Electrowinning Precious Metals from Cyanide Solution Using EMEW Technology

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Abstract:
The recovery of gold and silver from cyanide bearing solutions using electrowinning technology designed by Electrometals Technologies Ltd is reviewed. It has been successfully implemented in copper electrowinning applications, silver refining and in mining operations for recovery of gold and silver. The technology can be considered as a complete or partial replacement for Merrill Crowe technology and offers several advantages in the processing of high grade solutions. The advantages of the EMEW approach and actual plant applications and practices are evaluated and discussed.

1. Introduction

There are a number of approaches that have been proposed and used for the reduction of silver and gold from cyanide solutions. The most common is the Merrill Crowe approach which uses zinc cementation and the other is direct electrowinning of the silver and gold cyanide from solution. The Merrill Crowe approach has found extensive use as the process chemistry is simple and it can be applied directly to leach solutions from mining operations as well as to concentrated solutions produced by the elution of silver and gold absorbed onto activated carbon or ion exchange resins. It is also able to reduce gold and silver in solution to very low levels, typically below 1 ppm or less.

However, since the advent of concentration technologies based on activated carbon, electrowinning, using porous steel wool cathodes, has been extensively used to recover gold and silver from the more concentrated solutions produced by the activated carbon elution process. Electrowinning provides several advantages over the Merrill Crowe process including the use of more compact equipment, fewer process steps, reduced operating costs, the production of a higher grade doré and improved security of the high value product.

Often the decision regarding the choice of Merrill Crowe or electrowinning for final precious metals recovery is a critical part of the process flow sheet development. The decision will depend on the nature of the ore and the choice of upstream processes,
such as flotation, leaching, pre-concentration via the use of activated carbon, and the gold to silver ratios.

In fact, Merrill Crowe is often the recommended option for treating leach solutions with high silver to gold ratios – those exceeding 2:1 Ag:Au - due to the fact that large amounts of silver reduce the absorption of gold onto activated carbon and, for effective gold recovery, large amounts of activated carbon along with commensurately larger processing plants need are required. ¹, ²

Thus final reduction of precious metals from leach solutions leads to one of two processing schemes. The first one shown in Figure 1, or some variant thereof, is usually the one chosen for high gold ores.

![Figure 1: Activated carbon and electrowinning based flowsheet for the recovery of precious metals from cyanide solutions.](image)

The second, shown in Figure 2, is the one commonly considered for high silver deposits.

![Figure 2: Merrill Crowe based flowsheet for the recovery of precious metals from cyanide solutions.](image)

However practical engineering considerations and the drive to increase recoveries can result in a combination of these two flowsheets. In some operations, particularly silver ones, the concentration of silver in the leach solution, say from a flotation concentrate, is sufficiently high enough, >500 ppm, that an activated carbon concentration operation is not needed. In these applications the precious metals can be recovered directly by the Merrill Crowe approach. However, the tails from the pretreatment flotation operation can contain recoverable amounts of precious metals that a leach followed by activated carbon absorption and elution is warranted.
1.1 Electrowinning Precious Metals from Cyanide Solutions

The use of electrolysis for precious metals recovery from cyanide solution goes back to the 1890’s when the Siemens-Halske process, incorporating iron anodes and lead cathodes, was used. It was applied to the recovery of precious metals from dilute cyanide leach solutions in some applications. However improvements to the zinc cementation process by Merrill and Crowe involving the use of zinc dust, de-aeration of the solution and lead salts led to the complete displacement of the electrolysis approach. ³

The application of activated carbon technology in the 1980’s lead to a resurgence of the electrowinning approach as it was well suited to the recovery of precious metals from the more concentrated stream produced from the elution of activated carbon. A great deal of development ensued and most operations settled on an electrolytic cell of conventional design involving parallel anode/cathode configurations and the use of a porous cathode usually made of steel wool.

These electrowinning operations are a critical part of silver and gold recovery operations and a great deal of attention has been given to cell design and operating conditions. Some issues that are of concern include the following:⁴

- Cell design
- Operating conditions such as current, current densities, voltage, flowrate of solution through cells, etc.
- Recovery of silver and gold from cathode
- High temperature of operation
- Short circuits and fires
- Deposition of contaminants such as copper and mercury

As a result effective electrowinning of gold and silver from cyanide solutions requires a complex interplay of operating parameters, equipment design and safety issues.

For the most part these conventional electrolytic cells perform well on the concentrated leach solutions, but, over time, various other configurations have been proposed including high flow, fluidized bed and porous cathodes of various configurations.⁵ Many of these non-traditional designs have been focused on the recovery of precious metals directly from dilute leach solutions but none have been a commercial success.
2. **EMEW Technology Review**

The challenge associated with traditional electrowinning cell design with planar electrode configurations is that current efficiencies plummet once the concentration of the electrowon metal in solution decreases. Due to inadequate mixing, a zone of depletion forms around the cathode and at low concentrations side reactions such as hydrogen evolution occurs and other unwanted species are electrodeposited and the morphology of the electrodeposited metal changes. This compromises both the efficiency and selectivity of the electrowinning process.

In the 1990’s a cylindrical electrowinning cell was designed and tested by Electrometals Technologies Limited in Australia to overcome issues associated with poor solution contact with the cathode and boundary layer effects. The cell design became known as the EMEW cell, short for Electrometals Electrowinning, and involved an anode mounted in the center of a cylindrical cathode and featured the tangential introduction and helical flow of solution through and out of the electrowinning cell. Figure 1 shows the comparison of the planar and EMEW anode and cathode configurations as well as the solution flow through the EMEW cell.

![Image of conventional and EMEW cell designs](image)

**Figure 3: Conventional versus EMEW cell design.**

The helical solution flow substantially reduces the zone of depletion and boundary layer effects and as a result higher current efficiencies and selectivity can be maintained at lower metal concentrations. This improves the economies of metal recovery, produces a higher purity product and can also permit the discharge of spent electrowinning solutions with substantially lower metal concentrations.
The individual EMEW cells are constructed of 6” to 10” stainless steel cylinders with plastic end caps to direct and collect the solution flow. The anodes, made of stainless rods or dimensionally stable anode material are fitted through the center of the cell. The cells are arranged in an array and solution flow is split between the cells through a piping manifold. Figure 4 is a photograph of a bank of EMEW cells showing inlet and outlet piping manifolds and electrical connections.

Figure 4: A bank of EMEW cells showing the piping manifold and electrical connections.

The electrodeposited metal is plated out on the inside of the cylinder and Figure 5 shows the powdery deposit that is characteristic of silver. The nature of the silver deposit makes harvesting of the silver fairly easy. A short pulse of very high solution flow is effective at stripping most of the silver off the inside of the cylinder. The silver can then be recovered as a powder from solution in a simple filter. In contrast, for a metal like copper, which produces a solid coherent deposit, the top cap of the cylinder needs to be removed in order extract an inner cylinder of copper. See Figure 6 which shows the removal of a typical copper deposit.
Figure 5: Inside view of EMEW cell showing a powdery deposit of electrowon silver.
The key components of an electrowinning operation incorporating EMEW cells are:

- Array of cells
- Piping manifold
- Pump
- Rectifier
- Electrolyte tank
- PLC controller

The basic component configuration is shown in Figure 7. The regular mode of operation during electrolysis involves circulating the solution from the electrolyte tank through the
cells. The system is fully automated and controlled by a PLC. Periodically the solution flow through the cells is reversed and significantly increased to strip off the electrodeposited silver which is then separated from the electrolyte on a fine screen or some other filtration device. After the short strip cycle, the solution flow returns to its normal mode of circulation from the electrolyte tank through the cells.

Figure 7: Key Components and solution flows through an EMEW silver electrowinning operation

The EMEW design has been successfully applied to the electrolytic recovery of copper from sulfate solutions, silver from nitrate and cyanide solutions, nickel from sulfate solutions, and tin from hydroxide solutions. There are over 15 commercially operating EMEW plants around the world and many more are presently under consideration. Development work for the commercial application of the technology to lead, cadmium and other metals is underway.

3. Applications of EMEW Process for Precious Metals Recovery from Cyanide Solutions

As noted earlier, conventional cell configurations for the recovery of precious metals from concentrated cyanide solutions are tested and well established technologies. However it is in the treatment of the large volumes of concentrated cyanide solutions containing high levels silver that direct electrowinning using EMEW has proved to be a viable and cost efficient alternative and can be used in the place of the Merrill Crowe process shown in Figure 2.
Electrowinning using the EMEW approach offers the following advantages:

1. The final product is a higher grade material which produces a cleaner doré. In fact, the treatment of large amounts of zinc precipitates from some silver operations can become cumbersome and might even require the use of reverberatory furnaces to slag off much of the base metal contaminants in order to produce a clean doré. 

2. The process is simpler to operate. Essentially it is a silver reduction and filtration operation compared to the multiple unit operations, viz., clarification, de-aeration, lead addition, zinc addition, and filtration steps, in the Merrill Crowe operation.

3. The operating costs are lower than for Merrill Crowe operation. See Table 2

4. The labor requirement is typically lower than for the Merrill Crowe operation and is usually limited to monitoring the circuit and ensuring the effective operation of the automated harvesting of the silver product.

5. It is more robust than Merrill Crowe process where one has to be concerned about pH, oxygen content, cyanide concentration, temperature, lead additions, base metal contaminants, such as As and Sb, and scale forming compounds, like calcium sulfate and sodium silicate, as well as total suspended solids content. The EMEW based process operates effectively over a far wider range of conditions.

6. The design is modular and portable in nature so relocations and expansions are readily accommodated.

3.1 Operating Plant Data

The EMEW cell design has been successfully applied to the recovery of silver and gold from cyanide solutions at the Palmarejo Mine in Mexico. The Palmarejo gold and silver mine (owned and operated by Couer), located in the Chihuahua province in Northern Mexico, is largely a silver property that produced 9 million oz of silver and 125,000 oz of gold in 2011. It is reported as the 5th largest primary silver mine in the world. In 2009 an EMEW circuit, which is used to recover gold and silver from activated carbon eluates and concentrated leach solutions, was installed. In the 2011 the EMEW plant recovered 4,360,000 oz of silver and 69,800 oz of gold.

Due to the mineralogy of the Palmarejo deposit, which contains appreciable amounts of slow leaching silver sulfide and electrum, a processing approach was adopted that produces a high grade concentrate from flotation circuit. The concentrate is then directly leached with relatively high levels of cyanide to produce a concentrated solution typically containing 1000 ppm Ag and 10 ppm Au. The tail stream from the flotation circuit is subjected to a regular cyanide leach and precious metals recovery and
concentration step in a carbon-in-leach operation. The carbon is then eluted to produce solutions containing 1000 to 2000 ppm Ag and 10 to 20 ppm Au.

The unique aspect of the Palmerjo operations is that the direct electrowinning approach using EMEW technology was implemented to recover precious metals from both the concentrate leach solution and the eluate streams. Initial testing indicated that direct electrowinning would be sufficient to recover the bulk of the precious metals and that spent solution, containing ~50 ppm Ag, would be returned to the elution or leach circuits. At the time of the circuit implementation, cost assessments indicated that capital costs for the Merrill Crowe and EMEW were similar but the operating costs of the EMEW process were determined to be almost one half of those of the Merrill Crowe operation.\(^\text{10}\)

The EMEW operation at Palmerjo consists of 380 cells, each 48" in length and 8" in diameter powered by a bank of rectifiers. The voltage across each cell is typically 2.5 to 3 volts and current flows have ranged from 100 to 180 amps across each of the cells. However, it should be noted that higher current flows are possible and recent recommendations have included increasing current flows to 200 to 350 amps per cell. The cells are arranged in banks of 10 cells and the piping manifold is designed so that a single bank can be isolated from bulk solution flow so that cells can be worked on and repairs made without shutting down the whole circuit.

Solution, typically containing 800-1200 ppm Ag and 8-12 ppm Au, is recirculated from holding tanks through the cells for periods ranging from 6 to 12 hours with a goal of achieving precious metal concentrations less than 100 ppm. A typical depletion profile for gold and silver is shown in Figure 8. The selectivity of the process for precious metals is shown by the very small change in the copper concentration during this electrolysis run. Interestingly the reduction potential for silver from cyanide solutions is greater than that of gold\(^\text{11}\) and, especially at higher concentrations, silver will plate out preferentially over gold.\(^\text{12}\)
Figure 8: Depletion curves for silver, gold and copper in an EMEW circuit treating cyanide solutions

The silver deposits as a fine crystalline powder on the inside of the cathode similar to that shown in Figure 5. Solution flows are typically of the order of 2 m³/h/cell and every 15 minutes or so the solution flow is reversed and substantially increased to 10 m³/h/cell for about 10 seconds in the flush cycle. This high flow flushes the fine powdery silver out of the cell into a tank which is then pumped through a filter press to recover the precious metals.

Current efficiencies vary considerably over the depletion profile for the solution. Typically the overall current efficiency is of the order of 10 to 15% over the 1000 to 100 ppm concentration range which is low compared to conventional electrowinning circuits involving metal recovery from high concentrations of metal but better than the electrolytic recovery of solutions from low concentrations using conventional electrowinning cells.

As expected current efficiencies are highly dependent on solution concentrations and Figure 9 shows current efficiencies for silver recovery from multiple depletion runs plotted on the same chart. It can be observed at higher solution concentrations, current
efficiencies are of the order of 30-40% but then rapidly decrease to 5-10% at lower concentrations. This data is crucial to developing optimizing the performance of the EMEW operation and for developing the best operating regime for the EMEW process.

Figure 9: Current densities for silver recovery from cyanide solution in an EMEW circuit.

In practice the EMEW operation has worked well and has produced a lot of silver and gold. Challenges associated with the EMEW operation have included leaks, corrosion of cathode contacts, lack of maintenance and the absence of automated voltage monitoring on the individual cells plus the fact the EMEW operation is a more highly automated operation than the Merrill Crowe process and a higher level of operator training is required.

3.2 Electrowinning Versus Merrill Crowe – Complimentary Rather than Competing Technologies

Based on recent plant experience as well as the elevated precious metals prices over the past few years, the original concept for the EMEW technology as a direct and complete replacement for the Merrill Crowe process for the recovery of silver and gold from cyanide solution has been reconsidered. Initially it was proposed that direct electrowinning would be sufficient to recover all the precious metals and to produce spent solutions with 50 ppm levels of silver. However, plant practice has demonstrated, that for some operations, the EMEW process works better in conjunction with, rather than as a replacement, of the Merrill Crowe operation. The Palmarejo operation now incorporates both processes. EMEW is used for the recovery of the bulk of the silver and gold and the Merrill Crowe process is used as a polishing operation to achieve very
low concentration of precious metals in the spent solution. Or, if conditions require the treatment of large volumes of solution, the EMEW and Merrill Crowe processes can be operated in parallel resulting in a substantial increase in capacity. A simplified version of the Palmarejo flowsheet is shown in Figure 10.

The EMEW approach works very well for the recovery of silver from higher concentrations, >100 ppm Ag, and, even though low silver concentrations can be achieved in the EMEW process, lengthy residence times and low current efficiency result. On the other hand, the Merrill Crowe process is well suited for rapid recovery of low concentration of residual precious metals. In cases where the spent electrolyte is not recycled to the leach or elution circuits, mine operators may require a Merrill Crowe process onsite to polish silver to low concentrations before spent solutions are sent to tailings.

Figure 10: Basic processing scheme at Palmarejo operations

Running solutions through the EMEW process and then through Merrill Crowe process has the following advantages:

- The bulk of the precious metals are recovered in a easy to manage form that yields a higher grade doré material than that would be possible from the Merrill Crowe alone.
• Processing material through the EMEW process results in the removal of a good deal of the particulate content and clarification of solution which is often required before treating solutions in the Merrill Crowe process.
• The Merrill Crowe process at the end is an effective, rapid and efficient polishing step and produces spent solutions with low concentrations of precious metals.
• It allows operations personnel to make operating decisions based on the relative costs of the two process and in particular the costs of zinc vs. electricity.

The disadvantage is of the combined EMEW/Merrill Crowe approach is that it requires investment in both technologies as well as operating two very distinct processes.

Plant experience with EMEW in a cyanide operation over the past 4 years has led to the following lessons:

1. Higher current densities than those originally specified are achievable. This leads to faster silver recoveries as well as finer silver deposit which is more readily flushed from the cells
2. Preventative maintenance routines for the EMEW plant are necessary to ensure effective operation and precious metals recovery.
3. Automated individual cell voltage monitoring is important to ensuring rapid detection of short circuits. Low cell voltages have proved to be a reliable indicator of short circuiting problems and compromised performances in specific cells.
4. Even though there are opportunities for the EMEW process to directly displace Merrill Crowe for the recovery of precious metals from leach solutions, consideration should be given to considering them as complimentary process. This approach allows for the specific benefits of both processes to be realized. Using the EMEW process for the bulk of the precious metals recovery allows for the lower operating costs as well the production of a higher grade doré material. Using the Merrill Crowe process allows for the rapid recovery of precious metals from lower concentration solutions as well as the producing spent solutions with very low precious metals concentrations. Moreover when production demands increase it is possible to run the processes in parallel allowing for a large increase in production capacity

3.3 Kinetics of Electrolytic Silver Recovery in an EMEW Circuit.

The depletion profile for silver shown in Figure 11 has a typical first order exponential decay described by the following formula

\[ C_t = C_0 e^{-kt} , \]
or in natural log form by

\[ \ln \frac{C_t}{C_0} = -kt. \]

where \( C_t \) is the concentration at any time \( t \), \( C_0 \) is the starting concentration, \( t \) is time and \( k \) is a constant unique for each EMEW circuit and varies depending on the flowrate, number of cells, current, temperature, mass transfer coefficient and a host of other parameters.

A typical natural log plot for depletion curve for the electrolysis of silver from cyanide solution is shown in Figure 11.

![Natural log plot vs. time for the electrolytic recovery of silver from cyanide solution.](image)

Figure 11: Natural log plot vs. time for the electrolytic recovery of silver from cyanide solution.

The circuit constant for this run is determined from the slope to be \( 0.247 \text{h}^{-1} \). This circuit constant serves as a useful design and operations tool. It can be readily determined for each electrolysis run and serves as a useful confirmation that the circuit is operating close to design conditions. A large deviation from the design value would serve as an indicator of a short coming (or perhaps a short circuit!) in the operation.

Table 1 shows the variability and correlation coefficients for a series of runs for the same circuit running under similar conditions over a 10 day period.

<table>
<thead>
<tr>
<th>Run</th>
<th>Circuit Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.316</td>
</tr>
<tr>
<td>2</td>
<td>-0.375</td>
</tr>
</tbody>
</table>
It is noted that these depletion curves are similar to those observed for packed bed precious metal electrowinning units where the same first order relationship has been proposed.\textsuperscript{13} In these systems the kinetics are mass transfer controlled which leads to the first order relationship. On reflection an EMEW system with solution passing through hundreds of individual cells could be viewed as an approximation of a packed bed unit where the solution is passing through multiple openings in the packed bed. The key difference being that packed bed units show a voltage profile through the packed bed cathode, whereas, in each of the EMEW cells, the voltage profile is less pronounced and is close to identical in each individual cell.

3.4 Operating Cost Assessments

Our update of published costs projections for the EMEW and Merrill Crowe processes are shown in Table 2. It must be noted that these are our estimates only based on generic high silver operation and do not reflect the costs at the Palmarejo operations.

Table 2: Comparison of operating costs for the EMEW and Merrill Crowe process for the recovery of silver from cyanide solutions.

<table>
<thead>
<tr>
<th></th>
<th>EMEW</th>
<th>Merrill Crowe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labor</td>
<td>$7.46</td>
<td>$10.67</td>
</tr>
<tr>
<td>Zinc</td>
<td>$-</td>
<td>$4.00</td>
</tr>
<tr>
<td>Electricity</td>
<td>$5.18</td>
<td>$3.11</td>
</tr>
<tr>
<td>Reagents</td>
<td>$-</td>
<td>$0.23</td>
</tr>
<tr>
<td>General Consumables</td>
<td>$0.11</td>
<td>$0.33</td>
</tr>
<tr>
<td>Filter aid &amp; cloths</td>
<td>$0.13</td>
<td>$0.75</td>
</tr>
<tr>
<td>Maintenance</td>
<td>$0.74</td>
<td>$1.59</td>
</tr>
<tr>
<td>Crucible &amp; Refract</td>
<td>$0.13</td>
<td>$0.90</td>
</tr>
<tr>
<td>Fluxes</td>
<td>$0.01</td>
<td>$0.13</td>
</tr>
<tr>
<td>Diesel</td>
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<td>$0.46</td>
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<tr>
<td><strong>Total/kg Ag</strong></td>
<td><strong>$13.75</strong></td>
<td><strong>$22.16</strong></td>
</tr>
<tr>
<td><strong>Total/troy oz Ag</strong></td>
<td><strong>$0.43</strong></td>
<td><strong>$0.69</strong></td>
</tr>
</tbody>
</table>

Earlier analysis\textsuperscript{10} indicated operating cost of the EMEW operation were ~50% of the Merrill Crowe cost, however, with increased fossil fuel costs and commodity cost, adjustments and corrections were necessary. Our updates, shown in Table 2, indicate
that the difference has shrunk somewhat and the EMEW costs are ~60% of Merrill Crowe costs. In both operations, the labor costs are estimated to be the most significant. For the EMEW operation electricity costs are about $5.18/kg Ag whereas in the Merrill Crowe operation zinc and electricity cost are $7.11/kg Ag. For these cost estimates, highly conservative projections were used. High electricity and fuel costs, $0.50/kWh and $6/gal of diesel, as well as very low current efficiencies, 10%, were assumed. Lower electricity costs and improved current efficiencies would serve to further improve the price differential between the EMEW and Merrill Crowe options.

4. Conclusions

The cylindrical EMEW electrowinning cell - designed, developed and implemented by Electrometals - has been successfully implemented for the electrolytic recovery of a variety of base and precious metals. Notably the electrowinning of silver and gold from cyanide solution has been successfully implemented on a plant scale and as a result millions of troy oz of silver (along with some gold) are recovered every year using EMEW technology.

The EMEW operation results in substantial reductions in operating costs, it produces a cleaner precious metals doré, and it permits automatic harvesting of the silver product. In some cases, the EMEW process can be viewed a replacement for the Merrill Crowe zinc cementation process but plant experience has demonstrated that some circumstances might require both the implementation of the electrowinning and Merrill Crowe process to operate in a complimentary manner. The bulk of the precious metals recovery is done electrolytically to produce a low cost, higher precious metals content doré and the Merrill Crowe process is used to recover the residual amounts of precious metals in solution and to act, when necessary, as a second process to increase overall precious metals throughput.

Even though implementation has been successful there remain many opportunities for process improvement and optimization. These include voltage monitoring of individual cells, increases in current densities and the determination of first order circuit constants that can be used to monitor the performance of an EMEW circuit.

9 http://www.coeur.com/operations/palmarejo-mexico