A.K. KOIZHANOVA, D.R. MAGOMEDOV, E.A. TASTANOV, B.K. KENZHALIYEV, G.V. SEDELNIKOVA, A.N. BERKINBAYEVA

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INTENSIFICATION OF COPPER LEACHING FROM HEAPS USING BIOLOGICAL OXIDATION

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The article presents the results of experiments intended to leach copper from ore heaps of complex mineral composition biochemically. The processing of such heaps is complicated due to the presence of oxidized copper minerals among significant fragments of sulfide minerals and iron-calcium silicates. This factor does not allow to perform standard sulfuric acid leaching effectively without the use of additional oxidation catalysts, or to apply beneficiation methods for that kind of raw materials. Use of A. Ferrooxidans bacteria adapted to the composition of the copper dump, as a bio-catalytic agent, significantly accelerates the leaching process and increases the copper recovery degree into the productive solution.

Keywords: hydrometallurgy; copper; leaching; biochemistry; ferrooxidans bacteria.

INTRODUCTION

The characteristic feature of most copper deposits is decrease in reserves of rich raw materials, as well as the accumulation of significant volumes of non-commercial dumps with a low copper content of 0,1 – 0,5 %. This content makes the process of pyrometallurgical smelting of such raw materials completely unprofitable. At present, the practice of flotation beneficiation of ores and low copper content dumps mainly in the sulfide form has become widespread, and the standard hydrometallurgical technology - SX-EW (solvent extraction and electrowinning) is used to process non-commercial copper raw materials, represented mainly by the oxidized form of copper-bearing minerals.

However, there are numerous deposits with a complex mineralogical composition in addition to non-commercial ores and dumps that have a pronounced sulfide or oxidized form of copper in minerals. In most cases, the complex composition of such deposits is characterized by the presence of copper in an oxidized mineralogical form with a sufficiently high content of various impurities of sulfide and iron-bearing minerals, such as pyrite, arsenopyrite, etc.

The absence of sulfide copper minerals excludes the possibility of flotation concentration. At the same time, the presence of raw materials of sulfides of other metals, in particular iron, in the mineral composition can cause difficulties in standard hydrometallurgical processing. Despite the fact that oxidized forms of copper easily pass into solution during sulfuric acid leaching, sulfides of ferrous iron and other elements present in the mineralogical composition of the ore (dump) will significantly increase the consumption of sulfuric acid in the process of hydrometallurgical processing. Besides, the presence of minerals containing various combinations of iron, calcium, carbonates and silicates (tremolite, clinochlore, calcite, etc.) can also have a negative effect on the leaching process with sulfuric acid.

Iron compounds, often found in copper dumps, also have a significant impact on the leaching process. Iron ions passing into the productive solution, in the maximum oxidation state of +3, contribute to the further oxidation of the minerals containing copper during the circulation of the productive solution after the extraction stage (leaching with raffinate).

At the same time, the excess of the ferric ions concentration up to more than 10 g/L, has a negative effect on the extraction process, because reduces the selectivity of the organic extractant by copper resulting in deterioration in the quality of the electrolyte and the cathode copper obtained during the electrolysis. The specificity of the copper leaching and liquid extraction technology is disclosed in detail in a number of research works [1-3]. The role of Thiobacillus Ferrooxidans bacteria in the leaching of sulfide ores of is widely known [4-5]. In the biotechnological process, metals are converted from water-insoluble sulfides to soluble sulfates. Thiobacillus Ferrooxidans thionic bacteria oxidize all metal sulfides. They get the carbon required for the growth of bacteria from carbon dioxide. These bacteria develop in

A.K. Koizhanova (a.koizhanova@satbayev.university) Satbayev University, JSC “Institute of Metallurgy and Ore Beneficiation”, Almaty, Republic of Kazakhstan
D.R. Magomedov (davidmag16@mail.ru), E.A. Tastanov B.K. Kenzhaliyev, A.N. Berkinbayeva
Satbayev University, JSC “Institute of Metallurgy and Ore Beneficiation”, Almaty, Republic of Kazakhstan.
G.V. Sedelnikova (gsedelnikova@mail.ru)
JSC «Rosgeologia» Moscow, Russian Federation

an acidic environment (pH in the range of 1,0 – 4,8) at temperatures between 3 and 40 °C.

THE ROLE OF IRON COMPOUNDS IN COPPER LEACHING

In biotechnological leaching of metals, ore material or industrial waste containing metal sulfides is irrigated with sulfuric acid solutions, iron salts, and revivable thionic, iron-oxidizing bacteria are loaded. The usual oxidation of sulfide minerals most commonly found in copper dumps, for example, pyrite and chalcopyrite, can be described with the following reactions:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (1)$$

$$CuFeS_2 + 4O_2 \rightarrow CuSO_4 + FeSO_4 \quad (2)$$

However, the presence of iron (II) and other metals with a lower activity than copper in the solution can contribute to its precipitation if they are not in the maximum oxidation state, for example, this reaction:

$$Cu^{2+} + 2Fe^{2+} \rightarrow Cu^0\downarrow + 2Fe^{3+} \quad (3)$$

Oxidation processes in the sulfuric acid medium with atmospheric oxygen, will enable to transfer iron compounds from the oxidation state +2 to +3 according to the reaction:

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2H_2O + 2Fe_2(SO_4)_3 \quad (4)$$

The catalyzing factor in a sulfuric acid medium in the process promotes the acceleration of the transition of iron into the oxidized form +3 as illustrated by the example of the reactions:

$$2FeS_2 + 14H_2SO_4 \rightarrow \rightarrow 14H_2O + Fe_2(SO_4)_3 + 15SO_2 \quad (5)$$

$$2CuFeS_2 + 18H_2SO_4 \rightarrow \rightarrow 18H_2O + Fe_2(SO_4)_3 + 17SO_2 + 2CuSO_4 \quad (6)$$

The iron (III) compounds produced are capable of acting as an oxidizing agent. Iron ions passing into the product solution, in the maximum oxidation state 3+, contribute to the further oxidation of acid-absorbing minerals containing native copper during the circulation of the product solution after the extraction stage (leaching with raffinate).

The use of iron (III) sulfate as an oxidizing catalyst is known in practice. This compound in the leaching process can contribute to the dissolution of copper sulfide minerals by reactions:

$$CuFeS_2 + 2Fe(SO_4)_3 + 2H_2O + 3O_2 \rightarrow \rightarrow CuSO_4 + 2H_2SO_4 + 5FeSO_4 \quad (7)$$

$$2CuS + 2Fe(SO_4)_3 + 2H_2O + O_2 \rightarrow \rightarrow 2CuSO_4 + 2H_2SO_4 + 4FeSO_4 \quad (8)$$

At the same time, a widespread problem of hydrometallurgical industries which mine copper with high iron content is the accumulation of excess concentrations of iron ions in the productive solution. The excess of the concentration of ferric ions up to more than 10 g/l, has a negative effect on the extraction process, because it reduces the organic extractant selectivity for copper resulting in a deterioration in the electrolyte quality and the cathode copper quality obtained during the electrolysis. It is inexpedient to consider the addition of iron (III) sulfate as an oxidizing reagent in such cases. The cultivation of iron-oxidizing microorganisms, in this case, will enable to obtain the optimal concentration of iron 3+ ions from its initial content in the ore material.

STUDIES AND ANALYSIS

Adaptation and bacterial culture expansion on copper-containing mineral raw materials from the dump. The adaptation and growth of A. Ferrooxidans bacterial culture is usually accompanied by certain changes in the parameters of the solution [6-9], in particular, an active decrease in the concentration of Fe^{2+} and an increase in Fe^{3+} ions has been observed there. Copper compounds are often toxic to the standard A. Ferrooxidans strain that requires additional microbiological selection with the cultivation of an adapted culture. A. Ferrooxidans strains, adapted to the conditions of copper raw materials, enable bioleaching with an emphasis on copper sulfides. There is a known Acidithiobacillus Ferrooxidans-1333 strain sample bred in the Korean Center for Culture Collection [10] that showed high results of oxidation of Fe^{2+} in the chalcopyrite composition, due to the high immobilization of bacteria to the specificity of this mineral.

In the process of studying the copper-containing raw materials microflora, a dump sample from one of the deposits of Central Kazakhstan was taken as an object of research. The most revivable strains were selected on the sulfuric acid pulp of copper dump samples, with a total iron concentration of 10,8 g/L (Figure 1).

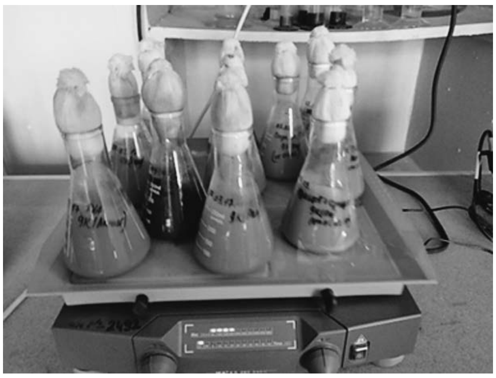

Figure 1 Selection of A. Ferrooxidans strains in the copper dump sulfuric acid pulp

As a result, the 3 most active A. Ferrooxidans strains were selected, adapted to the specifics of copper raw materials. The variant without use of bacterial culture with natural oxidation of the pulp with atmospheric oxygen was used for comparison. The content of the initial Fe^{3+} ions in the pulp samples was 0,3 g/L Fe^{2+} – 10,5 g/L. The pulp samples were monitored for an increase in Fe^{3+} ions for 10 days, (Figure 2). The use of strain 1 promoted the conversion of iron to the Fe^{3+} up to 6,1 g/L and use of strain 2 made it up to 6,6 g/L. The maximum increase in Fe^{3+} ions up to 7,8 g/L was noted when using strain 3. Natural oxidative processes, in the presence of atmospheric oxygen showed the lowest result of iron oxidation to the +3 rate in 10 days, so the analysis discovered only 2,7 g/L Fe^{3+} ions.

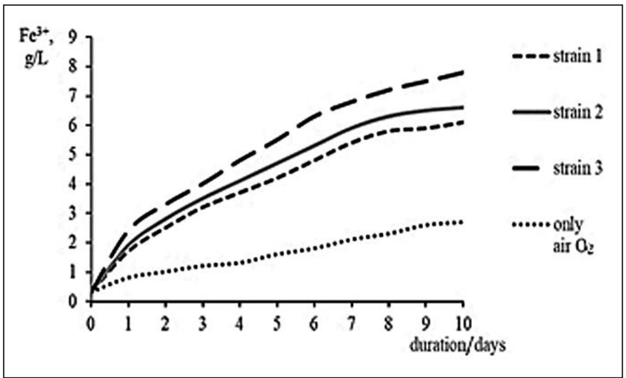

Figure 2 Dynamics of the increase in Fe^{3+} concentration during oxidation of copper-containing pulp.

EXPERIMENTAL PART

Previously studied samples from five dump points were taken for agitation leaching experiments. In order to select the optimal concentration, agitation leaching was performed with sulfuric acid solution with three concentration variants: 1,5, 2,0 and 2,5 %, with a S:L = 1:4 ratio during 6 hours. After the first stage of leaching, the solution was analyzed for copper content, the solid residue (cake) was subjected to the second stage of leaching. Based on the obtained copper concentrations in the solutions of the first and second leaching stages, the recovery was calculated for each stage. Preliminary data showed that 2,5 % is the most optimal concentration of sulfuric acid.

When the optimal 2,5 % concentration of sulfuric acid was selected, copper leaching experiments for the studied samples, using additional oxidizing reagents were performed. Iron (III) sulfate is most often treated as an oxidizing compound for the hydrometallurgical production of copper. Oxidized iron (III) compounds can be formed in the process of sulfuric acid leaching. However, in cases with sufficiently low iron content in the original ore raw materials, iron (III) sulfate is added to the leaching process as a catalyst for oxidative processes that enhance the dissolution of copper-bearing minerals.

At the same time, an excess of iron compounds in the productive solution is extremely undesirable, because it negatively affects the selectivity of the organic phase at the extraction stage. The use of common oxidizing agents based on chlorine and manganese compounds for liquid-extraction technology intended to process copper-containing raw materials is also impossible due to the deterioration and rapid wear of the organic phase by these components at the extraction stage. The use of sodium peroxide as oxidizing agent widespread in the hydrometallurgical processing of gold-bearing raw materials, in the case of heap leaching of copper dumps is unprofitable and is not very acceptable for sulfuric acid solutions.

Thus, iron (III) sulfate was chosen as a chemical catalyst for comparative experiments. The *A. Ferrooxidans* bacterial culture of strain 3, previously adapted to the composition of copper-containing raw materials, was used for experiments involving bio-oxidation. Preliminary bio-oxidation followed by leaching by the agitation method was performed with the weighed portions of the samples soaked in a bacterial solution of *A. Ferrooxidans* at a ratio of S:L = 1:1. Further leaching of the oxidized samples was performed with the sulfuric acid solution of 2,5 % concentration, with a ratio of S:L = 1:4.

For two stages of leaching, the recovery rate reaches 75,09 % on the sample from point 3 of the northern side of the dump, it reaches 67,59 % from the sample 1, and 73,97 % on the sample 5. Samples 3 and 4 in these experiments showed less significant results, 26,58 and 36,24 %, respectively. At the same time, a further increase in the concentration of sulfuric acid is impractical due to the formation of side impurities in the leaching process, as well as a decrease in the dynamics of increase in the rate of copper extraction into solution.

The results of the pre-oxidation leach experiments presented in Table 1 show marked increase in copper recovery over conventional two-stage sulfuric acid leaching. Thus, the use of preliminary bacterial oxidation on sample 1 makes it possible to extract 70,44 % of copper within 6 hours of leaching, while without oxidation in the first six-hour stage, this indicator is only 56,7 %, and in 12 hours – 67,6 %. A slight increase of 2 % recovery was also noted for sample 2 – in this case, it is also important to note a decrease in the leaching duration compared to the option without preliminary oxidation.

According to the experimental data of sample 2, it can be concluded that a longer acidification of the ore material in this area is required. The marked increase in recovery and halving of leaching duration, when using bio-oxidation, was noted at other sampling points. Thus, the extraction of copper from sample 3 increased from 75,09 to 88,65 %; samples 4 – from 36,2 to 45,18 %; sample 5 – from 73,97 to 87,3 %.

Table 1 **Results of oxidative leaching experiments**

Sample	Extraction / %		
	Only H_2SO_4 (12 hours)	$Fe_2(SO_4)_3$ + H_2SO_4 (6 hours)	A.Ferrooxidans + H_2SO_4 (6 hours)
1	67,6	63,91	70,44
2	26,59	18,71	28,58
3	75,09	83,5	88,65
4	36,24	35,46	45,18
5	73,97	85,71	87,3

The use of the chemical oxidation with iron (III) sulfate method, showed less efficiency compared to bio-oxidation but at the same time it contributed to the increase in the recovery rate of relatively simple sulfuric acid leaching.

CONCLUSION

During agitation leaching experiments, noticeable differences were found in the dynamics and efficiency of metal extraction into solution. Experiments with preliminary acidification of copper samples were performed using the chemical version of the oxidizing agent - iron (III) sulfate and with the version of biological oxidation with the A. Ferrooxidans bacterial culture adapted strain 3.

Subsequent leaching of oxidized samples showed a fairly high efficiency, enabled to intensify the copper extraction process into a product solution. The use of a chemical oxidizer - iron (III) sulfate, on a number of samples, allows to reach and sometimes even exceed within one six-hour stage the extraction rates of simple leaching obtained after two stages of 12 hours of leaching. However, the highest leaching efficiency, up to 88,65 %, was observed in experiments with preliminary bio-oxidation of samples with A. Ferrooxidans culture. Thus, the use of a catalyzing A. Ferrooxidans bacterial culture accelerates oxidative processes by many times and increases the degree of copper extraction by an average of 10 %.

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