

Bacterial Desulphurization of Brown Coals

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ABSTRACT

The objective of the paper was application of bacterial leaching on 2 brown coal samples from bore S 187 (CV) from locality Mine CSA Most. Based on the results of bacterial leaching and petrologic analyses of the given samples, it is possible to state that the individual samples are very similar, they contain significant shares of clay materials and pyrite is predominantly represented in a framboidal form, which intergrowths into a massive form. Applying bacterial leaching it is possible to remove from 32 to 38% of total sulphur and from 30 to 32% of pyritic sulphur from the coal; better results are obtained eliminating sulphate sulphur, i.e. up to 50% desulphurization.

Keywords: Bacterial leaching, *Thiobacillus ferrooxidans*, Desulphurization, Coal macerates

1 INTRODUCTION

Desulphurization of the fuels is a problem, which even with big effort of humans beings it has not been solved so as to the stop SO₂ introduction to air. It is well known that the high amount of sulphur in coal has adverse influence on its utilization and that contributes to environment contamination as the acid rain (Fecko et al. 1991, Fecko et al.1994, Fecko 1997). There are more evidences that the Czech Republic occupies one of the first positions in Europe in environment contamination by sulphur oxides, because our main source of energy is the combustion of solids fuels. In the amount of industrial emissions per km² the Czech Republic is second in the world (25 t km⁻²) and in the amount of emissions per inhabitant is third (0.2 t). Combustion depends on the concentration of sulphur which reaches somewhere around 12%.

2 MATERIALS AND METHODS

2.1 Distribution of sulphur in coal

Sulphur is presented in its organic and inorganic forms in coal. Free sulphur is presented only sporadically. Pyrite and marcasite are presented in large quantities but their proportions vary. Sulphates, mainly gypsum, originated primarily during the carbonisation process and secondarily during the weathering of pyrites. Organic sulphur is mainly bound to the structures of dibenzenethiophene,

benzenethiophene and thiols. Pyrite is presented in the epigenetic and syngenetic forms. Syngenetic pyrite was formed during the first phase of the coal forming process and that is, why it is interspersed within the coal substance. Epigenetic pyrite is geologically younger, therefore it acts as a filling material in the joints and fissures. It is less intergrown within the coal substance, it forms larger crystals and is easier to eliminate by suitable coal processing methods. A whole range of chemical techniques with the potential to separate pyrite from coal was reviewed, and also some microbiology techniques. The chemical techniques for desulphurization employ relatively non-specific reactions, functioning at high temperatures and pressures, and with relatively high consumption of chemicals. The methods of microbiology have the advantage of very specific reactions in a simple reactor, at ambient temperature and normal pressure, but they need a longer leaching time. The aim of this work is confirmation the viability of bacterial leaching applications on the samples of black coal from the different localities. [2, 3, 4]

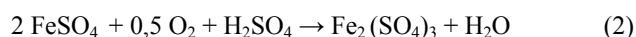
2.2 *Thiobacillus ferrooxidans*

They are aerobic, chemoautotrophic organisms that require atmospheric oxygen and inorganic compounds with CO₂ for production of their new biomass. They are non-sporulating gram negative bacteria. In appearance they are sticks of average 0.5-0.8 µm with length 0.9-1.5 µm. *Thiobacillus ferrooxidans* can get energy by oxidation of sulphur components and by oxidation of Fe²⁺. Optimal temperature for this bacteria is: 28-30 °C and optimal pH is in the range 1.8-2.2. [5]

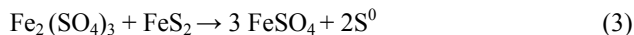
2.3 Principle of pyrite oxidation by *Thiobacillus ferrooxidans* bacteria

Bacterial leaching can be either direct or indirect. In the direct interaction the surface of the minerals is occupied by bacteria and metal sulphides are attacked by enzymatic oxidation.

Direct leaching oxidation of pyrite is best described by the following equations:



The bacteria create a leaching agent in indirect bacterial leaching. This agent oxidises sulphidic minerals. In acid solutions Fe^{3+} is the active agent. The solubility of pyrite can be written as:



2.4 Methods of bacterial leaching

For the bacterial leaching testwork a 10-litre airlift glass bioreactor patterned on the research of Deutsche Montan Technologie Company – Essen. (Bayer, 1988) was used. For bacterial leaching 2 brown coal samples from bore S 187 (CV) from Mine CSA Most (followed as S 23 and S 31) was used. After sterilization of the reactor, the prepared samples of coal were placed in it together with the medium 9K without FeSO_4 . After one hour of mixing and homogenising of the suspension, 1,000 ml of the bacterial culture *Thiobacillus ferrooxidans* was introduced into the reactor. Clean bacterial cultures of *Thiobacillus ferrooxidans* from the Czech-Slovak Collection of Micro-organisms in Brno were used for the test programme. The concentration of introduced bacteria in the process was 10^9 in 1 ml bacterial solution. The bioreactor was connected to the aquarium water aerator, which supplied the reactor with air. The air was cleaned in washers in 1 M H_2SO_4 solution to have more moisture and to remove airborne bacteria. Mixing of 5% suspension was using air. pH was measured by laboratory pH-meter “RADELKIS” and the pH was kept at the optimal value 1.8 – 2 during the whole experiment (28 days) to prevent formation of unwanted jarosite. The temperature was kept in the range 26-30 °C during the whole experiment.

During the leaching, after 1, 2, 3, and 4 weeks, samples of approximately 50 ml were taken from the bioreactor for analysis, was filtered on a Buchner funnel where the filtrate and the filter cake were separated, the content of total sulphur and its separate forms were determined in the filter cake. The cake was washed in 100 ml of 1M HCl and in 200 ml distilled water before the determination. [1]

2.5 Petrographic analysis

Measurement condition

Maceral analysis was performed on the grains according to CSN ISO 7404-2 [6] and CSN ISO 7404-3 [7] using a Zeiss NU-2 microscope. Planimetric analysis was evaluated in oil immersion, with refractive index $n_D = 1,515$, and the length wave $\lambda = 546 \text{ nm}$, temperature $t = 20 \text{ }^\circ\text{C}$, objective enlargement 32x.

Determination of sulphur

Sulphur was determined at the Research Coal Institute in Ostrava Radvanice on a LECO SC 132 instrument, directed by microprocessor with detection of SO_2 using infrared detector. Different forms of sulphur were

determined by thermal phase analyses at temperatures 420 °C (organic sulphur) 820 °C (pyrite sulphur) and 1,370 °C (total sulphur) with constant programme conditions. The sulphate sulphur was calculated.

3 RESULTS OF BACTERIAL LEACHING AND MINERALOGICAL-PETROLOGICAL ANALYSIS AND DISCUSSION

3.1 Sample No. 23

Results of petrologic analysis of Sample No. 23 – input

The maceral subgroup of humotelinite was chiefly formed by ulminite and textoulminite. There was less textinite than ulminite (euulminite). In the grains of humotelinite, corpohuminite was quite frequent, mineralized by clay minerals, formed by fine stripes or they were finely scattered in the coal mass. Its total abundance was 20.2 %.

Humocolinite was quite abundant (34.2 %). Gelinite grains were often disrupted by fissures of retreat. In corpohuminite there were liptinite group macerals – especially sporinite, less of suberinite.

Humodetrinite was represented by 11.4 %.

The maceral group of liptinite was mainly made up by sporinite and cutinite, less by suberinite. There was very little alginite. The total abundance of this group was 5.3 %. However, in some grains it accumulated to such a degree that monomaceral microlithotype of liptite was formed.

The maceral group of inertinite was very rare – planimetrically mainly funginite and fragments of fusinite were traced. Inertinite was represented by 2.6 %.

Inorganic impurities were frequent and formed predominantly by pyrite (17.5 %) and clay minerals (8.8 %). Pyrite prevailed as framboidal, which accumulated in places (Figure 1) but was often finely scattered in the coal mass.

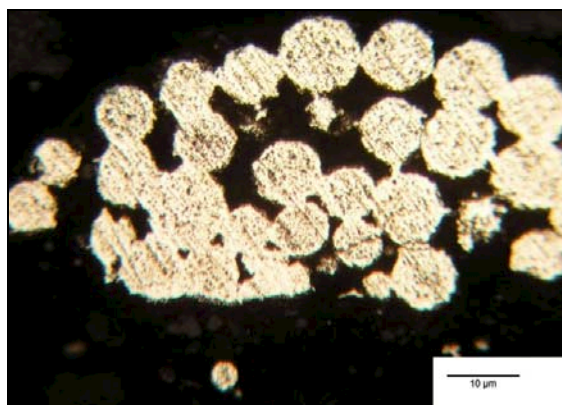


Figure 1. Accumulation of framboidal pyrite and its partial intergrowth with transition into massive pyrite.

Bacterial leaching results

Sulphur	Prior to leaching	Post leaching	Degree of desulphurization
	(%)	(%)	(%)
S _{total}	4.73	3.20	32.35
S _{pyritic}	2.93	1.99	32.08
S _{organic}	0.92	0.80	13.04
S _{sulphate}	0.88	0.41	53.41

Table 1. Results of bacterial leaching.

The results of bacterial desulphurization of the sample (See in the Table 1) imply that after one-month leaching it is possible to eliminate approximately 33 % of total sulphur, 32 % of pyritic sulphur and 53 % of sulphate sulphur from the sample. The elimination of organic sulphur is only about 14 %.

Results of petrologic analysis of Sample No. 23 post bacterial leaching

The maceral group of huminite was represented by the subgroup of humotelinite, which made 24.2 %. Textinite was rarer than ulminite or textoulminite. There are heavily jellified cell walls.

The humocolinite subgroup was made up by gelinite and corpohuminitite, in roughly comparable abundance; its total abundance was as high as 40 %.

The subgroup of humodetrinite was less frequent; its total abundance was 9 %. Attrinite and densite occurred in approximately same amounts. Some grains were mineralized by clay minerals or by finely intruded pyrite.

The liptinite group was primarily represented by sporinite and cutinite (Figure 2). In certain grains there was high occurrence of alginite. The total abundance of this group was 6.1 %.

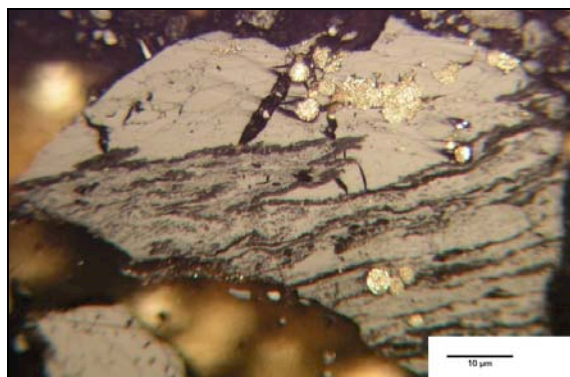


Figure 2. Cutinite with framboidal pyrite, partly leached and corpohuminitite.

Inertinite was represented by funginite and fragments of fusinite. It only totalled to 1 %.

Inorganic impurities were mainly represented by clay minerals, namely by 14.1 %. They formed separate grains or mineralized the individual macerals. Pyrite chiefly occurred

as framboidal, it often mineralized textinite – or as finely scattered it mineralized other macerals. Its total abundance was 6.2 %.

3.2 Sample No. 31

Results of petrologic analysis of Sample No. 31 - input

The humotelinite maceral subgroup was predominantly formed by textoulmite and ulminite. There was less textinite and it was often mineralized by finely intruded pyrite. Its total abundance was 26.2 %.

Humocolinite made 17.6 % and it was represented especially by gelinite, which had frequent fissures of retreat and corpohuminitite (flobafinite). Some grains were heavily jellified and they were labelled as colinite.

Humodetrinite was represented by attrinite and densinite. Its abundance was 14.2 %.

There was quite high occurrence of liptinite, namely as sporinite and cutinite. Alginite was rare. In places, liptinite transitioned into liptite. The sample contained 7.5 % of liptinite.

The macerals of inertinite were made up by fragments (fusinite) or funginite occurred. Both macerals were often mineralized by pyrite.

There was 14.0 % of pyrite. It was often massive or finely intruded. However, framboidal pyrite prevailed (Figure 3). Clay minerals mainly formed separate grains or mineralized humotelinite or humodetrinite. As a rule, humocolinite occurred without mineralization. The content of clay minerals in the sample was 15.8 %.

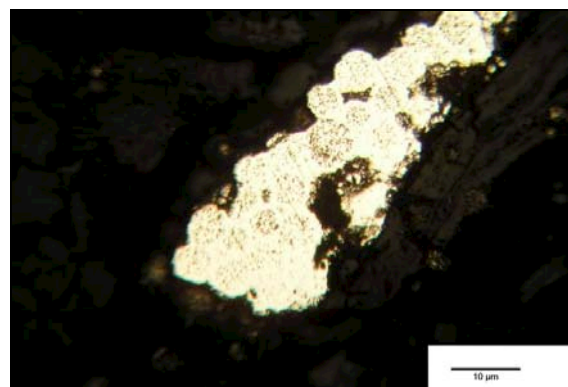


Figure 3. Ingrowths of framboidal pyrite with transition into massive pyrite.

Bacterial leaching results

It is apparent from the results of bacterial leaching (Table 2) that after one-month leaching there is an approximate 38 % desulphurization of coal, desulphurization of pyritic sulphur is about 29 % and sulphate sulphur desulphurization is about 53 %. Interestingly, there is high desulphurization of organic sulphur, i.e. as high as 54 %.

Sulphur	Prior to leaching (%)	Post leaching (%)	Degree of desulphurization (%)
S _{total}	8.15	5.08	37.67
S _{pyritic}	5.38	3.80	29.37
S _{organic}	1.83	0.84	54.10
S _{sulphate}	0.94	0.44	53.19

Table 2. Results of bacterial leaching.

Results of petrologic analysis of Sample No. 31 post leaching

The maceral group of humotelinite was represented by textinite, which was very often mineralized by pyrite and ulminite. Its total abundance was 17.6 %.

The group of humocolinite was characteristic for its abundance as high as 47.0 %. Gelinite slightly prevailed with typical fissures of retreat over corpohuminitite.

Humodetrinite was represented by mere 5.2 %. Both macerals of attrinite and densinite were present in almost identical amounts.

The liptinite maceral group was frequent in sporinite and cutinite. Suberinite (it was overtopped) and alginite were rare. The total abundance of liptinite was 9.0 %.

Inertinite was formed by rare fragments of fusinite and funginite.

Inorganic impurities were abundant in pyrite – 15.0 % and clay minerals – 6.2 %. Pyrite was finely intruded in textinite; clay minerals filled the cell space of funginite. In places, the occurrence of hematite was traced (Figure 4).

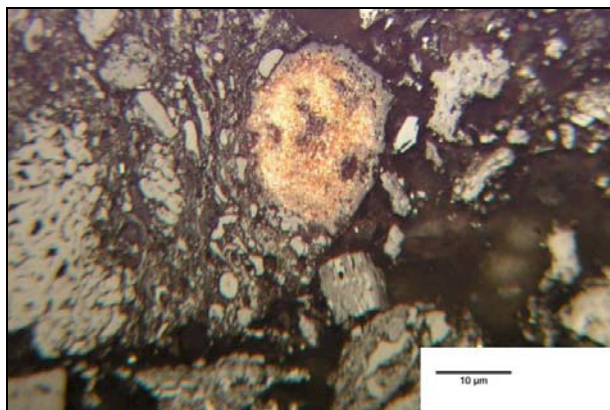


Figure 4. Secondary mineral post pyrite leaching – hematite.

4 CONCLUSION

The objective of the paper was application of bacterial leaching on 2 brown coal samples from bore S 187 (CV) from locality Mine CSA Most. Based on the results of bacterial leaching and petrologic analyses of the given samples. It is possible to state that the individual samples are very similar, they contain significant shares of clay materials and pyrite is predominantly represented in a framboidal form, which intergrowths into a massive form. Applying bacterial leaching it is possible to remove from 32

to 38 % of total sulphur and from 30 to 32 % of pyritic sulphur from the coal; better results are obtained eliminating sulphate sulphur, i.e. up to 50 % desulphurization. Desulphurization results could be improved under the following conditions:

- applying bacterial cultures of *Thiobacillus ferrooxidans* pre-adapted to a given coal type
- prolonging the leaching time
- applying mixed bacterial cultures of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*
- applying bacterial leaching post removal of clay materials, large shares of which in the sample complicate leaching, especially of pyritic grains.

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