Development and Commercialization of an Alternative Anode for Copper Electrowinning

S. Sandoval, C. Clayton, S. Dominguez, C. Unger, T. Robinson
Freeport-McMoRan Mining Company
4521 U.S. Highway 191
Morenci, USA

Abstract

In 2006, the Freeport-McMoRan Copper & Gold Inc. (FCX) Technology Center in Safford, Arizona undertook research to develop an alternative anode for copper electrowinning. The objectives of the development included a 15% voltage reduction versus conventional Pb-Ca-Sn anodes and the removal of lead and associated lead contamination from the copper electrowinning circuit. An anode development lab was established that included bench-scale electrowinning cells as well as accelerated life testing cells.

This paper describes the development of the FCX alternative anode including its structure and associated anode coating. In 2008, the Chino electrowinning plant was fully converted to the new FCX anode becoming the first electrowinning plant in the world to exclusively utilize non-lead anodes. A 15% electrowinning voltage reduction was achieved. Cleaning of electrowinning cells for lead sludge and addition of cobalt to the circuit for stabilizing lead anodes were discontinued. Lead content of copper cathodes measured less than 0.3 ppm.

Introduction

In 2006 Freeport-McMoRan Copper & Gold Inc. (FCX) Technology Center established an anode development lab at its SXEW Test Facility located in Morenci, Arizona. The purpose of the lab was to explore opportunities for replacing conventional Pb-Ca-Sn anodes in copper electrowinning with an alternative anode that would decrease energy consumption and remove lead contamination from the copper electrowinning circuit. A 15% voltage reduction target was established. The Lab operated on a 7-day 24-hr basis as part of the Technology Center’s SXEW Test Facility.

Figures 1, 2, and 3 display the anode development lab and associated testing cells. A dual approach was implemented for the development. Accelerated life testing cells were utilized to compare lifetime of anode coatings as a function of coating composition. The test coatings were applied to expanded titanium metal coupons. In addition voltage testing cells were utilized to compare voltage...
performance of candidate anodes coatings in copper electrolyte during copper electrowinning. Using this approach coating life was maximized while coating voltage was minimized.

Figure 1: Technology Center anode development lab.

The anode development lab incorporated ten accelerated life testers (on the right in Figure 1) containing eight coupon cells each (Figure 2) for a total lab capacity of 80 coupon cells that could be operated simultaneously. Each coupon cell contained a 1-inch by 3-inch coupon made of titanium expanded metal with one square inch of coating applied to the bottom of the coupon. The cathode utilized in the accelerated life cells was an uncoated coupon of titanium expanded metal. In the accelerated life cells the coupons were subjected to a 180 g/L sulfuric acid solution at room temperature. Current was 3.5 amps per square inch of 40% open expanded titanium. This calculates to a current density of 840 amps/ft$^2$ of titanium metal.

The anode development lab also incorporated ten voltage testing cells (on the left in Figure 1). In these cells a 3-inch by 6-inch coupon of 40% open expanded titanium with the candidate anode coating was tested (Figure 3). The voltage testing cells were fitted with 316L stainless steel cathodes having an immersed surface area of 3.5 inches by 4 inches. Electrolyte feed to the cells was 16 mL/min at a temperature of 120 °F. The copper electrolyte was lean electrolyte obtained from the FCX Morenci-Modoc solvent extraction plant. Current density was controlled at 30 amps/ft$^2$ on the cathode which equated to 50 amps/ft$^2$ of titanium metal on the anode.

Various coatings were evaluated for lifetime in the accelerated life cells and for voltage performance in the voltage testing cells. The anode coating development work focused primarily on mixtures of iridium oxide and tantalum oxide and the associated coating preparation and processing parameters. Coatings that met the 15% voltage reduction criteria and exceeded 3000 hours in the
accelerated life testing cells were carried forward to pilot testing in Test Facility cells, which contained full-scale commercial electrodes.

Figure 2: Accelerated life testing cells.

A strategic partnership was formed between FCX and Republic Alternative Technologies (Strongsville, Ohio) to develop an anode structure on which to apply the FCX anode coatings. Successful pilot testing of the resultant FCX anode led to in-plant demonstration of the alternative anode at FCX’s Chino (New Mexico, USA) SXEW plant. A successful demonstration led to the full conversion of Chino to alternative anodes in 2008. This paper provides an overview of the development of
Results and Discussion

Anode Coating Development

Anode coating development proceeded along two parallel paths, one to minimize voltage in the voltage testing cells and one to maximize lifetime in the accelerated life testers. Figure 4 displays progress made in reducing cell voltage by adjusting coating processing parameters.

![Figure 4: Voltage testing cell results showing progress in reducing cell voltage.](image)

Table 1 shows the processing parameter adjustments that were made in the coating development. Coating 1100-01 was made using conventional techniques that are well known [1]. Chloride salts of iridium and tantalum were mixed in a hydrochloric acid and n-butanol media in a 70:30 Ir to Ta molar ratio. The mixture as a paint was applied to the expanded titanium substrate which had been pickled to clean and roughen the surface. The painted substrate was cured in an oven at 520 °C to convert the paint into a crystalline Ir oxide/Ta oxide coating.

The first improvement in voltage performance was accomplished by developing individual organometallic resins of Ir and Ta that could be individually processed to remove excess hydrochloric acid and water. The resins were then mixed and processed in the same manner as 1100-01 to form coating 1100-01-A, which lowered cell voltage by about 100 mV. The second improvement in cell vol-
Development and commercialization of an alternative anode for copper electrowinning

tage was accomplished by adjusting the curing temperature of individual coatings and by using a combination of coats at different coating temperatures [2-3]. Coating 1100-01-A-520/340 utilized eleven total coats of paint. The first four coats were individually cured at 520 °C and then the next seven coats were individually cured at 340 °C. This lowered cell voltage by over 200 mV.

Table 1: Development summary of new FCX coating.

<table>
<thead>
<tr>
<th>Coating</th>
<th>Processing Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100-01</td>
<td>Prior art was utilized to mix chloride salts of Ir and Ta in hydrochloric acid and n-butanol to from the coating mixture.</td>
</tr>
<tr>
<td>1100-01-A</td>
<td>New art was developed where individual organometallic resins of Ir and Ta were prepared and additional processing steps were taken to remove excess hydrochloric acid and water from the resins before combining to form the coating mixture.</td>
</tr>
<tr>
<td>1100-01-A-520/340</td>
<td>Oven curing temperatures were adjusted so that higher temperature was used to cure the undercoats to form crystalline iridium oxide/tantalum oxide and lower temperature was used to cure the topcoats to form amorphous iridium oxide/tantalum oxide.</td>
</tr>
</tbody>
</table>

The combination of voltage reductions achieved more than met the 15% target, which was 300 mV savings versus conventional electrowinning with Pb-Ca-Sn anodes.

Accelerated life testing was carried out to maximize the lifetime of the new FCX coating. This testing, along with continuous co-minimization of voltage, led to the following adjustments to coating preparation:

- Molar ratio of Ir to Ta was adjusted from 70:30 to 80:20.
- Curing temperature of the undercoats was adjusted to 470 °C.
- Curing temperature of the topcoats was adjusted to 390 °C.

Figure 5 displays accelerated life results for individual coupons prepared using the improvements noted above. An average lifetime of 6500 hours was achieved. This exceeded the original 3000-hr target by over 100%. The variability noted in Figure 5 was due to varying amounts of initial Ir/Ta content of the coating. The small coupons were hand painted to place the individual coats, and this resulted in some variance in performance.
Figure 5: Lifetime hours of FCX anode coating in the accelerated life testers.

Anode Structure

The FCX alternative anode structure was composed of a copper hanger bar, six conductor rods attached to the hanger bar, and a titanium screen attached to the conductor rods on each side of the anode (Figure 6). The conductor rods were made by cold-rolling 5/8-inch titanium tube onto an aluminium core and sealing the end with titanium. The aluminium cores at the top of the rods were press-fitted into the copper hanger bar, and the titanium tubes were seated into the copper hanger bar to seal the rod/hanger bar connection from the tankhouse environment. Aluminium was chosen for the conductor rod core material (over copper) because of the cost differential that existed at the time of the Chino conversion. The screens were composed of expanded titanium metal that was 40% open and 0.022 inches thick.

The anode structure was designed so that the screens could be removed when the anode coating lifetime was spent, and the anode could be re-screened with a screen having a fresh coating. Thus the anode screen with coating became the consumable portion of the anode.
Chino SXEW Conversion and Performance

Voltage and Current Efficiency

Installation of FCX alternative anodes began at the Chino SXEW plant in January 2008 and was completed in July 2008. Figure 7 displays tankhouse rectifier voltage during and after installation. The Chino tankhouse consisted of an east and a west tankhouse each with its own rectifier.

The east and west tankhouses each utilized 80 electrowinning cells containing 63 cathodes and 64 anodes per cell. Current density varied from 15 to 30 amps/ft$^2$ depending on the time period. Lean electrolyte typically 34 g/L copper, 187 g/L sulfuric acid, and 3 g/L iron. Electrolyte temperature was typically 95 °F.

The west tankhouse continued operation with lead anodes while the east side was converted to alternative anodes. Figure 7 provides a unique picture of side-by-side tankhouse operation of lead anodes versus the FCX alternative anodes. With incremental installation of alternative anodes in the east tankhouse, east rectifier voltage decreased proportionally. A 15% reduction in rectifier voltage versus the west rectifier was achieved at full conversion of the east tankhouse. After conversion of the east tankhouse to alternative anodes, it was decided to take the east tankhouse down for maintenance to repair tankhouse beams and supports and to replace electrowinning cell paraliners. Production was shifted completely to the west tankhouse. Voltage increased on the west recti-
fier as current density was increased (Figure 7). After the maintenance period, production was shifted completely to the east tankhouse and the west tankhouse was shut down. Again the 15% voltage reduction was evident as production shifted from the west to the east tankhouse.

![Figure 7: Chino rectifier voltage on west tankhouse (with lead anodes) and on east tankhouse (with alternative anodes (AA)).](image)

![Figure 8: Chino tankhouse current efficiency with alternative anodes.](image)
The decrease in voltage at the end of Figure 7 was due to a decrease in production rate at the Chino plant.

Figure 8 displays tankhouse current efficiency using alternative anodes. An increase of 2% current efficiency was noted versus operation with Pb-Ca-Sn anodes. This was probably due to the increased care taken by Chino operators to control short circuits. The FCX alternative anodes are more easily damaged by short circuits than conventional Pb-Ca-Sn anodes. This is because the titanium screen becomes very hot locally during a short circuit and a hole is produced in the screen. Holes that become too large require repair, which is accomplished by spot welding a patch of screen over the hole. Control of short circuits decreases alternative anode repair rate. The keys to controlling short circuits in the Chino tankhouse were:

- Maintain straight cathode starter sheets in the electrowinning cells. The straightness of the cathode was the main factor affecting formation of short circuits. Chino inspected starter sheets for straightness during insertion into the cells and pulled the cathodes after two days of plating to press the cathodes flat.

- Remove “edge hair” or other inhomogeneities from the cathode starter sheet before insertion in the cell. This prevents formation of a dendrite that could lead to a short circuit.

- Maintain anode-cathode alignment in cells.

The steps noted above supported uniform current distribution in the electrowinning cell and minimized potential for short circuits. In addition, Chino had installed an FCX double-double contact system to distribute current to anodes and cathodes in each cell. The double-double contact system consisted of a main distributor bar with “sawtooth” contacts and equalizer bars on each side to aid current distribution in the cell. The sawtooth contacts provided two points of contact for each electrode and were particularly useful for lowering the contact resistance of the alternative anodes. The alternative anodes were lighter weight than conventional Pb-Ca-Sn anodes, weighing approximately 45 lbs.

Upon conversion of the Chino tankhouse to alternative anodes, addition of cobalt sulfate to tankhouse electrolyte ceased and cell cleaning to remove lead sludge was discontinued. Cobalt sulfate is typically added to tankhouse electrolyte to help stabilize Pb-Ca-Sn anodes. Both of these comprise operational savings to the plant.

**Anode Coating Wear Rate**

The wear rate of the FCX anode coating was monitored using in-plant XRF measurements. Sample anodes were periodically removed from solution, rinsed with water, and allowed to dry. A hand-held XRF unit was used to measure relative concentration of Ir and Ta remaining on the screen. Plots of the XRF measurements are shown in Figures 9 and 10.
Figure 9: Average of XRF scans of four anodes with top-coats cured at 380 °C.

Figure 10: Anode XRF scans as a function of top-coat curing temperature. Each plot is an average of three anodes.
Initially in the Chino conversion the top-coats of the anode coating were cured at 380 °C and the voltage savings versus Pb-Ca-Sn anodes measured 330 mV. Figure 9 displays the XRF Ir curves for a sample of these initial anodes. After 450 days about 20% of the initial Ir had been lost, but the slope of the curve was becoming less negative. The initial slope of this curve gave some cause for concern that the coating was degrading too quickly, and so the top-coat curing temperature was increased to 390 °C. This caused the voltage savings versus Pb-Ca-Sn anodes to decrease to 300 mV, and, as can be seen in Figure 10, decreased the coating degradation rate. An additional test cell was installed with top-coat curing temperature at 400 °C. Voltage savings at 400 °C top-coat temperature measured 270 mV. Based on these early results at Chino 390 °C was selected as the optimal top-coat curing temperature.

Coating lifetime was projected to be minimum 6 years based on testing in the anode development lab accelerated life testers. Figures 9 and 10 support this projection.

Cathode Quality

Two melts were conducted with 100% Chino cathode at FCX rod mills. The first melt was 163,529 lbs and was conducted at the El Paso (TX) rod mill. Lead content was analyzed using a Thermo Jerrell Ash Atom Comp 2000 DC Arc unit, and measured less than 0.3 ppm. The second melt was 100,524 lbs and was conducted at the Miami (AZ) rod mill. Lead content was analyzed using an Applied Research Laboratories 4460 Metal Analyzer Quantometer Arc Spark unit. Lead content was reported as less than 1 ppm. Cathode sulfur content was 2 to 4 ppm in the two melts. These results more than met FCX’s “AA” cathode quality specifications.

Learnings from the First Alternative Anode Installation

Targets for alternative anode voltage and coating life performance were met in the Chino conversion. A 15% voltage reduction was achieved and coating life projections were in agreement with estimations developed through anode development lab testing. With introduction of alternative anodes at Chino, cobalt addition to electrolyte ceased and cell cleaning for removal of lead sludge was discontinued. These were the key benefits that were projected, and they became reality. Lead content of cathode decreased below detection limits.

Learnings from the Chino installation were several, and are noted below.

- Chino used copper starter sheets for cathodes. During copper starter sheet plating, the cell electrolyte solution level was varied in order to plate copper up onto the loops that connect the starter sheet to the cathode hanger bar. This strengthened the loops.

When the Chino cell electrolyte level was set to its lowest level, one inch of anode screen protruded above solution level (and thus extended into the heat retention balls (HRB) floating on top of the cell). If a short circuit occurred and continued under these conditions, the
anode screen above solution level became very hot and ignited the HRB, producing a low-level cell fire.

It was found that the screen height could be decreased by 1 inch and still plate copper up onto the starter sheet loops. This would maintain the top of the alternative anode screens below solution level and prevent an HRB fire.

- Chino tankhouse operators reported that trading labor for cleaning of cells (to remove lead sludge) for labor to more diligently prevent short circuits (in the tankhouse) was a good trade.

- Spot welding was used to connect the anode screens to the anode conductor rods. In the initial anode production, the welds were not quite strong enough and some of the welds began to fail in operation. The welds were strengthened, and it was determined that the screens could still be removed for re-screening purposes when the anode coating life was spent.

- Around the perimeter of the alternative anode the screens were initially manufactured open, meaning that the screen on each side of the conductor rods did not connect, and there was a gap between the screens equal to the diameter of the conductor rods. During operation it was found that edges of the screens could become flared out towards the cathode, resulting in a potential short circuit. The anode design was improved by spot welding the screens together around the perimeter of the anode. This added strength and straightness to the anode, and also helped to feather the copper cathode deposit around the edges.

**Summary**

Freeport-McMoRan Copper & Gold Inc. (FCX) Technology Center developed an alternative anode for use in copper electrowinning at its SXEW Test Facility located in Morenci, Arizona. The anode was implemented at FCX’s Chino electrowinning plant in 2008 and has met targets for voltage reduction (15%) and coating lifetime projections (minimum 6 years).

Cleaning of electrowinning cells for lead sludge and addition of cobalt to the circuit for stabilizing lead anodes were discontinued with the alternative anodes. Lead content of copper cathodes decreased to less than 0.3 ppm.
References

