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COMPARISON OF KINETICS OF BLACK SHALE BIOLEACHING PROCESS USING STATIONARY AND AGITATED SYSTEMS

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In the study, the kinetics of black shale ore bioleaching process, carried out in small column and tank reactor, was investigated. During all experiments the concentration of Cu^{2+} ions in the leaching solution was determined as a function of leaching time. Based on the results obtained, kinetics of bioleaching processes in the agitated tank reactor and column reactor were compared. The rate of bioleaching in column was similar to that in agitated tank. For the experiments in column, two different types of packing materials (plastic bullets and sawdust) were tested in order to improve the bed porosity. The results showed that sawdust was the best packing material used in this study.

Key words: bioleaching, tank, column, black shale, packed bed, sawdust, plastic support, kinetic

INTRODUCTION

There are two fundamental mechanical systems using for bioleaching processes: dispersed (agitated) and stationary solid beds. The stationary solid bed can be applied for beds of a good porosity and permeability for the solvent. For the fine minerals particles agitated systems are more suitable.

The heap leaching process may be considered as heterogeneous fixed bed reactor, where the leaching solution circulates through the ore bed. The fractional void space occupied by the leaching solution depends on the particle size. During the bioleaching process, the bacteria diffuse from the leaching solution into porous medium and react with sulfide particles.

According to Lizama, (2004) the mechanics of heap leaching systems includes a particle size, particle composition and fluid flow phenomena inside the column. The fluid flow through the particle bed is important for the heap leaching operation. The

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leaching kinetics are proportional to the irrigation rate divided by heap height (Lizama et al., 2005).

Under these conditions, an important parameter is the effective external area of the solid particles wetted by the leaching solution and colonized by bacteria cells. The kinetic analyses of bioleaching data were interpreted according to the colonization shrinking core model (Lizama et al., 2005).

Bioleaching in column with recirculation of the leaching liquid is a lab-scale simulation of heap bioleaching processes (Long et al., 2004).

Understanding of the liquid flow phenomena inside the packed bed is important to enhance the bioleaching performance. The milli-Ct scanner has been used to determine the pore structure of the packed column before and after bioleaching. The application of this sophisticated technique give an opportunity to establish a fundamental relationship between pore microstructure and effective transport coefficient (Lin et al. 2004, 2005).

The purpose of this article is to compare the kinetics of bioleaching processes using stationary solid bed and dispersed solid systems. The paper considers also the effect of different materials (shavings, plastic) added to the mineral bed on the column bioleaching kinetic.

EXPERIMENTAL

MATERIALS AND MICROORGANISMS

The materials obtained from Lubin mine were fine powder with the mean particle size of 34.1 (sample A) and 43.3 µm (sample B). The particle size distribution for two black shale samples are presented in Fig. 1 and Fig 2. The chemical analysis has revealed that copper grade in these materials were 7.04 % and 2.32 % sample A and sample B, respectively.

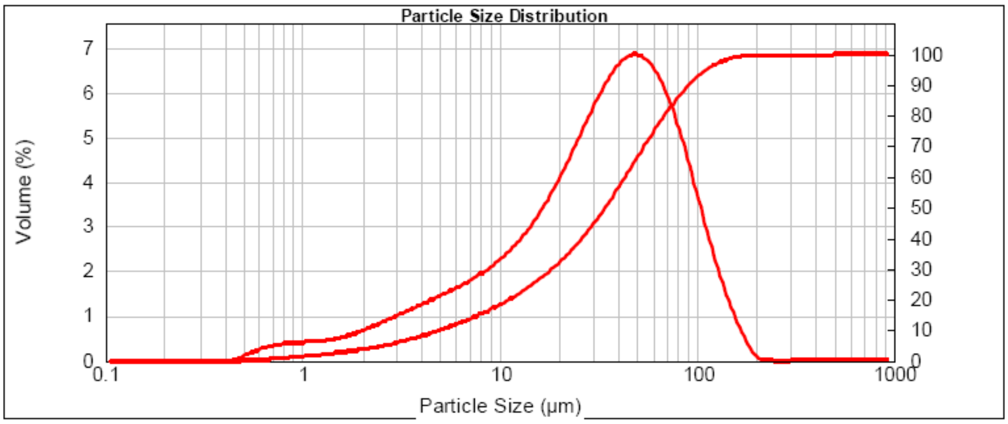

Fig. 1. Particle size distribution of black shale sample “A”

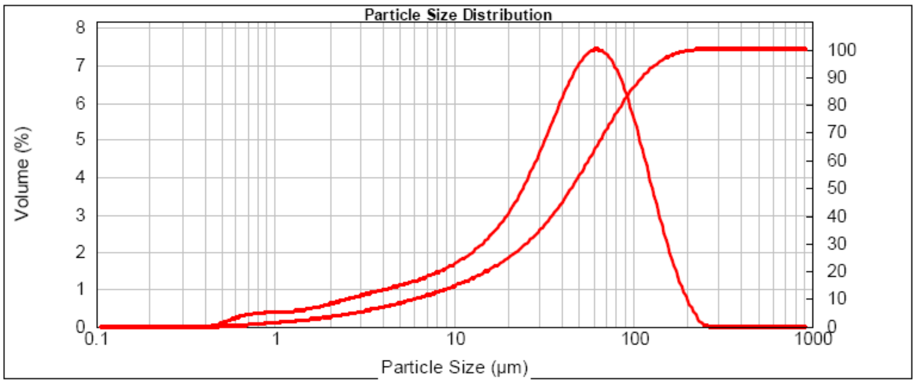

Fig. 2 Particle size distribution of black shale sample "B"

Support materials

The support materials used in this study were polyethylene spheres (3 mm in diameter) and wood sawdust (size range of 2-10 mm).

Bacteria strains

Microorganisms used in both column and tank leaching experiments can be classified as heterotrophic and autotrophic bacteria. The culture of *Streptomyces setonii* purchased from ATCC. The Actinomycetes *Streptomyces setonii* is known to degrade some types of coal organic compounds. The culture of chemolithotrophic bacteria such as *Acidithiobacillus ferrooxidans,* isolated from water samples taken from Zloty Stok old arsenic mine, was used to bioleaching procedure. The culture was adapted to grow with the high As and Cu ions concentration.

APPARATUS

Column bioleaching

Column leaching experiments were conducted in small column (37cm/5.0cm). The column was charged with 70 g of black shale material. The charges for column experiments when a support was used, were prepared by mixed 70 g of sawdust and 70 g of shale powder or 13.5 g of plastic bullets and 70 g of shale sample. The leaching solution (200 cm^3) was pumped from the feed container to the top of the column. Also, the gas (air) was introduced at the top of column, where a layer of leaching solution was created during the leaching tests.

Tank bioleaching

The leaching experiments were carried out in 8-dm^3 tank bioreactor with one propeller. The temperature and pH of the solution in the bioreactor were monitored and maintained at the designated pH by the addition of concentrated sulfuric acid. The temperature of the process was maintained at 30^0 C, using the circulating water bath.

Parameter measurement

The particle size distribution has been obtained by powder analysis using a laser diffractiometer Mastersizer 2000 (Malvern Instruments G.B). During the experiments Cu^{2+}, Fe^{2+}, Fe^{3+} ions and protein concentrations, as well as pH and Eh have been measured.

Two stage bioleaching process

The residues obtained in the heterotrophic leaching stage were treated with H_2SO_4 in order to remove carbonate minerals. The residues were then bioleached with autotrophic bacteria with fresh nutrient medium and new inoculum.

RESULTS

In black shales, the fine metal sulfide particles are dispersed in the carbon-organic matter. The role of heterotrophic microorganisms is biodegradation of organic matter compounds in order to release metals and metal sulphides from it.

TANK BIOLEACHING

The initial stage of the study was consisted in evaluation of effectiveness of the two stages bioleaching process, conducted in tank reactors, for two shale samples (A and B). The results of bioleaching by heterotrophic bacteria *Streptomyces setonii* are presented in Fig 3.

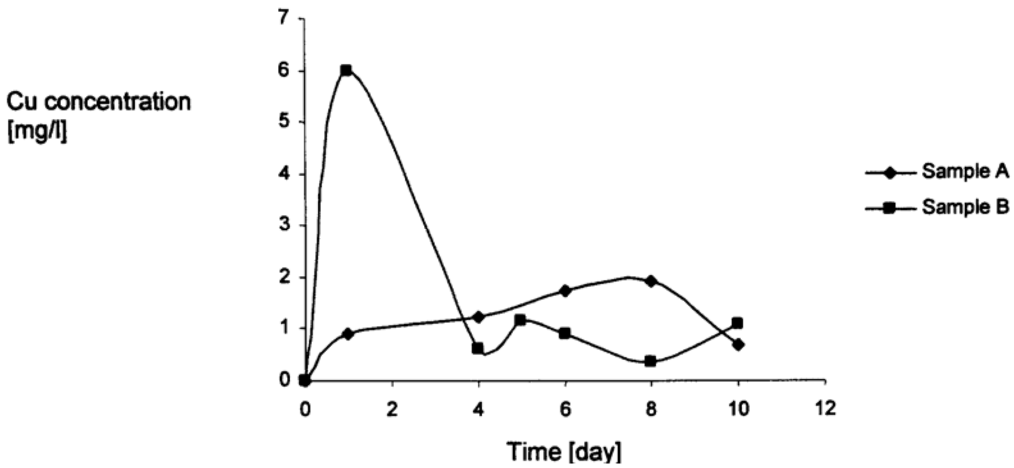

Fig. 3. Heterotrophic bioleaching of black shale samples

As can be seen, a low concentration of copper ions in the leaching solution resulted in a strong biosorption of Cu^{2+} ions by microbial cells.

The second stage of bioleaching procedure was preceded by carbonates neutralization with sulphuric acid (partially atmospheric leaching). From this reason the initial copper concentrations were much higher, then it was after heterotrophic bioleaching.

As can seen from Fig. 4, a continues increase of copper concentration was observed during two weeks autotrophic bioleaching. The differences in the yield of the process of the two samples is due to various content of copper in them.

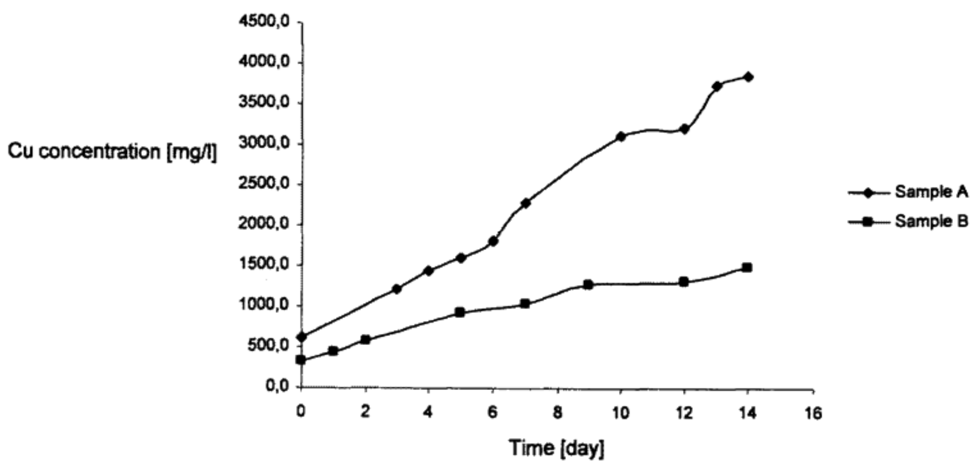

Fig. 4. Autotrophic bioleaching of black shale samples

COLUMN BIOLEACHING

The bed permeability is an essential process parameter, in the case of column bioleaching. The particle size distributions of shale samples (Fig. 1 and 2) showed that both materials contain a lot of fine particles. The amount of fine particles is a key parameter. It was recommended that the fine fraction should be less then 10 % (Lin et al., 2004, 2005).

The present work shows the influence of two supports (plastic and sawdust) on the bioleaching kinetics of shale samples in the trickle packed bed reactor (TBR).

It was observed that bioleaching rate rapidly increased with a sawdust as the support. This fact is connected with an immobilization of bacterial cells onto the sawdust surface. The decrease in the end of bioleaching can be connected with iron salts precipitation on the mineral surface and the occlusion of copper ions.

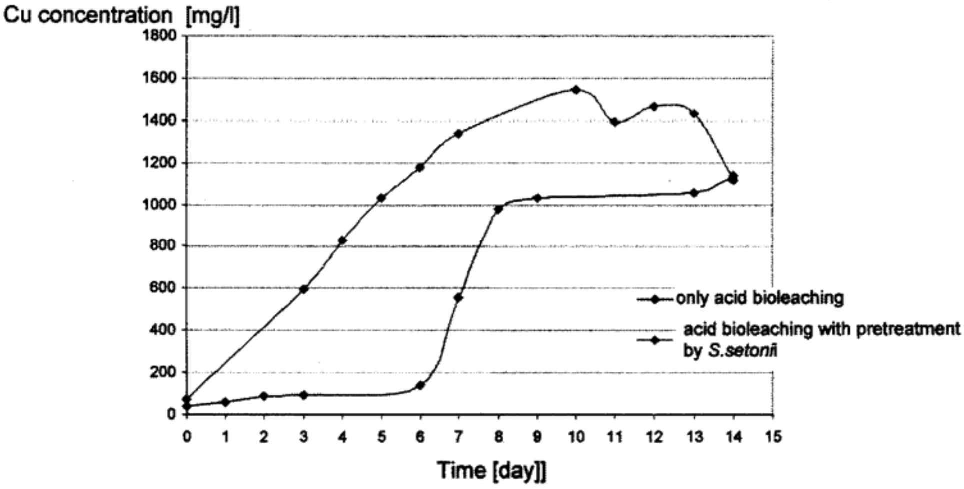

Fig. 5. Comparison of autotrophic bioleaching with or without heterotrophic leaching

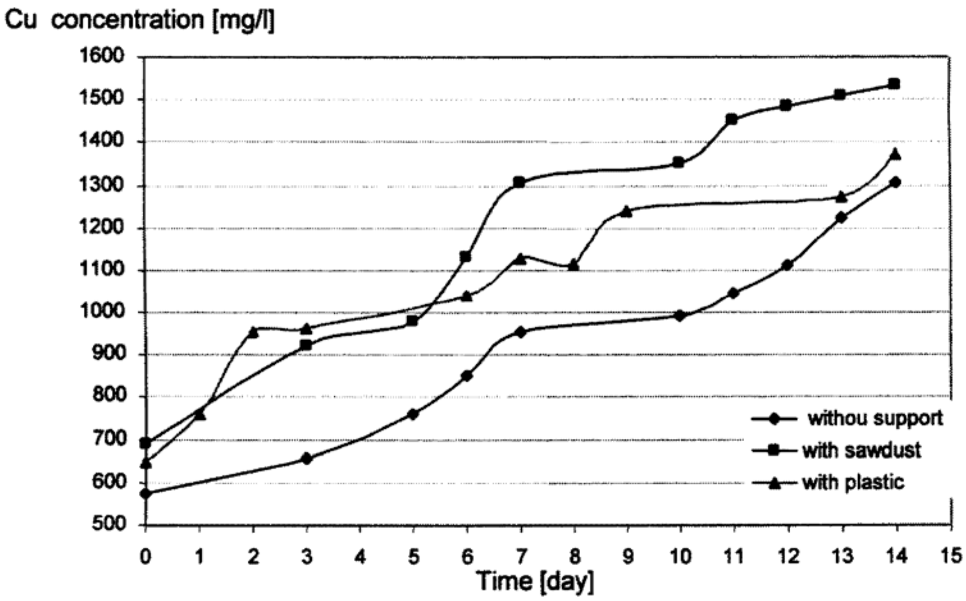

Fig. 6. Comparison of acid, autotrophic leaching with or without support for sample A

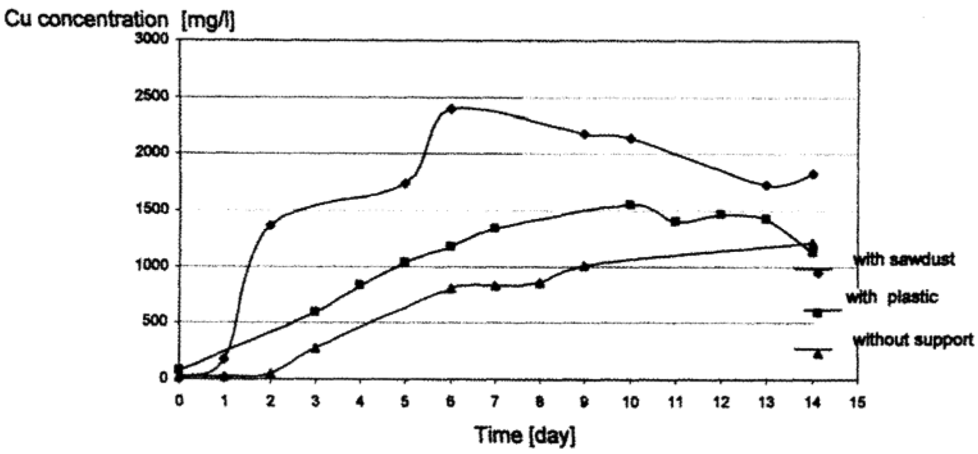

Fig. 7. Comparison of acid, autotrophic leaching with or without support for sample B

DISCCUSION

The bioleaching efficiency of the mineral particles in the column can be considered as a function of Reynolds number of the leaching solution flows through the bed. In the heap leaching practice, it is advisable to crush the mineral down to diameter of about 3 cm. The reduction of particles size can cause the plugging and channeling of the leaching solution. The porosity decrease influences an increase of the resistance of an internal mass transfer and an increase of bioleaching time considerably. (Bartlett, 1992) suggested a porosity range of 0.02 to 0.08 for typical minerals processed by heap leaching.

During the heap leaching the solution circulates from the top of the heap. At the steady state the liquid content in the bed becomes constant. The liquid flow is constant and was measured for each bead (Table 1).

Table 1. Leaching liquid flow through the column

Filler	Leaching liquid flow [cm^3/60s]	
	Shale sample "A"	Shale sample "B"
Without filler	12.37	11.86
Plastic spheres	13.58	13.34
Sawdust	17.3	17.1

The natural tendency of *Acidithiobacillus ferrooxidans* to grow on the solid surface makes it a potential microorganism able to be immobilized. Several solid supports have been used for cellular immobilization, including agar, polyurethane foam, glass beads, activated coal, sand and polyvinyl chloride. The immobilization of microbial cells offers significant advantages over the processes where the free cells are used (Giro et al., 2006).

An inhibitory effect of high ferrous ion concentration on the activity of immobilized *A. ferrooxidans* cells was observed (Long et al., 2004). In this work, a good effect of immobilization of A. *ferrooxidans* cells on the bioleaching of shale ores was achieved. On the other hand, the effect of the flow rate on the shale bioleaching was limited. As the flow rate increases, the mass transfer between the solid particles and the solution increases. In contrast, when the flow rate increases, the mean residence time of the solution in column decreased, resulting in relatively low bacteria cells in solution. The bioleaching of shale samples decreased.

CONCLUSIONS

The results of comparative tank and column tests using heterotrophic and autotrophic cultures indicate that bioleaching rates are similar in both cases. However, the bioleaching results of black shale samples indicated, that the column reactor with sawdust support for microbial cells immobilization, exhibited more suitable conditions for the metal leaching. The bacteria (*Acidithiobacillus ferrooxidans*) attached to the sawdust surface play a significant role in the bioleaching of shale samples. A higher copper recovery, for two investigated fillers, may be obtained for the shale sample mixed with wood shavings. The capillary model based on the hydraulic radius concept (Petersen et al., 2006) seems to adequate for the flow in porous media description.

ACKNOWLEDGMENTS

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W pracy przedstawiono wyniki doświadczeń przeprowadzonych na dwóch próbkach rudy łupkowej o zawartości miedzi 7,04 % (próbka A) i 2,32 % (próbka B). Obie próby materiału do badań zostały dostarczone przez Centrum Badawczo-Rozwojowe KGHM Cuprum. Przeprowadzone doświadczenia miały za cel porównanie procesu bioługowania próbek rudy łupkowej, który był prowadzony z bioreaktorze z mieszaniem i w kolumnie ze złożem stacjonarnym. W przypadku bioługowania w kolumnie użyto dodatkowo dwóch wypełniaczy, to jest plastikowych kulek i wiórów drewnianych. Bioługowanie prowadzono z wykorzystaniem bakterii heterotrofowych (*Streptomyces setoni* i mieszanka C) i autotrofowych (*Acidithiobacillus ferrooxidans).* Otrzymane wyniki sugerują, że kinetyka procesu bioługowania w bioreaktorze był lepsza od kinetyki procesu w kolumnie. Procesy, prowadzone w kolumnach z wypełnieniem, były korzystniejsze w porównaniu z procesami bez użycia wypełnienia. Z zastosowanych dwóch materiałów wypełniających, trociny okazały się być lepszym wypełniaczem. Może to być spowodowane bardziej porowatą strukturą materiału w kolumnie, o czym świadczy większa szybkość przepływu medium ługującego.