

Recovery of zinc during the pre-treatment of a refractory gold-bearing ore

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ABSTRACT

Mesophilic bacteria were enriched from samples collected from acid mine drainages in La Carolina (San Luis, Argentina). Two enrichments, E1 and E2, showed suitable rates of iron or sulphur oxidation, respectively. Both enrichment cultures were characterized by FISH and they were mainly composed by *Leptospirillum ferrooxidans* and *Acidithiobacillus ferrooxidans*. Studies with both, mixed and individual enrichment cultures, showed biooxidation (measured as iron solubilisation) of a refractory gold-bearing pyrite ore from Hualilán (San Juan, Argentina). Pyrite and sphalerite were the main mineral species in the ore with 7 % w/w and 8 % w/w of iron and zinc and approximately 25 ppm of gold. Leaching experiments (2 % w/v ore, 1.8 initial pH, 180 rpm and 30°C) were carried out with the addition of different alternative energy sources (6.67 g/L sulphur powder, 1 g/L iron(II), 0.02% w/v yeast extract). Redox potential, pH, iron(II) concentration and total Fe and Zn were measured regularly. A 100% of iron leaching (after 28 days in the best experimental condition) was observed in some of the cultures. In other systems high zinc release was obtained (100% of dissolution after 28 days in the best experimental condition). Our results strongly suggest that under the correct operating conditions, biooxidation pre-treatment can be used to recover zinc as a subproduct of gold extraction from refractory ore.

Introduction

Bioleaching is a bioprocess where products of microbial metabolism are applied to the recovery of metals like copper, cobalt, zinc and nickel, among others. Similarly, biooxidation is a pre-treatment that can be used to improve the recovery of gold from refractory sulphides ores. For many years, these processes have been successfully used in commercial scale applications. They present many advantages, like operational simplicity, low capital costs and they are also considered eco-friendly technologies to improve metal extraction [1-2].

Sphalerite is one of the most important sources of Zn in the world. According to mechanisms involved in metal (bio)leaching, sphalerite can be degraded by acidophilic autotrophic bacteria through a polysulfide pathway by the action of protons or ferric ion [3]. For many years *Acidithiobacillus ferrooxidans* was considered the most important microorganism in the bioleaching of sulphide ores operating at temperatures lower than 40 °C. Later, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans* have been found as dominant microbial populations in many bioleaching commercial applications [4].

The aim of this work was to study the possibility of recovering zinc as a second product during biooxidation of a refractory gold-bearing ore. Enrichment cultures mainly composed by *At. ferrooxidans* or *L. ferrooxidans* and a mixed cultures of them, were used as inocula in the biooxidation experiments. Additions of different alternative energy sources were tested in order to find suitable conditions for metals recovering.

Methodology

Microorganisms. Natural samples obtained from an acid mine drainage located in La Carolina (San Luis, Argentina) were enriched in media with sulphur and/or iron(II) as energy sources. Enrichments E1 and E2 showed the best performance of iron and sulphur oxidation respectively, and were selected for biooxidation experiments.

Molecular techniques. Both enrichments were characterized by FISH (fluorescent in situ hybridisation). Aliquots of 1 ml of active cultures E1 and E2 were used for FISH assays. Hybridisations were done following Amman's protocol [5], with Cy3 labeled probes TF539 and LF665 specific for *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, respectively.

Mineral. A refractory gold-bearing pyrite ore from Hualilán (San Juan, Argentina) was used in the experiments. Pyrite and sphalerite were the main sulphides in this sample. Gold was mainly associated to pyrite. The chemical composition of the ore was Fe 7 %, Zn 8%, S 9.1%, Mn 1.35%, Au 25.67 ppm and Ag 190.2 ppm. The mineral was finely grounded until 74 microns.

Bioleaching/Biooxidation. The experiments were carried out in Erlenmeyer flasks containing 150 ml of 0K medium (initial pH 1.8) with or without the addition of 1 g/L of iron(II) (medium 1K), sulphur powder (6.67%) (S⁰) and/or 0.02% w/v yeast extract (YE). A 2% w/v pulp density for the mineral was used in all systems.

Inocula were prepared from enrichment cultures E1 and E2 cultivated in 9K and 0K medium, respectively. Cells were harvested by filtering the cultures through 0.22 µm pore sizes membranes and suspended in basal salts medium. These suspensions (with bacterial population of approximately 5×10^8 cell/ml) were used to inoculate the flasks at 4.6% v/v. Distilled water was added periodically to the flasks to compensate evaporation losses. Experiments were carried out by duplicate. Sterile controls were also done, replacing the inoculum volume with fresh medium. During the bioleaching experiences 3 ml of sample were routinely drawn from flasks for analytical determinations.

Measurements and analysis. Determination of pH and Eh were done using specific electrodes, properly calibrated. Iron(II) concentration was determined through the orto-phenantroline colorimetric method. Dissolved zinc and total soluble iron were measured by atomic absorption spectrophotometry.

Results

According to hybridization with specific probes, *L. ferrooxidans* seemed to be the only species present in E1 enrichment cultures, while *At. ferrooxidans* seemed the predominant microorganism in E2 enrichment cultures.

Bioleaching/biooxidation experiments were carried out over a period of 43 days. In sterile systems pH rised to a value of 3.3, probably due to acid consumption in the neutralisation of carbonates and limonite contained in the ore. At the beginning of experiment, pH value in flasks inoculated with E1 showed a pH increase higher than in sterile flasks. The reasons for this pH rise may be similar to the one in the sterile controls, plus some acid consumption due to iron(II) oxidation catalysed by *L. ferrooxidans*. Cultures with YE addition showed a lower increase in pH value in comparison with the other cultures. After the initial increase, wards pH decreased probably due to ferric ion hydrolysis with the consequent precipitation of ferric compounds [6]. The lowest pH (1.2) was reached in flasks supplemented with sulphur powder and inoculated with E2 enrichment culture, supplemented or not with YE and/or iron(II). Similar final pH value was reached in flasks inoculated with E2 or E1+E2 when sulphur powder was the energy source while in the other cultures with the same inocula showed pH values close to 2.0 throughout the experience. This pH behaviour can be justified considering sulphur oxidation catalyzed by *At. ferrooxidans*, which is the main microorganism in E2 enrichment culture, or other possible sulphur-oxidiser present in the inoculum.

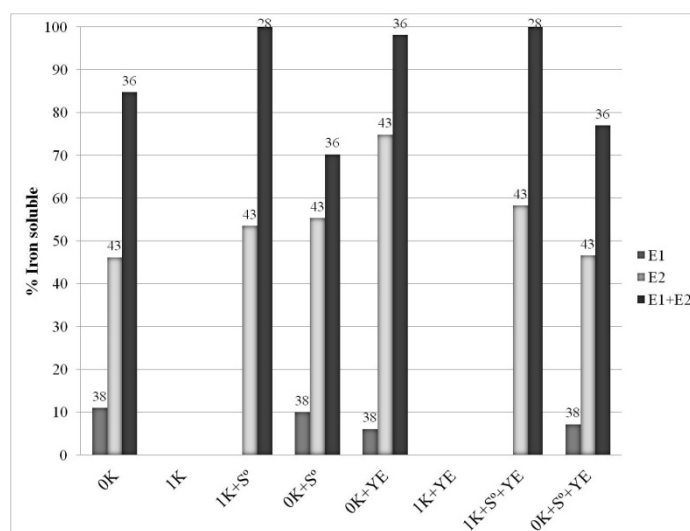


Figure 1. Percentages of soluble iron in the cultures. Numbers over bars indicate days necessary to achieve these percentages of solubilisation in each case.

In all cases, mixed culture (E1+E2) showed higher iron solubilisation than that observed in cultures inoculated only with E1 or E2. 100% of iron solubilisation was achieved by mixed cultures (E1+E2) in 1K+S° medium with or without yeast extract in 28 days. The addition of YE did not seem to have much effect on iron solubilization. E2 culture achieved better iron solubilisation than E1 culture. E2 showed the best performance in 0K+YE medium, reaching 74.9% of solubilisation in 43 days. The addition of sulphur powder was not significant, while the addition of YE only was relevant in 0K medium culture. However in 1K medium, the presence of sulphur powder and sulphur oxidizing bacteria (E2) seemed to be critical to maintain low pH and, consequently, keep iron in solution, as it can be seen in Figure 1. E1 cultures obtained iron solubilisations lower than 11%. Cultures grown in 1K medium (except those cultures with the addition of sulphur) showed high precipitation of some ferric compounds (probably jarosite, although it has not been confirmed yet) [7], and final soluble iron was lower than the initial iron in the medium (1 g/L). This is why the percentages of iron solubilised in those cultures were not included in Figure 1 (such values would be negative). The highest solubilisation obtained in sterile controls was 45% in 1K+YE medium in 31 days. Since iron solubilisation is closely related to gold release in biooxidation experiments (data not shown), total soluble iron was considered a reliable parameter to evaluate biooxidation efficiency (even when part of the iron solubilised can be later precipitated as other species).

Under most of the conditions assayed, zinc solubilisation was highest in mixed cultures. However, in the presence of sulphur and YE, E1 culture was more efficient (see Figure 2). Complete zinc solubilisation was reached in 1K medium for mixed culture after 28 days. Similar results were reached in 1K+S° and 0K media (98.7 and 95.5% of zinc solubilisation, respectively). E1 cultures solubilised 88-94% of zinc in 0K and 1K media with or without the addition of sulphur. The addition of YE showed negative effects on zinc solubilisation. E2 culture in 0K medium achieved 86.8% of zinc solubilisation after 35 days. The addition of sulphur powder and/or YE did not improve zinc solubilisation. In sterile controls zinc recovery was lower than 50% for all conditions assayed. When analysing iron and zinc solubilisations, mixed cultures showed better performance than single cultures. Besides, the addition of iron favoured zinc solubilisation but depressed the final amount of soluble iron in the cultures.

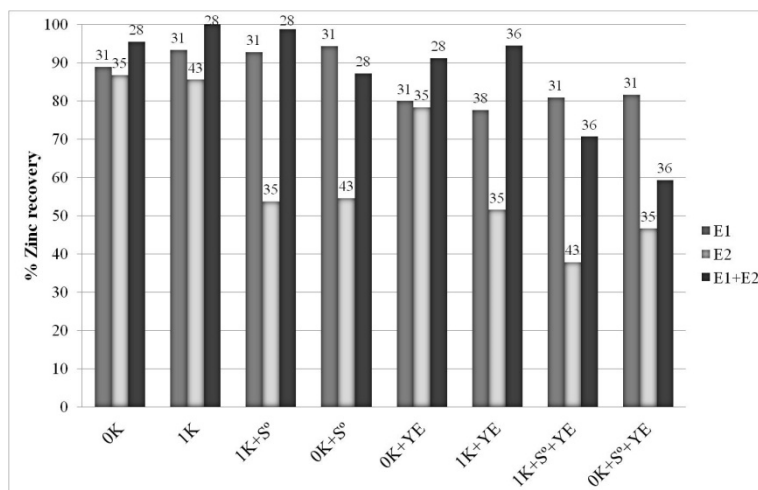


Figure 2. Percentages of zinc recovery from ore achieved by single and mixture cultures. Numbers on top of bars indicate the days necessary to reach the best performance in each case.

Conclusion

According to our results the best condition to recover zinc as subproduct without affecting iron solubilisation (and consequently gold recovery) was reached in mixed cultures of E1 and E2 in 1K+S° medium. Under this condition, 100% and 98% of iron and zinc solubilisation, respectively, were achieved in only 28 days.

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