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BIOOXIDATION OF MINING TAILINGS FROM ZŁOTY STOK

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The biooxidation of gold-bearing arsenic concentrate from mining tailing was investigated. The strain of *Thiobacillus ferrooxidans* isolated from the Złoty Stok tailing heaps was used. The chemical and biooxidation processes were monitored by checking the ferrous, ferric and arsenic concentration in the leaching solution. Leaching experiments were conducted using both coarse (-0.5 +0.125 mm) and fine (-0.045 mm) fractions. The samples were examined by means of the specific surface area measurements and the X-ray diffraction analysis. The small differences were observed during the oxidation of coarse and fine fractions. The slow chemical dissolution of loellingite (AsFe_2) a main arsenic-bearing mineral, was supported by X-ray diffragrams. In the case of a fine fraction oxidation, the precipitation of ferric arsenate was responsible for the lower Fe and As readings. The production of new phase was also supported by the FTIR spectra. Obtained results suggest that the direct biooxidation mechanism was responsible for the arsenic-bearing concentrate biooxidation.

Key words: bioleaching, loellingite, arsenopyrite, *Thiobacillus ferrooxidans*, gold, ferric arsenate

INTRODUCTION

Biooxidation pre-treatment of refractory gold ores and flotation concentrates is an alternative method to roasting and pressure oxidation (Ehrlich, Brierley 1990; Rossi 1990; Barret et al. 1993; and Rawlings 1997). Refractory gold ores contain gold as

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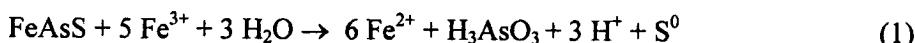
tiny inclusions in association with the sulphide, arsenosulphide and arsenic-bearing minerals (Wakao et al. 1988; Malatt 1999).

Bacterial oxidation of sulphide or arsenic refractory ores is mainly based on the action of the acidophilic, chemolithotrophic microorganisms such as *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans*. These microorganisms are used to accelerate the rate of minerals oxidation by breaking down the crystal lattice and thus liberation of the microinclusions of native gold.

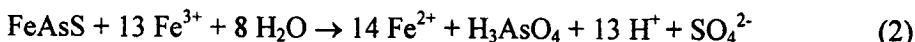
Generally, two broad mechanisms of bacterial oxidation have been proposed:

- i. the "direct" mechanism in which microbial cells are attached to the mineral surface and used an enzyme system with oxygen.
- ii. The "indirect" mechanism, in which the role of microorganism cells, is to produce ferric ions by oxidation of ferrous ions. The ferric ions participate in the chemical oxidation of minerals.

Most work with regard to the biooxidation has been done with pyrite and arsenopyrite (Adam et al. 1994; Nyashnu et al. 1999). The arsenopyrite was more rapidly and extensively destroyed than the pyrite. The biooxidation of arsenopyrite can be realised by the following way:



At the extreme oxidation condition, sulphur is completely oxidised to S(VI) and arsenic (III) is rapidly oxidised to arsenic(V):



Wakao et al. (1988) have suggested that *Thiobacillus ferrooxidans* was not responsible for arsenate oxidation. According to Wakao's paper, the potential energy derived from the arsenate oxidation is not necessary for the growth of bacteria.

Chilean refractory gold ores containing both enargite (Cu_3AsS_4) and cobalt bearing sulphides (Co,Fe) ($\text{AsS})_2$ as a gold matrix were also processed (Chimorro et al. 1998, Wiertz et al. 1999). The bioleaching process, in which the cobalt and arsenic were recovered, has been offered. It was found that bioleaching of enargite is governed by the indirect mechanism.

The aim of this study was to determine factors affecting the efficiency of arsenic-gold concentrate biooxidation in shake flask studies systems. The mechanism of bioleaching of arsenic-bearing minerals is also investigated.

MATERIALS AND METHODS

Tailings from a closed arsenic mine at Zloty Stok (Lower Silesia, Poland) contain gold-bearing minerals (loellingite and arsenopyrite), and were hand collected and used in laboratory experiments. The tailing samples were ground and wet-screened to obtain the three fractions: 0.5-0.125, 0.125-0.040 and -0.040 mm. The arsenic tailing assayed 27.98 % Fe, 4.99 % As, 15.78 % SiO₂, 8.65 % S, 2.81 % Mg, 2.41 % Ca, and Au 3-7 ppm. The carbonate minerals present in the feed material were dissolved using sulphuric acid.

The bacteria *Thiobacillus ferrooxidans* used in the biooxidation tests were isolated from slurries collected at the old arsenate mine Zloty Stok (Sadowski et al. 1998). The microorganism strain was initially adapted for growth in the presence of mineral feed prior to the biooxidation experiments.

Leaching and bioleaching experiments were performed in 250 ml Erlenmeyer flasks using 3 g of mineral sample in 100 ml of a nutrient solution. The slurry was conditioned in the medium 3K over 24 hours, then the inoculum was added to the bioleaching samples. Thymol, as a bacterial inhibitor was added to the chemical leaching samples. The flasks were shaken on a table shaker at the temperature equal to 30°C. Bacterial oxidation tests were performed at an initial pH = 2.

The flasks were periodically analysed for pH, iron(II) and total iron by the colorimetric method. The total arsenic concentration in the supernatant was determined by oxidation arsenic(III) to arsenic(V) and the concentration of molybdenum blue complex was measured at 865 nm.

Specific surface area of the mineral samples before and after of biotreatment was determined according to the BET method. Flow Sorb II 2300 (Micromeritics) was used to a surface area measurement.

The X-ray diffraction spectra of the mineral samples were obtained using Philips PW 1390 equipment, with CuK_a radiation and Ni filter.

Infrared spectra of sample obtained from after and before biooxidation were recorded on a Fourier Transformed Infrared Spectrometer Perkin Elmer Model 1600 FTIR. The sample was prepared by mixing 2 mg of mineral samples with 150 mg of KBr for transmission spectroscopy.

RESULTS

The initial bioleaching and chemical leaching experiments involving the arsenic bearing concentrate were carried at 12 % (w/v) of solid using -0.5+0.125 mm fraction. Figure 1 and 2 show the variation in the As, and Fe(III) concentrations during the leaching test. These data represent the average response of four particular tests. The

pH values were also recorded. The arsenic analyses were only performed on the liquid phase. In both cases, an increase of arsenic concentration was observed at the initial period. As can be seen from Fig. 1 and Fig. 2 the arsenic concentration in the bioleaching test was higher than that for the chemical leaching experiment.

Arsenic(III) is a primary product of the chemical and bacterial oxidation of loellingite and is normally oxidised by iron(III) to arsenic(V) in a secondary process. The predominance of arsenic(III) was observed at the early stage of oxidation period.

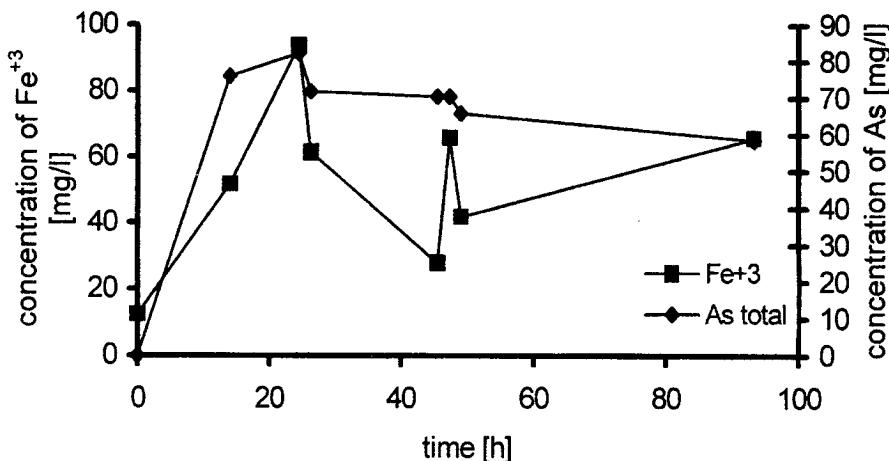


Fig. 1. Oxidation of arsenate concentrate (fraction $-0.5 +0.125$ mm)

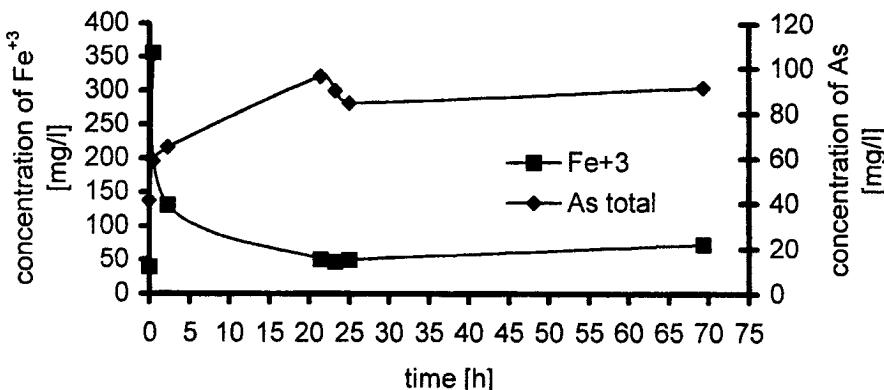


Fig. 2. Biooxidation of arsenate concentrate (fraction $-0.5 +0.125$ mm)

The leaching results are confirmed in the Table 1, where the surface areas of bioleaching samples are higher than the surface areas of chemical leaching samples.

Table 1. The surface areas of arsenic concentrate samples after the both chemical and bioleaching

Sample size [mm]	Surface area [m ² /g]			Time of leaching [h]	Nature
	Without Leaching	Chemical Leaching	Bioleaching		
-0.5 +0.125 (30%)	0.32	1.02	2.94	24	2K
-0.5 +0.125(12%)	0.32	5.55	7.49	70	2K
-0.040 (6%)	6.64	27.6	28.8	65	2K
-0.040(12%)	6.64	12.54	16.18	65	2K
-0.040(18%)	6.64	11.77	11.87	65	2K
-0.040(12%)	17.64	58.64	60.45	32 days	9K

The effect of density on the rate of oxidation was investigated using a fine fraction (-0.040mm) of arsenic bearing concentrate. It was found, by analysing the surface areas of leaching samples that the optimal biooxidation conditions correspond to the concentration of 12 % (w/v). The surface areas achieved for the same time period of bioleaching are also shown in Table 1.

The high concentration of solid may induce a limitation in agitation of suspension and inhibits the leaching of mineral. Consequently the surface areas of samples at the higher concentrations have been lower than in the case of 5% of solid (Table 1).

A part of X-ray diffraction spectra of samples before and after of bio- and chemical leaching are shown at the Figure 3. They confirm that a biooxidation of loellingite is more extensive than chemical oxidation.

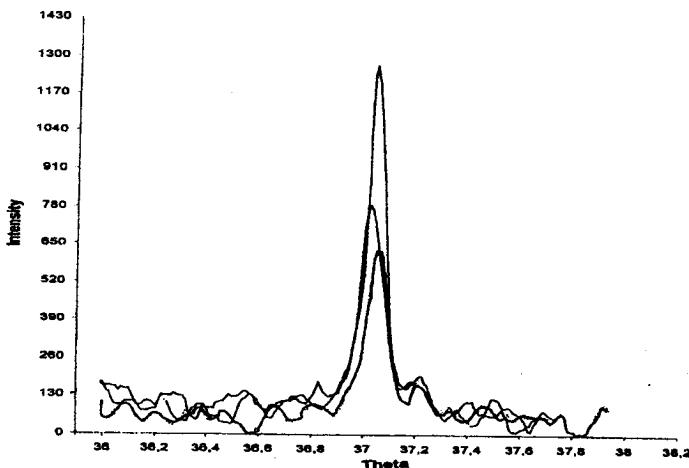


Fig. 3. A part of X-ray diffraction pattern of - 0.045 mm fraction of arsenate concentrate before and after both the chemical and bioleaching

As can be seen from Fig. 4 and 5, the fine fraction showed a similar trend in the course of the bioleaching and chemical leaching like the coarse samples.

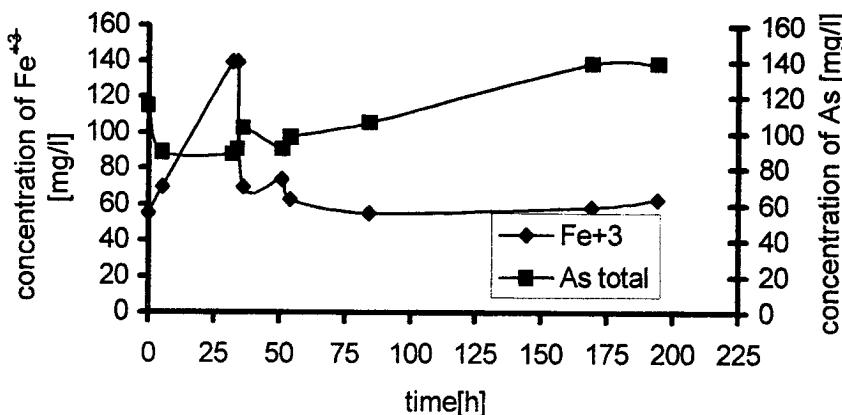


Fig. 4. Bioleaching of fine arsenate concentrate

Figure 5 indicates that the arsenic concentration in the solution slowly increased during the period of bioleaching. The evolution of arsenic concentrations, different from the leaching results of coarse fraction, can be attributed to the ferric arsenate precipitation.

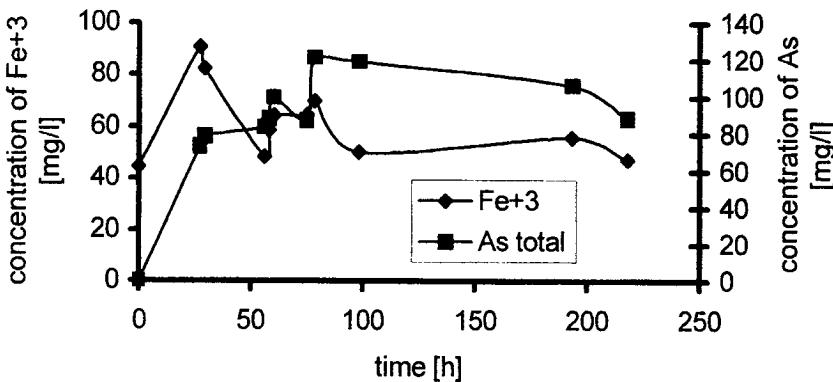
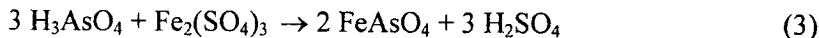


Fig. 5. Chemical leaching of fine arsenate concentrate

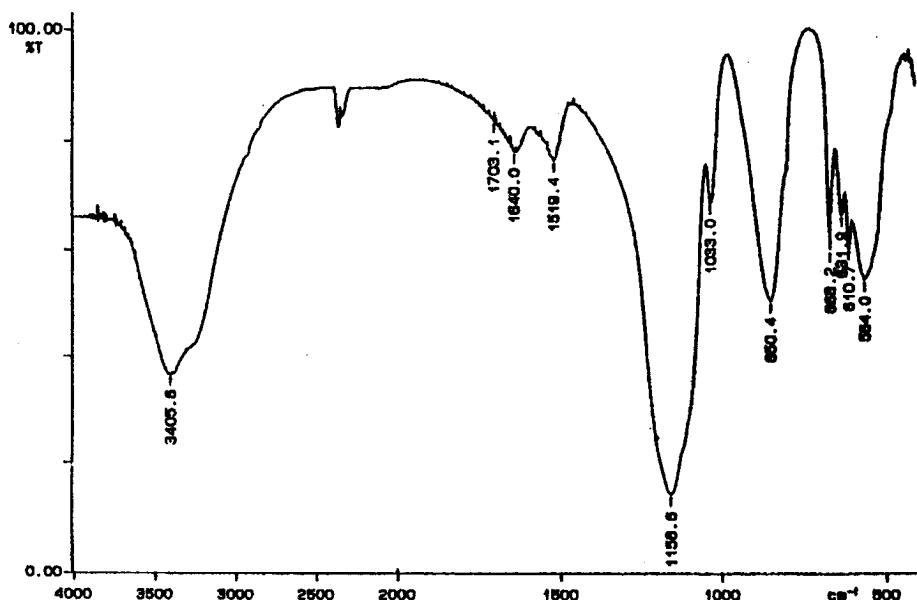
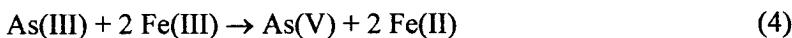


Fig. 6. FTIR spectra of ferric arsenate precipitated during the leaching tests

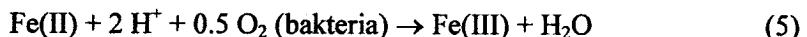
The precipitation of ferric arsenate was supported by the FTIR studies. From Fig. 6 it is apparent that the bands at 850 and 1033 cm^{-1} are assigned to the stretching vibration of ferric arsenate. The band at 1640 cm^{-1} corresponds to the stretching vibration of the structural water principally linked with ferric arsenate

DISCUSSION

The bacterial oxidation of mining tailing from Zloty Stok is not fully understood. It results from complex mineralogical composition of the tailings. According to early research (Norman, Snyman 1988; Komnitsas et al. 1994; Taxiarchou et al. 1994; Breed et al. 1996) the biooxidation of arsenic-bearing minerals results in a range of products with varying amounts of end forms of sulphur, iron and arsenic. Arsenic, for instance, may be present as As(III) or As(V). It was suggested that microbes did not oxidise arsenic (Fernandez et al. 1995, Cassity, Petic 1999). The potential energy derived from the arsenic oxidation is not necessary for the growth of the micro-organisms. For this reason, the As(III) ions are chemically oxidised by ferric iron.



The iron(II) produced in the above equation must be converted back to the iron(III) by bacterial oxidation process:



The variation of arsenic speciation is caused by a precipitation of FeAsO_4 . The precipitation of ferric arsenate can be realised at a Fe/As ratio higher than 3 (Reddy et al. 1987). During the bacterial leaching of arsenic-bearing mineral the $\text{Fe(III)}/\text{As}$ ratio was changed. Arsenic ions were found to dominate in the initial stage of the biooxidation of fine fraction of arsenic-bearing ore. When the concentration of Fe(III) was suitable, the precipitation of iron arsenate occurs. The concentration of arsenic ions in solution decreases at the end period of leaching (Fig. 1 and Fig. 5). It is interesting to note, that the biooxidation process of the fine arsenic bearing solid waste in the presence of nutrient 9K medium can not be controlled by a change of arsenic ions concentration. The chemical analysis revealed that the leach solution was free from arsenic ions. The absence of arsenic ions is likely to be due to the ferric arsenate precipitation. On the other hand, the arsenic toxicity to *T. ferrooedans* is well known (Cassity and Petic 1999). In general, the toxicity decreases upon precipitation of FeAsO_4 . It suggests that the bioleaching of arsenic bearing solid waste should be realised at a high ferric ion concentration. The concentration of arsenic ions in the leach solution can not be a parameter of biooxidation process.

CONCLUSIONS

1. Biooxidation of arsenic-bearing gold ore is a complex process, which occurs in a sequential way:
 - i. the first stage corresponds to biooxidation of iron and leaching
 - ii. in the second stage, arsenic(III) is oxidised to arsenic(V)
2. The recovery of arsenic was satisfactory for both coarse and fine fractions.
3. Concentration of As cannot be used to measure the extent of this process due to the precipitation of iron(III) arsenate during the fine fraction bioleaching.
4. The micro-organisms used for the biooxidation showed a good tolerance to the high arsenic concentration.

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Przeprowadzone wcześniejsze badania wskazują, że odpady górnicze zgromadzone na Hałdzie Jan koło Złotego Stoku stanowią potencjalny surowiec do otrzymywania złota. Przestawiona praca zawiera wyniki badań nad procesem bioutleniania próbek mineralnych pobranych z hałdy Jan. W badaniach użyto homogenicznych bakterii *Thiobacillus ferrooxidans* wcześniej wyselekcyjnowanych z tego złoża. Próbom biologowania poddano grubo- i drobnoziarnistą frakcję surowca. Przebieg procesu bioutleniania analizowane przez kontrole zmian stężenia jonów Fe(II), Fe(III), As oraz pH roztworu. Określono zmiany w powierzchni właściwej próbek mineralnych wywołane procesem bioutleniania. Zachowanie gruboziarnistej próbki mineralnej mało różni się od chemicznego i biologicznego utleniania materiału drobnoziarnistego. Badania rentgenowskie wskazują na łatwiejsze bioutlenianie loellingitu w porównaniu z procesem chemicznym. Zmniejszenie stężenia jonów arsenu w roztworze w końcowym okresie chemicznego fugowania należy tłumaczyć wytraceniem się arsenianu żelaza. W przypadku zastosowanie pożywki 9K do biologowania, stężenie arsenu w roztworze spadało do zera. Badania spektroskopowe potwierdzają powstanie arsenianu żelaza w procesie bioutleniania drobnoziarnistej frakcji odpadów górniczych z hałdy Jan.