ROOT-CAUSE ANALYSIS OF THE LACY COPPER PHENOMENON

* A. R. Almansa, T. Bravo, G. Ríos and R. Ramírez
ATLANTIC COPPER SLU (A Freeport McMoRan Company)
Avda. Francisco Montenegro s/n. Huelva, Spain 21001
*(*Corresponding author:* arodrigu15@fmi.com*)*

N. Aslin
GLENCORE TECHNOLOGY
160 Ann St 4000 Brisbane, Australia

ABSTRACT

Lacy copper has been an on-going concern at Atlantic Copper for at least 10 years and was first reported to Glencore Technology in mid-2010. Over the past 12 years, many of the plates were replaced due to age and general deterioration however; plate passivation and lacy copper issues have persisted. After analyzing all the possible causes of this phenomena, it was found that the problem is caused by a degradation of stainless steel as a consequence of the deposition of Sb oxides. These deposits act as passivating agents of stainless steel, which reduces the density of copper nuclei, causing defective copper deposit, with low thickness and ductility. After doing several tests for reducing/removing the phenomena, the over-riding factor was found to be the anode-cathode overlap. An adequate overlap eliminates the problem of "lacy copper". This was verified during an eight month trial with anodes extended 2.5cm in length. Longer anode not only avoids the appearance of lacy copper, but also recovers cathodes that already have lacy copper. On the other hand polishing of plates only gives rise to a temporary solution that requires on-going polishing, to avoid the re-appearance of lacy copper.

KEYWORDS

Cathode, Copper, Electrorefining, Steel.

INTRODUCTION

The electrolytic copper refinery of Atlantic Copper in Huelva (Spain) was commissioned in 1970 with an initial capacity of 40,000 t of cathodes per year. In 1975 the copper refinery was expanded to 108,000 t/year. From 1994 to 1996, a new expansion together with the implementation of ISA permanent cathode technology led to a capacity of 215,000 t/y. Since 1995, a progressive increase in the current density up to 350 A/m^2 has been accomplished, which together with an increase in the number of cells from 1,120 to 1,204, has led to the present cathode production capacity of 290,000 t/y

A lack of copper deposition in the lower part of the steel permanent cathodes was first reported in 2010. This phenomenon is known as “Lacy copper” because of the appearance of the copper deposit as it can be seen in Figure 1. The occurrence of this phenomena was relatively low and was assumed to be originated by an excessive anode scrapping. Nevertheless, in December 2015 Lacy Copper was observed in a significant amount of copper cathodes giving rise to the following issues:

- Increased tramp copper – housekeeping and maintenance problems
- Poor appearance of cathode deposit and untidy looking bundles

Figure 1. Lacy copper examples

Because of these issues, a project following the six sigma methodology (define, measure, analyze, improve and control) was launched in January 2016. This paper describes the main findings of this project and how the Lacy Copper problem was finally solved.

PHASE 1: DEFINE-MEASURE

Atlantic Copper refinery is operated following a three crops (5/6/5) schedule being the anode life 16 days. During December 2015 and January 2016, cathodes were visually inspected in the cathode stripping machines. More than 18000 cathodes were inspected being the main results that lacy copper was observed in 40 % of the 2nd crop cathodes and 55 % of the 3rd crop cathodes while only a 6 % of the 1st crop cathodes showed lacy copper. As a consequence of this results it was decided to keep this visual inspection and a monthly indicator for each crop was calculated in order to quantify the occurrence of the lacy copper phenomenon. The evolution of these monthly indicators from January 2016 to July 2017 is shown in Figure 2.

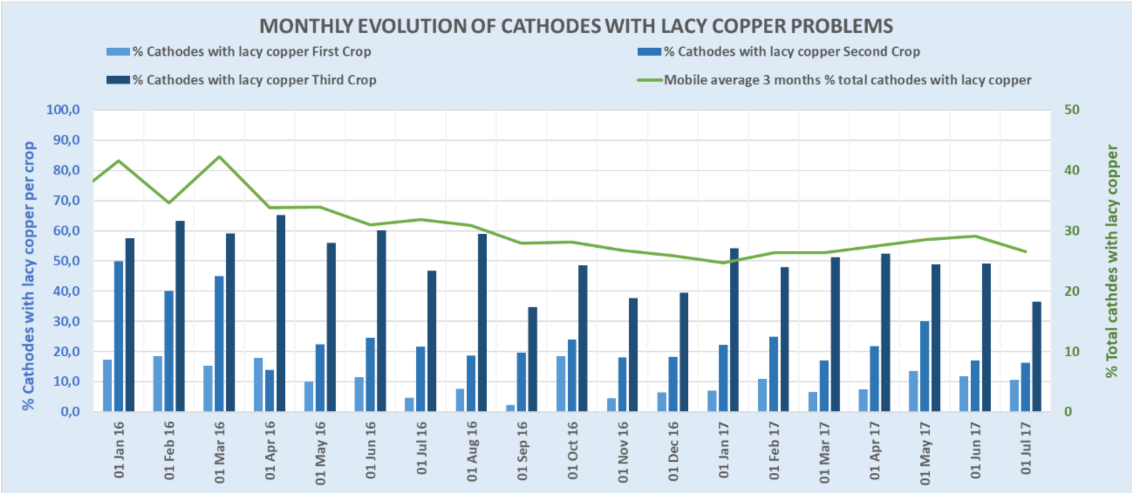

Figure 2. Monthly evolution of cathodes with lacy copper

Lacy copper micrograph

A sample of lacy copper was taken from the corner of a crop 3 cathode deposit and prepared for micro-structure analysis. The aim was to understand the growth pattern in the lacy copper region and especially to check the orientation and growth direction of the crystals. A picture of this sample and the location of the different micrograph samples is shown in Figure 3.

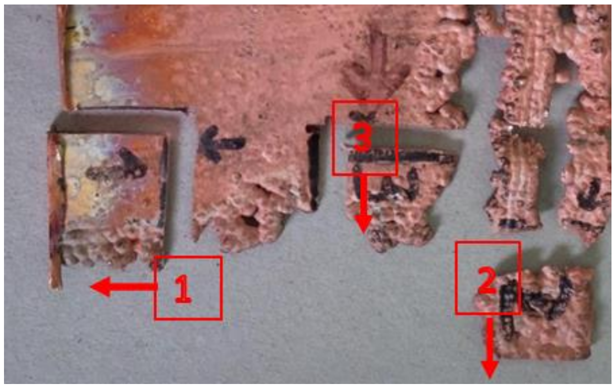

Figure 3. Lacy copper sample from bottom corner of cathode; Location of Micrograph samples

<u>Sample 1</u>

Sample 1 represents a vertical slice through the cathode at the bottom edge of the deposit (above the wax). Active part of the plate shows normal crystal structure which is fine-grained and perpendicular to the plate surface. Semi-passive part of the plate (Fig 4) with nodular appearance shows significantly different structure with only 3 or 4 active nucleation sites on the surface of the steel and crystals growing radially from these localized sites (Fig 4). This zone has a few isolated active sites while the vast majority of the surface is passive. Crystals are very coarse and typical of low current density growth in this area. Similar results were found in samples 2 and 3

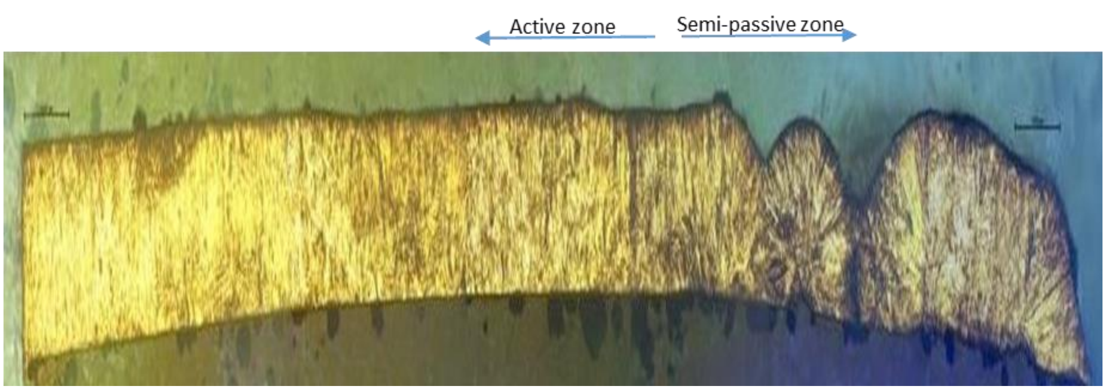

Figure 4. Sample 1 cross-section showing both active and semi-passive zones

A similar structure of copper was found by Vargas et. al (1995) during a study carried out in the starting sheet production circuit.

Steel permanent cathode (plate) analysis

Samples of the active and passive areas of the 316L steel plates, used as permanent cathodes, were analysed at the Avesta Research Centre (Sweden) and the Department of Materials Science of the University of Seville (Spain).

<u>Analysis of surface contamination</u>

This investigation was aimed at identifying any contaminants on the plate surface that could be responsible for passivation behavior of the plate. Samples of the plates were analysed by Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD)

The main difference between the passive and the active areas was the presence of C, O, Cu, S, As, and Sb. As shown in Figure 5, the XRD analysis of the passive area suggests that Sb oxides may be found on the steel surface. This finding would be consistent with Wesstrom (2014) in which the effect of Sb oxides is described as an "oxide layer" that decreases the number of nucleation sites.

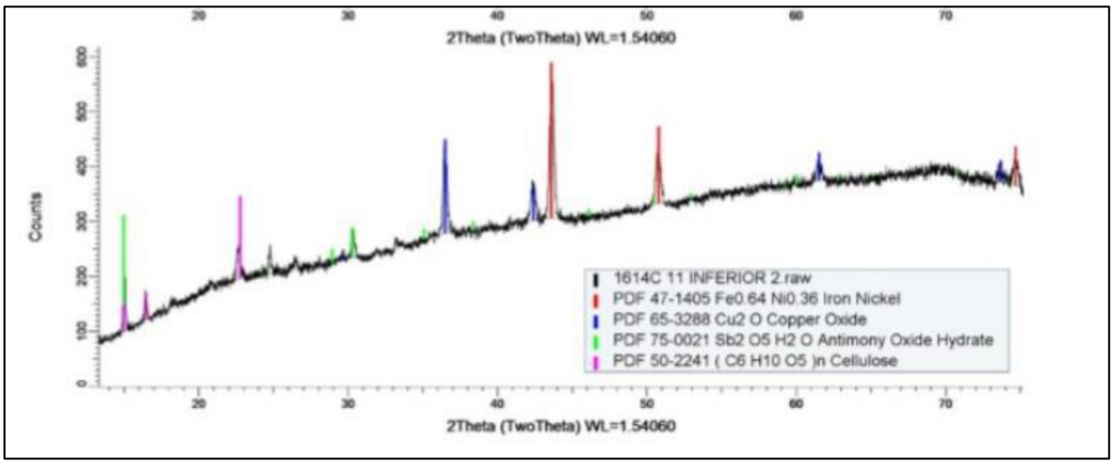

Figure 5. XRD analysis of a steel plate "passive" area

<u>Steel topography and surface roughness</u>

Active and passive areas of the plate were analysed for surface roughness and surface topography to identify any major differences in the physical profile of the surface that might affect adhesion, or indicate difference in corrosion between the "active" and "passive" areas of the steel. As depicted in Figure 6, results showed that the active area (middle of plate) had slightly lower surface roughness than Passive area near edge of plate; 0.5 μm Ra (active area) vs 0.8 μm (passive area). Both are still within new plate Ra spec 0.25 to 0.8 μm and should not have major effect on adhesion of the copper deposit

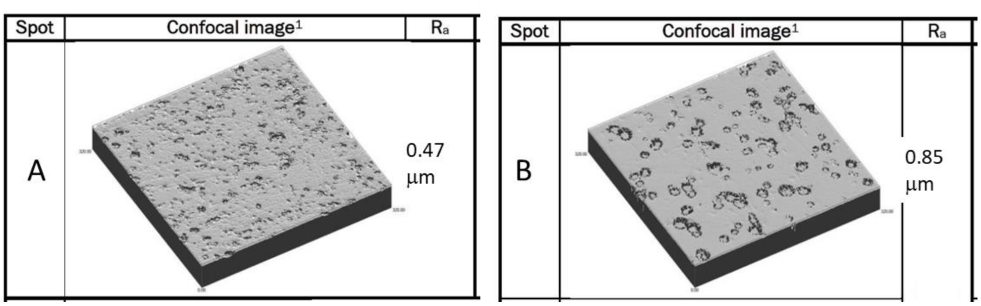

Figure 6. Topography image edge of a steel plate: (A) Active area (B) Passive area

PHASE 2: ANALYSE-IMPROVE

The next step in the project was to perform an analysis of causes of the observed lacy copper deposit. As this lacy copper deposit was associated with a low nucleation of copper on the steel surface, a cause effect matrix for this low nucleation was generated based on the observations of phase 1. This matrix is shown in Figure 7. As can be seen in this matrix, the following "improvement" actions were proposed:

- Linishing the plates
- Increase the dosification of thiourea
- Improve the anode cathode overlapping

CAUSE	Loss of the chemical properties of the plate	Low amount of thiourea	Geometry
EFFECT	Passivation of some areas of the steel surface	Low nucleation	Anode-cathode lower distance increase: It decreases current density in the lower area
1st CROP	High	Medium	Low
2nd CROP	High	Medium	Medium
3rd CROP	High	High	High
Proposed action	A1: Linishing test plates	A2: Increase test of thiourea	A3: Anode length increase

Figure 7. Lacy Copper cause effect matrix

Linishing the plates

The main objective of this practice was to remove the oxides and dirtiness layer that may have led to a "passivation" of the steel surface. Surface refurbishment was initially carried out by hand-linishing the plates and this was found to temporarily eliminate the lacy copper as it can be seen in Figure 8. As a result of this positive result, a horizontal belt-linisher was purchased by Atlantic Copper to refurbish all plates by midyear. Plate linishing eliminates lacy copper in the short term but re-linishing is required every 4-6 months. This is operationally expensive and likely to be harmful to the longterm longevity of the plates.

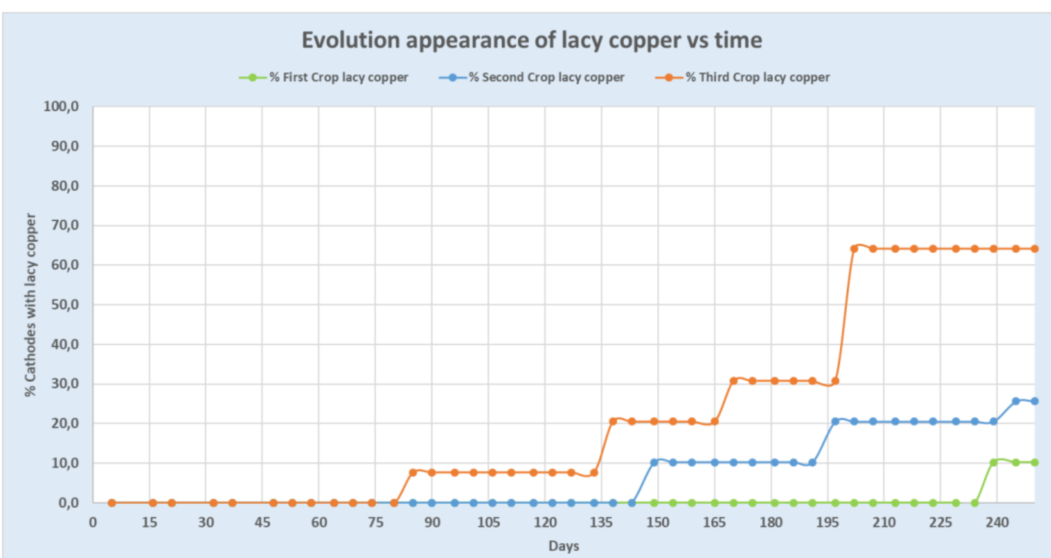

Figure 8. Effect of plate linishing on lacy copper occurrence

Thiourea tests

Stelter and Bombach (2007) have studied the influence of thiourea on the regular growth of copper along the entire surface of the cathode in depth. It is because of that an experimental set up was installed to increase progressively the thiourea dosification in one cell up to 100%. No influence of Thiourea on the lacy copper phenomenon was found (Figure 9).

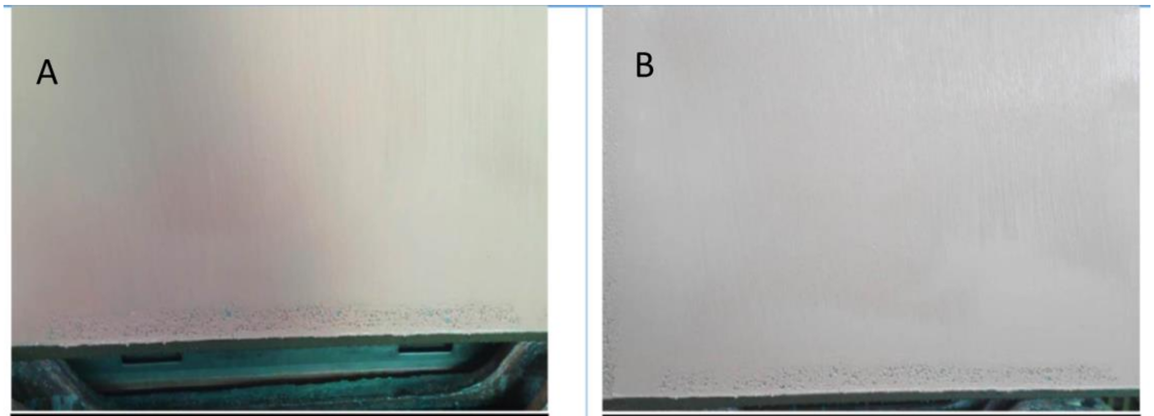

Figure 9. Effect thiourea on lacy copper. A before and B after 100 % thiourea overdosing

Bottom overlap tests

The purpose of the overlap between anode and cathode plate is to minimize rough growth around the edges of the cathode where current 'field lines' are concentrated (at the interface between copper deposit and edge-strip / wax). The optimum overlap dimension depends on cathode weight / thickness, however in practice a design overlap of 25–30 mm is a good compromise which accommodates a range of anode / cathode cycles and cathode weights. Plants with very light cathode (< 50 kg per side) would benefit from smaller overlaps (20–25 mm) while plants with heavier cathode (> 70 kg) would generally prefer larger overlaps (30–35 mm).

From the data presented in the literature bottom overlap ranges from 22 mm to 38 mm. Atlantic Copper had by far the largest bottom overlap, with 45 mm (Figure 10).

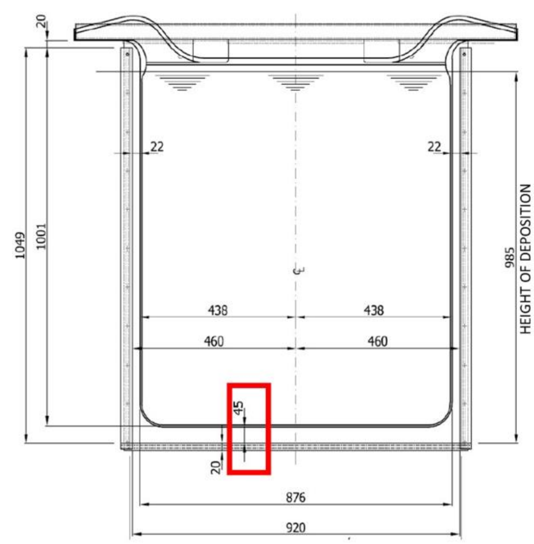

Figure 10. Atlantic Copper anode-cathode bottom overlap

A bottom overlap of 20 mm test was carried by casting anodes 25 mm longer. To do so some molds of the casting wheel was modified. At the same time the anode preparing machine (APM) had to be adjusted to handle these anodes when fed to the tankhouse. These "longer" anodes were fed in two cells for 11 anode cycles (173 days):

- Cell 1 in which the steel plates had shown lacy copper phenomena in the first crop
- Cell 2 in which all the plates had been linished.

The purpose of this test was to check the effect of this change of geometry on the lacy copper phenomena and on the duration of the positive effect linishing. The results achieved in cell 1 are depicted in Figure 11.

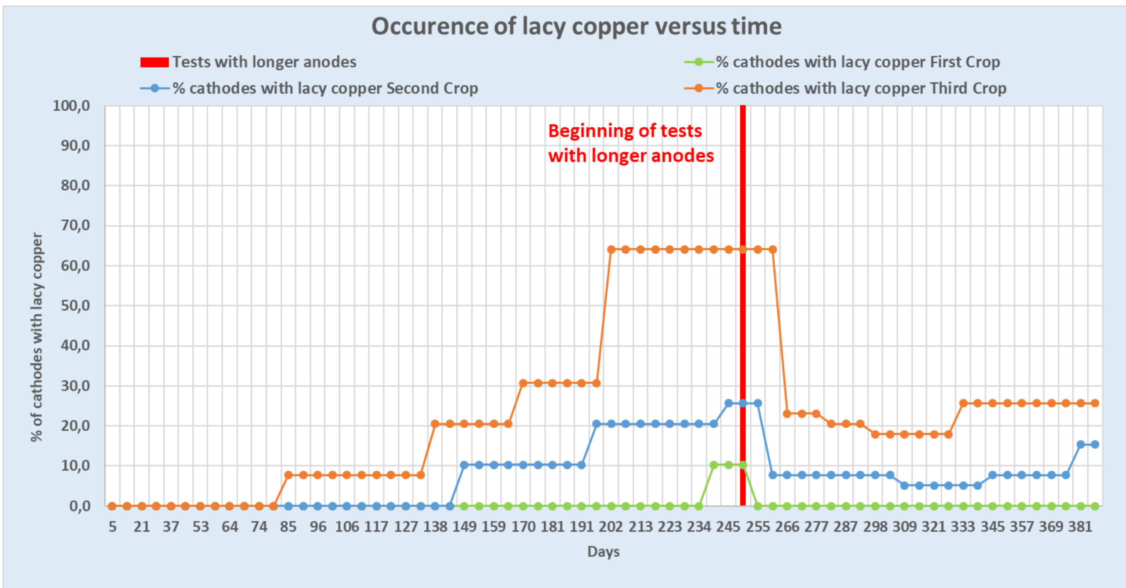

Figure 11. Overlap tests with 20 mm in Cell 1. Occurrence of lacy copper

As it can be seen in Figure 11, the positive effect of working with longer anodes is significant as the occurrence of lacy copper is reduced in the first anode cycle from 65 % to 23 % in the third crop. This positive effect is also depicted in the pictures shown in Figure 12.

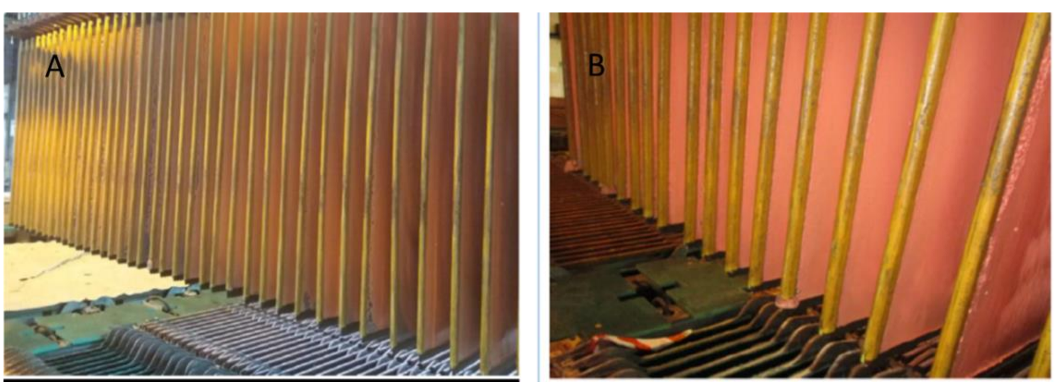

Figure 12. Overlap tests with 20 mm in Cell 1. A: cathodes before the test; B cathodes during the test

Regarding cell 2, the results were remarkable as none of the linished plated presented lacy copper after 228 days.

PHASE 3: CONTROL

As a consequence of the aforementioned promising results in June 2017 the decision of working with 25 mm longer anodes at full scale was made as well as reducing the radius on bottom corner of anodes from 64 mm to 20 mm.

The results of a combined linishing of the plates and a longer anode led to the minimization of the lacy copper problem, as it can be seen in Figure 13 and nowadays this phenomenon has almost disappeared.

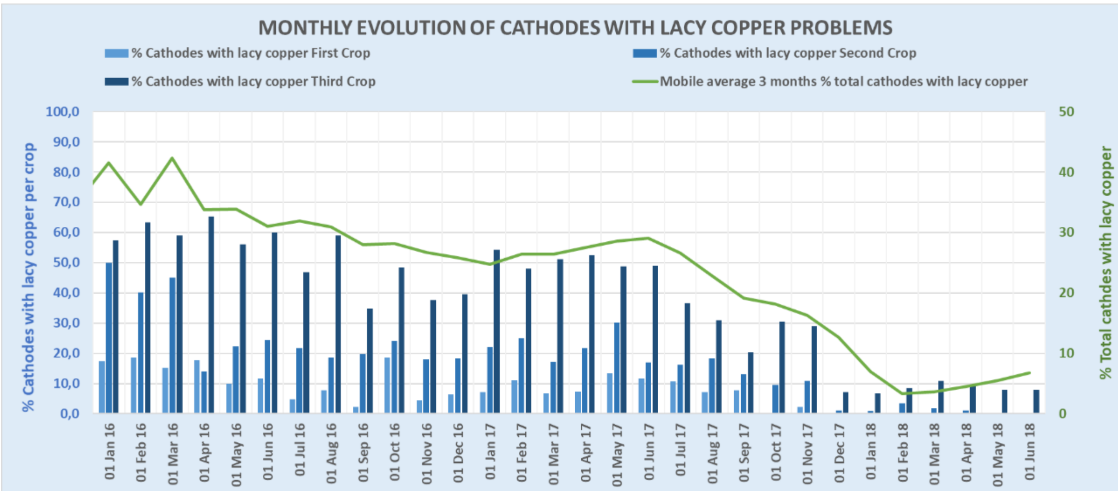

Figure 13. Effect of a 20 mm bottom overlapping on the monthly evolution of cathodes with lacy copper

At the end of September of 2018, the lacy copper problems disappear in all the blanks of the refinery and it was maintain over time.

CONCLUSIONS

- Micrograph analysis of a lacy copper sample showed two distinct zones with different growth behavior; center part of the plate showed normal crystal growth, fine-grained and perpendicular to the plate surface. Outer / transition zone where lacy copper was observed showed a few isolated sites where nucleation of large nodules occurred but the vast majority of the surface was completely passive. This region also has coarse crystal growth typical of low current density.
- Microscope imaging and surface roughness measurements showed the outer part of the cathode plate (passive area) had slightly lower roughness (µm Ra) than the active part of the cathode in the middle. Outer part had fewer, but deeper pits in the surface. The difference in surface condition would not significantly affect adhesion and did not show any significant corrosion.
- Chemical analysis of the passive steel areas using SEM, EDS and XRD showed that Sb oxides contaminated these areas.
- Lishinsing the plates may remove that "oxide layer" but plates have to be relisnished every six months. It is important to minimize the frequency and severity of linishing as this process can have adverse effect on plate life
- Anode cathode geometry plays in important role in current density distribution and hence have an effect on the lacy copper phenomenon
- Based on results to date lacy copper will be significantly reduced by installing longer anodes, and linishing all plates.

- The trials that are currently underway with long anodes and linished plates will indicate how long the plates can operate before they start to passivate, and how frequently they will need to be linished

ACKNOWLEDGEMETS

The authors wish to thank Atlantic Copper SLU and Glencore technology for the opportunity to publish this paper.

REFERENCES

Biswas, A. K., and W. G. Davenport. Extractive Metallurgy of Copper. Kent: Elsevier Science, 2014

Stelter, M., and H. Bombach. "Fundamentals and effects of aditives in copper electrorefining." Cu2007 - Volume V (2007)

Vargas T., Iturra F., Cifuentes L., Cifuentes M., Fuenzalida V., Rojas E., & Delgado C. (1995) The Effect of Antimony on the Electrocrystallization of Copper on Titanium During Electrorefining. In W.C. Cooper, D.B. Dreisinger, J.E. Dutrizac, H. Hein & G. Ugarte (Eds.) Copper 95-Cobre 95, Vol. III, Electrorefining and Hydrometallurgy of Copper (pp. 293-302) Montreal, Canada: The Metallurgical Society of CIM.

Wesstrom, B.C. “The effects of high antimony in electrolyte”. COM 2014