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## **BIOLEACHING OF GALENA FLOTATION CONCENTRATE**

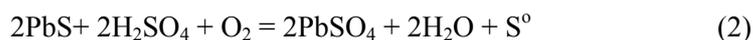
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The results of the bioleaching process of the galena flotation concentrates from ZGH Boleslaw S.A. by *Acidithiobacillus ferrooxidans* bacteria have been presented. It has been recorded that the final level of conversion of  $S_S$  into  $S_{SO_4}$  in bioleaching process is about 48% and it is two-fold higher than in the control examinations. However, in the course of reaction there is a gradual passivation of the galena surface caused by sparingly soluble  $PbSO_4$ . The analysis of raw materials and the products by X-ray analysis proved that there are differences in the composition of reaction products after the process of bioleaching and control leaching. The tested bacteria have been identified on the surface of the examined raw materials by scanning electron microscopy.

*Key words: Bioleaching, galena concentrate, x-ray analysis, passivation*

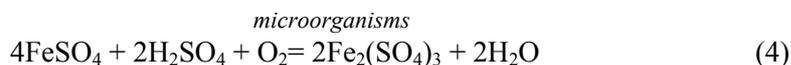
### INTRODUCTION

Galena is a sulphide mineral of great importance for lead metallurgy. Lead can be recovered from galena applying hydrometallurgical method, i.e. leaching by oxidant solutions, namely by iron(III) salt in the form of  $FeCl_3$  (Dutrizac, 1986). In the process of bioleaching chloride anion, which is toxic for microorganisms, is replaced by sulphate anion. The course of reaction of chemical and biological leaching of galena in acid medium by  $Fe_2(SO_4)_3$  can be presented by the following equations (Bang et al. 1995, Gonzales-Chaves et al. 2000):



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Using  $\text{Fe}_2(\text{SO}_4)_3$  as an oxidant in  $\text{H}_2\text{SO}_4$  solution, acid medium produces sparingly soluble  $\text{PbSO}_4$  (the product of the reaction). Therefore, hydrometallurgical process of lead recovery from sulphides should be modified and chloride solutions ought to be used again for lead extraction. Although this technology is considered as highly impractical, recent scientific reports present quite favourable opinions on the use of microorganisms for bioleaching of galena together with sphalerite in sulphide ores (Santhiya et al. 2001, Liao et al. 2004). *Acidithiobacillus ferrooxidans* bacteria are used in bioleaching process of lead and zinc sulphide minerals. This kind of bacteria can easily oxidize sulphur in reduced form (sulphide sulphur and elemental sulphur) into  $\text{S}_{\text{SO}_4}$  and they are also able to regenerate and reproduce in the process of leaching the  $\text{Fe}^{3+}$  ion (Karavaiko 1985, Torma, Bang et al., 1995). Another kind of sulphur bacteria which can be used as well are *Acidithiobacillus thiooxidans*, however they are able to oxidize only the reduced sulphur compounds (Santhiya et al. 2001). The effect of forming a passive film of elemental sulphur in the course of reaction is prevented by the action of *Acidithiobacillus thiooxidans* (reaction 3). Electrochemical interaction of Zn and Pb minerals in the process of biological leaching (da Silva et al. 2003) and their properties and functioning in the flotation process preceded by bioleaching have been examined as well (Santhiya et al. 2001).

The aim of this paper is to analyse and define suitability and applicability of *Acidithiobacillus ferrooxidans* bacteria for bioleaching of lead sulphide flotation concentrates, produced by mine Boleslaw (Poland). At this time, galena concentrate (PbS) has been used as a raw material for producing lead, applying pyrometallurgical methods.

## EXPERIMENTAL METHODS

### MATERIALS

Table 1 presents the chemical constitution of the examined flotation galena concentrate which was used in the bioleaching experiments. X-ray analysis revealed that raw concentrate of flotation galena was composed mainly of PbS (~80%). The percentage of other components was as follows: hydrocerusite (~5%), marcasite (~5%), sphalerite (~5%), pyrite (~4%) and minute quantities of gypsum and quartz (~2% in total).

Synthetic lead sulphide PbS (100%) of high purity made by IMN Gliwice has been used for a comparison.

Table 1. Constitution of flotation galena concentrate from ZGH Boleslaw S.A.

Constituent	H <sub>2</sub> O	Zn	Pb	S <sub>total</sub>	Fe	CaO	MgO	Sso <sub>4</sub>	Ss	SiO <sub>2</sub>	Cd
Contents [%]	7.5	2.44	69.3	18.4	6.21	0.77	0.22	0.33	18.09	0.50	0.02

#### BACTERIAL CULTURE

Strain of F3-02 *Acidithiobacillus ferrooxidans* bacteria of high activity in the oxidation process of iron(II) and reduced sulphur compounds have been used in the experiments. The strain of bacteria has been separated from ferruginous mineral water (Piwniczna-Lomnica). In preparation for the experiment the bacteria have been cultivated in a modified 2K medium. 2K liquid medium has got the following composition: (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>-3,0; KCl-0,1; MgSO<sub>4</sub> · 7H<sub>2</sub>O-0,5; Ca(NO<sub>3</sub>)<sub>2</sub>-0,01; K<sub>2</sub> HPO<sub>4</sub>-0,5; FeSO<sub>4</sub> · 7H<sub>2</sub>O - 9,84 (g/dm<sup>3</sup>) (Silverman 1959). The concentration of Fe(II) in 2K medium was 2,0 g/dm<sup>3</sup> and the application of 2M H<sub>2</sub>SO<sub>4</sub> solution allowed to obtain pH 2 medium which actually became the leaching solution for galena concentrate. The bacteria used in the experiments were not initially adapted to be with lead compounds.

#### BIOLEACHING EXPERIMENTS

The experiment was carried out in Erlenmeyer's flask of 300 cm<sup>3</sup> capacity. The quantity of galena concentrate was 5% weight/volume, the volume of solution was 100 cm<sup>3</sup>, whereas the strain of bacteria was 10 cm<sup>3</sup>. Laboratory shaker was used to aerate the leached samples, the number of cycles was 130 revolutions/min and the temperature was 25°C. Pb, Zn, Fe(II) concentration, oxidizing-reducing potential, pH, S<sub>total</sub> and S<sub>SO4</sub> contents in the residue after leaching have been analysed in the solution during the experiments. The method of spectral atomic absorption was applied to determine Zn and Pb concentration, whereas Fe(II) concentration was determined by manganometry method. S<sub>SO4</sub> was determined by weigh method, S<sub>S<sup>2-</sup></sub> was calculated as the difference between S<sub>total</sub> contents determined by weigh method and S<sub>SO4</sub>. The residue was analysed by X-ray method. The surface analysis were carried out by scanning microscopy method (SEM). The obtained results were verified by the examinations performed in sterile conditions.

#### X-RAY ANALYSIS

The examinations of phase composition of flotation galena samples before and after leaching process were carried out using PW 3710 X-ray diffractometer (produced by Philips). It was realised at the following measurement conditions: radiation Cu K<sub>α1</sub>; graphitoidal monochromator, 40kV voltage, 35mA intensity, counting time of the impulses - 2s, rate of meter shift - 0.02.

## STRUCTURAL ANALYSIS

The examinations of samples microstructure were performed using HITACHI S-4200 scanning microscope, which was coupled with EDS X-ray spectrometer and Voyager microanalysis system. The bioleaching residues were dried outdoors on the filter. The samples were prepared for analysis on a copper pad and were covered (sprayed) by gold.

## RESULTS AND DISCUSSION

## EXTRACTION OF METALS, Eh CHANGE, pH CHANGE

Table 2 presents the results which are the proof that in the process of bioleaching of flotation galena concentrate at the period of 288 h. As can be seen, *Acidithiobacillus ferrooxidans* bacteria caused rapid oxidation of Fe(II) into Fe(III) in biological leaching. It was resulted in growth of oxidizing-reducing potential measured in the slurry. This potential was increased from +408,6 mV to 560,8 mV after 288 h of bioleaching. The value of oxidizing-reducing potential (redox) in the control experiment was 286,5 mV at the same period of time. The increase of Fe(II) oxidation in the control solutions was entirely spontaneous due to atmospheric oxygen. For both the biological and control processes the total oxidation of Fe(II) ions was noticed after 384 h. It was found that there was a decrease of potential redox and it was connected with pH changes of the slurry.

The analysis of pH changes showed that the initial pH 2 of the slurry rises quite rapidly up to pH 4-5 which has been caused by abrupt course of chemical reaction of oxidizing PbS into PbSO<sub>4</sub> and sulphur S<sup>0</sup> (reaction 2). The next stage of reaction was possible due to the presence of *A. ferrooxidans* microorganisms and the biological reaction of oxidizing S<sup>0</sup> into H<sub>2</sub>SO<sub>4</sub> (reaction 3) which led to a gradual increase of acidity and a decrease of pH to lower values. In practice, it can indicate the progress of the reaction of biological oxidizing of sulphide PbS since in the control examinations no process of rapid acidifying of the solution is observed which means that the reaction of biological oxidizing of elemental sulphur into H<sub>2</sub>SO<sub>4</sub> does not take place.

It was found that there was an increase of the concentration of zinc released into the solution from 0,0 to 0,196 g/dm<sup>3</sup>. To compare, the zinc concentration in control experiments increased only up to 0,040 g/dm<sup>3</sup>. The function of zinc in the examined set was to indicate how the process precedes ( progress of the reaction). The lead concentration in the solution in the presence of sulphate ions ranged from 0,0019 to 0,0033 g/dm<sup>3</sup> but in the control examinations it was from 0,0021 to 0,0036 g/dm<sup>3</sup>. The highest concentration of Pb was reached in the leaching process of synthetic galena – 0,0098 g/dm<sup>3</sup>.

Table 2 presents, just for comparison, the results of biological oxidizing of pure synthetic sulphide PbS. It can be noticed that the initial rapid processs of neutralizing the solution as a result of chemical oxidation of PbS into PbSO<sub>4</sub> was the reason of

bacterial activity decline. The surface of galena is then covered with a passive film of lead sulphate, which makes further process of galena oxidizing impossible. The redox potential stays at low unchangeable level which indicates that there is no oxidizing of Fe(II). At the same time pH growth caused hydrolytic precipitation of iron salts which got down to the sediment.

Table 2. The results of bioleaching flotation galena concentrates by *A. ferrooxidans* F3-02 in 2K solutions. Marking: (b) - biological, (ktr) - control, (cz) - biological leaching of pure PbS

Nr	Czas [h]	PH	Eh, [mV] vs Ag/AgCl	Fe(II) [g/dm <sup>3</sup> ]	Zn [g/dm <sup>3</sup> ]	Pb [g/dm <sup>3</sup> ]
PbS1 (ktr)	0	2.2	413.4	2.159	0.00	0.00
PbS4 (b)		2.2	408.6	2.159		
PbS10(cz)		2.2	410.2	2.159		
PbS1 (ktr)	48	4.7	157.6	2.159	0.022	0.0036
PbS4(b)		3.2	433.2	1.127	0.025	0.0033
PbS10(cz)		5.2	130.1	1.985	0.005	0.0074
PbS1(ktr)	96	4.9	151.0	1.961	0.021	0.0030
PbS5(b)		3.3	415.0	0.392	0.090	0.0030
PbS10(cz)		5.1	130.6	2.00	0.005	0.0038
PbS1(ktr)	192	4.2	181.5	1.796	0.023	0.0032
PbS6(b)		3.2	428.8	0.561	0.091	0.0027
PbS10(cz)		5.0	133.9	1.904	0.005	0.0041
PbS2(ktr)	288	3.4	286.5	1.113	0.024	0.0022
PbS7(b)		2.7	560.8	0.00	0.157	0.0021
PbS11(cz)		5.0	156.4	1.041	0.003	0.0035
PbS3(ktr)	384	3.4	478.3	0.00	0.040	0.0021
PbS8(b)		2.2	534.5	0.00	0.196	0.0019
PbS12(cz)		5.4	174.0	0.555	0.004	0.0098

The best pH conditions for *A. ferrooxidans* bacteria are pH 2-3 [Karavaiko 1985]. Therefore, the alkaline medium is inappropriate for them. Lead sulphide in natural galena is not easily accessible in the process of biological oxidizing contrary to PbS in chemical reagent which is present there, thus there are differences in activity and state of the samples. These conclusions are similar to those presented in the paper by Cisneros-Gonzales, (1999).

#### THE LEVEL OF S<sub>S</sub> CONVERSION INTO S<sub>SO4</sub>

Chemical analysis of residues after bioleaching and control leaching regarding time relations has been presented in Table 3. The results prove that the dynamics of conversion reaction of sulphide sulphur S<sub>S</sub> into sulphate sulphur S<sub>SO4</sub> was higher in the case of bioleaching. The conversion of S<sub>S</sub> into S<sub>SO4</sub> amounted up to 42,39% after 192

h. The level of sulphide sulphur conversion into an oxidized form was 47,99% after 288 h of duration of leaching process by *A. ferrooxidans* bacteria but the level of conversion was only 27,25% in control leaching. Further biological oxidation of galena surface is quite different because of gradual passivation of its surface by lead sulphate, which has also been confirmed by other examination results [Bang et al. 1995, Gonzales-Chaves et al. 2000].

Table 3. Composition of residues after leaching of flotation galena in [%]

Serie	S <sub>SO4</sub>	S <sub>S</sub>	Zn	Pb	Fe	S <sub>SO4</sub> /(S <sub>tot.</sub> -S <sub>O4</sub> )*	Time, [h]
Control leaching	2.70	16.10	2.01	63.4	7.40	1.7	0
	2.72	15.07	1.91	63.4	7.94	18.05	96
	3.67	13.47	1.69	61.9	6.30	16.73	192
						27.25	288
Biological leaching	3.52	15.48	1.82	60.6	7.81	22.74	96
	5.32	12.55	1.59	57.8	8.37	42.39	192
	5.51	11.48	1.43	57.9	8.15	47.99	288
	5.54	11.13	1.40	56.9	7.41	49.78	384

\* The level of S<sub>S</sub> conversion into S<sub>SO4</sub>

There is a layer of PbSO<sub>4</sub> as a product of the reaction, on the grains of galena as shown in microscope pictures (Fig.2). *A. ferrooxidans* bacteria dipped in the base, partly covered with lead sulphate can be seen as well. Prolonging the time of leaching up to 384 h does not make any difference in the progress of oxidizing reaction of galena and the level of sulphide sulphur conversion into sulphate sulphur S<sub>SO4</sub>/(S<sub>total</sub> - S<sub>SO4</sub>) remains unchanged in biological examinations. Bacterial colonies were not present in bioleaching examinations of pure synthetic galena but its surface was covered with fine PbSO<sub>4</sub> crystals, which were formed by chemical reaction (2).

#### PHASE ANALYSIS OF RESIDUES

The analysis of X-ray radiography (Fig.1) showed that in the sample of galena flotation concentrate after the process of bioleaching by *A. ferrooxidans* microorganisms for 288h, the phase composition of the sample is as follows: galena PbS (~43%), anglesite PbSO<sub>4</sub> (~40%), pyrite FeS<sub>2</sub> (~8%), jarosite (H<sub>3</sub>O)Fe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub> (~6%), sulphur admixture (~3%).

In the sample of flotation galena after control leaching (288h) in iron salts (II) the following stages could be distinguished: galena PbS (~62%), anglesite PbSO<sub>4</sub> (~25%), pyrite (~6%), jarosite of mixed and difficult to identify composition (with H<sub>3</sub>O<sup>+</sup>, Pb<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>?) (~4%), marcasite FeS<sub>2</sub> (~3%). Trace amount of sulphur is also quite possible.

The composition of galena flotation concentrate in the process of biological leaching indicates that there is the higher concentration of oxidized sulphur compounds in the sample compared to the control tests.

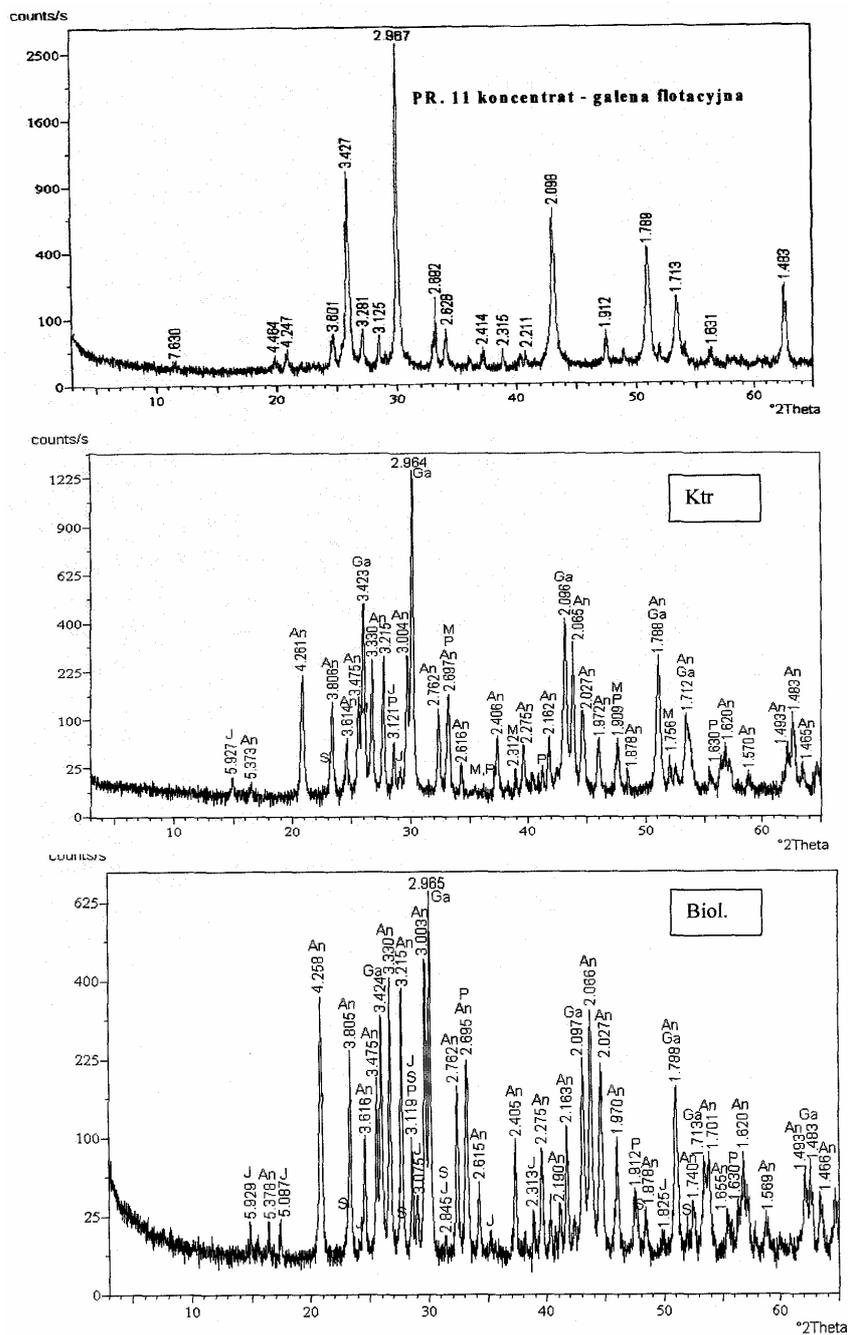


Fig. 1. Radiography of PbS flotation galena and control leaching residues (Ktr), biological leaching residues (Biol). Marking: J-jarosite, An-anglesite, Ga-galena, P-pyrite, M-marcasite

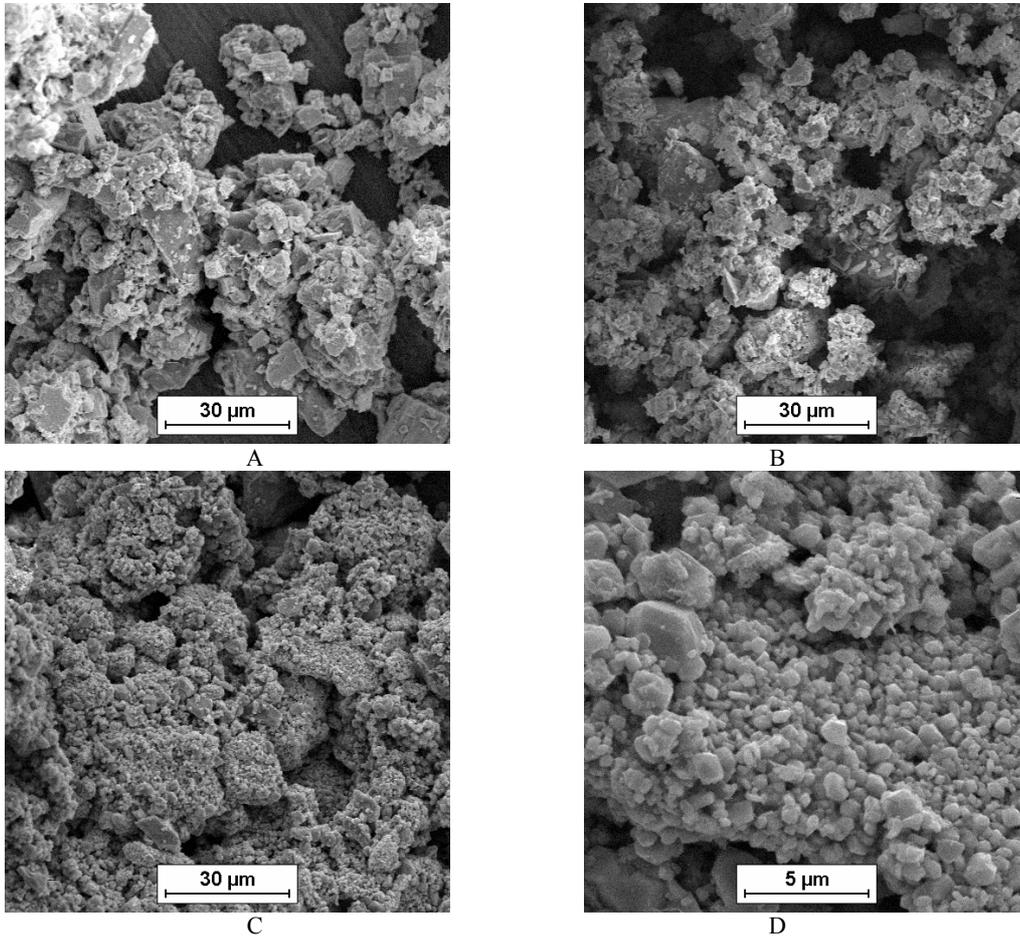


Fig. 2. SEM microphotographs of galena: A-raw galena flotation concentrate and B-after sterile control leaching (288h), 500x; C-galena flotation concentrate after bioleaching using *Acidithiobacillus ferrooxidans* (288 h) 500x, and D-3000x

#### MICROSCOPE ANALYSIS

The picture of the surface of raw concentrate of flotation galena after the process of bioleaching and control leaching in the solutions of iron salts has been presented in Fig. 2 and Fig.3. The method of scanning microscopy was applied. It can be noticed that the morphology of galena has been changed by the leaching solution. The surface of grains becomes covered and coated with a film of reaction products (Fig. 2). The film of reaction products ( $\text{PbSO}_4$  and most likely  $\text{S}^0$ ) can also be responsible for making the surface of galena passive as well as reducing the penetration of solution components and oxygen inside the grain. On the surface of galena in the process of bioleaching there were *Acidithiobacillus ferrooxidans* bacteria cells stuck to the surface and dipped in the leached base (Fig. 3).

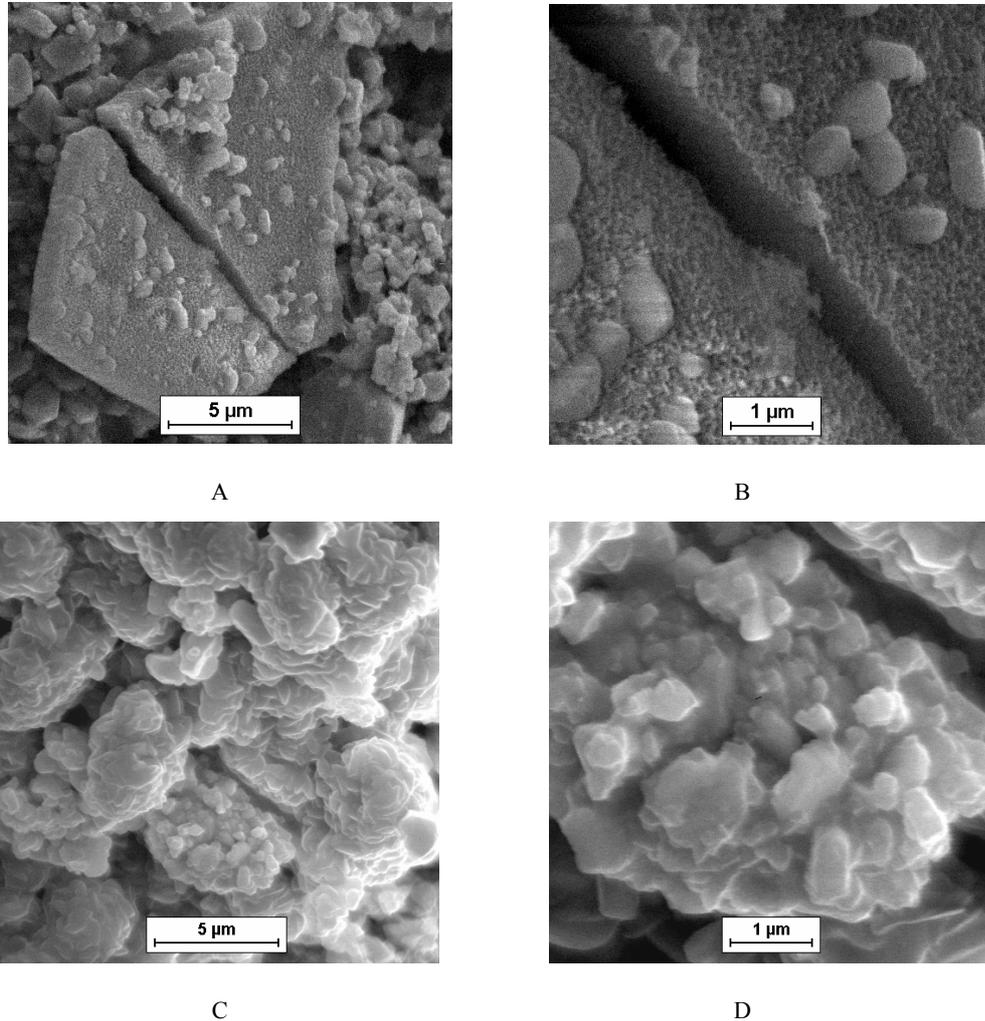


Fig. 3. SEM microphotographs of galena flotation concentrate surface after bioleaching using *Acidithiobacillus ferrooxidans*: (288 h) - A-3000x, B-10000x; and (384h) - C-3000x, D-10000x

### SUMMARY

The examinations on bioleaching of natural galena flotation concentrate in iron(II) salt solutions by *Acidithiobacillus ferrooxidans* bacteria allowed to draw some conclusions that the bacteria have an impact on higher yield in the course of reaction of oxidizing PbS into PbSO<sub>4</sub> as compared to the control data. The level of conversion of S<sub>S</sub> into S<sub>SO4</sub> after 288h of bioleaching amounted up to 47,99% whereas in the control examinations it was only 27,25%. After a period of time (384 h) though, there is a definite inhibiting of the course of S<sub>S</sub> oxidizing reaction. The possible cause of

inhibiting the reaction is the formation of passive film of products of galena oxidizing - lead sulphate - on the surface of leached galena and the fact that the access of the leaching agent and microorganisms inside the grain is made difficult.

#### ACKNOWLEDGEMENTS

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**Pacholewska M.**, *Biologowanie galenowego koncentratu flotacyjnego*, Physicochemical Problems of Mineral Processing, 38, (2004) 281-290 (w jęz. ang.).

W pracy przedstawiono wyniki procesu biologowania przy udziale bakterii *Acidithiobacillus ferrooxidans* naturalnych siarczkowych koncentratów ołowiu z ZGH” Bolesław” S.A. Stwierdzono, że końcowy stopień konwersji siarki Ss do Sso<sub>4</sub> w procesie biologowania wynosi około 48% i jest dwukrotnie wyższy w porównaniu z próbami kontrolnymi. W miarę postępu reakcji zachodzi jednak stopniowa pasywacja powierzchni galeny przez trudno rozpuszczalne produkty (prawdopodobnie PbSO<sub>4</sub>, S<sup>0</sup>). Analiza fazowa surowców i produktów metodą rentgenograficzną potwierdziła różnice w składzie produktów reakcji po ługowaniu biologicznym i kontrolnym. Na powierzchni badanych surowców zidentyfikowano testowane bakterie przy użyciu elektronowej mikroskopii skaningowej.