



Electrochemical behavior of galena in the presence of calcium and sulfate ions



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ABSTRACT

A study of the electrochemical behavior of galena and the effect of the Ca^{2+} and SO_4^{2-} species on the mineral behavior at different pH, was carried out using carbon paste electrodes. The Ca^{2+} and SO_4^{2-} ions were used to simulate the species that are most concentrated in the recycled water of sulfide mineral flotation processes. By means of electrochemical and SEM analysis, it was possible to identify the chemical species that are generated on the mineral surface by means of redox reactions. In the same way, it was observed that depending on the pH, Ca^{2+} and CaOH^+ species interact with the oxidized species of galena. Furthermore, at acidic pH, sulfate reacts with lead ions to form a passivating layer on the surface of the mineral, while at alkaline pH more than one species is generated on the mineral, which passivate its surface.

1. Introduction

The mineral galena (PbS), a lead sulfide, is the main source of lead metal worldwide with a current production of more than 4.35 million tons (ILZSG, 2016). The recovery of lead from its ores, involves aqueous operations and pyrometallurgical processes. The aqueous process consists of the flotation of the mineral to separate galena from other sulfides such as sphalerite (ZnS), iron sulfides (FeS_2 and FeS) and non-sulfide gangue. Subsequently, the mineral goes to the pyrometallurgical process which consists of the smelting and refining of metallic lead.

The galena, ground under the right conditions, is hydrophobic, so it can float naturally (Guy and Trahar, 1984). However, a collector is conventionally used (e.g., xanthate), since this gives a greater hydrophobicity so that the galena can be more easily and selectively attached to the bubbles during flotation.

It is well known that the galena flotation can be hindered by the presence of dissolved ions in the process water (Bulut and Yenial, 2016; Ikumapayi et al., 2012; Liu et al., 2013; Rao and Finch, 1989). These ions come from the recycle water, as the recycling practice is increasingly being used to minimize environmental impact, damage to health and/or international policies (Liu et al., 2013). The typical organic and inorganic pollutants found in the recycle water are: colloidal material, base metal ions (Pb^{2+} , Cu^{2+} , Zn^{2+} , Fe^{3+}), thiosalts, sulfite, sulfate,

sulfide, chloride, magnesium, calcium, sodium, potassium, reagents such as foaming agents, collectors and depressants (Bıçak et al., 2012). Many of these species may depress the flotation of the desired mineral or activate undesired ones, affecting the flotation selectivity (Liu et al., 2013; Rao and Finch, 1989).

Two of the ions commonly found in recycle water are calcium (Ca^{2+}) and sulfate (SO_4^{2-}) (Bulut and Yenial, 2016; Ikumapayi et al., 2012). Calcium presence is due to the dissolution of Ca-containing minerals, and to the addition of lime as pH regulator. While the presence of sulfate is due to the natural oxidation of the sulfide species (Sui et al., 1998). To this regard, some authors have found conflicting results, showing that calcium and sulfate have a depressant effect on galena (Ikumapayi et al., 2012), promote galena flotation (Liu and Zhang, 2000) or, depending on certain parameters, promote or depress its flotation (Bulut and Yenial, 2016).

It has been widely demonstrated that the flotation process, as well as mineral leaching, involves electron transfer reactions (Chmielewski and Lekki, 1989; Gardner and Woods, 1979; Pecina et al., 2006; Sun et al., 2016), so that such processes can be evaluated by means of electrochemical techniques to both understand and optimize them. However, insoluble solids present a challenge for their electrochemical study. If the solid is electrically conductive, it can be prepared and used as solid electrode, nevertheless, this type of electrodes can cause problems due to the difficult involved in the polishing of its surface, shows

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low reproducibility, low resolution and tendency to fracture. In addition, the physical properties of the mineral electrode, as sample size, is different from that used in flotation and/or leaching processes (Lázaro et al., 1995). As an alternative to the massive solid electrode, the solid can be pulverized, mixed with conductive powder such as graphite and agglomerated with an inert oil, thereby creating a carbon paste electrode (CPE) (Cisneros-González et al., 1999). This alternative has advantages such as particle size similar to that used in the mineral processing industry, a consistent surface, easy surface renewal, good selectivity and sensitivity and easy to make; furthermore, the electrochemical behavior of the CPE can represent the conditions under which actual flotation and leaching processes are conducted (Cisneros-González et al., 2000), since the electrode exhibits the electrochemical properties of the mineral added to the paste (Gerlach and Küzeci, 1983). Because of this, electrochemical techniques such as voltammetry coupled with carbon paste electrodes have proved to be very useful and versatile for the analysis of the electrochemical behavior of minerals (Nava and González, 2005).

Most of the studies of galena electrochemical behavior have been performed in acid media. Gardner and Woods (1979), Paul et al. (1978), Nicol et al. (1978) and Sivenas and Foulkes (1984), have conducted extensive studies on the electrochemical behavior of galena in perchloric acid, while Mikhlin et al. (2004) used nitric acid. In contrast, the behavior of the galena in neutral and alkaline solutions is more complex, so there are few studies under these conditions (Gardner and Woods, 1979; Urbano et al., 2016). However, no studies have been conducted on the electrochemical behavior of galena in the presence of calcium and sulfate ions in solution, as is the case in the industrial flotation of complex sulfide ores, where these ions can interfere and change the behavior of the mineral.

Due to the above reasons, the present work is an experimental study whose objective is to characterize the products of oxidation and reduction of the galena under acid and alkaline pH, as well as the mineral electrochemical behavior in the presence of the Ca^{2+} and SO_4^{2-} ions. Experiments were performed using carbon paste electrodes as an alternative to massive solid electrodes. It is important to mention that the measurements were carried out using cyclic voltammetry, and that these were supported and interpreted with the help of thermodynamic modeling of the system using Pourbaix diagrams.

2. Experimental

2.1. Samples

The galena sample was obtained from the Naica mine of Peñoles, Chihuahua, Mexico. Its mineralogical composition was determined by elemental analysis of metals by atomic absorption spectroscopy, while the sulfur quantification was carried out by mass balancing, associating it to the metals in their sulfide form. The galena used to prepare the carbon paste electrodes was ground in an agate mortar and pestle and sieved to -500 mesh ($-25 \mu\text{m}$).

2.2. Solutions and reagents

All reagents used are analytical grade. Deionized water was used for the preparation of solutions. The acid buffer was prepared by mixing sufficient quantities of a 0.1 mol L^{-1} solution of sodium acetate and 0.017 mol L^{-1} of acetic acid to obtain a pH 5.5. The alkaline buffer was prepared by dissolving sufficient amount of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ to obtain a pH 9.5. Solutions of 0.1 mol L^{-1} of NaOH or 0.1 mol L^{-1} of HNO_3 were used to adjust the pH of the solutions as required. The preconditioning solution of 880 ppm Ca^{2+} was prepared from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Preconditioning with sulfate was carried out using a solution of $0.02 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$. Collector preconditioning was conducted using a solution of 0.005 mol L^{-1} purified sodium isopropyl xanthate (SIPX).

2.3. Instrumentation

The electrochemical measurements were performed with an electrochemical analyzer-potentiostat (Radiometer Copenhagen model DEA332) coupled to an electrochemical interface (Radiometer Copenhagen model IMT102), using a typical three-electrode cell arrangement. An Alfa-Aesar graphite bar ($6.15 \text{ mm diameter} \times 152 \text{ mm long}$, 99.9995% purity), a saturated calomel reference electrode (all potentials are given vs. the reference electrode) was used as the counter electrode. The working electrode used was a galena-modified CPE (CPE-galena). The micrographs were obtained with a SEM-EDS Philips, model XL30ESEM. The diffractogram was obtained with a Bruker X-ray diffractometer model D8 Advance.

2.4. Preparation of carbon paste electrodes

The CPE-galena was prepared by mixing 0.16 g of graphite powder ($2\text{--}15 \mu\text{m}$, 99.9995% purity), 0.04 g galena and $80 \mu\text{L}$ silicone oil (Alfa Aesar, $\rho = 0.963$) in an agate mortar until a totally homogeneous paste is obtained. Once the paste was ready, it was packed in a polyethylene syringe of 3 mm internal diameter and 7 cm long, whose plunger is used to renew the electrode surface before each electrochemical test. Renewal is done by polishing the exposed surface of the electrode on a sheet of paper. The electrical contact between the potentiostat and the CPE was made with a copper wire. Once the electrode is prepared, it is left at rest for 24 h , immersed in deionized water. The unmodified CPE (CPE-blank) was prepared in the same way as the CPE-galena, but without mineral sample.

2.5. Procedures

The preconditioning of CPE-blank and CPE-galena in SIPX, Ca^{2+} and SO_4^{2-} solutions was done by immersing the electrode for 80 , 120 and 120 min , respectively. After preconditioning, the electrode was passed to the electrochemical cell containing the electrolyte buffer at the same pH as the preconditioning solutions, and the required electrochemical measurement was done. All measurements were performed at room temperature ($25 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$).

2.6. Thermodynamic modeling

Thermodynamic modeling consisted in determining the thermodynamically stable solid species on the mineral surface, as well as the aqueous species present in the solution, as a function of pH and potential. The Pourbaix diagrams were developed using the HSC Chemistry Software version 5.11.

3. Results and discussion

The elemental composition of the galena used in the preparation of the CPE-galena is shown in Table 1. In turn, the diffractogram of Fig. 1 shows that no other minerals species other than galena is present in the sample.

In order to study the effect of Ca^{2+} and SO_4^{2-} on the reactions in which the galena participates, both under acidic and alkaline pH, it is necessary to determine the electrochemical behavior of the mineral alone.

Table 1
Chemical composition of galena sample used in this work.

	Element (% wt.)					
	Pb	S	Cu	Fe	Zn	Insoluble
Galena (PbS)	81.7	12.6	0.08	0.24	0.43	4.95

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