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The effect of magnesium and zinc on indium cementation kinetics and deposit morphology in the presence of and without nonylphenylpolyethylene glycol

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ABSTRACT

Indium cementation on magnesium and zinc at 60 °C and pH 1.2 in the presence and absence of nonylphenylpolyethylene glycol (D1) is investigated. Indium cementation follows first-order kinetics in all experiments. The cementation agent affects indium cementation rate, a side reaction of hydrogen evolution and the morphology of the obtained deposit. Both highest cementation rate and most intensive hydrogen evolution accompanied with the highest dissolution of the cementation agent are found during indium cementation on magnesium. Surfactant D1 substantially inhibits all these processes. The rate of indium cementation on zinc in the presence and absence of D1 is 1.5 or 1.8 times lower compared with that on magnesium.

The variation of the fraction of deposited indium with time was examined according to the shrinking core model. A combination of ash diffusion model and chemical reaction model controls indium cementation on magnesium, while the chemical reaction model dominates during indium cementation by zinc.

Indium deposit morphology depends strongly on the cementation agent. A thick layer of indium (with large or small cracks as well as with formations of bubbles and flakes) is observed on the magnesium surface. A compact smooth deposit of fine crystallites is found on zinc. The presence of D1 causes deposition of more compact and refined deposits on both cementation agents.

The obtained results show two alternatives: using zinc-magnesium alloy and temperature higher than 60 °C to increase indium cementation rate on zinc or using low temperature and magnesium as a cementation agent of indium in the presence of surfactant D1.

1. Introduction

Indium occurs predominantly in the zinc-sulfide mineral sphalerite and is recovered mainly from residues generated during zinc ore processing (Alfantazi and Moskalyk, 2003; Kazanbaev et al., 2004, 2006). Indium content in zinc calcine, zinc cake and Waeltz-oxides varies in the range of 0.001–0.1%. It can also be obtained as a by-product in the course of lead, tin and copper production (Alfantazi and Moskalyk, 2003; Zelikman and Korshunov, 1991).

The cementation (metal displacement) reaction in which noble metal ions in the solution are reduced by a less noble metal (cementation agent) depends on various reaction conditions such as temperature, pH, cementation agent, presence of surfactants in solution, deposit morphology and side reactions (hydrogen evolution). A comparison of standard electrode potentials indicates that only a few metals can be used as cementation agents of indium (− .34 V): zinc (−0.76 V), aluminium (−1.66 V) and magnesium (−2.37 V). Indium cementation on zinc and aluminium was investigated by Vasil'ev et al., 2010. Our previous investigations on copper and silver cementation (Karavasteva, 2005, 2009) revealed an extremely slow cementation rate for aluminium used as a cementation agent.

The cementation of indium on zinc is used to recover it as a sponge material. The indium sponge is electrorefined to produce a cathode indium which is then used as an anode in a second electrorefining stage yielding high-purity indium.

Polyethylene glycols are long-chain nonionic surfactants which are used as levelling and foaming agents during zinc electrowinning and copper electrodeposition (Alfantazi and Dreisinger, 2003; Bozzini and Sgura, 2006; Bozzini et al., 2006; Karavasteva, 1994).

The deposition of metal ions on the surface of cementation agents is a heterogeneous electrochemical process. Electrons for reduction of metal ions are transferred from the anodic sites on the surface of cementation agents to the growing metal deposit. The adsorption of surfactants significantly affects both processes of the dissolution of cementation agent and the deposition of cemented metal. The presence of nonylphenylpolyethylene glycol (D1) during silver cementation on

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zinc, iron, copper and aluminium leads to inhibition of both the dissolution of cementation agents and the side reaction of hydrogen evolution (Karavasteva, 2009). On the other hand, surfactant D1 affects the cementation rate and morphology of the obtained silver deposits. On the other hand, our previous investigations on zinc dissolution in 0.5 M H_2SO_4 containing Co, Sb and Ge indicate that the surfactant D1 presence strikingly reduces both the hydrogen evolution and the quantity of dissolved zinc (Karavasteva, 2011).

The aim of the present paper is to investigate under equal conditions the effect of magnesium and zinc on indium cementation kinetics and deposit morphology in the presence and absence of nonylphenylpolyethylene glycol. The investigation is relevant for the development of hydrometallurgycal methods in manufacture of row indium from solutions obtained during the treatment of zinc calcine, zinc cake and Waeltz-oxides.

2. Experimental

Indium cementation on magnesium and zinc was carried out at 60 °C, at a constant stirring rate (300 min^{-1}) and with 5.10^{-3} mol of a cementing agent from sulphuric acid solutions (5 g H_2SO_4 L^{-1}, pH 1.2) containing 80 mg L^{-1} In^{+3}.The concentration of indium is in accordance with the hydrometallurgical methods in the manufacture of raw indium (Kazanbaev et al., 2004, 2006). The acidification was applied to prevent the deposition of hydroxide precipitates on the surface of the magnesium and zinc particles. The stirring was performed with a glass propeller with large surface. An oxygen-free environment was provided by passing purified nitrogen through the 250 mL thermostated cell 30 min before and during the experiments. Indium cementation was investigated in the absence of surfactant and with 0.030 g L^{-1} nonylphenylpolyethylene glycol (D1).

The magnesium and zinc samples (fractions with dimensions of $-100+80$ µm for magnesium and $-70+50$ µm for zinc) were treated with dilute sulphuric acid to remove any surface oxide layer and washed with twice-distilled water. Water remaining in the treated material was absorbed by pressing the latter with filter paper. The samples were weighed after the above mentioned treatment. Two parallel experiments were carried out for each of experimental series. During the kinetic investigations aliquots of 5 mL were taken from the sulphuric acid solution and analyzed for indium and the corresponding cementation agent using inductively coupled plasma spectrometry (ICPS). At the end of experiments the solution pH changes in the following ranges: from 1.2 to 1.25 for indium cementation on zinc and from 1.2 to 1.35 for indium cementation on magnesium. The cementation products were filtered, washed with twice-distilled water, dried at room temperature and prepared for SEM examination.

3. Results and discussion

3.1. Cementation kinetics

The current indium concentration (C_t) and its initial concentration (C_0) were used to characterize the cementation kinetics. Fig. 1 shows the variation of log (C_t/C_0) with time, obtained in the absence and presence of D1. It is evident that indium cementation follows first-order kinetics in all experiments. The rate constants (K_{Me}), the fractions of metal dissolved during the cementation (in %) and the stoichiometric molar ratio of cementing agent per deposited indium (R_{Me}) are shown in Table 1.

The obtained results indicate that the effect of magnesium and zinc on indium cementation is substantially different. The rate of indium cementation on magnesium in the presence and absence of D1 is 1.5 or 1.8 times higher than on zinc. The intensive hydrogen evolution taking place on magnesium along with indium cementation causes high consumption of magnesium per mol deposited indium. The presence of D1 inhibits both hydrogen evolution and magnesium dissolution resulting in magnesium consumption per mol deposited indium of 26% lower than in the absence of D1. On the other hand, hydrogen evolution during the magnesium dissolution in sulphuric acid solution is more intensive compared with that during the cementation of indium on magnesium.

The reaction occurring between the zinc and acid solution forming hydrogen and zinc ions during the indium cementation is very slow. Indium deposition on a zinc surface substantially inhibits both hydrogen evolution and zinc dissolution. These data are in agreement with the results of Sato et al. (1992) and Yano et al. (1998) concerning the

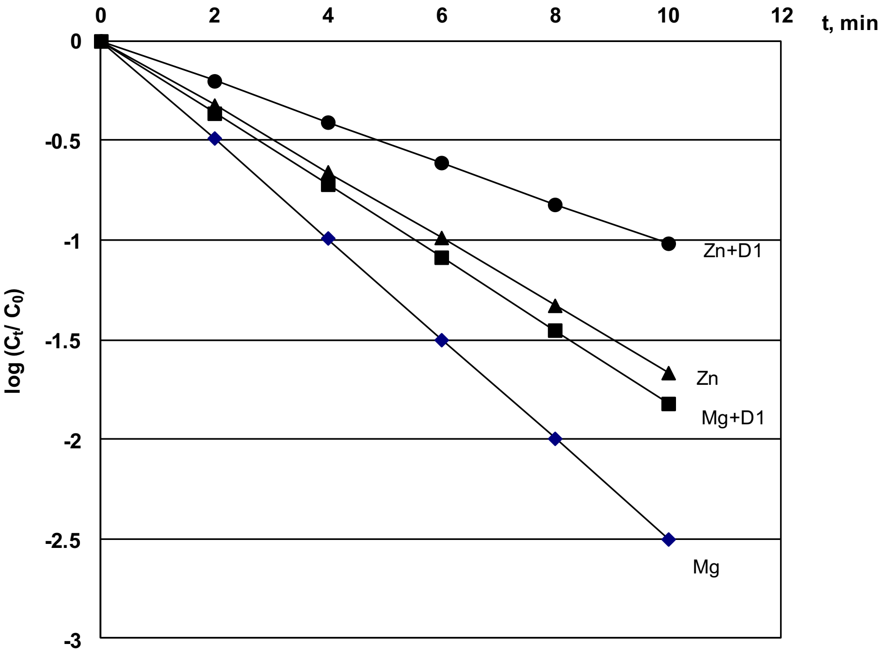

Fig. 1. The variation of log (C_t/C_0) with time t for indium cementation on magnesium and zinc at 60 °C, $5 \cdot 10^{-3}$ mol of cementation agents, pH 1.2 without and in the presence of 0.030 g L^{-1} nonylphenylpolyethylene glycol (D1).