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Electrochemical copper recovery from galvanic sludge

Pham T. Huyen[1], T.D. Dang[1], Mai T.Tung[1], Nguyen T.T. Huyen[1], T.A. Green[2] and S. Roy*[2],

[1]School of Chemical Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam

[2]Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, UK

Corresponding author:

*Prof. Sudipta Roy

Department of Chemical and Processing Engineering, University of Strathclyde, Glasgow,

United Kingdom

Tel: +44 141 548 2371

e-mail: sudipta.roy@strath.ac.uk

Abstract

The feasibility of recovering copper from electronic industrial waste mud (galvanic sludge) using a combination of leaching and electrowinning has been examined. Leaching with sulfuric acid was found to be the most efficient and cost-effective way of extracting the copper from the sludge, and the optimum acid concentration and time were determined. The copper was then extracted by electrowinning in a batch recirculation electrochemical reactor (Porocell™) employing a three-dimensional carbon felt cathode. The influence of applied current, flow rate and the presence of other metal ion contaminates on the rate and current efficiency of copper electrowinning was investigated. An analysis of the experimental data showed that the current efficiency was lower than unity even though the limiting current for copper deposition was not exceeded. This low current efficiency was attributed to the occurrence of a side reaction, most likely the reduction of dissolved oxygen or oxygen-induced corrosion. The influence of this side reaction can be minimized by operating at relatively high currents and low flow rates.

I. Introduction.

Metal finishing operations in the electronics industries typically produce high levels of waste whose disposal can pose a significant environmental challenge [1-3]. An example of such electronic waste is galvanic sludge which arises from the precipitation of rinse water and spent electrolytes and etchants in electroplating and electronics plants [1]. It is estimated that the European Union generates around 10^5 tons of such waste annually [2] while global production exceeds 10^6 tons per year [3]. The most common method of disposing of this waste is as landfill but this is not a very environmentally friendly approach.

An alternative to this is to stabilise the material in a cement or clay-based ceramic matrix so that potentially hazardous metal ions cannot be leached out [4-6]. For example, the material can be incorporated into clay bricks so they can be reused in the construction industry [6]. However, while this approach is more environmentally friendly than landfill, it has the disadvantage that the material is considered only as waste. Since electronic plants are increasingly being constructed in developing countries such as Vietnam an effective means of disposing of this waste which also allows the recovery of potentially valuable metals such as copper is highly desirable.

Other methods of treating galvanic sludge consider the material as a resource rather than as simple waste and are focussed on reclaiming high-value metals such as copper [7-16]. In general such methods have concentrated on pyrometallurgical [7,8] and hydrometallurgical [9-15] approaches for metal extraction or, in some cases, a combination of both [16]. Waste treatment methods employing pyrometallurgical techniques have received limited attention mainly because of disadvantages associated with its high energy consumption and the low purity

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of the final product [9]. Combined hydro- and pyro-metallurgical techniques have mainly focussed on sulphate roasting but the recovery rates of the target metals were generally low [16].

In contrast, hydrometallurgical routes to treating galvanic sludge appear more promising and a number of studies [9-15] have been performed. Typically this involves leaching using acidic or basic lixiviants, although in some cases [10] bio-leaching has also been employed. The advantage of leaching with sulphuric acid is the low cost and high efficiency but the selectivity to particular metals is low [17,18]. In contrast, base leaching with ammoniacal lixiviants is typically more selective but less efficient [17,18]. After leaching, metal ions can be recovered using a variety of techniques including cementation [9,11], solvent extraction [12], precipitation [13] and electrowinning [14,15]. The latter technique has the possibility of extracting metals with high efficiency, low energy consumption and with good compatibility with acidic and basic lixiviants, but has received relatively little attention.

In this paper, the treatment of galvanic sludge for copper recovery using a combination of leaching and electrowinning is described. The proposed process flowsheet is summarised in Figure 1. The initial stages involve acid or base leaching of the galvanic sludge followed by filtration to remove the insoluble residue. Subsequently, electrowinning of copper is performed from the filtered leaching solution. This employs a batch recirculation electrochemical reactor employing a low-cost, high surface area carbon felt electrode [19,20]. The high surface area/volume ratio of this three-dimensional (3-D) electrode allows the efficient extraction of metal ions even from relatively dilute solutions. The final process step, which is not presented here, involves incineration of the carbon felt in a furnace to obtain a high purity copper product.

The reactor employed in this study, along with other systems employing three-dimensional electrodes, is normally used to remove metal ions from dilute waste streams [21-23]. In this work we show that it can also be employed to electrodeposit metals from more concentrated solutions. A general problem with electrowinning from dilute solutions is that the extraction efficiency is often low, even if 3-D electrodes are employed [21,22]. This is compounded by the issues that metal ion concentrations typically have to be reduced to very low levels (e.g. < 10 mg l^{-1}) before they can be discharged into the environment [22]. However, this is not a requirement in the current process as the solution can be reused to leach additional batches of sludge (Figure 1) and the presence of even relatively high levels (e.g. 100 - 500 mg l^{-1}) of remaining copper is not expected to reduce the efficiency of the leaching.

II. Experimental.

2.1. Leaching

The leaching experiments were carried out in a 500 ml beaker with 100 ml of leach solution and the desired amount of copper-containing galvanic sludge. The sludge was obtained from the Hanoi Urban Environment One Member Limited Company (Urenco). The composition of the galvanic sludge was determined by ICP analysis after dissolution in nitric acid and dilution is shown in Table 1. The concentration of copper was approximately 21.5% wt.%. The contents were heated to 35 °C and stirred at 600 rpm for periods of 15 minutes to 3 hour. Each leaching experiment was performed at 3% or 10% (weight/volume) of waste sludge. The leaching solutions were then cooled and filtered. The copper concentration was determined using UV-Vis spectrophotometry (Jenway 7315 specrophotometer) after constructing a suitable calibration

curve. A wavelength of 805 nm was chosen [24] to avoid interference from the absorbance of ferric and nickel ions.

The concentration of copper and other trace metal ions was also measured by by ICP-MS (Perkin Elmer – Vietnam Metrology Institute). XRD analysis of the galvanic sludge and leaching residue were carried out at room temperature using Bruker D8 Advance diffractometer with Cu Kα radiation. The intensity data were measured by step scanning in the 2θ range between 5 and 70°, with 2θ step size of 0.05° and an acquisition time of 0.5 s per point.

2.2. Copper Electrowinning

The copper electrowinning experiments were performed using either simulated solutions prepared by dissolving $CuSO_4$ in 0.5 M H_2SO_4 or real solutions obtained by leaching 3% w/v galvanic sludge in 0.5 M H_2SO_4 and filtering it. The simulated solutions were initially used to characterise the metal ion recovery process, to avoid any complications arising from the co-deposition of impurity species. In both cases the nominal copper concentration was 7 g l^{-1}. The volume of the real and simulated solutions added to the reactor was 3 litres. The electrowinning experiments were performed under galvanostatic conditions using a DC power supply with the solution maintained at room temperature. No attempts were made to remove dissolved oxygen and O_2 evolution at the anode ensured that the solution was saturated with oxygen.

The electrowinning experiments were performed in a Porocell™ [19] batch recirculation electrochemical reactor (C-Tech Innovations). This system comprises a reservoir tank, electrochemical cell (Porocell), recirculation pump, flow-meter, drain and control valves and is similar in layout to earlier flow-channel reactors [20]. The electrochemical cell body is constructed from a cylindrical polypropylene housing fitted with a removable lid. The electrolyte

flow (typically 100 - 300 l h^{-1}) enters through an inlet at the bottom of the cell. It then flows radially outward through the cylindrical carbon felt electrode toward the anode before exiting the cell through an outlet in the lid (Figure 2). The cathode consists of carbon felt wrapped around a plastic mesh support. The 2D area is 150 cm^2 based on the cylindrical dimensions of the carbon felt cathode, but the actual (i.e. 3D) area is typically 10^2 - 10^3 times larger [19,22]. Figure 3 shows images of the unused carbon felt cathode and after repeated copper electrowinning experiments. A titanium cathode current feeder is positioned between the felt and the plastic mesh, and passes through the cell lid. The anode is a cylindrical titanium sheet with a coating of mixed tantalum/iridium oxides suitable for the evolution of oxygen. The anode is placed against the cell body and electrical connection is made directly through the cell wall.

The composition and microstructure of the unused and used carbon felt cathodes were analyzed using a Field Emission Scanning Electron Microscope (JEOL JSM-7600F in AIST, HUST, Vietnam). The concentration of copper in the electrolyte solution was analyzed by UV-Vis spectrophotometry using the method described in section 2.1.

III. Results

3.1 Leaching

To determine the optimum copper leaching process for the 3% w/v galvanic sludge, both basic and acidic lixiviants were trialled (Table 2). Copper concentrations were determined by UV-Vis spectrophotometry but also by ICP-MS. The difference between these two methods was approximately 7%. All other metals were determined by ICP-MS. The results in Table 2 indicate that sulphuric acid is more efficient for copper leaching than ammoniacal lixiviants but,

generally, not as selective. This is in good agreement with previous studies [17,18]. The ammoniacal lixiviants are more selective against iron and chromium the acidic ones, but selectivity against nickel and manganese is similar for all lixiviants. The presence of iron (especially in the form of Fe^{3+}) is particularly important as it may reduce the efficiency of the subsequent electrowinning step [25,26]. Despite this potential issue, the higher amounts of extracted copper and lower cost of the acid leachant made it the preferred option for developing the process.

The effect of the sulphuric acid concentration on the amount of copper extracted is shown in Figure 4. As expected, for the 10% w/v solution the amount of copper recovered is correspondingly higher than for the 3% w/v solution under equivalent conditions. The amount of recovered copper is relatively low for 0.1 M H_2SO_4 but is significantly higher as the acid concentration is increased. However, for the 3% w/v solutions there is little improvement in the amount of extracted copper 0.5 M H_2SO_4, so that all subsequent leaching trials were performed at that acid concentration. Similar behaviour was reported in a number of earlier studies [9,13,17]. Figure 5 shows the influence of leaching time on the amount of copper extracted at different acid concentrations. It can be seen that the initial increase in copper concentration is rapid but eventually reaches a limiting value after approximately 90 - 120 min. For this reason, 90 minutes was chosen as the processing time for the galvanic sludge leaching step. These findings are in good agreement with a number of previous studies [9,11,13,17] of the time and concentration dependence of copper leaching in sulfuric acid.

Figure S1(a) (supplementary information) shows the XRD patterns of the copper-containing waste sludge prior to leaching, and also the leaching residue. The data relating to their composition is shown in Table 3. The main composition of the galvanic sludge is calcite (94 - 96

wt% $CaCO_3$) with a trace amount of silica (1- 2 wt% SiO_2). This finding is not unexpected as the pre-treatment of electronic industrial waste water involves the addition of large amounts of calcite and calcium hydroxide to precipitate out the metal ions. Similar XRD studies of galvanic sludge have also shown predominantly calcite and quartz [9,10]. Copper in the form of $CuCO_3$ is also detected at a concentration of 2 - 3 wt%. Note that other metal precipitates may be amorphous in nature [9] or have lattice-anomalies [10] and are therefore not identifiable by XRD.

After leaching and filtering process, the remaining solid was also analysed by XRD and shown to be predominantly gypsum ($CaSO_4$) with a trace amount of SiO_2 (Figure S1(b) – supplementary information). No $CuCO_3$ was detected which confirms that the leaching process had removed the majority of the copper from the sludge. The $CaSO_4$ is formed by the reaction of calcite with sulfuric acid during the leaching process and has been reported in a number of other studies [9,17]:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \qquad (1)$$
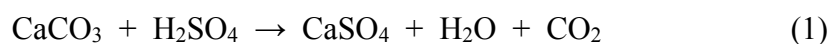
3.2 Electrowinning

Initially the recovery of copper ions from simulated leaching solutions containing 7 g l^{-1} copper in 0.5 M H_2SO_4 was investigated. The effect of the applied current on the rate of metal ion recovery at an electrolyte flow rate of 200 l h^{-1} is shown in Figure 6. As expected, the rate of copper depletion increases with current density, and at 18 A the concentration has been reduced to near zero in less than two hours. The change in metal ion concentration as a function of time in a batch recirculation electrochemical reactor under galvanostatic control has been studied

previously [27-29]. In the regime of current-limited control (i.e. below the limiting current) a linear decrease in concentration, C, is expected according to [28]:

$$C(t) = C_0 - \frac{\phi I t}{nFV} \qquad (2)$$

where C_0 is the initial concentration, ϕ is the current efficiency I is the applied current, t is the time, n is the number of transferred electrons, F is the Faraday constant and V is the solution volume. Below the limiting current, and in the absence of any electrochemical side reactions, it is expected that $\phi = 1$.

At some later time ($t = t'$) when the copper concentration is so depleted that the applied current exceeds the limiting current, the concentration decays exponentially with time according to [28]:

$$C(t) = C' \exp\left(\frac{-k_L A}{V}(t - t')\right) \qquad (3)$$

where k_L is the mass transport coefficient, A is the electrode area and C' is the concentration corresponding to $t = t'$. Closer inspection of Figure 6 indicates that at low applied currents and short times the metal ion recovery is occurring under current-limited control and a linear decrease in concentration is observed. At intermediate currents (6 – 9 A) the linear region extends to at least $C(t)/C_0 < 0.1$. However, the data obtained at highest current (18 A) displays some evidence of an exponential decay in concentration at longer times indicating the transition to mass transport control.

The influence of flow rate on the metal ion recovery is shown in Figure 7 for two different applied currents. As in the case of Figure 6 there is a general linear decrease in concentration with time for flow rates of 100 - 300 l h^{-1} which is indicative of a current-

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controlled process. Interestingly, reducing the flow rate tends to increase the rate of metal ion recovery. Referring to equation (2) the only plausible explanation for this behaviour is that the current efficiency, ϕ, is dependent on the flow rate. This is an important finding and will be analysed in detail in the Discussion section.

The final copper recovery experiment performed utilised a real solution obtained by leaching the copper-containing sludge (3% w/v) with 0.5 M H_2SO_4 and then filtering it. The initial copper concentration was 7 g l^{-1}, the flow rate 100 l h^{-1} and the applied current was 9 A. The results of this experiment are shown in Figure 8 alongside the equivalent data for the simulated leaching solution. In both cases the rate of metal ion recovery is very similar; indicating that the presence of trace metals (e.g. Fe, Mn and Ni) does not significantly influence the rate of metal recovery. It has been noted [25,26] that the presence of ferric ions can reduce the efficiency of copper electrowinning, but under the present electrochemical conditions this does not seem to be an issue.

3.3 Analysis and Processing of Carbon Felt Cathode

The structure of the carbon felt electrode was examined by SEM before and after electrowinning and representative images are shown in Figure S2 (supplementary information). The electrowinning conditions were as follows: $I = 9$ A, 200 l h^{-1} flow rate and an experimental duration of 3 hours. The micrographs indicate that the felt consists of an array of randomly dispersed, cylindrical carbon fibres with diameters of approximately 15 μm. This is comparable to the structures reported earlier [30,31] for carbon felt electrodes. In the post electrowinning images there is clear evidence of copper deposition on the individual fibres.

The carbon felt cathode can be re-used but once sufficient copper has been deposited so that the flow is reduced or blocked it has to be replaced. The metal loading of the cathode can be conveniently monitored by measuring the pressure drop across the reactor [21]. The final step of the process would normally be the incineration of the carbon felt in a furnace [30]. Only the carbon is consumed in the furnace leaving behind high purity copper. The presence of the carbon improves the quality of the recovered copper by scavenging oxygen or other constituents that would otherwise reduce its purity.

IV. Discussion

While the results obtained in the electrowinning experiments are broadly as expected, the unusual dependence of the metal ion recovery rate on the flow rate required further investigation. To enable this, equation (2) was fitted to the linear portion of the concentration versus time plots in order to extract the current efficiency. These results are summarised in Table 4 and Figure 9 for all of the electrowinning experiments performed. As noted earlier, because the limiting current is not exceeded in this linear region, $\phi = 1$ is often assumed. However, the results shown in Table 4 and Figure 9 indicate that $\phi < 1$ in all cases and it tends to be highest at low flow rates and high applied currents.

The most plausible explanation for the dependencies observed in Table 4 is that a side reaction is occurring at the cathode which reduces the overall current efficiency for copper deposition [29,32]. The current associated with this side reaction ($I_s = (1-\phi)I$) is shown in Table 4. At a fixed flow rate I_s is essentially independent of the total applied current, while at a constant total current I_s increases with the electrolyte flow rate. Collectively these results

indicate that the current efficiency is been influenced by a parasitic side reaction which is under mass transport control.

In order to identify the side reactions responsible for the loss of faradaic efficiency it is necessary to examine all possible electrochemical reactions occurring in the reactor. For the simulated solutions the electrochemical processes are:

Anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{4}$$

Cathode:

$$Cu^{2+} + 2e^- \rightarrow Cu \tag{5}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{6}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{7}$$

Ideally, below the limiting current for copper deposition only reaction (5) should occur and reaction (6) can only commence above it. However, the linear plots shown in Figure 6, 7 and 8 indicate the absence of mass transport control for copper deposition so this reaction can be ruled out as an explanation for the low current efficiencies observed. The anode reaction will leave the solution saturated with oxygen which can then be reduced according to cathode reaction (7). This reaction occurs at a more anodic potential than copper deposition and, due to its relatively low concentration, will generally occur under mass transport control [32].

In the case of the real solutions obtained by leaching galvanic sludge, the presence of trace metal ions allows the possibility of additional cathode reactions such as:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{8}$$

$$Ni^{2+} + 2 \text{ e-} \rightarrow Ni \qquad\qquad\qquad (9)$$

The reduction of ferric ions occurs at more noble potentials than for copper but the data in Table 4 indicates that at low concentrations it does not adversely influence the current efficiency of copper deposition. Nickel deposition occurs at less noble potentials than for copper so should not co-deposit unless the limiting current for copper deposition is exceeded.

The phenomenon of low faradaic efficiency in electrowinning when the limiting current for metal ion deposition has not been exceeded has been reported in a number of other studies employing three-dimensional cathodes [33-39]. For example, Tsapkh and Volkov [33] reported that during electrowinning with fluidised bed electrodes (FBE) the unusual mass transport and potential distribution of these 3-D electrodes can lead to an enhancement of the parallel oxygen reduction reaction thereby lowering the current efficiency. In contrast, under equivalent conditions using 2-D electrodes the influence of oxygen reduction is negligible. Other researchers [34-36] employing FBEs have also noted current efficiencies less than unity and its tendency to increase at higher currents. This has been attributed to corrosion of copper by oxygen generated at the anode [34,35] or by the development of anodic (i.e. dissolution) zones in the electrode bed [36]. In some cases the use of inert gas sparging or soluble anodes were shown [35] to improve the current efficiency, which seems to implicate oxygen either as a direct reduction or as a corrosion process.

Similar effects have also been observed in other three-dimensional electrode systems [37-39] and mainly arise from the highly non-uniform potential distribution [21,28]. These have been analysed [21] for a number of 3D flow-by electrodes with a cylindrical geometry, and these

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correspond closely to the Porocell configuration shown in Figure 2. Near the cathode feed the potential (i.e. the current density) is expected to be highest. However, moving radially outwards toward the anode, the potential and therefore the deposition rate will gradually decrease. Under some conditions the potential may become insufficient to allow deposition to occur [28]. It is also possible that sections of the cathode may adopt a potential close to the open circuit potential for oxygen or ferric ion induced copper corrosion. In these regions any electrodeposited copper will freely corrode.

As an example, during the electrowinning of copper using a spouted bed electrode (SBE) reactor [37] it was noted that the presence of oxygen reduced the rate of metal ion recovery and the current efficiency. This was attributed to the corrosion of copper by oxygen and the effect could be substantially reduced by sparging the solution with an inert gas. Similar corrosion effects were also observed during the recovery of nickel ions in a SBE [38]. Scott [39] also reported low current efficiencies during copper recovery in a moving bed electrode (MBE) and which increased with applied current. This was partially attributed to corrosion of the copper by oxygen generated at anode.

A 2012 study by Farrell [40] examining electrowinning from copper-loaded ion exchange media using a Renocell™ electrochemical reactor is particularly relevant. This system employs a 3-D carbon felt cathode in a configuration which is nearly identical to the Porocell [30]. For solutions containing 0.5 - 1 g l^{-1} Cu in H_2SO_4 at pH = 0.5 they observed: (i) current-limiting behaviour and (ii) a tendency for the metal ion recovery rate to decrease at high flow rates. They also reported that the current efficiency was higher at high currents (*cf.* ϕ = 0.42 - 0.61 at 7.5 A; ϕ = 0.34 - 0.48 at 5 A) and, at a fixed current, declined with increasing flow rate. Collectively, these results are in good agreement with the present study (Figure 9). The authors attributed

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some of the observed effects to hydrogen gas evolution blocking the active cathode area or, more plausibly, arising from the complex geometry and current distribution of the 3-D cathode. The possible influence of oxygen reduction or a corrosion process was not considered by the authors.

Comparing the present results to these previous findings it seem likely that the reduced current efficiency observed is due to either: (i) direct reduction of oxygen or (ii) oxygen induced corrosion. Regardless of the exact mechanism, the rate of this parasitic reaction will be necessarily controlled by the transport of to the electrode surface. The experimental results indicate that the influence of this side reaction can be minimised by operating at low flow rates and high applied currents. As reported by others [36-38] the use of inert gas sparging may also improve the current efficiency. Operating at higher temperatures would also reduce the solubility of O_2 and therefore its influence on the current efficiency for copper deposition, but with an increased energy cost. Another alternative is to use a 'divided' Porocell configuration which separates the anode and cathode processes using a cation exchange membrane [19]. This will prevent O_2 generated at the anode reacting at the cathode but with some increase in the complexity and cost of the reactor.

In the case of the real solutions, there is an additional possibility that the co-reduction of ferric ions also contributes to a loss in current efficiency. Analogous with the situation for oxygen, this can occur by a direct reduction or a corrosion process [25,26] and, due to the low iron concentration (< 1000 ppm), will generally occur under mass transport limited conditions. To investigate this possibility, we have calculated the ratio of the limiting current for O_2 and Fe^{3+} reduction using their respective concentrations and diffusion coefficients in 0.5 M H_2SO_4 [32,41]. These calculations indicate that, even if we assume all the iron in solution is in the form of Fe^{3+}, the limiting current is less than 25% that for O_2. The fact that the current efficiency is

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similar in the real and simulated solutions (Figure 8 and Table 4) also indicates that the role of ferric ion reduction is a relatively minor one.

A final consideration in the copper recovery experiments is the overall energy consumption [28]. The electrical energy requirements for experiments 1 - 4 have been calculated from the cell voltage and current efficiency, and are reported in Table 4. They typically ranged from 2.5 − 4.6 kWh kg. These results are comparable to the values obtained for other 3D electrodes when electrowinning from concentrated copper solutions [39,40] but higher than those reported [25] for conventional copper electrowinning (*ca*. 2 kWh kg). Notably, the conditions corresponding to the highest current efficiency also resulted in the highest energy consumption, so that optimisation of the copper recovery involves careful consideration of both of these factors.

V. Conclusion

A process flow for the recovery of copper from galvanic sludge waste using a combination of leaching, filtration and electrowinning has been developed. Acid leaching was found to be an effective means for extracting the copper from the sludge, and the optimum conditions were 0.5 M H_2SO_4 and leach time of 90 minutes. The leaching was not very selective compared to base leaching but the presence of trace metal ions such as manganese, iron and nickel did not adversely affect the subsequent electrowinning step.

Copper was then recovered by electrowinning in a batch recirculation electrochemical reactor employing a 3-D carbon felt cathode. The influence of applied current, flow rate and the presence of other metal ions on the rate and efficiency of copper electrowinning

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was investigated. It was found that the current efficiency was low (typically $\phi = 0.30 - 0.90$) even though electrowinning was performed below the limiting current for copper deposition. The low current efficiency arises due to the occurrence of a side reaction, most probably the reduction of dissolved oxygen or oxygen-induced corrosion.

The influence of this parasitic side reaction can be minimized by operating at relatively high currents and at low flow rates. For example, electrowinning at an applied current of 18 A and a flow rate of 200 l h^{-1} resulted in a current efficiency of $\phi = 0.90$ and > 99% of the copper was recovered in less than 2 hours. However, under these conditions the energy consumption was higher than at lower currents. Further optimisation of the electrochemical reactor is planned, and these results along will be reported in a subsequent paper. In addition, issues associated with the recycling of the leachant such as control of pH, viscosity and conductivity, and the build-up of impurities will also be addressed. This will be followed by an industrial-scale trial in Vietnam using galvanic sludge waste supplied by Urenco.

Acknowledgements

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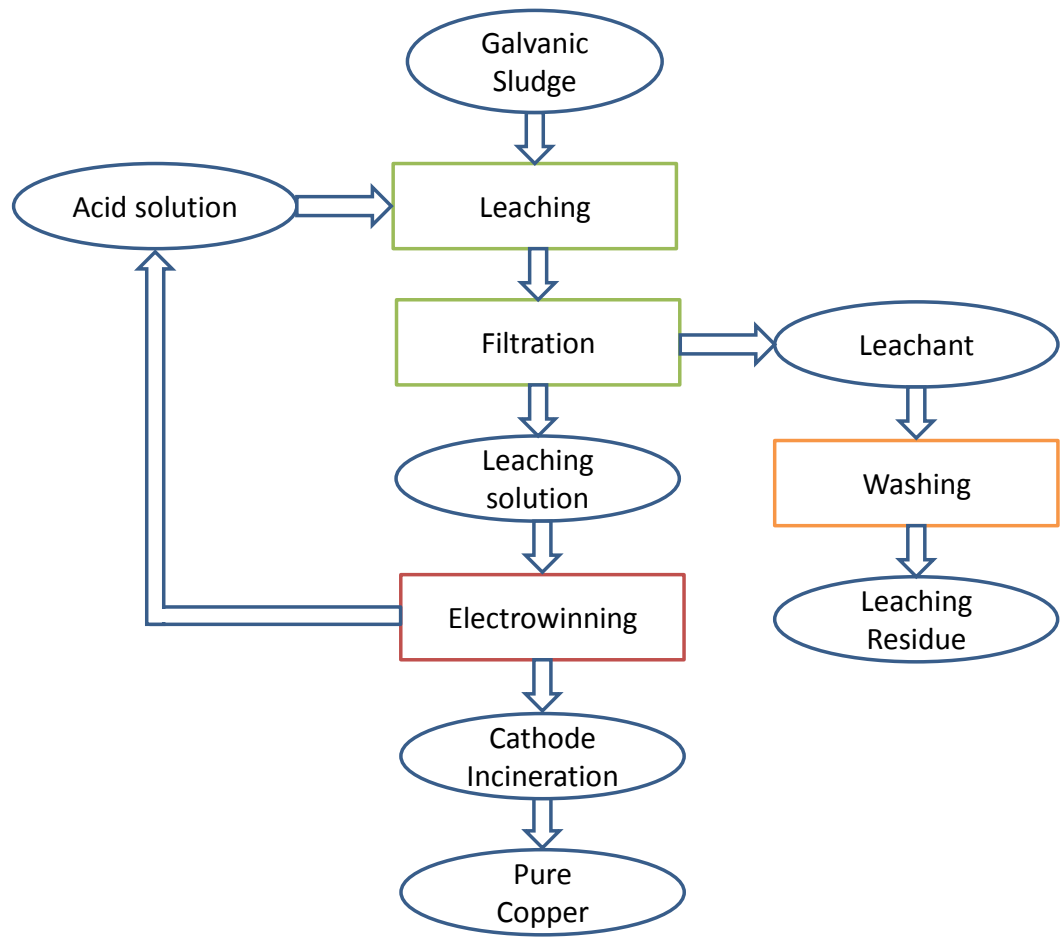
Figure 1: Proposed process flowsheet for recovery of copper from galvanic sludge waste.
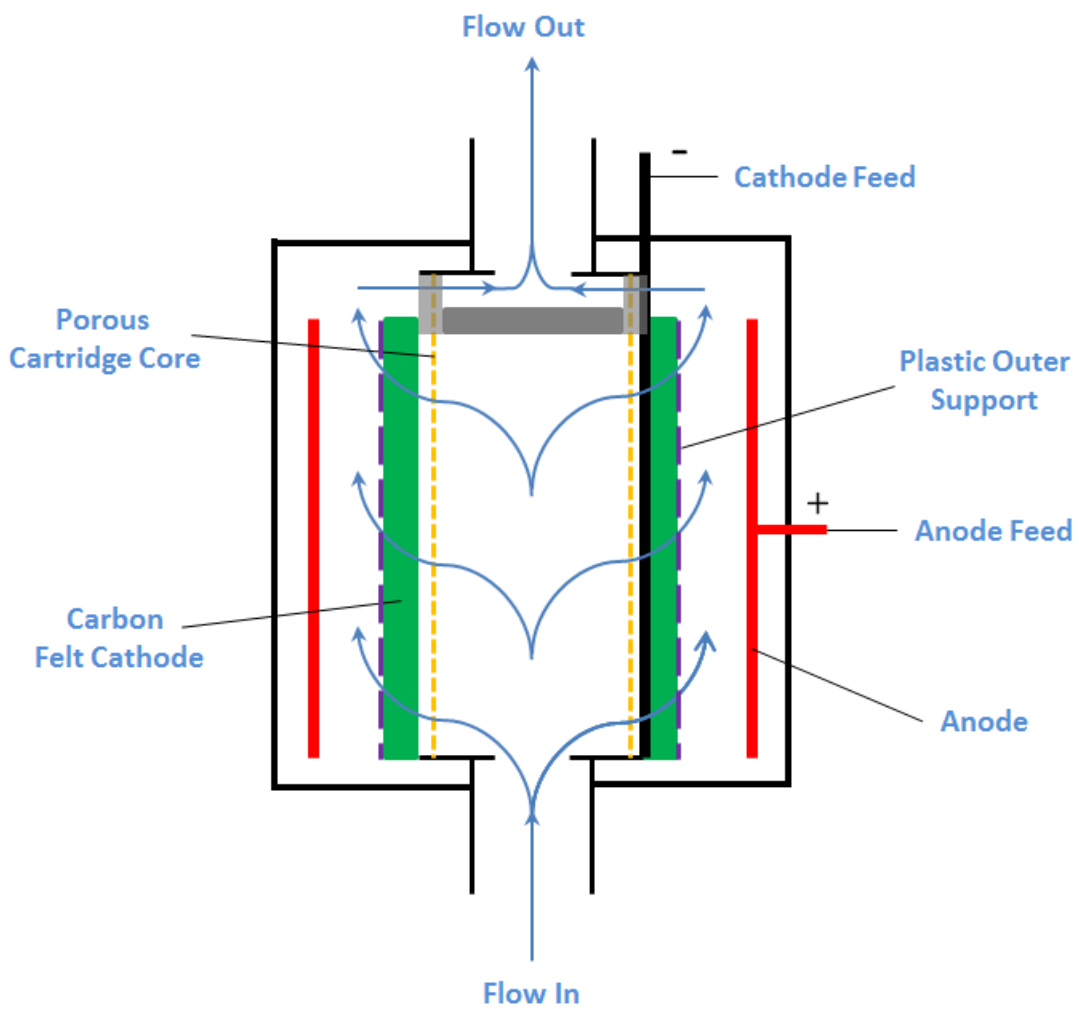
Figure 2. Schematic showing the internal structure of the Porocell reactor.
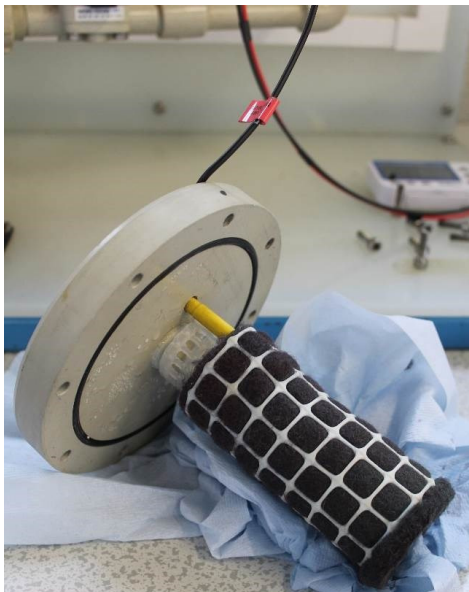
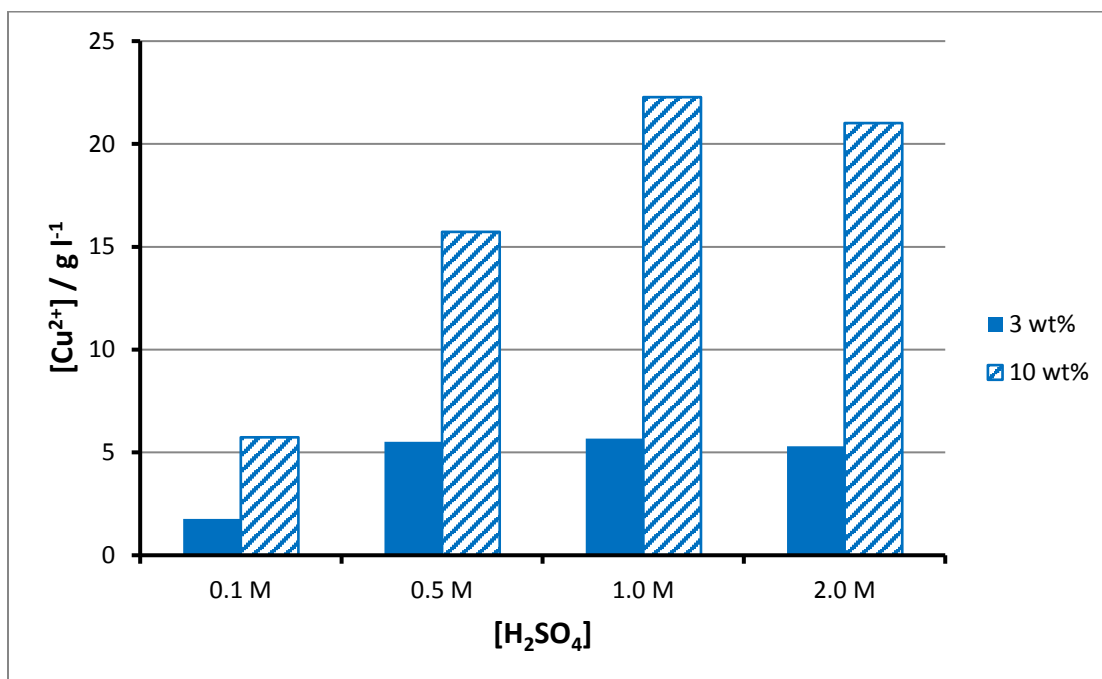Figure 3: Images of the carbon felt cathode before and after electrowinning.

Figure 4: Effect of the sulfuric acid concentration on the amount of copper recovered for the 3% w/v and 10% w/v solutions for a leaching time of 30 minutes.
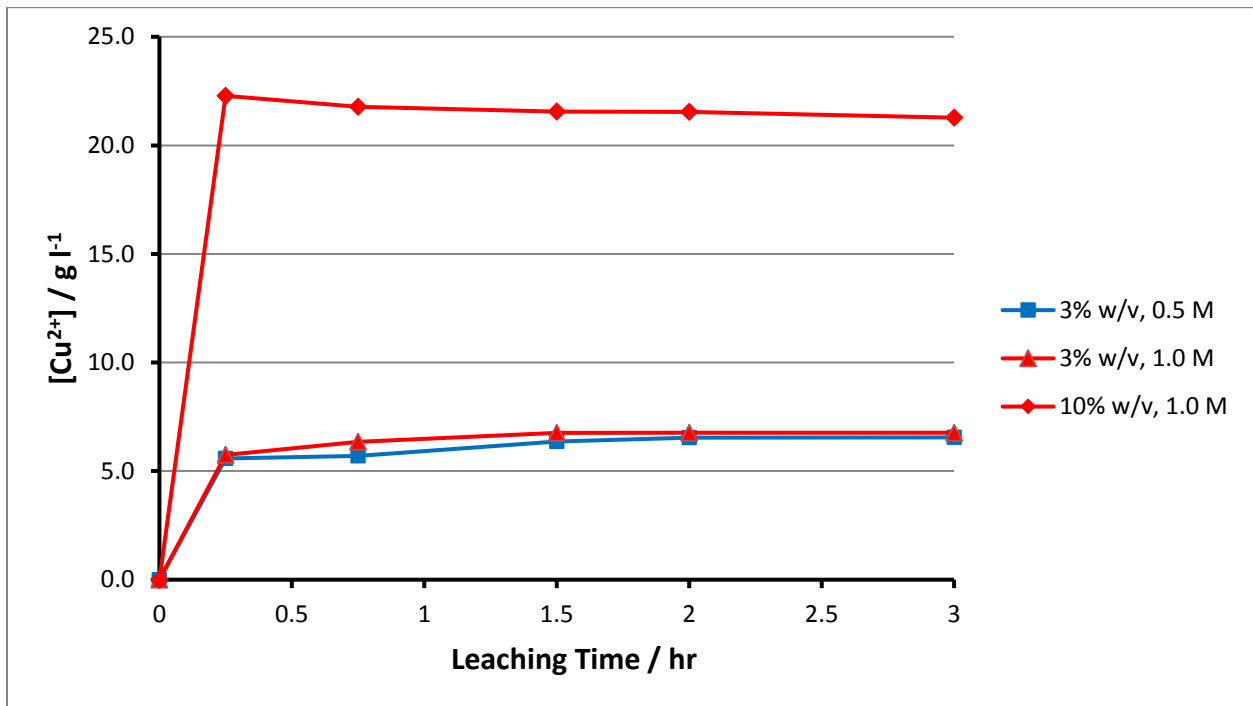
Figure 5: Effect of the leaching time and acid concentration (0.5 or 1.0 M H_2SO_4) on the amount of copper recovered.
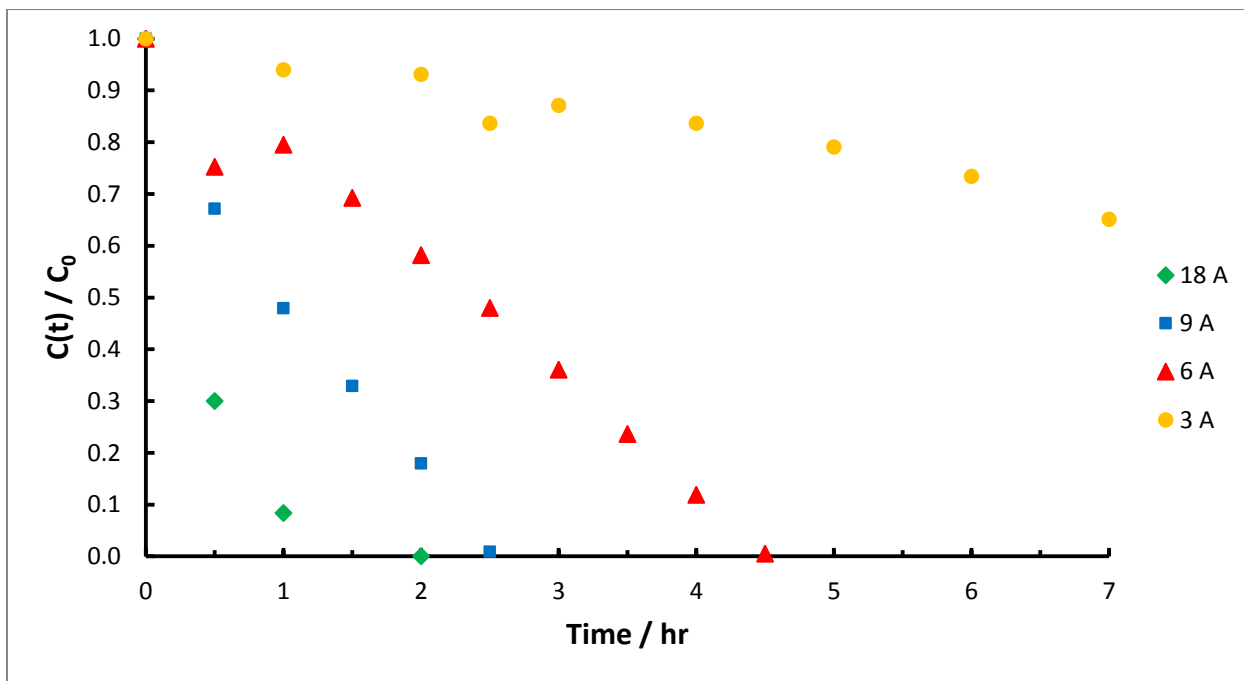
Figure 6: Change in the normalised copper concentration as a function of time and various applied current at a flow rate of 200 l h^{-1}.
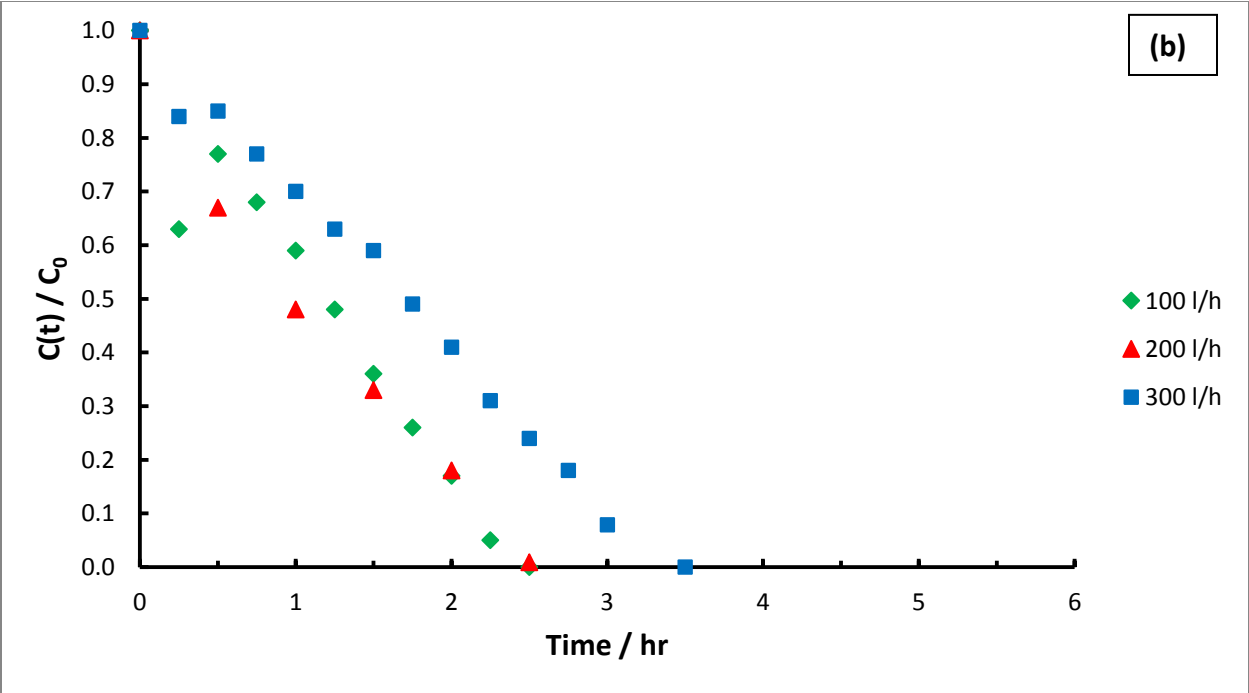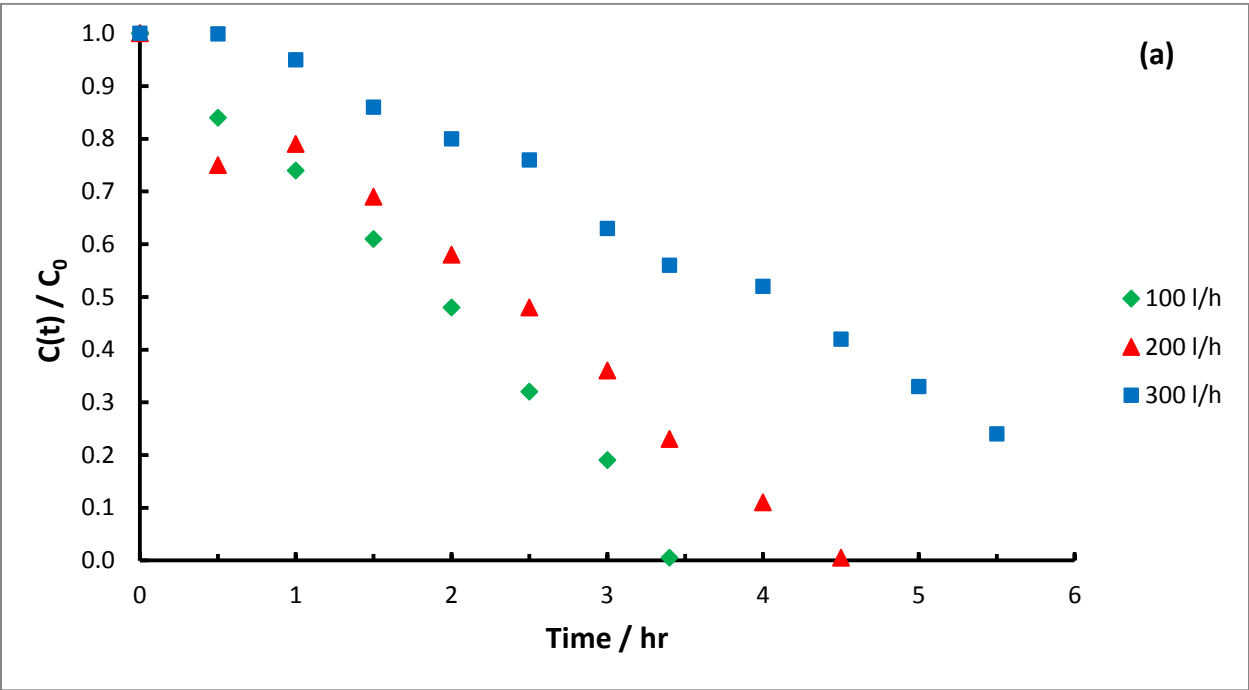
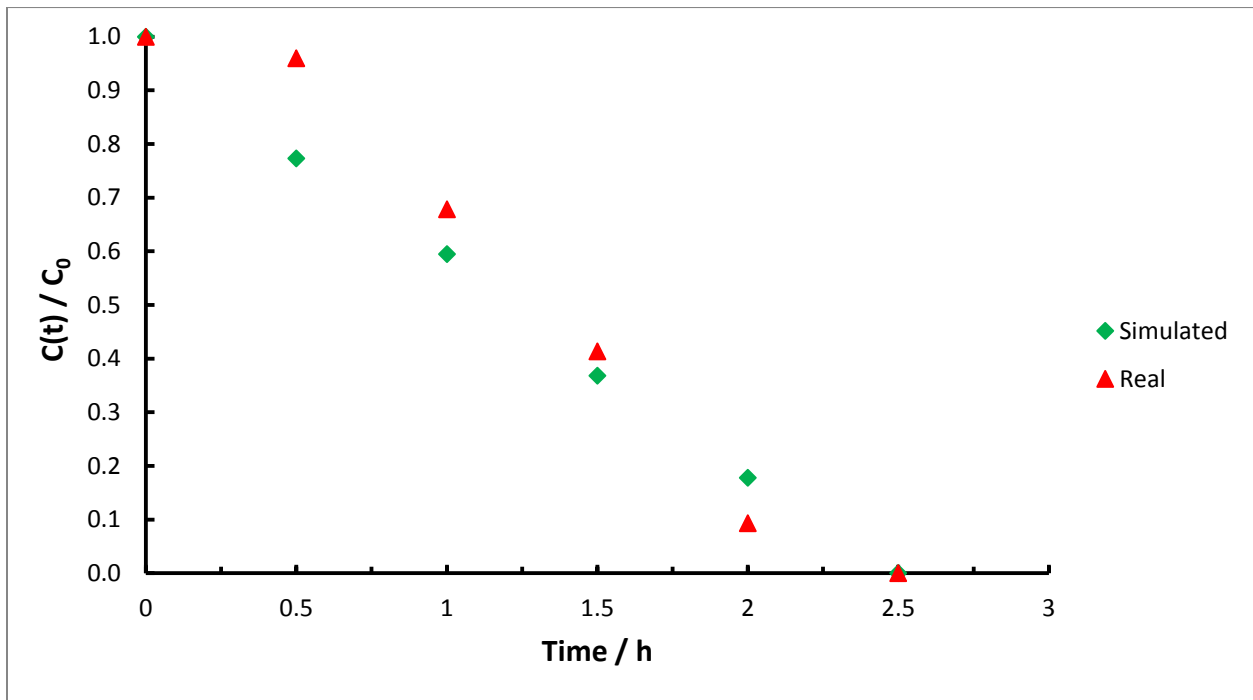Figure 7: Change in the normalised copper concentration as a function of time and flow rate. (a) 6 A, (b) 9 A.

Figure 8: Comparison of the metal recovery rate in simulated and real solutions. Electrowinning conditions: $I = 9$ Amps, $100 \, l \, h^{-1}$ flow rate.
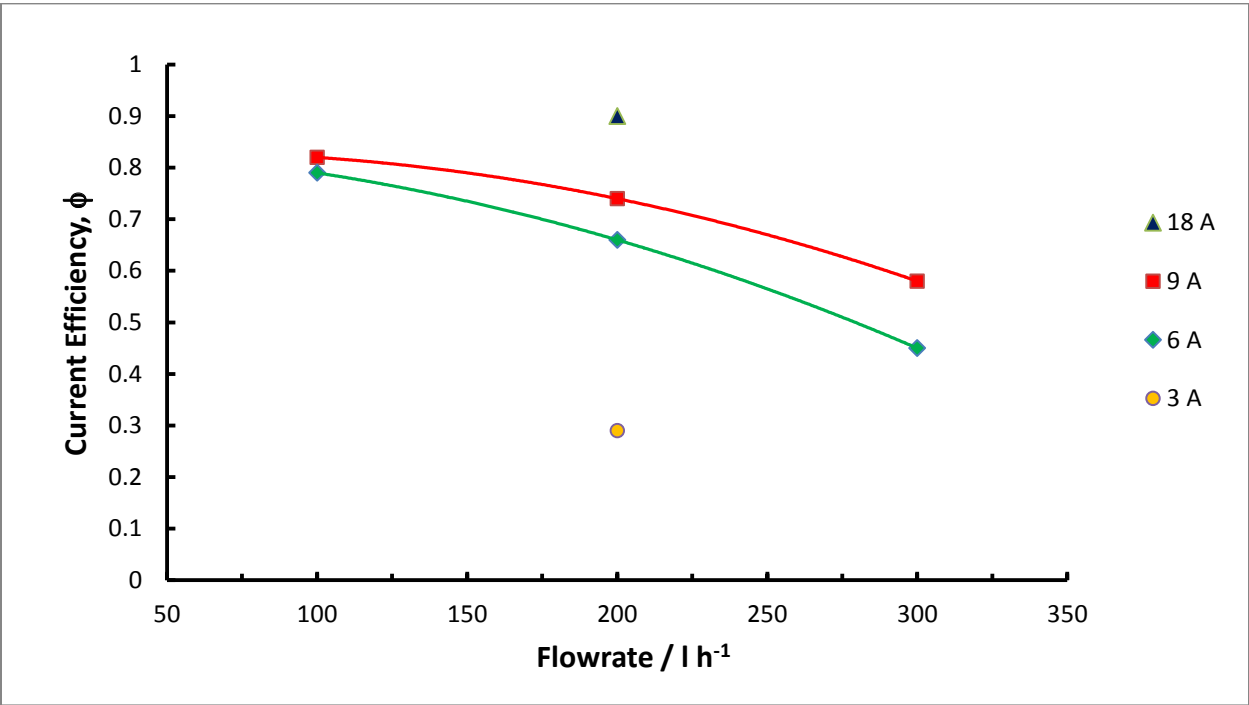
Figure 9: Dependence of the current efficiency for copper deposition on the applied current and flow rate.

Element	wt.%
Cr	0.01
Mn	1.37
Fe	6.78
Ni	0.12
Cu	21.5
Mg	3.32
Ca	20.7
Al	0.26

Table 1: Elemental composition of galvanic sludge determined by ICP analysis.

	1 M (NH$_4$)$_2$SO$_4$	2 M (NH$_4$)$_2$SO$_4$	1 M (NH$_4$)$_2$SO$_4$ + 1 M NH$_4$OH	0.5 M H$_2$SO$_4$	1.0 M H$_2$SO$_4$
Cr*	0.148	0.135	0.360	2.00	2.12
Mn*	44.7	68.0	12.7	159	218
Fe*	5.65	5.89	7.22	589	1005
Ni*	37.1	36.1	48.7	75.6	128
Cu*	1690	2805	4905	6330	7225
Cu†	-	-	-	5885	-

Table 2. Composition of solution (mg l^{-1}) leached from 3% w/v galvanic sludge using basic and acidic lixiviants. Concentrations determined by UV-Vis (†) and ICP-MS (*) measurements.

Sample	Compound	Composition wt%
Untreated galvanic sludge	Calcite - $CaCO_3$	94 – 96%
	$CuCO_3$	2 – 3 %
	Quartz – SiO_2	1 – 2 %
Galvanic sludge residue	$CaSO_4$	98 – 99%
	Quartz – SiO_2	1%

Table 3: Composition of untreated galvanic sludge and leach residue as determined by XRD.

Experiment	Flow rate (l h⁻¹)	Current, I (A)	Current Efficiency, ϕ	Side Reaction Current, $I_s = (1-\phi)I$ (A)	Cell Voltage (V)	Energy Consumption (kWh kg)
1	200	3	0.29	2.1	1.6	4.6
2	200	6	0.66	2.1	2.0	2.5
3	200	9	0.74	2.3	2.5	2.9
4	200	18	0.90	1.8	4.7	4.4
5	100	6	0.79	1.3	-	-
6	300	6	0.45	3.3	-	-
7	100	9	0.82	1.6	-	-
8	300	9	0.58	3.8	-	-
9	100	9	0.81	1.7	-	-

Table 4: Current efficiency data for each electrowinning experiment as a function of current, flow rate and solution composition. Also included are the mean cell voltage and the energy consumption. Experiments 1 – 8 were performed using simulated solution containing 7 g l⁻¹ of Cu^{2+} in 0.5 M H_2SO_4. Experiment 9 utilised a real solution obtained by leaching galvanic sludge (3% w/v) with 0.5 M H_2SO_4.
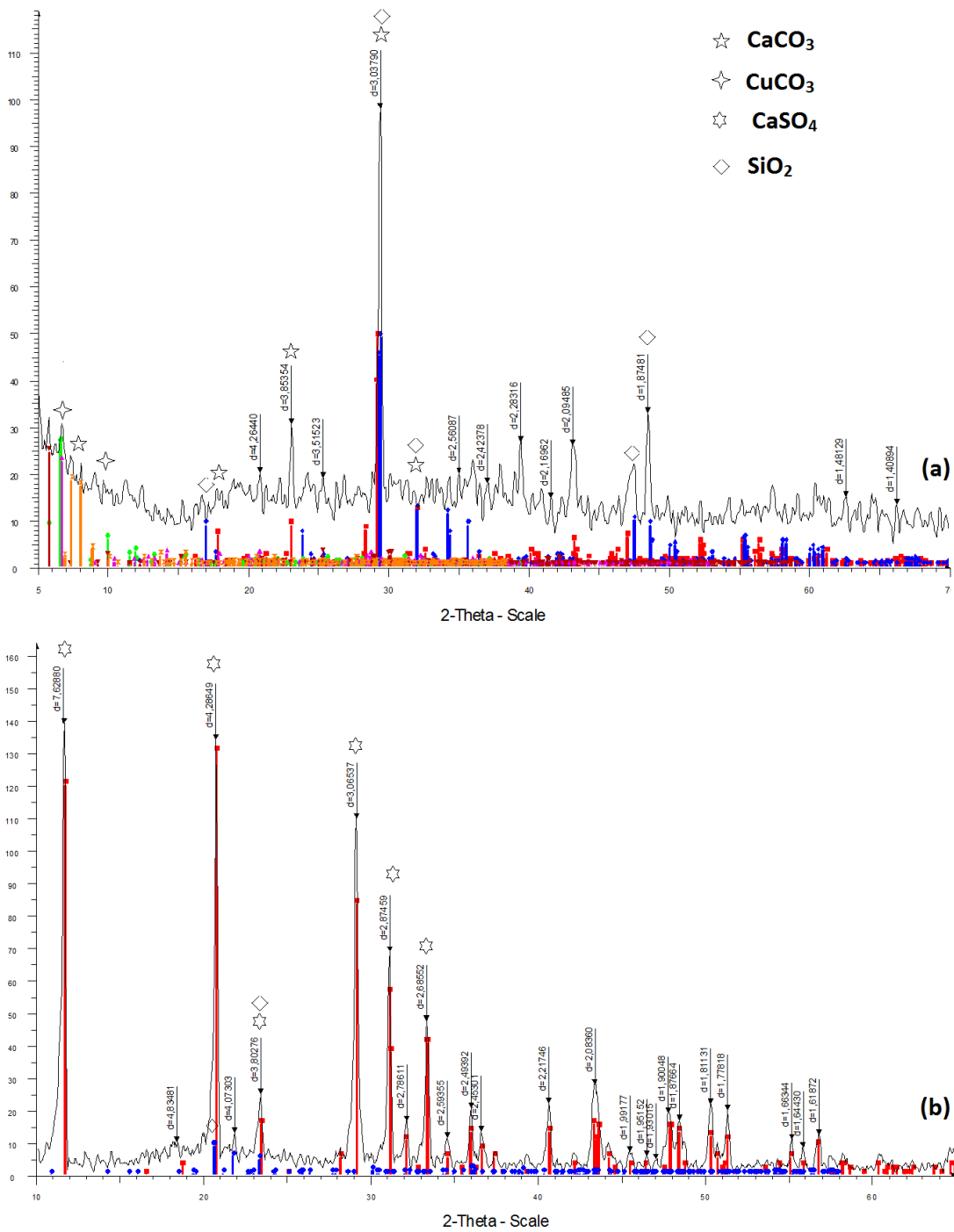
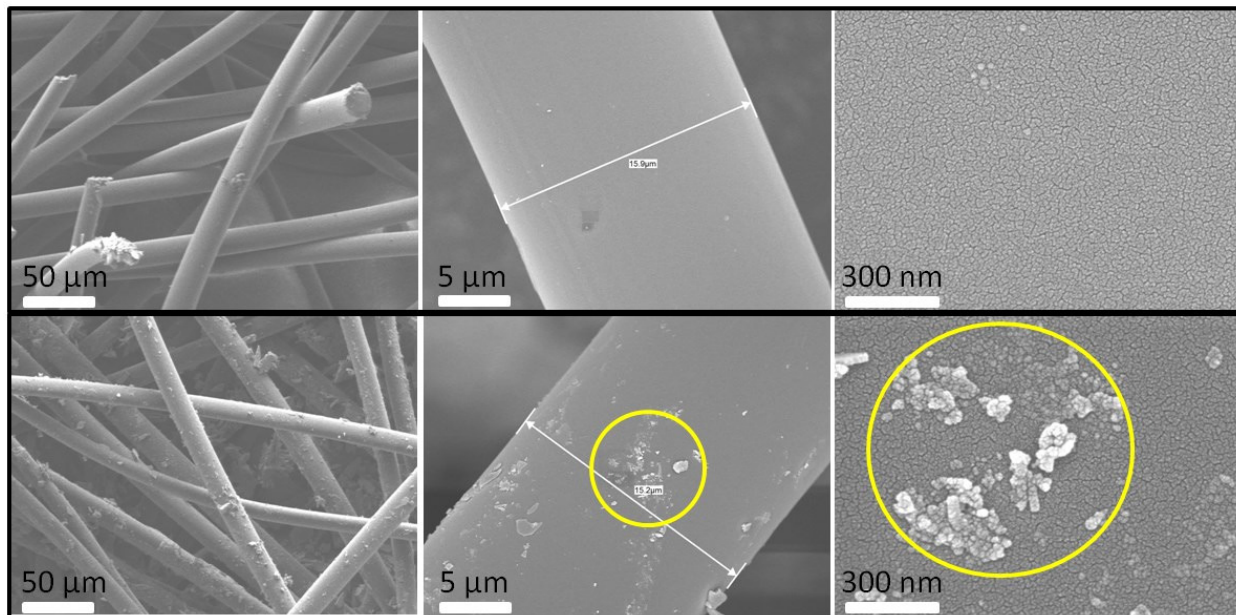Figure S1: X-ray diffractograms of (a) untreated galvanic mud (b) leaching residue.

Figure S2: SEM images of carbon felt electrode before (upper images) and after (lower images) after copper electrowinning at 9 A for 3 hours at a flow rate 200 l h^{-1}.