

BACTERIAL LEACHING OF BLACK SHALE COPPER ORE

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ABSTRACT. Black shale fraction of copper ore from the Lubin deposit, Poland, was leached in percolation columns initially by means of sulphuric acid and then by means of mixed culture of mesophilic, acidophilic, chemolithotrophic bacteria. The fraction contained 6.64 % copper, 3.05 % sulphur, 315 g/t silver, 10.94 % organic carbon and 22.5 % carbonates. Leach solutions containing ferric ions, sulphuric acid, dissolved oxygen and bacteria were used to irrigate the ore at rates between 40-120 l/ton. 24 hours. 80.2 % of the copper was leached within 150 days in this way. Copper was recovered from the pregnant solutions by means of cementation with metallic iron and cement copper concentrates containing about 82 % copper were obtained in this way. After the acidic leaching, the ore fraction was washed with water and was subjected to thiosulphate leaching to soluble silver. 51.6 % of this metal was leached within 30 days. The silver was recovered from the pregnant solutions by means of cementation with metallic zinc.

БАКТЕРИАЛНО ИЗЛУГВАНЕ НА МЕДНИ РУДИ, СЪДЪРЖАЩИ ЧЕРНИ ШИСТИ

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РЕЗЮМЕ. Фракция черни шисти от медна руда от находище Любин, Полша, бе излужена в перколационни колони първоначално посредством сярна киселина и после посредством смесена култура на мезофилни, ацидофилни хемолитотрофни бактерии. Фракцията съдържаше 6.64 % мед, 3.05 % сярна, 315 г/т сребро, 10.94 % органичен въглерод и 22.5 % карбонати. Излугвачи разтвори, съдържащи фери-йони, сярна киселина, разтворен кислород и бактерии, бяха използвани да оросяват рудата със скорости между 40-120 л/т. 24 часа. 80.2% от медта бе излужена за 150 дни по този начин. Медта беше извлечена от продукционните разтвори посредством циментация с елементарно желязо (Fe^0) и по този начин бяха получени циментационни медни концентрати, съдържащи около 82 % мед. След излугването в кисела среда рудната фракция бе промита с вода и бе подложена на излугване с тиосулфат, за да се разтвори среброто. 51.6 % от този метал бяха излужени за 30 дни. Среброто бе извлечено от продукционните разтвори посредством циментация с елементарен цинк (Zn^0).

Introduction

The black shale ore in the Lubin deposit, Poland, is an important source of some valuable metals, mainly copper and silver. At present, this ore is processed in commercial scale by flotation, as a result of which concentrate containing these metals is produced. However, the mineralogical composition and structure of this ore cause some problems to this way of treatment and this is the reason for studies on the possibility to process the ore by means of technological methods of different type. A special attention with this respect is paid to different hydrometallurgical methods, including such based on the action of microorganisms. Experiments for bioleaching of copper from the run-of-mine Lubin ore, from different mineralogical fractions of this ore, as well as from products and wastes from its processing have been carried out under laboratory conditions using both chemolithotrophic and heterotrophic microorganisms (Sklodowska et al., 1996; Sadowski et al., 2003; Farbiszewska-Kiczma et al., 2004; Groudev et al., 2006).

The present paper contains data about experiments on the different technological stages of a flowsheet connected with the processing of the run-of-mine Lubin ore: bioleaching of copper by means of acidophilic chemolithotrophic bacteria, recovery of copper from the pregnant solutions by means of

solvent extraction and electrowining, leaching of silver from the washed ore by means of thiosulphate, and recovery of silver from the pregnant solutions by means of cementation with metallic zinc (Zn^0).

Materials and methods

The sample of the run-of-mine Lubin ore used in this study contained 1.01% copper, 82 g/t silver, 1.19% sulphur, 1.2% organic carbon and 22.5% carbonates. Chalcocite was the main copper-bearing mineral in the ore but bornite, chalcopyrite, thenantite and covellite were also well present. Copper oxide minerals and pyrite were present in low quantities. The copper sulphides formed accretions with the host rock and were encapsulated in it. The sample had pH of 7.98 and was characterized by a highly positive net neutralization potential (+406 kg $CaCO_3$ /t).

Eight kg of the ore crushed to minus 8.0 mm were put into a plastic vessel to form a small heap (~ 30 cm long, 12 cm wide and 12 cm high). Data about the particle size of the ore are shown in Table 9. An aeration system consisting of several perforated plastic tubes was constructed in the vessel before adding the ore. The ore was supplied to the vessel in a way

that after the heap construction the aeration system was located inside the ore mass.

The ore was initially pretreated with sulphuric acid to decompose the carbonates and liberate the sulphide minerals from the carbonate matrix as well as to facilitate the adjustment of the ore pH to the levels suitable for the growth and activity of the acidophilic chemolithotrophic bacteria able to oxidize sulphide minerals. During the acidic pretreatment the carbonate content of the ore was decreased from the initial 22.5% to 1.7% and as a result of this the net neutralization potential of the ore was decreased from highly positive to very close to the neutral point (+2 kg CaCO₃/t). The acid consumption during the pretreatment amounted to 408 kg sulphuric acid/t ore. Approximately 18% of the copper was solubilized during the pretreatment within 48 hours. The carbonate and oxidizable mobility fractions were the main sources of the copper solubilized. Chalcocite was the only sulphide mineral solubilized efficiently during the pretreatment.

The acid pretreated ore was inoculated with a mixed culture of acidophilic chemolithotrophic bacteria (*At. ferrooxidans*, *At. thiooxidans* and *L. ferrooxidans*) preliminary adapted to the ore. 200 ml of active late-log-phase microbial culture containing about 10⁹ cells/ml grown on this ore was used as inoculum and was distributed evenly within the heap by means of diluted sulphuric acid solution with pH of 1.5 and containing Fe²⁺ ions (2 g/l) as well as ammonium and phosphate ions. The water content of the heap was adjusted to about 70-80 % from the maximum water retention capacity of the ore. Water-saturated air was injected through the aeration system to the ore by means of a small compressor to maintain the content of dissolved oxygen in the pore solution at levels higher than 5 mg/l. The wetted heap was maintained under such conditions for a period of 10 days during which most bacteria attached to the ore particles and started to oxidize the sulphide minerals. At the end of this period the ore was densely populated by bacteria, the redox potential of the pore solution was increased to about 570 mV and some copper and iron were solubilized from the ore.

Then the irrigation of the ore was started by diluted sulphuric acid solutions with a pH of about 1.7-1.8. The irrigation rate was in the range of 40-80 l/t ore per 24 h. The leach solutions were distributed evenly on the ore surface by means of perforated plastic tubules located on it. The aeration of the ore was continued and the content of ammonium and phosphate ions was maintained at 50 and 25 mg/l respectively, by means of periodic additions of these ions to the leach solutions.

Two different methods to recover copper from the pregnant heap effluents were used: cementation with metallic iron (Fe⁰) and solvent extraction + electrowinning.

The cementation process was carried out in glass vessels containing 200 g of iron shavings each. The copper-bearing solutions containing between 0.5–1.5 g/l copper ions were added at rates allowing residence times between 1–3 hours.

The solvent extraction of copper from the pregnant heap effluents was carried out by means of the reagent LIX 984N (10 volume percent in a kerosene diluent). The solvent extraction circuit consisted of two extraction stages and one stripping stage. The organic phase (reagent) and the aqueous phase (pregnant copper-bearing solution) were mixed at a 1:1 ratio. Mixing time of 3 minutes was needed to obtain loaded organic (approximately 80 % of the maximum loading capacity of the reagent). The loaded organic was separated from the aqueous phase and was subjected to stripping by means of strong solution of sulphuric acid. The copper transfer in the electrolytic cell was between 5-7 g/l copper. The final pregnant electrolyte was treated in the electrowinning cell in which the anodes were made of lead, and the cathodes were made of copper. Current density applied in the cell was between 200–230 amperes/m². The spent electrolyte contained about 30 g/l copper and 180–185 g/l sulphuric acid and was recycled to the stripping stage.

After the acidic copper leaching the heap was washed with water to remove the residual acidity and was subjected to alkaline leaching by means of solutions containing thiosulphate ions (added as ammonium thiosulphate) – 0.1 mol/l, copper ions (added as copper sulphate) – 0.005 mol/l, sulphite ions – 0.01 mol/l and ammonia to maintain the pH of these solutions in the range of 10.0-10.5.

The leach solutions were pumped to the top surface of the heap at a rate of 200 l/ton ore per 24 h. The solutions percolated through the ore mass and dissolved silver. The pregnant heap effluents were treated by means of cementation with metallic zinc to precipitate the dissolved silver. The depleted solutions from the cementation unit were collected in a regeneration vessel where make up water and reagents were added to the desired level. The leach solutions adjusted in this way were then recycled to the heap.

Measurement of ion concentrations in solutions was carried out by means of induced coupled plasma spectrometry. The isolation, identification and enumeration of microorganisms were carried out by methods described elsewhere (Groudev, 1990; Karavaiko et. al., 1988).

Results and discussion

The leaching of copper by the above-mentioned system was very efficient and 68% of the copper were solubilized within 150 days (Fig. 1). This amount, together with the 18% of copper solubilized during the acidic pretreatment of the ore, resulted in a final copper extraction of 86.4%. The concentration of copper in the pregnant heap effluents was usually between 0.5 and 1.0 g/l. Iron was solubilized together with copper during the leaching. Bacteria were able to maintain most of the iron in the ferric state and the redox potential of the pregnant solutions was usually higher 550 mV.

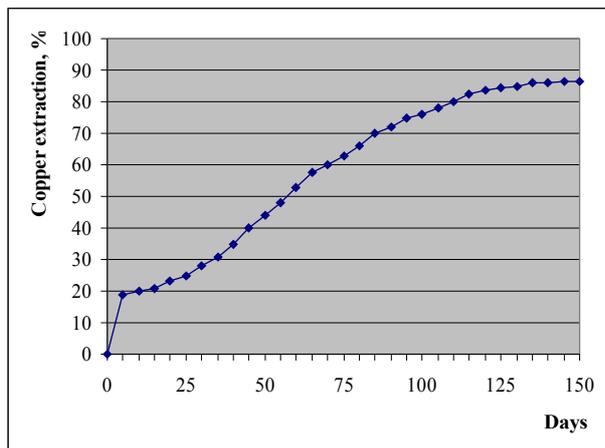


Fig. 1. Leaching of copper from the R-O-M Lubin ore

In some cases the concentration of iron in these solutions was low (less than 0.3-0.4 g/l). In these cases the heap was irrigated with leach solutions containing 1.5-2.0 g/l Fe^{3+} ions generated in bioreactor as a result of the bacterial oxidation of Fe^{2+} to Fe^{3+} ions by means of immobilized Fe^{2+} -oxidizing chemolithotrophic bacteria (*At. ferrooxidans* and *L. ferrooxidans*). Non-ferrous metals, mainly zinc and nickel, were also solubilized during the leaching but due to their low contents in the ore this solubilization is not of an economic interest. Lead was not solubilized but bacteria oxidized a portion of galena to the insoluble lead sulphate. Silver was also not solubilized. Its content in the ore after the acidic leaching was increased to 99 g/t due to the solubilization of other components (Table 1)

Table 1
Data about the chemical composition of the R-O-M Lubin ore at different stages of treatment

Component, %	Before treatment	After acidic pretreatment	After bioleaching
Copper	1.01	0.82	0.14
Total sulphur	1.19	1.37	0.25
Sulphide sulphur	0.93	0.91	0.16
C organic	1.2	1.5	1.4
C inorganic	10.2	0.37	0.08
Silver, g/t	82	96	99

The efficient leaching of the ore was connected with the suitable conditions created for the chemolithotrophic bacteria in the heap. The number of these bacteria in the heap was higher than 10^9 cells/g ore and that in the pregnant heap effluents varied between 10^8 - 10^9 cells/ml. In most samples tested during the leaching *L. ferrooxidans* was the prevalent microorganisms and this was due to its ability to grow well under very acidic conditions (at pH < 1.8). However, *At. ferrooxidans* was also well present and this was connected with its ability to oxidize, apart from Fe^{2+} ions, also the copper sulphide minerals.

The recovery of copper during the cementation exceeded 98%, and the content of copper in the cement concentrate was about 81–82%.

The cementation was connected with increase in the concentration of iron in the barren solutions (usually by 20–40 %). Most of the iron in these solutions was in the ferrous state due to the reaction between the Fe^{3+} ions in the pregnant effluents and the metallic iron. This resulted in decrease of the redox potential of the barren solutions to values lower than 350 mV. The pH of the barren solutions was increased to values higher than 2.0 due to the reaction between the sulphuric acid present in the pregnant solution and the metallic iron. For these reasons it was necessary to treat the barren solutions from the cementation in a way to turn them into efficient leach solutions. This was connected with increase of the concentration of Fe^{3+} ions and redox potential by mixing the barren solutions with solutions from the bioreactor for oxidation of Fe^{2+} to Fe^{3+} ions. The solutions from the bioreactor were characterized by high redox potential (> 550 – 600 mV), low pH (< 1.9) and high content of bacteria (usually between 1.10^8 – 3.10^8 cells/ml). In some cases diluted sulphuric acid solutions were added to compensate the water losses due to evaporation, to decrease pH to values between 1.7–1.8 and to decrease the total concentration of dissolved iron.

The consumptions of metallic iron during cementation amounted to about 2.0 – 2.2 g Fe^0 /g copper.

Copper with purity higher than 99.5% was produced in the electrolytic cell.

The leaching of silver from the ore after the acidic leaching was not very efficient. 51.2% of this precious metal was leached within 30 days (Fig. 2).

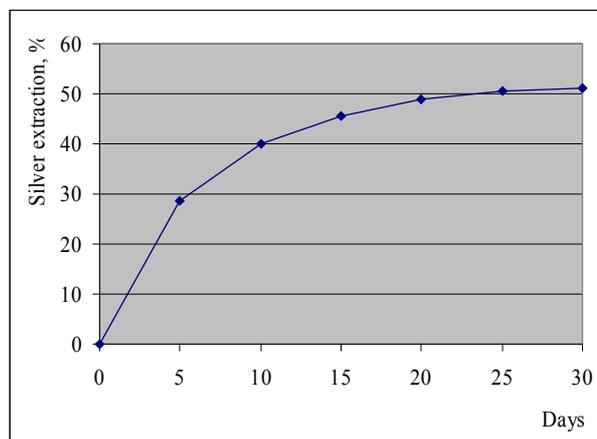


Fig. 2. Leaching of silver from the R-O-M Lubin ore by means of thiosulphate after its acidic leaching of copper

The degree of silver extraction from the pregnant solutions by means of cementation with Zn^0 was higher than 95%. The product from the cementation unit was silver concentrate, which contained also copper and zinc as valuable components. This concentrate can be processed by the well-known conventional methods for recovering pure silver.

The consumption of reagent during the leaching and cementation of silver amounted to 5.3 kg ammonium thiosulphate, 0.5 kg copper sulphate and 0.14 kg metallic zinc per ton of ore.

Similar extraction of silver was obtained by two other leaching methods: cyanidation and treatment by solutions containing hydrochloric acid and sodium chloride.

The final conclusion from this study is that the run-of-mine Lubin ore is suitable for recovering copper by means of acidic bioleaching with chemolithotrophic bacteria. However, the extraction of silver by means of different methods is not acceptable from an economic point of view. A more realistic approach involving the biotechnology as a component of the processing flow sheet is the bioleaching of flotation concentrate obtained from the same ore for copper solubilization and then chemical leaching of the solid residue for silver solubilization.

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