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BIOLEACHING OF POLISH BLACK SHALE

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Heterotrophic pretreatment combined with autotrophic bioleaching of Polkowice black shale were studied. Combination of these two processes was introduced as two-stage process which turned out to be more efficient in the terms of metals extraction. The sequence of preliminary heterotrophic and further autotrophic bioleaching was found as most reliable processing manner, since heterotrophic process provides the material's surface area expansion, and therefore strong influences rate and efficiency of autotrophic leaching. Besides, it was found that tube bioreactors designed specially for hereby research ensure better processing condition than Erlenmeyer flasks in the terms of extraction speed and efficiency.

Key words: heterotrophic bacteria, autotrophic bacteria, bioleaching, black shale, tube bioreactor, copper, silver, leaching

INTRODUCTION

During our studies on bioleaching of sulfide minerals, various experimental conditions were tested. The influence of various parameters (temperature, pH, stirring conditions, leaching medium composition and solid to liquid phase ratio) on bioleaching effectiveness and kinetics were investigated. However, acidophilic bacteria of *Acidithiobacillus* type were the only one considered so far (Farbiszewska et al.,1994,1996,2003). Therefore, we have introduced a combination of two processes: autotrophic bioleaching and heterotrophic pretreatment in our latest researches.

We assumed that heterotrophic leaching should provides better extraction of metals ions from organometallic compounds in shale ores. These organometallic compounds cannot be dissolved with autotrophic microorganisms. However, the results of heterotrophic bioleaching in neutral medium, using very active autochthonic bacteria

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strains, revealed a marginal role of organometallic compounds in examined mineral materials, thus almost complete lack of biooxidation and poor metal extraction (Farbiszewska-Kiczma et al., 2005). Therefore, alternative two-stage process was taken under consideration. It involves preliminary heterotrophic treatment and further autotrophic bioleaching.

Heterotrophic bioleaching process involves biooxidation of organometallic bonds as well as various organic bonds. This provides mineral's surface area expanding and thus increasing material susceptibility to further autotrophic bioleaching. As a result, great increase of extraction efficiency can be observed (Farbiszewska-Kiczma et al., 2004).

This procedure was introduced in studies on leaching of polymetallic shale ore, called Polkowice black shale. Tube bioreactors designed by our research team were used in these bioleaching experiments (Farbiszewska-Kiczma et al., 2006).

The aims of these researches were:

- evaluate bioleachability of Polkowice black shale ore;
- establish reliable lab-scale pilot operations of process;
- optimize configuration and settings.

MATERIALS AND METHODS

Examined material was black shale ore from Polkowice mine, containing among others 13.94% Cu and 148/t Ag. Particle size was within range of 0.4 to 2 mm. Bioleaching processes were carried out in Erlenmeyer flasks and in tube bioreactors with five beds.

BIOLEACHING IN ERLENMEYER FLASKS

Bioleaching in Erlenmeyer flasks was performed in two ways. First process was 35 days autotrophic bioleaching, while second included 25 days heterotrophic pretreatment and then 35 days autotrophic bioleaching.

In first process to each of three flasks containing 70 g of pretreated black shale ore, 350 dm^3 of leaching medium 2 K was added. Before that, leaching medium was inoculated with mixture of autochthonic bacteria strains *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. Mixture ratio was 1:1. Process was carried out 35 days at temperature 25ºC, pH=1.8. Another three control flasks were supplied with thymol – bacteriostatic substance. Both bacterial and control systems were aerated and stirred with magnetic stirrers, pH was regulated daily to value 1.8. At the end of process contents of Cu and Ag in treated ore were examined.

In second process 350 dm^3 of mineral solution was added to each of three flasks containing 70g of black shale ore. After that, flasks were inoculated with a mixture of active, autochthonic, non-antagonistic bacteria strains. Thymol was added to control flasks. Process was performed 25 days at temperature 25ºC. pH was regulated daily to value 7, and all flasks were stirred with magnetic stirrers. At the end of process, the

contents of Cu and Ag in treated ore were examined. Then, the material was dried and flushed with H_2SO_4 water solution, bringing pH value to 1.8. After that operation, autotrophic bioleaching was started using 2 K medium and autochthonic bacteria strains *Acidithiobacillus ferrooxidans* and *Acidithiobacillus* mixed in the ratio of 1:1. The control flasks were supplied with thymol. All flasks were placed on magnetic stirrers. Bioleaching process was performed 35 days at the temperature 25ºC, pH was regulated daily to value 1.8. At the end of process the contents of Cu and Ag in treated ore were examined.

BIOLEACHING IN BIOREACTORS

Process was carried out in tube bioreactors designed by our research team. Each bioreactor contained 1250 g of black shale ore (250 g per bed) and 3750 dm^3 of irrigating 2 K medium inoculated with autochthonic bacteria strains *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* mixed in the ratio of 1:1. Control system was supplied with thymol. Bioreactors were aerated with bubbler. Process was carried out 25 days at temperature 25ºC. At the end, the contents of Cu and Ag in treated ore were examined.

RESULTS AND DISCUSSION

After 35 days autotrophic bioleaching performed in Erlenmeyer flasks, black shale ore metallization decreased from 13.94% Cu and 148g/t Ag to 8.25% Cu and 132g/t Ag. It means that, 40.82% of Cu and 10.81% of Ag were extracted (Fig.1.). In control systems the contents of Cu and Ag were respectively 12.30% and 141g/megagram (Mg), it means that, 11.77% of Cu and 4,73% of Ag were extracted (Fig. 1.).

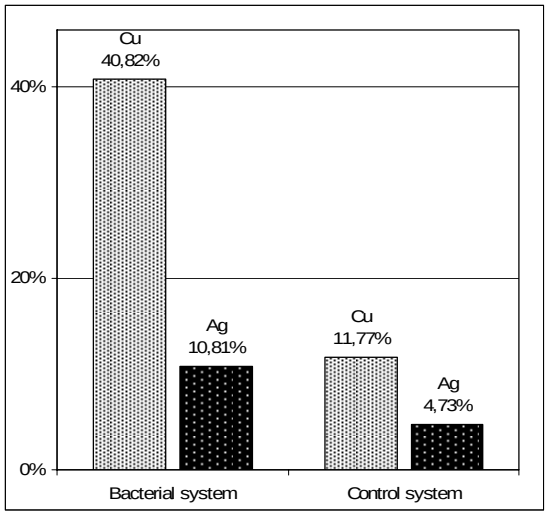

Fig. 1. Percentage of Cu and Ag extracted from ore after 35 days autotrophic bioleaching in Erlenmeyer flasks (process 1: autotrophic bioleaching only)

After 25 days heterotrophic bioleaching in Erlenmeyer flasks black shale ore the metallization decreased to 13.80% and 139 g/Mg of Ag. It means that the contents of Cu and Ag were decreased respectively by 1.0 and 6.08% (Fig.2.). The contents of Cu and Ag in control systems were 13.83% and 142 g/Mg (0.79% of Cu and 4.05% of Ag extracted) (Fig. 2.).

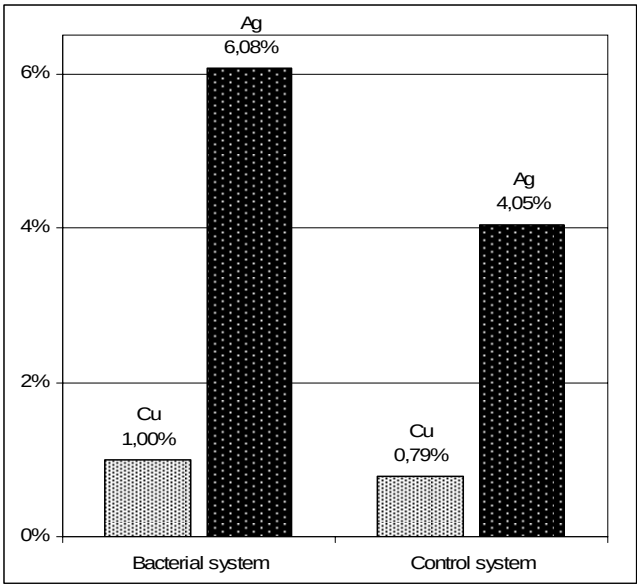

Fig. 2. Percentage of Cu and Ag extracted from ore after 25 days heterotrophic bioleaching in Erlenmeyer flasks (process 2 – stage 1: pretreatment)

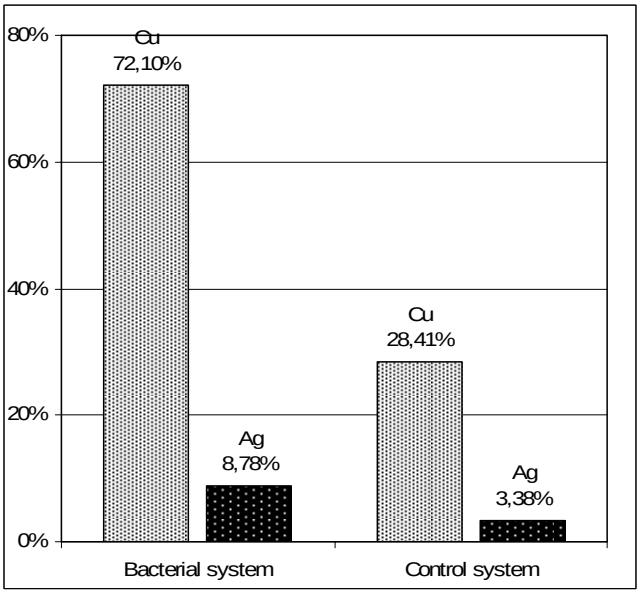

Fig. 3. Percentage of Cu and Ag extracted from pretreated ore (25 days heterotrophic treatment) after 35 days autotrophic bioleaching (process 2 – stage 2: autotrophic bioleaching)

After ore acidification to pH=1.8, further 35-days autotrophic bioleaching in Erlenmeyer flasks was carried out, at the end of bioleaching process 3.75% of Cu and 126g/t of Ag remained in ore. In this process 72.1% of Cu and 8.78% of Ag were extracted (Fig. 3). The contents of Cu and Ag in control systems were 9.87% and 137g/t (that means 28.41% of Cu and 3.38% of Ag were extracted) (Fig. 3.) In total, in both heterotrophic and autotrophic bioleaching experiments 73.1% of Cu and 14.86% of Ag were extracted. The chemical leaching has extracted 29.2% of Cu and 7.43% of Ag.

After 25 days autotrophic bioleaching in bioreactor, the contents of Cu and Ag in shale decreased to 3.33% and 75 g/Mg respectively (13.44% and 133 g/Mg in a control system). Thus, 76.17% of Cu and 49.32% of Ag were extracted in bacterial system, while 3.59% of Cu and 10.14% of Ag in control system (Fig. 4.). Autotrophic bioleaching in tube bioreactor, which lasted 25 days only, was more efficient (3.07% in case of Cu and right up to 34.46% in case of Ag) than two-stage bioleaching in Erlenmeyer flasks. One should notice that process in bioreactor lasted 35 days shorter. The amount of material was 18 times greater and the solid to liquid phase ratio was 1:3 instead 1:5.The percentage of extracted Cu (76.17%) in tube bioreactor was almost two times greater than in flask after 35 days (40.82% - autotrophic bioleaching) and comparable to those in flask after 60 days (73.1% - heterotrophic and autotrophic bioleaching). The percentage of extracted Ag in bioreactor was 4/3 times greater than those in flasks (for autotrophic/autotrophic after heterotrophic bioleaching respectively).

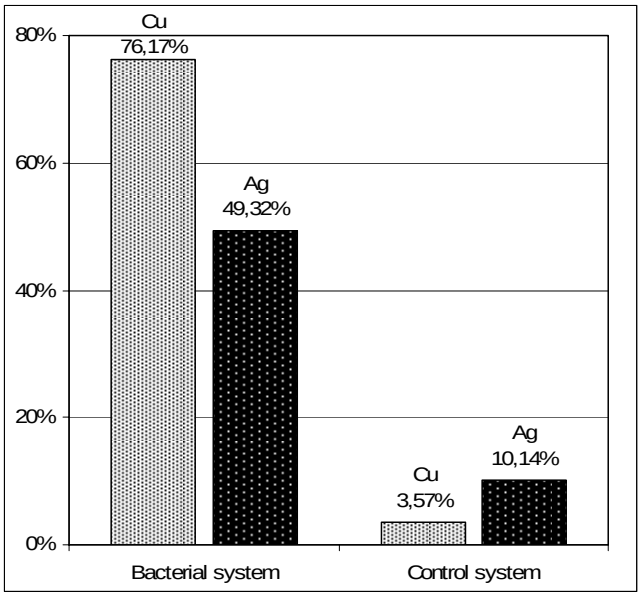

Fig. 4. Percentage of Cu and Ag extracted from ore after 35 days autotrophic bioleaching in tube bioreactors

CONCLUSIONS

1. Black shale ore from Polkowice mine is amenable to bioleaching.
2. Heterotrophic bioleaching of Polkowice ore provides the surface area expansion and an increase of efficiency of autotrophic bioleaching.
3. Bioleaching process runs more effective in tube bioreactors than in Erlenmeyer flasks.
4. The most reliable way to processing Polkowice black shale ore seems to be a two-stage bioleaching process (heterotrophic bioleaching prior to autotrophic) which will be conducted in tube bioreactors.

ACKNOWLEDGEMENT

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REFERENCES

FARBISZEWSKA T., CWALINA B., FARBISZEWSKA-BAJER J., Dzierżewicz Z., 1994, *The use of bacterial leaching in the utilization of wastes resulting from mining and burning lignite,* Acta BIOLOGICA CRACOVIENSIA, SERIAS: BOTANICA, 36,1-8.

FARBISZEWSKA T., CWALINA B., 1996, *Metabolic activity of autochthonous and museum strains of Thiobacillus ferrooxidans,* Acta Biologica Cracoviensia, serias: Botanica, 38, 1-8.

FARBISZEWSKA T., FARBISZEWSKA-KICZMA J., BĄK M., 2003, *Biological extraction of metals FROM A POLISH BLACK SHALE,* Physicochemical Problems of Mineral Processing, 37, 51-57.

FARBISZEWSKA-KICZMA J., FARBISZEWSKA T., 2005, *Isolation of bacteria that degrade organometallic compounds from metallic wastes,* Physicochemical Problems of Mineral Processing, 39, 263-267.

FARBISZEWSKA-KICZMA J., FARBISZEWSKA T., BĄK M., 2004, *Bioleaching of metals from polish black shale in neutral medium,* Physicochemical Problems of Mineral Processing, 2004, 38, p. 273-280.

FARBISZEWSKA-KICZMA J., FARBISZEWSKA T., GROBELSKI T., KICZMA B., 2006, *Bioleaching in tube reactors for utilization of metallurgical wastes,* Proceedings Central European Conference ECOpole ’06, Hradec-Kralove – Jamrozowa Polana, 18-20.

Grobelski T., Farbiszewska-Kiczma J., Farbiszewska T., *Bioługowanie polskiego czarnego łupka*, Physicochemical Problems of Mineral Processing, 41 (2007) 259-264 (w jęz. ang.).

Zostały przeprowadzone badania nad wykorzystaniem kombinacji procesów bioprzygotowania z użyciem bakterii heterotroficznych i bioługowania za pomocą bakterii autotroficznych próbek rudy łupkowej otrzymanej z kopalni Polkowice. Kombinacja tych dwóch procesów została przedstawiona jako proces dwu-stadialny, który zapewnia bardziej efektywniejszą ekstrakcje metali z surowca mineralnego. Kolejność realizacji procesu dwu-stadialnego okazała się być bardziej skuteczna, gdyż proces z użyciem heterotroficznych mikroorganizmów powoduje, że powierzchnia surowca staje się bardziej podatna na bioługowanie z użyciem autotroficznych mikroorganizmów. Dodatkowo zostało wykazane, że reaktory rurowe, specjalnie zaprojektowane do tych badań, były lepsze w porównaniu do procesu realizowanego w kolbach stożkowych.