Bioflotation as an Alternative Method for Desulphurization of Fine Coals - Part I

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Summary

Bioflotation might be developed as a new process for the removal of pyritic sulfur from fine coal. An application of bacteria to flotation would shorten the periods of the microbial removal of pyrite from some weeks by leaching methods to a few minutes. The bioflotation mechanism is based on rapid adhesion of bacterial cells with hydrophilic properties to the pyrite surface, which changes the properties of the mineral substance's surface from hydrophobic to hydrophilic. As a consequence, air bubbles form aggregates only with hydrophobic coal particles, and pyrite falls to the bottom of the flotation chamber as waste. This article shows that the possibility of using bacteria in the flotation process in place of toxic chemicals has significant environmental and economical benefit.

Keywords: bioflotation, desulphurization, bacteria, pyritic sulphur, coal

Introduction

Coal is a heterogenic, plant-derived sedimentary rock which, besides organic components, contains varying volumes of other elements, e.g. sulphur. Sulphur content is the main problem when using coal as a fossil fuel, since during the coal combustion process the majority of sulphur contained therein is transferred into waste gases in form of sulphur oxides, which are the main reason for the occurrence of acid rain.

EU regulations and directives aimed particularly at the power industry sector - the NEC[1] and LCP[2] directives - specify applicable limits for sulphur oxide emissions into the atmosphere. These limits are met through the implementation of diverse waste gas desulphurisation technologies adapted to the quality of the fuel and type of equipment used in mills, power plants and heat and power stations.

It seems, however, that the most favourable method of limiting pollutant emissions into the atmosphere would be to desulphurise coal prior to its combustion, that is, where the coal is mined. This would reduce transportation costs and the volume of waste generated as a result of fuel combustion, although more than 70% of this waste is subject to recycling, primarily in the mining industry, geotechnics and land reclamation (Gawenda and Olejnik 2008, Piotrowski 2008).

In Poland, the only desulphurisation method in use is gravitational separation of raw material. It is also possible to separate pyrite from coal in mills or magnetic separators, according to differences in material physical properties, enabling the removal of up to 80% of sulphur in a form which is later used e.g. for the production of sulphuric acid (VI) or pure iron. Enrichment by flotation is carried out in the case of particles under 0.5mm in size, which enables the removal of up to 40% of the iron persulfide(II) contained in coal. Major disadvantages of these physical and chemical desulphurisation techniques include high costs, production of waste materials, and/or insufficient selectivity. Biological methods may turn out to be an alternative. Their main advantages are: highly moderate reaction conditions compared to chemical reactions, little or no energy demand for biochemical reactions (microbiological processes run in normal ambient conditions), fewer chemical agents, and, above all, no loss of coal and no production of wastes generating serious problems for the environment.

Many studies have proven the usefulness of bacterial leaching with *Acidithiobacilllus ferrooxidans* bacteria (Aller et al. 2001, Cara et al. 2006, Cardona and Márquez 2009, Cwalina et al. 1994, Dastidari et al. 1998, 2000, Gomez et al. 1997, Hoffmann et al. 1981, Misra et al. 1996, Najafpour et al. 2001, Ohmura et al., 1992, Ohmura and Saiki 1996, Twardowska 1995, Wilczok et al. 1983) for the removal of pyritic sulphur from coal. This process is most effective when the raw material is fine, as then a large volume of pyritic sulphur is released and can be removed by bacteria. During the bioleaching process, microorganisms oxidise pyrite in coal to water-soluble sulphuric acid(VI), which enables the removal of 90-98% of the pyritic sulphur, whereas archea of the *Sulpholobus acidocaldarius* genus and *Rhodococcus rodochrous* bacteria enable the removal of not only pyritic sulphur, but organic sulphur as well. (Demirbas and Balat 2004; Kargi et al. 1982). The thermophilic, acidophilic archea *Acidianus brierleyi* are equally effective (Olsson et al. 1995).

Unfortunately, leaching by bacteria is a slow process, requiring at least a week (using specially aerated reactors), to obtain satisfactory results for the removal of pyritic sulphur from coal. The bioflotation method seems much more attractive in industrial practice, as in this method bacteria require only few minutes to adsorb on the pyrite surface and to separate it from coal.

[1] concerning countrywide ceiling values for emission of pollutants into the atmosphere, and specifying national emission limits for SO_2, NO_x, NH_3 and NHVOCs (non-methane volatile organic compounds)

[2] concerning reduction in emissions of some pollutants into the air from large combustion plants

General characteristics of the bioflotation method

Due to the hydrocarbon-like nature of their surfaces, coal grains have a high natural level of hydrophobicity depending on their mineral composition and ash content. Because of this, in the froth flotation process they are carried to the surface along with air bubbles. It should be observed that pyrite also shows hydrophobic properties and is subject to flotation along with coal (Demirbas 2002, Kawatra and Eisele 1997). Suppression of pyrite's floatability, and consequently its separation from coal, is possible with the use of certain bacteria species. The bioflotation mechanism is based on rapid adhesion of bacterial cells with hydrophilic properties to the pyrite surface, which changes the properties of the mineral substance's surface from hydrophobic to hydrophilic (Nagaoka et al. 1999, Vilinska and Hanumantha 2008, Pecina et al. 2009). As a consequence, air bubbles form aggregates only with hydrophobic coal particles, and pyrite falls to the bottom of the flotation chamber as waste. Bioflotation selectivity results from the specific structure of the bacterial outer membrane, which is hydrophilic and capable of adhesion to the pyrite surface. These properties, and thus bioflotation output, can be improved using genetic manipulation.

Factors conditioning the effectiveness of biological flotation

Many factors influence the effectiveness of the bioflotation process: the density of bacterial suspension, the type of bacteria, pH, contact duration, mineral particle size, the conditions of the microorganism culture, the nature of the bacterial cellular walls, and ash and sulphur content.

The cellular wall structure of bacteria has a significant effect on their adsorption process on mineral surfaces. Both in Gram-positive and Gram-negative bacteria, cellular walls contain many diverse organic functional groups (including carboxyl, hydroxyl, and amine), which show electrostatic, chemical and hydrophobic affinities to the mineral surface. The specific cell surface structure of *Acidithiobacillus ferrooxidans* is responsible for its selective adsorption on sulphide minerals. These microorganisms are capable of oxidising iron; thus they use minerals containing this chemical element as an energy source and growth substrate. Moreover, studies have proven that they adsorb on pyrite surfaces in the form of a monolayer through interactions other than hydrophobic and electrostatic (Ohmura et al. 1993). Apparently, a crucial role is played here by biological interactions linked to chemosensory systems, production of EPS (extracellular polymeric substances) and metabolic activity of cells (Tan and Chen 2012).

Tan and Chen studied the impact of environmental reaction on bacteria adsorption on pyrite surfaces. They proved that the greatest degree of coverage for the mineral surface (1.60%) is observed at pH ≤ 2.0, which may be the result of the high metabolic activity of bacteria in most favourable environmental conditions. However, within a pH range of 2-6, the impact of this parameter on coverage degree is not very great, which is connected with the almost invariable near-PZS (zero charge point) zeta potential for the mineral and bacteria.

Ohmura et al. (1992) have proven that there is a linear dependence between bacteria adhesion and depression of pyrite floatability connected with the number of linked bacterial cells of *Acidithiobacillus ferrooxidans*. They also observed that, independently of bacterial suspension density, reduction of floatability to a constant level occurs within a few seconds after adding bacteria, with no significant changes observed afterwards. Different observations were recorded by Zeky and Attia (1987). They found that extended duration of contact with bacteria significantly influences suppression of pyrite floatability. However, in spite of these differences both authors attained a pyrite floatability reduction of approximately 90%. Moreover, it has been proven that the pyritic sulphur removal process is also influenced by bacterial metabolites and such substances as proteins and lipids, contained in a nutrient medium and formed from destroyed cells. However, the authors have noted that these are live bacterial cells and their number in suspension determines changes in pyrite surface hydrophobicity.

There have also been studies carried out on the impact of nutrient medium and culture conditions of *A. ferrooxidans* bacteria on pyrite flotation (Misra et al. 1995, Sharma et al. 2003, Tan and Chen 2012). It was proven that nutrient medium affects bacteria surface properties, and consequently their hydrophobicity. This is due to the high nutritive requirements of microorganisms during their growth phase. Consequently deficiency or excess of some constituents causes alterations in the properties of the bacterial cell surface, e.g., phosphate deficiency enhances the ability of *A. ferrooxidans* to adhere to the surface of pyrite and elementary sulphur (Amaro et al. 1993). The authors have also proven that at low pH values, pyrite surfaces undergo surface oxidation, resulting in the development of an elementary sulphur layer which increases hydrophobicity. Bacteria oxidise this layer into soluble sulphates while they adsorb on the pyrite surface; as a result the mineral becomes hydrophilic.

Particle size impact on biological flotation results is demonstrated in the next section. The impact of the particle size of coal on the efficiency of biological-flotation-based pyrite separation from coal was analysed by Ohmura and Saiki (1996). Two size ranges were used in these studies: 53-75 μm and 38-53 μm, which corresponded to the content of completely freed pyrite particles: 30.3% and 64.4%, respectively. It was proven that finer coal grains required the use of a greater density of *Acidithiobacillus ferrooxidans* bacterial suspension. Moreover, less pyritic sulphur was removed in that case. For size range 53-75 μm, best results were obtained for a bacterial suspension density of 0.5•109 cells/cm^3. In these conditions, 75% of pyrite contained in the feed material became waste, while coal recovery reached 71%. In the case of size range 38-53 μm, best results were obtained for a bacterial suspension density of 1.5•109 cells/cm^3. In these conditions, 62% of pyrite contained in feed material became waste, and coal recovery reached 42%. According to the authors, these results indicate that a critical amount of bacteria is needed to change pyrite floatability, while an excessive amount of bacteria also adheres to coal particles, causing coal floatability suppression and reducing its recovery level. Moreover, the authors observed that fine pyrite particles do not sink when bacteria are added, which confirms the impact of both the level needed to free pyrite particles and of the size of these particles on the effectiveness of the bioflotation process for this component.

Comparison of the effectiveness of conventional and biological flotation

In the case of coal enrichment, feed material for the flotation process includes particles under 0.5mm, and sometimes even under 1mm. Particles with low-energy surfaces, showing high natural hydrophobicity and considerable flotation activity, become enriched, whereas a gangue particles are not subject to flotation, due to their high surface energy resulting from the petrographic inhomogeneity of this material. As mentioned before, organic coal substances have hydrophobic properties, whereas the degree of hydrophobicity, as measured by contact angle, varies depending on maceral constitution. On the other hand, mineral substance constituents are hydrophilic. Contact angle decreases with an increasing degree of particle surface coverage by the mineral substance. Contact angle value also depends on surface roughness and presence of microcracks (Brożek and Młynarczykowska, 2008).

Flotation results of raw material are determined by many factors, including the method of preparation of the feed and its quality, that is, mainly particle size (Saramak 2012, Brożek and Młynarczykowska 2013)

As regards coal, we may state that yield of concentrate decreases with increasing coal grain size. This is caused by the effect of separation of low-ash particles, which turn into waste. Thus, ash content in concentrate grows with decreasing particle size. This is connected with the effect of mechanical flotation of gangue particles (hydrophilic particles) to froth product. The intensity of the above phenomena is closely related to the size of particles subject to flotation, physicochemical and hydrodynamic conditions inside the flotation chamber, and flotation rate (Brożek and Młynarczykowska, 2010). We should remember that in real conditions feed material, which is heterogeneous as regards its surface properties is subject to flotation. Additionally, flotation, like all technological processes, proceeds in time while many random factors affect its results. Among them is the scale of interactions between particles and air bubbles including the following subprocesses: collisions, adhesion or detachment. Mathematical descriptions of the flotation process taking into account the impact of these factors and various models, like probabilistic, adsorptive or stochastic, are provided in the following publications: Brożek and Młynarczykowska 2006, 2007, Brożek et al. 2003a, b.

In conventional coal processing, froth flotation with modifiers, e.g. depressors, is used for the purposes of selective separation of organic material from inorganic wastes, depending on their nature. In the case of enriching sulphated coals, this function is performed by cyanides with reference to pyrite. In view of to their toxicity and harmfulness to the environment, the researchers examined their usability in the bioflotation method for coal enrichment (Amini et al. 2009). Flotation tests were carried out for coal samples originating from Tabas Mine, with particle sizes of 0150µm and content of ash 27%, pyritic sulphur 1.42%, total sulphur 2.7%, and volatile matter 2.5%. Conventional flotation was carried out in a Denver machine for solid phase content 14%, and pH reaction 7.2, using sodium cyanide as depressor (1kg/t), kerosene as collector (1.2kg/t) and MIBC (0.24kg/t) as frothing agent. In the case of biological flotation, the only alteration was the use of *A. ferrooxidans* bacteria, amounting to 109 cells per 1 g of coal, as a depressor. During the tests, concentrate and waste samples being taken were analysed for sulphur and ash content. The results are shown in Figures 1-3.

The diagrams show the impact of flotation conditions and chemical and biological depressor additive on sulphur and coal yield. In the case of conventional flotation it is apparent that approximately 94% of combustible parts and 89% of sulphur was recovered within 210 sec. after froth collection. The use of bacteria, changed coal and sulphur floatability, with the result that approximately 95% of combustible parts and 75% of sulphur was recovered within 210 sec. after froth collection. Total yield of sulphur in concentrate decreased by approximately 14% as a result of re-

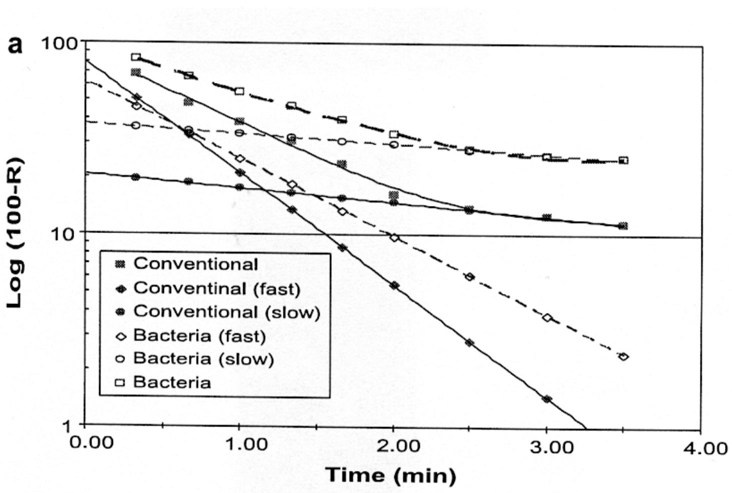

Fig. 1 Cumulative recovery of sulphur for conventional flotation and bioflotation (Amini E., 2009)

Rys. 1 Sumaryczny uzysk siarki we flotacji konwencjonalnej i bioflotacji (Amini E., 2009)

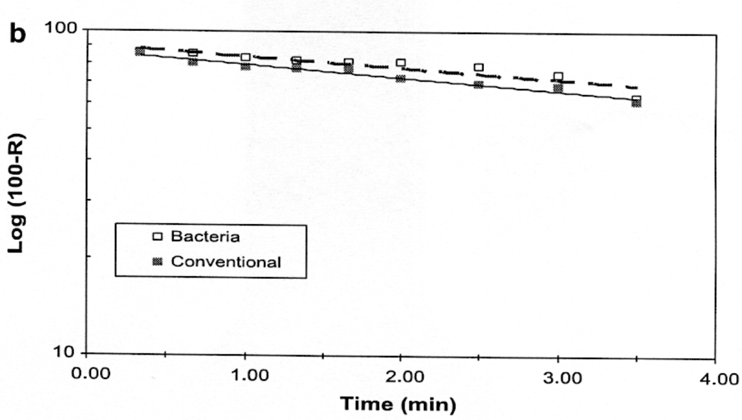

Fig. 2 Cumulative recovery of ash for conventional flotation and bioflotation (Amini E., 2009)

Rys. 2 Sumaryczny uzysk popiołu we flotacji konwencjonalnej i bioflotacji (Amini E., 2009)

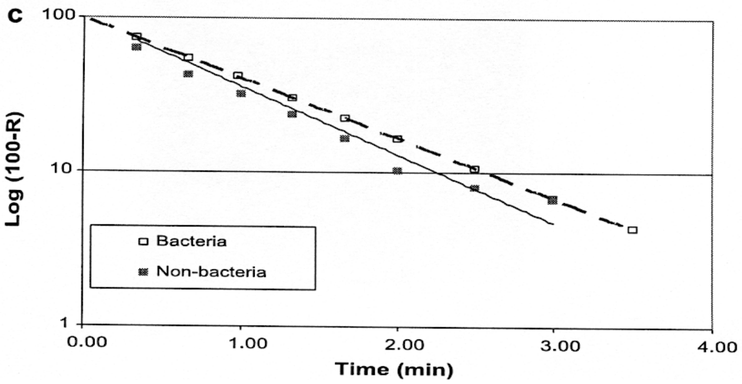

Fig. 3 Cumulative recovery of combustible materials for conventional flotation and bioflotation (Amini E., 2009)

Rys. 3 Sumaryczny odzysk części palnych we flotacji konwencjonalnej i bioflotacji (Amini E., 2009)

placing a conventional depressor, potassium cyanide, with *A. ferrooxidans* bacteria. The results indicate that microorganisms may be used as an alternative depressor for pyrite in the coal flotation process, thus affording an opportunity to replace detrimental chemical substances with bacteria, which are safer for the environment.

Summary

In the light of analyses carried out by researchers, developing technologies for full enrichment of power and coking coals should take into account the recycling of both enrichment products and non-coal products. Therefore, all studies should aim at developing methods for enrichment of ultra-fine coals, coal desulphurisation, removal of unwanted constituents from ash, and identification of agents enabling a reduction in costs and increased flotation effectiveness.

Taking into account the above trends of changes in coal processing technologies and ecological fuel production, biological desulphurisation would seem to be an attractive alternative to current methods for sulphur removal from fine coal. Using bacteria in the flotation process enables the duration of biological sulphur removal to be reduced from a few weeks, as in the leaching method, to a few minutes. Adsorption of microorganisms on the mineral surface reduces the pyrite flotation rate and improves selectivity of coal and waste rock separation. Moreover, it is possible to carry out flotation using bacteria instead of toxic substances, e.g. cyanides, eliminating the formation of aggressive flotation wastes.

Conducting a complex feasibility study may show the potential for using this method in processing plants which usually use flotation as a method for coal slurry enrichment. This technology may become highly ecological due to simultaneous coal desulphurisation.

In subsequent stages of their research, the authors will carry out verification of the described desulphurisation method for Polish coals with reference to variable conditions of the flotation process and selection of an optimal biological depressor guaranteeing proper operation under process conditions.

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Literatura - References

1. *Aller A., Martinez O., de Linaje J.A., Rosa Mendez R., Moran A., 2001. Biodesulphurisation of coal by microorganisms isolated from the coal itself. Fuel Processing Technology, 69, 45–57*
2. *Amaro A.M., Seeger M., Arredondo A., Moreno M., Jerez C.A., 1993. The growth conditions affect Thiobacillus ferrooxidans attachment to solids. Biohydrometallurgical Technologies, The Mineral, Metals and Material Society, 577-585*
3. *Amini E., Oliazadeh M., Kolahdoozan M., 2009. Kinetic comparison of biological and conventional flotation of coal. Minerals Engineering, 22, 344–347*
4. *Brożek M., Młynarczykowska A., Turno A., 2003a. The relationships between deterministic and stochastic models of flotation. Archives of Mining Sciences, 48, 3, 299-314*
5. *Brożek M., Młynarczykowska A., Turno A., 2003b. The distribution of the flotation rate constatnt in a sample of the to-component raw material. Archives of Mining Sciences, 48, 3, 521-532*
6. *Brożek M., Młynarczykowska A. (2006), Application of the stochastic model for analysis of flotation kinetics with coal as an example. Physicochemical Problems of Mineral Processing, 40, 31-44.*
7. *Brożek M., Młynarczykowska A. (2007), Analysis of kinetics models of batch flotation. Physicochemical Problems of Mineral Processing., 41, 51-65*
8. *Brożek M., Młynarczykowska A. (2008). The relation between the dispersive model of the particle and the distribution of permanent adhesion rate constant in the coal flotation process . Mineral Resources Management . 24 z. 4/1 s. 63–82*
9. *Brożek M., Młynarczykowska A (2010). Probability of detachment of particle determined according to the stochastic model of flotation kinetics. Physicochemical Problems of Mineral Processing. vol. 44 s. 23–34*
10. *Brożek M., Młynarczykowska A (2013). An analysis of effect of particle size on batch flotation of coal. Physicochemical Problems of Mineral Processing. vol. 49 s. 341–356*
11. *Cara J., Vargas M., Moran A., Gomez E., Martinez O., F.J. Garcia F.J., 2006. Biodesulphurization of a coal by packed-column leaching. Simultaneous thermogravimetric and mass spectrometric analyses. Fuel, 85, 1756–1762*
12. *Cardona I.C., Márquez M.A., 2009. Biodesulfurization of two Colombian coals with native microorganisms. Fuel Processing Technology, 90, 1099–1106*
13. *Cwalina B., Wilczok T., Dzierżewicz Z., Farbiszewska T., 1994. Bioekstrakcja siarki i metali z węgla oraz pyriteów węglowych. XII Międzynarodowy Kongres Przeróbki Węgla 23-27 maja 1994, Kraków*
14. *Dastidar M.G., Malik A., Roychoudhury P.K., 2000. Biodesulphurization of Indian (Assam) coal using Thiobacillus ferrooxidans. Energy Conversion & Management, 41, 375-388*
15. *Demirbas A., 2002. Demineralization and desulfurization of coals via column froth flotation and different methods. Energy Conversion and Management, 43, 885-895*
16. *Demirbas A., Balat M., 2004. Coal desulfurization via different methods. Energy Sources, 26, 541-550*
17. *Gawenda T., Olejnik T., (2008). Produkcja kruszyw mineralnych z odpadów powęglowych w kompanii węglowej S. A. na przykładzie wybranych kopalń,:. Mineral Resources Management. t. 24 z. 2/1 s. 27–42*
18. *Gomez F., Amils R., Marin I., 1997. Microbial ecology studies for the desulfurization of Spanish coal. Fuel Processing Technology, 52, 183-189*
19. *Hoffmann M.R., Faust B.C., Fern A.P., Hong H. Koo, Tsuchiya H.M., 1981. Kinetics of the Removal of Iron Pyrite from Coal by Microbial Catalysis. Appl. Environ. Microbiol., 42(2), 259-271*
20. *Juszczak A., Domka F., Kozłowski M., Wachowska H., 1995. Microbial desulfurization of coal with Thiobacillus ferrooxidans bacteria. Fuel, Vol 74, No. 5, 125-728*
21. *Kargi F., Robinson J.M., 1982. Removal of sulfur compounds from coal by thermofilic organism Sulfolobus acidocaldarius. Applied and Environmental Microbiology, vol.44, No.4, 878-883*

22. Kawatra S.K., Eisele T.C., 1997. Pyrite recovery mechanism in coal flotation. Int. Journal of Mineral Processing, 50, 187-201
23. Misra M., Bukka K., Chen S., 1996. The effect of growth medium of Thiobacillus ferrooxidans on pyrite flotation. Minerals Engineering, 9, 157-168
24. Nagaoka T., Ohmura N., Saiki H., 1999. A novel mineral flotation process using Thiobacillus ferrooxidans. Applied and Environmental Microbiology, 65, 3588-3593
25. Najafpour G.D., Azizan A., Harun A., 2001. Microbial desulfurization of Malaysian coal in batch process using mixed culture. IJE Transactions B: Applications, vol.15, No.3, 227-234
26. Ohmura N., Kitamura K., Saiki H., 1992. Mechanism of microbial flotation using Thiobacillus ferrooxidans for pyrite suppression. Biotechnology and Bioengineering, 41, 671-676
27. Ohmura N., Kitamura K., Saiki H., 1993. Selective adhesion of Thiobacillus ferrooxidans to pyrite. Applied and Environmental Microbiology, 59, 4044-4050
28. Ohmura N., Saiki H., 1996. Desulfurization of Pittsburgh coal by microbial column flotation. Applied Biochemistry and Biotechnology, 61, 339-349
29. Olsson G., Pott BM., Larsson L., Holst O., Karlsson H.T. Microbial desulfurization of coal and oxidation of pure pyrite by Thiobacillus ferrooxidans and Acidianus brierleyi. Journal of Industrial Microbiology 1995, Volume 14, Issue 5, pp 420-423
30. Pecina E.T., Rodríguez M., Castillo P., Díaz V., Orrantia E., 2009. Effect of Leptospirillum ferrooxidans on the flotation kinetics of sulphide ores. Minerals Engineering, 22, 462-468
31. Piotrowski Z., 2008. Properties of wet fly ash suspensions seasoned in hard coal mine underground. Gospodarka Surowcami Mineralnymi, Tom 24, Zeszyt 4/1
32. Saramak D.: Optimizing the performance of high-pressure grinding roll based ore enrichment circuits, Gospodarka Surowcami Mineralnymi, vol. 28 (4), 2012
33. Sharma P.K., Das A., Hanumantha Rao, Forssberg K.S.E., 2003. Surface characterization of Acidithiobacillus ferrooxidans cells grown under different conditions. Hydrometallurgy, 71, 285-292
34. Tan S.N., Chen M., 2012. Early stage adsorption behavior of Thiobacillus ferrooxidans on minerals I: an experimental approach. Hydrometallurgy, 119-120, 87-94
35. Twardowska I., 1995. Mikrobiologiczne odsiarczanie węgla. Przegląd Górniczy, 10, 29-33
36. Vilinska A., Hanumantha Rao K., 2008. Leptospirillum ferrooxidans sulphide mineral interactions with reference to bioflotation and bioflocculation. Transactions of Nonferrous Metals Society of China, 18, 1403-1409
37. Wilczok T., Buszman E., Cwalina B., Czogała J., 1981. Bakteryjne ługowanie pyriteu z węgla. Fizykochemiczne problemy mineralurgii, 13, 205-214
38. Zeky, M. E. L., Attia, Y. A., 1987. Coal slurries desulfurization by flotation using thiophilic bacteria for pyrite depression. Coal Prepar., 5, 15-37

Bioflotacja jako metoda alternatywna dla odsiarczania węgli – cz. I

Bioflotacja może być użyta jako proces usunięcia pirytu z węgla. Zaaplikowanie bakterii do flotacji z metodą ługowania skróciłoby okresy usuwania mikrobowego pirytu z kilku tygodni do kilku minut. Mechanizm bioflotacji bazuje na szybkim przyleganiu komórek bakterii o właściwościach hydrofilicznych do powierzchni pirytu, co zmieni cechy minerały z hydrofilicznych na hydrofobiczne. W konsekwencji powietrze wznosiłoby jedynie hydrofobiczne cząstki węgla, a piryt opadałby na dno komory flotacyjnej w postaci odpadu. Artykuł prezentuje możliwości użycia bakterii w procesie flotacji w miejsce toksycznych chemikaliów wraz z ich środowiskowymi i ekonomicznymi korzyściami.

Słowa kluczowe: bioflotacja, odsiarczanie, bakteria, siarczek pirytu, węgiel