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## **Influence of chemical and biogenic leaching on surface area and particle size of laterite ore**

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**Abstract:** Currently there is a decline in the world's nickel sulfide deposits, which are the main source of this metal. Due to the fact, that more than 70% of nickel reserves are in the form of oxide ores, more attention is nowadays paid on laterites. Leaching processes using different organic acids are widely described in the literature, but there is a lack of works linking influence of leaching process with the surface area and particle size distribution. Therefore, the main aim of this study was to examine how citric acid produced by microorganisms and citric acid added as chemical affected the specific surface and particle size distribution of mineral particles. The laterite ore was obtained from Szklary deposit, Poland. This study also compared the effect of chemical citric acid and filtrate after cultivation of *Aspergillus niger* on nickel extraction. It was observed that higher nickel recovery correspond to higher surface area of particles. The highest yield of nickel extraction was observed for a citric acid concentration of 1 mol/dm<sup>3</sup> (67%). The specific surface area after leaching was 159 m<sup>2</sup>/g. An analysis of particle size distribution showed increase in the median particle size of particles after leaching with citric acid. It may suggest that dissolution of Polish laterites follows a shrinking core-shrinking particle model.

**Keywords:** nickel, laterite ore, leaching, citric acid, *Aspergillus niger*

### **Introduction**

Nickel is an important metal used for a wide variety of applications. World deposits of this metal are in the forms of sulfide and oxide (laterites) ores. Currently, the majority of nickel is obtained by exploiting the sulfide ores. In laterites, nickel is associated with either iron oxide or silicate compounds and due to its complex structure it is difficult to treat the ore by flotation. This increases the expenditure of energy and generates costs of the process (Ministry of the Environment, 2001).

Due to the fact that more than 70% of the world reserves of this metal is in the form of non-sulfide ores, more attention is directed to laterites (Moskalyk and Alfantazi, 2002; Elias, 2002; Gleeson et al., 2003; Dalvi et al., 2004; Watling, 2008).

Starting from the 1950s, the world production of nickel from laterite has been increasing (Dalvi et al., 2004).

The laterites are usually treated using pyrometallurgical and hydrometallurgical processes. During past few decades, also bioleaching has been applied as environmentally friendly and low cost process. Metal recovery from non-sulfide ores using microorganisms is based on activity of heterotrophic fungi and bacteria. Extraction of metals is an effect of organic acid, chelating and complexing compounds “produced” by these microorganisms into the liquid medium. Most common microorganisms used are fungi like *Aspergillus* and *Penicillium* and also some chemolithotrophic microorganisms (*Acidithiobacillus ferrooxidans*, *Acidithiobacillus caldus*, *Leptospirillum ferrooxidans*) (Bosecker, 1986; Coto et al., 2001; Valix et al., 2001a; Alibhai et al., 1993; Tzeferis, 1994; Mohapatra et al., 2007; Simate and Ndlovu 2007, 2008; Simate et al., 2009).

Recently, *Acidithiobacillus ferrooxidans* bacteria are also used to bioleach laterite nickel ores under anaerobic conditions (Hallberg et al., 2011, du Plessis et al., 2011 and Behera et al., 2012). The obtained results are promising for extraction of metals from the low grade laterite ores. However, practical application of this method to the industry involves many difficulties to overcome.

Table 1. Chemical leaching of nickel oxide ore using different organic acids.

| Organic acid                               | Mineral material                                  | Metal | Yield of extraction, % | References            |
|--|---|-------|------------------------|-----------------------|
| Citric acid                                | Limonite, nontronite,                             | Co    | 65-95                  | Tang and Valix, 2006  |
| Lactic acid/Malic acid                     | New Caledonia                                     | Ni    | 15-35                  |                       |
| Citric acid                                | Laterites: After Caron process                    | Co    | 85                     | Coto et al., 2008     |
| Citric acid                                | Laterite ore, Indonesia                           | Co    | 55                     | Li al., 2010          |
| Citric acid + ammonium hydrogen bifluoride |   | Co    | 85.7                   |                       |
| Citric acid                                | Saprolite   | Ni    | 80                     | Valix et al., 2001b   |
|  | Weathered saprolite                               | Ni    | 60                     |                       |
|  | Limonite  |       |                        |                       |
|  | Nontronite  | Ni    | 20                     |                       |
|  |   | Ni    | 5                      |                       |
| Oxalic acid                                | Oxide ores, Gaspé, Canada                         | Cu    | 7                      | Mulligan et al., 2004 |
|  |   | Fe    | 35                     |                       |
|  |   | Ni    | 14                     |                       |
|  |   | Zn    | 32                     |                       |
| Citric acid                                | Oxide ores, Gaspé, Canada                         | Cu    | 30                     |                       |
|  |   | Fe    | 6                      |                       |
|  |   | Ni    | 60                     |                       |
|  |   | Zn    | 10                     |                       |
| Oxalic acid                                | Chromite Overburden, Sukinda Mines, Odisha, India | Ni    | 39                     | Behera et al., 2013   |
| Citric acid                                |   | Ni    | 21.5                   |                       |

To extract metal from laterites organic acids, both chemical grade and those produced by microorganisms, are used. It has been shown that the dissolution rate of metals depends on the concentration of acid in the broth. The mineral composition of ore also affects the effectiveness of metal dissolution (Alibhai et al., 1993; Burgstaller and Schinner, 1993; Tzeferis, 1994; Tzeferis and Agatzini-Leonardou, 1994; Castro et al., 2000). Different organic acids used as leaching reagents are presented in Table 1. Citric acid used as a lixiviant is considered to be most effective in selective extraction of nickel and cobalt from non-sulfide ores (Pradhan et al., 2006).

## Material and methods

The raw material used in the laboratory experiments was the laterite ore obtained from the Szklary deposit (Poland). Samples used in the experiment were crushed and milled.

An X-ray diffraction analysis (Fig. 1) showed the presence of magnetite ( $\text{Fe}_3\text{O}_4$ ), insignificant quantities of goethite grains ( $\text{FeOOH}$ ), small grains of silica minerals (mainly chalcedony), magnesite and magnesium silicate minerals and fragments of montmorillonites (pimelite, vermiculite and garnierite). The chemical analysis of the sample is presented in Table 2.

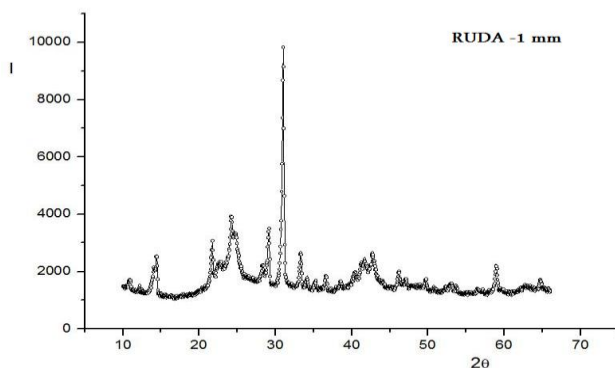


Fig. 1. X-ray diffraction pattern of laterite ore sample. Fraction –1 mm

Table 2. Chemical composition of nickel laterite ore from Szklary deposit

| Co, ppm | Fe, % | Mg, % | Ni, % |
|---------|-------|-------|-------|
| 177     | 8.51  | 7.31  | 1.17  |

The particle size distribution determined by laser diffraction using Malvern Mastersizer 2000 equipped with HydroMU dispersion unit (Malvern UK) showed that  $D_{10}$ ,  $D_{50}$ ,  $D_{90}$  sizes were 4.75, 28.62 and 303.70  $\mu\text{m}$  respectively. The particles specific surface area was measured by the Brunauer-Emmett-Teller (BET) method for the

helium/nitrogen mixture using a FlowsorbII apparatus (Micrometrics) and was 44.76 m<sup>2</sup>/g. The bulk density was 1.12 g/cm<sup>3</sup> and the density was found as 2.53 g/cm<sup>3</sup>.

Leaching experiments were carried out for different concentrations of citric acid (0.027, 0.25, 0.5 and 1.0 mol/dm<sup>3</sup>) at ambient temperature for 49 days. Samples contained 100 cm<sup>3</sup> of citric acid solution and 2.5% (w/v) of laterite ore. Deionized water and chemical grade reagents were used. The fungal culture filtrates were also used as the leaching reagent. A microorganism, *Aspergillus niger* Ł0581 producing mainly citric acid, was obtained from the Institute of Fermentation Technology and Microbiology, Lodz University of Technology.

First, nutrient broth was prepared. The Czapek-Dox growth medium was used (Table 3). Microorganisms were cultivated for four days and after this time the mixture was autoclaved and filtered to remove dead biomass. Only filtrates, citric acid concentration of 0.027 mol/dm<sup>3</sup>, were taken for further leaching experiments. Samples contained 100 cm<sup>3</sup> of broth and 2.5% (w/v) of laterite.

The process was monitored by analyzing changes of nickel concentration, specific surface area and particle size distribution of mineral particles. The ICP-OES method was used to measure concentration of nickel ions in the solution.

Table 3. Growth medium Czapek-Dox for microorganism *A. niger* Ł0581

| Component                            | Amount, g/dm <sup>3</sup> |
|--------------------------------------|---------------------------|
| NaNO <sub>3</sub>                    | 2.0                       |
| K <sub>2</sub> HPO <sub>4</sub>      | 2.0                       |
| KCl                                  | 0.5                       |
| MgSO <sub>4</sub> ·7H <sub>2</sub> O | 0.5                       |
| FeSO <sub>4</sub> ·7H <sub>2</sub> O | 0.02                      |
| ZnSO <sub>4</sub> ·7H <sub>2</sub> O | 0.02                      |
| CuSO <sub>4</sub> ·5H <sub>2</sub> O | 0.08                      |
| Sucrose                              | 30                        |

## Results and discussion

Nickel leaching recoveries for different leaching reagents are presented in Fig. 2. The highest yield of nickel extraction was observed for 1.0 (67%) and 0.5 mol/dm<sup>3</sup> citric acid (65%). The reported recovery of nickel for *A. niger* broth was very low, which suggested that it was not effective as a lixiviant. After two weeks of the process there was a decrease in the nickel concentration, probably due to either biosorption or complexation of metal by organic compounds present in the broth.

Except of changes in the nickel concentration during leaching process using different leaching reagents, also the effect of leaching process on the surface area of the laterite ore particles was examined. The results are shown in Fig. 3 and Table 4. In

the early leaching step of the process, the surface area decreased in all samples. To explain this phenomenon, samples of laterite ore were analyzed after contact with deionized water. Obtained results showed that decrease in the surface area of particles was caused by dissolution of the smallest grains. The smaller particle, the higher is the surface area, therefore reduce in the proportion of fine grains resulted in a decrease of the specific surface area of the sample.

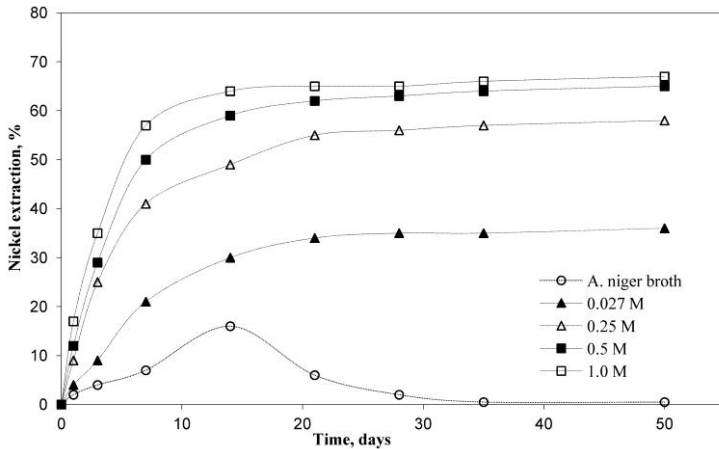


Fig. 2. Nickel extraction changes in time for different concentrations of citric acid and *A.niger* broth

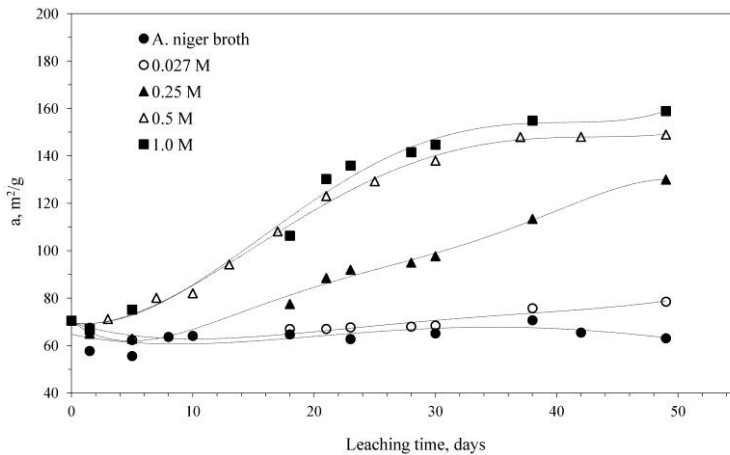


Fig. 3. Average values of specific surface area of Szklary laterite ore (fraction -1 mm) during leaching with different concentrations of citric acid and microbial broth of *A.niger*

For water suspension of ore, after decrease in the surface area during first days this value was maintained at a constant level (Table 4). In the case of leaching with different concentrations of citric acid (0.027-1.0 mol/dm<sup>3</sup>), after significant decrease in

the surface area the gradual increase of surface was observed in time. The largest increase in the specific surface area was obtained for the leaching process with 1.0 mol/dm<sup>3</sup> citric acid (159 m<sup>2</sup>/g), and the lowest value for the *A. niger* broth. The specific surface area was in this case only 63 m<sup>2</sup>/g.

Table 4. A specific surface area changes of laterite ore, during leaching and bioleaching

| Lixiviant             | <i>a</i> , m <sup>2</sup> /g |                       |                      |                           |
|-----------------------|------------------------------|-----------------------|----------------------|---------------------------|
|                       | <i>t<sub>i</sub></i>         | <i>t<sub>36</sub></i> | <i>t<sub>f</sub></i> | $\Delta a (t_f - t_{36})$ |
| Water                 | 70.5                         | 57.1                  | 55.9                 | (-) 1.2                   |
| <i>A. niger</i> broth | 70.5                         | 57.7                  | 63.1                 | 5.40                      |
| 0.027 M citric acid   | 70.5                         | 67.5                  | 78.5                 | 11.0                      |
| 0.25 M citric acid    | 70.5                         | 65.0                  | 130                  | 65.0                      |
| 0.5 M citric acid     | 70.5                         | 66.6                  | 149                  | 82.4                      |
| 1.0 M citric acid     | 70.5                         | 67.0                  | 159                  | 92.0                      |

*t<sub>i</sub>* – initial value, *t<sub>36</sub>* – specific surface area after 36 h, *t<sub>f</sub>* – final value (after 49 days)

A correlation of final surface area value with a yield of nickel extraction was observed. The higher degree of metal extraction corresponded to the higher specific surface area. Similar correlations for increasing the particle surface with greater yield of metal leached (black shale ore) was observed by Schubert (2007). Changes in the particle surface area during leaching processes can be explained by formation of a porous layer (also called a ash layer). The ash layer is formed by part of ore particle that has been difficult to leach (Levenspiel, 1999, Burghard and Bartelmus, 2001).

Table 5. *D<sub>10</sub>*, *D<sub>50</sub>*, *D<sub>90</sub>* for different lixivants determined at the beginning of the process (*t<sub>i</sub>*), after 36 h (*t<sub>36</sub>*) and 49 days (*t<sub>f</sub>*)

| Lixiviant             | Time                  | <i>D<sub>10</sub></i> , μm | <i>D<sub>50</sub></i> , μm | <i>D<sub>90</sub></i> , μm | <i>a</i> , m <sup>2</sup> /g |
|-----------------------|-----------------------|----------------------------|----------------------------|----------------------------|------------------------------|
| H <sub>2</sub> O      | <i>t<sub>i</sub></i>  | 4.75                       | 28.6                       | 304                        | 70.5                         |
|                       | <i>t<sub>f</sub></i>  | 4.46                       | 31.3                       | 480                        | 55.9                         |
| <i>A. niger</i> broth | <i>t<sub>36</sub></i> | 6.57                       | 36.4                       | 374                        |                              |
|                       | <i>t<sub>f</sub></i>  | 5.34                       | 42.1                       | 397                        | 63.1                         |
| 0.027 M citric acid   | <i>t<sub>36</sub></i> | 5.79                       | 36.7                       | 477                        |                              |
|                       | <i>t<sub>f</sub></i>  | 5.47                       | 36.6                       | 471                        | 78.5                         |
| 0.25 M citric acid    | <i>t<sub>36</sub></i> | 6.44                       | 38.2                       | 506                        |                              |
|                       | <i>t<sub>f</sub></i>  | 7.48                       | 42.8                       | 475                        | 130                          |
| 0.5 M citric acid     | <i>t<sub>36</sub></i> | 7.17                       | 43.2                       | 510                        |                              |
|                       | <i>t<sub>f</sub></i>  | 7.25                       | 47.6                       | 498                        | 149                          |
| 1.0 M citric acid     | <i>t<sub>36</sub></i> | 6.98                       | 45.5                       | 628                        |                              |
|                       | <i>t<sub>f</sub></i>  | 8.54                       | 49.6                       | 541                        | 159                          |

To properly determine changes taking place in the solid phase during the leaching process, measurements of particle size distribution of leachable material after 36 h and at the end of the process (after 49 days) were carried out. The results for the various concentrations of leaching solutions are shown in Table 5, which lists the volume fraction of the particles taken from the cumulative particle size distribution curve. All data were compared to initial values. It can be concluded that there is a correlation between the increase in the specific surface area and particle size distribution. The specific surface of the grains increased with increasing the concentration of citric acid. In the case of the lowest concentration ( $0.027 \text{ mol/dm}^3$ ) the distribution of particles after 49 days of leaching was similar to baseline (suspension of ore and water). The maximum surface area was obtained with  $1.0 \text{ mol/dm}^3$  citric acid concentration.

## Conclusions

The experiments demonstrated that citric acid may serve as an effective reagent for extraction of nickel from Polish laterites. It was observed, that specific surface area of laterite ore particles changed during leaching and it was correlated with the concentration of a lixiviant used in the process. Higher nickel recovery corresponded to higher surface area of mineral particles. The highest yield of metal extraction was achieved for  $1 \text{ mol/dm}^3$  citric acid and was equal to 67%. The specific surface area was in this case  $159 \text{ m}^2/\text{g}$ . The analysis of particle size distribution before and after the process showed the increase in the median particle size ( $D_{50}$ ), probably due to decrease of percentage of the smallest grains. It may suggest that leaching of the investigated laterite ore using citric acid follows the shrinking core-shrinking particle model.

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## References

- ALIBHAI K.A.K., DUDENEY A.W.L., LEAK D.J., AGATZINI S., TZEFERIS P., 1993. *Bioleaching and bioprecipitation of nickel and iron from laterites*. FEMS Microbiology Reviews, 11, 87–96.
- BEHERA S.K., PANDA P.P., PRADHAN N., SUKLA L.B., MISHRA B.K., 2012. *Extraction of nickel by microbial reduction of lateritic chromite overburden of Sukinda, India*. Bioresource Technology, 125, 17–22.
- BEHERA S. K., PANDA P. P., SAINI S. K., PRADHAN N., SUKLA L. B., MISHRA B. K., 2013. *Recovery of nickel from chromite overburden, Sukinda using Aspergillus niger supplemented with manganese*. Korean Journal of Chemical Engineering, 30(2), 392–399.
- BOSECKER K., 1986. *Leaching of lateritic nickel ores with heterotrophic microorganisms*. In: R.W. Lawrence, R.M.R. Branion, H.G. Ebner (Ed.), *Fundamental and Applied Biohydrometallurgy*, Elsevier, Amsterdam, 367–382.
- BURGSTALLER W., SCHINNER F., 1993. *Leaching of metals with fungi*. Journal of Biotechnology, 27, 91–116.

- BURGHARDT A., BARTELMUS G., 2001. *Inżynieria reaktorów chemicznych. Tom II Reaktory dla układów heterogenicznych*. Wydawnictwo Naukowe PWN, Warszawa.
- CASTRO I.M., FIETO J.L.R., VIEIRA R.X., TRÓPIA M.J.M., CAMPOS L.M.M., PANIAGO E.B., BRANDÃO R.L., 2000. *Bioleaching of zinc and nickel from silicates using Aspergillus niger cultures*. Hydrometallurgy, 57, 39–49.
- COTO O., BRUGUERA N., ABÍN L., GAMBOA J., GÓMEZ Y., 2001. *Bioleaching of Cuban nickeliferous serpentinite*. W: V.S.T. Ciminelli, O. Garcia (Ed.), *Biohydrometallurgy, Fundamentals, Technology and Sustainable Development, Part A*, Elsevier, Amsterdam, 175–182.
- COTO O., GALIZIA F., HERNÁNDEZ I., MARRERO J., DONATI E., 2008. *Cobalt and nickel recoveries from laterite tailings by organic and inorganic bio-acids*. Hydrometallurgy, 94, 18–22.
- DALVI A.D., BACON W.G., OSBORNE R.C., 2004. *The past and future of nickel laterites*. PDAC 2004 International Convention, Trade Show & Investors Exchange.
- du PLESSIS C.A., SLABBERT W., HALLBERG K.B., JOHANSON D.B., 2011. *Ferredox: A biohydrometallurgical processing concept for limonitic nickel laterites*, Hydrometallurgy, 109, 221–229.
- ELIAS M., 2002. *Nickel laterite deposits – geological overview, resources and exploitation*. In: Cooke C.R., Pontgratz J., (Ed.), *Giant Ore Deposits: Characteristics, Genesis and Exploitation*. CODES Special Publication. Centre for Ore Deposit Research, University of Tasmania, 205–220.
- GLEESON S.A., BUTT C.R.M., ELIAS M., 2003. *Nickel laterites: review*. Society of Economic Geologists (SEG) Newsletter, 54. Document on-line: [www.segweb.org](http://www.segweb.org)
- HALLBERG K.B., GRAIL B.M., du PLESSIS .A., JOHNSON D.B., 2011. *Reductive dissolution of ferric iron minerals: A new approach for bio-processing nickel laterites*. Minerals Engineering, 24, 620–624.
- LEVENSPIEL O., 1999. *Chemical Reaction Engineering*, 3rd ed. John Wiley & Sons, New York.
- LI G., RAO M., LI Q., PENG Z., JIANG T., 2010. *Extraction of cobalt from laterite ores by citric acid in presence of ammonium bifluoride*. Transactions of Nonferrous Metals Society of China, 20, 1517–1520.
- MINISTRY OF ENVIRONMENT, 2001. Document on-line: [ippc.mos.gov.pl/preview/pl/bref\\_met\\_nz.html](http://ippc.mos.gov.pl/preview/pl/bref_met_nz.html)
- MOHAPATRA S., BOHIDAR S., PRADHAN N., KAR R.N., SUKLA L.B., 2007. *Microbial extraction of nickel from Sukinda chromite overburden by Acidithiobacillus ferrooxidans and Aspergillus strains*. Hydrometallurgy, 85, 1–8.
- MOSKALYK R. R., ALFANTAZI A. M., 2002. *Nickel laterite processing and electrowinning practice*. Minerals Engineering, 15, 593–605.
- MULLIGAN C.N., BERNARD M.K., GIBBS F., 2004. *Bioleaching of heavy metals from a low-grade mining ore using Aspergillus niger*. Journal of Hazardous Materials, 110, 77–84.
- PRADHAN N., DAS B., GAHAN S.G., KAR N.R., SUKLA B.L. 2006. *Beneficiation of iron ore slime using Aspergillus niger and Bacillus circulans*. Bioresource Technology, 97, 1876–1879.
- SIMATE G.S., NDLOVU S., 2007. *Characterisation of factors in the bacterial leaching of nickel laterites using statistical design of experiments*. Advanced Materials Research, 20–21, 66–69.
- SIMATE G.S., NDLOVU S., 2008. *Bacterial leaching of nickel laterites using chemolithotrophic microorganisms: identifying influential factors using statistical design of experiments*. International Journal of Mineral Processing, 88, 31–36.
- SIMATE G.S., NDLOVU S., GERICKE M., 2009. *Bacterial leaching of nickel laterites using chemolithotrophic microorganisms: process optimisation using response surface methodology and central composite rotatable design*. Hydrometallurgy, 98, 241–246.



- SZUBERT A., KORZEKWA W., GROTOWSKI A., 2007. *Analiza bazy surowcowej oraz wytypowanie perspektywicznych surowców niklu: w ramach projektu PBZ-MNiSW-3/3/2006, pt.: Nowoczesne technologie oraz zaawansowane materiały i wyroby w zrównoważonym rozwoju przemysłu metali nieżelaznych*, KGHM Cuprum sp. z o.o. Centrum Badawczo-Rozwojowe, Wrocław.
- TANG J.A., VALIX M., 2006. *Leaching of low grade limonite and nontronite ores by fungi metabolic acids*. *Minerals Engineering*, 19, 1274–1279.
- TZEFERIS P.G., 1994. *Leaching of a low grade hematitic laterite ore using fungi and biologically produced acid metabolites*. *International Journal of Mineral Processing*, 42, 267-283.
- TZEFERIS P.G., AGATZINI-LEONARDOU S., 1994. *Leaching of nickel and iron from Greek non-sulphide nickeliferous ores by organic acids*. *Hydrometallurgy*, 36 (3), 345–360.
- VALIX M., USAI F., MALIK R., 2001a. *Fungal bioleaching of low grade laterite ores*. *Minerals Engineering*, 14 (2), 197–203.
- VALIX M., USAI F., MALIK R., 2001b. *The electro-sorption properties of nickel on laterite gangue leached with an organic chelating acid*. *Minerals Engineering*, 14 (2), 205-215.
- WATLING H.R., 2008. *The bioleaching of nickel-copper sulphides*. *Hydrometallurgy*, 91, 70-88.