Clean Technology for Coal Desulphuration to Reduce SO_2 Emissions from Coal Combustion in Thermal Power Plants

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Abstract

Power stations using the coal as energetically agent exhaust into the atmosphere large quantities of polluting agents having different forms. Burning of coal involves pollution of environment by means of powders exhausted from chimneys and by means of flying ash spoil dumps. Mechanical pollution is completed by chemical pollution produced as result of action of chemical substances in burned gases that can be even more dangerous than the solid ones, affecting the ecological balances of areas around the energetically complexes. In order to reduce the impact of gases onto the environment is required that in the future to be taken a range of measures aiming to monitor the noxious gases exhausted complying the national and international environment protection laws. Also, considering the toxicity of sulphurous gases over the flora and fauna, this paper analyses, based on original experiments, different methods (desulphurization by flotation, magnetic desulphurization, and bacterial desulphurization) for sulphur content reduction in coal before being used in thermal power plants.

Keywords: *coal combustion, desulphurization, SO_2 content, environmental protection, mechanical processing technologies, bacterial desulfurization of coal*

1. Introduction

One of the negative aspects of coal combustion is the generation of sulfur dioxide emissions, leading to acid rain occurrence. Therefore, given the increasing demands in environmental protection, there is needed a more advanced coal desulphurization in the pre-combustion phase.

The desulphurization of the coal used in the burning process in thermal power plants has the following advantages: eliminates investment needed to achieve gas desulphurization equipment, reduces the polluting elements of ash, slag and gas.

Desulfurization of coal can be carried out by flotation, gravitational procedures, magnetic separation or using bacteria.

The coal is a macromolecular compound with a very complex structure, the composition of which includes: C, H, O, N, S.

The element sulfur is found in coal in the following forms:

- Sulphate sulfur;
- Sulfur sulphide (pyrite and/or Marcasite);
- Organic sulfur.

Sulfur sulfate – is a minor element in the sulfur balance in coal, rarely going above 0.2%. The presence of sulphate sulfur is due to the oxidation of pyrite with the oxygen from atmosphere or water, leading to ferrous sulphate ($FeSO_4$). Sulfur sulfate is found in the form of $CaSO_4$, being brought by percolation water.

Sulphide sulfur – can be present as pyrite and marcasite. In coal, the pyritic sulfur is present in different amounts and forms, from very fine microscopic particles released into the mass of coal, up to thick granules of few millimeters.

The vast majority of pyrite in the Jiu Valley coal is finely disseminated into the coal mass, generally having sizes from 0.1 to 0.25mm.

Organic sulfur - is found in coal in three forms:

- sulfur in the form of -SH or H-S-S-H in a concentration of 2%, which by oxidation forms HSO_3;
- sulfur in the form of C = S, which after oxidation is removed in the form of SO_2;
- sulfur in an undefined form, highly resistant to chemicals reagents.

Sulfur is alongside other elements, an unwanted element in coal because by burning coal in power plants results a set of agents, one more harmful than the other, leading to a mechanical and a chemical pollution of the environment:

- mechanical pollution – represented by the particulates entrained in chimneys;
- chemical pollution – caused by the action of chemicals from the combustion of coal.

Chemicals resulting from burning coal have a complex impact on all environmental factors in their surrounding area (atmosphere, soil, water). Air pollution with SO_2 is very harmful to the human body. A concentration of 20 ppm SO_2 produces coughing and irritates the eyes, this compound also greatly affecting vegetation. On the wet leaves, sulfur dioxide dissolves forming sulfuric acid (H_2SO_3) which passes through oxidation in sulfuric acid (H_2SO_4) which is a harmful agent. This occurs especially in winter, so the conifers suffer primarily because they keep their leaves in winter.

Considering that by burning coal very harmful chemicals for flora and fauna are released, there it is required a purification of coal before burning, to reduce the sulfur content. This can be done either by traditional methods (gravitational concentration, flotation, and heavy media) or by chemical or biological methods.

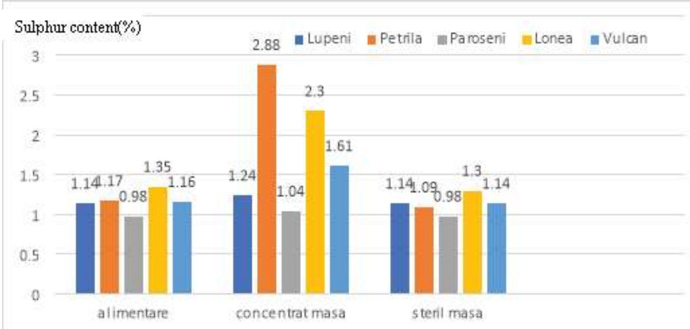

Fig. 1. Distribution of sulfur content in products and mining fields-mass concentration

Rys. 1. Rozkład zawartości siarki w produktach i polach wydobywczych – stężenie masowe

2. Experimental Part

The paper presents several methods tested in laboratory and pilot phase for reducing sulfur from coal before subjected to combustion, through various methods.

2.1. Research of desulphurization by separation processes in hydrogravitational and hydrocentrifugal fields

Hydrogravitational concentration processes are among the oldest concentration processes in both ore and coal. (Tomus N., Cismasiu M.C., Deak E.S, 2014)

Hydrogravitational separation is achieved easier when between the mineral species there is a difference of specific weight and when they fit into a close range granulometry, plus the difference in the form of granules.

Some examples of devices that use the water current concentration are: concentration tables, Reichart cones, and among the devices that are used in centrifugal field to concentrate we can mention hydrocyclonage, spirals, Knelson, Falcon or Mozley multigravitational concentrators.

The National Institute for Research and Development for Rare and Radioactive Minerals (NIRDRRM) Bucharest and the University of Petrosani performed experimental research using the Mozley concentrator and the concentration tables, on coal from different mining fields from Jiu Valley. Following the laboratory research several conclusions can be drawn:

- weight extraction of the mass concentrate varies between 1.76 and 7.14% depending on the mining field from which the coal originates;
- the content of sulfur in the mass concentrate is not much different from that in the feed, is a maximum of 2.88% for coal coming from E.M. Petrila, which means that a small amount of sulfur less concentrated in the mass concentrate; (figure 1)
- sulfur extraction in mass concentrate was calculated based on weight extraction and the ratio of sulfur in the concentrate and in the feed, obtaining a value below 10% for all the sorts of coal analyzed; (there were exceptions in Petrila and Lonea areas with the values 11,34% and 12.21%);
- as a general conclusion it can be said that coal desulfurization using Gemeni concentration table for less than 1 mm grain size coal is not justified given the very low sulfur extraction in the concentrate.

Desulfurization tests using Mozley concentrator, which is a device that combines the principle of the centrifugal field with the one of the hydrogravitational concentration led to the following conclusions:

- weight extraction of the concentrate is high enough (between 8 and 28%) for the coal coming from Jiu Valley Basin, but an inverse concentration of the sulfur is produced, this being explained by the fact that within the apparatus concentrate there were coarse size coal particles with lower sulfur content;
- based on the obtained results there can be stated that not even the Mozley concentrator gave the expected results for coal desulphurization (figure 2.)

2.2. Coal desulphurization by flotation

Flotation is a physical-chemical process which is based on the difference between superficial properties of the surface of particles of coal and sterile. This method is applied to fine grain classes, resulting in the reduction of pyritic sulfur content for class + 0,074 mm size up to 90% and class -0,074 mm size to 30%. (Krausz S., Sarbu R., Badulescu C., s.a, 2008).

The efficiency of the flotation process is influenced by the following parameters:

- the granulometry of the material, in coal the optimal class is from 1.17 to 0.30 mm;
- the degree of coal oxidation influences the surface characteristics of particles;
- the characteristics of the water (particularly pH), the optimum pH of coal is 6 -7.5;
- characteristics of reagents,
- flotation equipment used.

2.3. Magnetic desulphurization of coal

Magnetic separation was used to purify the small size coal particles. This process is based on the difference between the magnetic properties of coals and the associated minerals. Tests on magnetic concentration were carried out at different intensities of magnetic field. (Murray H.,1997)

After applying desulfurization by means of magnetic separation, the following conclusions can be drawn:

- for the process of magnetic separation to be applied, the tested material is necessary to be grinded down to 1 mm and an average size of 0.3 mm
- the weight extraction of magnetic product is between 6 and 26% (the mining areas with high weight extraction are Lonea and Petrila);
- the sulfur content in the magnetic product is as follows: 11.48% at Lupeni; 8.34% at Paroşeni, 6.4% at

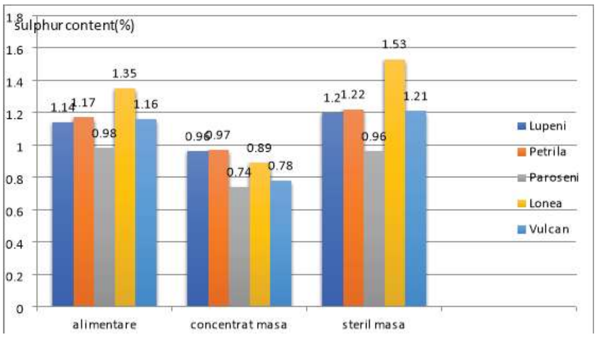

Fig. 2. Distribution of sulfur content in products and mining fields-Mozley concentrator
Rys. 2. Rozkład zawartości siarki w produktach i polach wydobywczych – koncentrator Mozley

Vulcan; 3.09% at Petrila; 5.85% at Lonea;

- the weight extraction of the non-magnetic product is between 76 and 94% (higher in the western part of the Jiu Valley and lower in the eastern part);
- the sulfur content in the non-magnetic product is as follows: Lupeni-0,48%S; Paroşeni-0,51 %S;Vulcan-0,57% S; Petrila-1,14%S; Lonea-1,12%S;
- in the non-magnetic product there remained between 40 and 54% of the sulfur existing in the original coal, which means that sulfur is not bound only to pyrite, but also to non- magnetic sulfates;
- the organic sulfur which is chemically bound to the carbon in the coal can be extracted only by chemical or biochemical processes, after the breaking of chemical bonds;
- between the iron and sulfur content of the magnetic products there is not necessarily a dependence because iron may be present in coal also in the form of oxides or silicates not only in the form of pyrite and marcasite.

It appears that much of the mineral impurities contained in coal are paramagnetic and may be removed by magnetic separation after advanced grinding to achieve the release of the mineral constituent species.

For a more efficient desulfurization, an increase in the magnetic properties of pyrite from coal is required using various methods. One such method is the selective wetting of the constituents with a water-based ferrofluid. The component wetted by ferrofluid and thus reported as magnetic product is, in this case, the mineral (pyrite, clay, silica). Magnetic susceptibility of coal will not be affected and they will form the non-magnetic fraction. To separate the "magnetized" component a high gradient magnetic separator (HGMS) was used, obtaining the following:

- the content of inorganic constituents was reduced from 17% to 5%;
- the sulfur content of a raw coal was reduced from 1.9% to 0.7%;
- the amount of SO_2 emitted into the atmosphere by the desulphurised coal combustion was three times lower than that of raw coal combustion.

2.4. Electrical desulphurization of coal

Electrical separation tests led to the following conclusions:

- separation is not achieved on conductive or non--conductive products with a significant sulfur content compared with the feed;
- during the electric field separation a division of the feed material in two fractions is obtained; the coarse fraction reaching in the conductive product due to centrifugal force that prevail in comparison with the and the fine fraction reaching in the non-conductive product because of electrical force;
- in the non-conductive product which has a relatively low weight extraction 8–15% and 10–17% sulfur extraction, there are distributed especially fine minerals from the grinding of sterile rocks in coal
- in addition to poor results in terms of reducing the sulfur content, if one takes into account that the separation in electric field requires the heating of the material to a temperature of at least 850C the application of this process is not justified.

2.5. Bacterial desulfurization of coal

The Jiu Valley coal is characterized by a great diversity of total sulfur, the mineral and organic sulfur ratio being 1:1. The sulfur content of coal is characterized by values ranging between 1.3–2.6% for the eastern part of the coal basin and from 2.4 to 3.3% for the western part.

The used mechanical processing methods have not given favorable results in reducing sulfur content due to very fine disseminated pyrite in the coal organic mass

In the first part of the research, microbiological and chemical analyzes of water samples collected from Lupeni mine were performed. During these analyses a wide range of culture media were used for the following:

- to highlight the chemoautotrophic mesophilic sulfur and iron oxidizing bacteria (genus Thiobacillus), the sulfate-reducing bacteria, the ferobacteria and heterotrophic aerobic bacteria
- to know the microflora of mine water
- to isolate chemoautotrophic sulfur and iron oxidizing bacteria.

The following chemoautotrophic sulfur and iron oxidizing bacteria species were found after the determination: T.thiooxidans, T.thioparus, T.neapolitanus, T.ferrooxidans, T.denitrificans, T.novellus.

The coal used for the next step of the research came from Lupeni mine, having a 2.81% total sulphur content. After the research the following can be concluded:

- Lupeni coal, due to its high content of carbonates do not provide the optimum conditions (pH of the cul-

Tab. 1. Reducing the sulfur content of coal from the Lupeni mine, Romania, after bacterial leaching
Tab. 1. Obniżenie zawartości siarki w węglu z kopalni Lupeni w Rumunii po ługowaniu bakteryjnym

Sulphur content	Before leaching (%)	After leaching (%)	Desulphurization degree (%)
Total sulphur	2.81	1.79	36.3
Pyritic sulphur	0.71	0.05	92.96
Organic sulphur	4.03	1.59	60.55
Sulphur sulphate	0,15	0,07	53,33

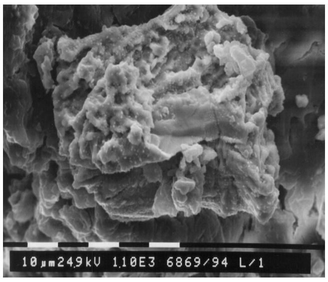

Fig. 3. Pyrite after a week of bacterial leaching
Rys. 3. Piryt po tygodniu wymywania bakteryjnego

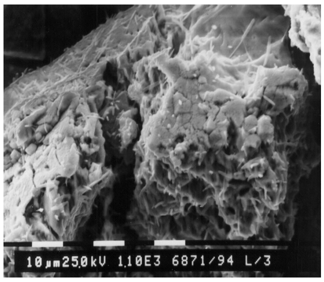

Fig. 4. Pyrite after bacterial leaching
Rys. 4. Piryt po wymywaniu bakteryjnym

ture medium tends to become neutral) for the development of bacteria belonging to the genus Thiobacillus, the sulfur was removed from the charcoal only in a proportion of 5–25 %;
- the success of bacterial desulfurization of coal depends on the composition, structure and dispersion of the sterile in coal, especially of the alkaline one. The reaction of coal sterile (which has the ability to fix the sulfuric acid) and sulfuric acid resulting from the action of bacteria, leads to the formation of alkaline sulfates, that are not consumed by bacteria;
- to perform desulphurization is necessary to create a culture medium for bacteria with a 2.5 pH by addition of hydrochloric acid;
- the duration of the desulphurization process is at least six days;
- by biological desulphurisation there can be removed approx. 20% of total sulfur, and can be locked in the form of a sulfate a percentage of 60% of the sulphide content;
- bacterial desulfurization capacity gradually decreases with increasing the size of coal particles;
- desorption of desulphurisation products is made through washing with warm water.

For the desulfurization of the hard coal from Lupeni mine by bacterial leaching means, the following were used:
- a 5 liter air-lift bioreactor of the Deutsche Montan Technology Research Institute in Essen
- 9K culture medium without $FeSO_4$
- Thiobacillus ferooxidans from the Czechoslovak Collection of Microorganisms in Brno
- the concentration of bacteria introduced into the process was of 109/1 ml.
- the pH of the solution was maintained between 1.8–2.0
- the duration of bacterial leaching was 28 days
- the temperature was 28–30°C.

Petrographic analysis carried out at the Institute of Geotechnics CAV in Prague revealed that coal from the Lupeni mine contains 84.4% vitrinite, 13.8% liptinite and 1.4% inertinite. The mineralogical composition consists of pyrite, clay minerals, particularly carbargilite. Pyrite is present in spheroidal form, the granules located in the mass of mineral coal. (P. Fecko, 2007).

After the bacterial leaching using Thiobacillus ferooxidans for one month, the total sulfur content was reduced from 2.81% to 1.79%, showing a degree of desulphurisation of 36.30%, pyritic sulfur being mainly reduced (92.96%) (Table 1).

Figures 3 and 4 present the image of the pyrite particle after a week and three weeks of leaching.

Conclusions

It can be said that coal desulfurization using Gemeni concentration table for less than 1 mm grain size coal is not justified given the very low sulfur extraction in the concentrate;

Researches using Mozley concentrator that combines field hydrocentrifugal at hydrogravitational revealed that even with this type of device cannot achieve a significant reduction of sulfur content in the desulphurized coal.

During the electric field separation a division of the feed material in two fractions is obtained; the coarse fraction reaching in the conductive product due to centrifugal force and the fine fraction reaching in the non-conductive product because of electrical force.

Desulfurization by flotation can be applied to fine grain classes, resulting in the +0,074mm class size a pyritic sulfur content of 90%.

Worth considering the results of the processes for desulfurization of coal in the magnetic field performed when a reduction of the sulfur content in coal to 50% is obtained.

The magnetic coal desulphurization applies to small size particles, with a reduction in the concentration of mineral components from 17% to 5% and the sulfur content from 1.9% to 0.7%.

By biological desulphurization approximately 20% of total sulfur can be removed.

After the bacterial leaching using Thiobacillus ferooxidans for one month, the total sulfur content was reduced from 2.81% to 1.79%, showing a degree of desulphurisation of 36.30%, pyritic sulfur being mainly reduced (92.96%).

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Czysta technologia odsiarczania węgla redukująca emisję SO_2 ze spalania węgla w elektrociepłowniach

Elektrownie wykorzystujące węgiel jako środek energetyczny emitują do atmosfery duże ilości zanieczyszczeń o różnej postaci. Spalanie węgla wiąże się z zanieczyszczeniem środowiska za pomocą pyłów wydobywających się z kominów oraz za pomocą lotnych hałd popiołów.Uzupełnieniem zanieczyszczeń mechanicznych są zanieczyszczenia chemiczne powstające w wyniku działania substancji chemicznych zawartych w spalinach, które mogą być jeszcze bardziej niebezpieczne niż stałe, naruszając równowagę ekologiczną terenów wokół kompleksów energetycznych. W celu ograniczenia oddziaływania gazów na środowisko wymagane jest podjęcie w przyszłości szeregu działań mających na celu monitorowanie emisji szkodliwych gazów zgodnie z krajowymi i międzynarodowymi przepisami ochrony środowiska.

Ponadto, biorąc pod uwagę toksyczność gazów siarkowych dla flory i fauny, w pracy przeanalizowano, na podstawie oryginalnych doświadczeń, różne metody (odsiarczanie flotacyjne, odsiarczanie magnetyczne, odsiarczanie bakteryjne) redukcji zawartości siarki w węglu przed zastosowaniem w elektrociepłowniach.

Słowa kluczowe: *spalanie węgla, odsiarczanie, zawartość SO_2, ochrona środowiska, technologie obróbki mechanicznej, Bakteryjne odsiarczanie węgla*