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## **APPLICATION OF SHRINKING CORE MODEL TO BIOLEACHING OF BLACK SHALE PARTICLES**

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Four size fractions of a black shale ore originating from the Lubin Copper Mine (Southwestern Poland) were leached in a small column using autotrophic bacteria (*Acidithiobacillus ferrooxidans*). The best results of bioleaching were obtained for the most fine fraction, where the copper recovery was 84%, and the surface area of the ore increased from 4.50 m<sup>2</sup>/g to 13.74 m<sup>2</sup>/g. Based on the shrinking core model, a new model describing bioleaching of the black shale type ore in a column is proposed. The model is based on assumption of dependence of copper recovery and surface area increase during the process.

*Key words: bioleaching, shrinking core model, black shale*

### **INTRODUCTION**

Much attention was focused on studies of shrinking core models in the last years (Brochot, 2004; Crundwell, 1997; Lapidus, 1992; Pritzker, 1996, 2003; Vegliò, 2001; Velardo, 2002, and others). They adapted earlier model equations to their experiments.

Liddell (2005) remarked that two facts about early development of shrinking core models have been overlooked. The first was focused mostly to gas-solid systems, and it was proposed by Levenspiel (1979). The author finds the shrinking core model as the simplest for reactions of gas with particles of unchanging size. He suggests, it must be a sharp reaction front between a porous product layer called "ash" and the fresh reactant, and shows that the three resistances controlling the shrinkage process are possible: diffusion of the reactant through the gas film surrounding the particle, diffusion of the reactant through the ash layer and a reaction at the unreacted core. Since 1960s, the use of shrinking core model for solid-liquid systems was examined (Chae, Wadsworth 1978, Veglio et al., 2001). The model considers the reaction of the

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reactant at the surface of the solid particle, which results in both aqueous and solid products which may form on the surface of the particle. As reaction proceeds, the unreacted core of the particle is reduced in size, while more solids and aqueous products are formed (Crundwell, 1995). It is important to notice that most of these models involve the pseudo-steady state (PPS) approximation (Liddell, 2005) to make the reactant concentration across the porous ash layer determination possible.

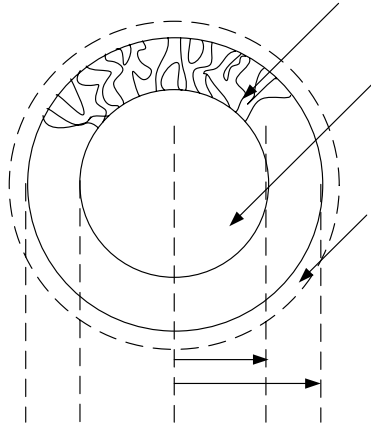


Fig. 1. Shrinking core particle

For a spherical particle (Fig.1) involving the quasi-steady state diffusion of the reactant through the previously reacted portion of the particle, followed by the chemical reaction at the surface of the unreacted core, it is useful to express the reaction rate in terms of fraction reacted (i.e. particle conversion) (Chae, 1979; Burghardt, 2001; Liddell, 2005). Describing the shrinkage process, the authors relate the fraction reacted ( $\alpha$ ) with reaction time ( $t$ ) in equations. If the process is controlled by the reactant diffusion through the fluid surrounding the particle (Burghardt, 2001):

$$\frac{t_f}{t_f^*} = 1 - \left(\frac{r_c}{R}\right)^3 = \alpha \quad (1)$$

where,  $t_f^*$  is the time required for the particle to react completely,  $r_c$  is the unreacted core radius at given time, and  $R$  is the initial particle radius. If the reaction is controlled by product layer diffusion (ash diffusion), then:

$$\frac{t_a}{t_a^*} = 1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3 = 1 - 3(1-\alpha)^{2/3} + 2(1-\alpha), \quad (2)$$

where, similarly to Eq. 1,  $t_a^*$  is the time required for the particle to react completely. When the process is controlled by the chemical reaction:

$$\frac{t_r}{t_r^*} = 1 - \left( \frac{r_c}{R} \right) = 1 - (1 - \alpha)^{1/3}. \quad (3)$$

There are different ways to find out the mechanism controlling the shrinkage process (Eq. 1-3), e.g. experiments using different particles radius ( $R_1$ ,  $R_2$ ) are carry out, regarding different times ( $t_1$ ,  $t_2$ ) necessary to attain the same particle conversion. In the case of the reactant diffusion through the fluid surrounding the particle control:

$$\frac{t_1}{t_2} = \left( \frac{R_1}{R_2} \right)^{1.5-2.0} \quad (4)$$

If the process is controlled by “ash diffusion”:

$$\frac{t_1}{t_2} = \left( \frac{R_1}{R_2} \right)^2 \quad (5)$$

For chemical reaction control:

$$\frac{t_1}{t_2} = \frac{R_1}{R_2} \quad (6)$$

In hydrometallurgy the shrinking core models are generally applied to describe the shrinkage of ore particles during mineral leaching reactions, which are a central unit operation in the hydrometallurgical ores treatment. The model is applied to description of the leaching process both for column or heap leaching (Lizama, 2004, 2005, Chae, 1979) and for stirred-tank reactors, including continuous systems (Crundwell, 1995). There are also literature data on the use of the shrinking core model for modelling of bacterial leaching processes. Most of the data concern sulphide ores bioleaching (Brochot, 2004; Conner, 2005, Leachy, 2005).

Bioleaching of sulphide minerals consists of oxidation of ferric ions, resulting in release of metal ions to the leaching solution, and formation of a sulphur layer (McGuire, 2001). At present, bioleaching processes are based on activity of chemolithotrophic bacteria like *Acidithiobacillus ferrooxidans*, which are able to act in an acid environment, and which convert metal sulphides via biochemical oxidation reactions into water-soluble metal sulphates (Bosecker, 1997). In principle, metal can be released from sulphide minerals by direct and indirect bacterial leaching (Sadowski, 2005).

Heap leaching is usually simulated in columns charged with ore where leaching solution percolates from the top (Lizama, 2004). At steady state conditions, metal leaching has been described as being pore-diffusion controlled by a reacted porous zone surrounding a region of unreacted ore, correlate to shrinking core model (Braun, 1974). However, Lizama (2004, 2005) proved that the shrinking core equation does not apply at the initial stages of bioleaching, which was due to an initial period of bacteria cells colonization on the ore surface.

In this study, a model for column bioleaching of Polish copper-bearing black shale ores is investigated to identify and understand aspects of bacteria in bioleaching applications, which can have implications in heap bioleaching operations. Based on general assumptions of the shrinking core model, new equation describing bioleaching of black shale particles is proposed. The primary assumption for this model equation is that the surface area of the more porous core increases with metal (copper) releasing from it, and that this dependence is constant. The final equation subordinates the black shale surface area from leaching time, taking into account the initial surface area (in  $m^2/g$ ).

## EXPERIMENTAL

The black shale ores used in this study was supplied by the Lubin Copper Mine (KGHM S.A.), Southwestern Poland, and it was in the form of broken core samples consisting of chunks of diameter  $<5.0$ mm. The material was screened into the four size fractions: 5.0 – 4.0 mm, 4.0 - 3.15 mm, 3.15 – 2.5 mm and 2.5 - 1.6 mm. Density ( $d$ ) of each fraction as well as the results of chemical analyses are presented in Table 1.

Table 1. Chemical analysis of four black shale fractions

Size fraction Chem.analysis	4.0 – 5.0 mm ( $d = 2.66 \text{ g/cm}^3$ )	4.0 - 3.15 mm ( $d = 2.56 \text{ g/cm}^3$ )	3.15 – 2.5 mm ( $d = 3.16 \text{ g/cm}^3$ )	2.5 - 1.6 mm ( $d = 3.40 \text{ g/cm}^3$ )
Cu [%]	6.02	6.05	6.24	7.03
Fe [%]	1.15	1.07	1.23	1.08
Ni [g/t]	436	440	335	387
V [g/t]	1050	1060	1110	1045
As [%]	0.09	0.085	0.06	0.075
Ag [g/t]	285	223	270	298
$C_{\text{tot}}^*$ [%]	11.1	11.3	11.12	11.3
$C_{\text{org}}^*$ [%]	7.42	6.85	6.4	7.85

\*  $C_{\text{tot}}$  – total carbon,  $C_{\text{org}}$  – total organic carbon

Autochthonous bacteria. *Acidithiobacillus ferrooxidans* (F701), obtained from the Practical and Experimental Biology Department of the University of Opole, was used for the bioleaching study. The cultures of 15% *inoculum* were grown at 32°C in shake flasks (170 rpm) at pH = 2.0 in the Silverman and Lundgren 9K nutrient medium (Silverman, 1959). The bioleaching experiments were carried out in small glass column (5/40cm). Figure 2 illustrates the system used in this study. For each experiment, the same weight of each fraction was used. The solid density in all cases was 10% (w/v) provided with 15% of bacterial *inoculum* in mineral medium 0K, containing:  $\text{KH}_2\text{PO}_4$ : 0.1 g/l and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ : 0.1 g/l. The solution was adjusted to pH=2 with 2M  $\text{H}_2\text{SO}_4$ . Each experiment started in reactors about 3 days before inoculation in order to neutralize carbonates and stabilize leaching solution to pH=2. Solution and solid samples were taken at regular intervals for analysis of copper concentration and the surface area ( $\text{m}^2/\text{g}$ ), respectively.

The bacterial growth was checked by Eh (mV),  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  measurements. The bacterial activity was found satisfied by observation of Eh changes from 285 mV at the beginning of the process to about 575 mV at the end. Because of relatively low content of iron in the ore, an increase of  $\text{Fe}^{3+}$  ion concentration and a rapid decrease of  $\text{Fe}^{2+}$  ions were observed only during 5-6 days of the process.

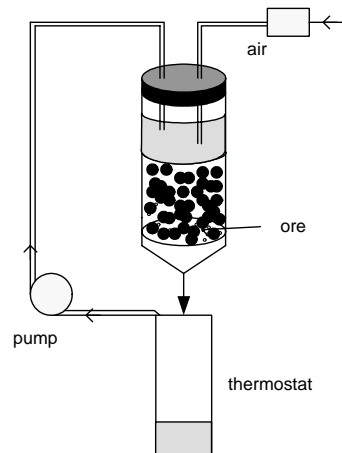


Fig. 2. Schematic representation of apparatus used for black shale ore bioleaching

## MATHEMATICAL FORMULATION

Bioleaching of copper-bearing black shale ores is usually described using formulas based on partial differential equation:

$$\frac{\partial c_{Cu}}{\partial t} = -w \frac{\partial c_{Cu}}{\partial x} + r_o, \quad (7)$$

where  $t$  denotes time, and  $x$  is the column length. In the case when “an ideal mixing” of ore in column is reached, an uniformity of the copper concentration gradient  $c_{Cu}$  within the column can be written as:

$$\frac{\partial c_{Cu}}{\partial x} = 0. \quad (8)$$

Based on Eq. 8 we receive a simple differential equation, including the reaction rate  $r_0$ :

$$\frac{\partial c_{Cu}}{\partial t} = -r_0. \quad (9)$$

The fact that the ore surface area [ $m^2/g$ ] increases during the process, which is due to bacterial penetration into ore particle making the core more porous, is important and helpful for description of the efficiency of copper-bearing ores bioleaching. The primary assumption for our model equation is that the increase of the surface area of the more porous core is directly proportional to decrease of copper concentration in the ore particle:

$$\frac{a - a_0}{c_{Cu}^0 - c_{Cu}} = const = \frac{1}{C}, \quad (10)$$

where  $a_0$  is the initial surface area of ore particles [ $m^2/g$ ], and  $c_{Cu}^0$  is the initial concentration of copper in the ore particle. By transforming and differentiating Eq. 10:

$$a - a_0 = C \cdot (c_{Cu}^0 - c_{Cu}), \quad (11)$$

$$da = C \cdot (-dc_{Cu}), \quad (12)$$

and by coupling these equations with Eq. 9, we receive:

$$\frac{\partial a}{\partial t} = C \cdot r_0. \quad (13)$$

The core-surface reaction rate is directly proportional to surface area ( $m^2/g$ ) changes:

$$r_0 = k \cdot a. \quad (14)$$

Substituting Eq. 14 with Eq. 13 we receive the first order differential equation:

$$\frac{\partial a}{\partial t} = C \cdot k \cdot a. \quad (15)$$

In order to make our calculations more simple, a constant  $B$  was introduced:  $C \cdot k = B$ . The solution of this equation for the initial condition:  $a(0) = a_0$  can be written as:

$$a(t) = a_0 e^{Bt}. \quad (16)$$

It is known that for an exponential function, as a function of real variable  $x$ , the plot of  $e^x$  is always positive and continuously increasing. That is why, the function is not useful for describing long-term processes, because going to infinity it assumes values, which don't possess any equivalent in nature. In order to limit the surface area  $a$  increasing values, coupled with reaction rate expression, we introduced the "limiting module"  $d \cdot (a_K - a)$ :

$$r_0 = k \cdot a \cdot d \cdot (a_K - a), \quad (17)$$

and received the new reaction rate equation:

$$\frac{\partial a}{\partial t} = C \cdot k \cdot d \cdot a \cdot (a_K - a). \quad (18)$$

The constants of the equation are included into constant  $B$ :

$$\frac{\partial a}{\partial t} = B \cdot a \cdot (a_K - a). \quad (19)$$

For initial condition:  $a(0) = a_0$ , after the variables separation the solution is:

$$a(t) = \frac{a_0 e^{Bt}}{1 - \frac{a_0}{a_K} (1 - e^{Bt})}. \quad (20)$$

To use Eq. 20 three process parameters have to be known: initial surface area  $a_0$ , reaction conversion parameter  $B$  and surface area  $a_K$ . The relevance of the parameter  $a_K$ , as the maximal surface area of ore increasing during the process can be found by analyses of Eq. 20 for very long periods of time:

$$\lim_{t \rightarrow \infty} \frac{a_0 e^{Bt}}{1 - \frac{a_0}{a_K} (1 - e^{Bt})} = \lim_{t \rightarrow \infty} \frac{a_0}{e^{-Bt} - \frac{a_0}{a_K} (e^{-Bt} - 1)} = \frac{a_0}{0 - \frac{a_0}{a_K} (0 - 1)} = \frac{a_0}{\frac{a_0}{a_K}} = a_K. \quad (21)$$

It is worth to notice that if the time goes to zero  $t \rightarrow 0$  we obtain:  $e^{Bt} = 1$  (for short periods of time). Thus, the above derived two-parameter Eq. 10 can be useful for determination of  $B$  parameter at the beginning of the process.

$$\lim_{t \rightarrow 0} \frac{a_0 e^{Bt}}{1 - \frac{a_0}{a_K} (1 - e^{Bt})} \approx \frac{a_0 e^{Bt}}{1 - \frac{a_0}{a_K} (1 - 1)} = a_0 e^{Bt}. \quad (22)$$

## RESULTS and COMMENTS

The overall behavior of copper-bearing shale bioleaching is revealed in Figure 3. As it can be seen there, the best copper recovery (84%) was attained for the most fined (2.5-1.6 mm) fraction. For the 3.15-2.5 mm fraction the percentage of copper recovery was 73%, and for 4.0-3.15 mm and 5.0-4.0 mm fractions the bioleaching yield was almost the same; 66-67%. In comparison to copper recovery, the percentage of Ni bioleaching was very low: the highest recovery of 19% was observed for the most fined fraction. For all fraction very low (about 3%) vanadium extraction was observed. However, in this case a slight decrease of vanadium concentration in leaching solution during the process could be seen. Even the yield of the process was quite low (e.g. in comparison to stirred tank bioleaching). It is worth to notice, that the heap leaching, a very slow process, is usually simulated in columns.

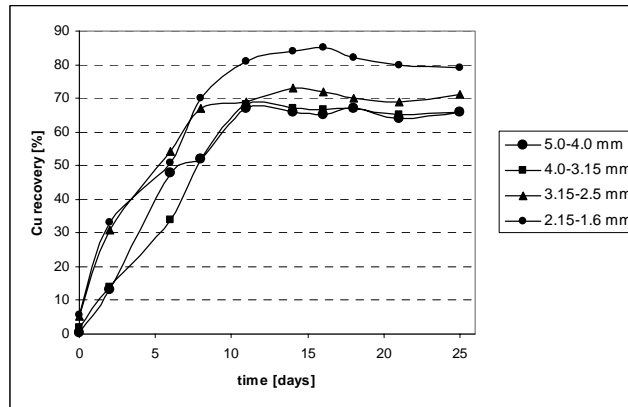


Fig. 3. Copper recovery from Polish black shales bioleaching from different ore size fractions

The kinetics of the process was followed by the iron ions concentration and redox potential Eh [mV] measurements. For the four fractions the increase of Eh from about 256 mV to 565 mV was observed. The most significant changes in Eh were seen during the first 10 days of bioleaching. Also, it was observed that, the  $\text{Fe}^{3+}$  ions concentration increases and  $\text{Fe}^{2+}$  ions concentration decreases during first 6-7 days of the process.



Correlating the data of copper recovery and surface area increase (Fig. 4) for all fractions, it is possible to notice that for the most fine fraction, where the copper recovery was the best, the surface area increase was the highest as well. For the others three fractions these values were lower, respectively.

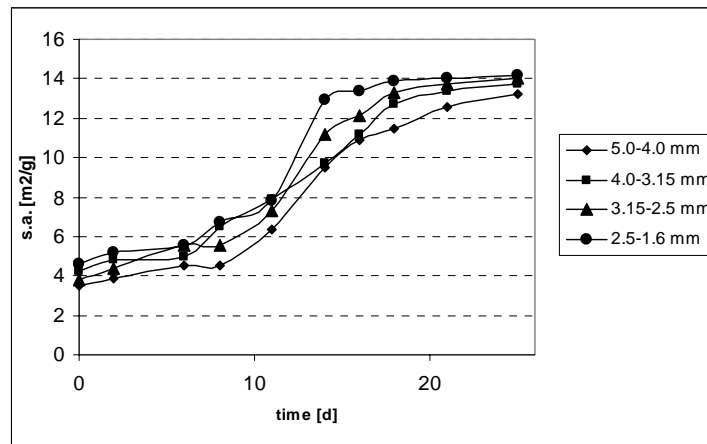


Fig. 4. Black shale surface area increment during bioleaching process

In order to make easier the modelling calculations, the surface area values obtained for all size fractions were averaged and presented in Fig. 5. Equation (14), which is also called the logistic equation, was transformed to the form

$$\ln\left(\frac{a}{a_K - a}\right) = a_K B t + \ln\left(\frac{a_0}{a_K - a_0}\right) = B \cdot a_K \cdot t + D \quad (23)$$

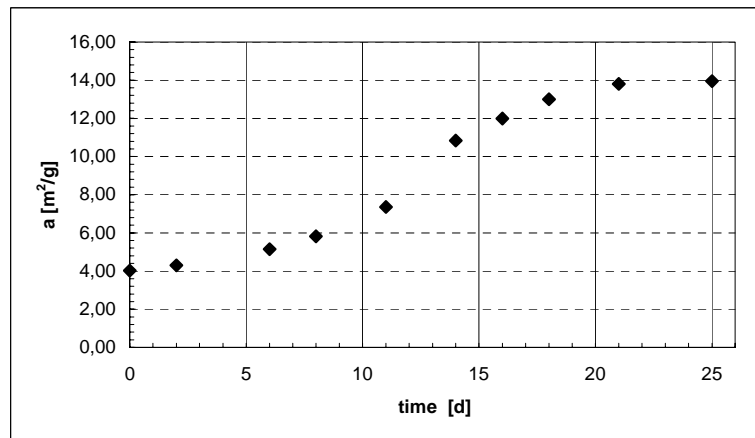


Fig. 5. Average of four size fractions values of surface area obtained during bioleaching process

Assuming  $a_K = 14$ , the following calculations (Table 2) of process results have been made:

Table 2. Experimental data for logistic equation (23)

l. p.	t	a	$\frac{a}{a_K - a}$	$\ln\left(\frac{a}{a_K - a}\right)$	$D_{theoret} = \ln\left(\frac{a_0}{a_K - a_0}\right)$
1	0	4.02	0.4032	-0.9084	-0.9093
2	2	4.30	0.4433	-0.8135	-0.9093
3	6	5.15	0.5810	-0.5430	-0.9093
4	8	5.83	0.7131	-0.3382	-0.9093
5	11	7.35	1.1061	0.1008	-0.9093
6	14	10.83	3.4164	1.2286	-0.9093
7	16	12.00	6.0000	1.7918	-0.9093
8	18	13.00	13.00	2.5649	-0.9093
9	21	13.80	69.00	4.2341	-0.9093
10	25	13.95	279.00	5.6312	-0.9093

The plotted dependence (Figure 6):  $\ln\left(\frac{a}{a_K - a}\right) = f(t)$  is a linear function only in a final stage of the process:

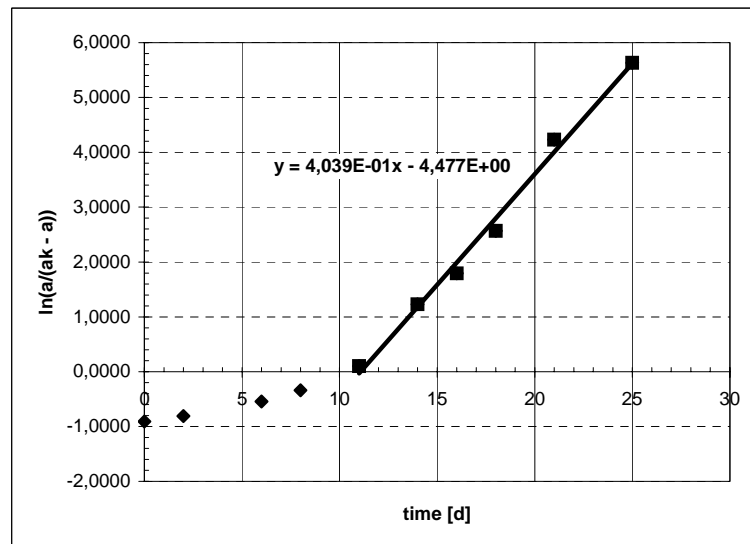


Fig. 6. Linear dependence  $\ln\left(\frac{a}{a_K - a}\right) = f(t)$  in the final stage of the process

Based on the correlation line equation (Fig. 6) it is possible to estimate the value of parameter  $a_k B$  value:  $a_k B=0.4039$ , and thus  $B=0.0993$  (g/(m<sup>2</sup> s)). The value of free-term coefficient  $D = -4.477$  differs from those theoretically determined one. It is due to deviations from the ideal model assumptions.

$$a = \frac{a_K}{1 + e^{-(a_K B t + D)}} = \frac{14}{1 + e^{-0,4039t + 4,477}} \quad (24)$$

The model obtained from Eq. (23) is illustrated in Figure 7. As it is seen, it is not possible to describe the first stage of the process using the logistic model due to simplifications assumed. The solution obtained can be useful only to describe the second stage of the black shale column bioleaching. The differences in a character of the two stages of the process can be due to the fact, that the beginning of the process is a period of bacteria cells colonization on the ore surface (Lizama, 2004, 2005).

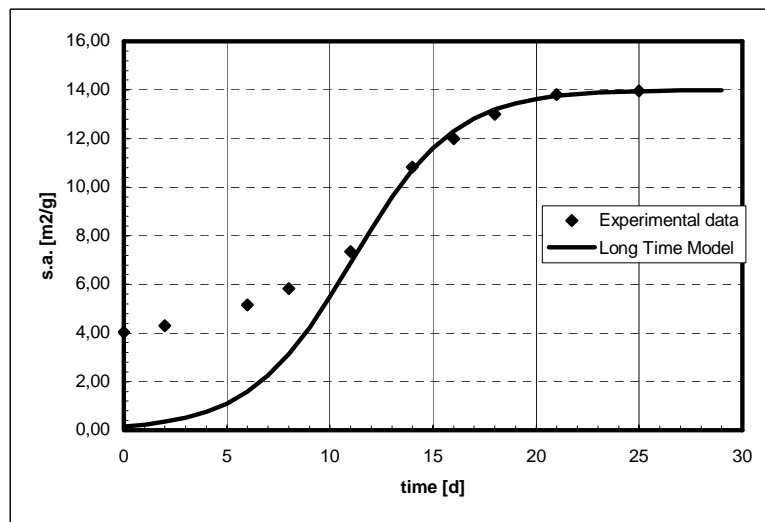


Fig. 7. Relationship between the Long Time Model calculated and experimental surface area data for black shale ore bioleaching

In order to describe the first stage of the process Eq. 16 was used. As above-considered, it is possible to simplify Eq. 16, which after transformation gives the form:

$$\ln(a) = B \cdot t + \ln(a_0). \quad (25)$$

The linear dependence:  $\ln(a) = f(t)$ , for the first stage process is presented in Fig. 8a. Figure 8b is a magnified Fig. 8a.

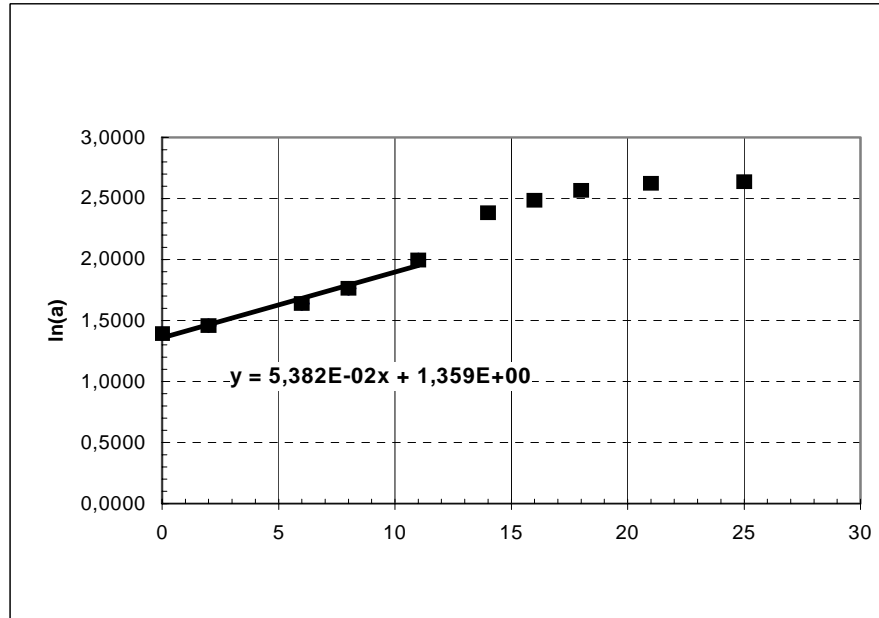


Fig. 8a. Linear dependence at the beginning of bioleaching process:  $\ln(a) = B \cdot t + \ln(a_0)$

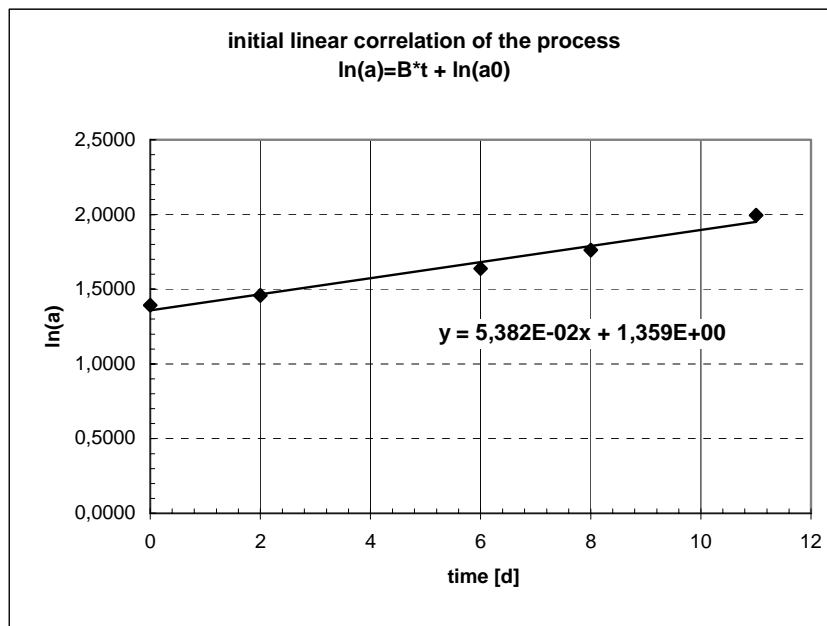


Fig. 8b. Linear dependence at the beginning of the bioleaching process:  $\ln(a) = B \cdot t + \ln(a_0)$

Based on the trend line equation (Fig. 8b) we obtained the value of  $B = 0.05382$ , and a value of the free-term coefficient:  $\ln(a_0) = 1,359 \rightarrow a_0 = 3,89$  which is in a great accordance with the experimental data of the initial surface area:  $a_0 = 4,02$ . It is then possible to assume the simplified model for the first stage of the bioleaching process:

$$a(t) = 3,89e^{0,05382t} \tag{26}$$

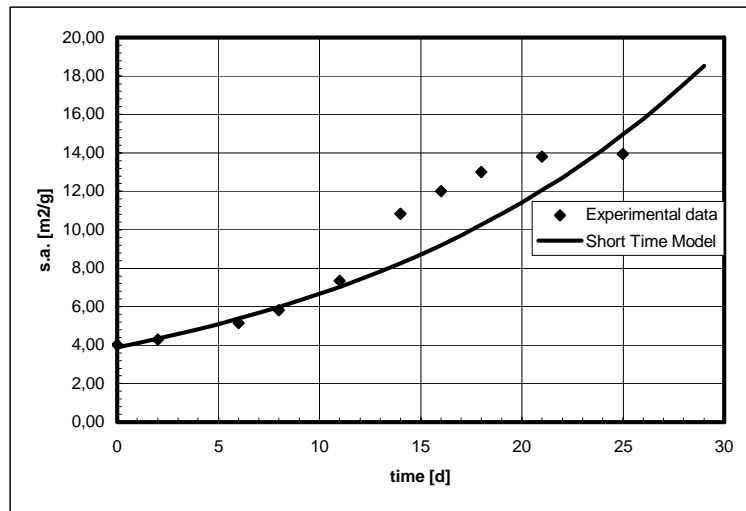


Fig. 9. Relationship between the Short Time Model calculated and experimental surface area data for black shale ore bioleaching

Taking into account both models: for the first and the second stage of the bioleaching process, we receive a correlation presented in Fig. 10.

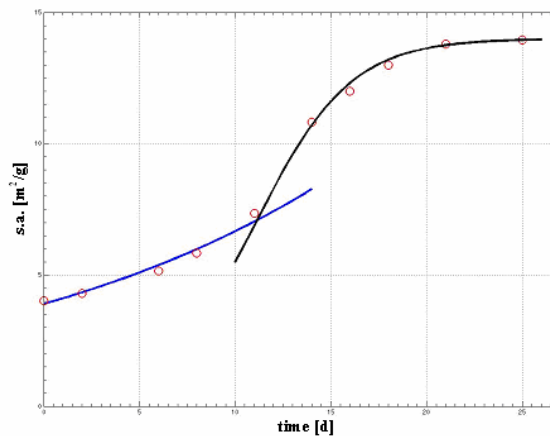


Fig. 10. Relationship between both Short Time and Long Time Models calculated and experimental surface area data for black shale ore bioleaching

## CONCLUSIONS

1. The kinetics of bioleaching of the copper-bearing black shale ores can be described using equations based on surface area “ $a$ ” ( $\text{m}^2/\text{g}$ ) of the ore.
2. For the beginning of the process description the logistic equation can be used, assuming its simplified form. It is necessary to take into account a separation of the first stage of the process from the second one. For the first stage the kinetics of the process has an exponential character, while the kinetics of the second stage is strongly limited by the character of the system.
3. For the first stage of the bioleaching only one parameter  $B_1$  has to be found. For the second stage two parameters are needed in order to describe the process more precisely:  $B_2$  and corrective factor  $D$ . This is due to complications resulting from a two-step transport of substrates (to the surface and through the porous layer). The parameters  $a_0$  and  $a_k$  are estimated taking into account the characteristics of the bioleached ore.
4. The assumption of correlation between the percentage of copper recovery and the surface area increase (Eq. 4) is correct.
5. The percentage of Cu recovery was the best for the most fine size fraction: 84%. For the other three fractions the area of the process was lower. The nickel recovery was also low, and no vanadium extraction was observed.
6. Bibliographic studies on simple mathematical models allowed to propose easy bioleaching model equations which can be used in practice.

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**Szubert A., Łupiski M., Sadowski Z.,** *Zastosowanie modelu kurczącego rdzenia do opisu bioługowania ziaren rudy łupkowej*, *Physicochemical Problems of Mineral Processing*, 40 (2006), 211-225 (jęz. ang.).

Cztery klasy ziarnowe rudy łupkowej, otrzymanej z kopalni Lubin (Polska Miedź S.A.), zostały poddane procesowi bioługowania w kolumnie. Do procesu bioługowania wykorzystano autotroficzne bakterie *Acidithiobacillus ferrooxidans*. W wyniku procesu bioługowania odzyskano 84 % miedzi z najdrobniejszej frakcji rudy (2,5-1,6 mm). W trakcie procesu bioługowania nastąpił wyraźny wzrost wielkości powierzchni właściwej ługowanych ziaren mineralnych. Początkowa wartość rozwinięcia powierzchni wynosiła 4,50 m<sup>2</sup>/g a po procesie bioługowania osiągnęła wartość 13,74 m<sup>2</sup>/g. Opracowany został nowy model bioługowania rudy łupkowej w kolumnie. Nowy model bazuje na istniejącym i opisanym w literaturze modelu kurczącego się rdzenia. Nowy model poprawnie opisuje otrzymane wyniki eksperymentalne.