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BIOLOGICAL EXTRACTION OF METALS FROM A POLISH BLACK SHALE

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The black shale ore is characterized by variable content of metals. In black shale metals occur in form of sulphides and sandwich compounds in which metals create organometalic connections with hydrocarbons. The method of flotation is successfully used to enriching sandstone and carbonate ores but this method is not effective for the shale ore. In existing technology of shale ore enriching, this ore is in considerable degree not used and passes to waste material. In this study, the bioextraction process was carried out with a Polish cupriferous black shale ore coming from Lubin-Głogów region on a large laboratory scale. This process was carried out in the „Biomel" batch reactor during 28 days with temperature control (40^o C), continuous aeration and mixing (300 r.p.m.). There were used two bacterial cultures *A.ferooxidans* F7-01 and *A.thiooxidans* T1- 01. Simultaneously, a control test was performed with thymol as a bacteriostatic substance. A concentration of Cu, Ni, Zn, Pb ions was determined by ASA method every three-four days. The results of investigations confirm our assumptions that Polish black shale ore could be a source of many metals by bioleaching in acid medium. We can suggest that 50% of copper contained in shale is a chalcocite because bioleaching of them was the most effective. The effect of bioleaching sphalerite contained in black shale ore was very low. We have not succeed in bioleaching galena. The following conclusion can be drown: batch strains used in our study convert PbS into $PbSO_4$, which is sparingly soluble and forms precipitate.

Key words: bioleaching, black shale ore

INTRODUCTION

The Lubin deposits of a black shale ore are structured from three litological forms: carbonate, sandstone, shale. The most interesting one and the most rich in copper and many of other metals is the shale layer.

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The black shale ore is characterized by variable content of metals and contains on average 5,5% Cu and also, among other metals, about 0,01% Ag, 0,03% V. This ore is created with bituminous shale, which consists mostly from clay minerals, carbonates, organic matter and detritus quartz (Kucha, Mayer, 1996).

In bituminous shale metals occur in form of sulphides and sandwich compounds in which metals create organometalic connections with hydrocarbons (Sawłowicz, Speczik, 1996).

The method of flotation is successfully used to enriching of sandstone and carbonate ores but this method is not effective for shale ore because of its properties. In existing technology of shale ore enriching, this ore is in considerable degree not used and passes to waste material. From several years it has been known, that shale ore should be enriched separately with usage of a new method.

MATERIALS AND METHODS

In this study, the bioextraction process was carried out with a Polish cupriferous black shale ore coming from Lubin-Głogów region. Our initial treatment of shale by sulphuric acid were aimed for removing base-forming minerals. After pre-treatment this shale contained 5,6% Cu, 0,017% Ni, 0,67% Pb, 0,2% Zn, 0,014% Mo, 0,035% V, 0,03% As. Samples of autochthonous *Acidithiobacillus* bacterial strains were isolated and adapted to Cu, Ni, As, Ag cations (Kelly et al. 2000). There were used two bacterial cultures *A.ferrooxidans* F7-01 and *A.thiooxidans* T1-01 stored in Practical and Experimental Biology Department of University of Opole (Farbiszewska et al. 2002).

Bioleaching process was carried out by 28 days in the „Biomel" batch reactor with temperature control (40^{o} C), continuous aeration and mixing (300 r.p.m.). There was placed 800 g black shale ore into 3200 cm^3 leaching medium (Mg^{2+}, SO_4^{2-}, K^+, HPO_4^{2-}, NH_4^+, Fe^{2+}) and 800 cm^3 inoculum. The active bacteria strains presented in culture were F7-01 and T1-01 in ratio 1:1. The concentration of ions in medium was determined as 5g in 1 dm^3. All pH measurements were performed at the reaction temperature and it held on a level pH 2.

Simultaneously there were two control systems, designing as K_1 and K_2. Control tests were performed with 800 g of a black shale ore and 4000 cm^3 leaching medium. There was introduced 25g thymol as a bacteriostatic substance to K_2. A concentration of Cu, Ni, Zn, Pb ions was determined by ASA method every three-four days.

RESULTS AND DISCUSSION

Bioleaching process of cupriferous shale was carried out in acid medium on a large laboratory scale. There were compared amounts (in percentages) of extracted Cu, Ni, Zn, Pb in succeeding days of process duration.

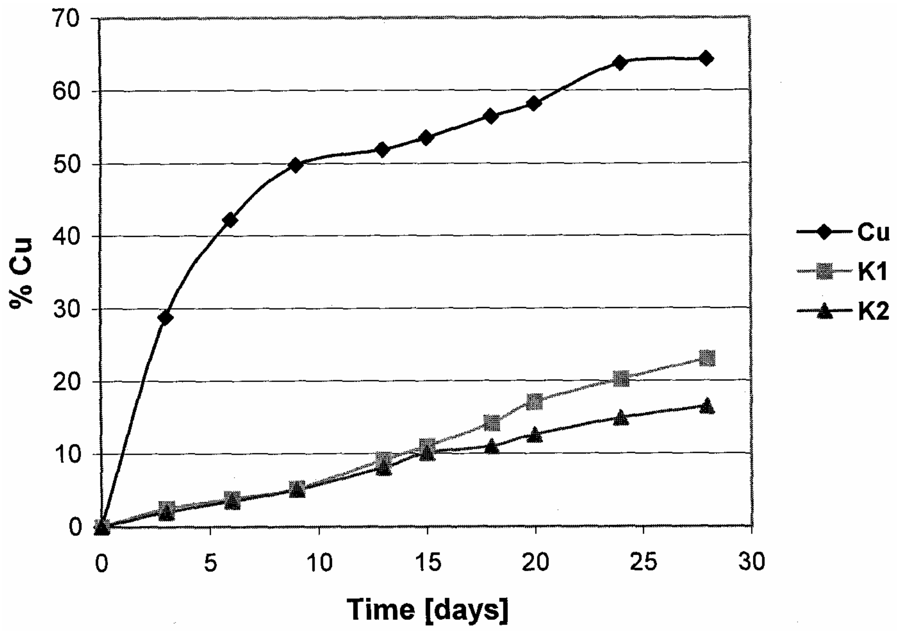

Fig. 1. Percent of copper leached with *A.ferrooxidans* F7-01 and *A.thiooxidans* T1-01

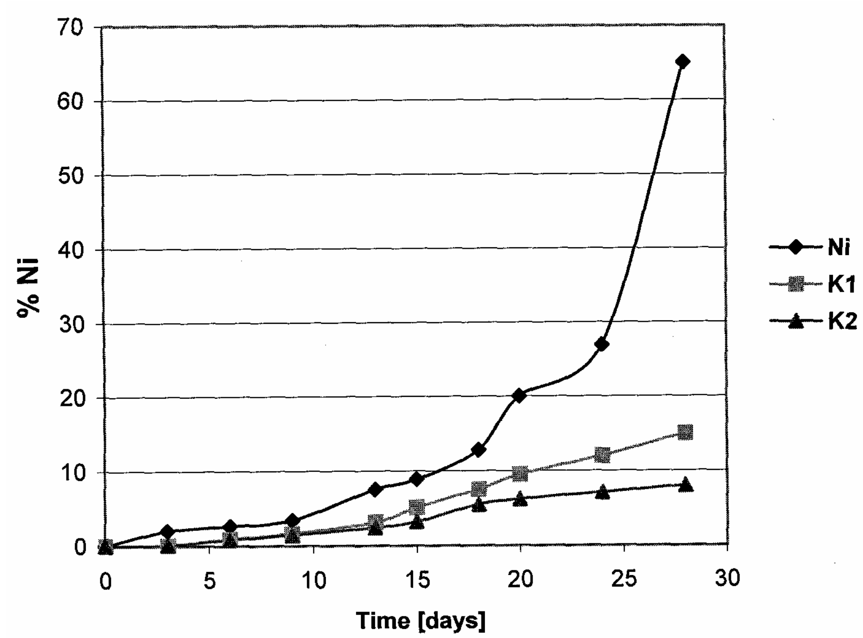

Fig. 2. Percent of nickel leached with *A.ferrooxidans* F7-01 and *A.thiooxidans* T1-01

Figure 1 shows extension of the leaching process in the batch and control systems. These results indicate that the process run most intensely in first six days of its duration. In this period 42,23% of copper contained in shale ore was leached. In simultaneous control test K_1 only 5,1 % of copper was extracted that imply a bioleaching character of this process. For next 22 days the dynamics of process grew smaller. In the batch system, control systems K_1 and K_2 adequate 64,3%, 23% and 16,5% of copper were extracted. We can conclude that 47,8% of copper in the batch system was obtained in a bioleaching process and 16,5% of copper obtained in K_2 system were chemically leached. The leaching process in the first phase coursed in K_1 control system similarly as in system K_2 and had a chemical character. Since thirteenth day a intensive growth of the leaching rate of copper was observed in K_1. We can state that considerably grew larger activity of chemolithoautotrophs batch delivered to system together with black shale ore. The initial activity of them was not large and their development occurred after dozen days.

Nickel bioleaching kinetics (see Figure 2) show quite different courses than copper bioleaching kinetics. In this case, leaching process in the batch system increases very slowly during first 13 days. When 50% of copper was extracted, impetuous nickel bioleaching begun than in creases. In 28 day of process duration 65% of nickel included in black shale ore was removed. Similar results, only with low efficiency were obtained in control system K_1. Comparing course of process in K_1 to changes in control system K_2 we could observe in this control test the bioleaching process by autochthonous bacteria strains besides chemical leaching.

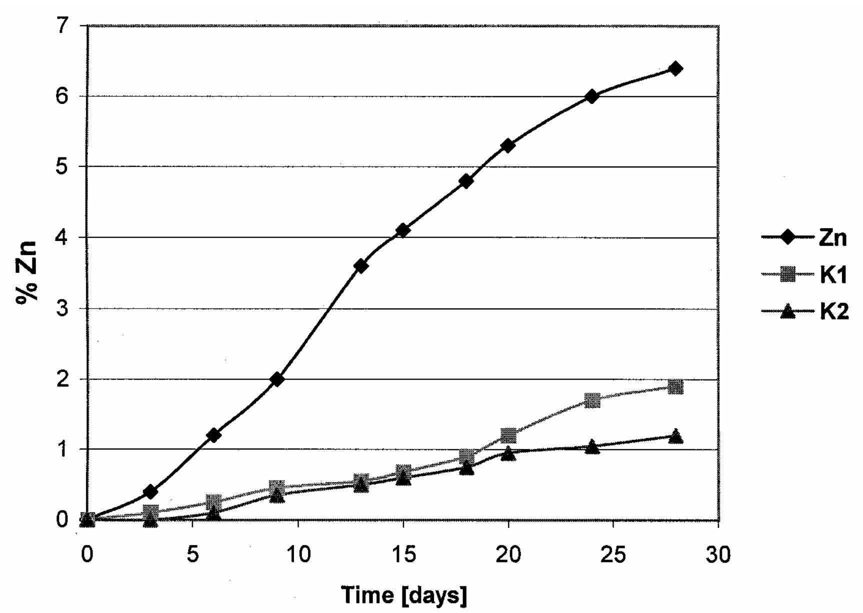

Fig. 3. Percent of zinc leached with *A.ferrooxidans* F7-01 and *A.thiooxidans* T1-01

Results, shown in Figure 3, reveal poor efficiency of zinc bioleaching process. In this manner, zinc minerals contained in black shale ore can be classified as slightly bioleachable. These results were consistent with those reported in literature (Muszer 2002).

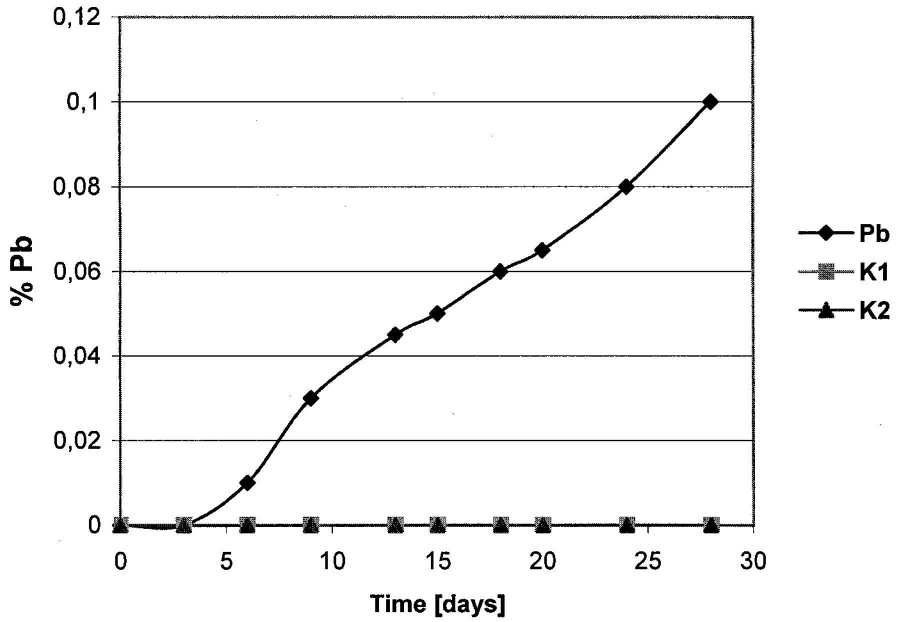

Fig. 4. Percent of lead leached with *A.ferrooxidans* F7-01 and *A.thiooxidans* T1-01

As shown in Figure 4 shape of curves proves that the lead sulfide, contained in black shale ore is biologically unleached and the results obtained agree with previous studies (Karavaiko et al. 1989).

CONCLUSIONS

The results of investigations confirm our assumptions that Polish back shale ore could be a source of many metals by bioleaching in acid medium. The initial stage of the process was bioleaching of copper sulphide. When 50% of this compound was extracted, a process of nickel bioleaching started. Considering our results, we can suggest that 50% of copper contained in shale is a chalcocite because bioleaching of them was the most effective (Karavaiko et al. 1989, Muszer 2002).

The effect of bioleaching sphalerite contained in black shale ore was very low. We have failed to bioleach galena. The following conclusion can be drown: batch strains used in our study convert PbS into $PbSO_4$, which is sparingly soluble and forms precipitate.

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Lubińskie złoża rud miedzi zbudowane są z trzech odmian litologicznych: węglanowej, piaskowcowej i łupkowej. Najbogatsza w miedź i wiele innych metali jest warstwa łupkowa. Charakteryzuje się ona zmienną zawartością metali i zawiera średnio 5,5% Cu, a także między innymi około 0,01% Ag, czy 0,03% V. Tworzą ją przede wszystkim łupki bitumiczne, które składają się głównie z minerałów ilastych, węglanów, substancji organicznej i detrytycznego kwarcu. W łupkach bitumicznych metale występują w formie siarczków i tzw. związków „sandwiczowych", w których metale tworzą połączenia organometaliczne z węglowodorami, np. porfiryny niklowe. Właściwości rudy łupkowej czynią ją niewzbogacalną metodą flotacji, stosowaną z pozytywnym skutkiem do wzbogacania rud piaskowcowych i węglanowych. W istniejących technologiach wzbogacania ruda łupkowa jest w znacznym stopniu niewykorzystana i przechodzi do odpadów. Od wielu lat wiadomo, że ruda ta winna być wzbogacana osobno, właściwymi dla niej metodami, ale dopiero od niedawna nowe technologie eksploatacyjne umożliwiają oddzielne pozyskiwanie łupka. W tej sytuacji wydaje się zasadne prowadzenie badań nad biohydrometalurgiczną przeróbką rudy łupkowej.

W pracy przedstawiono wyniki bioekstrakcji polimetalicznego, smolistego łupka miedzionośnego, pochodzącego z rejonu lubińsko-głogowskiego. Po wstępnej obróbce zawierał on: 5,6% Cu, 0,017% Ni, 0,67% Pb, 0,2% Zn, 0.014% Co, 0,014% Ag, 0,014% Mo, 0,035% V, 0,03% As. Materiał biologiczny stanowiły, wcześniej wyizolowane i zaadaptowane do jonów Cu, Ni, As i Ag, autochtoniczne szczepy bakterii rodzaju *Acidithiobacillus*. Były to szczepy *A.ferrooxidans* F7-01 i *A.thiooxidans* T1-01, przechowywane w muzeum szczepów Katedry Biologii Stosowanej i Eksperymentalnej Uniwersytetu Opolskiego. Proces prowadzono w dużej skali laboratoryjnej w bioreaktorze. Oceniając przebieg bioługowania porównano wyrażoną w procentach ilość wyługowanej miedzi, niklu, cynku i ołowiu w kolejnych dniach trwania procesu. Stwierdzono, że polski łupek miedzionośny bardzo łatwo ulega procesowi bioługowania w środowisku kwaśnym. Najpierw bioługują siarczki miedzi, a dopiero po ich połowicznym wyługowaniu rozpoczyna się bioługowanie niklu. Należy przypuszczać, że 50% miedzi zawartej w łupku to miedź chalkozynowa, gdyż minerał ten bioługuje się najłatwiej. Po wyługowaniu chalkozynu (Cu_2S) rozpoczyna się bioługowanie niklu. Zawarty w łupku sfaleryt (ZnS) bioługuje bardzo słabo, a bioługowania galeny PbS nie stwierdzono.