

COMPARATIVE VARIANTS OF BIOLOGICAL AND CHEMICAL LEACHING OF THREE DIFFERENT COPPER CONCENTRATES

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ABSTRACT. Two copper sulphide concentrates and a copper concentrate containing copper mainly in its elemental form were subjected to different variants of bacterial and chemical batch leaching in agitated bioreactors. The most efficient leaching of copper from the sulphide concentrates was achieved by means of a mixed culture of mesophilic chemolithotrophic bacteria at acidic pH maintained by sulphuric acid added from outside. The different variants of biological and chemical leaching of the third concentrate resulted in similar extractions of copper.

СРАВНИТЕЛНИ ВАРИАНТИ НА БИОЛОГИЧНО И ХИМИЧНО ИЗЛУГВАНЕ НА ТРИ РАЗЛИЧНИ МЕДНИ КОНЦЕНТРАТА

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РЕЗЮМЕ. Два медни сулфидни концентрата и един меден концентрат съдържащ мед главно в елементарна форма, бяха подложени на различни варианти на бактериално и химично излугване в периодичен режим биореактор с механично разбъркване. Най-ефикасно излугване на мед от сулфидните концентрати бе постигнато посредством смесена култура на мезофилни хемолитотрофни бактерии, развиващи се в присъствие на концентрата. Разтварянето на медта от третия концентрат бе ефикасно чрез химично излугване (посредством сярна киселина и фери йони), както и чрез хемолитотрофните бактерии при кисело рН, поддържано чрез сярна киселина добавена отвън. Различните варианти на биологично и химично излугване на третия концентрат постигнаха сходни извличания на медта.

Introduction

Different types of sulphide concentrates can be efficiently leached by means of chemolithotrophic bacteria. In some cases the leaching is connected with solubilization of one or more non-ferrous metals such as copper, zinc, nickel, cobalt, etc. from the concentrate being leached. In some other cases the bacterial leaching is used as a pretreatment procedure prior to conventional treatment. Such pretreatment procedure can be of different type: selective solubilization of some contaminant metals to upgrade the relevant concentrate with respect to the prevalent metal, e.g. solubilization of the copper, zinc and cadmium from off-grade complex lead concentrates; selective removal of some unwanted elements such as arsenic to make the relevant concentrate acceptable for conventional processing; oxidation of gold-bearing and silver-bearing sulphide minerals to liberate the gold (or silver) finely disseminated in the sulphide matrix and to facilitate its subsequent chemical extraction.

The bacterial leaching is carried out under batch or continuous conditions and is best performed in reactors with mechanical stirring. The optimum leach conditions can be established and controlled in such systems. Mixed cultures of different species of both mesophilic and thermophilic chemolithotrophic bacteria have been used in such operations (Groudev et al., 2005a; 2005b).

These bacteria oxidize the sulphide minerals by means of different mechanisms but both iron- and sulphur-oxidizing activities are needed to be present by the relevant bacterial communities for achieving high leaching rates. Some bacterial species are able to oxidize only the ferrous iron, other are able to oxidize only S^0 and sulphur reduced inorganic compounds but some species are able to oxidize both iron and sulphur (Norris, 2007; Rawlings, Johnson, 2007). Furthermore, the strains related to one and the same taxonomic species can differ considerably from each other with respect to the levels of their oxidative ability.

In some cases the chemolithotrophic bacteria are able to facilitate the leaching of metals present in the concentrates in their elemental zero-valency form or as oxides and carbonates.

The present paper contains some data about the leaching of three different copper concentrates by means of different variants of bacterial and chemical leaching.

Materials and Methods

Data about the chemical composition of the concentrates are shown in Table 1. The concentrate No 1 was a typical copper chalcopyritic concentrate. Covellite, chalcocite and bornite were also present but in much lower concentrations. The concentrate No 2 contained copper mainly in the secondary sulphides chalcocite and covellite. Chalcopyrite was also relatively well present, although in much lower concentration.

These two copper sulphide concentrates were relatively rich-in-pyrite. The contents of other non-ferrous metals such as zinc and lead were low. The concentrate No 3 was a typical polymetallic concentrate consisting of a mixed scrap from different sources, mainly from damaged electronic and machinery equipment. Apart from the copper, this concentrate contained also considerable amounts of lead and zinc, as well as of silver.

Table 1. Chemical composition of the concentrates

Component	Concentrate No 1	Concentrate No 2	Concentrate No 3
Cu total, %	21.7	35.2	40.4
Cu sulphidic, %	20.8	34.0	-
- primary, %	17.0	6.5	-
- secondary, %	3.8	27.5	-
Cu oxide, %	0.9	1.2	1.8
Cu elemental, %	-	-	98.2
Fe, %	25.5	18.1	14.5
S, %	32.9	28.0	0.32
Zn, %	0.21	0.12	8.2
Pb, %	0.48	0.33	12.7

The acidophilic chemolithotrophic bacteria used in this study were initially isolated as a mixed culture from a rich-in-pyrite and copper sulphides heap in the Vlaikov Vrah bioleaching operation. The culture consisted of *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans* and *Acidiphilium sp.* (probably *Ac. cryptum*). The culture was adapted to the concentrates used in this study by consecutive transfers of late-log-phase subcultures into the relevant concentrate suspensions with increasing pulp densities in a nutrient medium with the following composition (in g/l): $(\text{NH}_4)_2\text{SO}_4$ 0.50, KH_2PO_4 0.25, KCl 0.50, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 0.50, $\text{Ca}(\text{NO}_3)_2$ 0.01, with an initial pH of 1.8-1.9. The composition of the different microbial cultures originating from the mixed culture differed considerable in the presence of the different concentrates. The difference consisted mainly in the different ratios between the number of cells related to the different individual species of bacteria. These ratios depended on several factors such as pulp density, pH and composition of the nutrient medium, i.e. of the leach solution, and temperature during the leaching, as well as on the growth history of the relevant subculture. Some of these factors changed during the leaching and this was connected with changes of the species composition of the relevant mixed subculture.

The direct bacterial leaching of the concentrates was carried out under batch conditions in agitated 2 l baffled bioreactors containing 900 ml of the nutrient medium mentioned above, 100 g concentrate (with a particle size minus 0.074 mm) and 100 ml of an active microbial inoculum consisting of a late-log-phase bacterial culture preliminary adapted to the relevant concentrate and containing about 10^9 cells/ml. The leaching was carried out at stirring rate of 600 rpm, at 37 °C, for 10 days for the concentrate No 1 and No 2, and for 5 days for the concentrate No 3. Apart from the mechanical stirring, air containing 0.2 % CO_2 was injected into the bioreactors at a rate of 0.3 L/L mineral suspension. The pH was maintained within the range of 1.8 – 1.4 by addition of sulphuric acid or freshly ground limestone.

The indirect bacterial leaching was carried out by systems consisting of two different bioreactors. The first bioreactor was

of the same type as the bioreactors used for the direct bacterial leaching. The leach conditions were also the same but without the initial inoculation of the mineral suspensions with the relevant bacterial cultures. Instead this, acidified solutions of ferric sulphate generated in the second bioreactor as a result of the bacterial oxidation of ferrous ions in diluted sulphuric acid solutions were added to the first bioreactor. The addition of ferric ions to the first bioreactors was carried out in a way to follow the changes of the dissolved iron concentration during the direct bioleaching of the relevant concentrate.

The chemical leaching of the concentrates by means of acidified solution of Fe^{3+} ions was carried out in the same way as the indirect bacterial leaching by such ions but the leach solutions did not contain bacteria. In one variant the ferric ions were produced as a result of the chemical oxidation of ferrous sulphate in diluted sulphuric acid solutions by means of KMnO_4 . In a second variant the ferric ions were produced as a result of the bacterial oxidation of ferrous ions but then the bacteria were removed by means of vacuum filtration on the leach solutions.

The chemical leaching of the concentrates by means of sulphuric acid were carried out also in the baffled reactors of the same type and under the same experimental conditions but without bacteria and Fe^{3+} ions added from outside. The pH during the leaching was maintained within the range of 1.8-1.4.

The progress of the bacterial and chemical leaching was followed by analysis of the leach solutions for pH, Eh, dissolved oxygen and metals, and number of iron- and sulphur-oxidizing bacteria. Elemental analysis of the liquid samples was carried out by means of atomic absorption spectrometry and induced coupled plasma spectrometry. Elemental analysis of the solid samples was carried out by digestion and measurements of the ion concentrations in solutions by the above-mentioned methods. The isolation, identification and enumeration of microorganisms were carried out by methods described elsewhere (Karavaiko et al., 1988; Hallberg, Johnson, 1991).

Results and Discussion

The direct bacterial leaching was the most efficient way to solubilize copper from the concentrates No 1 and No 2 (Table 2 and Fig. 1). The extraction from the concentrate No 2 was much higher due to the presence of most copper in the forms of the secondary sulphide minerals chalcocite and covellite. These secondary sulphides are more amenable to bacterial leaching than the chalcopyrite. Regardless of this, the extraction of copper from the chalcopyrite, especially from the concentrate No1, was high, having in mind that the mesophilic bacterial leaching of chalcopyrite rarely exceeded 45% due to the formation of jarosites precipitated on its surface. The number of chemolithotrophic bacteria during the second half of the leaching period exceeded 10^9 cells/ml but most of the bacteria were firmly attached to the concentrate particles. *Leptospirillum ferrooxidans* was the prevalent bacterial species but *Acidithiobacillus ferrooxidans* was also well present. The number of *Acidithiobacillus thiooxidans* and *Acidiphilium sp.* was considerably lower (less than 10^4 and 10^2 cells/ml, respectively).

The indirect bacterial leaching by means of ferric ions was practically a combination of the direct and indirect leaching

since the Fe^{3+} -bearing solutions introduced into the relevant bioreactor (of the type No1) contained also considerable amounts of active iron-oxidizing bacteria. A large portion of these bacteria rapidly attached to the surface of the concentrate and started to oxidize the relevant sulphide minerals also by the direct mechanism. It must be noted that the continuous bacterial production of Fe^{3+} ions in the bioreactors of the type No 2 decreased considerably the number of *Acidithiobacillus thiooxidans* which was not able to oxidize the Fe^{2+} ions. However, the bioreactors No 1 were populated, apart from the iron-oxidizer *Leptospirillum ferrooxidans*, also by *Acidithiobacillus ferrooxidans* which possessed both iron- and sulphur-oxidizing abilities.

Table 2. Data about the leaching of concentrates by different methods used in this study

Copper-bearing substrates and forms of copper	Type of leaching			
	Direct bacterial	Indirect bacterial	Chemical by Fe^{3+}	Chemical by H_2SO_4
Copper extraction, %				
Concentrate No1				
- primary sulphidic Cu	46.5	33.5	25.3	16.8
- secondary sulphidic Cu	78.9	76.3	68.4	3.2
-oxide Cu	88.9	88.9	88.9	99.9
- total Cu	53.9	43.3	35.5	7.8
Concentrate No2				
- primary sulphidic Cu	44.2	40.1	25.8	1.5
- secondary sulphidic Cu	86.0	82.2	72.9	32.5
-oxide Cu	90.1	90.1	89.2	99.9
- total Cu	78.4	74.7	64.4	29.1
Concentrate No3				
- total Cu	90.1	92.5	92.1	91.4
- total Zn extraction	93.0	93.8	93.2	93.0

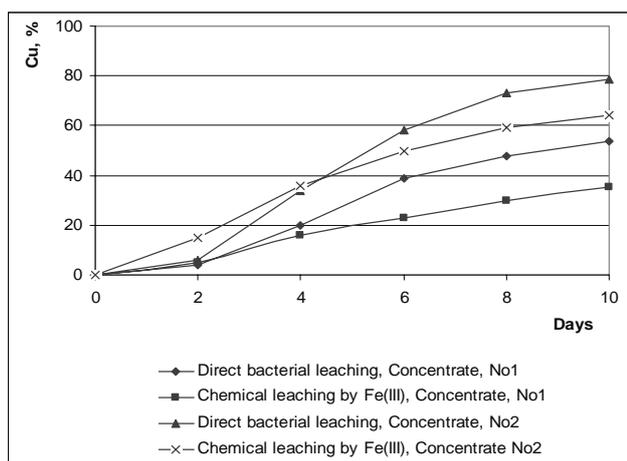


Fig. 1. Extraction of copper during the leaching of the concentrate No 1 and No 2

The copper leaching by this "indirect" bacterial action was not so efficient like the direct leaching. The copper extraction from the concentrate No 2 was much higher than that from the concentrate No 1 since the secondary copper sulphides were much more amenable to leaching (directly and by Fe^{3+} ions) than the chalcopyrite. Furthermore, it was found that the leaching by bacteria possessing only iron-oxidizing ability

(such as *Leptospirillum ferrooxidans*) was not efficient and that the presence of bacteria possessing sulphur-oxidizing ability (such as *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*) was necessary for the leaching of sulphide minerals.

The chemical leaching of the concentrate No 1 and No 2 by ferric ions (without bacteria) was less efficient than the bacterial leaching. The difference was more essential with the concentrate No 2. These data reflect the essential role played by bacteria in the oxidation of sulphide minerals. They also confirm the finding that both iron- and sulphur-oxidizing abilities are needed for achieving an efficient leaching of such minerals. The high sulphidic sulphur contents and the strongly negative net neutralization potentials made the bacterial leaching of these concentrates practically not connected with addition of sulphuric acid from outside.

The bacterial and chemical (by sulphuric acid and with or without ferric ions added outside) leaching of the concentrate No 3 resulted in similar extractions of copper, as well as of zinc and iron (Table 2; Fig. 2). This was connected with the efficient solubilization of the forms of these metals in this concentrate (mainly in the relevant elemental form and, in much lower concentrations, as oxides and carbonates). The acidophilic iron-oxidizing chemolithotrophic bacteria were able to grow in these leach systems only if sulphuric acid was added from outside to maintain the pH within the range suitable for these bacteria (i.e. at pH lower than 3.5). These bacteria used the ferrous ions solubilized from the concentrate by the sulphuric acid as the only energy source. The ferric ions produced as a result of the bacterial oxidation oxidized the elemental (zero-valency) metals to the relevant bivalent acid-soluble ions and in this way facilitated their solubilization. However, this effect was not very essential at leaching with 10% pulp density. Experiments carried out at higher pulp densities (12-15%) revealed that the presence of ferric ions increased to some extent the rate of metal solubilization. However, this positive effect was achieved only in systems in which the ferric ions were added from outside. This was due to the fact that the bacterial activity at these higher pulp densities (especially at 15%) was considerably decreased due to the higher concentrations of dissolved toxic metals.

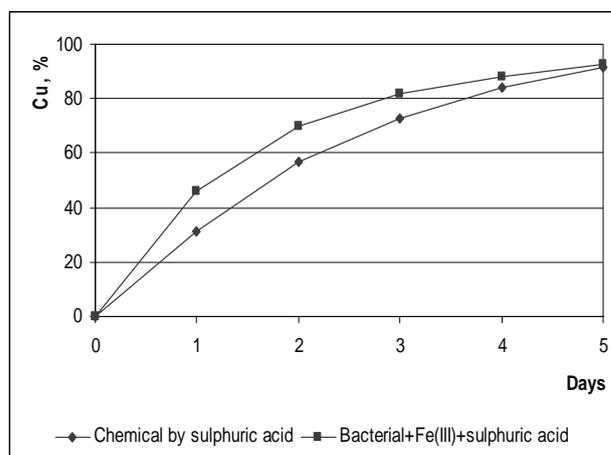


Fig. 2. Extraction of metals from concentrate No 3 during the chemical leaching by H_2SO_4 with and without Fe^{3+}

Some processes of cementation of metals (mainly of Cu^{2+} ions by the Fe^0) proceeded during the leaching but the resulted Cu^0 was also solubilized. The leaching of the concentrate No 3 was connected with high consumption of sulphuric acid added from outside (within the range of 203-215 g/100g concentrate at the different variants of leaching). The extraction of leach from all concentrates was very low due to the insolubility of PbSO_4 .

Conclusion

The data from this study demonstrates the essential role of the direct bacterial leaching in the extraction of copper from chalcopyrite, which is the most refractory sulphide mineral. The direct contact of the chemolithotrophic bacteria with the surface of this mineral as well as their ability to grow in a leach system containing high concentrations of heavy metals makes the preliminary adaptation of the relevant bacterial culture to the mineral substrate subjected to leaching an important stage in the development of the complex technological approach is needed also for an efficient extraction of copper from secondary copper sulphides, regardless of their higher amenability to oxidation by ferric ions. The indirect leaching by means of ferric ions obtained as a result of the bacterial oxidation of ferrous ions in diluted sulphuric acid solutions de facto creates a system for a combined direct and indirect leaching. Such system can operate even at high temperatures if thermophilic chemolithotrophic bacteria are used for production of the ferric ions-bearing solutions. Regardless of the fact that ferric ions are able to oxidize the elemental sulphur which is formed during the oxidation of sulphide minerals and is deposited on their surface, the presence of sulphur-oxidizing bacteria in the leach system enhance the removal of these passivation films and accelerate the leach rate. On the other side, the presence of chemolithotrophic bacteria in systems for chemical leaching by sulphuric acid of concentrates containing copper and other heavy metals in their elemental and oxide forms is not essential. In some cases,

however, the iron-oxidizing bacteria can facilitate this process by generating ferric ions in situ as a result of the bacterial oxidation of the ferrous ions which are chemically dissolved from the concentrate.

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