

## MICROBIAL OXIDATION OF THE MIXED PYRITE MILL TAILINGS

MAŁGORZATA PACHOLEWSKA

The Silesian University of Technology, Department of Metallurgy  
ul. Krasińskiego 8, 40-019 Katowice, Poland

Keywords: waste pyrite mill tailings, *Acidithiobacillus ferrooxidans*, diagram Eh-pH of Fe-S-H<sub>2</sub>O system.

### BIOLOGICZNE UTLENIANIE MIESZANYCH ODPADÓW PIRYTÓW POWĘGLOWYCH Z PRZEMYSŁU ENERGETYCZNEGO

Obecne metody składowania i wykorzystania mieszanych odpadów piryków powęglowych mają za zadanie przeciwdziałać skutkom zagrożenia dla środowiska – emisji związków siarki, metali ciężkich i kwaśnych odcieków. Celem pracy było przeprowadzenie w warunkach laboratoryjnych badań nad potencjalnym zagrożeniem spowodowanym przez biologiczne utlenianie mieszanych odpadów piryków powęglowych przy udziale bakterii, posiadających zdolność utleniania związków żelaza(II). Analizowano zmiany: stężenia Fe(II) i Fe(III) w roztworach, potencjału utleniająco-redukcyjnego Eh, pH, składu fazowego odpadów metodą rentgenograficzną, morfologii odpadów metodą mikroskopii skaningowej. Rezultaty badań wykazały, że w obecności mikroorganizmów występuje znaczny wzrost dynamiki roztwarzania związków Fe(II) z mieszanych odpadów oraz wzrost zakwaszenia roztworów w porównaniu z procesami chemicznego utleniania. Wykazano ponadto, że pomimo znacznej aktywności mikrobiologicznej w procesie utleniania związków Fe(II) do Fe(III), stopień uwolnienia żelaza z odpadów jest ograniczany przez strącanie trudno rozpuszczalnych związków żelaza(III) – jarosytów. Proces ten jest związany z osiąganiem stanu równowagi chemicznej i elektrochemicznej w układzie Fe-S-H<sub>2</sub>O.

#### Summary

The results of microbial oxidation under laboratory conditions of mixed pyrite mill tailings from power industry by *Acidithiobacillus ferrooxidans* bacteria have been presented in the paper. The analysis of the dynamics of Fe(II)/Fe(III) concentration changes, oxidizing-reducing potential Eh and pH as well as phase analysis revealed that despite a significant activity of microorganisms in microbial oxidation process, the level of iron releasing from wastes is limited by the process of precipitation of low-soluble iron(III) compounds. This process is connected with establishing the state of equilibrium in Fe-S-H<sub>2</sub>O system.

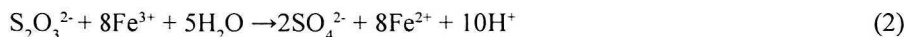
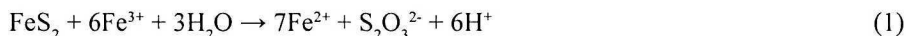
#### INTRODUCTION

Pyrite FeS<sub>2</sub> and other metal sulphides in mine tailings were transformed to sulphur compounds, heavy metal compounds, and acid waste waters resulting from natural processes of chemical and biological weathering of wastes stored in dumps. They have always been hazardous for the environment: the air, soil and water. The problems of storing and reusing pyrite mill tailings from power plants have been of great concern for quite

a long time [9]. Some serious research works have been carried out on the processes of microbiological desulfurization of coal and on extracting heavy metals from coal in order to reduce pollution of the environment [3–6, 10]. At present the best solution for storing pyrite mill tailings from the power plant (Jaworzno III Power Plant S.A.) seems to be mixing pyrite mill tailings with slag and decarbonized water sediments in the form of so-called mixed pyrite mill tailings [9].

The aim of the presented work was to carry out examinations in laboratory conditions on microbial oxidation of mixed pyrite mill tailings in water solutions and to obtain essential information on the dynamics of releasing pollutants into the environment and at the same time to define factors influencing the solubility process. The obtained results will be useful in further investigations undertaken in order to determine the behavior of pyrite and other minerals in the post-flotation tailings coming from the flotation process of complex Zn-Pb-Cd sulphide ore in ZGH Bolesław S.A. It is known that the oxidation rate of such minerals is greatly enhanced by the catalytic activities of acidophilic bacteria.

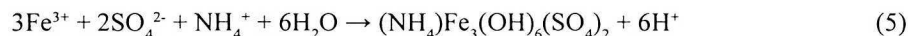
In this paper the wastes were inoculated with bacteria *Acidithiobacillus ferrooxidans* which can oxidize the reduced sulfur and iron compounds. The changes in concentration of Fe(II)/Fe(III) in solution as well as changes in Eh, pH were analyzed and compared with thermodynamic data in Eh-pH diagrams. X-ray radiography were used for the analysis of phase composition of the oxidation products. Scanning microscopy were used for observations of changes in the morphology of products. In natural conditions, first there is a process of oxidation in pyrite by Fe<sup>3+</sup> ion and then such products as Fe<sup>2+</sup> ions, sulfur, thiosulfates, tetrathionates and intermediate products are biologically oxidized into final products in accordance with the following mode [17, 18]:



Iron(II) ions can be biologically oxidized again in reaction (3):



Fe<sup>3+</sup> ion concentration in solution increases together with Eh oxidizing-reducing potential and acidity of the solutions also rises in the final stage of pyrite oxidizing (weathering) process [16]:



A stabilized state of equilibrium in Fe-S-H<sub>2</sub>O system results in precipitation of a part of iron(III) compounds from solutions. Precipitation reactions – equations (4) and (5), present the process of ferric hydroxide or ammonium jarosite forming from water solutions [12, 13, 19].

## EXPERIMENTAL METHODS

### *Bioleaching experiments*

Mixed pyrite mill tailings coming from Jaworzno III Power Plant S.A, containing 8.5%  $\text{FeS}_2$ , ground to 0.1–0.2 mm were used in bioleaching experiments. The experiments were carried out in the Erlenmeyer's flask of 300  $\text{cm}^3$  capacity. The quantity of tailings was 5% weight/volume, the volume of solution was 100  $\text{cm}^3$ . Strains of F1-02, F2-02, F3-02 *Acidithiobacillus ferrooxidans* bacteria of high activity in the oxidation process of iron(II) and reduced sulphur compounds, separated from ferruginous mineral water were used in the experiments [14]. The bacteria were cultivated in liquid nutrient medium, which actually became the leaching solutions for mixed pyrite mill tailings. The initial concentration of Fe(II) as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was 9.0  $\text{g}/\text{dm}^3$  in solution 9K and 0.0  $\text{g}/\text{dm}^3$  in solution B9K. Other components of solution were [ $\text{g}/\text{dm}^3$ ]:  $(\text{NH}_4)_2\text{SO}_4$  – 3.0, KCl – 0.1,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  – 0.5,  $\text{Ca}(\text{NO}_3)_2$  – 0.01,  $\text{K}_2\text{HPO}_4$  – 0.5. A laboratory shaker was used to aerate the leached samples, the number of cycles was 2 rev/s and the temperature was 20–22°C. The method of spectral atomic absorption was applied to determine the total iron concentration. The concentrations of Fe(II) and Fe(III) were determined by complexometry method using sulfosalicylic acid as indicator [11]. The pH analyses were carried out using pH-meter type Aquameter N5011, the Eh analyses were carried out using Solution Analyzer type N5173 with complex electrode Pt-Ag/AgCl/KCl saturated. All the electrode potentials in the text and figures were referred to electrode NHE. The obtained results were verified by the examinations in control leaching (chemical leaching) without inoculation of bacteria.

### *X-ray analysis*

The examinations of phase composition of solid residues samples before and after leaching process were carried out using PW 3710 X-ray diffractometer (Philips). It was realized at the following measurement conditions: radiation  $\text{Cu } \alpha_1$ , graphitoidal monochromator, 40 kV voltage, 35 mA intensity, counting time of the impulses – 2 s, rate of meter shift – 0.02.

### *Structural analysis*

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

### *Changes in Fe(II) and Fe(III) concentration*

The changes in Fe(II) and Fe(III) concentrations due to the activity of microorganisms in the process of biological leaching of mixed pyrite mill tailings were compared with concentration changes in the process of chemical leaching in solutions with different initial contents of Fe(II) and they are presented in Figs. 1 and 2. In nutrient medium solutions without iron, during the process of biological leaching, there was a close dependence between the growth of Fe(III) concentration in solution, then Fe(II) iron compounds



were spontaneously oxidized to Fe(III) – Fig. 1. Fe(III) concentration was from 1.05 to 1.19 g/dm<sup>3</sup> after 336 h in biological leaching examinations, whereas in chemical leaching examinations it was 0.35 g/dm<sup>3</sup>. It has been estimated that during that time the dynamics of iron releasing from 1 g of wastes into solutions in the process of biological leaching was about 0.067 mg/h while in the process of chemical leaching it was 0.021 mg/h. In the course of time the dynamics of leaching process of iron compounds from mixed pyrite mill tailings was reduced. In 504 h leaching process with microorganisms, Fe(III) concentration in solution was 1.26 g/dm<sup>3</sup>, whereas in solution after the process of chemical leaching it was 0.49 g/dm<sup>3</sup>. It meant that 0.050 mg/h of iron was released in the process of biological leaching and 0.019 mg/h in the process of chemical leaching. The obtained results are comparable to those presented in paper [7], where microbiological oxidizing of pyrite by bacteria which had been isolated from acid mine waters was examined. It was found out that such values can be obtained when there is low adherence of bacteria cells to the surface of pyrite.

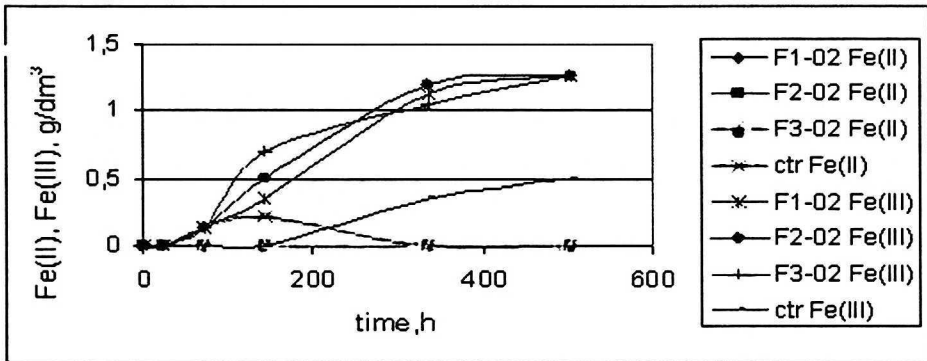


Fig. 1. Changes in Fe(II) and Fe(III) concentrations during bioleaching of mixed pyrite mill tailings by *Acidithiobacillus ferrooxidans* bacteria strains F1-02, F2-02, F3-02 in B9K solutions, ctr – control leaching

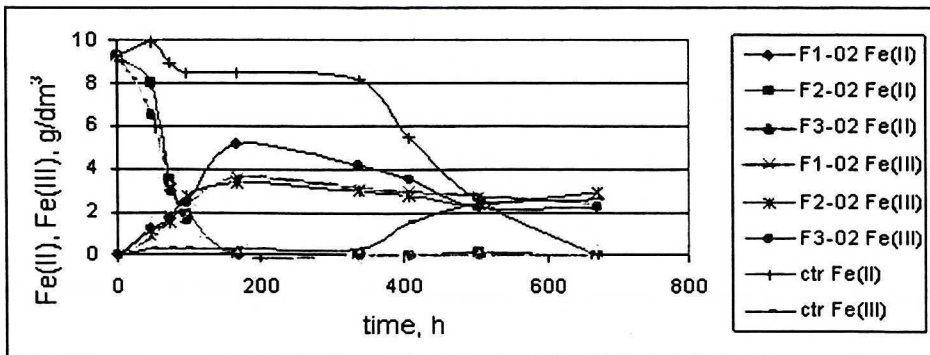


Fig. 2. Changes in Fe(II) and Fe(III) concentrations during bioleaching of mixed pyrite mill tailings by *Acidithiobacillus ferrooxidans* bacteria strains F1-02, F2-02, F3-02 in 9K solutions, ctr – control leaching

The decrease in pyrite leaching rate has been noticed in many research works [1, 5, 6, 16]. It is thought that inhibiting of the reactions depends on many factors, i.e. Fe(III) ions transportation up to the surface where the reaction takes place and Fe(II) ions away from the surface of the reaction, also on the ratio of Fe(III)/Fe(II) concentrations in solution, on microbiological activity and adherence of bacteria cells to the pyrite surface as well as on limiting pyrite accessibility by solid sparingly soluble products of the reaction.

The changes of Fe(II) and Fe(III) concentration in solutions during the leaching process of mixed pyrite mill tailings in nutrient medium solutions of Fe(II) initial concentration – 9.0 g/dm<sup>3</sup> have been presented in Fig. 2. Total oxidizing of Fe(II) added at the beginning of the process is of biological nature and lasts for 168 h. Fe(III) concentration in solution was 2.94–3.64 g/dm<sup>3</sup>, Fe(II) concentration was 0.00 g/dm<sup>3</sup> with pH of 2.28. In control examinations Fe(III) concentration was 0.28 g/dm<sup>3</sup> and Fe(II) concentration was 8.12 g/dm<sup>3</sup> with pH of 2.97. The value of oxidizing-reducing potential in biological examinations after 336 h was from +0.732 V to +0.775 V and it was +0.521 V for control tests. The dynamics of releasing iron compounds in chemical examinations was close to previous conditions. According to Rodriguez *et al.* [15], the rate of pyrite leaching is controlled, among other things, by competition of Fe(II) and Fe(III) ions in the process of chemisorptions on the surface of pyrite. The increase of Fe(II) concentration can be a diffusion barrier which restricts the growth of pyrite leaching rate.

### Change in pH

The change in solutions pH caused by pulping of the mixed pyrite mill tailings in the presence of *Acidithiobacillus ferrooxidans* bacteria and in the processes of chemical leaching has been presented in Figs. 3 and 4. Changes in pH featured growth and fall of pH which was connected with the following issues:

- releasing of alkaline components from wastes to solution,
- hydrolysis reactions and precipitation of iron(III) compounds into sediments.

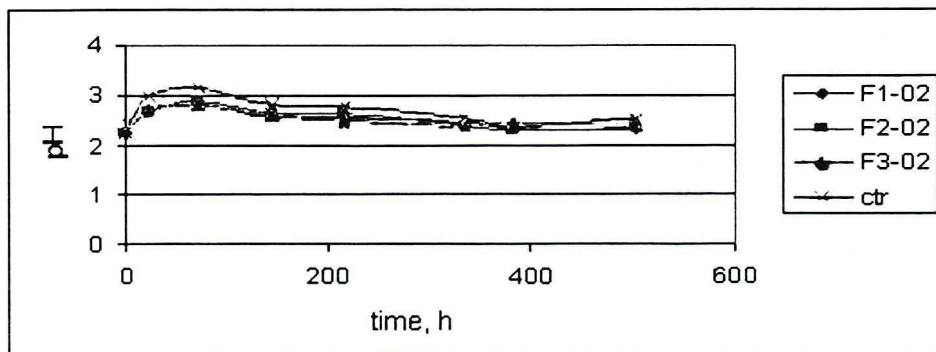


Fig. 3. Change in pH during bioleaching of mixed pyrite mill tailings by *Acidithiobacillus ferrooxidans* bacteria strains F1-02, F2-02, F3-02 in B9K solutions, ctr – control leaching

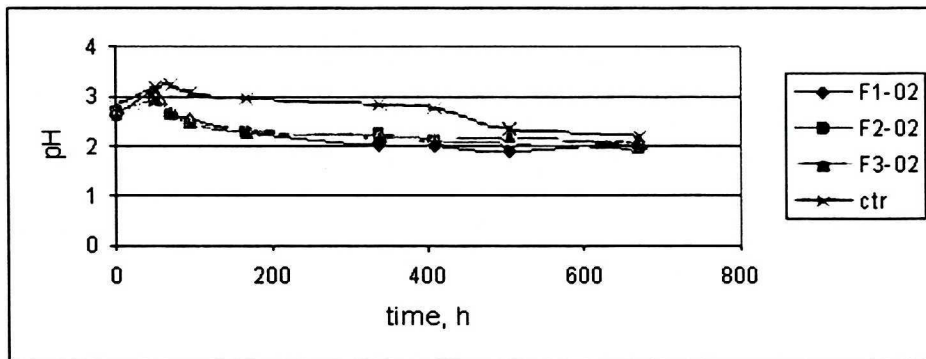


Fig. 4. Change in pH during bioleaching of mixed pyrite mill tailings by *Acidithiobacillus ferrooxidans* bacteria strains F1-02, F2-02, F3-02 in 9K solutions, ctr – control leaching

It has been established that the increase of acidity is stimulated by microorganisms, e.g. *At. ferrooxidans*. In the process of acid leachate and acid mine waters formation; rapid growth of acidity is a symptom of significant microbiological activity which can be compared to other abiotic environmental factors in weathering reactions of pyrite [8]. It has been confirmed by experimental data that the growth of the acidity of solutions occurred sooner in the course of biological leaching experiments than in the same conditions in chemical leaching experiments – Fig. 4. It has been found out that in the process of four-week biological leaching of mixed pyrite mill tailings when pH was not controlled in solutions of initial Fe(II) concentration of  $9.0 \text{ g/dm}^3$ , the average value of pH was 2.05 while in the process of chemical leaching the value of pH was 2.21.

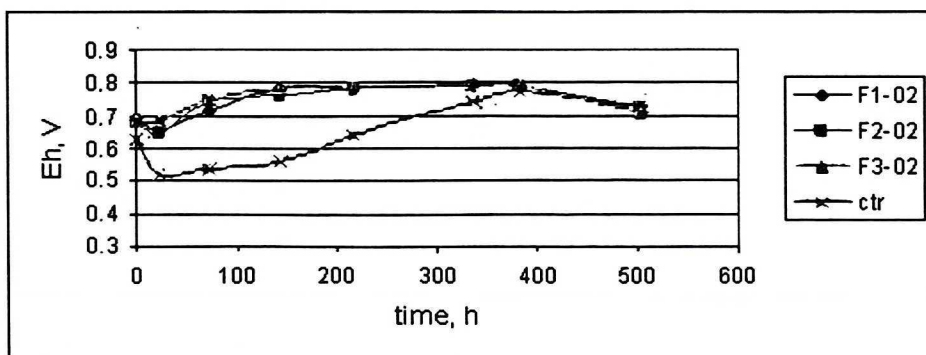


Fig. 5. Change in potential redox Eh during bioleaching of mixed pyrite mill tailings by *Acidithiobacillus ferrooxidans* bacteria strains F1-02, F2-02, F3-02 in B9K solutions, ctr – control leaching

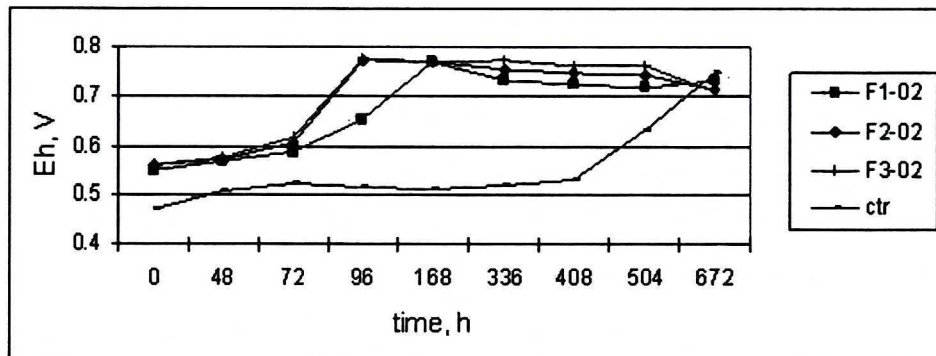


Fig. 6. Change in potential redox Eh during bioleaching of mixed pyrite mill tailings by *Acidithiobacillus ferrooxidans* bacteria strains F1-02, F2-02, F3-02 in 9K solutions, ctr – control leaching

### Changes in Eh potential

The course of the process of oxidizing of mixed pyrite mill tailings in water solutions was analyzed, taking into account the changes of Eh oxidizing-reducing potential in a given time – Figs. 5 and 6. The initial Eh value of solutions was from +0.520 to +0.550 V. Eh potential reached the level of +0.798 V to +0.792 V after 336 h for biological examinations (solutions without iron) and +0.732 V to +0.775 V (9K solutions), for chemical leaching examinations Eh value was +0.521 V. It has been noted that the value of Eh slightly dropped in the course of time which was probably caused by the change of Fe(II)/Fe(III) concentration. Such change was a result of the course of hydrolysis reaction and precipitation of iron III compounds into sediment. According to Hansford (quoted in [16]), the maximal value of Eh obtained in the process of bioleaching of pyrite in the presence of *At. ferrooxidans* can be about +0.850 V.

### Eh-pH diagram of Fe-S-H<sub>2</sub>O system

The state of equilibrium in Fe-S-H<sub>2</sub>O system has been presented in Eh-pH diagrams – Figs. 7a and 8a, for the case when the activity of iron ions in solutions is  $1 \cdot 10^{-6}$  and  $1 \cdot 10^{-2}$  mol/kg and the activity of sulfur is  $1 \cdot 10^{-3}$  mol/kg. It has been assumed that the level of activity of Fe and S compounds was appropriate to correspond to the ion concentration in real solutions. HCS Chemistry 4.1 – computer program and additionally some literature data [2, 19, 20] were used to present the diagrams. Zones of solid phase – FeS<sub>2</sub> pyrite, FeS pyrrhotine, iron(II) and (III) compounds – Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and Fe<sup>2+</sup>, Fe<sup>3+</sup> depending on Eh and pH were presented. Phase zones have been separated by equilibrium lines [2] and the most significant ones – (a), (b), (c) for the examined system have been presented below:



$$\text{Eh} = 0.728 - 0.059 \log \text{Fe}^{2+} - 0.177 \text{pH} \quad (7)$$



$$\log \text{Fe}^{3+} = -0.72 - 3\text{pH} \quad (9)$$





$$\text{Eh} = 0.771 \text{ [V]} \quad (11)$$

The diagrams indicate that together with the growth of ferric and ferrous ions activities, the zones of their thermodynamic stability decrease. Having reached the appropriate Eh-pH conditions,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  defined by equations (7) and (8), solid compounds of iron(III) are precipitated from solution.

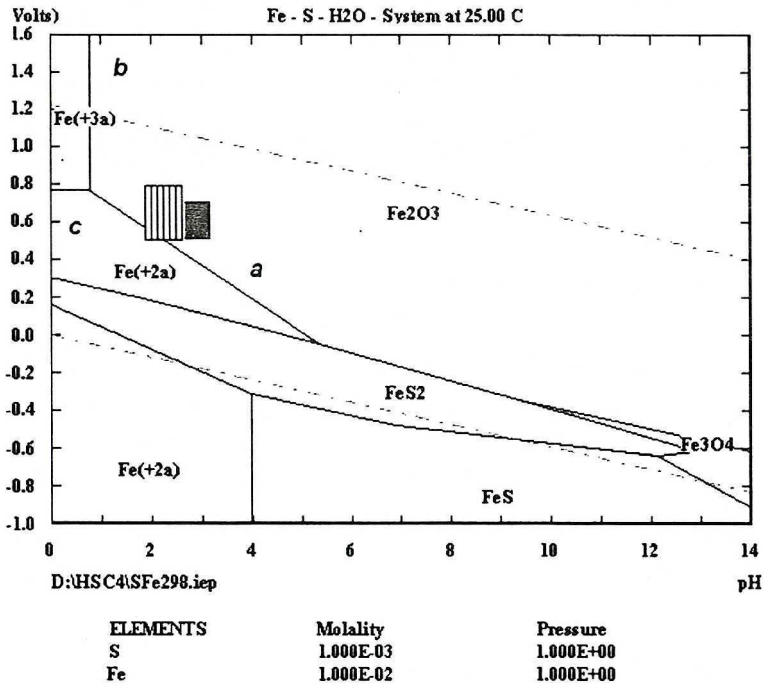


Fig. 7a. Diagram Eh-pH for the Fe-S-H<sub>2</sub>O system; activity of Fe(II)  $1 \cdot 10^{-2}$  mol/kg; marking: dashed area – results of Eh-pH in bioleaching experiments; dark area – in control experiments; line of equilibrium (a), (b), (c) – see more information in text

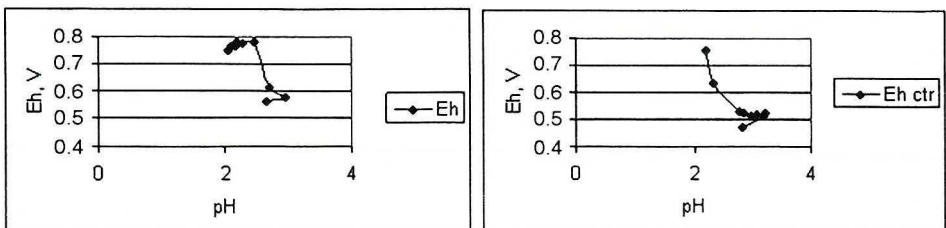


Fig. 7b. Experimental relationship Eh-pH for bioleaching – Eh and control leaching – Eh ctr of mixed pyrite mill tailings in 9K solutions



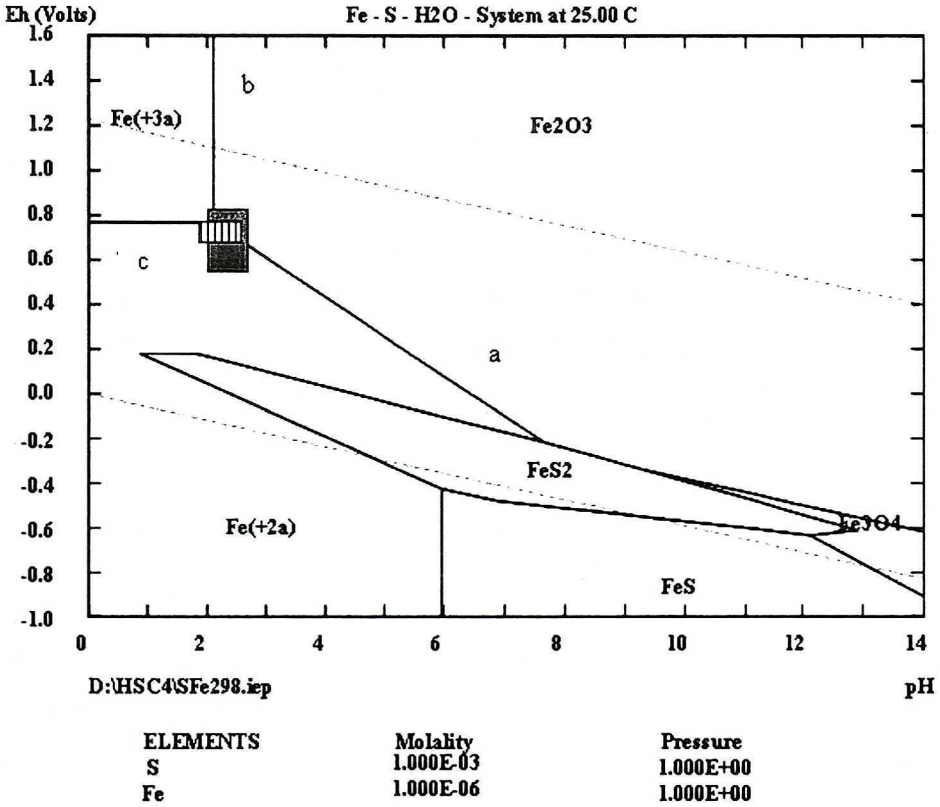


Fig. 8a. Diagram Eh-pH for the Fe-S-H<sub>2</sub>O system; activity of Fe(II)  $1 \cdot 10^{-6}$  mol/kg; marking: dashed area – results of Eh-pH in bioleaching experiments; dark area – in control experiments; line of equilibrium (a), (b), (c) – see more information in the text

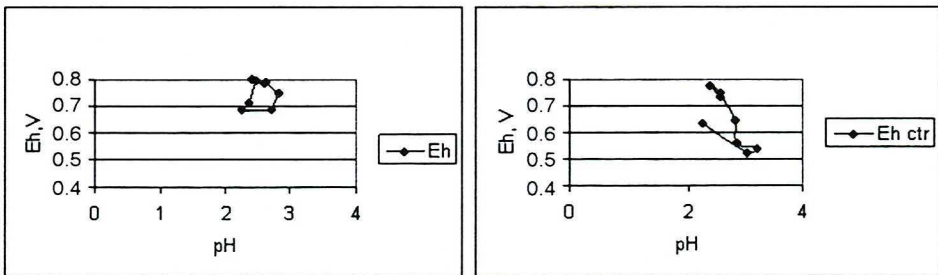


Fig. 8b. Experimental relationship Eh-pH for biological leaching – Eh and control leaching – Eh ctr of mixed pyrite mill tailings in B9K solutions

Some empirical data – Figs. 7b and 8b, marking Eh and pH boundary values from biological and chemical oxidizing process of mixed pyrite mill tailings have been additionally put on Eh-pH diagrams. The presented results indicate that the tested systems were about to reach the state of equilibrium which has been represented by lines (a), (b), (c). The value of pH coefficient (theoretically  $-0.177 \text{ V/pH}$  unit) gives evidence that there is convergence between Eh-pH empirical dependences and thermodynamic data. It has also been estimated that in the process of biological oxidation of pyrite mill tailings in 9K solutions and in chemical leaching examinations the coefficient is about  $-0.200 \text{ V/pH}$  unit. X-ray radiography analysis showed that iron(III) composites (jarosites) were precipitated from solution. However, in bioleaching examinations carried out in nutrient medium without iron, the system tends to reach the state of equilibrium expressed by equations (9) and (11), ( $E_h = 0.771 \text{ V}$ ).

#### *X-ray radiography analysis of residues after pyrite leaching process*

In order to identify the phases in residues after the process of biological and chemical leaching, X-ray radiography analysis of natural pyrite was carried out. Natural pyrite was exposed to biological and chemical leaching. The conditions of natural pyrite biological and chemical leaching were identical to those of pyrite mill tailings in 9K solutions. Pyrite compositions in [%]: Fe – 48.03, Ni – 0.0018, Mn – 0.61, Mg – 0.0027, K – 0.062, Al < 0.1, Ca – 0.31, Ss remaining part, ground 0.1 to 0.2 mm. The results of X-ray radiography analysis of residues from the process of biological leaching and chemical leaching have been compared in Fig. 9a, and 9b. The following phases were distinguished in the samples:

- $\text{FeS}_2$  regular pyrite,
- $\text{KFe}_3[\text{SO}_4]_2(\text{OH})_6$  potassium jarosite and  $(\text{H}_3\text{O})\text{Fe}_3[\text{SO}_4]_2(\text{OH})_6$  hydronium jarosite.

10% of jarosites were found in residue after the process of biological leaching. It confirms the results analysis [12, 13, 19] of sediments received from acid sulfate solutions which contain  $\text{Fe}^{2+}$  ions and which were subjected to the process of microbiological oxidizing by *At. ferrooxidans*. Elementary sulfur was not found. There were no new phases in pyrite residue after the process of chemical leaching since it is highly probable that the content of iron(III) compounds in residue was insufficient to be identified by X-ray radiography methods of analysis.

#### *Analysis of surface microstructure*

The image of pyrite surface structure received by electronic scanning microscopy has been presented in Fig. 10 and it is different before (Fig. 10a) and after the process of biological leaching (Fig. 10c) compared to the structure of crystals after the process of chemical leaching (Fig. 10b). Etching and spinning as well as brittleness of pyrite crystal edges due to the activity of *At. ferrooxidans* bacteria can be seen (Fig. 10c, d). The shape and size of pits on pickled surface suggest that pits correspond to the size of bacteria cells. The products of corrosion and presumably bacteria cells in the form of minute beams on the surface of pyrite have been presented in Fig. 10e, and f.

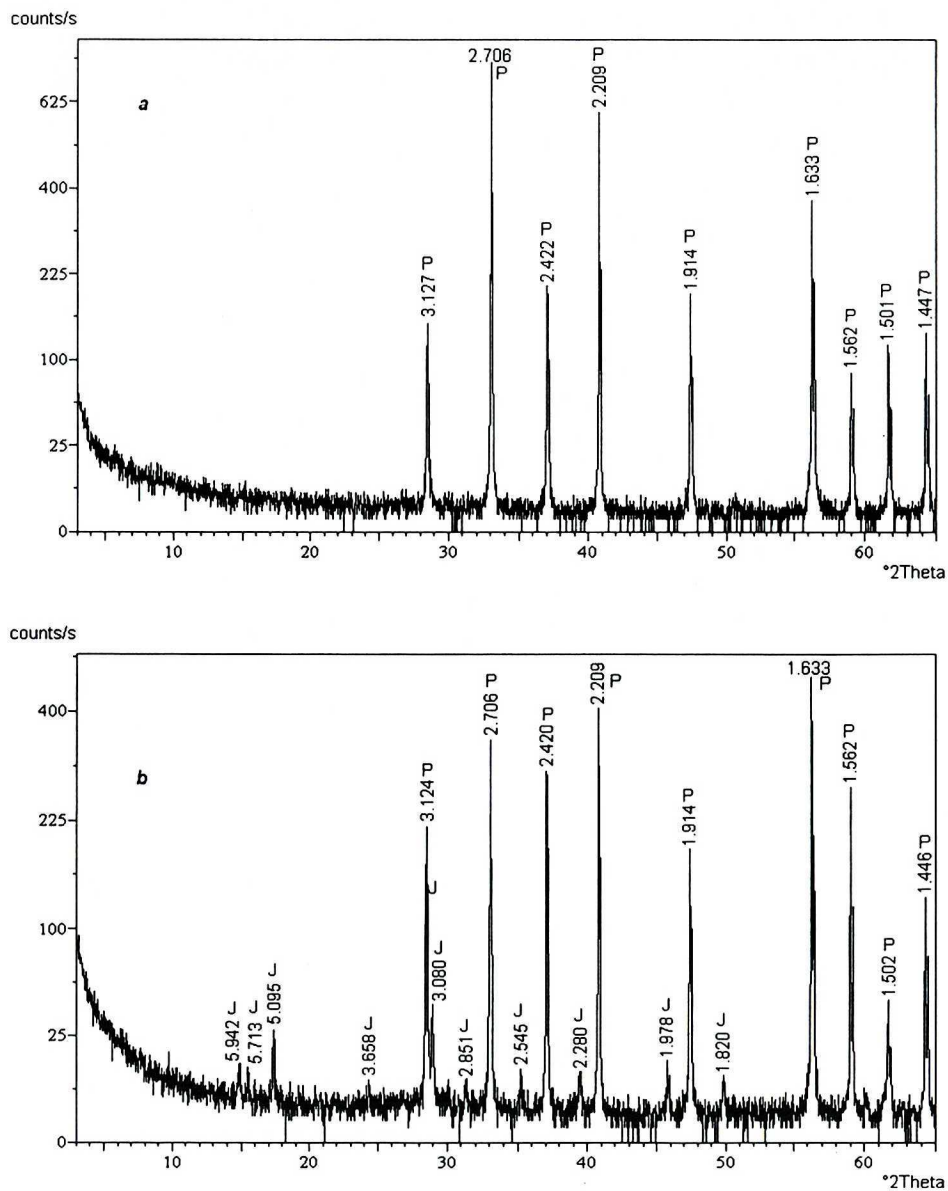


Fig. 9. Radiography of pyrite residues after control leaching – a, and biological leaching – b, in nutrient solution 9K; marking: J – jarosite, P – pyrite



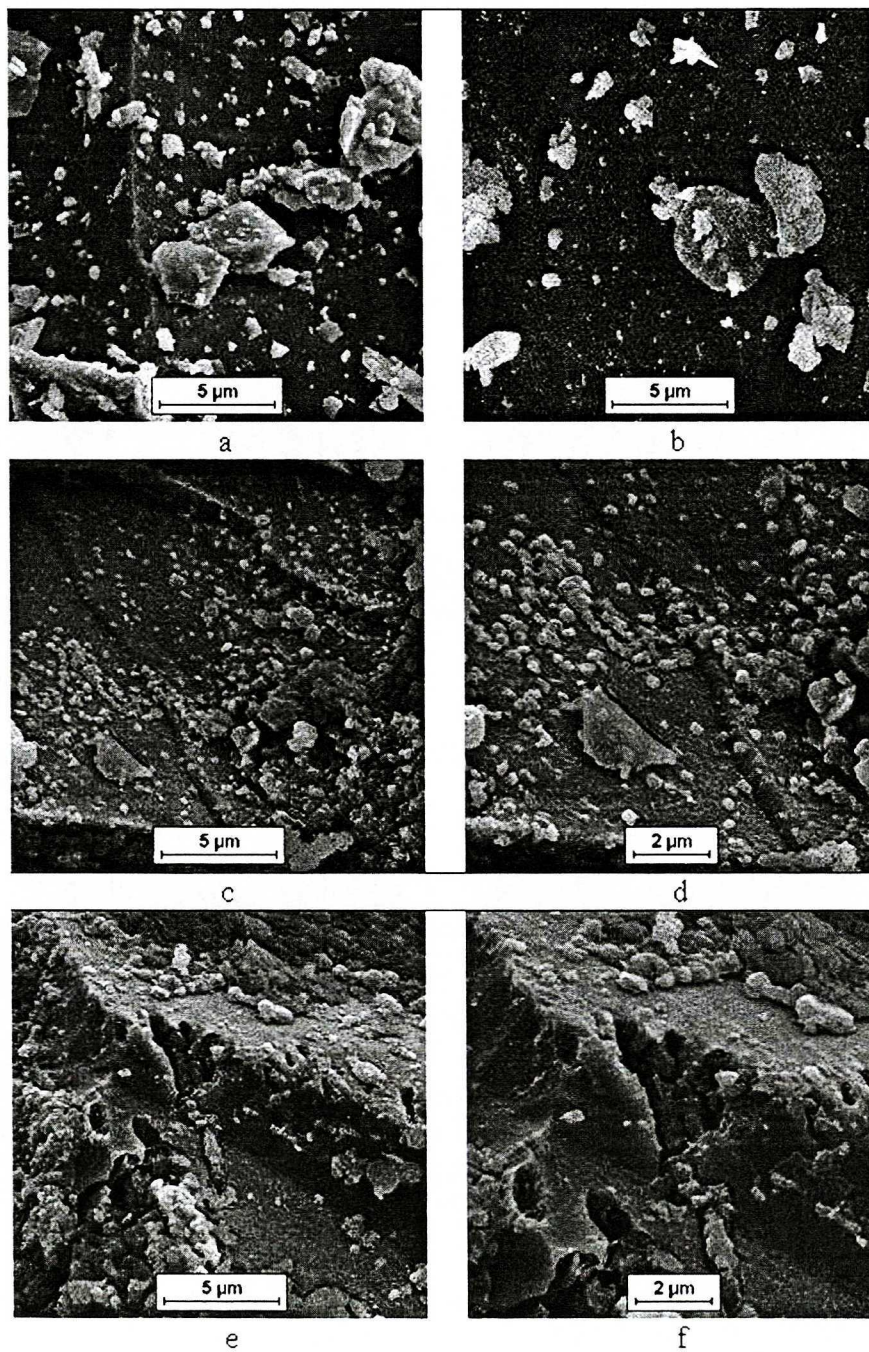


Fig. 10. SEM – scanning electron microscopy of pyrite surface; pyrite surface before leaching a – 3000x; pyrite surface after control leaching b – 3000x; pyrite surface after bioleaching in nutrient solution 9K using *Acidithiobacillus ferrooxidans*: c – 3000x, d – 5000x, e – 3000x, f – 5000x

## CONCLUSIONS

Basing on the results of Fe(II) and Fe(III) concentration changes in solutions and the values of Eh, pH oxidizing-reducing potential, it has been established that during the process of biological oxidizing of mixed pyrite mill tailings from power industry when *At. ferrooxidans* bacteria have been used as well as in the process of chemical oxidation, the process of pyrite oxidizing and iron releasing from wastes is more dynamic if bacteria are present. The change of Fe(II)/Fe(III) has a considerable impact on stabilizing Eh-pH state of equilibrium in Fe-S-H<sub>2</sub>O system. The stabilized Eh-pH parameters regulate the composition of solution at the same time. Despite the presence of bacteria which oxidize sulfur and iron compounds, iron compounds concentration in solutions coming from biological process was only 2–3 times higher than the iron compound concentration in solutions coming from the chemical process. On the basis of X-ray radiography, it has been suggested that such results are due to the reaction of iron(III) (jarosites) precipitation, when Fe-S-H<sub>2</sub>O system is trying to reach the state of equilibrium. As the final conclusion, it has to be emphasized that mixing pyrite mill tailings which come from power industry with other wastes of alkaline nature before storage is quite advantageous because they neutralize and prevent the process of releasing metals into the environment.

*Acknowledgements*

*This research work is being financed by funds for science for 2005–2008 as Research Sponsored Project PBZ-KBN-111/T09/2004.*

*The results in this paper were presented at the Conference VIII Ogólnopolskie Sympozjum Naukowo-Techniczne "Biotechnologia Środowiskowa" Wisła-Jarzębata, December 6–9, 2005. Author is grateful to Dr Grażyna Bzowska from Faculty of Earth Science, University of Silesia for X-ray analysis and to Dr Maria Sozańska from Faculty of Materials Science and Metallurgy, Silesian University of Technology for microstructure analysis SEM.*

## REFERENCES

- [1] Boon M., J.J. Heijnen: *Solid-liquid mass transfer limitation of ferrous iron in the chemical oxidation of FeS<sub>2</sub> at high redox potential*, Hydrometallurgy, **62**, 57–66 (2001).
- [2] Burkin A.R.: *The Chemistry of Hydrometallurgical Processes*, London 1966.
- [3] Cwalina B.: *Metabolizm siarki u Thiobacillus ferrooxidans w procesie ługowania metali z minerałów siarczkowych*, Wyd. UŚ, Katowice 1994.
- [4] Cwalina B., Z. Dzierżewicz: *Mikrobiologiczne odsiarczanie węgla – zalety i wady*, [w:] V Ogólnopolskie Sympozjum Nauk. Techn. Biotechnologia Środowiskowa, 205–211, 1997.
- [5] Cwalina B., P. Nogaj, A. Golek, L. Bułaś: *Bioekstrakcja metali z piritów węglowych w dużej skali laboratoryjnej*, Fizykochemiczne Problemy Mineralogii, **24**, 95–104 (1991).
- [6] Cwalina B., Z. Zawada: *Bioekstrakcja metali z piritów węglowych w obecności mikroflory autochtonicznej materiału ługowanego*, Przegląd Górniczy, **6**, 10–15 (1988).
- [7] Edwards K., M.O. Schrenk, R. Hamers, J.F. Banfield: *Microbial oxidation of pyrite: Experiments using microorganisms from an extreme acidic environment*, American Mineralogist, **83**, 1444–1453 (1998).
- [8] Garcia C., A. Ballester, F. Gonzalez, M.L. Blazquez: *Pyrite behavior in a tailings pond*, Hydrometallurgy, **76**, 25–36 (2005).
- [9] Hycnar J.: *Zagospodarowanie młynowych odpadów węglowych*, Gospodarka paliwami i Energia, **33**, 1–3 (1985).
- [10] Juszcak A., F. Domka, M. Kozłowska, H. Wachowska: *Microbial desulfurization of coal with Thiobacillus ferrooxidans bacteria*, Fuel, **74**, 5, 725–728 (1995).
- [11] Lipiec T., Z. Szmaj: *Chemia analityczna z elementami analizy instrumentalnej*. PZWL, Warszawa 1976.



- [12] Lopez-Delgado A., F.J. Alguacil, F.A. Lopez: *Recovery of iron from bio-oxidized sulphuric pickling waste water by precipitation as basic sulphates*, Hydrometallurgy, **45**, 97–112 (1997).
- [13] Nowaczyk K., A. Juszcak, F. Domka: *Microbial oxidation of the Waste Ferrous Sulphate*, Polish Journal of Environmental Studies, **8**, 6, 409–416 (1999).
- [14] Pacholewski A., M. Pacholewska: *Naturalne zdolności do utleniania jonu  $Fe^{2+}$  oraz  $S_2O_3^{2-}$  przez bakterie żelazowe ze źródeł wody mineralnej Łomniczanka*, [w:] Współczesne Problemy Hydrogeologii, t. X Ogólnopolska Konferencja Naukowa, Krzyżowa 2001, 389–396.
- [15] Rodriguez Y., A. Ballester, M.L. Blazquez, F. Gonzalez, J.A. Munoz: *New information on the pyrite bioleaching mechanism at low and high temperature*, Hydrometallurgy, **71**, 37–46 (2003).
- [16] Rohwerder T., T. Gehrke, K. Kinzler, W. Sand: *Bioleaching review part A: Progress in bioleaching: fundamentals and mechanisms of bacterial metal sulfide oxidation*, Applied Microbiology and Biotechnology, **63**, 239–248 (2003).
- [17] Sand W., T. Gehrke, P-G. Jozsa, A. Schippers: *(Bio)chemistry of bacterial leaching – direct vs. indirect bioleaching*, Hydrometallurgy, **59**, 159–175 (2001).
- [18] Schippers A., W. Sand: *Bacterial leaching of metal sulfides proceeds by two indirect mechanisms via thiosulfate or via polysulfides and sulfur*, Applied and Environmental Microbiology, **65**, 319–321 (1999).
- [19] Trupti D., K.G. Malay, R.C. Gautam: *Assessment of the significant parameters influencing the bio-oxidation and bio-precipitation of iron from industrial leach liquor*, Mineral Processing and Extractive Metallurgy (Transactions of the Institution of Mining and Metallurgy, Section C), **114**, 3, 57–64 (2005).
- [20] Wadsley M.: *Stoichiometric considerations in multicomponent aqueous stability diagrams*, Hydrometallurgy, **29**, 91–108 (1992).

Received: August 11, 2006; accepted: April 30, 2007.