



An alternative approach to recover lead, silver and gold from black gossan (polymetallic ore). Study of biological oxidation and lead recovery stages

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ABSTRACT

A novel procedure to recover lead, silver and gold from polymetallic sulphide ores, cleaner than the traditional hydrometallurgical route (hot brine leaching), is proposed. This process consists of a bio-oxidation stage, where sulphides are oxidised by the action of extremophiles, followed by an acid washing and a citrate leaching in which lead is recovered. The final solid obtained, mainly composed of quartz, is rich in silver and gold. This paper is focused on the biooxidation and the lead recovery of the black gossan, a polymetallic sulphide ore with valuable amounts of lead, silver and gold. Biooxidation performed with a mixed mesophilic culture (mainly *Acidithiobacillus ferrooxidans*) at 20% pulp density is able to dissolve the sulphide matrix, removing the gold refractory behaviour and producing jarosite, beaverite, gypsum and anglesite. A previous sulphuric acid washing of biooxidation residue greatly improves the lead recovery in the citrate stage. In the sulphuric acid washing, jarosite and beaverite are dissolved, being the most important variables the temperature and sulphuric acid concentration. The jarosite dissolution kinetics shows that the rate controlling step is the chemical reaction, with an activation energy of 86.4 kJ/mol. A linear relationship between the jarosite dissolved and lead recovered is found, reinforcing the necessity of a previous H₂SO₄ washing. The optimal pH range for lead recovery in the citrate solution is 5–9. Pulp densities higher than 5% produces an unstable solution, precipitating a part of the lead. A negative effect of gypsum has been confirmed through several citrate leaching tests performed with pure anglesite. The solid obtained after the studied stages is suitable to recover gold and silver that contains.

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1. Introduction

Polymetallic ores, specially sulphide minerals, such as pyrite (FeS₂) or galena (PbS), are the major sources for recovery of associated metal values such as gold and silver, and other base metals (Schippers et al., 2013). Recently, several factors are affecting the metal production, such as the discovery of ore deposits that are more difficult to exploit (complex mineralogy), a decrease in the grade of minerals, longer and more difficult environmental permitting process, higher capital and operating costs, and technological challenges. These changes drive to need for technological

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innovation, and specially biomining (Brierley, 2008; Norgate and Jahanshahi, 2010).

These polymetallic and low-grade ores are uneconomical to be treated by conventional metallurgical techniques, in contrast with the biohydrometallurgical technologies that have the potential to benefit them. Besides, bioleaching is more environmentally benign approach than traditional pyrometallurgical processes, as no SO₂ is generated, arsenic is fixed in a stable precipitate, and is able to dissolve the pyrite matrix in refractory gold and silver ores (Fomchenko et al., 2016; Kaksonen et al., 2014; Choi et al., 2018). A case of these polymetallic ores is the black gossan found in Las Cruces Mine (Spain). This ore, mainly composed of sulphides and calcite (CaCO₃), contains valuable amounts of lead, silver and gold. Tornos et al. (2014) reported 3.85 g/t of gold, 109 g/t of silver and 8.7% of lead in black gossan.

Hot brine leaching (HBL) to recover Pb, Ag and Au, especially from mining waste, is the process more widely studied. In the case

of gold recovery, an oxidising agent is necessary to provide an oxidation reduction potential (ORP) higher than 900 mV, some relevant studies found in the literature are Viñals et al. (1991), Frías et al. (2002), Behnajady and Moghaddam (2014) and Nesbitt et al. (1990). If Pb, Ag and Au are contained in a sulphide matrix, a previous step to dissolve the matrix will be necessary because Pb is found as PbS, and Au and Ag are occluded (Eymery and Ylli, 2000; Iglesias and Carranza, 1994). This pretreatment can be varied, such as roasting (Dunn and Chamberlain, 1997), pressure oxidation (Gudyanga et al., 1999), biooxidation (Fomchenko et al., 2016; Mubarak et al., 2017) or alkaline sulphide leaching (Celep et al., 2011).

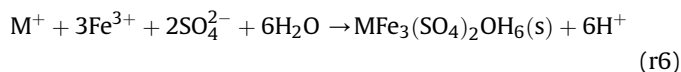
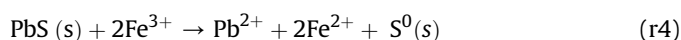
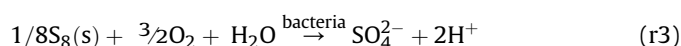
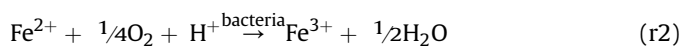
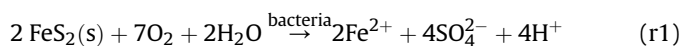
The implementation of HBL to dissolve the valuable metals (Ag, Au and Pb) from biooxidation residues could present some troubles:

- Chloride medium increases the industrial costs due to equipment corrosion (Gómez et al., 1997).
- Jarosite formed in bioleaching stage will be dissolved in an acid chloride medium forming a FeCl₃ dissolution that has environmental problems.
- Gold recovery in chloride media needs an oxidising agent, usually hypochlorite, which at pH values lower than 3.5 forms chlorine (Cl₂), and an acid medium is required to stabilise the lead chloride complex formed. Therefore, the simultaneous recovery of lead and gold will be complicated, leading to the chlorine formation, with environmental problems, or to lower lead recoveries (Nesbitt et al., 1990; Behnajady and Moghaddam, 2014).
- The addition of calcium hypochlorite could promote the co-precipitation of anglesite (PbSO₄) and gypsum (CaSO₄·2H₂O) (Behnajady and Moghaddam, 2014).

For these reasons an alternative hydrometallurgical process is proposed to recover Pb, Ag and Au from sulphide ores, mainly FeS₂. This proposal (Fig. 1) consists of a biological stage to oxidise the sulphide minerals, a second step to extract Pb from solid residue

using softer conditions than HBL, and a third stage where Ag and Au are recovered. The optimisation in the Pb, Ag and Au recovery in each stage is sought, as well as, the replacement of the HBL by the proposed novel hydrometallurgical technology to recover these target metals.

From a conceptual point of view, the first stage of this process is the sulphides oxidation, through biooxidation with extremophilic microorganisms. Biomining is an efficient technology to remove the refractoriness of these ores and to oxidise the lead sulphide (Mubarak et al., 2017; Fomchenko et al., 2016; Mahmoud et al., 2017). Reactions that take place in the biooxidation stage are the following (r1-r8):



r1-r3 (Iglesias and Carranza, 1994) are reactions catalysed by bacteria, pyrite dissolution, ferric ion regeneration and elemental sulphur oxidation, respectively. r4 is the indirect bioleaching of galena, being this reaction strongly dependent of ferric ion generated by r2. According to r5, the dissolved Pb²⁺ precipitates in sulphate medium remaining in the solid residue (Palencia et al., 1990). In the biooxidation processes usually precipitates jarosite (MFe₃(SO₄)₂OH₆) due to the presence of ferric ion, sulphate ion

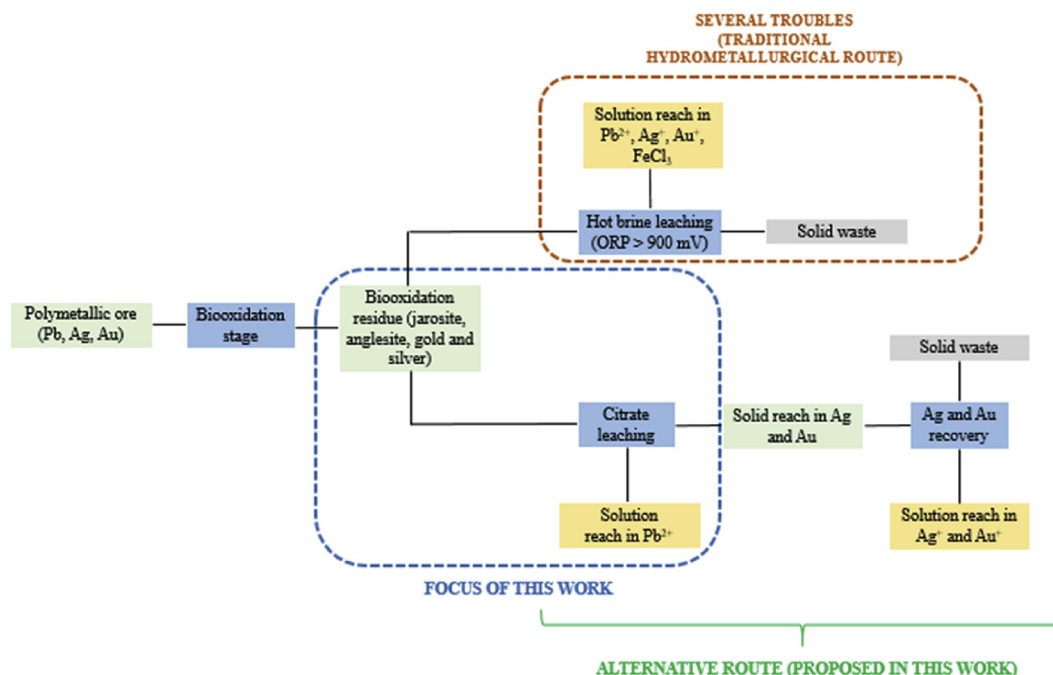


Fig. 1. Alternative hydrometallurgical process to recover Pb, Au and Ag from sulphide ores against hot brine leaching.

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