BIOTREATMENT OF TAILINGS FOR METAL RECOVERY

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ABSTRACT

In recent years, a widespreading interest towards biohydrometalurgy has been observed.

The importance of this technique for the biotreatment of metals results from its ability to take best advantage of mineral resources which otherwise could not be adequately recovered, mainly due to economic reasons (of conventional processing) and to the growing concern with environmental protection.

Bioleaching, in particular, is being regarded as one of the approaches to the solution of many such problems. Allowing a rational and comprehensive use of low grade and waste ores and decreasing the pollution of the environment to a great extent, it creates a real possibility for economic recovery of metals with a corresponding purification of industrial wastes from heavy metals. The highly acidic efluents may be partly recycled or easily neutralized. Other biotechnological ways of dealing with these efluents are also being developed.

This is the reason why scientific research on this field has blossomed on the last decade, recently culminating on the pilot and industrial implementation of bioleaching processes in several countries.

It is a known fact that Portugal possesses large mineral resources what combined with the growing demand for the development of less energetic techniques to process mineral raw materials justifies increasing scientific and technological research on this area.

INTRODUCTION

The solid and liquid effluents from mining activities present normally a major environmental problem. Among the most common are the acidic waters and metal contamination which are normally associated together causing water and soil contamination and presenting heavy toxicity effects on local bioresources, affecting the local ecosystems.

Due to these features it is not surprising to assume that biotechnological solutions may be considered to help in solving some of these problems if not all. Therefore many attempts have been done to research which biomethodologies could be most efficiently in dealing with these problems: bioleaching, biosorption and bioremediation (wetland technology) have been considerated as possible alternatives their applicability depending on the actual nuances of the concrete problem.

Although most of these technologies are on an active state of pre-competitive research, some of them are already offered at either pilot either commercial scale.

With the actual accelerated research efforts it is not too dreamfull to expect for better and improved biotechnologies will reach the market on the immediated future.

In this work we will be referring the application of new thermophilic microbial cultures to the treatment of the tailings from the flotation process in operation at Neves Corvo mining site. These tailings are mainly metal sulphides, pyrite and chalcopyrite with an unusual high copper concentration.

Our objective was to quantitativly solubilize the copper from these material in a contained process. Ways of dealing with the final effluents will be also postulated in the end of this paper.

THE ROLE OF MICROORGANISMS IN METAL LEACHING

Bacterial activity can be described by the indirect and direct leaching of metal sulphides. The microorganisms action may be indirect, whereby the microbes generate ferric iron, which oxidizes the mineral. In the direct leaching process the microbes contact and adhere to the mineral surface, oxidizing the mineral without the use of the ferric iron oxidant.

The fundamental reaction for the indirect leaching is the microbial oxidation of the ferrous iron (eq.1) in acid conditions for the purpose of energy generation.

$$4FeSO_4 + O_2 + 2H_2SO_4 \Longrightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad \text{(eq.1)}$$

The ferric sulphate which is generated serves to oxidize minerals such as chalcopyrite (eq.2).

$$CuFeS_2 + 2Fe_2(SO_4)_3 \Longrightarrow CuSO_4 + 5FeSO_4 + 2S \qquad \text{(eq.2)}$$

The resulting soluble metal sulphates may be recovered by solvent extraction, iron exchange or other methods.

The iron, now reduced to ferrous state, is reoxidized by the microorganisms according to eq.1.

The sulphur, which is often present as an end product of the metal solubilization may also be oxidized to sulphuric acid by the bacteria (eq.3). The production of sulphuric acid maintains pH at levels favourable to the bacteria and is also a leaching agent of the metal sulphides minerals.

$$2S + 2H_2O + 3O_2 \Longrightarrow 2H_2SO_4 \qquad \text{(eq.3)}$$

The direct mechanism of metal leaching takes place without ferrous iron as an oxidant. Pyrite may be oxidized directly by the microbes (eq.4).

$$FeS_2 + 3\tfrac{1}{2}O_2 + H_2O \Longrightarrow FeSO_4 + H_2SO_4 \qquad \text{(eq.4)}$$

These results in the solubilization of iron. The iron is subsequently oxidized according to eq.1 and the ferric iron than precipitates in the indirect leaching process.

Copper containing minerals, such as chalcopyrite, can also be leached by the direct process (eq.5).

$$2CuFeS_2 + 8\tfrac{1}{2}O_2 + H_2SO_4 \Longrightarrow 2CuSO_4 + Fe_2(SO_4)_3 + H_2O \quad \text{(eq.5)}$$

On the whole, microbial leaching is based on interlocking chemical and biochemical oxidation in which particular importance must be attributed to the iron cycle between ferrous and ferric ions.

MATERIALS AND METHODS

Mineral samples

Neves Corvo tailings of flotation were used as bacterial growth substrates and tested for biological metal extraction.

Chemical analysis of this mineral samples were undertaken. The main constituents for Neves Corvo tailings were sulphur (35.4%), iron (33.2%), silica (16.0%) and copper (1.2%).Other elements scarcer than 1% are presented in fig.1.

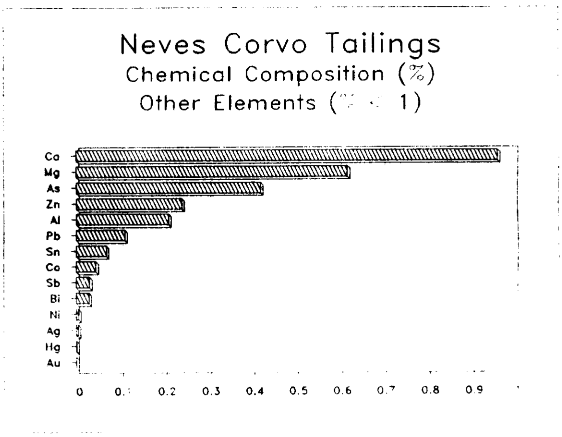

fig.1 - Neves Corvo tailings, elements < 1%

The mineralogical distribution of Neves Corvo tailings show that it contained mainly pyrite and quartz with some amount of chalcopyrite sphalerite, tetrahedrite, arsenopyrite, galena, pyrrhotite and carbonates.

The granulometric distribution is present in fig.2. Average particle size is around 13.5 μm.

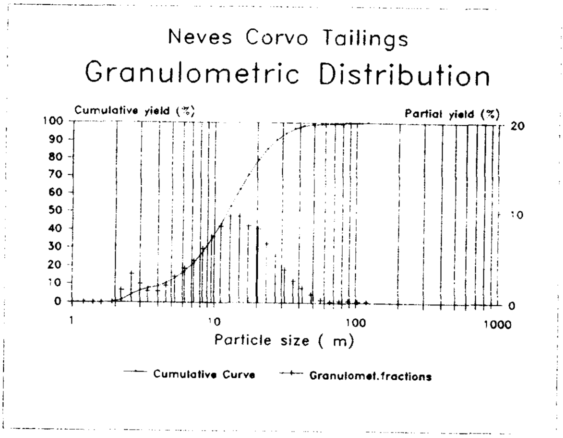

fig.2 - Granulometric distribution of Neves Corvo tailings

Microorganisms

A culture of thermophilic mineral oxidizing microorganisms was used in this studies. It was isolated by Duarte and Pereira (unpublished) from diverse spots in hot springs of S. Miguel (Açores).

Media

The bacterial tests were carried out using the mineral salts medium of Marsh and Norris (1983). This was designated medium S and contained (g/l): $(NH_4)_2SO_4$, 0.2;

$MgSO_4.7H_2O$, 0.4; K_2HPO_4, 0.1; KCL, 0.1. For convenience the medium was supplemented with o.2 g/l yeast extract.

Solution Analysis

Copper and total iron in solution were analysed by atomic absorption spectrophotometry. Ferrous iron was assayed by titration with ceric sulphate using phenanthroline-ferrous complex solution as end-pint indicator.

Approximate bacterial cell numbers were determined by direct cell count using a bacterial counting chamber.

Solution pH values were routinely measured.

Microbial Growth and Reaction System

The experimental studies here described were conducted in stirred tank reactors. The use of reactors offers the possibility of achieving a close control on the process and an efficient aeration.

The reactor consisted of a 500 ml baffled vessel fitted with a water jacket through which heated water circulated. In order to minimize evaporation each reactor was fitted with a condenser. The agitation was provided either by magnetic or mechanical stirring. The reactor was supplied with air at 1.5 vvm.

Initial choice of the optimal physiological parameters was done on an air lift type reactor with 400 ml working volume.

PHYSIOLOGICAL STUDIES WITH THERMIPHILIC MICROBIAL CULTURES

The work includes the study of some process parameters - temperature, initial pH, aeration rate, concentration of carbon dioxide, organic nutrient and solids in solution - which affect the bacterial activity (fig.3).

It was followed by a study of the performance of the reactor operating system.

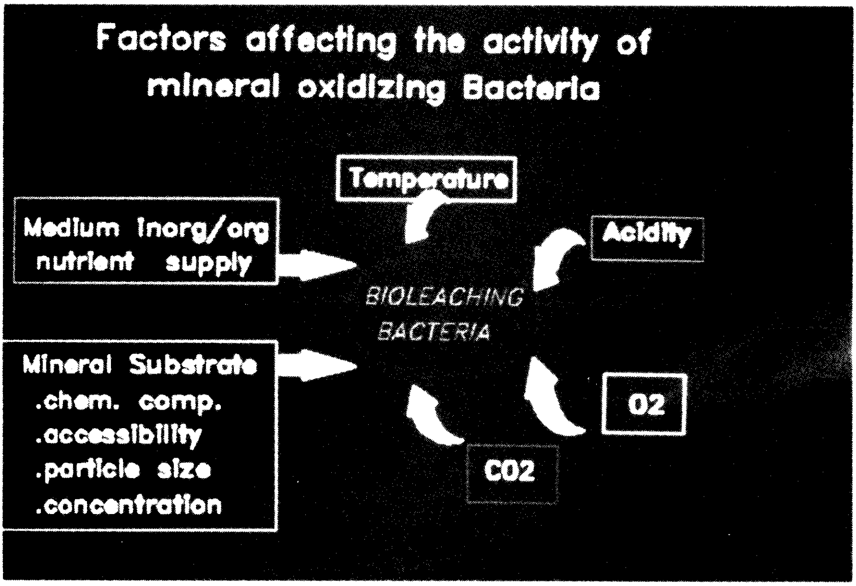

fig.3 - Factors affecting bacterial activity

Semicontinuous operation was also carried out in order to evaluate the effect of reduction in the residence time on copper and extraction rate and yield.

Optimal Physiological Parameters

All these experimental studies took place in air lift reactor system with the following set up conditions: temperature 70°C, yeast extract 0.2 g/l, initial pH 2.0, air flux 1.5 vvm and supplied with 1% (w/v) of the mineral tailings. These functioned as a source of iron and reduced sulphur and for a preliminary evaluation of copper leachability.

It was observed that the values of copper on the initial solution were already high. This unexpected behaviour might be attributed to an oxidation of the ore occurring after flotation and during sample preparation and storage.

Experience has shown that, depending on initial copper solubilization, different rates of extraction can be achieved. The problem of incomplete extraction of copper from chalcopyrite is explained by most authors with the formation, as the dissolution proceeds, of a solid reaction product located at chalcopyrite crystal surfaces. This material probably acts has a diffusion barrier, hindering the contact of the leaching solution with chalcopyrite crystal surfaces and thus retarding the dissolution process.

From the experiments a set of optimal values was found (table 1).

Table 1 - Optimal physiological parameters for bacterial activity and growth

parameter	covered range	best value	intial rate Cu?Cu^{2+} (mg/l.h)	initial rate Fe^{2+}?Fe^{3+} (mg/l.h)	final copper yield (%)
temperature (°C)	60-80	70	1.9	52.4	69.0
yeast extract (g/l)	0-0.3	0.2	1.3	45.9	76.0
initial pH	1.0-2.5	2.0	1.2	50.0	68.0
air flux (vvm)	1.0-2.0	1.5-2.0	1.2	50.9	75.0
carbon dioxide (%)	0-2	N.S.*	1.3	41.5	69.0

* no significative difference among the assays

Temperature

Temperature was the first parameter under study. It is a parameter that directly affects the microorganisms behaviour, and it was observed that small variations (± 5°C) in the operating temperature can lead to significant affect copper extraction rates. It can also be noted that at 80°C there is no bacterial activity. The extraction rate for copper obtained at 70°C was 1.9 mg/l.h.

Yeast extract supplement

Although growing autotrophically, the organic supplement, yeast extract, was found to be essential for optimal growth of these thermophiles. This was confirmed by the experiment set up with 0 g/l of yeast extract where no significant bacterial activity was observed. For all the other assayed values copper extraction rate was similar although the best value was 1.25 mg/l.h for 0.2 g/l of yeast extract in the culture media.

pH

The pH is an important parameter as it influences, not only bacterial growth but it also controls some important physic-chemical interactions in the system. In the experiment performed with different initial pH values the solubilization of copper was similar for all the assays except in what concerns to the lowest initial value of pH. In this particular case there was no important leaching activity.

Aeration

Once the temperature and the pH effects were studied it was necessary to evaluate the influence of aeration on the process, mainly to assess its effect as a potential limiting factor of bacterial activity. So, the air flux was varied and it was observed that the experiments performed with 2.0 vvm and 1.5 vvm had the best solubilization rates and achieve the highest copper extraction. All the other values which were assayed have lower rates for solubilized copper.

There was no significant difference between the oxidation rate when the medium was supplemented with yeast extract or the air enriched with carbon dioxide.

REACTOR STUDIES

One of the most important technological factors for evaluating the applicability of the bioleaching process concerns the maximum pulp density allowed to be used in these processes.

Pulp density may affect not only the hydrodynamics regime and reactor design but it also affects the microorganism behaviour.

It must be noticed that the economy of the process will be dependent on the volumetric rates which will be possible to achieve on the reactors.

On the table 2 it is shown the effect of the solid concentration on copper solubilization rates for the stirred reactor system.

Table 2 - Solid concentration effect

pulp density (% w/v)	maximum Cu concentration (mg/l)
5	627
10	989
15	1482

Stirred tank reactor allowed the used of high solid concentrations with good growth rates showing that there was no inhibition for these thermophiles until 15% (w/v) pulp density.

The maximum copper concentration in solution achieved was 1.5 g/l corresponding to the stirred reactor system operating with 15% (w/v) solid concentration after 164h of operation.

At the higher pulp densities high agitation rates are necessary for reaching a good homogenization what will originate high shear forces on the solids and the microorganism and this may well affect bacterial activity. Further studies are needed to evaluate the maximum solid concentration on the reactor without affecting the microbial activity.

SEMI CONTINUOUS OPERATION

After achieving the best values for the variables which directly affect the bioleaching process in a batch system it was desirable to have a semi continuous leaching experiment in order to evaluate the extraction rate and yields on a semi continuous basis.

Semi continuous operation in stirred tank reactor was performed with an initial pulp density of 10% (w/v). Each day 50 ml were removed from the 500 ml reaction medium and replaced by 50 ml of fresh medium. At the same time it was added 5 g of the solid substrate. Copper solubilization, pH values and bacterial cell numbers were determined daily.

Semi continuous operation system showed an increased in copper solubilization rate of approximately 7 mg/lh during all the test period.

On table 3 are shown the results of two experiments at two different residence times.

Table 3 - Influence of residence time on leaching of Neves Corvo tailing

residence time (days)	copper in solution (mg/l)	copper extracted (%)
8	1574	73
14	1712	83

These preliminary results show that a significant extraction of copper may occur from the tailings in relatively short residence times. Optimized solutions to this problem will require that an increased of the amount of solids extracted per unit volume of the reactor has to be achieved and that an economic design and operation of the reactor is found.

COMPARISON OF THE ORE BEFORE AND AFTER LEACHING

Representative samples of Neves Corvo flotation tailings were analysed in order to determined the mineralogical identification and distribution.

The mineral sample is mainly constituted by pyrite with quartz coming second in abundance. Chalcopyrite seems to occur more frequently in particles superior to 20μm grain size, although associated with pyrite (fig.4). This is the dominant type of association. Other sulphides are less frequent than chalcopyrite such as sphalerite, tetrahedrite, arsenopyrite, galena and pyrrhotite.

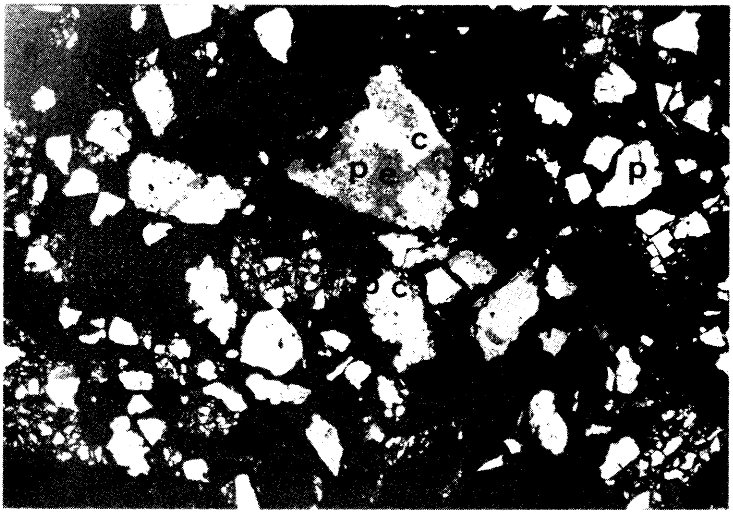

fig.4 - Mineral samples before leaching
(p-pyrite; c-chalcopyrite; q-quartz)

After five days of bacterial leaching in an air lift reactor the leached ore was subjected to a mineral examination (report performed by Dr.A.Belém LNETI/DTM).

Optical microscopic analysis of the ore surface showed that it mainly was quartz and jarosite. This was confirmed by X-ray diffraction technique. The electronic microscopic scanning technique was used to determine the presence of potassium type jarosite in the bioleached sample.

Sulphides, mainly pyrite and chalcopyrite, constitute a small percentage of the sample, being distributed in the matrix of jarosite and quartz. The particle size of the sulphides is inferior to 10μm.

Mineralogical examination showed that the decline in leaching rate during bacterial leaching can be attributed to blockage of the rock surface by precipitates of potassium jarosite type.

POTENTIAL FOR AN INTEGRATED COMPLETE BIOTREATMENT OF NEVES CORVO TAILINGS

This work points for the application of thermophilic bioleaching of the Neves Corvo tailings in order to quickly recover copper and most of the other important minerals present in this material.

After this treatment we are left with a much more easy to dispose solid residue and a liquid effluent witch contains most of the metals initially present and which could be a cause of environmental pollution.

Much of the iron has already been left on the solid residue as an oxide. The one present in the liquid can be cemented either after ore before copper and other metals recovery (e.g. solvent extraction, electrowinning, ion exchange) the final acidic effluent can be partly recycled due to the iron and bacterial nutrients present.

The net acidic drainage may be now in conditions that can satisfy the maximum allowed concentrations of metals (iron and manganese among others). However there remain the problem of dealing with the low pH of the effluent.

Recently biological solutions to this problem call for the action of the sulphate reducing bacterial witch in the present of sulphate rich medium can oxidize organic matter in an anaerobic process:

$$2CH_2O + SO_4^{2-} \Longrightarrow H_2S + 2HCO_3^- \qquad \text{(eq.6)}$$

This reaction will increase the pH and alkalinity of the medium therefore counteracting the acid generation of the bioleaching operation. The H_2S generated and the carbonate ions will also have and important action to precipitate many metals still present.

Bacterial sulphate reduction is very common in estuarine and marine sediments where all the necessary ingredients are abundant. Therefore their use either in on purpose built reactors either natural or constructed wetlands offer a great promise for closing the biological cycle of the metal and acid removal of effluent waters from mining operation and from the drainage of abandoned mines.

The integration of bioleaching with this biotreatment must reduce the costs of the whole treatment process alone. It is find out that the costs of constructing wetlands are recovery within one year through savings in chemicals. It is possible that the exploitation of sulphate reducing bacteria (with bioleaching where appropriate) for the biological treatment of mine wastewater may reduce those costs even further.

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