Bioleaching process for silver recovery: Structural and rheological studies

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ABSTRACT
In this work, we characterize the microstructural and rheological properties of silver manganese mineral pulps during a bioleaching process in a continuous stirred-tank reactor (CSTR). Analysis of the dissolution kinetics of Manganese in the pulp during the bioleaching process reveals a dissolution level of 20–23\% during 36–48 h. This percentage allows the extraction of large percentages of silver (Ag) during the cyanidation process, thus obtaining 64 wt\% of Ag. The maximum value of viscosity attained in the medium (especially between 48 and 72 h) is an important parameter, since it may cause processing setbacks such as in-homogeneous agitation and increase in transport energy. Several factors contribute to the continuous change of viscosity in the media such as mineral wearing, the presence of the excreted bacterial exopolysaccharide (EPS), pH changes, particle size modiﬁcations due to mineral wear (plus corrosion) and changes in density of the medium. For this reason, it is of great importance to monitor the rheological behavior of the mineral pulp during the bioleaching and cyanidation processes. The mineral pulp behaves as a weak gel as reported in linear viscoelastic measurements.

1. Introduction
In recent years, the mineral industry has shifted to the mining of low-grade ores due to the depletion of conventional high-grade ores. For low-grade ores resources, biological processing can be economically more effective and an environmentally friendlier alternative to traditional hydro-metallurgical and pyro-metallurgical processes (Sandström y Petersson, 1997; Eriüst et al., 2013). Bio-hydrometallurgy is a rapidly evolving biotechnology that has already provided rooted solutions to old problems associated with the recovery of metals by conventional pyro-metallurgy or chemical metallurgy (Boger, 2000; Sofrás and Boger, 2002). Patra et al. (2010) reported on the impact of pulp rheology on selective recovery of Ni and Cu ores, and found that factors such as shape, size and surface chemical properties of mineral particles affect pulp rheology. Ndlouvu et al. (2011) studied the influence of two phyllosilicate minerals on the rheology of mineral slurries. A complex rheological behavior of these systems arises due to the anisotropy in the surface charge and inter-particle orientation of the edges and faces of the non-spherical mineral particles in solution. Nosrati et al. (2011) studied the rheology of aging aqueous muscovite clay dispersions and found transient rheological behavior and microstructure evolution of the dispersions during aging. In addition, they observed thixotropy, yield stress, viscoelastic gel and strong rheoplectic behavior. Upon aging, the dispersions show a significant attenuation of the rheological parameters although they retain their predominant elastic properties. Zhang and Peng (2015) investigated the effect of clay...
minerals on pulp rheology and observed that clay minerals modify pulp rheology according to the type of minerals. Nonetheless, scarce literature is available to analyze the connection of the rheological properties of the system with the production of extracellular polymeric substances (exopolysaccharides, EPS) by bacteria during the bioleaching process. EPSs are mainly composed of polysaccharides and proteins, and form different structures that attach to the cell outer surface or they secrete into the growing medium, in fact, forming biofilms (Ruiz-Madiedo y de los Reyes-Gavilán, 2005). These structures are affected by particle size and particle size distribution (Cerpa et al., 1999, 2001; Pérez, 2004; Rivas and Colás, 2005), particle concentration and the mineralogical properties of the dispersed phase (Zamora, 2003), particle surface chemical properties and pH of the growing medium (Cerpa and Garcell, 1998; Garcell, 2001, 2004). Since a wealth of factors affect the rheology of a bioleaching process, a systematic analysis can achieve better understanding of the rheological properties of these systems in order to improve the recovery percentage upon minimizing operational failures associated with transport and pulp concentration. Efficiency parameters based on the rheological properties are then necessary, considering that as the bioleaching process evolves, the viscosity of the mineral pulp increases, complicating the washing operations for recovery of valuable minerals (for example cyanidation) which reduces the recovery efficiency.

Based on the above premises, in this work we characterize the microstructural and rheological properties of silver manganese mineral pulps during the bioleaching process.

2. Experimental

2.1. Materials and reagents

Samples of manganese silver minerals used in this study were provided by the First Majestic Silver Corp. Metallurgical Laboratory, corresponding to the cyanidation tails of the Encantada plant. Initially the ore has a head law of 331.5 g/t Ag and 3.1 wt% Mn. Cyanidation obtains only 60% of Ag dissolution, leaving a residue or tail grade of 130 g/t Ag and 2.7% Mn. This residue or tail law is what we use for the bioleaching tests and subsequent cyanidation. Mineral compositions of the ores tails (residue) are analyzed using quantitative X-ray diffraction (XRD) as shown in Table 1. The sample is mainly composed of calcite, with small amounts of quartz, hematite, goethite, loseyite, kaolinite, and nepheline (Na, K) AlSiO₄, and trace amounts of Pb, Mn, Fe, Zn oxides or their respective carbonates.

Table 2 discloses the elemental compositions of the ore.

2.2. Silver, mineralogy

Heavy liquid separation (HLS) at the specific gravity of 2.9 g/cm³ and 3.1 g/cm³ pre-concentrates the as-received samples, following by further concentration of the sink fraction by super-panning (SP). At this stage, we only observe few mineral grains of silver, wherein the major silver carriers are pyrolusite and rhodochrosite. Replacement of Mn by Fe, Pb and Zn, forms various manganiferous or Pb-manganiferous minerals and their pure carbonates, oxides and hydroxides.

Table 1

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Composition</th>
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<tbody>
<tr>
<td>Calcite</td>
<td>Quartz, hematite, goethite, loseyite, kaolinite, nepheline</td>
</tr>
<tr>
<td>Plumbojarosite dolomite, cerussite, rhodochrosite, oligorinite, ilmenite, pyrolusite, fluorite, quenselite, mimetite, bixite, hemimorphite</td>
<td></td>
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</table>

2.3. Microorganism and cultivation conditions

Separation of a native strain from the iron concentrate of La Encantada Mine (Durango, Mexico) provides a culture medium of 9 K with a pH of 2 (using H₂SO₄). This medium contains the following compounds: (NH₄)₂SO₄ 3.0 g/L, K₂HPO₄ 0.5 g/L, MgSO₄·7H₂O 0.5 g/L, KCl 0.1 g/L, Ca (NO₃)₂ 0.01 g/L and FeSO₄·7H₂O 44.2 g/L. Cultivation conditions include temperature of 30 °C, pH of 2.0 and rotational speed of 160 rpm (Dong et al., 2011). The native strain was cultivated and stepwise developed in 100 mL nutrient medium with 10 g iron concentrate, requiring three successive steps to achieve good quality of inoculum.

2.4. Bioleaching process

Bioleaching tests require a 10 L CSTR tank with paddle mixer, to which we add 9 K culture media with a microbial concentration of 10% (v/v). Operation conditions included agitation speed of 700 rpm, 1.5vvm (temperature and volume of air under standard conditions per volume of liquid per minute) aeration and a constant pH value of 4, solid content of 30%, granulometry of 70% – 200 mesh and 72 h retention time. Characterization of the pulp samples every 24 h provides the amount of Mn dissolved in silver.

2.5. Cyanidation process

The pulp obtained from the bioleaching process was washed and leached with sodium cyanide at a concentration of 1000 ppm during 72 h. Samples were extracted every 12 h for rheological characterization and filtered under vacuum (number 42 millipore paper). Analyses of the liquid and solid phases to determine Ag and Mn using atomic absorption spectroscopy also included liquid-phase titration to determine free cyanide using silver nitrate with a rhodanide indicator upon adding potassium cyanide up to the equilibrium point. pH values