# OPERATING EXPERIENCE RECOVERING ACID AND COPPER AT THE PHELPS DODGE EL PASO ROD MILL USING EMEW® TECHNOLOGY

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## ABSTRACT

The Phelps Dodge El Paso Rod Mill produces approximately 2.4 million pounds per day of copper rod from a Contirod® casting and rolling operation. The newly formed rod is treated to remove mill scale and oxides using a sulfuric acid and hydrogen peroxide solution which is bled periodically when the copper concentration reaches 30-35 g/L. The bleed solution is heated to 75° C to destroy the residual peroxide. Copper is then recovered in a 270 cell EMEW electrowinning plant. Clean acid is also regenerated in the EMEW plant and is returned to the rod cleaning circuit. The EMEW plant commissioned in January, 2006, has two operators and replaces a copper sulfate plant with fourteen operators. The EMEW plant has a capacity of 1700 kg/day of cathode copper at 2.1 kWh/kg copper deposited. The electrowinning plant operates in closed circuit with the rod mill returning up to 2600 kg/day of sulfuric acid resulting in zero discharge. Use of dimensionally stable anodes (DSA®) ensures that the acid quality is maintained in the closed loop operation. The operating conditions, performance and plant experience of the EMEW copper and acid recovery plant are discussed.

## INTRODUCTION

The El Paso Rod Mill produces about 2.4 million pounds per day of high purity copper rod from a continuous cast Contirod® process. The newly formed rod requires chemical cleaning to remove undesirable oxides and mill scale. The rod is cleaned in a heated Cleaning Solution consisting of sulfuric acid and hydrogen peroxide to simultaneously remove oxides, mill scale and etch the rod. The rod is thus chemically etched to make the surface bright and free from staining. This chemical treatment is referred to as the Dr. Otto Process. Purchasers of the rod also demand a bright, clean appearance. To preserve this appearance, a water-based wax coating is applied to inhibit oxidation and staining.

Process control of the copper and acid content of the Dr. Otto Process Cleaning Solution is maintained by continuously withdrawing a volume of Cleaning Solution and replacing this volume with new Cleaning Solution. This "bleed and feed" system produces about 38,000 to 53,000 liters per day of spent Cleaning Solution. The spent Cleaning Solution is an aqueous solution containing about 35 g/L copper sulfate, 200 g/L sulfuric acid, 0.50% hydrogen peroxide and a small amount of propylene glycol. The solution made to replace the withdrawn volume consists of pure water from reverse osmosis treated well water, purchased concentrated sulfuric acid and enough Dr. Otto Cleaning Solution to add some copper sulfate to the mix

Beginning in 1989, the spent Cleaning Solution was pumped to the El Paso Refinery Copper Sulfate Plant. The solution was utilized to produce copper sulfate pentahydrate. The copper sulfate process required the neutralization of acid by flowing the solution over a bed of copper chips. The peroxide was thermally decomposed or consumed by the chemical reaction with the copper chips. The copper sulfate crystallization process also required evaporation of significant volumes of the water. The continuous transfer of the spent Cleaning Solution to the Copper Sulfate Plant required that the production of copper sulfate must continue regardless of market conditions.

The Electrometals Electrowinning (EMEW) technology offered by Electrometals Technology, Limited (ETL) was selected in late 2004 to replace the existing process of making crystalline copper sulfate from spent Rod Mill Dr. Otto Cleaning Solution. The EMEW Plant offered three important opportunities for Rod Mill operations. First was the production of high purity copper cathode from the spent Dr. Otto Cleaning Solution. These cathodes could be returned directly to the casting furnace. Second was the recycle of regenerated sulfuric acid to the Dr. Otto process. The solution returned to the Dr. Otto process from the EMEW Plant contains about 5 g/L copper, 245 g/L sulfuric acid and zero peroxide. The composition of this returning solution was similar to the solution made from bulk acid and Cleaning Solution. Thus, there was little difficulty in returning the solution to the Dr. Otto acid tank. Third was the electrowinning of copper without the production of acid mist. The ease of EMEW operations and low manpower requirements were also taken into consideration. The EMEW Plant was designed to be staffed by two operators. This would replace fourteen operators, two mechanics and three supervisors at the Copper Sulfate Plant. The EMEW Plant was successfully commissioned in January of 2006. Simultaneously, operations at the Copper Sulfate Plant ceased.

## OPERATING CONDITIONS

The EMEW process is a novel variation of permanent cathode technology. The plating cell is tubular. A thin, rolled stainless steel split sleeve inserted into the cell functions as the cathode. A small diameter inert anode occupies the center of the cell. Solution enters the cell tangentially at the bottom and exits at the top of the cell. The resultant copper deposit is tubular. The cells are organized in modular 30 cell frames with two banks of 15 cells per frame. Small, low capacity cell arrangements with fewer cells are possible. Higher capacity plants are made by grouping the 30 cell frames into modules.

When the cathodes are harvested, the module is drained. The need to fill the module with water to dilute and purge any residual acidic solution was soon abandoned as it was found to be unnecessary. The top of the cell is removed and the copper cathode along with the split sleeve is extracted from the top of each cell. The split sleeve easily separates from the copper cathode and is inserted back into the cell. The top of the cell is replaced making the cell ready for service again. See Figure 1.

Figure 1 – Harvesting copper cathode from the plating cells. Copper cathode shown after removal of the split sleeve. The tops of cells with caps removed are visible. The operator in background is holding the split sleeve.

**Cathodes**

The harvested cathodes typically weigh about 23 kg each and are horizontally stacked in a holding frame. The frame is designed to stack up to 19 cathodes in a bundle. The bundle is secured with scrap copper rod. See Figure 2. The cathodes are not washed after harvesting. The cathode bundles are subsequently charged directly into the casting furnace at a controlled rate. The small quantities of residual sulfate deposits cause no difficulties in downstream processing.

Figure 2 – Copper cathodes secured in the bundle. This bundle has 15 cathodes - the product from one 15 cell bank. The bundle is weighed and the weight used to determine current efficiency.

**Plant Design**

The Phelps Dodge EMEW Plant was designed for batch processing and a capacity of 1,700 kg/day of cathode copper at 2.1 kWh/kg copper deposited. This capacity required 270 plating cells. These cells were organized into three independent modules of 90 cells each. Each 90 cell module was supplied with its own rectifier, solution circulation and means of physical isolation from the other two modules. Thus, any module can be isolated electrically and mechanically from the others for cathode harvesting or repairs.

Design of the EMEW Plant was straight forward with the design, fabrication and shipping of the EMEW modules and some ancillary equipment handled by ETL. An independent engineering firm was responsible for overall electrical and mechanical design of the plant. The only major variation from the typical design of the EMEW modules was the addition of structural members to extend the supporting legs of the modules to allow for better access and to accommodate the split level design of the plant building. As discussed below, the addition of a peroxide destruction circuit added to the complexity of the plant design. The circuit required an engineered skid-mounted package for heating and cooling the Cleaning Solution.

**Peroxide, organics and acid mist**

Three issues had to be resolved prior to final selection of the EMEW technology. The first was the effect of peroxide on plating efficiency. The second was the accumulation of impurities such as organics and metals in the recycling acid. The third was the generation of acid mist.

When first proposed, ETL indicated that the peroxide would decompose during solution storage and would have little effect on the plating of copper in the EMEW application. As such, it was determined that a peroxide destruction circuit was not necessarily required. As subsequently required by Phelps Dodge, an onsite plating bench test was conducted by an ETL representative to evaluate the effect of various concentrations of hydrogen peroxide in the feed solution. Tests revealed that the peroxide in the Cleaning Solution did not decompose during storage as rapidly as expected. The presence of peroxide in the expected concentrations caused a deleterious effect on the nature of the deposit and current efficiency. The copper deposit was found to be very porous. Current efficiency was lowered substantially, to around 72%, until the peroxide decomposed in the circulating feed solution by electrolysis. The current efficiency without any peroxide present was expected to be better than 92%.

A peroxide thermal destruction circuit was then incorporated into the design of the EMEW Plant. In this circuit, the incoming Cleaning Solution was heated to 75° C and agitated until the peroxide concentration was below 0.03%. The solution was then cooled to 54° C or less and stored for processing in the EMEW cells.

Another concern was the accumulation of organics in the recycling acid. Propylene glycol is routinely added to the Dr. Otto Cleaning Solution. The composition and effect of the accumulation of organic decomposition products was unknown and of great concern as a source of possible rod staining. Again, another bench test proved that the organics had little or no effect in regard to accumulation or rod staining. In summary, the test simulated the recycle of acid with the addition of propylene glycol and trace amounts of inorganic impurities such as iron and chromium. Oxidized rod samples were cleaned in the test solution, waxed and held to evaluate any tendency to stain. No unusual staining was observed in the month long test. Samples were periodically taken for analyses of the organic and inorganic constituents to determine the rate of accumulation. Even in this severe test with no withdrawal or dilution of the circulating solution, organics did not accumulate excessively. The discussion of the test methods and results are outside the scope of this paper. However, no objections were raised concerning the organic compounds and their concentrations. Analysis of the Rod Mill Cleaning Solution found these compounds were already present in the normal process solution. Routine solution loss through treatment of a bleed stream of rod rinse solution serves to prevent excessive accumulation of inorganic contaminants.

Generation of sulfuric acid mist in traditional electrowinning plants presents the operator with challenges in environmental control of the emissions, corrosion and industrial hygiene. The design of the EMEW cells circulates the electrolytic solution at a relatively high flow rate through each cell. The gases generated, principally oxygen, are swept along with the solution and return to a circulation tank. As the gases vent from the circulation tank, a small mist eliminator is completely adequate to separate any droplets from the gases. As a result of the sealed EMEW cells and release of gases in the circulation tank, the EMEW Plant is free of sulfuric acid mist.

## PERFORMANCE AND PLANT EXPERIENCE

From the viewpoint of the EMEW Plant, electrowinning of copper is the focus of operation. From the perspective of the Rod Mill, the EMEW Plant is an acid regeneration and copper recycle operation. Current operation of the plant is smooth and routine. However, a very tight construction and commissioning schedule caused difficulties which are discussed below.

Operationally, the requirement to destroy peroxide resulted in a more complex schedule for the daily batch processing of the solution. In summary, the daily process of receiving, heating and cooling solution, electrowinning and returning decopperized solution to the Rod Mill required careful management.

The need to cease operations in the Refinery Copper Sulfate Plant forced a very tight schedule for construction and plant start-up. The inability to expeditiously secure the release of the EMEW and other related equipment from customs seriously affected the very tight construction schedule.

### Start-up

Only two of the three modules were operational at start up. Various mechanical and electrical faults along with operational errors in solution handling caused a very difficult commissioning. Among these problems, the most serious was the sticking of the split sleeves in the cells and rectifier problems. As stated previously, the design of the EMEW cells requires that a stainless split sleeve, the permanent cathode, be removed and reinserted with each harvest of the copper cathode. The EMEW cell is constructed from a polished stainless steel tube with plastic end cap assemblies. The split sleeve has to be able to slide within the cell to be removed and inserted. The piping, tankage, split sleeves and cells were not adequately flushed to remove grit, dirt and other construction debris prior to initial insertion of the split sleeves into the cells. This debris caused the sleeves to stick within the cells making removal very difficult. When removed, the sleeves were often mechanically damaged requiring laborious hand polishing to remove burrs and scratches on the outside surfaces. In some cases, the sleeves bound up so tightly that the sleeve and copper cathode could not be removed without shutting down the frame and completely disassembling the affected cell. In addition to the problems with the sleeves, the rectifiers were unreliable. Frequent rectifier faults resulted in the unexpected shutdown of modules.

However, the operational flexibility inherent in the modular design of the EMEW units allowed continued operation with no impact on the Rod Mill operation. The ability to: a) electrically isolate individual cells within a frame, b) mechanically and electrically isolate individual frames within a module, and c) when necessary, mechanically and electrically isolate individual frames and swap rectifier connections, permitted quick reconfiguration to work around the difficulties.

## Copper analysis

A MIPAC Copper Concentration Monitor determines the copper concentration in each batch. A continuous sample of the solution circulating through the process tanks and the EMEW modules is provided to the monitor.

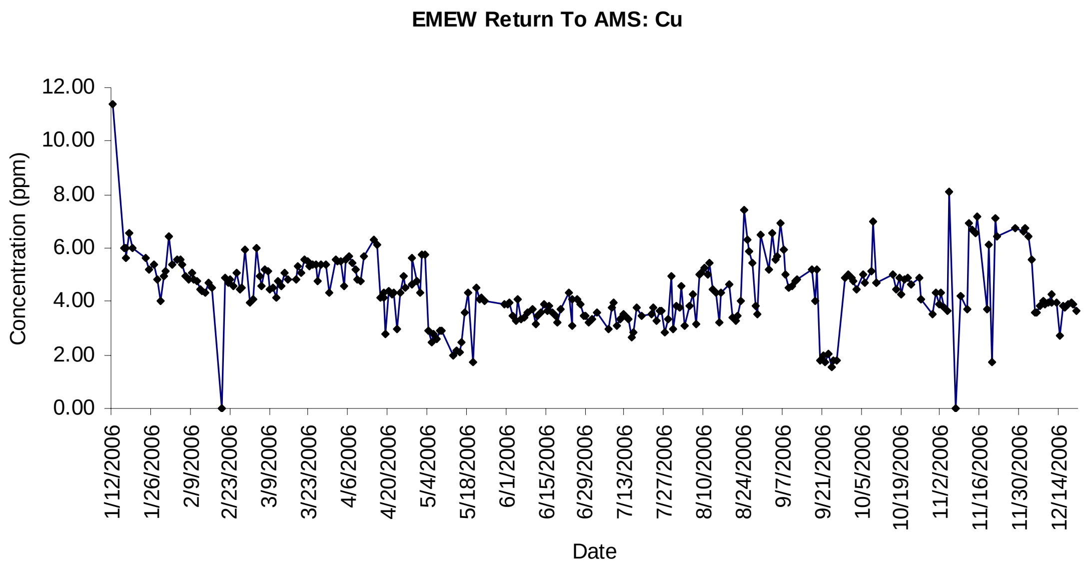


Figure 3 – Copper concentration in the Cleaning Solution returned to the rod cleaning process

The monitor compares the sample to a calibrated reference standard using proven colorimetric principle of measurement. This very useful instrument allows the plant operators to know at any time, without access to a laboratory, the copper concentration of the solution circulating through the EMEW cells. Adjustments to plant operations, such as plating rate, can be made quickly and accurately. Figure 3 shows the copper concentration in the return solution. The desired copper concentration is 5 g/L. The solution is often delivered with a copper content a little below 5 g/L at the request of the rod mill operators and due to operational considerations at the EMEW Plant. Automatic control of the rectifier current is possible by using the plant Programmable Logic Controller (PLC) and the MIPAC Copper Concentration Monitor output. This scheme has not yet been implemented at the Phelps Dodge El Paso EMEW Plant.

## Acid regeneration

As copper is deposited, the sulfuric acid content of the solution circulating in the EMEW cells increases. The concentration of acid in the solution returned to the rod mill is shown in Figure 4.

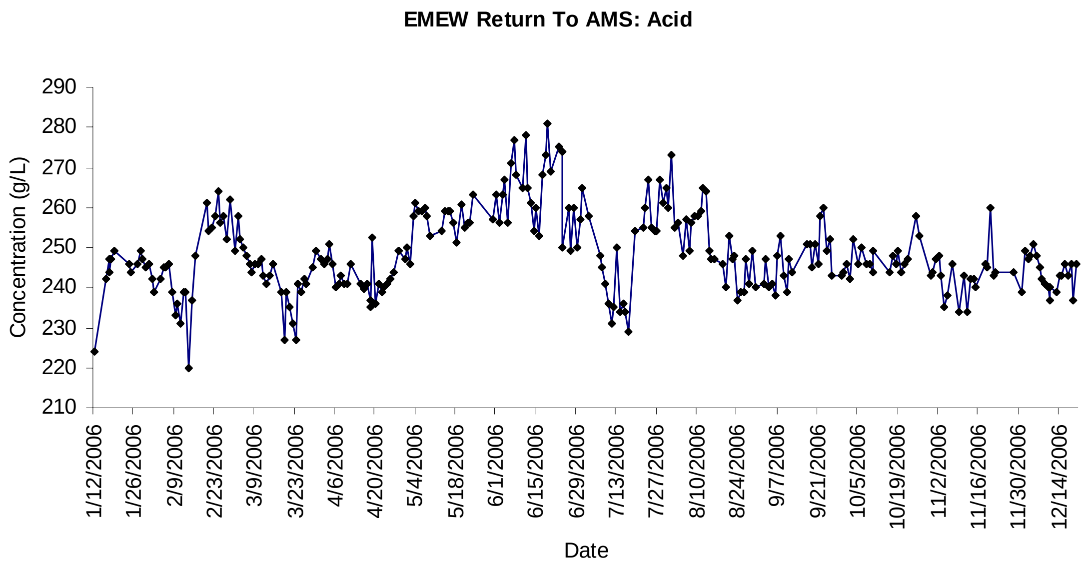


Figure 4 – Free acid concentration in the Cleaning Solution returned to the rod cleaning process

The acid content will vary depending on the initial sulfuric acid concentration of each batch, the total quantity of copper electrowon and incidental dilution from rinsing of cells. The recycle of acid from the EMEW Plant reduced the total annual consumption of sulfuric acid at the Rod Mill from about 1,800,000 liters in 2005 to about 340,000 liters in 2006.

## Control of impurities

As the rod exits the acid tank, water sprays in a rinse tank remove residual acidic solution. The acid content of the rinse tank is controlled by withdrawing a controlled volume of the rinse water. This withdrawal is sufficient to control impurities with the exception of iron. The acid lost in this withdrawn volume must be made up with bulk acid. The bulk acid used at the Rod Mill comes from a Phelps Dodge smelter and is often contaminated with minor amounts of $NO_X$. The principal source of iron addition to the recirculating Cleaning Solution is the bulk sulfuric acid.

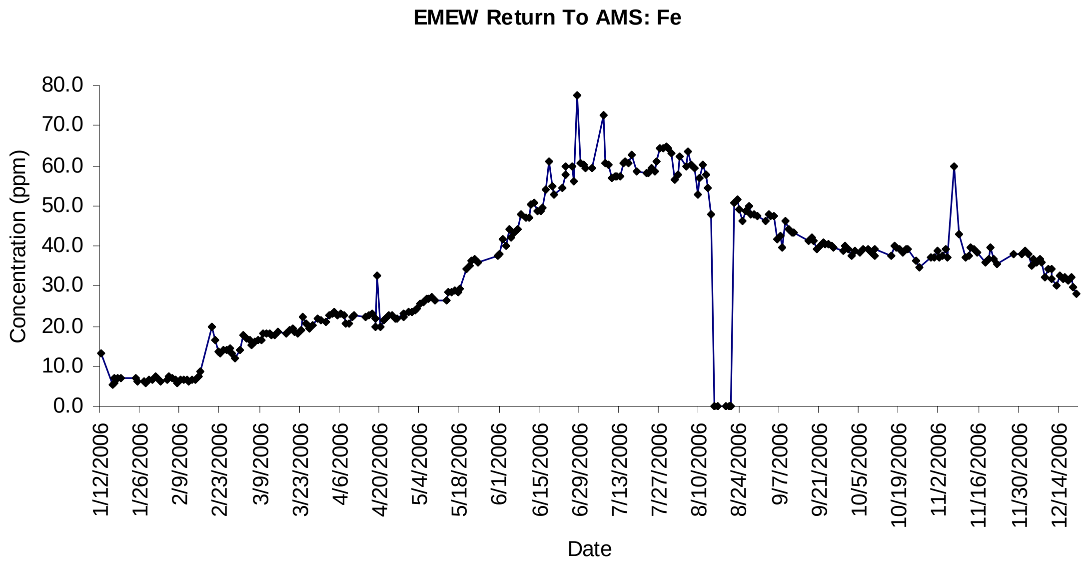


Figure 5 – Iron concentration in the Cleaning Solution returned to the rod cleaning process

The concentrated bulk sulfuric acid is stored in a carbon steel tank, as is typical for the storage of concentrated sulfuric acid. In the presence of $NO_X$, even in minor amounts, iron dissolves. Figure 5 shows the accumulation of iron in the Cleaning Solution. The lower iron content for the last half of 2006 is the result of a switch in acid supply from smelter acid to commercial concentrated sulfuric acid.

**Process Water Recovery**

The recycle Cleaning Solution contains high quality process water made by treating plant drinking water through a reverse osmosis process. Prior to commissioning the EMEW Plant, 38,000 to 53,000 liters per day of the process water in the spent Cleaning Solution was lost to the Refinery Copper Sulfate Plant. This process water was evaporated during the production of copper sulfate pentahydrate.

**Current efficiency**

Current efficiency is affected by many operational factors such as residual peroxide content, current density, variable copper content, on-off operation of the power supplies, and accuracy of record keeping. The current efficiency of the EMEW Plant is shown in Figure 6. The current efficiency is lower on average than the 92% originally forecast for the plant. However, the current efficiency is acceptable and does not adversely affect overall Rod Mill performance or cost expectations.

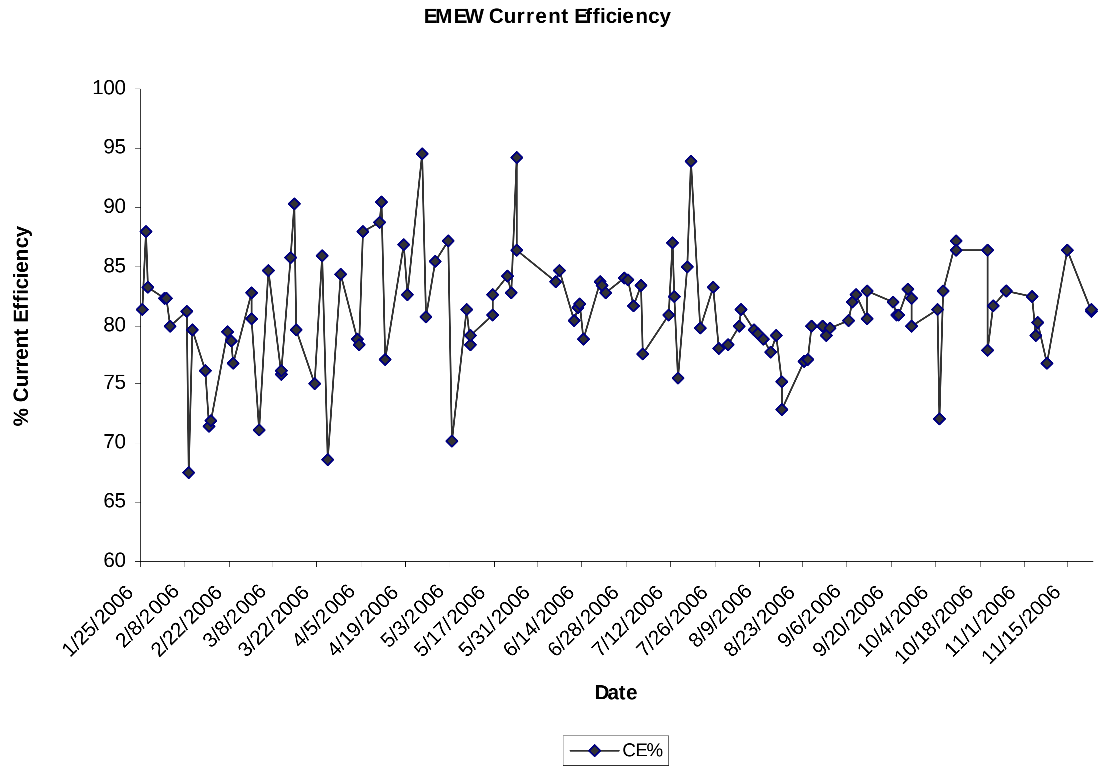


Figure 6 – Current efficiency of the EMEW Plant

## Staffing

The EMEW Plant is staffed by two full-time operators. Initially, an additional operator assisted for a few hours during each cathode harvest cycle. The additional operator was part-time and was assigned to the EMEW Plant from other Rod Mill work areas or from a temporary worker pool. Currently, the two operators harvest cathodes with each 90 cell module being harvested on a rotating schedule once per week. A Rod Mill supervisor, along with other duties, oversees the operation of the EMEW Plant. The plant is staffed only during the day shift. During off shifts, a Rod Mill operator makes periodic checks of the EMEW Plant. Few, if any, operator interventions are required.

## PROJECT SUMMARY

Capitol cost of the project was US$3.43 million. The construction period was four months. Considering elimination of Refinery Copper Sulfate Plant operating expenses, reduction in Rod Mill acid consumption, projected losses from the sale of copper sulfate, and operating costs of the EMEW Plant, cost savings from the implementation of the EMEW Plant exceed US$1.0 million per year.

## CONCLUSION

The implementation of the EMEW technology at the Phelps Dodge Rod Mill allowed for a number of positive operational changes. These changes include the recovery of metallic copper suitable for direct charging to the Rod Mill casting furnace, recovery and recycle of sulfuric acid and high quality process water, elimination of a high cost copper sulfate plant, and a reduction in the overall consumption of sulfuric acid. The EMEW Plant has proven to be operationally flexible and easy to operate. The EMEW Plant is operating at design capacity and has contributed to significant cost savings for the Phelps Dodge El Paso Refinery and Rod Mill.