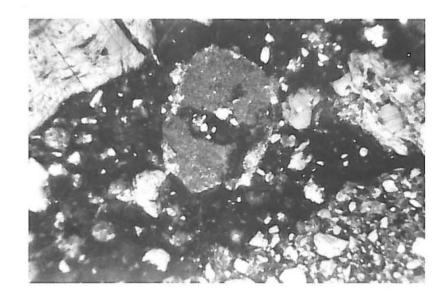


Fig. 9. Effect of bacteria — isolated residues of pyrite in edges

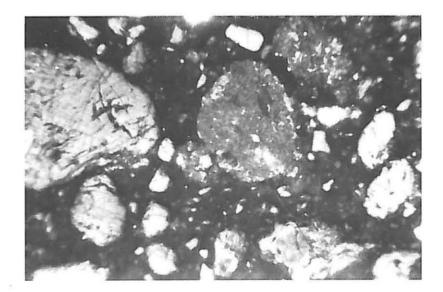


Fig. 10. Sample after 1 month of leaching — scraps of pyrite

This sample was composed of small fragments of separated macerate grains; more exact description would be difficult. Macerate group of huminite contained gelinite, flobafinite, and textinite. The humodetrinite was prevailing. Small fragments of rezinite were observed. Macerate group of inertinite was formed by scraps of sclerotinite and fuzinite. Inorganic additive was represented by 2% of clay minerals only; the rest was composed of different forms of pyrite. The framboidal and massive pyrite were represented approximately equally.

Only 6% of euhedral pyrite was substituted. The action of bacteria is shown on the Figure 4. In the central part of the picture, grains of the pyrite influenced by bacteria with slight residues of pyrite are shown.

Character of the sample after three weeks of leaching

This sample resembles previous sample from the micropetrographical point of view. Macerate group of huminite is represented by textinite, gelinite, and flobafinite. The textinite or its cell walls are filled up by very fine pyrite. Textinite is very often transformed totally to pyrite. Macerate group of liptinite is filling in sporinite and rezinite. Rezinite is often overshadowed by pyrite. In some grains, large groups of liptinite, transformed to liptite, are present. Macerate group of inertinite was formed in trimacerite with more-cell sclerotinite. Mineral additive was composed of different forms of pyrite. On the Figure 5, clusters of pyrite as well as massive pyrite that is affected at the edges by bacteria, are shown. The effect of bacteria can be better seen with green filter — on the Figure 6. The similar picture is in the Figure 7. The action of bacteria is clearly shown on the Figures 8 and 9. In the central part, a grain of pyrite after impact of bacteria, with isolated residues of pyrite at the edges, is shown.

Character of sample after one month of leaching

Macerate group of huminite was represented by textinite that was often "impregnated" by pyrite; similarly, the cell walls were underlined by pyrite. The gelinite and flobafinite were present, too. Macerate group of liptinite was composed of rezinite in flobafinite. In some places, the liptinite was mainly concentrated, and it could be defined as liptite. Structure of the rezinite was often emphasized by pyrite. Macerate group of inertinite was supplied with sporadic appearance of sclerotinite and fuzinite fragments. Mineral additive was composed of pyrite in framboidal form, and its many clusters were found. The lowest substitution of only 1.4% has euhedral pyrite. The effect of the bacteria is shown on Figure 10. In the grain after pyrite only scraps of pyrite are saved.

Fuzzy outline of some framboidal bodies were probably caused by the reduction of the sulphide mass.

CONCLUSION

The purpose of the work was the verification of bacteria leaching usefulness for desulphurisation of coal containing sulphur, from locality Nastup Tušimice. The results proved that bacteria leaching was possible as the leaching removed 71% of pyritic sulphur, with general desulphurisation of coal

of about 42%. The improved results were possible to achieve by application of the adapted culture of *Thiobacillus ferrooxidans* or of mixed culture of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, and if needed through the extension of leaching time.

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