BACTERIAL DESULPHURIZATION OF COAL FROM MINE CSA MOST

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Abstract

The objective of the paper was application of bacterial leaching on 3 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 24 to 40% of total sulphur and from 20 to 37% of pyritic sulphur from the coals.

1. Introduction

Desulphurization of the fuels is a problem, which even with great scientific efforts has not been solved to the stop SO$_2$ introduction to air [1-5]. It is well known that the high amount of sulphur in coal has adverse influence on its

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utilization and that contributes to environment contamination as the acid rain [3-5]. 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 km^2 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 somewere around 12%.

2. Experimantal conditions

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 CO_2 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 Fe^{2+}. 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:

$$FeS_2 + 3,5\ O_2 + H_2O = FeSO_4 + H_2SO_4 \tag{1}$$
$$2\ FeSO_4 + 0,5\ O_2 + H_2SO_4 = Fe_2(SO_4)_3 + H_2O \tag{2}$$

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:

$$Fe_2\ (SO_4)_3 + FeS_2 = 3\ FeSO_4 + 2S^O \tag{3}$$
$$2S^O + 3O_2 + 2\ H_2O = 2\ H_2SO_4 \tag{4}$$
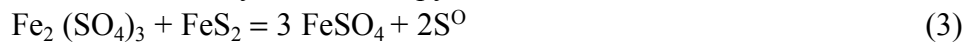
2.4. Methods of bacterial leaching

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 32. S36 and S 38) 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. 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 nD = 1,515, and the length wave λ= 546 nm, temperature t = 20 °C, objective enlargement 32x.

2.6. 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 and Discussion

3.1. Results of petrologic analysis of Sample No. 32 - input

The maceral group of humotelinite was mainly made up by textoulminite and euulminite (Fig. 1). There was much less textinite. The total abundance of this group was 22.8%.
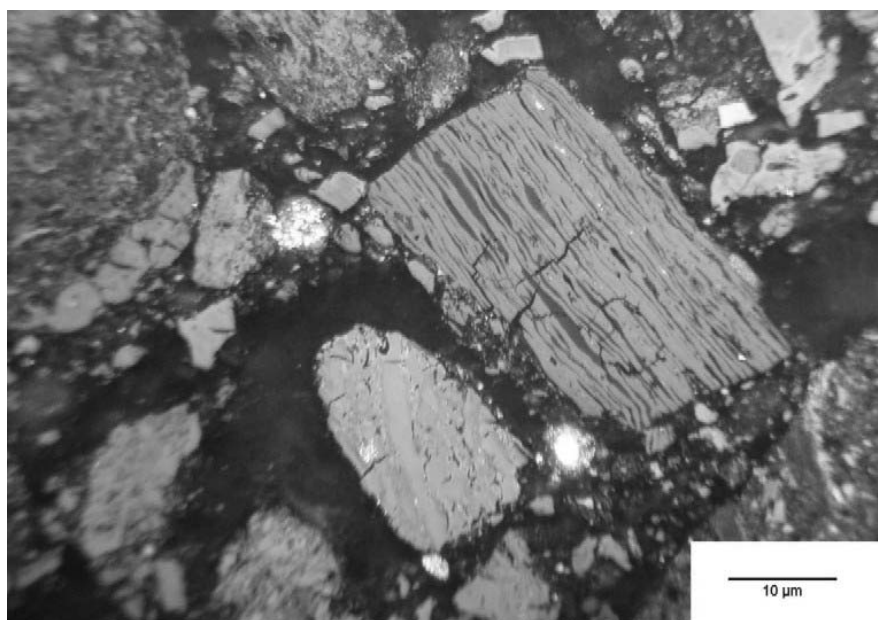
Fig. 1. A grain of euulminite

Humocolinite was the most abundant among all the macerals - 45.5%. Gelinite as well as corpohuminite (flobafinite) were present in roughly comparable amounts. In gelinite there were typical fissures of retreat. In some grains, virtitization progressed and the grains looked as colinite.

Humodetrinite was less frequent - 4.5%. Small grains of corpohuminite often occurred in the grains of humodetrinite.

The percentage abundance of the liptinite group was very high - 15.9%. Sporinite prevailed over suberinite and cutinite. In some grains there was

higher occurrence of alginite; though, its total abundance was very low.

The maceral group of inertinite was not planimetrically traced. In some grains, fragments of fusinite (or semifusinite) and funginite were preserved. Inorganic impurities were largely made up by pyrite - 6.8%, which formed clusters (mainly framboidal) and it finely intruded in textinite.

3.2. Results of bacterial leaching of Sample No. 32

It is apparent from the results of bacterial leaching of Sample No.32 that after the application of one-month bacterial leaching it is possible to eliminate approximately 40% of total sulphur, 34% of pyritic sulphur and about 30% of sulphate sulphur. In the given sample, also high desulphurization of organic sulphur was observed, namely up to 66%. See in the Table 1.

Table 1. Results of bacterial leaching

Sulphur	Prior to leaching	Post leaching	Degree of desulphurization
	(%)	(%)	(%)
S_{total}	5.31	3.18	40.11
$S_{pyritic}$	3.33	2.19	34.23
$S_{organic}$	1.09	0.37	66.10
$S_{sulphate}$	0.89	0.62	30.34

3.3. Results of petrologic analysis of Samples No. 32 post leaching

The maceral subgroup of humotelinite was represented by textinite and ulminite; the occurrence of textoulminite was also traced. Its total abundance was 18%. A high content was also typical for the maceral group of humocolinite - 50.0%. Humocolinite was primarily represented by gelinite - with frequent fissures of retreat and narrow light margins. Corpohuminite usually formed spherical bodies, the occurrence of which was bound to textinite, ulminite or the maceral subgroup of humodetrinite. Humodetrinite was represented by attrinite and densinite. Its abundance totalled 9.5%.

Liptinite group macerals were quite abundant - 12%. Sporinite prevailed over cutinite and suberinite. Alginite was also present. The maceral group of

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inertinite was formed by fragments of fusinite and funginite. The group had 2.0%. Inorganic impurities were represented by pyrite; framboidal pyrite dominated. Some framboids were more or less affected by leaching. The occurrence of pyrite was often bound to gelinite.

3.4. Results of petrologic analysis of Sample No. 36 - input

The maceral subgroup of humotelinite was mostly represented by textoulminite and ulminite. There was less textinite, which was mineralized by finely intruded pyrite. This subgroup had 28.4%. Humocolinite was made up by almost identical amounts of gelinite and corpohuminite. Its total abundance was 31.6%. Humodetrinite was represented by attrinite as well as densinite. In places there was corpohuminite. This subgroup was made up by 14.7%.

The maceral group of liptinite was predominantly represented by sporinite, less by cutinite and alginite as well as suberinite. It totalled to 10.6%. The maceral group of inertinite was not planimetrically traced in this sample.

In absolute majority, inorganic impurities were represented by clay minerals, which often formed separate grains or mineralized textinite, or other maceral. Sulphides were represented by pyrite, which prevailed as framboidal or finely dispersed. It was less frequent as massive. The total abundance of this impurity was 14.7%.

3.5. Results of bacterial leaching of Sample No. 36

The results of bacterial leaching (Table 2) of the given sample imply that after one-month leaching, the total desulphurization is only about 24% and desulphurization of other forms of sulphur is not high either.

3.6. Results of petrologic analysis of Sample No. 36 post bacterial leaching

Also in this sample more jellified macerals of the humotelinite subgroup dominated over less jellified ones. Therefore, textoulminite and euulminite were more frequent than textinite. The occurrence of finely intruded pyrite was bound to textinite; some grains carried the signs of leaching. The percentage abundance of this group was 17.1%.

Table 2. Results of bacterial leaching

Sulphur	Prior to leaching	Post leaching	Degree of desulphurization
	(%)	(%)	(%)
S_{total}	3.80	2.89	23.95
$S_{pyritic}$	2.40	1.92	20.00
$S_{organic}$	0.62	0.46	25.81
$S_{sulphate}$	0.78	0.51	34.62

The maceral subgroup of humocolinite was made up by gelinite and corpohuminite; their amounts were comparable. The grains of gelinite were often cracked; corpohuminite formed oval bodies in humotelinite or humodetrinite. The percentage abundance of this group was 35.4%. Humodetrinite was partly represented by attrinite and densinite; its total abundance was 22.3%.

The most frequently, the maceral group of liptinite was formed by sporinite and cutinite, less by suberinite. In some grains, alginite occurred. It totalled to 7.4%.

The maceral group of inertinite was not determined.

Inorganic impurities were made up by pyrite, either framboidal or little less massive. Some grains were partly leached and some changed to hematite. Its abundance was 4.1%. Clay minerals dominated with 13.7%. They very often formed separate grains or stripes in the coal mass, or they were finely intruded.

3.6. Results of petrologic analysis of Sample No. 38 - input

In small extent, the maceral subgroup of humotelinite was made up by textinite. Macerals with largely jellified walls prevailed, i.e. textoulminite to euulminite. Those macerals were mineralized by finely intruded pyrite.

The maceral subgroup of humocolinite was quite abundant in gelinite and corpohuminite. Gelinite had frequent fissures of retreat; in some grains it

occurred along with corpohuminite.

The maceral subgroup of humodetrinite was represented by little attrinite and densinite. Also in those grains, corpohuminite occurred.

The maceral group of liptinite was primarily made up by sporinite, cutinite, less by suberinite. In some grains there was suberinite and alginite in places. The high accumulation of macerals of this group led to the formation of a monomaceral microlithotype - liptite.

The inertinite maceral group was not determined.

Inorganic impurities were very abundant; i.e. over 40.0%, and therefore the percentage abundances of the individual maceral groups are not given. Unambiguously, clay minerals dominated and, as a rule, they formed separate grains. Pyrite was often in its framboidal stage; less often it was finely intruded or massive. In some grains, the intergrowths of framboidal pyrite transited to massive pyrite.

3.7. Results of bacterial leaching of Sample No. 38

Table 3. Results of bacterial leaching

Sulphur	Prior to leaching	Post leaching	Degree of desulphurization
	(%)	(%)	(%)
S_{total}	4.76	3.16	33.61
$S_{pyritic}$	3.30	2.08	36.97
$S_{organic}$	0.57	0.41	28.07
$S_{sulphate}$	0.89	0.67	24.72

It is apparent from the results of bacterial leaching of Sample No. 38 (See in Table 3) that after one-month bacterial leaching it is possible to remove roughly 34% of total sulphur and about 37% of pyritic sulphur from the sample.

3.8. Results of petrologic analysis of Sample No. 38 post bacterial leaching

The maceral subgroup of humotelinite was usually made up by textoulminite and euulminite, less by textinite.

Humocolinite was abundant in gelinite and corpohuminite. On some gelinite grains, light margins occurred which were of various widths. Gelinite had typical fissures of retreat. Its fragments made part of humodetrinite.

Humodetrinite was represented by attrinite and densinite. Its total abundance was very low.

The maceral group of liptinite was represented by sporinite, cutinite, less by suberinite and alginite. In terms of microlithotypes, some grains were classified as clarain, rarely as liptite.

The maceral group of inertinite was not determined.

Inorganic impurities were very abundant and therefore the percentage abundances of the individual maceral groups are not mentioned. Clay minerals clearly dominated. They usually formed separate grains or mineralized the individual macerals or occurred along with pyrite. Pyrite prevailed as framboidal; the individual framboids intergrew in places and transited to massive pyrite. There were partly leached grains or secondary mineral post pyrite - hematite.

4. Conclusion

The objective of the paper was application of bacterial leaching on brown coal samples from bore S 187 (CV). 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 approximately 24 to 40% of total sulphur and 20 to 37% of pyritic sulphur from the coal.

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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