
http://researchrepository.murdoch.edu.a/25259/
Accepted Manuscript

Role of organic reagents and impurity in zinc electrowinning


PII: S0304-386X(15)00008-0
DOI: doi: 10.1016/j.hydromet.2015.01.003
Reference: HYDROM 4023

To appear in: Hydrometallurgy

Received date: 11 November 2014
Revised date: 9 January 2015
Accepted date: 11 January 2015

Please cite this article as: Majuste, D., Martins, E.L.C., Souza, A.D., Nicol, M.J., Ciminelli, V.S.T., Role of organic reagents and impurity in zinc electrowinning, Hydrometallurgy (2015), doi: 10.1016/j.hydromet.2015.01.003

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Role of organic reagents and impurity in zinc electrowinning

Majuste, D.¹², Martins, E.L.C.³, Souza, A.D.³, Nicol, M.J.⁴, Ciminelli, V.S.T.¹²

¹ Department of Metallurgical and Materials Engineering, Universidade Federal de Minas Gerais, Belo Horizonte - MG, 31270-901, Brazil.
² INCT – Acqua (National Institute of Science and Technology on Mineral Resources, Water and Biodiversity), Belo Horizonte - MG, 31270-901, Brazil.
³ Votorantim Metais - Zinc, Três Marias - MG, 39205-000, Brazil.
⁴ School of Engineering and Information Technology, Murdoch University, Perth - WA, 6150, Australia.

*Corresponding author: Tel: +55 31 34091076 / Fax: +55 31 34091810 Email Address: daniel.majuste@demet.ufmg.br (D. Majuste).

Abstract

The role of organic reagents (flocculant and flotation collectors) and impurity (lubricating oil) in zinc deposition and in product quality are 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·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·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 were added to the solution. The observed trends have been interpreted in terms of the polar character and reactivity of the organic molecules to Zn²⁺ ion, and adsorption on the cathode surface.

*Keywords:* Electrowinning; zinc; organic impurities; current efficiency; nucleation overpotential.
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 sulphate 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).

\[
\text{Zn}^{2+}_{(aq)} + 2 \text{e}^- \rightleftharpoons \text{Zn}_{(s)} \quad \text{(Eq. 1)}
\]

\[
2 \text{H}^+_{(aq)} + 2 \text{e}^- \rightleftharpoons \text{H}_2(g) \quad \text{(Eq. 2)}
\]
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 Mureșan, 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.

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 understand of the behavior of these organic molecules in the zinc sulphate electrolyte will contribute to select 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$_2$SiO$_4$) (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 were 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 mm² each), and a central platinum anode (99.99% pure) in the form of a vertical rod (surface area ≈ 250 mm²). 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·m⁻²) under stirring (350 rpm). The metal was deposited for 6 h. The electrolyte consisting of 58 g·L⁻¹ Zn²⁺ and 160 g·L⁻¹ sulfuric acid was prepared with deionized water, analytical grade H₂SO₄ 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·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·t⁻¹ Zn, was calculated from the CV values, according to:

\[
SEC = \left( \frac{nFCV}{3.6\text{MCE}} \right)
\]  

(Eq. 3)
where \( n \) represents the number of electrons in the overall deposition reaction (2), \( F \) the Faraday constant (96485 C·mol\(^{-1}\)), \( M \) the zinc atomic weight (65.39 g·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:

\[
CE = \left( \frac{nFm}{ItM} \right) \times 100\%
\]  
(Eq. 4)

where \( m \) represents the weight of the deposit obtained after 6 h (g), \( I \) the total cell current (C·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 \( \approx 150 \text{ mm}^2 \)) and the reference electrode was a Ag/AgCl/KCl (3 mol·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·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 patterns were measured in the 2θ range of 10-120° using a scan rate of 0.06°/min. The patterns were identified using ICDD (International Centre for Diffraction Data) files as reference.

3. Results and discussion

3.1. Characterization of the organic compounds
Figure 1 shows the FTIR spectra of the analyzed compounds. The spectrum obtained by the analysis of Organic 1, the flocculant, indicated a wide FTIR band with relative high intensity at about 3436 cm\(^{-1}\) and FTIR shoulder at about 3300 cm\(^{-1}\) (Fig. 1a). The band at about 3436 cm\(^{-1}\) corresponds to the stretching mode of the N—H bond in primary (—CONH\(_2\)) and secondary (—CONH—) amide groups (Nakanishi and Solomon, 1977; Smith, 1999). The spectrum indicated a wide FTIR band with relative medium intensity at about 1636 cm\(^{-1}\) (Fig. 1a), which may be assigned to the stretching mode of the C=O bond in primary amide groups. The spectrum still indicated bands with relative low intensity at about 1419 cm\(^{-1}\) (Fig. 1a), which is diagnostic of the stretching mode of the C—N bond in primary amides, and at about 2926 and 2856 cm\(^{-1}\) (Fig. 1a), which correspond to the asymmetric and symmetric stretching modes, respectively, of the C—H bond in the —CH\(_2\)— groups, in alkanes. These FTIR bands exhibited shoulders at about 2950 and 2867 cm\(^{-1}\), which may be assigned to the asymmetric and symmetric stretching modes, respectively, of the C—H bond in the —CH\(_3\) groups, in alkanes. The FTIR analysis of Organic 1 did not show the band with relative high intensity at about 1515-1570 cm\(^{-1}\), which is typical of secondary amides.

The spectrum obtained by the analysis of Organic 2, the collector for zinc silicate, indicated thin, well-defined FTIR bands with relative high intensity at about 2956, 2929, 2869, and 2859 cm\(^{-1}\) (Fig. 1b). The band at about 2956 cm\(^{-1}\) is diagnostic of the asymmetric stretching mode of the C—H bond in the —CH\(_3\) groups, in alkanes, while the band at about 2869 cm\(^{-1}\) represents the symmetric stretching mode (Nakanishi and Solomon, 1977; Smith, 1999). The vibrations detected at about 2929 and 2859 cm\(^{-1}\) correspond to, respectively, the asymmetric and symmetric stretching modes of the C—H bond in the —CH\(_2\)— groups, in alkanes. FTIR bands with relative medium intensity at about 1465 cm\(^{-1}\) and relative low intensity at about 1380 cm\(^{-1}\) (Fig. 1b) were also detected, which represents, respectively, the asymmetric and symmetric bend modes of the C—H bond in the —CH\(_3\) groups, in alkanes.
The spectrum still indicated well-defined bands with relative medium intensity at about 1575 and 1115 cm\(^{-1}\) (Fig. 1b). While the vibration at 1575 cm\(^{-1}\) corresponds to the scissor mode of the N—H bond in primary amine (—NH\(_2\)) group, the band at 1115 cm\(^{-1}\) may be assigned to the asymmetric stretching mode of the C—O bond in the ether (—COC—) group, typically detected at 1140-1070 cm\(^{-1}\). It can also be observed a wide band with relative medium intensity at about 3276 cm\(^{-1}\) (Fig. 1b), which represents the symmetric stretching mode of the N—H bond in primary amines, typically detected at 3310-3280 cm\(^{-1}\). Regarding the detection of the corresponding asymmetric stretching mode, normally detected at 3380-3350 cm\(^{-1}\), the observed FTIR shoulder suggests a possible overlapping.

Regarding the FTIR analysis of Organic 4, the lubricating oil, the spectrum revealed thin, well-defined bands with relative high intensity at about 2953, 2924, 2872 and 2854 cm\(^{-1}\), and with relative medium intensity at about 1464 cm\(^{-1}\) and 1376 cm\(^{-1}\) (Fig. 1c). As earlier discussed, the molecular vibrations detected at 2924 and 2854 cm\(^{-1}\) correspond to, respectively, the asymmetric and symmetric stretching modes of the C—H bond in the —CH\(_2\)— groups, in alkanes, while those at 2953 and 2872 cm\(^{-1}\) are assigned to the asymmetric and symmetric stretching modes, respectively, of the C—H bond in the —CH\(_3\) groups, in alkanes. With regards to the FTIR bands at 1464 and 1376 cm\(^{-1}\), these are assigned to, respectively, the asymmetric and symmetric bend modes of the C—H bond in the —CH\(_3\) groups, in alkanes (Nakanishi and Solomon, 1977; Smith, 1999). A band with relative low intensity at about 1458 cm\(^{-1}\) was also detected (Fig. 1c), which corresponds to the scissors mode of the C—H bond in the —CH\(_2\)— groups, in alkanes. The FTIR analysis of Organic 4 revealed that the carbon chain of this compound has only single bonds between the atoms of carbon. Finally, the analysis of Organic 3, the collector for impurities, by GC detected different fatty acids, mainly hexadecanoic acid (C\(_{16}\)H\(_{32}\)O\(_2\)), octadecanoic acid (C\(_{18}\)H\(_{36}\)O\(_2\)), cis-9-octadecenoic acid (C\(_{18}\)H\(_{34}\)O\(_2\)), and cis,cis-9,12-octadecadienoic acid (C\(_{18}\)H\(_{32}\)O\(_2\)).
Therefore, Organic 3 is composed by saturated and unsaturated molecules containing the carboxyl (—COOH) group.

Table 1 summarizes the main findings obtained by the FTIR and GC analyses of the organics selected for this investigation. Only the polar amide and non-polar alkyl groups were detected in the molecule of the flocculant. The amide group can form hydrogen bonds with water, mainly through the C=O dipole due to the higher electronegativity of the O atom, and the negative charges available on the O and N atoms can attract the positively charged H\(^+\) and Zn\(^{2+}\) species, if there are no steric effects. In acid electrolytes, this organic molecule is protonated (Dean, 1999), which may favors its migration to the negatively charged Al/Zn cathode. The FTIR analysis of the collector for zinc silicate indicated the non-polar alkyl group and the polar ether and amine groups. The amine group contains a lone pair of electrons on the N atom, which allow bonding with water and H\(^+\) and Zn\(^{2+}\) species. In acid electrolytes, the migration of protonated amine molecules (Dean, 1999) to the negatively charged Al/Zn cathode may be favored as well. The ether group is slightly polar, despite of the two lone pairs of electrons on the O atom and, thus, its intermolecular reactivity is low, as well as its affinity for water. The FTIR analysis of the lubricating oil indicated only the non-polar alkyl group. This organic is a saturated compound, insoluble in water and electrostatically unreactive. The negative charges available on the O atoms of the carboxyl group, identified in the collector for impurities by means of GC analysis, may also attract the H\(^+\) and Zn\(^{2+}\) species, if there are no steric effects. In acid electrolytes, this organic group is protonated as well (Dean, 1999), and its migration to the negatively charged Al/Zn cathode may be favored.

3.2. Electrowinning
3.2.1. Effect of the organic impurities on the current efficiency

The average CE values obtained from the organic-containing electrolytes are summarized in Table 2. The CE obtained in the absence of organics in the solution was 93.7 ± 0.1%. In the presence of the collector for zinc, a significant negative impact was observed at both concentrations. With the addition of 50 mg·L\(^{-1}\), the CE dropped from 93.7 ± 0.1 to 21.6 ± 0.1%. The addition of the lubricating oil also resulted in negative effects at both concentrations. As it will be discussed later, Zn deposits obtained from solutions containing this compound exhibited residual amounts of oil and entrapped zinc sulfate (ZnSO\(_4\)) solution, even after thorough rinsing, which means that the CE values may be slightly smaller than those reported in Tab. 2.

For the other impurities (flocculant and collector for impurities), slightly positive effects on the CE can be observed at levels of 100 mg·L\(^{-1}\) of flocculant in the solution (Tab. 2). The average CE value obtained at this concentration is 1.19 units higher than that determined for the organic-free solution (93.7 %). The average CE values obtained in the presence of 50 mg·L\(^{-1}\) of flocculant or collector for impurities and 100 mg·L\(^{-1}\) of collector for impurities remain almost constant, within the experimental error. The Zn deposits obtained from solutions with the collector for impurities also exhibited residual amounts of entrapped ZnSO\(_4\) solution.

3.2.2. Effect of the organic impurities on the specific energy consumption

The average SEC values obtained from the organic-containing electrolytes are also summarized in Tab. 2. The average SEC value obtained from the organic-free solution was 2644 ± 3 kWh·t\(^{-1}\). As expected, an extremely negative effect was observed when the collector
for zinc was added to the solution at both concentrations. The addition of 50 and 100 mg·L⁻¹ of lubricating oil also increased the average SEC value. A slightly beneficial effect was observed only in the presence of 100 mg·L⁻¹ of flocculant in the solution. The average SEC value obtained at this concentration is 2% lower than that determined for the organic-free solution. The average SEC values obtained in the presence of 50 mg·L⁻¹ of flocculant or collector for impurities and 100 mg·L⁻¹ of collector for impurities remain almost constant, within the experimental error.

3.2.3. Effect of the organic impurities on the cell voltage

Figure 2 exhibits the cell voltage measured at 2, 4 and 6 h. Slight increases of the average CV values were observed in the presence of the collector for zinc silicate and lubricating oil in the electrolyte, but only with the collector for zinc this increase persisted along the 6 h. In the presence of the flocculant and collector for impurities in the solution, the CV values are statistically similar to those measured for the organic-free solution.

The energy consumption in the electrowinning cell is proportional to CV, which in turn is a function of the equilibrium potential for the anodic oxidation (E_{anode}) and cathodic reduction (E_{cathode}) reactions, their associated overpotentials (η_{anode} and η_{cathode}, respectively), and the ohmic potential drop through the cell, according to the simplified equation:

\[
CV = (E_{anode} - E_{cathode}) + \eta_{anode} - \eta_{cathode} + \frac{IL}{\kappa A} \quad \text{(Eq. 5)}
\]

where I is the current (A), L the inter-electrode distance (m), A the electrode reaction area (m²), and κ the specific conductivity of the electrolytic solution (S·m⁻¹). Voltage losses in the electrical contacts of the electrowinning cell were neglected. Assuming that E_{anode}, E_{cathode}, I,
L, and A are constants, the CV only depends on the $\kappa$, $\eta_{\text{anode}}$, and $\eta_{\text{cathode}}$ values. As mentioned in the experimental section, the voltages measured are those for a cell with a Pt anode, for which anodic polarization may be expected to be insignificant.

The effects of the addition of 50 and 100 mg·L$^{-1}$ of organics to the electrolyte on the specific conductivity were assumed to be negligible, according to the high concentrations of Zn$^{2+}$ ion (58 g·L$^{-1}$) and H$_2$SO$_4$ (160 g·L$^{-1}$). The slightly higher voltages measured in the presence of the collector for zinc and lubricating oil (Fig. 2) may be related to the behavior of the corresponding molecules at the reaction interface. This increase of the average CV value is assumed to be related to an increase of the nucleation overpotential for zinc deposition due to organic adsorption and interaction between the organic molecule and the Zn$^{2+}$ ion, as discussed later in this paper. The observed trends suggest a physical adsorption of the lubricating oil (insoluble compound) on the negatively charged Al/Zn surface, and specific adsorption of the collector for zinc (i.e., positively charged molecules due to the interaction between the N atom and the Zn$^{2+}$ ion). The drop of voltage from $t = 2$ h in the presence of the lubricating oil in the solution could be related to desorption of the non-polar molecules from the metal surface.

The CV measurements also revealed a gradual, very slight decrease of the cell voltage with time (Fig. 2). This trend was not affected by the type of organic molecule added to the solution, since it was observed for all the examined conditions. According to Eq. 5, a drop of voltage during electrowinning may be related to a decrease of the overpotential for zinc deposition on morphologically modified surfaces, and a slight increase in the electrolyte conductivity. Titration with 0.1 N sodium carbonate (Na$_2$CO$_3$) indicated that the free acidity of the organic-free electrolyte increased about 5% after 6 h, which is associated with the stoichiometric balance of the consumption of H$^+$ ions at the cathode (Eq. 2) and the production of H$^+$ ions at the Pt anode (Eq. 6).
H₂O ⇌ 2 H⁺(aq) + ½ O₂(g) + 2 e⁻  \hspace{1cm} (Eq. 6)

The zinc concentration in the electrolyte decreased less than 2%. Thus, the acid to zinc ratio slightly increased (from about 2.85 to 3.00), thereby increasing the conductivity. This result supports the observed, slight decrease of CV during electrowinning (from about 3.030 to 3.015 V).

3.3. Effect of the organic impurities on the nucleation overpotential for zinc deposition

The effects of the organic impurities on the nucleation overpotential (NOP) and rate of zinc deposition on the Al substrate were examined by means of cyclic voltammetry. The NOP values correspond to the difference between the initial potential for nucleation and the reversible potential for the Zn²⁺/Zn couple. Figure 3 shows replicate curves obtained using organic-free solutions. Low cathodic currents were observed until Zn deposition starts at point A. The cathodic current increased with polarization up to the potential at which the scan is reversed (point B). In the positive direction, the current decreased to the reversible potential (point C) and then became anodic, consistent with anodic oxidation of the Zn deposit. The region ABC, commonly termed the nucleation loop, provides the nucleation overpotential (i.e., E_A – E_C), which was found to be 74 ± 1 mV. The average cathodic peak current was (3.18 ± 0.03)x10⁻² A, which is equivalent to a current density of 405 A·m⁻². It is important to remark that this current is due to the simultaneous reduction of Zn²⁺ and H⁺ ions on the Al surface. In Figure 4, it can be seen a low cathodic current associated only with hydrogen evolution on the Al surface (peak in the range from -0.830 to -0.835 V), prior to Zn nucleation on this substrate. The observed decrease in hydrogen evolution when the
polarization increases is related to the formation of a zinc layer on the Al surface and slower reaction rate on the Zn substrate, which means that Al is a better substrate for this reaction, as previously discussed (Gabe, 1997).

The voltammograms obtained using solutions containing the organic compounds are shown in Figure 5. The addition of flocculant to the solution slightly increased the average NOP value from 74 ± 1 to 79 ± 3 mV, at 100 mg·L\(^{-1}\) (Fig. 5a). At 50 mg·L\(^{-1}\), no shift in the deposition potential was observed. This small shift of the zinc reduction potential in the negative direction suggests that the presence of flocculant in the solution slightly inhibits Zn nucleation at high concentrations. At 100 mg·L\(^{-1}\), the cathodic peak current decreased from (3.18 ± 0.03)x10\(^{-2}\) to (2.51 ± 0.15)x10\(^{-2}\) A, a decrease of 21%, while at 50 mg·L\(^{-1}\), a slight decrease (2%) was observed, from (3.18 ± 0.03)x10\(^{-2}\) to (3.12 ± 0.05)x10\(^{-2}\) A. The addition of this compound to the solution resulted in an increase of current efficiency during the zinc deposition experiments (Tab. 2). Therefore, the slight decrease of the cathodic current on the Al electrode suggests that the rate of hydrogen evolution may be lower on the deposit formed in the presence of this compound.

The voltammograms obtained using solutions containing the collector for zinc demonstrated a large decrease of the cathodic current over the whole potential range (Fig. 5b). A higher cathodic potential during deposition may support the increase of the cell voltage, as previously discussed. Therefore, this organic impurity has a strong inhibiting effect on the kinetics of zinc reduction, and the decrease of current efficiency when this collector is added to the synthetic solution may be predominantly driven by inhibition of the metal reduction reaction. This effect could be related to an interaction between the lone pair of electrons on the N atom of the amine group and the positively charged Zn\(^{2+}\) ion.

The voltammograms obtained using solutions with the collector for impurities revealed a slight increase in the average NOP value at 100 mg·L\(^{-1}\) (Fig. 5c). At 50 mg·L\(^{-1}\), no
shift in the deposition potential was observed. At 100 mg·L⁻¹, the average NOP valued increased from 74 ± 1 to 77 ± 3 mV and a slight decrease in the cathodic peak current was measured: from (3.18 ± 0.03)x10⁻² to (2.77 ± 0.02)x10⁻² A, which represents a decrease of about 13%. This shift in the zinc deposition potential in a negative direction indicates minor polarization, suggesting that the presence of this collector in the solution has a small inhibiting effect on metal nucleation.

Finally, in the presence of the lubricating oil, a significant increase in the average NOP value was observed from 74 ± 1 to 104 ± 1 mV, at 50 mg·L⁻¹, and to 114 ± 1 mV, at 100 mg·L⁻¹ (Fig. 5d). This large polarization confirms that the presence of this impurity in the solution has a high inhibiting effect on Zn nucleation, even at low concentrations, likely because of the physical adsorption of molecules on the electrode surface. In this case, as previously discussed, the reduction of Zn²⁺ occurs only at unblocked sites. The cathodic peak current dropped from (3.18 ± 0.03)x10⁻² to (1.19 ± 0.10)x10⁻² A, at 50 mg·L⁻¹, and to (0.52 ± 0.12)x10⁻² A, at 100 mg·L⁻¹, which represents decreases of about 63 and 84%, respectively. Therefore, the contamination of the solution with the lubricating oil causes the decrease of the cathodic current associated with zinc deposition resulting in decreased efficiency during electrowinning.

3.4. Characterization of the zinc deposits

3.4.1. Morphological analysis

SEM/EDS were used to describe the effects of the organic compounds on the morphology of the Zn deposits. Figure 6 shows typical micrographs. It can be observed that the clusters of hexagonal platelets grew randomly oriented in the organic-free synthetic
solution, and the deposits are apparently smooth (Fig. 6a and 6b). Fig. 6c-d reveals that the Zn deposits obtained in the presence of the flocculant in the solution consist of closely packed nodules of varying grain sizes. This nodular aspect of the metal deposit may be related to the competition between the two-dimensional nucleation (vertical growth) and lateral growth of monoatomic layers. This morphological change could be ascribed to the type of attachment of long organic molecules to the negatively charged Al/Zn surface, but such hypothesis remains to be better investigated.

The zinc deposits obtained from solutions containing the collector for zinc showed a different growth pattern (Fig. 6e). The hexagonal platelets grew predominantly perpendicular to the electrode surface (Fig. 6f), but platelets aligned at lower angles were also observed. This structural change of the metal deposit, which suggests that only nucleation occurs, was ascribed to the interaction between the polar amine group detected in this compound (Tab. 1) and the Zn\(^{2+}\) ion. When the collector for impurities was added to the solution, Zn deposits with a significant amount of pores were produced (Fig. 6g). It is well established that the hydrogen bubbles attached to the Al/Zn surface lead to the formation and growth of pores as the metal deposit forms around the bubbles, before their release. The interval by which the hydrogen bubbles remain attached to the metal electrode depends on the surface tension of the electrolyte (Gabe, 1997).

The zinc deposits obtained from solutions containing the lubricating oil are highly porous (Fig. 6h), which indicates a vigorous hydrogen evolution during electrowinning, and show areas without zinc deposition. The formation of “holes” on the surface may be ascribed to the initial, physical adsorption of organic molecules on the Al/Zn cathode, as discussed for the observed increase of cell voltages (Fig. 2). Thus, the adsorption of organics on the metal surface may affect significantly not only the process, but also the morphology of the deposit being formed.
As previously mentioned, analysis of the Zn deposits obtained from solutions containing the lubricating oil and collector for impurities revealed residual amounts of organics and entrapped ZnSO$_4$ solution on the zinc platelets. ZnSO$_4$ as needle-shaped crystals, were detected at high magnifications and their elemental analyses by EDS confirmed a high content of Zn, S and O. The EDS analysis revealed a high content of C in small spots or droplets visualized on the platelets. It is possible that the presence of small organic spots or droplets (organic films) on the Zn deposits hinder a total removal of zinc sulfate, even after thorough rinsing. The presence of residual ZnSO$_4$ and organics on the final product has practical implications, that is, a larger generation of slag during smelting.

Finally, it is important to report that the addition of organics to the electrolyte caused grain refinement; zinc platelets with minor sizes were visualized by SEM when the flocculant and flotation collectors were added to the solution. The highest effect was observed in the presence of the collector for zinc. It is known that the crystallite size is affected by the number of grain-producing dislocations during electrocrystallization (Oniciu and Mureșan, 1991). Thus, factors that promote disorder in the growing crystal contribute to reduce the grain size of the metal deposit. The adsorption of organic molecules on the Al/Zn surface may inhibit surface diffusion of ad-atoms towards the growing centers, thereby creating disorder during the incorporation of these ad-atoms into the crystal lattice.

3.4.2. Structural analysis

Table 3 shows the preferred orientations of Zn deposits obtained from organic-free and organic-containing solutions. Only peaks ascribed to hexagonal zinc (ICDD 04-0831) were detected by XRD. The preferred orientations of the Zn platelets detected in sample
obtained from the organic-free solution are (114), (103), (112), (102), and (101). A minor fraction of crystallites grew with the (100) and (002) orientations.

In the presence of the flocculant in the solution, the preferred orientations changed to (101), (002), (100), (201), and (102) (Tab. 3). In comparison with the growth pattern of the Zn deposit obtained from organic-free solutions, the contamination of the electrolyte with this impurity suppressed the growth of (114), (112), (103), and (102) planes. However, this organic promoted the growth of crystals with the (002) and (101) orientations. A relative increase in the growth rate of platelets with the (100) orientation was also observed. In the presence of the collector for zinc, the order of the preferred orientations of the Zn platelets changed to (110), (101), (112), (100) and (102) (Tab. 3). The contamination of the solution with this impurity suppressed completely the formation of platelets detected for samples obtained from organic-free solutions.

When the collector for impurities was added to the solution, the preferred orientations changed to (101), (103), (112), (102), and (002) (Tab. 3). The presence of this compound suppressed, in a minor extent, the growth of the (114), (112), (103), and (102) planes, but promoted the growth of crystals with the (101) and (002) orientations. These modifications did not cause significant effects on the morphology of Zn deposits. As earlier observed, the morphology of the deposits was mostly affected by the formation of pores (Fig. 6g). Finally, in the presence of the lubricating oil in the solution, the order of the preferred orientations changed to (101), (002), (103), (102) and (112) (Tab. 3). The growth of crystals with the (114), (112), (103), and (102) orientations was largely suppressed, and the growth of crystals with the (101) and mainly (002) orientations was favored.

The changes in the orientation of the zinc crystal support the hypothesis that the adsorbed organic molecules affect the electrodeposition of the metal ion. These molecules prevent the growth of platelets in one specific direction possibly by hindering the diffusion of
ad-atoms, thus inducing different growth rates for different crystal planes. These changes, coupled with the formation of pores on the Zn deposits, led to significant changes of the mechanical properties of this material, as will be discussed in a future publication. When the organic impurities were added to the zinc sulphate electrolyte, guided bend tests revealed the production of deposits with a higher resistance to deformation, but a lower ductility, which may affect the success of the striping stage.

On the basis of the observations made in the current investigation, simple control and optimization procedures were implemented in the industrial operation in order to minimize the detrimental effects caused by organic contamination, such as: (i) better control of the consumption of lubricating oils in all the machinery and installation of trays below the tankhouse cranes for collection of oil droplets; and (ii) optimization of the organic dosage in the flotation and thickening stages.

4. Conclusions

The experimental approach followed in the current investigation allowed identifying the role of some organics in zinc electrowinning, which may be present at residual amounts in the solution that feeds the electrowinning tankhouse, when zinc silicate ores are treated. A flocculant, a collector for zinc silicate, a collector for impurities and anti-foaming agent and a lubricating oil were selected for investigation. The results indicated strong inhibiting effects on zinc deposition when electrolyte is contaminated with non-polar hydrocarbon molecules and molecules containing the polar amine group. The addition of these compounds to the synthetic solution caused significant drops in the current efficiency and altered the morphology and crystal structure of the Zn deposits. In both cases, the organic molecule is assumed to restrict the access of Zn$^{2+}$ ion to the nucleation sites, however, by different
mechanisms: physical adsorption of the insoluble oil on the cathode surface and possible interaction between the amine group and the Zn$^{2+}$ ion. On the other hand, the addition of the flocculant and collector for impurities to the synthetic solution slightly increased the current efficiency, however, the behavior of long chain molecules containing the amide group (flocculant) at the reaction interface has altered the growth pattern of the hexagonal platelets.

Acknowledgements

The present work has been developed within the scope of the AMIRA Project P705B – Improved anode and cathode processes in the electrowinning of base metals. The authors are grateful to the Centre of Microscopy (Breno B. Moreira), XRD Laboratory (Andréia B. Henriques), and Laboratory of Ceramic Materials (Eduardo H. M. Nunes) (UFMG), for the analyses; and Votorantim Metals (Zinc) for providing samples and technical support. The financial support from the Brazilian agencies (CAPES/PROEX, CNPq, and FAPEMIG) is acknowledged as well.

References


Table 1. Functional groups of the organic compounds.

<table>
<thead>
<tr>
<th>Organic</th>
<th>Functional groups</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic 1 – flocculant</td>
<td>Alkyl</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>Amide</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Organic 2 – collector</td>
<td>Alkyl</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>for zinc</td>
<td>Amine</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>Ether</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Organic 3* – collector</td>
<td>Alkyl</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>for impurities and anti-</td>
<td>Carboxyl</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>foaming agent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic 4 – lubricating oil</td>
<td>Alkyl</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>

* Organic groups confirmed by gas chromatography.
Table 2. Zinc electrowinning: Effects of the organic compounds on the average values of CE and SEC.

<table>
<thead>
<tr>
<th>Organics</th>
<th>50 mg·L⁻¹</th>
<th>100 mg·L⁻¹</th>
<th>50 mg·L⁻¹</th>
<th>100 mg·L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic 1</td>
<td>94.1 ± 0.0</td>
<td>94.9 ± 0.0</td>
<td>2636 ± 8</td>
<td>2594 ± 5</td>
</tr>
<tr>
<td>Organic 2</td>
<td>21.6 ± 0.1</td>
<td>21.1 ± 0.1</td>
<td>11672 ± 9</td>
<td>11996 ± 31</td>
</tr>
<tr>
<td>Organic 3</td>
<td>94.2 ± 0.4</td>
<td>93.8 ± 0.1</td>
<td>2629 ± 10</td>
<td>2637 ± 7</td>
</tr>
<tr>
<td>Organic 4</td>
<td>90.7 ± 0.2</td>
<td>90.0 ± 0.1</td>
<td>2770 ± 35</td>
<td>2807 ± 91</td>
</tr>
</tbody>
</table>

Obs.: In the organic-free solutions, CE = 93.7 ± 0.1 % and SCE = 2644 ± 3 kWh·t⁻¹.
Table 3. Effect of the organic compounds on the crystalline structure of the zinc deposits.

<table>
<thead>
<tr>
<th>Organics</th>
<th>Preferred orientations – Miller indices (h k l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic-free</td>
<td>(1 1 4), (1 0 3), (1 1 2), (1 0 2), (1 0 1)</td>
</tr>
<tr>
<td>Organic 1</td>
<td>(1 0 1), (0 0 2), (1 0 0), (2 0 1), (1 0 2)</td>
</tr>
<tr>
<td>Organic 2</td>
<td>(1 1 0), (1 0 1), (1 1 2), (1 0 0), (1 0 2)</td>
</tr>
<tr>
<td>Organic 3</td>
<td>(1 0 1), (1 0 3), (1 1 2), (1 0 2), (0 0 2)</td>
</tr>
<tr>
<td>Organic 4</td>
<td>(1 0 1), (0 0 2), (1 0 3), (1 0 2), (1 1 2)</td>
</tr>
</tbody>
</table>
Fig. 1. FTIR spectra of Organics 1, 2, and 4, with the corresponding main vibrations.
Fig. 1. FTIR spectra of Organics 1, 2, and 4, with the corresponding main vibrations.

Organic 4

Asymmetric stretching mode
C=H (alkane)
Symmetric stretching mode
C=H (alkane)
Asymmetric bend mode
C–H (alkane)
Fig. 2. Effects of the organic compounds on the average values of CV during zinc electrowinning.

Legend: ◆ Organic-free solution; ● 0 mg·L⁻¹; ■ 100 mg·L⁻¹.
(Cont.) Fig. 2. Effects of the organic compounds on the average values of CV during zinc electrowinning.

Legend: ◆ Organic-free solution; ♦ 0 mg·L⁻¹; □ 100 mg·L⁻¹.
Fig. 3. Cathodic cycles (replicate) in organic-free solutions.
Fig. 4. Cathodic cycle in organic-free solutions: Details of the interval -0.81 to -0.87 V at low cathodic currents.
(a) Organic 1

(b) Organic 2
Fig. 5. Cathodic cycles in solutions containing (a) Organic 1, (b) Organic 2, (c) Organic 3, and (d) Organic 4. Legend: □ Organic-free; ○ 50 mg·L⁻¹; △ 100 mg·L⁻¹.
Fig. 6. Typical back-scattered electron images of Zn deposits obtained from (a-b) organic-free solution; solutions with 50 mg·L$^{-1}$ Organic 1 (c-d); Organic 2 (e-f); Organic 3 (g); and Organic 4 (h).
Highlights

- Amine-containing and non-polar compounds inhibited Zn nucleation;
- Amine-containing compound strongly affected current efficiency;
- Amide- and amine-containing compounds altered the growth pattern of Zn;
- Control and optimization procedures were implemented in the industrial unit.