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Role of organic reagents and impurity in zinc electrowinning

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ABSTRACT

The role of organic reagents (flocculant and flotation collectors) and impurity (lubricating oil) in zinc deposition and in product quality is described in this paper. In the presence of a flotation collector for zinc and a lubricating oil, characterized by polar amine and non-polar alkyl groups, respectively, by using Fourier transform infrared spectroscopy, an inhibition of the metal nucleation process was observed, which was found to be particularly significant for electrolyte contaminated with the amine-containing compound. The current efficiency (CE) dropped from 93.7% (organic-free solution) to 21.6% in the presence of 50 $mg \cdot L^{-1}$ of collector for zinc, and a negative but smaller effect was observed in the presence of similar amounts of the lubricating oil (90.7%). The addition of a flocculant and a collector for impurities, which contain the polar amide and carboxyl groups in their molecules, respectively, caused minor increases in the nucleation overpotential for zinc deposition and only at relatively high concentrations (100 $mg \cdot L^{-1}$). The addition of these compounds to the solution slightly increased CE. The characterization of the Zn deposits by X-ray diffraction and scanning electron microscopy revealed the formation of pores in deposits obtained from solutions containing the collector for impurities or lubricating oil, and different growth patterns were identified when the flocculant or collector for zinc was added to the solution. The observed trends have been interpreted in terms of the polar character and reactivity of the organic molecules to Zn^{2+} ion, and adsorption on the cathode surface.

1. Introduction

It is well-known that residual amounts of organic compounds can contaminate the feed solution of electrowinning tankhouses. The presence of organic impurities in the sulfate electrolyte during the electrowinning of zinc may significantly affect the current efficiency and the quality of the metal electrodeposited on the aluminum cathodes, which in turn may affect the mechanical properties of the Zn deposit and thereby the effectiveness of the stripping stage. Previous works which focused on the effect of organic compounds, such as acid mist suppressants (Hosny, 1993; Mackinnon, 1994; Dhak et al., 2011), extractants (Mackinnon et al., 1980), and surfactants added during pressure leaching (Mackinnon et al., 1988; Alfantazi and Dreisinger, 2003), confirmed these negative effects. A practical alternative to minimize the impacts of the organic impurities on zinc electrowinning involves their removal by means of adsorption on activated carbon. This practice is used with good results at a zinc operation which employs solvent extraction (Cole and Sole, 2002).

In the literature, the behavior of organic compounds in electrolyte solutions has been typically described in terms of adsorption on the cathode surface. The adsorption of organic molecules may affect the kinetics of the main electron transfer reaction of zinc deposition (Eq. (1)) due to the blockage of a fraction of the active sites available for nucleation. Other effects may involve interaction between the dissolved electroactive species and the organic reagents, such as the ability of some organic groups to act as proton (H^+) carriers that could affect the rate of the hydrogen evolution reaction (Eq. (2)).

$$Zn^{2+}{}_{(aq)} + 2\,e^- \leftrightharpoons Zn_{(s)} \tag{1}$$

$$2\,H^+{}_{(aq)} + 2\,e^- \leftrightharpoons H_{2(g)} \tag{2}$$

When the degree of organic adsorption on the cathode surface increases, increasing blockage of the nucleation sites may occur, resulting in increased cathode polarization (Oniciu and Mureşan, 1991). Thus, a higher driving force is required for deposition, which typically results in an increase of the cell voltage. Additionally, when the organic concentration in the electrolyte is high, the interfacial viscosity is likely to increase and, thus, the mass transfer of the metal ion to the nucleation sites can be affected.

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Winand (1992) distinguished the effects of organic compounds on metal deposition processes according to their hydrophilicity. Thus, adsorption of hydrophobic organic molecules was associated to strong inhibition in the rate of the cathodic reaction, while adsorption of hydrophilic molecules was related to small inhibition or even positive effects, as expected from additives. As will be discussed in the present paper, the results described here show that hydrophilic organic molecules may also cause strong inhibition of metal deposition and this effect may be even larger than that observed for hydrophobic compounds.

The present work is then motivated by the recognition that a better understanding of the behavior of these organic molecules in the zinc sulfate electrolyte will contribute to the selection of control and optimization procedures to be implemented in the industrial operation in order to minimize the adverse effects.

In this context, the purpose of the present paper is to describe the effect of some organic compounds, containing different functional groups, on (i) process parameters of zinc electrowinning, such as the current efficiency, cell voltage, and specific energy consumption; (ii) product quality, according to the morphology and crystal structure of the metal deposited; and (iii) nucleation overpotential for zinc deposition. The selected organic compounds are used in the industrial unit of Votorantim Metais, in Três Marias, Brazil. This industrial operation is unique as it combines processing of silicate and zinc sulfide ores, the latter involving the traditional roasting–leaching–electrowinning route. The treatment of the silicate ore comprises the flotation of zinc silicates and the removal of calcium and magnesium by pressure leaching, prior to the leaching of zinc from the silicate concentrate. Prior to electrowinning, impurities are removed by jarosite precipitation and cementation using Zn powder. The zinc production from silicate ores does not include roasting, applied to the extraction from sulfide concentrates, which normally destroys the organics used in the mineral processing stages.

2. Experimental

2.1. Characterization of the organic compounds

The selected organic compounds are a flocculant, added during thickening (Organic 1); a flotation collector for zinc silicate (willemite, Zn_2SiO_4) (Organic 2); a flotation collector for impurities (carbonates), which also acts as an anti-foaming agent in atmospheric leaching (Organic 3); and a lubricating oil, which is used in machinery, including the cranes (Organic 4). The characteristic functional groups of Organics 1, 2, and 4 were analyzed by Fourier transform infrared spectroscopy (FTIR) using a Perkin-Elmer (Paragon 1000) spectrometer. The spectral resolution was about 5 cm^{-1}, and a minimum of 150 scans with 10 s integration time was recorded. Due to the presence of water in Organic 3, this organic was analyzed by gas chromatography (GC) using a gas chromatography oven (Agilent 6890) attached to mass selective detector (Agilent 5973). Dichloromethane was used as the organic extractant.

2.2. Electrowinning

The electrowinning experiments were conducted in a four-electrode cell: three aluminum cathodes (99.5% pure) in the form of vertically aligned disks with 10 mm diameter (surface area ≈ 78 mm^2 each), and a central platinum anode (99.99% pure) in the form of a vertical rod (surface area ≈ 250 mm^2). Cathode and anode are distant by approximately 25 mm. The cell consisted of a 2 L Pyrex® reactor with a Teflon lid. Prior to each experiment, fresh cathode surface was prepared by wet mechanical polishing (SiC paper, grit size 1200) and rinsing with deionized water (Millipore® Milli-Q) in an ultrasonic bath for 15 min. The experiments were carried out at constant current density (500 $A \cdot m^{-2}$) under stirring (350 rpm). The metal was deposited for 6 h. The electrolyte consisting of 58 $g \cdot L^{-1}$ Zn^{2+} and 160 $g \cdot L^{-1}$ sulfuric acid was prepared with deionized water, analytical grade H_2SO_4 96% (FMaia®) and zinc sulfate heptahydrate >99% (Sigma-Aldrich®). In order to keep nearly constant the acid to zinc ratio during electrowinning, a small deposition area in a large volume of solution (1 L) was used. The temperature of the electrolyte solution was kept constant at 38.0 ± 0.5 °C using a temperature-controlled hot plate (IKA® RET basic). The organic compounds were added to the electrolyte in two concentrations, namely 50 and 100 $mg \cdot L^{-1}$. All the experiments were performed in duplicate.

Cell voltage (CV) measurements were taken at 2, 4, and 6 h, using a Minipa (ET 2615 A) multimeter. This parameter was measured between each Al cathode and the central Pt anode. The average specific energy consumption (SEC), in $kWh \cdot t^{-1}$ Zn, was calculated from the CV values, according to:

$$SEC = \left(\frac{nFCV}{3.6MCE}\right) \tag{3}$$

where n represents the number of electrons in the overall deposition reaction (2), F the Faraday constant (96485 $C \cdot mol^{-1}$), M the zinc atomic weight (65.39 $g \cdot mol^{-1}$), and CE the current efficiency. After the electrowinning, the deposits (in the range of 59–273 mg) were manually stripped from the Al cathodes, rinsed with deionized water in an ultrasonic bath for 15 min, and dried in a furnace at 60 °C for 30 min. The average mass of the three Zn deposits produced in each test was measured by an analytical balance with high degree of precision and readability up to 0.1 mg (Mettler AE200). The CE was determined according to:

$$CE = \left(\frac{nFm}{ItM}\right) \times 100\% \tag{4}$$

where m represents the weight of the deposit obtained after 6 h (g), I the total cell current ($C \cdot s^{-1}$), and t the deposition time (s).

2.3. Electrochemical measurements by cyclic voltammetry

The electrochemical measurements by cyclic voltammetry were conducted in a conventional three-electrode cell. The working electrode was Al (99.5% pure) in the form of a vertically aligned disk with 10 mm diameter, the counter-electrode was Pt (99.99% pure) in the form of a vertical rod (surface area ≈ 150 mm^2) and the reference electrode was a Ag/AgCl/KCl (3 $mol \cdot L^{-1}$) (+0.197 V vs. SHE at 38 °C). The cell consisted of a 1 L Pyrex® reactor with a Teflon lid. Prior to each measurement, fresh working electrode surface was prepared by wet mechanical polishing (SiC paper, grit size 1200) and rinsing with deionized water in an ultrasonic bath for 15 min. All the measurements by cyclic voltammetry were conducted in triplicate by using an Autolab® (PGSTAT 20) potentiostat, equipped with the GPES (v.49) data acquisition system. The measurements started at −0.60 V with an initial scan towards negative potentials, and reversed at −0.905 V towards positive potentials. As the focus of this investigation is the deposition process, only the cathodic cycles will be discussed. The measurements were conducted at a low scan rate (1 $mV \cdot s^{-1}$), after an equilibration time of 10 min, and under stirring (350 rpm). All the potentials are reported versus the SHE scale.

2.4. Characterization of the zinc deposits

The morphology of the Zn deposits obtained from organic-free and organic-containing electrolyte was analyzed by scanning electron microscopy (SEM) coupled to energy dispersive spectrometry (EDS), using a JEOL (JSM 6360 LV) microscope equipped with a Thermo Noran (Quest) spectrometer. The micrographs were obtained using a 15 kV accelerating voltage. The crystalline structure of the Zn deposits was analyzed by X-ray diffraction (XRD), using a PANalytical (Empyrean) X-ray diffractometer, and Cu Kα1 (λ = 1.5406 Å) radiation. The XRD