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Copper recovery from tin stripping solution: Galvanostatic deposition in a batch-recycle system

S. Silva-Martínez [a,b,*], S. Roy [a]

[a] School of Chemical Engineering and Advanced Materials, Merz Court, University of Newcastle, Newcastle Upon Tyne NE1 7RU, UK
[b] Research Center in Engineering and Applied Science, Autonomous University of Morelos State, Av. Universidad 1001, Col., Chamilpa CP 62209, Mexico

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ABSTRACT

Tin stripping is employed widely for the manufacture of printed circuit boards. At the end of stripping process, in general, 2–40 g/l of Cu along with 150 g/l SnO_2 and ferric and nitrate ions remain in solution. The performance of an electrochemical batch recycle reactor for copper recovery from simulated tin stripping waste solutions was examined by galvanostatic plating. Galvanostatic control was achieved by the application of decreasing constant current steps which followed the concentration decay of metal ions in solution. The concentration decay was predicted by a model based on the batch recycle reactor operating under mass transport control. The current required to reduce the copper ions at the mass transfer limit at each time step was predicted from the model. These were matched against copper reclamation experiments from simulated tin stripping waste solutions using a single volumetric mass transfer coefficient as a fitting parameter. The prediction of the concentration decay of copper ions was in good agreement with the experimental data. It was found that the current efficiency for copper deposition was lowered by nitrates and oxygen present in the electrolyte due to their co-reduction at the cathode. Dissolved Fe^{3+} ions also influenced current efficiency for copper recovery due to the simultaneous reduction of ferric ions. The current efficiency was between 70% and 90% throughout the electrolytic process, which suggests that electrochemical copper reclamation may be a viable process.

1. Introduction

Spent acidic cupric chloride etchant waste and tin stripping waste from printed circuit board (PCB) industry are classified as hazardous wastes [1–3]. The process of stripping the tin from the copper circuit board is usually carried out with a nitric acid based solution, along with a ferric salt to increase the oxidising power of the solution, and other additives [1–4]. Strict environmental directives have been imposed due to the environmental impacts and human health toxicity from PCB manufacturing industry [2–4]. In addition, tin stripping solutions and waste printed circuit boards contain lots of valuable resources which are considered attractive for metal recovery and as secondary resources [5,6].

Copper recovery has been carried out using several processes such as adsorption [7], leaching [2], plating and deposition [8–12], polymer supported ultrafiltration process [13], solvent extraction [14], copper leaching aided with ultrasound [15] and electrocoagulation [16] among others.

Although some researchers have investigated the possibility of recovering metals from simulated tin-strip solutions [1,10–12], a practical process has yet to be conceived. In general, the separation schemes involve filtration to remove the acid and SnO_2 followed by the electrodeposition of metals [3,11,12]. Although these investigators have simulated tin-strip solutions using acidified copper-nitrate solutions, they have used unusually high concentrations of nitric acid [17] or not included ferric ions [12,18], which are not applicable in practice.

Thermodynamic [17] and kinetic [19] analysis for the feasibility of copper and tin reclamation from spent tin-strip solutions have been reported. The thermodynamic work [17] showed that a recovery process is feasible if they consisted of the following stages: (1) HNO_3 recovery could proceed until the solution was pH 3.4, (2) SnO_2 should then be separated from the dissolved copper by filtration, (3) copper could be electrodeposited, and (4) the remaining iron could be recycled or precipitated. Such a process enables both acid and metal recovery, bringing one closer to a zero-emission target. The kinetic analysis of the solution focused on the current efficiency of Cu^{2+} deposition from solutions containing Cu^{2+} and HNO_3 only or HNO_3 with Fe^{3+} ions [19]. That investigation showed that copper could be recovered from acidified solutions at relatively high current efficiencies; the presence of ferric ions in solution

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* Corresponding author at: Research Center in Engineering and Applied Science, Autonomous University of Morelos State, Av. Universidad 1001, Col., Chamilpa CP 62209, Mexico. Tel.: +52 (777) 329 70 84; fax: +52 (777) 329 79 84.
E-mail address: ssilva@uaem.mx (S. Silva-Martínez).

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can compromise the efficiency of the process significantly due to a corrosion reaction.

In this work we have examined the performance of the copper deposition in a batch recycle reactor using simulated tin-strip solutions (after the acid and tin separation steps). The simulated solutions therefore contain $CuNO_3$, HNO_3 and ferric ions. The solution concentration of copper was 0.03 or 0.3 M with 0.1 M HNO_3, and a ferric ion concentration of 0.01 and 0.05 M. The range of metal ion concentration reflects the low and high concentrations of metal which may exist in the waste tin strip solution. A batch recycle reactor with a flat Cu cathode plate and a platinized Ti-mesh anode were used in metal recovery. The advantage of this system is that once the metal is plated out, a highly pure copper plate is obtained, which could be directly sold in the market. The system was operated under galvanostatic control, using a mass transfer controlled metal plating model. Such an operation should enable metal to be plated at the highest possible rate and maximum current efficiency.

The specific aims of this work are (a) to study the influence of ferric ions on the electrochemical recovery of copper from acidic nitrate electrolytes under galvanostatic mode in a batch recycle electrochemical reactor since these had been identified as contributors to lower current efficiencies and (b) to assess the performance of the galvanostatic approach used for copper recovery which is based on the application of controlled constant current steps. The current steps are calculated using a theoretical analysis similar to that used for potentiostatic control which predicts the concentration of depositing ions at the electrode. The prediction of the copper concentration decay during the electrochemical process assumes that copper was deposited under mass transport control.

2. Model

Copper can be reduced at the highest possible rate under the mass transport limiting conditions. If the concentration of copper concentration were known (or predictable), at each time step (j), then it can be used to fix the applied current to the mass transfer limiting value ($I_L(t_j)$) corresponding to the instantaneous metal concentration at that time ($C(t_j)$). The limiting current for two-dimensional electrode is related to the ion concentration:

$$I_L(t_j) = -nFV_R k_m A_s C(t_j) \tag{1}$$

where $I_L(t_j)$ is the limiting current at each time step j, n is the number of electrons involved, F is the Faraday constant, V_R is the reactor volume, k_m is the mass transport coefficient, A_s is the active electrode area per unit reactor volume, and $C(t_j)$ is the concentration at time t_j. The combined parameter $k_m A_s$ (known as 'volumetric' mass transport coefficient [20]) is commonly used as a figure of merit for the electrochemical process because the changes on the electrode surface during the deposition make difficult the calculation of k_m and A_s separately [20].

Taking into account the concentration–time relationship for a two-dimensional electrode given by Eq. (2) [21,22], the limiting current, $I_L(t_j)$ from Eq. (1), can be expressed by Eq. (3),

$$C(t_j) = C(0)\exp(-k_m A_s t_j) \tag{2}$$

$$I_L(t_j) = -nFV_R k_m A_s[C(0)\exp(-k_m A_s t_j)] \tag{3}$$

where $C(0)$ is the initial metal concentration in solution. Eq. (2) can be re-written in a logarithmic form [22], as shown below

$$\ln\left[\frac{C_L(t_j)}{C(0)}\right] = -k_m A_s t_j \tag{4}$$

This means that a batch recycle system under mass transport will show a linear dependence of $\ln[C(t)/C(0)]$ *vs.* t [21]. From the $\ln[C(t)/C(0)]$ *vs.* t plot the 'volumetric' mass transport coefficient ($k_m A_s$) is equal to the slope, S, value ($k_m A_{s(Slope)} = S$). Using this new value, Eq. (2) is transformed into:

$$C(t_j) = C(0)\exp(-S\, t_j) \tag{5}$$

Eq. (5) allows one to predict the metal concentration decay, $C(t)$, with time under the actual experimental conditions.

The current efficiency, $\Phi(t_j)$, for each time step can be calculated independently from the relationship between charge passed for metal recovery and the total charge passed in the recovery process, given by Eq. (6):

$$\Phi(t_j) = \left(\frac{\sum_{j=1}^{n}[I_{L(slope)}(t_{j-1}) * (t_j - t_{j-1})]}{\sum_{j=1}^{n}[I_L(t_{j-1}) * (t_j - t_{j-1})]}\right)100 \tag{6}$$

where $I_{L(Slope)}$ can be calculated from Eq. (3) using the $k_m A_{s(Slope)}$ value.

The model shows that for a current efficiency of 100% for metal recovery, the profile of the concentration decay, can be obtained for each time step (or by varying t from $t = 0$ to $t = t_j$) calculating $C(t_j)$ with Eq. (2). $I_L(t_j)$ can be also calculated for each time step as a guide for changing the applied current to the cathode. In this case, the applied current is decreased at each time according to the decrease in the limiting current due to diminishing copper concentration in the electrolyte as the deposition progresses.

An example of this analysis is presented in Fig. 1. The figure shows the approach for model predictions of the copper concentration decay (solid line) and the controlled current steps (dashed lines), using Eqs. (2) and (3) respectively, for copper recovery under mass transport control, considering the 'volumetric' mass transport coefficient ($k_m A_s$, from Table 2). This figure shows that 17 controlled current steps are needed to be applied to the cathode to remove 90% of copper ions from the electrolyte solution over a period of 17 h, if the current efficiency were 100%.

This approach should allow maximum yield for metal recovery whilst maintaining the lowest energy consumption (since the potential is fixed at a minimum value). The number of time steps can be fixed by estimating the time required to deplete 90% of metal ion assuming mass transfer controlled metal deposition conditions. Although any number of current steps can be used, in practice, 4–7 steps should be sufficient to provide reasonable agreement with theoretical predictions.

3. Experimental

3.1. Electrolyte composition of simulated tin-strip solution

As has been shown in previous work the copper concentration in the waste solution can vary between 0.03 and 0.3 M [17,19].

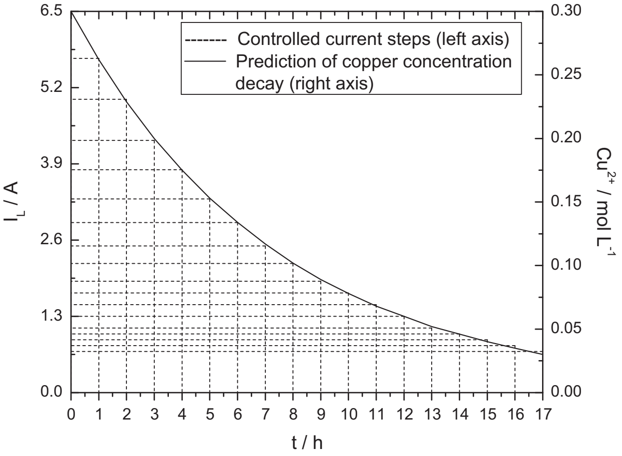

Fig. 1. Model predictions of copper concentration decay and the controlled current steps *vs.* time, for a batch recycle reactor from an electrolyte initially containing 0.3 mol L^{-1} of copper ions.