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BIOLEACHING OF Zn-Pb-Ag SULPHIDIC CONCENTRATE

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ABSTRACT
Polymetallic or complex Zn-Pb-Ag sulphide concentrates can be treated by bioleaching combined with proper hydrometallurgical processes.
Indirect bioleaching is a biotechnology that presents important advantages when apply to bioprocessing of zinc and zinc polymetallic concentrates such as high metals recovery, fast kinetic of 4-5 hours to get full metals extraction, sulphur oxidation to elemental sulphur (avoiding sulphuric acid generation, while pyrite mineral remains untouched), and use of conventional reactors (aeration is not required) and normal process equipments.
Indirect bioleaching of Zn-Pb-Ag sulphide concentrates is based on applying ferric leaching of the polymetallic concentrates by means of bio-regenerated ferric sulphate solution.
Keywords: biotechnology, metal bearing sulfide minerals

1. INTRODUCTION
All mineral processing technologies have an effect on the environment. Therefore, the development of innovative, environmentally friendly technologies will be extremely important and minimising waste generation and using wastes to produce useful by-products maintaining economic viability is a goal for the process, and biotechnology is one of the most promising solutions to deal with those mining problems compared to pyrometallurgical routes.
Biological processes are carried out under mild conditions, usually without addition of toxic chemicals. The products of biological processes end up in aqueous solution (hydrometallurgy) which is more amenable to containment and treatment than gaseous wastes or slags, which are typical in pyrometallurgical processes.
Due to the variety and complexity of the mineral resources, the collective Zn-Pb-Ag sulfide concentrate has taken in consideration in order to identify the most promising ways of minerals bioprocessing. Indirect bioleaching technique is considered.

2. INDIRECT BIOLEACHING OF POLYMETALLIC CONCENTRATES
Indirect bioleaching of Zn-Pb-Ag sulphide concentrates is based on applying ferric leaching of the polymetallic concentrates by means of bio-regenerated ferric sulphate solution. After ferric sulphate leaching zinc is dissolved and recovered by the electrowinning. The leaching residue is treated under oxidant conditions in a brine circuit to recover lead and silver. Descriptive diagram of the process is presented in Figure 1.

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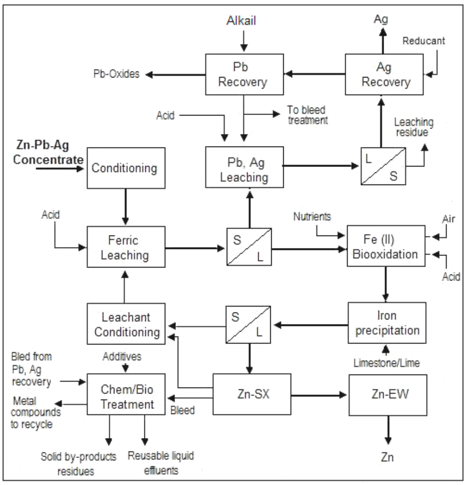

Figure 1. Indirect bioleaching of Zn-Pb-Ag sulphide concentrates

3. PROCESS DESCRIPTION

The indirect bioleaching processing route for Zn-Pb-Ag concentrates starts with a chemical leaching step where the zinc is extracted from the solid to the aqueous phase by means of the chemical oxidation process using ferric sulphate as main reaction. Major areas shown in the diagram are: Ferric leaching, Bio-oxidation, Iron precipitation, Iron redissolution, Zn Solvent extraction and electrowinning, Brine process (lead and silver recovery), Effluent treatment.

The process flowsheet for the indirect bioleaching of Zn-Pb-Ag concentrates is shown in next Figure 2. As a conceptual block diagram it shows the main steps and streams for the zinc and lead recovery [1].

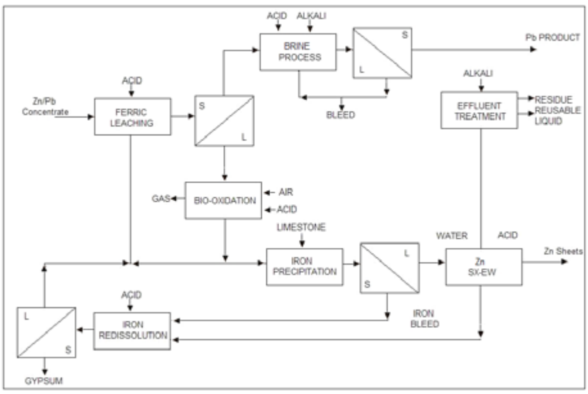

Figure 2. Indirect bioleaching block diagram

3.1. Ferric Leaching

According to flowsheet for the indirect bioleaching of Zn-Pb-Ag concentrate presented in Figure 2, the indirect bioleaching processing route for polymetallic bulk concentrates starts with a chemical leaching step. Zinc is extracted from the solid to the aqueous phase by means of the chemical oxidation process using ferric sulphate according to the following main reaction.

$$ZnS + Fe_2(SO_4)_3 = ZnSO_4 + 2\ FeSO_4 + S0$$

Lead sulphide is transformed in lead sulphate remaining in the solid phase due to the low solubility of this compound in sulphate media. Lead sulphide is transformed to lead sulphate according to chemical reaction:

$$PbS + Fe_2(SO_4)_3 = PbSO_4 + 2FeSO_4 + S0$$

Silver follows a similar pathway. Under conditions of high temperature, low acidity, and high ferric ion concentration, silver precipitated as insoluble silver jarosite (AgFe3(SO4)2(OH)6) [2]:

$$AgS\ (Ag_2SO_4) + Fe_2(SO_4)_3 = AgSO_4 + 2FeSO_4 + S0$$

The ferric leaching step is composed of stirred tank reactors arranged in cascade so that the pulp passes from one tank to the next by overflowing. The feed is made up of a high density pulp of the Zn-Pb-Ag concentrate and a part of the leaching residue. The feed flow is mixed at the leaching reactors at a ratio corresponding to 7-8 % solids with ferric solutions coming from the biooxidation and iron redissolution steps. Flow of ferric solution is set so as ratio of ferric ion to zinc and lead in the concentrate is in excess of 25 %. The temperature is set at 90°C. The pH is regulated at 1.25 by adding H2SO4.

3.2. Biooxidation and iron precipitation

The biooxidation step is composed of one stage in biooxidation pool arranged in parallel. Air is injected through a system of membrane disk diffusers installed in the bottom of the pools. The clarified ferrous solution from the previous stage enters the bioreactors at a temperature of 30ºC. The air flowrate to the bioreactors is 20 Nm3/hm2. Conversion efficiency of ferrous to ferric ion is high, Fe(II) concentration at the outlet is 0.5 g/l. Biooxidation step is presented as chemical reaction:

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow \text{T. ferrooxidans} \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

The bio-solution which is not recycled back to ferric leaching, is sent to a precipitation step. Iron precipitation step is performed in reactors arranged in cascade.
Iron precipitation step is presented as chemical reaction:

$$Fe_2(SO_4)_3 + 3CaCO_3 + 3H_2O = 2Fe(OH)_3 + 3CaSO_4 + 3CO_2$$

Iron is precipitated by means of limestone addition at pH 4. Addition of a small amount of H2O2 is needed to assure all iron is ferric.

3.3. Iron redissolution

The iron precipitation step is composed of reactors arranged in cascade. Iron is redissolved by means of sulphuric acid addition at pH 1. Part of the acid needed comes from the acid aqueous raffinate produced at solvent extraction. Iron redissolution is presented as chemical reaction:

$$2Fe(OH)_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6H_2O$$

Rest of acid needed to reach the pH setpoint is supplied as concentrated sulphuric acid.

3.4. Zinc Solvent Extraction

Solvent extraction Unit consists of the following stages: Extraction, Washing, Stripping, Depletion, Bleed neutralization and Organic regeneration, At solvent extraction, through a series of extraction/stripping stages, a zinc sulphate purified solution is obtained using Solvent Extraction proces:

Extraction:

$$2[RH]org + [Zn^{2+}]aq + 2[SO_4^{2-}]aq \rightarrow [R2Zn]org + 2[H^+]aq + 2[SO4^{2-}]aq$$

Stripping:

$[R2Zn]org + 2[H+]aq + 2[SO4^{2-}]aq \rightarrow 2[RH]org + [Zn^{2+}]aq + 2[SO4^{2-}]aq$

3.5. Zinc Electrowinning

This purified Zn loaded solution is sent to the electrowinning step to obtain Zn cathodes.

$Zn^{2+}aq + 2^{e-} \rightarrow ZnOs$

The zinc deposition on the cathodes is carried out with a current efficiency of 91 %. No significant side reactions (except from hydrogen evolution) are considered.

3.6. Effluent treatment

In order to produce a final effluent free of metals it is necessary to implement a bleed treatment stage. No design parameters and flowsheet is given for this area since it is considered as conventional technology.

3.7. Lead and silver recovery

The process route of lead recovery from the leaching residue follows a first step where it is leached in a hot brine solution and a second one, a precipitation step where lead in solution is recovered in form of carbonate concentrate. Chemical reactions involved in the leaching process of lead and silver are.

$PbSO_4 + 4NaCl = Na_2PbCl_4 + Na_2SO_4$

$AgFe_3(SO4)_2(OH)_6 + 4NaCl = NaFe_3(SO_4)_2(OH)_6 + Na_3AgCl_4$

Finally, the silver is recovered from solution using a proper reductant, e.g. lead powder, producing metallic cement that is purified to obtain silver bullion for the market. Lead is precipitated with an alkali to produce pure lead oxides or carbonate concentrate ready to be commercialized

4. CONCLUSIONS

To date, biohydrometallurgy has been industrially applied to recover copper and gold from ores and concentrates; while copper is recovered through heap bioleaching, gold is extracted using stirred bioreactors. Within BioMinE [3] project, an European consortium composed of industriesand top experts in biohydrometallurgy have developed an inovative indirect bioleaching application dealing with zinc concentrates and zinc polymetallic concentrates; hopefully, the achieved successful results will open the way for bioprocessing of a wide variety of zinc and lead polymetallic or complex minerals deposits that are abundant and can be found in Europe and worldwide.

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