

TWO-STAGE LEACHING OF COPPER AND SILVER FROM CLINKER, AN WASTE PRODUCT FROM THE ZINC METALLURGY

Irena Spasova, Marina Nicolova, Plamen Georgiev, Stoyan Groudev

University of Mining and Geology "St. Ivan Rilski" Sofia, 1700, e-mail: spasova@mgu.bg

ABSTRACT: A sample of the clinker, an waste product from the zinc pyrometallurgy, was subjected to a gravimetric treatment to separate the valuable metals (mainly copper and silver) from the coke. The heavy fraction (with a particle size less than 0.074 mm) containing 1.20% copper and 95 g/t silver was subjected to a two-stage leaching in agitated reactors for extracting these metals. The first stage was carried out by means of different acidophilic chemolithotrophic bacteria and 88.0% of the copper was solubilized for 168 hours by a culture of extreme thermophiles at 70 °C. The copper was recovered from the pregnant solution by means of solvent extraction plus electrowinning. The residual solid mineral mass after the bioleaching was subjected to leaching by an alkaline solution containing thiosulphate and amino acids of microbial origin as silver – complexing agents. 86.2% of this metal was extracted in this way for 48 hours. Silver was recovered from the pregnant solution by means of cementation with metallic zinc (Zn⁰).

ДВУСТАДИЙНО ИЗЛУГВАНЕ НА МЕД И СРЕБРО ОТ КЛИНКЕР -ОТПАДЪЧЕН ПРОДУКТ ОТ МЕТАЛУРГИЯТА НА ЦИНКА

Ирена Спасова, Марина Николова, Пламен Георгиев, Стоян Грудев

Минно-геоложки университет "Св.Иван Рилски" София 1700, e-mail: spasova@mgu.bg

РЕЗЮМЕ. Проба от клинкер – отпадъчен продукт от пирометалургията на цинка, бе подложена на гравитационно третиране за отделяне на ценните метали (главно мед и сребро) от кокса. Тежката фракция (с едрина на частиците под 0.074 mm), съдържаща 1.20% мед и 95 g/t сребро, бе подложена на двустадийно излугване в реактори с разбъркване за извличане на тези метали. Първият стадий бе проведен посредством различни ацидофилни хемолитотрофни бактерии и 88.0% от медта бе разтворена за 168 часа чрез култура на екстремни термофили при 70 °C. Медта беше извлечена от продукционния разтвор чрез течна екстракция и електролиза. Остатъчната неразтворена минерална маса след биологичното излугване бе подложена на излугване чрез алкален разтвор, съдържащ тиосулфат и аминокиселини от микробен произход, като комплексирани агенти за среброто. 86.2% от среброто бе извлечено по този начин за 48 часа. Среброто бе извлечено от продукционния разтвор чрез циментация с метален цинк (Zn⁰).

Introduction

The clinker from the zinc pyrometallurgy is an waste product still containing some valuable components such as coke and several heavy metals, mainly copper and silver but also lead, iron and zinc. It has been shown that it is possible to extract considerable portions of these components by means of a flowsheet in which the first step is the gravimetric separation to obtain a light fraction (consisting mainly of coke) and a heavy fraction (containing the valuable non-ferrous metals, silver and iron) (Genchev and Groudev, 1979).

The utilization of the coke obtained in this way is not a problem. However, the different properties of the metals present in the heavy fraction is connected with the application of selective methods for obtaining acceptable extractions of these metals. Previous experiments have shown that copper is solubilized efficiently by means of acidified ferric sulphate solutions produced as a result of the prior bacterial oxidation of ferrous sulphate. Copper extractions in the range of 75 – 80 % were obtained by leaching with such solutions of the heavy

fraction (crushed to minus 5.0 mm) in percolation columns for a period of 120 days. Considerable amounts of the iron and zinc were also solubilized together with copper. Lead and silver were not solubilized. The leaching was connected with a great consumption of sulphuric acid added from outside (about 4.5 – 5.0 g/g Cu solubilized). Copper was recovered from the pregnant leach solutions by means of cementation with metallic iron (Fe⁰).

The main objectives of the present study were as follows:

- to increase both the rate and the level of copper extraction by testing the possibilities for bacterial leaching of finely ground heavy fraction of the clinker in agitated bioreactors;
- to extract the lead and silver from the solid residue after the bacterial leaching by means of leach solutions with composition suitable for solubilization of these metals.

Materials and Methods

The heavy fraction of the clinker used in this study contained 1.20 % copper, 0.41 % lead, 0.12 % zinc, 13.6 % iron, 95 g/t silver and 2.84 % sulphur. The phase analysis of copper revealed that 31.4 % of this metal was present in oxide minerals, 47.5 % in secondary sulphides (mainly in chalcocite) and 21.1 % in chalcopyrite. However, a portion of the copper (about 8 %) can be related to an inert fraction which was very refractory to leaching. This fraction consisted of very fine sulphides (with a size in the range of about 1 – 5 µm) disseminated in a silicate glass-type matrix. The larger portion of this inert fraction was separated in the light fraction during the gravimetric treatment of the initial clinker sample. Most of the lead (64.4 %) was present as galena but lead-bearing oxides were also well present. Most of the iron was present in the metallic form (Fe⁰) but significant portions were present in sulphides (mainly in pyrite and chalcopyrite) and in some ferrite associations with copper. Data about the phase distribution of silver are shown in Table 1.

Table 1.
Phase composition of the silver in the heavy fraction of clinker

Phases	Content	
	g/t	% from the total
Free silver	-	-
Silver encapsulated in iron oxides and hydroxides	35.5	37.4
Silver finely disseminated in sulphides	56.2	59.1
Silver finely disseminated in silicates	3.3	3.5
Total content of silver	95.0	100.0

The heavy fraction was characterized by a highly positive net neutralization potential (170 kg CaCO₃/t) due to the presence of several acid-consuming components (carbonates, oxides and Fe⁰). The experiments for leaching of metals were carried out with finely ground material (with a particle size less than 74 microns) in glass cylindrical baffled reactors with a working volume of 2 l at 20 % pulp density and 320 rpm stirring rate.

Four types of leaching were applied:

- Leaching by means of acidophilic chemolithotrophic bacteria growing in the presence of the material being leached. In this case bacteria will grow on the sulphides still present in this material and/or on the ferrous ions which are dissolved from the material under the acidic conditions created by means of the sulphuric acid added from outside or partially generated in the leach system. In these experiments diluted sulphuric acid (with an initial pH of 1.8) containing (NH₄)₂SO₄ and KH₂PO₄ in concentrations 0.50 and 0.25 g/l, respectively, was used as a leach solution. This solution was inoculated by a late-log phase mixed culture of mesophilic acidophilic chemolithotrophic

bacteria of the species *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*. The culture was preliminary adapted to the clinker fraction by consecutive transfers in clinker suspension with a step by step increasing pulp density. The leaching by the inoculated solution was carried out at 35 °C for a period of 168 h. The progress of the leaching was followed by analysis of liquid samples for dissolved metals, as well as for pH, Eh, and number of chemolithotrophic bacteria. The pH during the leaching was maintained to 1.7 – 1.8 by adding sulphuric acid from outside.

Similar experiments were carried out also by mixed cultures of both moderately thermophilic (at 45 °C) and extremely thermophilic (at 70 °C) bacteria.

The mixed culture of the moderate thermophiles consisted of *Sulfobacillus thermosulfidooxidans* and *Acidithiobacillus caldus*, and the mixed culture of the extreme thermophiles contained bacteria related to the genus *Sulfolobus*;

- The clinker fraction initially was pretreated by sulphuric acid to neutralize the acid-consuming components, and then the leaching was carried out by means of the above-mentioned bacterial cultures;
- Leaching by means of ferric sulphate solutions generated by means of the prior bacterial oxidation of ferrous ions in separate bioreactor at different temperatures (35, 45 and 70 °C) and still containing the relevant active chemolithotrophic bacteria. The leaching by these solutions was carried out at 20 % pulp density and at the relevant temperature. In this case the ferric ions will be the main leaching agent but bacteria can also directly solubilize the sulphides present in the material being leached and can regenerate ferric ions by the in situ oxidation of the ferrous ions;
- Control chemical leaching by means of solutions containing different concentrations of sulphuric acid and/or ferric ions.

The solid residues after the leaching of copper and zinc were washed with distilled water and then were subjected to chemical leaching by solutions of FeCl₃ to solubilize the lead. This leaching was carried out in agitated reactors at 35 and 70 °C for different periods of time.

The solid residues after the leaching of lead were washed with distilled water to about neutral pH and then were subjected to leaching of silver by alkaline solutions containing microbial protein hydrolysates, thiosulphate, sulphite and copper ions, and ammonia in different concentrations to find the optimum composition of the leach solutions towards the clinker fraction used in this study (Groudev et al., 2008, Spasova et al., 2009). The protein hydrolysates contained different silver-complexing amino acids and were mixed together in suitable proportions. The leaching of silver by such solutions was carried out in agitated reactors at 20 % pulp density and 35 °C for 48 h.

Elemental analysis of the liquid samples was carried out by means of atomic adsorption spectrometry and induced coupled plasma spectrometry. Elemental analysis of the solid samples

was carried out by digestion and measurement of ion concentrations in solution by the above-mentioned methods.

The isolation, identification and enumeration of microorganisms were carried out by methods described elsewhere (Karavaiko et. al., 1988; Hallberg and Johnson, 2001).

Results and Discussion

The chemolithotrophic bacteria were able to solubilize efficiently copper and zinc from the clinker fraction (Figure 1). The best results were obtained by means of the mixed culture of extreme thermophiles. However, these results were very similar to those obtained by the mesophilic and moderately thermophilic bacteria. The bacterial growth and activity were possible only in systems in which sulphuric acid was added from outside to maintain the pH within the range suitable for these acidophilic bacteria. The sulphuric acid was an effective leaching agent towards the oxide minerals, chalcocite and metallic iron present in the clinker fraction (Figure 2).

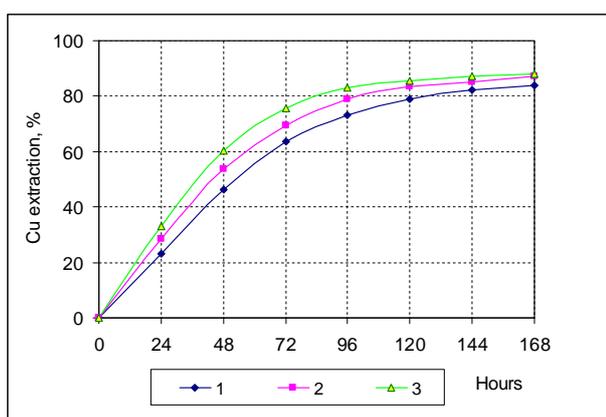


Fig. 1. Leaching of copper from the clinker heavy fraction by means of mixed cultures of chemolithotrophic bacteria growing at different temperatures. 1 – 35°C, 2 – 45°C, 3 – 70°C

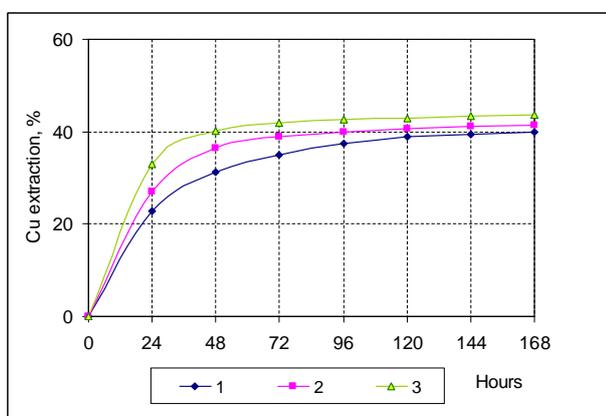


Fig. 2. Leaching of copper from the clinker heavy fraction by means of sulphuric acid at different temperatures. 1 – 35°C, 2 – 45°C, 3 – 70°C

Iron was solubilized from the relevant oxide minerals and Fe^0 as ferrous ions (Fe^{2+}) and, as a result of this, during the lag-phase of bacteria the redox (Eh) potential of the leach solutions was low (in the range of about 260 – 290 mV). However, the chemolithotrophic bacteria oxidized efficiently the ferrous ions to the ferric state (Fe^{3+}) and the Eh steadily increased reaching values higher than 600 mV at the end of leaching. The ferric ions were an efficient oxidant towards the secondary copper sulphides, sphalerite and galena and, to some extent, towards the chalcopyrite. The main role of bacteria in these systems was to regenerate the Fe^{3+} ions and maintain a high Fe^{3+}/Fe^{2+} ratio.

The pregnant solutions at the end of leaching contained about 2.0 – 2.1 g/l copper, about 230 mg/l zinc, and about 11 g/l total dissolved iron. These concentrations reflected final copper extraction of about 40 – 41%. Lead and silver were not solubilized, although a portion of galena (PbS) was oxidized to anglesite ($PbSO_4$). The number of iron-oxidizing chemolithotrophic bacteria in these experiments exceeded 3.5×10^8 cells/ml at the end of leaching.

The leaching by means of ferric sulphate solutions obtained as a result of the prior bacterial oxidation of Fe^{2+} ions and still containing the relevant active bacteria (with pH 1.7 – 1.8 maintained by sulphuric acid) gave similar results (Figure 3), regardless of the fact that the total concentrations of dissolved iron in these systems were higher (about 14 g/l at the end of leaching).

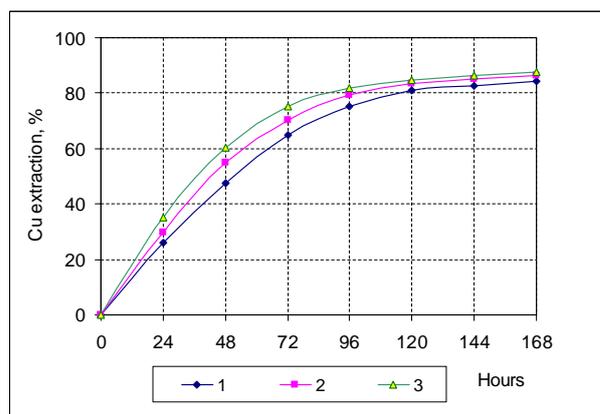


Fig. 3. Leaching of copper from the clinker heavy fraction by means of ferric ions at different temperatures. 1 – 35°C, 2 – 45°C, 3 – 70°C;

The initial concentration of Fe^{3+} ions was 3.0 g/l. In all experiments the pH of the leaching suspensions was maintained to 1.7 – 1.8 by means of sulphuric acid added from outside.

Copper and zinc can be recovered from the pregnant solutions by means of solvent extraction plus electrowinning. The dissolved iron can be precipitated by increasing the pH to the desired levels to obtain pigments with different composition and structure and characterized by a specific colour and particle size.

The solid residues after the copper and zinc extraction were efficiently leached by means of $FeCl_3$ solutions to

solubilize the lead. 94.5% of this metal were extracted by leaching in agitated reactors at 70 °C for 72 h by means of solution containing 3 g/l FeCl₃ and with a pH of 1.7 (maintained by hydrochloric acid).

Some silver was also solubilized during this leaching. It was possible to increase the silver extraction by using leach solutions containing FeCl₃ and much higher concentrations of hydrochloric acid.

The solid residues after the lead extraction were subjected to an alkaline leaching for solubilization of silver. The highest extraction of 86.2% was obtained by means of solution containing 15 g/l thiosulphate ions, 3 g/l microbial protein hydrolysate, 0.5 g/l copper ions, 3 g/l sulphite ions, and 3.5 g/l ammonia. The leaching was carried out in an agitated reactor, at 20% pulp density and 35°C for 48 h. The treatment of the pregnant leach solution by cementation with metallic zinc (Zn⁰) resulted in the production of a concentrate which, apart from the silver, contained also zinc and a very small amount of copper.

*Recommended for publication by
Department of Engineering Geoecology*

References

- Genchev, F.N. and Groudev, S.N., (1979). Leaching of copper from clinker, an waste product from the zinc metallurgy, *Annual of the University of Mining and Geology, Sofia*, 25, 159 – 170.
- Groudev, S.N., Spasova, I.I., Nicolova, M.V. and Georgiev, P.S., (2008). Biological and chemical leaching of copper and silver from black shales, In: *Proc. 12th Conference on Environment and Mineral Processing*, 5 – 7 June 2008, Ostrava, Part I.
- Hallberg, K.B. and Johnson, D.B., (2001). Biodiversity of acidophilic microorganisms, *Advanced and Applied Microbiology*, 49, 37-84.
- Karavaiko, G.I., Rossi, G., Agate, A. D., Groudev, S.N. and Avakyan, Z.A., (eds.), (1988). *Biogeotechnology of Metals. Manual*, GKNT Center for International Projects, Moscow.
- Spasova, I.I., Nicolova, M.V. and Groudev, S.N., (2009). Extraction of copper and silver from a black shale ore by means of chemical and biological leaching, *Proc. XIII Balkan Mineral Processing Congress*, Bucharest, vol. II, 576 – 581.