

Ewa JAŹDŹYK, Zygmunt SADOWSKI\*

## **EFFECT OF ARTIFICIAL POLYMER FILM ON BIOOXIDATION OF ARSENOPIRYTE WASTES**

*Received March 2003, reviewed, and accepted May 15, 2003*

The effect of polymer film on the biooxidation of arsenopyrite tailings was examined. Adsorption of a typical sugar polymer, dextrin, on the mineral particles was studied. The effect of pH on the adsorption at the biooxidation range was determined. The microelectrodes were used to measure the dissolved oxygen concentration in the polymer film. Based on these results, the oxygen diffusion coefficient has been calculated to be  $1.6 \cdot 10^{-5} \text{ cm}^2/\text{s}$ . The biooxidation results show that polymer film plays a key role in both the immobilization of microbial cells and oxygen diffusion. For effective biooxidation of arsenopyrite tailings the presence of polymer film onto the solid surface is indispensable.

*Key words: biooxidation, biofilm, dextrin, Acidithiobacillus ferrooxidans, diffusion coefficient*

### **INTRODUCTION**

Gold in the refractory ores is encapsulated as fines in the crystal structure of the arsenopyrite matrix. To effectively extract gold from these ores an oxidative pretreatment is necessary to break down the arsenopyrite matrix. Biological pretreatment of the refractory gold ores is the most popular method for the gold recovery (Karas, Sadowski, 2002).

The concept of the microbial cells immobilization was checked by (Karamanev et al. 2001). Immobilization of microbial cells prevent them from moving freely. The oxygen mass-transport rate in the immobilized system (biofilm) is very high. Formally, molecular diffusion is considered the predominant mechanism for the oxygen transport in the biofilm (De Beer et al., 1997).

The term biofilm encompasses a variety of extracellular polymer substances (EPS), which microbial cells colonized. The diffusion through these biofilms controls the microbial oxidation reaction. Microbial activity in biofilms is controlled by transport

---

\* Technical University of Wrocław, Institute Chemical Engineering and Heating Equipment, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, [sadowski@iic.pwr.wroc.pl](mailto:sadowski@iic.pwr.wroc.pl)

process (Lewandowski et al., 1998, Rasmussen et al., 1998 a). The biopolymer film is capable of transportation of trace organic and inorganic compounds. The oxygen diffusion through the biofilm controls the microbial oxidation of minerals. The diffusion coefficient of dissolved oxygen through a biofilm formed by filtering nitrifiers through a membrane filter was found between 80 and 100% of its value in water (Lewandowski et al., 1991).

The studies of the migration of oxygen within structurally heterogeneous biofilm demonstrated the importance of biofilm architecture to the oxygen transport (Rasmussen et al., 1998 b, Stoodley et al., 1998).

The goal of this paper was to calculate the diffusion coefficient of the polymer film created onto the mineral surface.

## MATERIALS AND METHOD

### MINERAL SAMPLES

The material used in this study was obtained from the out-of-operation arsenic mine at Zloty Stok (Lower Silesia, Poland) The sample tailing was collected from the "Jan" heap and it contained gold-bearing minerals such as loellingite and arsenopyrite. The samples were ground and wet-screened to obtain -0.5 +0.125 mm size fraction. The results of chemical analysis of this size fraction is presented in Table 1.

Table 1. Chemical composition of arsenic sample

Elements	Composition [%]
Fe	24.65
As	3.22
Si	13.02
S	7.42
Al	2.41

The specific surface area of the mineral samples was determined by the BET method using FlowSorb II 2300 and was equal to 1.63 m<sup>2</sup>/g.

### BACTERIA

*Acidithiobacillus ferrooxidans* was used in this work. This strain was isolated from mine water from the Zloty Stok mine. A part of culture was adapted to grow in the high As ion concentration solutions. *A.ferrooxidans* was grown in 300 ml Erlenmeyer flasks at 30°C while shaking at 150 rpm using 130 ml 9K medium of composition presented at Table 2. The pH of this medium was adjusted to 2.0. A 10% (v/v) inoculum of the 4 days old culture was used for bacterial iron oxidation studies.

The microorganism cells concentration correlates to the protein concentration. Protein concentration was determined by reacting the proteins with copper ions to form a purple copper-protein complex. The complex concentration was determined by using a spectrometer.

#### REAGENTS

The polymer film was created by a polysaccharide (DEXTRIN) adsorption on the solid surface. Dextrin was purchased from Sigma Chemical Co. and used without further purification.

#### OXIDATION PROCEDURE

The packed-bed reactor was used for the biooxidation experiments. We utilized a glass column with 210 mm-high and 47 mm-inside diameter. The perforated glass plate supported the mineral material at the bottom. The column works in a flooded way with recycling the medium using a peristaltic pump. Air was supplied to the supernatant at the rate of 960 ml/min. The experiments were run at 25°C. The biooxidation process was monitored by measurements of the following parameters: pH, Eh, Fe<sup>3+</sup>, Fe<sup>2+</sup>, total As and proteins concentrations.

#### POLYMER ADSORPTION

Adsorption experiments were conducted in plastic 100 ml bottles. Solid samples of 1.0g were mixed with 100 ml of polymer solution. The suspensions were equilibrated for 10 hours. The solid particles were centrifugated for 15 minutes at 4500 rpm and about 10 ml of supernatants was pipetted out for analysis. Dextrine concentration after adsorption was determined by colorimetric method (Dubois et al., 1956). The adsorbed amount of polymer was calculated by depletion.

#### DETERMINATION OF OXYGEN PROFILE

Oxygen profiles were measured by a microelectrode connected with a micromanipulator. The electrodes were mounted on a micromanipulator (Model MM33) World Precision Instruments. The electrodes were moved from the bulk solution down through the polymer film.

#### EXPERIMENTALS AND DISCUSSION

Figure 1a shows the adsorption behaviour for pH of the suspension between 1.85 and 4.09. This narrow pH range corresponds with the biooxidation conditions. It is evident that the adsorption density is almost independent of pH in the investigated pH range. The results of dextrin adsorption are presented in Fig. 1b. It shows that the isotherm exhibits Langmuirian behaviour. It is apparent that the equilibrium adsorption density was about 0.9 mg/m<sup>2</sup>.

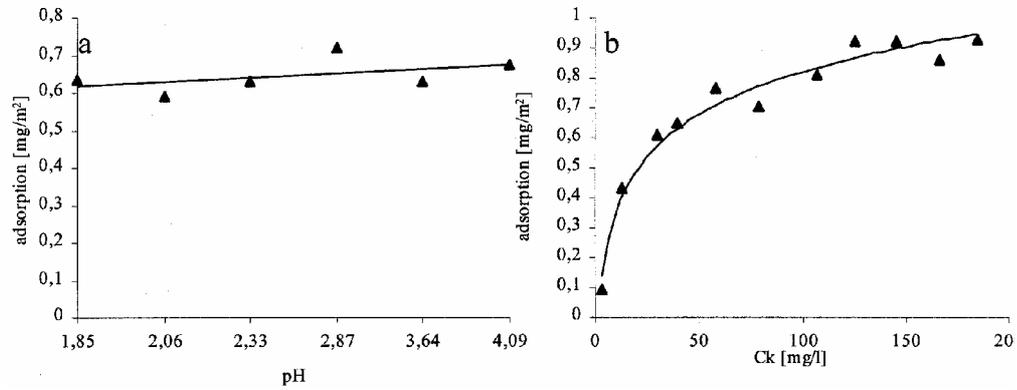


Fig. 1. Isotherms of dextrin adsorption onto the +0.125 –0.5 mm fraction of arsenic waste: a) effect of different values of pH, b) effect of different dextrin concentrations ( $C_k$ )

Dissolve oxygen profiles were also measured. Figure 2 shows the oxygen concentration profiles at various locations inside the polymer film. The numbers from 1 to 5 show different places of microelectrode.

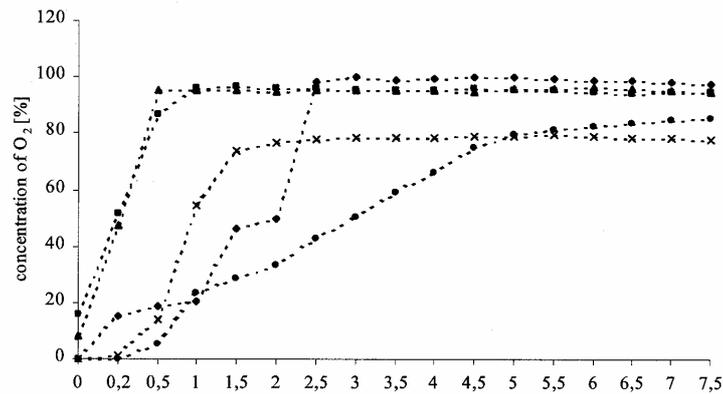


Fig.2. Oxygen concentration profiles

The rate of change of oxygen concentration inside the polymer film can be described by the equation resulting from differential mass balance (Lewandowski et al., 1991).

$$\frac{\partial c}{\partial t} = D_f \left( \frac{\partial^2 c}{\partial x^2} - \frac{V_{MAX} c}{K_S + c} \right), \quad (1)$$

where:  $D_f$  is the diffusion coefficient for the dissolved oxygen [ $\text{cm}^2/\text{s}$ ];  $c$  is the oxygen concentration at the point  $x$  ( $x = 1,2,3,4,5$ );  $V_{MAX}$  is the rate of oxygen consumption [ $\text{mg}/\text{dm}^3 \text{ s}$ ] and  $K_S$  is the oxygen saturation concentration [ $\text{mg}/\text{dm}^3$ ].

If the polymer film is partially penetrated, the above equation can be transformed to the form:

$$\frac{\partial c}{\partial x} = \sqrt{2 \frac{V_{MAX}}{D_f} \left( c - K_f \ln \frac{K_S + c}{K_S} \right)}. \quad (2)$$

The first derivative  $\frac{\partial c}{\partial x}$  should be linearly related to  $\sqrt{c - K_f \ln \frac{K_S + c}{K_S}}$ .

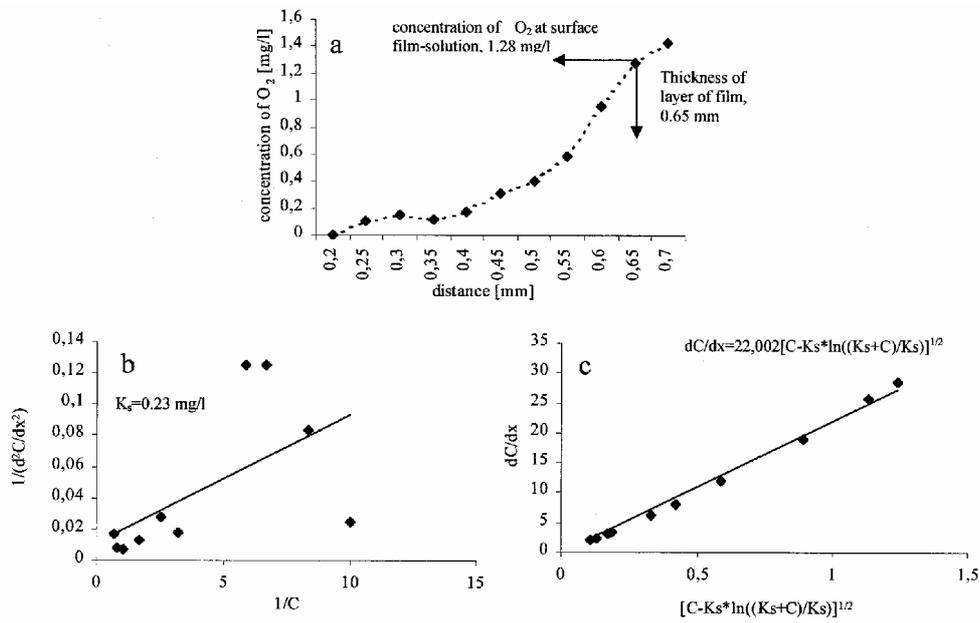


Fig. 3a. The dissolved oxygen profile within the distance of 0.2 to 0.7 mm; 3b. Determination of the half saturation coefficient (K<sub>s</sub>); 3c. Determination of diffusion coefficient for oxygen

The slope of the line from Fig. 3b divided by the intercept gives K<sub>s</sub>. For dissolved oxygen concentration K<sub>s</sub> is 0.23 mg/l. The regression line is shown in Fig 3b and Equation 3.

$$\frac{\partial c}{\partial x} = 22.002 \left[ c - K_S \ln \frac{K_S + c}{K_S} \right]^{\frac{1}{2}}. \quad (3)$$

The flux of oxygen must be preserved at the polymer film - solution interface. The oxygen diffusion coefficient can be calculated from the equation:

$$D_f \left( \frac{dC}{dx} \right)_f = D_w \left( \frac{dC}{dx} \right)_w \quad (4)$$

The mass transfer coefficients for the biofilm obtained by Lewandowski (Yaung et al., 1995) were 0.0003 and 0.00034  $\text{m} \cdot \text{s}^{-1}$  and the diffusion coefficient for oxygen in the biofilm was  $1.75 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . The diffusion coefficient of dissolved oxygen in water is  $D_w = 2.0 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . In our experiments the diffusion coefficient for oxygen is  $1.6 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .

The arsenopyrite oxidation data for both cases, that is in the presence and absence of polymer film are presented in Fig.4. The data indicate that in the presence of polymer the kinetics of biooxidation of arsenopyrite was enhanced. The total arsenic concentration obtained, when the polymer film was presented, was around 30 mg/l. The measurements of the protein concentration showed an increasing trend for both cases. However, we found that the protein concentration in the solution was lower in the presence of the biofilm. It can explain by the low diffusion of the protein through the polymer film. In contrast to arsenic, iron(III) ions the extraction from the tailing was low. It results from the  $\text{FeAsO}_4$  precipitation (Sadowski et al., 2001).

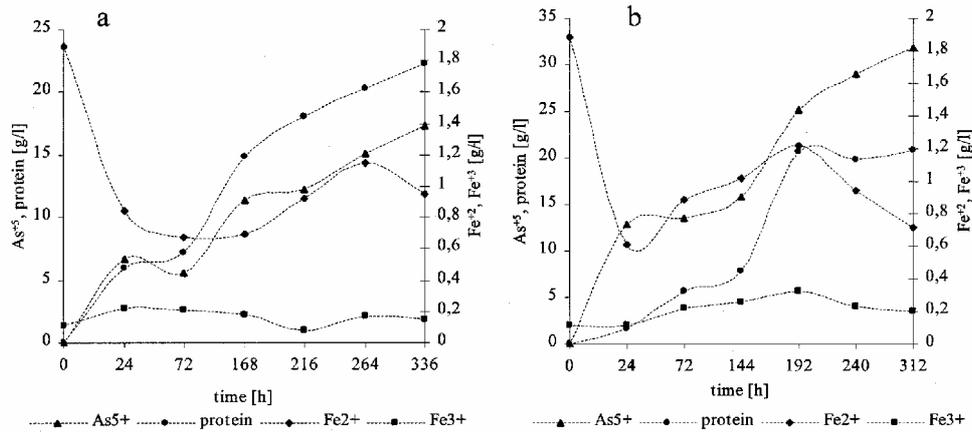


Fig. 4. Variation of  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{As}^{+5}$  ions and protein concentration in bioleaching of arsenic refractory ores in percolator: a) without polymer film, b) with polymer film

Table 2 shows the surface areas of the mineral powder used for biooxidation. It is evident that the presence of polymer film causes an increase of the surface area. An increase in the surface area from 1.63 to  $42.68 \text{ m}^2/\text{g}$  in the presence of polymer film was observed.

Table 2. The surface area of fine fraction after biooxidation of arsenic refractory wastes

Following samples	Surface area [m <sup>2</sup> /g]	Increase of surface area after biooxidation
Initial sample	1.63	
After biooxidation without polymer film	30.87	18.94
After biooxidation with polymer film	42.68	26.18

## CONCLUSION

In conclusion, we can say that:

- The adsorption of dextrin onto the mineral surface creates a special polymer film which improves oxygen diffusion
- According to the differential mass balance model the diffusion coefficient of oxygen in the polymer film is  $D_f = 1.6 \cdot 10^{-5} \text{ cm}^2/\text{s}$ . It is comparable with the literature data
- An application of the polymer film provides a strong improvement of the biooxidation of arsenopyrite waste
- After the biooxidation process, the surface area of arsenopyrite increases from 1.63 to 42.68 m<sup>2</sup>/g. It is 7.24 – fold greater than the biooxidation process without the polymer film

## REFERENCES

- RASMUSSEN K., LEWANDOWSKI Z., (1998), *The accuracy of oxygen flux measurements using microelectrodes*, *Wat. Res.*, 32 (12), 3747-3755.
- RASMUSSEN K., LEWANDOWSKI Z., (1998), *Microelectrode measurements of local mass transport rates in heterogeneous biofilms*, *Biotechnol. Bioeng.*, 59 (3), 302-309.
- De BEER D., STOODLEY P., LEWANDOWSKI Z., (1997), *Measurement of local diffusion coefficients in biofilms by microinjection and confocal microscopy*, *Biotechnol. Bioeng.*, 53 (2), 151-158.
- STOODLEY P., LEWANDOWSKI Z., BOYLE D.J., LAPPIN-SCOTT M.H., (1998), *Oscillation characteristics of biofilm streamers in turbulent flowing water as related to drag pressure drop*, *Biotechnol. Bioeng.*, 57 (5), 536-544.
- LEWANDOWSKI Z., CUNNINGHAM B.A., (1998), *Biofilm process fundamentals*, in *Bioremediation: Principles and Practice*, volume 1, S.K.Sikdar, R.L. Irvine (Eds.), Technomic Publishing, Co., Inc., Lancaster, Basel, 511-546.
- KARAS H., SADOWSKI Z., (2002), *Biometalurgia metali nieżelaznych, podstawy i zastosowanie*, W.Charewicz (Ed.), Wrocław, CBPM Cuprum, Uniwersytet Wrocławski, 40-50.
- KARAMANEV D., MARGARITIS A., CHONG N., (2001), *The application of immobilization to the bioleaching of refractory gold concentrate*, *Int. J. Miner. Process.*, 62, 231-241.
- YAUNG S., LEWANDOWSKI Z., (1995), *Measurement of local mass transfer coefficient in biofilm*, *Biotechnol. Bioeng.*, 48, 737-744.
- LEWANDOWSKI Z., WALSE G., CHARACKLIS W.G., (1991), *Reaction kinetics in biofilms*, *Biotechnol. Bioeng.*, 38, 877-882.

- DUBOIS M., GILLES K.A., HAMILTON J.K., REBERS P.A., SMITH F., (1956), *Colorimetric method for determination of sugars and related substances*. Anal. Chem., 28 30, 350-356.
- SADOWSKI Z., JAZDZYK E., FARBISZEWSKA T. FARBISZEWSKA-BAJER J. (2001), *Biooxidation of arsenic refractory ores in the presence of polymer film*, Biohydrometallurgy: Fundamentals, Technology and Sustainable Development, V.S.T.Ciminelli, O.Garcia Jr. Eds., Elsevier, 217-223.

**Jażdżyk E., Sadowski Z.,** *Wpływ sztucznego filmu utworzonego z polimeru na proces bioutleniania odpadów arsenopirytowych*, Physicochemical Problems of Mineral Processing, 37 (2003) 69-76 (w jęz. ang.).

Określono wpływ filmu utworzonego z dekstryny na proces bioutleniania odpadów arsenopirytowych. Zbadano proces adsorpcji typowego polimeru cukrowego, dekstryny, na powierzchni materiału mineralnego. Określono wartości odczynu pH dla procesu bioutleniania odpadów arsenopirytowych. Stosując mikroelektrodę tlenową określono profile stężeń tlenu w filmie z polimeru. Korzystając z uzyskanych wyników obliczono współczynnik dyfuzji tlenu w warstwie utworzonego filmu. Współczynnik ten wyniósł  $1.6 \cdot 10^{-5} \text{ cm}^2/\text{s}$ . Wyniki uzyskane dla procesu bioutleniania wskazują na to, że film utworzony z polimeru odgrywa kluczową rolę zarówno w procesie unieruchomienia komórek bakteryjnych jak i w dyfuzji tlenu. W celu zintensyfikowania procesu bioutleniania odpadów arsenopirytowych niezbędna wydaje się być obecność filmu z polimeru na powierzchni ciała stałego.