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Development of a rapid measurement of current efficiency in the electrowinning of zinc

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A B S T R A C T

A method for the rapid measurement of current efficiency for the deposition of zinc by a computer controlled anodic stripping technique has been successfully developed and evaluated in the laboratory and in a zinc tankhouse. This method provides rapid measurement of the efficiency within about 3 min from 1 to 2 L of electrolyte at a fixed temperature. Minimum preparation time is involved as the pure lead wire cathode surface can be easily renewed by simply cutting the coated wire to expose a new surface. Reproducible results have been achieved which compare very favourably with those obtained by longer term conventional methods.

It has been demonstrated that the technique can also prove to be useful as a convenient method for the study of cathode morphology and for the nature of the potential/time transients during nucleation and growth of zinc deposits under various conditions. Thus, the effects of the concentrations of various impurities such as selenium, antimony and cobalt on the current efficiency and the morphology of the zinc deposits have been studied. The effects of the addition of additives such as glue and gelatine have similarly been evaluated. The results have been shown to be consistent with published data.

1. Introduction

Approximately 11 million tonnes per year of zinc are produced around the world (Hassall and Roberts, 2010) and it is expected to continue growing at 2–3% per year. About 85–90% of the total is produced by electrowinning. Generally, the electrowinning of zinc is carried out in an electrolyte containing about 60 g/L of zinc and 170 g/L of H_2SO_4 with aluminium cathodes and anodes made of a lead-silver alloy.

The deposition process is known to be accompanied by the reduction of protons with the evolution of hydrogen. The corresponding anodic reaction is the oxidation of water with oxygen evolution.

$$Zn^{2+} + 2e = Zn \qquad E^\circ = -0.76\ V \tag{1}$$

$$2H^+ + 2e = H_2 \qquad E^\circ = 0\ V \tag{2}$$

$$2H_2O = O_2 + 4H^+ + 4e \qquad E^\circ = 1.23\ V \tag{3}$$

The relative rates of Reactions (1) and particularly (2) are known to be extremely sensitive to the impurities present in the electrolyte (Bestetti et al., 2001; de Souza and Tenorio, 2002; Dhak et al., 2011; Guillaume et al., 2007; Ivanov, 2004; Ivanov and Stefanov, 2002; Recendiz et al., 2007; Tripathy et al., 2004). Even though the electrolytic processing of zinc has been widely established and practiced for many years, there continues to be various problems related to the current efficiency of the cathodic process. Zinc producers often use the current efficiency as a key performance indicator given its importance in determining the overall energy consumption. Theoretically, 1.6 kWh is required to deposit 1 kg of zinc but typical energy consumption for zinc electrowinning in current industrial practice is 3.25–3.40 kWh/kg of zinc with 85–95% current efficiency (Huang et al., 2010; Parada and Asselin, 2009). It is not unusual to experience periods of low current efficiency (as low as 75%) at various times in most tankhouses.

The primary source of low current efficiency is the presence of certain metal impurities which enhance the rate of Reaction (2) (Gabe, 1997). In addition, the presence of some organic compounds in the feed solution has also been reported (Majuste et al., 2015) to have an effect on the cathode current efficiency.

In order to counteract the harmful effects of the impurities, various organic additives are added to the electrolyte to inhibit the hydrogen evolution reaction and promote a smoother surface morphology of the cathodes. Numerous researchers have studied various additives and their effect on the current efficiency (Das et al., 1996; Das et al., 1997; de Souza and Tenorio, 2002; Dhak et al., 2011; Guillaume et al., 2007; Ivanov, 2004; Ivanov and Stefanov, 2002; Majuste et al., 2015; Merrin et al., 1997; Stefanov and Ivanov, 2002; Tripathy et al., 1997; Tripathy et al., 1998a; Tripathy et al., 1998b; Tripathy et al., 1999a; Tripathy et

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al., 1999b; Tripathy et al., 2004). Generally, current efficiency is evaluated in small, batch cells employing parallel plates of aluminium as the cathodes and lead-silver alloy as the anode with deposition times varied between 2 and 48 h. The weight of the deposited zinc then is compared to the theoretical weight of the deposit using Faraday's law. Although this method simulates the actual plant operation, it is time-consuming and does not lend itself to rapid evaluation or control of solution purity.

It is clear that there exists a significant opportunity for the development of a method which can rapidly assess the current efficiency achievable by a particular solution. In addition to the need for a measurement that is rapid, the method should also be simple to operate with minimal operator interference. While it is recognized that such measurements have been developed in the past, there are, as far as we are aware, no such units operating in practice. It is further recognized that the effects of some metallic impurities (such as nickel) on the current efficiency are often only apparent after several hours of deposition. Thus, it is unlikely that any such method will be able to produce results in minutes which will agree in absolute terms with those obtained on the plant over 48 h. However, a rapid method may still be able to produce useful relative values that will reflect the quality of the electrolyte.

This paper summarizes results obtained using a simple automated anodic stripping method for the measurement of current efficiency in a period of minutes. In addition, the data collected also gives information on the potential-time transients associated with nucleation and growth of the deposits and allows for relatively rapid preparation of samples for evaluation of deposit morphology.

2. Experimental details

2.1. Cathode materials

Various materials (Al, Sn, Pb, Pb–Ag alloy, graphite) were evaluated as potential cathode materials and were either imbedded in resin or, in the case of wires, insulated with heat-shrink tubing with only the cross-section exposed. Unless stated, the surface of the cathodes were wet polished using 800 and 1200 grit papers and rinsed with deionised water prior to all tests.

2.2. Experimental method

Solutions consisting of 50 g/L of zinc and 170 g/L of sulfuric acid were prepared from a purified stock solution of zinc sulphate and Analar grade sulfuric acid. The addition of nickel and cobalt impurities was made by adding the required volume of the appropriate aqueous solution from respective stock solutions. Antimony was added as potassium antimony tartrate and gelatine and glue were added from stock solutions of 5000 ppm. The temperature of the electrolyte was maintained at 35 °C using a temperature controlled hot plate.

Comparative electrowinning tests in a mini-cell were conducted in a temperature-controlled 2 L glass cell using Pt wire as a central anode surrounded by four identical vertical circular disk cathodes with an inter electrode spacing of 50 mm as shown in Fig. 1.

The cathodes were prepared from pure aluminium (alloy H1S) disks with a diameter of 11.3 mm that were imbedded in circular resin disks. The cathodes were polished with 400 grit silicon carbide paper, washed with deionised water and air-dried before being placed in the cell. At the end of the designated (generally 6 h) deposition time, the zinc deposits were peeled from the substrate and were washed thoroughly with deionised water and allowed to air dry before weighing. Current efficiencies were obtained from the mean of the four masses. The results from the four cathodes agreed to within 1%.

The electrolysis cell used to initially evaluate the measurement of current efficiency by anodic stripping consisted of a 2 L glass beaker with a Perspex lid provided with slits to accommodate the electrodes. A $Hg/Hg_2SO_4/K_2SO_4$(sat) electrode immersed into a Luggin capillary and a platinum wire served as reference and counter electrode respectively. A PAR Model 173 potentiostat-galvanostat was used which was controlled by a data acquisition system based on LabVIEW. The software enabled the system to automatically program the potentiostat to deposit and anodically strip zinc.

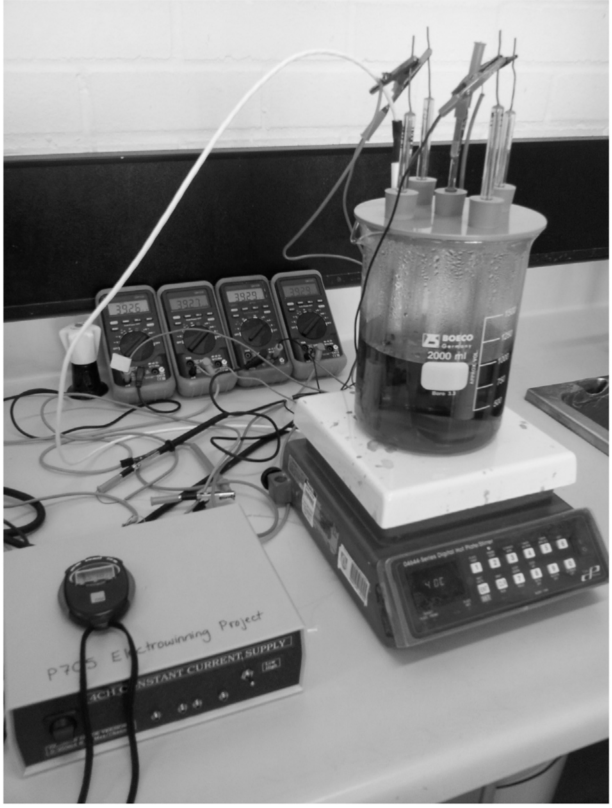

Fig. 1. Mini-cell set-up.

In a typical sequence of operations, a constant cathodic current density of 500 A/m^2 (as practiced in the zinc industry) was first applied to the working electrode in order to produce a zinc deposit for a fixed period of time. The total cathodic charge is obtained by integrating the current over the plating cycle. At the end of plating period, a suitable anodic current is applied to strip the zinc and the potential of the zinc during stripping is monitored. The completion of stripping is signalled by a rapid positive rise in the potential (Fig. 2) and this enables the anodic charge to be obtained. Initial testwork showed that it is necessary to conduct the anodic stripping in two stages in order to ensure that all of the zinc is oxidised from the surface. Most but not all of the zinc is stripped in the first stage at a relatively high current density (current = I_{ah}). A lower current density (current = I_{al}) is applied in the second stage to gently strip the remaining zinc without oxidizing the electrode surface. It was found that a short "cleaning" cycle (current = I_c) at a suitable potential was also desirable after the anodic stripping cycle to remove the last traces of zinc. The overall cycle which generally takes only several minutes can then be repeated a number of times.

The zinc current efficiency in each cycle is the ratio of anodic charge to the cathodic charge .

$$\text{Efficiency} = -\frac{[(I_{ah} \times t_{ah}) + (I_{al} \times t_{al}) + (I_c \times t_c)]}{(I_d \times t_d)} \times 100\% \qquad (4)$$

in which I_{ah} is the high anodic current, t_{ah} time for high anodic current, I_{al} low anodic current, t_{al} time for low anodic current, current, I_c anodic cleaning current, t_c time for anodic cleaning current, I_d the deposition current and t_d the plating time.

Fig. 2 shows the variations in current applied to the electrode (positive currents are anodic) and the corresponding potentials for